Photocatalytic Reaction in Monolithic Optical Fiber Reactor with Inverse Opal Catalyst

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PHOTOCATALYTIC REACTION IN MONOLITHIC OPTICAL FIBER REACTOR WITH INVERSE OPAL CATALYST

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 Department of Chemical Engineering

by
Maoming Ren
B.S., Tianjin University, China, 2001
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Abstract

The development of photocatalytic reactor is essential for the successful application of heterogeneous semiconductor in environmental study, which has been shown to be photoactive and effective to oxidate organic pollutant and photoreduce CO2 to useful compounds. In this dissertation, a monolithic optical fiber reactor (MOFR) coated with inverse opal titania, which uses optical fibers as light-transmitting conductor and support of catalyst, was developed for both photodegradation and photoreduction. 1,2-dichlorobenzene, a volatile organic compound (VOC), was selected as the organic pollutant. This configuration of reactor and catalyst provides a high surface area, enhances mass transfer within the catalyst, manipulates photons transmission within fibers, and provides higher quantum efficiency. The effects of flow rate, UV intensity, humidity (water vapor pressure) and temperature were investigated for the photodegradation in gaseous phase. The results show that flow rate and UV intensity determine the reaction regime simultaneously. Higher humidity can significantly decrease the photoreaction. Inverse opal titania shows higher quantum efficiency than conventional P25 catalyst in this study. This configuration can also work in an aqueous phase to degrade organic compounds. With inverse opal titania doped with Cu, MOFR can be used to photoreduce CO2 to methanol at mild experimental conditions. The effects of water vapor pressure, flow rate and UV intensity were investigated in detail and optimized. The results show there is an optimal value for the water vapor pressure in this study. In addition, inverse opal catalyst shows higher quantum efficiency for reduction.

A three-dimensional model was developed to simulate the process of photodegradation both in gaseous phase and aqueous phase. A convection diffusion model, reaction kinetics model and UV radiance model in optical fiber were incorporated. Reasonable agreement between experimental results and model-predicted results was found. This model certainly explains the experimental results. So it is used to select optimal value for each experiment parameters in MOFR.
Chapter 1. Introduction

1.1 PhotocatalyticDegradation

The presence of hazardous organic compounds in gaseous phase from chemical industries, power plants, landfills, oil production plants and agricultural sources is an interesting topic of global concern. Traditional treatment processes include biodegradation treatment, thermal and catalytic oxidation, chemical treatment using chlorine, potassium permanganate, ozone, hydrogen peroxide, combustion and high-energy ultraviolet light (Ollis et al, 1989; Legrini et al, 1993; Mills et al, 1993; Roberts et al, 2002). All these treatment processes currently in use have their own limitations and none is cost-effective: (i) Phase transfer methods can remove unwanted organic pollutants from waste gas or water, but they do not eliminate the pollutants entirely; (ii) Cost of biological treatment is low, however, some of the toxic compounds present are found to be lethal to microorganisms intended to degrade them, and there is a class of non-biodegradable organic compounds noted as bio-recalcitrant organic compounds; (iii) While chemical treatments based on hydroxyl radical chemistry are powerful to oxidize toxic organic compounds, these processes either use high-energy ultraviolet light or strong chemical oxidants and therefore, undesirable nature. Moreover, several intermediates, which are even more hazardous, are formed in these processes, and because of very low efficiencies, overall treatment cost becomes high if destruction of intermediates and complete mineralization are to be achieved, especially for degrading dilute compounds. Photocatalysis is one way to degrade volatile organic compounds (VOC) in the air and in wastewater.

The heterogeneous photocatalysis on semiconductor metal oxide is one method which has plenty of advantages compared with other methods.

1. Photocatalysis can decompose the hazardous organic compound in the gaseous and aqueous phase more efficiently.

2. Photocatalysis can decompose some non-biodegradable organic compounds.
3. Degradation on photocatalyst can take place at mild experimental conditions, such as ambient temperature and normal pressure.

4. Photocatalyst has higher efficiency when pollutants are diluted.

Although photocatalytic degradation has so many merits, its degradation is determined by several parameters, such as catalyst surface area, the light irradiation and mass transfer of reactants. Since the efficiency of photocatalyst is still low, its application in the industry is still in the cradle.

Enhancing catalytic efficiency is a big challenge not only in the industry but also in academic area. Currently TiO2 is widely used as photocatalyst. The common TiO2 reactors are slurry bed reactor and immobilized reactor. It has been shown that the immobilized bed TiO2 reactor has higher efficiency than the slurry bed reactor. Monolithic optical fiber reactor (MOFR) with immobilized TiO2 shows higher efficiency. However, the light transmission within optical fibers, the active surface area and mass transfer within catalyst limit its efficiency. So based on these limitations of MOFR, my current study was to attempt to find a better way to decrease or eliminate these limitations to enhance efficiency. This is the main aspect of my study.

In order to achieve these goals, inverse opal or photonic bandgap (PBG) TiO2 was grafted on optical fibers. Inverse opal TiO2 can provide more active surface area and increase mass transfer compared with the common P25 TiO2 because of its porosity. Also, the PBG properties of the periodically porous TiO2 can control the propagation of light within certain wavelength range. Therefore, UV photons can be distributed more evenly within the reactor. Experiments were designed to compare the efficiency of inverse opal TiO2 and common P25 TiO2 at same experimental conditions. Therefore, MOFR coated with inverse opal TiO2 was developed. In this study, two kinds of immobilized reactors (figure 1.1) were figured out. The first one uses lamps external to the reactor with inverse opal TiO2 coated on glass rod. The other one, MOFR, uses bundled optical fibers as the light source and substrate for inverse opal TiO2 coated on optical fibers.
The designed MOFR with inverse opal TiO2 can also be utilized to photocatalyze the trace hazardous organic compounds in wastewater. Some experiments were designed to show this application.

![Figure 1.1](image)

Figure 1.1. The schematic of photocatalytic reactors, (a) the immobilized reactor with external light source; (b) monolithic optical fiber reactor

1.2 Photoreduction

Greenhouse gases such as CO2 and CH4 are the primary causes of global warming. The atmospheric concentration of CO2 has steadily increased due to the human activities, especially the fossil fuel consumption. The Kyoto Protocol of the United Nations Framework convention on Climate Changes (UNFCCC) mandated a return of CO2 emission levels to these of 1990. Besides decreasing CO2 emission, conversion of CO2 to usable hydrocarbon would be one of the most promising routes to overcome the effect of global warming. Study has shown that CO2 can be photoreduced by some metal oxide catalyst, such as CuO-Al2O3, CuO-ZnO, TiO2, and CuO (Hirano et al, 1992; Kuwabata et al, 1994; Yamashita et al, 1998; Wu et al, 2005)).

In this dissertation, Cu-loaded inverse opal TiO2 on MOFR is used to photocatalytically reduce CO2 to methanol.
1.3 Overview

The main theme of this work is to develop a more efficiency reactor to photodegrade hazardous organic compounds in gaseous and aqueous phases and to photoreduce.

Chapter 2 introduces the background of photodegradation and photoreduction mechanism. This chapter will also include the optical properties of inverse opal titania.

Methodology of synthesizing inverse opal TiO2 was described in detail and inverse opal TiO2 was characterized by SEM, XRD and UV-vis transmission spectra to show its physical and optical properties. The synthesis and characterization will be included in chapter 3.

Chapter 4 describes the degradation of the pollutant in a batch reactor with inverse opal titania illuminated by external light source. The efficiency of inverse opal catalyst is compared with P25 titania. The effects of several experimental parameters on the degradation were studied in detail.

In chapter 5 we develop a monolithic optical fiber reactor (MOFR) with inverse opal TiO2 and show the experimental detail and the effects of several parameters on the photodegradation.

Chapter 6 will set up a 3-dimensional model of the MOFR and simulate the decomposition in gaseous phase. Comparison between experimental results and simulated results verify the accuracy of our model.

Chapter 7 describes the procedure of photodegradation in aqueous phase by MOFR and a modified model was set up to simulate the process. Both experimental and simulated results were discussed in detail.

Chapter 8 shows the application of MOFR with Cu-loaded inverse opal TiO2 to reduce CO2 to usable organic. The procedure of fabricating catalyst and its photoreduction were described in detail.

Major conclusions and future work preview will be in chapter 9.
Chapter 2. Background of Photocatalysis

2.1 Introduction

Since 1977, when Frank and Bard first examined the possibility of using TiO₂ to decompose cyanide in water (Frank et al, 1977), there has been increasing interest in the environmental applications of TiO₂ to decompose organic compounds (Ollis et al, 1989; Legrini et al, 1993; Mills et al, 1993; Roberts et al, 2002; Hoffmann et al, 1995; Herrmann, 1999; Ollis et al, 1993; Linsebigler et al, 1995; Stafford et al, 1996; Mills et al, 1997; Pelizzetti et al, 1999; Lin, 2005; Heller et al, 1981; Fujishima et al, 2000; Nozik et al, 1996; Fujishima et al, 1999; Sato et al, 1998; Compton et al, 1999; Bull et al, 1976; Wrighton, 1979; Sze, 1981). Thousands of patents and paper about heterogeneous photocatalysis in either aqueous or gaseous system have been published.

Table 2.1. List of organic compounds which have been proved to be photodegradeable on TiO₂ (revised based on reference (Herrmann, 1999; Lin, 2005))

<table>
<thead>
<tr>
<th>Class</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkanes</td>
<td>methane, isobutane, pentane, heptane, cyclohexane,</td>
</tr>
<tr>
<td>Haloalkane</td>
<td>mono-, di-, tri- and tetrachloromethane, tribromoethane, 1,1,1-trifluoro-2,2,2-trichloroethane</td>
</tr>
<tr>
<td>Aliphatic alcohols</td>
<td>methanol, ethanol, isopropyl alcohol, glucose,</td>
</tr>
<tr>
<td>Aliphatic carboxylic acids</td>
<td>ethanoic, dimethylethanoic, propanoic, oxalic acids</td>
</tr>
<tr>
<td>Alkenes</td>
<td>propene, cyclohexene</td>
</tr>
<tr>
<td>Haloalkanes</td>
<td>perchloroethene, 1,2-dichloroethene, 1,1,2-trichloroethene,</td>
</tr>
<tr>
<td>Aromatics</td>
<td>benzene, naphthalene, phenanthrene, pyrene</td>
</tr>
<tr>
<td>Haloaromatics</td>
<td>chlorobenzene, 1,2-dichlorobenzene, bromobenzene</td>
</tr>
<tr>
<td>Nitrohaloaromatics</td>
<td>3,4-dichloronitrobenzene</td>
</tr>
<tr>
<td>Phenols</td>
<td>phenol, hydroquinone, catechol, 4-methylcatechol, resorcinol</td>
</tr>
<tr>
<td>Halophenols</td>
<td>2-,3-,4-chlorophenol, pentachlorophenol, 4-fluorophenol, 3,4-difluorophenol</td>
</tr>
<tr>
<td>Aromatic carboxylic acids</td>
<td>benzoic, 4-aminobenzoic, salicylic, m- and p-hydroxybenzoic,</td>
</tr>
<tr>
<td></td>
<td>chlorohydroxybenzoic acids</td>
</tr>
<tr>
<td>Polymers</td>
<td>polyethylene, poly(vinyl chloride) (PVC)</td>
</tr>
<tr>
<td>Surfactants</td>
<td>sodium dodecylsulphate (SDS), polyethylene glycol, sodium dodecyl benzene sulphonate, trimethyl phosphate, tetrabutylammonium phosphate</td>
</tr>
<tr>
<td>Herbicides</td>
<td>methyl viologen, atrazine, simazine, prometon, propetryne, bentazon</td>
</tr>
<tr>
<td>Pesticides</td>
<td>DDT, parathion, lindane</td>
</tr>
<tr>
<td>Dyes</td>
<td>methylene blue, rhodamine B, methyl orange</td>
</tr>
</tbody>
</table>
The general formula to describe the photocatalysis is generalized in equation (2.1).

\[
\text{Organic compound} + O_2 \xrightarrow{hv, TiO_2} CO_2 + H_2O + \text{Mineral Acid}
\]  

(2.1)

A variety of organic compounds have been proved to be photodegradable via equation (2.1). Table 2.1 shows a summary of these organic compounds. More and more compounds would be added to the list with the research going on.

Greenhouse gases such as CO2 are the primary causes of global warming. The atmospheric concentration of CO2 has steadily increased due to the human activities, especially the fossil fuel consumption. The Kyoto Protocol of the United Nations Framework convention on Climate Changes mandated a return of CO2 emission levels to those of 1990. Besides of reducing Co2 emission, conversion of CO2 to usable hydrocarbon would be one of the most promising routes to overcome the effect of global warming.

Since the energy grade of CO2 is lower from a thermodynamic perspective than organic compounds, CO2 is a rather inert and stable compound. Any transformation of CO2 to hydrocarbon needs huge energy input. Solar energy is one of the cheapest and best candidates as energy source because it is abundant and produces no greenhouse gas. Consequently, the photoreduction of CO2 using solar energy is attractive and it can work like the natural photosynthesis. It has been shown that CO2 can be reduced in water vapor or solvent by photocatalysts such as TiO2 and ZnS (Yamashita et al, 1998; Kuwabata et al, 1994). Equation (2.2) describes the overall reaction.

\[
CO_2 + 2H_2O \xrightarrow{hv} CH_4O + \frac{3}{2}O_2
\]  

(2.2)

This method needs relatively mild experimental conditions, such as mild temperature and pressure. The efficient photoreduction of CO2 is a challenging task for photocatalyst.
2.2 Titanium Dioxide

Titanium dioxide, the most widely used environmental photocatalyst, is nearly an ideal photocatalyst in several aspects because it is relatively inexpensive, highly chemically stable, photoactive and nontoxic (Kuwabata et al, 1994). Titanium dioxide has three natural polymorphs (table 2.2): anatase, rutile and brookite. Among these three polymorphs, anatase has the highest photocatalytic activity (Stafford et al, 1996; Hoffmann et al, 1995; Linsebigler et al, 1995; Mills et al, 1997; Szczepankiewicz et al, 2000; Lin et al, 1999). Although rutile TiO$_2$ has higher refractive index (which is an important parameter for photonic crystals), the photocatalytic activity of rutile TiO$_2$ is rather low due to its low band gap energy and its fast hole-electron recombination rate. Due to its poor photocatalytic performance, rutile is only used in the cosmetic and paint industries. Brookite is the least common of the three polymorphs and is rarely used commercially (Lin et al, 1999).

Table 2.2. Properties of three polymorphs of titanium dioxide (Xu et al, 2006)

<table>
<thead>
<tr>
<th>Properties</th>
<th>Rutile</th>
<th>Anatase</th>
<th>brookite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystalline form</td>
<td>Tetragonal</td>
<td>Tetragonal</td>
<td>Orthogonal</td>
</tr>
<tr>
<td>Density (g/cm$^3$)</td>
<td>4.27</td>
<td>3.90</td>
<td>4.13</td>
</tr>
<tr>
<td>Refractive index</td>
<td>2.72</td>
<td>2.52</td>
<td>2.63</td>
</tr>
<tr>
<td>Energy bandgap (eV)</td>
<td>3.0</td>
<td>3.2</td>
<td></td>
</tr>
<tr>
<td>Moh’s hardness</td>
<td>7.0-7.5</td>
<td>5.5-6.0</td>
<td>5.5-6.0</td>
</tr>
<tr>
<td>permittivity</td>
<td>114</td>
<td>48</td>
<td>78</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>1825</td>
<td>Transformation to rutile</td>
<td>Transformation to rutile</td>
</tr>
</tbody>
</table>

* The refractive index of rutile and anatase is a little bit different in various sources (Xu et al, 2006; Mori; http://www.kalpaperchem.com/titan.htm). The value in this table is from reference (http://www.kalpaperchem.com/titan.htm).

Another reason that anatase TiO$_2$ is more popular is that it is much easier to be synthesized than rutile. In most papers about synthesis of rutile titania, anatase is obtained first and then is calcinated to be converted to rutile beyond about 700°C. Some calcination even needs a temperature higher than 1000°C. However, high temperature calcinations will bring new problems such as agglomeration and deformation when the catalyst is porous (Wijnhoven et al, 1998; Thorne, 2004; Turner et al, 2001; Subramania et al, 1999). There are many methods of producing TiO$_2$ nanopowders,
such as chemical vapor deposition (CVD) (Agillon et al, 1999), oxidation of titanium tetrachloride (Akhtar et al, 1991; Jang et al, 1997), thermal decomposition or hydrolysis of titanium alkoxides (Shimakawa et al, 1993), and sol–gel technique (Gablensz et al, 1998). In this experiment, sol-gel method combined with liquid phase chemical reaction is combined to produce inverse opal TiO$_2$.

### 2.3 Photocatalytic Mechanism

In semiconductor, there are valence bands and conduction bands, which are separated by an energy gap. Usually, when the photon’s energy is equal to or greater than the gap energy, the electron in the valence band will be excited to the conduction band and leave a positive hole in the valence band (Ollis et al, 1993; Poniakowski et al, 1994; Boer, 1990). The energy gap of anatase titanium dioxide is about 3.2eV and the light wavelength should be less than 388nm (see the detail in the origin of photonic band gap in chapter 2.7). Before the excited electrons recombine with the positive holes within a few nanoseconds, if they encounter separately the electron acceptors and electron donors, the photochemical reaction will take place (Figure 2.1) (Roberts et al, 2002; Gerischer et al, 1991).

![Figure 2.1. The schematic of photocatalytic mechanism](image)
The mechanism of the photocatalytic reaction is complicated and is still under study. The most accepted mechanism is as follows (Roberts et al, 2002; Rothenberger et al, 1985; Martin et al, 1994):

I. Charge carrier generation:

\[ TiO_2 + hv \rightarrow h_{cb}^+ + e_{cb}^- \]

II. Charge carrier trapping:

\[ h_{cb}^+ + >Ti^{IV}\text{OH} \rightarrow \{ >Ti^{IV}\text{OH}^* \}^+ \]
\[ e_{cb}^- + >Ti^{IV}\text{OH} \rightarrow \{ >Ti^{III}\text{OH} \} \]
\[ e_{cb}^- + >Ti^{IV} \rightarrow Ti^{III} \]

III. Charge carrier recombination:

\[ e_{cb}^- + \{ >Ti^{IV}\text{OH} \}^+ \rightarrow Ti^{IV}\text{OH} \]
\[ h_{cb}^+ + \{ >Ti^{III}\text{OH} \} \rightarrow Ti^{IV}\text{OH} \]

IV. Interfacial charge transfer

\[ \{ >Ti^{IV}\text{OH}^* \}^+ + \text{Reductant} \rightarrow >Ti^{IV}\text{OH} + \text{Reductant}^* \]
\[ (>Ti^{III}\text{OH}) + \text{oxidant} \rightarrow \text{oxidant}^- + Ti^{IV}\text{OH} \]

Where >TiOH represents the primary hydrated surface functionality of TiO2, \( h_{vb}^+ \) is a valence band hole, \( e_{cb}^- \) is a conduction band electron, \( e_{tr}^- \) is trapped electron, \( \{ >Ti^{IV}\text{OH}^* \}^+ \) is the surface-trapped valence band hole, and \( \{ >Ti^{III}\text{OH} \} \) is the trapped electron on conduction band. Characteristic times for the various steps range from 10 ps to 100 ns, except for electron scavenging by oxidant that is as slow as milliseconds. Geris cher and Heller have suggested that reduction of oxygen is the rate-limiting step in most photocatalytic oxidations (Pelizzetti et al, 1999; Thorne, 2004; Gerischer et al, 1991).

The mechanism of photoreduction of CO2 is still unknown. However, most studies have focused on coupling TiO2 with other metals or metal oxides to stabilize charge carriers or using metal dopants as electron sinks (Xu et al, 2000; Adachi et al, 1994; Malati et al, 1984; Sasirekha et al, 2006; Armelao et al, 2006; Chen et al, 2009).
2.4 Photocatalytic Kinetics

As mentioned previously, the mechanism of photocatalytic oxidation is complicated and it is difficult to get the exact reaction kinetics from the elementary reaction steps. The reaction rate depends on the light irradiance and the photocatalysis. The mechanism on general catalysis is well known, however, the mechanism of photocatalysis is more complicated. A variety of models have been derived to describe the kinetics of photocatalysis. The most famous model, which is widely used, is the Langmuir-Hinshelwood (LH) kinetic model (Martin et al, 1994; Al-Ekabi et al, 1986; Cunningham et al, 1991; Peill et al, 1998). The LH model relates the covered surface by reactants with the reaction rate. It is described in the followed equation.

\[
\frac{dC}{dt} = k_{LH} \theta_0 = \frac{k_{LH} C_0}{1 + K C_0}
\]  (2.3)

where \( \theta_0 \) is the covered site fraction of the reactant on the surface of the catalyst. However, when the LH model is applied to photocatalysis, the \( k_{LH} \) should be one parameter which is related with the light irradiance. But the relationship between \( k_{LH} \) and light irradiance remains unknown.

An empirical power rate law including the influence of light irradiance was also proposed in equation (2.4) (Peill et al, 1998):

\[
r = k C_0^m I^n
\]  (2.4)

where \( I \) is the light intensity. This model can fit most of the individual experiments but with different power-law exponents, \( m \) and \( n \), which means that \( m \) and \( n \) are related with other experimental variables, such as the diffusion, temperature and so on. Also \( m \) and \( n \) are interrelated rather than independent (Fujishima et al, 2000), which also make the model more complicated.

2.5 Photocatalytic Reaction Design

A number of photocatalytic reactors have been designed specifically for degradation of hazardous contaminants, such as the fixed bed reactor where the TiO2 particles are packed (Duffy et al, 2000), immobilized TiO2 on an annular glass rod (Hoffmann et al, 1995), and a multiannular
photocatalytic reactor (Lin, 2005; Yamazaki et al, 1993). Now the most popular reactor is monolithic optical fiber reactor (MOFR), where optical fibers support catalyst and transfer light. Several studies have been focused on MOFR (Danion et al, 2006; Wu et al, 2005; Krauss, 2006, http://en.wikipedia.org/wiki/Photonic_crystal; Sajeev, 1987). Although current MOFR increases the efficiency and attracts more attention, there are some limitations for the scale-up. First, current MOFR can transfer light only in a short distance. This restricts the scale-up. In addition, the efficiency of MOFR with immobilized catalyst is still low due to the low mass transfer within catalyst.

In a photochemical reactor, titania is used in an immobilized form and coated on inert substrates. Titania loses some of its activity and surface area when it is spread on surfaces. The so-called “shadow effect” makes most of the titania surface unavailable for UV illumination (Gogate et al, 2004). In order to overcome this, titania in the macro or mesoporous form or with nanohole arrays has been manufactured and used (Arabatzis et al, 2003; Hamaguchi et al, 2005; Zhang et al, 2005). It provides ways to distribute photons more evenly and increase mass transfer in a photoreactor. Moreover, in order to increase the overall quantum efficiency of the reaction we should prevent electron–hole recombination on the titania surface. Several investigators have used stripped fiber optic cables simultaneously as the support for powdered titania (P-25 form) and as a light delivery mechanism (Marinangelli et al, 1977; Peill et al, 1995; Peill et al, 1996). The ineffective light utilization by powdered titania P-25 coated on fiber optics is the limiting factor in this reactor design. Photonic band-gap materials, “photonic crystals”, are spatially ordered crystalline materials in which electromagnetic wave propagation is forbidden in a certain frequency range [35,73]. In other words, they are the equivalent of semiconductors for electron propagation. The three-dimensional array of interconnected void spaces within a photonic band gap titania allows for specific localization of photons dependant on the pore size (Joannopoulos et al, 1995; Srinivasan et al, 2007; Mihi et al, 2005; Tan et al, 2006; Rodriguez et al, 2005). The advent of photonic crystals has opened up a number of applications that use photonic band gaps. When titania has the structure of photonic crystal, we can
now confine, control, and manipulate both photons and electrons in a single system. The confinement and slowdown of photons have been used in enhancing the photoactivity of titania. Photonic titania is useful in removing pollutants from wastewater (Lichtin et al, 1996; Rizzo et al, 2007; Zhang et al, 2006; Sharma et al, 2005; Ilisz et al, 2002). We have shown that it is also useful in the photocatalytic degradation of pollutants in gaseous and aqueous phases (Ren et al, 2006).

2.6 Photonic Crystal

2.6.1 Photonic Band Gaps (PBG)

Photonic crystals are composed of periodic dielectric or metallo-dielectric nanostructures that affect the propagation of electromagnetic waves (EM) in the same way as the periodic potential in a semiconductor crystal affects the electron motion by defining allowed and forbidden electronic energy bands. Essentially, photonic crystals contain regularly repeating internal regions of high and low dielectric constant. Wavelengths of light that are allowed to travel are known as modes, and groups of allowed modes form bands. Forbidden bands of wavelengths are called photonic band gaps.

Photonic crystal is characterized by a filled valence band and an empty conduction band. When the electron within the valence band is excited by a photon, whose energy is equal to or greater than the band gap energy, the electron will be excited from the valence band into the conduction band to leave a positive hole in the valence band (figure 2.2) (Fukuda, 1998; Hoffmann et al, 1995).

The band gap energy, \( E_g \), corresponds to a forbidden energy band for the electrons and its energy is given by

\[
E_g = E_c - E_v
\]

where \( E_c \) is the minimum energy in the conduction band, \( E_v \) is the maximum of the valence band, and the \( E_g \) is the minimum energy needed to excite the electrons from the valence band to conduction band. In titanium dioxide, the most popular material for an applied photonic crystal, the energy band gap is about 3.2eV (Boer et al, 1990)). With the photon energy equation, \( E_{\text{photon}} = h C / \lambda \), the maximum wavelength needed is calculated as follows.
\[
\lambda_{\text{max}} = \frac{h \cdot c}{E} = \frac{6.6260 \times 10^{-34} \text{J} \cdot \text{s} \times 3 \times 10^8 \text{m/s}}{3.2\text{eV} \times 1.6021 \times 10^{-19} \text{j/eV}} \times 10^9 \text{nm/m} = 388\text{nm}
\]

Since the needed energy can be shifted to 3.4eV (the band structure depends on the material and bonding structure, and also on the orientation in crystal because the arrangement of atoms varies in different crystal orientations) (Gray; Stier et al, 2002), the maximum wavelength is chosen as 365nm as a conservative value. It is in the range of UV. In this study, UVA lamp has been chosen to be the light source.

2.6.2 Photonic Crystal Preparation Method

Many methods for synthesizing three-dimensional (3D) photonic crystals for the visible or the near infrared have been proposed (Stier et al, 2002), such as layer-by-layer lithography, e-beam fabrication, chemical vapor deposition (CVD), woodpile crystal, holographic lithography and inverse opal (Johnson et al, 2000; Lin et al, 1998; Sharp et al, 2002; Colvin et al, 1999; Vlasov et al, 2001). Figure 2.2 shows some process and photonic crystals (Chan et al, 2005).

Figure 2.2. Example methods for photonic crystals fabrication

The most popular method is the sol-gel method (or colloidal method). Sol-gel method is to use microporous polymers, such as polystyrene (PS) spheres and poly (methyl methacrylate) (PMMA) as template. There are many methods to arrange the spheres in close-packed structures, including gravity sedimentation, centrifugation, vertical deposition, templated deposition, electrophoresis, patterning,
and controlled drying (Míguez et al, 2001). In this method, polystyrene is used as the template and coated on the substrate. After that, liquid phase chemical reaction (sol-gel) is used to fabricate a 3-D photonic crystal.
Chapter 3. Photonic Crystal Fabrication and Characterization

3.1 Introduction

Photonic crystal has a periodic optical structure that is designed to affect the propagation of photons in a similar way that periodicity of a semiconductor crystal controls the motion of electrons. Photonic crystals contain regularly repeating internal regions of high and low dielectric constant (Peill et al, 1998). In particular, these photonic crystals have photonic band gaps (PBG) such that light within certain frequencies is prevented from propagating in certain or all directions within the material (Sajeev, 1987; Yablonovitch, 1987).

Many methods for synthesis of three-dimensional photonic crystals for the visible or the near infrared have been proposed (Cangiani, 2002; http://www.aph.uni-karlsruhe.de/ag/wegener/phc/phc.en.html). 3-D inverse opal titania or Photonic Crystals (PC) are fabricated by many methods. Nanomachining (Fleming et al, 1999), lithography (Divliansky et al, 2003), chemical vapor deposition (CVD) and 3-D holography (Miklyaev et al, 2003; Campbell et al, 2000) are a few of the most commonly used but they suffer from being complex, and expensive.

The most popular method is the sol-gel method (or Colloidal assembly). It uses microporous polymers, such as polystyrene (PS) and poly (methyl methacrylate) (PMMA) as templates. There are many methods to arrange the spheres in close-packed structures, including gravity sedimentation, centrifugation, vertical deposition, templated deposition, electrophoresis, patterning, and controlled drying (Míguez et al, 2001).

In this research, polystyrene is used as the template and a liquid phase chemical reaction (sol-gel method) is used to fabricate a 3D photonic crystal (Kuai et al, 2003; Lin et al, 2004; Ni et al, 2002; Wijnhoven et al, 2001; Subramanian et al, 1999; Wijnhoven et al, 1998; Colvin et al, 2001).
3.2 Fabrication of Photonic Crystal

3.2.1 Materials

Quartz rod (3mm in diameter), optical fibers (1mm in diameter, manufactured by Thor Labs, New Jersey), quartz sheet, sandpaper (Norton), polystyrene sphere (120 nanometer in diameter, Duke Scientific), titanium ethoxide (Aldrich), DI water, anhydrous ethyl alcohol (EMD), CH₂Cl₂ (OmniSolv), 1,2-dichlorobenzene (EM Science), hexane (EMD), P25 titania dioxide (Degussa Corporation, Akron, PA).

3.2.2 Fabrication of Photonic Crystal

In this study, a liquid phase chemical reaction method is used. Polystyrene spheres (PS) are used as template. Figure 3.1 shows the schematic of the synthesis process. The methodology used for the production of photonic band gap titania on a substrate was that employed by Colvin and co-workers (Divliansky et al, 2003). The process began with roughening the surface of a quartz plate by sandpaper to make it easier to coat the polystyrene spheres. The roughed plate was subsequently washed repeatedly with deionized water and finally wiped with a soft cloth to remove any attached particles. Polystyrene (PS) latex spheres suspension (different diameter, Duke Scientific Corporation, Palo Alto, CA) was diluted to 0.5% (v/v). The quartz was dipped in the diluted PS solution for 5 minutes and dried in an oven at 50-60 °C for about 20 min. The process was repeated three times. A glove box was prepared with a nitrogen blanket and the coated quartz plate was transferred to the box. Inside the glove box a solution of 288 µL distilled, deionized water was mixed with 50 mL of ethyl alcohol and stirred. 136 µL of titanium ethoxide in ethyl alcohol was added slowly into the liquid with constant stirring. When the liquid became cloudy, the polystyrene-coated quartz plate was dipped into it and suspended in the middle of solution for 8h while stirring. The titania precursor would diffuse into the spaces between PS spheres. Then the liquid reaction takes place inside PS layer. The plate was then removed out of the solution and dried at 60 °C for 2 h in oven to remove the solution. Thereupon the plate was dipped in pure methylene chloride overnight to remove the polystyrene template. The
Figure 3.1. Process of preparing the photonic crystal on glass rod/optical fiber

1. Roughen the surface on sand paper
2. Coat PS
3. Dry in the oven
4. Washing with DI water
5. Calcinate in the oven
6. Remove PS in CH₂Cl₂
7. Dry in the oven
8. Coat Ti(EtO)₄
9. N₂
10. Magnetic stirrer
resulting titania coated plate was air-dried to evaporate methylene chloride. Then it was placed into an oven to calcinate. The temperature increases from room temperature to 450°C at the rate of 50°C/h and remained at 450 °C for 12 h. Finally the structure was cooled for characterization and photodegradation.

3.3 Characterization of Photonic Crystal

3.3.1 Scanning Electron Microscope

Scanning electron microscopy (SEM) is a valuable tool for probing the structure and morphology of material at the nanometer to micron length scale. Here we use the SEM to determine the type and orientation of the porous titania. Visual evidence of sample defects is also shown in the pictures.

Figure 3.2. Scanning electron microscope images of coated PS and the resulting porous titania. (A) 100 nm PS microspheres templates (B) x30K magnification of the PBG titania and (C) x45K magnification of the PBG titania synthesized using PS template. Scale bar is one micron for each.
The samples were mounted on a glass slide using colloidal graphite glue and coated with gold by sputtering. The coated samples were examined under SEM to obtain secondary electron images. SEM pictures were obtained on a Hitachi Instruments Model S-3600N. Figure 3.2 shows SEM images from the PS templates and the resulting macroporous titania generated on quartz plate. The image of the PS templates shows that the PS spheres are highly ordered except some defects on the surface. This results in the defects on the surface of macroporous titania. It is clear from the image that a highly ordered macroporous structure is obtained with pores of diameter about 100-150 nm, which can provide the photonic crystal titania with PBG which covers the UV range theoretically. This was confirmed by the UV transmission spectra of the sample.

3.3.2 X-Ray Diffraction

The refractive index of the titania in the samples is dependent on the particular crystalline phase. Titania has several polymorphic forms. Two phases relevant to the photonic materials are the anatase (n~2.52) and rutile (n~2.72) forms of titania, which have high refractive index. The rutile phase of titania needs very high temperature to synthesize. Usually the anatase titania was synthesized first and was calcinated at high temperature (usually higher than 1000°C) to transform to rutile. However, the high temperature would ruin the porous structure completely. So anatase titania is actually used in photonic crystal.

The particular phase was experimentally determined by X-ray diffraction (XRD). A Bruker-Siemens D5000 automated powder x-ray diffractometer with a Psi solid-state detector and Rietvald analysis software was used to obtain the XRD spectra of the sample. Some sample was scratched from the substrate and ground into powder. Then it was placed onto a plastic plate that was mounted onto the sample holder of the diffractometer. The phase of powder can best be distinguished by the presence of the diffraction peak at for the (101) crystalline anatase phase 2θ= 25.2°, or for (110) rutile at 2θ = 27.3°.
Figure 3.3. Powder XRD diffraction pattern of the synthesized anatase titania and the peaks of commercial anatase and rutile titania

Figure 3.3 shows the XRD spectrum of the sample of titania synthesized in our lab. The spectral features clearly reveal that the form of synthesized titania is indeed of the anatase form which has a refractive index of ~ 2.5. According to Wijnhoven and Vos, such a refractive index is necessary to achieve band gaps for the UV-visible spectrum.

3.3.3 UV Transmission

Photonic crystals (or PBG materials) have a spatially periodic structure fabricated from materials having different dielectric constants. These are capable of influencing electromagnetic waves in a similar manner to electrons in a semiconductor. In other words, photonic crystals exclude the passage of photons of a chosen range of frequencies thereby helping to confine, control and manipulate
photons in three dimensions. According to modified Bragg’s law (equation 3.1), by controlling the pore size in the photonic crystal, the band gap can take place at certain wavelength. The relationship between the band gap and pore size is described.

\[
\lambda_{\text{max}} = 2d_{111}\sqrt{n_{\text{eff}}^2 - \sin^2 \theta}
\]

\[
n_{\text{eff}} = n_{\text{TiO}_2} f + n_{\text{air}} (1 - f)
\]

where \(n_{\text{TiO}_2}\) and \(n_{\text{air}}\) are the refractive index of TiO\(_2\) and air respectively, \(f\) is TiO\(_2\) phase volume percentage. Usually \(f=0.74\) for fcc structure, \(d_{111}\) is associated with the pore size by equation 3.3

\[
d_{111} = \sqrt{\frac{2}{3}} D
\]

where, \(D\) is the distance between neighboring air spheres. Photonic band gap is an important optical property of photonic crystal. It determines the range of light frequencies, which will be prevented to propagate inside. This objective of this characterization is to show that the PBG is within UV range.

Two quartz sheets, one coated with PBG titania and a blank sheet without any coating, was used to obtain the UV transmission of the titania. First, the blank slide was used to get the baseline of the slide. Then the slide coated with PBG titania was exposed to UV light in a specially fitted sample holder. UV transmission was measured under scan mode between the wavelengths of 500 and 190 nm. Then the baseline of the slide was subtracted. Transmission spectra of the coated titania samples were collected to ascertain the wavelength of UV absorption by the photonic crystal titania coating using a HACH 4000 UV/Vis spectrophotometer. Photonic crystal titania were prepared with different PS size, 500nm, 60nm, and 120nm. The UV transmission spectra of photonic titania with 500 nm PS template shows that the PBG is beyond UV range and the spectra with 60 nm PS template shows that the PBG is less than UV range.

Figure 3.4 shows the UV transmission spectra of different coatings of titania on a quartz slide. The spectra from the PBG titania with 120 nm PS coating clearly shows a drop in transmission at
around 350 nm. Figure 3.4 also shows the transmission spectra from two other non-photonic crystal configurations: a) titania layer obtained using the sol-gel reaction without the polystyrene (PS) template and b) P25 titania obtained by dip-coating the slide in P25 titania powder solution. Both of them show low transmission for all wavelengths analyzed thereby not exhibiting the distinct band gap shown by the PBG titania layer. This clearly illustrates the band gap phenomenon within UV range for photonic crystal titania, thus causing UV light to be trapped within the PBG catalyst layer. The transmission spectra shown is not normalized to the thickness of the three samples because the primary objective was to look for the location of the band gap if there is one and absolute transmission values of the samples were not a matter of concern here.

Figure 3.4. UV Transmission spectra of photonic band gap titania and powdered titania.
3.4 Conclusions

The characterization of the synthesized inverse opal titania shows that it has the optical properties of photonic crystal and has a PBG within the UV range. SEM images show that it has 3-D macroporous structure and the pore size is between 100-150nm. The XRD diffraction of the powder shows the titania is in anatase phase, which has a relatively high photo activity and whose refractive index is high enough to produce a PBG within UV range. The PBG for the macroporous titania with 120nm PS template has a band gap in the UV range.
Chapter 4. Photodegradation on Inverse Opal Titania in a Batch Reactor

4.1 Introduction

Photocatalysis is the use of UV or visible light to activate catalysts such as semiconductors that can potentially oxidize organic and inorganic materials in air or water. The literature is replete with references to this technology in both laboratory and pilot-scale (Legrini et al, 1993; Mills et al, 1993). In most cases, titania in the powdered form is the preferred catalyst because it is cheap, easily available, and is not easily degraded. The application of UV light excites an electron from its valence band to the conduction band leaving a positive hole in the valence band. Both excited electrons and holes are capable of oxidizing adsorbed organic species. Titania can be doped with substances to make it useful even in the visible range of the light spectrum. In the design of photochemical reactors, the choice to immobilize powdered titania on solid supports is commonly used so that its recovery and reuse is facilitated. A number of volatile organic compounds have been subject to photooxidation using titania in various reactor types (Roberts et al, 2002; Hoffmann et al, 1995; Herrmann, 1999). However, the problem of low efficient photon utilization within the reactor still limits the use of this technology on a large scale (Ollis et al, 1989).

Photonic crystals (photonic band gap (PBG) materials) have a spatially periodic structure fabricated from materials having different dielectric constants (Ollis et al, 1993). They are capable of influencing electromagnetic waves in a similar manner to electrons in a semiconductor. In other words, photonic crystals exclude the passage of photons of a chosen range of frequencies thereby helping to confine, control and manipulate photons in three dimensions. A variety of templating procedures have been used to produce photonic crystals of titania (Linsebigler et al, 1995; Stafford et al, 1996; Mills et al, 1997; Pelizzetti et al, 1999; Fujishima et al, 2000). A number of investigators have produced systematic periodic structures of TiO2 crystals with air spheres filling the uniform voids using colloidal templates (Linsebigler et al, 1995; Pelizzetti et al, 1999; Fujishima et al, 2000). These photonic crystals possess high surface areas, offer a high refractive index contrast, and have optical
properties in the UV/visible wavelength region. These properties make them conducive for applications requiring high photonic efficiency. However, their use in photocatalytic applications has not been investigated thus far.

In this chapter, we report a proof-of-concept study of the application of PBG titania on the photocatalytic degradation of an air pollutant – 1,2-dichlorobenzene (DCB) vapor. The in-situ fabrication of the appropriate periodic structure of titania necessary for the band gap on a quartz glass rod support is described in Chapter 3. Experiments to examine the photocatalytic efficiency of the PBG titania were conducted in a tubular reactor with UV illumination. The effects of flow rate, temperature, UV intensity and moisture content on DCB degradation were explored. The degradation efficiency of a photonic band gap titania reactor is compared to that using a thin coat of P25 titania powder to illustrate the effect of the photonic band gap. The objective in this chapter is to demonstrate the relatively higher efficiency of inverse opal titania for photocatalysis and the effects of experimental conditions on its degradation rate.

4.2 Experimental

The fabrication and the characterization (SEM, XRD, UV-transmission) of photonic band gap TiO2 was described in details in chapter 3. SEM images show the periodic structure of in-situ PBG catalyst. The XRD spectra show that the phase of in-situ TiO2 catalyst is anatase, which has relatively high refractive index. The UV transmission spectra illustrate the photonic band gap within the UV range for the in-situ catalyst. Therefore, the in-situ catalyst fabricated with 120 nm polystyrene has the properties of anatase TiO2 with photonic band gap structure.

4.2.1 Materials

1,2-dichlorobenzene (DCB) of 98% purity was obtained from EM Sciences, Gibbstown, NJ. Powered titania (P25) donated from Degussa Corporation, Akron, PA was used as the photocatalyst. The TiO2 crystallites had a mean surface area of 60-70 m² g⁻¹, a mean particle diameter of 20 nm and the point of zero charge at a pH of 6.8. DI water was obtained from the Mega-Pure System
manufactured by Barnstead company. Titanium (IV) ethoxide purchased from Aldrich was used as titanium precursor. Anhydrous ethyl alcohol purchased from EMD was used to sol-gel reaction. Quartz rod (3mm in diameter) was used as the substance for supporting catalyst. Sandpaper (Norton) was used to roughen the rod surface. Hexane from EMD used to absorb gaseous DCB was measured by GC/MS.

4.2.2 Reactor Setup

![Figure 4.1. A schematic of the reactor set-up used for photocatalytic degradation of 1,2-dichlorobenzene vapor, the inset on the right-top corner is a draft of the cross section of quartz rod coated with PBG TiO2.](image)

The experimental assembly for the photoreaction of 1,2-dichlorobenzene is shown in Figure 4.1. The reactor system consisted of a glass quartz tube (11 cm in length, 1.2 cm in diameter). The PBG titania-coated glass rod was placed in the middle of the tube. The inset on top right in Figure 4.1 is a schematic of the cross section of the coated glass rod with PBG TiO2. The gas flow was introduced from the inlet at the bottom of the quartz tube by a mini air-pump and flowed out from the
exit of the quartz tube. Two UV lamps (Model XX-15L UVP Inc., Upland, CA) placed on either side of the reactor supplied the necessary UV light (with $300 < \lambda < 380$ nm) for the reaction. The lateral position of the UV lamps on either side of the reactor tube could be varied to obtain different UV light intensities incident on the reactor. The light intensity was measured by a UVX-36 radiometer (UVP Inc., Upland, CA). The entire reactor assembly was placed inside a temperature-controlled stainless box so that the reaction can be carried out at different temperatures. The box could also eliminate the damage of UV light to the surrounding by covering the UV source inside. The temperature of the reactor was measured and controlled by a J-Kem temperature controller. When the temperature measured is below the set temperature, the controller would turn on the heater until the temperature reached the set point.

The reaction was designed to be operated in a semi-batch (recirculating) mode. A known volume (77mL) of DCB vapor at a selected initial concentration (about 200ppm) was recirculated through the reactor for a given length of time using a mini air-pump. Pure DCB vapor was generated outside the insulated box from small volume (~10 mL) of pure liquid DCB in a gas bubbler, through which air was recirculated. An empty bubbler was placed immediately after the bubbler vapor exit in order to minimize any entrained liquid DCB from entering the reaction system. DCB vapor was sampled through a gas-tight sampling port by a liquid sealed syringe. The sampled gas was sealed by hexane liquid at both sides of the syringe. The volume of the sample gas was the difference of the reading at both sides. Then the sample was injected into the hexane liquid and stored for analysis. The DCB sample in hexane was analyzed by a gas chromatograph/ mass spectrometer. The detail of the GC/MS method was given in the following section. When the desired initial concentration of DCB in the vapor phase was achieved, the DCB vapor was switched to a loop that by-passed the vapor generator tube with the pure DCB liquid and the empty tube. To measure the effect of moisture on the photoreaction, the pure DCB liquid in the vapor generator was covered by a layer of DI water. When the DCB vapor was generated, the flow passed the water layer to increase the water vapor pressure in
the flow. A thermohygrometer was connected to the system immediately after the empty bubbler to measure relative humidity (water vapor content).

4.2.3 DCB Analysis

DCB solution adsorbed in hexane was analyzed using a gas chromatography/mass spectrometer (Agilent GC Model HP 6890 with HP 5973 MS detector). The GC column used for analysis was Agilent 19091s-433 or HP-5MS (30m × 0.25mm × 0.25μm). The column temperature was initially set to 70 °C and increases at 15 °C.min⁻¹ to 270 °C and held for 7 minutes. Then the temperature was increased at the same rate until 300 °C. Before injection, solvent hexane was used to wash the syringe three times. The flow rate was set at 54.4 mL.min⁻¹. The injection pulse pressure was 25 psi until 0.25m. The purge flow to split vent was 50mL.min⁻¹ @ 1.00m. Figure 4.2 shows the GC/MS spectra of DCB in hexane analyzed by our current method.

![GC/MS spectrum of DCB](image)

Figure 4.2. Typical GC/MS spectrum of DCB by our method

4.3 Experimental Results and Discussion

The well known Langmuir-Hinshelwood mechanism for photodegradation on titania is given by equation (4.1).
\[ -r = \frac{kK C_S}{1+KC_S} \]  

(4.1)

where, \( k \) is the intrinsic surface reaction rate constant (mol.L\(^{-1}\).min\(^{-1}\)), \( K \) is the Langmuir-Hinshelwood adsorption constant (L.mol\(^{-1}\)), \(-r\) is the reaction rate, \( C_S \) is the concentration near to the surface. For 1,2-DCB, the value of Langmuir-Hinshelwood (L-H) constant is about 2700 L.mol\(^{-1}\). So consider the low concentration in our case, the \( KC_S \) term is relatively lower than 1. Therefore, the L-H model can be simplified to first-order reaction

\[ -r = kKC_S \]  

(4.2)

At steady state, the overall mass balance on the catalyst is shown below:

\[ k_m a_v (C - C_S) = kKC_S \]  

(4.3)

where, where \( k \) is the intrinsic surface reaction rate constant (mol. L\(^{-1}\). min\(^{-1}\)), \( K \) is the Langmuir-Hinshelwood adsorption constant (L.mol\(^{-1}\)), \( k_m \) is the mass transfer coefficient (cm.min\(^{-1}\)) and \( a_v \) is the surface area of PBG titania per unit volume of the reactor (cm\(^2\).cm\(^{-3}\)). After rearranging equation (4.1) and (4.2),

\[ -r = kK \frac{k_m a_v C}{k_m a_v + kK} = k^* C \]  

(4.4)

Where, \( k^* \) is the pseudo first-order rate constant (min\(^{-1}\)). The pseudo first-order rate constant is composed of two factors, the reaction at the surface and the mass transfer of the vapor toward the catalyst surface (Sauer et al, 1994).

\[ \frac{1}{k^*} = \frac{1}{k_m a_v} + \frac{1}{kK} \]  

(4.5)

By integrating equation (4.4), the concentration declined with time went on. The concentration is expressed in equation (4.6)

\[ \frac{C(t)}{C_0} = \exp(-k^*t) \]  

(4.6)

Where \( C_0 \) is the initial concentration.
4.3.1 Radiant Flux Intensity

Radiant flux intensity is always an important parameter in photoreaction through photocatalyst since the intensity affects the number of active sites on the catalyst. The kinetic expression is the Langmuir-Hinshelwood model. When UV radiant flux is high, the surface of the active catalyst will provide more excited holes and electrons. The photoreaction would be faster. Also the effect of radiant flux depends on the concentration of absorbed reactants on surface. It was confirmed that for all photochemical reactions the rate is linear to the radiant flux up to a certain value. The effect of UV intensity would be first-order. Above that value, the rate dependency would decrease from a first-order to a lower order (Galvez et al, 2001). The transition value depends on the chemical compound, the catalyst and reactor configuration.

When the reactant concentration is higher, the adsorbed reactant concentration on the surface is higher. Thus, the overall reaction rate may depend on radiant flux rather than the mass transfer. Therefore, the kinetic rate expression becomes first-order reaction of the intensity and pseudo zero-order of reactant concentration. On the other hand, when the concentration is very low and the intensity is high, the external mass transfer would affect the overall reaction rate significantly. The effect of radiant flux might not be significant so that the kinetic rate expression becomes a pseudo-zero order on radiant flux and first-order of reactant concentration. Exclusive those two extreme conditions, both the UV intensity and the concentration would affect the reaction rate together.

The UV intensity was varied by changing the distance between the lamps and the reactor. Figure 4.3 shows the effect of radiant flux intensity at the reactor wall upon the overall degradation of DCB vapor from the air stream. The initial DCB concentration is about 200ppm. It is obvious that the DCB concentration declined with the increase of irradiation time. A blank experiment (control experiment) without UV irradiation was done to illustrate photoreaction of DCB in dark. It is clear that for the control experiment in the absence of the UV light the reaction is negligible. And the other experiments under UV irradiation showed significant degradation. This clearly demonstrates that the
in-situ photonic band-gap titania is photoactive in the UV wavelength range. Thus, it can be concluded that the rate of a photochemical reaction is generally proportional to radiant flux at low values up to \( \approx 25 \text{ mW.cm}^{-2} \), beyond which it is only proportional to the square root of the radiant flux [4] as has been noted for powdered titania [17]. In our study, the PBG titania shows a discrepancy in this respect and the rate constant is proportional to the radiant flux intensity even at intensities higher than 25 mW.cm\(^{-2}\).

**UV Intensity Effect**

![Graph showing the effect of UV radiant flux intensity on the degradation of DCB on inverse opal titania at 324K and 436mL.min\(^{-1}\) and relative humidity=50% at room temperature.]

**Figure 4.3.** Effect of UV radiant flux intensity on the degradation of DCB on inverse opal titania at 324K and 436mL.min\(^{-1}\) and relative humidity=50% at room temperature.

**Table 4.1.** The fitted reaction rate coefficient at first-order reaction assumption

<table>
<thead>
<tr>
<th>UV intensity /mW.cm(^{-2})</th>
<th>( k^* / \text{min}^{-1} )</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>66</td>
<td>0.0023 ± 0.00012</td>
<td>0.983</td>
</tr>
<tr>
<td>114</td>
<td>0.0038 ± 0.00041</td>
<td>0.926</td>
</tr>
</tbody>
</table>
The pseudo first-order rate constant, $k^*$, was obtained by fitting equation (4.6) for each UV intensity. The fitted rates were shown in 4.1. When UV intensity is 114 mW.cm$^{-2}$, the reaction rate coefficient is 0.0038 min$^{-1}$, which is much higher than the rate constant at 66 mW.cm$^{-2}$. This means that the reaction rate depends on the radiant flux very much at our experimental conditions and reactor configuration.

4.3.2 Effects of Mass Transfer

As mentioned in equation (4.5), the mass transfer of reactant might significantly affect the reaction rate. If the mass transfer part, $k_m a_v$, is dominant compared with the reaction part, $kK$, then the superficial reaction rate would depend on the mass transfer. Equation (4.5) would be simplified to

$$k^* = k_m a_v \tag{4.7}$$

If the reaction portion is dominant compared with the mass transfer portion, equation (4.5) would be simplified to

$$k^* = kK \tag{4.8}$$

In this chapter, we just do several experiments on the effect of flow rate. Figure 4.4 shows effect of flow rate at our experimental condition range. For our present case, the gas flow rate was found to have minimal effect on the overall rate coefficient (table 4.2).

<table>
<thead>
<tr>
<th>Flow rate / mL.min$^{-1}$</th>
<th>k* / min$^{-1}$</th>
<th>R$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>186</td>
<td>0.0018 ± 0.0003</td>
<td>0.937</td>
</tr>
<tr>
<td>436</td>
<td>0.0023 ± 0.0002</td>
<td>0.852</td>
</tr>
</tbody>
</table>

*experimental conditions: 53°C, 66mW.cm$^{-2}$, saturated water
4.3.3 Effects of Water Vapor Pressure

Water vapor pressure in the stream easily condenses on the surface of catalyst. It would compete efficiently with DCB for the adsorption sites on the surface. Once there is a layer of condensed water on the surface of the catalyst, the mass transfer of DCB and the oxidant (O₂) from the bulk to the active sites will be limited. Also the availability of the active sites for DCB and oxygen will decrease. So increase of water vapor pressure in the stream would decrease the photoreaction. Figure 4.5 shows that the saturated DCB stream significantly decreases the degradation under our experimental conditions by about 26% compared with the stream with dry stream (table 4.3).
Figure 4.5. Water vapor effects on DCB photodegradation at 326K, 436mL.min\(^{-1}\), 66mW.cm\(^{-2}\)

Table 4.3 The fitted model for first-order reaction for moisture effect

<table>
<thead>
<tr>
<th>moisture</th>
<th>k* / min(^{-1})</th>
<th>R(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saturation at 25°C</td>
<td>0.0023±0.0003</td>
<td>0.9824</td>
</tr>
<tr>
<td>Dry</td>
<td>0.0031±0.0003</td>
<td>0.9455</td>
</tr>
</tbody>
</table>

* Experimental conditions: 324K, 436mL.min\(^{-1}\), 66mW.cm\(^{-2}\)

4.3.4 Effects of Temperature

The effect of temperature on catalytic reaction is relatively complicated. Increasing temperature will decrease the adsorption of reactant on the catalyst surface. However, it will accelerate the surface reaction. The delineation of those two steps was not attempted in this chapter.
Temperature Effect

Figure 4.6. Temperature effects on DCB degradation at 436mL.min\(^{-1}\), 66mW.cm\(^{-2}\) and dry air

In this part, we only show the overall effect of temperature on both steps. Figure 4.6 shows that higher temperature will have faster degradation rate of DCB under our experimental conditions. The rate constant increases from 0.0017 min\(^{-1}\) at 303 K to 0.0031 min\(^{-1}\) at 324 K. A plot of \(\ln k^*\) versus \(1/T\) gives the following equation for the temperature dependence:

\[
\ln(k^*/\text{min}^{-1}) = -\frac{2950K}{T} + 3.24 \quad \text{with} \quad (R^2=0.956) \tag{4.9}
\]

Table 4.4. The fitted first-order reaction for the temperature effect

<table>
<thead>
<tr>
<th>Temperature</th>
<th>(k^*/\text{min}^{-1})</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>51°C</td>
<td>0.0031±0.0002</td>
<td>0.9602</td>
</tr>
<tr>
<td>43°C</td>
<td>0.0028±0.0006</td>
<td>0.9745</td>
</tr>
<tr>
<td>30°C</td>
<td>0.0017±0.0001</td>
<td>0.987</td>
</tr>
</tbody>
</table>

*Experimental conditions: 436mL.min\(^{-1}\), dry gas, 66mW.cm\(^{-2}\)
4.3.5 Comparison between P25 and PBG TiO2

P-25 titania is a commercially available form of anatase titania (from Degussa Corporation) that has been frequently used in fixed film titania photocatalysis applications and also as a reference sample to compare the relative photonic efficiency of any synthesized titania sample. In the present work, a P-25 titania coating on the glass rod was achieved by a dip-coating method described previously from our laboratory and used in the reactor set-up described in this work. Comparison was done under same UV light intensity, relative humidity, vapor flow rate, temperature, initial DCB concentration, and catalyst thickness. Figure 4.7 is the rate of change of DCB in the air in the two cases as a function of time. Significant improvement in the overall rate constant was observed with PBG titania.

![Figure 4.7](image_url)

Figure 4.7. Comparison of the first order degradation rate of DCB in the semi-batch reactor using P25 titania powder and PBG titania on the quartz glass rod.

The initial photonic efficiencies were calculated as

\[
\xi = \frac{r_{DCB}^0 \text{ (mol.m}^{-3}.s^{-1})}{I_0 \text{ (Einstein.m}^{-3}.s^{-1})}
\]  

(4.10)
where \( r^0_{\text{DCB}} \) is the initial reaction rate and \( I_0 \) is the incident photon flow per unit volume of reactor (\( I_0 = 0.16 \text{ Einstein.m}^{-3}.\text{s}^{-1} \)) determined by radiometric measurements as described in the experimental section. The value of \( \xi \) obtained were \( 1.6 \times 10^{-5} \text{ mole.Einstein}^{-1} \) for PBG titania and \( 4.6 \times 10^{-6} \text{ mole.Einstein}^{-1} \) for P25 titania. Thus, a 248% increase in the photonic efficiency was observed for the PBG crystal in this work. From SEM images of the cross-sections of the coated quartz rods, the average thickness of the photonic crystal titania layer on the quartz rod was estimated to be 2 µm, while that of the P25 titania layer was 4 µm. This implied that on the basis of either film thickness or catalyst mass, the PBG titania exhibits higher photonic efficiency and is therefore a more efficient photocatalyst. The effectiveness of the photonic crystal titania in a larger scale multichannel monolith reactor is currently being investigated in our laboratory.

Table 4.5. Comparison of the efficiency between PBG catalyst and P25 titania layer

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>( k^* / \text{min}^{-1} )</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>P25 titania layer</td>
<td>0.0013±0.0001</td>
<td>0.926</td>
</tr>
<tr>
<td>PBG TiO2</td>
<td>0.0037±0.0003</td>
<td>0.943</td>
</tr>
</tbody>
</table>

4.4 Conclusions

This chapter showed that the PBG TiO2 is photoactive under UV illumination. The effects of UV intensity, flow rate, moisture, and temperature, are studied thoroughly. Increase of UV intensity and temperature will significantly enhance the photoreaction of DCB. Saturated gas will decrease the reaction rate. The PBG TiO2 catalyst significantly increased the efficiency of photodegradation compared to the commercial P25 titania layer under similar experimental conditions.
Chapter 5. Development of a Monolithic Optical Fiber Reactor for Photocatalysis in Gas

5.1 Introduction

The selection of an appropriate reactor configuration for catalysis is of utmost importance in a large-scale reactor to provide a large amount of activated photocatalyst per unit volume. The majority of photocatalytic reactors, which is a variation of the annular or tubular reactors, have several drawbacks such as low light utilization efficiency due to the absorption and scattering of the light and the restricted processing capability due to mass transport limitations.

In order to meet this reactor design challenge, a novel approach to solving these problems by employing optical fibers as a means of light transmission and substrate of catalyst was first proposed by Ollis and Marinangeli (1977, 1980, 1982). Experimental application of the idea was demonstrated by Hofstadler et al. (1994) who designed a TiO2-coated quartz fiber reactor and used it to carry out the oxidation of 4-chlorophenol. Peill and Hoffmann (1995, 1996, 1998) developed, characterized, and modeled an optical fiber reactor (OFR) system for photomineralization of pentachlorophenol, 4-chlorophenol, dichloroacetate, and oxalate in water. Similar OFR systems were easily devised to oxidate gaseous organic pollutants such as benzene or acetone in air streams (Choi et al, 2001; Lin et al, 2005). The OFR system enhances the uniformity and distribution of the UV light and thus can be used for the in-situ treatment of contaminated sites in the environment. However, immobilization of TiO2 on an optical fiber also has its own problems. In an OFR system, since the contaminants diffusion direction is opposite to the light transmission direction, the excited electrons and holes are generated relatively far from the flow-catalyst interface and, consequently, are more susceptible to recombination loss (Choi et al, 2001). Another drawback of an OFR reactor is that the configuration does not effectively utilize the entire reactor volume. Considering that the optical fiber is very thin, the OFR could provide very low surface area. Also to efficiently utilize the reactor volume, the OFR should be very small. All those drawbacks limit the OFR to laboratory-scale.
On the other hand, a multi-channel monolithic optical fiber reactor (MOFR) was suggested by Lin et al (2005). The whole MOFR consists of a lot of OFR and utilizes the reactor volume more efficiently and provides a larger surface area than OFR. Another advantage of MOFR is that the reactor can be scaled up to a relative larger volume reactor, which makes it more useful. However, MOFR still has some drawbacks. The light transmission within the fiber is limited to the range within several centimeters. Beyond that, the catalyst on the fiber was not fully utilized in the oxidation. Therefore the efficiency of MOFR is still relatively low. Because optical fibers are inserted in a small channel, it is not easy to uninstall the reactor once it is constructed. This disadvantage also limits the replacement of optical fibers once some fibers were broken. Titania loses some of its activity and surface area when it is coated on surfaces. Also, because of the so-called “shadow effect”, most of the titania surface will be unavailable for UV illumination (Kakimoto et al, 1999).

In chapter 4, the inverse opal catalyst was proven to have higher efficiency than conventional catalyst. In this chapter, a monolithic optical fiber reactor (MOFR) with inverse opal TiO2 catalyst coated on the fibers, which combine the advantage of MOFR and inverse opal catalyst, was constructed and tested to provide relative large surface area and more efficient light transmission. In this configuration, stripped optical fibers, which allow UV light to radially refract out of the fibers, were used as both light distributors and support for photocatalysts. Inverse opal TiO2 catalyst coated on fibers shows a photonic band gap, which controls the light transmission and increases the surface area due to its porous property. Thus, a higher overall reaction efficiency can be reached. 1,2-dichlorobenzene (DCB) is selected as the model contaminant in air as we did in our preliminary work (Ren et al, 2006). Experiments were performed under conditions that were relevant to the evaluation MOFR with inverse opal titania.
5.2 Experimental

5.2.1 Materials

1,2-dichlorobenzene (DCB) of 98% purity was obtained from EM Sciences, Gibbstown, NJ. Powered titania (P25) donated from Degussa Corporation, Akron, PA was used as the photocatalyst. The TiO2 crystallites had a mean surface area of 60-70 m² g⁻¹, a mean particle diameter of 20 nm and the point of zero charge at a pH of 6.8. DI water was obtained from the Mega-Pure System manufactured by Barnstead company. Titanium (IV) ethoxide purchased from Aldrich was used as titanium precursor. Anhydrous ethyl alcohol purchased from EMD was used to sol-gel reaction. Optical fibers (1mm in diameter, FT1.0 UMT) were purchased from ThorLabs Inc. Sandpaper (Norton) was used to roughen the rod surface. Hexane from EMD used to absorb gaseous DCB was measured by GC/MS.

5.2.2 Monolithic Optical Fiber Reactor

The methodology used for fabrication of photonic band gap titania on an optical fiber substrate was that employed by Colvin and co-workers (Peng et al, 2001; Colvin et al, 2002). The detail was described in chapter 3 and 4.

Figure 5.1. The schematic of monolith optical fiber reactor.

Figure 5.1 illustrates a schematic of the MOFR utilized in our experiment. Twelve optical fibers with photonic TiO2 were bundled together and distributed evenly in the reactor using a distributor plate at the bottom. The evenly distributed fibers in the distributor were inserted in a quartz
tube (0.7cm inner diameter, 30 cm in length) and sealed to form the monolith reactor. The light will be allowed to radiate from the end without distributor.

5.2.3 MOFR Setup in Gaseous System

The MOFR was installed into the experimental setup in figure 5.2. The whole setup includes the MOFR, a light source, pollutant source (bubbler), flowmeter, sampling section and an air pump. The end of the reactor without distributor was connected to the equipment providing UV light. So the light can not only transmit within the fiber core but illuminate on the surface directly to enhance the adsorption of photons. Thus more light can be used in the experiment. The UV lamp, Osram XBO W/H, was obtained from Spectral Energy Corporation, NY. Light was delivered to the fiber optic bundle from the UV light source, through a collimator, a reflecting mirror, a UV band pass filter (310-380 nm), a condenser lens and finally focused on the fiber optic. The incident angle is adjusted at 85°.

![Cross section of coated fiber](image)

Figure 5.2. A schematic of MOFR setup in gaseous system
The sampling section was set before the inlet of the MOFR. It contains a septum with Teflon coating to prevent the possible leakage. And no leakage at the sampling section was detected. Airtight syringes were used to take samples. To observe the volume of the sample more accurately, those samples was sealed by hexane within the syringe at both ends. In order to avoid the possibility of liquid DCB into the system, two bubblers were used in the system, the smaller one with pure DCB liquid and the larger one empty. When the air passes the bubbler with pure DCB, it passes the bigger empty bubbler immediately to remove the possible liquid DCB in the flow. The energy of the flow was provided with a small air pump.

After ascertaining that there were no leaks in the system, the pump was turned on introducing DCB vapor. Before introducing DCB vapor, the system was purged by fresh air. Once the concentration in the vapor generator reached 4000-5000ppb, the vapor generator was switched off and the flow directed to the reactor recirculation system. A steady concentration of DCB in the vapor was reached via recirculation without UV light. Once steady state was assured, the power supply to the UV lamp was turned on and the reaction was allowed to occur. Samples of DCB were taken from the recirculation loop using a gas-tight syringe and injected into 1mL hexane. A gas chromatograph (Model HP 6890 Series) with a mass selective detector (MS 5973) manufactured by Agilent was used to analyze DCB in the hexane. To test the whole mass balance, another loop was added to absorb the product after reaction. Two bubblers were used, one with NaOH solution to adsorb inorganic products (HCl) and the other with hexane to absorb organic products of reaction. The vapor stream from the reactor was allowed to go through them sequentially and the resulting solutions from the bubblers were analyzed.

5.2.4 Methodology and Analysis

DCB in hexane was analyzed by a Hewlett-Packard gas chromatograph/mass spectrometer (Model HP 6890) with a mass selective detector (HP 5973). A glass capillary column (60 m long, 0.53 mm I.D.) coated with SPB-20 was obtained from Supelco Inc. The oven temperature was set at 70°C
initially, with a temperature ramp of $6^\circ \text{C. min}^{-1}$ to a final temperature of $100^\circ \text{C}$. The injector temperature was $180^\circ \text{C}$ and the detector temperature was also $180^\circ \text{C}$. The carrier gas was helium at 0.565 ml min$^{-1}$. Compound identification was done using the NBS mass spectral library. Chloride analysis was accomplished using a standard argentometric titration method [16].

5.3 Results and Discussion

5.3.1 Catalyst Properties

Figure 5.3. SEM images: (a) the SEM image of coated polystyrene template on the fiber, (b) the inverse opal titania on the fiber. Note the difference in scale.

Figure 5.3 (a) shows the SEM of the polystyrene template on optical fiber surface. The thickness of the template coating is about 3 $\mu$m. It shows clearly the homogeneous packing of the spherical PS particles (120 nm) with some minor imperfections. Figure 5.3 (b) shows the ordered macroporous photonic titania structure obtained on the template. As can be seen the photonic structure is not as well ordered as the template from which it is formed. This is due to the fact that the hydrolysis reaction to form titania within the template occurs on a tiny cylindrical fiber. As we have noted before, the difficulty of controlling removal rate of the template makes the hollow inverse opal photonic titania structure somewhat less ordered than the template from which it originated. Nevertheless, the mean diameter of the macropores is 100-200 nm. The porous structure of the material was clear and the air voids occupied those spaces originally occupied by the PS spheres. The
successive layers of air spheres were visible in some of the SEM images suggesting an interconnected 3-dimensional network of photonic titania. The template thickness on the fiber was approximately 3 \( \mu \text{m} \) and the PBG titania thickness was approximately 2 \( \mu \text{m} \). That showed considerable shrinkage of the template during the hydrolysis, condensation and calcinations.

The XRD spectrum of titania obtained by this templating procedure indicated (101) crystalline anatase phase. The refractive index of this material is near 2.5 which is necessary to achieve band gaps for the UV-visible spectrum (Wijnhoven et al, 1998). Figure 5.4 shows the UV transmission spectra for photonic band gap titania made from various size templates and P25. The transmission spectrum for the 220 nm PS template shows a sharp stop band gas at 540 nm, whereas that for the 120 nm PS template shows a broad band gap between 200 and 300 nm, and only an indication of increased transmission below 200 nm. However, that of P25 shows low UV transmission within the range 200 nm-500 nm. Clearly the photon localization for the 120 nm PS template overlaps the electronic excitation wavelength for anatase titania. Thus, we confirm that the material we prepared are indeed photonic band gap materials. The optical spectrum of the 120 nm and 220 nm template show Bragg diffraction. With increasing template size, the stop-band gap red-shits, but the transmission in the dip becomes narrower. The calculated bad gap position agrees fairly well with the observed center of band gap.

However, we noted relatively large differences in the optical responses of the crystal as the PS size decreased possibly as a result of structural disorders. Also shown for comparison is the UV transmission spectrum obtained from conventional powdered titania P25 (non-photonic configuration) coated on the film. The low transmission for all wavelengths and the fact that there is no jump in UV transmission show the non-photonic nature of the P25. It is known that the inverse opal titania has a transparent window in the visible range, but in the anatase form it exhibits a broad stop band gap, not a full band gap (Stein et la, 2001).
5.3.2 Kinetics of Photodegradation of DCB

The photocatalytic degradation rate of DCB depends on the concentration of adsorbed reactant on the catalyst and could be explained by Langmuir-Hinshelwood kinetics (Lin et al, 2002, 2003). The reactor was operated in a semi-batch mode with recirculation of the gas stream through the reactor. The overall rate of disappearance of DCB from the gas stream is given by the following equation (Lin et al, 2005; Ren et al, 2006)

\[
\frac{C(t)}{C_0} = \exp(-k^* t)
\]  

(5.1)

where \(C(t)\) is the concentration at any time \(t\) relative to the initial concentration \(C_0\). The first order rate constant, \(k^*\) is composed of two terms (Lin et al, 2005)

\[
\frac{1}{k^*} = \frac{1}{k_m a_v} + \frac{1}{kK}
\]  

(5.2)

where each term on the right hand side represents a resistance. The term \(1/k_m a_v\) is the mass transfer diffusion resistance and \(1/kK\) is the intrinsic reaction resistance. By determining \(C(t)/C_0\) as a function
of time and fitting the data to Equation (5.1) above we can obtain the overall rate constant, $k^*$. Figure 5.5 shows the result of one experiment and the fitted 1st-order reaction curve based on equation (5.1).

Figure 5.5. Photodegradation of DCB in a typical semi-batch recirculating mode: $I_{UV}=36.70 \text{mW.cm}^{-2}$, flow rate=$100 \text{mL.min}^{-1}$

5.3.3 Effects of PS Template Pore Size

The PS template size determines the photonic band gap for titania. This will also determine the overall porosity of the PBG titania. Early experiments have shown that the UV absorption bands vary non-linearly with template size (Manoharan et al, 2001). In general, the degradation of DCB will improve when the photons are efficiently utilized by the titania. Therefore, an even distribution of the photons within the photonic band gap will result in a higher reaction rate constant. The dependence of 1,2-dichlorobenzene degradation on the pore size of the template used is shown in Table 5.1. The overall rate constant is 0.0145 min$^{-1}$ for the 120 nm PS templated titania when UV intensity is 40 mW.cm$^{-2}$. The conversion of 1,2-DCB with 120 nm PS is 1.8 times greater than that with 500 nm PS within the range of 20-120 mW/cm$^2$ under the same experimental conditions. This is presumably
caused by the improved transmission capability within the porous TiO\textsubscript{2} due to the enhancement of “slow photon” intensity on the red-edge of the photon stop gap (Chen et al, 2006, 2007). A significant portion of the improvement may also be caused by a reduction in light scattering associated with the regularity of the photonic titania pore structure. As shown in Figure 7.4(b), the photonic band-gap of 120nm pore size lies within the electronic band-gap of anatase titania, while that of 500 nm is believed to be out of that range. Hence, we conclude that most of the photons will be utilized efficiently in the case of the inverse opal created using the 120 nm PS template.

Table 5.1. Effects of PS sphere size on degradation rate

<table>
<thead>
<tr>
<th>Pore size</th>
<th>k*/ min(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>500nm</td>
<td>0.00818</td>
</tr>
<tr>
<td>120nm</td>
<td>0.0145</td>
</tr>
</tbody>
</table>

*Experimental condition: \(I_{UV}=57\) mW.cm\(^{-2}\), flow rate=77mL.min\(^{-1}\)

5.3.4 Effects of Flow Rate

Flow rate affects the overall removal efficiency as shown in Figure 5.6. Clearly there are two regimes – up to about 50 mL.min\(^{-1}\), the rate constant increases linearly with flow rate and reaches an asymptotic limit of 0.8 h\(^{-1}\) at higher flow rates. After that, the increase becomes slower. The result can be explained by equation (5.2). At a low flow a rate (superficial velocity), the reaction is within mass-transfer controlled regime so the diffusion of DCB to the porous photonic titania determines the rate. In this regime the mass transfer rate can be improved by increasing the flow rate. At high flow rates, the rate is limited by the rate of surface reaction on the catalyst surface and becomes less dependent on mass transfer.

In addition to the flow rate, the primary macroscopic design variables for the multiple optical fiber reactor include the length and diameter of the fiber optic cables and their number and spacing. The inlet air flow will be through the pores in the inverse opal film and in the spaces between the individual optical fiber within the monolith. The configuration and distribution of the monolithic fiber arrangement inside the reactor will determine the cross sectional area for flow between the optical
fibers within the monolith. This will influence the overall flow pattern and interstitial velocity inside the voids and this can also vary with flow rate.

Figure 5.6. Flow rate effects on the reaction rate constant, experimental conditions: UV intensity 36.7mW.cm$^{-2}$

Figure 5.7. Cross section of MOFR: the left panel is the schematic of our MOFR; the right one shows the schematic after adding four smaller fibers to our MOFR
We first conducted a CFD simulation of the flow pattern by solving the equations for flow. The cross section of the reactor is showed in figure 5.7. The left panel of figure 5.7 shows the cross section of the MOFR in our experiment. The green part is the channel for stream. The twelve white circles represent optical fibers with catalyst layer. The flow direction is vertical to the cross section. As we can see that there are some big spaces within the stream channel (four corners). The flow rate at that corner will be much faster than that next to the fibers. Considering there is no catalyst around, the bypass will decrease the efficiency of MOFR. In order to minimize the bypass effect on the removal efficiency, we insert four optical fibers with smaller diameter (0.8mm) as shown in the right panel of figure 5.7. Those smaller fibers will redistribute the flow within the MOFR and increase the velocity next to the fibers. Therefore, the mass transfer next to the catalyst will be faster and removal efficiency of MOFR per pass will increase.

Since there is no velocity within the cross section, the continuous equation (equation 5.3) can be simplified by equation 5.4 to equation 5.5 (the stream flows along z direction).

\[
\frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y} + \frac{\partial u_z}{\partial z} = 0 \tag{5.3}
\]

\[
\frac{\partial u_x}{\partial x} = 0, \quad \frac{\partial u_y}{\partial y} = 0 \tag{5.4}
\]

\[
\frac{\partial u_z}{\partial z} = 0 \tag{5.5}
\]

The momentum equation in the z direction is described by equation 5.6.

\[
\frac{\partial u_z}{\partial \theta} + u_x \frac{\partial u_z}{\partial x} + u_y \frac{\partial u_z}{\partial y} + u_z \frac{\partial u_z}{\partial z} = g \frac{1}{\rho} \frac{dP}{dz} + \mu \left( \frac{\partial^2 u_z}{\partial x^2} + \frac{\partial^2 u_z}{\partial y^2} + \frac{\partial^2 u_z}{\partial z^2} \right) \tag{5.6}
\]

There are some assumptions to the flow in our MOFR.

1. Assume steady state. \( \frac{\partial u_z}{\partial \theta} = 0 \)
2. Assume that there is only flow in the \( z \) direction. So \( u_x = 0, u_y = 0 \)

3. The gravity effect can be neglected for the gas system

4. \( \frac{\partial u_z}{\partial z} = 0, \frac{\partial^2 u_z}{\partial z^2} = 0 \)

Those assumptions combined with equation 5.5 simplify equation 5.6 to equation 5.7.

\[
\frac{\partial^2 u_z}{\partial x^2} + \frac{\partial^2 u_z}{\partial y^2} = \frac{1}{\mu} \frac{dP}{dz}
\]  \( (5.7) \)

The boundary conditions for the configuration of MOFR:

1. The velocity on the surface of the fiber and the quartz tube is zero;

2. The integration of velocity in \( z \) direction over the whole cross section is equal to the actual flow rate, which is \( \iint_{\text{crosssection}} u_z = Q \)

MATLAB was used to solve the partial differentiation equation. The results are given in Figure 5.8. From figure 5.8 (a), we observed that flow bypassing occurs within the reactor which can decrease the efficiency. The velocity at the four corners is much faster than the other area. Inserting four smaller fibers decreased the bypassing and increased the velocity closer to the fibers in the reactor. Thus, the diffusion of DCB becomes fast and so does the reaction. Figure 5.8 (b) presents the velocity distribution within MOFR after four additional fibers (0.8 mm) are inserted. The velocity distribution is more homogeneous. The velocity next to the fibers is much faster than that with bypassing when the overall flow rate is the same. In order to support the CFD simulation, we carried out the reaction by inserting 4 fibers into the reactor to rectify the flow bypassing. Thus, for the initial experiments where only 12 fibers of 1 mm diameter each were used (Figure 5.8 (a)), we inserted four additional fibers of 0.8 mm each where flow bypassing was noted (Figure 5.8 (b)). The DCB degradation rate constant in the two cases is presented in Table 5.2. We observed an increase of 25% in the rate constant in the second case.
Figure 5.8. Velocity distributions within the MOFR; (a) with only 12 1mm fibers evenly distributed, (b) With four additional 0.8 mm diameter fibers inserted to block flow bypassing.
Table 5.2 Effects of velocity maldistribution (flow bypassing) in the monolith on degradation rate

<table>
<thead>
<tr>
<th></th>
<th>$k^*/\text{min}^{-1}$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MOFR</td>
<td>0.0146</td>
<td>0.9262</td>
</tr>
<tr>
<td>MOFR with 4 smaller fibers</td>
<td>0.0182</td>
<td>0.9722</td>
</tr>
</tbody>
</table>

* Experimental conditions: $I_{UV}=57 \text{ mW.cm}^{-2}$, flow rate=100mL.min$^{-1}$

5.3.5 Effects of UV Transmission and UV Intensity

A major consideration is the rate of attenuation of the light intensity along the length of the fibers. Refraction of light out of the fiber and into the photocatalytic coating of PBG titania is the primary loss mechanism as light travels down the fiber (Peill et al 1998). We have previously shown that the attenuation length increases with fiber diameter (Lin et al, 2006). It is important to ascertain the capability of the fiber to transmit UV light radially outward as the fiber is coated with the inverse opal. Figure 5.9 shows the radial transmission of UV light within the fiber as a function of the fiber length under various treatment conditions. The UV light within inverse opal titania can be transmitted to a longer distance than non inverse opal titania.

![Figure 5.9. Light transmission as a function of the fiber length (I is the intensity at the end of the fiber)](image)
The photon intensity plays an important role in the photocatalytic reaction. The reaction takes place with first-order regime or half-order regime (Ollis et al., 1991, Wang et al., 1998; Jacoby et al., 1995). Figure 5.10 shows the effect of UV intensity under laminar flow and room temperature on the overall degradation of DCB vapor in the system. Obviously with the increase of UV intensity, the reaction rate constant increases. However, when the intensity is low, the reaction is almost first-order reaction, which means that it depends on how many photons are available. When there are plenty of photons available, the reaction will not only depend on the intensity itself but also depend on some other parameters. From figure 5.10, the effect of UV intensity on the reaction rate constant can be described in the following equation (Ren et al., 2008), which is more accurate to describe the real effect.

\[ k^* = \frac{aI}{1 + bI} \]

(5.8)

Where, \(a\) and \(b\) are functions of the other experimental conditions, \(I\) is the UV intensity, \(k^*\) is the overall reaction rate constant. When the intensity is relatively low, the product of \(bI\) is smaller when compared with 1. So the effect of UV intensity on reaction is proportional to the intensity and it is 1\textsuperscript{st}-order. While with the increase of intensity, \(bI\) part becomes important. So the effect of intensity is become 1\textsuperscript{st}-order and 0\textsuperscript{th}-order. When the intensity is so large that 1 is relatively smaller than \(bI\) part, the effect of overall reaction rate constant becomes negligible and become 0\textsuperscript{th}-order, which means that it provides plenty of active sites on the surface of the catalyst and the reaction is completely controlled by mass transfer. In order to obtain the exact relationship between intensity and overall reaction rate constant, the reciprocal of equation 5.8 gives equation 5.9.

\[ \frac{1}{k^*} = \frac{1}{a} \frac{1 + bI}{aI} \]

(5.9)

Figure 5.11 shows \(\frac{1}{k^*}\) is almost linear with \(\frac{1}{I}\) if only the UV intensity was changed. So the relationship can be expressed in equation 5 after fitting the data by linear regression.

\[ k = \frac{0.0025 \times 1}{1 + 0.1639 \times 1} \]

(5.10)
The figure shows that the data fits the model very well (figure 5.11).

Figure 5.10. Effects of UV intensity on overall reaction rate constant. Flow rate =100mL.min⁻¹, room temperature.

Figure 5.11. The fitted linear regression based on equation 5.10
5.3.6 Combined Effect of Flow Rate and UV Intensity

The effects of flow rate and UV intensity were studied separately. However, these two parameters affect the overall reaction rate constant simultaneously. In order to obtain the co-effects of those two parameters, a 3×3 factorial experiment was designed as shown in table 5.3. The results represent that they two parameters are not independent. By fitting the result in the format of equation 5.10, Figure 5.12 shows the co-effect of flow rate and UV intensity on reaction rate constant. From figure 5.12, the highest overall reaction rate constant is achieved at 100mL.min$^{-1}$ and 113.65 mW.cm$^{-2}$ within our experimental condition range. And we can approximately predict the overall reaction rate constant within the experimental condition range.

Table 5.3. Results of designed experiments

<table>
<thead>
<tr>
<th>Experiment #</th>
<th>Intensity /mW.cm$^{-2}$</th>
<th>Flow rate /mL.min$^{-1}$</th>
<th>K*/min$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>36.7</td>
<td>70</td>
<td>0.012</td>
</tr>
<tr>
<td>2</td>
<td>77</td>
<td>0.0131</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>100</td>
<td>0.0135</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>70</td>
<td>0.0136</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>77</td>
<td>0.0145</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>100</td>
<td>0.0146</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>70</td>
<td>0.014</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>77</td>
<td>0.0146</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>100</td>
<td>0.0148</td>
<td></td>
</tr>
</tbody>
</table>

Figure 5.12. 3-dimensional plot of rate constant against UV intensity and flow rate
5.4 Conclusions

This study successfully developed a monolith optical fiber reactor with inverse opal TiO2 to decompose 1,2-dichlorobenzene. From the effects of pore size, it is obviously that higher efficiency is obtained when the photonic band gap is within the UV range. The effect of flow rate will depend on the range of the flow itself. When the flow rate is less than about 50 mL.min\(^{-1}\), the reaction rate constant increases linearly. When the flow rate is large than that, the constant increase becomes slower. The order of photocatalytic reaction is between 0th-order and first-order when the UV intensity is within the range of 20-120mW.cm\(^{-2}\). The bypass flow decreases the overall efficiency. This can be explained by the velocity simulation results.
Chapter 6. Simulation of Monolithic Optical Fiber Reactor

6.1 Introduction

The modeling and simulation of the monolithic reactor is essential for the future industrialization, scale-up and commercialization of the heterogeneous photoreactor with PBG as an alternative method for decomposing organic pollutants in gaseous phase (Hoffmann et al., 1995; Alfano et al., 2000). This model includes several sub-models: fluid dynamics, radiation field and the reaction kinetics. These sub-models are interconnected; therefore it complicates solving the whole system. A numerical simulation is needed to solve these cross-linked sub-models (Alfano et al., 2000; Cassano et al., 1995; Brandi et al., 2004). Considering the complication of the reactor system, a simpler structure with all essential components of sub-models is easier to be used for simulation (Puma et al., 2004). This simple and useful model is especially important to the future improvement, scale-up and optimization of photocatalytic reactors.

The most widely used photoreactor design is the annual flow configuration and the modeling of this annular reactor is extensively developed. However, our design of the reactor is not as simple as annular design. In our system, the gas flows along the optical fibers rather than within a cylindrical channel. Therefore, the annular flow is not fit for our system.

One eighth of one fiber (a triangular prism) can represent the whole fibers. Figure 6.1 illustrates this model and this model will simplify the simulation since it doesn’t consider the effect of the reactor wall. However, according to the simulation in chapter 5, the effects of the reactor wall and the bypass in the corners are really significant. Ignoring those effects will result in worse simulation results. So a more complicated model which considers effect of reactor wall and the bypass was developed.

6.2 Model Development

The whole reactor includes a large number of the triangle cells in figure 6.1. However it doesn’t represent the whole reactor since it ignores the area next to the reactor wall. In order to see whether
This prism can represent the entire monolith reactor or not, the velocity distributions within the entire monolith reactor and the triangular prism were simulated and showed in figure 6.2 and 6.3. The simulation of the entire monolithic optical fiber reactor shows some bypass of the flow next to the reactor wall which affects the velocity distribution in the reactor. However, the triangular prism model in figure 6.3 shows that the velocity is relatively faster than the simulated one in the entire reactor. And that would increase the mass transfer of the reactants and products. That would mislead us to draw a fault conclusion. So the simple triangle cell model doesn’t represent the real reactor.

Although we can simulate the velocity distribution of the entire MOFR, the reaction kinetics model cannot be simulated as easily as the velocity simulation since the catalyst layers were not active during the velocity simulation. Because the photocatalyst layer is really thin, several millions of meshes more would be produced when they are active and it is beyond the capacity of our current computer.
Figure 6.2. Simulated velocity distributions in the entire MOFR
Figure 6.3. Simulated velocity distributions within the triangular prism model

One fourth of the entire reactor (figure 6.4 (a)) was used to simplify the simulation. It not only simplifies the simulation but also includes all the necessary parts in the reactor, such as the effects of
reactor wall and bypass in the corner. It doesn’t have any assumption on the structure of the reactor.

We will set up a quarter cylinder model which includes the fluid dynamics sub-model, mass transfer model, and the reaction kinetics sub-model. Also it will consider the light transmission within the fibers. We make the following assumptions in order to simplify the problem:

1. Steady state conditions;
2. Isothermal conditions along the reactor;
3. The velocity field at the inlet is uniformly distributed;
4. The initial inlet concentration is set to 4000 ppb;
5. The inlet concentration in the following circulation is set to the average concentration of the outlet of the previous loop;
6. The flow coming out of the outlet is directly circulated to the inlet after the space time it takes to pass the tubing;

Figure 6.4. A schematic of the quarter cylinder model. The blue cylinders represent optical fibers; the red arrows represent the direction of UV light; the black arrows represent the flow: (a) quarter cylinder model; (b) quarter cylinder model with block
7. The mixture caused by the pump is neglected;
8. The possible adsorption by the small pump is negligible;
9. Incompressible Newtonian fluid with constant physical properties;(verified by the tiny pressure change within the reactor)
10. There is no deterioration of the catalyst. The activity of the photocatalyst remains the same during the reaction;
11. The catalyst coating has the uniform thickness throughout of the reactor;
12. Dilute pollutant within the reactor. The activity sites are never saturated;
13. The UV intensity is uniform at each length of fiber

In order to prove the effect of bypass next to reactor wall, the quarter cylinder model was modified by adding a smaller optical fiber in the area of the bypass, where the velocity is relatively fast. The modified quarter cylinder model is shown in figure 6.4 (b). The diameter of the smaller optical fiber is 0.08 cm. The purpose of this smaller optical fiber is to block the bypass. It has no catalyst layer on the surface.

6.2.1 Fluid Dynamic Sub-Model

Although we have assumed that the flow is steady-state, unidirectional, incompressible, continuous under a fully developed laminar regime within the reactor, the velocity profile within the quarter cylinder model cannot be expressed in a simple equation. The profile can only be expressed by the differential equations, the incompressible Navier-Stokes equation (equation 6.1) and the continuous equation (equation 6.2).

\[
\frac{\partial u_z}{\partial \theta} + u_x \frac{\partial u_z}{\partial x} + u_y \frac{\partial u_z}{\partial y} + u_z \frac{\partial u_z}{\partial z} = g - \frac{1}{\rho} \frac{dP}{dz} + \frac{\mu}{\rho} \left\{ \frac{\partial^2 u_z}{\partial x^2} + \frac{\partial^2 u_z}{\partial y^2} + \frac{\partial^2 u_z}{\partial z^2} \right\} \tag{6.1}
\]

\[
\frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y} + \frac{\partial u_z}{\partial z} = 0 \tag{6.2}
\]
Where \( u_x, u_y \) and \( u_z \) are the velocities at different directions respectively and direction \( z \) is along the flow from the bottom of the reactor to the top; \( g \) is the gravity coefficient; \( P \) is pressure at each point; \( \rho \) is the density of the flow. Based on the unidirectional flow and the assumptions that gravity effect can be negligible for gas flow and pseudo steady state (similar to the part in chapter 5), the equations can be simplified to yield:

\[
\frac{\partial^2 u_z}{\partial x^2} + \frac{\partial^2 u_z}{\partial y^2} = \frac{1}{\mu} \frac{dP}{dz}
\]

(6.3)

The boundary conditions for the above equation are

\[ u_x = u_y = 0, u_z = u_0 \quad z=0 \] (6.4)

\[ u_x = u_y = u_z = 0 \quad \text{at surface of catalyst and wall} \] (6.5)

Therefore, the dynamic distribution cannot be solved by traditional ways. And the differential equation with all the boundary conditions needs to be solved by numerically simulation.

### 6.2.2 Reaction Kinetics Sub-Model

The kinetic rate equation used in the present model is derived based on the following: (i) the photocatalytic destruction rate of organic contaminants can be fitted by a Langmuir-Hinshelwood kinetic rate equation; (ii) the kinetic rate constant follows a power law expression of the radiation on the catalyst surface (Herrmann et la, 1999; Peill et la, 1998).

\[
r = -k I_z^n \frac{KC}{1+KC}
\]

(6.4)

Where \( K \) refers to the adsorption equilibrium constant of 1,2-DCB on porous TiO2; \( I_z \), the intensity at length \( Z=z \) \((Z=0 \text{ at the bottom of the reactor})\), is a function of position \( z \); \( n \) is the power law coefficient which varies according to the light intensity; \( C \) is the reactant concentration. Since the pollutant is dilute and the assumption that the active sites are never saturated, \( KC<<1 \) and the equation is simplified to yield:

\[
r = -k_{obs} I_z^n C
\]

(6.5)
Based on the effect of light intensity on the experimental degradation, the power is approximate 0.2. Here we used the light intensity distribution along the fiber (results of chapter 5) to express the function of light intensity at different length.

\[ I^n_z = I^n_{z=L} \times e^{-\beta n (L-z)} \]  

(6.6)

Where \( \beta \) is the UV intensity attenuation rate along the length of fibers, which can be obtained by the regression of UV transmission within the fibers by assuming that the intensity decreases exponentially with length; \( L \) is the total length of the MOFR; \( z \) is the distance from the flow inlet (\( z=0 \) at the inlet and \( z=L \) at the outlet); \( I^n_{z=L} \) is the inlet or initial light intensity at the top of the reactor. \( K_{obs} \) is the observed reaction rate constant that excludes the major factors that affect the overall destruction rate. It is based on experimental decomposition under the range of our experimental conditions (flow rate 70-100mL.min\(^{-1}\), UV intensity 36.7-113.65mW.cm\(^{-2}\)). It is an average result within the experimental conditions after excluding the effect of intensity and flow rate.

6.2.3 Mass Balance

The equation of convection and diffusion of reactants in this MOFR is expressed in equation 6.7 (Comsol Multiphysics, Chemical engineering module).

\[ \nabla \cdot (-D \nabla c) = R - u \cdot \nabla c \]  

(6.7)

Where \( c \) is the concentration of reactant DCB; \( D \), diffusion coefficient of reactant DCB, which can be the diffusion coefficient in air or within the porous catalyst, depends on where the point is; \( u \) is the vector of velocity of the stream; The value of the velocity within the main channel is determined by the simulated solution of fluid dynamics sub-model. \( R \) represents the reactions within MOFR. Within the main channel, there is no reaction and \( R \) is equal to zero. Within the catalyst layer, the reaction part would be determined by the reaction kinetics discussed in previous section.

The diffusion coefficient of DCB in gas stream was calculated according to the Fuller-Schettler-Giddings equation (http://www.epa.gov/athens/learn2model/part-two/onsite/ed-background.html).
\[ D_{AB} = \frac{10^{-3}r^{1.75}\left(\frac{1}{M_A} + \frac{1}{M_B}\right)^{1/2}}{P[\Sigma V_A^{1/3} + \Sigma V_B^{1/3}]^2} \]  

(6.8)

Where P is the total pressure in atm; \( M_i \) is the molecular weight of component \( i \); \( D_{AB} \) is the diffusivity coefficient between component A and B (cm\(^2\).s\(^{-1}\)); \( T \) is the temperature in Kelvin; \( \Sigma V_i \) is the sum of the diffusion volume for component \( i \). The diffusion in our catalyst is Knudson diffusion because the pore size in our catalyst is within the range of Knudson diffusion. The Knudson diffusion coefficient in the porous catalyst was calculated by the following equations.

\[ D_k^e = \frac{\varepsilon_p}{\tau} \frac{D_k}{2 \frac{\sqrt{8RT\varepsilon_p}}{3\pi M\tau}} \]  

(6.9)

Where \( D_k^e \) is the Knudson diffusion coefficient in the porous catalyst; \( \varepsilon_p \) is the porosity of the catalyst; \( \tau \) is the tortuosity of the channel where the component diffuses through; \( r \) is the average radius of the channel; \( R \) is the universal gas constant; \( T \) is the temperature in Kelvin; \( M \) is the molecular weight of the gas.

### 6.2.4 Model Simulation

The model equations including the sub-model equations of radiation field in chapter 5 constitute a system of nonlinear differential equations with complex nonlinear boundary conditions. COMSOL is used to solve for a single pass conversion. In this model, the convection and diffusion sub-model utilize simulated velocity result of the dynamic sub-model. The model will integrate numerically the nonlinear differential equations to obtain the conversion.

In a continuous reactor system in which all the flow emerging from the outlet of the photoreactor is recirculated back to the inlet passing through the pump and the tubing. Since there is no reservoir, we can treat the whole system as the outlet flow would be directly recirculated back to the inlet after the space time of the tubing between the inlet and outlet.

\[ C_{\text{outlet}}^{n+1}(t) = C_{\text{inlet}}^{n}(t + \tau_{\text{tubing}}) \]  

(6.10)
Where the average concentration of reactant at the outlet of $n^{th}$ loop is equal to the average concentration at the inlet of $n+1^{th}$. $\tau_{tubing}$ is the space time of the tubing between the outlet of the reactor and the inlet of the next loop.

The number of passes $N_p$ of the gaseous solution through the reactor in a given time $t$ is:

$$N_p = \frac{t}{\tau_{MOFR} + \tau_{tubing}} = t \frac{Q}{V_{MOFR} + V_{tubing}}$$

(6.11)

Where $Q$ is the current volumetric flow rate; $V_{tubing}$ is volume of the tubing between inlet and outlet; $V_{MOFR}$ is the volume of MOFR channel where the flow passes by.

### 6.2.5 Estimation of Parameters

The parameters and constants in the quarter cylinder model are summarized in Table 6.1. Once these parameters have been estimated, the predicted reactor conversions can then be computed for given values of the volumetric velocity, inlet concentration, temperature and input light intensity. The geometrical and fluid dynamic parameters can be easily measured or calculated. The UV radiance

**Table 6.1. Optical fiber monolithic reactor model parameters**

<table>
<thead>
<tr>
<th>Model parameter</th>
<th>Values</th>
<th>Unit</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Geometry</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$D_{fiber}$</td>
<td>0.1</td>
<td>cm</td>
<td>Diameter of optical fiber coated with photonic catalyst</td>
</tr>
<tr>
<td>$D_{block, fiber}$</td>
<td>0.08</td>
<td>cm</td>
<td>Diameter of optical fiber for blocking the bypass</td>
</tr>
<tr>
<td>$D_{reactor}$</td>
<td>0.7</td>
<td>cm</td>
<td>Inner diameter of reactor</td>
</tr>
<tr>
<td>$\delta$</td>
<td>0.001</td>
<td>cm</td>
<td>Thickness of the catalyst layer</td>
</tr>
<tr>
<td>$L$</td>
<td>27</td>
<td>cm</td>
<td>Length of the reactor</td>
</tr>
<tr>
<td>$\varepsilon_p$</td>
<td>0.84</td>
<td>dimensionless</td>
<td>Porosity (C. C. Cheng and A. Scherer)</td>
</tr>
<tr>
<td>$\tau$</td>
<td>3.0</td>
<td>dimensionless</td>
<td>Tortuosity (Newton et al., 2004)</td>
</tr>
<tr>
<td><strong>Fluid Dynamics</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$u$</td>
<td>60~100</td>
<td>mL.min$^{-1}$</td>
<td>Volumetric velocity in the reactor</td>
</tr>
<tr>
<td><strong>Mass Transfer</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$D_{atm}$</td>
<td>6.624*10$^{-6}$</td>
<td>m$^2$.s$^{-1}$</td>
<td>Diffusion coefficient of DCB in atmosphere (Lin et al., 2005)</td>
</tr>
<tr>
<td>$D_{Porous}$</td>
<td>1.21*10$^{-7}$</td>
<td>m$^2$.s$^{-1}$</td>
<td>Diffusion coefficient of DCB in porous media of our catalyst layer</td>
</tr>
</tbody>
</table>
transmission along the fiber is given in Chapter 5. The diffusion coefficients of the substrates (DCB) in atmosphere and porous media are found in the literature. The adjustable parameters of the model, the observed rate constant \( k^* \), can be estimated by fitting the model to the experimental results under different operation conditions.

6.3 Results and Discussion

6.3.1 Dynamics Sub-model Results

Using the model described in the previous sections, the dynamics of quarter cylinder model is simulated to obtain the velocity distribution. Figure 6.5(a) shows the velocity distribution within the quarter cylinder model. When compared with monolith reactor (figure 6.2), the quarter cylinder reactor model shows exactly the same velocity distribution. That proves that the quarter cylinder reactor model can precisely represent the whole monolith reactor. And the quarter cylinder reactor has only 25% of the meshes when the dimension of the meshes is the same and the simulation is faster than that of the whole MOFR model.

Figure 6.5 shows the simulated velocity on the surface for both quarter cylinder model and quarter cylinder model with block at same volumetric velocity. The figure clearly shows that there is bypass flow in the corner whose velocity is really faster than that in the other area. After adding a smaller fiber to that area, the velocity within the MOFR was redistributed and the flow at the other area especially the area next to the catalyst is much faster and that will increase the mass transfer of the reactant. The simulated reaction rate constants in the following section will prove that. The velocity contour on the outlet (Figure 6.6) shows the redistribution of velocity.

In order to figure out the velocity distribution inside the model, the velocity profile of the model on the side face was shown in figure 6.7. The velocity becomes stable very quickly after the flow enters the inlet. After about 10% of the total length, the velocity distribution becomes fully developed. The pressure contour on the side face of the quarter cylinder model (figure 6.8) shows that
Figure 6.5. Simulated velocity distributions on the surface of the model (Q=77mL.min⁻¹): (a) quarter cylinder model; (b) quarter cylinder model with block
Figure 6.6. Simulated velocity contour on the outlet of the MOFR (Q=77mL.min⁻¹): (a) quarter cylinder model; (b) quarter cylinder model with block
the different pressure between inlet and outlet is tiny and negligible. This proves that the assumption of incompressible Newtonian flow is acceptable.

Figure 6.7. Simulated velocity contour on the side face along the flow (Q=100mL.min⁻¹) for quarter cylinder model

Figure 6.8. Pressure contour on the side face of quarter cylinder model (Q=100mL.min⁻¹)
6.3.2 Convection and Diffusion Model Results

Figure 6.9 presents the concentration distribution within the model in one pass of the flow at \(Q=100\text{mL.min}^{-1}\) and \(I_{\text{UV}}=57.09\text{mW.cm}^{-2}\). The concentration on slices at different length paralleled to the inlet is uniformly distributed. This proves the diffusion of DCB within the reactor is really fast under the experimental conditions. Even the concentration next to the rod is still almost the same as concentration at other area at each \(Z=z\) slide. Therefore, the reaction within the reactor is controlled by the reaction itself rather than the diffusion. This would be testified by the result of the simulated results late on. Similar results were obtained under different volumetric velocity and UV intensity within the range of our experimental conditions.

![Concentration contour of quarter cylinder model](image)

6.3.3 Comparison between Simulation and Experimental Results

The quarter cylinder model was simulated continuously by setting the inlet concentration by the outlet concentration of the previous loop. The total time passed by was calculated as the product of the number of loops and space time per loop. The simulation was done at our experimental conditions to compare with our experimental results.
Figure 6.10 Simulated photodegradation results at 70mL.min\(^{-1}\)

Figure 6.10 gives some simulated result of the quarter cylinder model at 70mL.min\(^{-1}\). From the fitted regression according to exponential decay, the observed reaction rate constant can be obtained to be used to compare with the experimental one.

Table 6.2 Simulation result compared with the experimental data

<table>
<thead>
<tr>
<th>Flow rate /mL.min(^{-1})</th>
<th>Intensity /mW.cm(^{-2})</th>
<th>experimental reaction rate constant, (k^*)</th>
<th>simulated reaction rate constant, (k^*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>70</td>
<td>36.7</td>
<td>0.012</td>
<td>0.010167</td>
</tr>
<tr>
<td></td>
<td>57.09</td>
<td>0.0136</td>
<td>0.011</td>
</tr>
<tr>
<td></td>
<td>113.65</td>
<td>0.014</td>
<td>0.012667</td>
</tr>
<tr>
<td>77</td>
<td>36.7</td>
<td>0.0131</td>
<td>0.010231</td>
</tr>
<tr>
<td></td>
<td>57.09</td>
<td>0.0145</td>
<td>0.011541</td>
</tr>
<tr>
<td></td>
<td>113.65</td>
<td>0.0146</td>
<td>0.012735</td>
</tr>
<tr>
<td>100</td>
<td>36.7</td>
<td>0.0135</td>
<td>0.010481</td>
</tr>
<tr>
<td></td>
<td>57.09</td>
<td>0.0146</td>
<td>0.11672</td>
</tr>
<tr>
<td></td>
<td>113.65</td>
<td>0.0148</td>
<td>0.012835</td>
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</tbody>
</table>
Table 6.2 gives the details of the simulated reaction rate constant and the experimental reaction rate constant under various experimental conditions. After comparison between them, the trend of the effects of UV intensity in the model is similar to the trend of our experimental results. As the intensity increases, the reaction becomes faster and the observed reaction rate constant becomes bigger. Obviously the simulated one is smaller than our experimental one under same experimental conditions. This shows that there are still some limitations in our model. The possible way that causes the relatively smaller simulated rate constant is that there is extra UV light illuminated on the catalyst. In our MOFR, in order to obtain higher reaction rate, the light not only can transfer within the fibers but also can illuminate on the surface directly because the light was illuminated on the quartz top directly rather than the optical fiber bundle. So the actual UV intensity on the surface is higher than that in our model. Therefore, the experimental rate constant is higher than the simulated one.

![Graph](image)

**Figure 6.11.** Comparison of reaction rate constant between experimental and simulated data: flow rate is 70mL.min⁻¹

The effects of flow rate on reaction rate constant are tiny from our simulation result. From the concentration distribution (figure 6.9), the concentration at each length level is almost the same, which
means the diffusion of reactants within the main channel of MOFR is fast enough and the reaction is not controlled by that diffusion. So increasing flow rate doesn’t really affect the reaction rate. Although increase of flow rate can decrease the reaction time per loop, it will increase the number of loops within same period.

**6.3.4 Effects of the Block in MOFR**

In the model considering the block, we use optical fibers with smaller diameter (0.8mm) to block the bypass. This model will show the how the bypass influence the degradation. From the velocity distribution in figure 6.5 and figure 6.6, the smaller fiber really significantly changes the velocity distribution and minimizes the bypass. That will increase the chance of contact between reactant and active sites. Therefore the reaction rate constant should be higher. Figure 6.12 shows the concentration distribution within the block model. Figure 6.13 shows the block effect on the degradation compared with that without block. The block removes the bypass and therefore increases the degradation.

![Concentration distribution](image)

Figure 6.12. Concentration distribution in quarter cylinder model with block
Figure 6.13. Contrast between quarter cylinder model and quarter cylinder model with block ($I_{uv}=36.7\,\text{mW}\cdot\text{cm}^{-2}$, flow rate=$77\,\text{mL}\cdot\text{min}^{-1}$)

6.4 Conclusions

A three-dimensional heterogeneous convective-diffusion-reaction model is developed to simulate the performance of a monolithic optical fiber monolith reactor. With the assumption of symmetry, the MOFR model is reduced to the quarter cylinder model without losing the essential elements of the reactor. The reactor model incorporated an empirical radiation field sub-model, flow dynamics model and a Langmuir-Hinshelwood kinetics sub-model. Reasonable agreement is found between the model-predicted and experimental photodegradation conversion data.

The quarter cylinder model with block significantly changes the flow distribution within the model and blocks the bypass. Therefore it increases the chance of contact between reactant and catalyst surface and increases the photoreaction.

Although simulated result trend of quarter cylinder model fit that of experimental results, the simulated reaction rate constant is generally lower than the experimental one. Because this model didn’t consider the UV light that directly illuminates on the surface and the reaction due to that portion
of UV light. Also in the actual MOFR, the outlet is not at the top as in the model. There is 2 cm between the top end of MOFR and the outlet. Therefore there is dead corner at the top of MOFR that will change the flow within MOFR and decrease the reaction rate of MOFR.
Chapter 7. Photocatalytic Reaction in Wastewater with MOFR Using Inverse Opal Titania

7.1 Introduction

The presence of hazardous organic compounds in the discharge of wastewater from chemical plant, landfill, and agricultural sources is also a topic of global concern. There are some traditional methods to remove the harmful compounds in wastewater. However, none of them is cost-effective when the harmful compound is diluted in water. They can either produce more hazardous intermediates or has some other limitations (Legrini et al, 1993; Mills et al, 1993; Ollis et al, 1989; Roberts et al, 2002).

Heterogeneous photocatalysis on metal oxide semiconductor particles is an advanced oxidation technology, which has been shown to be an effective means of removing organic pollutants from water streams (Roberts et al, 2002; Lin et al, 2002). Compared with traditional oxidation processes, heterogeneous photocatalysis has a lot of advantages as discussed in chapter 2. Titanium dioxide is commonly used as photocatalyst since it has a lot of advantages compared with other materials.

There are several kinds of design of photocatalytic reactor. The monolithic optical fiber reactor (MOFR) is proven to be more efficient than the other reactor designs in water phase (Lin et al, 2002, 2003). Our study shows that the inverse opal catalyst has higher efficiency to degrade hazardous organic compound in gaseous phase than traditional catalyst (Ren et la, 2006, 2008). Chapter 5 proves that MOFR with inverse opal catalyst has higher efficiency in gaseous phase than MOFR with P25 TiO2 catalyst layer.

In this study, MOFR with inverse opal titania will be used to degrade diluted 1,2-dichlorobenzene in water. The design of MOFR with inverse opal titanium dioxide was described in chapter 5. The effects of flow rate and UV intensity on decomposition were also studied. A modified quarter cylinder model was developed to simulate the degradation in water within the MOFR.
7.2 Experimental

7.2.1 Materials

1,2-dichlorobenzene (DCB) of 98% purity was obtained from EM Sciences, Gibbstown, NJ. DI water was obtained from the Mega-Pure System manufactured by Barnstead company. Titanium (IV) ethoxide purchased from Aldrich was used as titanium precursor. Optical fibers (1mm in diameter, FT1.0UMT) were purchased from ThorLabs Inc. Sandpaper (Norton) was used to roughen the rod surface. Hexane from EMD used to absorb gaseous DCB was measured by GC/MS.

7.2.2 Experimental Setup

Optical fibers with inverse opal TiO2 was bundled together and evenly distributed within the reactor (see details in chapter 5). The initial concentration of the DCB in the reservoir was set at 5% of the saturated DCB in water (7mg.L\(^{-1}\)) at room temperature. The reservoir volume was 400 mL. The reaction was carried out in a semi-batch (recirculating) mode. DCB solution was sampled by syringes both at the inlet and exit stream of the MOFR as shown in figure 7.1. The UV light was provided by a UV lamp (310-380 nm, manufactured by Osram, obtained from Spectral Energy Corporation, NY) powered by a UV housing system.

7.2.3 Experimental Procedure

The MOFR with inverse opal TiO2 was installed in the experimental setup (figure 7.1). The volume of the reservoir is 400mL. The liquid in the reservoir is stirred by a magnetic stirrer to mix the solution. After ascertaining that there were no leaks in the system, the feed recirculating pump was turned on for 24h before reaction to reach equilibrium in the whole system. Once steady state was assured, the power supply to the UV lamp was turned on and the reaction was allowed to occur. Samples of DCB solution were taken from the recirculation loop both on the inlet and exit of the reactor with tight syringes every 20 minutes. The concentration of DCB in the aqueous phase was analyzed by a Hewlett-Packard gas chromatograph (Model HP 6890 Series I) coupled with a mass spectrometer (HP 5973).
7.2.4 Methodology and Analysis

DCB sample in the aqueous phase was analyzed using a Hewlett-Packard gas chromatograph (Model HP 6890 Series) coupled with a mass spectrometer (HP 5973). A glass capillary column (60 m long, 0.53 mm I.D) coated with SPB-20 was obtained from Supelco, Inc. The oven temperature was set at 70 °C initially, with a temperature ramp of 6 °C.min⁻¹ to a final temperature of 100 °C. The injector temperature was 180 °C and the detector temperature was also 180 °C. The carrier gas was helium at 0.565 ml. min⁻¹. Compound identification was done using the NBS mass spectral library.

7.3 Results and Discussion

7.3.1 Kinetics of Photodegradation of DCB in the MOFR

The reactor system was operated in a semi-batch mode with recirculation of the 1,2-DCB solution in the reservoir through the reactor (figure 7.1). The fractional removal of DCB from the liquid stream in one pass is given by the following equation.
\[ x = 1 - \frac{C_{\text{exit}}}{C_{\text{feed}}} = 1 - \exp(-k^*t) \]  

(7.1)

Where \( C_{\text{exit}} \) is the concentration at the exit of the reactor and \( C_{\text{feed}} \) is the feed concentration at the inlet.

The first order rate constant, \( k^* \), is composed of two terms using the Langmuir–Hinshelwood kinetics (Lin et al., 2002; Lin et al., 2003; Ren et al., 2008; Ollis et al., 1991; Wang et al., 1998).

\[ \frac{1}{k^*} = \frac{1}{k_m a_v} + \frac{1}{kK} \]  

(7.2)

where each term on the right hand side represents a resistance. The term \( 1/k_m a_v \) is the mass transfer diffusion resistance and \( 1/kK \) is the intrinsic reaction resistance.

Figure 7.2. DCB concentration in the outlet and inlet streams as well as the overall removal efficiency as a function of time. The flow velocity was 12mL.min\(^{-1}\). The UV intensity was 113.65mW.cm\(^{-2}\).

Figure 7.2 shows an example of the degradation in the reactor system. The reactant concentration in the exit and inlet of the MOFR as well as the overall removal efficiency as a function of reaction time are shown in the figure. The concentration at both ends of the reactor decrease as time
goes on. The overall conversion of DCB per pass from aqueous phase remained constant under the experimental conditions. Therefore, the process is at steady state. A steady-state conversion in one pass is about 23.2% under the experimental conditions (flow velocity, \( Q = 12\text{mL.min}^{-1} \), UV intensity \( I=113.65\text{mW.cm}^{-2} \)).

7.3.2 Effects of UV Intensity

The photon intensity always plays an important role in the photocatalytic reaction. The reaction takes place within first-order regime or half-order regime for intensity. Since the average removal efficiency (ARE) in one pass is almost constant within the experimental range, the ARE in one pass can be used to represent the rate of photoreaction. Figure 7.3 shows the effect of UV intensity on ARE per pass at \( 12\text{mL.min}^{-1} \) and room temperature. With the increase of UV intensity the ARE in one pass increases. The trend shows that the ARE in one pass increases linearly when the intensity is low and the increase becomes slower when the intensity is high. The effects of UV intensity on reaction will be illustrated by the concentration distribution within the reactor of the simulation.

![Figure 7.3](image)

Figure 7.3. UV intensity effects on the average removal efficiency in one pass on DCB solution. The flow velocity was \( 12\text{mL.min}^{-1} \) and room temperature.
7.3.3 Flow Rate Effects

Flow rate affects the photoreaction by the mass transfer of the reactant and the number of passes through the reactor. Since the retention time during one pass will decrease as the flow rate increases, the ARE in one pass cannot clearly show the effect of flow rate on the reaction. The experimental results show that the reaction is faster when the flow rate increases. Figure 7.4 shows the ARE in one pass decreases as flow rate increase, which means that the retention time is dominant rather than the reaction rate. It will be used to be compared with the simulated results. From chapter 4 and 5, we can see that flow rate and UV intensity affects the reaction simultaneously. They would determine whether the reaction is within mass transfer controlled regime or surface reaction controlled regime. The simulation results will illuminate their co-effects.

Figure 7.4. Flow rate effects on DCB average removal efficiency in one pass. The UV intensity was 113.65mW.cm$^{-2}$. 
7.4 Quarter Cylinder Model in Aqueous Phase

7.4.1 Quarter Cylinder Model Assumptions

1. Steady state conditions;
2. Isothermal conditions along the reactor;
3. The velocity field at the inlet is uniformly distributed;
4. The initial inlet concentration is set at 5% saturated DCB in water at 25°C;
5. The inlet concentration in the following circulation is set to the average concentration of the outlet of the previous loop;
6. The flow coming out of the outlet is directly circulated to the inlet after the residence time it takes to pass the tubing;
7. The mixture caused by the pump is neglected;
8. The possible adsorption by the small pump is negligible;
9. Incompressible Newtonian fluid with constant physical properties;(verified by the tiny pressure change within the reactor)
10. There is no deterioration of the catalyst. The activity of the photocatalyst remains the same during the reaction;
11. The catalyst coating has the uniform thickness throughout of the reactor;
12. Dilute pollutant within the reactor. The activity sites are never saturated;
13. The UV intensity is uniform at each length of fiber
14. The reaction is 1st order of DCB and independent of oxygen concentration

7.4.2 Fluid Dynamic Sub-Model

Although we have assumed that the flow is steady-state, unidirectional, incompressible, continuous under a fully developed laminar regime within the reactor, the velocity profile within the quarter cylinder model cannot be expressed in a simple equation. The profile can only be expressed by
the differential equations, the incompressible Navier-Stokes equation (equation 7.1) and the continuous
equation (equation 7.2).

\[
\frac{\partial u_z}{\partial \theta} + u_y \frac{\partial u_z}{\partial x} + u_y \frac{\partial u_z}{\partial y} + u_x \frac{\partial u_z}{\partial z} = g - \frac{1}{\rho} \frac{dP}{dz} + \frac{\mu}{\rho} \left( \frac{\partial^2 u_z}{\partial x^2} + \frac{\partial^2 u_z}{\partial y^2} + \frac{\partial^2 u_z}{\partial z^2} \right)
\]

(7.1)

\[
\frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y} + \frac{\partial u_z}{\partial z} = 0
\]

(7.2)

Where \( u_x, u_y \) and \( u_z \) are the velocities at different directions respectively and direction \( z \) is along the
flow from the bottom of the reactor to the top; \( g \) is the gravity coefficient; \( P \) is pressure at each point; \( \rho \)
is the density of the flow. Based on the symmetric properties of the reactor and the assumptions that
gravity effect can be negligible for gas flow and pseudo steady state (similar to the part in chapter 5),
the equations can be simplified to yield:

\[
\frac{\partial^2 u_x}{\partial x^2} + \frac{\partial^2 u_z}{\partial y^2} = \frac{1}{\mu} \frac{dP}{dz} - \frac{g \rho}{\mu}
\]

(7.3)

The boundary conditions for the above equation are

\[
\left. u_x \right|_{Z=0} = \left. u_y \right|_{Z=0} = 0, \left. u_z \right|_{Z=0} = u_0
\]

(7.4)

\[
\left. u_x \right|_{at \ wall} = \left. u_y \right|_{at \ wall} = \left. u_z \right|_{at \ wall} = 0
\]

(7.5)

Therefore, the dynamic distribution cannot be solved by traditional ways. And the differential
equation with all the boundary conditions needs to be solved by numerically simulation.

7.4.3 Reaction Kinetics Sub-Model

The reaction kinetics sub-model in aqueous phase is very similar to that in gaseous phase.
Langmuir-Hinshelwood kinetics is used and the power law effect of the UV intensity is the same with
that in chapter 6. The difference is that the observed reaction rate constant \( K_{obs} \) is calculated based on
the observed reaction rate within the experimental range. \( K_{obs} \) is the observed reaction rate constant
that takes into account the major factors that affect the overall destruction rate. It is based on
experimental decomposition under the range of our experimental conditions (flow rate 70~100mL.min−1}
1, UV intensity 36.7~113.65mW.cm\(^{-2}\)). It is an average result within the experimental conditions after excluding the effect of intensity and flow rate.

### 7.4.4 Mass Balance

The equation of convection and diffusion in the main channel of this MOFR is

\[
\nabla \cdot (-D_k \nabla c) = R - u \cdot \nabla c
\]

(7.6)

Where \(c\) is the concentration of reactant DCB; \(D_k\), diffusion coefficient of reactant DCB, which can be the diffusion coefficient in air or within the porous catalyst, depends on where the point is, in the channel or within the catalyst layer; \(u\) is the vector of velocity of the stream; The value of the velocity within the main channel is determined by the simulated solution of fluid dynamics sub-model. The velocity within the catalyst channel and wall of is set to zero since \(R\) represents the reactions within MOFR. Within the main channel, there is no reaction and \(R\) is equal to zero. Within the catalyst layer, the reaction part would be determined by the reaction kinetics discussed in previous section. The diffusion coefficient of DCB in water, \(D_k = 0.89 \times 10^{-5} \text{ cm}^2\cdot\text{s}^{-1}\), was found in literature [11]. The diffusion coefficient within the catalyst layer, \(D_k^\varepsilon\), was calculated by equation (7.7).

\[
D_k^\varepsilon = \frac{\varepsilon_p}{\tau} D_k
\]

(7.7)

Where \(D_k^\varepsilon\) is the Knudsen diffusion coefficient in the porous catalyst; \(\varepsilon_p\) is the porosity of the catalyst; \(\tau\) is the tortuosity of the channel where the component diffuses through.

### 7.5 Simulation Results

#### 7.5.1 Dynamics Sub-Model Results

Figure 7.5 shows the simulated velocity on the surface of the quarter cylinder model at 12mL.min\(^{-1}\). The figure clearly shows that there is bypass flow in the corner whose velocity is really faster than that in the other area in the main channel of the quarter cylinder model. Also the velocity can show that the flow is laminar flow, which is similar to the simulated result in chapter 6. From the velocity distribution on the symmetric face, the velocity becomes stable very quickly after the flow
comes into the inlet. The bypass in the corner will reduce the efficiency of the reactor based on the similar results in chapter 6.

Figure 7.5. Simulated velocity distribution on the boundary of quarter cylinder model of MOFR at 12mL.min$^{-1}$

### 7.5.2 Convection and Diffusion Model Results

Figure 7.6 presents the concentration distribution on the boundary within the quarter cylinder model in one pass of the flow at $Q=12$mL.min$^{-1}$ and $I_{UV}=113.65$mW.cm$^{-2}$. The concentration on slices at different length paralleled to the inlet is not as uniformly distributed as the result of gaseous phase. At the end next to the inlet, the reaction is really slow and the diffusion and convection of the reactant is faster than the degraded amount of the reactant. Thus, at that area, the reaction is controlled by the reaction and the concentration is almost uniformly distributed as each length. At the end next to the inlet of UV light (the exit of the flow), the reaction is relatively fast and concentration is not uniformly distributed. This means that the diffusion and convection of reactant limits the reaction and the reaction is controlled by diffusion and convection. Between these two areas, there is an area where the reaction
is controlled by both photoreaction on the surface and the diffusion of reactant. The concentration contour on the surface at the whole UV intensity range and experimental flow rate is similar to that shown in figure 7.6(a). This can prove that the effects of flow rate on the overall efficiency in one pass are significant and it can increase the mass transfer in the area next to the exit and therefore increase the reaction there. Figure 7.6(b) shows the concentration distribution within one pass on the side face of the quarter cylinder model. It can clearly prove the conclusion made above.

Figure 7.6. Concentration contours. (a) on the boundary of the quarter cylinder model in one pass at 12mL.min$^{-1}$ and 113.65mW.cm$^{-2}$; (b) on the side face of quarter cylinder model. UV intensity is 43.91mW.cm$^{-2}$; flow rate is 12mL.min$^{-1}$. 
7.5.3 Effects of UV Intensity

The simulated value and the experimental value are shown in table 7.1 at same experimental conditions. In the table, the trend of the simulated value fits the experimental one very well. Obviously with the increase of UV intensity, average removal efficiency in a pass increases. If we focus on figure 7.6, we will find that the effect of UV intensity is important. At the exit of the reactor, the intensity is really high and reaction is faster. At the inlet, the intensity is low and the reaction is really slow. In the middle range of the reactor, there is a range where both intensity effect and other parameters plays important role in the reaction. Overall, both experimental and simulated results show that increasing UV intensity in that range (30-110mW.cm$^{-2}$) would increase the average removal efficiency in one pass under the current flow rate and temperature.

<table>
<thead>
<tr>
<th>UV intensity /mW.cm$^{-2}$</th>
<th>Experimental ARE in one pass</th>
<th>Simulated ARE in one pass</th>
</tr>
</thead>
<tbody>
<tr>
<td>113.65</td>
<td>0.2320</td>
<td>0.2080</td>
</tr>
<tr>
<td>57.09</td>
<td>0.1420</td>
<td>0.1630</td>
</tr>
<tr>
<td>43.91</td>
<td>0.0990</td>
<td>0.1260</td>
</tr>
<tr>
<td>36.70</td>
<td>0.0870</td>
<td>0.1120</td>
</tr>
</tbody>
</table>

*experimental conditions: flow rate=12mL.min$^{-1}$ and room temperature

7.5.4 Effects of Flow Rate

The average removal efficiency in one pass not only depends on the reaction itself but also depends on the residence time within the reactor for the reactant. Higher flow rate can increase the mass transfer within the reactor and therefore can increase the reaction. However, it also can decrease the residence time significantly. Those two effects are contradicted. Figure 7.7 shows the concentration contour at the exit of the reactor at different flow rate. When all the other conditions are same, the ARE will decrease with the increase of flow rate. This proves that the effect of residence time is dominant in the system. Table 7.2 also shows that the residence time for the reactant is dominant.
Figure 7.7. DCB concentration contour at the outlet in one pass at different flow rate. UV intensity is 43.91mW.cm\(^2\). The concentrations at the inlet are the same.
Table 7.2 Flow rate effects on ARE in one pass for simulation and experiment

<table>
<thead>
<tr>
<th>flow rate / mL.min(^{-1})</th>
<th>Experimental average removal efficiency in one pass</th>
<th>Simulated average removal efficiency in one pass</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>0.2320</td>
<td>0.2080</td>
</tr>
<tr>
<td>10</td>
<td>0.2580</td>
<td>0.2280</td>
</tr>
<tr>
<td>6.2</td>
<td>0.3290</td>
<td>0.2950</td>
</tr>
<tr>
<td>4</td>
<td>0.3680</td>
<td>0.3740</td>
</tr>
</tbody>
</table>

* UV intensity is 113.65 mW.cm\(^{-2}\) and room temperature

7.6 Conclusions

The monolithic optical fiber reactor with inverse opal titania was utilized to degrade organic contaminant in wastewater system. From the experimental results, the MOFR can also be utilized to decompose organic compound in wastewater system. Increase of UV intensity will significantly enhance the average removal efficiency in one pass through the reactor. Increase of flow rate will decrease the space time and therefore decrease the average removal efficiency. The model used in chapter 6 was modified to simulate the aqueous phase degradation and explain the effect of the UV intensity and flow rate in the experiment from simulation point of view.
Chapter 8. Photoreduction of CO2 to Methanol via Cu/TiO2 Catalyst on MOFR

In chapter 5, we showed that the monolithic optical fiber reactor (MOFR) with inverse opal TiO2 can decompose dichlorobenzene efficiently. Another possible application of the MOFR in photoreaction is illustrated in this chapter.

8.1 Introduction

Greenhouse gases such as CO2 and CH4 are the primary causes of global warming. The atmospheric concentration of CO2 has steadily increased due to the human activities, especially the fossil fuel consumption. Recently, the Kyoto Protocol of the United Nations Framework convention on Climate Changes mandated a return of CO2 emission levels to those of 1990. Besides of reducing the emission of CO2, conversion of CO2 to usable hydrocarbons would be one of the most promising routes to overcome the effect of global warming. Since the energy grade of CO2 is lower from a thermodynamic perspective than organic compounds, it is a rather inert and stable compound. Any transformation of CO2 to hydrocarbon needs huge energy input. The solar energy is one of the cheapest and best candidates as energy source because it is abundant and produces no greenhouse gas. Consequently, the photo reduction of CO2 using solar energy is attractive and can possibly mimic the natural photosynthesis.

To convert CO2, severe conditions of high temperature and high pressure are required. However, CO2 can be photocatalytically reduced to methanol or methane by various photocatalysts under relatively mild experimental conditions. Typically, there are two ways to photocatalytically reduce CO2. One is the reaction where hydrogen takes part in. This one requires high energy input, high pressure and high temperature (equation 8.1).

\[
CO_2 + 3H_2 \xrightarrow{hv} CH_4O + H_2O
\]  

(8.1)

It has been shown that CO2 can be reduced by mixed oxide catalysts, such as CuO-Al2O3, CuO-ZuO, CuO supported on MgO, La2O3, Sm2O3, ThO2-K and ZrO2, and ZnO supported on MgO, Al2O3, SiO2, TiO2, ZrO2 and Nb2O5.
The second way is that CO2 can be photoreduced in the pressure of water vapor or a solvent with photocatalysts such as TiO2 and ZnS (Yamashita et al, 1998; Kuwabata et al, 1994). Equation 8.2 describes the overall photoreduction of CO2 with H2O (Hirano et al, 1992).

\[
CO_2 + 2H_2O \xrightarrow{hv} CH_2O + \frac{3}{2}O_2
\] (8.2)

This method needs relatively mild experimental conditions, such as lower temperature (room temperature) and lower pressure (around atmospheric pressure).

The efficient photoreduction of CO2 is a challenging task. Titania catalyst with a bandgap of 3.2eV (for anatase phase) is widely used as a photocatalyst. It has been shown that TiO2 supported copper plays a crucial role in the photoreduction (Tseng et al, 2002; Wu et al, 2005; Hirano et al, 1992; Seneviratna et al, 2005; Rajh et al., 1998; Goeringer et al, 2001). There are various heterogeneous supports on which Cu/TiO2 can be used, including glass surface (Al-Ekabi et al, 1988; Yatmaz et al, 2001), reactor wall (Kumara et al, 1999), quartz rod (Lin et al, 2003; Ren et al, 2006), and monoliths (Sánchez et al, 1999; Hossain et al, 1999; Ren et al, 2008; Lin et al, 2006).

In this chapter, we will utilize the technology of inverse opal TiO2 (described in detail in chapter 3) on MOFR. Photoreduction of CO2 to methanol under various conditions is explored.

8.2 Experimental

8.2.1 Preparation of Catalyst

Inverse opal TiO2 on the fibers was prepared by a sol-gel method (Tseng et al, 2002). Figure 8.1 shows the schematic of the methodology. The titania precursor, titanium ethoxide (97%, Aldrich, USA), ethanol and acetic acid were mixed and stirred by a magnetic stirrer at low relative humidity (less than 25% at room temperature). Water needed for hydrolyzing titania precursor was slowly released by the esterification of the ethanol and acetic acid. A typical batch contained 0.02 mol titanium ethoxide, 0.08 mol anhydrous ethanol and 0.08 mol anhydrous acetic acid. The hydrolysis of the titania precursor was allowed to take place for 8 h. Subsequently polyethylene glycol (PEG) was added into the solution. The ratio of the TiO2 solution to PEG was 2:1. 0.1 mol/L of nitric acid was
added into the solution with a 1:6 volume ratio of titanium ethoxide to HNO3. The appropriate amount of the copper precursor, CuCl₂·2H₂O, was then added to obtain the desired Cu loading (wt %) on titania. The solution was heated to 80 °C for 8 h. Then the optical fibers coated with PSL were dipped into the solution vertically. To evaporate the solution faster, the fibers were heated by a heat gun. The procedure was repeated thrice. Then the coated fibers were calcined in an oven at a rate of 5°C per minute from the ambient temperature to 450°C and maintained for 8 hours for calcination.

![Diagram](image)

Figure 8.1. The schematic of the process of synthesizing inverse opal catalyst with Cu loaded

8.2.2 Modification of Optical Fibers

Quartz optical fibers (3M Power-Core FT-1.0-UMT) were purchased from Thorlabs, Newton, NJ and were used as the light conductor and supporter of the catalyst. The fibers were cut into small pieces with equal length of 0.4 m. A section of the single fiber was then stripped to a desired length (0.21 m). Firstly, the fibers were completely stripped off its protective buffer using a wire stripper and
the inner polymer cladding was then removed mechanically with a sharp razor. The surface of the fiber cores was then roughened using fine sandpaper. The roughened fibers were then coated with 120 nm polystyrene (PSL) latex microspheres (Duke Scientific Corporation) by dipping into a 0.5 % (w/w) solution of PSL for 5 minutes and drying with a heat gun at room temperature. The process of dip-coating was repeated thrice.

8.2.3 Characterization of the Catalyst

Scanning electron microscopy (SEM) was used to inspect the microscopic structure of the film on the fiber. A small piece of the fiber (approximately 1 cm) with in-situ catalyst (Cu/io-TiO2) was glued on to a plate and gold coated. SEM images of the fiber with PC TiO2 were obtained using a FEI Quanta 200 Scanning Electron Microscope. The TiO2 phase was probed using an x-ray diffractometer (XRD). XRD measurements were obtained using a Bruker-Siemens D5000 automated powder X-ray diffractometer with a Psi Solid-State Detector. Elemental analysis was conducted using an x-ray photoelectron spectrometer (XPS). XPS measurements were made by mounting the catalyst on the fiber to the sampling tray of the XPS (AXIS 165, Kratos Analytical Limited). The catalyst was coated on a quartz microscope slide and analyzed using a UV spectrophotometer (HACH 4000Uv-Vis spectrophotometer, Loveland, CO) to obtain the transmission characteristics and the stop band gap.

8.2.4 Reactor Setup

32 optical fibers with inverse opal Cu/TiO2 were bundled together by epoxy and inserted into a stainless tube (Figure 8.2). The gas-phase reactants flow in from the bottom of the reactor and flows out from the top. The UV light is introduced from the top of the reactor. A 500 W lamp (Osram, Spectral Energy Corporation, NY) provided UV light (310-380 nm). The entire reaction set up is shown in Figure 8.3. Pure helium was used as the carrier gas into the reactor. Supercritical CO2 was used as the reactant and was provided from a gas cylinder (Airgas, USA). The carrier gas flows through a water vapor generator (bubbler) and then flowed into the reactor. After passing through the reactor, the flow was forced to pass through a desiccant to absorb the extra water vapor. Then the flow
passed through an absorbent (chloroform) to absorb the product methanol. The absorbent was placed in an ice-bath to minimize evaporation of methanol and chloroform. The reaction section was heated to 70°C and maintained at that temperature. Before the UV light was turned on, He gas flow was used to rinse the system to assure that there are no organic compounds left in the reactor. After reaction, the absorbent and the product were analyzed by GC-MS.

(a) Individual fiber (magnified)  (b) Reactor schematic.

Figure 8.2. A schematic of the monolithic optical fiber reactor: (a) individual fiber with catalyst; (b) MOFR with heating system

8.2.5 Methodology and Analysis

The solution of chloroform containing methanol was analyzed using a gas chromatography/mass spectrometer (Agilent GC Model HP 5890 Series II with HP 5971 MS detector). The GC column used for analysis was DB-200 (30m × 0.25mm × 0.20μm) manufactured by Agilent J&W. The column temperature was programmed to vary from 45 to 145°C at a rate of 20°C.min⁻¹ with an initial holding time of 7 min. The column inlet pressure was 8.2 psi. Split injection with a split ratio of 0.7 mL.min⁻¹ and a split ratio of 1:1 was used. Nitrogen (UHP) was used as the carrier gas.
Figure 8.3. A schematic of the experimental reactor setup
8.3 Results and Discussion

8.3.1 Catalyst Properties

Figure 8.4(a) shows the SEM micrograph of the Cu/io-TiO2 film on the optical fiber. The thickness of the catalyst thin layer on the fiber is about 2 μm. Due to the existence of Cu, and the consequent charge developed on the sample, a high resolution SEM could not be obtained. The generated catalyst Cu/io-TiO2 was ground to a powder to analyze using the X-ray diffractometer. Figure 8.4(b) is the XRD of a 10 wt% Cu/io-TiO2 sample which shows the existence of copper (the Cu peak is at 2θ=43.3°) and anatase TiO2. No Cu peak was observed in the 2 wt% Cu/io-TiO2 sample, either due to the low Cu loading or the extremely small Cu clusters within the photonic titania structure. The XRD spectrum indicated the (101) crystalline anatase phase. The anatase titania is necessary to achieve the necessary electronic band gap of 3.2 eV for the UV-Vis spectrum (λ: 290 - 390 nm). The UV-Vis transmission spectra of Cu/io-TiO2 are shown in Figure 8.4(c). A polystyrene sphere (template) with 120 nm diameter, that results in an inverse opal titania of porosity 0.45 and refractive index of 2.5 by sol-gel method gives rise to an optical peak of 352 nm. If we assume a band width of 90 nm, the upper edge of the photonic band gap would be 397 nm. In this case, the entire transmitted UV light falls within the photonic band gap edge. Thus, the 120 nm PSL-templated Cu/io-TiO2 possesses an electronic band gap that overlaps with the photonic band gap for the UV-Vis spectrum. This should result in considerable slow down of the photons in the transmitted UV. Figure 8.5 is the XPS spectra of the Cu/io-TiO2 sample. The binding energies of Ti 2p3/2 and 2p1/2 of the Cu/io-TiO2 are the same as those of the pure titania at 459.4 and 463.3 eV respectively, which indicates that the integrity of the io-TiO2 structure was retained even with Cu doping. The binding energies of Cu 2p3/2 and 2p1/2 were 32.8 and 952.8 eV respectively corresponding to CuO. The shapes of the spectra showed that the majority of the copper species was CuO with minor amounts of Cu2O. The XPS data also showed that the component analysis gave a weight ratio of Cu/Ti of 0.173, 0.133 and 0.118 for 6.8 wt%, 3 wt% and 2 wt% Cu respectively with a surface ratio higher than the bulk.
Figure 8.4. Characterization of the catalyst on fibers; a) SEM image of the film of catalyst on fibers; b) XRD spectra of 10 Wt% Cu/TiO$_2$ catalyst; c) UV-vis spectra of the thin film of catalyst.
ratio, indicating that Cu is mainly dispersed on the surface of the structure. This is in agreement with the values obtained by Tseng et al (2002) on Cu/Ti ratios for sol-gel derived Cu/TiO2 catalysts.

Figure 8.5. XPS spectra of Cu/TiO2 catalyst; a) XPS of Cu 2p on catalyst; b) XPS of Ti 2p on catalyst 6.8 wt% Cu/TiO2
8.3.2 Effects of Flow Rate

Figure 8.6 shows that the overall production rate of methanol (0.0364±0.00141μmol.g-cat\(^{-1}.h^{-1}\)) is independent of feed flow rate (when flow rate >5mL min\(^{-1}\)) under our experimental conditions, such as UV intensity, CO2 and H2O partial pressures. Typically, if mass transfer resistance is significant, then the diffusion of CO2 and H2O towards the catalyst will be important and the overall rate of conversion will be dependent on the feed flow rate and the reaction is likely controlled by mass transfer. The overall reaction rate constant \(k^*\) is composed of two parts, the reaction at the surface and the mass transfer of the vapor toward the catalyst surface.

\[
\frac{1}{k^*} = \frac{1}{k_a} + \frac{1}{kK} \tag{8.3}
\]

where \(k\) is the intrinsic surface reaction rate constant (mol.L\(^{-1}.min^{-1}\)), \(K\) is the Langmuir-Hinshelwood adsorption constant (L . mol\(^{-1}\)), \(k_m\) is the mass transfer coefficient (cm/min) and \(a_v\) is the surface area of PBG titania per unit volume of the reactor (cm\(^2\).cm\(^{-3}\)).

![Effect of flow rate on production rate](image)

Figure 8.6. Flow rate effects on methanol yield rate. UV intensity=113.65mW.cm\(^2\), temperature is 70 °C, CO2 pressure is 1.5bar and H2O pressure is 0.032 bar.
In our experiments, within the feed rates range used the methanol production rate is only dependent on the reaction rate and not on the diffusion of the reactants towards the catalyst surface. The space velocity of CO2 gas and H2O vapor varied from 5-31mL.min⁻¹ for these series of experiments which were conducted at a constant temperature of 70°C.

8.3.3 Effects of Water Vapor Pressure

The rate of methanol formation on the catalyst can be assumed to occur via a Langmuir-Hinshelwood surface reaction mechanism, wherein both H2O and CO2 adsorb simultaneously on the Cu/io-TiO2 surface and react to form CH₃OH. The rate of methanol formation is given by (Wu et al, 2005)

\[
r_{CH₃OH} = \frac{kP_{H₂O}P_{CO₂}I^\beta}{(1+K_{H₂O}+K_{CO₂})^3}
\]

where \(k\) is the rate constant (μmol.g-cat⁻¹.bar⁻¹.h⁻¹), \(I\) is the light intensity (W.cm⁻²), \(\beta\) is the power intensity, \(K_{CO₂}\) and \(K_{H₂O}\) are respectively the adsorption equilibrium constants (bar⁻¹) for CO2 and H2O. Wu et al (2005) noted that for adsorption on titania at their experimental conditions, \(K_{H₂O}\) is much larger than \(K_{CO₂}\) and \(K_{CO₂}P_{CO₂}\) can be neglected when compared with \(K_{H₂O}P_{H₂O}\) and 1. Therefore, the denominator can be simplified and the equation (8.4) can be simplified to the following

\[
r_{CH₃OH} = \frac{kP_{H₂O}^2P_{CO₂}I^\beta}{(1+K_{H₂O})^3}
\]

Rearranging the above equation one obtains

\[
(rate * P_{H₂O})^{-1/3} = (kI^\alpha P_{CO₂})^{-1/3}P_{H₂O}^{-1} + K_{H₂O}^{-1/3} \]

Thus a plot of the LHS versus \(P_{H₂O}^{-1}\) gives the intrinsic rate constant \(k\) from the slope as

\[k = (slope)^{-3}(P_{CO₂}I^\beta)^{-1}\]

and \(K_{H₂O} = \frac{intercept}{(slope)}\). Experiments were conducted by varying the partial pressure of water vapor while keeping the partial pressure of CO2, UV intensity and temperature constant. Figure 8.7 is a plot of the methanol formation rate as a function of the partial pressure of water at \(P_{CO₂} = 1.5\) bar at a temperature of 70°C and \(I\) of 113 mW.cm⁻². The methanol yield increased gradually to 0.039 μmol.g-cat⁻¹.h⁻¹ at a water partial pressure of 0.038 bar and then declined as the
water partial pressure increased further. This indicated a competitive adsorption for the reactants CO₂ and H₂O on the titania active sites as implied by the Langmuir-Hinshelwood formalism. Figure 8.8 gives the plot of equation (8.6) from which the values of k = 2536 μmol.g-cat⁻¹.h⁻¹.bar⁻³ and K_H2O = 56.5 bar⁻¹ were obtained. The goodness of the fit was shown by the correlation coefficient of 0.98. The value of β was obtained independently as described in the next section. The reaction rate parameters for Equation (8.5) are summarized in Table 8.1, which can be used to obtain the rates for other conditions using the photonic titania catalyst.

![Figure 8.7](image)

**Figure 8.7.** Effects of water vapor pressure on methanol yield rate. Reaction temperature 70°C, CO₂ pressure 1.5 bar, UV intensity=113.65mW.cm⁻², flow rate=31mL.min⁻¹.

**Table 8.1.** Adsorption constant and rate parameters in the L-M model for the photonic titania

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>k(μmol/g-cat-hr-bar³)</td>
<td>2536.4</td>
</tr>
<tr>
<td>α</td>
<td>0.737±0.020</td>
</tr>
<tr>
<td>K1 (bar⁻¹)</td>
<td>56.47</td>
</tr>
</tbody>
</table>

*Experimental conditions: P_{CO2} = 1.5bar; P_{H2O} = 0.031bar; T = 70°C; 2 wt% Cu/io-TiO2, UV range: 37-113 mW.cm².*
8.3.4 Effects of UV Light Intensity and Quantum Efficiency

As described in chapter IV and chapter V, UV intensity effect on the reaction will be first-order when intensity is relatively small. With the increase of intensity, the power for intensity dependence will decrease (Lin et al., 2006). Figure 8.9 shows the dependence of the UV intensity of the lamp on the methanol production rate with all other experimental conditions fixed. Increasing UV intensity from 37 to 113 mW cm\(^{-2}\) increased the methanol production. The rate varies as \(I^\beta\) with \(\beta = 0.737 \pm 0.02\) if we fit the rate versus intensity by power model. Ideally the photoactivity will be proportional to the value of I. However, if the light flux exceeds the photon demand for a reaction, the power for intensity dependence will decrease. Table 8.2 lists the standard deviation of methanol production rate with increasing I. Good reproducibility in the overall rates of methanol production was observed at different intensities. A comparison of the UV intensity effect in a comparable optical fiber reactor, but with conventional powdered titania reported earlier (Wu et al., 2005) showed that the intensity variation was

Figure 8.8. The regression of equation (8.6) for the Langmuir-Hinshelwood model
much lower with $\beta = 0.20 \pm 0.16$. Wu et al (2005) used intensities as large as 1-16 W.cm$^{-2}$, which is three orders of magnitude higher than the range that we used in our experiments.

Figure 8.9 Effects on UV intensity on methanol yield rate. The power regression is also displayed in the figure. Reaction temperature 70°C, CO2 pressure 1.5 bar and H2O pressure 0.032 bar, UV intensity=113.65Mw.cm$^{-2}$.

Table 8.2 Effects of UV light intensity on the methanol formation and the quantum efficiency of the reaction.

<table>
<thead>
<tr>
<th>UV intensity, I /mW.cm$^{-2}$</th>
<th>Methanol yield /μmol.g-cat$^{-1}$.hr$^{-1}$</th>
<th>$\Phi E$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>113.65</td>
<td>0.0368 ± 0.0011</td>
<td>0.4701</td>
</tr>
<tr>
<td>57.09</td>
<td>0.0216 ± 0.0006</td>
<td>0.5493</td>
</tr>
<tr>
<td>43.91</td>
<td>0.0182 ± 0.0003</td>
<td>0.6018</td>
</tr>
<tr>
<td>36.70</td>
<td>0.0163</td>
<td>0.6448</td>
</tr>
</tbody>
</table>

*Note: $P_{CO2} = 1.5$ bar; $P_{H2O} = 0.031$ bar; $T = 70°C$; 2 wt% Cu/io-TiO2.

The fact that our experiments which were conducted at much lower UV intensities shows methanol production rates comparable to those of Wu et al who conducted experiments at high UV light intensities, indicates that photonic (inverse opal) titania on fiber optic tubes is superior to
conventional powdered titania in light utilization. It has also been shown from chapter IV and chapter 
V that macroporous inverse opal (photonic crystals) titania formed by a sol-gel technique is superior to 
commercial powdered titania (Magpantay, 2008). We offer the following explanation for the superior 
performance of Cu/io-TiO2 on fiber optic tubes for photoreduction: Fiber optic tubes provide a 
medium to deliver light effectively to the photocatalyst. Light absorption by the titania photocatalyst 
produces charge separation. The inverse opal (photonic crystals) configuration serve to promote light 
absorption by increasing the effective light path through the catalyst material. Instead of allowing the 
photon to escape the material, the inverse opal arrangement will increase the probability of electronic 
excitation by increasing the contact time for light within the photocatalyst. The photoreduction of CO2 
involves the generation of e/h+ pair on the inverse opal TiO2 catalyst and subsequent reaction of e- 
with CO2 to form CH3OH. The presence of Cu delays the e/h+ recombination on the inverse opal 
TiO2 catalyst, thereby increasing the excited sites and the reaction rate. The combination of slow 
photons and delayed e/h+ recombination on Cu/io-TiO2 improves the quantum efficiency in the 
MOFR configuration.

In order to confirm the above we calculated the overall quantum efficiency of the process. The 
quantum efficiency is defined as (Tseng et al, 2002)

\[ \psi_Q(\%) = \left( \frac{6\times\text{moles of methanol yield}}{\text{moles of UV photon available}} \right) \times 100 \]  

Equation (8.7) is based on the stoichiometry of the reaction wherein 6 moles of electrons are required 
to yield 1 mole of CH3OH and one e/h+ pair is formed for each photon. The total yield of methanol 
and photons absorbed were based on 24 hours of reaction. The total photon flux is calculated as the 
product of the UV light intensity (mW.cm⁻²), the cross sectional area of one fiber, the number of fibers 
per reactor, the radiation time and divided over the energy per photon. The energy per photon is hc/λ= 
5.68×10⁻¹⁹ J for λ = 350 nm. Table 8.2 summarizes the quantum efficiency as a function of intensity I. 
Figure 8.10 also shows the intensity effect on quantum efficiency. It is clear that the quantum 
efficiency decreased as the photon flux increased due to the fact that the abundance of photons exceeds
the number of photons required in the reaction. Thus, very high light intensities are not optimal for the process. We use power regression to fit the relationship. Since the quantum efficiency can be proportional to dividing reaction rate by intensity, the quantum efficiency should be proportional to the power $I^{\beta-1}$, which is $I^{0.27}$. So the quantum efficiency regression result fits the result of intensity effect on reaction rate constant.

![Graph showing the relationship between UV intensity and quantum efficiency](image)

Figure 8.10. Effects of UV intensity on quantum efficiency and the regression relationship between them

### 8.4 Conclusions

This chapter shows the fabrication and operation of a MOFR. The technique of photonic (inverse opal) titania on optical fibers was utilized to improve the conventional optical fiber reactor. Copper supported on inverse opal titania generated in-situ by sol-gel technology on optical fibers is effective in improving the photon utilization rate in a photocatalytic reactor. Inverse opal titania allows the slowdown of photons and improves the quantum efficiency for the photoreduction of
gaseous CO$_2$ to CH$_3$OH in the presence of water vapor and UV light. Methanol production rates were comparable to those of a conventional fiber optic reactor using Cu supported on unstructured titania, but required much lower light intensities. The production rate was independent of the feed rate indicating that the reaction is not mass-transfer controlled under our experimental conditions. The production rate increased with UV radiation intensity as $I^{0.74}$ in contrast to $I^{0.20}$ for unstructured titania.
Chapter 9. Conclusions and Recommendations

9.1 Conclusions

The application of photocatalysis for organic pollutant in exhaust gas and wastewater treatment and purification on an industrial scale can be assisted by the development of new photoreactor designs and application of new structured catalyst. A good photoreactor design should meet the following challenges: high ratio of the illuminated catalyst area to the volume of the reactor; uniform light distribution; high overall removal efficiency; high quantum efficiency; high throughput; low power consumption; and easily scale-up capability. To overcome these challenges, it is urgently important to have more efficient catalyst and reactor. And the phase and structure of catalyst is really important.

In this work, a novel monolithic optical fiber photocatalytic reactor coated with inverse opal titania was designed. The MOFR has the inherent advantages of a fixed-bed design. It can enhance the light distribution with the reactor and utilize the photons more efficiently. Also this configuration can provide more surface area given reaction volume. Using optical fiber instead of lamp to deliver UV light can save reactor space and remotely control the reactor. Inverse opal titania can control the light propagation in the fibers and distribute light more efficiently. The porous structure would increase mass transfer of reactant and provide more catalytic active surface. 1,2-dichlorobenzene, a major class of volatile organic compounds (VOC) contaminant, is selected as the contaminant in gas and water to prove the efficiency of the reactor. In addition, this reactor with inverse opal Cu/TiO2 catalyst was synthesized to photoreduce CO2 to methanol with the illumination of UV light.

Preliminary experiments were done to synthesize inverse opal catalyst and prove its higher efficiency than conventional P25 layered catalyst in gaseous phase. SEM images of inverse opal titania showed its photonic crystal structure. XRD spectra gave the details of its components and phase state. From XRD spectra, the in-situ synthesized catalyst is mainly anatase titania. UV-vis spectra were done to show its photonic bandgap properties. The spectra clearly showed there is a bandgap within the UV range when the template is 120nm polystyrene spheres. The inverse opal titania was grafted on quartz
rods and applied to a batch reactor. The experiments in the batch reactor showed about 250% higher efficiency than conventional P25 layered catalyst and faster reaction rate constant. The effects of UV intensity, flow rate, water vapor pressure and temperature were investigated. The results showed that UV intensity really affects the reaction rate. Mass transfer is not significant in the reactor system. Saturated water vapor in the gas flow decreases the reaction due to its condensation on the catalyst. Higher temperature increases the reaction.

A laboratory-scale monolithic optical fiber reactor with inverse opal titania was then designed and tested for its performance in photodegradation. Experimental results showed that inverse opal titania with PBG in UV range has faster reaction rate than inverse opal titania without PBG in UV range. This clearly showed that PBG plays a significant role in the reaction. The light distribution within optical fiber with inverse opal titania can transfer light to a longer distance. Flow rate and UV intensity effects were studied. The results showed that they worked simultaneously. With increase of flow rate and UV intensity, the reaction becomes faster. The bypass within the reactor was studied by blocking it by smaller optical fibers. By blocking the bypass, the actual flow rate increases and faster reaction is achieved. The change of velocity distribution within the reactor by blocking the bypass was proved by the simulation result of the velocity distribution.

A three-dimensional heterogeneous convection-diffusion-reaction model of MOFR was developed by incorporating radiant distribution model, flow dynamics model and Langmuir-Hinshelwood kinetics model. The simulation results fit the experimental results, such as the effects of UV intensity and block effect.

This MOFR was also utilized to degrade dilute DCB in wastewater. Experimental results showed it can work at aqueous phase and gaseous phase. The effects of flow rate and UV intensity on the reaction in aqueous phase were investigated. The model used in the gaseous phase was modified to simulate the result of aqueous phase. Simulation results explain the experimental results.
MOFR with inverse opal Cu/TiO2 catalyst was used to photoreduce CO2 to organic compound. New experimental equipment was designed. Inverse opal titania allows slowdown of photons and improves the quantum efficiency for the photoreduction of gaseous CO2 to CH3OH in the presence of water vapor and UV light. The production rate is comparable to those of unstructured catalyst with the similar reactor. The reduction is independent of mass transfer of CO2. UV intensity affects the reduction significantly.

**9.2 Recommendations**

One of the obstacles impeding the commercial use of the photocatalysis on degradation of organic compounds is due to the high energy consumption of the artificial UV light source. Thus solar photocatalysis is a more promising process since use of sunlight is much more economical and clean. Cost-effective technological applications of photocatalysis would require the development of photocatalysts that can use the visible light (400 nm < λ < 700 nm), the main part of the solar spectrum. Fe atom is found to insert into the TiO2–SiO2 lattice during sol–gel process, resulting in the full visible light absorption as well as the effect on product selectivity of the derived catalyst (Li et al., 2005). The visible-light-driven photocatalysis can be achieved through modifying the optical absorption of TiO2, i.e., extending the absorption of bulk TiO2 into visible region through narrowing the bandgap of TiO2 or introducing new absorption band. The bandgap of TiO2 can be narrowed by incorporating with anions such as F, C, N, Cr, F or S (Li et al., 2005; Khan et al, 2002; Asahi et al, 2001; Gole et al, 2004; Sakthivel et al, 2004), or cations such as Cr, Fe, W or V (Wu et al, 2008; Wu et al, 2006; Gao et al, 2006). When the doped TiO2 is used in the MORF, a sunlight collector, instead of the expensive short-arc light source, can be used to provide photons for the photoreaction.

Our experimental results in photoreduction show that the quantum efficiency is still far from commercial application. Although the inverse opal catalyst increases the efficiency, more work need to be done. The mechanism of photoreduction of CO2 is still not clear by now. In order to enhance quantum efficiency and increase reduction rate, photoreduction mechanism is vital. It determines what
kinds of measurements can be done to increase the reaction rate and quantum efficiency. In addition, decreasing the electron-hole recombination is another aspect. Doping cations can slow down the recombination and increase available active catalytic site for reaction. Attempt to find best doped TiO2 catalyst might significantly increase the quantum efficiency and make its commercial application possible.
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Appendix : List of Publications and Presentations

Publications


Presentations

Vita

Maoming Ren was born in 1979 in the People’s Republic of China. He received his Bachelor of Science and Master of Science degrees from Tianjin University in July 2001 and March 2004, both in chemical engineering. In August 2004, he came to Louisiana State University to pursue his doctoral degree in chemical engineering.