Heterogeneous catalyzed macromolecular hydrogenations in oscillating systems

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HETEROGENEOUS CATALYzed MACROMOLECULAR HYDROGENATIONS IN OSCILLATING SYSTEMS

A Dissertation

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Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
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in

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by

Alan Bussard
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Nomenclature

\( a \) interfacial area, \( m^2/m^3 \)
\( a_{in} \) surface fluid amplitude, m
\( A \) forcing or piston amplitude, m
\( C \) concentration, mol/m\(^3\)
\( C^* \) saturation concentration, mol/m\(^3\)
\( C_{Ao} \) initial concentration of aromatic, mol/m\(^3\)
\( C_{Ho} \) initial concentration of hydrogen, mol/m\(^3\)
\( C_{HR} \) reference concentration of hydrogen, mol/m\(^3\)
\( d \) diameter, m
\( D \) molecular diffusivity, m\(^2\)/s
\( D_e \) effective diffusivity, m\(^2\)/s
\( E_a \) energy of activation, J/mol
\( f \) pulsing frequency, 1/s
\( g \) gravitational constant, m/s\(^2\)
\( G/L \) gas/liquid volumetric ratio, dimensionless
\( IV \) iodine value, dimensionless
\( k \) mass transfer coefficient, m/s; or reaction rate constant, mol/(g Pd·s)
\( k_0 \) rate constant, mol/(g Pd·s)
\( K \) equilibrium constant, m\(^3\)/mol; or apparent diffusivity, m\(^2\)/s
\( k_{in} \) characteristic eigenvalue, dimensionless
\( k_{obs} \) \( f \) first order observed rate constant, L/(g Pd·s)
\( k_{obs} \) second order observed rate constant, L\(^2\)/(g Pd·s·mol)
\( L \) characteristic length scale, m

\( m \) mass of sample, g

\( N \) molar flux, mol/m\(^2\)/s; or normality, mol/L

\( N_{H_2} \) moles of \( H_2 \) consumed per unit volume, mol/m\(^3\)

\( N_1 \) impeller speed, 1/s

\( N_0 \) impeller constant (0.8 for marine propeller), dimensionless

\( P \) pressure, MPa

\( p_m \) as in Eq. 3.8, dimensionless

\( P_v \) Power per unit volume, kg/(m·s\(^3\))

\( q_m \) as in Eq. 3.9, dimensionless

\( r \) rate, mol/(g\(_{Pd}\)·s); or pore radius, m

\( r_{H_2} \) rate of hydrogen consumption, mol/(g\(_{Pd}\)·min)

\( R_{H_2} \) rate of hydrogen consumption, mol/(g\(_{cat}\)·s)

\( R \) gas constant, J/(K·mol)

\( S \) selectivity, dimensionless

\( t \) time, s

\( T \) temperature, K; or dimensionless time, \( \omega t/2 \)

\( T_1, T_2 \) function shown in equation 6.25, dimensionless

\( u \) superficial velocity, m/s

\( V \) volume of liquid, cm\(^3\)

\( V_0 \) titration volume for blank test, ml

\( v_0 \) liquid volumetric flow rate, L/s

\( V_s \) titration volume for sample, ml

\( W \) weight, g
\( \Delta x \) amplitude of fluid pulsation, m

\( X \) fractional conversion, dimensionless

**Greek letters**

\( \alpha \) Womersley number, dimensionless

\( \beta = \alpha \cdot Sc^{0.5} \), dimensionless

\( \delta \) liquid film thickness, m

\( \epsilon \) hold-up, dimensionless

\( \epsilon_c \) catalyst porosity, dimensionless

\( \Phi \) Thiele modulus, dimensionless

\( \Phi_{WP} \) Weisz-Prater modulus, dimensionless

\( \nu \) kinematic viscosity, m\(^2\)/s

\( \rho_{cc} \) catalyst loading, kg/m\(^3\)

\( \tau \) tortuosity, dimensionless

\( \eta \) effectiveness factor, dimensionless

\( \mu \) viscosity, Pa\cdot s

\( \rho \) density, g/m\(^3\)

\( \sigma \) surface tension, N/m

\( \omega \) frequency \((2\pi f)\), rad/s

**Dimensionless numbers**

\( Ca \) Capillary number \(=\mu u_{TP}/\sigma\)

\( Re \) Reynolds number \(=\rho uLdch/\mu\)

\( Re_I \) impeller Reynolds number \(=\rho Nd_l^2/\mu\)

\( Sc \) Schmidt number \(=\mu/\rho D\)

\( Sh \) Sherwood number \(=kL/D\)
We Weber number (=$\rho N_t^2 d_i^3/\sigma$)

Subscripts

b bubble
c catalyst
ch channel
film film
G gas
GL gas-liquid
GS gas-solid
H hydrogen
I impeller
L Liquid
LS liquid-solid
M methane
obs observed
Oil oil
ov overall
p particle
Pd Palladium
S solid
TP two phase
slug slug
surf surface
UC unit cell
TAG triglycerides
Abstract

An examination of novel oscillatory (alternating gas and liquid phase) reactors and heterogeneous catalysts for multi-phase macromolecular reactions was carried out. A monolith-containing square die with Pd/Al₂O₃ catalysts was used to successfully hydrogenate poly(styrene) (PS). The inherent pulse behavior of the extruder was found to be sufficient to approach intrinsic kinetics at low polymer concentrations. At higher (10 wt% PS) concentrations, forced pulsing was shown to have a greater impact on observed reaction rates. Selectivity with this extruder-fed reactor was better than with a stirred tank in all cases, due to a more plug-flow-like residence time distribution. While accurate control over the exit distribution of forced pulses was difficult due to gas back mixing, an optimal frequency of forced pulsation was observed for the 10 wt% PS system.

Mesoporous catalysts for macromolecular hydrogenations were synthesized and tested for PS hydrogenation. They were shown to be more active than microporous catalysts. The type of support was shown not to have a large influence on activity, but high dispersion of the active metal was critical. The addition of a second inactive metal did improve hydrogenation selectivity, but it was observed that having a chloride-free support is even more important in achieving high activity.

For the hydrogenation of a low molecular weight species (α-methylstyrene) (AMS) in a piston oscillating monolith reactor (POMR), oscillations gave improvements in reaction rate of up to 84%. With no oscillations, the activity was still higher than in a stirred tank operated at an equivalent power per unit volume. Selectivity in the POMR was as good as or better than in a stirred tank. It was also found that the Pd crystallite size had a large influence on activity.
For the hydrogenation of soybean oil, the POMR gave a higher activity than a stirred tank at identical conditions. The hydrogenation rate increased by as much as 112% with oscillations. It was shown that this improvement was unrelated to external mass transfer; rather it arised from improved intraparticle mass transfer limitations or surface wetting. Stereo-selectivity was largely unaffected by the reactor system but was instead dependent on intraparticle diffusion lengths.
Chapter 1 Introduction

1.1 Heterogeneous Catalysis and Multiphase Systems

Heterogeneous catalysis has been an important field of study ever since the German scientist Johann Wolfgang Döbereiner first popularized a cigarette lighter based on hydrogen and oxygen flow over a platinum sponge in 1823. By World War I, Germany was using iron to catalyze the reaction between nitrogen and hydrogen (Haber process) to produce ammonia on a large scale. Today, most commercially produced chemicals involve the use of catalysis at some point in their manufacture. Research into new catalytic materials is still at the forefront in both industry and academia as a way to both improve traditional processes and develop new classes of reactions for the production of novel compounds.

With continuing discovery of new raw materials for chemical feedstocks and energy production, especially higher molecular weight materials (cellulosics, tar sands, etc.), the design of catalysts for three-phase systems will have to be better understood. The demands on both the catalysts and the reactor systems are increasing; many problems must be addressed before new products can be successfully brought to market. In this dissertation, heterogeneous catalyzed hydrogenations of low and high molecular weight systems are used as case studies to improve the design of multiphase reaction catalysts and reactors.

1.1.1 Polymer Modification

Some 70% of the world polymer market is devoted to just four parent polymers: polystyrene (PS), polyethylene (PE), polypropylene (PP), and polyvinylchloride (PVC). With the flood of new plastics applications, these four simple polymers cannot satisfy the need for all specialized materials. Specialty polymers are available (PTFE, PEEK, etc.), but at much higher costs. Innovative uses demand polymers that are stronger, better able to resist chemical attack, and possess a wider temperature range of usage, have better environmental stability, but are still
easy to produce. Eventually, the increased costs of petrochemical feedstocks will demand sources for commodity materials not dependent on the simple monomers in common use. In some cases, polymers with improved attributes will be produced by derivatization, i.e., post-polymerization reactions. Catalyzed hydrogenations or dehydrogenations are just two types of modifications that are possible, but they are important ones. Derivatization is convenient because it builds on the more available polymers, meaning no new investments are required for monomer or biopolymer production. Also, certain polymeric structures can only be obtained through post polymerization modification.

One example of a useful polymer formed upon hydrogenation of PS is polyvinylcyclohexane (PVCH). PVCH has a $T_g$ that is 42°C higher than PS, meaning it can be used at elevated temperatures where PS would melt or soften.\textsuperscript{1} Figure 1.1 shows the reaction. Dow Chemical explored the use of PVCH in advanced optical recording media because of its superior optical clarity and low birefringence. Another advantage of PVCH is that some of the cost of hydrogenation can be recouped since PVCH has a lower density than PS, and while bulk polymers are often sold based on weight, they are used based on volume. Another similar post-polymerization reaction is the hydrogenation of nitrile butadiene rubber (HNBR), which has better resistance than NBR to degradation by prolonged oil contact and to abrasion at elevated temperatures. This makes HNBR an excellent choice for automotive applications.\textsuperscript{2}

Polymer modifications are a relatively new area for heterogeneous catalysis and reaction engineering. These reactions often pose a significant barrier to mass transfer of the gas phase reactants, due to high solution viscosity. Solid catalyst and reactor technologies are often ill-equipped to deal with viscous feeds, including polymer melts or concentrated solutions. Furthermore, the behavior of polymer chains in confining media at high concentrations and in the presence of a gas phase is poorly understood. This is largely because the preferred techniques
to study polymer diffusion, such as dynamic light scattering, require polymer concentrations far less than what is often encountered in an industrial process, and will not work with porous catalysts and a pressurized gas phase. With concentrated solutions or melts, the polymers are often highly entangled, creating additional barriers to mass transport.

![Figure 1.1](image)

**Figure 1.1** The hydrogenation of PS to PVCH, where “n” indicates number of repeat units.

### 1.1.2 Edible Oil Hydrogenation

Another area where improvements in three-phase catalytic processing could affect an existing industry is the partial hydrogenation of edible oils. In this case, the goal is to control the hydrogenation of a polyunsaturated fatty acid. An example of a triglyceride is shown in Figure 1.2 with three fatty acid chains connected by a glycerol backbone. Saturated edible fats (e.g., animal lard and butter) have long been popular for their shelf life and pleasant texture, yet health concerns in the 1980s led to an increased demand for healthier unsaturated oils. However, the presence of unsaturation makes these oils inherently less stable than saturated fats. Also, unsaturated fats are liquid at room temperature. The hydrogenation of these polyunsaturated oils, in the form of C\textsubscript{18} triglycerides of fatty acids, promotes stability, i.e., better resistance to oxidation and a higher melting point.\(^3\)

Edible oil hydrogenations exhibit many of the same characteristics as polymer hydrogenations. For instance, serial pathway selectivity is important, because hydrogenation to complete saturation is undesired. Edible oils come with varying degrees of double bonds —
stearic and palmitic acids are saturated, oleic is monounsaturated, linoleic has two double bonds, and linolenic has three double bonds.\textsuperscript{4} To a varying degree, all of these components will be found in natural food-grade oils. Stereo-selectivity is another important factor, as the production of cis- configured fatty acids is preferable to the trans- configuration for health reasons.\textsuperscript{5} The reaction pathways for soybean oil hydrogenation are illustrated in Figure 1.3.

![Figure 1.2 A triglyceride composed of three fatty acids bonded to a glycerol backbone. “CX:Y” denotes a fatty acid of X carbons and Y double bonds.](image)

Due to consumer concerns, the FDA mandated that all nutritional labels separately list trans-fatty acid content beginning in 2006. Natural edible oils come in the cis- only configuration, but unselective hydrogenation leads to trans formation. This is further complicated
by the trans configuration being thermodynamically more stable.\textsuperscript{6} An ideal hydrogenation would react all linolenic to linoleic fatty acids, while not changing the concentration of saturated or monounsaturated fatty acids, and preventing any cis-trans isomerization. The most popular reaction from the literature is the hydrogenation of soybean oil, which contains about 7 wt% linolenic, 54 wt% linoleic, 23 wt% oleic, with the remainder saturated.\textsuperscript{5-7}

1.2 New Directions for Catalysis in Multiphase Systems

Several future catalytic bioprocessing applications are closely related and pose similar challenges for the future role of heterogeneous catalysts in multiphase systems. One such example is the hydrogenation of levulinic acid to form the monomer $\alpha$-methylene-$\gamma$-valerolactone (MeMBL).\textsuperscript{8} Levulinic acid is readily available from biomass processing and incorporating MeMBL into a polymer raises the glass transition temperature ($T_g$) 100°C higher than a conventional acrylic such as poly(methyl methacrylate) (PMMA).\textsuperscript{8} Multiphase systems consist of reactants present in both the gas and liquid phases, with the reaction taking place only on the surface of the solid catalyst. Multiphase systems often suffer from the effects of poor mass transfer, because the gas phase reactant must first diffuse from the bulk gas into the bulk liquid solvent, then from the bulk solvent to the solid catalyst surface, and then finally into the catalyst pores. A schematic of this mass transfer process is shown in Figure 1.4. Traditionally, three-phase reactions are operated at high pressures to maximize solubility of the gaseous reactant and thereby minimize transport resistances.

For three-phase catalytic systems, the liquid phase reactant must also access catalyst pores. Lower molecular weight reactants do not pose the same diffusional problems that polymers do; polymer chains can be entangled either with other chains or with pore surfaces, greatly increasing molecular friction for intraparticle diffusion. The use of certain solvents can help disentangle the chains, but at increased feed and separations costs. Polymer chains that
cannot diffuse into the pore space can only react on the outer surface of the catalyst, in which case the number of active sites is severely limited.

![Mass transfer schematic](image)

**Figure 1.4** A process schematic showing the mass transfer steps required for a three-phase system.

A high concentration of polymer dissolved in the liquid phase is desired from an economic point of view to facilitate more production. As the concentration of polymeric systems increases the viscosity increases dramatically. This can lead to serious problems in obtaining a proper (generally, uniform) liquid phase distribution over the surface of the catalyst, a phenomenon commonly referred to as “surface wetting”. Poor surface wetting behavior can lead to significant temperature gradients inside the reactor (i.e., hotspots) and areas where the liquid reactant cannot access active sites.

### 1.2.1 Activity vs. Selectivity in Hydrogenation Reactions

Unwanted side reactions typically include hydrocracking, which results in chain scission for a polymer, marked by an increase in polydispersity, a decrease in molecular weight, and a decrease in $T_g$. A tradeoff between catalyst activity and selectivity towards desired products is a recurring theme in catalytic hydrogenations. For instance, for the hydrogenation of 1,3 butadiene, selectivity towards n-butane varied from 5-40 mol% as the turnover frequency varied...
between 0.6-1.3 s\(^{-1}\) for four different hydrogenation catalysts operated under identical conditions.\(^1\) In this case, the formation of side products (but-1-ene, trans-but-2-ene, and cis-but-2-ene) depended greatly on the catalyst structure. In the case of polymer hydrogenations, the temperature is usually increased to improve activity. However, at these higher temperatures the catalyst operates unselectively.\(^1\) An ideal catalyst would be highly active for the desired hydrogenation reaction only. Because most of the side reactions follow a serial pathway (i.e., hydrogenation to an intermediate state of saturation, sometimes followed by complete saturation, followed by cracking), this suggests that the internal transport should facilitate the diffusion of intermediate product out of the catalyst pores before further reaction. External mass transfer should therefore be high enough for proper surface renewal. Hotspots would favor hydrocracking over hydrogenation because it is well known that these reactions have a higher activation energy. Lower molecular weight compounds can also undergo isomerization, or be alkylated by hydrocracked fragments to disproportionation / coupling products. An example here is the hydrodechlorination of CCl\(_2\)F\(_2\) to CH\(_2\)F\(_2\). In this reaction, significant amounts of methane (4-50 mol\%) and traces of ethane, propane, CHClF\(_2\), and CH\(_3\)Cl were all present in the product distribution.\(^1\)

1.2.2 Reactor Design for Three-Phase Catalytic Reactions

Typical reactors for three-phase systems include stirred tanks where the catalyst is present as a powdered slurry and trickle beds where the catalyst is present as pellets in a packed tower, with liquid and gas in co-current downflow. Trickle beds are often desired in high-volume industrial processes because catalyst separation is not required. The hydrodynamic behavior of trickle beds during scale-up is also well known. Stirred tanks are usually relegated to smaller scale processes, either continuous or batch, or for research purposes. With stirred tanks the catalyst / reactant combinations are easily changed, and for higher throughput several reactors
can be run in parallel. Stirred tanks are typically not as easy to scale up. Both trickle bed and
stirred tank systems usually rely on high pressures to obtain suitable concentrations of the
gaseous reactant at the catalyst.

Another important factor in a three-phase reactor system is achieving high interfacial
areas, especially for gas and liquid. Unless the catalyst is partially wetted, the higher the gas-
liquid interfacial area, the higher the flux rate of the gaseous reactant through the liquid film to
the catalyst surface. Wetting distribution phenomena are not widely understood because each
reaction system will operate the most efficiently (with regards to activity and selectivity) under
different heat and mass transfer regimes. High interfacial areas are of particular importance for
viscous macromolecular systems because these systems are often characterized by larger bubble
sizes. They are also typically shear thinning, so more agitation or higher flow rates can result in
higher shear rates and lower viscosities, which in turn enhances mass transfer. Figure 1.5 shows
that the viscosity of a typical polystyrene (PS) solution decreases rapidly as shear rates are
increased. Higher flow and agitation rates can also assist in the transport of the product away
from the catalyst surface, before it has a chance to re-adsorb and further react to an undesired
product.

Systems where the catalyst is present as a washcoated layer on a monolith or other
structured packing have only recently been examined for three-phase reactors. There are few
large scale processes based on such reactors at present. Monolith and other reactors with
structured packings have traditionally been restricted to automotive and combustion applications
where low pressure drop is particularly desirable. They also offer a high specific surface area per
unit volume and, usually, good liquid distribution.

Regardless of the reactor chosen, the overall goal of the system is to control the catalyst
pore environment in such a way as to maximize activity and selectivity. The usual methods of
changing temperature, pressure, and agitation rate / superficial velocities over the surface of the catalyst are currently the control methods of choice.

![Figure 1.5](image)

**Figure 1.5** Plot of PS solution viscosity (Pa·s) vs. shear rate (s⁻¹) for average molecular weight 6.7 x 10⁵ Da, 10 wt% PS in THF/cyclohexane, 25°C.

### 1.2.3 Catalytic Deactivation in Hydrogenation Reactions

Another serious issue with three-phase catalytic systems is the decrease in catalytic activity as a function of time on stream due to deactivation. This problem can manifest itself as a poison irreversibly adsorbing on an active metal site, metal leaching into solution, pore blockage due to coke or heavy oligomer formation, gradual oxidation of the metal, or a loss in surface area due to sintering (the migration and coalescence of metal particles). A process that must be frequently halted to regenerate the catalyst or even replace it is undesirable from an economic standpoint. This is especially true when the catalyst utilizes a precious metal such as Pt, Pd, Ru, or Rh supported on a porous metal oxide or carbon. For high temperature hydrogenations / dehydrogenations (>400°C), the prevalent deactivation mechanism is surface coking. In this case, the surface becomes covered in a layer of carbon which blocks active sites. An example is the hydrogenation of aromatics in pyrolysis gasoline (PYGAS) where a high hydrogen partial
pressure is required to limit deactivation due to coking\cite{13}. Lower temperature reactions such as the three-phase hydrogenation of nitrile during the recycling of nylon 6,6 show the deactivation here is actually the formation of heavy oligomers by catalytic coupling; the oligomers take up the active sites\cite{14}.

As the demands on heterogeneous catalysis in multiphase systems grow, due in particular to uses related to bio-renewable resources, the prevention of catalytic deactivation will become even more important. This is because many bio-derived feedstocks are inherently impure compared to petrochemical feedstocks, and these impurities can lead to significant deactivation. While the traditional processing of products from crude oil typically involves catalysis related exclusively to hydrocarbons, the complexity of bio-feedstocks means they will also contain residual materials such as proteins and nucleic acids, as well as traces of common catalyst poisons such as sulfur, phosphorous and alkali. Also, many of these bio-systems include an aqueous phase in addition to an organic liquid phase, thereby making the reactor system four phase.

### 1.2.4 The Role of the Supports

While the choice for the active metal used to carry out a catalytic reaction is usually an easy one, the role of the porous support is not always as clear. Supports such as zeolites (microcrystalline alumino-silicates) are often chosen in the petrochemical industry because they offer possibilities for product shape selectivity, related to their well-defined pore network. They are also useful because they can be ion-exchanged modify their acid or base strengths. However, they are not the first choice for most three-phase reactions because they only offer microporous (< 2 nm) pore diameters. Since mass transfer is usually the limiting factor in these reactions, larger pore sizes would be desired to facilitate easier diffusion. The trade-off here is that as pore
sizes increase, the support’s surface area tends to decrease, leaving less area over which the catalytically active metal can disperse.

Another important consideration is the chemical nature of the support. Supports such as silicas, aluminas, and activated carbons have varying levels of interaction with both the reactants and the active metal. Activated carbons are often considered the most chemically inert of the supports, but even they can exhibit strong interactions when the surface is not graphitized. Support interaction with the active metal changes the behavior of the catalyst on both an electronic – electron donation or withdrawal between the metal and support – and geometric – site blockage if the support “decorates” the metal crystallite. Sometimes the supports even play a completely independent role in the reaction mechanism. Because some multiphase systems include a fourth aqueous phase, the relative hydrophilicity of the catalytic surface can play an important role if some reactants are present in the aqueous phase.

1.3 Outline of Dissertation

Chapter 1 of this dissertation gives an overview of the role of heterogeneous catalysis in three-phase reacting systems, and some of the research problems that must be addressed before certain emerging technologies can be brought to market. Specific systems of interest include polymer modifications, edible oil hydrogenations, and bio-feedstock conversions. While much of the current heterogeneous catalysis / reactor design research is still focused on traditional hydrocarbon processing, design of catalysts and reactors for multiphase systems involving oligomeric and polymeric reagents will become increasingly important research areas.

Chapter 2 presents a review of the literature on current methods for catalytic hydrogenation. In particular, the differences between homogeneous and heterogeneous catalysis for macromolecular hydrogenations are contrasted. Current reactor designs and heterogeneous
catalysts are explored in detail, describing the advantages and disadvantages of both. Finally, the
theory behind polymer transport in porous media is explored.

The remaining chapters of this dissertation cover the research done in fulfillment of my
Ph.D. Chapter 3 investigates a novel reactor system used for the hydrogenation of a high
molecular weight reactant and compares it to a conventional stirred tank. This chapter (authored
by A. Bussard and K. Dooley) is a paper accepted for publication (accepted 12/31/07) by *AIChe
Journal*. An earlier, shorter version appeared in *ACS Polymer Preprints*¹⁵, and portions have
been presented at the 2006 AIChE National Meeting in San Francisco, California. Chapter 4
details results from catalyst syntheses of materials that may be useful in hydrogenation of heavy
feedstocks and polymers. Portions of this work have been presented at the 20⁶th Meeting of the
North American Catalysis Society and the final paper (authored by A. Bussard and K. Dooley)
will be submitted to *Applied Catalysis A: General*. Chapter 5 discusses the development of a
novel reactor for three-phase catalytic reactions and its application to a test hydrogenation
reaction, comparing its performance to a stirred tank, and to other three-phase catalytic reactions
proposed in recent work. This chapter (authored by A. Bussard, Y. Waghmare, K. Dooley, and
F.C. Knopf) has been submitted to *Industrial Engineering & Chemistry Research*. Portions have
also been presented at the 2007 AIChE National Meeting in Salt Lake City, Utah. Chapter 6
details how this same reactor is applicable to a bio-feedstock (edible oil) hydrogenation. This
chapter (authored by Y. Waghmare, A. Bussard, F.C. Knopf, and K. Dooley) will be submitted
to *Industrial Engineering & Chemistry Research*. Chapter 7 summarizes the results and
discusses possible future work.
Chapter 2 Literature Review

2.1 Homogeneous Catalysis

Many polymer hydrogenation reactions are carried out using homogeneous catalysis, where the catalyst is present in the same liquid phase as the polymer. The main advantages of this catalysis are typically mild reaction conditions, high activities, simple stirred tank reactors, and the ability to better realize high conversions. The degree of hydrogenation is usually measured by monitoring the hydrogen uptake into the reactor system. Over the past several decades, most polymer hydrogenation research has been in homogeneous catalysis. Each hydrogenation reaction has been studied with many different transition metal complexes and solvents. The original homogeneous catalysts were Ziegler-type metallocenes (i.e. titanocene), which are still used today due to their low cost. These types of catalysts are often used in high concentrations (especially if at low temperatures and pressures) relative to polymer in order to achieve good reaction rates. However, this results in having to remove the catalyst from the product by expensive post-hydrogenation chemical treatments, such as precipitating the metals without degrading the polymer. Removing the metal is especially important for Ziegler-type catalysts since they can catalyze further reactions such as chain scission.

Research into using group 9 and 10 metal complexes to selectively hydrogenate C=C double bonds has also shown promise. Rhodium complexes such as Wilkinson’s Catalyst (Figure 2.1) can be used to hydrogenate NBR, styrene-butadiene rubber (SBR) and poly-butadiene (PBD) polymers without loss of sensitive functional groups. Excess PPh₃ ligands are usually added to the polymer / catalyst solution to prolong activity by blocking the reduction of Rh to the metal at elevated reaction temperatures.

Ruthenium complexes can also be used to catalyze polymer hydrogenations, though they are typically not as active as Rh complexes. Ru complexes often require ketone-based solvents to
prevent gel formation. Excess PPh₃ ligands are not necessary for this system, but the tradeoff is that Ru tends to promote crosslinking in NBR via reduction of nitrile groups to secondary amines. This means crosslinking inhibitors (e.g., CoSO₄ or carboxylic acids) must be added to the solution. Much recent research into homogeneous catalysts for polymer hydrogenations focuses on Ir- or Os-based organometallics with exotic ligands designed to increase selectivity to the desired level of hydrogenation. Post-reaction separation is important for these catalysts, not only to prevent further undesired product formation, but also to recover the precious metal.

![Figure 2.1 Wilkinson’s Catalyst, PPh₃ = triphenylphosphine.](image)

The best homogeneous catalyst for each reaction is generally known. The inherent weakness of all homogenous catalytic methods is the expensive and complicated polymer / catalyst separation requirement. Therefore, the future of polymer hydrogenation research lies in improving the heterogeneous catalysts and reaction methods.

2.2 Heterogeneous Catalysis

Palladium and platinum are the most useful active metals for polymer hydrogenation, although Pt is often avoided because it is much more active than Pd in catalyzing hydrocracking. Much still has to be learned about the relative activities of hydrogenation vs. chain scission, and about long-term catalyst deactivation, in order to see what will work economically.

2.2.1 Palladium Alloy Catalysts for Selective Hydrogenations

One method for improving selective hydrogenations is alloying or mixing the active metal with a less active transition or near-transition metal. Binary metal crystallites have been studied extensively, and it is believed that the ensembles of the active metal are disrupted by the
presence of the inactive metal in the crystallite. Increasing the Pd-Pd nearest neighbor atomic distance on the support prevents two adjacent carbons from both adsorbing on the surface. This step is believed necessary for chain scission to occur. A schematic of this process is shown in Figure 2.2.

![Figure 2.2 Schematic of chain scission mechanism on catalyst surface: (a) denotes surface adsorption, (b) denotes C-C bond breaking, (c) denotes hydrogenation followed by desorption.](image)

This brings about an important aspect of certain heterogeneous catalyzed reactions denoted “structure sensitivity”, which means a catalytic reaction’s selectivity depends upon the crystallite face or plane exposed, and its concentration of active metal. Structure sensitivity is believed to be dependent on two semi-independent factors: geometric and electronic effects. Diluting the active metal with a less active one can result in significant changes in d-band electron density; the d-band electrons are responsible for the \( \pi \)- and \( \sigma \)-bonding of the active metal to a hydrocarbon. The ensemble geometry can be altered even if there are only slight changes to d-band density, in effect creating islands of the active metal. Of course, alloying can also alter the crystallite structure significantly, producing new types of active sites - e.g. high energy steps, corners, and dislocations versus smooth planes of atoms.

An example of alloying to enhance the selectivity of PS hydrogenation is the 5 wt% Pd/BaSO\(_4\) catalyst of Gehlsen and Xu and coworkers. Gehlsen hydrogenated PS at 140°C and 3.4 MPa H\(_2\) in a stirred tank, saturating PS homopolymers with only minor amounts of chain scission, although the reactions required >12 h contact time. Conversely, Xu obtained high conversions in less than 10 h under conditions similar to Gehlsen et al. (1995), but with a
different solvent (decalin vs. 10% THF/cyclohexane for Gehlsen et al.). The role of the solvent on catalytic activity for polymer reactions is unclear.

The most common alloying element for Pd is Cu, although other metals such as Ag, Fe, Sn, Ni and Zn have also been used.\textsuperscript{25-29} The alloying effect of the second metal is particularly effective at Pd loadings greater than 1 wt\%.\textsuperscript{30} The key is to break up active metal clusters (geometric effect) while not significantly affecting the hydrogenation activity (electronic effect). Studies on CO and NO oxidation have shown that a homogeneous Pd/Cu bimetallic catalyst resists sintering by stabilizing zero-valent Pd.\textsuperscript{27,31} This same group also indicated that the bimetallic state was more thermodynamically stable than the monometallic one. Alloy catalysts can also lead to enhanced serial pathway selectivity in hydrogenations,\textsuperscript{25} which is of particular importance for polymer systems where it is believed chain scission occurs after hydrogenation to saturation.

Pd alloy catalysts are commonly made using co-impregnation techniques on dried supports, starting with the corresponding nitrate salt solutions at a pH of ~8.\textsuperscript{27,30,31} These salts are used because of their high water solubility, meaning higher loadings can be achieved, since a dry support will only imbibe a fixed volume at incipient wetness. More sophisticated methods such as atomic layer epitaxy\textsuperscript{29} or impregnation using organometallic solutions\textsuperscript{25} are also used, but it is not clear whether these methods are better than conventional impregnations. Wetted catalysts are dried, calcined in flowing O\textsubscript{2} or air, and reduced in dilute H\textsubscript{2} for several hours.

A key step in forming well-mixed metal solutions or alloys is to reduce the catalyst at >280°C, a temperature considerably higher than for Pd monometallic catalysts.\textsuperscript{30} Diagrams of different levels of metal interaction are shown in Figure 2.3. Good Pd/Cu interaction after reduction was shown through EXAFS/XANES, and the breakup of Pd surface clusters was shown via CO chemisorption, FT-IR spectroscopy of the CO adsorption bridging mode, and
XPS. But studies on \( \gamma \)-alumina have shown that surface segregation of Cu eventually occurs,\(^{29}\) probably due to the large difference in Pd/Cu atomic radii.\(^{30}\)

![Figure 2.3 Bimetallic metal cluster formation (dark atoms represent Pd, light atoms represent M, where M = Cu, Sn, Ag, Au): (a) M covering Pd; (b) Pd covering M; (c) metal segregation; (d) alloy formation.](image)

Even though the literature suggests some surface segregation (i.e., Cu covering Pd),\(^{29}\) the effect on activity may be small. This is because the surface composition at UHV or other vacuum is rarely observed under actual reaction conditions. The presence of strongly adsorbing species (e.g. olefins) can “trap” active metal at the surface,\(^{32}\) increasing activity beyond what was predicted from surface characterization methods. Venezia et al. (1996) indicated that for Ag-Pd systems a layer of Ag atoms covered the Pd (at UHV), yet the catalyst was still active.

Cu and Zn cluster with Pd with minimal electronic effect,\(^{25,33,34}\) only a slight charge redistribution from 4d to 5sp states at Pd sites.\(^{27,35}\) Such charge redistribution favors Pd/second metal interaction, slightly reducing the strength of alkenene/alkyne-Pd bonds, but with minimal effect on the Pd-H interactions. In theory, this type of clustering should result in better selectivity in (e.g.) alkyne hydrogenations to alkenes, with little effect on activity, as is indeed the case.\(^{34,36-38}\) It could also result in fewer closely-spaced multiple contacts of polymer with the metal surface, which presumably contribute to hydrogenolysis.

Alloy catalysts can also improve edible oil hydrogenations. For example, a 2.5 wt% Pd/Ag bimetallic alloy / silica catalyst lowers trans-fat formation by 10-20%.\(^{39}\) This same group also used a 2.1 wt% Ni/Ag catalyst and noted that while activity and saturation selectivity
improved, higher cis-trans isomerization occurred than for a pure Ni catalyst. While a Pd/Cu catalyst better resists sintering, and the oil hydrogenation kinetics are still largely dominated by the Pd, the presence of Pd may force Cu to the zero-valent state after reduction, and this state is less selective than Cu\textsuperscript{+1}. Engelhard (now BASF Catalysts) has examined precious metal catalysts to replace Ni. Their most recent “second generation” Pt catalyst produces no more saturated fats than Pd or Ni, but also lowers trans isomer formation to below 10 wt\%.

The most common method for making Pd bimetallic catalysts is non-selective deposition using an impregnation method and inorganic salt precursors. A bimetallic Pd/Cu/Al\textsubscript{2}O\textsubscript{3} catalyst (alloy formation confirmed using EXAFS and XANES) can be made by the incipient wetness impregnation of an aqueous Pd(NO\textsubscript{3})\textsubscript{2} and Cu(NO\textsubscript{3})\textsubscript{2} solution to achieve a pre-determined loading, followed by drying at \textasciitilde70-80°C, calcination in air at 400°C, and reduction at 280°C in pure H\textsubscript{2}. Another method may be to impregnate one metal followed by drying and reduction before adding the second metal.

One important consideration here is the order in which the metals are added to the support. Skoda showed that when Cu(NO\textsubscript{3})\textsubscript{2} was added to Pd/Al\textsubscript{2}O\textsubscript{3}, the result consisted of a Pd core surrounded by Cu (Figure 2.4). However, when they deposited Pd acetate onto CuO/Al\textsubscript{2}O\textsubscript{3}, they found good alloying in the surface layer. The same Pd/Cu bimetallic catalyst can also be made using a redox method where hydrogen is pre-adsorbed on Pd before addition of a Cu precursor. This is an example of a selective deposition where interaction occurs as a result of Cu being reduced by the PdH, leading to Pd\textsubscript{2}Cu formation. For these methods a final reduction step of no less than 400°C in 10% H\textsubscript{2}/N\textsubscript{2} was presumably required to homogenize the mixed metal. It is important to note that both non-selective and selective deposition methods typically do not show alloy formation until after reduction. This indicates that the selective deposition methods do nothing to further Pd/second metal interaction.
Since Cu has relatively “neutral” interactions with Pd, Sn can be chosen to study the effect of a metal that more influences the electronic structure of Pd. Sn will likely be present in a mixed oxide state, even after reduction at high temperature (up to 500°C). This is especially true as the Sn/Pd ratio increases. This suggests that Pd would act as an electron donor. However, Choi and Lee (2000) used XANES data to show that Pd in Pd/Sn/Al₂O₃ behaved similar to metallic Pd. Therefore, the exact nature of Pd/Sn interactions is not well understood. Another issue here is the possible formation of tin aluminates during reduction, for an alumina-supported catalyst.

These catalysts can be made using a wetness impregnation technique similar to Cu/Pd, although the Sn precursor is typically SnCl₂. An important consideration here is that Cl⁻ may induce support acidity, leading to significant sintering during reduction. The fact that bimetallic catalysts always need higher temperature reductions makes the sintering even worse. Choi and Lee (2000) reported a Pd dispersion of just 5.2% at a 2.0 wt% loading using the SnCl₂ precursor.

**2.2.2 Catalyst Supports for Macromolecular Hydrogenation**

As stated in Chapter 1, macromolecules can have difficulty diffusing into microporous catalytic supports, suggesting the need for larger pore sizes. For example, researchers at Dow Chemical used Pt on ultra-wide pore (UWP) silica to give a catalyst exhibiting modest activity for PS hydrogenation at low temperatures (~150ºC) and relatively high polymer concentrations (~15-25% polymer by weight), with little to no chain degradation. The UWP catalyst had a
surface area of 16.5 m²/g, a pore volume of 1.57 cm³/g, and an average pore diameter of 380 nm. Typically, catalysts with such large pores are avoided because of the correspondingly low surface areas. It is unknown why Dow made the UWP pore sizes so large, considering they are roughly 15 times the radius of gyration \( R_g \) of PS at reactor conditions. Chang\(^{12} \) hydrogenated triblock copolymer (SBS rubber) solutions at 80-180°C and 3.4 MPa using 0.5 wt% Pd/γ-Al₂O₃ and found an optimal average pore diameter of 39 nm, 64 m²/g surface area. However, they still encountered pore diffusion problems, resulting in >10 h for complete conversion. It might therefore be beneficial to use large surface area mesopore (2-50 nm pores, as defined by IUPAC) supports. The larger pore sizes also prevent pore blockage by coke or heavy oligomer formation.

Another important role of supports that has not been investigated for polymeric modification is how the support interacts with the reactant, and whether this will change the reaction dynamics. For instance, Monte Carlo simulations have shown polymer chain diffusion is significantly more hindered for a strongly adsorbing surface than a weakly adsorbing one.\(^{45} \) This would indicate that a more inert support such as a partly graphitized activated carbon would be better for hydrogenation reactions because it would make pore transport faster.

Polymer solutions do not always obey “no-slip” boundary conditions on the molecular level.\(^ {46,47} \) Slip is thought to occur because the chains exclude themselves from non-interacting surfaces, due to a reduction of possible chain conformations near the surface. The exclusion leaves a solvent-rich region near the wall lower in viscosity,\(^ {46} \) which may allow the polymer to more easily “slide” along the catalyst surface in pore diffusion. But this same exclusion of chains from the walls can also hinder the diffusion of polymers in some porous media, because the chain must exit the bulk solution to enter the pore environment in the first place (Figure 2.5). The pore itself is a confined space with fewer degrees of freedom – i.e., lower entropy. Although not explicitly stated in the literature, this would suggest intraparticle mass transfer might be
enhanced when non-interacting surfaces and long pores are present, while worsened in shorter pores, relative to interacting surfaces.

![Figure 2.5 Model of polymer diffusion from an area of maximum number of chain conformation to a pore (diameter d) that reduces the number of possible conformations.]

While an inert support like a hydrophobic carbon may enhance intraparticle transport, a support which interacts more with the polymer can promote intrinsic activity. Slightly acidic supports such as silica and alumina exhibit higher specific activities for the model hydrogenation of benzene over Pd, compared to powdered Pd,48 even though it is believed the reaction mechanism is unchanged. This has been attributed both to a metal-support interaction leading to structural modification of the metal and to the creation of additional sites at the metal-support interface.48,49 However, this increased activity from acidic sites can also translate into worse selectivity due to acid-catalyzed isomerizations.50 Whether or not this behavior would extend to the aromatic hydrogenation of PS has not been studied.

One problem with most Group VIII metal on carbon catalysts is low (4-15%) measured dispersions (using H₂ or CO chemisorption) at typical loadings of 0.4-3 wt%.51-53 The former
showed that the dispersion based on TEM particle size measurements (~20%) was substantially higher than that based on H₂ and CO chemisorption (~2-6%). Carbon from the support migrates into the bulk Pd crystals during reduction (e.g., at 300°C with 20% H₂/He) and occupies interstitial sites, and carbon layers partially cover the Pd crystal surface, blocking active sites and suppressing formation of the β-PdH phase (thought to catalyze hydrocracking) in the presence of H₂. This is significant for this project because it shows that a carbon support can alloy with Pd in a manner similar to bimetallic catalysts, where the second metal also usually disrupts formation of the β-PdH phase.\textsuperscript{26,38} The introduction of C into bulk Pd without forming surface carbon overlayers would be ideal, since chemisorption might be unaffected. Krishnankutty and Vannice (1995) showed that calcinations in 2% O₂ at 300°C was sufficient to burn off the carbon overlayer, but they also burned off the interstitial carbons. Subsequent reduction at 300 °C re-established both the carbon overlayer and the interstitial carbon. But according to others, carbon on the Pd surface is necessary to stabilize the presence of carbon in the bulk Pd crystal.\textsuperscript{54,55} It is unlikely that Pd/C catalysts can be made with carbon present in only the bulk Pd phase and not also present as an overlayer.

\textbf{2.2.2.1 Mesoporous Silicas and Aluminas}

Silica-based mesoporous supports (MCM-41, MCM-48) were first synthesized by Mobil Chemical in the early 1990s. MCM-41 has 2-D hexagonal symmetry while MCM-48 has a 3-D wormhole structure. MCM supports are made using cationic surfactants such as cetyltrimethyl ammonium bromide (CTAB), which strongly interact with anionic silica oligomers, forcing them to self-assemble into mesoscopically ordered composites.\textsuperscript{56,57} These supports typically have average pore sizes in the lower end of the mesopore spectrum, at 2-5 nm.\textsuperscript{58,59} MCM-41 can exhibit long range hexagonal order, yet much of the support may also adopt disorganized “wormhole” morphology.\textsuperscript{59} The disadvantage of MCM materials is that they cannot withstand
high temperature/moisture conditions found in most industrial processes, with pore collapse after exposure to boiling water for several hours. Increasing the MCM synthesis temperature generally increases the hydrothermal stability, until surfactant demicellization occurs. However, even by judiciously controlling synthesis conditions such as pH and temperature, MCM materials quickly degenerate when exposed to steam at ~600°C. They last only 150 h at ~100°C before complete collapse under hydrothermal conditions. Furthermore, silicas are less compatible with Pd, as they are known to form Pd silicides, which can deactivate the metal.

In recent work, steps have been taken to improve the stability of mesoporous silicates by incorporating minor amounts of Al into the structure using modified MCM-type synthesis procedures. These aluminosilicates typically have Si/Al molar ratios from 10-100. They can be formed by mesostructure templating around zeolitic seed precursors such as types beta or Y. These seeds are believed to improve hydrothermal stability by forming the basis for a zeolite-like wall structure containing some secondary building units, even though the walls remain somewhat disordered. The SiO₂ and Al₂O₃ precursors are usually tetraethylorthosilicate and aluminum isopropoxide, respectively. The organic templating agent is typically an amine (e.g., triethanolamine), which hydrogen bonds to silica or alumina precursors at a basic pH. Adding different types of zeolite to the mesophase has the secondary effect of inducing a desired level of acidic functionality to the support. These materials are steam-stable up to 800°C for short times. However, literature sources do not show how to give pore diameters greater than ~5 nm. Varying the surfactant/precursor concentration does not show a direct correlation with either pore size or distribution, nor is there a strong link between synthesis conditions and pore geometry.

In an effort to extend MCM-type synthesis to larger pore silicates, SBA-type materials have been synthesized from amphiphilic block copolymers. Using this method, pore sizes up to
30 nm are possible with both 2-D hexagonal and 3-D wormhole morphologies. SBA aluminosilicates have thicker walls than MCMs, leading to better hydrothermal stability.

In the most recent work, attention has turned to synthesizing mesophases based entirely on alumina. While these synthesis methods are similar to those for silica, achieving a long-range ordered structure as in MCM materials is difficult. It is unclear if long-range order is even required for hydrothermal stability. This is because most synthesis papers do not expose supports to adverse conditions for longer than a few (6-10) hours. Virtually all synthesis methods use templates (structure directing agents), and an alcoholic (EtOH, IPA) solvent.

Syntheses using alkyl carboxylic (e.g. lauric, stearic) acids as templates are driven by interactions between the acids and clusters of aluminum hydroxide. The mixture is aged at RT followed by thermal treatment at 80-200°C from 0-48 h, then dried and calcined using air at 400-600°C. The resulting mesoporous aluminas have pore sizes from 2-3 nm and surface areas as high as 600-700 m²/g. There is no correlation between length of surfactant chains, synthesis conditions, or calcination procedure and the resulting structure. However, pore size can be adjusted by adjusting the water/Al ratio. At water/Al molar ratios of ~50, pore diameters as high as 8 nm and surface areas of 400 m²/g can be produced. This may be due to a swelling effect of solvent micelles from the additional water. Adding iso-octane as a hydrophobic component in 1/1 molar ratio with the alcohol can also improve pore uniformity and increase pore diameter by ~1 nm. The pore structure is thermally stable to 550°C, but the PSD is broad.

Non-ionic surfactants used as templates include primary amines, polyethylene glycols (PEGs), and poly(ethylene oxide/propylene oxide/ethylene oxide) triblock copolymers (PEO/PO/EO). The triblocks are sold under the BASF trade name Pluronic® in various component ratios. These surfactants complex and/or H-bond to aluminum hydroxide clusters, with these precursors assembling around micelles and liquid crystalline phases.
The reagent used in this procedure is not the typical alkoxide, but instead a salt such as Al(NO$_3$)$_3$.\textsuperscript{67} This may be to provide a pH buffering effect. In a typical synthesis the surfactant/Al precursor/water mixture is adjusted to pH ~8, aged 6 h at RT, then hydrothermally treated for 24 h at 100°C. This results in a boehmitic alumina phase made of lamellar walls. After calcination for 4 h at 500°C, lathlike $\gamma$-alumina walls are formed.\textsuperscript{67} This is significant because no previous mesoporous synthesis method has resulted in such a well-defined wall structure. Pore diameters from 4-10 nm with surface areas of 250-350 m$^2$/g were obtained, but it proved difficult to remove the entire template. Hicks et al. (2003) reported carbonaceous contamination of the mesostructure after calcination. This is not surprising considering Pluronic surfactants have average MWs in the thousands and are prone to coking. While the resulting alumina was stable in air to 800°C, any significant amount of moisture will quickly reduce the porosity, even at room temperature.\textsuperscript{67} There was no observed connection between block copolymer composition and pore properties.

The difficulty of template removal during calcination motivated the Pinnavaia group to use primary amines (octylamine, dodecylamine) in place of Pluronic triblocks. The Al precursor is an alkoxide and the synthesis consists of aging for 20 h at RT, no hydrothermal treatment, and calcination at 325°C.\textsuperscript{66} This low temperature calcination resulted in amorphous boehmite materials with pore sizes 3-5 nm and surface areas 325-460 m$^2$/g. The PSD is characterized by a long tail and a FWHM of ~4 nm. As with syntheses using triblock templates, there was no link between amine chain length and pore size or surface area. The primary amine probably functions similarly to the block copolymers, mediating the size of boehmite nanoparticles.\textsuperscript{66} Why this method does not require hydrothermal treatment is not explained. The main advantage of the method is that all of the amine can be removed during calcination. The mesoporous boehmite can be further calcined to $\gamma$-alumina with a pore diameter as large as 7 nm at a surface area of 440 m$^2$/g.\textsuperscript{66}
Low molecular weight (200) PEGs have also been used as non-surfactant organic templates by Shan et al. (2003) to give alumina-based mesophases. The procedure consists of RT overnight aging of the PEG/Al alkoxide/water/alcohol suspension followed by drying and hydrothermal treatment for 2-24 h.\textsuperscript{65} Calcination results in wormhole-like morphology with pore sizes ranging from 4-20 nm and FWHM PSD of 1-2 nm.\textsuperscript{65} Calcination of the template does not result in residual contamination. Pore sizes can be tailored by lengthening the time or increasing the temperature of hydrothermal treatment. The literature claims the result is an alumina stable to 800°C in air, but effects of moisture are not discussed.\textsuperscript{65}

\subsection*{2.2.2.2 Mesoporous Carbons}

Most commercial activated carbon supports were micropores until recently. The only common method for producing mesoporous carbons is to use mesoporous silica as a template for the impregnation of a carbon precursor (a “replica” technique). The precursor is decomposed to carbon at \textasciitilde 900°C in inert gas, then the silica template is dissolved in strong acid or base. This leaves behind the inverse image of the silica — the pores of the carbon are located where the walls of the silica were. A schematic of the process is shown in Figure 2.6. Few groups have investigated the use of these materials as catalysts, which is significant because often the most difficult step in making a carbon-supported catalyst is to functionalize it with active metal. It is unclear how the steps required to produce a mesoporous carbon affect adsorption of Pd precursors.

Typical carbon precursors in these syntheses include sucrose solution,\textsuperscript{72-75} polystyrene dissolved in toluene,\textsuperscript{76} or furfuryl alcohol.\textsuperscript{77-80} Most of the literature focuses on aqueous-phase impregnation of the mesoporous silica, but a few papers examine deposition from the vapor phase.\textsuperscript{77,81} For the furfuryl alcohol carbon source, the precursor is polymerized by mild heating at
~80°C after impregnation in silica. Sometimes an organic acid catalyst such as p-toluene sulfonic acid (p-TSA) is added.\textsuperscript{79} This polymerization locks the carbon precursor in the pore space.

The most popular silica precursors are SBA–type, because the thick SBA walls (7-11 nm, vs. ~4 nm for MCMs) lead to larger carbon mesopores after template removal. At least one group\textsuperscript{80} makes the SBA silica in situ during the carbon synthesis, but most make the silica separately in order to verify the structure. A key choice is the desired crystal structure of the silica precursor. Many in the literature start with SBA-15 which results in an ordered 2D array of carbon pores. However, for catalytic purposes this may be a poor choice, because a 2D pore network is more easily blocked. 3D structures such as MCM-48 and SBA-16 therefore have an advantage for catalytic applications even though their pore networks are less ordered.

Figure 2.6  Replica technique for making mesoporous carbons: (a) represents adding carbon precursor to the pores of the silica template and carbonizing; (b) represents removal of the silica template; (c) represents addition of active metal to pores of the mesoporous carbon.
Another way to produce mesoporous carbons, this time as films, is by a template method using a block copolymer template instead of a mesoporous silica.\textsuperscript{82,83} For example, a Pluronic, an organic acid catalyst (p-TSA), a homopolymer (poly-acrylic acid (PAA)), and an alcoholic solvent can be coated on a substrate and annealed. A carbon precursor (furfuryl alcohol) is infused into the template matrix under supercritical CO\textsubscript{2} conditions to enhance the solubility by swelling the block copolymer. The as-impregnated film is then carbonized. The advantage of this method is that there is no need to pre-synthesize a mesoporous silica, and so the carbon can be directly coated onto a pre-fabricated structure such as a monolith. The homopolymer addition acts to strengthen the resulting carbon film.\textsuperscript{83}

\textbf{2.2.3 Macromolecular Transport in Confined Media}

Experimental evidence has shown the turnover frequency for aromatic hydrogenation using a Pd/metal oxide catalyst decreases as: benzene $>$ toluene $>$ p-xylene $>$ m-xylene $>$ o-xylene even though activation energies are similar for all compounds (Figure 2.7).\textsuperscript{50} This trend is probably due to steric hindrances arising from the presence and location of the methyl group. Clearly if one extends this trend to macromolecules it is obvious that they will experience much more resistance to intraparticle diffusion inside microporous catalysts.

\begin{center}
\begin{tikzpicture}
\node (benzene) at (0,0) {\includegraphics[width=1cm]{benzene.png}};
\node (toluene) at (1.5,0) {\includegraphics[width=1cm]{toluene.png}};
\node (p-xylene) at (3,0) {\includegraphics[width=1cm]{p-xylene.png}};
\node (m-xylene) at (4.5,0) {\includegraphics[width=1cm]{m-xylene.png}};
\node (o-xylene) at (6,0) {\includegraphics[width=1cm]{o-xylene.png}};
\end{tikzpicture}
\end{center}

\textbf{Figure 2.7} Various aromatic compounds arranged in decreasing activity for hydrogenation activity.
The “hindered diffusion” mechanism of polymer transport into mesoporous pores has been studied both experimentally and by numerical simulation, usually configurational Monte-Carlo methods. The biggest shortcoming of both the experiments and the simulations is that they used highly dilute solutions, whereas actual reaction systems consist of more concentrated solutions. Many simulations assume hard sphere polymer geometry and perfectly cylindrical pores. Approximating a dendritic polymer chain as a hard sphere and a flexible linear polymer as a random coil diffusing into a cylindrical pore are supposedly valid at size ratio $\lambda<0.25$ ($\lambda$ is the ratio of the polymer hydrodynamic radius ($R_h$)/pore radius ($R_p$)). However, $\lambda$ is not always the defining length scale that dictates diffusion in porous media. Others used dynamic light scattering (DLS) to show a highly branched polymer will diffuse slower than a linear one, even when the hydrodynamic radii are equal. Easwar and Langley noted that for linear polymers the characteristic scaling dimension for diffusion was only half of $R_h$, but was $\sim R_h$ for highly branched polymers. The idea that the effective $R_h$ for a polymer in a pore can be smaller than in bulk solution originated with De Gennes. In other words, pore wall/polymer chain interactions (attraction or repulsion) play an important role in affecting the polymer’s conformation inside the pore, which is something not taken into account in most simulations. Another shortcoming of most numerical simulations is that they are based on a single pore, as opposed to the reality of a random, often interconnecting pore network. These simulations often do not accurately predict the effects of varying pore size distributions, tortuosity, or pore constrictions (i.e., “ink bottle” effects) on rates of diffusion.

In the limit of highly confining pores ($\lambda>0.6$), Muthukumar and Baumgartner proposed a reptation model that is dominated by entropic barriers or traps limiting diffusion of polymer chains. The traps were simulated as bottlenecks that connected an infinite array of cubic boxes. This theory has been confirmed by DLS experiments of Easwar et al., whose data followed the
model predictions — the diffusion rate decays exponentially as chain length N increases for weakly confined polymers, but is independent of N, depending on the pore cross section, for strongly confined chains. Guo and co-workers observed surface (silica, 10-20 nm pores) interaction effects with the diffusing polymer (linear polystyrene in fluorobenzene, a good solvent) using forced Rayleigh scattering. They noted that strongly adsorbing surface sites (hydroxyls) greatly impeded the rate of diffusion, in contrast to non-interacting surfaces.89

Inside pores, good solvents disentangle the polymer while in poor solvents the polymer adopts a globular conformation. But there have been few experimental studies of solvent effects on polymer diffusion in porous materials. Light scattering experiments require the solvent to nearly match the refractive index of the porous glass medium that must be used. Another complication is the impact of high temperatures/pressures. Light scattering experiments are usually done at room temperature and atmospheric pressure. It is unknown how actual reactor conditions in hydrogenations will affect intrapore polymer configurations and therefore the effective hydrodynamic radius \(R_h\) or radius of gyration \(R_g\). A high shear rate near a surface will also disentangle polymer chains, reducing intramolecular interactions so that the solution behaves like it is less concentrated.90

Most recently, Sikorski and Romiszowski (2007) have used Monte Carlo simulations to examine the transport of a polymer chain trapped between two parallel planes (slit) with random rod-like barriers inside the slit. They found the interesting result that for a slit with no barriers, the containing cyclic groups had the highest mobility followed by the star polymer. The linear polymer had the lowest diffusivity.91 However when the barriers are present, the linear polymers exhibit the highest mobility followed by the star polymer and finally the cyclic polymer. The star behaves similarly to the linear polymer for low values of chain number (N~70-100) but the differences are magnified at N~200-1000, where the diffusion coefficient for the star polymer is
two orders of magnitude less, with barriers. They attributed the difference in transport behavior between the linear, star, and cyclic containing polymers to differences in the allowed molecular motion for each polymer. Therefore, this shows that the pore morphology (constrictions, etc.) can have a pronounced impact on intraparticle transport depending on the polymer geometry.

2.3 Reactor Systems for Continuous Polymer Modification Reactions

Virtually all current PS hydrogenation papers use conventional stirred tank reactors run in batch or semi-batch mode. These papers focused on PVCH characterization rather than the effects of the reactor system or catalyst. Other hydrogenations of less viscous non-polymeric materials (e.g., nitrobenzenes, acetylene, styrene, α-methylstyrene (AMS), isolefins) have been examined in continuous systems. The reactors most commonly examined are those containing a catalyst monolith or other structured packing, or trickle beds.

2.3.1 Packed Bed Reactors

While trickle beds offer several advantages, including the ability to operate reliably over a relatively wide range of gas-to-liquid (G/L) ratios, a significant problem for them remains maldistribution — concentration of liquid in rivulets that reduce wetting efficiency. This is especially true for downflow trickle beds that operate under low liquid superficial velocities in order to avoid large pressure drops. In the case of a gas mass transfer-limited hydrogenation, maldistribution may sometimes increase global reaction rates as some particles have thin liquid films, and these present less resistance to mass transfer of the gas. This explains why, for trickle bed operation at low pressure and/or high liquid feed concentration (i.e., gas mass transfer-limited), downflow outperforms upflow operation. At high pressures and/or low liquid feed concentrations (liquid mass transfer-limited), the improved liquid contacting efficiency of upflow is desired. The differences become minute as liquid flow rates increase past the trickle flow regime. Poor liquid distribution can lead to reactor hot spots, catalyst deactivation, and poor
selectivity. These problems have given rise to specialized catalyst-coated packings to try to make flow distribution as even as possible.

One method which can improve liquid distribution in packed bed reactors is to introduce a pulsing flow by periodically modulating gas or liquid flows.\(^{96-101}\) In other words, the trickle bed is operated in an unsteady-state mode such that during the gas-rich cycle the gas phase reactant can easily diffuse through a thin or nonexistent liquid film to the surface of the catalyst. The liquid-rich cycle provides liquid phase reactant and flushes product from the surface, while also providing good heat transfer rates. Khadilkar et al. (1999) and Lange et al. (1994) reported activity enhancements up to 60% and 10%, respectively for AMS hydrogenation in a pulsed trickle bed using a Pd/Al\(_2\)O\(_3\) catalyst. Pulsing may also prove favorable for serial pathway selectivity, where the goal is to remove the desired intermediate product from the surface of the catalyst. Wilhite and co-workers (2003) noted a 45% increase in styrene selectivity during phenylacetylene hydrogenation by pulsing the liquid feed.\(^{102}\)

The pulse behavior in trickle beds is largely governed by column dimensions and superficial gas and liquid velocities. Boelhouwer et al. (2002) performed an in-depth analysis, and they noted the inherent impracticality of liquid feed pulsing at relatively high frequencies, where pulse coalescence of the shock waves occurs down the length of the column. For instance, for an on-off cycled feed the time between liquid pulses had to be at least 120 s in a column that was only 3.2 m tall in order to avoid shock wave coalescence. However, they did show that by increasing superficial gas velocities and keeping pulse times short, stable pulse behavior at up to 1 Hz could be attained, even though the shock waves still decayed somewhat. Boelhouwer et al. (2002) showed that pulse properties such as liquid holdup and velocity are only dependent on superficial gas velocities, while superficial liquid velocities only affect pulse frequency.
Nevertheless, controlling pulse behavior inside of a trickle bed is difficult and only feasible over a narrow operating range of frequency, superficial velocities and column length.

![Figure 2.8 Schematic of a packed bed reactor operated in countercurrent mode.]

2.3.2 Catalyst Monolith Reactors

Catalyst monolith reactors have traditionally been restricted to automotive and combustion applications where a low pressure drop is particularly desirable. Their use in three-phase reactors has only recently been studied. They do offer a high specific surface area per unit volume and good liquid distribution. When compared to packed beds, monoliths are several times more efficient on a volume basis in many transport-limited reactions, due to the thin, well-mixed liquid films that can develop when gas slugs are forced through the channels. Monoliths may also require only a fraction of the energy input for mixing when compared to a stirred tank.
reactor at equivalent performance.\textsuperscript{104} Unlike trickle beds, which typically operate with gas/liquid volumetric ratios of 2:1 to 10:1 or greater, hydrodynamically stable monoliths usually operate between 1:1 to 3:1 ratios.\textsuperscript{105} Most of the monolith literature is devoted to studying the two phase slug (Taylor) flow (Figure 2.9). The thin film separating the gas slug from the catalyst-coated monolith minimizes the gas-solid diffusion length.\textsuperscript{93} Plug flow-like behavior exists inside the monolith because the gas slugs in Taylor flow force the reactants through the channels with little backmixing. This hydrodynamic behavior has the effect of improving reaction selectivity since the residence time distribution is tightly controlled.\textsuperscript{106} With Taylor flow, there is inherent pulsing behavior because the gas and liquid slugs alternate down the channel.

![Figure 2.9](image)

**Figure 2.9  Schematic of Taylor flow in a cylindrical capillary channel.**

Some argue that catalyst monolith reactors are already sufficiently active for hydrogenations in the Taylor flow regime.\textsuperscript{104,107} However, they are far from ideal at the more common gas/liquid volumetric rates (G/L >1) where trickle beds are typically used. At these conditions, liquid/gas distribution is just too uneven. There are other reactor parameters that greatly affect performance. One of these is the design of the gas distributor. Since gas slugs are responsible for the enhanced performance of the catalyst monolith, having a distributor that gives a homogeneous bubble dispersion is critical. Significant variations in hydrodynamic behavior have been noted for different distributor designs and positions within monolith reactors.\textsuperscript{108} For distributors placed too close to the monolith segments, preferential gas flow through the center was observed. Placing the distributor far away led to flow along the walls of the reactor, around
the monolith stack. For an optimal reactor design, the location of the distributor will clearly have a large impact on performance.

Although most monolith reactor research deals with the conversion of low molecular weight reactants, viscous effects can also play an important role in flow behavior. MRI studies from Heibel et al. (2003) noted that a sucrose solution with twice the viscosity of water led to an increase in the thickness of the liquid film surrounding the gas slugs. This is in agreement with earlier work which noted higher viscosities leading to more favorable conditions for column flooding. A thicker liquid film would reduce the rates of mass transfer by increasing the diffusion length.

2.4 Concluding Remarks

PS hydrogenation is interesting as a case study, but the ultimate goal of the project is to improve the heterogeneously catalyzed hydrogenations/dehydrogenations of macromolecules, both from an activity and selectivity standpoint, and especially in more viscous solutions or melts. PS, AMS and edible oil hydrogenations are simply ways to test the effectiveness of our reactors and catalysts. Though not directly part of this project, I believe other reactions such as the reforming of biomass can benefit from what is learned here. Current hydrogenation reactor/catalyst schemes have significant shortcomings including selectivity problems and low activity due to poor rates of mass transfer. These problems can be addressed by the simultaneous study of novel reactor designs along with new catalytic materials.
Chapter 3 Polymer Hydrogenation in Pulsed Flow Systems with Extrusion

3.1 Introduction

The ability to chemically modify polymers has recently engendered increased interest as a way to economically develop new materials. With chemical modification, there is no need to develop a new process for the monomer(s), and certain structures of commercial interest are only available synthetically through polymer modification reactions. Such reactions may also improve material properties such as resistance to chemical degradation and mechanical strength. Therefore, polymer modification reactions provide another way to individually tailor polymer architectures for a specific use. One type of reaction that has been researched extensively is the modification of poly(butadiene) (PBD). Alternating double bonds in PBD allow the addition of functional groups by either homogeneous or heterogeneous catalysis. The simplest PBD modification reaction is hydrogenation. More elaborate modifications such as the synthesis of PBD polyols are also possible, but only with careful control of the extent of backbone functionalization and the prevention of cross-linking.

While several PBD modifications have been successful, the heterogeneously catalyzed hydrogenation of poly(styrene) (PS) to poly(vinylcyclohexane) (PVCH) (Figure 3.1) has proved more difficult. This is because the stabilizing effect of the aromatic ring resists hydrogenation at mild reaction conditions. While PBD can be completely saturated at 343 K and 3.5 MPa, PS hydrogenation conditions typically range from 412-473 K at pressures of 3.5–6.9 MPa, while still requiring 8-24 h for near-complete conversion. These high temperatures can also reduce molecular weight (MW) through backbone chain scission. High pressures are particularly necessary in stirred tanks because the catalyst particle is fully wetted, meaning hydrogen must always overcome gas-liquid and liquid-solid mass transfer resistances.

literature studies have focused exclusively on processing in batch stirred tanks,\textsuperscript{9,10,24,92,111} while one source has investigated the use of catalyst-coated monoliths mounted on stirrers.\textsuperscript{101} Stirred tanks, where the catalyst is present in the form of a slurry, are less practical since the catalyst must be filtered from the products post reaction. Continuous processing is also usually preferred over batch mode.

\begin{center}
\begin{tikzpicture}
    \node (polystyrene) [circle, draw, minimum size=1cm] {
        \includegraphics[width=1cm]{polystyrene.png}
    };
    \node (catalyst) [above right of=polystyrene, xshift=0.5cm, yshift=-0.5cm] {catalyst};
    \node (polyvch) [right of=polystyrene, xshift=1cm] {
        \includegraphics[width=1cm]{polyvch.png}
    };
    \node (h2) [above of=catalyst, yshift=-0.5cm] {3H$_2$};
    \draw[->] (catalyst) -- (polyvch);
\end{tikzpicture}
\end{center}

\textbf{Figure 3.1} \textit{Hydrogenation of poly(styrene) to poly(vinylcyclohexane).}

Current commercial three-phase reactors, such as packed beds operated in trickle flow mode, are ill-equipped to deal with polymer systems. As is well known, these reactors can suffer from rivulet formation and inhomogeneous residence time distributions (RTD); higher viscosity polymer solutions exacerbate these problems. A large variation in RTD can also contribute to poor reaction selectivity where the pathway is serial in nature and an intermediate product is desired.\textsuperscript{100} Research to improve mass transfer rates and control surface wetting for three-phase systems has recently focused on pulsed-flow operation, where alternating gas- and liquid-rich conditions exist at the surface of a catalyst.\textsuperscript{96-98,100,112,113} Pulsed flow can realize certain advantages of partial catalyst wetting. During the gas-rich cycle, the gas is supplied to the surface with minimal liquid film resistance. The liquid-rich cycle supplies fresh reactant, while flushing away product and providing a high rate of heat transfer. This method of deliberate unsteady-state operation has been shown to enhance reaction rates for the hydrogenation of
alpha-methylstyrene (AMS) in a packed bed.\textsuperscript{96} It is also believed this type of flow can enhance serial pathway selectivity by giving a more uniform RTD.\textsuperscript{100} Boelhouwer et al.\textsuperscript{100} noted there should be an optimal frequency for such pulsing in order to minimize side products, and that this optimum would be governed by the rates of heat generation and reaction. However, they also noted the inherent impracticality of pulsing trickle beds at high (beyond 1 Hz) frequencies in large (>3 m) columns where pulses would coalesce and decay unless other operating conditions, such as superficial gas velocity, were not within a narrow range.\textsuperscript{100} Predicting optimal pulsing conditions (e.g. frequency, amplitude) is difficult since they are a function of reactor dimensions, operating conditions, and certain characteristics of the reaction.

Monolith reactors operated in the Taylor (slug) flow regime have also been investigated for improved three-phase reactor operation.\textsuperscript{105,107,114,115} They have also shown rate enhancements for AMS hydrogenation compared to conventional stirred tanks.\textsuperscript{115} Taylor flow consists of inherent pulsing behavior in monolith channels, with intermittent gas slugs. Such flow exhibits high rates of mass transfer because each liquid slug is well-mixed and the gas slugs are surrounded by only a thin liquid film, minimizing the gas diffusion length.\textsuperscript{116} These reactors can also approach plug flow behavior,\textsuperscript{115} thereby improving serial pathway selectivity in some hydrogenations, compared to trickle beds.\textsuperscript{115} Heibel et al.\textsuperscript{108} noted that increasing viscosities would give thicker films surrounding gas slugs, which would presumably reduce the rates of mass transfer.

Because the extension of these pulsed systems to the modification of polymers has never been realized, it would be beneficial to examine the effects of pulsed operation on a model reaction like PS hydrogenation. Extruders, commonly used for polymer melt processing, exhibit flow instabilities as a result of partial screw filling.\textsuperscript{117} In this mode of operation (i.e., liquid-starved), alternating regions of gas and polymer are transported along the extruder barrel where
they affect flow at the exit die (e.g., surging or spurt flow). Therefore, extrusion in gas-liquid systems also exhibits unsteady flow behavior similar to that of monoliths and pulsed trickle beds. While most researchers have tried to limit oscillatory extruder behavior because it is often detrimental to materials processing, our goal is to use this behavior to our advantage in the reaction. This paper focuses on the applicability of pulsed flows to polymer modification reactions, and on combining the inherent unsteady flow of the extrusion process with heterogeneous catalysis in a novel reactor system that can improve polymer hydrogenation.

3.2 Experimental

3.2.1 Catalyst Preparation

A Pd/\(\gamma\)-Al\(_2\)O\(_3\) catalyst was prepared by ion exchange. Pseudoboehmite (UOP Versal V-250) was calcined at 773 K in flowing air to dehydroxylate to the \(\gamma\)-phase. A Pd(NH\(_3\))\(_4\)(NO\(_3\))\(_2\) solution was prepared from PdCl\(_2\) by dissolving in excess aqueous ammonia and NH\(_4\)NO\(_3\) at a pH of 11. The Cl\(^-\) was removed by contacting the solution with an ion exchange resin (IRA-400, Rohm and Haas). This solution was then mixed with the alumina at 333 K overnight. The resulting solid was filtered, dried at 353 K, then calcined at 773 K in flowing air, and finally reduced at 403 K in 10\% H\(_2\)/N\(_2\). The catalyst had a final Pd content of 0.5 wt\% (determined by ICP-AES) after three consecutive ion exchanges, with drying, calcining, and reduction done after each exchange.

This catalyst was either washcoated on 100 cells per square inch cordierite monoliths with cylindrical channels (0.2 cm channel diameter, 1.2 cm length) or pressed into 20-35 mesh pellets. Washcoating took place from a stirred aqueous slurry, at 25 wt\% solids content, with 0.1 mol/L nitric acid added dropwise during the process to maintain the pH at 3.5-4. An acidic pH creates charge barriers that prevent the alumina particles from aggregating\(^{118}\). The slurry was then ball milled for 90 min to reduce the average particle size below 10 \(\mu\)m. This was verified by
examining the particles before and after milling by SEM. Ball-milled samples were stable for
days without stirring. Dry, bare monoliths were dipped into the slurry and excess slurry removed
with compressed air. As-coated monoliths were dried at 363 K, calcined at 773 K, and reduced at
403 K in 10% H₂/N₂. This resulted in repeatable washcoat loadings of 4 wt% at a coating
thickness of 100 µm. The final catalyst had a BET surface area of 290 m²/g (determined using a
Quantachrome AS-1) and a dispersion of 74% by H₂ chemisorption (determined using a
Micromeritics 2700). Using the Barrett-Joyner-Halenda algorithm, the average pore size was
found to be 10 nm with a full width at half maximum of 4 nm based on the desorption branch.

3.2.2 Reactor Setup and Procedure

The pulsed reactor was based on a research grade twin-screw extruder (Haake Rheocord
9000). A schematic of the system is shown in Figure 3.2. The counter-rotating screws have a L/D
aspect ratio of 13. Custom-made dies housing the catalyst (packed bed or monolith) was placed
at the exit of the extruder. The square die held square catalyst-coated monoliths (5.75 cm sides,
1.2 cm length), and was shaped to match the monolith dimensions. The cylindrical die (1.75 cm
diameter, 15.5 cm length) held a packed bed of catalyst particles. The mean residence times were
from 10-56 min for the monolith die and 16-73 min for the packed bed die. The PS (Dow Styron,
MWₗ = 230 kg/mol) was dissolved in a mixture of 10 vol% THF/cyclohexane⁹ (cyclohexane,
Sigma-Aldrich, 99+%; THF, Fisher, 99.9%) at a concentration of 2 or 10 wt%. This solution was
pre-mixed with hydrogen at high pressures in a stirred tank before both phases were fed to the
extruder at the screw head. The screw speed was held constant at 10 rpm. Heating bands around
the barrel and die provided temperature control. A photocell positioned at the die exit recorded
flow instabilities in the form of voltage changes. In order to better control pulse frequency, a
computer-controlled solenoid valve was attached to the extruder barrel so that additional
hydrogen could be injected into the system at user-defined intervals. This mode of operation is
referred to as forced pulsing. The polymer solution was fed by a piston pump (Eldex B-100-S-4) such that the level in the stirred tank was constant. Hydrogen flow into the system was recorded by mass flow controller (Brooks 5850C). When not in operation, the reactor was left under 0.34 MPa hydrogen partial pressure to keep the Pd catalyst in the reduced state.

Figure 3.2  Schematic of the pulsed extruder-reactor.

Several experiments using a high pressure stirred tank (Autoclave Engineers Zipperclave, 500 cm$^3$) reactor were also done for comparison purposes. The impeller was a three-bladed marine propeller with no gas sparger or baffles. The catalyst was present as either a powder or a catalyst-coated monolith placed at the bottom of the reactor. The stirred tank was operated at 2600 rpm and 423-453 K with 2 and 10 wt% PS solutions. The reactor could be intermittently
sampled through a dip-tube. This reactor was also maintained under hydrogen purge between runs to maintain the catalyst’s reduced state.

Conversion was determined using a Jasco V-570 UV-Vis spectrometer, by monitoring the decrease in absorbance of the aromatic peak at 262 nm of samples diluted in chloroform (Mallinckrodt, 99.9%). This absorbance was correlated to the conversion of aromatic groups using a linear calibration developed from $^1$H-HMR data on samples reacted to various conversions in a stirred tank. The NMR data were related to aromatic group conversion according to Gehlsen et al. The reactor was operated in single-pass mode with a limited amount of catalyst, such that PS conversions were low (2-7%). Polymer molecular weight changes were monitored by performing intrinsic viscosity measurements on product samples dissolved in toluene based on standard Mark-Houwink constants for polystyrene. Selected liquid samples with the polymers removed through distillation were analyzed by GC-MS (HP 5972). Key extruder / reactor measurements were interfaced to LabView® through an MIO-16E data acquisition card (National Instruments).

3.3 Results and Discussion

3.3.1 Flow Behavior in the Pulsed Reactor

The range of two-phase flow for PS hydrogenation in the extruder-fed reactor was from G/L (ratio of volumetric flow rates at reaction conditions) of 0.5 at 2.0 MPa to G/L = 1.2 at 3.5 MPa. Below 2.0 MPa, there were periods of little to no gas exiting the extruder. Above 3.5 MPa, G/L did not significantly increase. The range of superficial gas and liquid velocities ($u_G$ and $u_L$) explored in this study was 1-16 cm/h, calculated using the channel diameter. To our knowledge, no previous work to develop flow regime maps at such low flow rates and with viscous polymeric systems has been published. However, extrapolating data from flow maps in similarly sized circular channels indicates operation in the slug flow regime, which is confirmed by
experimental data from the photocell. Figure 3.3 shows the time evolution of gas holdup for the two phase flow exiting the die as recorded by the photocell. The flow is discontinuous with alternating gas (low photocell voltage) and liquid slugs (high photocell voltage), characteristic of a liquid-starved extruder. These regions of discontinuous gas- and liquid-rich flow arise within the screw flights and persist through the monolith channels inside the die. Taylor (slug) flow is usually the desired mode of operation for three-phase monolith reactors, when reactions are highly gas mass-transfer limited.

Figure 3.3(a) shows the natural pulsing behavior of the reactor while Figure 3.3(b) shows the effects of forced pulsing at 0.1 Hz. Forced pulsing resulted in periodic spikes in gas flow in the monolith. These large gas slugs are superimposed on the pulses inherent to the system. Spikes in gas flow appear as lower voltages of ~20 s duration, centered around 40 s and 90 s in Fig. 3.3(b). The exit age distribution of these spikes could not be controlled by varying the inlet pulsing frequencies from 0.1-0.5 Hz for either the 2 or 10 wt% PS solutions. Other attempts to control the exit distribution of these spikes by varying flow rates, pressures, and screw speed were also unsuccessful. Pulsing at 0.5 Hz did result in longer gas spikes exiting the extruder, but nevertheless the average pulse frequency at the exit was similar to that for 0.1 Hz and for unforced operation (Table 3.1). In other words, the impact on the average frequency of occasional large gas slugs was small, but the average amplitude of the exit pulses did decrease as the forced pulsing frequency increased (Table 3.1), indicating more foam.

No changes in the die or barrel pressure greater than 25 kPa were measured in any experiment, either with natural or forced pulsing. The inability to control the average exit pulse frequency is most likely due to gas backmixing in the extruder barrel and bubble coalescence prior to the die exit. Problems associated with controlling pulse behavior due to coalescence have also been reported in previous work on pulsed trickle beds.
Figure 3.3  Alternating gas/liquid flow from catalyst monolith operated under: (a) unforced (natural) pulsing conditions, with flow initiated at 45 s; (b) forced pulsing, 0.1 Hz. Voltages near 220 mV in (a) and 230 mV in (b) represent slugs of gas; voltages near 240 mV in (a) and 250 mV in (b) represent slugs of liquid.

Table 3.1  Average pulse characteristics for forced and unforced pulsing.

<table>
<thead>
<tr>
<th>Forced Oscillation Frequency</th>
<th>Average Outlet Frequency</th>
<th>Average Amplitude</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Hz)</td>
<td>(Hz)</td>
<td>(mV)</td>
</tr>
<tr>
<td>None</td>
<td>0.13</td>
<td>8</td>
</tr>
<tr>
<td>0.1</td>
<td>0.14</td>
<td>6.5</td>
</tr>
<tr>
<td>0.5</td>
<td>0.16</td>
<td>2.5</td>
</tr>
</tbody>
</table>
3.3.2 Hydrogenation Studies

The only observed product was hydrogenated PS (PVCH). Previous work\textsuperscript{24} has shown PS hydrogenation over Pd catalysts to be first order in aromatic concentration ($C_A$) and zero order in hydrogen concentration ($C_H$) for $\leq 3$ wt$\%$ PS in stirred tanks at greater than 3.0 MPa. At high rates of agitation (e.g., $>2000$ rpm) there were no significant external liquid, intraparticle, or gas-phase concentration gradients. Below 3.0 MPa, the dependence on hydrogen concentration was linear.\textsuperscript{24} Using these results, observed rate constants for the reactor at lower pressures were determined by modeling the system mass balance as a plug flow reactor with first-order kinetics dependencies for both reactants (Eq. 3.1), using the reaction stoichiometry of Fig. 3.1. In the limit of zero resistances to mass transfer, the $k_{obs'}$ in Eq. 3.1 is the intrinsic rate constant for the reaction. From $k_{obs'}$ a pseudo-first order (in aromatic group) rate constant ($k_{obs}$) was calculated (Eq. 3.2) by multiplying by a reference hydrogen concentration $C_{Hr}$ ($0.238 \text{ mol H}_2/\text{L}$, the solubility in cyclohexane at 3.4 MPa and 453 K). In this manner we obtained a $k_{obs}$ that was independent of $H_2$ pressure. Both $C_{Hr}$ and the feed concentration $C_{Ho}$ were obtained using the Henry’s Law coefficient for hydrogen solubility in cyclohexane,\textsuperscript{121} thereby assuming that the small amounts of THF and PS did not significantly impact the solubility of $H_2$ in the solvent.

\begin{equation}
W = \frac{v_o}{k_{obs'}} \int_0^X \frac{1}{(C_{Ho} - 3 \cdot X \cdot C_{Ao})(1 - X)} dX \quad (3.1)
\end{equation}

\begin{equation}
r_{obs} = k_{obs'} C_A C_{Hr} ; \quad k_{obs} = k_{obs'} C_{Hr} \quad (3.2)
\end{equation}

The pulsed reactor was operated at lower pressures and power/volume (P/V) ratios than the agitated vessel, but gave similar results for $k_{obs}$. For the agitated vessel at $>3.0$ MPa, $k_{obs}$ was computed using a batch reactor mass balance, with kinetics dependencies of first order in aromatic concentration and zero order in hydrogen. This method allowed rough quantitative comparisons between the two modes of operation.
To investigate the effects of washcoating the catalyst on a ceramic monolith, reactions were performed in the agitated vessel using the catalyst present as either a powder ground to 100-120 mesh or as a washcoated monolith at the bottom of the stirred tank. The results of these runs are summarized in Table 3.2. At temperatures of both 423 and 453 K, \( k_{\text{obs}} \) was independent of catalyst form, proving the washcoated monolith is chemically identical to the powdered version. Increasing the hydrogen partial pressure to 5.5 MPa did not result in a higher rate of reaction, indicating that the \( k_{\text{obs}} \) values at high rpm in Table 3.2 are representative of the intrinsic kinetics at their respective conditions, and that these kinetics are indeed zero-order in \( \text{H}_2 \) at high pressures. Xu et al.\textsuperscript{24} reported intrinsic activities of \( 3.2 \times 10^{-5} \text{ L} \cdot \text{s}^{-1} \cdot \text{gPd}^{-1} \) at 423 K and \( 1.4 \times 10^{-4} \text{ L} \cdot \text{s}^{-1} \cdot \text{gPd}^{-1} \) at 453 K for a 5 wt% \( \text{Pd/BaSO}_4 \) catalyst. These values are similar to those reported in Table 3.2 for both powdered and monolith-supported catalysts. However, a direct comparison between the intrinsic activities of the catalysts used by Xu et al. and in this study is difficult due to differences in catalytic properties (e.g., Pd dispersion) as well as the effects of the solvent (Xu et al. used decahydronaphthalene).

To determine if intraparticle gradients were present, Weisz-Prater moduli\textsuperscript{122} (C\text{WP}) were computed based on the highest observed rates for both the monolith-supported and powdered catalysts at 2 wt% PS. The diffusivity of \( \text{H}_2 \) was calculated using the Wilke-Chang correlation,\textsuperscript{123} and from this an effective diffusivity was obtained using average catalyst properties. The hydrogen solubility was obtained from the literature.\textsuperscript{121} The modulus for 2 wt% PS was 0.02 for the powdered catalyst and 0.03 for the monolith-supported catalyst. This confirms that for the 2 wt% PS system, pore diffusion is neither limiting nor significant.

Figure 3.4 shows results for the hydrogenation of a 2 wt% PS solution for a monolith die, no forced pulsing. Also plotted is a correlation for the gas to liquid mass transfer coefficient times the interfacial area per volume (\( k_{\text{gl}} a_{\text{gl}} \)) for slug flow in monoliths. The \( \text{H}_2 \) concentration
gradient in the liquid multiplied by $k_{gl}a_{gl}$ is the observed rate ($r_{obs}$). The correlation for $k_{gl}a_{gl}$ is shown as Eqs. 3.3$^{124}$ and 3.4$^{116}$. Eq. 3.4 adjusts the methane-water coefficient to the present system. $L_{slug}$ was approximated as the length of a monolith channel, although its magnitude will not affect the shape of the curve.

$$
(k_{gl} \cdot a_{gl})_M = \frac{0.133 \cdot u_{tp}^{1.2}}{L_{slug}^{0.5}}
$$

(3.3)

$$
(k_{gl} \cdot a_{gl}) = (k_{gl} \cdot a_{gl})_M \cdot \left(\frac{D_{H}}{D_{M}}\right)^{0.5}
$$

(3.4)

Higher two-phase velocities ($u_{tp} = u_L + u_G$) through the die result in faster mass transfer from gas to liquid, and this is closely reflected in the observed rate of reaction under unforced conditions (Fig. 3.4); the results confirm that the reaction is gas mass-transfer limited at these lower pressure conditions. At high liquid space velocities (0.5-1.25 cm$^3 \cdot s^{-1} \cdot$gPd$^{-1}$) the observed rate constants are within 30% of the intrinsic rate constant at this temperature ($\sim 9 \times 10^{-5}$ L$\cdot$s$^{-1}$·gPd$^{-1}$, see Table 3.2).

Figure 3.4 Hydrogenation of 2 wt% PS, 453 K, 3.13 MPa, no forced pulsing, G/L (volumetric) $\sim$ 1.2.
Table 3.2  Agitated vessel experiments for powdered and monolith supported catalysts.\(^1\)

<table>
<thead>
<tr>
<th>Run</th>
<th>Pressure</th>
<th>Temperature</th>
<th>(k_{\text{obs}}) (\text{L}^{-1}\text{s}^{-1}\text{gPd}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>powder_1</td>
<td>3.4</td>
<td>150</td>
<td>(3.1 \times 10^{-5})</td>
</tr>
<tr>
<td>monolith_1</td>
<td>3.4</td>
<td>150</td>
<td>(2.9 \times 10^{-5})</td>
</tr>
<tr>
<td>powder_2</td>
<td>3.4</td>
<td>180</td>
<td>(9.0 \times 10^{-5})</td>
</tr>
<tr>
<td>monolith_2</td>
<td>3.4</td>
<td>180</td>
<td>(9.1 \times 10^{-5})</td>
</tr>
<tr>
<td>powder_3(^2)</td>
<td>3.4</td>
<td>180</td>
<td>(1.1 \times 10^{-4})</td>
</tr>
</tbody>
</table>

\(^1\) All runs at 2600 rpm, 2 wt% PS unless otherwise noted
\(^2\) 10 wt% PS feed

Figure 3.5  Hydrogenation of 2 wt% PS, 453 K, 2.65 MPa, 0.1 Hz forced pulsing, G/L (volumetric) ~ 1.2.

The added effect of forced pulsing at 0.1 Hz on PS hydrogenation is shown in Figure 3.5. Because the G/L ratio and reactor pressure could not be varied independently in the pulsed reactor, and because the \(H_2\) pressure dependence on the kinetics was known, the pressure for the forced pulsing experiments was decreased somewhat to keep the G/L volumetric ratio the same as in the unforced experiments. In this manner, any changes in \(k_{\text{obs}}\) could be attributed to the effects of the pulsing itself. When the pressure differences are taken into account assuming first-
order kinetics in H₂, the observed rates for either natural or forced pulsing are virtually identical (compare Figs. 3.4 and 3.5). In other words, for a low viscosity (zero-shear viscosities of 2.2 mPa·s for 2 wt% PS, 37.2 mPa·s for 10 wt% PS, at 296 K) 2 wt% PS solution, the inherent, natural oscillations caused by the extruder are sufficient to give reaction rates near those of an intensely agitated tank.

The maximum $k_{\text{obs}}$ for a 2 wt% PS solution is approximately $7 \times 10^{-5}$ L·s$^{-1}$gPd$^{-1}$ at high superficial velocities, where the resistance to gas-liquid mass transfer is minimized. Again, $k_{\text{obs}}$ scales well with the computed $(k_{\text{gl}}a_{\text{gl}})$ for slug flow, indicating that gas-to-liquid mass transfer is still limiting. Attempts to increase the superficial velocities further in order to eliminate the remaining transport resistances resulted in flow instabilities and a transition to a purely foam-type flow, accompanied by a decrease in $k_{\text{obs}}$. We conclude that there is a well-defined optimal superficial velocity giving the hydrodynamic environment that minimizes resistance to external mass transfer in the monolith-supported catalyst.

![Graph](image)

**Figure 3.6** Hydrogenation of 10 wt% PS, 453 K, no forced pulsing, monolith die, inverse liquid space velocity of 13.8 s$^{-1}$gPd$^{-1}$ cm$^{-3}$. 

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Figure 3.6 shows the effect on the reaction of varying the system pressure for a 10 wt% PS feed. As seen, the pseudo first-order rate constants for the pulsed reactor vary slightly over the pressure range 2.4-3.4 MPa. This variation can be explained by concomitant variation in G/L, which increases noticeably at >3.0 MPa. A higher G/L results in thinner liquid films surrounding the gas slugs, and so often enhanced gas-solid mass transfer. Changes in G/L of this magnitude typically have minimal effects for inviscid Newtonian systems. However, the effects of G/L here are greater, as these solutions are shear-thinning, and therefore more affected by the shearing behavior of the liquid film.

In order to accurately measure $k_{\text{obs}}$ for more concentrated (and less reactive) feeds, more catalyst was required, and so for reasons of synthetic ease we switched from a monolith to particulate catalyst, present as a packed bed. The catalyst was still contained in the die of the extruder, and other operating conditions were also unchanged. The exit pulse characteristics described in Table 3.1 were also maintained. In Figure 3.7, we show $k_{\text{obs}}$ for 10 wt% feeds, for both unforced and forced (0.1 and 0.5 Hz) pulsing modes. The data again show an increase in $k_{\text{obs}}$ with liquid flow rate. However, the observed rates for the 10 wt% PS solutions are approximately one order of magnitude less than for the 2 wt% solutions, findings consistent with much greater diffusional resistance associated with higher viscosity. The 0.5 Hz data show a decrease in $k_{\text{obs}}$ compared to both the unforced and 0.1 Hz runs. This decrease can be attributed to the longer period of the flow instabilities, consisting of intervals of large gas slugs and almost dry catalyst (see Figure 3.8). Clearly the highly liquid-starved condition over an extended period is not conducive to macromolecular hydrogenation. In Figure 3.8, note the extended periods of the large gas slugs at 0.5 Hz forced pulsing. For 0.1 Hz forced pulsing, G/L of 1.2, $k_{\text{obs}}$ computed by Eqs. 3.1 and 3.2 is 20-40% higher than for unforced operation, depending on the space velocity (Fig. 3.7). This indicates that forced pulsing can either increase or decrease the observed
rate constant for more viscous and shear-thinning feeds, depending upon the frequency and the space velocity. For low frequency and high space velocity, there is a definite increase in $k_{obs}$.

![Graph](image)

**Figure 3.7** Hydrogenation of 10 wt% PS at 453 K, packed bed die. Pressures are 3.24 MPa for unforced pulsing, 2.65 MPa for 0.1 and 0.5 Hz forced pulsing.

![Graph](image)

**Figure 3.8** Gas/liquid behavior at die exit for 0.5 Hz forced pulsing, 10 wt% PS, packed bed die. Voltages near 216 mV represent slugs of gas; voltages near 225 mV represent slugs of liquid.
Note that increasing the PS concentration from 2 to 10 wt% in the agitated vessel reaction experiments (Table 3.2) left $k_{\text{obs}}$ virtually unchanged, while similar experiments in the pulsed reactor resulted in a nine-fold decrease. This highlights the important role of solution viscosity on the mass transfer. While the natural or forced pulsing of the extruder-fed reactor can affect the wetting behavior by alternating mostly gas and mostly liquid slugs, it has less effect on viscosity, because the average shear rates for the continuous reactor experiments are low. However, in the agitated vessel at high stirrer speeds, the shear rates are large near the agitator, resulting in a low viscosity for the shear-thinning polymer solution. We examined the viscosity of the 10 wt% solution at ambient conditions in a cone and plate viscometer, and found that shear rates $>4$ s$^{-1}$ resulted in approximately a 90% reduction in viscosity from the zero-shear value. At the high rpm conditions of Table 3.2, the shear rate at the tip of the agitator was greater than 500 s$^{-1}$. Assuming no gas in the packed bed, the shear rates here were only 0.03-0.07 s$^{-1}$. Therefore, it is not surprising that the agitated vessel experiments showed no effect of feed concentration.

Since the particles used in the packed bed were necessarily larger than the powdered catalyst in the stirred tank experiments (to avoid large pressure drops), the Weisz-Prater moduli $C_{WP}$ were also computed for 10 wt% PS feed. In the stirred tank with powdered catalyst, $C_{WP}$ was 0.07, indicating negligible pore diffusion resistance. For the packed bed system, $C_{WP}$ was 0.21, suggesting modest intraparticle gradients. Therefore the Thiele modulus ($\phi$) and effectiveness factor ($\eta$) were computed assuming spherical pellet geometry, giving $\eta = 0.93$ for the packed bed catalyst at 10 wt% PS. The reaction was still largely limited by the resistance to gas-liquid mass transfer, as has been well documented for this system.

To examine reactor effects on the selectivity of hydrogenation, certain product samples from the stirred tank and pulsed reactor experiments were analyzed by intrinsic viscosity measurements. No samples (natural or forced pulsing) from the extruder-fed reactor showed any
decrease in molecular weight at the conversions obtained in this study. However, the stirred tank samples did show some hydrocracking at similar conversions. For instance, the average molecular weight was reduced from 230 to 200 kg/mol at a PS conversion of 6% in the stirred tank. This result is significant because it demonstrates there is a clear advantage in using a structured catalyst with alternating gas- and liquid-rich conditions at the surface. Selectivity enhancements have also been found previously for catalyst monoliths operated in slug flow when applied to low molecular weight hydrogenations. These enhancements are presumed to arise from more uniform residence times on the catalyst surface (for the polymer) and more plug flow-like behavior. The present work shows that these selectivity enhancements can be extended to polymer systems as well. The natural pulsing behavior of the extruder system is sufficient to “flush” PS from the surface of the catalyst before a chain scission event can occur, because we found that the longer gas slugs arising from forced pulsing did not give any further selectivity enhancements.

\[ P = N_o \rho N^3 d_i^5 \]  \hspace{1cm} (3.5)

\[ P = \frac{1}{2} \rho L^2 \omega^3 V \]  \hspace{1cm} (3.6)

A perhaps more illuminating way to compare stirred tank performance to the pulsed reactor is by examining the power input to each system. The power input (P) to the stirred tank was calculated using Eq. 3.5\(^{125}\) where \(N_o\) is a constant depending on the impeller shape (0.8 for a three-bladed marine propeller).\(^{125}\) The power input for the extruder-fed reactor was approximated by multiplying the volumetric flow rate by the pressure drop across the die. Calculations of the power input due to the pulsing were estimated from Eq. 3.6\(^{126}\) where \(L\) is the length of the monolith and \(\omega\) represents the pulsing frequency. This power input term was negligible compared to the power input due to the pressure drop, for all runs.
Dividing the input power by the respective liquid reactor volumes gave power per unit volume (P/V), with the result that even for the extruder-fed reactor operating at its highest flow rate, with a 2 wt% PS solution its input P/V ($1.2 \times 10^4$ W/m$^3$) is only 16% of the stirred tank value at 2000 rpm. For a 10 wt% PS solution in the packed bed die, P/V is only 5% of the stirred tank value at 2000 rpm. The agitator speed required to attain negligible external mass transfer gradients at low PS concentration in typical autoclaves is ~2000 rpm, based on our own and others’ results. Note that at lower speeds $k_{obs}$ is reduced substantially (last entry, Table 3.2). So we can conclude that not only can a reactor with extrusion-generated pulses approach the $k_{obs}$ of a stirred tank for solutions of low to moderate polymer concentration, with better selectivity, but that this system also requires a lower input P/V at otherwise comparable conditions.

It is also instructive to compare the optimal pulsing frequency of the extruder system to other pulsed reactors (trickle beds), and with correlations that have been developed for finding optimal frequencies based on hydrodynamic models. The pulsed trickle bed literature on the hydrogenation of AMS over a similar Pd catalyst showed that the optimum condition depends on liquid holdup, gas superficial velocity, reaction rate and heat transfer requirements. For this reaction, very low frequencies (~0.002 Hz) were observed as optimal in pulsed trickle beds. However, other reactions have been shown to benefit from faster pulsing frequencies. For instance, the hydrogenation of 2-ethylanthraquinones over a similar Pd catalyst in a pulsed trickle bed showed an optimum at 0.01-0.02 Hz. For the case of the extruder-fed reactor, the optimum forced pulse frequency appears to be higher (~0.1 Hz) for the PS system. PS hydrogenation is kinetically much slower than AMS hydrogenation, and slower than anthraquinone hydrogenation, since an aromatic ring is being hydrogenated versus an unsaturated ring substituent. This suggests that as the reaction becomes kinetically more difficult, a faster pulsing frequency is advantageous. This may be because for an “easy” hydrogenation
like AMS, the need for a high fugacity of adsorbed hydrogen atoms is less. The effects of surface tension may also play an important role in determining optimal pulsing conditions. Haure et al. showed that the application of water pulses to remove oxidized SO$_2$ as H$_2$SO$_4$ from activated carbon benefited from a pulsing frequency of 0.008 Hz, but pulsing at much lower frequencies ($\sim 3 \times 10^{-4}$ Hz) was not effective.$^{128}$

Previous work$^{129}$ has shown that the onset of unstable operation and thus optimal pulsing frequency for gas-liquid systems could be predicted based on the Benjamin-Ursell bubble stability theory for an inviscid solution.$^{130}$ This theory states that the stability is governed by Mathieu equations:

\[
\frac{d^2 a_m}{dT^2} + \left[ p_m - 2q_m (\cos(2T)) \right] a_m = 0 \tag{3.7}
\]

\[
p_m = \left( \frac{4 k_m \tanh(k_m L)}{\omega^2} \right) \cdot \left( g + \frac{k_m^2 \sigma}{\rho} \right) \tag{3.8}
\]

\[
q_m = 2 k_m A \cdot \tanh(k_m L) \tag{3.9}
\]

where subscript $m$ represents the $m$th zero of the derivative of the $l$th order Bessel function based on zero velocity at the channel wall.

The Benjamin-Ursell theory was applied to the extruder system by solving Eqs. 3.8 and 3.9 for the frequencies leading to bubble instability. Physical values for density and surface tension were taken from simulations performed in HYSYS® 2.2 for the liquid mixture at reaction conditions. Since the forcing amplitude from previous work was based on mechanical vibrations, while the pulsing in the extruder die arose from a periodic gas flow, the derivation of pulsing amplitude was necessarily modified. The amplitudes (length of the gas slugs) inside the monolith and the packed bed were calculated from the photocell data. The pulse amplitudes were computed from the observed gas flow rate during individual gas slugs, divided by the cross
sectional area and multiplied by the time it took a slug to exit the die (e.g., see Figure 3.3(b)). In the monolith die, this gave amplitudes of 0.01 and 0.27 cm for natural pulsing and 0.1 Hz forced pulsing, respectively. In the packed bed die, the amplitudes were 0.02, 0.4, and 0.8 cm for natural pulsing, 0.1 Hz, and 0.5 Hz forced pulsing, respectively.

Table 3.3 Prediction of instability onset from Benjamin-Ursell Theory.

<table>
<thead>
<tr>
<th>Die type</th>
<th>Forced pulsing frequency</th>
<th>Frequency onset of instability, from Benjamin and Ursell</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Hz</td>
<td>Hz</td>
</tr>
<tr>
<td>Monolith</td>
<td>N/A</td>
<td>92</td>
</tr>
<tr>
<td>Monolith</td>
<td>0.1</td>
<td>64</td>
</tr>
<tr>
<td>Packed bed</td>
<td>N/A</td>
<td>292</td>
</tr>
<tr>
<td>Packed bed</td>
<td>0.1</td>
<td>92</td>
</tr>
<tr>
<td>Packed bed</td>
<td>0.5</td>
<td>126</td>
</tr>
</tbody>
</table>

Calculating the onset of instability based on \( m = 4 \) and \( l = 1 \), which have been shown to provide good fits to experimental data from bubble columns for the air-water system,\(^\text{129}\) gives the results shown in Table 3.3. The predicted onset of instability according to Benjamin-Ursell theory occurs at much higher frequencies than what we observed as optimal in the monolith die for 10 wt% PS. Other \( m \) values (1-4) for \( l \) values of 0 or 1 give similar results. This shows that the effects of pulsing on \( k_{\text{obs}} \) in solid-catalyzed systems do not arise from the onset of bubble instability. These findings also confirm the assumption, based on available data in both trickle bed and extruder-fed systems, that the wetting behavior controls the overall rate of the process. An additional complication is that Benjamin-Ursell theory was developed for large columns of free-standing liquid (i.e., bubble columns) and does not take into account secondary forces such as viscous effects. Knopf et al.\(^\text{129}\) have shown that for low viscosity bubble columns, pulsing does not appreciably enhance the rates of mass transfer except at the critical frequencies leading to bubble instability, as predicted by Benjamin-Ursell theory. But clearly such considerations have little applicability to solid-catalyzed systems, whether present as monoliths or packed beds.
3.4 Conclusions

Reactors based on pulsed flow generated by an extruder are an attractive alternative to agitated vessels for three-phase polymer modification reactions, especially at low to moderate polymer concentrations. In addition to offering the advantages of continuous processing with no catalyst separation requirement, the extruder-fed reactor can reduce the input power/volume requirement compared to an agitated vessel, while exhibiting comparable productivity and a higher hydrogenation selectivity. For poly(styrene) hydrogenation in the pulsed reactor, observed rates are highly dependent upon gas-liquid mass transfer rates. As the solution viscosity increases with increased concentration of polymer, the observed rates do decrease, although the pulse hydrodynamics remain similar.

For poly(styrene) hydrogenation there is an optimal pulsing frequency, one especially observable with more concentrated solutions. The pulsing frequency regulates the liquid wetting distribution – higher frequencies leading to more foam-like behavior and decreased pulse amplitudes in the reactor. At low polymer concentrations, the pulsing frequency inherent in a liquid-starved extruder is sufficient to give an optimal wetting distribution, to the extent that even the maximum productivity of a stirred tank is approached. When processing higher concentrations of polymer, reaction productivity benefits from forced pulsing at a specific frequency, resulting in longer periods of gas-rich flow over the catalyst. However, an extension of the hydrodynamic theory that predicts high optimal pulsing frequencies for bulk liquid-gas systems is not applicable to confined polymer systems, as studied here. Also, accurately controlling the die exit behavior of the forced pulses is made difficult due to pulse coalescence, with the result that frequencies higher than optimal significantly decrease the observed rates of reaction due to liquid starvation of the catalyst. Compared to previous work on pulsed trickle beds for kinetically facile hydrogenations, this work shows the importance of increased pulsing
frequency for a difficult gas-liquid reaction, one that is more sensitive to the concentration of adsorbed hydrogen.
Chapter 4 Palladium Catalysts for the Hydrogenation of Poly(styrene) to Poly(vinylcyclohexane)

4.1 Introduction

The heterogeneous catalysis of poly(styrene) (PS) hydrogenation (Figure 4.1) is of interest as a test bed for gas-liquid reactions of large molecules. Also, the saturated product poly(vinylcyclohexane) (PVCH) has some attractive properties, for example an increased $T_g$ and lower birefringence relative to PS, making it an alternative for optical recording media. Another advantage is that PS is one of the largest volume commodity polymers and is available as a low cost feedstock. For this hydrogenation, the majority of past studies used Pd or Pt catalysts on BaSO$_4$ or SiO$_2$ supports. An in-depth investigation of the effects of catalyst properties on the activity and selectivity of the reaction has not appeared, as the focus has been more on product PVCH characterization. However, Hucul and Hahn reported significant gains in activity and selectivity when using a Pt/SiO$_2$ support with an average pore diameter of 380 nm. They argued that megaporous supports of this type were needed to overcome diffusional limitations that a polymer chain encounters in more typical microporous and mesoporous supports. These internal transport limitations (i.e., hindered transport) are a result of the entropic barrier associated with polymer chain confinement in a pore, which limits the number of chain conformations available. The megaporous catalyst support had a correspondingly low surface area of 16.5 m$^2$/g. Other catalysts such as a 5 wt% Pd on BaSO$_4$ had even larger pore diameters (1300 nm), with correspondingly smaller surface areas (4.6 m$^2$/g). It would be beneficial if mesopores (2-50 nm) with larger surface areas could be used without sacrificing the ability of the polymer to access pores. Chang and Huang have reported optimal rates and selectivities for hydrogenation of SBS elastomer when using a catalyst in the mesoporous range (39 nm), and
speculated that an optimal pore size results from the balance of intraparticle transport rates with metal dispersion (which decreased with increasing surface area).12

The main reaction competing with hydrogenation is chain scission; the PS backbone is hydrocracked with a decrease in the average molecular weight. In order to achieve a high activity, temperatures are often increased to the point where the catalyst no longer operates selectively. Previous work has also shown the solvent can affect selectivity. Gehlsen et al. found that the addition of 10 vol% THF to cyclohexane reduced chain scission.9 Chang and Huang found that using toluene instead of cyclohexane led to greater selectivity in hydrogenating olefinic over aromatic groups in SBS rubber.12 They attributed this result to a competing adsorption of toluene’s phenyl group.

Bimetallic catalysts can sometimes enhance hydrogenation selectivity through both geometric and electronic effects arising from disruption of site ensembles. For instance, it is believed that the hydrogenolysis of ethylene to methane proceeds over larger ensembles of the active (Ni) sites, while smaller ones favor hydrogenation to ethane.35,132 However, the effect of another less active metal on a Pd or Pt catalyst has not been explored for PS or other polymer hydrogenation.

The reactor for PS hydrogenation is typically a stirred batch vessel operated at 423-453 K and 3.4-6.7 MPa, with a powdered catalyst.9,10,24,92,131 At least one source used instead an agitated tank where the impeller blades consisted of catalyst coated monoliths.133 No post reaction separation step was needed to recover the product. Xu et al. have shown that external mass transfer limitations can be minimized for a 3 wt% PS /decahydronaphthalene (DHN) solution hydrogenated at 3.4 MPa and 423 K, with a stirring rate of 2000 rpm and a powdered catalyst.24 They fitted their kinetics data as first order in aromatic group concentration and zero order in hydrogen. As the PS concentration increased, external resistances to mass transfer also
increased due to the higher solution viscosity. Higher PS concentrations can also affect the intraparticle diffusion rate, because the polymer chains become more entangled and their hydrodynamic diameter increases. The mechanism by which entanglement occurs is not widely understood, because diffusion measurements based on dynamic light scattering require the polymer to be at a fraction of its overlap concentration. Similarly, molecular simulations (e.g., Monte-Carlo) are limited, because they generally assume idealized systems (e.g., a polymer modeled as a hard sphere in a cylindrical channel\textsuperscript{134}), whereas a typical catalyst support consists of a random network of pores with varying tortuosity and constrictive effects. For dilute polymer solutions, it has been shown that polymer transport in porous media depends on polymer architecture, with a higher degree of branching leading to decreased polymer mobility.\textsuperscript{85}

Figure 4.1 Hydrogenation of PS to PVCH.

This chapter focuses on improving the activity and selectivity of PS hydrogenation by specifically tailoring catalyst properties for high molecular weight reactants. Specifically, the extension of bimetallic catalysts to polymeric systems is explored. We also examine the role of support materials and their relative chemical inertness on the reaction. Work in polymer hydrogenation has focused on typical alumina and silica supports; more hydrophobic supports such as activated carbons have not been investigated. Guo and co-workers\textsuperscript{89} showed that polymer interaction with hydroxyl groups on silica further hindered diffusion of linear polystyrene. This indicates support-polymer interactions can play an important role in the transport of polymers inside porous catalysts.
4.2 Experimental

4.2.1 Catalyst Preparation

Our first catalyst (Pd_A1) was a monometallic Pd on γ-Al₂O₃, prepared by ion exchange. PdCl₂ (Pressure Chemical, 99%) was converted to Pd(NH₃)₄(NO₃)₂ by dissolving in excess aqueous ammonia and ammonium nitrate. Excess Cl⁻ was removed by contacting the solution with a bed of Amberlite IRA-400 ion exchange resin (Rohm and Haas), and complete removal confirmed using ICP-AES elemental analysis. Support A1 was pseudoboehmite (UOP V-250), pre-calcined in flowing air at 773 K for 6 h to convert it to the gamma phase. Phase change was confirmed by monitoring weight loss via TGA. The γ-Al₂O₃ was contacted with the ion exchange solution under stirring at 333 K overnight. The catalyst was filtered, dried at 363 K, calcined in flowing air at 773 K, and re-introduced to the ion exchange solution two more times to achieve a higher Pd loading with the drying and calcination steps repeated after each impregnation. It was finally reduced in 10% H₂/N₂ at 403 K for 4 h. This catalyst served as a baseline material.

Pd/Cu bimetallic catalysts were also prepared on the same γ-Al₂O₃ support (denoted A11) by incipient wetness impregnation (IWI) from Pd(NO₃)₂·2H₂O and Cu(NO₃)₂·2H₂O (both Sigma-Aldrich, 99+%) precursors dissolved in de-ionized water (~0.01-0.03 g/mL). After addition of a metal precursor, the catalyst was dried at 363 K under vacuum, and for sequentially impregnated materials a second metal precursor added. The catalyst was re-dried under vacuum at 363 K, calcined in flowing air at 773 K, and finally reduced in 10% H₂/N₂ at 553 K. A higher reduction temperature for bimetallic catalysts was chosen consistent with previous work on Pd/Cu alloy formation. Another γ-Al₂O₃ support (A12) was prepared by calcining a different pseudoboehmite (Sasol 23N4-80) under identical conditions as A11, and impregnated by the same IWI method.
We tried several different supports in order to investigate the role of different pore sizes and support types. These supports included commercial microporous activated carbons (Calgon PCB) (C3) and mesoporous aluminas (Sasol Hta-101) (Al3), all of which were functionalized by IWI from Pd(NH₃)₄(NO₃)₂. HMS-C8 (S1) and MCM-48 mesoporous silicas were synthesized from the starting material tetraethyl orthosilane (Aldrich, 98%) and sodium silicate (Aldrich, 99%) respectively, as described elsewhere.¹³⁵,¹³⁶

In an effort to investigate mesoporous carbons with pore diameters greater than the mostly microporous commercial carbons commonly available, our syntheses followed the inverse replica method of Ryoo et al.⁷⁵,¹³⁷,¹³⁸ HMS-C8 (disordered, wormhole morphology) or MCM-48 (cubic) silicas were impregnated with a carbon precursor, either aqueous sucrose or furfuryl alcohol (both Aldrich, 99%). For a sucrose precursor (sucrose/H₂SO₄/water = 1.25/0.14/6 wt ratio), the catalyst was dried first at 373 K, and then at 433 K overnight between each of three separate impregnation steps, with the drying repeated between each step. The furfuryl alcohol precursor was added to the mesoporous silica under stirring at 363 K, partially polymerizing the alcohol within the pore volume. Carbonization and silica template extraction were the same for both precursors - carbonization at 1173 K in flowing N₂ for 6 h, then silica extraction using 10 wt% aqueous HF under stirring at 333 K, three separate times. After the final extraction, the solution was analyzed by ICP-AES to check for complete silicon removal. The carbons were filtered, rinsed in excess deionized water, then dried in a static oven at 363 K and then at 573 K in flowing N₂.

The mesoporous carbons were activated for impregnation with Pd by boiling in deionized water, contacting with 5% aqueous HNO₃ for 6 h at 353 K under reflux, then rinsing with deionized water and drying at 353 K. The carbons were then functionalized by IWI from
palladium acetate dissolved in acetone (0.0125 g/mL). The catalysts were dried at 353 K, treated at 573 K in flowing N₂, and reduced in 10% H₂/N₂ at 403 K for 4 h.

4.2.2 Catalyst Characterization

Dispersion measurements were made on a Micromeritics 2700 using pulse chemisorption. To check that the supports themselves did not adsorb hydrogen, several runs were performed using bare supports (UOP V-250, Sasol 23N4-80, Sasol Hta-101). In all cases the supports failed to adsorb measurable quantities of hydrogen at ambient conditions. All catalysts were cleaned at 573 K in flowing N₂ before being exposed to fixed-volume pulses of H₂ at 298 K. For carbon-supported samples, CO was used instead of H₂. This was done as a result of a large difference in the measured dispersions of some carbon supports between H₂ and CO. For instance, catalyst Pd_C2 had a measured dispersion of 30% with CO and 94% with H₂. This observation is attributed to the effects of H₂ spillover, which was less evident on alumina- or silica-supported samples. To check for differences in dispersion between H₂ and CO, measurements on Pd_Al1 using both gases were performed, with CO giving a slightly lower value (68% vs. 74% for H₂). The assumed adsorption stoichiometry for hydrogen chemisorption was 0.5 mol H₂/mol active metal and 1 mol CO/mol active metal. Attempts to further reduce the catalysts by monitoring dispersion before and after progressively higher reduction temperatures were also carried out to ensure our procedures were sufficient for complete reduction. BET surface areas and pore size distributions (PSD) (computed from the desorption branch of the isotherms by the Barrett-Joyner-Halenda algorithm) were obtained by N₂ adsorption-desorption using a Quantachrome AS-1, after drying under vacuum at 573 K. Elemental analysis was determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES), after dissolving the catalysts in boiling concentrated acid under reflux. Powder XRD spectra of samples ground to >100 mesh were obtained at the LSU Center for Advanced Microstructures.
and Devices (CAMD) using CuKα radiation on the XPD beamline. Samples were scanned from 0.5-10.0° in 2θ using a step size of 0.02° with sample spinning. An internal standard (Mica 675, NIST) was used to verify the correct 2θ offset. Spectra were background subtracted and pattern smoothed, using MDI Jade® software. SEM-EDS measurements were made using a JEOL 840A SEM of a catalyst support (Al1) that was washcoated on a monolith. Prior to taking the EDS, the monolith was mounted in cold cure epoxy and ground into a thin (<1 mm) cross sectional slice. The sample was polished with progressively finer diamond cloths and finally carbon coated.

4.2.3 Kinetics Studies

The PS used was Dow Styron® with an average molecular weight of 230 kg/mol, measured using intrinsic viscometry. Solvents used were cyclohexane (Sigma-Aldrich, 99+%) and tetrahydrofuran (Fisher, 99.9+%). The polymer was dissolved in a mixture of 10 vol% THF/cyclohexane at a concentration of 2 or 10 wt% PS. All reactions were carried out in semi-batch mode in an Autoclave Engineers 20 mL Microclave equipped with gas sparger and radial impeller. All catalysts were first ground between 100-120 mesh. The catalyst and liquid feed were charged to the reactor and purged with N2 twice. The reactor was then purged with H2 and left under ~0.1 MPa before being brought up to temperature with mild stirring to ensure a uniform liquid temperature. Once the operating temperature was reached, agitation was increased to 2600 rpm and the system pressurized. This marked the start of a run, which lasted between 4 and 12 h. The hydrogen supply valve was left open to replace any reacted H2 and to keep the pressure constant. At the end of a run, stirring was stopped and the reactor allowed to cool to room temperature before bleeding off H2. The catalyst was separated from the liquid phase by centrifugation. Excess methanol was added to the liquid to precipitate PS and PVCH. The polymer was dried at room temperature and then overnight under vacuum at 383 K. Conversion was determined using UV-Vis spectroscopy (Jasco V-570), examining the decrease in aromatic
absorbance at 262 nm of polymer samples dissolved in chloroform (Mallinckrodt, 99.9+%). The UV-Vis calibration line was determined using \(^1\)H-NMR data from selected samples of varying PS conversion, measuring the relative areas of the aromatic (6-7 ppm) versus aliphatic (1-3 ppm) proton resonances.

Specific activity was determined by using a batch reactor mass balance with the kinetics reported by Xu et al.\(^{24}\) in order to find the rate constant \(k'\) in L/s/g\(_{\text{Pd}}\). Selectivity was determined for selected samples using capillary viscometry to find the intrinsic viscosity in toluene, then calculating the average molecular weight of the product using tabulated Mark-Houwink constants for PS/toluene.\(^{119}\) The selectivity (S) is here defined as the ratio of final to initial molecular weight measured using intrinsic viscosity measurements \((S = MW_f / MW_i)\).

4.3 Results and Discussion

4.3.1 Catalyst Characterization

Mono- and bimetallic catalyst weight loadings, methods of preparation, and physical properties are summarized in Table 4.1. Catalysts PdCu0_Al1 – PdCu5_Al1 were made either by co-impregnation or sequential impregnation, where the order of metal addition was also varied. For comparison purposes some commercial catalysts were examined, such as 5 wt% Pd on activated carbon (CP-97, Engelhard; MPT-5, Sud-Chemie), denoted Pd_C1 and Pd_C2 respectively. A 5 wt% Pd on BaSO\(_4\) (Pd_Ba1) (Aldrich) similar to that of Xu et al was also tested.\(^{24}\)

As expected, lower Pd loadings generally resulted in higher metal dispersions for monometallic catalysts; also, with the exception of PdCu0_Al1, the ion exchange (IX) technique for loading Pd onto Pd_Al1 gave the highest dispersion. This is because IX relies on a pH driving force to adsorb the metal, exchanging cationic Pd with Brønsted acid groups. IWI is less selective, relying on saturating the pore volume with Pd solution through capillary action. It is
more difficult to impregnate the carbons (e.g., compare Pd_C3 to PdCu0_Al1 in Table 4.1), because they are typically more hydrophobic than aluminas or silicas, leading to poorer wetting by aqueous solutions.

\[ \text{PdCu}_1\text{Al1, PdCu}_2\text{Al1, PdCu}_3\text{Al1, PdCu}_4\text{Al1, and PdCu}_7\text{Al2 were all made by} \]
\[ \text{IWI, with sequential Pd and Cu impregnations from their respective nitrate salts in water. However, PdCu}_1\text{Al1 and PdCu}_2\text{Al1 were made by adding Pd first, while PdCu}_3\text{Al1, PdCu}_4\text{Al1, and PdCu}_7\text{Al2 were made by adding Cu first. The order of metal addition influenced the final dispersions. For the case of Pd-first addition, dispersions were the lowest of all catalysts studied, 17-19\%. This is likely because Cu covered most of the Pd sites during the second addition. However, when Cu was added first, the higher Pd dispersions were mostly retained, compared to monometallic PdCu0\text{Al1 (Table 4.1).}} \]

\[ \text{Samples PdCu}_5\text{Al1 and PdCu}_6\text{Al2 were co-impregnated by IWI. This method leads to lower dispersions on support Al1 than adding Cu first, but higher than adding Pd first. These results demonstrate the importance of preparation method and order of metal addition on final catalyst properties, as also observed in past work on alloy catalysts.}^{42} \text{ However, for support Al2, the dispersions of both co-impregnated and Cu-first impregnated catalysts were identical. To estimate the precision of dispersion measurements, three separate chemisorption tests were performed on the same catalyst sample (Pd\text{Al1). The sample was cleaned by N}_2 \text{ flow for 2 h at 573 K in between each test. The average dispersion was 74\% with a coefficient of variation of 4.7\%, showing good repeatability. To examine the accuracy of the surface area measurements, the correlation coefficient was examined for each multipoint BET plot. For a perfect fit, a plot of the BET data for relative pressures below 0.35 should fit a straight line (see Appendix B). In all cases, the correlation coefficient was >0.99. This indicates that the catalyst support samples are well described by the BET equation.} \]
Table 4.1 Properties of catalysts used for PS hydrogenation.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pd</th>
<th>Cu</th>
<th>BET area</th>
<th>Dispersion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>wt %</td>
<td>m²/g</td>
<td>%</td>
<td></td>
</tr>
<tr>
<td>Pd_Al1</td>
<td>0.5</td>
<td>250</td>
<td>74</td>
<td></td>
</tr>
<tr>
<td>PdCu0_Al1</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>80</td>
</tr>
<tr>
<td>PdCu1_Al1</td>
<td>1</td>
<td>1</td>
<td>-</td>
<td>17</td>
</tr>
<tr>
<td>PdCu2_Al1</td>
<td>1</td>
<td>0.5</td>
<td>-</td>
<td>19</td>
</tr>
<tr>
<td>PdCu3_Al1</td>
<td>1</td>
<td>1</td>
<td>-</td>
<td>67</td>
</tr>
<tr>
<td>PdCu4_Al1</td>
<td>1</td>
<td>0.5</td>
<td>-</td>
<td>50</td>
</tr>
<tr>
<td>PdCu5_Al1</td>
<td>1</td>
<td>0.5</td>
<td>130</td>
<td>47</td>
</tr>
<tr>
<td>PdCu6_Al1</td>
<td>1</td>
<td>0.5</td>
<td>47</td>
<td></td>
</tr>
<tr>
<td>Pd_Al2</td>
<td>0.5</td>
<td>-</td>
<td>-</td>
<td>70</td>
</tr>
<tr>
<td>Pd_Al3</td>
<td>0.5</td>
<td>-</td>
<td>81</td>
<td>67</td>
</tr>
<tr>
<td>Pd_Ba1</td>
<td>5</td>
<td>-</td>
<td>4.6</td>
<td>24</td>
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<tr>
<td>Pd_C1</td>
<td>5</td>
<td>-</td>
<td>1100</td>
<td>35</td>
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<tr>
<td>Pd_C2</td>
<td>5</td>
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<td>800</td>
<td>29</td>
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<td>860</td>
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<td>Pd_S1</td>
<td>1</td>
<td>-</td>
<td>970</td>
<td>62</td>
</tr>
</tbody>
</table>

* Measured using mercury porosimetry by Xu et al. (2003)

1 sequential impregnation: Pd(NO₃)₂ first, then Cu(NO₃)₂

2 sequential impregnation: Cu(NO₃)₂ first, then Pd(NO₃)₂

3 co-impregnation

Table 4.2 Preparation and catalyst properties, mesoporous carbon supports.

<table>
<thead>
<tr>
<th>Carbon precursor</th>
<th>Silica template</th>
<th>Pd</th>
<th>BET Area</th>
<th>Dispersion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd_MC1</td>
<td>Furfuryl alcohol</td>
<td>HMS-C8</td>
<td>1</td>
<td>870</td>
</tr>
<tr>
<td>Pd_MC2</td>
<td>Furfuryl alcohol</td>
<td>MCM-48</td>
<td>1</td>
<td>1280</td>
</tr>
<tr>
<td>Pd_MC3</td>
<td>Sucrose</td>
<td>HMS-C8</td>
<td>1</td>
<td>500</td>
</tr>
<tr>
<td>Pd_MC4</td>
<td>Sucrose</td>
<td>MCM-48</td>
<td>1</td>
<td>490</td>
</tr>
</tbody>
</table>

The composition and physical properties of the mesoporous carbon catalysts (Pd_MC1-4) are summarized in Table 4.2. All carbon precursors and silica templates result in high surface area supports. The furfuryl alcohol precursor gave higher surface areas for both the HMS-C8 and MCM-48 silica templates. However, the catalysts prepared from furfuryl alcohol-derived carbons
showed lower Pd dispersions. Kim et al.\textsuperscript{142} used different aromatic precursors (naphthalene, anthracene, pyrene) and sucrose to show that the nature of the carbon precursor can affect the carbon morphology. Our results confirm this, while also showing that the precursor affects the ability to impregnate with active metal. In all cases, Pd dispersions were lower than for the monometallic catalysts on alumina supports (Table 4.1). Catalyst Pd\textsubscript{C3} was prepared from a commercial microporous activated carbon using the same oxidation (with aqueous HNO\textsubscript{3}) pretreatment, and it gave a relatively high (43\%) dispersion at 1 wt\% Pd loading. The Pd\textsubscript{C3} was impregnated from aqueous Pd(NH\textsubscript{3})\textsubscript{4}(NO\textsubscript{3})\textsubscript{2}; however, attempts to use this method on the mesoporous carbons resulted in poor (8-14\%) dispersions.

The palladium acetate/acetone impregnations produced carbon catalysts with consistently better dispersions. During impregnation the carbons imbibed the organic solution much more readily than an aqueous one. This observation is likely a consequence of the aggressive HF treatment used to dissolve the silica template, because the HF can generate a partially fluorided, hydrophobic surface.\textsuperscript{143} This also suggests that the treatment at 573 K in N\textsubscript{2} does not remove all of the surface fluoride.

The difficulty associated with functionalizing mesoporous carbons prepared by acidic surface treatments has been shown previously; the contact pH of the mesoporous carbon after HF treatment but before metal addition was \textasciitilde3.\textsuperscript{144} The HNO\textsubscript{3} treatment is believed to promote anchoring of metal precursors to the support by creating carboxyl and lactone groups on the surface that bonds the metal precursors. However, the side effect is the surface can be made even more acidic, as proven by a decrease in the zero-point charge upon HNO\textsubscript{3} treatment of a commercial activated carbon.\textsuperscript{145} The relative strength of the HNO\textsubscript{3} solution then becomes important as some oxygen-containing groups on the surface are important but not at the expense of making the surface overly-acidic.
Figure 4.2 shows PSDs for the mesoporous aluminas and silicas (Al1, Al2, Al3, S1) used here. All four supports are in the mesoporous range. The average pore sizes of aluminas Al1, Al2 and Al3 are 10, 14 and 35 nm, respectively. Al1 and Al2 have similar distributions (4-5 nm full-width at half maximum, FWHM), while Al3 has a much broader distribution (FWHM ~20 nm). Figure 4.2 also shows the PSD for the silica support (S1), which is on the low end of the mesoporous range but has a homogeneous PSD (FWHM <1 nm); this is typical for a disordered wormhole silica.135 Both commercial carbon catalysts (Pd_C1 and Pd_C2) had PSDs mostly in the microporous range, with a distribution that tailed off at pore diameters >2 nm, indicating some population of pores in the lower end of the mesoporous range. The average pore diameters for Pd_C1 and Pd_C2 were 2.8 and 1.9 nm, respectively.

Figure 4.3 shows the PSDs for the mesoporous carbons that were synthesized using the inverse replica technique. Clearly the biggest influence on the PSD is the type of carbon precursor. Mesoporous carbons MC1 and MC2 were derived from furfuryl alcohol and displayed a bimodal distribution. The first peak in MC1 is small and is centered at 1.9 nm (0.3 nm FWHM) while the second much larger peak is at 4.1 nm (1.7 nm FWHM). For MC2, the first peak is centered at 2 nm (1 nm FWHM) while the second is centered at 3.8 nm (1 nm FWHM). Both supports show a broad distribution of pores with sizes from 5 nm down to well into the microporous range. The existence of mesopores as well as some microporosity for carbons prepared by this method is consistent with previous work.137 The PSDs of MC3 and MC4 (prepared from sucrose) are narrower but there are three discernible peaks in each distribution. For MC3, the first peak is centered at 2.2 nm (0.3 nm FWHM), the second peak is the major one, at 3.7 nm (0.5 nm FWHM), and the third small peak is at 9.4 nm (2.1 nm FWHM). MC4 has a similar shaped PSD with peaks at 2.1 nm (0.5 nm FWHM), 3.4 nm (0.8 nm FWHM), and 9.6 nm...
(3.7 nm FWHM). The computed average pore sizes are 3.7 nm, 2.9 nm, 4.7 nm, and 4.8 nm for MC1, MC2, MC3, and MC4 respectively.

![Pore size distributions (PSDs) of catalyst supports Al1, Al2, Al3, and S1, computed by the BJH method.](image)

**Figure 4.2** Pore size distributions (PSDs) of catalyst supports Al1, Al2, Al3, and S1, computed by the BJH method.

Figure 4.4 shows the XRD spectra for the mesoporous silica templates HMS-C8 and MCM-48. The HMS-C8 spectrum is typical to that which has been reported previously, with similar d-spacing (3.3 nm) and FWHM (~1°). The MCM-48 spectrum shows less crystalline order than in some previous work, which sometimes shows minor higher angle peaks corresponding to the (220), (420), and (332) reflections of the Ia3d space group. However, the dominant (211) peak is evident in Fig. 4.4, with the correct d-spacing (3.5 nm) and a FWHM (~0.75°) that is narrower than for the HMS-C8 silica, which is what is typically found for these two silica supports.
Figure 4.3  PSDs of mesoporous carbons (a) MC1 and MC2 and (b) MC3 and MC4.
Figure 4.4  Powder XRDs of silica precursors (a) MCM-48 and (b) HMS-C8 used as templates for mesoporous carbon synthesis.

Figure 4.5  Powder XRDs of mesoporous carbons, (a) MC1; (b) MC2; (c) MC3; (d) MC4.
Figure 4.5 shows the XRD spectra for the mesoporous carbons (MC1-MC4) with the d-spacings for each reflection labeled. The disorder of the mesoporous silica templates results in similarly disordered mesoporous carbons, exhibiting no higher angle reflections. All samples showed a shift towards higher d-spacings compared to the silica templates. Karandikar et al. noted a tendency for mesoporous carbons to shift to slightly lower d-spacings as compared to the silica template materials. They attributed this to shrinkage of the carbon framework during carbonization and silica removal. However, Ryoo et al. observed additional peaks at lower angles (higher d-spacings), assumed to result from structural changes, specifically transitions to different space groups. For instance, they reported a sharp (110) peak at (~1.6°) in a mesoporous carbon derived from MCM-48. This reflection is not present in the \textit{Ia3d} space group. They suggested that the transitions result from strain in the carbon structure during the template removal. They also showed that the resulting carbon is not an identical geometric inverse of the silica material (i.e., carbon pore size identical to silica wall thickness). Therefore the presence of additional reflections in the carbon materials not seen in the silica templates is not surprising. Furthermore, a slightly disordered support is often more advantageous in catalytic applications; a well-defined 2-D hexagonal structure such as MCM-41 can result in more intraparticle diffusion resistance after a long period of use than a similar pore size material with a more random 3-D structure. Low intraparticle diffusion resistance would be more critical in the case of polymer transport.

Wall thicknesses were estimated for each mesoporous carbon assuming cylindrical pores for HMS and cubic pores for MCM-48 derived materials by taking the primary d-spacing minus the pore diameter and dividing by 2. For MC1 with a primary d-spacing of 11 nm and a pore diameter of 4.1 nm, the predicted wall thickness is 3.5 nm. Similarly, supports MC2, MC3, and MC4 had computed wall thicknesses of 2.5, 1.0, and 1.9 nm respectively.
4.3.2 Reactor Studies

4.3.2.1 Activity

Catalytic activities in the form of observed rate constants were determined using the batch mass balance (Eq. 4.1). Previous work has shown that for supported Pd catalysts the kinetics are zero order in hydrogen \( (C_H) \) and first order in aromatic concentration \( (C_A) \) at \( H_2 \) pressures above 3.4 MPa. Integrating Eq. 4.1 gives Eq. 4.2, where \( X \) is the fractional conversion of aromatic rings and \( t \) is the reaction time. In Eq. 4.3, \( k_{obs} \) for each catalyst was computed on a per gram of Pd basis by dividing by the catalyst concentration \( (C_{cat}) \). Turnover frequencies (TOFs) were also computed based on the initial reaction rate \( (r_i) \), so the data could be compared on a metal surface site basis (Eq. 4.4). \( V_L \) is the liquid volume and \( mol_{Pd} \) is the total mols of Pd. These results are summarized in Table 4.3.

\[
- r_A = -\frac{dC_A}{dt} = k' C_A \quad (4.1)
\]

\[
- \ln(1 - X) = k' t \quad (4.2)
\]

\[
k_{obs} = \frac{k'}{C_{cat}} \quad (4.3)
\]

\[
TOF = \frac{r_i \cdot V_L}{mol_{Pd} \cdot dispersion} \quad (4.4)
\]

Figure 4.6 shows the effects of the Pd dispersion on \( k_{obs} \) for the catalysts listed in Table 4.1. This figure also shows the method of preparation and support type reflected by the style of points. There are two distinct data groups, one at high dispersions with high \( k_{obs} \), and one at low dispersions with low \( k_{obs} \). There is a noticeable increase in the overall activity on a weight basis of catalysts with higher dispersion. This confirms that our dispersion measurements are relevant to the hydrogenation reaction, even for bimetallic catalysts.
While the performance on a per gram of Pd basis is clear from Figure 4.6, it is also desirable to compare catalyst performance on a per active site basis. This behavior is commonly referred to as TOF (defined by Eq. 4.4) and is represented in Figure 4.6 by the line between the origin and Pd_A11. While catalysts above this line may exhibit a lower activity on a per gram of Pd basis, they have a higher activity on a per surface site basis.

![Figure 4.6](image_url)

**Figure 4.6** Effects of metal dispersion on $k_{\text{obs}}$ at 453 K, 2600 rpm, 5.5 MPa H$_2$, for the catalysts of Table 4.1 supported on Al$_2$O$_3$, SiO$_2$, and BaSO$_4$. Circles denote Al$_2$O$_3$ supported catalysts prepared by different techniques.

To estimate the range of experimental error around this line, the maximum and minimum TOFs were computed for catalyst Pd_A11 based on multiple runs for both the dispersion and rate measurements. The calculated relative error in TOF was $\pm$ 17% and the upper and lower bounds are represented by the two dotted lines. Points residing above this error range are therefore conclusively more active and points below it are less active on a per site basis. From this, it can be seen that there are in fact two catalysts (PdCu2_A11 and PdCu4_A11) that have
higher activities on a per surface site basis. An interesting point is that they are both bimetallic catalysts, prepared by sequential impregnations with different orders of metal addition but with identical amounts of metals (1 wt% Pd, 0.5 wt% Cu). This implies that these catalysts could actually outperform Pd_Al1 if they could be prepared at a similar (~74%) dispersion, although this would be difficult to accomplish given the tendency of Cu to lower the dispersion of Pd catalysts as discussed earlier. Below the lower bound are three catalysts: two made from co-impregnations and one from a sequential impregnation (1 wt% Pd, 1 wt% Cu). A similar conclusion can be made by examining the tabulated TOFs in Table 4.3. This also suggests there may be a minimum requirement of Pd sites on the surface (ensembles) to obtain a high activity for aromatic ring hydrogenation, since both the dispersion and $k_{obs}$ dropped precipitously upon Cu addition.

Table 4.3 gives the observed activities for the catalysts listed in Table 4.1. Results from run 23 demonstrate that our reactor system can be operated free of external mass transfer limitations, as the computed $k_{obs}$ is virtually identical to the intrinsic rate constant of Xu et al. (2003), for the same catalyst (Pd_Ba1) at the same conditions. However, as can be seen from runs 1, 2, and 4, increasing the hydrogen pressure from 2.5 to 5.5 MPa did increase $k_{obs}$ by 15%, suggesting that for Pd/Al$_2$O$_3$ catalysts either the reaction order for H$_2$ is slightly greater than zero, or there are modest external mass transfer resistances at pressures less than 5.5 MPa. Note that when compared at the same reaction conditions, high dispersion Pd/Al$_2$O$_3$ catalysts are much more active on a weight basis than lower dispersion Pd/BaSO$_4$ ones (compare runs 1 and 22, Table 4.3), and so the former are more likely to be mass transfer limited.

The solvent greatly affected the catalytic activity, as seen by comparing run 5 (DHN solvent) to run 1 (THF/cyclohexane). DHN is a much worse solvent for PS than THF/cyclohexane; the time to dissolve 2 wt% PS in DHN is several days, compared to ~4 h for
10 vol% THF/cyclohexane. These results suggest dissolving a polymer in a poor solvent, where it adopts more of a globular conformation, facilitates intraparticle transport. In even poorer solvents such as CO$_2$/toluene, PS can adopt an even more collapsed conformation, as was confirmed by a decreasing mean-square radius of gyration with increasing CO$_2$ pressure. Therefore while previous work has shown that the addition of a good solvent such as THF can improve selectivity, this can come at the expense of poorer observed activity resulting from increased polymer-solvent interactions, with a corresponding increase in the polymer’s hydrodynamic radius. Previous work examining the effects of chain conformation on intraparticle diffusion coefficients has shown that a more compact disk-like conformation as found in, e.g., porphyrins enhance intraparticle diffusion compared to linear PS, even when the molecular weight of the porphyrin is higher. We conclude that when a solvent reduces a severely confined polymer’s hydrodynamic radius, a higher effective pore diffusivity results.

An important result is that when increasing the PS concentration from 2 to 10 wt%, $k_{obs}$ changes little - compare runs 2 and 4 with 6 and 7, or 19 with 20-21. Another way to see this is to note that for Pd_A11 and Pd_A13 the TOF scales linearly with PS concentration. Therefore the rate is roughly first order in aromatic concentration, and the higher viscosity of the 10 wt% polymer solution had little effect on the kinetics. This is in slight contrast to some previous work, where an agitation rate of 4500 rpm was required to observe the intrinsic kinetics with a 9 wt% PS solution. However, in that work a higher molecular weight (332 kg/mol) of PS was used (so higher viscosity), which might account for the different behavior. Our rheological measurements using a cone and plate viscometer for 10 wt% PS solutions at 298K showed a decrease in viscosity by as much as 90% when comparing shear rates $>$4 s$^{-1}$ to those at $<$1 s$^{-1}$. The calculated shear rate near the impeller blades under reaction conditions is $>$500 s$^{-1}$. Such high shear rates greatly reduce the viscosity of shear-thinning polymer solutions,
thereby increasing the rate of external mass transfer. Other methods to lower PS solution viscosity such as processing in supercritical CO$_2$ have also resulted in enhanced catalytic activities, but at the price of more catalyst deactivation, due to the formation of CO from a reverse water-gas-shift reaction.$^{149}$

**Table 4.3** Catalyst activities at 453 K, 2 wt% PS in 10 vol% THF/cyclohexane, except as noted.

<table>
<thead>
<tr>
<th>Run #</th>
<th>Catalyst</th>
<th>Particle size</th>
<th>Pressure</th>
<th>$k_{\text{obs}} \cdot 10^5$</th>
<th>TOF $\cdot 10^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Mm</td>
<td>MPa</td>
<td>L/s/g$_{\text{Pd}}$</td>
<td>1/s</td>
</tr>
<tr>
<td>1</td>
<td>Pd$_1$Al$_1$</td>
<td>0.13-0.15</td>
<td>5.5</td>
<td>9.74</td>
<td>0.24</td>
</tr>
<tr>
<td>2</td>
<td>Pd$_1$Al$_1$</td>
<td>0.13-0.15</td>
<td>3.4</td>
<td>8.67</td>
<td>0.21</td>
</tr>
<tr>
<td>3$^1$</td>
<td>Pd$_1$Al$_1$</td>
<td>0.13-0.15</td>
<td>2.5</td>
<td>8.45</td>
<td>0.20</td>
</tr>
<tr>
<td>4</td>
<td>Pd$_1$Al$_1$</td>
<td>0.13-0.15</td>
<td>5.5</td>
<td>169</td>
<td>4.12</td>
</tr>
<tr>
<td>6$^3$</td>
<td>Pd$_1$Al$_1$</td>
<td>0.13-0.15</td>
<td>3.4</td>
<td>10.9</td>
<td>1.31</td>
</tr>
<tr>
<td>7$^3$</td>
<td>Pd$_1$Al$_1$</td>
<td>0.13-0.15</td>
<td>2.5</td>
<td>7.74</td>
<td>0.93</td>
</tr>
<tr>
<td>8$^3$</td>
<td>Pd$_1$Al$_1$</td>
<td>0.5-0.84</td>
<td>3.4</td>
<td>6.88</td>
<td>0.83</td>
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<tr>
<td>9$^3$</td>
<td>Pd$_1$Al$_1$</td>
<td>0.5-0.84</td>
<td>2.5</td>
<td>4.68</td>
<td>0.56</td>
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<td>PdCu$_1$Al$_1$</td>
<td>0.13-0.15</td>
<td>5.5</td>
<td>8.88</td>
<td>0.20</td>
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<td>11</td>
<td>PdCu$_1$Al$_1$</td>
<td>0.13-0.15</td>
<td>5.5</td>
<td>1.6</td>
<td>0.17</td>
</tr>
<tr>
<td>12</td>
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<td>0.13-0.15</td>
<td>5.5</td>
<td>5.03</td>
<td>0.48</td>
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<tr>
<td>13</td>
<td>PdCu$_3$Al$_1$</td>
<td>0.13-0.15</td>
<td>5.5</td>
<td>5.41</td>
<td>0.15</td>
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<tr>
<td>14</td>
<td>PdCu$_4$Al$_1$</td>
<td>0.13-0.15</td>
<td>5.5</td>
<td>9.89</td>
<td>0.36</td>
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<td>15</td>
<td>PdCu$_5$Al$_1$</td>
<td>0.13-0.15</td>
<td>5.5</td>
<td>2.37</td>
<td>0.11</td>
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<td>16</td>
<td>PdCu$_6$Al$_2$</td>
<td>0.13-0.15</td>
<td>5.5</td>
<td>2.31</td>
<td>0.09</td>
</tr>
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<td>17</td>
<td>PdCu$_7$Al$_2$</td>
<td>0.13-0.15</td>
<td>5.5</td>
<td>2.3</td>
<td>0.09</td>
</tr>
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<td>18</td>
<td>Pd$_1$Al$_2$</td>
<td>0.13-0.15</td>
<td>5.5</td>
<td>8.71</td>
<td>0.22</td>
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<tr>
<td>19$^3$</td>
<td>Pd$_1$Al$_3$</td>
<td>0.5-0.84</td>
<td>5.5</td>
<td>11.4</td>
<td>1.52</td>
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<tr>
<td>20</td>
<td>Pd$_1$Al$_3$</td>
<td>0.13-0.15</td>
<td>5.5</td>
<td>10.7</td>
<td>0.29</td>
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<tr>
<td>21</td>
<td>Pd$_1$Al$_3$</td>
<td>0.13-0.15</td>
<td>3.4</td>
<td>11.6</td>
<td>0.31</td>
</tr>
<tr>
<td>22</td>
<td>Pd$_1$Ba$_1$</td>
<td>0.13-0.15</td>
<td>5.5</td>
<td>2.36</td>
<td>0.18</td>
</tr>
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<td>23$^2$</td>
<td>Pd$_1$Ba$_1$</td>
<td>0.13-0.15</td>
<td>5.5</td>
<td>13.9</td>
<td>1.04</td>
</tr>
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<td>24</td>
<td>Pd$_1$S$_1$</td>
<td>0.13-0.15</td>
<td>5.5</td>
<td>7.4</td>
<td>0.22</td>
</tr>
</tbody>
</table>

$^1$ at 423 K

$^2$ using Decahydronapthalene (DHN) solvent

$^3$ using 10 wt% PS

Using the Al$_3$ alumina, with a much larger pore diameter but lower surface area (Table 4.3, runs 20 and 21), shows almost no change in $k_{\text{obs}}$ compared to Al$_1$ (although a slightly larger
TOF). This finding also differs from some previous work,\textsuperscript{9,10,24,92,131} where it was postulated that pore diameters as large as 380 nm were necessary to eliminate intraparticle diffusion limitations in PS hydrogenation using cyclohexane solvent. However, again the conditions for mass transfer were less favorable (15-25 wt% PS, molecular weights ~370 kg/mol) than here. Therefore, it is possible that the higher polymer concentrations and molecular weights could explain the differences in results.

Note that as the catalyst particle size increases from a powder (runs 6 and 7, Table 4.3) to small spherical particles (runs 8 and 9, Table 4.3) there is a decrease in $k_{\text{obs}}$. This indicates that for the more concentrated 10 wt% solution the catalyst particle size (diffusion path length) plays a more important role in attaining the maximum catalytic activity than does pore size. The effective diffusivity ($D_e$) was approximated for catalyst Pd-Al1 in the 10 wt% PS system by assuming the powdered catalyst is not internally (intraparticle) diffusion limited ($\eta=1$). The rate constant $k'$ in Eq. 4.2 will then equal the intrinsic rate constant $k$. From this, $D_e$ was calculated from Eqs. 4.5-4.7 assuming spherical particle geometry and a first order reaction.

\[ \phi = \frac{R}{3} \left( \frac{k}{D_e} \right)^{0.5} \]  
\[ \eta = \frac{3}{\phi^2} \left( \phi \cdot \coth(\phi) - 1 \right) \]  
\[ -\ln(1 - X) = \eta kt \]  

where $R$ is the pellet radius, $\phi$ is the Thiele modulus, and $\eta$ is the effectiveness factor. The calculated $D_e$ for the pellet catalyst was $1.5 \times 10^{-13}$ m$^2$/s with an $\eta$ of 0.73, indicating internal mass transfer resistances for the pellet geometry. Comparing the calculated $D_e$ to values from the literature for PS diffusion in porous media leads to some interesting observations. Light scattering experiments\textsuperscript{89,134} on highly dilute PS samples across a wide range of MWs (50-1130
kg/mol) and pore diameters (20-178 nm) in porous glasses have shown $D_e$ values in the range of $\sim 10^{-10}$-10$^{-11}$ m$^2$/s. Molecular simulations$^{150}$ have predicted similar values for the effective diffusivity at comparable conditions for a network of interconnected, cylindrical pores. However, one study$^{151}$ has used a novel imaging technique to obtain $D_e$ values at PS concentrations near the overlap concentration. For PS (MW=90 kg/mol) diffusing into a porous glass bead with a pore diameter of 15 nm, the measured $D_e$ values were $\sim 1 \times 10^{-13}$ m$^2$/s. These values are close to our calculated value of $D_e$, showing the importance of chain entanglement at above the overlap concentration to intraparticle mass transfer. Using a scaling correlation from the literature$^{152}$ for PS in cyclohexane at ambient conditions, the calculated radius of gyration is 14 nm for the PS used in this study. From this, the overlap concentration ($C^*$)$^{87}$ was calculated as 0.034 g/cm$^3$. The 10 wt% PS solution used to calculate $D_e$ exceeded the overlap concentration by a factor of $\sim 3$.

For the bimetallic catalysts, it is clear that those prepared with a Pd/Cu atomic ratio $>1$ (PdCu2_Al1 and PdCu4_Al2) give higher TOFs. These activities are substantially higher than those of the monometallic catalysts. This behavior can be attributed to previous work where it was found that hydrogenation catalysts with Pd/Cu $>1$ exhibit less surface segregation of Cu,$^{27}$ which would presumably enhance activity. This also explains the two seeming outliers of the two groups in Figure 4.6, located at 19% and 67% dispersion, with similar activities. These are catalysts PdCu2_Al1 (run12) and PdCu3_Al1 (run 13), respectively. While PdCu2_Al1 was made by sequential impregnation with Pd before Cu, PdCu3_Al1 was made by adding Cu before Pd. This would suggest that PdCu3_Al1 should have a higher activity due to Pd being buried underneath Cu in PdCu2_Al1. However, PdCu2_Al1 has a Pd/Cu atomic ratio $>1$, which has been shown to give higher activity in Pd/Cu bimetallic catalysts,$^{42}$ while PdCu3_Al1 has a ratio $\sim 1$. So there is a competing effect between the order of metal addition and the Pd/Cu atomic ratio, with control of the Pd/Cu ratio being the more important consideration in obtaining a
catalyst with a high TOF. The fact that PdCu2_Al1 was able to maintain a fairly high intrinsic activity despite a low dispersion suggests that its synthesis conditions should be further modified to enhance the amount of surface Pd. But note that the co-impregnated samples (Table 4.3, runs 15 and 16) showed low specific activities, regardless of the alumina support. These catalysts also had significantly lower TOFs and would have activities lower than the baseline Pd_Al1 catalyst even at the same dispersion (as shown in Fig. 4.6).

Table 4.4 Catalyst activities of micro- and mesoporous carbons. All data at 453 K, 2 wt% PS in 10 vol% THF/cyclohexane.

<table>
<thead>
<tr>
<th>Run #</th>
<th>Catalyst</th>
<th>Particle Size</th>
<th>Pressure kPa</th>
<th>k\textsubscript{obs} \cdot 10^5</th>
<th>TOF \cdot 10^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>Pd_C1</td>
<td>0.13-0.15</td>
<td>3.4</td>
<td>0.8</td>
<td>0.04</td>
</tr>
<tr>
<td>26</td>
<td>Pd_C2</td>
<td>0.13-0.15</td>
<td>3.4</td>
<td>1.1</td>
<td>0.07</td>
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<td>27</td>
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<td>3.4</td>
<td>1.1</td>
<td>0.05</td>
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<td>Pd_MC1</td>
<td>0.13-0.15</td>
<td>3.4</td>
<td>4.1</td>
<td>0.23</td>
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<td>0.20</td>
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<td>3.4</td>
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<td>Pd_MC4</td>
<td>0.13-0.15</td>
<td>3.4</td>
<td>5.4</td>
<td>0.21</td>
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</tbody>
</table>

For the activated carbon supports, the mostly microporous carbons (both commercial carbons and the one sample prepared here) showed a k\textsubscript{obs} (Table 4.4, runs 25-27) 4-5 times lower than our mesoporous carbons, even at higher H\textsubscript{2} pressures, and even though the dispersions were similar. This shows that there is a minimum ratio of pore diameter to hydrodynamic radius required to eliminate intraparticle concentration gradients. Even disordered wormhole morphology mesoporous silica, which has a PSD at the low end of the mesoporous range, gives high activity with a 2 wt% PS solution (Table 4.3, run 24). This critical diameter ratio would depend on polymer structure - degree of branching, chain conformation in solution, and molecular weight. Table 4.4 also shows that the mesoporous carbons are equally as active as the Pd_Al1 baseline catalyst, when compared on a surface Pd basis by TOF. These results indicate that a more inert catalyst support is not necessarily better for hydrogenation, even though this
was suggested by PS diffusion experiments in silica which showed a porous support with hydroxyl groups interacts with PS chains, impeding molecular diffusion.\textsuperscript{89}

Another important result is that the TOFs of the mesoporous carbons are virtually identical to that of the baseline catalyst (Pd\_Al1). This shows that the more inert nature of the carbon supports does not enhance the catalytic activity as suggested by the diffusion studies of Guo et al.\textsuperscript{89} In other words, the type of support used does not affect macromolecular hydrogenation activity, and the key to obtaining a highly active catalyst is more dependent upon the ability to attain high metal dispersion.

4.3.2.2 PVCH Selectivity

Table 4.5 shows the results of intrinsic viscosity experiments used to determine the degree of chain scission for selected catalyst runs. Particular attention was paid to determining the effects on selectivity of Cu addition and of the catalyst support. By far the best catalyst for reducing hydrocracking was Pd\_S1. This could be because this mesoporous silica was prepared from a pure organometallic precursor (TEOS),\textsuperscript{135} while the other supports were prepared from industrial boehmitic aluminas or activated carbons. For example, Figure 4.7 shows SEM-EDS elemental analysis of support Al1, with some Cl present as an impurity. Carbon is also present due to the conductive coating. Further analysis by ICP-AES showed supports Al1 and Al2 had a Cl concentration of \textasciitilde0.5 wt\% while S1 did not have Cl present in detectable quantities. The presence of Cl gives rise to stronger acid sites on an Al\(_2\)O\(_3\) support, and such sites in conjunction with Pd can catalyze cracking reactions. Another important consideration is therefore the source of the active metal precursor. Many commonly available precious metal salts include Cl (e.g. PdCl\(_2\), H\(_2\)PtCl\(_6\), RuCl\(_3\), etc.), and the results here suggest that these precursors should be avoided if hydrocracking selectivity is a concern. In Table 4.5, comparing runs 2 and 6 shows there is little effect of PS concentration on hydrocracking. Run 6 did have a slightly lower MW\(_f\)/MW\(_i\),
but at a higher overall conversion. Comparing runs 2, 6, 14 and 15 shows that the addition of Cu to Pd either by co- or sequential impregnation reduces the rate of hydrocracking. Run 14 showed a MW\textsubscript{i}/MW\textsubscript{i} almost identical to run 2, and greater than run 6, but at a conversion almost three times higher than run 2. Run 15 showed a MW\textsubscript{i}/MW\textsubscript{i} approximately 30% higher than run 2, at almost the same conversion. Catalysts Pd_C2 and Pd_Al2 were both similar to Pd_Al1 in selectivity. Therefore, while the most important consideration in reducing chain scission is to reduce surface acidity as much as possible, alloying Pd with less active metals also reduces polymer chain scission.

Table 4.5 Molecular weights (MW\textsubscript{i}) of hydrogenation products. MW\textsubscript{i}=230 kg/mol.

<table>
<thead>
<tr>
<th>Run #</th>
<th>Catalyst</th>
<th>Conversion</th>
<th>MW\textsubscript{i}</th>
<th>MW\textsubscript{i}/MW\textsubscript{i}</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Pd_Al1</td>
<td>22.1</td>
<td>119</td>
<td>0.52</td>
</tr>
<tr>
<td>6</td>
<td>Pd_Al1</td>
<td>57.2</td>
<td>106</td>
<td>0.46</td>
</tr>
<tr>
<td>14</td>
<td>PdCu4_Al1</td>
<td>68</td>
<td>120</td>
<td>0.52</td>
</tr>
<tr>
<td>15</td>
<td>PdCu5_Al1</td>
<td>23.9</td>
<td>158</td>
<td>0.69</td>
</tr>
<tr>
<td>18</td>
<td>Pd_Al2</td>
<td>34.2</td>
<td>121</td>
<td>0.53</td>
</tr>
<tr>
<td>24</td>
<td>Pd_S1</td>
<td>28.9</td>
<td>227</td>
<td>0.99</td>
</tr>
<tr>
<td>26</td>
<td>Pd_C2</td>
<td>43.2</td>
<td>118</td>
<td>0.51</td>
</tr>
</tbody>
</table>

Figure 4.7 SEM-EDS of Al1 catalyst support. Presence of carbon is due to conductive coating.
4.4 Conclusions

The heterogeneous catalyzed hydrogenation of PS to PVCH was investigated in an agitated tank reactor for the purposes of evaluating novel Pd catalysts designed for large molecule hydrogenations. Catalyst support type, pore size, influence of a second metal, and preparation method on the activity and selectivity were all examined. A monometallic Pd/Al₂O₃ catalyst was used as a baseline material for comparison. Mesoporous carbon supports were synthesized using an inverse replica technique from mesoporous silica and carbon-forming precursors. The performance of catalysts obtained from these supports was compared to commercial supports.

Kinetics results show the reaction to be internal diffusion-limited for traditional microporous catalysts, but not for powdered mesoporous catalysts with pore diameters above a certain threshold limit. For catalysts in the form of spherical pellets, some internal gradients were observed. Calculated effective diffusivities were comparable to those observed experimentally for PS diffusion into porous media with a similar pore diameter at concentrations approaching the overlap limit, and approximately two orders of magnitude smaller than what is observed for highly dilute solutions.

It was shown that the critical factor in determining catalytic activity was the active metal dispersion, with higher dispersions leading to a higher specific activity. The relative inertness of the support was found not to impact the activity. Calculated turnover frequencies did show two bimetallic catalysts with higher per active site activities. Both of these catalysts were prepared using sequential impregnation techniques and had a metal ratio of 1 wt% Pd / 0.5 wt% Cu. These catalysts still had lower specific activities relative to Pd_A11 because of difficulties in getting high dispersions when Cu is present. For bimetallic supports, the ratio of the two metals and the order of addition were found to have the biggest impacts on activity. Adding Pd before Cu
tended to lower the dispersions and specific activities by covering Pd atoms with less active Cu. In all cases, catalysts made from co-impregnations had lower TOFs than the baseline material.

Selectivity results show the biggest contributor to chain scission reactions is the amount of impurities present in the catalyst support. Support Al1 was found to have Cl impurities that foster acid-catalyzed cracking reactions and a decrease in the average molecular weight. Supports prepared in our lab from clean precursors exhibited a much higher selectivity. It was also found that the addition of a second, less active metal such as Cu also reduces chain scission relative to a monometallic catalyst. It is believed this mechanism occurs by the less active metal “diluting” the Pd and preventing multiple adsorptions that would lead to a C-C bond cleavage from occurring.
Chapter 5 Hydrogenation of Alpha-Methyl Styrene in a Piston Oscillating Monolith Reactor

5.1 Introduction

Reactors based on monolithic catalysts have traditionally been utilized in gas phase cleanup (e.g. de-NOₓ) for the automotive industry. More recently, interest has turned to using these reactors in three-phase systems as an alternative to stirred tanks, where the catalyst is present as a slurry, or to trickle bed reactors. Three-phase monolith reactors are sometimes attractive alternatives to stirred tanks for fine chemicals production, with higher reaction rates at lower power input. Selectivities with the monolith reactors are typically unaffected; for example, Cybulski et al. observed selectivities equal to or better than a stirred tank, in the hydrogenation of 3-hydroxypropanal to 1,3-propanediol. Furthermore, by coating the catalyst on a monolith there is no need to separate catalyst from product.

The primary advantage of monolith over packed bed reactors is in fluid phase transport-limited reactions, where monolith reactors are often several times more efficient on a volume basis. As is well known, packed trickle beds suffer from poor catalyst wetting phenomena due to rivulet formation. This behavior leads not only to highly variable concentration gradients in gas to solid transport, but also to variations in residence time distribution. Both phenomena can worsen reaction selectivity, especially in serial reaction pathways. It appears that monolith reactors offer improvements in both areas, as is also the case for other reactor types with well-defined geometry and simpler gas-liquid hydrodynamics, for example the tubular supported catalytic membrane reactor.

At relatively low gas-to-liquid (G/L) volumetric ratios, both gas and liquid flow through a monolith as discrete, alternating slugs, the Taylor regime (Figure 5.1). Plug flow-like behavior exists because gas slugs in Taylor flow force the reactants through the channels with little back
mixing. Because intense mixing takes place in the liquid slug, and because only a thin film separates the gas slug from the catalyst-coated monolith, the rates of liquid-solid and gas-solid transport can be high. Some argue that monolith reactors are already sufficiently active for certain hydrogenations in the Taylor flow regime, however, they are far from ideal at the more common volumetric rates (G/L >> 1) where trickle beds can operate. At these conditions, liquid/gas distribution in a monolith is uneven and can result in significant under-performance of the reactor.

**Figure 5.1 Schematic of Taylor Flow behavior in a capillary with alternating slugs of gas and liquid. N_x denotes molar flux.**

Other design parameters greatly affect monolith reactor performance, for example the geometry of the gas distributor. Uniform gas bubble dispersion is critical. Significant variations in hydrodynamic behavior have been noted for different distributor designs. For distributors placed too close to the first monolith segments, preferential gas flow through the center of the monolith was observed. Placing the distributor far away led to gas flow along the outer walls of the reactor.

Although most monolith three-phase reactor research deals with low molecular weight reactants, viscous effects can affect the hydrodynamics. In magnetic resonance imaging (MRI) studies, a sucrose solution with twice the viscosity of water led to an increase in the thickness of the liquid film surrounding gas slugs. Higher viscosities can also lead to more liquid loading in
packed beds.\textsuperscript{105} A thicker liquid film would decrease mass transfer rates by increasing the diffusion length, $\delta$.

One method to improve hydrodynamics in packed bed reactors is to periodically modulate liquid loading,\textsuperscript{96-101} such that during the gas-rich cycle the gas phase reactant can more easily diffuse to the catalyst surface. The liquid-rich cycle provides liquid phase reactant and flushes product from the surface while also ensuring high rates of heat transfer. Khadilkar et al.\textsuperscript{95} and Lange et al.\textsuperscript{101} reported enhancements in time averaged conversion of up to 60\% and 10\% respectively for AMS hydrogenation in a pulsed trickle bed using a Pd/Al$_2$O$_3$ catalyst. Castellari and Haure\textsuperscript{96} noted reaction rates can be enhanced up to 400\% for the same reaction in a pulsed trickle bed. Pulse behavior within trickle beds is largely governed by column dimensions and superficial gas and liquid velocities.

Boelhouwer and co-workers\textsuperscript{100} performed an in-depth analysis of pulsing behavior in trickle beds. They concluded that there were inherent impracticalities at relatively high imposed frequencies of 1 Hz and greater, where a shock wave decays rapidly along the length of the bed. For an on-off cycled feed the time between liquid pulses had to be at least 120 s in a bed 3.2 m in length to avoid shock wave coalescence. However, at high superficial gas velocities and short liquid pulsing times, stable pulses up to 1 Hz could be attained over the entire bed length. Apparently, controlling pulse behavior inside a trickle bed is difficult and in most cases practical only over a narrow operating range.

The piston oscillating monolith reactor (POMR) is an extension of previous work\textsuperscript{126,129,156} on pulsed bubble columns to three-phase reactors with a structured catalyst. Since a key challenge to most three-phase reactors is the transport of gas to the catalyst surface, we believed that the previously observed enhanced gas-liquid mass transfer rates arising from pulsed flow would increase observed rates. Other important aspects of such reactions, such as the surface
wetting distribution and the residence time distribution within the monolith channels, might also be effectively controlled using forced pulsing. The POMR represents a novel way to tune the catalyst pore environment, as opposed to the more traditional methods of varying temperature, pressure, and superficial velocities/agitation rates.

The hydrogenation of α-methylstyrene (AMS) to cumene (Figure 5.2) is often used to investigate the performance of three-phase reactor systems, because of its mild reaction conditions (~50-100°C and ~0.1-0.68 MPa) and fast kinetics. It is typically limited by gas mass transfer. At sufficiently high AMS concentration (>0.5 wt%), the reaction is zero order in AMS and first order in H₂.

\[
\text{AMS} + \text{H}_2 \rightarrow \text{Cumene}
\]

Figure 5.2 Hydrogenation of AMS to cumene.

5.2 Experimental

5.2.1 Catalyst Preparation

The Pd/Al₂O₃ catalysts used were prepared via an ion exchange (IX) technique. PdCl₂ was first converted into Pd(NH₃)₄(NO₃)₂ by dissolving in an aqueous solution containing excess aqueous ammonia and NH₄NO₃ at a pH of 11. Excess Cl⁻ was removed from solution by contacting with an ion exchange resin (Amberlite IRA-400, Rohm and Haas). Pseudoboehmite (Versal V-250, UOP) was converted at 500°C in flowing air to γ-Al₂O₃, which was then
contacted with the Pd solution at 60°C overnight. The sample was filtered, dried at 80°C and then calcined at 500°C in flowing air. Finally, it was reduced at 130°C in 10% H₂/N₂.

The catalyst powder was washcoated onto cordierite ceramic monoliths with cylindrical channels (200 cpsi, 5 x 5 x 1.2 cm, 1.3 mm hole diameter, 26.5 g bare weight), from an aqueous slurry (25 wt% solids). The slurry was first ball milled for 90 min after which a stable alumina suspension was obtained. Then 0.1 M HNO₃ was added to bring the pH to 3.5-4. Upon removal from the slurry, compressed air was used to blow out excess slurry and clear any blocked channels.

For pretreatment 1, the as coated monoliths were dried in air at 90°C and then calcined at 500°C in flowing air before being reduced at 130°C in 10% H₂/N₂. For pretreatment 2, a catalyst that had already been used in reaction experiments was then subjected to additional calcination at 500°C in flowing air, then reduction at 130°C in 10% H₂/N₂. As explained below this additional treatment alters the surface structure of the Pd catalyst.

5.2.2 Piston Oscillating Monolith Reactor (POMR) System

The POMR consists of a 1 L stainless steel square vessel in which three catalyst coated monoliths and heat exchangers are alternately stacked in a “sandwich” arrangement (Figure 5.3). This arrangement sits above a gas distributor. The external dimensions of the steel vessel containing the monoliths is 10.8 x 10.8 x 8.2 cm. At the bottom of the reactor is a flexible Teflon diaphragm connected to a cam/motor arrangement. The diaphragm can be used to impose oscillatory behavior on the reactor system. The diaphragm has a diameter of 17.8 cm. The frequency (f) can be controlled between 0-50 Hz at a maximum amplitude (A) of 25.4 mm.

Experiments were performed at frequencies of 0-17.5 Hz and amplitude 2.5 mm due to equipment limitations. The POMR process flow diagram is shown in Figure 5.4. The reactor is operated in batch mode with respect to the liquid. Hydrogen is continually recycled through the
system by a gas booster and additional hydrogen is allowed to enter the system to replace any that is lost due to reaction. The gas booster is a positive displacement pump with its own oscillatory frequency of 0.5 Hz as it constantly circulates gas even when the diaphragm oscillations are shut off.

Figure 5.3  Schematic of the Piston Oscillating Monolith Reactor (POMR).

Figure 5.4  POMR process flow diagram.
5.2.3 Procedure for Reactor Studies

AMS and cyclohexane (both 99+%, Sigma-Aldrich) were used. The polymerization inhibitor (15 ppm p-tertbutylcatechol) present in AMS can deactivate hydrogenation catalysts,\textsuperscript{116,158} so it was removed by contacting the AMS with adsorption grade alumina beads and complete removal verified by GC/MS. Cyclohexane was contacted with molecular sieve to remove traces of water.

A mixture of 13 mol% AMS/cyclohexane was charged to the reactor, which was brought to temperature (46°C) under 0.1 MPa of H\textsubscript{2}, then pressurized to 0.44 MPa H\textsubscript{2}. The piston/cam oscillator and gas booster were then started and the gas recirculation flow rate set. Gas superficial velocity was held constant at 18 cm/s. Analysis of 1 mL liquid samples withdrawn at defined intervals was by GC (HP 5890, FID detector) with an Alltech EC-1 capillary column (30 m x 0.25 mm ID). Ethylbenzene was added as an internal standard. Trace side products were identified by GC/MS (HP 5972).

For comparison purposes, a stirred reactor (500 mL Autoclave Engineers Zipperclave, 6.8 cm marine propeller) was also used at the same pressure and temperature. The catalyst was reduced in situ (130°C) and a constant H\textsubscript{2} purge maintained on the system when not in use. A catalyst-coated monolith identical to those used in the POMR was held stationary 3.5 cm below the propeller, with approximately 20 mL fluid volume beneath the monolith.

5.3 Results and Discussion

5.3.1 Catalyst Characterization

For the alumina washcoat, the BET surface area was 290 m\textsuperscript{2}/g. The BJH pore size distribution of the washcoat was also measured, based on the desorption isotherm. The average pore diameter was 10 nm with a FWHM of 4 nm. Pd weight loadings after ion exchange were determined by ICP-AES; results are summarized in Table 5.1. The impregnation from the first
Pd ion exchange was only 0.23 wt%. In order to obtain higher Pd loadings the same catalyst underwent sequential exchanges. Each time, the catalyst was dried, calcined, and reduced before being re-introduced to the ion exchange solution. This resulted in a final weight loading of 0.5 wt%. Monolith loading after washcoating is also shown in Table 5.1. Weight loadings were consistently ~4 wt% with coating thicknesses of ~100 µm. Metal dispersion was measured on a Micromeritics 2700 by pulse chemisorption of H₂. The pretreatment 1 catalyst showed a dispersion of 74% and the pretreatment 2 catalyst was 60%. To ensure that 130°C was sufficient to fully reduce the catalyst, the sample was exposed to increased temperatures (150-180°C) under H₂ flow, but no further increases in dispersion were measured.

Table 5.1  ICP results showing Pd and washcoat loadings.

<table>
<thead>
<tr>
<th>Ion Exchange</th>
<th>Pd wt%</th>
<th>Monolith</th>
<th>Loading</th>
<th>Catalyst wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.23</td>
<td>1</td>
<td>4.05</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.38</td>
<td>2</td>
<td>3.92</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.50</td>
<td>3</td>
<td>3.98</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>4</td>
<td>3.97</td>
<td></td>
</tr>
</tbody>
</table>

5.3.2 Visualization Studies

Visualization experiments were performed to better understand the hydrodynamics of the POMR. Photographs of the acrylic mock up in operation (air-water) were taken with a high speed camera (Photron Fastcam PCI-R2). In the absence of oscillations, channeling of gas took place at low gas superficial velocities (0.4-6.3 cm/s). The preferential flow of gas through certain channels decreased as superficial gas velocities increased over this range. Using an MRI technique, Gladden et al.¹⁵⁹ found that at low gas superficial velocities (approximately 0.85 cm/s – 2.5 cm/s), gas flowed through only 70% of monolith channels. From a reaction perspective, this means that only 70% of the catalyst will take part in reaction at any one time. Unequal flow distribution also results in inhomogeneous liquid residence times through the monolith stack,
which can give poor selectivities in serial reactions where a portion of the reactant will spend more time in contact with the catalyst, giving a higher probability for further reaction.

Upon application of oscillation, even gas distribution across the monolith cross section was obtained as shown in Figure 5.5. The oscillations induced both rapid gas expulsion and liquid suck back, in different parts of the cycle. During the liquid-rich part of the cycle, the gas velocity decreased due to the downward force on the liquid (Fig. 5.5a). After the onset of the

Figure 5.5 One complete cycle of oscillation, air-water in monolith mock-up assembly with oscillation: 121 channels (11x11) each 1.59 mm diameter; Amplitude = 2.46 mm; Frequency = 2 Hz; Gas superficial velocity = 6.2 cm/s.
upward stroke, liquid is expelled from the channels; gas flows through almost all channels in a uniform distribution (Fig. 5.5c).

5.3.3 Reactor Studies

5.3.3.1 Activity

Figure 5.6 shows reactant and product concentrations as a function of time on stream in the POMR at typical pulsing conditions of 8 Hz frequency and 2.5 mm amplitude. The best-fit slope of this line (mol/L/min) was used to calculate the rate in mmol/g\textsubscript{Pd}/s. From these rate data it was determined that the rate is independent of AMS concentration at these conditions, consistent with earlier work which also shows the reaction is first order in H\textsubscript{2} concentration.\textsuperscript{154,157,160} The slopes of the AMS and cumene lines are identical but opposite in sign; this shows there is a good mass balance on the system.

Figure 5.6 also shows the catalyst used here does not noticeably deactivate over the time scale of a reactor experiment. Some catalyst deactivation for the pretreatment 1 catalyst was noted between successive reactor runs. In these reactor experiments, attempts to reproduce rates by re-reducing the catalyst in-situ before each run resulted in partial regeneration only. Rates of hydrogenation varied from 1.5 - 6.0 mmol/g\textsubscript{Pd}/s for the pretreatment 1 catalyst in the POMR. Therefore, thermogravimetric analysis (TGA) of the used pretreatment 1 catalyst sample was performed to investigate the source of deactivation. In Figure 5.7(a) the sample was treated in a manner similar to the in-situ reduction preceding most runs. Regardless of gas chosen, the low-temperature treatment only decreases the starting weight by \textasciitilde7%. In Figure 5.7(b) it is shown that an oxidative treatment at 500°C removed up to 17% of the initial weight. Because traces of oligomer were observed in the liquid samples by GC/MS, we conclude that the deactivation we observed is caused not by loss of reduction, but rather by the formation of AMS oligomers blocking sites on the catalyst surface, for fresh catalysts. We believe this to also be the cause of
previously observed catalyst deactivation for AMS hydrogenation in stirred tanks.\textsuperscript{161} While previous literature\textsuperscript{116,161} has noted that deactivation could be minimized by maintaining a high hydrogen partial pressure between reactor runs, we found that by itself this action was insufficient to fully restore activity in multiple successive runs. In previous work the catalyst was simply replaced when deactivation affected the results.\textsuperscript{116} Our strategy was instead to calcine (500°C, air) and then reduce (130°C, 10% H\textsubscript{2}/N\textsubscript{2}) the once-used catalyst, one time only, in order to completely regenerate the activity (denoted “pretreatment 2”). Reaction rates for the catalyst after pretreatment 2 were approximately an order of magnitude higher than for pretreatment 1, and cumene selectivity was higher. Therefore, this treatment protocol not only regenerated the catalyst, but also greatly improved its performance in all subsequent runs. The pretreatment 2 catalyst required no additional regeneration steps, even after multiple successive runs.

Figure 5.8 summarizes the differences in activity at different oscillation frequencies for the pretreatment 2 catalyst. Due to the operation of gas booster and the applied piston oscillations, the pressure inside the reactor oscillates, and these pressure oscillations at different frequencies are reported in Table 5.2.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5_6.png}
\caption{Concentration of cumene (product) and AMS (reactant) versus time in the POMR. Conditions: frequency = 8 Hz, piston amplitude = 2.5 mm, 46°C, 0.44 MPa H\textsubscript{2}.}
\end{figure}
Figure 5.7  (a) Low temperature TGA of used Pd/Al₂O₃ catalyst in N₂ (0-160 min), air (160-280 min), and H₂ (280-400 min). Ramp of 5°C/min to 120°C. (b) High temperature TGA in air. Ramp at 5°C/min to 130°C with hold for 2 h, followed by ramp at 5°C/min to 500°C.
The POMR runs labeled as 0.5 Hz were performed with the piston-oscillated diaphragm off. However, this is not a true run at zero frequency since the gas booster is used to introduce and recycle hydrogen, and the booster’s characteristic frequency is 0.5 Hz. It can be considered a gas-pulsed, but not “actively forced” (simultaneous pulsing of both gas and liquid by the diaphragm) run. The other runs used the diaphragm and are labeled with its pulsing frequency. At zero frequency (recycle gas booster off) there was no measurable reaction rate, therefore less than 0.1 mmol/gPd/s.

The results (Fig. 5.8) show that low frequency, low amplitude oscillations by active forcing greatly enhance observed reaction rates for this highly gas mass transfer-limited system. The POMR pulsing frequency can be varied over a wider range than previous work in pulsed trickle beds which showed lower activity and difficulty in controlling the pulsing over a wide range of process variables such as reactor length and superficial velocities.97,98,101

Table 5.2 Experimental values for POMR studies at different frequencies, pretreatment 2 catalyst.

<table>
<thead>
<tr>
<th>f Hz</th>
<th>uL cm/s</th>
<th>Avg. P MPa</th>
<th>P. Std. Deviation MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0</td>
<td>0.44</td>
<td>0.05</td>
</tr>
<tr>
<td>8</td>
<td>45</td>
<td>0.46</td>
<td>0.07</td>
</tr>
<tr>
<td>17.5</td>
<td>97</td>
<td>0.43</td>
<td>0.08</td>
</tr>
</tbody>
</table>

AMS hydrogenations with the same type monoliths were carried out in a stirred tank. Results of these runs are compared to the POMR runs in Figure 5.8. Experiments were performed at 400 and 800 rpm. Doubling the agitation rate had the effect of increasing the activity from 5.1 - 8.5 mmol/gPd/s for the pretreatment 2 catalyst. To ensure the results from the monolith supported catalyst in the stirred tank were not a result of poor liquid circulation through the monolith, an additional experiment was carried out with the washcoat removed and run as a
slurry at identical temperature and pressure. The observed rate was 6.1 mmol/gPd/s at 400 rpm, showing the activity results with monolith or powdered catalyst do not differ significantly. This result is also shown in Fig. 5.8 as the experiment with particle catalyst. To further compare POMR to stirred tank performance, the power per unit volume ($P_v$) input into the system was calculated for each system. For the POMR, $P_v$ was calculated based on Eq. 5.1 at 8 and 17.5 Hz. These results were used to find the corresponding agitated tank rpm at identical $P_v$ based on the correlation of Pandit et al. for a stirred tank with marine propeller and no gas sparger (Eq. 5.2).

$$P_v = \rho_L \left( g u_G + \frac{A^2 \omega^3}{2} \right)$$  \hspace{1cm} (5.1)

$$P_v = N_o \rho_L N_i^1 d_i^5$$  \hspace{1cm} (5.2)

At 8 Hz and 2.5 mm amplitude, $P_v = 1.63 \times 10^3$ W/m$^3$, which is equivalent to an agitated tank at 520 rpm. For 17.5 Hz, the equivalent $P_v$ is at 730 rpm. Because the observed rates in the stirred tank at both 400 and 800 rpm are below all observed rates for the POMR, we conclude that the POMR is superior to a stirred tank at similar $P_v$ and otherwise comparable conditions.

The reason for the regenerative effect of pretreatment 2 is obvious as the heavy oligomers are combusted at sufficiently high temperature. The reason for the greatly enhanced activity is more subtle. Dispersion measurements for the catalyst subject to pretreatment 2 showed a decrease in Pd dispersion from 74% to 60%. Therefore, Pd crystallite size increased relative to a purely reductive pretreatment. It is well known that Pd crystallite size can have an important influence on hydrogenations (i.e. structure sensitivity). An in-depth analysis of the structure sensitivity of AMS hydrogenation is not available, but based on results from similar hydrogenations it is believed that structure sensitivity is dependent on both geometric and electronic effects. From an electronic standpoint, smaller crystallites behave less like bulk
Pd and are more electron deficient. For instance, XPS data indicate that decreasing Pd crystal size from 40 to 10 Å results in a Pd 3d\textsubscript{5/2} binding energy increase of 0.6 eV, consistent with a higher Pd oxidation state.\textsuperscript{163} The turnover frequency of the 10 Å crystallites was an order of magnitude less for vinyl acetate hydrogenation, compared to crystals larger than 40 Å. For crystals larger than 40 Å, turnover frequency was largely independent of crystal size. This shows there is typically a critical particle size where structure sensitivity comes into play, and this threshold will depend on the type of reaction in question. Smaller Pd crystals also have more coordinately unsaturated atoms located at edges and corner sites; and these sites are often associated with lower hydrogenation activity. The lower initial activity of the higher dispersion catalyst can be explained in these terms.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.8.png}
\caption{Comparison between hydrogenation rates in the POMR and stirred tank for the pretreatment 2 catalyst. Other conditions are same as in Figure 5.6.}
\end{figure}

5.3.3.2 Selectivity

Previous work with the AMS hydrogenation test reaction has focused almost exclusively on activity, because the hydrogenation of AMS with Pd-based catalysts is highly selective under
normal operating conditions. However, a product breakdown by GC/MS shows several minor side products. The heavier ones are identified in Figure 5.9 and will be referred to as products 1-5 for simplicity. These are mostly disproportionation products, formed by the serial pathway of cracking followed by alkylation and in some cases hydrogenation. Though not shown in Figure 5.9, there are also positional isomers of these products, a small amount of AMS dimer, and a noticeable light hydrocarbon peak (C$_1$-C$_3$) in the GC spectrum. The wt% of light hydrocarbons was similar to the sum of the wt% of the peaks identified in Figure 5.9.

Selectivity ($S_x$) for each product in Figure 5.9 was defined on a molar basis (Eq. 5.3). The selectivity to cumene was always >98%, and it is likely that such products would be undetectable with less active catalysts. However, a complete product breakdown is important because it indicates how selectively the catalyst/reactor might behave in more important reactions that are not as simple. A selectivity comparison between the POMR and stirred tank is shown in Figure 5.10. The effect of catalytic pretreatment is also shown. In all cases the POMR with the pretreatment 2 catalyst showed the best overall selectivity, although the effects of pretreatment far outweighed those of reactor type. Products 3-5 were not even formed at detectable limits.

Since the pretreatment 2 catalyst has larger Pd crystallites and therefore fewer edge and corner sites that are more active for hydrocracking reactions, it follows that it would give higher hydrogenation selectivity. Products 3-5 especially are so complex that they would require longer time on the surface to form. The decrease of these products for the pretreatment 1 catalyst in the POMR suggests that the primary products do not remain on the surface for very long times. The increased selectivity may also explain why the pretreatment 2 catalyst also showed superior long-term stability. Along with fewer hydrocracking and alkylation products, there were also fewer oligomers formed. This may also explain why some of the previous literature notes deactivation issues while some do not.
Figure 5.9  AMS hydrogenation side products identified by GC/MS.

Figure 5.10  Molar selectivities of different reactor systems. (a) POMR vs. stirred tank (400 rpm), (b) POMR - pretreatment 2 catalyst. Other conditions same as in Figure 5.6.
5.3.4 Comparison to Previous Work

The hydrogenation of α-methylstyrene is generally mass transfer controlled because of its “fast” intrinsic kinetics. It is important to take into account both rates of mass transfer and the intrinsic kinetics when comparing observed reaction rates to previous work. In monolith channels, there are three external (to the catalyst) mass transfer steps for the transport of hydrogen to the catalyst surface, namely, gas to liquid, liquid to solid and gas to solid, as indicated in Fig. 5.1. Different correlations that have been used to calculate the volumetric mass transfer coefficients for each step are listed in Table 5.3. Gas to liquid and liquid to solid mass transfer occurs in series; these are in parallel with gas to solid mass transfer.

\[ S_x = \frac{(\text{Mol})_x \times (#C)_x}{\sum (\text{Mol})_x \times (#C)_x} \times 100 \]

(5.3)

Table 5.3 Mass transfer correlations used to calculate mass transfer rates in catalyst monoliths, three-phase reactions.

<table>
<thead>
<tr>
<th>Mass transfer step</th>
<th>Correlation</th>
<th>Investigator</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas to liquid through bubble cap</td>
<td>[ k_{GL}a_{GL} = \frac{0.111\mu_{TP}^{1.2}}{0.57\varepsilon L_{UC}} ]</td>
<td>Bercic and Pintar (1997) (^{124})</td>
</tr>
<tr>
<td>Liquid to solid</td>
<td>[ k_{LS} = \frac{D_{LH}}{d_{ch}} 20 \left( 1 + 0.003 \left( \frac{L_{UC}}{d_{ch}} \right)^{-0.7} \right) ]</td>
<td>Kreutzer et al. (2001) (^{116})</td>
</tr>
<tr>
<td></td>
<td>[ a_{LS} = \frac{4\varepsilon_L}{d_{ch}} ]</td>
<td></td>
</tr>
<tr>
<td>Gas to solid through liquid film</td>
<td>[ k_{GS} = \frac{D}{\delta} ]</td>
<td>Irandoust and Andersson (1989) (^{155})</td>
</tr>
<tr>
<td></td>
<td>[ \delta = (d_{ch} - d_b)/2 ]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[ d_{ch}b_{ch} = 0.64 + 0.36\exp(-3.08Ca^{0.54}) ]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[ a_{GS} = \frac{4(1 - \varepsilon_L)}{d_{ch}} ]</td>
<td></td>
</tr>
</tbody>
</table>
By combining these three steps the overall volumetric mass transfer coefficient \(k_{ov}a\) can be determined as:

\[
k_{ov}a = k_{GS}a_{GS} + \frac{1}{k_{GL}a_{GL}} + \frac{1}{k_{LS}a_{LS}})^{-1}
\]  

(5.7)

Using these equations, the values of the individual volumetric mass transfer coefficients were computed at the conditions of this study (Table 5.4). The gas superficial velocity was fixed for all experiments based on the gas recycle rate. However, the liquid superficial velocity is a function of pulse frequency. The velocities are 45 and 97 cm/s at respective frequencies of 8 and 17.5 Hz. These values were calculated based on the volume of fluid displaced by each upward stroke per time and divided by the cross sectional area of the monolith channels. At pulsing conditions, the liquid hold up \(\varepsilon_L\) is \(\frac{u_L}{u_L + u_G}\), while at no pulsing conditions, the liquid superficial velocity was taken to be zero and \(\varepsilon_L\) is \(1 - \frac{L_{slug}}{L_{ch}}\), with \(L_{slug}\) taken as 3 \(d_{ch}\).116

Table 5.4  Computed values for POMR studies at different frequencies, pretreatment 2 catalyst.

<table>
<thead>
<tr>
<th>f</th>
<th>(P_v)</th>
<th>(k_{ov}a)</th>
<th>Rate min.</th>
<th>Rate max.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hz</td>
<td>W/m³ x 10³</td>
<td>s⁻¹</td>
<td>mmol g_Pd⁻¹ s⁻¹</td>
<td>mmol g_Pd⁻¹ s⁻¹</td>
</tr>
<tr>
<td>0.5</td>
<td>1.32</td>
<td>0.86</td>
<td>15</td>
<td>29</td>
</tr>
<tr>
<td>8</td>
<td>1.63</td>
<td>1.5</td>
<td>26</td>
<td>49</td>
</tr>
<tr>
<td>17.5</td>
<td>4.53</td>
<td>2.4</td>
<td>40</td>
<td>76</td>
</tr>
</tbody>
</table>

The overall volumetric mass transfer coefficients obtained from these calculations (Table 5.4) are similar to values reported by Kreutzer et al.116 for gas-liquid co-current flow in a monolith catalyst at similar superficial velocities. For a 200 cpsi monolith Kreutzer et al.116 reported volumetric mass transfer coefficients between 0.5–1 s⁻¹ at gas and liquid superficial velocities varying between 10–40 cm/s. Because the visualization studies showed liquid-
dominated flow on the piston down-stroke (half the cycle), a minimum volumetric mass transfer coefficient \((k_{\text{ova}})_{\text{min}}\) was estimated as \(0.5k_{\text{ova}}\).

Using the calculated maximum and minimum values of \(k_{\text{ova}}\), it is possible to compute maximum and minimum theoretical observed rates by equating the mass transfer rate to the kinetic rate. We used the rate expression of Meille et al.\(^{25}\) as follows:

\[
\begin{align*}
\text{rate} \ (\text{mol} \ \text{s}^{-1} \ \text{g}^{-1} \ \text{Pd}) &= A_o \exp \left( -\frac{E_a}{RT} \right) \frac{K_H C_H}{(1 + \sqrt{K_H C_H})^2} \\
\end{align*}
\]

where \(A_o = 8.5 \times 10^6 \ \text{mol/gPd/s} \); \(E_a = 38.7 \ \text{kJ/mol} \) and \(K_H = 1.4 \times 10^{-2} \ \text{m}^3/\text{mol} \). From this expression, the rate constant \(k_o \ (0.055 \ \text{m}^3/\text{gPd/s}) \) was calculated by lumping together \(A_o\), the exponential term, and \(K_H\) to give:

\[
\begin{align*}
\text{rate} \ (\text{mol} \ \text{s}^{-1} \ \text{g}^{-1} \ \text{Pd}) &= k_o \frac{C_H}{(1 + \sqrt{K_H C_H})^2} \\
\end{align*}
\]

This rate expression was chosen because the hydrogenation was studied under conditions similar to ours (up to 50°C and 0.6 MPa). Also, it gave the highest observed rates from all of the literature reviewed. The internal diffusion resistance was accounted for by calculating the Thiele modulus:

\[
\Phi = \sqrt{\frac{k_o' \ L}{D_e}} \tag{5.10}
\]

where \(L\) is the characteristic length scale which is taken as the thickness of the washcoat (100 \(\mu\)m) and \(D_e\) is the effective diffusivity \((2.4 \times 10^{-5} \ \text{cm}^2/\text{s})\). The rate constant \((k_o)\) has been multiplied by the catalyst particle density and catalyst active metal loading to obtain \(k_o'\) with units of \((\text{m}^3\ \text{fluid/}\text{s/m}^3\ \text{catalyst})\). Because \(C_H\) is small, the kinetics are effectively first order, so the effectiveness factor becomes:

\[
\eta = \frac{\tanh(\Phi)}{\Phi} \tag{5.11}
\]

For the present conditions, \(\eta \sim 1\). Equating the mass transfer and reaction rates gives:
where $C^*$ is saturation concentration (20.4 mol/m³) of H₂ in the reaction mixture and $C_{surf}$ is the reactant concentration at the surface. $\rho_c$ is the catalyst reactor loading expressed as total grams of Pd divided by the liquid volume of monolith channels (553 g Pd/m³). From Eq. 5.12 it is possible to calculate concentration of reactant at the external catalyst surface. The observed rate of reaction is then:

$$r_{obs} = \eta r(C_{surf})$$  \hspace{1cm} (5.13)$$

In all cases, the surface concentration of hydrogen ($C_{surf}$) was <10% of $C^*$, showing that the assumption of effectively first order kinetics for computing the Thiele modulus is valid. The expected observed reaction rates for both minimum and maximum $k_{ov,a}$ at different frequencies are reported in Table 5.4. The rates calculated at $(k_{ov,a})_{min}$ are in broad agreement with the experimentally determined reaction rates, which varied from 16 – 30 mmol/gPd/s at 0.5 to 17.5 Hz in the POMR. This suggests that the effective $k_{ov,a}$ for the reactor is in fact closer to $(k_{ov,a})_{min}$ as shown by the high speed photographs where the liquid rich duration is half the cycle.

Similarly, we computed the expected observed reaction rates using the mass transfer correlations of van Baten and Krishna. These correlations were developed from CFD and model the mass transfer from Taylor bubbles by accounting for the contributions of the “cap” and “film” regions. Predicted rates of reaction and overall mass transfer coefficients are summarized in Table 5. Results show the predicted rates of reaction are similar to those obtained using the correlations of Table 3 and are in excellent agreement with what was experimentally observed in the POMR for $(k_{ov,a})_{min}$.

The AMS hydrogenation reaction has been extensively studied using many different reactor configurations. It is interesting to compare the performance of the POMR with other reactor systems at similar temperature and H₂ pressure, all using supported
Pd/Al₂O₃ catalysts. In Figure 5.11 the observed reaction rates of several systems are compared. In constructing the graph we only used data where the rate on a metal weight basis could be determined, at relatively high liquid superficial velocities (or as high as reported in the paper). We excluded some data where the catalyst appeared to be of lower intrinsic activity, and only used data at conditions leading to maximum activity for the reactor in question, within the temperature and pressure constraints. Further details can be found in Appendix C.

Table 5.5 Computed values for POMR studies at different frequencies using the correlation of van Baten and Krishna.²⁶⁵,²⁶⁶

<table>
<thead>
<tr>
<th>f</th>
<th>k_0v a</th>
<th>Rate min.</th>
<th>Rate max.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hz</td>
<td>s⁻¹</td>
<td>mmol g⁻¹ s⁻¹</td>
<td>mmol g⁻¹ s⁻¹</td>
</tr>
<tr>
<td>0.5</td>
<td>1</td>
<td>18</td>
<td>35</td>
</tr>
<tr>
<td>8</td>
<td>1.5</td>
<td>26</td>
<td>50</td>
</tr>
<tr>
<td>17.5</td>
<td>1.8</td>
<td>30</td>
<td>58</td>
</tr>
</tbody>
</table>

The performance of the POMR is superior except for stirred tank data where all transport resistances were carefully eliminated by operating at high rates of agitation (>1500 rpm) and with powdered catalysts.²²,³⁶ The POMR is at least an order of magnitude more productive than a conventional monolith reactor, and greatly superior to either conventional or advanced (pulsed, rotating) trickle beds. Only certain membrane and metal mesh microreactors approach the performance of the POMR. For the former there is segregation of liquid and gas phases, which is likely to give small liquid film thicknesses, similar to what we observe for the POMR. For the latter the liquid film thickness is kept small by the geometry of the microreactor.

The stirred tank data have been included in Fig. 5.11 to show how far the normal operating conditions for this reaction are from those conditions where rates are not transport-limited, and also to demonstrate the considerable spread of intrinsic (not transport-limited) catalyst activities which have been observed. As previously mentioned, our transport-limited data for pretreatment 2 are consistent with the intrinsic kinetics of Meille et al., whose data were
used to determine the kinetic constants in Eq. 5.8. Their activity data can be considered as an upper bound for all Pd/Al₂O₃ catalysts in the AMS hydrogenation.

Our transport-limited data for pretreatment 1 are consistent with the intrinsic kinetics of Germain et al.⁴⁶ There are other reports of intrinsic activities for even less active Pd catalysts, but these catalysts may have been poisoned by either AMS inhibitor or oligomeric reaction products.

![Reaction rate comparison](image)

**Figure 5.11** Comparison of reactor performance for different types of reactors.

5.4 Conclusions

The POMR is a viable alternative to stirred tanks, trickle beds, and conventionally operated monoliths. By using actively forced pulsing (piston-cam arrangement) we were able to increase the AMS reaction rate by 84% over an unforced run where the gas flow is pulsed at low frequency (0.5 Hz). The POMR gave rates 200% higher than a stirred tank reactor operated at similar power input, both using the same catalyst monolith. The enhanced activities arise because the POMR alters the surface wetting phenomena, minimizing liquid film thickness over at least part of a pulse cycle, thereby enhancing rates of external mass transport. High speed photography
reveals both gas- and liquid-rich conditions within the monolith stack during pulsing, as well as an even distribution of bubbles in each monolith channel. These findings are consistent with our previous work on actively forced bubble columns.\textsuperscript{126,129,156}

While the effects of catalyst preparation and pretreatment can often mask the advantages of novel reactors, we have shown that by using a correctly pretreated catalyst of larger Pd crystallite size, we can realize the benefits of the novel reactor design in the standard test reaction of AMS hydrogenation, while also achieving high selectivity to cumene and a stable catalyst. Volumetric mass transfer coefficients calculated based on literature correlations but adapted to the internal flows of the POMR were used to predict observed rates of reaction at our reaction conditions, and these values are in broad agreement with the experimental data. The large variation in catalyst preparation characteristic of some previous studies may explain some of the large discrepancies in observed rates.

So in conclusion the POMR provides for rapid mass transfer rates in gas-liquid transport limited reactions, superior to several other reactors of advanced design, and even superior to a stirred tank when compared on a power-per-volume basis. The POMR comes with the added advantage of a fixed-bed catalyst, in a conventional package – a monolith. It is the type of oscillations (low frequency and amplitude), and how they are generated (by a piston-cam arrangement), that set the POMR apart from previous work in the area of novel gas-liquid contactors.
Chapter 6 Partial Hydrogenation of Soybean Oil in a Piston Oscillating Monolith Reactor

6.1 Introduction

The heterogeneous catalyzed hydrogenation of edible oils has long been an important process for the food industry, because it provides improved resistance to oxidation and better textural properties (e.g., a higher melting point). This reaction is traditionally carried out in a three-phase agitated tank at 0.1-0.7 MPa and 150-200°C using a Ni-based catalyst present as a slurry. While Ni-based catalysts are prevalent in industrial applications, supported Pd catalysts have also been investigated because of their higher activity, allowing for lower catalyst loadings and temperatures. Several continuous flow laboratory reactors have also been studied for this reaction, such as trickle beds, tubular reactors, and bubble columns. Winterbottom et al. showed a packed bubble column exhibited less trans product formation than a slurry bubble column, possibly due to a more plug-like flow pattern. Boger et al. noted a similar selectivity effect for soybean oil hydrogenation with a monolithic catalyst, compared to a slurry stirred tank, but they attributed this effect to differences in mass transfer.

While a high catalyst activity is desired, the selectivity to the intermediate mono- and diunsaturated triglycerides in the serial hydrogenation pathway is also important. The reaction has historically been operated in the external gas mass transfer-limited regime to avoid excessive hydrogenation. Furthermore, recent health concerns regarding the adverse effects of trans fatty acids (TFA) on LDL/HDL cholesterol ratios has spurred research into minimizing the formation of TFAs. Raw soybean oil has no trans-fat content and so the formation of TFAs is the result of stereoisomerization. Previous work has shown that a higher hydrogen concentration on the catalyst surface lowers the rate of TFA formation. The easiest way to increase the surface H₂
concentration is by increasing the H₂ pressure and the rate of agitation. Unfortunately, this will in turn worsen the serial pathway selectivity, promoting the formation of saturates.

The effects of intraparticle mass transfer limitations have also been investigated. It has been shown that both the serial pathway selectivity and the stereoselectivity decrease when the reaction is pore diffusion-limited with respect to the triglycerides; under these conditions the partially hydrogenated triglycerides diffuse more slowly from the pores, giving them more opportunity to react further. Intraparticle diffusion limitations with respect to hydrogen have the opposite effect and improve selectivities by decreasing the average hydrogen pressure in a pore.

While agitated tank slurry reactors are now common for this process, it would be beneficial if a structured catalyst could be used instead, obviating an additional separation step. The presence of catalyst particles or dissolved transition metal is particularly troublesome for a food product. Previous work on three-phase structured reactors has shown they are a viable alternative for gas mass transfer-limited reactions such as hydrogenations. The two most common such systems are monoliths operated in the slug (Taylor) flow regime and trickle beds. Boger et al. did an economic evaluation of a process where a monolith reactor is used for the hydrogenation of edible oil, and showed that cost reductions up to 40% can be achieved when compared to the conventional slurry reactor process. Monolith reactors in slug flow show improved surface wetting compared to trickle beds, which are known to suffer from rivulet formation and radial gradients in liquid concentrations at the catalyst external surface.

Improvements in trickle bed performance are possible when inducing pulsed flows, through the periodic modulation of the liquid feed flow. By alternating between gas- and liquid-rich conditions over the surface of the catalyst, the gradients in the gaseous reactant’s concentration can be reduced and the rate of mass transfer increased. Catalyst
monolith reactors exhibit alternating gas and liquid slugs passing over the catalyst surface, with the hydrodynamics approaching plug flow. However the liquid phase reactants used in these systems have typically been characterized by low molecular weights and viscosities. Therefore, the logical extension of soyoil hydrogenation to a structured catalytic system is complicated by the higher viscosity and its effect on the mass transfer. One MRI study has shown that a sucrose solution with twice the viscosity of water increases the film thickness surrounding gas slugs in monoliths,\textsuperscript{185} presumably reducing mass transfer.

A piston oscillating monolith reactor (POMR) has previously been used to show activity enhancements of up to 84\% and equal or better selectivity for the hydrogenation of alpha-methyl styrene (AMS) to cumene, compared to a stirred tank reactor at the same conditions.\textsuperscript{186} These improvements result from low frequency/amplitude oscillations that enhance external gas mass transfer to the surface, while also altering the surface wetting behavior. The liquid films are apparently reduced in thickness for at least part of the cycle. This work is an extension of the oscillating reactor system, exploring a more complex reacting system of higher viscosity and more possible products than present in the AMS hydrogenation work.

6.2 Experimental

6.2.1 Catalyst Preparation

The Pd/$\gamma$-Al$_2$O$_3$ catalyst was prepared by an ion-exchange technique. Pseudoboehmite (UOP V-250) was first calcined at 500°C in flowing air to de-hydroxylate it to the gamma phase. The Pd precursor used was PdCl$_2$. This was converted to Pd(NH$_3$)$_4$(NO$_3$)$_2$ by dissolving in excess NH$_3$OH and NH$_4$NO$_3$ at a pH of 11. Excess Cl$^-$ was removed from this solution by contacting with an ion exchange resin (Amberlite IRA-400, Rohm and Haas). The solution was then contacted with $\gamma$-Al$_2$O$_3$ at a temperature of 60°C overnight. The sample was filtered, dried at 80°C and then calcined at 500°C in flowing air. The impregnation step was repeated two more
times with drying and calcination steps performed in between. Finally, the catalyst was reduced at 130°C in 10% H\textsubscript{2}/N\textsubscript{2}. This gave a final Pd loading of 0.5 wt% by ICP-AES analysis. The catalyst had a BET surface area of 290 m\textsuperscript{2}/g, a pore volume of 0.46 cm\textsuperscript{3}/g and an average pore diameter of 10 nm. Dispersion measured by H\textsubscript{2} chemisorption was 74%.

The catalyst was washcoated on 200 cpsi cordierite monolith supports (5 x 5 x 1.2 cm, 0.13 cm channel diameter) from an aqueous slurry of 25 wt% solids, maintained at pH 3.5-4 by the addition of 0.1 M HNO\textsubscript{3}. The slurry was ball milled for 90 min before the washcoating in order to lower the average alumina particle size to <10 µm, as confirmed by SEM. The bare monoliths were dipped in the slurry, and compressed air was used to clear any blocked channels. The coated monolith was dried in air at 90°C and then calcined at 500°C in flowing air before being reduced again at 130°C in 10% H\textsubscript{2}/N\textsubscript{2}. The final coating thickness was ~100 µm.

### 6.2.2 Reactor Tests

An Autoclave Engineers Zipperclave (500 mL) agitated tank reactor was used for comparison purposes. The reactor was equipped with a 3-bladed marine propeller. The reactor was charged with 350 mL soybean oil (Soy Beginnings manufactured by Thumb Oilseed Producer's Cooperative, bleached, refined, de-odorized) and catalyst (either as a powder or a submerged monolith), and then it was purged to remove air. The reactor was brought to temperature under mild stirring and ~0.1 MPa H\textsubscript{2}. Once the reactor attained the operating temperature the system was pressurized and the agitator set to the desired rate. This represented the start of a run. Samples were periodically obtained from a dip tube.

The POMR consists of three catalyst-coated monoliths separated by customized cross-flow heat exchangers arranged in a “sandwich” arrangement above a gas distributor (Figure 6.1). This assembly sits in a 1 L stainless steel square vessel. An immersion circulator was used to pump the heat exchange fluid (Duratherm S) through the heat exchangers, thus providing
temperature control. The $\text{H}_2$ is distributed in upflow through the monoliths and recycled using a gas booster. The gas booster is a positive displacement pump with its own oscillatory frequency of 0.5 Hz. A superficial gas velocity through the monoliths of 17.5 cm/s was maintained using the recycle loop. Beneath the monolith/distributor stack is a piston/cam arrangement that allows for a maximum of 25.4 mm amplitude and 0-50 Hz frequency. Experiments were performed at frequencies of 0-17.5 Hz and amplitude 2.5 mm. A schematic of the entire system is shown in Figure 6.2.

![Schematic of the piston oscillating monolith reactor (POMR) reactor body.](image)

Previous work has shown this arrangement provides an oscillatory flow of both gas and liquid inside the monolith stack, as observed by high speed photography\(^{186}\) (Figure 6.3). It has also been shown that this arrangement allows for a more homogenous gas distribution and higher interfacial areas due to enhanced bubble breakage. The reactor is operated in semibatch mode as $\text{H}_2$ is allowed to enter the reactor to replace the $\text{H}_2$ consumed. The POMR was charged with 1 L of soybean oil and brought to temperature under 0.1 MPa of $\text{H}_2$. It was then pressurized and the oscillations started, marking the beginning of a run.
6.2.3 Analysis

Samples from the reactors were analyzed using a gas chromatograph (HP 5890) equipped with a FID and a SP-2560 (Supelco) capillary GC column (100 m x 0.25 mm). The GC was operated isothermally with an oven temperature of 200°C. Reactor samples were first converted to their corresponding fatty acid methyl esters (FAMEs) using IUPAC method II.D.19\(^8\). Chromatograms were analyzed both for degree of saturation of the FAMEs (C\(\text{xx:}\text{y}\), where xx is the alkyl group chain length and y is the number of double bonds) and for trans/cis conformations. Positional isomers were lumped together. The relative error in the GC measurements was always less than 11% as shown in Table 6.1.

![Figure 6.2 Flowsheet for the POMR system.](image)

The overall degree of oil unsaturation was measured in terms of iodine value (IV), calculated using IUPAC method II.D.7\(^8\). The IV is given by Equation 6.1 where \(N\) is the normality of sodium thiosulphate titrating solution, \(V_0\) is the titration volume of this solution for a blank, \(V_s\) is the titration volume for the sample, and \(m\) is the mass of the oil sample. The relative error in the IV measurement was found to be less than 2%.
\[ IV = \frac{12.69 \cdot N \cdot (V_0 - V_s)}{m} \] (6.1)

Figure 6.3 One complete cycle of oscillation, air-water in monolith mock-up assembly with oscillation: 121 channels (11x11) each 1.59mm diameter; Amplitude = 2.46 mm; Frequency = 2 Hz; Gas superficial velocity = 6.2 cm/s.

6.3 Results and Discussion

Figure 6.4 shows a graph of oil composition changing with respect to time during a typical run. Figure 6.5 shows a graph of IV vs. time for a typical run. The overall reaction rate (rate of hydrogen consumption, \( r_{H_2} \)) was calculated from the IV measurements. IV represents the grams of iodine required to saturate all double bonds in 100 g of oil. The number of moles of \( H_2 \) required to decrease the IV of soy oil by an amount \( \Delta IV \) is defined in Eq. 6.2.
Using Eq. 6.2, the rate of hydrogen consumption can be calculated as:

$$r_{H_2} = N_{H_2} \times \frac{V}{W_{Pd} \Delta t} \left[ \frac{mol}{g_{Pd} \cdot min} \right]$$  \hspace{1cm} (6.3)

where $V$ is the volume of reaction mixture, $W_{Pd}$ is the weight of the active metal (Pd) in the catalyst, and $\Delta t$ is the time over which $\Delta IV$ was measured. The rate $r_{H_2}$ was calculated based on the first two data points of a run. As seen in Figure 6.4 the decrease in the slope is gradual.
Therefore the rate of H₂ consumption we report is the maximum observed rate for the batch reaction.

Alternatively, the rate of hydrogen consumption can be obtained from the change in the concentration of the individual oil components as monitored by GC. The hydrogenation reactions can be represented as:

\[
\begin{align*}
\text{C18:3} & \xrightarrow{k_3} \text{C18:2} & \xrightarrow{k_2} \text{C18:1} & \xrightarrow{k_1} \text{C18:0} \\
\text{H}_2 & & \text{H}_2 & \text{H}_2 \\
\end{align*}
\]

(6.4)

Let the concentration of individual component C18:X be represented as \( C_{Xi} \), where \( i \) is the sample number. Considering the serial reaction pathway and stoichiometry, the hydrogen consumption \( (N_{H_2}) \) can be calculated as:

\[
N_{H_2} = (C_{i0} - C_{i1}) + 2(C_{20} - C_{21}) + 3(C_{30} - C_{31})
\]

(6.5)

\[\begin{array}{c|c|c|c|c|c|c}
\hline
\text{Time, t [min]} & 0 & 10 & 20 & 30 & 40 & 50 \\
\text{IV} & 0 & 20 & 40 & 60 & 80 & 100 \\
\hline
\end{array}\]

Figure 6.5  Plot of iodine value (IV) vs. time in stirred tank. Conditions: T = 110°C, P = 0.4 MPa, 2000 rpm, 1 g of 0.5% Pd/Al₂O₃ powdered catalyst.

A detailed derivation of Equation 6.5 is presented in Appendix D. Once \( N_{H_2} \) is calculated, the overall rate of hydrogen consumption was obtained from Equation 6.3 as before. Selectivities
were computed based on the kinetic model of a serial hydrogenation pathway as shown in Equation 6.4. The selectivities are defined as:

\[ S_{32} = \frac{k_3}{k_2} \text{ and } S_{21} = \frac{k_2}{k_1} \]  

(6.6)

The rate constants \( k_1, k_2, \) and \( k_3 \) were obtained by fitting the concentration vs. time data for all of the components. Let the concentration of C18:X be denoted \( C_x \). Then according to Eq. 6.4, the differential equations for the concentrations become:

\[ \frac{dC_3}{dt} = -k_3 C_3 \]  

(6.7)

\[ \frac{dC_2}{dt} = k_3 C_3 - k_2 C_2 \]  

(6.8)

\[ \frac{dC_1}{dt} = k_2 C_2 - k_1 C_1 \]  

(6.9)

\[ \frac{dC_0}{dt} = k_1 C_1 \]  

(6.10)

Equation 6.10 is not used in the calculation of rate constants because it is not independent. The differential forms of Equations 6.7–6.9 are not desirable for the calculation of the selectivities; we smoothed the data through integration, in the process algebraically combining Equations 6.7–6.9 as shown below. The selectivities are obtained as the inverse slopes of Equations 6.11 and 6.12.

\[ \int [C_1 + C_2 + C_3]_0 - [C_1 + C_2 + C_3]_0 \, dt = \int \frac{k_1}{k_2} \left( \frac{C_2}{C_3} \right) d(C_2 + C_3) \]  

(6.11)

\[ \int [C_2 + C_3]_0 - [C_2 + C_3]_0 \, dt = \int \frac{k_2}{k_3} \left( \frac{C_2}{C_3} \right) dC_3 \]  

(6.12)

6.3.1 Observed Catalyst Activities

The soy oil hydrogenation rate was measured in the POMR at pulsing frequencies of 0, 8, and 17.5 Hz, keeping other operating parameters constant at \( T = 110^\circ C, P = 0.41 \, MPa \). While the
rates shown in Figure 6.6 were calculated from IV measurements, we found that rates calculated from concentration data were in good agreement. Figure 6.6 shows that the reaction rate increases with the frequency of oscillation. Enhancements of >100% can be achieved with 17.5 Hz vibrations, as compared to no forced vibrations. It should be noted that when no piston oscillations are applied to the reactor, the system is still subjected to inherent low frequency (0.5 Hz) and amplitude vibrations, due to the pulsation of the gas booster in the H₂ recycle loop. Previously it has been also reported that oscillations cause pressure fluctuations in the reactor. \(^{186}\) The standard deviation of the reactor pressure at various frequencies is listed in Table 6.2.

![Figure 6.6](image)

**Figure 6.6** Effect of frequency on hydrogenation rate in the POMR, 0.5% Pd/Al₂O₃ on monolith catalyst. Stirred tank data shown for comparison. Conditions: T = 110°C, P = 0.4 MPa, A = 2.5 mm.

For comparison purposes, soy oil hydrogenation was also carried out in a stirred vessel using the same type of monolithic catalyst as in the POMR and under identical temperature (110°C) and pressure (0.41MPa) conditions. From Figure 6.6 it can be seen that the reaction rate in the stirred tank was substantially lower than in the POMR even without forced oscillations.
These higher rates can be attributed to higher rates of mass transfer, as will be shown subsequently.

Table 6.2 Summary of pressure data and power input for POMR.

<table>
<thead>
<tr>
<th>f</th>
<th>P_v</th>
<th>Avg. pressure</th>
<th>Pressure std. deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hz</td>
<td>W/m^3 x 10^-3</td>
<td>MPa</td>
<td>MPa</td>
</tr>
<tr>
<td>0.5</td>
<td>1.47</td>
<td>0.41</td>
<td>0.04</td>
</tr>
<tr>
<td>8</td>
<td>1.81</td>
<td>0.40</td>
<td>0.07</td>
</tr>
<tr>
<td>17.5</td>
<td>5.05</td>
<td>0.43</td>
<td>0.08</td>
</tr>
</tbody>
</table>

Equivalent power input per unit volume (P_v) is a commonly used criterion for comparing two different reactor systems. For the POMR, P_v was calculated (Eq. 6.13) as shown in previous work.\(^{129}\) This P_v was then used to find the corresponding agitated tank rpm at identical P_v using the correlation of Pandit et al.\(^{125}\) for a stirred tank with a marine propeller and no gas sparger (Eq. 6.14).

\[
P_v = \rho_L \left( g \mu_G + \frac{A^2 \omega^3}{2} \right)^5
\]

\[(6.13)\]

\[
P_v = N_o \rho_L N_i d_i^5
\]

\[(6.14)\]

At 8 Hz and 2.5 mm amplitude, P_v = 1.81 x 10^3 W/m^3 (Table 6.2), which is equivalent in power to the agitated tank operated at 520 rpm. When the corresponding reaction rates are compared, it is seen that the rate in the POMR is about three times higher than the rate in the agitated tank at an equivalent power input. To understand the effect of agitation speed on the reaction rate in the stirred tank, an additional experiment was carried out at 2000 rpm. No difference was observed in the reaction rate at 2000 rpm, compared to 520 rpm. This observation suggests that the reaction is not externally mass transfer-controlled in the stirred tank at typical operating conditions for the monolith catalyst.

Additional experiments were performed using a powdered catalyst to discern the governing rate-limiting mechanism. The effect of catalyst particle size on the observed reaction
rate was studied. The results of these experiments are summarized in Table 6.3. Hydrogen consumption rates obtained by both methods (IV and concentration data) are shown in the table and it is seen that the rates obtained by both methods are in reasonable agreement.

It was observed that the increasing particle diameter results in decreasing reaction rates. This suggests that the rate was limited by the intraparticle resistance to diffusion. For a reaction of arbitrary kinetics, the rate at constant temperature and bulk fluid concentrations should be inversely proportional to the characteristic pore diffusion length at high Thiele modulus.

For spherical particles this characteristic pore diffusion length, \( L \), can be taken as \( d_p/6 \), while for the slab-like monolith-supported catalyst \( L \) corresponds to the washcoat thickness. A plot of \( r_{H_2} \) vs. \( L^{-1} \) (Figure 6.7) shows that the assumption of high Thiele modulus for the monolith looks correct, while for the smallest particle size we are approaching the true intrinsic kinetic rate of reaction.

Table 6.3 Summary of results obtained in stirred tank reactor.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>T</th>
<th>P</th>
<th>RPM</th>
<th>Mean size, diameter or thickness</th>
<th>( r_{H_2} ) (conc)</th>
<th>( r_{H_2} ) (IV)</th>
<th>( \Phi_{WPH_2} )</th>
<th>( \Phi_{WPTAG} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monolith</td>
<td>110</td>
<td>0.41</td>
<td>2000</td>
<td>100</td>
<td>0.21</td>
<td>0.21</td>
<td>10</td>
<td>3.0</td>
</tr>
<tr>
<td>Monolith</td>
<td>110</td>
<td>0.41</td>
<td>520</td>
<td>100</td>
<td>0.19</td>
<td>0.23</td>
<td>11</td>
<td>3.3</td>
</tr>
<tr>
<td>Powder</td>
<td>110</td>
<td>0.41</td>
<td>2000</td>
<td>38</td>
<td>4.7</td>
<td>5.0</td>
<td>0.97</td>
<td>0.3</td>
</tr>
<tr>
<td>Powder</td>
<td>110</td>
<td>0.41</td>
<td>2000</td>
<td>63</td>
<td>4.5</td>
<td>3.9</td>
<td>2.1</td>
<td>0.6</td>
</tr>
<tr>
<td>Powder</td>
<td>110</td>
<td>0.41</td>
<td>2000</td>
<td>166</td>
<td>3.3</td>
<td>3.3</td>
<td>12</td>
<td>3.7</td>
</tr>
<tr>
<td>Powder</td>
<td>110</td>
<td>0.69</td>
<td>2000</td>
<td>63</td>
<td>8.8</td>
<td>8.8</td>
<td>4.7</td>
<td>1.4</td>
</tr>
</tbody>
</table>

To verify this hypothesis, Weisz-Prater moduli for both the hydrogen and triglyceride reactants were calculated based on the observed reaction rates as shown in equations 6.15 and 6.16. Qualitatively, the Weisz-Prater modulus is the ratio of the observed reaction rate to the internal diffusion rate inside a catalyst particle. Values >>1 indicate internal gradients are present while values <<1 indicate the reaction is not internally mass transfer limited.
Figure 6.7 Effect of diffusion length on the rate of reaction.

\[
\begin{align*}
\Phi_{WPH_2} &= \frac{\left(R_{H_2} \rho_c \right)_{obs} L^2}{D_{eH_2} C_{H_2}^s} \\
\Phi_{WPTAG} &= \frac{\left(R_{H_2} \rho_c \right)_{obs} L^2}{D_{eTAG} C_{TAG}}
\end{align*}
\]  

(6.15)  

(6.16)

where \( R_{H_2} \) is the observed rate of hydrogen consumption in mol g\(^{-1}\) s\(^{-1}\), \( \rho_c \) is the catalyst density (833 g/L), \( C_{H_2}^s \) is the concentration of hydrogen at the catalyst surface, which was assumed to be equal to the saturation concentration of hydrogen. It will be shown subsequently that this assumption is valid. Due to lack of data for the physical properties of soyoil at reactor conditions, we used physical data for cottonseed oil to get the corrected soyoil properties at the conditions of interest as follows:

\[
(Property \ at \ T_i)_{soybeanoil} = \frac{(Property \ at \ T_0)_{soybeanoil}}{(Property \ at \ T_0)_{cottonseed \ oil}} \times (Property \ at \ T_i)_{cottonseed \ oil}
\]

(6.17)

It can be seen from Table 6.4 that the physical properties of soyoil are similar to those of cottonseed oil. The saturation concentration of H\(_2\) was taken as \( C_{H_2}^s = 1.05 \times 10^{-2} \text{ mol/L} \). The
concentration of triglycerides, $C_{TAG}$, was calculated from the density and average molecular weight of soy oil. $D_{ei}$ is the effective pore diffusivity of compound $i$:

$$D_{ei} = \frac{D_i \varepsilon_c}{\tau} \quad (6.18)$$

Due to lack of data, the molecular diffusivity of H$_2$ in soy oil, $D_{H_2}$, was taken as $10.7 \times 10^{-5}$ cm$^2$/s at 110°C. The molecular diffusivity of trioleate in cottonseed oil was used ($D_{TAG} = 1.2 \times 10^{-6}$ cm$^2$/s). The porosity $\varepsilon_c$ was determined from N$_2$ adsorption data, while the tortuosity $\tau$ was taken as 3, a typical value for this type of catalyst. Calculated values of the Weisz-Prater moduli are shown in Table 6.3. It can be seen that for the smallest size particle both Weisz-Prater moduli are $< 1$, suggesting effectiveness factors near 1. For the monolith catalyst, both moduli are $>>1$, suggesting strong intraparticle resistances to mass transfer. For the intermediate-sized particles, we are in the transition region between intrinsic kinetics control and large intraparticle resistances. This is qualitatively in agreement with the results in Figure 6.7.

These results are also in agreement with previous work showing that it is difficult to completely eliminate intraparticle diffusion limitations in the hydrogenation of triglycerides. Veldsink claimed that even at particle diameters as small as 12 µm, pore diffusion limitations occur in the hydrogenation of methyl linoleate over Pd/C catalysts. In the present work, $\Phi_{WTAG} / \Phi_{WPH}$ is $\sim 0.3$, which is in agreement with observations made by Jonker et al. on the ratio of Weisz-Prater moduli in the hydrogenation of mono-saturated edible oils.

It is known that the hydrogenation of soybean oil reaction is first order with respect to concentration of double bonds and first order with respect to hydrogen concentration. When the H$_2$ pressure was increased from 0.41 to 0.69 MPa we observed that the reaction rate based on concentration data changed from 4.5 to 8.8 mol g$_{Pd}^{-1}$ min$^{-1}$ for a constant catalyst particle size. In other words, the rate increased 1.9 times when pressure was increased 1.7 times. Thus the
observed reaction rate does show an approximate first-order dependence on hydrogen concentration. This provides further support for the assumption that the smallest powdered catalyst is almost intrinsic in its activity.

**Table 6.4  Comparison of physical properties of cottonseed oil and soybean oil.**

<table>
<thead>
<tr>
<th>Property</th>
<th>Cottonseed oil</th>
<th>Soybean oil</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>P (MPa)</td>
<td>T (°C)</td>
</tr>
<tr>
<td>Density (kg/m³)</td>
<td>- 100</td>
<td>860</td>
</tr>
<tr>
<td>Viscosity (Pa s)</td>
<td>- 99</td>
<td>7.2 x 10⁻³</td>
</tr>
<tr>
<td>Solubility of hydrogen (mmol/kg of oil)</td>
<td>0.1</td>
<td>72</td>
</tr>
<tr>
<td>Diffusivity of hydrogen (m²/s) at T/µ = 4.5x10⁴ KPa⁻¹s⁻¹</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

The reaction rates obtained in the stirred tank reactor are comparable to those reported in the literature for Pd catalysts. Thomson and Winterbottom reported that for a silica-supported Pd catalyst, observed rates of ~1.5 mol g⁻¹ Pd min⁻¹ were obtained in a stirred tank at 2000 rpm, 110°C, 0.1 MPa for a catalyst of particle size 150 µm. This rate can be corrected for pressure assuming a first-order reaction with respect to hydrogen as discussed previously, giving a predicted reaction rate of 6.3 mol g⁻¹ Pd min⁻¹ at 0.41 MPa, near our value for the smallest size Pd/Al₂O₃ catalyst. A list of reaction rates from the literature using Pd catalysts is provided in Table 6.5.

**6.3.2 Selectivity**

As discussed earlier the selectivity and catalytic activity are equally important for this system. Two serial pathway selectivities, \( S_{32} \) and \( S_{21} \) (Equation 6.6), and also the selectivity toward trans isomer formation were determined. Of the two serial pathway selectivities, \( S_{21} \) is more important because it dictates formation of saturates. Formation of saturated triglycerides is undesirable and so a high value of \( S_{21} \) is desired. The selectivity results for the POMR and for the stirred tank are listed in Table 6.6.
Table 6.5  Reaction rates for hydrogenation of soyoil (unless noted) over a Pd catalyst in a stirred tank. Rates are corrected for H₂ pressure = 0.41 MPa assuming first order kinetics with respect to H₂.

<table>
<thead>
<tr>
<th>Investigator</th>
<th>T</th>
<th>rpm</th>
<th>d₀ or L</th>
<th>Catalyst loading</th>
<th>r_H₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thomson and Winterbottom³⁹</td>
<td>110</td>
<td>2000</td>
<td>150</td>
<td>2.5</td>
<td>6.3</td>
</tr>
<tr>
<td>Parry and Winterbottom⁶</td>
<td>160</td>
<td>-</td>
<td>-</td>
<td>2.2</td>
<td>0.1</td>
</tr>
<tr>
<td>Savchenko and Makaryan¹⁹²</td>
<td>102</td>
<td>-</td>
<td>-</td>
<td>0.5</td>
<td>3.0</td>
</tr>
</tbody>
</table>

Table 6.6  Selectivities for POMR and stirred tank runs. All runs done at 110°C.

<table>
<thead>
<tr>
<th>Reactor</th>
<th>Catalyst</th>
<th>f</th>
<th>rpm</th>
<th>P</th>
<th>L</th>
<th>S₂₁</th>
<th>S₃₂</th>
<th>Trans fat at IV = 75</th>
</tr>
</thead>
<tbody>
<tr>
<td>POMR</td>
<td>Monolith</td>
<td>0</td>
<td>N.A.</td>
<td>0.41</td>
<td>100</td>
<td>8.7</td>
<td>1.4</td>
<td>0.42</td>
</tr>
<tr>
<td>POMR</td>
<td>Monolith</td>
<td>8</td>
<td>N.A.</td>
<td>0.41</td>
<td>100</td>
<td>11.8</td>
<td>2.0</td>
<td>0.42</td>
</tr>
<tr>
<td>POMR</td>
<td>Monolith</td>
<td>17.5</td>
<td>N.A.</td>
<td>0.41</td>
<td>100</td>
<td>10.8</td>
<td>2.5</td>
<td>0.39</td>
</tr>
<tr>
<td>Stirred tank</td>
<td>Monolith</td>
<td>2000</td>
<td></td>
<td>0.41</td>
<td>100</td>
<td>10.2</td>
<td>1.6</td>
<td>0.37</td>
</tr>
<tr>
<td>Stirred tank</td>
<td>Powder</td>
<td>N.A.</td>
<td>2000</td>
<td>0.41</td>
<td>38</td>
<td>14.8</td>
<td>1.6</td>
<td>0.26</td>
</tr>
<tr>
<td>Stirred tank</td>
<td>Powder</td>
<td>N.A.</td>
<td>2000</td>
<td>0.41</td>
<td>63</td>
<td>15.2</td>
<td>1.7</td>
<td>0.31</td>
</tr>
<tr>
<td>Stirred tank</td>
<td>Powder</td>
<td>N.A.</td>
<td>2000</td>
<td>0.41</td>
<td>166</td>
<td>11.4</td>
<td>1.8</td>
<td>0.28</td>
</tr>
<tr>
<td>Stirred tank</td>
<td>Powder</td>
<td>N.A.</td>
<td>2000</td>
<td>0.69</td>
<td>63</td>
<td>9.9</td>
<td>1.4</td>
<td>0.25</td>
</tr>
</tbody>
</table>

For the POMR, we observed increases in selectivity with respect to frequency for S₂₁ and S₃₂, the latter being more marked. Figure 6.8 shows a plot of S₂₁ vs. the characteristic diffusion length scale. It can be seen that within the experimental error, S₂₁ does not change with diffusion length. For linoleate hydrogenation over 1 wt% Pd/C (T = 121°C, P = 0.31 MPa), Cordova and Harriot¹⁷⁹ has shown S₂₁ attains a constant value for length scales larger than 10 µm. Data from Cordova and Harriot¹⁷⁹ is also plotted in Figure 6.8 for comparison purposes. They showed that S₂₁ decreases for diffusion lengths between 2-10 µm due to the intraparticle concentration gradients of the triglycerides, in agreement with theory for series reactions in pores¹⁸⁸. Figure 6.8 also shows that the selectivity S₂₁ for a monolith catalyst in a stirred tank is similar to the selectivities obtained with a POMR. This suggests that S₂₁ is more dependent on catalytic
chemistry than pore structure. For the stirred tank runs, $S_{32}$ remained constant with increasing particle diameter, to within the precision of the data.

![Graph showing selectivity $S_{21}$ as a function of characteristic length scale of the catalyst.](image)

**Figure 6.8** Selectivity $S_{21}$ as a function of characteristic length scale of the catalyst.

Trans fatty acid production was higher for the monolith catalyst irrespective of the reactor system. The monolith catalyst showed a trans fatty acid content $\sim 40\%$ as opposed to $\sim 28\%$ for a powder catalyst at similar operating conditions. This behavior can be attributed to both the higher internal diffusion resistance (with a larger catalyst) and differences in overall observed reaction rates. Veldsink\textsuperscript{181} claimed that the increase in observed reaction rate (either by increasing stirrer speed or by increasing hydrogen partial pressure) results in a decrease in trans fatty acid formation. However, that does not appear to be the case here as the rate more than doubled in the POMR with only a slight decrease in the trans product concentration observed. More data are necessary to come to a definite conclusion here.

**6.3.3 Analysis of Mass Transfer**

Hydrogenation of soy oil is kinetically “fast” at normal reaction conditions. It is important to establish the effects of mass transfer on the observed rates of hydrogenation and on
the selectivities. In the stirred tank, the catalyst surface is fully wetted and H₂ must dissolve in
the soy oil and then be transported through the liquid phase. The turbulence provided by the
intense agitation results in a homogeneous bulk liquid with only a small boundary layer region
near the catalyst. On the other hand, in monolith channels there are three external mass transfer
steps for the transport of H₂ to the catalyst surface - gas to liquid, liquid to solid, and gas to
solid⁹³,¹⁸². Mass transfer coefficients for the individual steps were estimated through literature
correlations that are listed in Table 6.7. A more detailed discussion of these mass transfer
calculations can also be obtained from our previous work.¹⁸⁶

<table>
<thead>
<tr>
<th>Mass transfer step</th>
<th>Correlation</th>
<th>Investigator</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas to liquid through bubble cap</td>
<td>( k_{GL}a_{GL} = \frac{0.111u_{TP}^{1.2}}{\xi L_{UC}^{0.57}} )</td>
<td>Bercic and Pintar (1997)¹²⁴</td>
</tr>
<tr>
<td>Liquid to solid</td>
<td>( k_{LS} = \frac{D_n}{d_{ch}} 20 \left( 1 + 0.003 \left( \frac{L_{UC} / d_{ch}}{Re Sc} \right)^{0.7} \right) )</td>
<td>Kreutzer et al. (2001)¹¹⁶</td>
</tr>
<tr>
<td>Gas to solid though liquid film</td>
<td>( k_{GS} = \frac{D}{\delta} )</td>
<td>Irandoust and Andersson (1989)¹⁵⁵</td>
</tr>
<tr>
<td></td>
<td>( \delta = (d_{ch} - d_b) / 2 )</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \frac{d_b}{d_{ch}} = 0.64 + 0.36 \exp(-3.08Ca^{0.54}) )</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( a_{GS} = \frac{4(1 - \xi L)}{d_{ch}} )</td>
<td></td>
</tr>
</tbody>
</table>

By combining these three steps the overall volumetric mass transfer coefficient \((k\text{,}_a\text{,}a)\)
can be determined as¹¹⁶:

\[
k\text{,}_a\text{,}a = k_{GS}a_{GS} + \left( \frac{1}{k_{GL}a_{GL}} + \frac{1}{k_{LS}a_{LS}} \right)^{-1}
\]  (6.22)
Using these equations, the values of the individual volumetric mass transfer coefficients were computed at the conditions of this study. The gas superficial velocity was fixed for all experiments based on the gas recycle rate. However, the liquid superficial velocity is a function of pulse frequency. The velocities are 45 and 97 cm/s at respective frequencies of 8 and 17.5 Hz. These values were calculated based on the volume of fluid displaced by each upward stroke per time, then divided by the cross sectional area of the monolith channels. At pulsing conditions, the liquid hold up $\varepsilon_L$ is $\frac{u_L}{u_L + u_G}$, while at no pulsing conditions, the average liquid superficial velocity was taken to be zero and the liquid hold up $\varepsilon_L$ as $1 - \frac{L_{\text{slug}}}{L_{ch}}$, with $L_{\text{slug}}$ taken as 3 $d_{ch}$.116 The results are summarized in Table 6.8.

Increasing the frequency of the oscillations should result in increased mass transfer coefficients in the POMR, because the time-averaged superficial velocity of liquid in the monolith channels also increases, and because for at least part of the cycle (the upstroke of the piston) the liquid film thickness is small and gas flow dominates. This has been the typical explanation for the positive effects of pulsating flows on reaction rates97,101,116,186 To establish the extent of the external mass transfer resistance, the external mass transfer rate of hydrogen was equated with the observed reaction rate as follows.

$$k_c a(C_{H_2}^* - C_{H_2}^0) = R_{H_2} \rho_{cc}$$  \hspace{1cm} (6.23)

Here, $C_{H_2}^*$ is the solubility of hydrogen in soy oil, $C_{H_2}^0$ is the concentration of hydrogen at the catalyst surface and $\rho_{cc}$ is the catalyst loading expressed as kg of catalyst/ m$^3$ of liquid volume inside all monolith channels. The hydrogen concentration at the catalyst surface was obtained from Equation 6.23 and the value of $C_{H_2}^*/ C_{H_2}^0$ was calculated. From Table 6.8 it is seen that this ratio is less than unity indicating presence of external mass transfer limitations. Weisz -
Prater moduli were calculated based on the calculated surface concentration of hydrogen and the observed reaction rates in the POMR. High values of moduli (see Table 6.8) confirmed the existence of internal diffusion limitations. This suggests that the reaction is limited by both the external and the internal mass transfer in the POMR.

<table>
<thead>
<tr>
<th>( f )</th>
<th>( u_L )</th>
<th>( k_{\text{La}} )</th>
<th>( C_{H_2}^* / C_{H_2}^* )</th>
<th>( \Phi_{WPH_2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hz</td>
<td>cm/s</td>
<td>1/s</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>0</td>
<td>0.47</td>
<td>0.10</td>
<td>230</td>
</tr>
<tr>
<td>8</td>
<td>45</td>
<td>1.14</td>
<td>0.50</td>
<td>64</td>
</tr>
<tr>
<td>17.5</td>
<td>97</td>
<td>1.97</td>
<td>0.55</td>
<td>94</td>
</tr>
</tbody>
</table>

Similarly, it is possible to compute the ratio \( C_{H_2}^* / C_{H_2}^* \) for the stirred autoclave using Eq. 6.23. The overall volumetric mass transfer coefficient for the autoclave reactor was calculated using the correlation proposed by Albal et al.\(^{193}\)

\[
Sh = 1.41 \times 10^{-3} Sc^{0.5} Re^{0.67} We^{1.29}
\]

where the Sherwood number is \( Sh = \frac{k_{\text{La}} a d_i^2}{D} \), and the other dimensionless quantities are defined as usual. Using Equation 6.24, \( k_{\text{La}} \) was found to be \( \sim 11 \text{ s}^{-1} \) at 2000 rpm. For the smallest catalyst size, this gives \( C_{H_2}^* / C_{H_2}^* = 0.99 \). This shows that the reaction is not external transport-limited in stirred tank, as the intraparticle resistance scales more strongly with catalyst size.

Since both external and internal mass transfer limitations exist in the POMR, improvements in POMR performance with increasing frequency suggest that either one or both of the limitations are altered. Improvements in the rate of reaction due to enhancements in the external mass transfer have already been shown in our previous work\(^ {25}\) and can also be seen from increasing \( k_{\text{La}} \) values (Table 6.8). The possibility of improving reaction rates by altering the internal transport also exists. Recently Bakker et al.\(^ {194}\) showed that the alternating flow of gas...
bubbles and liquid slugs in a monolith can enhance internal convective diffusion in a macroporous structured catalyst. They used a honeycomb monolith structure made up of interlocked elongated mullite grains with interstitial voids of ~45 µm size. The silica used for the coating had an average pore size of 4.2 µm. They did not investigate the effect of frequency of the alternating gas-liquid slug flow.

In a previous study, Chandhok et al.\textsuperscript{195} achieved up to two orders of magnitude enhancement in $k_{La}$ with pulsating flow through a liquid membrane, at frequencies in the 1 Hz range. Leighton and McCready\textsuperscript{196} explained that the enhancement of transport in membranes due to oscillating flows can result from enhanced Taylor dispersion in the pores themselves, and that such dispersion can explain the enhancements observed in liquid membrane transport.\textsuperscript{195} They proposed that the mass transfer enhancement in pores is a function of Womersley number $\alpha = r(\omega/\nu)^{0.5}$ ($r$ is pore radius) and Schmidt number $Sc = \nu/D_e$ as shown in Equation 6.25.

$$\frac{K}{D_e} = 1 + \left(\frac{\Delta x}{r}\right)^2 \left(1 - \frac{4}{\beta} \frac{T_1(\beta)}{T_2(\beta)}\right)$$

(6.25)

where:

$\beta = \alpha Sc^{0.5}$

$T_1(\beta) = \text{ber} \beta \text{ber}' \beta + \text{bei} \beta \text{bei}' \beta$

$T_2(\beta) = \text{ber} \beta \text{bei}' \beta + \text{ber}' \beta \text{bei} \beta$

$K$ is the apparent diffusion coefficient due to pulsations, $\Delta x$ is the amplitude of fluid pulsation penetrating inside the pores and the functions $\text{ber} \beta$ and $\text{bei} \beta$ are Kelvin functions, related to the Bessel function $I_0$ by $I_0(\beta^{1/2}) = \text{ber} \beta + i \text{bei} \beta$. This equation is only valid for a limiting case of $\alpha \to 0$ and $Sc \to \infty$, but $\beta$ of order one. For this study, $\alpha \sim 10^{-5}$, $Sc \sim 10^4$, and $\beta \sim 0.1$. 

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Using the above equation, predicted enhancements in pore transport were calculated for our runs. Values of macropore radius \(r\) were obtained from SEM images of washcoated monoliths, which showed both larger (~10 µm) and smaller pores (~1 µm average radius) pores. To obtain the upper and lower bounds, two extremes were considered for \(\Delta x\). The largest possible value of \(\Delta x\) was taken as the product of washcoat thickness and tortuosity which gives a value of 300 µm. The conservative estimate was obtained by assuming that fluid is only able to penetrate to a distance of one tenth of the washcoat thickness \((\Delta x = 30 \mu m)\).

Calculated values of the transport enhancement, \(K/D_e\), for the combination of two different pore radii and two different \(\Delta x\) values are reported in Table 6.9. Enhancements were calculated for 8 Hz, 17.5 Hz and also for 0.5 Hz which is the true frequency at no forced pulsing conditions due to the gas recycle booster. The values of \(K/D_e\) for \(r = 10 \mu m\) and \(\Delta x = 30 \mu m\) are of order 1-10, relative to a true run at 0 Hz. Since the smallest frequency was 0.5 Hz, the observed improvement in the performance relative to this frequency is the ratio 
\[
\left( \frac{K/D_e}{K/D_e} \right)_{8Hz} / \left( \frac{K/D_e}{K/D_e} \right)_{0.5Hz}
\]
(keeping \(r\) and \(\Delta x\) values constant). For \(r = 10 \mu m\) and \(\Delta x = 30 \mu m\), this ratio is 1.8 and 1.9 for 8 and 17.5 Hz respectively. These values can be compared to the actual ratios of reaction rates obtained in the POMR, namely 1.3 and 2.1 for 8 and 17.5 Hz respectively. The enhancement theory results do scale qualitatively with the experimental observations. With better estimates of \(r\) and \(\Delta x\), it might be possible to theoretically better predict the enhancements observed in the POMR.

The present work suggests that significant enhancements to pore diffusion / convection can be achieved in the catalyst washcoat. The pulsations are propagated into the pore space, at least to some extent. It was shown by Leighton and McCready that the smaller the pore diffusivity and the larger the ratio of amplitude to pore size, the greater the enhancement. This
result suggests that for reactions of even heavier molecules the POMR would be an ideal reactor. But further investigation is required to systematically discern the effects of pulse frequency and amplitude on internal diffusion in the POMR.

Table 6.9  Transport enhancements in the POMR.

<table>
<thead>
<tr>
<th>f (Hz)</th>
<th>r (µm)</th>
<th>Δ x (µm)</th>
<th>K/De</th>
<th>(K/De)_f Hz/(K/De)_0.5 Hz</th>
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<tr>
<td>0.5</td>
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<td>5</td>
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<tr>
<td>0.5</td>
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<td>300</td>
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<td>100</td>
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6.4 Conclusions

It was shown that by using low frequency and low amplitude mechanical oscillations, up to a 112% enhancement in the hydrogenation rate of soybean oil can be achieved in the POMR. On a power per unit volume basis, the POMR performs better than a stirred tank with an identical monolith catalyst. Experiments with a powdered catalyst having a shorter diffusion length did show higher reaction rates in the stirred tank. Experimental observations confirmed by Weisz-Prater moduli calculations showed that the reaction is intraparticle diffusion-limited for larger catalyst sizes including the monolith in the stirred tank. For the stirred tank, external mass transfer calculations showed that the reaction is not external mass transfer controlled. For the POMR, calculations showed that both external and internal mass transfer limitations exist. Due to higher intraparticle diffusion resistances, the monolith catalyst (in both the stirred tank and the POMR) exhibited slightly smaller serial pathway selectivity (S21) towards the formation of monounsaturated fatty acids, but the POMR showed equal or better selectivity to diunsaturated...
fatty acids ($S_{12}$). Formation of trans fatty acids was also higher in the monolith catalyst as compared to the powdered catalyst. A theory proposed by Leighton and McCready\textsuperscript{196} for pulsed diffusion in liquid membranes was used to calculate the mass transport enhancement in the monolith catalyst washcoat. The theoretical predictions were in order of magnitude and qualitative agreement with experimental observations. The current work suggests that it is possible to achieve significant internal mass transfer enhancements in the washcoat of monoliths using low amplitude and low frequency pulsations in the fluid. Improved internal transport combined with the enhanced external mass transfer from pulse effects give higher activity for the POMR.
Chapter 7 Summary and Future Work

7.1 Summary

The heterogeneous catalyzed hydrogenation of macromolecules and low molecular weight species was investigated in novel oscillatory reactors. These reactors were based on a polymer extruder and a bubble column design (POMR), but with deliberate unsteady state flows induced by alternating gas and liquid flows over the catalyst surface. In the case of the extruder-fed monolith die, the oscillatory behavior was provided by the alternating liquid- and gas-filled screw sections that propagated down the extruder barrel to the die containing the catalyst. For the bubble column design, the oscillations were provided by a piston/camshaft arrangement. Significant gains in activity and some gains in selectivity were observed as compared to more conventional reactors (e.g., agitated vessels). We have shown that controlling the catalyst wetting phenomena can play a key role in enhancing activity and selectivity by controlling surface renewal of reactive species. In addition, the advantage of having the catalyst fixed in the reactor as either a monolith or packed bed is also advantageous in catalyst/product separation.

The hydrogenation of poly(styrene) over a Pd/Al₂O₃ catalyst was studied in a novel pulsed extruder, which feeds the monolith die. The activity and selectivity of the reaction was investigated over a range of flow rates, polymer concentrations and natural and forced pulsing regimes. Observed activities were highly related to gas-to-liquid mass transfer rates provided by correlations for slug flow in catalyst monoliths. Results show a naturally pulsed reactive extruder is an attractive choice for hydrogenation at low polymer concentrations (2 wt%), where intrinsic rates are approached. Higher concentrations (10 wt%) lead to significant mass transfer barriers and a decrease in activity. But for this case, forced pulsing has a greater effect on productivity, and an optimum pulsing frequency was evident. However, at higher concentrations a stirred tank was able to outperform the extruder system due to the effect of higher shear rates near the
impeller blades that lower the viscosity of the shear thinning polymer solutions. Selectivity was higher and power input lower than in a stirred tank at comparable conditions. Enhanced selectivity was attributed to a more plug flow-like residence time in the monolith channels and improved surface renewal of reactants. The optimal frequency was higher than found in previous work on hydrogenations in low molecular weight systems. However, control of the exit age distribution of pulses proved to be difficult beyond that which was attainable using the natural characteristic frequency of the extruder.

The hydrogenation of alpha-methyl styrene to cumene was investigated in a novel piston oscillating monolith reactor (POMR). Low frequency (0 – 17.5 Hz) and amplitude (2.5 mm) mechanical oscillations were applied to the three-phase system at 46°C and 0.44 MPa H₂. For comparison purposes the reaction was also carried out in a stirred tank at identical temperatures and pressures, and at similar power input per volume. Results show activity improvements of up to 84% for 17.5 Hz, 2.5 mm piston oscillations over low frequency pulsed gas flow conditions. The POMR also gives as good or better selectivity towards cumene than a stirred tank at identical conditions. While the effects of catalyst pretreatment and its impact on Pd crystallite size also have an important role in determining catalyst activity and long term stability in AMS hydrogenation, these results suggest that the impact of low frequency and amplitude oscillations, applied to structured reactors, is considerable. It was also shown that the POMR can exhibit superior activity over other structured reactors such as trickle beds and conventional monoliths and even approach the highest rates quoted in the literature for a pelletized catalyst in a stirred tank. We were able to use correlations for volumetric mass transfer coefficients in monoliths to predict the enhancement of observed reaction rates in the POMR, and these predicted enhancements are in good agreement with the experimental values.
It has been shown that the use of low frequency, low amplitude oscillations can directly benefit the performance of gas mass transfer-limited reactions. This was shown for both low molecular weight hydrogenations (AMS) and for the hydrogenation of a polymer (PS). Flow oscillations in gas-liquid reactions not only provide a way to improve gas mass transfer by producing higher interfacial areas by bubble breakage, but also by affecting the catalyst surface wetting. Since the optimal surface wetting distribution for each reaction will vary, the POMR has the particular advantage of being able to accurately control the pulsing frequency over a wide range, to generate the optimal wetting environment.

New hydrogenation catalysts were synthesized to address the shortcomings of current catalysts for polymeric systems. The role of pore diameters, support type, preparation method, and the influence of a second metal were investigated in a laboratory stirred reactor for the hydrogenation of PS. The largest improvement in activity (~1 order of magnitude) came from changing the organic solvent from 10 vol% THF/cyclohexane to decahydronapthalene (DHN). This was attributed to the effects of polymer chain conformation; in a relatively good solvent (THF/C₆H₁₂) the polymer chains expand due to interactions with solvent molecules, while in a bad solvent (DHN), the polymer collapses to a state of minimal hydrodynamic radius.

It was found that the method of preparation of the bimetallic catalyst has a large impact on the observed activities. In particular, the order of metal addition and the Pd/Cu atomic ratio were major factors that determined hydrogenation activity. In fact, the only catalysts that had a higher activity per active site (TOF) than a monometallic baseline catalyst were Pd/Cu catalysts at a ratio of 1 wt% Pd / 0.5 wt% Cu. It was also shown that the addition of the second inert metal (Cu) enhances selectivity by limiting chain scission reactions compared to a monometallic catalyst. However, the best improvement in selectivity came from using a catalyst support free from acidic (chloride) impurities that can catalyze side reactions. It was found that the catalyst
pore diameter did not greatly influence the reaction rate, provided it was above a certain critical value in the low end of the mesoporous range (2-3 nm). Catalyst supports in the microporous range (<2 nm) did exhibit poor performance. The critical pore diameter is likely to be influenced by polymer morphologies, molecular weights, and concentrations in solution, as these all affect the conformation of polymer chains inside pores. Relatively inert mesoporous carbon supports did not exhibit an advantage over aluminas and silicas, as might be expected based on polymer diffusion experiments. Instead, the ability to make a catalyst with a high dispersion proved to be the controlling factor in obtaining a high specific activity.

For the hydrogenation of soybean oil, the POMR also showed significant gains in activity over a stirred tank operated at identical power per unit volume. Pulsing was found to improve observed hydrogenation rates by more than double. Analysis showed that the reaction was not limited by external mass transfer. Instead the size of catalyst particles was shown to have a significant impact on hydrogenation activity. This suggests that the reaction is limited by internal mass transfer in both the stirred tank and POMR. Therefore, the two phase pulsed flow directly influenced the intraparticle environment, either by enhancing pore diffusion or altering the surface wetting of the monolith washcoat. It is difficult to conclude the exact cause from our experiments. Serial pathway selectivity ($S_{32}$) was shown to improve as pulsing frequencies were increased while no conclusion could be made over $S_{21}$. However, the monolith structured catalyst exhibited worse stereo-selectivity regardless of reactor system.

7.2 Future Work

The hydrogenations of AMS and PS have some, albeit limited industrial importance. Therefore, they serve primarily as case studies for proof of principle type reactions, and in this respect they were successful. The final goal of this project is to use the catalysts and reactors
developed here in emerging markets where we feel the use of a structured catalyst inside of an oscillating reactor can benefit the most.

One such possible direction is in the area of gas-to-liquids (GTL) technology. GTL (Fischer Tropsch) reactions involve the transformation of syngas (H₂ and CO) into synthetic gasoline and diesel. The fuels produced from GTL are typically much cleaner than those from crude oil, making them ideal as blending stock for increased environmental regulations. Even though FT technology was originally pioneered by the Nazis in WWII to provide fuel for the war effort, current crude oil prices and the easy availability of syngas feedstocks (particularly coal and biomass) in the United States has made this an attractive field for ongoing research. Also, depending upon reactor configuration, higher value products can be made such as poly(alpha olefins) and surfactants. In the low temperature (220-230°C) Fischer Tropsch reactor (LTFT), the system is operated in three-phase mode with unconverted syngas, solid catalyst, and a liquid phase product at ~3 MPa.

The two commercial scale LTFT reactors are fixed bed tubular and bubble column slurry reactors. The original FT reactors used in Germany were based on an array of fixed tubes arranged in a shell and tube type design. This was required because the FT reaction is highly exothermic, necessitating rapid rates of heat removal to limit catalyst deactivation via coking and the formation of low molecular weight products (primarily methane). The catalyst was fixed in the form of spherical particles inside the tubes. Syngas was flowed from the top and as it converted to liquid hydrocarbons, the heavier liquid phase flowed under gravity to a knockout pot at the bottom. The size of catalyst particles is relegated by pressure drop concerns and the active metal chosen. Co catalysts are much more reactive than Fe based ones and therefore require smaller particles for better heat transfer. However, due to the inherent radial and axial temperature gradients present in this system, only a small section of the reactor operates at the
optimum temperature. The main advantages of this reactor are that impurities will only poison the catalyst near the entrance and the easy scale-up from one tube to a bundle.

The other reactor is based on a bubble column where the catalyst is present as a slurry suspended in the liquid “wax” phase and the syngas is discharged from the bottom by a distributor. While bubble columns have been in use as mass transfer systems (e.g., gas scrubbers) for many years, this reactor type has only recently been commercialized. This is because of problems related to separation of fine catalyst particles from the liquid. This reactor has significant advantages over the tube design in the form of better heat transfer and the ability to use catalyst with diameters <100 µm. Smaller diameter particles also mean a lower active metal loading is required to prevent reactor runaway, which translates into lower catalyst costs. In this reactor catalyst poisoning is a serious issue due to lower loadings and all of the catalyst being exposed to the entrance syngas. However, in-situ catalyst replacement is possible using this design whereas the fixed tube reactors require shut down. Bubble columns also have a cost advantage as the reactor train costs ~25% of a fixed bed for a given throughput.

A system similar to the POMR could have significant advantages over both the fixed bed and slurry bubble column reactors. The similarities between a slurry bubble column and the POMR are obvious. However, the POMR would have superior cooling ability from the alternating heat exchanger/monolith stack and the fixed catalyst would sidestep the separation requirement that prevented the quick implementation of this type of reactor. Washcoat thicknesses in the range of the particles that are currently used are easily attainable using the results presented in this dissertation. As this dissertation has shown, one of the key abilities of oscillations is the ability to control the surface wetting of the catalyst and the residence times of species on the surface. This could be greatly beneficial to GTL technology because the desired products are formed via a chain growth mechanism and pulsing could be used to optimize the
reactor for the production of species in certain molecular weight ranges. Current LTFT reactors generally produce mainly diesel and other heavier molecular weight products. Because FT reactors produce a variety of products, post-FT treatment (e.g., distillation) and further product upgrading is required. Optimizing the FT reactor for one particular product slate would lessen these post FT requirements.

The POMR could be used to produce heavier species than what is normally attainable in a LTFT slurry bubble column. This is because if higher loadings are used, the viscosity of the liquid “wax” increases to the point where there are significant heat and mass transfer gradients. The pulses provided by the POMR have been shown to greatly improve gas distribution through all monolith channels even with viscous liquids. These pulses can also provide a greater mixing effect to make the reactor more isothermal. The mesoporous catalyst supports prepared in this project can also find relevance in GTL reactions because while light gas phase reactants are used, the products are heavier liquids and in some cases polymers. This can create intraparticle barriers to product diffusion out of the catalyst, effectively trapping products and resulting in the chains growing longer than desired.

Another area where the benefits of this project can be realized is the heterogeneous catalyzed production of bio-diesel. Bio-diesel is composed of methyl ester analogous of fatty acids. These fatty acids are typically obtained from edible oil sources. Diesels derived from bio-based feedstocks are not only attractive because they are renewable and would increase energy independence, but also because bio-diesel is inherently superior to petroleum based diesel. Bio-diesel has a higher cetane number, is almost free of Sulfur, has better lubricity, and gives lower soot emissions. Even if it is not feasible to convert all diesel production to edible oil feedstocks, bio-diesel is can still be used as a high quality blending component for petroleum based diesels in order to meet strict new government standards for (15 ppm) levels of Sulfur.
The transesterification reaction to produce bio-diesel takes the edible oil and reacts it with methanol over an alkaline or acid catalyst to produce the fatty acid methyl ester (FAME) and glycerol as a byproduct. Homogeneous catalysts (e.g. NaOH) are commonly used on the small scale by independent producers because they offer high activities and are soluble in MeOH. However, for large scale production a heterogeneous catalyst is clearly superior to avoid separation issues. Heterogeneous catalyst such as basic zeolites, alkaline earth metals, and solid acids can be used in this application. The addition of a solid phase effectively makes the system three-phase because the two liquid phases (edible oil and MeOH) are immiscible. This problem can be avoided by adding a co-solvent such as THF but at much higher costs. Also, the co-solvent must then be recovered for re-use. Therefore, the transesterification reaction is usually highly mass transfer limited in three-phase systems.

One method for improving on bio-diesel production is by processing in super critical methanol with no catalyst present. However, while this method gives high rates of reaction the capital costs are very large because the temperatures range from 350-400°C and pressures from 10-25 MPa. In comparison, the use of a heterogeneous catalyst will allow processing at 40-85°C and ~0.2 MPa. The key is overcoming mass transfer related issues. Clearly there are concerns on the external side regarding the contacting of the two immiscible liquid phases. However, internal mass transfer can be a concern regarding the transport of triglycerides into the porous catalyst pellet. As was shown in Chapter 6, we have shown improvements in intraparticle mass transfer for soyoil using the catalysts from this project. Therefore, the mesoporous catalyst supports studied in this project could be used as a basis for designing new mesoporous catalysts with an acidic or basic nature for bio-diesel production. The POMR would be a good choice for studying the influence of a structured catalyst with pulsing on the direct production of bio-diesel. Some modifications would need to be made from the existing apparatus since a gas phase does not
need to be re-circulated. This project has made it clear that low frequency, low amplitude pulses can directly benefit activity and selectivity by alternating the distribution of gas and liquid slugs. The question then becomes how well the pulses can distribute two immiscible liquid phases.
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Appendix A Supplementary Material for Chapter 3

A.1 Reactive Extruder Operating Procedure

1. Catalyst loaded in die (monolith or packed bed form) and attached to end of extruder barrel. For packed bed die, pack catalyst particles between silanized glass wool. Housing for monolith die holds 2 monoliths (5.5 x 5.5 x 1.2 cm) plus a steel backing plate. Packed bed die is 1” stainless steel pipe with Autoclave fittings. Die must be well insulated.

2. System is purged with H₂ flow to remove all traces of air and left at ~1 atm of H₂ pressure. Exhaust fan above extruder must be on.

3. Ceramic band heaters and heating tape used to slowly bring reactor up to temperature.

4. When at operating temperature, flow of polymer and hydrogen started, system pressurized. Start stirrer on autoclave (~400 rpm). Set extruder screw rpm.

5. Polymer solution flow set using Eldex B-100-S4 piston pump. Liquid flow is also checked by timed collection at outlet.

6. Gas flow into system recorded using Brooks 5850C MFC. This voltage data is recorded on computer using LabView software.

7. Flow at the outlet of the die is regulated by micrometer needle valve.

8. Gas flow rates measured using bubble meter (for instantaneous measurements) and the time to fill a gas bag of known volume (for time averaged measurements).

9. Once steady flow observed at exit, forced pulsing (optional) started using a LabView® (National Instruments) interface via computer-controlled solenoid. Record of photocell voltage (LabView) also started. Pressure across pulsing valve maintained at ~69 kPa.

10. The reactive extruder was run to pass ~60 mL of fluid before a sample was taken.

11. The polymer was recovered from solution by precipitating in excess tech grade methanol and drying under vacuum overnight at 120°C. This polymer was then dissolved in chloroform (for conversion analysis) or toluene (for intrinsic viscosity experiments).

A.2 Calibration for Brooks 5850C Mass Flow Controller

Brooks 5850C MFC, 0-100 sccm range, S/N# 80506HC026816

H₂ regulator set to 3.44 MPa. Output recorded using bubble meter attached to MFC exit.

Desired flow set using 10-turn potentiometer. Voltage corresponding to flow recorded using voltmeter for calibration and LabView® for experiments.
Figure A.1  Calibration of Brooks 5890C MFC. Output voltage used to determine flow into system in sccm. Flow controlled using potentiometer wired to MFC.

Figure A.2  MFC data from a typical reactive extruder run. Note unsteady state nature of H₂ flow.

A.3 Photocell on Die Exit

The photocell used to record flow instabilities at the die exit consists of a 1/8” Teflon tube surrounded by a plastic enclosure that slides tightly on the tube. On one side of the
enclosure is the light source: a 550 nm red laser diode connected to a variable power supply set at 2.0 Vdc.

Opposite the laser is a photodiode (photovoltaic cell) that outputs a voltage depending upon the impinging light intensity. The laser passes perpendicular to the Teflon tube. As gas and liquid slugs flow through the tube the intensity of light that impinges on the photodiode varies because the index of refraction changes. This voltage signal is recorded in LabView®. Low voltages correspond to gas-rich conditions and high voltages correspond to liquid-rich conditions. The LabView® program works as a stripchart recorder and measures the different voltages as a function of run-time.

Figure A.3  Schematic of photocell on die exit used to record alternating gas and liquid rich conditions.
A.4 PS Conversion Analysis

PS conversion was determined for all experimental runs using UV-Vis spectroscopy. This method determines the conversion from a regressed calibration line. The calibration line was determined using an absolute method for aromatic conversion — $^1$H-NMR, which is able to distinguish if protons are near carbon-carbon single or double bonds.

![Figure A.4 Baseline data of photocell under no flow. Deviation in baseline is +/- 1 mV.](image)

Table A.1 $^1$H-NMR acquisition and processing parameters for Bruker ARX-300.

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Figure A.5  Sample $^1$H-NMR spectra for PS (not hydrogenated). Triplet at $\sim$5.3 ppm is residual undeuterated solvent (CH$_2$Cl$_2$) used for setting the chemical shift.

Figure A.6  Sample $^1$H-NMR spectra for PS partially hydrogenated to PVCH. Note the increase in relative area of low ppm (aliphatic) peaks relative to high ppm (aromatic peaks), compared to Figure A.5. This is the basis for determining conversion.
From Figures A.5 and A.6, PS conversion based on $^1$H-NMR data was calculated by integrating the aromatic resonance protons at ~6-7.5 ppm and the aliphatic resonance protons at ~0.5-2 ppm and comparing the relative areas. For the purposes of this study, resolving each peak is not necessary. Therefore, one can treat all peaks at high ppm chemical shift as one common component when integrating and similarly with the low ppm chemical shift peaks.

For PS to PVCH:

![Diagram showing the conversion of PS to PVCH](image)

H$_1$-H$_3$ represent aliphatic protons and H$_4$-H$_8$ represent aromatic protons in PS, and H$_1$-H$_{13}$ represent aliphatic protons in PVCH. Therefore, upon complete conversion 5 aromatic protons $\rightarrow$ 0 aromatic protons and 3 aliphatic protons $\rightarrow$ 13 aliphatic protons.

Define PS fractional conversion ($X$) as:

$$R = \frac{Area_{aromatic}}{Area_{total}}$$  \hspace{1cm} (A.1)  \\

$$N = \frac{5 - 8R}{R + 1}$$ \hspace{1cm} (A.2)  \\

$$X = \frac{N}{5}$$ \hspace{1cm} (A.3)  \\

where at 100% conversion, $R = 0$ and $N = 5$ which correctly gives $X = 1$. At 0% conversion, $R = 0.625$ and $N = 0$ which correctly gives $X = 0$. 

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Figure A.7  Calibration line for maximum absorbance at 262 nm versus PS conversion from the Jasco V-570 UV-Vis Spectrometer. PS samples dissolved in spectrophotometric grade chloroform at 0.01 wt% concentration. PS Conversion determined using the $^1$H-NMR method shown in Table A.1.

For UV-Vis sample analysis, one must select baseline subtraction and verify a flat baseline before performing the analysis. From Figure A.7, the PS fractional conversion ($X$) for all reactive extruder samples was determined using:

$$X = \frac{Abs - 2.993}{-0.030} \quad \text{(A.4)}$$

Table A.2  Jasco V-570 UV-Vis spectrometer parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>starting $\lambda$</td>
<td>400 nm</td>
</tr>
<tr>
<td>ending $\lambda$</td>
<td>200 nm</td>
</tr>
<tr>
<td>scan rate</td>
<td>40 nm/min</td>
</tr>
<tr>
<td>photometric mode</td>
<td>Abs</td>
</tr>
<tr>
<td>Data pitch</td>
<td>0.1 nm</td>
</tr>
<tr>
<td>Band width</td>
<td>2.0 nm</td>
</tr>
<tr>
<td>solvent</td>
<td>chloroform</td>
</tr>
<tr>
<td>polymer concentration</td>
<td>0.01 wt%</td>
</tr>
<tr>
<td>response</td>
<td>medium</td>
</tr>
<tr>
<td>number of cycles</td>
<td>1</td>
</tr>
</tbody>
</table>
A.5 Determination of Observed Rate Constant (k<sub>obs</sub>)

To calculate the pseudo-first order rate constant k<sub>obs</sub> for poly(styrene) hydrogenation:

1. Model reactive extruder as plug flow reactor (PFR) and stirred tank as a batch reactor.
2. Units on k<sub>obs</sub> must be in L/s/gPd for comparison to stirred tank work.
3. Fractional conversion determined using UV spectroscopy (Section A.4).
4. Liquid volumetric flowrate measured at die exit.
5. Reaction assumed first order in aromatic and hydrogen concentrations based on Xu et al. data for pressures <3.44 MPa, first order in aromatic and zero order in hydrogen for pressures >3.44 MPa
6. Computed second-order rate constants made pseudo-first order by multiplying by C<sub>Hr</sub>.
7. Concentration of hydrogen dissolved in liquid obtained from Henry’s Law based on data from Snijder et al.
8. k<sub>obs</sub> depends on the system used (i.e. die type, PS concentration): detailed in sections A.5.1-A.5.4.

For a PFR in differential form:

\[ F_{Ao} \frac{dX}{dW} = -r_A \quad (A.5) \]

where \( X \) is the fractional conversion of species A, \(-r_A\) is the rate of reaction of species A, \( W \) is the weight of catalyst, and \( F_{Ao} \) is the molar flow rate entering the reactor. Integrating Eq. A.5 gives:

\[ W = F_{Ao} \int_0^X \frac{dX}{-r_A} \quad (A.6) \]

For a reaction that is first order in hydrogen and aromatic concentrations, A.6 simplifies to:

\[ W = \frac{v_o}{k_{obs}} \int_0^X \frac{dX}{(C_{Ho} - 3XC_{Ao})(1 - X)} \quad (A.7) \]

where \( v_o \) is the volumetric flow rate, \( C_{Ho} \) is the initial concentration of hydrogen, and \( C_{Ao} \) is the initial concentration of aromatics.
**A.5.1 2 wt% PS in Monolith Die**

\( v_o := 1.67 \cdot 10^{-5} \ \text{L/s} \) \quad \text{liquid volumetric flowrate}

\( P := 3.03 \cdot 10^6 \ \text{Pa} \) \quad \text{system pressure}

\( \text{Conv} := 0.0558 \) \quad \text{fractional conversion from UV}

\( V := 0.0224 \ \text{L} \) \quad \text{volume of monolith channels}

\( C_{\text{cat}} := 1.0267 \ \frac{\text{gPd}}{\text{L}} \) \quad \text{concentration of Pd}

\( C_{\text{Ao}} := 0.1686 \ \frac{\text{molA}}{\text{L}} \) \quad \text{concentration of aromatic}

\( W := C_{\text{cat}} V \ \frac{\text{gPd}}{\text{mol}} \) \quad \text{calculate weight of Pd in reactor}

\( R := 82.06 \) \quad \text{gas constant}

\( T1 := 273 + 180 \ \text{K} \) \quad \text{convert temp to K}

\( K_{\text{H2}} := 6.93 \cdot 10^{-5} \) \quad \text{Henry's constant at 180 C in cyclohexane from Snijder et al. (1994) JCED}

\( C_{\text{Ho}} := \frac{K_{\text{H2}} P}{1000} \)

\( C_{\text{Ho}} = \frac{21}{100} \ \frac{\text{mol}}{\text{L}} \) \quad \text{concentration of H2 in cyclohexane}

\( C_{\text{Hr}} := 0.238 \ \frac{\text{mol}}{\text{L}} \) \quad \text{solubility at reference conditions 180C, 3.4 MPa}

\[
W = \frac{v_o}{k_{\text{obs}}} \int_0^{\text{Conv}} \frac{1}{\left(C_{\text{Ho}} - 3 \cdot X \cdot C_{\text{Ao}}\right) \cdot (1 - X)} \, dX \cdot \text{solve} \ k_{\text{obs}} \rightarrow 2.1338250740437101319 \times 10^{-4} \text{L}^2 \frac{s}{\text{gPd} \cdot \text{mol}}
\]

\[
2.1338 \cdot 10^{-4} \cdot C_{\text{Hr}} = \frac{1}{10000} \\frac{L}{s \cdot \text{gPd}}
\]
A.5.2 10wt% PS in Monolith Die

\[ v_o := 1.67 \times 10^{-6} \text{ L/s} \] liquid volumetric flowrate

\[ P := 2.86 \times 10^6 \text{ Pa} \] system pressure

\[ \text{Conv} := .022 \] fractional conversion

\[ V := 0.0224 \text{ L} \] volume of monolith channels

\[ C_{\text{cat}} := 1.0267 \text{ gPd/L} \] concentration of Pd

\[ C_{A_0} := 0.843 \text{ molA/L} \] concentration of aromatic

\[ W := C_{\text{cat}} \cdot V \text{ gPd} \] calculate weight of Pd

\[ R := 82.06 \] gas constant

\[ T_1 := 273 + 180 \text{ K} \] convert temp to K

\[ K_{H2} := 6.93 \times 10^{-5} \] Henry's constant at 180'C in cyclohexane from Snijder et al. (1994) JCE

\[ C_{H_o} := \frac{K_{H2} \cdot P}{1000} \] from Snijder et al. 1994 solubility of H2 in cyclohexane

\[ C_{H_o} = 0.198 \text{ mol/L} \] concentration of H2 in cyclohexane

\[ C_{H_r} := 0.238 \] solubility at reference conditions 180'C, 3.4 MPa

\[ W = \frac{v_o \cdot \text{Conv}}{k_{\text{obs}}} \int_{0}^{\text{Conv}} \frac{1}{(C_{H_o} - 3 \cdot X \cdot C_{A_0}) \cdot (1 - X)} \, dX \text{ solve } k_{\text{obs}} \rightarrow 9.572439918604832213 \times 10^{-6} \text{ L}^2 \text{s}^{-1} \text{gPd}^{-1} \text{mol}^{-1} \]

make pseudo-first order:

\[ 9.57244 \times 10^{-6} \cdot C_{H_r} = 2.278 \times 10^{-6} \frac{L}{s \cdot \text{gPd}} \]
A.5.3 10 wt% PS in Packed Bed Die

\[ v_0 := 8.33 \cdot 10^{-6} \text{ L s}^{-1} \quad \text{liquid volumetric flowrate} \]

\[ P := 2.55 \cdot 10^6 \text{ Pa} \quad \text{System pressure} \]

\[ \text{Conv} := 0.055 \quad \text{fractional conversion} \]

\[ V := 0.035 \text{ L} \quad \text{volume of packed bed die} \]

\[ C_{\text{cat}} := 5.714 \text{ gPd L}^{-1} \quad \text{concentration of Pd} \]

\[ C_{\text{Ao}} := 0.843 \text{ molA L}^{-1} \quad \text{concentration of aromatic} \]

\[ W := C_{\text{cat}}V \text{ gPd} \quad \text{calculate weight of Pd} \]

\[ R := 82.06 \quad \text{gas constant} \]

\[ T_1 := 273 + 180 \quad \text{K} \quad \text{convert temperature to K} \]

\[ K_{\text{H2}} := 6.93 \cdot 10^{-5} \quad \text{Henry's constant at 180C in cyclohexane from Snijder et al. (1994) JCED} \]

\[ C_{\text{Ho}} := \frac{K_{\text{H2}}P}{1000} \]

\[ C_{\text{Ho}} = 0.177 \text{ mol L}^{-1} \quad \text{concentration of H2 in cyclohexane} \]

\[ C_{\text{Hr}} := 0.238 \quad \text{solubility at reference conditions 180C, 3.4 MPa} \]

\[ W = \frac{V_0}{k_{\text{obs}}} \int_0^{\text{Conv}} \frac{1}{(C_{\text{Ho}} - 3 \cdot X \cdot C_{\text{Ao}}) \cdot (1 - X)} \text{d}X \text{ solve, } k_{\text{obs}} \rightarrow 2.6391190067840883288 \cdot 10^{-5} \text{ L}^2 \text{s}^{-1}\text{gPd}^{-1}\text{mol}^{-1} \]

\[ \text{make pseudo-first order:} \]

\[ 2.639 \cdot 10^{-5} \cdot C_{\text{Hr}} = 6.281 \times 10^{-6} \frac{L}{s\text{gPd}} \]
A.5.4 Stirred Tank

At the stirred tank conditions the reaction is first order in aromatic concentration and zero order in hydrogen concentration as shown by Xu et al. (2003).

\[ t := 36000 \text{ s} \quad \text{reaction time} \]

\[ C_{\text{cat}} := 0.133 \frac{\text{gPd}}{\text{L}} \quad \text{concentration of Pd} \]

\[ \text{Conv} := 0.373 \quad \text{fractional conversion} \]

\[ k_{\text{obs}} := \frac{-\ln(1 - \text{Conv})}{C_{\text{cat}} t} \quad \text{for first order reaction in a batch reactor} \]

true first order rate constant

\[ k_{\text{obs}} = 9.75 \times 10^{-5} \frac{\text{L}}{\text{s}\cdot \text{gPd}} \]

A.6 Intrinsic Viscosity

Intrinsic viscosity was used to detect the side reaction (chain scission), which results in a decrease in molecular weight. Toluene was the solvent used. The Mark Houwink constants were obtained from Polymer Handbook, 4th edition, Section VII, pg. 23119. The viscometer was a Cannon-Fenske #J744, size 100.

define relative viscosity:

\[ \eta_{\text{rel}} = \frac{t_{\text{soln}}}{t_{\text{toluene}}} \quad (A.8) \]

where \( t_{\text{soln}} \) is solution efflux time, \( t_{\text{toluene}} \) is pure solvent efflux time.

define specific viscosity:
\( \eta_{sp} = \frac{\eta_{soln} - \eta_{toluene}}{\eta_{toluene}} = \frac{t_{soln} - t_{toluene}}{t_{toluene}} \)  
(A.9)

define reduced viscosity:
\[ \eta_{red} = \frac{\eta_{sp}}{c} \]  
(A.10)

where \( c \) is concentration in g/dL.

define intrinsic viscosity:
\[
[\eta] = \lim_{c \to 0} \frac{\eta_{sp}}{c} 
\]
(A.11)

\[
[\eta] = K M^a
\]
(A.12)

where \( K = 8.48 \cdot 10^{-5} \text{ dL/g} \) and \( a = 0.748 \) and \( M \) is molecular weight (g/mol)

For un-hydrogenated Dow Styron PS dissolved in toluene:

<table>
<thead>
<tr>
<th>Sample</th>
<th>Concentration g/dL</th>
<th>( t_{soln} ) s</th>
<th>( t_{toluene} ) s</th>
<th>( \eta_{sp} )</th>
<th>( \eta_{red} ) dL/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.0</td>
<td>97.5</td>
<td>46.2</td>
<td>1.11</td>
<td>1.11</td>
</tr>
<tr>
<td>2</td>
<td>0.75</td>
<td>83.0</td>
<td>n/a</td>
<td>0.80</td>
<td>1.06</td>
</tr>
<tr>
<td>3</td>
<td>0.5</td>
<td>69.2</td>
<td>n/a</td>
<td>0.50</td>
<td>1.00</td>
</tr>
<tr>
<td>4</td>
<td>0.25</td>
<td>56.7</td>
<td>n/a</td>
<td>0.23</td>
<td>0.91</td>
</tr>
</tbody>
</table>

Sample calculation of MW using y-intercept from Fig. A.8:

\[
a := 0.748 \quad K_1 := 8.48 \cdot 10^{-5} \quad \eta := 0.8551
\]

\[
M := \left( \frac{\eta}{K_1} \right)^a
\]

\[
M = 2.251 \times 10^5 \quad \text{g/mol}
\]
A.7 Mass Transfer Calculations

A.7.1 External Mass Transfer

An example of a gas-to-liquid mass transfer coefficient calculation is shown for two representative gas and liquid superficial velocities.

\[
(k_{gl} \cdot a_{gl})_M = \frac{0.133 \cdot u_{tp}^{1.2}}{L_{slug}^{0.5}}
\]  
(A.13)

\[
(k_{gl} \cdot a_{gl}) = (k_{gl} \cdot a_{gl})_M \cdot \left(\frac{D_H}{D_M}\right)^{0.5}
\]  
(A.14)

where \(u_{tp}\) is the two phase velocity (cm/s), \(L_{slug}\) is the length of a gas slug (cm), \(D_H\) and \(D_M\) are the diffusivities for hydrogen and methane respectively (cm²/s). Eq. A.13 was used to calculate the gas-to-liquid mass transfer coefficient, which is based on a correlation for methane-water. Eq. A.14 was used to scale this coefficient to the hydrogen / solvent system using the ratio of liquid-phase diffusivities.

Figure A.8  Plot of reduced viscosity vs. concentration. y-intercept is \([\eta]\).
Calculate diffusivity of H2 in cyclohexane from ChemSep data at 180°C, assuming no contribution from dissolved PS

\[ T_1 := 453 \quad \phi_b := 1 \quad V_a := 108.9 \]
\[ \mu_b := 0.8 \quad M_b := 84.16 \]

modified stokes einstein equation using Wilke and Chang corellation (1955) AIChE J

\[
\frac{D_{ab} \mu_b}{T_1} = \frac{7.4 \times 10^{-8} \left( \frac{\phi_b M_b}{M_b} \right)^5}{V_a^{0.6}} \]

solve: \[ D_{ab} \rightarrow 2.304496592518479398110^{-5} \text{ cm}^2 \text{ s}^{-1} \]

\[ D_{ab} := 2.3 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \]
\[ L_{slug} := 1.2 \text{ cm} \quad \text{assuming length of 1 monolith for a length of slug} \]
\[ U_g := 4.8 \times 10^{-4} \text{ cm s}^{-1} \quad \text{gas superficial velocity} \]
\[ U_l := 3.6 \times 10^{-4} \text{ cm s}^{-1} \quad \text{liquid superficial velocity} \]

\[ u_p := U_g + U_l \quad \text{two phase velocity} \]
\[ k_{gl1_a_m} = \frac{0.133 \left( \frac{u_p}{L_{slug}} \right)^{1.2}}{0.5} \]

corellation from Bercic and Pintar (1997) CES

\[ k_{gl1_a_m} = 2.474 \times 10^{-5} \]
\[ D_m := 2.38 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \]

adjustment to hydrogen/cyclohexane system from Kreu (2001) CES

\[ k_{glagl_h} = k_{gl1_a_m} \left( \frac{D_{ab}}{D_m} \right)^{0.5} \]

\[ k_{glagl_h} := 2.432 \times 10^{-5} \text{ s}^{-1} \quad \text{gas to liquid mass transfer coefficient times interfacial area} \]

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A.7.2 Internal Mass Transfer

Internal (intraparticle) mass transfer gradients were estimated using the Weisz-Prater modulus from H.S. Fogler\textsuperscript{122}:

\[
C_{wp} = \frac{\text{rate}_{\text{observed}}}{\text{rate}_{\text{diffusion}}} = \frac{\text{rate} \cdot \rho_c \cdot L^2}{D_e \cdot C_{He}}
\]  \hspace{1cm} (A.15)

\[
D_e = \frac{D_H \phi_p}{\tau}
\]  \hspace{1cm} (A.16)

where \(\text{rate}\) is the maximum observed rate as calculated in section A.5, but converted to hydrogen consumption and put on a per catalyst mass basis (mol H/s/gcat), \(\rho_c\) is the catalyst density (g/cm\(^3\)), \(L\) is the diffusion length (cm), \(D_e\) is the effective diffusivity defined in Eq. A.16, \(C_{He}\) is the concentration of hydrogen at the surface (mol H/cm\(^3\)), \(D_H\) is the hydrogen diffusivity (cm\(^2\)/s), \(\phi_p\) is the catalyst porosity (dimensionless), and \(\tau\) is the catalyst tortuosity (dimensionless). A summary of the Weisz-Prater parameters for each catalyst are shown in Table A.4.

Table A.4 Calculated Weisz-Prater Parameters.

<table>
<thead>
<tr>
<th>Reactor</th>
<th>PS concentration</th>
<th>(C_{wp})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>wt%</td>
<td></td>
</tr>
<tr>
<td>agitated tank</td>
<td>2</td>
<td>0.02</td>
</tr>
<tr>
<td>agitated tank</td>
<td>10</td>
<td>0.03</td>
</tr>
<tr>
<td>monolith die</td>
<td>2</td>
<td>0.07</td>
</tr>
<tr>
<td>packed bed die</td>
<td>10</td>
<td>0.21</td>
</tr>
</tbody>
</table>

A.8 Power Input

The power input for the stirred tank was computed using a correlation from Pandit et al.\textsuperscript{125}:

\[
P = N_o \rho N^5 D^5
\]  \hspace{1cm} (A.17)

where \(P\) is power input (W), \(N_o\) is the impeller constant, \(\rho\) is liquid density, \(N\) is revolution per seconds (1/s), and \(D\) is impeller diameter (m).
\[ D := 0.068 \text{m} \quad \text{diameter of impeller} \]

\[ N := 33s^{-1} \quad \text{revolution per second 33rps for 2000 rpm} \]

\[ N_0 := 0.8 \quad \text{constant for marine propeller from pandit et al (1989)} \]

\[ \rho := 610 \frac{\text{kg}}{\text{m}^3} \quad \text{density of mixture} \]

\[ V := .00035 \text{m}^3 \quad \text{volume of liquid} \]

\[ P := N_0 \rho \cdot N^3 \cdot D^5 \quad \text{from pandit et al Chem Eng Sci (1989) for 3 blade marine propeller no sparger} \]

\[ P = 25.498 \text{W} \]

\[ P_v := \frac{P}{V} \]

\[ P_v = 7.285 \times 10^4 \frac{\text{kg}}{\text{ms}^3} \quad \text{in watts/m}^3 \]

The power input for the reactive extruder was calculated using the pressure drop times volumetric flow rate:

\[ Q := 4.17 \times 10^{-8} \frac{\text{m}^3}{\text{s}} \quad \text{volumetric flowrate} \]

\[ \Delta P := 3.1 \times 10^6 \text{Pa} \quad 450 \text{ psi pressure drop} \]

\[ V := 1.12 \times 10^{-5} \text{m}^3 \quad \text{volume of monolith} \]

\[ P := Q \cdot \Delta P \quad \text{assuming incompressible newtonian} \]

\[ P = 0.129 \text{W} \]

\[ P_v := \frac{P}{V} \]

\[ P_v = 1.154 \times 10^4 \frac{\text{kg}}{\text{ms}^3} \quad \text{in watts/m}^3 \]

For the packed bed die:
\[
Q := 4.17 \cdot 10^{-8} \text{ m}^3 \text{ s}^{-1}
\]

\[
\Delta P := 2.7 \cdot 10^6 \text{ Pa}
\]

400 psi pressure drop

\[
P := Q \cdot \Delta P
\]

assuming incompressible newtonian fluid

\[
P = 0.113 \text{ W}
\]

\[
P_v := \frac{P}{V}
\]

\[
P_v = 1.005 \times 10^4 \frac{\text{kg}}{\text{m} \cdot \text{s}^3}
\]

in watts/m^3

The power input due to pulsing is negligible, as determined using the relationship from Waghmare et al.\textsuperscript{126}:

\[
P = \frac{1}{2} A^2 \omega^3
\]

(A.18)

where \(A\) is the forcing amplitude (m), and \(\omega\) is the pulsing frequency (2\(\pi f\)).

\[
A := .012 \text{ m}
\]

length in m of monolith as amplitude

\[
f := .5 \text{s}^{-1}
\]

frequency of pulsing in Hz at max pulse rate

\[
\omega := 2 \cdot \pi \cdot f
\]

\[
P_m := \frac{1}{2} A^2 \omega^3
\]

power per mass

\[
P_m = 2.232 \times 10^{-3} \frac{\text{m}^2}{\text{s}^3}
\]

\[
\rho := 610 \frac{\text{kg}}{\text{m}^3}
\]

fluid density at rxn conds in kg/m^3

\[
P_v := P_m \rho
\]

\[
P_v = 1.362 \frac{\text{kg}}{\text{m}^3 \cdot \text{s}^3}
\]

so power input due to pulsing is insignificant
A.9 Bubble Instability Calculation

The onset of bubble instability in the liquid was calculated based on Benjamin-Ursell\textsuperscript{130} theory, where instability is governed by a series of Mathieu equations:

\[
\frac{d^2 a_m}{dT^2} + [p_m - 2q_m (\cos(2T))]a_m = 0 \tag{A.19}
\]

\[
p_m = \left( \frac{4k_m \tanh(k_m L)}{\omega^2} \right) \left( g + \frac{k_m^2 \sigma}{\rho} \right) \tag{A.20}
\]

\[
q_m = 2k_m A \cdot \tanh(k_m L) \tag{A.21}
\]

where \(a_m\) is the surface fluid amplitude, \(T\) is \(\omega t/2\) (\(t\) is time in s), \(k_m\) is the characteristic eigenvalue, \(L\) is the length of the monoliths (cm), \(\omega\) is the forcing frequency (rad/s), \(g\) is the acceleration due to gravity (cm/s\(^2\)), \(\sigma\) is the surface tension (dyn/cm), \(\rho\) is the liquid density (g/cm\(^3\)), and \(A\) is the forcing amplitude (cm). The subscript \(m\) represents the \(m\)th zero of the derivative of the \(l\)th order Bessel function based on zero velocity at the channel wall. Values for \(k_m\) are determined by multiplying the radius of cross-section of total flow area by the constant 11.7 obtained from the paper for \(m=4, l=1\). The parameter \(q\) equals \(2Ak_m\) and the corresponding \(p\) values are given in the paper. Then \(\omega\) is computed from these values and Eq. A.20. The forcing amplitudes \((A)\) are calculated below.

Calculate forcing amplitude \(A\):

for monolith die

\(A_C := 9.33 \text{cm}^2\) total cross sectional area of monolith

\(Q_{p.01} := 7.8 \text{cm}^3/\text{min}\) flow rate in the die for forced pulsing calculated from bubble meter data at NTP and adjusted using ideal gas law

\(Q_{np} := 1.8 \text{cm}^3/\text{min}\) flow rate in the die for natural pulsing calculated from bubble meter data at NTP and adjusted using ideal gas law
Duration of gas slugs

\[ t_{p0.1} := 20 \text{s} \quad 0.1 \text{ Hz} \]

\[ t_{np} := 3 \text{s} \]

Calculate forcing amplitudes

\[ A_{np} := \frac{Q_{np}}{A_c} t_{np} \quad A_{np} = 9.646 \times 10^{-3} \text{ cm} \quad \text{for unforced pulsing} \]

\[ A_{p0.1} := \frac{Q_{p.01}}{A_c} t_{p0.1} \quad A_{p0.1} = 0.279 \text{ cm} \quad \text{for 0.1 Hz forced pulsing} \]

for packed bed die

\[ A_c := 2.5 \text{ cm}^2 \quad \text{total cross sectional area of monolith} \]

\[ Q_{p.01} := \frac{3 \text{ cm}^3}{\text{min}} \quad \text{flow rate in the die for forced pulsing calculated from bubble meter data at NTP and adjusted using ideal gas law} \]

\[ Q_{np} := \frac{1.2 \text{ cm}^3}{\text{min}} \quad \text{flow rate in the die for natural pulsing calculated from bubble meter data at NTP and adjusted using ideal gas law} \]

Duration of gas slugs

\[ t_{p0.1} := 20 \text{s} \quad 0.1 \text{ Hz} \]

\[ t_{p0.5} := 40 \text{s} \quad 0.5 \text{ Hz} \]

\[ t_{np} := 3 \text{s} \]

Calculate forcing amplitudes

\[ A_{np} := \frac{Q_{np}}{A_c} t_{np} \quad A_{np} = 0.024 \text{ cm} \quad \text{for unforced pulsing} \]

\[ A_{p0.1} := \frac{Q_{p.01}}{A_c} t_{p0.1} \quad A_{p0.1} = 0.4 \text{ cm} \quad \text{for 0.1 Hz forced pulsing} \]

\[ A_{p0.5} := \frac{Q_{p.01}}{A_c} t_{p0.5} \quad A_{p0.5} = 0.8 \text{ cm} \quad \text{for 0.5 Hz forced pulsing} \]
A.10 Raw Data

A.10.1 Data Summary for Reactive Extruder

Table A.5  Summary of data for unforced reactive extruder runs: 2 wt% PS, 180°C, 3.03 MPa, monolith die.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Inverse liq space velocity</th>
<th>Rate Constant</th>
<th>( (k_{gl}a_{gl}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS_1_29</td>
<td>6.9</td>
<td>7.6E-06</td>
<td>2.4E-05</td>
</tr>
<tr>
<td>PS_1_30</td>
<td>4.6</td>
<td>1.8E-05</td>
<td>3.1E-05</td>
</tr>
<tr>
<td>PS_1_31</td>
<td>5.2</td>
<td>1.4E-05</td>
<td>2.9E-05</td>
</tr>
<tr>
<td>PS_1_33</td>
<td>3.3</td>
<td>3.7E-05</td>
<td>5.5E-05</td>
</tr>
<tr>
<td>PS_1_34</td>
<td>5.5</td>
<td>1.8E-05</td>
<td>2.9E-05</td>
</tr>
<tr>
<td>PS_1_35</td>
<td>2.5</td>
<td>4.0E-05</td>
<td>7.3E-05</td>
</tr>
<tr>
<td>PS_1_36</td>
<td>2.1</td>
<td>4.8E-05</td>
<td>9.3E-05</td>
</tr>
<tr>
<td>PS_1_37</td>
<td>1.8</td>
<td>4.8E-05</td>
<td>1.0E-04</td>
</tr>
<tr>
<td>PS_1_38</td>
<td>1.2</td>
<td>6.3E-05</td>
<td>1.6E-04</td>
</tr>
<tr>
<td>PS_1_39</td>
<td>1.0</td>
<td>5.3E-05</td>
<td>1.9E-04</td>
</tr>
<tr>
<td>PS_1_40</td>
<td>0.9</td>
<td>6.2E-05</td>
<td>2.2E-04</td>
</tr>
<tr>
<td>PS_1_41</td>
<td>0.8</td>
<td>6.8E-05</td>
<td>2.5E-04</td>
</tr>
<tr>
<td>PS_1_43</td>
<td>1.4</td>
<td>5.1E-05</td>
<td>1.4E-04</td>
</tr>
</tbody>
</table>

Table A.6  Summary of data for 0.1 Hz forced pulsing reactive extruder runs: 2 wt% PS, 180°C, 2.55 MPa, monolith die.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Inverse liq space velocity</th>
<th>Rate Constant</th>
<th>( (k_{gl}a_{gl}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS_1_58</td>
<td>1.7</td>
<td>6.1E-05</td>
<td>1.4E-04</td>
</tr>
<tr>
<td>PS_1_59</td>
<td>3.3</td>
<td>3.6E-05</td>
<td>4.7E-05</td>
</tr>
<tr>
<td>PS_1_60</td>
<td>2.8</td>
<td>2.9E-05</td>
<td>6.8E-05</td>
</tr>
<tr>
<td>PS_1_61</td>
<td>2.4</td>
<td>2.9E-05</td>
<td>8.0E-05</td>
</tr>
<tr>
<td>PS_1_62</td>
<td>4.4</td>
<td>2.0E-05</td>
<td>3.7E-05</td>
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<tr>
<td>PS_1_63</td>
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<td>1.1E-05</td>
<td>1.6E-05</td>
</tr>
<tr>
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<td>6.9</td>
<td>1.3E-05</td>
<td>2.1E-05</td>
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<td>PS_1_65</td>
<td>5.5</td>
<td>1.6E-05</td>
<td>2.6E-05</td>
</tr>
<tr>
<td>PS_1_66</td>
<td>9.2</td>
<td>8.3E-06</td>
<td>1.4E-05</td>
</tr>
<tr>
<td>PS_1_67</td>
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<td>4.8E-05</td>
<td>1.4E-04</td>
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<tr>
<td>PS_1_68</td>
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<td>1.0E-04</td>
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<td>PS_1_69</td>
<td>1.2</td>
<td>6.1E-05</td>
<td>1.8E-04</td>
</tr>
<tr>
<td>PS_1_70</td>
<td>0.8</td>
<td>7.8E-05</td>
<td>2.8E-04</td>
</tr>
<tr>
<td>PS_1_71</td>
<td>0.7</td>
<td>6.9E-05</td>
<td>3.2E-04</td>
</tr>
<tr>
<td>PS_1_72</td>
<td>0.6</td>
<td>5.7E-05</td>
<td>4.3E-04</td>
</tr>
</tbody>
</table>
Table A.7  Summary of data for unforced reactive extruder runs: 2 wt% PS, 180°C, 13.8 s g_{Pd} mL^{-1} inverse liquid space velocity, monolith die.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pressure</th>
<th>Rate Constant</th>
<th>( (k_{\text{w}}a_{\text{p}}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(MPa)</td>
<td>L s^{-1} g_{Pd}^{-1}</td>
<td>s^{-1}</td>
</tr>
<tr>
<td>PS_10_15</td>
<td>2.41</td>
<td>2.5E-06</td>
<td>6.0E-06</td>
</tr>
<tr>
<td>PS_10_16</td>
<td>2.86</td>
<td>2.3E-06</td>
<td>6.1E-06</td>
</tr>
<tr>
<td>PS_10_17</td>
<td>3.10</td>
<td>2.6E-06</td>
<td>7.9E-06</td>
</tr>
<tr>
<td>PS_10_18</td>
<td>3.36</td>
<td>2.9E-06</td>
<td>8.0E-06</td>
</tr>
</tbody>
</table>

Table A.8  Summary of data for unforced reactive extruder runs: 10 wt% PS, 180°C, 3.17 MPa, packed bed die.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Inverse liq space velocity</th>
<th>Rate Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>s g_{Pd} mL^{-1}</td>
<td>L s^{-1} g_{Pd}^{-1}</td>
</tr>
<tr>
<td>PS_10_100</td>
<td>18.0</td>
<td>6.8E-06</td>
</tr>
<tr>
<td>PS_10_103</td>
<td>26.7</td>
<td>6.2E-06</td>
</tr>
<tr>
<td>PS_10_104</td>
<td>14.4</td>
<td>8.0E-06</td>
</tr>
<tr>
<td>PS_10_105</td>
<td>42.4</td>
<td>5.6E-06</td>
</tr>
<tr>
<td>PS_10_106</td>
<td>6.0</td>
<td>7.9E-06</td>
</tr>
<tr>
<td>PS_10_107</td>
<td>23.2</td>
<td>6.7E-06</td>
</tr>
<tr>
<td>PS_10_108</td>
<td>42.4</td>
<td>5.9E-06</td>
</tr>
<tr>
<td>PS_10_109</td>
<td>72.0</td>
<td>4.3E-06</td>
</tr>
<tr>
<td>PS_10_110</td>
<td>32.7</td>
<td>6.0E-06</td>
</tr>
<tr>
<td>PS_10_111</td>
<td>22.5</td>
<td>6.7E-06</td>
</tr>
<tr>
<td>PS_10_112</td>
<td>13.6</td>
<td>8.2E-06</td>
</tr>
<tr>
<td>PS_10_113</td>
<td>16.0</td>
<td>7.4E-06</td>
</tr>
</tbody>
</table>

Table A.9  Summary of data for 0.1 Hz forced pulsing reactive extruder runs: 10 wt % PS, 180°C, 2.55 MPa, packed bed die.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Inverse liq space velocity</th>
<th>Rate Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>s g_{Pd} mL^{-1}</td>
<td>L s^{-1} g_{Pd}^{-1}</td>
</tr>
<tr>
<td>PS_10_200</td>
<td>18.0</td>
<td>8.4E-06</td>
</tr>
<tr>
<td>PS_10_202</td>
<td>7.2</td>
<td>1.1E-05</td>
</tr>
<tr>
<td>PS_10_203</td>
<td>14.4</td>
<td>9.6E-06</td>
</tr>
<tr>
<td>PS_10_204</td>
<td>5.3</td>
<td>1.2E-05</td>
</tr>
<tr>
<td>PS_10_205</td>
<td>10.3</td>
<td>9.7E-06</td>
</tr>
<tr>
<td>PS_10_206</td>
<td>16.7</td>
<td>8.6E-06</td>
</tr>
<tr>
<td>PS_10_207</td>
<td>20.6</td>
<td>8.0E-06</td>
</tr>
<tr>
<td>PS_10_208</td>
<td>12.4</td>
<td>1.0E-05</td>
</tr>
</tbody>
</table>
Table A.10 Summary of data for 0.5 Hz forced pulsing reactive extruder runs: 10 wt % PS, 180°C, 2.55 MPa, packed bed die.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Inverse liq space velocity</th>
<th>Rate Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>s g Pd mL⁻¹</td>
<td>L s⁻¹ g Pd⁻¹</td>
</tr>
<tr>
<td>PS_10_209</td>
<td>9.0</td>
<td>6.2E-06</td>
</tr>
<tr>
<td>PS_10_210</td>
<td>6.0</td>
<td>7.0E-06</td>
</tr>
<tr>
<td>PS_10_211</td>
<td>24.0</td>
<td>6.3E-06</td>
</tr>
</tbody>
</table>

A.10.2 Summary of Selectivity Data

Table A.11 Summary of data for capillary viscometry on extruder, stirred tank and unreacted samples. No extruder samples showed any detectable loss of MW upon comparing the time it takes a 1 g/dL solution to flow through the viscometer. Only the unreacted samples showing a lowered time had dilutions and MW determined.

<table>
<thead>
<tr>
<th>Run</th>
<th>Reactor</th>
<th>Conversion</th>
<th>Time at 1 g/dL</th>
<th>MW</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS_unreacted1</td>
<td>N/A</td>
<td>0</td>
<td>109.00</td>
<td>224.7</td>
</tr>
<tr>
<td>PS_unreacted2</td>
<td>N/A</td>
<td>0</td>
<td>108.30</td>
<td>225.8</td>
</tr>
<tr>
<td>Pd_Al1_1</td>
<td>autoclave</td>
<td>22.1</td>
<td>82.05</td>
<td>119.3</td>
</tr>
<tr>
<td>Pd_Al1_2</td>
<td>autoclave</td>
<td>6.4</td>
<td>97.89</td>
<td>203.5</td>
</tr>
<tr>
<td>PS_1_29</td>
<td>extruder</td>
<td>4.3</td>
<td>108.67</td>
<td>N/A</td>
</tr>
<tr>
<td>PS_1_33</td>
<td>extruder</td>
<td>9.0</td>
<td>107.63</td>
<td>N/A</td>
</tr>
<tr>
<td>PS_1_35</td>
<td>extruder</td>
<td>7.8</td>
<td>110.37</td>
<td>N/A</td>
</tr>
<tr>
<td>PS_1_40</td>
<td>extruder</td>
<td>4.7</td>
<td>111.30</td>
<td>N/A</td>
</tr>
<tr>
<td>PS_1_41</td>
<td>extruder</td>
<td>4.6</td>
<td>109.21</td>
<td>N/A</td>
</tr>
<tr>
<td>PS_1_58</td>
<td>extruder</td>
<td>6.5</td>
<td>107.81</td>
<td>N/A</td>
</tr>
<tr>
<td>PS_1_60</td>
<td>extruder</td>
<td>5.3</td>
<td>109.04</td>
<td>N/A</td>
</tr>
<tr>
<td>PS_1_63</td>
<td>extruder</td>
<td>6.1</td>
<td>109.41</td>
<td>N/A</td>
</tr>
<tr>
<td>PS_1_64</td>
<td>extruder</td>
<td>6.0</td>
<td>109.45</td>
<td>N/A</td>
</tr>
<tr>
<td>PS_1_70</td>
<td>extruder</td>
<td>4.4</td>
<td>108.79</td>
<td>N/A</td>
</tr>
<tr>
<td>PS_1_72</td>
<td>extruder</td>
<td>2.2</td>
<td>109.93</td>
<td>N/A</td>
</tr>
<tr>
<td>PS_10_15</td>
<td>extruder</td>
<td>2.0</td>
<td>110.25</td>
<td>N/A</td>
</tr>
<tr>
<td>PS_10_17</td>
<td>extruder</td>
<td>2.7</td>
<td>108.13</td>
<td>N/A</td>
</tr>
<tr>
<td>PS_10_100</td>
<td>extruder</td>
<td>6.2</td>
<td>107.78</td>
<td>N/A</td>
</tr>
<tr>
<td>PS_10_105</td>
<td>extruder</td>
<td>7.9</td>
<td>107.74</td>
<td>N/A</td>
</tr>
<tr>
<td>PS_10_107</td>
<td>extruder</td>
<td>6.9</td>
<td>110.1</td>
<td>N/A</td>
</tr>
<tr>
<td>PS_10_110</td>
<td>extruder</td>
<td>7.5</td>
<td>111.06</td>
<td>N/A</td>
</tr>
<tr>
<td>PS_10_113</td>
<td>extruder</td>
<td>6.1</td>
<td>109.78</td>
<td>N/A</td>
</tr>
<tr>
<td>PS_10_205</td>
<td>extruder</td>
<td>4.5</td>
<td>109.33</td>
<td>N/A</td>
</tr>
<tr>
<td>PS_10_206</td>
<td>extruder</td>
<td>5.4</td>
<td>107.80</td>
<td>N/A</td>
</tr>
</tbody>
</table>
Appendix B Supplementary Material for Chapter 4

B.1 Microclave Agitated Tank Reactor Operating Procedure

1. Load desired amount of ground catalyst powder and 15 mL of polymer solution into reactor. Adding greater than 18 mL will cause overflow.

2. Ensure Inconel metal washer is in place and seal reactor. Anti-seize compound on the threads is not needed for temperatures below 200°C.

3. Slip on the ceramic heating band and then the two thermocouples at the bottom. The type-J thermocouple is for heater control and the type-K is for the digital readout. Ensure the ceramic heating band is in direct contact with the metal reactor body by tightening the two nuts.

4. Leak test and purge the system with N₂ low pressure line. Then leak test at high pressure with the H₂ line at ~7 MPa. The rupture disk is set to ~14 MPa, the Microclave MAWP. For added safety, an escape line can be attached to the rupture disk assembly to facilitate ventilation should the rupture disk fail.

5. The most efficient way to monitor for leaks is to observe the pressure gauge and look for a drop in pressure because the gas volume in the reactor is small. Some time must be given to allow the gas to diffuse into the liquid.

6. The leak-free system should be bled down to ~100 kPa of H₂ with agitation and heating started. For high working temperatures (>100°C), coolant (50/50 ethylene glycol/water) must be supplied to the top half of the drive unit.

7. Once the reactor is at reaction temperature the H₂ line is opened and set to the desired run pressure. This marks the start of a run.

8. After the desired run time, the run is terminated by first closing the H₂ line and turning the heater off. For faster cooling, the ceramic heater band can be removed.

9. Once the reactor has cooled to near ambient temperature, the remaining pressure is bled off. This must be done slowly through the needle valve to avoid the liquid from being entrained with the gas through the exit port. The reactor is opened and the liquid/catalyst separated using a centrifuge. Most of the catalyst will have settled on the bottom by then.

10. The polymer is recovered by precipitating it in excess methanol followed by drying at ambient conditions and then under vacuum at 120°C overnight. The polymer is then dissolved in chloroform (for conversion analysis) or toluene (for intrinsic viscosity experiments).

11. The reactor assembly that contacts the fluid (impeller blade and cup) must be cleaned with toluene in between each run because some polymer will accumulate on these surfaces and dry out.
B.2 PS Analysis

PS conversion and molecular weight were determined using the same methods specified in Appendices A.4 - A.6.

B.3 Catalyst Preparation

B.3.1 Washcoating Monoliths

Figure B.1 is a flowchart that demonstrates how the monolithic catalysts were created by dipcoating in an aqueous slurry.

Figure B.1  Monolith washcoating procedure.
A critical step in obtaining a stable solids suspension is wet-ball-milling the slurry before dipcoating. The average particle size was reduced to <10 µm as confirmed by SEM (Figure B.2). Figure B.3 shows SEM images of a monolith coated three consecutive times with a 25 wt% solids slurry. It can be seen in Figure B.2 (a) that this method results in some channels having a significantly higher loading. The washcoat also exhibits some cracking due to contraction during calcination. Therefore to achieve a uniform channel-to-channel washcoat, the coating process was performed only once on subsequent monoliths.

**Figure B.2** SEM images of catalyst support in aqueous slurry (25 wt% solids) before milling (a) and after milling for 90 min (b).

**Figure B.3** SEM images of a coated monolith cross section showing cylindrical channels washcoated with catalyst (a) and a magnified view of the channel-washcoat-monolith interface (b).
B.3.2 Thermogravimetric (TGA) Analysis

Figure B.4 shows TGA results for the calcination of catalyst support Al1 with flowing air for a 2°C/min ramp from 50°C to 500°C, then a 2 h hold, then a ramp to 650°C. It can be seen from the weight derivative that the phase change to γ-Al₂O₃ is complete by 500°C. This confirms
that the 500°C calcination temperature is sufficient given a long enough soak time to completely convert the pseudoboehmite.

B.4 Catalyst Characterization

B.4.1 Elemental Analysis

Elemental analysis was performed using inductively coupled plasma atomic emission spectroscopy (ICP-AES). A known amount of catalyst sample was dissolved in boiling acid under reflux, and then diluted with DI water. The ICP concentrations of the calibration samples are shown in Table B.1. Table B.2 shows the repeatability for catalyst loading on a monolith from the 25 wt% slurry. All monoliths were dipcoated into the same slurry and allowed to dry before calcination. Excess slurry on the outside of the monolith was scraped off using a spatula.

Table B.1   ICP calibration.

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Expected conc.</th>
<th>Al 308 ppm</th>
<th>Al 394 ppm</th>
<th>Al 396 ppm</th>
<th>Average ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al_std0</td>
<td>0</td>
<td>0.049</td>
<td>0.056</td>
<td>0.054</td>
<td>0.053</td>
</tr>
<tr>
<td>Al_std10</td>
<td>10</td>
<td>10.25</td>
<td>9.92</td>
<td>10.36</td>
<td>10.18</td>
</tr>
<tr>
<td>Al_std100</td>
<td>100</td>
<td>101.7</td>
<td>99.7</td>
<td>103.5</td>
<td>101.63</td>
</tr>
<tr>
<td>Al_std500</td>
<td>500</td>
<td>490.5</td>
<td>483.5</td>
<td>496.8</td>
<td>490.27</td>
</tr>
<tr>
<td>Al_std1000</td>
<td>1000</td>
<td>979</td>
<td>968</td>
<td>985</td>
<td>977.33</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Pd 229 ppm</th>
<th>Pd 340 ppm</th>
<th>Pd 344 ppm</th>
<th>Pd 360 ppm</th>
<th>Average ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd_std0</td>
<td>0</td>
<td>0.089</td>
<td>0.280</td>
<td>0.235</td>
<td>0.182</td>
</tr>
<tr>
<td>Pd_std1</td>
<td>1</td>
<td>1.10</td>
<td>0.71</td>
<td>1.12</td>
<td>1.11</td>
</tr>
<tr>
<td>Pd_std10</td>
<td>10</td>
<td>12.13</td>
<td>11.88</td>
<td>11.95</td>
<td>11.9</td>
</tr>
<tr>
<td>Pd_std100</td>
<td>100</td>
<td>99.7</td>
<td>100.4</td>
<td>96.2</td>
<td>98.1</td>
</tr>
<tr>
<td>Pd_std500</td>
<td>500</td>
<td>493.5</td>
<td>508</td>
<td>497</td>
<td>494.8</td>
</tr>
<tr>
<td>Pd_std1000</td>
<td>1000</td>
<td>1000</td>
<td>986</td>
<td>993</td>
<td>994</td>
</tr>
</tbody>
</table>

Table B.2   Catalyst loadings measured by ICP-AES.

<table>
<thead>
<tr>
<th>Monolith</th>
<th>Al308 ppm</th>
<th>Al396 ppm</th>
<th>Avg. ppm</th>
<th>Catalyst g</th>
<th>Monolith loading wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>281.2</td>
<td>278</td>
<td>279.60</td>
<td>1.68</td>
<td>4.05</td>
</tr>
<tr>
<td>2</td>
<td>280</td>
<td>277.8</td>
<td>278.90</td>
<td>1.67</td>
<td>3.92</td>
</tr>
<tr>
<td>3</td>
<td>282</td>
<td>278.1</td>
<td>280.05</td>
<td>1.68</td>
<td>3.98</td>
</tr>
<tr>
<td>4</td>
<td>282.1</td>
<td>278.1</td>
<td>280.10</td>
<td>1.68</td>
<td>3.97</td>
</tr>
</tbody>
</table>
B.4.2 Adsorption Analysis – Pore Size Distribution

The physical adsorption isotherm for N$_2$ was measured on a Quantachrome Autosorb AS-1. To obtain the pore size distribution, a full adsorption/desorption experiment was run with 20 data points on each branch. Each sample was degassed at 300°C under vacuum for at least 2 h prior to analysis. An isotherm for a typical catalyst is shown in Figure B.5. The adsorption/desorption branch hysteresis is the result of pores filling and emptying differently (i.e., capillary condensation and evaporation occur at different rates depending on the relative pressures and meniscus size as described by Eq. B.1.

![Figure B.5 Adsorption/desorption isotherm for a typical mesoporous catalyst (Pd_A11).](image)

The Barrett-Joyner-Halenda (BJH) algorithm was used to calculate the pore size distribution (PSD) for all mesoporous materials. The BJH method is generally considered appropriate for mesoporous materials. The method assumes cylindrical pores. Capillary condensation in the pores is assumed to follow the Kelvin equation (Eq. B.1), which assumes a
hemispherical geometry for the liquid-vapor meniscus in each pore. The Kelvin equation is not considered accurate for microporous materials because as pore diameters shrink to the size of the adsorbate molecules, the concept of a vapor-liquid meniscus at equilibrium loses physical meaning.

\[
\ln \left( \frac{P}{P_o} \right) = \frac{2\gamma V_m}{r_k RT} \tag{B.1}
\]

In Eq. B.1, \( P/P_o \) is the relative pressure, \( \gamma \) the surface tension, \( V_m \) the molar volume, \( r_k \) the Kelvin radius, \( R \) the gas constant, and \( T \) the temperature. For a typical adsorption experiment, \( T, \gamma, R, \) and \( V_m \) are known. The Kelvin equation inherently underestimates the actual pore radius because prior to condensation some adsorption takes place on the pore walls. The thickness of this film is commonly referred to as \( t \). So the actual pore radius \( r_p \) is defined as:

\[
r_p = r_k + t
\]

The BJH method calculates \( t \) in Angstroms as:

\[
t = \left[ \frac{13.99}{\log(P_o / P) + 0.034} \right]^{0.5} \tag{B.2}
\]

The pore volumes (\( V_p \)) at each relative pressure step “\( n \)” on the desorption branch of the isotherm are given by:

\[
V_{pn} = \left( \frac{r_{pm}}{r_{km} + 0.5\Delta t_n} \right)^2 \Delta V_n - \Delta t_s \sum_{j=1}^{n-1} Ac_j \tag{B.3}
\]

c is given by:

\[
c = \frac{r_p - t}{r_p} \tag{B.4}
\]

and \( A \) is the area of each pore assuming cylindrical geometry:

\[
A = \frac{2V_p}{r_p} \tag{B.5}
\]
B.4.3 Adsorption Analysis – Surface Area

The Brunauer-Emmett-Teller (BET) method is the most widely used procedure for determining the surface area of porous samples. The BET equation is:

\[
\frac{1}{W ((P/P_o) - 1)} = \frac{1}{W_m C} + \frac{C - 1}{W_m C} \left( \frac{P}{P_o} \right) \tag{B.6}
\]

where \(W\) is the weight of gas adsorbed at a relative pressure \(P/P_o\), \(W_m\) is the weight of one monolayer of adsorbate, and \(C\) is the BET constant. This equation has the form \(y = mx + b\) where \(P/P_o\) is \(x\). A plot of this equation for a typical experiment is shown in Figure B.6. From the BET equation, \(W_m\) is determined from the slope \(s\) and the y-intercept \(i\):

\[
s = \frac{C - 1}{W_m C} \tag{B.7}
\]

\[
i = \frac{1}{W_m C} \tag{B.8}
\]

Figure B.6 BET plot of catalyst support (Pd_Al1).
Surface areas were computed by the multipoint BET method at the relative pressure range 0.05-0.35. In all cases, the correlation coefficient of the BET plot was > 0.99. The total surface area of the samples was calculated using Eq. B.9 where $S_i$ is the area, $N$ Avogadro’s number, $A_{cs}$ the cross sectional area a N$_2$ molecule occupies on the surface (16.2 Å$^2$), and $M$ the molecular weight of N$_2$. This total area is divided by the sample mass to obtain the specific area.

$$S_i = \frac{W_m N A_{cs}}{M}$$  \hspace{1cm} (B.9)

### B.4.4 Dispersion Measurements

All metal dispersion measurements were taken using a Micromeritics Pulsesorb 2700. A fixed volume of analysis gas is introduced into a sample chamber that is under a constant flow of inert gas. The Pulsesorb detects the amount of gas that does not adsorb on the sample by a thermal conductivity detector. Therefore, the inert and active gas phases must have significantly different thermal conductivities. For CO as the adsorbing gas, He is the inert. For H$_2$ as the adsorbing gas, N$_2$ is the inert. Larger loop volumes are used for samples with higher metal loadings. Results from a typical experiment are shown in Table B.3.

<table>
<thead>
<tr>
<th>Injection #</th>
<th>Loop Volume (cm$^3$)</th>
<th>TCD Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0891</td>
<td>0.00</td>
</tr>
<tr>
<td>2</td>
<td>0.0891</td>
<td>0.06</td>
</tr>
<tr>
<td>3</td>
<td>0.0891</td>
<td>0.40</td>
</tr>
<tr>
<td>4</td>
<td>0.0891</td>
<td>0.49</td>
</tr>
<tr>
<td>5</td>
<td>0.0891</td>
<td>0.50</td>
</tr>
<tr>
<td>6</td>
<td>0.0891</td>
<td>0.50</td>
</tr>
<tr>
<td>7</td>
<td>0.0891</td>
<td>0.50</td>
</tr>
</tbody>
</table>

The calibration constant (k) value for this run is 0.0891/0.50, or 0.1782 cm$^3$. The total volume of gas chemisorbed is:
1st injection: 0.0891 – 0 = 0.0891
2nd injection: 0.0891 – (0.06 x 0.1782) = 0.0784
3rd injection: 0.0891 – (0.40 x 0.1782) = 0.0178
4th injection: 0.0891 – (0.49 x 0.1782) = 0.0018

total volume: 0.1871 cm³

The volume is brought to STP using the ideal gas law. The percent dispersion $D$ is calculated as:

$$D = \frac{V_{ads} \cdot M \cdot S}{W \cdot V_m \cdot f} \cdot 100$$  \hspace{1cm} (B.10)

where $V_{ads}$ is the total volume adsorbed at STP, $M$ is the molecular weight of the catalytic metal, $S$ the adsorption stoichiometry (in mol active metal/mol test gas), $W$ the weight of catalyst sample, $V_m$ the molar volume at STP (22414 cm³/mol), and $f$ the weight fraction of catalyst metal on the support. All of these parameters are well known except $S$. There is some uncertainty in how different types of adsorbates bond to active metals on a surface. It is generally accepted that one molecule of H₂ will dissociate and occupy two active metal sites, $S = 0.5$. It is generally assumed that $S = 1$ for CO, although CO bonds in both linear (to a single metal site) and bridged (to multiple metal sites) modes. In reality, the adsorbing nature of CO on Platinum group metals is a mix of several modes governed by factors such as crystallite size and dominant exposed faces (e.g. (111), (100), etc.).

Continuing the example above, for H₂ adsorption on a 0.5 wt% Pt/Al₂O₃ catalyst the dispersion is:

$$D = \frac{0.1871 cm³ \cdot 195.1 g/mol_{Pt} \cdot 2 mol_{Pt} / mol_{H₂}}{0.8353 g \cdot 22414 cm³/mol_{H₂} \cdot 0.005} \cdot 100 = 77.9\%$$

Therefore, 78% of all Pt sites are assumed to be surface-active.

To ensure that only the catalyst metal sites were adsorbing the test gas, blank runs were performed using bare supports. A typical result for a blank run is shown in Table B.4. The data indicate the amount of H₂ adsorbed (0.008 cm³) is small compared to the amount adsorbed in a
typical experiment using a metal-supported catalyst, for a similar sample mass. Table B.5 shows data for a run using an empty sample cell. These data shows that the TCD detector error is +/- 0.01 area units for a 0.097 cm$^3$ loop. For a 0.206 cm$^3$ loop, the TCD error is +/- 0.03 area units. Therefore the results in Table B.4 for a blank sample are within the error detection limit of the experiment (5-6%).

Table B.4  Typical experimental data for a H$_2$ chemisorption experiment using a blank catalyst support (Al1).

<table>
<thead>
<tr>
<th>Injection #</th>
<th>Loop Volume (cm$^3$)</th>
<th>TCD Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.206</td>
<td>0.47</td>
</tr>
<tr>
<td>2</td>
<td>0.206</td>
<td>0.49</td>
</tr>
<tr>
<td>3</td>
<td>0.206</td>
<td>0.49</td>
</tr>
<tr>
<td>4</td>
<td>0.206</td>
<td>0.49</td>
</tr>
<tr>
<td>5</td>
<td>0.206</td>
<td>0.49</td>
</tr>
</tbody>
</table>

Table B.5  Experimental data for empty sample chamber.

<table>
<thead>
<tr>
<th>Injection #</th>
<th>Loop Volume (cm$^3$)</th>
<th>TCD Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.097</td>
<td>0.22</td>
</tr>
<tr>
<td>2</td>
<td>0.097</td>
<td>0.22</td>
</tr>
<tr>
<td>3</td>
<td>0.097</td>
<td>0.21</td>
</tr>
<tr>
<td>4</td>
<td>0.097</td>
<td>0.20</td>
</tr>
<tr>
<td>5</td>
<td>0.097</td>
<td>0.20</td>
</tr>
<tr>
<td>6</td>
<td>0.097</td>
<td>0.21</td>
</tr>
<tr>
<td>7</td>
<td>0.097</td>
<td>0.20</td>
</tr>
<tr>
<td>8</td>
<td>0.097</td>
<td>0.20</td>
</tr>
</tbody>
</table>

Repeatability experiments were also carried out on the same sample with “cleaning” steps performed between each analysis. This treatment was done at high temperature (300°C) with inert gas flow for 2 h in order to remove the adsorbate prior to another analysis. The results for a run with a 0.5 wt% Pd/Al$_2$O$_3$ catalyst are shown in Table B.6.
Table B.6  H₂ chemisorption repeatability for 0.5 wt% Pd/Al₂O₃ catalyst (Pd_Al1).

<table>
<thead>
<tr>
<th>Loop Volume cm³</th>
<th>TCD Area Run 1</th>
<th>TCD Area Run 2</th>
<th>TCD Area Run 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Injection #1</td>
<td>0.206</td>
<td>0.45</td>
<td>0.49</td>
</tr>
<tr>
<td>Injection #2</td>
<td>0.206</td>
<td>0.95</td>
<td>0.84</td>
</tr>
<tr>
<td>Injection #3</td>
<td>0.206</td>
<td>0.99</td>
<td>1.06</td>
</tr>
<tr>
<td>Injection #4</td>
<td>0.206</td>
<td>1.03</td>
<td>1.07</td>
</tr>
<tr>
<td>Injection #5</td>
<td>0.206</td>
<td>1.07</td>
<td>1.09</td>
</tr>
<tr>
<td>Injection #6</td>
<td>0.206</td>
<td>1.07</td>
<td>1.09</td>
</tr>
<tr>
<td>% Dispersion</td>
<td>74.6</td>
<td>76.9</td>
<td>70.1</td>
</tr>
<tr>
<td>Average</td>
<td>73.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Std Dev</td>
<td>3.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

CO was used as the adsorbate for carbon-supported samples because there can be problems associated with hydrogen spillover onto certain carbons. The phenomenon of spillover is still not fully understood but is believed to occur when molecules that are adsorbed on the active metal diffuse onto the support. Therefore, just because the bare support does not chemisorb the test gas (as shown in Table B.4) is not sufficient evidence that spillover cannot occur. It is also believed that spillover can be influenced by certain surface groups (e.g., hydroxyls, silanols, etc.) which vary greatly depending upon the carbon precursor and preparation method. To illustrate that spillover was a potential problem for some of the carbon supports, Table B.7 shows chemisorption data for catalyst Pd_C2 using both CO and H₂ as test gases. There is a large discrepancy between the observed dispersion values for this catalyst; the sample adsorbs many more H-atoms than CO.

To compare the difference in dispersion between H₂ and CO on the same catalyst in the presumed absence of spillover, measurements were made on Pd_A11 using both gases. The results using H₂ are shown in Table B.6. The CO chemisorption results are summarized below in Table B.8. The results show that percent dispersions calculated from CO chemisorption are typically lower than those calculated from H₂. This is qualitatively consistent with CO having a
higher tendency to adsorb in bridged modes without perfect surface coverage. However, the two dispersion values (74% for H₂ and 68% for CO) are still close enough to facilitate comparisons.

Table B.7  Chemisorption results for Pd_C2 carbon-supported catalyst using (a) CO and (b) H₂ detection test gases.

(a) CO adsorbate

<table>
<thead>
<tr>
<th>Injection #</th>
<th>Loop Volume (cm³)</th>
<th>TCD Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5</td>
<td>0.07</td>
</tr>
<tr>
<td>2</td>
<td>0.5</td>
<td>0.56</td>
</tr>
<tr>
<td>3</td>
<td>0.5</td>
<td>0.65</td>
</tr>
<tr>
<td>4</td>
<td>0.5</td>
<td>0.76</td>
</tr>
<tr>
<td>5</td>
<td>0.5</td>
<td>0.91</td>
</tr>
<tr>
<td>6</td>
<td>0.5</td>
<td>0.91</td>
</tr>
<tr>
<td>7</td>
<td>0.5</td>
<td>0.91</td>
</tr>
</tbody>
</table>

Dispersion: 36%

(b) H₂ adsorbate

<table>
<thead>
<tr>
<th>Injection #</th>
<th>Loop Volume (cm³)</th>
<th>TCD Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>0.5</td>
<td>0.2</td>
</tr>
<tr>
<td>3</td>
<td>0.5</td>
<td>1.42</td>
</tr>
<tr>
<td>4</td>
<td>0.5</td>
<td>2.33</td>
</tr>
<tr>
<td>5</td>
<td>0.5</td>
<td>2.33</td>
</tr>
<tr>
<td>6</td>
<td>0.5</td>
<td>2.33</td>
</tr>
<tr>
<td>7</td>
<td>0.5</td>
<td>2.33</td>
</tr>
</tbody>
</table>

Dispersion: 91%

Table B.8  Chemisorption analysis of Pd_Al1 using CO as the test gas.

<table>
<thead>
<tr>
<th>Injection #</th>
<th>Loop Volume (cm³)</th>
<th>TCD Meter Reading</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.206</td>
<td>0.18</td>
</tr>
<tr>
<td>2</td>
<td>0.206</td>
<td>0.25</td>
</tr>
<tr>
<td>3</td>
<td>0.206</td>
<td>0.35</td>
</tr>
<tr>
<td>4</td>
<td>0.206</td>
<td>0.35</td>
</tr>
<tr>
<td>5</td>
<td>0.206</td>
<td>0.35</td>
</tr>
<tr>
<td>6</td>
<td>0.206</td>
<td>0.35</td>
</tr>
<tr>
<td>7</td>
<td>0.206</td>
<td>0.35</td>
</tr>
</tbody>
</table>

Dispersion: 68%
B.4.5 X-Ray Diffraction (XRD)

Powder XRD of mesoporous catalysts was performed at the Center for Advanced Microstructures and Devices (CAMD) on the XPD beam line using CuK$_\alpha$ radiation. A summary of acquisition parameters is shown in Table B.9. Samples were prepared by powdering to <100 mesh and placing in stainless steel rotating sample holders.

**Table B.9 XRD acquisition parameters.**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Start angle</td>
<td>0.5°</td>
</tr>
<tr>
<td>End angle</td>
<td>10°</td>
</tr>
<tr>
<td>Step size</td>
<td>0.02°</td>
</tr>
<tr>
<td>Spin speed</td>
<td>200</td>
</tr>
<tr>
<td>Integration time</td>
<td>2.0 s</td>
</tr>
<tr>
<td>Acquire Integration</td>
<td>1.0 s</td>
</tr>
<tr>
<td>Beamline current</td>
<td>&gt;2.0 mA</td>
</tr>
</tbody>
</table>

Spectra were processed using MDI Jade® software. They were first background subtracted and then pattern smoothed. The correct 2$\theta$ offset was verified using an internal standard. For low angles, the standard was Mica 675, a certified synthetic fluorophlogopite sample from NIST. This sample has a d-spacing of 9.98104 Å which corresponds to a 2$\theta$ of 8.853° if using CuK$_\alpha$ radiation. Several flakes were added to the top of the sample. Once the correct 2$\theta$ values were determined, d-spacings were calculated from the Bragg equation:

$$n\lambda = 2d \cdot \sin(\theta)$$  

where $n = 1$, $\lambda$ is the wavelength of radiation (1.5418° for CuK$_\alpha$), $d$ the d-spacing, and 2$\theta$ the peak location. A raw data file for an MCM-48 silica is shown in Figure B.7 (a).

The large decay from high initial intensity at very low angle (~0.75°) is an instrumental artifact. The shoulder located at ~2.5° represents the sample peak and the strong reflection at higher angle is the internal standard. The sample peak is convoluted with the decay from high intensity. The background was therefore manually chosen to subtract the decay artifact. The
processed version shown in Figure B.7 (b) still retains some of the original decay artifact but shows the sample peak much more clearly.

Figure B.7 XRD spectrum of MCM-48 mesoporous silica: (a) raw data; (b) processed data after background subtraction and smoothing.
## B.5 Kinetics Data Summary

### Table B. 10 Kinetic data summary.

<table>
<thead>
<tr>
<th>Run #</th>
<th>Catalyst</th>
<th>wt% Pd</th>
<th>wt% Cu Loading</th>
<th>Particle size P</th>
<th>Rxn time</th>
<th>Conversion</th>
<th>$k_{obs} \cdot 10^5$</th>
<th>g Pd/L</th>
<th>mm</th>
<th>MPa</th>
<th>h</th>
<th>fractional</th>
<th>L/s/g Pd</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pd_Al1</td>
<td>0.5</td>
<td>0</td>
<td>0.133</td>
<td>0.13-0.15</td>
<td>5.5</td>
<td>10.00</td>
<td>0.373</td>
<td>9.74</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Pd_Al1</td>
<td>0.5</td>
<td>0</td>
<td>0.133</td>
<td>0.13-0.15</td>
<td>3.4</td>
<td>6.00</td>
<td>0.220</td>
<td>8.67</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Pd_Al1</td>
<td>0.5</td>
<td>0</td>
<td>0.133</td>
<td>0.13-0.15</td>
<td>3.4</td>
<td>6.00</td>
<td>0.082</td>
<td>2.97</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Pd_Al1</td>
<td>0.5</td>
<td>0</td>
<td>0.133</td>
<td>0.13-0.15</td>
<td>2.5</td>
<td>12.00</td>
<td>0.385</td>
<td>8.45</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Pd_Al1</td>
<td>0.5</td>
<td>0</td>
<td>0.133</td>
<td>0.13-0.15</td>
<td>5.5</td>
<td>2.00</td>
<td>0.802</td>
<td>169.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Pd_Al1</td>
<td>0.5</td>
<td>0</td>
<td>0.133</td>
<td>0.13-0.15</td>
<td>3.4</td>
<td>12.00</td>
<td>0.465</td>
<td>10.90</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Pd_Al1</td>
<td>0.5</td>
<td>0</td>
<td>0.133</td>
<td>0.13-0.15</td>
<td>2.5</td>
<td>12.00</td>
<td>0.359</td>
<td>7.74</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Pd_Al1</td>
<td>0.5</td>
<td>0</td>
<td>0.133</td>
<td>0.5-0.84</td>
<td>3.4</td>
<td>8.00</td>
<td>0.232</td>
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1 at 150°C
2 using Decahydropanthalene (DHN) solvent
3 using 10 wt% PS
## B.6 Selectivity Data Summary

Table B.11  Selectivity data summary.

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<td>227</td>
<td>0.99</td>
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</table>
Appendix C Supplementary Material for Chapter 5

C.1 POMR Operating Procedure for AMS Hydrogenation

1. Charge AMS/cyclohexane reactant mixture to POMR via sampling port. POMR holds 1 L of fluid.

2. POMR kept under ~1 atm H₂ purge when not in use. Gas exit of POMR opened to bubbler to provide gas seal.

3. Fill POMR to above monolith stack with piston at bottom of stroke.

4. Seal reactor and heat using the recirculation bath. Set bath temp ~10°C higher than desired POMR temperature.

5. Apply ~1 Hz pulsing to mix reactants to uniform temperature at top and bottom thermocouples.

6. Allow reactant mixture to go ~5°C above desired set-point because gas flow (once started) will have cooling effect.

7. Start gas flow using gas booster and instrument air regulator.

8. Set POMR piston to desired frequency.

9. System is now pressurized to start reaction. Must pressurize top and bottom of diaphragm at nearly identical rates (no more than 10 psi differential or you risk deforming or damaging the diaphragm).

10. Record pressure (transducer) in LabView software.

11. During run, keep both H₂ and N₂ valves to POMR open to account for minor leaks and for H₂ consumed by reaction.

12. Sample during the run occurs through a needle valve on the POMR body, ~1 mL samples. Purge dead volume in valve before sampling to ensure accuracy.

13. Shut down
   - Stop both piston and heater
   - Decrease instrument air pressure until booster stops pumping
   - Let reactor cool down
   - Once cool, system is de-pressurized by bleeding gas to fume hood vent
   - De-pressurize top and bottom of diaphragm at similar rates
   - ~800 mL of fluid is drained through bottom port on POMR process side
   - To completely remove all reactant, POMR must be disassembled to access the diaphragm for complete cleaning and removal of liquid phase
14. In-situ catalyst treatment

- Maximum temperature in POMR is 120°C with silicone heat transfer fluid (Duratherm S, silicone based heat transfer fluid)
- System is slightly pressurized with desired gas (H₂ for reduction) and bubbler is connected to gas outlet
- Gas flow is set using the needle valve at the gas outlet
- The heater is started and the POMR is slowly brought up to temperature

C.2 Agitated Tank Operating Procedure

1. The agitated tank used here is an Autoclave Engineers Zipperclave with 3-bladed marine propeller. Heat is supplied by wrapping the vessel in heating tape, connected to a Vari-AC (<100°C).

2. Place catalyst-coated monolith at bottom of vessel. Reduce in situ if desired by heating until thermocouple reads ~130°C under hydrogen purge which exits through bubbler.

3. After cooling, fill system through dip-tube using 100 mL glass syringe and maintain 1 atm H₂ purge by venting through bubbler.

4. After filling to 350 mL (completely submerging impeller), begin heating while applying ~50 rpm stirring.

5. Once at desired temperature, increase stirring to desired rpm and pressurize system.

6. Sample using the dip-tube connected to a needle valve. Must purge ~ 2 mL of dead volume from system before sampling to ensure representative sample.

7. For reactor shut-down, stop stirring and heating. Once cooled, de-pressurize system using purge valve through bubbler.

8. System can be drained using dip-tube and fresh reactant re-introduced without air entering system, using a 100 mL syringe. However, ~100 mL of liquid will remain in the vessel because dip-tube does not go to bottom.

9. If complete liquid removal is required, vessel must be removed.

C.3 Pressure Transducer Calibration, POMR

Moody Price model # MPILPG15AA, 0-5000 psi 1-5 VDC span.

The transducer recorded pressure in LabView. However, an analog (Bourdon) gauge was used to record pressure fluctuations for both the top and bottom sides of the diaphragm because the span of the transducer was too large for accurate measurements.
C.4 AMS Conversion Analysis

The AMS to cumene conversion was determined using capillary gas chromatography (GC, Hewlett-Packard 5890 Series II, FID detector. An Alltech Econo-Cap EC1 capillary column (30 m x 0.25 mm ID) was used for separation. The concentration of the components was determined by adding a known amount of ethylbenzene (0.01 mL) as internal standard to a 0.99 mL reactor sample. GC operating parameters are listed in Table C.1 and retention times are listed in Table C.2. The cyclohexane area is not needed and the cyclohexane solvent saturated the detector anyway.

The concentrations were determined by first equating area% and wt%, then calculating mol and volume% using the molecular weights and densities. The area% / wt% equality relationship was confirmed by injecting a standard composed of 10 wt% AMS/ cyclohexane with 1 wt% ethylbenzene. Equating a ratio of the areas of AMS and ethylbenzene to the wt% ratio gives 10.1 wt% AMS, showing good agreement. AMS and cumene concentrations vs. time were plotted and showed zero order dependence of rate on AMS concentration (Figure C.4).
specific activity (mol cumene/g\textsubscript{Pd}/s) was computed by taking the slope (mol cumene/L/min), multiplying by liquid volume (L) and dividing by g\textsubscript{Pd} present.

Table C.1  GC data acquisition parameters.

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<th>Value</th>
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<td>Initial Time (min)</td>
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<td>Ramp (°C/min)</td>
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<td>Injector Temperature (°C)</td>
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<td>Detector Temperature (°C)</td>
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<tr>
<td>Column flow rate (mL/min)</td>
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Table C.2  Average retention times for major species in AMS hydrogenation reaction.

<table>
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<th>Species</th>
<th>Retention time (min)</th>
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<td>Cyclohexane</td>
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<tr>
<td>ethylbenzene</td>
<td>3.5</td>
</tr>
<tr>
<td>cumene</td>
<td>4.6</td>
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<tr>
<td>AMS</td>
<td>5.6</td>
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</table>

Figure C.2  Typical chromatograms for a reactor run using pretreatment 1 catalyst: (a) start of reaction; (b) at 60 min. Note small peak just before cyclohexane, corresponding to light components due to catalytic cracking side reaction. Some cumene is present at start of reaction as residue from previous run.
(Figure continued)

Figure C.3. Typical GC spectra for a reactor run using pretreatment 2 catalyst: (a) start of reaction; (b) at 40 min. Some cumene is present at start of reaction as residue from previous run.
Figure C.4  Typical plot of concentration of AMS and cumene. Note that the slopes are opposite in sign but approximately equal in magnitude.
C.5 AMS Selectivity Analysis

Five minor side products at retention times greater than AMS were identified from MS spectra using a Hewlett Packard 5972 Mass Spectrometer attached to an H-P 5890 GC. Figure C.5 shows the structure of the side products. Also, there is a light component present (C\textsubscript{1}-C\textsubscript{3} hydrocarbons) at ~1.2 min, but it was not quantified exactly, because the components could not be separated at the analytical conditions (see Figure C.2 (b)).

![Chemical structures of side products](image)

**Figure C.5** 5 side products formed during hydrogenation of AMS.

Define selectivity of component \( m \) on a carbon basis as \( S_m \):

\[
S_m = \frac{\text{mol}_m \cdot \#C_m}{\sum \text{mol}_m \cdot \#C_m} \cdot 100
\]  \hspace{1cm} (C.1)

where \( \text{mol}_m \) is the number of moles of species \( m \) and \( \#C_m \) is the number of carbons present in \( m \).

**Table C.3** Approximate retention times for the five side products identified in Figure C.5.

<table>
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<th>Retention time (min)</th>
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<td>1</td>
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Figure C.6 Magnified view of GC chromatogram baseline showing the five minor side products at $t > 6$ min and the light components prior to the solvent peak.

C.6 Mass Transfer Rate Calculations

The first step is to calculate the individual external mass transfer steps, which include gas-solid, gas-liquid, and liquid-solid. Gas-liquid and liquid-solid transport are in series, accounting for the liquid-rich portion of the microchannel, while their combination is in parallel with gas-solid mass transfer, which accounts for the gas-rich portion. The objective here is to compare correlations for $k_{ov}:a$ to values determined experimentally using the acrylic bubble column mock-up, and to determine if there is agreement between the air-water system and the H$_2$/AMS/cyclohexane system. Also, the $k_{ov}:a$ can be used to back-calculate the expected observed rate of reaction for comparison purposes to what was actually observed. This is done by equating the rate of mass transfer to the catalyst pellet to the observed rate of reaction and calculating the surface concentration of the hydrogen. From this concentration, the intrinsic rate times the effectiveness factor gives the theoretical rate. The calculation is shown below.
Compute overall mass transfer coefficient from literature correlations

Physical parameters

\[ L := 0.132 \text{ cm} \quad \text{characteristic length equal to monolith channel diameter} \]

\[ L_{\text{slug}} := 3L \quad \text{assumed length of a slug} \]

\[ d_{\text{channel}} := 0.132 \text{ cm} \quad \text{diameter of single monolith channel in cm} \]

\[ U_g := 17.5 \frac{\text{cm}}{s} \quad \text{superficial velocity of gas at operating conditions in cm/s} \]

\[ U_l := 31.8 \frac{\text{cm}}{s} \quad \text{superficial velocity of liquid at operating conditions cm/s} \]

\[ \epsilon_1 := \frac{U_l}{U_l + U_g} \quad \text{definition of liquid holdup} \]

\[ \Phi_{\text{slug}} := \frac{L_{\text{slug}}}{d_{\text{channel}}} \quad a := \frac{4 \epsilon_1}{d_{\text{channel}}} \quad \text{compute interfacial area} \]

\[ v_1 := U_g + U_l \quad \text{two phase velocity} \]

Compute diffusivity of H2 in cyclohexane at reaction conditions from correlation from Snijder et al. JCED (1994)

\[ \text{Diff(TV)} := \exp\left(-\frac{3239}{TV}\right) \cdot 4.78 \cdot 10^{-4} \frac{\text{m}^2}{\text{s}} \]

\[ D_{\text{H2}} := \text{Diff(323)} \]

\[ D_{\text{H2}} = 2.11 \times 10^{-8} \frac{\text{m}^2}{\text{s}} \]

Calculate liquid-solid mass transfer coefficient

Correlation from Kreutzer et al. (2001)

\[ k_{\text{ls}} := \frac{D_{\text{H2}}}{L} \cdot 20 \left[ 1 + 0.003 \left( \frac{\Phi_{\text{slug}}}{\left( \frac{L}{U_l} \right)} \right)^{-0.7} \right] \]

\[ k_{\text{ls}} = 7.737 \times 10^{-4} \frac{\text{m}}{\text{s}} \]

\[ k_{\text{ls\_a}} := \frac{k_{\text{ls}} \cdot a}{1} \]

This is the predicted liquid to solid mass transfer coefficient times the interfacial area in 1/s
Calculate gas-solid mass transfer coefficient

Correlation from Irandoust and Andersson (1989)

\[
\begin{align*}
\sigma &:= 17.2 \times 10^{-3} \ \text{kg} \ \text{s}^{-2} \quad \text{surface tension} \\
\eta &:= 5.1 \times 10^{-4} \ \text{Pa} \cdot \text{s} \quad \text{viscosity} \\
Ca &:= \frac{\eta \cdot v_1}{\sigma} \quad Ca = 0.015 \\
D_{\text{methane}} &:= 2.38 \times 10^{-5} \ \text{cm}^2 \ \text{s} \\
\frac{d_{\text{bb}}}{d_{\text{channel}}} &:= \left[ 0.64 + 0.36 \cdot e^{-3.08 \cdot Ca^{0.54}} \right] \\
d_{\text{bb}} &= 1.192 \times 10^{-3} \ \text{m} \\
\delta &:= \frac{d_{\text{channel}} - d_{\text{bb}}}{2} \quad \delta = 6.411 \times 10^{-5} \ \text{m} \quad \text{film thickness surrounding a bubble} \\
\frac{d_{\text{channel}}}{d_{\text{bb}}} &:= \frac{D_{\text{H2}}}{\delta} \quad k_{\text{gs}} = 3.292 \times 10^{-4} \ \text{m} \ \text{s}^{-1} \\
a &:= \frac{4 \cdot (1 - \varepsilon_l)}{d_{\text{channel}}} \\
k_{\text{gs}\_a} &:= k_{\text{gs}} \cdot a \\
k_{\text{gs}\_a} &= 0.354 \ \text{s}^{-1} 
\end{align*}
\]

This is the gas-solid mass transfer coefficient times the interfacial area.
Calculate overall gas mass transfer coefficient

\[ k_{ov} := \left( \frac{1}{k_{ls\_a}} + \frac{1}{k_{gl\_a}} \right)^{-1} + k_{gs\_a} \]

\[ k_{ov} = 1.476 \frac{1}{s} \]

this is the overall mass transfer coefficient for the POMR

Use computed overall mass transfer coefficient to compute expected observed rate const:

Kinetics from Meille et al. IECR (2002) give highest observed rate from literature will use this for comparison

\[ RR := 8.314 \frac{J}{mol K} \]

\[ T1 := 320K \]

\[ C_{\text{star}} := 20.4 \frac{mol}{m^3} \]

solubility of H2 in AMS at rxn conditions from Snijder et al. JCED (1994)

\[ rM(CH,TV) := 8.5 \times 10^{-6} \exp \left( \frac{-38700}{RR \cdot TV} \right) \frac{CH \cdot 1.4 \cdot 10^{-2} \frac{m^3}{mol}}{1 + \left( CH \cdot 1.4 \cdot 10^{-2} \frac{m^3}{mol} \right)^0.5} \]

\[ \rho_c := 8.333 \times 10^{-2} \frac{kg}{m^3} \]

catalyst density of typical alumina

calculate effective diffusivity

\[ D_e := \frac{\rho_c \cdot 0.46 \frac{cm^3}{gm}}{3} \]

tortuosity of 3

\[ D_e = 2.697 \times 10^{-5} \frac{cm^2}{s} \]

calculate Theile Modulus

\[ \Phi := 8.5 \times 10^{-6} \cdot 1.4 \times 10^{-2} \exp \left( \frac{-38700}{RR \cdot T1} \right) \frac{1}{mol} \cdot s^{-1} \]

\[ L := 1.076 \times 10^{-4} \frac{m}{s} \]

diffusion length
\[ \Phi := \left( \frac{\Phi}{D_e} \right)^{0.5} \cdot L \]
\[ \Phi = 0.496 \]

Calculate effectiveness factor

\[ \eta := \frac{\tanh(\Phi)}{\Phi} \]
\[ \eta = 0.925 \quad \text{(This shows internal mass transfer not significant)} \]

\[ C_s := 4.0 \frac{\text{mol}}{\text{m}^3} \quad \text{Hydrogen surface concentration} \]

\[ \rho_{cc} := 5.532 \times 10^{-1} \frac{\text{kg}}{\text{m}^3} \]

Given

\[ k_{ov}(C_{star} - C_s) = \eta \cdot rM(C_s, T1) \left( \frac{\text{mol}}{\text{gm} \cdot \text{s}} \right) \rho_{cc} \]

\[ C_{ss} := \text{Find}(C_s) \]

\[ C_{ss} = 1.235 \frac{\text{mol}}{\text{m}^3} \]

\[ r_{obs} := \eta \cdot rM(C_{ss}, T1) \quad \text{calculate theoretical observed rate} \]

\[ r_{obs} = 0.051 \quad \text{in mol/s/g Pd} \]

So the theoretical observed rate using highest observed kinetics from the literature results in a rate comparable to the rates observed in the POMR for pretreatment 2 catalyst

Can also calculate theoretical observed rate for autoclave using Albal et al. (1983)

\[ N := 400 \frac{1}{\text{min}} \quad \text{impeller speed} \]
\[ \mu_o := 0.98 \times 10^{-3} \cdot \text{Pa} \cdot \text{s} \quad \text{viscosity at RT} \]
\[ \rho_L := 772 \frac{\text{kg}}{\text{m}^3} \quad \text{liquid density} \]
\[ D_i := 68 \text{mm} \quad \text{impeller diameter} \]
\[ \mu_1 := \mu_o \left( \frac{320}{298} \right) \left( 9.17 \times 10^{-5} \frac{\text{cm}^2}{\text{s}} \right) \frac{1}{D_{H2}} \]
\[ \mu_1 = 4.572 \times 10^{-4} \frac{\text{kg}}{\text{ms}} \]
This value is the theoretical observed rate and is similar to the 400 rpm result for the agitated tank experiment.

The following GC data presented in Table C.4 are typical for an AMS hydrogenation experiment. A similar table was made for each individual reaction run in the agitated tank or the POMR. Each Excel table automatically computes the relevant concentrations of each component from the supplied GC areas. From these tables, average values were obtained across different runs.

C.7 Raw Data

C.7.1 Catalyst Activity Data

The following GC data presented in Table C.4 are typical for an AMS hydrogenation experiment. A similar table was made for each individual reaction run in the agitated tank or the POMR. Each Excel table automatically computes the relevant concentrations of each component from the supplied GC areas. From these tables, average values were obtained across different runs.
Table C.4  Typical data obtained from GC for a typical reactor run for either the POMR or the agitated tank. All weight percentages determined vs. ethylbenzene internal standard. These concentrations are then used to produce a figure of type Figure C.4, for determination of hydrogenation rate.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>time (min)</th>
<th>EB A1</th>
<th>Cumene A2</th>
<th>AMS A3</th>
<th>A2/A1</th>
<th>A3/A1</th>
<th>A2+A3</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1S0</td>
<td>0</td>
<td>2.79</td>
<td>2.74</td>
<td>42.77</td>
<td>0.98</td>
<td>15.33</td>
<td>16.31</td>
</tr>
<tr>
<td>A1S1</td>
<td>20</td>
<td>4.58</td>
<td>12.02</td>
<td>63.27</td>
<td>2.62</td>
<td>13.81</td>
<td>16.44</td>
</tr>
<tr>
<td>A1S2</td>
<td>40</td>
<td>3.96</td>
<td>18.03</td>
<td>35.76</td>
<td>4.55</td>
<td>9.03</td>
<td>13.58</td>
</tr>
<tr>
<td>A1S3</td>
<td>60</td>
<td>3.13</td>
<td>25.80</td>
<td>23.12</td>
<td>8.24</td>
<td>7.39</td>
<td>15.63</td>
</tr>
</tbody>
</table>

**Autoclave Run 1**

Rate = 4.0 mmol/g_{Pd}/s

| RPM      | 400 |
| Temp (C) | 45  |
| Press (kPa) | 345 |

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Cumene wt%</th>
<th>AMS</th>
<th>Mole fraction</th>
<th>Volume (mL)</th>
<th>Conc (mol/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1S0</td>
<td>0.98</td>
<td>15.33</td>
<td>0.01</td>
<td>1.14</td>
<td>16.92</td>
</tr>
<tr>
<td>A1S1</td>
<td>2.62</td>
<td>13.81</td>
<td>0.02</td>
<td>3.04</td>
<td>15.24</td>
</tr>
<tr>
<td>A1S2</td>
<td>4.55</td>
<td>9.03</td>
<td>0.04</td>
<td>5.28</td>
<td>9.97</td>
</tr>
<tr>
<td>A1S3</td>
<td>8.24</td>
<td>7.39</td>
<td>0.07</td>
<td>9.56</td>
<td>8.15</td>
</tr>
</tbody>
</table>
Table C.5  Summary of catalyst activities (hydrogenation reaction rates) for the agitated tank.

<table>
<thead>
<tr>
<th>Pretreatment 1 Catalyst</th>
<th>Pretreatment 2 Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run #</td>
<td>rpm</td>
</tr>
<tr>
<td>mmol/g Pd/s</td>
<td>mmol/g Pd/s</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>1</td>
<td>400</td>
</tr>
<tr>
<td>2</td>
<td>400</td>
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<td>3</td>
<td>400</td>
</tr>
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<td>4</td>
<td>400</td>
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<td>5</td>
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<td>400</td>
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<tr>
<td>8</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td>800</td>
</tr>
</tbody>
</table>

Table C.6  Summary of catalyst activities (hydrogenation rate) for the POMR.

<table>
<thead>
<tr>
<th>Run #</th>
<th>Freq.</th>
<th>Rate</th>
<th>Reduced in situ before the run?</th>
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</thead>
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<td>Hz</td>
<td>mmol/g Pd/s</td>
<td></td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td></td>
</tr>
<tr>
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<td>1</td>
<td>6.2</td>
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<tr>
<td>2</td>
<td>0</td>
<td>5.9</td>
<td>Yes</td>
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<tr>
<td>3</td>
<td>17.5</td>
<td>2.2</td>
<td>Yes</td>
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<tr>
<td>4</td>
<td>1</td>
<td>1.5</td>
<td>No</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>3.3</td>
<td>Yes</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>2.3</td>
<td>No</td>
</tr>
<tr>
<td>7</td>
<td>1</td>
<td>4.2</td>
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</tr>
<tr>
<td>8</td>
<td>8</td>
<td>5.1</td>
<td>Yes</td>
</tr>
<tr>
<td>9</td>
<td>17.5</td>
<td>0.9</td>
<td>Yes</td>
</tr>
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<td>10</td>
<td>8</td>
<td>3.1</td>
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<td>11</td>
<td>0</td>
<td>3.6</td>
<td>No</td>
</tr>
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<td>12</td>
<td>1</td>
<td>2.7</td>
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<td>13</td>
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<td>15</td>
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<td>1.5</td>
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<td>8</td>
<td>2.3</td>
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</tr>
<tr>
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<td>17.5</td>
<td>33.3</td>
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</tr>
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<td>0</td>
<td>21.1</td>
<td>No</td>
</tr>
<tr>
<td>23</td>
<td>8</td>
<td>24.0</td>
<td>No</td>
</tr>
</tbody>
</table>
## C.7.2 Catalyst Selectivity Data

The following GC data are for a typical run and were used to compute the selectivities to the minor products.

### Table C.7 Sample GC data used to obtain molar selectivity results. All weight percentages determined vs. ethylbenzene internal standard.

<table>
<thead>
<tr>
<th>Side Product Peak</th>
<th>Peak Area</th>
<th>Sample #</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>Side Product Peak</th>
<th>wt%</th>
</tr>
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<tbody>
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<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td>EB</td>
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<td></td>
<td></td>
<td></td>
<td>1</td>
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<td>4</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>5</td>
</tr>
</tbody>
</table>

| R13S3             | 0.082    | 0.042    | 0.114 | 0.095 | 0.024 | 4.62 | 0.0177 | 0.0091 | 0.0247 | 0.0206 | 0.0052 |
| R22S3             | 0.055    | 0.05     | 0     | 0.018 | 0     | 4.37 | 0.0126 | 0.0114 | 0      | 0.0041 | 0      |
| R19S3             | 0.049    | 0.025    | 0.028 | 0.026 | 0.006 | 4.35 | 0.0113 | 0.0057 | 0.0064 | 0.0060 | 0.0014 |

<table>
<thead>
<tr>
<th>Side Product Peak</th>
<th>mole</th>
<th>Sample #</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>Side Product Peak</th>
<th>Concentration (mole/L)</th>
</tr>
</thead>
<tbody>
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<td></td>
</tr>
</tbody>
</table>

| R13S3             | 1.3E-04  | 6.9E-05  | 2.1E-04 | 1.6E-04 | 3.2E-05 | 1.1E-03 | 5.5E-04 | 1.6E-03 | 1.2E-03 | 2.6E-04 |
| R22S3             | 9.4E-05  | 8.7E-05  | 0      | 3.1E-05 | 0      | 7.5E-04 | 6.9E-04 | 0      | 2.5E-04 | 0      |
| R19S3             | 8.4E-05  | 4.4E-05  | 5.4E-05 | 4.5E-05 | 8.5E-06 | 6.7E-04 | 3.5E-04 | 4.3E-04 | 3.6E-04 | 6.8E-05 |

<table>
<thead>
<tr>
<th>Side Product Peak</th>
<th>molar selectivity</th>
<th>Sample #</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
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<td></td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| R13S3             | 3.2E-03  | 1.7E-03  | 4.5E-03 | 3.8E-03 | 9.4E-04 |
| R22S3             | 2.4E-03  | 2.2E-03  | 0      | 8.0E-04 | 0      |
| R19S3             | 2.0E-03  | 1.0E-03  | 1.2E-03 | 1.1E-03 | 2.4E-04 |
C.8 Power Input Calculations

Power per volume input for AMS hydrogenation in POMR

\[
\rho_1 := 0.772 \frac{\text{gm}}{\text{cm}^3} \quad A := 0.25 \text{ cm} \\
\rho_l := 1.631 \times 10^3 \frac{\text{kg}}{\text{ms}^3} \quad \text{correlation from Knopf et al. AIChE J (2006)}
\]

\[
P_v := \rho_1 \left( \rho_l \cdot u_g + \frac{A^2 \cdot \omega^3}{2} \right)
\]

\[
P_v = 1.631 \times 10^3 \frac{\text{kg}}{\text{ms}^3}
\]

This is power per volume input for POMR at 8 Hz

Power per volume input for AMS hydrogenation in stirred tank

\[
N := 13.33 \frac{1}{s} \quad \text{impeller speed} \\
D_i := 6.8 \text{ cm} \quad \text{impeller diameter} \\
V := 350 \text{ mL} \quad \text{liquid volume}
\]

\[
P_v := \frac{0.8 \cdot \rho_1 \cdot N^3 \cdot D_i^5}{V} \quad \text{Correlation from Pandit et al. CES (1989) for stirred tank with marir propeller}
\]

\[
P_v = 6.077 \times 10^3 \frac{\text{kg}}{\text{ms}^3}
\]

This is power per volume input for the stirred tank at 800 rpm

Now calculate the equivalent rpm in a stirred tank for actual power put into POMR

Given

\[
1.631 \times 10^3 \frac{\text{kg}}{\text{ms}^3} = \frac{0.8 \cdot \rho_1 \cdot N^3 \cdot D_i^5}{V}
\]

\[
\text{NN} := \text{Find}(N)
\]

\[
\text{NN} = 8.599 \frac{1}{s}
\]

\[
\text{RPM} := \text{NN} \cdot 60 \frac{s}{\text{min}}
\]

\[
\text{RPM} = 515.911 \frac{1}{\text{min}} \quad \text{So POMR conditions translate to a stirred tank RPM of 516}
\]
C.9 Supplementary Material for Figure 5.11


For the *slurry reactor*, the rates were computed from the regressed kinetics equation (Eq. (1) of paper) at 46°C and 0.44 MPa, for 0.5 wt% Pd/Al₂O₃. These were determined in cumene solvent (50–100 mol% AMS, zero order) at 2000 rpm stirring speed. Germain et al. demonstrated by the usual particle size and variable speed tests that the mass transfer resistances were negligible under these conditions.

\[ \text{Rate} = 55 \text{ mmol/(s* gPd)} \]


For the *slurry reactor*, the rates were computed from the regressed kinetics equation (Eq. (4) of paper) at 46°C and 0.44 MPa, for 1 wt% Pd/Al₂O₃. These were determined in methycyclohexane solvent (0.5–100 wt% AMS, zero order) at 1500 rpm stirring speed. Meille et al. demonstrated by the usual particle size and variable speed tests that the mass transfer resistances were negligible under these conditions.

\[ \text{Rate} = 460 \text{ mmol/(s* gPd)} \]


For the *trickle bed reactor*, data were obtained at variable temperature due to heat effects (but 50°C max.) and 0.3 MPa, with hexane solvent at 1582 mol/m³ AMS, using a small diameter 0.5% Pd/Al₂O₃. The slope of the initial rate plot (conversion vs. residence time) was taken from Fig. 2 of the paper and multiplied by the initial concentration of AMS, and divided by the catalyst density and fraction of Pd to give the result. The calculated liquid and gas superficial velocities are 0.03 and 6.6 cm/s, respectively.

\[ \text{Rate} = 0.112 \text{ mmol/(s* gPd)} \]

For the *pulsed trickle bed reactor*, data were obtained at similar conditions except 1484 mol/m³ AMS, with a pulse frequency of $1.7 \times 10^2$ Hz and a split (on flow/total flow for the liquid pulse) of 0.25. The slope of the initial rate plot was taken from Fig. 3a of the paper and multiplied by the initial concentration of AMS, and divided by the catalyst density and fraction of Pd to give the result.

\[ \text{Rate} = 0.162 \text{ mmol/(s* gPd)} \]
For the **trickle bed reactor**, data were obtained at 41°C and 0.1 MPa, with pure AMS using a 2 mm eggshell 0.5% Pd/Al₂O₃. The rate in mmol/(gcat*s), from Fig. 2 of the paper, was divided by the fraction of Pd to give the result. The calculated liquid and gas superficial velocities are 0.45 and 3.0 cm/s, respectively.

\[
\text{Rate} = 0.2 \text{ mmol/(s* gPd)}
\]

For the **pulsed trickle bed reactor**, data were obtained at similar conditions with a pulse frequency of 1.7 x 10⁻³ Hz and a split (on flow/total flow for the liquid pulse) of 0.3. The rate in mmol/(gcat*s), from Fig. 6 of the paper, was divided by the fraction of Pd to give the result.

\[
\text{Rate} = 0.86 \text{ mmol/(s* gPd)}
\]


For the **rotating trickle bed reactor**, the rates were measured at 40°C and 1 bar, with pure AMS. The rate for the 1% Pd/Al₂O₃ catalyst (1.5 mm spheres) was used, at rotation speed 2200 rpm, the maximum rate at the maximum rotational speed. The rate per bed volume from Fig. 5 of the paper, 40 x 10⁻⁷ mol/(cm³ bed*s), was divided by the catalyst density (1.17 g/cm³, Table 1) and by the Pd loading to give the rate in mmol/(s*g Pd). The liquid superficial velocity for this calculation was 0.12 cm/s, approximately the highest used here. The gas flow rate was not given.

\[
\text{Rate} = 0.34 \text{ mmol/(s* gPd)}
\]


For the **tubular membrane reactor**, the rate was interpolated from Fig. 7 of the paper, at 46°C and 0.1 MPa, with pure AMS. This rate is in mmol/(s*g cat), which is multiplied by (100/2) to put in mmol/(s*g Pd), since there was 2% Pd on the membrane catalyst. The computed velocities at reaction conditions are: 0.15 cm/s for liquid, 27 cm/s for gas.

\[
\text{Rate} = 1.0 \text{ mmol/(s* gPd)}
\]

For the slurry reactor, rate data were taken from Fig. 3, for a 0.5% Pd/Al$_2$O$_3$ catalyst at 1 MPa, 53°C, >1600 rpm, 50 vol% AMS in cumene. At these conditions, Purnama et al. estimated no intraparticle or external limitations to mass transfer, and found first-order behavior with respect to H$_2$ pressure. At 4 MPa H$_2$, the rate was 4 mmol/(s*g Pd) with 80% conversion in 52 min, for the most active catalyst. For the same catalyst at 1 MPa, the conversion was 80% in 25 min, so the rate ~ (4)(52/25).

**Rate = 8.3 mmol/(s*g Pd)**

For the flow-through membrane reactor, the reaction conditions are: 0.1 MPa, 40°C, 0.35 mol/L AMS in heptane, at maximum liquid flow rate. The rate was taken from Fig. 5, using the maximum rate. The computed liquid superficial velocity is 0.37 cm/s. The H$_2$ was dissolved in the liquid (1600 rpm) prior to contact with the membrane.

**Rate = 9.0 mmol/(s*g Pd)**


For the metal mesh microreactor, the rate was measured at 0.28 MPa, 40°C, pure AMS, with a 1% Pd/Al$_2$O$_3$ catalyst. The observed rate in mol/(m$^3$ liquid*s) was taken from Table 1 of the paper, multiplied by the ratio of liquid to catalyst volume (155/15), then divided by the catalyst density and the Pd loading to give the rate in mmol/(s*g Pd). The calculated liquid and gas superficial velocities are 0.036 and 0.11 cm/s, respectively.

**Rate = 8.6 mmol/(s*g Pd)**


For the monolith reactor, the rates were determined at 46°C and 1 MPa from Fig. 6 of the paper. The first-order rate constant is given, which is then multiplied by the equilibrium concentration of H$_2$ in the liquid to obtain an overall rate on a reactor volume basis. A hydrogen solubility in toluene of 36.5 mol/m$^3$ was used, extrapolating from the data of Yin and Tan.


The liquid superficial velocity was 15 cm/s, the gas velocity 20 cm/s.

**Rate = 2.1 mmol/(s*g Pd)**

Data were obtained at 40°C, 0.1 MPa, with no solvent – pure AMS feed. The liquid superficial velocity is the highest used. The gas superficial velocity is 1.1 cm/s.

\[ \text{Rate} = 0.8 \text{ mmol/(s*g Pd)}. \]
Appendix D Supplementary Material for Chapter 6

D.1 POMR Operating Procedure for Soyoil Hydrogenation

1. Charge the POMR with 1L of pure soyoil from the top. Soyoil brand was Soy Beginnings (Thumb Oilseed Producer's Cooperative) and has been bleached, refined, and de-odorized.

2. POMR was kept under ~1 atm H₂ purge when not in use.

3. For a desired run temperature of 110°C, set heater bath temperature to 140°C. All heat exchanger lines were insulated. A centrifugal pump supplied the heat transfer fluid (Duratherm S, Duratherm Extended Life Fluids) to the exchangers, with the flow started in bypass mode (ball valve to heat exchangers closed, needle valve on return line to bath wide open). The flow through the exchangers was slowly increased by opening the ball valve and slowly closing the needle valve until the pressure gauge on the heat transfer fluid inlet was ~35 psig. This set the flow rate to ~100 mL/min. Other flow rates were set by adjusting the needle valve.

4. Pulse at ~1 Hz to make the system temperature uniform. It took ~1.5 h to reach the operating temperature.

5. Allow the reactant mixture to go ~5°C above desired set-point because the gas flow (once started) will have a cooling effect.


7. Set POMR piston to desired frequency.

8. The system is pressurized. Care was taken to pressurize the top and bottom of the diaphragm at near identical rates (no more than 10 psi differential).

9. Record pressure transducer voltage with LabView® software.

10. Keep both H₂ and N₂ valves to the POMR open to account for any minor leaks and for H₂ consumed by reaction.

11. Sample (~1 mL) during a run using the needle valve connected to the POMR body (similar to a dip-tube) attached to sample into vial at periodic intervals. Care must be taken to first purge dead volume in the valve before taking the sample.

12. Shutdown
   a. Stop oscillations and heating.
   b. Decrease instrument air to booster until it stops pumping.
   c. System is depressurized by bleeding gas to the fume hood vent. Care was taken to depressurize the top and bottom of the diaphragm at similar rates.
d. Drain ~800 mL of fluid through the bottom port on the process side. Drain oil at high temperature (~80°C), because it solidifies at room temperature.

e. POMR must be disassembled to access the diaphragm for complete cleaning and removal of the oil phase.

13. In-situ catalyst treatment
   a. The maximum temperature in the POMR was 120°C with silicone heat transfer fluid.
   b. Pressurize with desired gas (H₂ for reduction) and connect bubbler to gas outlet.
   c. Set gas flow using the needle valve at the gas outlet.
   d. Start heating, bring to temperature.

D.2 Agitated Tank Operating Procedure

1. The agitated tank was an Autoclave Engineers Zipperclave (500 mL) with a 3-bladed marine propeller. Heat was supplied by wrapping the vessel in heating tape controlled by a Variac.

2. Place catalyst-coated monolith at bottom of vessel. Reduce in situ (if desired) by heating until thermocouple reads ~120°C under hydrogen purge, exiting through a bubbler.

3. After cooling, fill the system through the dip-tube using a 100 mL glass syringe and maintaining 1 atm H₂ purge by venting through the bubbler.

4. After filling to 350 mL to completely submerge the impeller blade, begin heating the system while applying ~50 rpm stirring.

5. Once the reactor is at the desired temperature, increase the stirring rate and pressurize the system.

6. Sample at regular intervals using the dip-tube connected to a needle valve. Purge ~2 mL of dead volume from the system before sampling. The valve was also wrapped with heating tape to avoid hardening of the oil.

7. For reactor shutdown, stop the stirring and heating. Depressurize the system using the purge valve, through the bubbler.

8. For repeated runs, the system can be drained using the dip-tube, and fresh reactant re-introduced via the syringe. However, ~100 mL of liquid will remain in the vessel because the dip-tube does not go all the way to the bottom. Remove liquid when still hot to avoid solidification.

9. If complete liquid removal is required, the vessel must be removed.
D.3 Analysis

D.3.1 Conversion to FAME

This section describes how to convert triglycerides from the hydrogenation reaction to fatty acid methyl esters (FAME) for GC analysis. The procedure follows IUPAC Method II.D.19 (*Standard Methods for the Analysis of Oils and Derivatives*, Sections 1 and 22, 6th edition, 1979).

Equipment:

- 50 mL ground glass round-bottom flask
- reflux condenser
- gas adapter to flask (x2)
- 250 mL separatory funnel (optional)
- sample vials (~2 mL)
- 10 mL pipette
- glass boiling stones

Reagents:

- chromatographic quality heptane (Fisher, HPLC)
- sodium sulfate, anhydrous (Mallinckrodt, 99%)
- 0.5 M NaOH methanolic solution, made by dissolving 2g anhydrous NaOH (Mallinckrodt, 98.8%) into 100 mL of methanol (Fisher, HPLC) pre-dried with 5A molecular sieve
- Boron trifluoride, 12-25% methanolic solution (Acros, 99%)
- sodium chloride (Fisher, ACS) saturated aqueous solution
- nitrogen (industrial)
- methyl red, Fisher, ACS (optional)
- hexane, Fisher, HPLC (optional)

Procedure:

To be done in a fume hood.

1. Obtain ~350 mg sample of triglycerides from reactor.

2. Add triglycerides and boiling stones to 50 mL round bottom 2- or 3-neck flask.

3. Attach condenser and flow N₂ through the system to a bubbler.

4. Add 6 mL of 0.5M NaOH methanolic solution.
5. Boil under reflux with N₂ purge, until oil droplets disappear (5-10 min).

6. Add 7mL boron trifluoride (BF₃) methanolic solution through top of condenser.

7. Continue boiling for 1 min.

8. Add 2-5 mL heptane through top of condenser.

9. Continue boiling for 1 min.

10. Cool flask and remove condenser.

11. Add a small amount of saturated NaCl solution and swirl. Precipitation should occur instantly. Continue addition until the liquid level is even with the neck of the flask.

12. Allow phases to separate and transfer ~1 mL of the upper heptane layer into a PTFE-capped sample vial.

13. Add a little sodium sulfate to remove traces of water.

14. This solution contains 7-17% FAMEs and can be directly injected into a GC column (Supelco SP2560, 100 m, 0.25mm) for analysis.

If the dry FAMEs are desired:

15. Transfer the flask contents from step 11 to a separatory funnel. Separate layers.

16. Extract the saline solution twice with 50 mL portions of hexane.

17. Combine the heptane solution and the two extracts and wash with 20 mL portions of water until free from acid. Use methyl red as an indicator.

18. Dry over sodium sulfate, filter and evaporate solvent over a boiling water bath with a N₂ purge.

This procedure performs the reactions shown in Figure D.1, giving the fatty acid methyl ester analogs of the triglycerides. The first reaction is a saponification to remove the glycerol backbone from the fatty acids. The second step is an esterification catalyzed by BF₃ to produce the FAMEs. The FAMEs are soluble in heptane and as a result will preferentially partition into the top organic layer.
**Figure D.1** Reaction to transform triglycerides to FAMEs. R, R’ and R” represent alkyl and alkenyl groups.

**D.3.2 Determination of the Iodine Value**

This section describes the procedure to determine the iodine value (IV) of soybean oil at various levels of hydrogenation. The iodine value is a measure of the total amount of unsaturation. The Procedure follows IUPAC Method II.D.7 (*Standard Methods for the Analysis of Oils and Derivatives*, Section 1 and 22, 6th edition, 1979).

**Equipment:**
- 250 mL wide neck glass bottles with ground glass stoppers
- 50 mL burette, 0.1 mL increments

**Reagents:**
- Wijs reagent (0.1 M iodine monochloride in acetic acid/carbon tetrachloride, Riedel-de Haen)
- 0.1 M sodium thiosulfate aqueous solution Sigma Aldrich, >98%)
- 100 g/L potassium iodide (Sigma, >99%) aqueous solution, free from iodine or iodate
- carbon tetrachloride (Acros, >99%)
- 10 g/L natural starch aqueous dispersion (must be remade every 1-2 weeks)

**Procedure:**
To be done in a fume hood.

1. For an expected IV of 101-150, need ~0.13 g of sample, for 51-100, ~0.20 g, and for 21-50, ~0.40 g. While the exact amount is not critical, recording the weight to 0.001g is necessary.

2. Dissolve the oil in 15 mL carbon tetrachloride. Add 25 mL Wijs reagent and shake container.

3. Place container in the dark for ~1 h.

4. Add 20 mL potassium iodide solution and 150 mL water.

5. Titrate with sodium thiosulfate solution using starch solution as an indicator until the blue color just disappears after shaking. Do not add the starch indicator until the titration is near its endpoint (when the color starts to turn straw yellow). If the starch does not make the solution turn blue upon addition, it has decomposed and needs to be replaced with a fresh starch solution.

Calculate IV based on: 
\[ IV = \frac{12.69 \cdot N \cdot (V_s - V_o)}{m} \]

where \( N \) is exact normality of sodium thiosulphate solution (0.1 M), \( V_s \) is the volume used to titrate a standard (sample with no oil present), \( V_o \) is the volume used to titrate the oil sample, \( m \) is the mass of the oil sample.

**D.3.3 GC Calibration**

The GC retention times of species C18:3, C18:2, C18:1, C18:0, C16:0, and the relative retention times of the trans and cis isomers (to find out what order the cis/trans components were in each species), were obtained using calibration standards from Sigma-Aldrich. The following calibration standards were used:

1. Linoleic acid methyl ester (C18:2) cis/trans FAME mixture
   Sigma Stock # 47791
   10 mg/mL in methylene chloride (as total weight)

   \( \text{cis-9, cis-12-Octadecadienoic acid methyl ester 10 \% (w/w)} \)

   \( \text{cis-9, trans-12-Octadecadienoic acid methyl ester 20 \% (w/w)} \)

   \( \text{trans-9, cis-12-Octadecadienoic acid methyl ester 20 \% (w/w)} \)

   \( \text{trans-9, trans-12-Octadecadienoic methyl ester 50 \% (w/w)} \)
Figure D.2  Plot of decreasing iodine value as a function of run time for a typical hydrogenation reaction. Starting IV is ~136 and final IV is ~75 at the desired level of hydrogenation.

2. Linolenic acid methyl ester (C18:3) cis/trans FAME mixture
   Sigma Stock # 47792
   10 mg/mL in methylene chloride (as total weight)

   cis-9, cis-12, cis-15-Octadecatrienoic acid methyl ester 3 % (w/w)
   cis-9,cis-12,trans-15-Octadecatrienoic acid methyl ester 7 % (w/w)
   cis-9,trans-12,cis-15-Octadecatrienoic acid methyl ester 7 % (w/w)
   cis-9,trans-12,trans-15-Octadecatrienoic acid methyl ester 15 % (w/w)
   trans-9,cis-12,cis-15-Octadecatrienoic acid methyl ester 7 % (w/w)
   trans-9,trans-12,cis-15-Octadecatrienoic acid methyl ester 15 % (w/w)
   trans-9,trans-12,trans-15-Octadecatrienoic acid methyl ester 30 % (w/w)

3. Oil Reference Standard, AOCS RM-2
   Sigma Stock # O7131-1AMP
   pkg of 100 mg, stored in freezer

   All cis forms:
   Methyl linoleate 36 wt. %
   Methyl linolenate 34 wt. %
   Methyl oleate 18 wt. %
   Methyl palmitate 7 wt. %
   Methyl stearate 5 wt. %
Table D.1  HP 5890 GC data acquisition parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial Temperature (°C)</td>
<td>200</td>
</tr>
<tr>
<td>Initial Time (min)</td>
<td>0</td>
</tr>
<tr>
<td>Ramp (°C/min)</td>
<td>0</td>
</tr>
<tr>
<td>Final Temperature (°C)</td>
<td>200</td>
</tr>
<tr>
<td>Final Time (min)</td>
<td>45</td>
</tr>
<tr>
<td>split ratio</td>
<td>1:40</td>
</tr>
<tr>
<td>sample size (µL)</td>
<td>1.0</td>
</tr>
<tr>
<td>Injector Temperature (°C)</td>
<td>220</td>
</tr>
<tr>
<td>Detector Temperature (°C)</td>
<td>220</td>
</tr>
</tbody>
</table>

Table D.2  Approximate retention times for all major species used in soyoil hydrogenation reaction. GC parameters listed in Table D.1. Data obtained using AOCS RM-2 sample.

<table>
<thead>
<tr>
<th>Species</th>
<th>Retention time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C16:0</td>
<td>23.8</td>
</tr>
<tr>
<td>C18:0</td>
<td>27.7</td>
</tr>
<tr>
<td>C18:1</td>
<td>30.6</td>
</tr>
<tr>
<td>C18:2</td>
<td>33.6</td>
</tr>
<tr>
<td>C18:3</td>
<td>38.0</td>
</tr>
</tbody>
</table>

Analysis of the standards for FAME trans-cis mixtures for linolenic and linoleic FAMEs show that first all trans- species are eluted, then trans/cis mixed species, and finally all cis- species.

D.3.4 GC Analysis

Figure D.3 shows the chromatogram for an unreacted sample of soyoil. Only cis-isomers are present in this sample. Figure D.4 shows a typical sample after reaction. The additional peaks present under each C18:X species are cis/trans and positional isomers that are being separated by the column. Positional isomers were lumped together since they do not affect the definition of selectivity (i.e., all cis/trans/trans, trans/cis/trans, and trans/trans/cis areas added together to represent all C18:3 with one cis and two trans species). These figures do not show the heptane solvent peak at ~10 min. In all cases, the
heptane peak saturates the detector. Minor peaks shown in Figure D.3 (36-38 min) indicate some conversion immediately before this sample was taken.

Figure D.3  Chromatogram of unreacted soy oil feed.

Figure D.4  Chromatogram of a typical sample after reaction.
D.3.5 Determination of Activity

D.3.5.1 Based on Iodine Value (IV) Measurements

The overall reaction rate (rate of hydrogen consumption, \( r_{H_2} \)) was calculated using IV measurements. The iodine value represents grams of iodine required to saturate all the double bonds in 100 grams of oil. Based on the definition of IV, the number of moles of \( H_2 \) required to decrease IV by amount \( \Delta IV \) can be given as:

\[
N_{H_2} = \frac{\Delta IV}{100} \times \frac{\rho_{oil}}{\text{Mol. Wt. } I_2} \left[ \text{mol} / m^3 \right]
\]  
(D.1)

Using Eq. D.1 the rate of hydrogen consumption can be calculated as:

\[
r_{H_2} = N_{H_2} \times \frac{V}{W_{Pd} \Delta t} \left[ \text{mol} / g \text{Pd} \cdot \text{min} \right]
\]  
(D.2)

where \( V \) is the volume of reaction mixture, \( W_{Pd} \) is the weight of active Pd metal used, and \( \Delta t \) is the time over which \( \Delta IV \) was measured. \( \Delta IV \) was measured using the first two sample points, meaning \( r_{H_2} \) represents the maximum observed rate for a positive order batch reaction.

D.3.5.2 Based on Concentration Data

The hydrogenation reaction for the individual compounds can be represented as:

\[
\text{C18:3} \xrightarrow{k_3} \text{H}_2 \xrightarrow{k_2} \text{C18:2} \xrightarrow{k_1} \text{C18:1} \xrightarrow{k_1} \text{C18:0}
\]

(D.3)

Let the concentration of individual components C18:X be represented as \( C_{iX} \), where \( i \) is the sample number. We desire to calculate the hydrogen consumption at each step of the reaction:

1. Consumption of \( H_2 \) due to step 1 = \( x \) mol/L
C18:3 $\xrightarrow{k_3} \text{H}_2 \rightarrow \text{C18:2}$

$x = C_{30} - C_{31}$

2. Consumption of H$_2$ due to step 2 = y mol/L

C18:2 $\xrightarrow{k_2} \text{H}_2 \rightarrow \text{C18:1}$

Note that C$_2$ increases by amount x due to step 1, and decreases by amount y due to step 2. Hence the total change in C$_2$ concentration is:

$C_{20} - C_{21} = y - x$

$y = (C_{20} - C_{21}) + x = (C_{20} - C_{21}) + (C_{30} - C_{31})$

3. Consumption of H$_2$ due to step 3 = z mol/L

C18:1 $\xrightarrow{k_1} \text{H}_2 \rightarrow \text{C18:0}$

Note that C$_1$ increases by amount y due to step 2, and decreases by amount z due to step 3. Hence the total change in C$_1$ concentration is:

$C_{10} - C_{11} = z - y$

$z = (C_{10} - C_{11}) + y = (C_{10} - C_{11}) + (C_{20} - C_{21}) + (C_{30} - C_{31})$

Combining steps 1, 2 and 3, we get for total H$_2$ consumption, $N_{H_2} = x + y + z$

$N_{H_2} = (C_{10} - C_{11}) + 2(C_{20} - C_{21}) + 3(C_{30} - C_{31})$ \hspace{1cm} (D.4)

Once the hydrogen consumption $N_{H_2}$ is calculated, the overall rate of hydrogen consumption can be obtained from equation (D.2) as before.

**D.3.6 Determination of Selectivity**

**D.3.6.1 Serial Pathway Selectivity**
Selectivity was determined from the chemical composition supplied by GC analysis. Define two selectivities $S_{32}$ and $S_{21}$ for the serial reaction:

$$C18 : 3 \xrightarrow{k_3} C18 : 2 \xrightarrow{k_2} C18 : 1 \xrightarrow{k_1} C18 : 0$$

$$S_{32} = \frac{k_3}{k_2} \quad \text{(D.5)}$$

$$S_{21} = \frac{k_2}{k_1} \quad \text{(D.6)}$$

Higher values of $S_{32}$ and $S_{21}$ correspond to less formation of saturates and higher consumption of tri-unsaturates. The rate constants $k_3$, $k_2$, $k_1$ were obtained by regression using the differential equations for a first-order serial reaction pathway:

$$\frac{dC_3}{dt} = -k_3C_3 \quad \text{(D.7)}$$

$$\frac{dC_2}{dt} = k_3C_3 - k_2C_2 \quad \text{(D.8)}$$

$$\frac{dC_1}{dt} = k_2C_2 - k_1C_1 \quad \text{(D.9)}$$

$$\frac{dC_0}{dt} = k_1C_1 \quad \text{(D.10)}$$

To obtain $S_{32}$ and $S_{21}$, rearrange Eqs. D.7-D.10 into integral forms. Eqs. D.7 and D.8 become:

$$\frac{d(C_3 + C_2)}{dC_3} = \frac{k_2C_2}{k_3C_3} \quad \text{(D.11)}$$

Integrating D.11 gives:

$$(C_3 + C_2) - (C_3 + C_2)_0 = \frac{k_2}{k_3} \int \frac{C_2}{C_3} dC_3 \quad \text{(D.12)}$$

Rearranging D.8 and D.9 give:
\[
\frac{dC_1}{d(C_2 + C_3)} = \frac{k_2C_2 - k_1C_1}{-k_2C_2}
\]

integrating D.13 gives:

\[
(C_1 + C_2 + C_3) - (C_1 + C_2 + C_3)_0 = \frac{k_1}{k_2} \int \frac{C_1}{C_2} d(C_2 + C_3)
\]

where \(S_{32}\) and \(S_{21}\) can be obtained from D.12 and D.14 by inserting the concentrations of C18:3, C18:2, and C18:1 that are known from the GC data. The integrals in the equation D.12 and D.14 were obtained by fitting a power low expression to experimental data and then calculating the analytical integral at that particular point. Figure D.5 shows a typical fit used for calculating the integral \(\int (C_2 / C_3) dC_3\) in equation D.12.

![Figure D.5 Plot illustrating the power law fit used for calculating integral in equation D.12.](image)

\[y = 2.0947x^{-0.4981}\]

\[R^2 = 0.9992\]

The expressions in equation D.12 and D.14 were plotted in the form of \(y = mx\), where the inverse slopes of the lines correspond to \(S_{32}\) and \(S_{21}\). This integral method was chosen to smooth measurement errors (see Table D.3).
Figure D.6  Plot of Eq. D.12 for a typical hydrogenation. The inverse of the slope (1.66) is the ratio $k_3/k_2$, which is $S_{32}$. Data are limited to three points because at high conversion $C_3$ approaches zero, leading to a division by zero error.

Figure D.7  Plot of Eq. D.14 for a typical hydrogenation. The inverse of the slope (15.98) is the ratio $k_2/k_1$, which is $S_{21}$. 
The errors in these serial pathway selectivities were quantified by computing the average percent error:

\[
\% Error = \left[ \frac{\sigma}{y_{\text{mean}}} \right] \times 100 \quad \text{where} \quad \sigma = \sqrt{\frac{\sum (y_{\text{exp}} - y_{\text{fit}})^2}{N - 1}}
\] (D.15)

where \(y_{\text{exp}}\) is the experimental y-value from the plots used to determine selectivity (i.e. Figures D.6 and D.7), \(y_{\text{fit}}\) is the corresponding y-value from the line of best fit and \(y_{\text{mean}}\) is mean value of all \(y_{\text{exp}}\). Data that resulted in excessively high % errors (>20%) were discarded as being unreliable and were not used in subsequent calculations.

**D.3.6.2 Stereoselectivity**

Stereoselectivity was monitored by adding up all of the trans content from the chromatograms and expressing it as a weight fraction. This method is consistent with the typical method used in the literature. As shown in Figure D.8, the formation of trans species is approximately linear with respect to time. For low activity runs where a final IV of near 75 was not reached, the final trans content at IV \(\sim 75\) was approximated using the line of best fit from the data. In this manner the total trans content was compared at identical IV values; trans content is a strong function of double bond conversion. Species with both trans and cis double bonds (i.e. C18:2ct) were treated as purely trans in this analysis. However, the trans content primarily resulted from C18:1t species, which comprised \(\sim 90\%\) of all trans species after reaction. The contribution from species with both cis and trans species was mostly negligible.

**D.4 Summary of Data**

To estimate the error present in the GC analysis, the same sample was injected into the GC four times. For each shot, the areas were obtained and the weight fractions
calculated for each species. An Excel spreadsheet was setup to automatically take the GC areas and perform the necessary calculations. From these data, the mean and standard deviations were calculated. Percent errors were obtained from the standard deviations divided by the means. These results show that the highest uncertainty was in the trans content, with an error of 11%.

![Total trans content of the oil as a function of run time. The final IV for this run was 85, at 80 min.](image)

**Figure D.8** Total trans content of the oil as a function of run time. The final IV for this run was 85, at 80 min.

**Table D.3** Experimental error analysis for multiple GC injections.

<table>
<thead>
<tr>
<th>Shot #</th>
<th>C16:0</th>
<th>C18:0</th>
<th>C18:1 tot</th>
<th>C18:2 tot</th>
<th>C18:3 tot</th>
<th>trans tot</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>wt. fraction</td>
<td>wt. fraction</td>
<td>wt. fraction</td>
<td>wt. fraction</td>
<td>wt. fraction</td>
<td>wt. fraction</td>
</tr>
<tr>
<td>1</td>
<td>0.110</td>
<td>0.066</td>
<td>0.515</td>
<td>0.288</td>
<td>0.022</td>
<td>0.160</td>
</tr>
<tr>
<td>2</td>
<td>0.110</td>
<td>0.064</td>
<td>0.493</td>
<td>0.316</td>
<td>0.018</td>
<td>0.160</td>
</tr>
<tr>
<td>3</td>
<td>0.102</td>
<td>0.061</td>
<td>0.507</td>
<td>0.311</td>
<td>0.019</td>
<td>0.191</td>
</tr>
<tr>
<td>4</td>
<td>0.101</td>
<td>0.061</td>
<td>0.505</td>
<td>0.314</td>
<td>0.019</td>
<td>0.194</td>
</tr>
<tr>
<td>Mean</td>
<td>0.106</td>
<td>0.063</td>
<td>0.505</td>
<td>0.307</td>
<td>0.019</td>
<td>0.176</td>
</tr>
<tr>
<td>Std. Dev.</td>
<td>0.005</td>
<td>0.002</td>
<td>0.009</td>
<td>0.013</td>
<td>0.002</td>
<td>0.019</td>
</tr>
<tr>
<td>% Error</td>
<td>4.4</td>
<td>3.6</td>
<td>1.8</td>
<td>4.2</td>
<td>9.4</td>
<td>10.8</td>
</tr>
</tbody>
</table>
Table D.4  Summary of runs in agitated vessel, $T=110^\circ$C. Blank cells represent selectivity data where the $R^2$ values are >0.5 or the APRD was >60%. Blank cells indicate runs that were discarded due to errors > 20%.

<table>
<thead>
<tr>
<th>Run #</th>
<th>Catalyst</th>
<th>P</th>
<th>RPM</th>
<th>particle size</th>
<th>$k$</th>
<th>$r_H^1$</th>
<th>$r_H^2$</th>
<th>$S_{21}$</th>
<th>$R^2$</th>
<th>Error</th>
<th>$S_{32}$</th>
<th>$R^2$</th>
<th>Error</th>
<th>IV$_{final}$</th>
<th>Trans at IV$_{final}$</th>
<th>Trans at IV=75</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Monolith</td>
<td>0.2</td>
<td>2000</td>
<td>100</td>
<td>0.078</td>
<td>0.30</td>
<td>0.34</td>
<td>9.16</td>
<td>0.90</td>
<td>13</td>
<td>1.70</td>
<td>0.96</td>
<td>16</td>
<td>102</td>
<td>0.11</td>
<td>0.22</td>
</tr>
<tr>
<td>2</td>
<td>Monolith</td>
<td>0.4</td>
<td>2000</td>
<td>100</td>
<td>0.053</td>
<td>0.31</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>108</td>
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<td>0.25</td>
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<td>3</td>
<td>Monolith</td>
<td>0.3</td>
<td>2000</td>
<td>100</td>
<td>0.026</td>
<td>0.12</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td>0.07</td>
<td>0.43</td>
</tr>
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<td>Monolith</td>
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<td>2000</td>
<td>100</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>111</td>
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<td>0.39</td>
</tr>
<tr>
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<td>2000</td>
<td>100</td>
<td>0.041</td>
<td>0.23</td>
<td>0.18</td>
<td>9.49</td>
<td>0.97</td>
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<td>11</td>
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<td>0.19</td>
<td>0.39</td>
</tr>
<tr>
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<td>0.3</td>
<td>2000</td>
<td>100</td>
<td>0.044</td>
<td>0.19</td>
<td>0.21</td>
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<tr>
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<td>0.043</td>
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<td></td>
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<td>0.49</td>
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<td>2000</td>
<td>100</td>
<td>0.041</td>
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<td>0.19</td>
<td>11.99</td>
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<td>0.99</td>
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<td>0.22</td>
<td>0.36</td>
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<tr>
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<td>Monolith</td>
<td>0.3</td>
<td>520</td>
<td>100</td>
<td>0.042</td>
<td>0.19</td>
<td>0.24</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>111</td>
<td>0.18</td>
<td>0.38</td>
</tr>
<tr>
<td>10</td>
<td>Powder</td>
<td>0.3</td>
<td>2000</td>
<td>44&lt;x&lt;74</td>
<td>1.260</td>
<td>6.80</td>
<td>6.41</td>
<td>12.44</td>
<td>0.85</td>
<td>21</td>
<td>1.74</td>
<td>0.98</td>
<td>6</td>
<td>62</td>
<td>0.40</td>
<td>0.34</td>
</tr>
<tr>
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<td>Powder</td>
<td>0.3</td>
<td>2000</td>
<td>44&lt;x&lt;74</td>
<td>0.980</td>
<td>6.24</td>
<td>4.58</td>
<td>19.58</td>
<td>0.94</td>
<td>17</td>
<td>2.14</td>
<td>0.94</td>
<td>9</td>
<td>68</td>
<td>0.38</td>
<td>0.31</td>
</tr>
<tr>
<td>12</td>
<td>Powder</td>
<td>0.3</td>
<td>2000</td>
<td>44&lt;x&lt;74</td>
<td>0.730</td>
<td>4.31</td>
<td>2.96</td>
<td>15.68</td>
<td>0.99</td>
<td>5</td>
<td>1.47</td>
<td>0.97</td>
<td>4</td>
<td>73</td>
<td>0.36</td>
<td>0.33</td>
</tr>
<tr>
<td>13</td>
<td>Powder</td>
<td>0.3</td>
<td>520</td>
<td>44&lt;x&lt;74</td>
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<td>2.59</td>
<td>1.78</td>
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<td>0.790</td>
<td>2.98</td>
<td>2.95</td>
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<td>0.95</td>
<td>20</td>
<td>1.56</td>
<td>0.99</td>
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<td>76</td>
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</tr>
<tr>
<td>15</td>
<td>Powder</td>
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<td>2000</td>
<td>44&lt;x&lt;74</td>
<td>0.990</td>
<td>4.49</td>
<td>5.27</td>
<td>14.27</td>
<td>0.99</td>
<td>6</td>
<td>1.70</td>
<td>0.99</td>
<td>1</td>
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<td>0.37</td>
<td>0.31</td>
</tr>
<tr>
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<td>2000</td>
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<td>1.020</td>
<td>5.48</td>
<td>4.68</td>
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<td>0.99</td>
<td>4</td>
<td>1.41</td>
<td>0.95</td>
<td>6</td>
<td>69</td>
<td>0.27</td>
<td>0.25</td>
</tr>
<tr>
<td>17</td>
<td>Powder</td>
<td>0.6</td>
<td>2000</td>
<td>44&lt;x&lt;74</td>
<td>1.973</td>
<td>8.79</td>
<td>8.77</td>
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<td></td>
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<td>71</td>
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<td>0.25</td>
</tr>
<tr>
<td>18</td>
<td>Powder</td>
<td>0.3</td>
<td>2000</td>
<td>&lt;44</td>
<td>0.900</td>
<td>4.30</td>
<td>4.99</td>
<td>14.83</td>
<td>0.85</td>
<td>30</td>
<td>1.56</td>
<td>0.98</td>
<td>6</td>
<td>70</td>
<td>0.29</td>
<td>0.26</td>
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<tr>
<td>19</td>
<td>Powder</td>
<td>0.3</td>
<td>2000</td>
<td>150&lt;x&lt;180</td>
<td>0.730</td>
<td>3.32</td>
<td>3.28</td>
<td>11.38</td>
<td>0.94</td>
<td>31</td>
<td>1.75</td>
<td>0.97</td>
<td>7</td>
<td>73</td>
<td>0.33</td>
<td>0.28</td>
</tr>
</tbody>
</table>

1 $r_H$ calculated from GC data (see section D.3.5.2)

2 $r_H$ calculated from IV data (see section D.3.5.1)
Table D.5  Data for agitated tank with averaged values from the runs performed at identical conditions in Table D.4.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>T</th>
<th>P</th>
<th>RPM</th>
<th>particle size</th>
<th>mean size</th>
<th>L scale</th>
<th>k</th>
<th>R_{th}^1</th>
<th>R_{th}^2</th>
<th>S_{21}</th>
<th>S_{32}</th>
<th>Trans at IV=75</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>wt. fraction</td>
</tr>
<tr>
<td>Monolith</td>
<td>110</td>
<td>0.31</td>
<td>2000</td>
<td>100.000</td>
<td>100</td>
<td>0.045</td>
<td>0.21</td>
<td>0.21</td>
<td>10.21</td>
<td>1.61</td>
<td>0.37</td>
<td></td>
</tr>
<tr>
<td>Monolith</td>
<td>110</td>
<td>0.31</td>
<td>520</td>
<td>100</td>
<td>100</td>
<td>0.042</td>
<td>0.19</td>
<td>0.23</td>
<td>-</td>
<td>-</td>
<td>0.44</td>
<td></td>
</tr>
<tr>
<td>Powder</td>
<td>110</td>
<td>0.31</td>
<td>2000</td>
<td>44&lt;x&lt;74</td>
<td>63</td>
<td>0.950</td>
<td>4.51</td>
<td>3.94</td>
<td>15.15</td>
<td>1.72</td>
<td>0.31</td>
<td></td>
</tr>
<tr>
<td>Powder</td>
<td>110</td>
<td>0.58</td>
<td>2000</td>
<td>44&lt;x&lt;74</td>
<td>63</td>
<td>1.970</td>
<td>8.79</td>
<td>8.77</td>
<td>9.88</td>
<td>1.41</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td>Powder</td>
<td>110</td>
<td>0.31</td>
<td>2000</td>
<td>44&lt;x&lt;74</td>
<td>38</td>
<td>0.900</td>
<td>4.67</td>
<td>4.99</td>
<td>14.83</td>
<td>1.56</td>
<td>0.26</td>
<td></td>
</tr>
<tr>
<td>Powder</td>
<td>110</td>
<td>0.31</td>
<td>2000</td>
<td>150&lt;x&lt;180</td>
<td>166</td>
<td>0.730</td>
<td>3.32</td>
<td>3.28</td>
<td>11.38</td>
<td>1.75</td>
<td>0.28</td>
<td></td>
</tr>
</tbody>
</table>

1 \( r_{th} \) calculated from GC data (see section D.3.5.2)
2 \( r_{th} \) calculated from IV data (see section D.3.5.1)

Table D.6  Summary of POMR data at T=110°C, P=0.31 MPa. Blank cells represent selectivity data where the \( R^2 \) values are >0.5 or the APRD was >60%. Blank cells indicate runs that were discarded due to errors > 35%.

<table>
<thead>
<tr>
<th>Run #</th>
<th>Freq.</th>
<th>k</th>
<th>( r_{th}^1 )</th>
<th>( S_{21} )</th>
<th>( R^2 )</th>
<th>Error</th>
<th>( S_{32} )</th>
<th>( R^2 )</th>
<th>Error</th>
<th>IV_{final}</th>
<th>Trans at IV_{final}</th>
<th>Trans at IV=75</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Hz</td>
<td>L/g_{Pd}/min</td>
<td>mol/g_{Pd}/min</td>
<td>%</td>
<td>%</td>
<td>wt. fraction</td>
<td>wt. fraction</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>17.5</td>
<td>0.27</td>
<td>1.12</td>
<td>10.82</td>
<td>0.98</td>
<td>5</td>
<td>2.46</td>
<td>0.93</td>
<td>7</td>
<td>65</td>
<td>0.45</td>
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<tr>
<td>2</td>
<td>8</td>
<td>0.17</td>
<td>0.56</td>
<td>11.83</td>
<td>0.99</td>
<td>9</td>
<td>2.01</td>
<td>0.97</td>
<td>8</td>
<td>71</td>
<td>0.41</td>
<td>0.43</td>
</tr>
<tr>
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<td>0</td>
<td>0.097</td>
<td>0.493</td>
<td>8.72</td>
<td>0.94</td>
<td>17</td>
<td>1.41</td>
<td>0.97</td>
<td>9</td>
<td>97</td>
<td>0.25</td>
<td>0.41</td>
</tr>
<tr>
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<td>0.998</td>
<td>12.31</td>
<td>0.99</td>
<td>12</td>
<td>2.24</td>
<td>0.97</td>
<td>12</td>
<td>62</td>
<td>0.47</td>
<td>0.39</td>
</tr>
<tr>
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<td>8</td>
<td>0.180</td>
<td>0.782</td>
<td>19.24</td>
<td>0.40</td>
<td>35</td>
<td>2.28</td>
<td>0.92</td>
<td>12</td>
<td>71</td>
<td>0.43</td>
<td>0.41</td>
</tr>
<tr>
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<td>0.503</td>
<td>82</td>
<td>0.43</td>
<td>0.42</td>
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</tr>
<tr>
<td>7</td>
<td>17.5</td>
<td>0.23</td>
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<td>72</td>
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<td>0.22</td>
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<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

1 \( r_{th} \) calculated from IV data (see section D.3.5.1)
Table D.7  Typical raw data collected for a single experimental run.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Sample time</th>
<th>oil mass</th>
<th>Volume for titration</th>
<th>Computed IV</th>
<th>k</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>min</td>
<td>g</td>
<td>mL</td>
<td>L/gpol/min</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0.1815</td>
<td>30.5</td>
<td>133.5</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>45</td>
<td>0.1696</td>
<td>35</td>
<td>109.2</td>
<td>4.46E-03</td>
</tr>
<tr>
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<td>0.2014</td>
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<td>90.1</td>
<td>4.37E-03</td>
</tr>
<tr>
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<td>135</td>
<td>0.1997</td>
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<td>72.4</td>
<td>4.53E-03</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Area</th>
<th>C16:0</th>
<th>C18:0</th>
<th>C18:1t</th>
<th>C18:1c</th>
<th>C18:1 total</th>
<th>C18:2 tt</th>
<th>C18:2 ct &amp; tc</th>
<th>C18:2 cc</th>
<th>C18:2 total</th>
<th>C18:3 ttt</th>
<th>C18:3 ttc+tcc</th>
<th>C18:3 ccc</th>
<th>C18:3 total</th>
</tr>
</thead>
<tbody>
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<td>7.10</td>
<td>3.41</td>
<td>0.00</td>
<td>15.47</td>
<td>15.47</td>
<td>0.00</td>
<td>0.00</td>
<td>35.68</td>
<td>35.68</td>
<td>0.00</td>
<td>0.00</td>
<td>4.73</td>
<td>4.73</td>
</tr>
<tr>
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<td>3.44</td>
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<td>0.21</td>
<td>0.89</td>
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<td>20.88</td>
<td>0.15</td>
<td>0.24</td>
<td>1.62</td>
<td>2.00</td>
</tr>
<tr>
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<td>5.42</td>
<td>15.71</td>
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<td>0.22</td>
<td>0.99</td>
<td>12.91</td>
<td>14.11</td>
<td>0.10</td>
<td>0.16</td>
<td>0.87</td>
<td>1.13</td>
</tr>
<tr>
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<td>4.67</td>
<td>11.00</td>
<td>22.11</td>
<td>33.11</td>
<td>0.53</td>
<td>2.21</td>
<td>13.05</td>
<td>15.79</td>
<td>0.09</td>
<td>0.17</td>
<td>0.82</td>
<td>1.08</td>
</tr>
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</table>

<table>
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<tr>
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Appendix E Copyright Permission Letters

E.1 Permission Letter for Chapter 3

Dear Dr. Bussard,

Permission is granted. Please fully cite the publication of your article in the *AIChE Journal*.

Thank you very much.

Sincerely,

Arthur Baulch,
*AIChE Journal*

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Hoboken, NJ 07030-5774
Tel: 201-748-6971; Fax: 201-748-6182
abaulch@wiley.com

"Alan Bussard"
<abussa1@lsu.edu>
01/21/2008 05:53 PM

Hi Arthur,

I am working on my PhD dissertation and wanted to include the paper *Polymer Hydrogenation in Pulsed Flow Systems with Extrusion* by Alan Bussard and Kerry Dooley. This paper was accepted 12/31/07 by the AIChE Journal for publication and the copyright has been transferred to John Wiley & Sons. Can you send me an e-mail confirming it is OK to put a copy of this paper in my dissertation? Thank you.

Alan Bussard
Graduate Student
Gordon A. and Mary Cain Department of Chemical Engineering
Louisiana State University
abussa1@lsu.edu

01/21/2008 05:53 PM

Subject Copyright request for PhD dissertation
Vita

Alan G. Bussard was born to C.W. and W.E. Bussard in the month of October, 1981, in San Mateo, California, a suburb just south of San Francisco. He completed his undergraduate studies at the University of California at Berkeley, where he earned the degree of Bachelor of Science in Chemical Engineering in 2003. A glutton for punishment, he left the great state of California and enrolled at Louisiana State University in the Department of Chemical Engineering where he worked under the tutelage of Dr. Kerry M. Dooley. He looks forward to an industrial career involving chemical reaction engineering and catalysis.