Catalysts for the Positional Isomerization of Internal, Long-Chain Olefins

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CATALYSTS FOR THE POSITIONAL ISOMERIZATION OF INTERNAL, LONG-CHAIN OLEFINS

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy

in

The Gordon A. and Mary Cain Department of Chemical Engineering

by

James Bruno
B.S., Western Michigan University, 2010
M.S., Louisiana State University, 2012
August 2015
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ABSTRACT

Double-bond isomerization of internal C_{16}-C_{18} olefins is a necessary step in the production of paper sizing agents. In this work, the properties that enable long-lasting solid acid catalysts (both commercial and lab-synthesized) were identified, the efficacy of regenerated solid acid catalysts was tested, and the feasibility of organometallic chain-walking catalysts (both homogeneous and polymer-supported) for olefin isomerization was evaluated.

Hexadecene isomerization was investigated using perfluorinated ion exchange resins (Nafion®) supported on SiO₂ or Al₂O₃, sulfonated poly(styrene-co-divinylbenzene) resins (PS-DVBs), tungstated zirconias, and acidic zeolites. Selected catalysts underwent lifetime studies. Oversulfonated PS-DVBs (e.g., Amberlyst 35) were reasonably selective with long lifetimes, only gradually deactivating due to poisoning by surface oligomers. Amberlyst® 70, Amberlyst® XN1010, ZSM-35 and SAPO-11 were evaluated because of their lower acid site densities and degree of crosslinking (for the PS-DVBs). None of these catalysts were optimal for various reasons. Both beneficial and harmful effects arising from the cooperativity of acid sites in close proximity were observed. Enhanced acid strength was associated with multiple adjacent sites, but at the expense of more rapid deactivation due to olefin oligomerization.

Used SAC-13 catalysts were regenerated by solvent extraction. Nonpolar m-xylene was the most effective in reopening pore volume. The catalysts regenerated by ethanol were active in octadecene isomerization, but deactivation was relatively rapid. Small pores volumes and a small fraction of surface sites resulted in both a diffusion limitation within the catalyst and enhanced deactivation from fewer oligomerization events.

Homogeneous Fe(CO)₅ was an extremely effective catalyst capable of highly selective double bond isomerization (100% selective) with a high (80%) conversion of alpha olefins to
internal olefins. The optimal batch reactor conditions to isomerize 2 L of 1-hexadecene were 500 ppm of Fe(CO)$_5$ at 180°C for 1-4 h.

Iron pentacarbonyl was also immobilized on a functionalized PS-DVB. Iron carbonyls were detected on the surface, though it was unclear whether they were physisorbed or bonded to surface groups. The catalyzed reactions of octadecenes were slow with a very low conversion and internal olefins were being removed from the product. Therefore, the heterogeneous iron carbonyls synthesized here were ineffective for generating internal double bonds.
CHAPTER 1: INTRODUCTION

1.1 The Paper Machine and Wet End Chemistry

Paper is commonly manufactured in a four-part process: the forming section (based on a Fourdrinier machine), a press section, a drying section, and a calendering section (Figure 1.1). A dilute suspension of pulp (~4% solids, mostly cellulose and hemicellulose) is evenly distributed from the Headbox to the fast-moving “wire” made up of a woven polymer fabric. The paper is mechanically treated by various presses and then dried to form the final product (~96% solids).

The forming section of the paper machine is called the “wet end” where a variety of chemical additives are combined with the furnish. Additives can include defoamers, drainage aids, mineral fillers (CaCO$_3$, e.g.), sizing agents, etc. The interaction between the pulp and wet end additives is the basis of Wet End Chemistry, a diverse area of research and development in paper science and engineering.

1.2 Alkenyl Succinic Anhydride

This research is based on the synthesis of alkenyl succinic anhydride (ASA), a sizing agent and a common wet end additive (Figure 1.2). Sizing agents reduce the ability of fluids to penetrate the paper. Rosin/Al$_2$(SO$_4$)$_3$ systems were initially used as sizing agents because the amphipathic (hydrophilic/hydrophobic) system formed non-reactive hydrostatic bonds with the hydrophobic cellulose and hemicellulose paper stock. ASA also has amphipathic effects (anhydride groups bond to paper stock, alkenyl groups resist aggregation of water) with the advantage of operating at neutral pH.

1.2.1 Synthesis of ASA

ASA is synthesized by the reaction of an olefin with maleic anhydride (Figure 1.3). Wurzburg established that internal olefins react faster than alpha olefins and produce higher
quality ASA. Most companies use C_{16}-C_{18} olefins as feedstock. Olefin feedstock is typically made up of alpha olefins where the double bond is in the terminal position, so the process begins with double bond isomerization, which can be accomplished by either precious metals (Pt, Pd, e.g.), acid and base catalysts, or organometallic “chain-walking” catalysts. Alternatively, internal double bonds can be generated by olefin self-metathesis, a double displacement reaction with an internal olefin product and ethylene, though it is uncommon in industrial processes.
1.3 Catalysts for Positional Isomerization of Olefins

Liquid acids such as H₂SO₄ are capable of the isomerization, but industrial usage carries the risks of equipment corrosion and environmental disposal. Solid acid catalysts are used to sidestep these issues because they are non-corrosive and easily separated from effluent streams. The most common types of solid acid catalysts used for positional isomerization are sulfonated poly(styrene-co-divinylbenzene) (PS-DVB’s)⁵, acidic zeolites⁶, solid bases (such as K-based catalysts for the Shell Higher Olefin Process)¹¹, and perfluorinated ion exchange resins⁷.

The supported metal catalysts are more useful in converting alpha olefin double bonds to the beta and gamma positions. Strong acid catalysts are more useful in further internalizing the double bond via hydride shift, with a goal of converting most of the alpha and beta olefins. However, strong acid catalysts can also promote side reactions that include skeletal isomerization (alkyl shift), cracking (β scission), and oligomerization (alkylation). A scheme of these reaction mechanisms are in Figure 1.4.

Organometallic catalysts are selective for the positional isomerization of terminal olefins to internal, trans olefins (see mechanisms in Chapter 4.1).¹² However, these homogeneous catalysts must be separated from the product because their toxicity and subsequent reactivity
may incur additional process costs. Homogeneous catalysts may be bound to a solid support to create a heterogeneous catalyst.

![Diagram of mechanisms](image)

Figure 1.4: Mechanisms of the acid catalyzed reactions of olefins: (1) hydride shift; (2) alkyl shift; (3) cracking; and (4) dimerization

### 1.4 Purpose of Research

The purpose of this work was to find improved catalysts for the positional (double bond) isomerization of hexadecenes and octadecenes (C_{16}-C_{18}), especially internalization of the double bond to the gamma, delta, epsilon etc. positions. Ideal catalysts should be reusable and selective to internal double bonds while minimizing oligomerization, skeletal isomerization (“branched”
olefins), or cracking. A secondary purpose was to obtain a better understanding of how the oligomers, which are catalyst poisons, are generated on the active sites.

This research especially focuses on three classes of catalysts. These are sulfonated poly(styrene-\(\text{co}\)-divinylbenzenes) (Chapter 2), perfluorinated, sulfonated ion exchange resins (Chapters 2-3), and iron carbonyls, both homogeneous and heterogeneous (Chapter 4). However, certain other catalysts such as acidic zeolites and tungstated zirconias are also considered for comparison purposes. Catalytic reaction studies include examination of initial activities, catalyst lifetimes under industrially relevant conditions, and regeneration studies for a few promising catalysts. Selected catalysts were also characterized by a variety of techniques. Examples include measurements of total acid sites and acid site distributions, by thermogravimetric and titration methods. Further examples include surface characterization by Fourier Transform Infrared (FTIR) Spectroscopy, and bulk characterization by elemental analysis.
CHAPTER 2: DOUBLE-BOND ISOMERIZATION OF HEXADECENES WITH SOLID ACID CATALYSTS*

2.1 Introduction

Internal, long-chain alkenes (>C₁₀) are feedstocks in the manufacture of paper sizing agents and deep-sea drilling fluids.¹³,¹⁴ Alkenyl succinic anhydrides (ASA), common sizing agents, are synthesized by reacting maleic anhydride with a long-chain alkene. The sizing properties of ASA increase with extent of olefin double bond isomerization,¹³ so there is interest in methods that maximize internal alkenes. Practical methods include isomerization by either solid acids,¹⁵ organometallic “chain-walking” catalysts,¹⁰ or metathesis.¹⁰

We have evaluated solid acid catalysts for the selective double bond isomerization of hexadecenes (C₁₆). Sulfonated poly(styrene-co-divinylbenzene) (PS-DVB), perfluorinated ion exchange resins, and acidic zeolites are most frequently used.⁶,¹⁴,¹⁶-¹⁹ Both skeletal isomerization (branching) and oligomerization compete with positional (double bond) isomerization. Oligomerization is slower with internal alkenes when using weaker, primarily Lewis acid, catalysts.²⁰,²¹ Selectivity to internal alkenes decreases with respect to both increasing temperature (usually at >150°C) and acid strength.²²,²³

Perfluorinated polymers with pendant sulfonic acid groups (e.g., Nafion®) are of interest as catalysts for these and other acid-catalyzed reactions such as alkylation and Claisen condensation. These catalysts are characterized by high acid strengths and thermal stability up to 280°C.²⁴ However, given their inherently low surface areas, the polymers must be supported, usually on SiO₂. The silica-polymer composites are weaker acids than Nafion itself, with relatively low crush strengths.²⁵-²⁷ Interaction of the sulfonic acid groups with the silanols can

(*Chapter 2 previously appeared as [Bruno, J.E.; Dooley, K.M. “Double-bond isomerization of hexadecenes with solid acid catalysts.” Applied Catalysis A: General, 497, 176-183, 2015]. It is reprinted by permission of Elsevier - see the letter copied in Appendix B.)
have other malign effects, such as increasing deactivation rates.\textsuperscript{25} Using both a higher crush strength and a more amphoteric support (e.g., certain catalytic aluminas) may improve catalyst lifetime. We note that Harmer et al reported difficulties in distributing Nafion in porous silica by wet impregnation,\textsuperscript{28} and that Bringue et al found that a Nafion/Al\textsubscript{2}O\textsubscript{3} had at least some catalytic activity for the dehydration of 1-pentanol.\textsuperscript{29}

In this work, the activity of materials prepared by various methods of impregnation of Nafion/Al\textsubscript{2}O\textsubscript{3} was investigated. These new Nafion materials were compared directly to the presumably weaker sulfonated PS-DVBs, and to commercial Nafion/SiO\textsubscript{2}. Furthermore, we tested commercial zeolites and tungstated zirconia (WZ), comparing both selectivity to internal alkenes and turnover frequency. Lifetime studies and acid site characterizations were performed to elucidate how the structure and acid strengths of the active sites may contribute to the catalyst deactivation.

2.2 Experimental Procedures

2.2.1 Catalyst Preparation

Commercial catalysts were provided by several manufacturers: the PS-DVBs were Amberlyst 15 (AM-15, Dow), Amberlyst 35 (AM-35, Dow), Amberlyst 70 (AM-70, Dow), Amberlyst XN1010 (AM-XN1010, Dow) and Lewatit K2620 (K2620, Sybron). The supported Nafion/SiO\textsubscript{2} was SAC-13, provided by BASF. The tungstated zirconia was XZO 1251, provided by Magnesium Elektron. The zeolites included SAPO-11 (6C USA) and ZSM-35 (Alfa Aesar). Prior to use, SAPO-11 and ZSM-35 were calcined in flowing air for 3 h at 450°C and cooled under N\textsubscript{2} (bottled while still hot). XZO 1251 was calcined in flowing air at 800°C for 3 h (also bottled while hot). The PS-DVBs and supported Nafion catalysts were dried for 16 h under vacuum at 90°C and 110°C, respectively.
Nafion/Al$_2$O$_3$ catalysts were prepared by wet impregnation in two ways starting with Nafion NR50 beads (Ion Power, 1100 EW). For the preparation of BCPR5, the Nafion was first dissolved (1 L 316SS autoclave, overnight, 220°C, 500 rpm) in water/propan-2-ol (50% v/v) to a 0.8 wt% solution, then 225 mL of solution was contacted with 15 g Al$_2$O$_3$ (Engelhard Al-3945 E, 2.1 mm) in a rotary evaporator under 5.0 mbar pressure for 6 h. For BCPR4, an Al$_2$O$_3$ support (LaRoche A 201 5x8 alumina spheres, 15 g) was wet impregnated overnight in the 1 L autoclave concurrent with the Nafion dissolution (750 mL of the 0.8 wt% solution, 220°C, 100 rpm). All Nafion/Al$_2$O$_3$ catalysts underwent filtration and three separate ion exchanges (125 mL of 0.05 M HCl for 2 h). Catalysts were then washed with DI water and vacuum dried for 3 h at 120°C. Nafion content was determined by thermogravimetric analysis (Perkin Elmer TGA 7), where temperature was ramped from 50-550°C in flowing He.

### 2.2.2 Catalyst Characterization

Acid sites were characterized by both wet titration and TPD of propan-1-amine (1-PA, Alfa Aesar 99+%). Wet titration was performed by stirring 0.1 g catalyst in 20 mL of 2 M NaCl (12 h) followed by titration with 0.01 M NaOH to a phenolphthalein endpoint. For TPD (Perkin Elmer TGA-7), the 1-PA was adsorbed at 50°C for 15 min, then held at 50°C until constant weight, then ramped to 300°C at 5°C/min. Samples of effluent gas were analyzed by GC/MS (HP 5890 Series II/5927 MSD) using an SP-1000 column (Supelco, 30 m, 0.32 mm ID). The surface area and pore volume was calculated by N$_2$ physisorption. Adsorption/desorption isotherms at -196°C were measured using a Quantachrome Autosorb 1 porosimeter.

### 2.2.3 Isomerization Studies

The positional isomerization of C$_{16}$ alkenes was studied in packed bed reactors (316 SS, 12.7 mm ID, 0.36 m long) at 130°C except where noted. Each reactor was filled with 20 mL of
catalyst with α-alumina as bed support. After drying under N₂ flow at 130°C overnight, the reactor was fed with 1 mL/min [LHSV ~ 3 mL feed/(h•mL catalyst)] of partially isomerized feedstock (~70 wt% 1-, 2-, and 3-C₁₆). Samples were collected every hour for 3 h.

Lifetime studies were performed on selected catalysts in a larger but otherwise similar reactor at the same LHSV (15.5 mm ID, 0.61 m length, 30 mL catalyst). Samples were collected every 12 h. Catalysts were regenerated where necessary by pumping solvent (50 vol% propan-2-ol/ 50% m-xylene) through the system.

Product samples were analyzed by GC/FID. An HP 5890 GC equipped with an SP-1000 column (Supelco, 30 m, 0.32 mm ID) was used. The initial temperature of 70°C was increased 15°C/min to 145°C, then 2°C/min to 160°C with a final hold time of 2.5 min. Industrial olefin mixtures (see Appendix) were used as analytical standards.

Gel Permeation Chromatography (GPC) was used to measure dimer content. A 20-50 mg sample was dissolved in HPLC-grade THF (Fisher) and analyzed in an Agilent 1100 HPLC with THF carrier using an Agilent 1200 DRI detector. The column was a Phenogel 10µ, 7.8 mm ID x 300 mm length (Phenomenex). The solvent flow rate was set to 1.0 mL/min with each test lasting 20 min. Each sample was run at least twice.

Solvents used in catalyst regenerations were analyzed by matrix-assisted laser desorption ionization (MALDI) MS (Bruker Omniflex), with α-cyano-4-methoxycinnamic acid (Aldrich) as the target.

2.3 Results and Discussion

2.3.1 Catalyst Characterization

The Nafion loadings (by TGA) and acid site densities (by 1-PA TPD) of three representative Nafion/Al₂O₃ catalysts are listed in Table 2.1, along with those of SAC-13. The
Nafion polymer in SAC-13 decomposed between 305-355°C and 410-510°C (Figure 2.1), corresponding to desulfonation and depolymerization, respectively. The total weight loss for both regions (13 wt%) exactly matched the reported Nafion loading. It can be seen from Figure 2.1 that the alumina-supported Nafion materials underwent similar transitions but at a slightly higher desulfonation temperature range.

Table 2.1: Nafion Content and Acid Site Density of SAC-13 and Nafion/Al₂O₃ Catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Wt% Nafion</th>
<th>Acid Site Density by 1-PA TPD, a</th>
<th>Sulfonate Groups by TGA, b</th>
<th>BET Surface Area (m²/g)</th>
<th>Pore Volume (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAC-13</td>
<td>13</td>
<td>0.72 meq/g</td>
<td>0.21 meq/g</td>
<td>300</td>
<td>1.3</td>
</tr>
<tr>
<td>BCPR4</td>
<td>15</td>
<td>~0 meq/g</td>
<td>0.07 meq/g</td>
<td>39</td>
<td>0.043</td>
</tr>
<tr>
<td>BCPR5</td>
<td>1.5</td>
<td>0.32 meq/g</td>
<td>0.14 meq/g</td>
<td>240</td>
<td>0.29</td>
</tr>
</tbody>
</table>

aFor the alumina-supported catalysts the contribution from the pure Al₂O₃ has been subtracted. bThe sulfonate group content is calculated assuming SO₂ is formed by decomposition of sulfonate in the TGA.

For the supported Nafion catalysts, the acid site densities varied according to the method of impregnation. The GC/MS samples taken during the 1-PA TPD established that the desorption peak centered between 130-140°C for SAC-13 (Figure 2.2) was associated with Hofmann elimination to give propene and NH₃. This reaction is generally considered diagnostic for Brønsted sites, with lower temperature features associated with desorption of 1-PA. The entire range of the feature was from 90-180°C for SAC-13. Therefore, only the weight loss at greater than 90°C was used to generate the 1-PA acid site densities reported in Table 2.1. This weight loss was further corrected by subtracting the weight loss of the support at >90°C.

The catalyst prepared in the rotary evaporator after complete Nafion dissolution (BCPR5) exhibited the same strong acid feature by 1-PA TPD as SAC-13 (Figure 2.2), but with fewer total sites. However, the preparation method based upon simultaneous polymer dissolution /
Figure 2.1: Thermal analysis of supported Nafion resins, SAC-13 and BCPR4

Figure 2.2: Propan-1-amine (1-PA) TPD for SAC-13 and two Nafion/Al\(_2\)O\(_3\) catalysts

impregnation (BCPR4) was less successful. In general, there was no correlation between Nafion loading and total acid site density, as measured by either gas-phase titration with a base, or by sulfonate decomposition in the TGA measurements.
An alternate way of measuring the acid content of the supported Nafion catalysts is wet back-titration of the liberated protons. We measured an acid site density of 0.41 meq/g for SAC-13, which differs from literature values on similar Nafion composites, but it should be noted that these cover a wide range: ~0.13-0.15, 29,33,34 0.32, 30 and 0.67 meq/g. 35 The theoretical value assuming all measured acid sites are associated with only the sulfonate groups of a Nafion of typically spaced sulfonate groups is ~0.14 meq/g, per the manufacturer’s specification. However, SiO₂ contains silanol groups that can be acidic (especially in the presence of nearby sulfonate groups) and adsorb 1-PA or undergo ion-exchange in aqueous solution. 30,34,36 Such proximate Si-OH groups probably account for the widely observed discrepancies from the specified value, and for the discrepancies observed with the other titrations such as with 1-PA. Other acid groups, whether initially present in the silica support, or induced in the silica by proximate sulfonate groups, could be relevant in the catalysis. The same could be true for the alumina support.

We also measured the TGA weight loss associated with desulfonation. Assuming the weight loss feature from –SO₃H decomposition corresponds to SO₂ generation, the sulfonate content for SAC-13 was calculated from the TGA data as ~0.21 meq/g (Table 2.1). This measured sulfonate content was still lower than the acid site density by 1-PA TPD for most of the Nafion composite catalysts. We can again conclude that some of the base must adsorb, and remain adsorbed at >90ºC on either non-sulfonic acid sites or on sites not characteristic of a single –SO₃H; this conclusion is consistent with the wet titration values. Conversely, for BCPR4 there were more sulfonate groups measured by TGA than by 1-PA titer, especially after subtracting for 1-PA adsorption by the bare support. This suggests that many of these sulfonate groups for BCPR4 are inaccessible to adsorption by 1-PA. The sites that are accessible do appear to be strong (Figure 2.1), as the lone peak in the 1-PA is associated with Hofmann elimination.
The names and acid site densities of the non-Nafion catalysts are listed in Table 2.2. The wet titration values are given for the sulfonated PS-DVB’s (instead of the values from 1-PA TPD), because both the desulfonation of PS-DVB’s and the Hofmann elimination reaction for these catalysts take place in the 150-300°C range. Therefore, it is impossible to deconvolute the two reactions and compute an acid site density by 1-PA titration. The measured density by 1-PA TPD for the tungstated zirconia XZO 1251 is less than the value measured for a similar material by combined NH$_3$ adsorption/FTIR (by a factor of 3-4, see Appendix), but NH$_3$ is known to adsorb on many types of sites and even very weak acid sites. As our goal is to compute a turnover frequency for a low-temperature isomerization reaction where only stronger sites would participate, the value determined from 1-PA TPD would be more appropriate.

Table 2.2: Properties of Solid Acid Catalysts

<table>
<thead>
<tr>
<th>Name</th>
<th>Active Material</th>
<th>Manuf.</th>
<th>Acid Site Density (meq/g)</th>
<th>BET Surface Area (m$^2$/g)</th>
<th>Pore Vol. (cm$^3$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>XZO 1251</td>
<td>Tungst. Zirconia</td>
<td>MEL</td>
<td>0.032$^a$</td>
<td>26</td>
<td>0.026</td>
</tr>
<tr>
<td>AM-15</td>
<td>Sulf. PS-DVB</td>
<td>Dow</td>
<td>4.8$^b$</td>
<td>37$^c$</td>
<td>0.20$^c$</td>
</tr>
<tr>
<td>AM-35</td>
<td>Sulf. PS-DVB</td>
<td>Dow</td>
<td>5.4$^b$</td>
<td>41$^c$</td>
<td>0.22$^c$</td>
</tr>
<tr>
<td>AM-70</td>
<td>Sulf. PS-DVB</td>
<td>Dow</td>
<td>2.7$^b$</td>
<td>1.0$^c$</td>
<td>0.002$^c$</td>
</tr>
<tr>
<td>AM-XN1010</td>
<td>Sulf. PS-DVB</td>
<td>Dow</td>
<td>2.4$^b$</td>
<td>410</td>
<td>0.37</td>
</tr>
<tr>
<td>K2620</td>
<td>Sulf. PS-DVB</td>
<td>Sybron</td>
<td>5.2$^b$</td>
<td>27</td>
<td>0.025</td>
</tr>
<tr>
<td>SAPO-11</td>
<td>Acid Zeolite</td>
<td>6C USA, Ltd.</td>
<td>1.4$^a$</td>
<td>230$^d$</td>
<td>0.25$^d$</td>
</tr>
<tr>
<td>ZSM-35</td>
<td>Acid Zeolite</td>
<td>Alfa Aesar</td>
<td>1.5$^{a}$</td>
<td>350$^e$</td>
<td>0.31$^e$</td>
</tr>
</tbody>
</table>

$^a$ 1-PA TPD  $^b$ Wet Titration  $^c$ From $^{38}$  $^d$ From $^{39}$  $^e$ From $^{40}$

Selected catalysts were chosen for the isomerization reaction study. BCPR4 and BCPR5 represent each of the Nafion/Al$_2$O$_3$ synthesis methods. All catalysts were compared to SAC-13. The macroporous resins (AM-XN1010, -70, -15, K2620, AM-35) have acid site densities that increase in this order, but each is also unique in structure. For AM-70 (8% crosslinking) there are chloride groups on the aromatic ring. AM-15 is fully sulfonated, with a rigid structure (20%...
crosslinking). AM-35 is similar in structure to AM-15 (20% crosslinking), but is “over-sulfonated”, i.e., >1 pendant sulfonic acid group on some of the aromatic rings. The K2620 is similar to AM-35. AM-XN1010, while similar in acid site density to AM-70, had a far more rigid structure (80% crosslinking). Therefore, each sulfonated PS-DVB catalyst was evaluated on the effect of a common structural modification: crosslinking, over-sulfonation, or the presence of additional groups that are electron-withdrawing, presumably near the sulfonate groups.

The tungsten content for XZO 1251 is 15 wt%. It has a low acid site density, but, based on 1-PA TPD results, there are Brønsted acid sites of widely varying strengths, especially compared to the sulfonated PS-DVBs and zeolites. The ZSM-35 catalyst, a Ferrierite, features a two-dimensional intersecting pore structure (10- and 8-ring channels), the larger channel consisting of elliptical 4.2 x 5.4 Å pores; the SAPO-11 is of framework type AEL, with one-dimensional straight, elliptical 4.0 x 6.5 Å pores. SAPO-11 and ZSM-35 have similar acid site densities (Table 2.2), both with some Brønsted sites of similar strength on the basis of 1-PA TPD
data (Figure 2.3, the large desorption feature at >400°C). However, there are fewer strong sites in SAPO-11. SAPO-11 is a proven double bond isomerization catalyst at <200°C, and was shown to be superior for this purpose to other common SAPOs and AlPOs.

### 2.3.2 Catalyst Testing – Alkene Isomerization

Each catalyst was tested in a packed bed, at 130°C except where noted, with a partially isomerized C\textsubscript{16} feed, similar to what is often present industrially (See Section 2.3 for details). The products of reaction were determined by comparing the GC/FID results of the feed (~30 wt% hexadec-1-ene, 40 wt% hexadec-2-ene and hexadec-3-ene and ~5 wt% skeletal [branched] alkenes) using both standards and product samples (see Appendix for product determinations and sample chromatograms). Alkenes with the double bond at the 3- and higher positions are denoted “Target”; double bonds at the 1- and 2- position are denoted “Terminal”. Conversion to internal alkene (X\textsubscript{i}), selectivity to internal alkene (S\textsubscript{i}) and turnover frequency (TOF) based on the measured acid site densities are defined by Equations (2.1-2.3). To provide a more accurate comparison of different catalysts at greatly different conversion levels, an alternate TOF can also be computed from calculated first-order rate constants (see Appendix C). Results for all the catalysts are in Table 2.3; the TOFs in Table 2.3 were determined from the calculated first-order rate constants, although in practice these numbers are very similar to what is found using Equation (2.3). Because dimer could not elute from the GC column, both the GC and

\[
X_i = \left(1 - \frac{\text{mol(Terminal, Product)}}{\text{mol(Terminal, Feed)}}\right) \times 100\%
\]  

\[S_i = \frac{[\text{moles(Target,Product)}]-[\text{moles(Target,Feed)}]}{[\text{moles(Target+Branched+2\times Dimer,Product)}]-[\text{moles(Target+Branched+2\times Oligomer,Feed)}]} \times 100\% \]
\[
\text{TOF} = \frac{X_i(\%) \times (\text{mL C16})}{100 \times \text{min}} \times \left( \frac{0.783 \text{ g C16}}{\text{mL C16}} \right) \times \left( \frac{\text{mol C16}}{224 \text{ g C16}} \right) \times \left( \frac{\text{g catalyst}}{\text{meq g catalyst}} \right) \times \left( \frac{1000 \text{ meq}}{\text{mol}} \right) \times \left( \frac{1 \text{ min}}{60 \text{ s}} \right) \quad (2.3)
\]

GPC results had to be used in order to compute \( S_i \) and TOF. Only dimer was detected in the GPC runs. The data are in large part representative of the intrinsic kinetics, as standard diffusion calculations (Appendix) based on the assumption of fixed pores showed that intraparticle and external film concentration gradients were minimal. The conversion and selectivity data in Table 2.3 also show that even at these low space velocities the catalysts are operating far from equilibrium.

**Nafion-Based Catalysts**

Isomerization results for BCPR4 and BCPR5 are presented in Figure 2.4. SAC-13 was the most active among these supported Nafion catalysts. The selectivity of SAC-13 and BCPR5 to internal alkenes is also high. It might be thought that the high acid strength of perfluorosulfonicacid groups, caused by the electron-withdrawing fluorine atoms, would preferentially convert the linear alkenes to branched isomers and oligomers; but this is not always the case in the low temperature range used here.

This behavior can be partly explained by the 1-PA TPD results (Figure 2.2) and the morphologies (Table 2.1). The \( \text{NH}_3 \) and propene, products of the Hofmann elimination, appeared in the desorption feature centered between 130-140\(^\circ\)C for SAC-13. The reaction is generally considered to be diagnostic for Brønsted sites.\(^{31,32}\) For BCPR4 there is little desorption overall with almost nothing in this temperature range, and this correlates with its low activity and low selectivity. For BCPR5 there are some sites in the relevant range and its activity and selectivity are higher. By some measures a Nafion/SiO\(_2\) catalyst may be considered weakly acidic, with maximum acid strength only comparable to the zeolite H-Beta,\(^{25}\) but this is not the case where
the reaction chemistry of alkenes is considered, or for the Hofmann elimination, or other Brønsted acid-catalyzed reactions such as the Claisen rearrangement.\textsuperscript{36}

Table 2.3: Solid Acid Catalyst Results for 3 h Packed Bed Reactor Study, 130°C

<table>
<thead>
<tr>
<th>Material</th>
<th>(X_i) (%)</th>
<th>(S_i) (%)</th>
<th>TOF (\times 10^3) (s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAC-13</td>
<td>82</td>
<td>65</td>
<td>36</td>
</tr>
<tr>
<td>XZO 1251</td>
<td>51</td>
<td>55</td>
<td>27</td>
</tr>
<tr>
<td>XZO 1251\textsuperscript{a}</td>
<td>98</td>
<td>-30</td>
<td>120</td>
</tr>
<tr>
<td>SAPO-11</td>
<td>74</td>
<td>83</td>
<td>2.3</td>
</tr>
<tr>
<td>ZSM-35</td>
<td>74</td>
<td>66</td>
<td>4.1</td>
</tr>
<tr>
<td>K2620</td>
<td>79</td>
<td>70</td>
<td>0.81</td>
</tr>
<tr>
<td>AM-15\textsuperscript{b}</td>
<td>23</td>
<td>78</td>
<td>0.14</td>
</tr>
<tr>
<td>AM-35</td>
<td>74</td>
<td>76</td>
<td>0.75</td>
</tr>
<tr>
<td>AM-70</td>
<td>7.1</td>
<td>24</td>
<td>0.062</td>
</tr>
<tr>
<td>AM-XN1010</td>
<td>74</td>
<td>43</td>
<td>1.3</td>
</tr>
<tr>
<td>BCPR4</td>
<td>4.2</td>
<td>31</td>
<td>1.3</td>
</tr>
<tr>
<td>BCPR5</td>
<td>15</td>
<td>74</td>
<td>4.2</td>
</tr>
<tr>
<td>BCNA2</td>
<td>0</td>
<td>N/A</td>
<td>0</td>
</tr>
</tbody>
</table>

\textsuperscript{a} 185°C
\textsuperscript{b} 110°C

Figure 2.4: Alkene isomerization with supported Nafion catalysts (3 h on stream, 130°C)
Furthermore, the temperature range of the TPD feature associated with Hofmann elimination in SAC-13 is relatively narrow compared to other supported acids, such as H-MFI, where the feature also appears at much higher temperatures.\textsuperscript{32} The narrowness suggests that the sites are more uniform in acid strength than in acidic zeolites; uniformity of acid strengths would be expected to promote reaction selectivity. Branching and oligomerization usually take place selectively at higher temperatures for these and other acid catalysts such as H-ZSM-5 and tungstated zirconia.\textsuperscript{43-45} Therefore, the presence of these Brønsted sites in this particular temperature range suggests a correspondence between the location of this feature in the 1-PA TPDs and the catalysts’ selectivity towards double bond isomerization.

All of the Nafion/Al\textsubscript{2}O\textsubscript{3} catalysts were less active than SAC-13, although still more active on a site basis than the PS-DVBs (Table 2.3). The acid sites of these alumina-supported catalysts are apparently less accessible, buried within large polymer domains. This feature accounts for their relatively low acid site densities and pore volumes (Table 2.1) – polymer domains could be blocking pore mouths. Low surface acidities for Nafion/Al\textsubscript{2}O\textsubscript{3} were also recorded by Bringue et al.,\textsuperscript{29} and Harmer et al. used TEM/EDX micrographs to observe the lack of sufficient Nafion penetration into the pores of Al\textsubscript{2}O\textsubscript{3} supports.\textsuperscript{28} This suggests that many of the acid sites are inaccessible in the interior of larger microparticles near the external surface of the alumina support. The preparation better able to disperse the polymer throughout the pore structure is one where the Nafion is completely dissolved in a partly aqueous solution and then wet-impregnated over a long time period, as in BCPR5.

**Sulfonated PS-DVB Catalysts**

While the TOFs for the sulfonated PS-DVB catalysts in Table 2.3 may seem low, these are considerably higher on a site basis relative to SAC-13 than is the case in many other
Brønsted acid-catalyzed reactions. For example, the relative rate of SAC-13 to AM-15 is two times higher in the isomerization of 1-dodecene, \(^{17}\) five times higher in the alkylation of benzene with benzyl alcohol, \(^{46}\) and four times higher in toluene alkylation. \(^{38}\) The latter study noted that oversulfonated AM-35 is at least twice as active as AM-15, which is also the case here.

The branched isomer and the dimer contents for the PS-DVB and zeolite catalysts are given in Figure 2.5. The branched isomer production is similar across all of the catalysts except SAC-13, which is less selective to the linear products. The most notable results for the dimers are their higher production for the more active catalysts within a class. For example, ZSM-35 is more active than SAPO-11, and so makes more dimer both on an absolute (Figure 2.5) and relative (Table 2.3) basis. Also, AM-15 is both the least active PS-DVB and the most selective (note: AM-15 was reacted at 110°C to avoid the desulfonation known to take place at 130°C).

The oversulfonated PS-DVBs K2620 and AM-35 have some acid sites that are close together on the same phenyl ring which provides more opportunity for the interaction of two acid sites. As the dimerization is generally considered to consist of a bimolecular rate-determining step in either a Langmuir-Hinshelwood or Eley-Rideal mechanism, \(^{16,43}\) such interaction would be expected to promote oligomerization, as observed here.

The same cooperativity phenomenon can be deduced from Figure 2.6, which plots TOF for the sulfonated PS-DVB catalysts as a function of acid site density. Both TOF and dimer content appear to be relatively insensitive to site density until >5 meq/g site density. The results for the oversulfonated AM-35 and K2620 are qualitatively different at >5 meq/g. Adjacent acid sites on PS-DVBs must either promote carbenium ion formation or help stabilize the carbenium ions, because enhanced activities on a strong acid site basis for reactions with AM-35 and similar
oversulfonated PS-DVBs have also been observed in alkylation and alcohol dehydration catalysis,\textsuperscript{38,47} along with enhanced heats of adsorption of NH\textsubscript{3}.\textsuperscript{47}

![Figure 2.5: Branching and dimer content (wt % of total product) for sulfonated, sulfated and silicate catalysts (LHSV = 3, 130°C, except 110°C for AM-15).](image)

Farcasiu hypothesized that the relative weakness (by conventional measurements of acid strength such as NH\textsubscript{3} heats of adsorption or shifts in ν\textsubscript{OH} in IR spectra upon adsorption of base probes) of supported versus liquid-phase sulfonic acids arises from the rigidity of the solids, which prevents the acid sites from cooperating in the transfer of a hydron.\textsuperscript{27} If so, then any factor promoting cooperativity, such as the presence of adjacent –SO\textsubscript{3}H (AM-35, K2620), or even adjacent –OH (SAC-13), would be expected to increase the observed turnover frequency. This same concept was postulated by Gates 20 years earlier to explain the TOFs for alcohol condensations in sulfonated PS-DVBs.\textsuperscript{48} More substantial evidence has recently appeared. The cooperativity of –OH and –SO\textsubscript{3}H groups in enhancing the acid-catalyzed hydrolysis of
benzaldehyde dimethyl acetal was observed for mixed sulfonic acid-hydroxy polymer brushes,\textsuperscript{49} and also for sulfonated mesoporous silicas in esterification reactions, where both the heat of adsorption and the TOF increased substantially upon increasing the acid site density.\textsuperscript{50} In these cases there were no complicating effects of different levels of crosslinking or different pore structures. By this same hypothesis, alkyl-tethered sulfonated silicas should be more active on a site basis for any Brønsted acid-catalyzed reaction than the more rigid sulfonated PS-DVBs with one \(-\text{SO}_3\text{H}\) per ring. This has been observed - significantly so - in previous studies of esterification catalysis,\textsuperscript{51} and in both ketone acetalization and amine acylation.\textsuperscript{52} We conclude that the enhanced activities of both SAC-13 relative to the alumina-supported Nafions, and of the oversulfonated relative to the other PS-DVBs result from better acid site cooperativity.

**Tungstated Zirconias and Zeolites**

Most of the remaining catalysts were initially selective for double bond isomerization, although XZO 1251 deactivated quickly (noticeable even over 3 h time on stream). The SAPO-
11 and ZSM-35 catalysts gave initial results similar to sulfonated PS-DVB catalysts (Table 2.3); upon calculating first-order rate constants, this SAPO-11 is similar to the one studied by Gee et al. for tetradecene isomerization at similar conditions (see Appendix).\(^6\) ZSM-35 also deactivates, but far more slowly than tungstated zirconia (at a similar rate to AM-35, vide infra). This deactivation can be attributed to pore mouth poisoning. The pores of ZSM-35 have been shown to fill with carbonaceous species by Khitev et al.\(^{53}\) Unlike the polymers, many internal sites are inaccessible once a few mouths are closed. The polymer catalysts, with many possible swelling paths, are less impacted by a few oligomerization events.

Overall activity for tungstated zirconia (XZO-1251) was very high on a site basis (Table 2.3), but far less so on a weight basis. The selective temperature range is narrow: note from Table 3 that increasing the reaction temperature to 185°C results in a catalyst that is highly selective for dimers and skeletal isomers. The negative selectivity reported in Table 2.3 is a consequence of the presence of some target alkenes in the feed (see Equation 2.2); these were also converted to (mostly) dimer.

The order of the TOFs in Table 2.3 for non-sulfonated acid catalysts matches the relative rankings of acid strengths as determined by NMR shifts of basic probe molecules: tungstated zirconias > zeolites > SAPOs.\(^{54,55}\) However, the high isomerization activity of tungstated zirconias is accompanied by rapid dimerization (Figure 2.5). The oligomer buildup on the 3 h used catalyst XZO 1251 was so large that it could easily be observed and measured by TPO (in Appendix C).

### 2.3.3 Lifetime Studies of PS-DVBs

Lifetime studies were performed on PS-DVBs to explore the relationship between acid site density and deactivation. A typical result for a sulfonated PS-DVB catalyst is shown in
Figure 2.7. AM-35 partly deactivated over an extended time period (18 d), but without significant selectivity loss. Deactivation is expected because of dimer production (Figure 2.5), and the dimers can irreversibly adsorb on the acid sites. This adsorption would decrease the further production of dimers (Figure 2.8). While such oligomerization has sometimes been assumed to be responsible for the deactivation,\textsuperscript{19} the connection has not been directly established for the reactions of alkenes. In this work, aside from the quantification of dimers versus time on-stream, which correlates with deactivation (compare Figure 2.7 and 2.8), we also washed the used AM-35 with 300 mL 50\% v/v propan-2-ol/m- xylene (10 times catalyst bed volume) and then re-used it. The wash partially restored the activity (Figure 2.7), and the presence of dimers (400-500 m/z) and trimers (600-700 m/z) in the extract was confirmed through MALDI MS (Figure 2.9).

**Figure 2.7: Lifetime study of fresh and regenerated ("Regen") AM-35 (130°C, LHSV = 3)**

Lifetime tests with AM-70 and AM-XN1010 were intended to test the hypothesis that catalysts with fewer immediately adjacent acid sites could have a longer lifetime due to lower
dimer production. The crosslinking for each catalyst varied substantially (8% and 80% respectively) from that of AM-35 (20%). For high crosslinking, the rigidity of the chains results
in a more permanent microparticle structure\textsuperscript{17,43,56} of high BET surface area (Table 2.2), in which there should be essentially no $-\text{SO}_3\text{H}$ interactions due to swelling. For low crosslinking the opposite should hold, if the catalyst is swollen.

However, AM-70 was totally inactive until the pores were swollen with polar solvent. Dried catalyst remained inactive for the first 6 days, despite doubling the LHSV to 6 and raising the temperature to 160°C (Figure 2.8 and 2.10). On day 6, the catalyst was treated with 150 mL methanol and then 150 mL xylene at 90°C in order to swell the microparticles. This treatment immediately increased the TOF, followed by a steady decrease over the next two days (Figure 2.10). A similar trend was observed with dimer production (Figure 2.8). The importance of polar solvent swelling to AM-70 was noted previously both in alcohol condensation and oligomerization\textsuperscript{43,57} The extra $-\text{Cl}$ groups change the swelling behavior of the resins to prefer more hydrophilic solvents. However, once swollen it did deactivate at a faster rate than AM-
XN1010 (Figure 2.10), as would be expected if more –SO\textsubscript{3}H interaction at low crosslinking results in more oligomerization.

We found that AM-XN1010 deactivated faster than did AM-35 (Figure 2.10), but with dimer production similar to AM-35 (Figure 2.9). Therefore, crosslinking is only one factor controlling the oligomerization. AM-XN1010 is so highly crosslinked and the pore structure so rigid that most of the sulfonation takes place near the surfaces of the microparticles – this is why the acid site density (Table 2.2) is so low and the BET surface area so high. By measuring the rates of reaction with various-sized catalyst particles in sucrose inversion, it was estimated that >50\% of the –SO\textsubscript{3}H groups are on the microparticle surfaces, versus <5\% for AM-15 with 20\% crosslinking.\textsuperscript{58} Therefore AM-XN1010, while low in overall site density, has its –SO\textsubscript{3}H sites concentrated at microparticle surfaces, and therefore acts as if it were oversulfonated, accounting for its relatively fast dimerization rate.

The sulfonic acid groups in any sulfonated PS-DVB can be separated by as few as two methylene groups, and groups from one chain can interact with those of another chain upon swelling. There are two different ways the proximity of acid sites can explain deactivation. Clusters of sulfonic acid groups can facilitate the interaction of more than one adsorbed alkene, or of strongly adsorbed and weakly adsorbed alkenes. Therefore, a greater intermolecular distance between acid sites should decrease the likelihood of oligomerization. Alternatively, in a catalyst with greater intermolecular distance between sulfonic acid groups, fewer acid sites might be poisoned by the growing oligomer.

However, the above analysis is complicated by the fact that internal alkenes produce oligomers at a slower rate,\textsuperscript{20,21} so active isomerization catalysts at lower temperatures (where isomerization dominates) would generate fewer oligomers even if they are intrinsically more
active for oligomerization of the 1-alkenes. This supposition can be deduced from the greatly
decreasing rates of oligomerization in batch oligomerization reactions. The TOFs in batch
reactors at longer times are more than two orders of magnitude less (10\(^{-4}\) – 10\(^{-3}\) s\(^{-1}\) at
temperatures below 170°C) than the initial rates. Therefore it is difficult to establish
quantitative relationships between site density and oligomerization rate, although a qualitative
connection undoubtedly exists, as shown in Figure 2.6.

2.4. Conclusions

For the double-bond isomerization reaction, several features must be present to engender
an active, selective and relatively long-lasting acid catalyst. First, the sites must be of sufficient
acid strength to enable operation at the low temperatures where oligomerization and skeletal
isomerization will not dominate. Second, the proximity of acid sites affects both the activity and
lifetime of the catalysts. Factors that lead to strong acid sites that can interact cooperatively also
lead to greater rates of both isomerization and oligomerization. Third, catalysts with some very
strong acid sites, such as tungstated zirconia, are more prone to produce oligomers even though
there are probably no nearby acid sites. The oversulfonated PS-DVB catalysts such as AM-35
and K2620 show relatively high rates of oligomerization (but less than a tungstated zirconia),
and yet still have relatively long lifetimes because they lack a fixed pore structure within their
microparticles. They instead rely on swelling to create pores, enabling creation of new paths to
bypass adsorbed oligomers. Conversely, certain modified polymer catalysts such as AM-70 (a -Cl group on the ring) change the thermodynamics of swelling to the extent that the catalyst can
be rendered almost inactive for reactions of hydrocarbons unless the pores are pre-swollen.

Finally, it was shown that the selectivity of certain supported Nafions for double-bond
isomerization can be traced to Brønsted sites of a particular strength as quantified by propan-1-
amine desorption. This metric might be used in the future to help develop even more selective catalysts. While an active alumina-supported Nafion can be prepared by a wet impregnation technique whereby the polymer is completely dissolved in aqueous alcohol prior to contact with the support, it is catalytically inferior to standard silica-supported Nafion.
3.1 Introduction

The isomerization of olefins plays an important part in certain fine chemical processes, and is also important in its effect on the hydroisomerization of paraffins.\textsuperscript{61,62} An example of the former is the double-bond isomerization of C\textsubscript{16}-C\textsubscript{18} olefins in the synthesis of alkenyl succinic anhydride (ASA),\textsuperscript{4} a paper sizing agent.\textsuperscript{2} Another is double-bond and skeletal isomerization in the manufacture of lube oils and drilling fluids.\textsuperscript{63-65} One commonality among all these isomerization processes is the formation of unsaturated polyalkenyl surface species that are also postulated as intermediates in the isomerizations. Another is that the double bond isomerizations are easier than the skeletal ones, and that both can be accomplished by either precious metals (Pt, Pd, e.g.) or by acid catalysts.\textsuperscript{4-7}

Liquid acids such as H\textsubscript{2}SO\textsubscript{4} can isomerize olefins, but industrial usage carries the risks of equipment corrosion and significant disposal problems. Solid acid catalysts can sidestep these issues because they are non-corrosive and easily separated from effluent streams. The most common types of solid acid catalysts used for positional (double bond) isomerization are sulfonated poly(styrene-co-divinylbenzene) (PS-DVB’s),\textsuperscript{5} acidic zeolites,\textsuperscript{6} solid bases (such as K-based catalysts for the Shell Higher Olefin Process),\textsuperscript{11} and perfluorinated ion exchange resins.\textsuperscript{7} Regeneration of this last one is the focus of this study.

Nafion is comprised of a PTFE backbone with perfluorinated side-chains and pendant sulfonic acid groups. The electron-withdrawing fluorine atoms enable acid sites that are as strong as 100\% sulfuric acid on a Hammett acidity scale (-H\textsubscript{o} ~ 12.0).\textsuperscript{42} Nafion resins are also more
thermally stable than PS-DVB’s, but high cost and low initial surface area (limiting applicability to polar media that can swell it) often inhibits adoption.\textsuperscript{66,67} In order to offset the low surface area, Nafion-H was can be deposited on metal oxide supports. Sol-gel synthesis has been used to create high-surface area 13 wt\% Nafion / balance SiO\textsubscript{2} composites, which have proven active for a wide variety of acid-catalyzed reactions.\textsuperscript{17,28,30} This composite would eventually be commercialized as SAC-13\textsuperscript{®}.

Some of these industrial isomerization processes use SAC-13 to position the terminal double bond of $\alpha$-olefins to the middle of a long-chain olefin.\textsuperscript{4} There is interest in extending the lifetime of SAC-13 through regeneration. Several studies have noted continual loss of activity for SAC-13 in successive reactor experiments.\textsuperscript{68-70} Regenerations in the literature are usually limited to contacting with concentrated acid solutions. For example, both SAC-13 and a Nafion-modified large-pore silica were regenerated to a high percentage of the initial catalytic activity for anisole acylation by boiling the catalyst in 20\% HNO\textsubscript{3}.\textsuperscript{70-73} Concentrated nitric acid was also used for SAC-13 regeneration in the alkylation of isobutane with 1-butene.\textsuperscript{33} Also, it is impossible to determine from one or a few batch experiments whether the initial sites were actually regenerated. Regeneration with strong acids could merely impregnate the silica with the aqueous acid. These highly acidic regenerations are often inappropriate in industrial reactors due to corrosion of the equipment and disposal of the low-pH waste. Also, it is impossible to determine from one or a few batch experiments whether the initial sites were regenerated. Regeneration with strong acids could simply impregnate the silica with aqueous acid. Therefore, the purpose of this work was to evaluate alternative solvents in regeneration of SAC-13. We used the positional isomerization of octadecenes as a test reaction. Reaction studies included those in a batch reactor and extended lifetime studies in a continuous reactor.
3.2 Experimental Procedures

3.2.1 Regeneration Methods

Used SAC-13 (BASF) was obtained by isomerizing hexadecenes and octadecenes until
the catalyst was almost completely inactive. The used catalyst was sieved to a 20-40 mesh (0.42-
0.85 mm) fraction prior to regeneration experiments.

Regeneration solvents included deionized water, m-xylene (Aldrich, 99%), ethanol
(Omnisolv, 95%), isobutanol (Fisher), cycloheptane (Aldrich, 95%), hexane isomers (mixture of
2,3-dimethylbutane and methylcyclopentane, Phillips, tech.), and n-hexadecane (Chemsampco,
95-96%). Used SAC-13 (2 g) was contacted with 100 mL solvent and heated under reflux,
except for hexadecane, where heating was to 110°C. After 1 h the mixture was cooled and the
solvent decanted. The wash procedure was performed twice for each catalyst, then it was dried
for 3 h at 110°C and vacuum dried overnight at 150°C. The vacuum drying, subsequently
referred to as “heat treatment”, was also conducted at 250°C for certain samples.

The acid sites for the catalysts were then reactivated by two ion exchanges with 100 mL
of 2 M H$_2$SO$_4$ at 60°C and 220 rpm for 1 h. Finally, catalysts were once again dried for 3 h at
110°C and vacuum dried overnight at 150°C.

Selected catalysts were regenerated in packed bed reactors (316 SS, 12.7 mm ID), at
85°C except where noted, with α-alumina as bed support. The contents were contacted with N$_2$
at 85°C overnight and then fed with 0.5 mL/gcat/min solvent. Either a fixed solvent volume was
used or the flow was continued until the solvent became clear (each instance is noted).

3.2.2 Characterization

The physisorption of N$_2$ was used to determine the surface area, pore volume and pore
size distribution of the regenerated catalysts (Quantachrome Autosorb 1 porosimeter). The BJH
method was used to calculate the pore size distributions from the adsorption-desorption isotherms. Thermogravimetric analysis (TA SDT Q600 TGA/DSC) was used to quantify the decomposition of both oligomers and Nafion under N₂ flow. The temperature was programmed from 50-250°C at 5°C/min, a 20 min hold, then 2°C/min to 550°C. FTIR spectra were recorded in transmission mode (5 mg catalyst per 100 mg KBr wafers) on a Nicolet 380 FTIR. Potentiometric titrations were performed by stirring 150 mg catalyst in 20 mL 2 M NaOH overnight and then titrating the solution with 0.0120 M NaOH until the pH equaled that of the pure 2 M NaCl solution (~ 9.7).

3.2.3 Reaction Studies

Batch reactions were conducted in glass round bottom flasks. The catalyst was loaded at a 10:1 feed to catalyst ratio. The feed was a partially isomerized octadecene mixture (~40-45 mol% 1-, 2-, and 3-octadecene). Prior to reaction, the feed was passed over a column of 5A molecular sieve at room temperature. The reaction mixture was reacted with stirring at 130°C for 6 h. Product olefin was filtered through a 0.2 μm PTFE membrane prior to GC analysis. In some experiments a small sample was collected at 6 h and the reaction was allowed to continue another 10 h. In other experiments the filtered solid catalyst was returned to the reactor, more feed was loaded, and the experiments repeated until almost complete catalyst deactivation was observed.

Selected catalysts were tested in packed bed reactors (316 SS, 12.7 mm ID, 0.36 m long) at 130°C with the same feed except where noted. The LHSV (mL/h/gcat) was fixed for each run at 3. Samples were collected every 12 h, until almost complete deactivation was observed.

All products were analyzed by an HP 5890 Series II GC with a flame ionization detector and a Supelco DB-5 column (30 m, 0.32 mm ID). The temperature was programmed at 50°C for
1.0 min, ramped 10°C/min to 100°C, held for 5 min, ramped again at 5°C/min to 260°C, with a final hold of 17 min. Further analytical details can be found in a previous study.\textsuperscript{7} GC/MS samples were analyzed on an HP 5890 Series II GC equipped with an HP 5972 Mass Selective Detector and a Supelco DB-1 column (30 m, 0.32 mm ID). The initial temperature of 100°C was held for 1 min, ramped at 5°C/min to 260°C, then held for 52 min. Sample injections were 0.1 µL for GC and 1.0 µL for GC/MS.

3.3 Results and Discussion

3.3.1 Characterization of Fresh and Used Catalysts

The BET surface area of the used (completely deactivated) SAC-13 was 1.2 m\textsuperscript{2}/g, >99\% less than fresh SAC-13 (Table 3.1). The pore volume had decreased from 1.1 to 0.098 cm\textsuperscript{3}/g. Both results are indicative of deactivation by either complete coverage of the surface by oligomers or pore mouth poisoning. However, the TGA results for the used catalyst (vide infra) indicate the former.

Table 3.1: N\textsubscript{2} Physisorption of Fresh and Used SAC-13

<table>
<thead>
<tr>
<th></th>
<th>Surface Area (m\textsuperscript{2}/g)</th>
<th>Pore Volume (cc/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh SAC-13</td>
<td>300</td>
<td>1.1</td>
</tr>
<tr>
<td>Used SAC-13</td>
<td>1.2</td>
<td>0.098</td>
</tr>
</tbody>
</table>

Both TGA results and FTIR spectra for fresh and used SAC-13 show regions where surface hydrocarbons can be detected and quantified. Desulfonation of Nafion at atmospheric pressure starts at ~280°C and there is extensive depolymerization of -CF\textsubscript{2} groups by 550°C (Figure 3.1).\textsuperscript{7,24} The Nafion content of fresh SAC-13 was calculated from the weight loss in Figure 1 to be ~14.0 wt\%, which is close to the nominal 13 wt\%.\textsuperscript{30} However, used SAC-13 lost significantly more mass, starting at 120°C, indicating hydrocarbon deposits. The used catalyst
lost an additional 4.8 wt% between 250°C and 550°C. This loss must correspond to heavier (possibly coke-like) species. Overall the used SAC-13 contained ~43 wt% hydrocarbons, which includes olefins, oligomers, and heavier material. As this is enough to fill the pores (as Table 3.1 suggests), the surface would be almost entirely covered (as Table 3.1 also suggests). Note that TGA experiments with the temperature ramped up to 700°C did not show further weight loss, so all surface species have decomposed and desorbed from the remaining SiO$_2$ by 550°C.

The presence of surface hydrocarbons was also confirmed by FTIR. Saturated C-H vibrations at 2800-3000 cm$^{-1}$ appeared in used SAC-13 (Figure 3.2). Also shown in Figure 3.2 are spectra of hexadecenes composed of either the unreacted olefin feed (“α-Olefins”, AlphaPlus® 1-hexadecene, Chevron) or mostly internal (3- and greater) olefins post-reaction. The composition of these α-olefins is given in Appendix C.2, and the composition of the internal olefins was 73 mol% internal olefins (3-position and higher), 20 mol% terminal olefins (1- and 2-positions), and 7.0 mol% branched olefins. The surface hydrocarbons were predominately
Figure 3.2: FTIR results for Fresh and Used SAC-13 (2800 cm$^{-1}$-3100 cm$^{-1}$). Parameters: 512 scans at 4 cm$^{-1}$ resolution.

Internal olefins as evidenced by absorption bands in the 425-1675 cm$^{-1}$ range (Figure 3.3). The 1-hexadecene has C-H bands at 884, 908, and 989 cm$^{-1}$ which correspond to bending modes for vinylidenes, alpha olefins, and internal olefins respectively.\textsuperscript{16} The quantity of alpha olefins decreased in the internal olefins sample, with the C-H bending mode shifting to 964 cm$^{-1}$. This band was also observed in used SAC-13, suggesting that internal olefins were predominant on the surface. Additionally, the used SAC-13 sample contained absorption bands at 719, 1367, and 1461 cm$^{-1}$, all of which were not present in fresh SAC-13 but were observed in both alpha and internal olefin samples.

3.3.2 Regeneration of SAC-13 by Solvent Treatment

Initial Characterization

Several polar and nonpolar solvents and solvent mixtures were screened in an attempt to regenerate used SAC-13 (Table 3.2). Oligomers and higher molecular weight species were
extracted by refluxing at the solvent’s boiling point (unless noted). The residual oligomer content was calculated by subtracting the initial Nafion content (14.0 wt%) from the overall TGA weight loss at 550°C. Most of the solvents removed between 75-90% of the initial deposits on a mass basis.

FTIR absorbance spectra were measured for each sample and apparent integrated intensities were calculated. The area beneath the saturated C-H vibrations (2800-3000 cm⁻¹) was divided by the area beneath the Si-O stretching mode (980-1330 cm⁻¹). This apparent integrated intensity (AII) ratio, according to the Beer-Lambert law, would represent the ratio of concentrations of oligomer and SiO₂ times the ratio of their respective extinction coefficients. Both the concentrations of SiO₂ and extinction coefficients should be constant, so the variations in Table 3.2 give a rough idea of residual hydrocarbon concentrations. Variations in the concentration of Si-OH groups of the used catalysts (the absorbances of the Si-O bands varied

Figure 3.3: FTIR results for fresh and used SAC-13 (425 cm⁻¹-1675 cm⁻¹). Parameters: 512 scans at 4 cm⁻¹ resolution.
somewhat from 960 cm\(^{-1}\) and 1350 cm\(^{-1}\), suggesting more than one type of Si-OH group is present) prevent this analysis from being more than qualitative.

Table 3.2: Solvent Treatments

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Wt. %</th>
<th>Oligomer</th>
<th>(\varepsilon_{\text{olig}}C_{\text{olig}}/\varepsilon_{\text{SiO2}}C_{\text{SiO2}})</th>
<th>Surface Area (m(^2)/g)</th>
<th>Pore Volume (cm(^3)/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None (Fresh SAC-13)</td>
<td>0</td>
<td>0</td>
<td>300</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td>None (Used SAC-13)(^1)</td>
<td>43(^5)</td>
<td>0.40</td>
<td>-0(^3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>None (Used SAC-13)(^2)</td>
<td>n.d.(^3)</td>
<td>0.21</td>
<td>44</td>
<td>0.045</td>
<td></td>
</tr>
<tr>
<td>A47 H(_2)O</td>
<td>13</td>
<td>0.12</td>
<td>60</td>
<td>0.055</td>
<td></td>
</tr>
<tr>
<td>A23 m-Xylene</td>
<td>4.1</td>
<td>0.033</td>
<td>210</td>
<td>0.21</td>
<td></td>
</tr>
<tr>
<td>A24 Ethanol</td>
<td>12</td>
<td>0.081</td>
<td>100</td>
<td>0.11</td>
<td></td>
</tr>
<tr>
<td>A25 Isobutanol</td>
<td>9.0</td>
<td>0.19</td>
<td>120</td>
<td>0.14</td>
<td></td>
</tr>
<tr>
<td>A26 Cycloheptane</td>
<td>8.5</td>
<td>0.066</td>
<td>100</td>
<td>0.089</td>
<td></td>
</tr>
<tr>
<td>A27 Cyclohexane/ethanol (1:1 v/v)</td>
<td>3.8</td>
<td>0.082</td>
<td>130</td>
<td>0.12</td>
<td></td>
</tr>
<tr>
<td>A44 Hexane/ethanol (65:35 v/v)</td>
<td>9.5</td>
<td>0.044</td>
<td>140</td>
<td>0.14</td>
<td></td>
</tr>
<tr>
<td>A45 Hexadecane(^4)</td>
<td>4.6</td>
<td>0.19</td>
<td>N/A</td>
<td>N/A</td>
<td></td>
</tr>
</tbody>
</table>

1: Vacuum dried at 120°C  
2: Vacuum dried at 250°C  
3: None detected  
4: Solvent wash at 110°C  
5: Initial Wt. % also includes both olefins and oligomers

Much of the surface area could be restored by solvent extraction. In one case (for m-xylene, A23), 66% recovery was possible. However, there was little improvement in pore volume with most extracted catalysts only showing 10% of the initial 1.1 cm\(^3\)/g. This suggests that larger pores can only be partly cleared of oligomer, creating what are essentially small pores.

Pore size distributions of SAC-13 and used SAC-13 are shown in Figure 3.4. The average pore diameter for SAC-13 was 150 Å. Once deactivated, there were no detectable pore diameters below 100 Å, and little total pore volume. To be completely effective, solvents must be able to
regenerate both micropores (<20 Å) and mesopores (20-500 Å).

Pore size distributions for selected regenerated catalysts are shown in Figure 3.5. Despite varying amounts of residual oligomers (Table 3.2), each solvent recovered some pore volume
with diameters characteristic of both micropores and mesopores. The aromatic solvent m-xylene (A23) recovered almost twice the volume of micropores and smaller mesopores than the more polar solvents ethanol (A24) and isobutanol (A25), which gave very similar pore size distributions of the regenerated catalysts. The diminished volume of the larger mesopores (>100 Å) suggests that pores cannot be completely extracted, i.e., smaller open pores are formed from partly cleared larger pores. Therefore, some of the internal acid sites in all the pores remained unavailable for reaction despite extensive solvent extraction.

**Batch Reaction Studies**

Reaction studies were conducted on the catalysts of Table 3.2 in batch reactors. Both conversion of terminal olefins \( X_i \) (Equation 3.1) and selectivity to internal olefins \( S_i \) (Equation 3.2) were calculated by comparing the reaction products to the partially isomerized feedstock where “Terminal” olefins were 1-, and 2-octadecene (52 mol% ±0.70 mol%), “Target” olefins were at the 3- and higher position (44 mol% ±0.80 mol%), and “Branched” olefins were skeletal isomers of octadecene (4.3 mol% ±0.20%).

\[
X_i = \left(1 - \frac{\text{mol(Terminal, Product)}}{\text{mol (Terminal, Feed)}}\right) \times 100\% \tag{3.1}
\]

\[
S_i = \frac{[\text{moles(Target, Product)}-\text{moles(Target, Feed)}] \times 100\%}{[\text{moles(Target+Branched, Product)}-\text{moles(Target+Branched, Feed)}]} \tag{3.2}
\]

Catalytic activity in these batch experiments could be almost completely recovered using either m-xylene (A23), EtOH (A24), cycloheptane (A26), or 1:1 v/v cycloheptane/EtOH (A27). The conversions of the terminal olefins were between 59%-71% for the most active catalysts.
(Figure 3.6) with selectivities to internal olefins between 80%-100% compared to the 70% conversion and 93% selectivity for fresh SAC-13. A23 had the lowest selectivity because it contained 100% more branched compounds than the feed (11 mol%), although there were also increases in branched compounds observed for A24 and A27. These increases could reflect subtle differences in acid group orientation of catalysts regenerated with various solvents.

In general, the results show that both highly polar solvents such as ethanol, or aromatic/naphthenic ones such as m-xylene or cycloheptane are effective solvents. Only the first type are good swelling solvents for Nafion, but the latter would be better at extracting oligomers on the Nafion surface. Interestingly, the solvent most like the feed itself, hexadecane, is ineffective. The comparison of ethanol (A24) and isobutanol (A25) shows that the inclusion of

Figure 3.6: Batch reaction results for SAC-13 and regenerated SAC-13. [used1: vacuum dried at 120°C; used2: vacuum dried at 250°C.]
an even more surfactant-type of solvent (with the same –OH group) will not improve regeneration.

The used SAC-13 that was vacuum dried at 250°C was inactive. No oligomer content could be measured by TGA (Table 3.1), although the oligomer AII ratio measured by FTIR is half that of untreated SAC-13, so not all the oligomer was removed from the surface. This result might be possible if the sulfonic acid groups decomposed during the heat treatment. In previous studies, the –SO$_3$H groups in Nafion largely decomposed between 280°C and 350°C, although gradual weight loss could be observed as early as 250°C. The acid groups may be more readily decomposed in the used SAC-13 due to the low pressure (<5 mmHg).

Mixtures of polar and nonpolar solvents yielded better oligomer removal (Table 3.1), but the regeneration of catalytic activity was either insignificantly or adversely affected. For example, the 1:1 v/v ethanol/cycloheptane treatment (A27) gave similar reaction results to A24 (ethanol alone) and A26 (cycloheptane alone), while a 65:35 v/v of hexane/ethanol treatment (A44) resulted in a relatively inactive catalyst.

The m-xylene-treated catalyst (A23) resulted in regeneration of the most sites that could be classified as strongly acidic. This is based on a higher selectivity to branched olefins in the batch data of Figure 3.6. Alkyl group shifts (skeletal isomerization) are usually associated with stronger acid sites, as with tungstated zirconia at 180°C$^{7,22,62}$ and HZSM-5, CoAPO and SAPO molecular sieves between 250°C-550°C. The m-xylene apparently regenerated these stronger acid sites more than water (A47), ethanol (A24), isobutanol (A25), and cycloheptane (A26). We and others have presented evidence for the hypothesis that the strongest sites in catalysts containing sulfonic acid groups are associated with adjacent acid groups.$^{7,38,48,75-78}$ Given the FTIR (Table 2), pore volume (Table 3.2), pore size distribution (Figures 3.4 and 3.5) and surface
area results (Tables 3.1 and 3.2), it appears as if m-xylene removed the most surface oligomers, and therefore would also have been expected to facilitate more interaction between adjacent acid sites.

**Stability of Regenerated SAC-13**

The ethanol-regenerated catalyst (A24) was tested in a continuous packed bed reactor with results compared to those for fresh SAC-13. Overall catalytic activity was measured by the turnover frequency (TOF), calculated using Equation 3.3:

\[
\text{TOF} = \frac{X_1(\%) \times (\frac{\text{mL C16}}{60 \text{ s}}) \times (\frac{0.789 \text{ g C18}}{\text{mL C18}}) \times (\frac{\text{mol C18}}{252 \text{ g C18}}) \times (\frac{\text{g catalyst}}{(0.21 \text{ meq/\Phi}) \times \text{g catalyst}}) \times (\frac{1000 \text{ meq}}{\text{mol}})}{100}\]

(3.3)

The acid site density of Fresh SAC-13 was determined as 0.21 meq/g, the value measured by temperature programmed desorption of 1-propylamine (1-PA) in previous work. The surface oligomers cover some acid sites, causing the true site density to be lower than 0.21 meq/g. However, TPD measurements of the regenerated catalysts are unreliable because some residual oligomer simultaneously decomposes with 1-PA. Wet titration of acid sites with indicators is also impossible, because both the catalyst fragments and the residual oligomer turn the solution dark, obscuring the color-changing indicators. Therefore an estimate of the acid site density of a regenerated catalyst was made by ratioing its wet titer to that of the fresh SAC-13 by potentiometric titration. The results for this ratio are 0.32 for the ethanol-treated catalyst and 0.83 for the catalyst treated with continuous flow of 65/35 ethanol/methylcyclopentane.

The TOF for the ethanol-treated A24 is less active than Fresh SAC-13: up to 75% of the TOF after 1 d, but then to 2-3 times less after 2.5 d (Figure 3.7). The TOF might be expected to decrease in this case because with only 10% pore volume recovery (Table 3.2) the system would...
be much more diffusion-limited. The second key feature of the results in Figure 3.7 is that the catalyst lost 66% of its activity after 3 d whereas the TOF of Fresh SAC-13 dropped below 0.020 s\(^{-1}\), losing 20% of its initial activity after 5.5 d. So the regenerated catalyst deactivated somewhat faster.

Figure 3.7: Long-term activity of fresh SAC-13, A24 (ethanol-regenerated SAC-13) and A40 (continuous flow regeneration with 65/35 ethanol/methylcyclopentane) in a packed bed reactor

In an attempt to further increase the surface area and pore volume, used SAC-13 was solvent-treated in packed bed reactors (Section 3.2.1). Packed bed reactors can increase the number of extraction stages above the two used in Table 3.2 (two batch extractions). Sample A40 was produced in the reactor by contacting used SAC-13 at 80\(^\circ\)C with 65:35 v/v ethanol/hexane flowing at 60 mL/g\(_{\text{cat}}\)/h until the effluent turned from a brown-orange color to clear. The cumulative extract from the first 4 h and the final 4 h were analyzed by GC/MS. While this solvent was only moderately effective in removing oligomer (residual hydrocarbons
decreased in the batch extractions using this solvent from 43 wt% to 9.5 wt% - see A44 in Table 3.2), the goal was to determine what surface species were being removed. Octadecene isomers and dimer were observed in both the first and last 50 mL of solvent (components heavier than dimers were too heavy to be detected by GC-MS). Residual octadecenes decreased from 68% to 50% abundance, and dimers increased from 4.7% to 9.4% abundance (the balance are branched compounds).

Sample A40 was characterized by TGA, FTIR, and porosimetry, showing 7.1 wt% residual oligomers (TGA), an oligomer relative AII of 0.036, a surface area of 120 m\(^2\)/g, and a pore volume of 0.11 cm\(^3\)/g. Each value is within 25% of that found for sample A44, which is from the batch regeneration using the same solvent pair. Therefore, continuous solvent treatment (except possibly with the best solvents) cannot completely remove surface oligomers, and continuous treatment was only slightly more effective than batch regeneration.

After ion-exchange to ensure that protons occupied the cationic sites, sample A40 was tested in the packed bed reactor for octadecene isomerization and was found to be completely inactive after 1.5 d (Figure 3.7). This suggests, when compared to sample A24, that there is some threshold amount of oligomers that must be removed in order to prevent rapid deactivation.

The effects of continuous regeneration were also examined using successive batch reactions. The continuously regenerated sample A40 had 44% conversion of terminal olefins after an initial 17.5 h (A40_1, Figure 8). The products of reaction were removed by filtration and replaced with fresh feed for several repeat experiments (Figure 3.8). For the third and fourth runs, samples were taken after both 6 and 18 h to follow the reaction progress. The conversion was still increasing at long times within a run, but steady deactivation to a minimal activity was observed over the course of four runs. This behavior conforms to what might be expected based
on the deactivation observed during the continuous flow reactor experiments (Figure 3.5). It can be concluded that the rate of deactivation increased for those catalysts already containing surface oligomers above a certain threshold amount.

![Figure 3.8: Successive batch reactions of used SAC-13 (65:35 v/v ethanol/hexane regeneration in packed bed). The solid bars represent conversion, the hatched bars selectivity.](image)

**3.3.3 Discussion**

The behavior observed in Figures 3.7-3.8 could result from greater diffusional limitations in the regenerated catalysts leading to more reaction events in a given pore that ultimately result in surface oligomers. Alternatively, smaller (on average) pores in regenerated catalysts could be more susceptible to complete blockage after fewer oligomerizations. Finally, certain sites more likely to be found in the regenerated catalysts might preferentially catalyze oligomerization, and, by inference, deactivation. We consider these three possibilities, starting with the last.

Strong liquid acids (e.g., concentrated sulfuric acid) react with olefins to directly form carbenium ions, but in heterogeneous systems the mechanisms are subtly different. The
reactant must either bond to the surface or abstract a proton into the liquid phase. Once bonded to the surface, octadecene can undergo a hydride shift (leading to double bond isomerization), an alkyl shift (leading to skeletal isomerization), or oligomerization (dimer, trimer, etc.). Cracking is assumed negligible due to the low system temperature; cracking is significant for several classes of acid catalysts when the temperature is about 275°C. There is sparse information about the relative rate of oligomerization of olefins in the C\textsubscript{18} range versus the competing isomerizations. Gee et al. conducted a kinetic study on the dimerization of hexadecenes on a sulfonated ion exchange resin, but the model did not consider branched olefins or the catalyst deactivation. \textsuperscript{16} We studied a similar sulfonated ion exchange resin and did not observe significant deactivation for several days’ reactions of hexadecene, although what deactivation there was could be traced to oligomer coverage of the surface. \textsuperscript{7}

Kazansky and others have theorized that olefins on acidic zeolites form intermediates more resembling surface alkoxide cationic species. \textsuperscript{81,82} DFT studies have confirmed this, e.g., for ethylene adsorbed on high silica zeolite, the most stable species was calculated to be a surface ethoxide covalently bonded with the proton, although the transition state for both proton addition and partial carbonyl dissociation resembles a carbenium ion. \textsuperscript{82}

In the case of a reaction similar to oligomerization, the alkylation of isobutane with butene, Janik et al. determined that in phosphotungstic acid the alkylation reaction barrier for both t-butyl and s-butyl alkoxide intermediates was lower than hydride transfer, and this contributed to the observed deactivation with coke formation. \textsuperscript{83} For the same alkylation on Nafion/SiO\textsubscript{2} composites it was found that the strongest acid sites were the alkylation sites, but that oligomerization of 2-butene was the dominant reaction after the strongest sites deactivated. \textsuperscript{25} These studies suggest that surface alkoxides could preferentially form oligomers. However,
Gorte observed that weaker acid sites on H-MFI, like SiOH, can adsorb butenes proximate to acid sites, which also enhances oligomerization. More recently, carbenium ions were found to be stabilized by the zeolite frameworks of HZSM-5, HY, and Hβ and exist as ion pairs instead of surface alkoxy species. Stable t-butyl carbenium ions were found to be energetically more favorable than t-butoxy species in H-MOR, HZSM-5, and HZSM-22. Both studies found that catalysts with high acid strength are more likely to form carbenium ions than surface alkoxy species. These studies prove that the surface-stabilized intermediate is not universal in solid acid catalysts, so we cannot assume that the intermediate for SAC-13 is a carbenium ion or an alkoxy species without extensive spectroscopic and computational (DFT) work. In summary, there is no consensus on the type of site leading preferentially to oligomer formation on SAC-13, and whether this site might be different in nature in the partly regenerated SAC-13.

On the other hand, pore morphology certainly contributes to the observed catalytic activity. The pore size distribution of fresh SAC-13 (Figure 3.4) is in agreement with Harmer and Sun, who reported 150-200 Å pore diameters via SEM. For regenerated catalysts 10%-20% of the initial pore volume was recovered, mostly in the 10 to 100 Å range, and the catalyst where the most was recovered (A23, m-xylene) was also the most active. But most of the regenerated catalysts displayed some degree of isomerization activity, and there is no obvious relationship between activity and the recovery of either pore volume or surface area. The presence of some larger pores may be critical; de Klerk observed that 1-hexene and 1-octene, undergoing oligomerization on sulfated zirconia, deactivated at a slower rate when pore diameters >100 Å were present. Interestingly, stronger acids, such as sulfated zirconia, HZSM-5, and HY zeolites formed oligomers and deactivated regardless of the pore size at lower temperatures where there was no cracking.
The average pore diameters for selected catalysts are in Table 3.3. Each of the regenerations gave an average pore diameter between 24-28% of fresh SAC-13. This means that only smaller channels through the large pores are fully opened. The critical diameter of 1-octadecene was calculated to be 6.3 Å and the diameter based on the van der Waals volume was calculated to be 8.4 Å. This means that the size of an octadecene molecule is ~20% that of an average pore diameter, putting the diffusion process at least partly in the configurational or surface regime. The effects of these greater diffusion limitations are evident in Figure 3.8, where successive reactions took longer periods of time to reach even lower conversions. We suspect that some pore mouth poisoning occurred, further limiting site access in the channels.

Table 3.3: Average pore diameters of selected catalysts

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Average Pore Diameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None (Fresh SAC-13)</td>
<td>150</td>
</tr>
<tr>
<td>A47 H₂O</td>
<td>37</td>
</tr>
<tr>
<td>A23 p-Xylene</td>
<td>42</td>
</tr>
<tr>
<td>A24 EtOH</td>
<td>42</td>
</tr>
<tr>
<td>A25 iBuOH</td>
<td>45</td>
</tr>
<tr>
<td>A26 Cycloheptane</td>
<td>37</td>
</tr>
<tr>
<td>A27 Cycloheptane/EtOH (1:1 v/v)</td>
<td>36</td>
</tr>
<tr>
<td>A44 Hexane/EtOH (65/35 v/v, batch)</td>
<td>39</td>
</tr>
<tr>
<td>A40 Hexane/EtOH (65/35 v/v, continuous)</td>
<td>36</td>
</tr>
</tbody>
</table>

Regardless of the mechanism, it is indisputable that regenerated SAC-13 deactivated at a faster rate than the fresh catalyst. It was observed that the deactivation of long path-length MFI zeolites increased with higher olefin chain-lengths. For incompletely regenerated catalysts, adsorbed olefins are more likely to be adjacent to adsorbed oligomers, which would increase the rate of bimolecular reactions (Langmuir Hinshelwood mechanism for chemisorbed olefins, Eley-Rideal mechanism for physisorbed olefins). Oligomerization of C8-C24 olefins was found to be
a first order Eley-Rideal mechanism by Gee et al. for PS-DVB’s, with surface oligomers reacting with adsorbed monomers faster than adsorbed monomers reacted with each other.\textsuperscript{16} Granollers et al. found that a first order Eley-Rideal mechanism best-described isoamylene dimerization on PS-DVB’s, although multiple order reactions best described higher order oligomerization.\textsuperscript{89} Regardless of the exact mechanism, the surface olefins are in close proximity to surface oligomers in the partly regenerated catalysts, so the oligomerization can be expected to take place at a higher rate. Due to the decreased pore volumes and diameters, relatively few of these reactions are necessary to poison the pores.

3.4 Conclusions

Used SAC-13 was regenerated in both batch and continuous processes with both polar and nonpolar solvents. Most solvents removed between 75\%-90\% of the initial hydrocarbon deposits with up to 66\% of the initial surface area and 10\% of the initial pore volume recovered. All solvents were able to recover pore volume within the micropores and mesopores, but the diminished volume in the larger mesopores (>100 Å) indicated that smaller pores were formed from partially-regenerated larger pores, and that some of the internal acid sites were physically covered, rendering them inaccessible to reactants.

Catalysts regenerated with both polar and nonpolar solvents were active in the batch isomerization of octadecenes. More nonpolar solvents (m-xylene, cycloheptane) were more effective at removing oligomer thus exposing acid sites, but the polar solvents would have been more effective at swelling the Nafion. The m-xylene-regenerated catalyst had the most strongly acidic regenerated sites. When tested in a continuous process, catalysts regenerated by ethanol and ethanol/hexane (65/35 v/v) had, at most, 75\% of the Fresh SAC-13 TOF. Given the rapid
deactivation of some catalysts after relatively short time periods (48 h), there seems to be a
growing diffusion limitation that is accelerated when above a threshold of surface oligomers.
4.1 Introduction to Chain-Walking Catalysts

Certain transition metals have shown good activity for olefin isomerization by double bond migration. These “chain-walking” catalysts are common in polymerization. Crabtree describes two possible mechanisms of alkene isomerization (Figures 4.1 and 4.2). Figure 4.1 is a “stepwise” isomerization: an alkene ligand bonds to a generic, electron rich (d\(^8\) and above) metal center (“M”), then migratory insertion of hydrogen yields an alkyl, followed by β-hydride elimination and ligand dissociation. Instead of immediate dissociation, another migratory insertion can take place and further isomerize the alkene. Figure 4.1 is a “multiple” isomerization mechanism: the alkene bonds to the metal center, oxidative addition forms an η\(^3\) allyl complex, and reductive elimination gives an isomerized alkene.

Figure 4.1: Stepwise Isomerization Mechanism
Figure 4.2: Multiple Isomerization Mechanism

The mechanisms differ in several ways. Stepwise isomerization moves the double bond one position while multiple isomerization moves the double bond two positions. Stepwise isomerization involves an oxidized metal center while the metal center is both oxidized and then reduced in the multiple isomerization mechanism. Crabtree reasons that an olefin/catalyst system lacking sufficient H₂ partial pressure will follow the multiple isomerization mechanism.¹⁰

4.1.1 Literature Review of Organometallic Double-Bond Isomerization by Fe(CO)₅

Organometallic catalysts for double bond isomerization are typically group VI, VII, and VIII transition metals. Iron pentacarbonyl is the only chain-walking catalyst used in long-chain olefin isomerizations.⁹¹,⁹² Iron Pentacarbonyl, Fe(CO)₅, is a stable, 18 electron complex with the five carbonyl ligands arranged in a trigonal bipyramid, with an iron formal oxidation state of zero. Carbonyl ligands show a high degree of pi backbonding,¹⁰ so the high electron density of Fe(0) is shared.
Due to its stability, Fe(CO)$_5$ is a poor catalyst, but it activates upon thermal and photolytic decarbonylation, which was monitored by several studies.$^{8,9,93-100}$ After impregnation onto zeolites, TiO$_2$, SiO$_2$, Ni(100), and Au(111), the degree of decarbonylation was measured by in-situ FTIR. Hauchard and Rowntree determined that losing the first carbonyl was rate-determining.$^9$ Every study found that the most abundant intermediate had between three and four carbonyl ligands and both photolytic and thermal decarbonylation are appropriate for generating the active species.$^{93-97}$

The active species formed from iron pentacarbonyl is an effective catalyst for olefin isomerization. Casey and Cyr established that the reaction followed the “multiple” isomerization mechanism (Figure 4.2).$^9$ Manuel found that 1-hexene, a terminal olefin, reacted faster than internal C$_6$ isomers, with over 98% conversion.$^{12}$ Although terminal olefins are weak pi backbonding ligands due to open antibonding orbitals, the high electron density of iron compensates, especially since one or more carbonyl ligands are no longer bonded to the metal center.$^{12}$ Manuel completed his experiments using Fe$_3$(CO)$_{12}$, which was later shown to decompose to Fe(CO)$_3$ complexes.$^4$ Casey and Cyr also found Fe(CO)$_3$ primarily responsible for isomerization of 3-ethyl-1-pentene,$^9$ Kane et al. observed Fe(CO)$_4$ intermediates in the isomerization of 1-hexene and 1-octene,$^9$ and Whetten et al. postulated that either the observed Fe(CO)$_4$ species was active and following the same mechanism as Fe(CO)$_3$, or that it decomposed to Fe(CO)$_3$, which quickly isomerized 1-pentene.$^{100}$ There are two 1-hexadecene isomerization experiments using iron pentacarbonyl in the patent literature. Peters used a feed of 1-hexadecene with 550 ppm Fe(CO)$_5$ resulting in 88-94% internal olefin at 220 °C.$^8$ Weber and Springer used 500 ppm Fe(CO)$_5$ at 180 °C and found 60% internal olefins past the fourth position (87% internal olefins overall).$^9$
In this chapter, iron pentacarbonyl is used for the positional isomerization of hexadecenes and octadecenes as a homogeneous catalyst. Attempts at tethering iron pentacarbonyl to a polystyrene support are also detailed.

4.2 Experimental Procedures

4.2.1 Experimental Materials

Batch reactor studies were conducted with 1-hexadecene (AlphaPlus® 1-Hexadecene, Chevron), which is 93 mol% 1-hexadecene and 6 mol% vinylidenes (“branched” olefins) with the balance 2- and 3-hexadecenes and alkanes.\(^{101}\) Batch reactor studies on a smaller scale were conducted with 1-octadecene (AlphaPlus® 1-Octadecene, Chevron). The technical data sheet listed the composition as 91 mol% 1-octadecene and 7.0 mol% vinylidenes (“branched” olefins).\(^{102}\)

Iron pentacarbonyl (Fe(CO)\(_5\)) was obtained from Sigma Aldrich (>99.99%). The syntheses of the heterogeneous catalysts started with brominated poly(styrene-co-divinylbenzene) (Aldrich, 2.5 mmol Br/g, 2% DVB crosslinking). The syntheses made use of a variety of solvents and reagents: THF (Aldrich, >99.9%, with and without 250 ppm BHT inhibitor), 0.5 M LiPPh\(_2\) in THF (Aldrich), benzene (>99.9%, Aldrich), ethylbenzene (99.8%, Aldrich), diethylether (>99.0% with BHT inhibitor, Aldrich), acetone (>99.5% histological grade, Aldrich), and methanol (>99.9%, Aldrich). One synthesis used lithium ribbon (>99.9%, Aldrich).

4.2.2 Homogenous Reactions

Batch reactions were performed in a 4 L stainless steel reactor with automatic stirring and heating controls. The reactor was loaded with 2 L of 1-octadecene. A 20 mL sample was withdrawn and spiked with Fe(CO)\(_5\) in a glove box. The quantity of Fe(CO)\(_5\) corresponded to
250, 500, 750, and 1000 ppm (by weight) of the 2 L batch (between 0.40 g and 1.60 g catalyst). The spiked sample was added to the 2 L batch, the autoclave sealed, then it was purged three times with 10 psig of UHP N₂. The temperature was raised to 180°C and the contents agitated at ~200 rpm. Aliquots were withdrawn at 1 and 4 h after the temperature reached 180°C. After 4 h the heaters were shut down and the vessel cooled overnight. A sample was taken of the final product. Samples were analyzed as discussed in Section 4.2.5.

4.2.3 Heterogeneous Catalyst Synthesis

PSFE1, PSFE2, and PSFE3

The reaction apparatus for all syntheses was a 250 mL three-neck round bottom flask (glass) equipped with a UHP N₂ or Ar inlet (PTFE tubing in reactor), pressure-equalizing addition funnel, mercury thermometer, and condenser (as needed). The funnel was fitted with a rubber septum cap. Effluent gas passed through a mineral oil bubbler, sealing the reaction from the atmosphere.

Brominated poly(styrene-co-divinylbenzene) (Br-PS-DVB) was added to the reaction vessel with 50 mL THF, then degassed by bubbling UHP N₂ for 1 h. PSFE1 and PSFE2 contained 3 g of support while PSFE3 contained 0.998 g. The mixture was stirred for an hour in order to swell the polymer. A volume of 0.5 M LiPPh₂ in THF was injected through the septum cap and added to the solution dropwise such that the PPh₂ to Br molar ratio was 2:1 (30 mL PSFE1 and PSFE2; 10 mL PSFE3). Lithiation and phosphination took place for 24 h (PSFE1 and PSFE3), and 16 h (PSFE2) at 25°C under flowing N₂.

Lithiation/phosphination was quenched with 100 mL of acetone/water (3:1 molar ratio). The mixture was stirred for approximately 2 h. The excess solvent was decanted with an autopippette. Nitrogen flow was increased to ensure that the polymer was not exposed to air. The
solvent was replaced with 100 mL of the acetone/water mixture for another 2 h. The process of
decanting solvent, replacing it, and letting it stir for 2 h was repeated with benzene and methanol.

After decanting the methanol, the thermometer was replaced with a stopcock adapter and
the pressure-equalizing addition funnel and N₂ inlet were quickly replaced with glass stoppers.
The polymer was then vacuum dried for 6 h at 130°C with the pressure decreasing from 10
mmHg to 3 mmHg.

The reaction apparatus was placed back under flowing N₂ and covered in aluminum foil
to prevent photolytic decarbonylation, and 80 mL of benzene was added to the dried polymer
with stirring. In a glove box, 20 mL of benzene was spiked with 1.5 g Fe(CO)₅ (3:1 Fe/P molar
ratio) and then added to the polymer slurry. A condenser (also covered in foil) was attached with
its top covered by a rubber septum cap. A syringe needle was placed into the cap to allow gas to
escape into a tube connected to a mineral oil bubbler. The benzene was refluxed at 90°C for 24 h.

The reaction apparatus was then vacuum dried at 90°C, 10 mmHg. The final product was
removed from the flask in a glove box, weighed, and stored in aluminum-covered sample
containers.

**PSFE4**

The reaction apparatus for PSFE4 was the same as the first three catalysts. All glass
pieces were heated to at least 110°C prior to assembly and the Br-PS-DVB support (1.024 g) was
vacuum dried at 5 mmHg and 110°C overnight. All solvents were degassed by bubbling UHP N₂
for 1 h prior to use. Changes to the synthesis were adapted from Bernard et al.¹⁰³

The catalyst support was contacted with 50 mL of THF for 45 min without stirring. The
reaction vessel was simultaneously cooled to 3°C. The 0.5 M LiPPh₂ solution was added
dropwise at 3°C (11 mL), followed by an additional 50 mL THF, and then warmed to 25°C. The
reaction proceeded for 3 d at 25°C before it was quenched with the 3:1 molar ratio acetone/water solution (50 mL). The support was filtered in a ground glass filter under UHP N₂ purge and washed with 50 mL methanol and 70 mL diethylether. The support was then vacuum dried at 100°C.

Reaction with Fe(CO)₅ was done the same way as before with the following exceptions: ethylbenzene was used instead of benzene (here and for PSFE9 and PSFE10), 1.5 g Fe(CO)₅, and a 24 h reaction time at 100°C. Solid products were filtered in the N₂-purged glass filter using 50 mL ethylbenzene to rinse the catalyst. The ethylbenzene was degassed by freeze-pump-thaw, which was used on every solvent from this point onward. All drying and bottling procedures were also the same as the previous section.

**PSFE9**

All THF solvents were distilled from a sodium/benzophenone still. The resin (2.006 g) was swollen in 50 mL THF for 1 h, then 25 mL of 0.5 M LiPPh₂ was added dropwise. The addition funnel was replaced with a condenser, and then the temperature was increased to reflux for 2 d. The reaction was quenched with 25 mL of a 2:1 molar ratio of acetone/water for 4 h. The support was filtered under N₂, rinsed with 50 mL cyclohexane, and then vacuum dried in situ overnight (10 mmHg).

The support was removed from the filter by adding 50 mL of ethylbenzene. The reactor was charged with the support slurry and 15 mL of ethylbenzene spiked with 1.5 g iron pentacarbonyl. The mixture was heated to 75°C for 24 h. The catalyst was filtered again under N₂, rinsed with 50 mL ethylbenzene, vacuum dried in situ at 10 mmHg and 25°C overnight, and then moved to a glass tube for vacuum drying at 115°C for 20 h at 5 mmHg, also overnight. About 2 g of catalyst was recovered.
All THF and diethylether was passed through an activated alumina column prior to use. The LiPPh\textsubscript{2} was prepared separately by stirring 50 mL THF, 0.77 g lithium, and 10 mL ClPPh\textsubscript{2} in a UHP Ar-purged 3 neck round bottom flask with condenser for 1.5 h\textsuperscript{104}. The mixture turned deep red. The flask was then heated to reflux for 6 h. The 1 M LiPPh\textsubscript{2} product was removed and the residual lithium was hydrolyzed with acetone.

The procedure to phosphinate the support was the same as before (1.451 g Br-PS-DVB). The support was swollen in 25 mL THF for 1 h, at which point 30 mL of the 1 M LiPPh\textsubscript{2} solution was added (8.2:1 P:Br molar ratio). The slurry was heated to reflux at 70°C for 2 d before it was cooled and quenched with 25 mL of acetone/water at a 3:1 molar ratio. The support was filtered under N\textsubscript{2} and rinsed with 50 mL of acetone/water at a 3:1 molar ratio, and 100 mL of diethylether. The support was vacuum dried in situ overnight at 10 mmHg and 25°C.

The support was recovered with 25 mL ethylbenzene. The mixture was heated to 80°C, then 20 mL of ethylbenzene with 2.0 g Fe(CO)\textsubscript{5} were added. The reaction lasted 2 d at 80°C. The catalyst was recovered, filtered, rinsed with cyclohexane, vacuum dried in situ at 10 mmHg and 25°C, then vacuum dried at 110°C and 5 mmHg overnight.

**4.2.4 Catalyst Characterization**

Heterogeneous catalysts were characterized by FTIR and ICP-AES. FTIR spectra were recorded in transmission mode on a Nicolet 380 FTIR. Solid samples (5 mg catalyst per 100 mg KBr wafers) were pneumatically pressed at 1700 psig. Elemental analysis was performed by dissolving 100 mg of sample in 150 mL aqua regia. Samples were boiled for 3 d. The acid was then slowly evaporated and replaced with deionized water to lower the acid content to about 5 vol\%. The solutions were analyzed by ICP-AES to measure P and Fe concentrations.
4.2.5 Heterogeneous Reactions

Catalysts were loaded into a 3-neck round bottom flask fitted with a mercury thermometer, a magnetic stir bar, and two purge gas tubes for either Ar or UHP N₂ (PTFE tubing). The purge gas flow rate was controlled by a needle valve. The outlet was insulated from the atmosphere by a mineral oil bubbler. Approximately 500 mg of catalyst was added to the flask, followed by an olefin feed at either an 80:1, 50:1, or 10:1 feed/catalyst ratio by mass. The feed was either an α-olefin mixture of 95 mol% 1-octadecene and 5.0 mol% branched olefin or a partially isomerized octadecene consisting of 4.3 mol% branched olefins, 52 mol% terminal olefins (1- and 2-octadecene), and 44 mol% internal olefins (3-position and higher octadecenes). The flask was immersed in a peanut oil bath and heated to 130°C and reacted for 6 h (some reactions lasted 19 h). The products were filtered and analyzed.

4.2.6 Product Analysis

Olefin products were analyzed on an HP 5890 GC with a flame ionization detector. Hexadecene products were analyzed on a Supelco SP-1000 column (30 m, 0.32 mm ID). The initial temperature of 70°C was increased 15°C/min to 145°C, then 2°C/min to 160°C with a final hold time of 2.5 min. Octadecene samples were tested on a Supelco DB-5 column (30 m, 0.32 mm ID). The initial temperature of 50°C was held for 1.00 min, increased at a rate of 10°C/min to 100°C, held for 5 min, ramped again at 5°C/min to 260°C, with a final hold time of 17 min. Additional details about the GC analysis are in Appendix A; peak identities were determined in the same way as Appendix C.

Ultraviolet-Visible Spectroscopy (UV-Vis) was used to test selected product samples. Samples were diluted in isopropanol and tested on a Jasco V 750 spectrometer. Samples and standards were loaded into 5 mL optical glass cuvettes.
4.3 Results and Discussion

4.3.1 Homogeneous Fe(CO)\(_5\) study

Iron pentacarbonyl was initially tested under homogeneous reaction conditions with 1-octadecene. The batch experiments were adapted from the patents of Weber et al. and Peters et al.: 2 L of \(\alpha\)-olefin in a batch reactor for 2-6 h with 250-1000 ppm catalyst.\(^8,9\) The conversion of terminal olefins (\(X_i\), Equation 4.1), number of turnovers (Equation 4.2), and selectivity to internal olefins (\(S_i\), Equation 4.3) were calculated from the GC analysis.

\[
X_i = \left(1 - \frac{\text{mol(Terminal, Product)}}{\text{mol(Terminal, Feed)}}\right) \times 100\% \quad (4.1)
\]

\[
\text{Turnovers} = \frac{X_i(\%) \times (\text{mL C18}) \times \left(\frac{0.789 \text{ g C16}}{\text{mL C16}}\right) \times \left(\frac{\text{mol C18}}{252 \text{ g C18}}\right) \times \left(\frac{195.9.8 \text{ Fe(CO)5}}{\text{g Fe(CO)5}}\right)}{100\%} \quad (4.2)
\]

\[
S_i = \frac{\text{moles(Target, Product)} - \text{moles(Target, Feed)}}{\text{moles(Target+ Branched, Product)} - \text{moles(Target+ Branched, Feed)}} \times 100\% \quad (4.3)
\]

The optimal reaction time was confirmed by withdrawing samples from the batch reactor at 1, 4 and 5 h with an initial concentration of 1000 ppm Fe(CO)\(_5\) in 1 L of 1-hexadecene. Most of the reaction took place within the first hour (430 turnovers, 69% conversion), with an additional 20 turnovers and 3% conversion per hour (Figure 4.3). All homogeneous catalysts used here were 100% selective to internal olefins. The conversion of the final batch was nearly the same as the 5 h sample (not shown), so the reaction reached equilibrium some time before 5 h. It is possible that, for industrial applications, the residence time should be lower (e.g. < 2 h) to eschew the energy costs for marginal conversion. However, the residence time of future tests was

60
Figure 4.3: 1-Hexadecene isomerization with 1000 ppm Fe(CO)$_5$ at 180°C

Figure 4.4: Batch reactions of Fe(CO)$_5$ in 1-hexadecene at 180°C for 4 h

chosen as 4 h to ensure that batches with a lower catalyst concentration could approach equilibrium. It may be desirable for industrial processes to use shorter residence times (~1 h) in case the increase in turnovers (~10/h) does not justify the energy costs.
The optimal catalyst concentration was the determined by reacting the 2 L batches at 180°C for 4 h (250, 500, 750 and 1000 ppm Fe(CO)$_5$). The optimal concentration was 500 ppm (Figure 4.4), which maximized the number of turnovers while minimizing catalyst usage. These results are in agreement with Weber et al., who had a similar conversion at 4 h with 350 ppm catalyst.$^9$

Partially isomerized hexadecenes were also tested in the batch reactor with 1000 ppm Fe(CO)$_5$ for 4 h at 180°C. The composition of the feed was 4.4 mol% branched olefins, 26 mol% internal olefins (1- and 2-hexadecene), and 71 mol% terminal olefins (3-octadecene and higher), as determined by GC. The conversion of terminal olefins was only 16%, giving 36 mol% internal olefins in the final product. The catalyst was therefore three times less active with the partially isomerized feed when compared to the α-olefin feed on a number of turnovers basis (140 versus 480 turnovers at 1000 ppm for 4 h). This difference arises from the slower isomerization of long-chain E- and Z-octenes with the double bond in the 2- and higher position; when these olefins bond to the catalyst, the alkyl portions of the molecule exhibit suppressed rotation due to steric hindrance, diminishing their reactivity.$^{105}$

One of the major challenges of homogeneous catalysis is the separation of the catalyst and product. The product solution changed color from clear to amber, indicating the presence of dissolved iron carbonyls. This iron would be expected to oxidize over the course of the reaction into a solid compound that can be filtered. Precipitates were observed in the reaction products, likely due to iron oxide formed from residual oxygen in the olefin and purge gases, and adventitious O$_2$. If the reactor was not purged as described in Section 4.2.2, then there was no observed catalytic activity at all – the catalyst is completely oxidized.$^9$ Elemental analysis of the product olefin by ICP-AES was performed, but there was not enough iron in the sample to obtain
acceptable results. Therefore, the quantity of dissolved iron must be low. A sample of 1-octadecene spiked with 35 ppm Fe(CO)$_5$ was tested by UV-Vis Spectroscopy with Fe chromophores detected at 272 nm and 282 nm (Figure 4.5). These features were not observed in reaction products, so the quantity of iron remaining must have been less than 35 ppm as the sum of all iron carbonyls.

Figure 4.5: UV-Vis spectra of 1-octadecene spiked with 35 ppm Fe(CO)$_5$, then diluted in isopropanol. The final concentrations are shown in the legend.

4.3.2 Heterogeneous Iron Carbonyl Catalysts

Synthesis Method Selection

Depositing an iron carbonyl on a heterogeneous support would sidestep the issues of homogeneous catalyst separation. The initial method of deposition was to phosphinate a polystyrene support and, though a ligand exchange, tether the iron carbonyl to the polystyrene (Figure 4.6). This method mainly follows the work of Pittman et al, who synthesized iron
carbonyl tethered to polystyrene via phosphines for 1-pentene isomerization.\textsuperscript{106,107} Similar lithiation/phosphination procedures were also carried out by several other groups.\textsuperscript{103,104,108-110}

![Reaction schematic for supported Fe(CO)$_5$](image)

Figure 4.6: Reaction schematic for supported Fe(CO)$_5$\textsuperscript{107}

The literature discusses two major considerations when designing this experiment: the optimal level of crosslinking of the PS-DVB support and the use of n-butyllithium versus LiPPh$_2$ as reagent. The crosslinking levels were either 2\% DVB or 12-20\% DVB; polymers with higher crosslinking are more structurally rigid. Chou et al. observed that Fe(CO)$_5$ reacted four times slower with the 12\% than the 2\% crosslinked support.\textsuperscript{111} Grubbs et al. found that there was less chelation of a functionalized PS-DVB with the metal complexes when it was 20\% crosslinked.\textsuperscript{112} Excessive chelation might not be desired for the tethered iron carbonyl, because to function catalytically the Fe must exchange at least one -CO group for an olefin. Pittman et al. compared their supported iron carbonyl catalyst to homogeneous Fe(CO)$_4$PPh$_3$ and Fe(CO)$_3$(PPh$_3$)$_2$, finding similar reaction results for all the catalysts.\textsuperscript{107} The literature is unclear on the exact structure of the tethered catalyst. Regardless of its identity, less rigid supports are better-suited for the ligand exchange, and several other studies have found that < 3\% DVB crosslinking was preferable to macroporous systems with higher crosslinking, which were 12\% and 20\%
crosslinking. \textsuperscript{103,109,113,114} Therefore we used a 2% crosslinked Br-PS-DVB support in favor of one with higher crosslinking.

Next, the chemicals used in lithiation of the Br-PS-DVB were chosen. In the Chou study, \textit{LiPPh}_2 was preferred over \textit{n}-butyllithium because the phosphination consisted of one step instead of three steps (exchange lithium with surface bromide, followed by phosphine exchange with \textit{ClPPh}_2, followed by lithium elimination). \textsuperscript{108} Even though \textit{n}-butyllithium phosphination (at 60°C) yielded two times more surface phosphorus than \textit{LiPPh}_2 (at 25°C), the former method also left more residual bromine groups on the polymer, and these could interfere with future reactions. \textsuperscript{108} In another study, Bernard et al. found that when reacting \textit{ClPPh}_2 with \textit{n}-butyllithium the reaction did not go to completion, so the 2% crosslinked Br-PS-DVB ultimately contained fewer active sites than its \textit{LiPPh}_2 counterpart. \textsuperscript{103} For all these reasons we conducted lithiation with \textit{LiPPh}_2.

The rest of the synthesis was similar to what is found in the literature; we filtered the phosphinated polymer under inert conditions, washed with various solvents, and dried under vacuum (0.007 bar) using Schlenk techniques. \textsuperscript{103,106} The phosphinated polymer was contacted with \textit{Fe(CO)}_5 in a nonpolar solvent under inert gas, refluxed for several days, and then filtered, washed, dried, and transferred to a glove box. The exact syntheses are in Section 4.2.3.

\textbf{Catalyst Characterization}

For the synthesized samples, elemental analysis (ICP-AES) for iron and phosphorous was performed with results presented in Table 4.1. According to the manufacturer, the Br-PS-DVB support contained 2.5 meq Br/g, so 2.5 meq/g would be the maximum P and Fe content by ICP-AES, assuming both were present only bound to the aromatic ring. The earliest syntheses (PSFE1-PSFE3) only converted 5-10\% of the elemental bromine to phosphorous (Table 4.1).
These values are far lower than suggested by the literature, where 50-100% conversion of Br to P was possible. In all cases, the iron content was at least double the amount of the phosphorous.

Table 4.1: Elemental Analysis of Iron Carbonyl Supported on PS-DVB (before reaction with olefins)

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<th>Catalyst</th>
<th>P (mmol/g)</th>
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<tr>
<td>Br-PS-DVB</td>
<td>0.00</td>
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<tr>
<td>PSFE1</td>
<td>0.21</td>
<td>1.00</td>
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<tr>
<td>PSFE2</td>
<td>0.17</td>
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<td>0.12</td>
<td>0.42</td>
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<td>PSFE4</td>
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<tr>
<td>PSFE9</td>
<td>0.01</td>
<td>0.42</td>
</tr>
<tr>
<td>PSFE10</td>
<td>0.07</td>
<td>0.90</td>
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There are several possible explanations for the low P and Fe contents. First, unbound species may have been extracted during washings (7.5 mmol Fe(CO)$_5$ was used per 2.5 mmol P). Second, impurities in the solvents (peroxides, e.g.) may have affected the lithiation reaction. Third, the brominated support may not have been cleaned well enough. Fourth, phosphorous may have been cleaved from the surface into the iron solution. Fifth, phosphorous may have been cleaved during a drying step.

Some steps were then modified with a goal of increasing the amount of lithiation. A glass filter, operated under flowing N$_2$ or vacuum, was used in PSFE4, PSFE9, and PSFE10 to possibly improve the solvent washing. The solvents were further degassed by either bubbling N$_2$ through them for 1 h (PSFE2, PSFE3) or by successive freeze-pump-thaw cycles (PSFE4, PSFE9, PSFE10). Additionally, unstable solvents such as THF and diethylether were further purified either by distillation from sodium and benzophenone (PSFE9) or by passage through a packed column of activated alumina (PSFE10). The supports were all oven-dried, vacuum-dried,
and swollen in THF prior to reaction. The contact time with LiPPh$_2$ was altered from 18 h at 25°C (PSFE1, PSFE2) to either 2 d at room temperature (PSFE3, PSFE4) or to 2 d under reflux (PSFE9, PSFE10). The contact time with Fe(CO)$_5$ was increased from 1 d (PSFE1, PSFE2, PSFE3, PSFE9) to 2 d (PSFE4, PSFE10). New LiPPh$_2$ was synthesized from ClPPh$_2$ and Li(0) in THF for PSFE10 in case the purchased 0.5 M LiPPh$_2$ (in THF) was contaminated. Finally, prior to elemental analysis, all samples were boiled in aqua regia for 3 d in order to completely dissolve the P and Fe components. As seen from Table 4.1, none of these steps were sufficient to increase the amount of phosphorous detected on the catalysts, at least as quantified by ICP-AES. Currently, we are attempting to digest the polymer by either adding an initial high temperature treatment (“ashing”) or a different combination of acids or bases.

The supported iron carbonyl catalysts were characterized by FTIR prior to reaction. The CO stretching bands in the 1800-2100 cm$^{-1}$ range were examined. According to the Sanner et al., the polymer (PS-DVB) (PPh$_2$)$_{1-2}$ Fe(CO)$_{3-4}$ displays stretching bands at 1876, 1932, 1968, and 2045 cm$^{-1}$, in contrast to Fe(CO)$_5$ (2000 and 2025 cm$^{-1}$), mono-coordinated Fe(CO)$_4$PPh$_2$ (1942, 1978, and 2054 cm$^{-1}$), and bis-coordinated Fe(CO)$_3$(PPh)$_2$ (additional band at 1893 cm$^{-1}$). The mono-coordinated bands were present in PSFE1, PSFE2, and PSFE3 (Figure 5). The bis-coordinated band around 1875-1880 cm$^{-1}$ appears to be present in PSFE2 and PSFE3, but it overlaps with the absorption of the support at 1880 cm$^{-1}$, so it is not possible to make a definitive conclusion. The support also shows absorption centered at 1940 cm$^{-1}$. The sample PSFE2 showed a carbonyl band centered at 1930 cm$^{-1}$. PSFE10 did not exhibit clearly resolved bands, but the absorbance at ~2070 cm$^{-1}$ and the increase in absorbance at 1900-2025 cm$^{-1}$ suggests that it also contains CO and/or PPh$_2$. Chou et al. described using supported iron concentrations on the
order of 35 ppm in order to achieve the resolution necessary for quantitative analysis of mono- and bis-coordinated phosphines. This level of resolution is not present in Figure 4.7, but the lack of a defined 1875-1880 cm\(^{-1}\) band shows that PSFE1, PSFE2, PSFE3, and PSFE10 contain primarily mono-coordinated phosphines of supported iron.

PSFE4 and PSFE9 do not display any carbonyl features and closely resemble the Br-PS-DVB support. This is entirely consistent with the results in Table 4.1. Therefore, analysis by FTIR is a far quicker method than ICP-AES to determine if there was a problem with the synthesis.

The overlap with bands of the support in the C-Br region of the spectrum makes it impossible to determine whether residual bromide is present. However, it is possible that some Fe is tethered to the support through an acyl ligand, as absorption at 1747 cm\(^{-1}\) (PSFE10) and 1732 cm\(^{-1}\) (PSFE3) was noted.

Figure 4.7: IR spectra in CO stretching range of fresh catalysts
Reactions with Heterogeneous Iron Carbonyl Catalysts

Selected supported iron carbonyl catalysts were tested in the glass batch reactors. In the first series of tests the isomerization of 1-octadecene with these catalysts was compared to that of homogeneous Fe(CO)$_5$, for 6 h at 130°C (Figure 4.8). Both PSFE1 and PSFE2 were evaluated at an 80:1 feed/catalyst ratio (by mass). The conversion to internal olefins was < 1.5% but with 100% selectivity to internal olefins. This amounts to only 4 and 13 turnovers, respectively, based on the amount of Fe. This compares to 83% conversion but only 10 turnovers for 50:1 octadecene/Fe(CO)$_5$ reaction over the same time frame, so the rates are similar.

![Figure 4.8: Conversion of 1-octadecene with supported iron carbonyls (6 h, 130°C). Not shown: $X_i = 83\%$ for Fe(CO)$_5$, Turnovers $= 10$ at a 50:1 feed/catalyst ratio.](image)

PSFE3 was then tested at both 50:1 and 10:1 feed/catalyst ratios in order to obtain a higher conversion. At 10:1 the conversion increased to 2.5%. The conversion of PSFE1 was
almost the same as PSFE4 (1.8%), so PSFE2 and PSFE4 were the most active supported catalysts on a site basis, giving the most turnovers over the fixed time frame. The iron content was greatest in PSFE1 (Table 4.1), and so its higher activity corresponds to its increased iron content, whether or not all of the Fe was tethered to the PS-DVB surface. If the excess iron is physisorbed Fe(CO)$_x$ (x ≤ 5), then the observed activity could also be caused by the small quantities of physisorbed or even dissolved Fe(CO)$_x$.

The low conversion of 1-octadecene was difficult to quantify via GC (small internal olefin peaks overlap with large alpha olefin peak), so PSFE9 and PSFE10 were tested using partially isomerized octadecenes (44 mol% internal olefins, 52 mol% terminal olefins, and 4.3 mol% branched olefins). The partially isomerized mixture gave a lower overall conversion of internal olefins, as determined using Equation 4.1 in Section 4.3.1. However, the small conversions were more accurately quantified due to the smaller interfering α-olefin peak.

Despite the lack of detectable carbonyl bands for PSFE9 (Figure 4.7), there was still conversion to internal olefins. Note that the partially isomerized olefin contained only about half the amount of 1-octadecene as the pure 1-octadecene feed, so the 3 mol% increase in internal olefins upon reaction is reflected in Figure 4.1 as 6.8% conversion. This conversion is notable; assuming the ICP analyses are correct, then the phosphorous ligand may not be needed for the iron-catalyzed isomerization.

The conversion of PSFE10 was -4.4% because the quantity of terminal olefins increased by 2.5 mol%. This strange behavior was further investigated in a batch reaction that lasted 19 h with temperature starting at 130°C the first 6 h, then raised to 180°C for the last 13 h. The final sample showed a decrease in internal olefins of 3.2 mol%. These reactions proceed slowly, as evidenced by the low conversion over the long residence time at a higher temperature.
The exact reason why internal olefin content decreased is unknown. The olefin could be selectively retained on the iron particle or catalyst support, or consumed in a reaction such as polymerization. The latter is more likely. The firm conclusion is that the supported iron catalysts prepared here are not completely selective for double bond isomerization to internal olefins.

**4.4 Conclusions**

Homogeneous Fe(CO)$_5$ is an effective catalyst for the selective double bond isomerization of 1-hexadecene into internal olefins. In order to obtain optimal conversion of terminal olefins, $\alpha$-olefins (1-hexadecene) were optimally converted to internal olefins when 2 L of 1-hexadecene was mixed with 500 ppm Fe(CO)$_5$ (by mass) at 180°C for 4 h. The $\alpha$-olefins are preferred as feed over mixtures of partially isomerized olefins because the Fe(CO)$_5$ is three times less active for partially isomerized olefins on the basis on the basis of turnover rate. Small quantities of dissolved or colloidal iron remain in the product solution, although the identities of these species are unknown.

Iron carbonyls were tethered to Br-PS-DVB supports via PPh$_2$. Initial ICP-AES analysis indicated that less than 10% of surface Br groups were exchanged with P and the Fe:P ratio was between 10:1 and 2:1. The Fe could be tethered to the surface through PPh$_2$ or acyl ligands, or physisorbed to the PS-DVB surface. Carbonyl bands were detected for most of the catalysts. None of the supported iron carbonyl catalysts were very selective for double bond migration. One catalyst, PSFE10, actually decreased the quantity of internal olefins. The mechanism of reaction and the active catalyst species are at this time unknown.
REFERENCES


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(99) Kane, V. V.; Light, J. R. C.; Whiting, M. C. Polyhedron 1985, 4, 533.


APPENDIX A: GC AND GC-MS DETAILS

Table A1: GC Method, Chapter 2

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APPENDIX B: PERMISSION LETTER FOR CHAPTER 2

Applied catalysis. A, A: general

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- Publication Type: Journal
- Volume:
- Issue:
- Start page:
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APPENDIX C: CHAPTER 2 SUPPORTING INFORMATION

C.1 Acid Site Densities for Tungstated Zirconia

The computed acid site densities from two 1-PA adsorption / desorption experiments are 0.0315 and 0.0321 mmol/g, taking into account product (propene and NH$_3$) desorption from 150 to 300°C. Note the desorption essentially stops at 300°C (Figure C1). Baertsch et al. reported a Brønsted site density for a similar tungstated zirconia as 3-4 times this value (using their Figure 5 and Table 2), but they calculated this number on the basis of all NH$_3$ molecules desorbed (after NH$_3$ adsorption) at up to 900°C.

![Figure C1: 1-propylamine TPD for tungstated zirconia XZO-1251](image)

C.2 Identification of GC Products

GC Products were identified by comparing the chromatograms of three industrial hexadecene samples also analyzed elsewhere: alpha olefin (AlphaPlus® hexadec-1-ene, Chevron), a partially isomerized olefin product from a reaction over a precious metal catalyst
(sample B35A1), and a product from the long contact time reaction of sample B35A1 over SAC-13 (sample PSAC). The GC column was a Supelco SP1000, 30 m, 0.32 mm ID. This is a moderately polar column. The information gained from the retention times of these standards helped determine the double bond positions of specific products.

According to the technical information supplied by Chevron, there is 92.5 wt% hexadec-1-ene, 6.2 wt% vinylidenes (grouped with “branched compounds”), 0.18 wt% hexadec-2-ene, and 0.25 wt% alkanes. The major peak in Figure C2 is at 9.5 min and constitutes 88 area% of the sample with 6.5 area% eluting between 8.5-8.8 min and 5.2 area% eluting after 9.5 min. The peak at 9.5 min therefore corresponds to hexadec-1-ene, with the branched olefins eluting at 8.5-8.8 min.

[Graph: Figure C2: C16Alpha and B35A1 (partial isomerization of alpha olefin). Alpha olefin eluted at 9.5 min and terminal olefins eluted at 9.8 min.]

The transformation of C16Alpha to B35A1 occurs over a precious metal catalyst below 150°C at atmospheric pressure, and a high degree of isomerization is not observed. Large
peaks appeared at 9.8 and 10.1 min (Figure C2), and because the primary products from this catalyst are the 2- and 3-enes (Valerie Massie-Boyer, Bercen Inc., personal communication), these peaks can be taken as characteristic of the 2-ene and the 3-ene, respectively. But in addition, the B35A1 chromatogram shows two other smaller sets of peaks, at 8.0-8.8 min and 8.8-9.4 min.

The final reaction of B35A1 to PSAC takes place over a solid acid catalyst below 150°C (Figure C3), to give both internal and branched olefins. The peak areas between 8.8-9.4 min are sharply increased, and because it is known that the highly internal olefins are the primary products (Valerie Massie-Boyer, Bercen Inc., personal communication), these peaks must represent (primarily) internal olefins. The areas beneath the three peaks after 9.5 min decreased, strengthening the conclusion that they represent terminal and near-terminal olefins. Sojak et al., also using a column with a polar stationary phase, concluded that primarily cis double bonds at the 2- or 3-ene position had a more polar character (and so eluted later than the 1-alkene), while olefins with double bonds at the 6-, 7-, and 8-ene position were more nonpolar. While it is likely that some of the area in one of the peaks eluting prior to hexadec-1-ene at 8.8-9.4 min was due to the 2-trans alkene isomer, the results for sample B35A1 suggest this contribution was rather small.

The peak areas between 8.0-8.8 min increased upon converting the C16Alpha mixture to the PSAC mixture, and as seen previously it is likely that these represent branched compounds. In order to confirm their designation as branched compounds, the PSAC olefins were hydrogenated using Gee et al.’s (ref. 6 of paper) procedure: 1 mL of PSAC olefin was diluted in 9 mL of tridecane, combined with 0.10 g Pd/C catalyst (10 wt% Pd), and stirred with H₂
bubbling into the liquid at 40°C. We observed results similar to Gee et al., with several smaller peaks eluting prior to the main alkane, hexadecane. The weight percentage of compounds in the 8.0-8.8 min range after hydrogenation was about 30 wt% higher than in the corresponding initial olefin mixture. Therefore we conclude that the compounds in this range must be branched in nature.

C.3 First-Order Rate Constants

For the total isomerization reaction, the first-order rate constant on a site basis in L/(mol•s) can be calculated as:

\[ k = -\ln(1-X) \frac{1000 F'}{W S} \]  

Where X is the total fraction conversion of terminal alkene, F’ is the feed volumetric flow rate in L/s, W is catalyst weight in g, and S is the acid site density in meq/g. Multiplication of this “k”
by the feed concentration gives the turnover frequency, which is why the units for “k” are not s\(^{-1}\).
The k’s for SAPO-11 and ZSM-35 are 2.3 \times 10^{-3} and 4.1 \times 10^{-3}\text{ L/(mol•s)}, respectively.

Now compare these to the first-order k’s of a similar reaction and catalyst, taken from the Gee et al.\(^6\) Their data are for the batch isomerization of 1-tetradecene by a SAPO-11 catalyst. Based on these data, they presented regression results for several first-order rate constants describing double bond migrations, skeletal isomerization, and dimerization. Using their \(k_1\) rate constant A (pre-exponential factor) and E (activation energy) for the double-bond migration of a 1-tetradecene (Table 2 of their paper), we compute \(k_1 = 0.36\text{ h}^{-1}\) at 130°C. They report actual data at 142°C so the extrapolation to 130°C is justified. To put it on the same basis as ours (where multiplication by the 1-alkene concentration will give the TOF) we must multiply this \(k_1\) by their batch volume and divide by the catalyst weight and acid site density. Gee et al. do not report site densities so we used our own site density for SAPO-11, giving a final \(k_1\) on a site basis of 1.8 \times 10^{-3}\text{ L/(mol•s)}.\(^6\) This compares favorably to our results given above.

C.4 Computation of Weisz-Prater Moduli to Check for Diffusion Limitations

We computed the Weisz-Prater moduli for the two most active catalysts (AM-35 and SAC-13) at 130°C. The standard formulation of the Weisz-Prater modulus \(\Phi\) is:

\[
\Phi = \frac{r_{v,obs} L^2}{D_e C^s}
\]  
(C2)

where \(r_{v,obs}\) is the observed rate on a catalyst volume basis, \(L\) is the characteristic intraparticle diffusional distance, \(D_e\) is the effective diffusivity of the reactant, and \(C^s\) is the concentration of the reactant at the external surface.\(^{117}\) For 1-hexadecene at 130°C, \(C^s\) is 3.5 \times 10^{-3}\text{ mol/cm}^3 (assuming no external film gradient), and the self-diffusivity (which would approximate the diffusivity of one isomer in another) is 1.7 \times 10^{-5}\text{ cm}^2/s. The concentration was computed using a process simulator (ASPEN HYSYS v.8.6) while the diffusivity was computed using the
correlation of Sun and Chen.\textsuperscript{118} To obtain $D_e$, we multiplied the diffusivity by the porosity squared (i.e., assumed the random pore value for the tortuosity).

AM-35: The particles are spherical, so $L \sim$ diameter/6. Physical properties are given in refs. 28 and 45, and Table 2. The particle density (1.10 g/cm$^3$) and porosity (0.23) were computed from the total pore volume (0.21 cm$^3$/g; 0.22 cm$^3$/g)$^{38,57}$ and the solid density measured of 1.54 g/cm$^3$.\textsuperscript{57} The mean spherical particle diameter of the almost dry catalyst was determined by sieving a freshly dried batch, to give 0.47 mm. Using the TOF from Table 2.3, the computed $r_{v,obs}$ is $4.5 \times 10^{-6}$ mol/(cm$^3$$\cdot$s) and the computed $\Phi$ for the mean diameter is 0.086. This is well within the range associated with minimal intraparticle concentration gradients. For example, for a 1$^{st}$ order irreversible reaction, $\Phi = \phi \tanh(\phi)$, where $\phi$ is the Thiele modulus. For $\Phi = 0.086$, $\phi = 0.3$, and the effectiveness factor $\eta = 0.97$.

SAC-13: The particles are cylindrical, so $L \sim$ diameter/4. Physical properties were obtained from various references.\textsuperscript{18,29,30} The particle density (0.76 g/cm$^3$) and porosity (0.64) were computed from the total pore volume (0.84 cm$^3$/g, average from the above refs.) and the typical solid density (2.1 g/cm$^3$). The mean cylindrical diameter is 1.0-1.1 mm. Using the TOF from Table 2.3, the computed $r_{v,obs}$ is $5.6 \times 10^{-6}$ mol/(cm$^3$$\cdot$s) and the computed $\Phi$ is 0.15-0.18. This is within the range normally associated with minimal intraparticle concentration gradients. For example, for a 1$^{st}$ order irreversible reaction, for $\Phi = 0.15$, $\phi = 0.4$, and the effectiveness factor $\eta = 0.94$. For $\Phi = 0.18$, $\phi = 0.44$, and $\eta = 0.94$.

**C.5 Computation of External Film Concentration Gradients**

The dimensionless film gradient can be computed from the implicit equation:

$$\frac{C^b - C^s}{C^b} = \left(\frac{k_e}{D_e}\right) L \frac{\eta}{k_e C^b}$$  \hspace{1cm} (C3)
Where $C_b^b$ is the bulk concentration of reactant, $C_s^s$ the concentration of reactant at the external surface, $r_v^s$ is the rate at the external surface on a catalyst volume basis, $L$ is the characteristic intraparticle diffusional distance, $k_c$ the mass transfer coefficient (units of velocity) and $\eta$ is the effectiveness factor accounting for intraparticle transport. The value of $C_b^b$ is the same as used for $C_s^s$ in the computation of intraparticle gradients, and the $L$-values and $r_v^s$ values are the same as used previously.

The maximum possible gradient corresponds to $\eta = 1$. From the previous section, we know $\eta$ is close to 1. The correlations for $k_c$ used were those recommended for spheres and cylinders by Welty et al.\textsuperscript{119} The viscosity of hexadecane (used for hexadecane here) at elevated temperatures was found in the Dortmund databank: $\sim 0.7 \text{ mPa}\text{s}$.\textsuperscript{120}

For AM-35, using the correlation for spheres of Brian and Hales, a $k_c$ of $1.5 \times 10^{-3} \text{ cm/s}$ was computed, which when substituted into eq. (C3) gives a 4% concentration gradient, i.e., a maximum of 4% of the bulk concentration value at $L = 0.47 \text{ mm}/6$.\textsuperscript{121}

For SAC-13, using the correlation for the Nusselt number for flow perpendicular to a long cylinder, and the Chilton-Colburn analogy between heat and mass transfer, the maximum gradient is 5.5-6.5% at $L = 1-1.1 \text{ mm}/4$.

Therefore while external film gradients exist, they are relatively modest, especially considering $\eta$ is slightly $< 1$.

**C.6 TPO of Fresh and Used XZO 1251**

The temperature programmed oxidation (TPO) for a typical tungstated zirconia is shown below in Figure C4. Oligomer buildup on the used sample took place over a 3 h test.
Figure C4: Results for XZO 1251, temperature programmed oxidation (TPO).
VITA

James Bruno was born to Jack and Shari Bruno in August 1986. He grew up in Lansing, Illinois, a suburb south of Chicago, enjoying a lively household as the oldest of four boys.

He graduated from Marian Catholic High School in 2005. He attended Western Michigan University that fall. During his Undergraduate career he became heavily involved in student leadership organizations, worked as a Resident Assistant for three years, and resolved to make mentorship and teaching a part of his career. He graduated in May 2010 with a Bachelor of Science in Chemical Engineering and minors in Chemistry, Mathematics, and Environmental Studies. He started graduate school at Louisiana State University in August 2010. He joined Dr. Dooley’s catalysis group in January 2011 and completed his Master of Science in Chemical Engineering in December 2012. This dissertation will complete the requirements for a Ph.D. in Chemical Engineering.

Apart from his work at LSU, he was part of LSUSL (a campus gaming group), volunteered at the Baton Rouge Crisis Intervention Center for two years, and can usually be found blowing off steam at Rocket’s Hideout Cards and Games.