Abstract

Dawei Xu. Heterogeneous Catalytic Hydrogenation of Polymers Facilitated by Supercritical Carbon Dioxide. (Under the direction of Dr. George W. Roberts, Dr. Douglas J. Kiserow and Dr. Ruben G. Carbonell).

The heterogeneous catalytic hydrogenation of polystyrene (PS) in decahydronaphthalene (DHN) was studied in a batch reactor using 5%Pd/BaSO₄ as the catalyst. The effects of temperature and H₂ pressure were investigated over the ranges from 90 to 180°C and 250 to 1000 psig. At high H₂ pressure, the rate of PS hydrogenation was approximately first order with respect to aromatic ring concentration, with an apparent activation energy of 59.6 kJ/mol. For the hydrogenation of 3wt% PS solution at 150°C and with agitation above 2000 rpm, the resistance to gas-liquid mass transfer was negligible. Calculations indicated that influences of liquid-solid mass transfer and pore diffusion were minimal during hydrogenation of PS solutions at concentrations of 3wt% or less. The resistance to mass transport became severe in the hydrogenation of PS solutions at concentrations of 4.5wt% or higher.

Precipitation of PS from different solvents under high pressure CO₂ was investigated. DHN was selected as the solvent for PS hydrogenation in the presence of supercritical CO₂ (scCO₂) due to the high precipitation pressure and the saturated structure of DHN. It was found that H₂ solubility in CO₂-swollen DHN was substantially higher than in pure DHN at a constant H₂ pressure. Deactivation of 5%Pd/BaSO₄ was observed during PS hydrogenation in CO₂-swollen DHN above 150°C. The analysis of the gas phase showed that about 50 ppm CO was formed at 150°C, which could poison the catalyst. It was found that 65%Ni/Al₂O₃/SiO₂ could effectively convert CO to CH₄. Therefore, the bimetallic catalyst
system (5%Pd/BaSO₄ plus 3wt% 65%Ni/Al₂O₃/SiO₂) showed improved resistance to CO poisoning during PS hydrogenation in CO₂-swollen DHN.

The irreversible adsorption of PS on the surface of catalyst was found to lead to a lower hydrogenation rate. The adsorption of PS from DHN onto solid catalyst was studied. At equilibrium, the amount of adsorbed PS increased with increasing temperature. The presence of high pressure CO₂ significantly reduced the adsorption of PS. Assuming PS adsorption to be irreversible, a kinetic model of PS adsorption was developed and was demonstrated to be consistent with the experimental results at temperatures from 25 to 150°C.

**Keywords:** Polystyrene, Polycyclohexylethylene, Hydrogenation, Kinetics, Mass transfer, Supercritical CO₂, Phase equilibrium, Equation of state, CO poisoning, Reverse water gas shift reaction, Methanation, Start-up procedure, PS adsorption
Heterogeneous Catalytic Hydrogenation of Polymers
Facilitated by Supercritical Carbon Dioxide

By
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Approved by:

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Chair of Advisory Committee

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Biography

Dawei Xu was born in Xianghe, Hebei, P. R. China on December 22, 1975. He graduated from Xianghe High School in the July of 1994. In September of 1994, he attended Tianjin University and graduated with a Bachelor of Science in Chemical Engineering in June of 1998. In September of 1998, he entered the graduate program at Tianjin University and received a Master of Science in Chemical Engineering under the direction of Professor Zhentao Mi in June of 2000. In August of 2000, he enrolled as a Doctoral candidate in the Department of Chemical Engineering at North Carolina State University.
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Chapter 1

Introduction

The hydrogenation of polymers has been investigated as a post-polymerization process to modify the properties of the precursor polymers\textsuperscript{1-5}. Generally, the hydrogenated polymers show improved thermal and oxidative stability. For example, the hydrogenated styrene-butadiene-styrene copolymer, Kraton G\textsuperscript{®} (Shell)\textsuperscript{6}, exhibits excellent weatherability and improved thermal, oxidative and UV stability. This polymer has been used in laminating films, high performance adhesives, and sealants. The hydrogenated nitrile-butadiene rubber, Therban\textsuperscript{®} (Bayer)\textsuperscript{7}, has been used in seals, hoses, and belts in automobiles and oilfields due to its excellent thermal stability and improved resistance to oil and chemicals. Hydrogenated polystyrene (PS), polycyclohexylethylene\textsuperscript{4, 8}, exhibits enhanced thermal and oxidative stability, as well as excellent optical properties, and has been proposed for use in optical media.

Currently, there are two approaches to hydrogenating polymers, non-catalytic and catalytic. The non-catalytic technique is achieved by diimide reduction using a hydrazide reagent, such as $p$-toluenesulfonylhydrazide (TSH)\textsuperscript{9}. The diimide formed from the thermal decomposition of TSH reacts with C=C bond, adding hydrogen across the double bond and releasing the N$_2$. Although this method circumvents the use of high-pressure equipment, polymer chain scission during hydrogenation and contamination by the sulfur-containing residue in the polymer limit its application.
The catalytic technique includes both homogeneous and heterogeneous hydrogenations. The homogeneous hydrogenation utilizes a soluble metal complex as the catalyst. The homogeneous catalyst usually has a high activity for saturating the C=C bond in a polymer structure. However, separation and recycle of the catalyst from the hydrogenated polymer are complicated and expensive\textsuperscript{10}. Moreover, the residual metal in the polymer may influence the properties of the hydrogenated polymer and catalytically degrade the polymer\textsuperscript{11}. Heterogeneous catalysts are composed of active metal or metals supported on porous materials, which are insoluble in the polymer solution. Hence, heterogeneous catalysts are easier to separate after the hydrogenation, such that there is little or no metal contamination in the polymer. Recently, a new platinum catalyst supported on wide pore silica\textsuperscript{8, 12} was developed and demonstrated to be very active for hydrogenation of aromatic polymers, which had been rarely achieved by homogeneous catalysts.

However, mass transfer of H\textsubscript{2} and the unsaturated polymer to the catalytic sites on the heterogeneous catalyst can be slow or even controlling steps in the hydrogenation process. This is especially true when concentrated polymer solutions are to be hydrogenated. The low reaction rates, poor selectivity, and difficult scale-up that can be associated with the various mass transfer resistances can be impediments to the development of heterogeneous hydrogenation technology.

The motivation of this research is to use supercritical CO\textsubscript{2} (scCO\textsubscript{2}) as a processing aid for the hydrogenation of polymers. It is known that scCO\textsubscript{2} can increase the H\textsubscript{2} solubility in the liquid phase\textsuperscript{13, 14}, reduce the viscosity of polymer solutions\textsuperscript{15-18}; and increase the diffusion coefficient of the polymer in the solutions\textsuperscript{15}. All of these factors should increase the reaction rate and improve the selectivity. Moreover, the lower viscosity should make it possible to use
a continuous fixed-bed reactor for polymer hydrogenation, which eliminates the tedious step of separating small catalyst particles from the final polymer solution.

This research explores the feasibility of the hydrogenation of polymers in the presence of scCO₂. Heterogeneous hydrogenation of PS is chosen as the model reaction. The kinetics, mass transport, phase equilibrium, and catalyst deactivation in the hydrogenation of PS are studied.

Chapter One starts with an introduction to the properties and applications of hydrogenated polymers, with emphasis on hydrogenated aromatic polymers. Then, the homogeneous hydrogenation of polymers is briefly discussed. The heterogeneous hydrogenations of olefinic and aromatic polymers are discussed in detail. The mechanism and corresponding evidence of heterogeneous hydrogenation of polymers are presented. Following a brief introduction to supercritical fluids, the potential advantages of utilizing supercritical fluids in heterogeneous catalysis are explained. The applications of scCO₂ in heterogeneous hydrogenation are then reviewed.

Chapters Three and Four focus on kinetics and mass transport in the hydrogenation of PS in pure H₂, which is the baseline for subsequent studies in scCO₂. The reaction processes and analytic methods are discussed in Chapter Three. Then, the effects of temperature (90–180°C) and H₂ pressure (250-1000 psig) on PS hydrogenation are studied. It is found that partially hydrogenated PS consists of polymer with about 80% of the rings hydrogenated, plus some polymer that is lightly hydrogenated. This behavior is attributed to the 'blocky' hydrogenation mechanism, i.e. 80% of the aromatic rings in an individual polymer chain are hydrogenated after the polymer chain adsorbs on the catalyst surface and before the polymer chain desorbs. Then the polymer chain with about 80% of the rings saturated desorbs due to
the change of the thermodynamic driving forces between polymer, surface and solvent. Subsequent adsorption steps are required to achieve fully hydrogenated polymer. A kinetic model based on the above mechanism is developed and is found to be consistent with the experimental results. Finally, the apparent activation energy of PS hydrogenation is obtained as 59.6 kJ/mol.

The mass transfer processes in PS hydrogenation are investigated in Chapter Four. The viscosity and diffusivity of PS solutions are measured, which are necessary for calculating mass transfer rates in PS hydrogenation. It is found that mass transfer has minimal influence on the hydrogenation when the PS concentrations are 3wt% or less. The influence of mass transfer becomes serious when PS concentration is increased to 4.5wt% or higher.

Phase equilibrium is of great importance in supercritical technology. Before conducting hydrogenation in the presence of scCO$_2$, the phase equilibria involved in this process have to be investigated in order to understand the phase behavior and the equilibrium composition in each phase. These results are necessary for the design and control of the hydrogenation process. Carbon dioxide is an anti-solvent for PS, which causes PS to precipitate from a solution at certain pressures. The polymer precipitates are likely to block the catalyst surface and cause catalyst deactivation. Hence, Chapter Five starts with an investigation of the precipitation of PS from different solvents. Decahydronaphthalene (DHN) is selected as the solvent for PS hydrogenation in the presence of scCO$_2$ because of the high precipitation pressure and the stable structure of DHN. The volume expansions of DHN and PS-DHN solutions by high pressure CO$_2$ are investigated at various temperatures, pressures, PS molecular weights and PS concentrations. The phase equilibria of DHN-CO$_2$-
H₂ are calculated using the Peng-Robinson equation of state. It indicates that the increase of H₂ solubility in the liquid phase depends on the operating conditions and the properties of each compound in the system.

Catalyst deactivation is always a concern in heterogeneous catalysis. It has been reported that serious catalyst deactivation by carbon monoxide (CO) poisoning can take place during heterogeneous hydrogenation in the presence of scCO₂ because of the reverse water gas shift reaction¹⁹, ²⁰. In Chapter Six, the deactivation of 5%Pd/BaSO₄ in the presence of scCO₂ is observed during PS hydrogenation above 150°C. The analysis of the gas phase indicates that about 50 ppm CO is formed during hydrogenation at 150°C, which could poison the catalyst. A deactivation model is developed and is demonstrated to fit the experimental results reasonably well. The catalyst deactivation by CO poisoning is overcome by adding methanation catalyst (65%Ni/Al₂O₃/SiO₂) into the reaction, which converts CO to CH₄ effectively. The bimetallic catalyst system (5%Pd/BaSO₄ and 65%Ni/Al₂O₃/SiO₂) shows improved resistance to CO poisoning during PS hydrogenation.

The start-up procedures for PS hydrogenation are investigated in Chapter Seven. It is found that the irreversible adsorption of PS onto catalyst prior to the initiation of hydrogenation can cause a decrease in hydrogenation rate. Heating catalyst and PS solution separately until the desired temperature then adding them together and initiating the hydrogenation shows the highest hydrogenation rate. Moreover, the adsorption of PS onto catalyst is studied. The equilibrium amount of adsorbed PS on catalyst is found to increase with temperature. A kinetic model is developed to interpret the adsorption results.
References


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(7) [www.therban.com](http://www.therban.com).


Chapter 2

Literature Review:

Catalytic Hydrogenation of Polymers and Catalytic Hydrogenation in the Presence of Supercritical CO₂

2.1 Introduction

Hydrogenation of polymers is an important method for modifying the chemical and physical properties of the precursor polymer by reducing the unsaturated units in the polymer chain. The saturated polymers usually exhibit enhanced thermal and oxidative stability. Hydrogenation of polymers also can generate model polymers or copolymers with well-controlled microstructure, which is especially useful in fundamental studies1.

Homogeneous and heterogeneous catalytic hydrogenations are the two primary techniques for hydrogenating polymers2, 3. Generally, the homogeneous catalyst has a high activity and selectivity under mild reaction conditions. However, metal contamination in the hydrogenated polymers may cause polymer degradation. Heterogeneous hydrogenation usually requires more rigorous conditions, such as a higher H₂ pressure. The catalyst separation and reusability as well as the absence of the metal contamination in the produced polymers are the major advantages of heterogeneous hydrogenation.

The high viscosity and low diffusivity of a polymer solution can lead to a low mass transfer rate, which can influence or even control the overall hydrogenation rate. To enhance the mass transfer rate, more energy associated with heating or agitating will be needed.
Furthermore, the separation of small catalyst particles from a viscous polymer solution can be difficult.

Recently, supercritical CO$_2$ (scCO$_2$) has gained increased attention as a hydrogenation medium$^{4-6}$. Carbon dioxide can be miscible with H$_2$ to form a homogeneous phase, which avoids the gas-liquid interface and the corresponding gas-liquid mass transfer resistance. The low viscosity and high diffusivity of scCO$_2$ also will facilitate mass transfer from the fluid phase to the surface and into the interior of the solid catalyst. Therefore, hydrogenations that are limited by low mass transfer rates may be faster in the presence of scCO$_2$.

This chapter includes a review of the homogeneous and heterogeneous hydrogenation of polymers, with emphasis on the heterogeneous hydrogenation of aromatic rings in polymers. Furthermore, the properties of supercritical fluids and their application in catalysis are discussed in this chapter.

### 2.2 Hydrogenated polymers

Generally, a polymer hydrogenation process includes dissolution of polymer, hydrogenation, separation and drying. The extra cost for hydrogenation is always a major factor that inhibits the application of hydrogenated polymers. Hence, the hydrogenation of polymer is used only when polymer with a particular structure is difficult to synthesize by monomer polymerization alone$^3, 7$. However, the polymer hydrogenation technique should become more and more commercially viable due to the growth of the research in this field and the demand for high performance polymeric materials.

Hydrogenated polymers usually exhibit improved thermal and oxidative stability compared with the precursor, unsaturated polymers. Polymers that have been studied for
hydrogenation include polybutadiene, polyisoprene, styrene-butadiene-styrene copolymer (SBSC), nitrile butadiene rubber (NBR), polystyrene (PS), etc. Among them, hydrogenations of the butadiene units in SBSC and in NBR have been commercialized, producing the well-known Kraton G® (Shell) and Therban® (Bayer) polymers1.

Hydrogenation of polybutadiene produces polyethylene or poly(ethylene-co-butylene) depending on the structure of the precursor polybutadiene. As shown in Figure 2.1, the hydrogenation of 1,4-polybutadiene converts this elastomer to a tough semicrystalline polyethylene plastic1, 8. The properties of hydrogenated 1,4-polybutadiene and low density polyethylene are compared in Table 2.11. On the other hand, the hydrogenation of polybutadiene containing a moderate amount of 1,2-polybutadiene will give an elastomeric polymer, poly(ethylene-co-butylene), as shown in Figure 2.1.

\[
(-\text{CH}_2\text{-CH}=\text{CH}-\text{CH}_2-) + \text{H}_2 \rightarrow (-\text{CH}_2\text{-CH}-\text{CH}_2\text{-CH}_2-)
\]

\[
(-\text{CH}_2\text{-CH}=\text{CH}-\text{CH}_2-)(-\text{CH}_2\text{-CH}_2-) + \text{H}_2 \rightarrow (-\text{CH}_2\text{-CH}-\text{CH}_2\text{-CH}_2-)(-\text{CH}_2\text{-CH}_2-)
\]

Figure 2.1 Hydrogenation of polybutadiene

<table>
<thead>
<tr>
<th>Property</th>
<th>Hydrogenated 1,4-polybutadiene</th>
<th>Low density polyethylene</th>
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<td>Tensile strength, MPa</td>
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<td>Elongation, %</td>
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<td>Refractive index</td>
<td>1.50</td>
<td>1.51</td>
</tr>
</tbody>
</table>

Table 2.1 Properties of hydrogenated 1,4 polybutadiene and low density polyethylene1

The selective hydrogenation of butadiene units in SBSC produces the well-known ‘Kraton G’ polymer, as shown in Figure 2.2. This polymer consists of an ethylene-butylene
rubber phase with separated styrene units. The hydrogenated SBSC exhibits enhanced oxidation and weather resistance, higher service temperatures and increased stability, which allow it to be used as adhesives, sealants, coatings, etc.

Figure 2.2 Selective hydrogenation of styrene-butadiene-styrene copolymer

Hydrogenated NBR (HNBR, Therban) was developed during 1970s due to the requirement from automotive and oil industries for an elastomer with improved heat and oil resistance. Since then, HNBR has been well known for its dynamic properties at elevated temperatures, excellent resistance to ozone, hot air, oil and abrasion, and good low temperature behavior. Currently, HNBR is widely used as seals, hoses, and belts in automobiles, oilfields, etc.

Figure 2.3 Selective hydrogenation of nitrile butadiene rubber

Hydrogenated PS, polycyclohexylethylene or PCHE, exhibits unique physical properties, such as a higher glass transition temperature (147°C) than PS (105°C), which allows this new material to be used in high temperature environments. PCHE also shows
improved thermal, oxidative and UV stability. The density, dielectric constant and water absorption decrease after the aromatic rings of PS are saturated. Moreover, atactic PCHE, a highly transparent material, exhibits a twenty-four fold reduction in the stress optical coefficient compared to PS\textsuperscript{13}, which allows it to be used as an optical material. Table 2.2 lists the major properties of PCHE.

![Figure 2.4 Hydrogenation of PS](image)

**Table 2.2. Typical physical properties of polystyrene and polycyclohexylethylene\textsuperscript{11}\)**

<table>
<thead>
<tr>
<th>Physical Property</th>
<th>PS</th>
<th>PCHE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tg(°C)</td>
<td>105</td>
<td>147</td>
</tr>
<tr>
<td>Density (g/cm), 23°C</td>
<td>1.06</td>
<td>0.947</td>
</tr>
<tr>
<td>Heat Capacity (J/g.K), 25°C</td>
<td>1.22</td>
<td>1.39</td>
</tr>
<tr>
<td>Dielectric Constant, 1kHz</td>
<td>2.53</td>
<td>2.26</td>
</tr>
<tr>
<td>Refractive Index, 589nm</td>
<td>1.59</td>
<td>1.506</td>
</tr>
<tr>
<td>Water Absorption at 23°C,24h (%)</td>
<td>0.06</td>
<td>0.025</td>
</tr>
<tr>
<td>Coefficient of Thermal Expansion&lt;Tg (µm/m°C)</td>
<td>69</td>
<td>64</td>
</tr>
<tr>
<td>Flexural Modulus (Gpa), 25°C</td>
<td>3.1</td>
<td>2.8</td>
</tr>
<tr>
<td>Plateau Modulus, G\textsubscript{N}\textsuperscript{o} (Pa)</td>
<td>200,000</td>
<td>81,000</td>
</tr>
<tr>
<td>Entanglement Molecular Weight (M\textsubscript{e})</td>
<td>18,000</td>
<td>39,000</td>
</tr>
<tr>
<td>Backbone Atoms between Entanglements</td>
<td>170</td>
<td>350</td>
</tr>
<tr>
<td>Stress-Optical Coefficient (Brewsters, 10\textsuperscript{-12}Pa\textsuperscript{-1})</td>
<td>-4700</td>
<td>-160</td>
</tr>
</tbody>
</table>

The application of PCHE has been focused on utilizing its excellent optical properties as digital video disc substrates\textsuperscript{12}. The high transparency of PCHE in the near UV region gives rise to the potential to replace polycarbonate in manufacturing high density DVDs because
polycarbonate exhibits high absorption in this region\textsuperscript{13, 14}. Moreover, the low stress optical coefficient of PCHE leads to a low birefringence and the low water adsorption gives easy control of deformation during molding\textsuperscript{12}. The lower density of PCHE can compensate part of the cost of hydrogenation because the polymer will be sold by weight but used by volume as the material for optical storage media\textsuperscript{13}.

On the other hand, the bulky cyclohexane rings in PCHE hinder the polymer chains from coiling tightly and cause a higher entanglement molecular weight (\(M_e\)) as shown in Table 2.2\textsuperscript{11}. Normally glassy polymers must have a molecular weight more than ten times \(M_e\) to achieve acceptable toughness\textsuperscript{13}. The high entanglement molecular weight of PCHE and therefore its brittle glassy behavior may limit its applications. Recently, Bates et al.\textsuperscript{13, 15, 16} attempted to improve the toughness of PCHE by incorporating rubbery saturated diene blocks into PCHE chain to form a block copolymer. They found the hydrogenated butadiene-styrene pentablock copolymer showed significant improvements in toughness. They reported that this hydrogenated copolymer could be used in thin-wall injection-molded applications, such as optical media discs, due to its excellent combination of mechanical and optical properties.

PCHE and its copolymers also have been proposed as a dielectric layer in capacitor films because of their high \(T_g\), high breakdown voltage and low moisture absorption\textsuperscript{17}. High temperature insulating foams prepared from PCHE-based polymers have also been reported. The high \(T_g\), improved thermal stability and UV stability, and good weatherability allow these foams to be used in extreme environments\textsuperscript{18}. The use of PCHE-containing polymers as positive photoresist substrates\textsuperscript{19} and elastic fibers\textsuperscript{20} has also been reported. Recently, Wolf and Hillmyer\textsuperscript{21} synthesized PCHE monoliths with nanoporous structure. These PCHE
monoliths showed improved thermal stability, oxidative stability and solvent resistance compared to PS, therefore it can be used as templates for synthesizing nanomaterials.

The hydrogenations of PS derivatives or other polymers containing aromatic rings also have been reported. Gehlsen et al.\textsuperscript{22} studied the hydrogenation of poly(methylstyrene). Higher glass transition temperature was found for the hydrogenated poly(methylstyrene). Later, high $T_g$ materials were synthesized by hydrogenation of polyindene\textsuperscript{23}, poly(styrene-co-1,1-diphenylethylene)\textsuperscript{24} and poly(styrene-co-methylstyrene)\textsuperscript{25}, indicating that catalytic hydrogenation of aromatic polymers could be an efficient way to create high $T_g$ materials.

\textbf{2.3 Homogeneous hydrogenation of polymers}

Homogeneous hydrogenation catalysts are usually well-defined metal complexes, which are soluble in solution. The homogeneous catalysts for polymer hydrogenation include\textsuperscript{7}: Ziegler-type catalyst, rhodium complexes, ruthenium complexes, palladium complexes, and iridium complexes. For example\textsuperscript{7, 26}, the well-known Wilkinson's catalyst, RhCl($\text{PPh}_3$)$_3$, shows high selectivity and high yield in hydrogenation of NBR. The presence of the nitrile groups and the saturated diene units in HNBR is responsible for its excellent resistance to oils, fuels and chemicals. Hence high selectivity to the C=C bond is essential in NBR hydrogenation to maintain its unique properties. On the other hand, the nitrile group in the NBR chain may coordinate with the catalyst, which can inhibit the catalyst activity. Therefore, a catalyst that has high activity for hydrogenating the C=C bond, without causing significant reduction of the CN group and without being inhibited by the presence of the CN group is necessary for NBR hydrogenation. Hence, Wilkinson's catalyst has gained growing interest for NBR hydrogenation. A detailed mechanism and kinetics of NBR hydrogenation
catalyzed by this catalyst have been reported\textsuperscript{26}. Hydrogenation of C=C bonds in other polymers catalyzed by the ‘Wilkinson’ catalyst has also been studied\textsuperscript{8, 27, 28}.

The cost of rhodium catalyst is always a concern in polymer hydrogenation. Therefore, homogeneous hydrogenation of polymers catalyzed by other metal complexes has been investigated. The lower cost of ruthenium or palladium complexes allows them to be alternatives to the expensive Rh complexes\textsuperscript{7}. A comprehensive review of the homogeneous hydrogenation of polymers has been published by McManus and Rempel\textsuperscript{7}.

Homogeneous catalysts usually has high activity and selectivity for polymer hydrogenations. Thus hydrogenation processes can be carried out under mild conditions, which is important to avoiding unwanted side reactions, such as chain scission or crosslinking. However, it is difficult and expensive to recover the homogeneous catalyst from a polymer solution\textsuperscript{29, 30}. Moreover, the residual metal in the hydrogenated polymer can catalytically degrade the polymer\textsuperscript{30, 31}. These factors limit the application of homogeneous catalysts in polymer hydrogenation.

2.4 Heterogeneous hydrogenation of polymers

The heterogeneous hydrogenation catalysts are composed of transition metals (e.g., Ni, Pd, Pt, Rh) supported on a porous material, such as alumina, silica, barium sulfate, etc. Reactant molecules diffuse into the catalyst, adsorb on the metal crystallites and react with H\textsubscript{2}. Due to the large dimension of polymer molecules, the rate of diffusion of polymer chains into the heterogeneous catalyst is always a concern. The low diffusion rate will cause a low hydrogenation rate. Large pore catalyst supports can lower the resistance to pore diffusion. However, the low surface area and the low metal dispersion that often are associated with large pore supports can lead to a low concentration of active sites and a corresponding low
rate of hydrogenation. Thus a proper balance between the pore size and the surface area is necessary for polymer hydrogenation.

The early heterogeneous hydrogenation of polymers was called ‘destructive hydrogenation’, which produced low molecular weight fuels\(^2\). In 1950s, successful nondestructive hydrogenation of polymers was conducted by using Ni/kieselguhr and Pd/CaCO\(_3\) as catalysts\(^2\). However, the low activity of heterogeneous catalysts made them unfavorable compared with homogeneous catalysts. Later, Rachapudy et al.\(^{32}\) compared homogeneous hydrogenation and heterogeneous hydrogenation of 1,2-polybutadiene. The results indicated that only heterogeneous hydrogenation could produce fully saturated polymer, without incorporation of foreign groups. From then on, heterogeneous catalytic hydrogenation of various polymers has been studied extensively for both fundamental and practical interests.

2.4.1 Heterogeneous hydrogenation of olefinic polymers

In 1979, Rachapudy et al.\(^{32}\) reported the hydrogenation of polybutadiene with Ni/kieselguhr and Pd/CaCO\(_3\). Later, hydrogenation of poly(vinylethylene)\(^{33}\), poly(1,3-dimethyl-1-butenylene)\(^{34}\) and polyisoprene\(^{35}\) with Pd/CaCO\(_3\) were studied. Other heterogeneous catalysts, such as Pd/C\(^{36}\), Pd/BaSO\(_4\)\(^2\).\(^{37}\) and Pd/Al\(_2\)O\(_3\)\(^{31}\), have also been investigated for the hydrogenation of C=C bonds in polymers. After studying the hydrogenation of SBSC catalyzed by Pd/Al\(_2\)O\(_3\) with different pore sizes, Change and Huang\(^{31}\) reported that catalyst with an average pore diameter of 38.9 nm presented the highest conversion and selectivity for hydrogenating the olefinic structure in this copolymer. They concluded that catalyst having larger pores had lower mass transfer limitations, but had a low metal dispersion at the same time, which could cause a poor activity. Hence, a catalyst
with a proper pore diameter would show the highest activity because of the good balance between mass transfer and catalytic site dispersion. However, the low activation energy observed in Change and Huang's work\textsuperscript{31} suggested that mass transport might still influence hydrogenation kinetics with this Pd/Al\textsubscript{2}O\textsubscript{3} catalyst. On the other hand, Hucul\textsuperscript{38} studied the hydrogenation of styrene-isoprene-styrene copolymer and polybutadiene. It was found that catalysts with pore sizes in a range of 1000 to 5000 nm showed the best performance. Although these two articles claimed different optimum pore sizes for heterogeneous hydrogenation of polymers, both groups concluded that catalysts with well-controlled pore size exhibited high activity.

In 1984, Schulz and Worsfold\textsuperscript{39} studied the heterogeneous hydrogenation of polyisoprene with 5\%Pd/CaCO\textsubscript{3}. They found that partially hydrogenated polymers from heterogeneous hydrogenation were cloudy, whereas similar homogeneously hydrogenated polymers were clear. This indicated some inhomogeneity in the polymers from heterogeneous hydrogenation. In subsequent investigation, it was realized that partially hydrogenated polymers were composed of fully hydrogenated polymer and polymers that contained no appreciable hydrogenation. Hence, Schulz and Worsfold proposed the 'blocky' mechanism for heterogeneous hydrogenation of polymers, i.e., that the polymer chain was not readily desorbed once adsorbed on the catalyst surface until most of the monomer units had been hydrogenated.

Later, Rosedal and Bates\textsuperscript{40} confirmed the 'block' hydrogenation mechanism by studying the heterogeneous hydrogenation of poly(vinylethylene). They extracted a polymer sample with 47\% units hydrogenated using 1-octanol. It was found that the extracted polymer showed 85\% of the repeat units hydrogenated. Thus they concluded that partially
hydrogenated polymer consisted of essentially unhydrogenated precursor polymer and 85% hydrogenated polymer. Furthermore, they qualitatively interpreted the above results by a 'blocky' mechanism as followings: 85% of the repeat units in an individual polymer chain were hydrogenated during a single adsorption step. Subsequent adsorption steps were necessary to achieve complete hydrogenation. Furthermore, they estimated the equilibrium fraction of adsorbed polymer segments in an individual polymer chain as 30%, which was less than the conversion (85%) in the first adsorption. Thus conformational rearrangement of polymer chains must occur during the first adsorption step to present the unsaturated units to the catalyst surface for hydrogenation. The conversion in the first adsorption step can be influenced by some factors. For example, unhydrogenated polymer chains in solution can compete for the metal surface with the adsorbed polymer chains. Polymer concentration could influence the competition between unhydrogenated polymer chains and adsorbed polymer chains and therefore influence the conversion in the first adsorption step. On the other hand, the dynamics of conformational rearrangement might be too slow to allow the adsorbed polymer to compete for catalytic sites with unadsorbed polymer molecules. Desorption then would occur. Hence, factors that could influence the conformational rearrangement rate, such as polymer molecular weight, could affect the conversion in the first adsorption step. In 1998, Cassano et al. studied the heterogeneous hydrogenation of polybutadiene and demonstrated that the hydrogenation followed a similar 'blocky' mechanism. It was found that the 'blocky' hydrogenation mechanism was independent of the solvent and catalyst used in the hydrogenation process.
2.4.2 Heterogeneous hydrogenation of aromatic polymers

The hydrogenation of aromatic ring is more difficult than the hydrogenation of C=C structures\textsuperscript{40}. Few homogeneous catalysts have been successfully utilized for the hydrogenation of aromatic rings. On the other hand, heterogeneous catalytic hydrogenation of aromatic rings in small molecules is common\textsuperscript{42-45}. The mechanism and kinetics of hydrogenation of aromatic rings have been studied in detail\textsuperscript{43-45}. Consequently, the hydrogenation of aromatic rings in polymers catalyzed by heterogeneous catalysts have also been investigated\textsuperscript{2, 3, 11, 46-50}.

Polystyrene is the most common polymer that has been studied for the hydrogenation of aromatic rings in polymers. The first study of PS hydrogenation appeared over 70 years ago\textsuperscript{51}. From then on, this reaction has been studied by many research groups. Various heterogeneous catalysts and solvents have been used for this reaction. Table 2.3 summarizes the results from different research groups.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>T (°C)</th>
<th>P\textsubscript{H2} (psi)</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raney Ni\textsuperscript{52}</td>
<td>250</td>
<td>3820</td>
<td>DHN</td>
</tr>
<tr>
<td>10%Rh/Charcoal\textsuperscript{53}</td>
<td>200</td>
<td>2000</td>
<td>DHN</td>
</tr>
<tr>
<td>75%Ni/Kieselgur\textsuperscript{54}</td>
<td>165</td>
<td>2939</td>
<td>CYH/THF</td>
</tr>
<tr>
<td>5%Pd/BaSO\textsubscript{4}\textsuperscript{22, 37}</td>
<td>140</td>
<td>500</td>
<td>CYH/THF</td>
</tr>
<tr>
<td>5%Pd/BaSO\textsubscript{4}\textsuperscript{55, 56}</td>
<td>190</td>
<td>1740</td>
<td>MCYH</td>
</tr>
<tr>
<td>66%Ni/SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3}\textsuperscript{49, 57}</td>
<td>160</td>
<td>1450</td>
<td>CYH/THF</td>
</tr>
<tr>
<td>5%Pt/SiO\textsubscript{2}\textsuperscript{46, 47}</td>
<td>150</td>
<td>875</td>
<td>CYH</td>
</tr>
</tbody>
</table>

DHN---Decahydronaphthalene, CYH---Cyclohexane, THF---Tetrahydrofuran, MCYH---Methylcyclohexane

Among the results in Table 2.3, the last process developed by Dow Chemical Company\textsuperscript{46, 47} has the highest hydrogenation rate. Most conventional hydrogenation catalysts usually have high surface area and small pore size, which can limit the access of large
polymer molecules to the catalytic sites inside the pores of catalysts. Thus, these catalysts have fewer catalytic sites available for PS hydrogenation, and therefore show a lower activity than large pore catalysts. Traditional catalysts with large pores also exhibit a low activity for polymer hydrogenation due to low surface area and poor metal dispersion. Hence, a catalyst with a good combination of high surface area and metal dispersion as well as reasonably large pore size is desirable for polymer hydrogenation. Dow's 5\%Pt/SiO_{2} catalyst has a surface area of 16.5 \text{ m}^{2}/\text{g} and average pore size 380 nm. Moreover, this catalyst has a narrow pore size distribution which is well controlled between about 80 nm and 1000 nm. The unique large pore structure of Dow’s 5\%Pt/SiO_{2} catalyst allows large polymer molecules to rapidly diffuse into the catalyst, and then rapidly diffuse back into the solvent after the surface reaction. Hence, this catalyst shows superior catalytic performance for PS hydrogenation.

Bayer AG’s patents\textsuperscript{49, 57} claim that the addition of another solvent, such as THF, promotes the hydrogenation rate. It has been suggested that the additional solvent enhances the miscibility of PS in the solvents and increase its radius of gyration\textsuperscript{2, 58}. The change of the solvent quality also may favor the adsorption and conformational rearrangement of polymer chains on the metal crystallites. Thus, the hydrogenation rate can be increased. However, the function of solvent on polymer hydrogenation is still a subject of speculation. Effects of solvent on polymer hydrogenation need further investigation.

Similar to the 'blocky' mechanism for the heterogeneous hydrogenation of C=C bonds in polymers, the commonly accepted mechanism for heterogeneous hydrogenation of PS is\textsuperscript{12}: diffusion of PS into the pores of catalyst, adsorption of PS onto the catalyst surface, hydrogenation reaction, conformational rearrangement of the PS chain on the catalyst surface
to further hydrogenate other unsaturated units in this PS chain, and desorption. Desorption occurs once most of the aromatic units in the PS chain have been saturated. This hydrogenation mechanism leads to a mixture of fully saturated (or mostly saturated) polymer and unsaturated (or lightly saturated) polymer. Nakatani et al.\textsuperscript{56} found that partially hydrogenated PS showed phase-separated morphologies, which suggested that partially hydrogenated PS consisted of a mixture of saturated and unsaturated chains. Weimann\textsuperscript{3} extracted a 40% saturated PS sample with hexane. The extracted polymer was 83% saturated while the residual undissolved polymer was only 20% saturated. This result is consistent with the 'blocky' hydrogenation mechanism. Ness et al.\textsuperscript{59} studied the effect of molecular weight on the PS hydrogenation catalyzed by Dow's Pt/SiO\textsubscript{2}. It was found that the initial rate of hydrogenation was inversely proportional to the molecular weight. Based on the above hydrogenation mechanism, they attributed the effect of molecular weight on the hydrogenation rate to the influence of molecular weight on the dynamics of polymer conformational rearrangement on the metal crystallite. Finally they suggested that catalysts with metal crystallite larger than the dimension of polymer chain should yield the highest activity for polymer hydrogenation.

2.5 Supercritical fluids

As shown in Figure 2.5, the temperature-pressure phase diagram of a substance is composed of four regions: gas (G), liquid (L), solid (S) and the supercritical region. When the temperature and pressure of a substance is above its critical temperature ($T_c$) and critical pressure ($P_c$), it is termed a supercritical fluid. A supercritical fluid possesses physical properties similar to both gases and liquids, as shown in Table 2.4. The density of a supercritical fluid is close to a liquid, which gives it a strong dissolving ability compared to a gas. Substances that
cannot be dissolved by a gas often can be dissolved by a supercritical fluid. Supercritical fluids have higher heat capacity than gases, which can lead to better temperature control of a process. The diffusivity of components in supercritical fluids is about an order of magnitude higher than in liquids, and the viscosity of supercritical fluids is at least an order of magnitude lower than the viscosity of liquids, all of which lead to faster mass transfer rates. Another important property of supercritical fluids is their 'tunability'. Physical properties of supercritical fluids can be adjusted by simply changing temperature or pressure. Although properties of gases or liquids can be changed by changing temperature and pressure, such changes are much smaller than those in the supercritical state. This gives one more flexibility in using supercritical fluids.

Figure 2.5 P-T phase diagram of a substance
Table 2.4 Typical physical properties of gas, liquid and supercritical fluid

<table>
<thead>
<tr>
<th></th>
<th>Density (kg/m³)</th>
<th>Viscosity (cP)</th>
<th>Diffusion Coefficient (cm²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas</td>
<td>1</td>
<td>0.01</td>
<td>0.1</td>
</tr>
<tr>
<td>Supercritical Fluid</td>
<td>300-800</td>
<td>0.03-0.1</td>
<td>0.001</td>
</tr>
<tr>
<td>Liquid</td>
<td>1000</td>
<td>1</td>
<td>0.00001</td>
</tr>
</tbody>
</table>

Table 2.5 lists the critical conditions of some commonly used supercritical fluids. Among them, carbon dioxide has gained the greatest attention because its critical condition is relatively mild and it is non-toxic and inexpensive. Hence, carbon dioxide has been successfully used in many academic researches and industrial processes, such as extraction and separation, reaction, material processing, microelectronics processing, and so on. The following sections will be focused on the utilization of supercritical fluids in heterogeneous catalysis.

Table 2.5 Critical conditions of commonly used supercritical fluids

<table>
<thead>
<tr>
<th></th>
<th>Tc (°C)</th>
<th>Pc (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Dioxide</td>
<td>31.1</td>
<td>73.8</td>
</tr>
<tr>
<td>Ethane</td>
<td>32.2</td>
<td>48.8</td>
</tr>
<tr>
<td>Ethene</td>
<td>9.3</td>
<td>50.4</td>
</tr>
<tr>
<td>Propane</td>
<td>96.7</td>
<td>42.5</td>
</tr>
<tr>
<td>Propene</td>
<td>91.9</td>
<td>46.2</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>280.3</td>
<td>40.7</td>
</tr>
<tr>
<td>Isopropanol</td>
<td>235.2</td>
<td>47.6</td>
</tr>
<tr>
<td>Benzene</td>
<td>289.0</td>
<td>48.9</td>
</tr>
<tr>
<td>Toluene</td>
<td>318.6</td>
<td>41.1</td>
</tr>
<tr>
<td>p-Xylene</td>
<td>343.1</td>
<td>35.2</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>344.0</td>
<td>36.0</td>
</tr>
<tr>
<td>Chlorotrifluoromethane</td>
<td>28.9</td>
<td>39.2</td>
</tr>
<tr>
<td>Trichlorofluoromethane</td>
<td>198.1</td>
<td>44.1</td>
</tr>
<tr>
<td>Ammonia</td>
<td>132.5</td>
<td>112.8</td>
</tr>
<tr>
<td>Water</td>
<td>374.2</td>
<td>220.5</td>
</tr>
</tbody>
</table>
2.5.1 Supercritical fluids in heterogeneous catalysis

A heterogeneous catalytic reaction can occur at the internal or external surface of a heterogeneous catalyst. Hence, mass transfer steps are necessary prior to and after the surface reaction in order to transfer the reactants to the catalytic sites and to transfer the products back into the bulk fluid. A supercritical fluid can significantly affect the chemical reaction on the surface of the catalyst and the mass transfer steps\textsuperscript{6,60}.

Pressure can influence the equilibrium and kinetics of many chemical reactions. Therefore, the pressure associated with supercritical conditions can have a significant effect on the equilibrium and kinetics of a chemical reaction. The reaction rate and equilibrium constant of a chemical reaction at supercritical conditions can be much different from those in a liquid or gas phase. Moreover, the change of solubility and density from a liquid or gas to a supercritical fluid can influence the rate and equilibrium of a chemical reaction. The effect of changing reaction conditions from a liquid or gas to the supercritical regime is different for different reactions. Thus the selectivity of a reaction network can be affected by changing the reaction conditions to supercritical regime. Therefore, the reaction rate and selectivity can be adjusted by properly changing the reaction conditions to the supercritical regime.

Mass transfer is very important in heterogeneous catalytic reactions. The chemical reaction cannot take place until the reactants have been transferred to the catalytic sites. The reaction cannot be continued if the products are not transferred away from the catalyst in order to leave the catalytic sites available for the fresh reactants. Hence, the overall reaction rate can be influenced or even controlled by the mass transfer rates. A supercritical fluid eliminates the gas-liquid interface and therefore the gas-liquid mass transfer resistance,
which could be the rate-limiting step in some catalytic reactions. Moreover, the viscosity of a supercritical fluid is lower than a liquid and the diffusivity of substances in a supercritical fluid is higher than in a liquid. Both of these will enhance the mass transfer rate. Hence, mass transfer controlled reactions can be accelerated by changing conditions to the supercritical regime. On the other hand, a supercritical fluid has higher heat capacity and thermal conductivity than a gas. The temperature control of a reaction at supercritical conditions can be much better than in the gas phase\(^4\). Better temperature control can lead to an improvement in reaction selectivity and process safety.

The solubility of heavy organics is higher in supercritical fluids than in gases. The deposition of heavy organics on the surface of catalyst can cause catalyst deactivation. The high solubility and high diffusivity of heavy organics in supercritical fluids can accelerate the removal of heavy organics from the catalyst surface and extend the catalyst lifetime\(^6\). Moreover, the pressure tunable property of supercritical fluids can be used to vary the solubility of reactants and products, which could facilitate the separation of products from reactants. Finally, a supercritical solvent can be easily recovered by releasing pressure after reaction\(^6\).

Supercritical fluids have been successfully used in many heterogeneous catalytic reactions, such as alkylation, amination, esterification, Fischer-Tropsch synthesis, isomerization, oxidation and hydrogenation\(^6, 60\). The cost of high-pressure equipment associated with supercritical operation is one of the factors that can limit the applications of supercritical fluids. However, the chemical industry has already learned how to handle a high-pressure process. Many of the above catalytic reactions have been operated at high-pressure without using supercritical technology. Moreover, the fast reaction rate, high
selectivity and extended catalyst lifetime in a supercritical reaction will require a smaller reactor and will allow the reaction to be operated for a longer time. All of these can compensate the cost of high-pressure equipment and make the catalytic reaction at supercritical conditions economically feasible.

2.5.2 Heterogeneous hydrogenation in supercritical CO₂

In a typical heterogeneous hydrogenation in the liquid phase, H₂ has to diffuse through the gas-liquid interface into the liquid and then diffuse to and into the catalyst to access the catalytic sites. The solubility of H₂ in organics is usually low, which can lead to a low gas-liquid mass transfer rate. The low mass transfer rate can affect the overall hydrogenation rate. Therefore, more energy associated with agitation or heating is required to enhance the mass transfer rate. On the other hand, hydrogenation in a supercritical fluid can eliminate the gas-liquid mass transfer resistance due to the absence of the gas-liquid interface. Hence hydrogenation in a supercritical fluid has attracted the interest of many academic and industrial research groups.

CO₂ exhibits totally miscibility with H₂ above 304K, which allows them to form one phase at most commonly used hydrogenation temperatures. CO₂ is a non-flammable gas. It can expand the non-explosive regime of H₂ and air so that the safety of a hydrogenation process can be improved. Moreover, CO₂ possesses a mild supercritical condition and is non-toxic and inexpensive. Hence, supercritical CO₂ has gained substantial attention for supercritical hydrogenation.

Tacke et al. studied the hydrogenation of fats and oils in scCO₂. The hydrogenation was conducted in a continuous fixed bed reactor and 6 fold increase of the space time yields was observed. Moreover, the selectivity was improved and the catalyst lifetime was extended
by using scCO$_2$. Hitzler et al.$^{64}$ investigated the hydrogenation of cyclohexene in scCO$_2$ in a continuous reactor that was operated at constant pressure. The hydrogenation process achieved high liquid hourly space velocity ($300$ h$^{-1}$) and space-time yield ($2.5 \times 10^5$ kg/h/m$^3$). The reaction medium was a single phase at the beginning of the reactor. To assure that it remained one phase, Hitzler et al.$^{64}$ monitored the temperature gradient along the reactor at different flow rates of cyclohexene. Then, phase diagrams at different temperatures were generated using the Peng-Robinson equation of state. The phase diagrams confirmed that the reaction took place in a single phase along the whole reactor. Some general conclusions were drawn from this phase equilibrium study, which could be applied to other supercritical hydrogenation systems: (a) the miscibility of the system improved with reducing H$_2$ concentration, (b) above $60^\circ$C, the regions of miscibility increased apparently with increasing temperature, (c) only a small amount of CO$_2$ was required to form one phase system at high temperatures. Subramanian et al.$^{4,65,66}$ also examined the hydrogenation of cyclohexene in scCO$_2$. By tuning the pressure and temperature, such that the reaction mixture had a liquid-like heat capacity, they demonstrated that the reaction temperature could be effectively controlled at 343K for an olefin space velocity of $20$ h$^{-1}$, and that the catalyst activity remained stable for a 22 hour run at cyclohexene conversion exceeding 80%. Tschan and coworkers carried out the selective hydrogenations of phenylacetylene$^{67}$ and propargylic alcohol$^{68}$ in scCO$_2$. They found that the ideal reaction medium was a single-phase fluid created by high pressure CO$_2$. High conversion and good selectivity were achieved in these single-phase reactions. Philai et al.$^{69}$ investigated the single-phase hydrogenation of 4-oxoisophorone in a supercritical medium. Higher conversions are achieved in scCO$_2$ compared with those obtained in conventional organic solvents. Furthermore, CO$_2$-organic
cosolvent systems were investigated. No advantage was found from CO₂-organic cosolvent systems in this research. Burgener et al.\textsuperscript{70} investigated the hydrogenation of citral in a continuous fixed-bed reactor and a batch reactor. The reaction rate was remarkably higher in the presence of CO₂ at a single-phase condition than in conventional organic solvents. The influences of reactor type, pressure and feed composition on the reaction rate and product distribution were observed. Bhanage et al.\textsuperscript{71} studied the selective hydrogenation of α,β-unsaturated aldehydes. The selectivity to unsaturated alcohols is higher in scCO₂ than in organic solvents. The selectivity depended mainly on CO₂ partial pressure, while the conversion depended on both CO₂ and H₂ partial pressures. Finally, the authors mentioned that one more advantage in this process was the easy separation of catalyst at reduced pressure after reaction.

Heterogeneous hydrogenation in the presence of high pressure CO₂ has also been investigated at two fluid phase conditions: a gas-like fluid phase and a liquid-like fluid phase. The two fluid phase condition usually requires low pressure compared with single fluid phase system. The presence of CO₂ in the liquid-like fluid phase can enhance the solubility of H₂ in the liquid and therefore improve the reaction rate and mass transfer rate\textsuperscript{5}. Devetta et al.\textsuperscript{72} studied the catalytic hydrogenation of an unsaturated ketone in scCO₂ at two fluid phase conditions. Internal and external mass transfer were investigated and detailed kinetic models were developed to interpret the experimental data. Devetta et al.\textsuperscript{72} explored the effect of CO₂ on the solubility of H₂ in the liquid phase using the Peng-Robinson equation of state. The H₂ solubility approached a maximum when the ratio of CO₂ to organics was around one. Consequently, maximum reaction yield was obtained at a ratio of CO₂ to organics around one, which indicated the high solubility of H₂ led to a faster rate. Phiong et al.\textsuperscript{73} studied the
three-phase catalytic hydrogenation of α-methylstyrene in scCO₂. It was found that scCO₂ significantly enhanced the rate of hydrogenation, which was attributed to the enhanced solubility of H₂ in the liquid. A maximum reaction rate was obtained with 50wt% CO₂ (H₂-free basis) in the system, which was consistent with Devetta's work. Chouchi et al.⁷⁴ reported that hydrogenation of α-pinene in scCO₂ exhibited higher reaction rate at two fluid phase conditions than at single-phase conditions. The faster reaction rate was attributed to the higher concentration of α-pinene in the medium surrounding the catalyst under two fluid phase condition.

Although scCO₂ exhibits many advantages in hydrogenation reactions, such as increasing H₂ solubility and improving mass transport, the low solubility of organics in scCO₂ can limit its application. The solubility problem can be obviated by using a co-solvent in scCO₂ to enhance its solvation power⁶. Philai et al.⁶⁹ reported the uselessness of co-solvent in the hydrogenation of 4-oxoisophorone in scCO₂. But this conclusion may not be true for all hydrogenation reactions. Co-solvents are still a potential tool to enhance the solvation power of scCO₂ in order to expand its applications in hydrogenation.

2.6 Conclusions

Hydrogenation of polymers offers great potential to modify their properties. Hydrogenated SBSC and NBR have been demonstrated to be high performance materials in a wide spectrum of applications. Hydrogenated styrenic polymer or copolymers are not commercially available. However, they have gained great attention due to their unique properties. Many potential applications using these new materials have been proposed.
Catalytic hydrogenation of polymers holds the promise of preparing novel polymeric material that cannot be synthesized by direct polymerization alone. Development of proper catalysts and understanding of the hydrogenation mechanism remain important in polymer hydrogenation. Homogeneous hydrogenation of polymers has been studied by many groups. Kinetic models based on proposed hydrogenation mechanism have been reported and been found to fit experimental results well. On the other hand, the mechanism of heterogeneous hydrogenation of polymers is still the subject of much speculation. A full understanding of the heterogeneous hydrogenation mechanism and the development of corresponding kinetic models will facilitate the design of hydrogenation process and the design of catalyst for polymer hydrogenation. Hence, further investigation on the heterogeneous hydrogenation of polymers is still interesting to academic and industrial researchers.

Mass transfer resistance is a barrier to be overcome in many hydrogenation processes. Mass transfer limitations become more serious when one hydrogenates viscous polymer solutions. Recently, supercritical technology has been successfully used in catalytic reactions, in which mass transfer resistance can be significantly reduced. Hence, supercritical technology opens a potential way to improve the mass transport in polymer hydrogenation.

Among the commonly used supercritical fluids, scCO₂ has gained more attention because of its mild critical condition, its low cost, and its non-toxic and inflammable properties. Hydrogenation in the presence of scCO₂ can be conducted in a single fluid phase or in two fluid phases. The former eliminates the gas-liquid interface and therefore avoids the gas-liquid mass transfer resistance. Although the gas-liquid mass transfer resistance remains under two fluid phase conditions, the increase of H₂ solubility and the decrease of viscosity in the liquid phase due to the presence of CO₂ can effectively improve mass transport. Hence,
many successful results using scCO₂ in hydrogenations have been reported. High reaction rate, high selectivity, extended catalyst lifetime and better temperature control have been demonstrated.

References


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Chapter 3

Kinetics of Heterogeneous Catalytic Hydrogenation of Polystyrene

3.1 Introduction

The hydrogenation of unsaturated polymers can improve the properties of the precursor polymers\textsuperscript{1-3}. For example, the thermal and oxidative stability of a polymer can be improved by hydrogenation of the unsaturated units in the polymer. When a polymer with desirable properties cannot be produced easily by direct polymerization, hydrogenation of a commercially-available unsaturated analog may be a viable alternative.

Most polymer hydrogenations have been carried out using either homogeneous or heterogeneous catalysis. Homogeneous hydrogenation catalysts provide high activity and operate at mild reaction conditions. Therefore homogeneous hydrogenations of polymers have been given great attention since the 1960s\textsuperscript{4}. Various homogeneous catalysts have been used for polymer hydrogenation. Detailed kinetics and reaction mechanisms have been reported. The difficulty in removing the homogeneous catalyst from the hydrogenated polymer is one of the major drawbacks in this technique\textsuperscript{5,6}. The residual metal in the polymer can catalytically degrade the hydrogenated polymer\textsuperscript{6,7}.

Heterogeneous catalysts are easier to separate after the hydrogenation, such that there is little or no metal contamination of the polymer. However, mass transfer of H\textsubscript{2} and the unsaturated polymer to the sites on the heterogeneous catalyst can be a slow, or even
controlling step in the overall process. This is especially true when relatively concentrated polymer solutions are to be hydrogenated. The low reaction rates, poor selectivity, and difficult scale up that can be associated with the various mass transfer resistances can be impediments to the development of heterogeneous hydrogenation technology.

Qualitative investigation on the mechanism of heterogeneous hydrogenation of polymers has been reported. A commonly accepted explanation is that the hydrogenation of polymer chains occurs in a ‘blocky’ manner\(^3\), \(^8\)\(^-\)\(^10\). The majority of unsaturated units in a polymer chain are hydrogenated in a single adsorption step. Then the chain desorbs from the surface of catalyst due to the reduction of the thermodynamic driving force for chain adsorption. Further hydrogenation of the remaining unsaturated units requires subsequent adsorption steps. Few quantitative kinetics of heterogeneous hydrogenation of polymers have been reported\(^4\), \(^11\). All the published kinetic models are based on empirical, power law rate equations. Further investigation on the kinetics of heterogeneous hydrogenation of polymers is necessary.

This research uses the heterogeneous hydrogenation of polystyrene (PS) as the model reaction. Studies were conducted in a batch reactor. Detailed procedures and analytical methods are discussed. The reaction mechanism and kinetics of PS hydrogenation are studied.

3.2 Background

3.2.1 Kinetics of homogeneous hydrogenation of polymers

One of the most commonly used homogeneous catalysts is the Wilkinson’s catalyst (RhCl(PPh\(_3\))\(_3\)), which has been successfully used in saturating polydienes (e.g. polybutadiene)
and polymers containing polydiienes and other functional groups (e.g. styrene-butadiene copolymer or acrylonitrile-butadiene copolymer). Complete and informative research on homogeneous hydrogenation of C=C bonds in polymers has been performed by Rempel and coworkers\textsuperscript{2, 12-15}. Detailed hydrogenation mechanisms and the corresponding kinetic models have been reported. For example, the hydrogenation of polybutadiene catalyzed by Wilkinson’s catalyst can be described by the following paths as shown in Figure 3.1\textsuperscript{12}.

![Figure 3.1 Mechanism of homogeneous hydrogenation of polybutadiene\textsuperscript{12}

In Figure 3.1, the steps A\textsubscript{o}-A'-B'-C-D is called 'unsaturated path'\textsuperscript{12}, in which the interaction between catalyst A\textsubscript{o} and C=C bond occurs prior to the interaction between A\textsubscript{o} and H\textsubscript{2}. Further investigation showed this path did not represent the actual hydrogenation kinetics. The path A\textsubscript{o}-A-B-C-D is called the 'hydride path'\textsuperscript{12}. The H\textsubscript{2} interacts with catalyst
prior to the interaction between catalyst and C=C bond. By assuming the step B-C is the rate-limiting step in the 'hydride path', the rate equation (3.1) is obtained, which is found to be in good agreement with the experimental results\textsuperscript{12}. Here, [C=C], [H\textsubscript{2}] and [Rh]\textsubscript{T} are the concentrations of olefinic units, H\textsubscript{2} and rhodium respectively. K, K\textsubscript{1}, and K\textsubscript{4} are the equilibrium constants of corresponding steps. k\textsubscript{2} is the rate constant of B-C step.

\[
\frac{-d[C = C]}{dt} = \frac{k2KK_{1}K_{4}[Rh][H_{2}][C = C]}{K_{4}[PPh_{3}] + KK_{4}[PPh_{3}][H_{2}] + KK_{1}K_{4}[H_{2}]} \quad (3.1)
\]

The kinetic equation (3.1) indicates some general trends in the homogeneous hydrogenation of polymers. The hydrogenation rate is first order in the concentration of C=C bonds, and first order in the concentration of rhodium in the system. At a relative low H\textsubscript{2} concentration, the hydrogenation rate is first order in [H\textsubscript{2}], but it changes to a zero order dependence at high H\textsubscript{2} concentration. All of these features are in good agreement with actual experimental results\textsuperscript{12, 14}. Similar kinetic models can be derived for homogeneous hydrogenation of other polymers catalyzed by Wilkinson’s catalyst\textsuperscript{14, 15}.

### 3.2.2 Kinetics of heterogeneous hydrogenation of polymers

The mechanism of the heterogeneous hydrogenation of polymers has not been studied directly\textsuperscript{3}. Based on the evidence obtained by the examination of partially hydrogenated polymers, a ‘blocky’ mechanism is commonly accepted\textsuperscript{3, 8-11}. Firstly, polymer diffuses into the catalyst pore and adsorbs on the metallic crystallite. The desorption of adsorbed polymer takes place only if most of the unsaturated units in the polymer chain have been saturated. Subsequent adsorption steps are necessary to saturate the remaining unsaturated units. A detailed description of the ‘blocky’ mechanism and the corresponding evidence have been discussed in Chapter Two and in other articles\textsuperscript{3, 8, 9, 11}. 

\[\text{pph}\]
In 1993, Gehlsen reported the first quantitative kinetic study of heterogeneous polymer hydrogenation. The hydrogenation of poly(isoprene) obeyed pseudo first order kinetics with respect to the C=C bond, as shown by equation (3.2). Here, \([C=C]\) is the concentration of unsaturated C=C bonds; \(k\) and \(t\) are the apparent rate constant and reaction time respectively. The apparent activation energy of this reaction was found to be 8684 cal/mol. After checking the effect of agitation and catalyst concentration on the apparent rate constant, Gehlsen concluded that the mass transfer limitations were minimal in this kinetic study. Several comparison experiments were done to investigate potential catalyst deactivation. The first was a hydrogenation initiated at \(t=0\) by adding \(H_2\) into the reactor. The other one had a 60 minute induction period before the initiation of hydrogenation, i.e., the polymer solution was held with catalyst at reaction temperature for 60 minutes before adding \(H_2\). The later showed a 30\% decrease in apparent reaction rate constant. Gehlsen attributed this to the irreversible adsorption of polymer chains on the catalyst surface, which led to catalyst deactivation.

\[
\frac{-d[C=C]}{dt} = k \ [C=C] \quad (3.2)
\]

Later, Weimann studied the kinetics of heterogeneous hydrogenation of PS catalyzed by Pt/SiO\(_2\). A similar pseudo first order rate equation with respect to the unsaturated aromatic rings was used to describe the kinetics of PS hydrogenation. The apparent activation energy was found to be 31.2 kJ/mol or 60.2 kJ/mol for different batches of catalyst. Furthermore, Weimann examined a 40\% hydrogenated PS sample by extracting the sample with hexane. Polymer extracted by hexane showed a 83\% degree of hydrogenation and the remaining polymer showed a 20\% degree of hydrogenation. This result indicated that PS
hydrogenation followed a similar ‘blocky’ mechanism to that observed with diene polymer hydrogenations\(^9,10\). Recently, Ness et al.\(^8\) studied the heterogeneous hydrogenation of PS catalyzed by Pt/\(\text{SiO}_2\). A zero order rate equation depending on the aromatic rings was obtained.

All three researchers found that the hydrogenation rate decreased as the polymer molecular weight increased. By qualitative calculations, Ness et al.\(^8\) excluded the possibility of mass transfer limitation due to the increase in viscosity with increasing molecular weight. They attributed this behavior to the conformational dynamics of polymer coils on the metal surface, i.e. the conformational dynamics of the polymer coil on the surface of catalyst is the rate limiting step. Therefore the hydrogenation rate decreased as polymer molecular weight increased because of the low rates of conformational rearrangement of longer polymer chains. They suggested that catalysts with metal crystallite size equal to or larger than the polymer coil size should yield a faster hydrogenation rate. Rosedale and Bates\(^9\) suggested that the degree of polymerization, polymer concentration, polymer-solvent, polymer-surface, and solvent-surface interaction energy could influence the polymer adsorption and conformational rearrangement and therefore influence the hydrogenation. Moreover, Ness et al.\(^8\) mentioned that the polymer interchain interaction might also influence the conformational dynamics of adsorbed polymers in concentrated polymer solutions.

### 3.3 Materials and procedures

3.3.1 Materials

The 5\%Pd/\(\text{BaSO}_4\) catalyst was obtained from Aldrich and was used as received. The 5\%Pd/\(\text{BaSO}_4\) catalyst was examined by scanning electron microscopy (SEM). The particles had an irregular shape, with an approximate aspect ratio of 2:1:1. The average equivalent
spherical diameter was about 20 µm as shown in Figure 3.2. A true density of 4.42 g/cm³ was measured by gas displacement, a BET surface area of 4.6 m²/g was measured by N₂ adsorption, and an average pore diameter of 1.3 µm and a porosity of 71.7% were measured by mercury porosimetry. The Pd metal dispersion of 0.29% was obtained by CO chemisorption assuming the ratio of CO/Pd is 2.0. Commercial PS (Nova 172) with a weight average molecular weight of approximately 290,000 g/mol was used as received. Decahydronaphthalene (DHN) (Aldrich, 99%) was used as received. Hydrogen (99.99%) was supplied by National Welders.

Figure 3.2 SEM image of 5%Pd/BaSO₄
3.3.2 Procedures

A. Hydrogenation reaction

The hydrogenation reactions were performed in a 50 mL batch reactor. An axial flow impeller with two pairs of pitched blades was used to agitate the fluid. Four vertical baffles were installed in the reactor. A schematic of the hydrogenation equipment is shown in Figure 3.3. The catalyst was loaded into the reactor, then the polymer solution was loaded into the reactor. The reactor was sealed and flushed with either N\(_2\) or CO\(_2\) to remove air. After flushing with H\(_2\), the reactor was heated to the reaction temperature with agitation adjusted to 1500 rpm gradually. The time required to reach the temperature was about 15 minutes. Once the system was at the desired temperature, it was pressurized with H\(_2\) to the desired pressure through a tube located above the liquid surface and the agitation was adjusted to 2500 rpm. Counting of the reaction time began once the desired pressure was reached, typically a few seconds after pressurization began. The system was run for a specified time, between 2 and 10 hours. The agitation was stopped and the reactor was allowed to cool to room temperature. The pressure was then released.
B. Measurement of degree of hydrogenation

A UV-VIS spectrophotometer (Jasco V-550) was used to determine the degree of hydrogenation of the aromatic rings. First, the UV-VIS was calibrated with PS in DHN solution at 261.5 nm. A calibration curve, i.e., a plot of absorption versus aromatic ring concentration, was obtained, as shown in Figure 3.4. After hydrogenation, the hydrogenated PS solution was filtered to remove the catalyst and then diluted with DHN. The absorption of the diluted sample was measured at 261.5 nm. The concentration of aromatic rings after hydrogenation can be obtained according to the measured absorption and the calibration
curve. The degree of hydrogenation (H.D.), which is the conversion of aromatic rings (X), was calculated from $X = H.D. = 1 - \frac{C_A}{C_{Ao}}$. Here, $C_A$ is the concentration of aromatic rings after hydrogenation, and $C_{Ao}$ is the initial concentration of aromatic rings. The hydrogenated product then was precipitated into excess methanol. The precipitated polymer was dried in a vacuum oven (about 23 Torr) at 60°C for 48 hours. The molecular weight of the dried polymer was determined using gel permeation chromatography (GPC) with tetrahydrofuran as the mobile phase.

![Figure 3.4 Calibration curve of UV-VIS](image-url)
Some of the dried hydrogenated PS samples were examined by FTIR to confirm the saturation of the aromatic rings. As shown in Figure 3.5, the green spectrum and the blue spectrum represented PS and 45% hydrogenated PS respectively. The two red spectra represented 97% hydrogenated PS. The disappearance of peaks at 1500, 1600 and 3030 cm$^{-1}$ demonstrated the saturation of aromatic rings. The increase of peaks at 2860 cm$^{-1}$ demonstrated the formation of alkyl structure, which could represent the formation of cyclohexane rings.
C. Solvent Extraction

Partially hydrogenated PS was dissolved in hexane (PS/hexane \(\approx 0.04 \text{ g/g}\)). The supernatant solution was separated from the undissolved polymer using a pipette. Then the undissolved polymer was dissolved in tetrahydrofuran. Both the hexane solution and the tetrahydrofuran solution were dried in vacuum oven (70°C and about 23 Torr) to remove the solvents. The dried polymer samples were dissolved in DHN and then were measured by UV-VIS to determine the degree of hydrogenation.

3.4 Results and discussion

3.4.1 Effect of temperature

Figure 3.6 shows the effect of temperature on the reaction. The hydrogenation reactions were conducted at 750 psig H\(_2\) pressure, 2500 rpm agitation rate and with a 5%Pd/BaSO\(_4\) to PS ratio of 1.0 (wt./wt.). The rate of ring hydrogenation increases as the temperature increases.

The side reaction, scission of the polymer backbone was significant at higher temperatures. The weight-average molecular weight of the polymer at the end of reaction at 120°C, 150°C and 180°C was 259,910 g/mol, 205,731 g/mol and 178,296 g/mol respectively. Apparently, the rate of chain scission increases with increasing temperature. In order to exclude the possibility of thermal degradation of PS, the 3wt% PS solution was heated at 180°C for three hours with 2500rpm agitation and 750psig H\(_2\) or N\(_2\), without any catalyst. By measuring the intrinsic viscosity, the weight-average molecular weight were determined as 332,385 g/mol, 291,825 g/mol and 301,910 g/mol for the original PS and PS after heated in H\(_2\) or N\(_2\) respectively. Although the molecular weight from intrinsic viscosity is slightly
higher than that from GPC, the difference of molecular weight between the virgin PS and the PS after heating was not as apparent as the difference between virgin PS and hydrogenated PS. Hence, the significant reduction of molecular weight after hydrogenation was mostly due to the catalytic side reaction. However, the final degrees of hydrogenation are different at different temperatures. It may be that the rate of chain scission depends on the degree of hydrogenation. In any event, the occurrence of chain scission will influence the properties of the hydrogenated polymer and should be avoided. Thus the relative rates of ring hydrogenation and chain scission will be an important element in the final choice of catalyst and process conditions.

Figure 3.6 The effect of temperature on the degree of hydrogenation (3wt% PS in DHN, 1g 5%Pd/BaSO₄/g PS, 750psig H₂, 2500rpm)

◊ 90 °C, □ 120 °C, ∆ 150 °C, × 180 °C
3.4.2 Effect of H₂ pressure

Figure 3.7 shows the effect of hydrogen pressure on the degree of hydrogenation, at otherwise fixed conditions. At lower pressures, hydrogen pressure has a strong influence on the reaction rate. Above about 500 psig, the reaction rate appears to be essentially independent of H₂ pressure. This implies that the surface of catalyst is essentially saturated with H₂ above about 500 psig, so that the reaction rate does not change with a further increase in H₂ pressure.

![Figure 3.7 The effect of H₂ pressure on the degree of hydrogenation](image)

(3wt% PS in DHN, 150 °C, 1g 5%Pd/BaSO₄/g PS, 2500rpm, 10hr reaction time)
3.4.3 Partially hydrogenated PS

As shown in Table 3.1, the partially hydrogenated PS was separated into two materials. One has a degree of hydrogenation close to 80%, and the other one has a low degree of hydrogenation. The results can be explained by the ‘blocky’ hydrogenation mechanism, i.e., after a PS chain was adsorbed on the catalyst surface, it would not desorb until about 80% of the aromatic rings on this chain had been hydrogenated. The undissolved polymer also showed some extent of hydrogenation. This could result from a limitation of the extraction experiment, i.e., the supernatant was not completely separated from the undissolved polymer. On the other hand, it could be because of the 'unstable' adsorption of some PS chains on the catalyst. The adsorption of PS depends on the dimensions of the PS coil and the metallic crystallite on the catalyst surface. If the metallic crystallite was too small, PS would adsorb unstably because the metallic crystallite could contact only a few aromatic rings on the PS chain, which might not hold the polymer due to an insufficient interaction driving force. The PS chain could desorb before 80% of its aromatic units had been hydrogenated. Weimann\(^1\) reported that a 40% hydrogenated PS was separated into two materials with 83% and 20% degree of hydrogenation respectively. The lightly hydrogenated PS showed lower degree of hydrogenation than this work. This might be due to a difference in the crystallite size distribution of the catalysts used in both works. Ness et al.\(^8\) mentioned that larger metal crystallites should exhibit higher activity for PS hydrogenation. Larger crystallites should exhibit less possibility for the 'unstable' adsorption of PS and should lead to a lower quantity of lightly hydrogenated PS. That might explain the higher activity of Weimann’s 5%Pt/SO\(_2\) compared to the 5%Pd/BaSO\(_4\) used in this work.
Table 3.1 Separation of partially hydrogenated PS

<table>
<thead>
<tr>
<th>Overall HD</th>
<th>HD of extracted polymer</th>
<th>HD of undissolved polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>42%</td>
<td>82%</td>
<td>31%</td>
</tr>
<tr>
<td>69%</td>
<td>79%</td>
<td>44%</td>
</tr>
<tr>
<td>32%</td>
<td>74%</td>
<td>13%</td>
</tr>
</tbody>
</table>

3.4.4 Kinetics of PS hydrogenation

The mechanism and kinetics of the hydrogenation of aromatic rings in small molecules are well known\textsuperscript{16-19}. Various kinetic equations have been derived according to different hydrogenation mechanisms. The heterogeneous polymer hydrogenation might be described by similar mechanisms.

It has been observed that heterogeneous polymer hydrogenation follows a ‘blocky' mechanism, and the adsorption and conformational rearrangement of polymer chains on the catalyst surface dominates the overall hydrogenation. In Figure 3.8, the black and blue dots represent aromatic rings, and the red dots represent saturated aromatic rings. First, the PS chain adsorbs on a metallic crystallite on the catalyst surface. Some of the aromatic rings (black dots) will contact the surface and react with H\textsubscript{2}. Then, conformation rearrangement presents other aromatic rings (blue dots) to the surface, which do not contact the surface at the beginning. Then H\textsubscript{2} reacts with these aromatic rings and other aromatic rings are presented to the surface again, until most of the aromatic rings in this chain have been saturated. Then the PS chain desorbs due to the change of the interaction between polymer, catalyst surface and solvent, i.e., the cyclohexane rings are not as strongly adsorbed as the aromatic rings.
Figure 3.8 Schematic of adsorption, conformational rearrangement and hydrogenation of PS

Hence, the following hydrogenation steps can be assumed to describe the mechanism of heterogeneous polymer hydrogenation.

\[ H_2 + 2\beta \xrightarrow{K} 2H\beta \]  
\[ A + \delta \xrightarrow{k} A\delta \]  
\[ A\delta + H\beta \xrightarrow{K_3} AH\delta + \beta \]  
\[ AH\delta + H\beta \xrightarrow{K_4} AH_2\delta + \beta \]  
\[ AH_2\delta + H\beta \xrightarrow{K_5} AH_3\delta + \beta \]  
\[ AH_3\delta + H\beta \xrightarrow{K_6} AH_4\delta + \beta \]  
\[ AH_4\delta + H\beta \xrightarrow{K_7} AH_5\delta + \beta \]  
\[ AH_5\delta + H\beta \xrightarrow{K_8} AH_6\delta + \beta \]  
\[ AH_6\delta \xrightarrow{K_9} AH_6 + \delta \]
Where $\beta$ and $\delta$ denote the active sites for adsorbing $H_2$ and aromatic rings respectively. A is the aromatic ring in PS and $AH_i$ is the partially or fully saturated aromatic ring. For example, $AH_6$ represents a cyclohexane ring. Here, step (3.3) represents the adsorption of $H_2$. Steps (3.5-3.10) represent the surface reaction. Step (3.11) represents the desorption of cyclohexane ring. Step (3.4) represents the adsorption of aromatic rings on the active site and is presumed to be the rate-limiting step in this mechanism. However, step (3.4) has a different meaning from the adsorption step in a small molecule hydrogenation, due to the unique properties of polymer chains. This step includes two possible ‘adsorptions’: the adsorption of aromatic rings in a free PS chain, which is represented by the black dots in Figure 3.8; and the ‘adsorption’ of aromatic rings of an adsorbed PS chain which is represented by the blue dots in Figure 3.8. In other words, the former represents the adsorption of a free PS chain and the later represents the conformational rearrangement of the PS chain. Therefore, $k$ should be influenced by any factors that can influence the adsorption and conformational rearrangement of PS, such as temperature, solvent, catalyst, molecular weight and concentration of PS, polymer interchain interaction and so on.

The overall hydrogenation rate can be written as

$$-r_A = r_2 = kC_A\theta_\delta$$  \hspace{1cm} (3.12)

Here, $\theta_\delta$ denotes the fraction of vacant active sites $\delta$ and $C_A$ is the concentration of aromatic rings. The other steps are assumed to be in quasi-equilibrium. Therefore, the equilibrium of step (3.3) gives

$$K_1 = \frac{\theta_H^2}{C_{H2} \cdot \theta_\beta^2}$$  \hspace{1cm} (3.13)
Here, $\theta_\beta$ is the fraction of vacant active sites $\beta$, $C_{H2}$ is the concentration of $H_2$ and $\theta_{H\beta}$ is the fraction of active sites $\beta$ occupied by $H_2$.

Equation (3.5) to (3.11) can be added together

$$A\delta + 6H\beta \xrightarrow{K_{3-9}} AH_6 + \delta + 6\beta$$  \hspace{1cm} (3.14)

At equilibrium

$$K_{3-9} = \frac{C_c \cdot \theta_A \cdot \theta_\delta^6}{\theta_{A\delta} \cdot (\theta_{H\beta})^6}$$  \hspace{1cm} (3.15)

Here, $C_c$ is the concentration of fully hydrogenated aromatic rings and $\theta_{A\delta}$ is the fraction of active sites $\delta$ occupied by aromatic rings. From equation (3.13), we have

$$\frac{\theta_\beta}{\theta_{H\beta}} = \frac{1}{(K_1 \cdot C_{H2})^{0.5}}$$  \hspace{1cm} (3.16)

An active site balance for $\delta$ gives

$$\theta_\delta + \theta_{A\delta} + \theta_{AH\delta} + \theta_{AH2\delta} + \theta_{AH3\delta} + \theta_{AH4\delta} + \theta_{AH5\delta} = 1$$  \hspace{1cm} (3.17)

It has been reported that the catalyst surface is dominated by aromatic rings during liquid phase hydrogenation of aromatic hydrocarbons$^{16}$. In other words, step (3.5) could be the next slowest step in this process. Therefore the sites occupied by partially hydrogenated intermediates are neglected in equation (3.17). Hence, equation (3.17) can be simplified to

$$\theta_\delta + \theta_{A\delta} = 1$$  \hspace{1cm} (3.18)

The combination of equations (3.15), (3.16) and (3.18) gives
\[ \theta_{\delta} = \frac{1}{1 + \frac{C_C}{K_{3-9}} \left( \frac{1}{K_1 \cdot C_{H_2}} \right)^3} \]  

(3.19)

Thus, the overall hydrogenation rate can be obtained as

\[ -r_A = \frac{kC_A}{1 + \frac{C_C}{K_{3-9}} \left( \frac{1}{K_1 \cdot C_{H_2}} \right)^3} \]  

(3.20)

The hydrogenation of aromatic rings can be considered to be irreversible\(^{16}\), thus the equilibrium constant \(K_{3-9}\) is a fairly large number. When the concentration of \(H_2\) is also high, i.e. \(C_{H_2}\) is a large number, the second term in the denominator can be significantly less than 1 and therefore it can be canceled from equation (3.20). Thus a first order rate equation with respect to aromatic rings is obtained as shown by (3.21). Figure 3.7 showed that the hydrogenation degree increased with \(H_2\) pressure at low \(H_2\) pressure and it became independent of \(H_2\) at high \(H_2\) pressure, which is consistent with the above analysis.

\[ -r_A = kC_A \]  

(3.21)

\[ \frac{1}{W} \cdot \frac{dN_A}{dt} = kC_A \]  

(3.22)

\[ \frac{dC_A}{dt} = kC_{cat} C_A \]  

(3.23)

To fit the experimental results, equation (3.21) is re-written as (3.22). Dividing by the liquid volume, equation (3.22) can be further re-written as equation (3.23). Here, \(W\) is the weight of catalyst, \(N_A\) is the total moles of aromatic rings, \(C_{cat}\) is the concentration of catalyst. Equation (3.23) can be used to test the experimental results. As shown below, equation (3.23) can fit the experimental data well.
A power law rate equation has a simple format but retains the accuracy to express the kinetics of a reaction. When the reaction mechanism is not completely understood, the power law rate equation becomes the only alternative. Furthermore, kinetics described by a power law rate equation can be compared with the mass transport and used for process design conveniently. Hence, the following power law rate equation was tested to fit the experimental data.

\[-r_A = -\frac{1}{W} \frac{dN_A}{dt} = kC_A^aC_{H_2}^b\]  

(3.24)

Here, \(C_A\) is the molar concentration of aromatic rings in solution, and \(C_{H_2}\) is the hydrogen concentration in liquid phase. Dividing by the liquid volume

\[-\frac{dC_A}{dt} = k_{cat} C_A^aC_{H_2}^b\]  

(3.25)

The kinetic experiments were carried out at 90-180°C and 750 psig \(H_2\) pressure using different PS concentrations and different catalyst/PS ratios. The PS concentration was between 1 and 3wt%. Since the partial pressure of \(H_2\) was constant in all of the experiments that will be analyzed below, equation (3.25) can be simplified to

\[-r_A = -\frac{dC_A}{dt} = k' C_{cat} C_A^a\]  

(3.26)

Where \(k' = k_{cat} C_{H_2}^b\). In general, \(k'\) will depend on the concentration of hydrogen. Moreover, all the kinetic experiments were performed at a constant \(H_2\) pressure of 750 psig and Figure 3.7 shows that hydrogenation is independent of \(H_2\) pressure at pressures above 500 psig, i.e., \(b=0\) in this regime. Therefore \(k'\) was essentially constant.
The reaction order ‘a’ was assumed to be 0, 1, 1.5, 2, and 3. The corresponding integrated forms of equation (3.26) then were tested against the experimental data.

The integration of equation (3.26) is shown by equations (3.27-3.31). Here, X is the fractional conversion of aromatic rings i.e., the degree of hydrogenation, and t is the reaction time. For \(a=1\), at a constant temperature, the slope of a plot of \(-\ln(1-X)\) vs. \(C_{cat}t\) will give the reaction rate constant \(k'\). Figure 3.9 shows such a plot for the hydrogenations at 150°C. The value of \(k'\) at 150°C was determined to be \(1.61 \times 10^{-6}\) L/(s·g). The rate constants at the other three temperatures were determined similarly.

The other rate equations can be tested in a similar manner. The results are summarized in Table 3.2. It is found that ‘a’ of 1 and 1.5 fit the data equally well. The hydrogenation mechanism shown previously also leads to a first order rate equation. Furthermore, the first order rate equation can be easily used to compare the reaction rate with the mass transfer rate. Hence, the first-order rate equation (\(a=1\)) was chosen as the kinetic model in this work.

\[
X = k'C_{cat}t / C_{AO}
\]

\[a=0\] (3.27)

\[-\ln(1-X) = k'C_{cat}t\]

\[a=1\] (3.28)

\[2(1-X)^{-0.5} - 2 = k'C_{cat}tC_{AO}^{0.5}\]

\[a=1.5\] (3.29)

\[
\frac{X}{1-X} = k'C_{AO}C_{cat}t
\]

\[a=2\] (3.30)

\[(1-X)^{-2} - 1 = 2k'C_{AO}^{2}C_{cat}t\]

\[a=3\] (3.31)
Figure 3.9  First order kinetic model

(PS in DHN (≤ 3wt%), 750 psig H₂, 150°C, 5%Pd/BaSO₄, 2500rpm)

Table 3.2 Correlation results of hydrogenation kinetics

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>( a=0 )</th>
<th>( a=1 )</th>
<th>( a=1.5 )</th>
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<tr>
<td></td>
<td>( k' )</td>
<td>( R^2 )</td>
<td>( k' )</td>
</tr>
<tr>
<td>90</td>
<td>4.04E-8</td>
<td>0.993</td>
<td>1.62E-7</td>
</tr>
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<td>120</td>
<td>1.28E-7</td>
<td>0.972</td>
<td>6.15E-7</td>
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<tr>
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<td>0.478</td>
<td>1.61E-6</td>
</tr>
<tr>
<td>180</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>T (°C)</th>
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<th>( a=3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( k' )</td>
<td>( R^2 )</td>
</tr>
<tr>
<td>90</td>
<td>6.53E-7</td>
<td>0.997</td>
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</tr>
<tr>
<td>150</td>
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<td>0.952</td>
</tr>
<tr>
<td>180</td>
<td>1.50E-4</td>
<td>0.838</td>
</tr>
</tbody>
</table>

R - Correlation coefficient
Assuming that $k'$ obeys the Arrhenius relationship,

$$\ln k' = \ln A - \frac{E}{RT} \quad (3.32)$$

Here $E$ is the activation energy (J/mol), $R$ is the gas constant (J/K/mol) and $T$ is the reaction temperature (K). An Arrhenius plot of the first-order rate constants from Table 3.2 is shown in Figure 3.10. The activation energy was determined to be 59.6 kJ/mol from the slope of the line. The good fit of the experimental data in Figure 3.10 indicates that the rate equation given by equation (3.33) can provide a reasonable description of the hydrogenation of aromatic rings in PS in DHN over 5%Pd/BaSO$_4$ catalyst.
Turnover frequency (TOF) is defined as the rate that H\textsubscript{2} molecules are converted per metal atom on the catalyst surface per second, as shown by equation (3.34). Typically, TOF is between 0.1 and 10 second\textsuperscript{-1} for an industrial reaction\textsuperscript{20}. The TOFs for hydrogenation of 3wt\% PS solution at the beginning of the reaction were calculated. As shown in Table 3.3, the TOFs for PS hydrogenation are greater than 0.1 at 120, 150 and 180°C, which are in the range of the TOFs of typical industrial reactions. However, the catalyst concentration in this study is normally 1 gram of catalyst per gram of PS, which is higher than the commonly used catalyst concentration. As shown above, the 5\%Pd/BaSO\textsubscript{4} has a surface area of 4.6 m\textsuperscript{2}/g and metal dispersion of about 0.29\%. The low surface area and low metal dispersion lead to fewer catalytic sites for PS hydrogenation. Therefore large amount of catalyst had to be used to achieve a reasonable hydrogenation rate.

\[
TOF = \frac{\text{atoms } H_2}{\text{atom Pd, time}} = \frac{k^\prime C_A \times 106.4 \times 3}{5\% \times 0.29\%} \tag{3.34}
\]

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>TOF (s\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>90</td>
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<tr>
<td>120</td>
<td>0.364</td>
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<tr>
<td>150</td>
<td>0.953</td>
</tr>
<tr>
<td>180</td>
<td>5.64</td>
</tr>
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</table>

3.5 Conclusions

The heterogeneous hydrogenation of PS catalyzed by 5\%Pd/BaSO\textsubscript{4} in DHN was studied. It was found that the hydrogenation rate increased with temperature. However, the
polymer chain scission became serious at high temperatures. The hydrogenation rate depended on H\textsubscript{2} pressure at low H\textsubscript{2} pressures, and became independent of H\textsubscript{2} pressure at high H\textsubscript{2} pressures, above about 500 psi. The partially hydrogenated PS was extracted with hexane. The extracted polymer showed a degree of hydrogenation of about 80\%, while the unextracted polymer showed a much lower degree of hydrogenation. This result was attributed to the ‘blocky’ hydrogenation mechanism. A kinetic model based on the ‘blocky’ hydrogenation mechanism was developed. At high H\textsubscript{2} pressure, this model could be simplified to a pseudo first order (in the concentration of aromatic rings) rate equation. Power law rate equations with different powers over the concentration of aromatic ring were tested against the experimental data. It was found that the first order rate equation fit the experimental results well, consistent with the rate equation derived from the ‘blocky’ hydrogenation mechanism. Assuming the hydrogenation rate constants obey Arrhenius relationship, the apparent activation energy was obtained as 59.6 kJ/mol for the hydrogenation of PS at concentrations of 3wt\% or less.

References


Chapter 4

Transport Processes in Heterogeneous Hydrogenation of Polystyrene

4.1 Introduction

The heterogeneous hydrogenation of polystyrene (PS) is a solid-liquid-gas three phase reaction. Five different mass transport steps are required, as shown in Figure 4.1. The H$_2$ in the gas phase must: 1) be transported from the bulk gas phase into the bulk liquid; 2) be transported from the bulk liquid to the external surface of the catalyst particle; 3) diffuse into the catalyst to access the catalytic sites on the pore wall. For PS, only the last two transport steps are required, transport from the bulk liquid to the external surface of the catalyst, and diffusion into the catalyst. The hydrogenated PS requires the reverse transport processes as PS, transferring from the interior of catalyst to the bulk liquid phase.

Hydrogenation occurs on the active sites on catalyst, which are generally inside the pores of the catalyst. The apparent hydrogenation rate will be a combination of the surface reaction rate and the mass transfer rates. The slowest steps will dominate the apparent hydrogenation rate. Hence, if one of the transport processes is very slow, the observed hydrogenation rate will be determined by the rate of that step. To avoid limitations of mass transfer, more energy associated with rigorous agitation, or heating will be required.
Figure 4.1 Mass transport and concentration gradients

The mass transport processes involved in the hydrogenation of small molecules have been studied in detail\textsuperscript{1,2}. However, few investigations about mass transport in heterogeneous polymer hydrogenation have been reported\textsuperscript{3-6}. Due to the large dimension of polymer molecules, mass transfer limitations can be even more severe during the hydrogenation of polymers. The high viscosity of polymer solutions and low diffusivity of polymer molecules tend to reduce the rates of mass transfer. Hence, a thorough study of the mass transport during polymer hydrogenation will be necessary.

This chapter will include a brief review of the gas-liquid mass transfer, liquid-solid mass transfer and pore diffusion, with emphasis on the necessary correlations for quantitatively evaluating mass transfer rates. The effect of polymer concentration and molecular weight on the viscosity and diffusivity of polymer solution will be discussed.
influence of overlap concentration and non-Newtonian properties of polymer solution will also be discussed briefly. The viscosity and diffusivity of PS solutions were measured at various temperatures. The liquid-solid mass transfer coefficients and effectiveness factors of pore diffusion were calculated to compare with the kinetics studied in the previous chapter.

4.2 Background

4.2.1 Gas-liquid mass transport

As shown in Figure 4.1, a concentration gradient exists from the bulk gas phase to the interior of catalyst, which is the driving force for mass transport. According to Fick’s law, the mass transfer rate \( N_i \) (g•mole/s) can be expressed as

\[
Ni = -D_i A \frac{dC_i}{dx}
\]  
(4.1)

Here, \( D_i \) is the diffusion coefficient of species \( i \) (m\(^2\)/s); \( A \) is the plane through which species \( i \) transfers; \( dC_i/dx \) is the concentration gradient. For gas-liquid mass transport, a relatively stagnant gas layer exists on the gas side of the gas-liquid interface and a relatively stagnant liquid layer exists on the liquid side of the gas-liquid interface. These two stagnant layers, so-called boundary layers, constitute the major resistance for gas-liquid mass transfer. For the mass transfer through these boundary layers at the gas-liquid interface, a simplified Fick’s law, as shown by (4.2), can be used to describe the gas-liquid mass transport of \( \text{H}_2 \).

\[
-r_{\text{H}_2} = N_{\text{H}_2} = k_{gl} A_{gl} (C^*_{\text{H}_2} - C_{\text{H}_2})
\]  
(4.2)

Here, \(-r_{\text{H}_2}\) is the mass transfer rate of \( \text{H}_2 \); \( k_{gl} \) is the gas-liquid mass transfer coefficient; and \( A_{gl} \) is the interfacial area between gas and liquid phase; \( C^*_{\text{H}_2} \) is the equilibrium concentration of \( \text{H}_2 \) in liquid phase, which is primarily influenced by the partial pressure of \( \text{H}_2 \), temperature
and the properties of liquid; $C_{H_2}$ is the actual concentration of $H_2$ in liquid phase. The difference between $C_{H_2}^*$ and $C_{H_2}$ represents the driving force for gas-liquid mass transfer. The product of $k_{gl}$ and $A_{gl}$ is a key factor that influences the rate of gas-liquid mass transport. However, a quantitative estimation of $k_{gl}A_{gl}$ is difficult because of too many affecting factors, such as reactor type, internal geometry of the reactor, properties of gas and liquid phase, agitation, temperature, pressure, etc⁷.

Moreover, particles suspended in the liquid phase also can influence the rate of gas-liquid mass transport. Lee and Foster⁸ summarized the results of previous researchers and concluded that a small volume (up to 2-3%) of fine particles has little effect on $k_{gl}A_{gl}$. The $k_{gl}A_{gl}$ will increase as the volume fraction of particle increases (up to 7-9%) and $k_{gl}A_{gl}$ will decrease with further increase of particle load (above 10% volume fraction).

### 4.2.2 Liquid-solid mass transport

The concentration gradient in the bulk liquid phase is negligible due to the intensive agitation. However, a stagnant film exists on the external surface of catalyst particle, which comprises the major resistance to liquid-solid mass transfer. Thus, a significant concentration gradient occurs through this stagnant layer. The liquid-solid mass transfer rate for PS hydrogenation can be expressed as⁹:

\[-r_{H_2} = k'_{ls} A_{ls} (C_{H_2,l} - C_{H_2,s}) \quad (4.3)\]

\[-r_{PS} = k_{ls} A_{ls} (C_{PS,l} - C_{PS,s}) \quad (4.4)\]

Where, $k_{ls}$ and $k'_{ls}$ are the liquid-solid mass transfer coefficients, $A_{ls}$ is the total external surface area of catalyst particles, $C_{PS,l}$ and $C_{H_2,l}$ are the concentrations of PS and $H_2$
in the bulk liquid phase respectively, and $C_{PS,s}$ and $C_{H2,s}$ are the concentrations of PS and H$_2$ at the external surface of catalyst particles, respectively.

Assuming the catalyst particles are spheres, $A_{ls}$ can be calculated by the following equation,

$$A_{ls} = \frac{6 \cdot W_{cat}}{d_p \rho_p} \quad (4.5)$$

Here, $W_{cat}$ is the total weight of catalyst, $d_p$ is the particle diameter and $\rho_p$ is the density of catalyst particle.

Brian and Hales found that the liquid-solid mass transfer coefficient $k_{ls}$ between a sphere and surrounding fluid could be calculated from

$$\left(\frac{k_{ls}d_p}{D}\right)^2 = 4.0 + 1.21N_{pe}^{2/3} \quad (4.6)$$

$$N_{pe} = \frac{d_p V}{D} \quad (4.7)$$

where $D$ is the diffusivity of reactant in the liquid phase and $V$ is the relative velocity of the catalyst particle to the surrounding liquid. The velocity of a particle falling freely through a fluid can be expressed as

$$V = \frac{gd_p^2(\rho_a - \rho_l)}{18\mu} \quad (4.8)$$

Here, $\rho_l$ is the liquid density and $\rho_a$ is the apparent density of the catalyst particle in the liquid phase. The viscosity of liquid phase is $\mu$ and $g$ is the acceleration due to gravity.

Thus equation (4.6) can be rewritten as.

In the hydrogenation reactor, vigorous agitation is necessary to prevent the catalyst particle from settling. Hence, the actual relative velocity between catalyst particle and surrounding liquid is somewhat higher than the free settling velocity. However, the catalyst are fine particles (<50μm in most slurry reactor), thus the increase of the relative velocity is quite small. Therefore, the actual $k_{ls}$ is usually 1 to 4 times greater than the $k_{ls}^*$ that is based on the free settling velocity. As an estimation, the actual $k_{ls}$ can be assumed as twice of $k_{ls}^*$. Thus the actual $k_{ls}$ can be calculated by the equation (4.10)$^{1,2}$:

$$\left(\frac{k_{ls} d_p}{D}\right)^2 = 16 + 4.84 \left[\frac{g d_p^3 (\rho_s - \rho_l)}{18 \mu D}\right]^{2/3}$$

4.2.3 Pore diffusion

The diffusion of reactants inside the pores of catalyst is a parallel process with the hydrogenation reaction$^1$. PS molecules diffuse into the pore and may adsorb on any active sites along the pore and react with H$_2$ as shown by Figure 4.2. To simplify the complexity between the surface reaction and pore diffusion, an effectiveness factor, $\eta$, is defined to describe the effect of pore diffusion$^2$.

$$\eta = \frac{\text{actual reaction rate}}{\text{intrinsic reaction rate}}$$
Thus the hydrogenation rate corrected by the effect of pore diffusion is

\[ -r_A = -\frac{dN_A}{dt} = \eta k_{\text{Cat}} C_A \]  \hspace{1cm} (4.11)

Assuming: 1) the catalyst particles are spheres; 2) the temperature gradient inside catalyst is negligible; 3) the diffusion of reactants in catalyst pores follows the Fick’s law, and 4) the reaction is first order, the effectiveness factor can be calculated by

\[ \eta = \frac{3}{\phi} \left( \frac{1}{\tanh \phi} - \frac{1}{\phi} \right) \]  \hspace{1cm} (4.12)

Here \( \phi \) is a dimensionless variable, which is called Thiele modulus and can be calculated according to equation (4.13)

\[ \phi = \frac{d_p}{2} \sqrt{\frac{k_v}{D_{\text{eff}}}} \]  \hspace{1cm} (4.13)
Here $k_v'$ is the reaction rate constant per unit of gross volume of catalyst and $D_{\text{eff}}$ is the effective diffusion coefficient, which can be calculated from $D_{\text{eff}} = \frac{\theta \cdot D}{4}$. Here $\theta$ is the porosity of the catalyst. If the effectiveness factor $\eta$ is greater than 0.95, the influence of pore diffusion is negligible during reaction. If $\eta$ is less than 0.5, the influence of pore diffusion is significant.

4.2.4 Mass transfer in polymer solution

Polymer solutions generally have high viscosity, low diffusivity and non-Newtonian behavior. Hence, mass transfer in polymer solutions is more complex than in small molecule solutions. The properties of polymer solutions depend on molecular weight and concentration of polymer, the interaction between polymer and solvent and the interaction between polymer and polymer.

At low concentration, polymer chains are isolated from each other by the surrounding solvent molecules. The polymer chain interacts mainly with the solvent. The solution behaves like an ideal, so-called dilute solution. When the polymer concentration increases to a certain value, $C^*$, the polymer chains start to interact with each other. The concentration $C^*$ is called overlap concentration and the solution is generally called semidilute solution. When the polymer concentration is much greater than $C^*$, polymer chains become fully entangled as shown in Figure 4.4, which is called a concentrated solution. The semidilute and concentrated polymer solutions generally exhibit high viscosity and low diffusivity due to the inter-penetration and entanglement between polymer chains. The movement of each polymer chain is constrained by the neighboring chains. The diffusion behavior of individual polymer chains in a concentrated solution can be illustrated by the tube model and reptation theory.
The polymer chain can be assumed to be in a tube-like region which is surrounded by the neighboring chains. The movement of the polymer chain is effectively confined in the 'tube' and can be described as a snake slithering on earth, so called reptation theory as shown in Figure 4.4\textsuperscript{10}.

![Dilute, Semidilute, Concentrated Concentration regimes of polymer solutions](image)

**Figure 4.3 Concentration regimes of polymer solutions\textsuperscript{11}**

The crosses represent the intersection of the neighboring chains.

As described above, mass transport in hydrogenation is related to viscosity and diffusivity. The high viscosity of, and low diffusivity in, concentrated polymer solutions will
influence the mass transport significantly in the hydrogenation of polymers. Moreover, the non-Newtonian behavior of polymer solutions can make the situation even more complex. Generally, polymer solutions show shear-thinning behavior, i.e. the viscosity decreases with shear rate. Hence, the viscosity of polymer solutions can decrease due to the shear created by the agitation during hydrogenation. Moreover, the overlap concentration can be increased under shear. Thus it is possible that the polymer solution transfers from the concentrated or semidilute region to the dilute region under agitation. In that case, viscosity and diffusivity will undergo significant changes and corresponding changes of mass transport will be expected.

4.3 Materials and procedures

4.3.1 Materials

The 5%Pd/BaSO₄ catalyst was obtained from Aldrich and was used as received. The 5%Pd/BaSO₄ catalyst was examined by scanning electron microscopy (SEM) as shown in Figure 3.2. The particles had an irregular shape, with an approximate aspect ratio of 2:1:1. The average equivalent spherical diameter was about 20 µm. A true density of 4.42 g/cm³ was measured by gas displacement, a BET surface area of 4.6 m²/g was measured by N₂ adsorption, and an average pore diameter of 1.3 µm and a porosity of 71.7% were measured by mercury porosimetry. Commercial PS (Nova 172) with a weight average molecular weight of approximately 290,000 g/mol was used as received. Standard PS with molecular weight of 126,000 and 412,000 g/mol were obtained from Polymer Source, Inc. and used as received. Decahydronaphthalene (Aldrich, 99%) was used as received. Hydrogen (99.999%) was supplied by National Welders. Certified viscosity standards were obtained from Cambridge Applied Systems.
4.3.2 Procedures

A. Hydrogenation reactions

The hydrogenation reactions were carried out in a 50 cc autoclave. The hydrogenation procedure is same as described in Chapter 3. To investigate the effect of mass transport, the experiments in this chapter were focused on the effect of PS concentration, catalyst concentration and agitation.

B. Viscosity measurement

![Figure 4.5 Schematic drawing of SPL440 viscometer](image-url)
The viscosity of PS solutions was measured with a SPL440 viscometer from Cambridge Applied Systems. As shown in Figure 4.5, the piston in the viscometer is moved by the magnetic coils. The time that takes the piston to move from top to bottom is recorded and is converted into the viscosity of the measured solution according to the internal calibration function. The accuracy of the viscometer has been verified by measuring the viscosity of certified standards. The measured viscosity showed less than 3% deviation from the certified viscosity at different temperatures as, shown by Figure 4.6.

![Figure 4.6 Verification of SPL440 viscometer](image)

The SPL440 viscometer is sensitive to contamination. The following procedure must be followed in order to achieve accurate results.

1) Clean the viscometer thoroughly with tetrahydrofuran (THF).
2) Dry the viscometer in air.

3) Rinse the measurement chamber and piston with PS solution to be measured.

4) Fill the chamber with PS solution and insert the piston.

5) Heat the viscometer to the desired temperature and start measurement.

6) Dump out the PS solution, rinse the measurement chamber and piston with PS solution and refill the viscometer with the same PS solution.

7) Measure the viscosity at the same temperature as step 5.

8) If the difference between the results from step 5 and 7 are within 3%, the viscometer is performing properly. Increase temperature and measure the viscosity at different temperatures.

9) If the difference between the results from step 5 and 7 are outside of 3%, the viscometer may be contaminated by the residual THF.

10) Dump out the solution, and repeat steps 6 and 7.

11) If the difference between the results from step 10 and 7 is within 3%, the contaminant has been removed and the viscometer can produce accurate results. Continue measuring the viscosity at different temperatures.

12) If the difference between step 10 and 7 is out of 3%, re-cleaning of the viscometer by THF is required. Start from step 1 and do the other steps again.

C. Dynamic light scattering

The diffusivity of PS solution was measured in a view cell by dynamic light scattering with a 90° scattering angle. The dynamic light scattering measures the scattered intensity autocorrelation function, G(q, t), which is then fitted to the following relationship (4.14)\textsuperscript{13}. 
\[ G(q,t) = \langle I(q,t)I(q,0) \rangle = A_1(1 + A_2 \exp(-A_3t)) \] \hspace{1cm} (4.14)

Here, \( A_1, A_2 \) and \( A_3 \) are constants. A typical experimental result, i.e., a plot of \( G(q, t) \) versus \( t \) is shown in Figure 4.7. The constant \( A_3 \) can be obtained from fitting the curve in Figure 4.7 with equation (4.14). The constant \( A_3 \) is related to the scattering vector \( q \) and diffusivity \( D \) by \( A_3 = 2q^2D \); \( q \) can be calculated by equation (4.15).

\[ q = \frac{4\pi n}{\lambda} \sin\left(\frac{90^\circ}{2}\right) \] \hspace{1cm} (4.15)

The diffusivity \( D \) can be calculated from (4.16) once \( A_3 \) is determined.

\[ D = \frac{A_3}{2\times\left(\frac{4\pi n}{\lambda} \sin\left(\frac{90^\circ}{2}\right)\right)^2} \] \hspace{1cm} (4.16)

Here, \( n \) is the reflective index of solvent, which is 1.475 for DHN, and \( \lambda \) is wavelength of the laser, 514 nm in this work.

Figure 4.7 A typical measurement from dynamic light scattering
4.4 Results and discussion

4.4.1 Gas-liquid mass transport

Changing the rotational speed of the agitator is a standard technique to study the influence of the gas-liquid transport resistance. The effect of agitation on the hydrogenation rate was explored using 3wt% PS in DHN. The temperature was 150°C, the H₂ pressure was 750 psig, and the ratio of catalyst to PS was 1 g/g for all experiments. The degree of hydrogenation (i.e., the fractional conversion of aromatic rings to cyclohexane rings in a fixed reaction time (10hr)) was used to represent the reaction rate. Figure 4.8 shows that the degree of hydrogenation increases as the agitation rate increases in the region between 500 and 2000 rpm. When the agitation rate exceeded 2000 rpm, there was no significant change in the degree of hydrogenation after 10 hours with increasing agitation rate. It appears from these results that the resistance of gas-liquid mass transfer is not significant above an agitation rate of about 2000 rpm, at these conditions.
Figure 4.8 Effect of agitation rate on the degree of hydrogenation

(3wt% PS in DHN, 150 °C, 750 psig H₂, 1g 5%Pd/BaSO₄/g PS, 10hr reaction time)

Figure 4.9 is a plot of the first order rate constant k’ versus catalyst concentration C\text{cat} for a series of experiments at 150°C. The value of k’ is essentially independent of C\text{cat} over a wide range of C\text{cat}. Although the values of k’ scatter considerably, there is no obvious trend with C\text{cat}. If the reaction were controlled by H₂ transfer from the gas to the liquid, the value of k’ would have been proportional to \( \frac{1}{C_{\text{cat}}} \). The data in Figure 4.9 obviously do not obey this relationship. This supports the previous conclusion that gas-liquid mass transfer was not an important resistance for these experiments.
Figure 4.9 Dependence of rate constant on catalyst concentration

(PS in DHN (≤ 3wt%), 750 psig H₂, 150°C, 5%Pd/BaSO₄, 2500rpm)

The average and the standard deviation (δ) were calculated using all 11 data points

4.4.2 Liquid-solid mass transport

Normally, a reaction that is controlled by external mass transport, either gas-liquid or liquid-solid mass transport, has an activation energy less than about 15kJ/mol ¹,¹⁴. Therefore, the observed activation energy of about 60 kJ/mol, reported in the previous chapter, suggests that the influence of both gas-liquid and liquid-solid mass transport was negligible in this study. In order to test the influence of liquid-solid mass transport, the liquid-solid mass transfer coefficient $k_{ls}$ was estimated for PS using the correlation (4.10). Here $d_p$ is the diameter of an equivalent spherical catalyst particle, taken to be 20 μm, and $D$ is diffusivity of PS in DHN. In this study, the liquid density $\rho_l$ was about 1 g/mL. The density $\rho_a$ was
calculated from $\rho_a = \rho_p \theta + \rho_p (1 - \theta)$, where $\theta$ is the catalyst porosity and $\rho_p$ is the true density of the catalyst particle. The calculated value of $\rho_a$ was 1.97 g/mL.

The viscosity of PS-DHN solutions (3wt%-9wt%) was measured between 50 and 150°C, and the results are shown in Figure 4.10. The viscosity decreases with temperature significantly, especially for concentrated PS solutions. At the same temperature, the viscosity increases with PS concentration. The diffusivity of 3wt% PS-DHN solution was measured between 25 and 150°C, as shown in Figure 4.11. The diffusivity increases with temperature. The effect of molecular weight on the diffusivity is minimal at low temperatures, and becomes apparent at high temperatures. The experimental viscosity and diffusivity were extrapolated to 180°C according to $\mu = A \exp\left(\frac{B}{T}\right)$\textsuperscript{15} and $D = D_\infty \exp\left(-\frac{E_D}{RT}\right)$\textsuperscript{16}. Thus the liquid-solid mass transfer coefficient $k_{ls}$ can be calculated for different temperatures according to equation (4.10). The calculated results are shown in Table 4.1.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>$\mu$ (cp)</th>
<th>$D \times 10^{11}$ (m$^2$/s)</th>
<th>$k_{ls}$ (m/s)</th>
<th>$\frac{k_{ls} A_{ls}}{k'C_{cat} V}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>90</td>
<td>1.49*</td>
<td>2.95*</td>
<td>1.60E-05</td>
<td>6.68E+03</td>
</tr>
<tr>
<td>120</td>
<td>1.02*</td>
<td>4.88*</td>
<td>2.55E-05</td>
<td>2.81E+03</td>
</tr>
<tr>
<td>150</td>
<td>0.731*</td>
<td>7.52*</td>
<td>3.82E-05</td>
<td>1.61E+03</td>
</tr>
<tr>
<td>180</td>
<td>0.549</td>
<td>10.9</td>
<td>5.41E-05</td>
<td>3.85E+02</td>
</tr>
</tbody>
</table>

* - experimental data. (Other viscosity and diffusivity are from the extrapolation of experimental data).
Figure 4.10 Viscosity of PS-DHN

Commercial PS (Nova 172, Mw ≈ 290000 g/mol)

Figure 4.11 Diffusivity of PS in DHN solution

Standard PS (Mw = 126000 g/mol or 412000 g/mol)

Commercial PS (Nova 172, Mw ≈ 290000 g/mol)
Assuming that \( k_{ls} \) can be expressed by an Arrhenius relationship, \( k_{ls} = A \exp\left(-\frac{E_a}{RT}\right) \), the activation energy for liquid-solid mass transport can be calculated as 18.6 kJ/mol. This value is much lower than the experimentally determined activation energy for PS hydrogenation, 59.6 kJ/mol, which further confirm that the influence of liquid-solid mass transfer is minimal at these conditions.

At steady state, the mass transfer rates and the reaction rate must be the same. Hence, combining (4.4) and (4.11), the overall hydrogenation rate can be written as (4.17). If the reaction was controlled by liquid-solid mass transport, the first term in the denominator of (4.17) is negligible and the reaction rate can be written as, \( -r_A(ls) = k_{ls}A_{ls}C_A \). Thus, the ratio of the rate of reaction controlled by liquid-solid mass transfer of PS to the actual reaction rate is given by \( \frac{k_{ls}A_{ls}}{k'C_{cat}V} \). As shown in table 4.1, the calculated ratios are greater than 385 for all the experimental temperatures, which means the liquid-solid mass transfer resistance was negligible in these experiments.

\[
- r_A = \frac{C_{PS}}{1 + \frac{1}{\eta W_{cat}k + k_{ls}A_{ls}}} \quad (4.17)
\]

4.4.3 Pore diffusion

Based on a comparison of the catalyst pore size and the radius of gyration, \( R_{g,c} \), for PS, Ness et. al.\(^4\) concluded that pore diffusion probably did not influence the kinetics of PS hydrogenation over Pt/SiO\(_2\) catalyst. In order to test the effect of pore diffusion in the present study, values of the effectiveness factor were estimated. The catalyst particles were assumed
to be spheres with a diameter of 20 µm. The Thiele modulus was \( \phi = \frac{d_p}{2} \sqrt{\frac{k_v}{D_{\text{eff}}}} \) and the effectiveness factor was \( \eta = \frac{3}{\phi} \left( \frac{1}{\tanh \phi} - \frac{1}{\phi} \right) \). Here \( k_v \) can be estimated from \( k_v = k' \rho_p (1 - \theta) \). Calculated values of the effectiveness factor are shown in Table 4.2. These values suggest that the effect of pore diffusion was insignificant for these experiments.

### Table 4.2 Calculations of pore diffusion

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>k' (L/g/s)</th>
<th>k_v' (s^{-1})</th>
<th>D_{\text{eff}} (m^2/s)</th>
<th>\phi</th>
<th>\eta</th>
</tr>
</thead>
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<tr>
<td>90</td>
<td>1.62E-7</td>
<td>2.03E-4</td>
<td>5.29E-12</td>
<td>0.0196</td>
<td>1.00</td>
</tr>
<tr>
<td>120</td>
<td>6.15E-7</td>
<td>7.70E-4</td>
<td>8.75E-12</td>
<td>0.0938</td>
<td>0.999</td>
</tr>
<tr>
<td>150</td>
<td>1.61E-6</td>
<td>2.01E-3</td>
<td>1.35E-12</td>
<td>0.122</td>
<td>0.999</td>
</tr>
<tr>
<td>180</td>
<td>9.53E-6</td>
<td>1.19E-2</td>
<td>1.95E-12</td>
<td>0.247</td>
<td>0.996</td>
</tr>
</tbody>
</table>

Due to the small size of H_2 molecules compared with PS, the rates of liquid-solid mass transfer and pore diffusion of H_2 molecules should be much faster than PS. Because the gas-liquid and liquid-solid mass transfer resistances were negligible as shown above, and the effectiveness factors are close to 1, the kinetic model (3.32) obtained in Chapter Three can be assumed to express the intrinsic kinetics of PS hydrogenation under these conditions.

### 4.4.4 Concentrated PS solutions

The results presented above show that the mass transport resistances are negligible for 3wt% or less PS-DHN solutions, at agitation rates greater than about 2000 rpm. However, Weimann^5 has reported that the kinetics of PS hydrogenation depend on the solution
viscosity, which is related to PS concentration and molecular weight. To further investigate the influence of mass transfer, the PS concentration was increased in the hydrogenation reactions. Figure 4.12 shows that the observed reaction rates in experiments with PS concentrations of 4.5wt% and higher are much lower than those predicted by Equation (3.32). This implies that some mass transfer process may be influencing the reactions at these higher PS concentrations.

Figure 4.12 Experiments with higher PS concentrations

(PS in DHN, 150 °C, 750 psig H₂, 5%Pd/BaSO₄, 2500rpm)

◊ PS conc. ≤ 3wt%, Δ PS conc. > 3wt%
To test whether gas-liquid mass transport had become a significant resistance at these higher PS concentrations, the agitation rate was increased, with the results shown in Figure 4.13. An increase of agitation rate from 2500rpm to 3500rpm caused the observed hydrogenation rate to increase for the 4.5wt%, 6.5wt% and 7.5wt% solutions. The points for these three concentrations at 3500 rpm are close to the line representing the intrinsic kinetic equation (3.32). However, the 9wt% solution required an agitation rate of 4500 rpm to bring the reaction rate close to intrinsic hydrogenation rate.

![Figure 4.13 Experiments with higher PS concentrations at higher agitation rates](image)

(PS in DHN, 150 °C, 750 psig H₂, 5%Pd/BaSO₄, 2500rpm)

- Intrinsic kinetic equation, Δ 2500rpm, O 3500rpm, × 4500rpm
In viscous fluids, both $k_{gl}$ and $k_{ls}$ depend on the liquid viscosity\textsuperscript{1, 2, 7}. The viscosity increase caused by the increased PS concentration tends to reduce both gas-liquid and liquid-solid mass transfer rates. Moreover, the variables that affect the solution viscosity and diffusivity, e.g., PS concentration and molecular weight, also can influence the effectiveness factor because the effectiveness factor will depend on these variables. Generally, the primary effect of a higher agitation rate is to increase the gas-liquid interfacial area $A_{gl}$, and therefore increase the gas-liquid transfer rate. The liquid-solid mass transport and pore diffusion resistance will not be influenced by the agitation significantly\textsuperscript{1}. Figure 4.13 might imply that the hydrogenation of concentrated PS solution was influenced by gas-liquid mass transport. However, the non-Newtonian behavior of polymer solution could make it different. The decrease of viscosity due to the shear stress created by agitation may enhance the gas-liquid mass transport as well as liquid-solid mass transport. It has been reported that the overlap concentration will increase under shear\textsuperscript{12}, which may imply less entanglement between polymer chains. Therefore, the diffusivity of polymer in solution may also increase under shear, which would improve the liquid-solid mass transport. Hence, whether the lower hydrogenation rate in these concentrated PS solutions is caused by a lower rate of gas-liquid mass transport or liquid-solid mass transport can not be distinguished at this point. Additional measurements of viscosity and diffusivity in the concentrated regime and under shear, and further quantification of the mass transfer rates at these conditions, are necessary. Furthermore, the apparent hydrogenation rate constant $k'$ is related to the adsorption and conformational dynamics of PS molecules as discussed in Chapter Three. The high viscosity and heavy entanglement in concentrated PS solutions could influence the adsorption and conformation rearrangement of PS coils, which would also influence the hydrogenation rate.
4.5 Conclusions

The mass transport processes in heterogeneous hydrogenation of PS were studied. The viscosity of PS (Mw≈290000) solutions was measured at various temperatures and concentrations. The diffusivity of PS solutions (3wt%) was measured at various temperatures and PS molecular weights. The rate of hydrogenation of 3wt% PS solution became independent of agitation above 2000 rpm, which indicated that gas-liquid mass transfer was a negligible resistance at these conditions. Moreover, the hydrogenation rate constant was found to be independent of catalyst concentration, which further confirmed the negligible influence of gas-liquid mass transport at these conditions. Calculations of the liquid-solid mass transfer coefficient and the effectiveness factor demonstrated that the resistances of liquid-solid mass transport and pore diffusion were negligible in hydrogenation of PS solution at 3wt% and at 90°C to 180°C. At these conditions, the actual reaction rates were at least 385 times lower than the rates of reaction for the case of liquid-solid mass transfer control. And the effectiveness factors were higher than 0.996 for all temperatures.

The hydrogenation rate decreased when the PS concentration was increased above 4.5wt%. Further investigation showed that the rate of hydrogenation of concentrated PS solutions could be increased by increasing the agitation rate. Hence, the gas-liquid mass transport might influence the hydrogenation in concentrated solutions. Further investigation is necessary to confirm this conclusion.
References


Chapter 5

Phase Equilibria for the Hydrogenation of Polystyrene in the Presence of Supercritical CO$_2$

5.1 Introduction

Catalytic hydrogenation is a major method for modifying the physical and chemical properties of polymers. However, the high viscosity of a polymer solution will cause low mass transfer rates, which can influence the overall hydrogenation rate. Generally, the viscosity of a polymer solution will increase with polymer molecular weight and concentration. Thus, the influence of viscosity on mass transport and the overall hydrogenation rate will become severe in the hydrogenation of high molecular weight and concentrated polymer solutions.

It has been known that supercritical CO$_2$ (scC$_2$) can swell a polymer solution$^{1-3}$ or melt$^4,5$ and cause a significant decrease in viscosity. Moreover, scCO$_2$ can increase the diffusion coefficient of a polymer in solution$^6$, as well as the H$_2$ solubility in the liquid phase$^7,8$. All of these factors will improve the rate of mass transport in polymer hydrogenations. Hence, hydrogenation of polymers in the presence of scCO$_2$ is a potential way to overcome the barrier of low mass transfer rates. The application of scCO$_2$ in heterogeneous hydrogenation has gained great interest. The improvement of hydrogenation rate and selectivity and the extension of catalyst lifetime have been demonstrated in the presence of scCO$_2^9$. A comprehensive review about utilizing scCO$_2$ as hydrogenation media has been presented in Chapter Three.
This chapter will focus on the phase behavior for polystyrene (PS) hydrogenation in the presence of scCO₂. The precipitation of PS from different solvents will be studied. The proper solvent suitable for hydrogenation of PS in the presence of scCO₂ will be selected. The volume expansions of PS solutions will be investigated at different conditions. The phase equilibria of CO₂-H₂-solvent and PS-solvent-CO₂ will be studied using the Peng-Robinson equation of state (PR-EOS) and the Sanchez-Lacombe equation of state (SL-EOS). Furthermore, the effect of CO₂ on the solubility of H₂ and viscosity of PS solution will be studied.

5.2 Background

Supercritical CO₂ is one of the most commonly used supercritical fluids because of its mild critical conditions (T<sub>c</sub>=31.1°C and P<sub>c</sub>=73.8bar). Moreover, CO₂ is non-toxic, nonflammable, and inexpensive, which make it more attractive in the modern chemical industry. Supercritical CO₂ shows unique properties similar to both gas and liquid. For example, the density, heat capacity and solvent strength are close to a liquid, but the viscosity and diffusivity are similar to a gas. Processes limited by mass transport resistances in the liquid phase become faster under supercritical conditions. Processes limited by the solubility or heat capacity in the gas phase become favorable under supercritical conditions. Thus scCO₂ has been successfully used in many chemical processes, such as: enzymatic reactions, polymerization reactions, catalytic reactions, extraction and separation, gas antisolvent crystallization, microelectronics processing, etc.⁸,¹⁰

5.2.1 Phase behavior of CO₂-solvent-polystyrene

Although scCO₂ shows many potential advantages for chemical processes, the low solubility of most hydrocarbons in CO₂ can limit its application. It has been reported that
hydrocarbons with more than eight carbon atoms cannot be dissolved by CO$_2$ completely$^{11}$. Consequently, as a hydrocarbon macromolecule, the solubility of PS in scCO$_2$ is virtually zero under commonly used temperatures and pressures. Moreover, CO$_2$ can be termed as an anti-solvent for PS. Carbon dioxide will cause PS to precipitate from an organic solution as its fraction in the solution increases. The PS precipitate might block the pores of solid catalyst and lead to catalyst deactivation. Hence, a detailed investigation of the precipitation of PS from different solvents will be necessary prior to conducting hydrogenation in the presence of CO$_2$. Furthermore, controlling the hydrogenation conditions, especially the CO$_2$ partial pressure during hydrogenation, is also necessary to avoid the precipitation.

The precipitation of a solute from solutions by an anti-solvent gas has been studied by several research groups. Different theoretical and empirical models have been developed in order to predict the precipitation conditions. The classical definition of volume expansion, as shown by Equation (5.1), has been used as the criterion for the precipitation$^{12}$. In Equation (5.1) $V_L$ is the total volume of the liquid phase, $X_1$ is the fraction of anti-solvent gas in the liquid phase and $V_2$ is the total volume of the pure solvent at the same temperature and a reference pressure (normally atmospheric pressure).

$$\frac{\Delta V}{V} = \frac{V_L(T, P, X_1) - V_2(T, P_o)}{V_2(T, P_o)}$$  \hspace{1cm} (5.1)

Equation (5.1) can also be written as (5.2), where $v_L$ is the molar volume of the liquid mixture, and $v_2$ is the molar volume of the solvent.

$$\frac{\Delta V}{V} = \left(1 - \frac{1}{v_2(T, P_o)}\right) \frac{v_L(T, P, X_1)}{v_2(T, P_o)} - 1$$  \hspace{1cm} (5.2)
It has been observed that $v_L/v_2$ is close to one with low and moderate mole fractions of gas in the liquid phase, i.e., the change of the molar volume of liquid is negligible with increasing pressure\textsuperscript{12}. Thus the volume expansion mainly depends on the mole fraction ($X_1$) of gas in the liquid phase, as shown by (5.3).

\[
\frac{\Delta V}{V} \approx \frac{1}{1 - X_1} - 1 \tag{5.3}
\]

The precipitation of a solute by an anti-solvent gas may be a consequence of the liquid phase volume expansion. Hence, according to equation (5.3), the mole fraction of gas anti-solvent in the liquid phase can be another criterion for the precipitation. Kikic et al.\textsuperscript{13} investigated the precipitation of naphthalene from toluene by high pressure CO$_2$. It was found that the precipitation of naphthalene was influenced only by the amount of CO$_2$ dissolved in the liquid phase, which demonstrated that $X_1$ could be used as the criterion for precipitation.

Recently, it was found that the behavior of volume expansion is similar for different solvents. The volume expansion can not distinguish the difference between different solvents and therefore the definition of volume expansion can not be used as a universal criterion for predicting precipitation. Hence, the relative molar volume expansion\textsuperscript{12} and relative partial molar volume reduction\textsuperscript{14} have been proposed as more appropriate thermodynamic criteria for gas anti-solvent precipitation processes.

On the other hand, investigation of the volume expansion of a polymer solution in the presence of high pressure CO$_2$ is one of the primary methods to study the phase equilibrium of the polymer-solvent-CO$_2$ ternary system. The volume expansion can be correlated with an equation of state to determine the binary interaction parameters, which then can be used to
calculate other properties, such as the composition of the gas and liquid phases, density of each phase, critical conditions, etc.

5.2.2 H₂ solubility in the presence of CO₂

The solubility of H₂ is a major concern for three-phase hydrogenation reactions. Poor H₂ solubility can cause low reaction rates and low mass transfer rates. A commonly accepted idea is that CO₂ can swell a liquid and increase the H₂ solubility in the liquid⁸. Hence, the increase of H₂ solubility could benefit a liquid-phase hydrogenation in the presence of CO₂.

Under single-phase conditions, H₂, CO₂ and organic substrates may form a homogeneous phase such that the H₂ solubility will be essentially the same as the initial fraction of H₂ added into the system. However, when two fluid phases are present, the H₂ solubility will be different from the initial fraction of H₂ in the system because of the phase equilibrium between the light and heavy phases. Hence, any factor that can affect the phase equilibrium, such as temperature, pressure, and properties of organic substrates will affect the H₂ solubility in the liquid phase.

![Figure 5.1 H₂ solubility in CO₂-swollen liquid at different CO₂ to organic feed ratios](image-url)
Devetta et al.\textsuperscript{7} studied the phase equilibrium of H\textsubscript{2}-CO\textsubscript{2}-organic liquid under two-phase conditions. The organic liquid was a mixture of unsaturated ketones. They found that the H\textsubscript{2} solubility in the liquid phase went through a maximum when the overall fraction of CO\textsubscript{2} in the system was increased, as shown in Figure 5.1. However, the H\textsubscript{2} solubility is defined on a CO\textsubscript{2} free basis in Devetta’s work, which will be different from the actual H\textsubscript{2} solubility in the liquid phase.

Besides the ternary phase equilibria of H\textsubscript{2}-organics-CO\textsubscript{2}, ternary phase equilibria of H\textsubscript{2} and organics with other supercritical fluids have been investigated. Schiemann\textsuperscript{15} studied the phase equilibrium of H\textsubscript{2}-sunflower oil-propane. A large increase in the fraction of H\textsubscript{2} in the liquid phase was observed with adding propane into the system. However, further investigation of the same ternary system by other researchers did not show the same behavior as shown in Figure 5.2\textsuperscript{16}, which raised doubts about Schiemann’s results. Due to the variety of organic substrates and supercritical fluids, it is not reasonable to draw a general conclusion about the influence of supercritical fluids on the H\textsubscript{2} solubility in liquid phase. Further study of the phase equilibrium of H\textsubscript{2}-organics-CO\textsubscript{2} will be necessary to understand the effect of scCO\textsubscript{2} on H\textsubscript{2} solubility.
5.2.3 Viscosity of PS-solvent-CO$_2$

When CO$_2$ is dissolved in polymer solutions, the volume of polymer solution will expand significantly. Consequently, the solvent strength and the interaction between polymer and solvent will change. This can affect the conformational state of polymer chain$^3$. Most polymers, such as PS, cannot be dissolved in scCO$_2$. Therefore, it has been suggested that the CO$_2$-rich phase of a polymer-organic-CO$_2$ ternary system is free of polymer$^{17, 18}$. Hence, the volume expansion by scCO$_2$ virtually dilutes the original polymer solution. All of the above factors can influence the viscosity of a polymer solution.

The viscosity of polymer solutions in the presence of scCO$_2$ has been investigated by different researchers$^{1-3, 6}$. The viscometer that is widely used in this field is the ‘falling body' type viscometer$^{19-21}$. It measures the falling speed of a sinker in a chamber filled with the polymer solution and high pressure CO$_2$. The viscosity is determined using the falling speed,
the density difference between the sinker and solution and the calibration constant of the viscometer.

It was found that the viscosity of polymer solution decreased with the addition of CO2 into the solution\(^1\,^6\). The largest reductions in viscosity occurred at low temperatures and at high polymer concentrations. The decrease of viscosity in the presence of CO2 could, in part, arise from the dilution of polymer solution due to volume expansion. However, Yeo and Kiran\(^1\) found the viscosity of PS solution in CO2-swollen toluene was lower than that in pure toluene at the same overall polymer concentration. In other words, polymer solution diluted by high pressure CO2 showed lower viscosity than that diluted by organic solvent. Ideally, the viscosity of a liquid mixture can be expressed by a linear equation, \(\eta = \sum_i X_i \eta_i\). Here, \(\eta_i\) and \(X_i\) are the viscosity and mole fraction of component \(i\), respectively. Due to the low viscosity of scCO2, a polymer solution diluted by scCO2 can have a lower viscosity than a polymer solution with the same polymer concentration in the organic solvent. On the other hand, the solvent quality could change significantly in the presence of CO2, which will influence the conformation of the polymer chain. Li et al.\(^3\) observed that the apparent mean-square radius of gyration of PS in toluene decreased with increasing CO2 pressure. Hence, less interaction between polymer chains will be expected due to the decrease of the dimension of the polymer coil in the presence of CO2. This decrease may reduce the viscosity of polymer solution as well.
5.3 Materials, procedures and calculations

5.3.1 Materials

Commercial PS (Nova 172) with a weight average molecular weight of approximately 290,000 g/mol was used as received. Standard PS samples (Mw=212,000 and Mw=114,000) were obtained from Aldrich and were used as received. Standard PS samples (Mw=412,000 and Mw=10,500) were obtained from Polymer Source Inc. and were used as received. The following hydrocarbons were obtained from Aldrich and used as received: n-hexane, tetradecane, n-hexylcyclohexane, tetrahydrofuran, cyclohexane (CYC), methylcyclohexane (MCYC), ethylcyclohexane, α-phellandrene, decahydroquinoline, DHN (76% trans-DHN and 24% cis-DHN), dicyclohexyl, cyclohexylbenzene, tetrahydronaphthalene and perhydrofluorene. Isopropyl benzoate was obtained from TCI and used as received. Carbon dioxide (>99.99%) were supplied by National Welders.

5.3.2 Phase behavior and volume expansion

Phase behavior was studied in a view cell with a constant volume of 21 mL. The experimental set-up is shown in Figure 5.3. Solutions with a known concentration of PS and a known volume were loaded into the view cell. The system was flushed with low pressure CO₂ to remove air, heated to the desired temperature, and pressurized with CO₂ to different final pressures. The phase behavior was observed through two sapphire windows. Once the system was at equilibrium, a digital camera was used to record the phase behavior.
Volume expansion measurements were carried out in a similar system, but with a different view cell that was designed to constrain the expansion of the polymer solution to one dimension. The inside of the cell was rectangular with dimensions of 0.635 cm (width), 1.587 cm (depth) and 1.587 cm (height). The volume of the cell was approximately 2.1mL. The corners of the interior of the cell were machined to minimize curvature in order to maintain a rectangular shape. A detailed drawing of the view cell is available elsewhere. A digital camera (Pulnix TM-7 CN) was used to capture images of the expansion of the polymer solution under high pressure CO₂. The images were transferred to a computer through an image capture board (Scion Corp LG3). The volume of the solution was measured by Scion imaging software. After DHN or PS-DHN was loaded into the cell, the cell was sealed and flushed with CO₂ to remove air and heated to the desired temperature. Once the temperature was stable, the Scion software was calibrated and the original height (h₀) of the

Figure 5.3 Schematic diagram of the apparatus for recording the phase behavior
polymer solution was measured. The cell was pressurized with CO$_2$ to the desired pressure and the height of the solution was measured periodically until it did not change with time. The height ($h_e$) of the solution at equilibrium then was measured. Volume expansion ($V.E.$) is defined as $V.E. = V_e/V_o$. Here, $V_e$ and $V_o$ are the equilibrium and initial volumes of the solution, which can be calculated according to the dimension of the view cell and the height $h_o$ and $h_e$.

5.3.3 Equation of state

A. Peng-Robinson equation of state

The phase equilibria of CO$_2$, DHN and H$_2$ were calculated using the PR-EOS$^{23}$ with classical mixing rules as shown below. Pure trans-DHN was assumed for all calculations of phase equilibria. The pure-component characteristic properties for PR-EOS calculation are listed in Table 5.1. The binary interaction parameters $k_{ij}$ are obtained from Aspen Plus or from fitting the PR-EOS to published experimental data. The binary interaction parameters for the PR-EOS are listed in Table 5.2. The comparisons between calculated phase equilibria and published experimental results can be found in Appendix A. All of the PR-EOS calculations were performed in Aspen Plus.

The PR-EOS is

$$P = \frac{RT}{v - b} - \frac{a(T)}{v(v + b) + b(v - b)}$$

(5.4)

$$a = \sum_{i=1}^{2} \sum_{j=1}^{2} X_i X_j a_{ij}$$

$$a_{ij} = (a_i a_j)^{0.5} (1 - k_{ij})$$
\[ b = \sum_{i=1}^{2} \sum_{j=1}^{2} X_i X_j b_{ij} \]

\[ b_{ij} = \frac{b_i + b_j}{2} \]

where X is the mole fraction, and k_{ij} is the binary interaction parameters. The parameters \(a\) and \(b\) are constants in the PR-EOS and can be calculated by the following relations:

\[ a = a(T_c) \alpha(T) \]

\[ a(T_c) = 0.45724 \frac{(RT_c)^2}{P_c} \]

\[ \alpha(T) = \left[ 1 + \beta(1 - \sqrt{T/T_c}) \right]^2 \]

\[ \beta = 0.37464 + 1.54226 \omega - 0.26992 \omega^2 \]

\[ b = 0.07780 \frac{RT_c}{P_c} \]

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<tr>
<th>(M_w)</th>
<th>(\omega)</th>
<th>(P_c) (Pa)</th>
<th>(T_c) (K)</th>
</tr>
</thead>
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<td>(CO_2)</td>
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<td>(MeOH)</td>
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<td>8084000</td>
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<tr>
<td>(DHN)</td>
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<td>32000000</td>
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<td>(CYC)</td>
<td>84.16128</td>
<td>0.208054</td>
<td>4080000</td>
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<td>(MCYC)</td>
<td>98.18816</td>
<td>0.236055</td>
<td>3480000</td>
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</table>

All the properties are from Aspen Plus.

MeOH - Methanol
Table 5.2. Binary interaction parameters for PR-EOS

<table>
<thead>
<tr>
<th></th>
<th>(k_{ij})</th>
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<tbody>
<tr>
<td>(\text{H}_2)-(\text{CO}_2)^*</td>
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<td>(\text{H}_2)-(\text{DHN})^*</td>
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<tr>
<td>(\text{CO}_2)-(\text{DHN})^{24, 25}</td>
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</tr>
<tr>
<td>(\text{H}_2)-(\text{CYC})^{26}</td>
<td>0.17</td>
</tr>
<tr>
<td>(\text{CO}_2)-(\text{CYC})^*</td>
<td>0.105</td>
</tr>
<tr>
<td>(\text{CO}_2)-(\text{MCYC})^{27}</td>
<td>0.10</td>
</tr>
<tr>
<td>(\text{H}_2)-(\text{MeOH})^{28}</td>
<td>-0.19</td>
</tr>
<tr>
<td>(\text{CO}_2)-(\text{MeOH})^*</td>
<td>0.05</td>
</tr>
</tbody>
</table>

* Aspen Plus default value

B. Sanchez-Lacombe equation of state

The SL-EOS\(^{29-32}\) is based on a lattice-fluid model, in which the pure components are broken into parts or "mers" that are placed into a lattice and are allowed to interact with a mean-field-type intermolecular potential. To account for the compressibility of a solution or the free volume, an appropriate number of holes are also introduced into the lattice. The SL-EOS has a simpler form and fewer parameters than other equations of state that can be used for polymer-related systems. Hence, the SL-EOS has been widely used in polymer-sc\(\text{CO}_2\) related phase equilibrium calculations\(^{17, 18, 22}\).

The SL-EOS is

\[
\rho^2 + P + T \left[ \ln(1 - \rho) + (1 - \frac{1}{r}) \rho \right] = 0 \tag{5.5}
\]

Here, \(\rho\), \(P\), and \(T\) are the reduced density, pressure and temperature respectively. The size parameter, \(r\), represents the number of lattice sites occupied by a molecule. The reduced parameters for a pure component are defined as follows:
Here, \( T^* \), \( P^* \) and \( \rho^* \) are the characteristic pressure, temperature, and close-packed mass density respectively, \( \varepsilon^* \) is the mer-mer characteristic interaction energy, and \( R \) is the universal gas constant. The characteristic parameters of polymers are obtained by fitting pure-component PVT data to the SL-EOS\(^{33}\). The characteristic parameters for low molecular weight substances can be determined using the vapor pressure curve of the substances and their molar volume at the normal boiling point\(^{29,31}\). The pure-component characteristic parameters for PS, trans-DHN and \( \text{CO}_2 \) are given in Table 5.3.

<table>
<thead>
<tr>
<th>Substance</th>
<th>( \rho^* ) (g/cm(^3))</th>
<th>( P^* ) (bar)</th>
<th>( T^* ) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CO}_2 )(^{18})</td>
<td>1.510</td>
<td>5745.0</td>
<td>305.0</td>
</tr>
<tr>
<td>DHN(^{29})</td>
<td>0.935</td>
<td>3150.4</td>
<td>621.0</td>
</tr>
<tr>
<td>PS(^{18})</td>
<td>1.105</td>
<td>3570.0</td>
<td>735.0</td>
</tr>
</tbody>
</table>

In order to apply the SL-EOS to mixtures, the mixing rules for the characteristic parameters must be defined. The mixing rule for the characteristic close-packed molar volume \( v^*_{\text{mix}} \) is

\[
v^*_{\text{mix}} = \sum_{i=1}^{N} \sum_{j=1}^{N} \phi_i \phi_j v^*_{ij}
\]
with

\[ v^*_i = \frac{n^*_i + n^*_j}{2} (1 - n^*) \]

where \( \eta_{ij} \) is the binary interaction parameter, which corrects for the deviations from the arithmetic mean. The subscripts \( i \) and \( j \) refer to the two components in the system. \( \phi_i \) is defined as

\[ \phi_i = \frac{m_i}{\sum_{j=1}^{n} \rho_i v^*_i} \]

where \( m_i \) is the mass fraction of component \( i \), and \( \rho_i^* \) and \( v_i^* \) are the characteristic mass density and close-packed molar volume of component \( i \). The mixing rule for the characteristic interaction energy of the mixture \( \varepsilon_{mix}^* \) is

\[ \varepsilon_{mix}^* = \frac{1}{v_{mix}} \sum_{i=1}^{n} \sum_{j=1}^{n} \phi_i \varepsilon_{ij}^* v_j^* \]

with

\[ \varepsilon_{ij}^* = \sqrt{\varepsilon_{ii}^* \varepsilon_{jj}^* (1 - k_{ij})} \]

Here \( k_{ij} \) is a binary interaction parameter that accounts for specific binary interactions between components \( i \) and \( j \). \( \varepsilon_{ii}^* \) and \( \varepsilon_{jj}^* \) are the characteristic mer-mer interaction energies for component \( i \) and \( j \). The mixing rule for \( r_{mix} \) is

\[ \frac{1}{r_{mix}} = \sum_{j=1}^{n} \frac{\phi_j}{r_j} \]
Here, \( r_j \) is the number of sites that molecule \( j \) occupies in the lattice. At equilibrium,

\[
T^L = T^V
\]

\[
P^L = P^V
\]  \hspace{1cm} (5.6)

\[
\mu^L_i = \mu^V_i \quad (i=1, 2, 3)
\]

where \( \mu \) is the chemical potential and the superscripts \( L \) and \( V \) refer to the gas and liquid phases. The chemical potential for component \( i \) in a mixture can be derived as

\[
\mu_i = RT \left[ \ln \phi_i + \left( 1 - \frac{r_i}{r} \right) \right] + r_i \left\{ \rho \left[ \frac{2}{v^*} \left( \sum_{j=1}^{i} \phi_j v_{ij}^* \epsilon_{ij}^* - \epsilon_{ij}^* \sum_{j=1}^{i} \phi_j v_{ij}^* \right) + \epsilon^* \right] + \right\}
\]

\[
+ r_i \left\{ RT \left( 1 - \rho \right) \ln(1 - \rho) + \frac{\rho}{r_i} \ln(\rho) \right\} + P \left( 2 \sum_{j=1}^{i} \phi_j v_{ij}^* - v^* \right) \]  \hspace{1cm} (5.7)

The Fortran programs proposed by McHugh and Krukonis\(^3\) were used to solve the above equations (5.5 - 5.7) to obtain the equilibrium composition and density of each phase. To calculate the phase equilibria of PS, DHN and CO\(_2\), the SL-EOS was fit with the experimental results to get the binary interaction parameters, as described in Appendix A. To simplify the calculation, the binary interaction parameter \( \eta_{ij} \) was set to zero, and DHN was assumed to be pure trans-DHN for all calculations. The obtained binary interaction parameters \( k_{ij} \) are listed in Table 5.4.
Table 5.4. Binary interaction parameters for SL-EOS

<table>
<thead>
<tr>
<th></th>
<th>k_{ij}</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO_2-DHN</td>
<td>0.057</td>
</tr>
<tr>
<td>CO_2-PS^{35}</td>
<td>0.066</td>
</tr>
<tr>
<td>PS-DHN</td>
<td>-0.06</td>
</tr>
</tbody>
</table>

5.4 Results and discussion

5.4.1 Phase behavior of PS in various solvents

Figure 5.4 summarizes the phase behavior of 10 wt.% PS dissolved in various solvents at 120°C and different CO_2 pressures. The + in Figure 5.4 represents one type of biphasic behavior, as shown in Figure 5.5a. The light (upper) phase is primarily CO_2, and the heavy (bottom) phase is the CO_2-swollen solvent with PS dissolved in it. The _ represents PS precipitation. Therefore, a + with _ overlaid denotes three-phase behavior — one CO_2 rich phase, one solvent rich phase and one polymer rich phase as shown in Figure 5.5b. When the CO_2 pressure is sufficiently high, the solvent and CO_2 can become miscible and form one homogeneous phase. The × represents a condition where only one fluid phase exists. A × with _ overlaid denotes a second type of biphasic behavior — one fluid phase containing CO_2 and solvent and one polymer rich phase, as shown in Figure 5.5c.
Figure 5.4 Phase behavior of 10wt% PS in various solvents at 120°C

1--n-hexane, 2--tetradecane, 3--n-hexylcyclohexane, 4--tetrahydrofuran,
5--CYC, 6--MCYC, 7--ethylycyclohexane,
8-- α-phellandrene, 9-- isopropyl benzoate, 10--decahydroquinoline, 11--DHN, 12--
dicyclohexyl, 13--cyclohexylbenzene, 14--tetrahydronaphthalene, 15--perhydrofluorene

 insoluble, × one fluid phase, + two fluid phases, _ precipitation

For the solvents studied in this research, precipitation of PS occurred at biphasic conditions as the CO₂ pressure was increased, forming the three-phase system shown in Figure 5.5b. In some cases, a further increase in CO₂ pressure led to two-phase behavior, a polymer rich phase and solvent-CO₂ rich phase, as shown in Figure 5.5c.
Figure 5.5. Typical phase behavior of PS-solvent-CO$_2$
(a) shows two phases—one CO$_2$ rich phase and one solvent rich phase with PS dissolved in it;
(b) shows three phases—one CO$_2$ rich phase, one solvent rich phase and one PS rich phase;
(c) shows two phases—one CO$_2$-solvent phase and one PS rich phase.

Among the solvents shown in Figure 5.4, CYC$^{36, 37}$, MCYC$^{38, 39}$ and DHN$^{40}$ have been used for the hydrogenation of PS. Therefore it is interesting to compare their phase behavior. The precipitation pressures for these three solvents at 120°C are summarized in Table 5.5. It has been suggested that the fraction of CO$_2$ dissolved in the liquid is the major reason for precipitation$^{13}$. Therefore, the phase equilibrium of the CO$_2$-solvent system (without PS) at the precipitation pressure was calculated using the PR-EOS. The calculated mole fractions of CO$_2$ are given in Table 5.5. The mole fraction of CO$_2$ in DHN is similar at different temperature and their corresponding precipitation pressures. Considering the error caused by neglecting PS in this calculation, the results in Table 5.5 imply that CO$_2$ fraction in liquid is the major reason for PS precipitation from DHN. CYC and MCYC had a much lower precipitation pressure than DHN at 120°C. The calculated fraction of CO$_2$ at precipitation was found to be very different for different solvents. For the three solvents at 120°C, the lower precipitation pressure, the lower the fraction of CO$_2$ at precipitation.
Table 5.5. Precipitation pressure of PS by CO₂ and mole fraction of CO₂ in the liquid phase
3wt% PS in solvent

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Temperature (°C)</th>
<th>Precipitation pressure (psig)</th>
<th>mole fraction of CO₂*</th>
</tr>
</thead>
<tbody>
<tr>
<td>DHN</td>
<td>40</td>
<td>1200</td>
<td>0.69</td>
</tr>
<tr>
<td>DHN</td>
<td>80</td>
<td>2000</td>
<td>0.65</td>
</tr>
<tr>
<td>DHN</td>
<td>120</td>
<td>2720</td>
<td>0.66</td>
</tr>
<tr>
<td>DHN</td>
<td>150</td>
<td>3000</td>
<td>0.65</td>
</tr>
<tr>
<td>DHN</td>
<td>180</td>
<td>3000</td>
<td>0.62</td>
</tr>
<tr>
<td>CYC</td>
<td>120</td>
<td>1150</td>
<td>0.37</td>
</tr>
<tr>
<td>MCYC</td>
<td>120</td>
<td>780</td>
<td>0.28</td>
</tr>
</tbody>
</table>

* calculated from PR-EOS, neglecting influence of PS

The fraction of CO₂ in the solvent should be a major cause of the decrease in viscosity of the polymer solution upon application of CO₂ pressure. Hence, it is likely that the viscosity of PS-CYC and PS-MCYC will decrease less before precipitation than the viscosity of PS-DHN. However, a measurement of the viscosity of PS in different solvents at different CO₂ pressures will be necessary to confirm this speculation. Because of its high precipitation pressure and high corresponding CO₂ content, DHN was selected as the solvent for hydrogenation of PS in this research. The phase behavior of the DHN-PS-CO₂ system then was studied in more detail, as described below.

Table 5.5 also shows the effect of temperature on the precipitation pressure for 3wt% PS in DHN. At low temperatures, PS precipitates at relatively low pressures. As the temperature is increased, the precipitation pressure increases to an apparent asymptote of about 3000 psig. If the CO₂ concentration in the liquid is essentially constant at precipitation, the observed increase of precipitation pressure with temperature is reasonable, since the solubility of CO₂ in the liquid should decrease with temperature at a fixed pressure. The
asymptote in precipitation pressure at the highest temperatures may be due to increased
dissolution of DHN into the vapor phase, which tends to concentrate PS in the liquid.

During hydrogenation, aromatic rings in PS become saturated. This may change the
interaction between the solvent and polymer and influence the phase behavior of the system.
Table 5.6 shows the precipitation pressure of hydrogenated and partially hydrogenated PS at
150°C. Partially hydrogenated PS (X≅0.50) shows the same behavior as PS. Fully
hydrogenated PS (X≅0.99) precipitates at a slightly higher pressure than PS. The solvent,
DHN, is fully saturated which may make hydrogenated PS somewhat more soluble than PS
itself. Moreover, the results in Table 5.6 suggest that polymer does not precipitate during the
hydrogenation reaction.

Table 5.6. Precipitation pressure of PS and hydrogenated PS
3wt% polymer in DHN at 150°C

<table>
<thead>
<tr>
<th>Hydrogenation degree of PS, X</th>
<th>Precipitation pressure (psig)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 (PS)</td>
<td>3000</td>
</tr>
<tr>
<td>50%</td>
<td>3000</td>
</tr>
<tr>
<td>99%</td>
<td>3100</td>
</tr>
</tbody>
</table>

5.4.2 Volume expansion of DHN and PS-DHN

The volume expansion of pure DHN by high pressure CO₂ at different temperatures is
shown in Figure 5.6a and 5.6b. Generally, the volume of DHN increases as the pressure of
CO₂ increases until DHN becomes completely miscible with CO₂ and forms one
homogeneous phase. However, at 40°C, the V.E. goes through a maximum with CO₂
pressure. This may be the result of the density of CO₂ at 40°C becoming so high that a
substantial quantity of DHN dissolved into the CO₂-rich phase at high CO₂ pressures, causing the volume of the solvent-rich phase to decrease. The V.E. calculated from the PR-EOS is shown by the lines in Figure 5.6a and 5.6b. The calculated V.E. was consistent with the experimental values at high temperatures but deviated from the experimental results at low temperatures, especially at 80°C.

Figure 5.6a Volume expansion of DHN
According to the phase rule for nonreacting systems, there are three degrees of freedom in a ternary system with two phases. Hence, the volume expansion results for the PS-DHN solutions under high pressure CO₂ depend on the mass ratio of each compound as well as temperature and pressure. The experiments with three components were done at conditions similar to those of the reaction, i.e. about 40-50% of the total volume was filled with PS solution in both the volume expansion experiments and the hydrogenation reactions. Thus, the volume expansion results are expected to explain the phase behavior in the hydrogenation system reasonably well.
Figure 5.7 shows the volume expansion of 3wt% PS-DHN solution at different temperatures. Generally, the volume of the PS solution increases with the CO₂ pressure. The PS solution can obtain approximately 40% expansion at each temperature, except at 180°C. The solution expanded only about 20% before precipitation occurred at 180°C. This is probably because more DHN dissolved in the CO₂ rich phase at 180°C, which reduced the volume of the heavy phase.

5.4.3 Effect of PS concentration and molecular weight on volume expansion

Figures 5.8 and 5.9 show the effect of PS concentration and molecular weight on volume expansion at 150°C. The solid lines in both figures represent the volume expansion of DHN. Figure 5.8 shows that the volume expansions of 'dilute' PS solutions (<6wt%) are similar to the pure DHN. The volume expansions of 'concentrated' solutions (>9wt%)
become lower than pure DHN as the PS concentration increases. These data suggest that PS in 'dilute' solutions does not influence the phase equilibrium significantly. For 'dilute' solutions, the volume expansion and liquid phase CO₂ fraction can be calculated based on the CO₂-DHN binary system, neglecting the presence of PS. In the 'concentrated' solutions, PS starts to influence the phase equilibrium significantly, which causes a decrease of volume expansion at the same CO₂ pressure. Thus a phase equilibrium calculation that considers the effect of PS is necessary to describe the ternary system in this regime.

Figure 5.9 shows that variation of PS molecular weight does not change the volume expansion significantly at a concentration of 3wt% PS. Hence, the influence of molecular weight on the phase equilibrium can be neglected at these conditions.

![Figure 5.8 Effect of PS concentration on volume expansion at 150°C](image)

Commercial PS with molecular weight about 290000 g/mol
The SL-EOS was fit with the volume expansion data in Figure 5.9 to determine the binary interaction parameter for PS-DHN. As shown in Appendix A, one set of binary interaction parameter $k_{PS-DHN} = -0.06$ can represent the volume expansions of all of the different molecular weight PS in DHN solutions at 3wt%. The binary interaction parameters for CO$_2$-DHN and PS-CO$_2$ were determined by fitting the SL-EOS with experimental data as shown in Appendix A. The volume expansions of commercial PS in DHN solutions at 150°C were calculated using the SL-EOS with the obtained binary interaction parameters. The calculated volume expansions decrease with increasing PS concentration as shown in Figure 5.10a, which is consistent with the measured volume expansions (Figure 5.8). However, Figure 5.10b shows the deviations between calculated volume expansions and measured
volume expansions become significant at concentrations above 3wt%, which can be attributed to the high polydispersity of the commercial PS.

Figure 5.10a Calculated volume expansions of PS-DHN at 150°C

Figure 5.10b Calculated volume expansions of PS-DHN at 150°C
5.4.4 Effect of CO₂ on H₂ solubility in DHN

It has been suggested that one of the advantages of carrying out a hydrogenation reaction in a CO₂-swollen liquid is that the H₂ solubility in the liquid is higher than in the pure liquid. Devetta et al.⁷ studied the phase equilibrium of H₂-CO₂-organic mixture using the PR-EOS. Here, the organic mixture was an unsaturated ketone and its isomers. They found that H₂ solubility (moles of H₂ dissolved per mole of organic mixture) could be increased up to three-fold if the total ratio of CO₂ to organic mixture was around one. In the current study, the phase equilibria of DHN-H₂ and DHN-H₂-CO₂ was calculated using the PR-EOS. Figure 5.11 shows the phase equilibrium of the DHN-H₂-CO₂ ternary system at 150°C and 3000 psig total pressure. The mole fraction of H₂ in the DHN-rich heavy phase decreases as the amount of CO₂ in the system increases. As a check, the phase equilibria of CYC-H₂-CO₂ and methanol-H₂-CO₂ were calculated using the same method. The same general trend was obtained, as shown in Appendix A.

The H₂ solubility based on the volume of liquid phase is usually used in the study of kinetics and mass transport. Hence, the H₂ solubility based on liquid volume was calculated using the PR-EOS, as shown in Figure 5.12. The H₂ solubility based on liquid volume also decreased upon adding CO₂. In order to illustrate the effect of pressure on the H₂ solubility in the liquid phase, ternary phase diagrams of CO₂-H₂-DHN were calculated at 150°C and at various pressures. An apparent increase of H₂ solubility with the addition of CO₂ occurred only at very high pressures, as shown in Figure 5.13. As a check, ternary phase diagrams of CYC-H₂-CO₂ and methanol-H₂-CO₂ were calculated at various pressures as shown in Appendix A. The same behavior as the DHN system was obtained, i.e. an increase of H₂
solubility with adding CO$_2$ occurs only at high pressures. The lowest pressure at which this 'switchover' of H$_2$ solubility occurs depends on the organic itself and the conditions.

![Graph](image)

**Figure 5.11 Phase equilibrium of DHN-H$_2$-CO$_2$ at 150°C and 3000 psig**

The above calculations indicate that H$_2$ solubility in the liquid phase does not necessarily increase with adding CO$_2$ at a constant total pressure. In some cases, the addition of CO$_2$ can cause a decrease of H$_2$ solubility. Chouchi et al.$^{41}$ investigated the hydrogenation of $\alpha$-Pinene in the presence of scCO$_2$ at constant total pressure but various H$_2$ and CO$_2$ partial pressures. It was found that reaction rates were much faster under two fluid phase conditions than under one fluid phase conditions. This result was attributed to the higher concentration of $\alpha$-Pinene in the fluid surrounding catalyst under two fluid phase conditions.
However, the authors did not present the ternary phase diagram of H₂-CO₂-α-Pinene. If that ternary phase diagram exhibits the same behavior as the DHN system, the faster reaction rate can also be attributed to the higher H₂ concentration surrounding the catalyst under two fluid phase conditions. Hence, the calculation of a ternary phase diagram is necessary to investigate the hydrogenation in the presence of scCO₂. It should be noted that the addition of CO₂ in the system could cause a decrease of H₂ solubility at constant total pressure, which may reduce the overall hydrogenation rate.

Figure 5.12 Solubility of H₂ in the CO₂-swollen DHN at 150°C and 3000 psig
Figure 5.13a Ternary phase diagram of DHN-CO$_2$-H$_2$ at 150°C and 5000 psig

Figure 5.13b Ternary phase diagram of DHN-CO$_2$-H$_2$ at 150°C and 20000 psig
However, the above analysis is based on the assumption of constant total pressure. Table 5.7 shows the phase equilibria at typical hydrogenation conditions used in this work, which is at constant volume. The first two rows are the phase equilibria of H$_2$-DHN in the 50cc reactor at 750 psig and 3000 psig respectively. The solubility and mole fraction of H$_2$ in the liquid phase increase as H$_2$ pressure increases. However, the volume expansion of the liquid phase do not change significantly. The H$_2$ solubility in the liquid with 750 psig H$_2$ and 2250 psig CO$_2$ (3000 psig total pressure) is lower than that with 3000 psig H$_2$. However, the volume fraction of CO$_2$ plus H$_2$ is much higher than that with just 3000 psig H$_2$. Because the gas fraction in a swollen liquid could be one of the major reasons for the decrease in viscosity of a liquid, a significant decrease in viscosity of the CO$_2$-swollen liquid is expected. Moreover, the calculations also show that the solubility of H$_2$ in the CO$_2$-swollen liquid is about twice that in pure solvent, at a constant H$_2$ partial pressure of 750 psig. The first and third rows in Table 5.7 are the usual hydrogenation conditions in this work. Hence, the
possible decrease in viscosity and the increase of H₂ solubility should benefit the PS hydrogenation under the conditions used in this research.

Table 5.7 Simulation of the phase equilibrium under hydrogenation conditions at 150°C\(^\text{a}\)

<table>
<thead>
<tr>
<th>Pressure</th>
<th>H₂ solubility (mol/mL)</th>
<th>H₂ and CO₂ mol. frac.</th>
<th>H₂ and CO₂ vol. frac.</th>
<th>V.E.</th>
</tr>
</thead>
<tbody>
<tr>
<td>750 psig H₂</td>
<td>2.0×10⁻⁴</td>
<td>0.036</td>
<td>0.013</td>
<td>1.0</td>
</tr>
<tr>
<td>3000 psig H₂</td>
<td>7.3×10⁻⁴</td>
<td>0.12</td>
<td>0.048</td>
<td>1.1</td>
</tr>
<tr>
<td>3000 psig H₂ and CO₂(^b)</td>
<td>4.3×10⁻⁴</td>
<td>0.50</td>
<td>0.33</td>
<td>1.3</td>
</tr>
</tbody>
</table>

\(^{a}\) phase equilibrium of liquid phase for H₂-DHN and H₂-CO₂-DHN
\(^{b}\) pressurize the reactor with 750 psig H₂ then increase the total pressure to 3000 psig by adding CO₂

5.4.5 Effect of CO₂ on viscosity of PS solutions

It was found that high pressure CO₂ could reduce the viscosity of PS-DHN solutions significantly\(^6\). The effect of CO₂ on the viscosity of polymers has been studied in detail\(^4, 5, 42\). The change of polymer viscosity with CO₂ can be represented by free volume models based on Doolittle's equation\(^43\). However, the free volume model failed to represent the change of the viscosity of PS-DHN solution upon application of high pressure CO₂. Hence, Equation (5.8) is used to represent the effect of CO₂ on the viscosity of PS-DHN solutions.

As shown in Figure 5.14a and 5.14b, the viscosity of PS-DHN solutions with high pressure CO₂ could be represented by the following linear equation.

\[ \eta = A \cdot (\eta_{CO₂} \cdot X_{CO₂} + \eta_{PS−DHN} \cdot X_{PS−DHN}) \]  \hspace{1cm} (5.8)

Here, \( \eta \) is the viscosity of PS solution with CO₂ at a given temperature and pressure\(^6\), \( \eta_{CO₂} \) is the viscosity of CO₂ at the same temperature and pressure\(^44\) and \( \eta_{PS-DHN} \) is the
viscosity of PS-DHN solution at the same temperature and ambient pressure\(^6\). \(X_{\text{CO}_2}\) is the mole fraction of \(\text{CO}_2\) in the liquid phase and \(X_{\text{PS-DHN}}\) is the mole fraction of PS and DHN in the liquid phase, both of which are obtained from SL-EOS. \(A\) is a fitting parameter, which is obtained as 0.902 for 126,000 g/mol PS in DHN solutions and as 0.277 for 412,000 g/mol PS in DHN solutions. The viscosity deviation \(\Delta \eta\) that is defined by equation (5.9)\(^{45}\) represents the deviation of the system from an ideal mixture. It will be close to zero when the mixture contains similar components. Mixtures containing very different molecules will exhibit a large viscosity deviation. As shown in Figure 5.15, the viscosity deviation is greater for the high molecular weight PS solution, which can be explained by the greater difference between high molecular weight PS solution and \(\text{CO}_2\). The viscosity deviation becomes greater as the viscosity increases for both molecular weight PS solutions. The high viscosity occurs at low temperatures and high PS concentrations. The difference between PS-DHN solution and \(\text{CO}_2\) could be greater at these conditions, which leads to a larger viscosity deviation.

The swelling of PS solution by \(\text{CO}_2\) will cause a dilution of PS solution, which can reduce the viscosity of the solution. The 'dilution' effect of \(\text{CO}_2\) on the viscosity of PS solution can be represented by equation (5.10), which leads to a viscosity \(\eta_{\text{mix}}\). As shown in Figure 5.15, \(\eta_{\text{mix}}\) is always higher than the actual viscosity \(\eta\). Hence, the decrease of viscosity of PS solution not only depends on the dilution by \(\text{CO}_2\), but also depends on other factors, such as the conformation change of PS coils in the presence of \(\text{CO}_2\).

\[
\Delta \eta = \eta - (\eta_{\text{CO}_2} \cdot X_{\text{CO}_2} + \eta_{\text{PS-DHN}} \cdot X_{\text{PS-DHN}}) \quad \text{(5.9)}
\]

\[
\eta_{\text{mix}} = \eta_{\text{CO}_2} \cdot X_{\text{CO}_2} + \eta_{\text{PS-DHN}} \cdot X_{\text{PS-DHN}} \quad \text{(5.10)}
\]
Figure 5.14a. Viscosity correlation for PS (126,000 g/mol) in DHN solution
Concentration: 1.1wt%-10.0wt%, Temperature: 90 and 150°C, Pressure: 700-3000psi
Solid points are experimental data obtained from Whittier⁶

Figure 5.14b. Viscosity correlation for PS (412,000 g/mol) in DHN solution
Concentration: 1.12wt%-12.5wt%, Temperature: 90 and 150°C, Pressure: 700-3000psi
Solid points are experimental data obtained from Whittier⁶
Figure 5.15 Viscosity correlation for PS-DHN solution

- 412000 g/mol PS in DHN solution
- 126000 g/mol PS in DHN solution

5.5 Conclusions

The precipitation of PS in different organic solvents by high pressure CO$_2$ was investigated. DHN was chosen as the solvent for PS hydrogenation in the presence of high pressure CO$_2$. Volume expansions of PS-DHN solution were measured at different temperatures and CO$_2$ pressures. About 40% volume expansion can be obtained for 3wt% PS solutions at temperatures from 40 to 150°C. The effect of PS molecular weight on the volume expansion is insignificant for 3wt% PS solution at 150°C. It was found that the volume expansion of PS-DHN solutions at 150°C started to decrease with PS concentration.
when the PS concentration was above 9wt%. The volume expansions of PS solution calculated from SL-EOS were consistent with the experimental results.

Ternary phase diagrams for DHN-CO₂-H₂ at constant total pressure indicated that H₂ solubility in the liquid phase decreased with adding CO₂ into the system. Only at very high pressures, H₂ solubility in the liquid phase started to increase with adding CO₂ into the system. The same general trend can be obtained from the ternary phase diagrams of CYC-CO₂-H₂ and methanol-CO₂-H₂. However, at constant volume, the H₂ solubility in the liquid phase increases with increasing CO₂ partial pressure. The H₂ solubility with 750 psig H₂ and 2250 psig CO₂ can be twice as high as that with 750 psig H₂ only.

The viscosity of PS-DHN solution under high pressure CO₂ can be represented by a linear equation. The viscosity deviation from ideal liquid mixture increased with increasing PS molecular weight. And the highest deviation was found for the solution with highest viscosity. Besides the dilution effect caused by CO₂ swelling, the conformational change of PS coil in the presence of CO₂ could affect the viscosity of PS solutions.

References


(20) Dindar, C. High-Pressure Viscosity and Density of Polymer Solutions at the Critical Polymer Concentrction in Near-Critical and Supercritical Fluids. MS, Virginia Polytechnic Institute and State University, 2001.


Chapter 6

Hydrogenation of Polystyrene in the Presence of Supercritical CO₂

6.1 Introduction

The transport properties of supercritical fluids generally fall between those of the corresponding liquid and gas. Therefore liquid-phase processes that are limited by transport resistances become faster under supercritical conditions. Hence, supercritical fluids have been widely investigated for both fundamental interest and practical application. Among the commonly used supercritical fluids, supercritical carbon dioxide (scCO₂) has gained more attention because its supercritical state is easily accessible (Tₓ=31.1°C and Pₓ=1070 psi), and because CO₂ is non-toxic, nonflammable, recyclable and inexpensive. Hence, scCO₂ has been used in a wide range of applications, such as reaction, separation, processing, etc¹.

Heterogeneous catalytic hydrogenation in the liquid phase is of great importance in the chemical industry. Catalysts play an important role in heterogeneous hydrogenation. Catalyst can influence the reaction rate, selectivity and process cost. Reactants have to transfer to the surface of the catalyst prior to reaction, as described in Chapter Three. No matter how active the catalyst may be, it only affects the rate of the surface reaction. If one of the mass transport steps is the rate-limiting step, the overall hydrogenation rate will be controlled by the mass transfer rate. Therefore, heterogeneous catalytic hydrogenations conducted in scCO₂ have been investigated in order to achieve rapid mass and heat transfer during reaction.

The reverse water gas shift reaction (RWGSR) between H₂ and CO₂ can occur during hydrogenation in the presence of scCO₂. The carbon monoxide (CO) that is formed can
strongly absorb on the catalyst and cause it to deactivate. Deactivation of the catalyst can severely impact the viability of a hydrogenation process in the presence of supercritical CO₂. In this chapter the hydrogenation of polystyrene (PS) in the presence of scCO₂ is studied. The mechanism of catalyst poisoning by CO and solutions to the catalyst poisoning problem are investigated.

6.2 Background

6.2.1 Hydrogenation in CO₂-swollen liquids

Supercritical CO₂ (scCO₂) is recognized as an alternative hydrogenation medium. The good miscibility of H₂ with CO₂ enables this system to easily form a single phase. Elimination of the gas-liquid interface in a single-phase system avoids the gas-liquid mass transfer limitation. Hence, many hydrogenation reactions have been investigated under single-phase conditions created by the presence of supercritical CO₂. Successful results from these researches have been reported as described in Chapter Two.

The conditions required to form a single phase may not be suitable for some hydrogenation processes. For example, the reactant or product might precipitate from the solution as the pressure is increased to form a single phase; or the pressure required for a single phase may be too high to be acceptable at a certain temperature and H₂ fraction. Hence, a two-phase system, a so-called 'CO₂-swollen' or 'CO₂-expanded' liquid, becomes an alternative to the single-phase hydrogenation medium. The CO₂-swollen liquid exhibits lower viscosity and higher diffusion coefficient than the unswollen liquid, which can benefit mass transfer during hydrogenation. Furthermore, enhanced H₂ solubility in a CO₂-swollen liquid has been reported at certain conditions. Therefore, a hydrogenation reaction that is limited by a low mass transfer rate or low H₂ solubility should exhibit a higher rate in
a CO₂-swollen liquid. Devetta et al.⁹ studied the selective hydrogenation of an unsaturated ketone under two-phase conditions. It was found that hydrogenation of the CO₂-swollen ketone was faster than hydrogenation of the unswollen ketone. Phiong et al.¹⁰ also showed an increased rate of α-methylstyrene hydrogenation when using scCO₂ to swell α-methylstyrene. Furthermore, Chouchi et al.¹¹ studied the hydrogenation of α-pinene at single-phase and two-phase conditions and found that the hydrogenation rate was higher in CO₂-swollen α-pinene.

All these researches indicate that a single-phase condition is not necessary to take advantage of scCO₂ in a hydrogenation reaction. The enhanced H₂ solubility, improved diffusivity and reduced viscosity in a CO₂-swollen solvent can also benefit the hydrogenation reaction and improve the mass transport.

6.2.2 Catalyst poisoning

Catalyst deactivation is a major concern for any hydrogenation process. Besides the traditional deactivation pathways, such as poisoning by impurities in the reactant or solvent, the loss of metal surface due to fouling or sintering, etc.¹², catalyst poisoning in scCO₂ by CO formed via the RWGS (6.1) has also received increased attention.

\[ \text{CO} + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O} \]  

Minder et al.¹³, ¹⁴ reported complete catalyst deactivation by CO during the hydrogenation of ethyl pyruvate catalyzed by 5%Pt/alumina in scCO₂. Hydrogen consumption was terminated immediately when CO₂ was added into the system as shown by Figure 6.1. FTIR measurement showed that bridge-bonded CO covered the Pt on the used catalyst as shown by Figure 6.2, which verified that catalyst poisoning by CO occurred...
during hydrogenation. Later, Hutchenson et al.\textsuperscript{15} confirmed the formation of CO under hydrogenation conditions in the presence of CO\textsubscript{2}. In further investigations, they claimed that CO poisoning was not significant under flow conditions with a residence time shorter than 20 minutes\textsuperscript{16}. To date, catalyst deactivation by CO has not been reported for continuous hydrogenation reactions in the presence of CO\textsubscript{2}. However, the results from batch hydrogenations are conflicting. Some researchers did not report catalyst poisoning by CO\textsuperscript{10, 11, 17} while others reported significant catalyst poisoning by CO\textsuperscript{13, 14}. Besides Minder and Hutchenson, Pillai et al.\textsuperscript{18} also studied catalyst deactivation during hydrogenation in the presence of CO\textsubscript{2} at batch conditions. They showed a loss of metal dispersion in successive hydrogenation runs but did not clearly attribute this to CO poisoning. In another paper, Pillai et al.\textsuperscript{19} studied the hydrogenation of 4-oxoisophorone in scCO\textsubscript{2} and organic solvents. A lower extent of deactivation was observed in scCO\textsubscript{2}, which should exclude the possibility of catalyst poisoning by CO.

Figure 6.1 The influence of CO\textsubscript{2} addition on H\textsubscript{2} consumption during reduction of ethyl pyruvate in ethanol\textsuperscript{13}.  

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6.2.3 Hydrogenation of carbon oxides

The RWGSR (6.1) is a reversible and endothermic chemical reaction. Higher temperatures favor the formation of CO. The CO can poison the catalyst and severely impact the economic viability of hydrogenations in the presence of CO₂. In addition to the RWGSR, methanation reactions (6.2) and (6.3) between hydrogen and carbon oxides may also occur during hydrogenations in scCO₂.

\[
\begin{align*}
3\text{H}_2 + \text{CO} & \rightleftharpoons \text{CH}_4 + \text{H}_2\text{O} \quad (6.2) \\
4\text{H}_2 + \text{CO}_2 & \rightleftharpoons \text{CH}_4 + 2\text{H}_2\text{O} \quad (6.3)
\end{align*}
\]

The mechanism, kinetics and equilibrium of the RWGSR have been studied in detail\textsuperscript{20-26}. Several empirical equations have been reported for calculating the equilibrium constant of the RWGSR at various temperatures\textsuperscript{24-26}. Mills and Steffgen showed that the enthalpy of the RWGSR is not greatly influenced by temperature. Thus the equilibrium constant at different temperatures can be calculated using the van't Hoff relationship (6.4).
Here, K is equilibrium constant at any temperature, T is the temperature (in Kelvin). R is the gas constant (8.314 mol·K/J), ΔrH° is the enthalpy of formation at 298.15 K, which is 41.2kJ/mol for the RWGSR, K° is the equilibrium constant at 298.15 K (9.75×10⁻⁶ for the RWGSR), and T° is 298.15 K. Figure 6.3 shows the calculated CO mole fraction at equilibrium conditions with an initial mole ratio of CO₂/H₂=5, which is similar to the ratio of CO₂ to H₂ during the present PS hydrogenation experiments. Figure 6.3 shows that the CO concentrations at equilibrium, as calculated from various empirical and theoretical equations are consistent. Figure 6.3 also shows that the equilibrium CO concentrations are very substantial.

![Graph showing CO mole fraction at equilibrium conditions with a CO₂/H₂ ratio of 5.](image)

Figure 6.3 CO mole fraction at equilibrium conditions with a CO₂/H₂ ratio of 5

The equilibrium constant was obtained from publications of Bissett²⁵, Newsome²⁴ and Mills²⁶, and van't Hoff relationship (6.4).
6.3 Materials and procedures

6.3.1 Materials

The 5%Pd/BaSO₄ catalyst was obtained from Aldrich and was used as received. The 65%Ni/Al₂O₃/SiO₂ catalyst was obtained from Aldrich and was reduced at 177°C for 4 hours before use. The catalysts were characterized by scanning electron microscopy (SEM) as shown in Figures 3.2 and 6.4. The particles have an irregular shape, with an average equivalent spherical diameter of approximately 20 µm for 5%Pd/BaSO₄ and 10 µm for 65%Ni/Al₂O₃/SiO₂. 5%Pd/BaSO₄ has a true density of 4.42 g/cm³, a BET surface area of 4.6 m²/g, an average pore diameter of 1.3 µm and a porosity of 71.7%. CO chemisorption showed a metal dispersion of 0.29% assuming a Pd/CO ratio of 2.0. The 65%Ni/Al₂O₃/SiO₂ catalyst has a BET surface area of 142 m²/g, an average pore diameter of 0.033 µm and a pore volume of 1.088 cm³/g. The metal dispersion is 7.7% by CO chemisorption measurement assuming a Ni/CO ratio of 1.0. 10%Pd/activated carbon, 10%Pd/alumina, 5%Pt/alumina, and 10%Pt/activated carbon were obtained from Aldrich and used as received. 5%Rh/alumina was obtained from Alfa Aesar and used as received.

Commercial polystyrene (Nova 172) with a weight average molecular weight of approximately 290,000 g/mol was used as received. Decahydronaphthalene (76% trans-DHN and 24% cis-DHN) was obtained from Aldrich and used as received. Hydrogen (>99.999%) and carbon dioxide (>99.998%) were supplied by National Welders and used as received.
6.3.2 Procedures and analysis

A. Hydrogenation of PS

Hydrogenation reactions were carried out in a 50 mL batch reactor at various temperatures (90 - 180°C) and with H₂ and CO₂ partial pressures of 250 - 1000 psig and 250 - 2250 psig respectively. H₂ and CO₂ were added into the reactor through a dip tube located beneath the liquid surface, below the lowest impeller. The pressure was controlled by pressurizing with H₂ first and then adjusting the total pressure to the desired pressure by adding CO₂. Hydrogen was fed periodically during each experiment to maintain the desired total pressure. The agitation rate was 2500 rpm for all the experiments to assure the minimal influence of gas-liquid mass transfer as shown in Chapter Four. Details on the hydrogenation process are described in Chapter Three.
After the reactor was cooled down to room temperature, the pressure was released slowly. The hydrogenated PS solution then was filtered to remove the catalyst and was diluted with DHN. The absorption of the diluted sample was measured at 261.5 nm with a UV-VIS spectrophotometer (Jasco V-550) to determine the concentration of aromatic rings. The degree of hydrogenation (HD), which is equivalent to the conversion of aromatic rings $X$, was calculated using $HD = X = 1 - \frac{C_A}{C_{Ao}}$, where the $C_A$ is the concentration of aromatic rings after hydrogenation and $C_{Ao}$ is the initial concentration of aromatic rings.

B. Hydrogenation of carbon oxides

To investigate the hydrogenation of carbon oxides during PS hydrogenation, some reactions were performed in order to measure the CO and CH$_4$ concentration in the gas phase. The experiments are similar to the PS hydrogenation experiments but no polymer was present in the reactor. The catalyst concentration, reaction temperature and time, H$_2$ and CO$_2$ partial pressures and agitation rate were kept same as the corresponding PS hydrogenation.

After the reactor was cooled down to room temperature, the pressure was released slowly and the gas was passed through a ten port valve that sent a 1 mL gas sample to a gas chromatograph (GC). The GC had a 30-foot column packed with Hayesep DB 100/120 (Alltech) and was operated at 100°C with helium as the carrier gas. Quantitative results were obtained for CH$_4$. Due to the low concentration of CO in the gas, only qualitative results were obtained for CO. The rest of the gas was collected in a gas bag. A pump was used to draw a known volume of gas from the bag through a CO detection tube (Dräger Tube, CO 10/b or 2/a). The CO concentrations were obtained by measuring the length of the tube that was discolored.
6.4 Results and discussion

6.4.1. Effect of CO₂ partial pressure and temperature

Figure 6.5 shows a set of experiments with a constant H₂ partial pressure and varying CO₂ partial pressures. Apparently, the presence of CO₂ has a negative impact on the hydrogenation of PS. The degree of hydrogenation in 10 hours decreases with CO₂ pressure until it becomes independent of CO₂ partial pressure above about 1200 psig.

![Figure 6.5 Effect of CO₂ pressure on the hydrogenation of PS](image)

3wt% PS in DHN, 150°C, 750psig H₂, 1g 5%Pd/BaSO₄/g PS, 2500 rpm, 10hrs

The effect of CO₂ varies with reaction temperature. Figure 6.6 shows that the negative effect of CO₂ on PS hydrogenation is negligible below about 120°C, but becomes significant at higher temperatures. It is clear that CO₂ inhibits catalyst activity during PS hydrogenation at high CO₂ partial pressures and high reaction temperatures.
CO₂ is an antisolvent for PS. As the fraction of CO₂ in DHN increases with increasing CO₂ pressure, the solvent strength of CO₂-swellen DHN decreases and eventually PS precipitates from DHN at a certain CO₂ pressure. For example, PS will precipitate from DHN at 150°C when CO₂ pressure is greater than about 3000 psig. The PS precipitate may block the surface of catalyst and cause deactivation. However by controlling the CO₂ partial pressure, the precipitation of PS can be avoided. Based on previous studies on the precipitation of PS in DHN at various conditions (as shown in Chapter Five), the precipitation of PS will not occur at the hydrogenation conditions used in this work. Thus the possibility of a PS precipitate blocking the catalyst surface can be excluded and catalyst deactivation during hydrogenation was caused by other factors, most likely by CO poisoning.

![Figure 6.6. Effect of temperature on the hydrogenation of PS](image)

3wt% PS in DHN, 1g 5%Pd/BaSO₄/g PS, 2500rpm, 10hrs
× 750 psig H₂, ◊ 750 psig H₂ and 2250 psig CO₂

6.4.2 Effect of H₂ partial pressure
Figure 6.7 shows the effect of H₂ partial pressure on PS hydrogenation. As H₂ partial pressure increases, the degree of hydrogenation in DHN increases at low H₂ pressures but approaches a constant value above 500 psig. This behavior implies that the active sites are saturated by H₂ and therefore a further increase in H₂ pressure does not increase the hydrogenation rate. Hydrogenation in CO₂-swollen DHN shows catalyst deactivation at higher H₂ partial pressures, as shown in Figure 6.7. However, no catalyst deactivation is apparent at 250 psig of H₂ partial pressure. This might be because PS hydrogenation dominates the consumption of H₂ at low H₂ partial pressures. As the H₂ partial pressure increases, the concentration of H₂ in the liquid phase increases, which increases the likelihood of the RWGSR. This is particularly true when all the active sites are saturated by H₂, including the active sites in the small pores that PS cannot access; the RWGSR may occur at those sites.

Figure 6.7 Effect of H₂ partial pressure on the hydrogenation of PS
3wt% PS in DHN, 1g 5%Pd/BaSO₄/g PS, 150°C, 2500rpm, 10hr
(Reactions in H₂ and CO₂ were controlled at a total pressure of 3000 psig)
6.4.3 Carbon monoxide concentration

Table 6.1 shows measured CO concentrations in the gas phase at different temperatures and times. The reactions catalyzed by 5%Pd/BaSO₄ produce significant amounts of CO at higher temperatures, but less than 10 ppm CO is produced in 10 hours below 120°C. The CO concentrations produced in all these reactions are much lower than the equilibrium concentration as shown in Table 6.1, which indicates the RWGSR is far from equilibrium at the experimental conditions.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>T (°C)</th>
<th>t (hr)</th>
<th>CO (ppm)</th>
<th>CO* (ppm)</th>
<th>CH₄ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5%Pd/BaSO₄</td>
<td>90</td>
<td>10</td>
<td>2</td>
<td>5057</td>
<td>0</td>
</tr>
<tr>
<td>5%Pd/BaSO₄</td>
<td>120</td>
<td>10</td>
<td>10</td>
<td>8406</td>
<td>0</td>
</tr>
<tr>
<td>5%Pd/BaSO₄</td>
<td>150</td>
<td>10</td>
<td>50</td>
<td>12918</td>
<td>0</td>
</tr>
<tr>
<td>5%Pd/BaSO₄</td>
<td>180</td>
<td>10</td>
<td>150</td>
<td>18614</td>
<td>0</td>
</tr>
<tr>
<td>5%Pd/BaSO₄</td>
<td>150</td>
<td>5</td>
<td>48</td>
<td>12918</td>
<td>0</td>
</tr>
<tr>
<td>5%Pd/BaSO₄</td>
<td>150</td>
<td>15</td>
<td>58</td>
<td>12918</td>
<td>0</td>
</tr>
</tbody>
</table>

a. the reactions were carried out with 3wt% 5%Pd/BaSO₄, 750 psig H₂ and 2250 psig CO₂, and 2500 rpm.

b. 0 denotes that no CH₄ is detected by GC

CO* - the calculated equilibrium concentration according to Equation (6.4)

CO can strongly absorb on the metal surface and occupy the active sites needed for PS hydrogenation, leading to a decrease in PS hydrogenation rates. For example, a hydrogenation of PS at 150°C and 750 psig H₂ showed a 83% conversion in 10 hours, while the hydrogenation at the same conditions but with 15 psig CO only showed a 2% conversion in 10 hours. Figures 6.5 and 6.6 showed the effect of CO₂ partial pressure and temperature on
PS hydrogenation. At high temperature and high CO₂ pressure, the rate of PS hydrogenation in CO₂-swollen DHN was lower than in DHN. In a parallel manner, the rate of the RWGS reaction will be high at high temperature and CO₂ pressure, producing higher concentrations of CO, as shown in Table 6.1. The rate of PS hydrogenation in CO₂-swollen DHN was much lower than the rate in pure DHN under conditions that favor CO formation. Therefore, it is very likely that CO poisoning is responsible for the lower rates of PS hydrogenation in CO₂-swollen DHN.

Methane can also be formed by the hydrogenation of CO or CO₂ as shown by equations (6.2) and (6.3). CO₂ methanation may occur via the intermediate formation of CO or via the formation of a complex on the catalyst surface²⁶. However, it has been reported that direct methanation of CO₂ does not occur in the presence of a significant amount of CO²⁶. Table 6.2 shows that the equilibrium constants for the methanation of carbon oxides are much larger than those for the RWGS reaction indicating that the methanation of carbon oxides is much more favorable thermodynamically than the RWGS reaction at these conditions. The occurrence of methanation during hydrogenation can significantly alter the gas composition, which will influence PS hydrogenation.

### Table 6.2 Equilibrium constants for methanations and RWGS reaction²⁶

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>K₁</th>
<th>K₂</th>
<th>K₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>90</td>
<td>1.68×10⁻⁴</td>
<td>5.20×10¹⁸</td>
<td>9.05×10¹⁴</td>
</tr>
<tr>
<td>120</td>
<td>4.54×10⁻⁴</td>
<td>1.67×10¹⁶</td>
<td>7.58×10¹²</td>
</tr>
<tr>
<td>150</td>
<td>1.09×10⁻³</td>
<td>1.15×10¹⁴</td>
<td>1.23×10¹¹</td>
</tr>
<tr>
<td>180</td>
<td>2.38×10⁻³</td>
<td>1.55×10¹²</td>
<td>3.55×10⁹</td>
</tr>
</tbody>
</table>

K₁, K₂ and K₃ are equilibrium constants for reaction (1), (2) and (3) respectively.
Finally it should be noted that the choice of catalyst is a key factor for the hydrogenation of carbon oxides. The catalyst can influence the rate of the RWGSR or methanation significantly.

6.4.4 Presumed mechanism of catalyst deactivation

In Chapter Three, we studied the kinetics of PS hydrogenation catalyzed by 5%Pd/BaSO₄ and obtained a first order kinetic equation with respect to the concentration of aromatic rings, as shown in (6.5).

\[-\frac{dC_A}{dt} = k' C_{\text{cat}} C_A\]  \hspace{1cm} (6.5)

In this chapter, the following kinetic scheme for the RWGSR is proposed in order to explain catalyst deactivation during PS hydrogenation. Assuming that the rate of the RWGSR can be expressed by a power-low rate equation, then

\[\frac{dC_{\text{CO}}}{dt} = k_i C_{\text{cal}} \frac{C_{\text{CO}_2} C_{\text{H}_2}^b}{C_{\text{CO}_2} C_{\text{H}_2}^b} \]  \hspace{1cm} (6.6)

It is assumed that the second term is negligible because the RWGSR is so far from equilibrium, and \(k_i = k_i \frac{C_{\text{CO}_2} C_{\text{H}_2}^b}{C_{\text{CO}_2} C_{\text{H}_2}^b}\) because CO₂ and H₂ are in excess, and are constant, during the reaction. Then, (6.6) can be simplified to

\[\frac{dC_{\text{CO}}}{dt} = k_i' C_{\text{cat}}\]  \hspace{1cm} (6.7)

The concentration of active catalyst is assumed to be \(C_{\text{cat}} = C_{\text{cat}}^\alpha (1 - \alpha C_{\text{CO}})\), i.e., the concentration of poisoned catalyst is proportional to the CO concentration. Here \(C_{\text{cat}}^\alpha\) is the initial catalyst concentration and \(\alpha\) is a constant. Thus
\[
\frac{dC_{CO}}{dt} = k'_i C_{cat} = k'_i C_{cat}^\circ (1 - \alpha C_{CO}) \tag{6.8}
\]

Integrating equation (6.8) from \(C_{CO}=0\) at \(t=0\) to \(C_{CO}\) at \(t\), the result is

\[
C_{CO} = \frac{1}{\alpha} (1 - e^{-\alpha k'_i C_{cat}^\circ t}) \tag{6.9}
\]

and

\[
C_{cat} = C_{cat}^\circ (1 - \alpha C_{CO}) = C_{cat}^\circ e^{-\alpha k'_i C_{cat}^\circ t} \tag{6.10}
\]

These results show an exponential decay of the concentration of active catalyst.

Substituting \(C_{cat}\) into equation (6.5) and integrating from \(t=0\) to \(t\), then

\[
\ln(1 - X) = \frac{k'}{\alpha k'_i} (e^{-\alpha k'_i C_{cat}^\circ t} - 1) \tag{6.11}
\]

In equation (6.11), if \(t\), the reaction time, is long enough, the exponential term will be significantly smaller than one and can be neglected. Hence, a long-time asymptote of the degree of hydrogenation exists:

\[
X = 1 - \exp\left(-\frac{k'}{\alpha k'_i}\right) \quad \text{as} \quad t \to \infty \tag{6.12}
\]

Figure 6.8 shows that this proposed mechanism is consistent with experimental results, noting that the degree of hydrogenation of PS in the presence of \(CO_2\) does approach a long-time asymptote.
According to the above analysis, three major factors will influence the extent of CO poisoning on a catalyst: $k'$, $\alpha$ and $k_1'$. $k_1'$ is the apparent rate constant for the RWGSR. It is influenced by the activity of the catalyst for the RWGSR, along with the CO$_2$ and H$_2$ partial pressures. $\alpha$ is a constant describing the adsorption of CO on the metal surface of the catalyst. If either $\alpha$ or $k_1'$, or both, are small, i.e., the formation rate of CO or the adsorption of CO on the catalyst is low, CO poisoning should be negligible. This conclusion can be demonstrated as follows:

$$e^{-\alpha k_1'C_{cat}^o t}$$

can be expressed as

$$e^{-\alpha k_1'C_{cat}^o t} = 1 + (-\alpha k_1'C_{cat}^o t) + \frac{1}{2}(-\alpha k_1'C_{cat}^o t)^2 + \frac{1}{3!}(-\alpha k_1'C_{cat}^o t)^3 + \cdots$$
As $\alpha k'_1$ approaches zero, the third and following terms can be ignored. Thus

$$
e^{-\alpha k'_1 C_{cat}^0 t} \approx 1 + (-\alpha k'_1 C_{cat}^0 t)$$

(6.13)

Inserting (6.13) into equation (6.11), gives

$$\ln(1 - X) = -k'C_{cat}^0 t$$

(6.14)

This is the integrated form of the first order rate equation (6.5) for PS hydrogenation without CO poisoning as shown in Chapter Three.

If $k'$ is large, i.e., the catalyst is very active for the PS hydrogenation, the degree of hydrogenation of PS can be close to 100% at long times according to (6.12). However catalyst deactivation by CO still can exist as shown in Figure 6.9. Due to the fast rate of PS hydrogenation, it may be difficult to notice the deactivation of catalyst during hydrogenation. Moreover, the possible increase in the hydrogenation rate due to the presence of scCO$_2$ may compensate for catalyst deactivation such that a comparison of hydrogenation in scCO$_2$ and organic solvents does not shed light on whether or not there is CO poisoning. Therefore detecting CO in the reaction system is critical to determining whether catalyst poisoning by CO might be important.
Figure 6.9 Catalyst deactivation behavior with $k'/k_1'=\alpha=3$

The results were obtained from Equation (6.11) and (6.14).

Figure 6.10 shows several possible types of catalyst behavior, as calculated from equation (6.11). In all cases, the long-time asymptote is given by $(k'/\alpha k_1')$. However, the rate at which the asymptote is approached depends on $k'$. The black line shows a hydrogenation in pure DHN, with no CO poisoning $(\alpha k_1')$. The value of $k'$ ($1.61 \times 10^{-6}$ L/g/s) was obtained from experiments in pure DHN at 150°C as shown in Chapter Three. The value of $C_{cat}^0$ (28 g/L) is typical of those experiments.

The three colored lines in Figure 6.10 all have a value of $k'/\alpha k_1'=0.58$, which gives an asymptotic hydrogenation degree of 44%, consistent with Figure 6.8. However, these three lines have values of $\alpha k_1'$ that differ by two orders of magnitude, as do the corresponding values of $k'$. The lower the value of $\alpha k_1'$, the lower the value of $k'$. 

Figure 6.10 Catalyst deactivation behavior with $k'/k_1'=\alpha=3$

The results were obtained from Equation (6.11) and (6.14)
The data for the experiment with H$_2$ and CO$_2$ are replotted as points in Figure 6.10. The data correspond quite well with the curve for $\alpha k_1' = 2.76 \times 10^{-6}$. This curve was calculated using $k'/\alpha k_1' = 0.58$ and $k' = 1.61 \times 10^{-6}$ L/g/s, which was obtained from the experiments.

As expected, Figure 6.10 shows that the rate of approach to the asymptote increases as the value of $k'$ increases. Behavior such as that shown by the curve for $\alpha k_1' = 2.78 \times 10^{-7}$ could be mistaken for very low catalyst activity, rather than for poisoning by CO. Once again, this emphasizes the need to measure the CO formed during the reaction.

![Simulation of catalyst poisoning by CO](image)

Figure 6.10 Simulation of catalyst poisoning by CO

- $a - \alpha k_1' = 2.76 \times 10^{-6}$
- $b - \alpha k_1' = 2.76 \times 10^{-5}$
- $c - \alpha k_1' = 2.76 \times 10^{-7}$
- $d$ - No poisoning,
- $e$ - experimental data

6.4.5 Solutions to catalyst deactivation by CO poisoning
CO poisoning during hydrogenation can be avoided or maintained at a negligible level. As shown above, reducing $k_1'$ is one approach. $k_1'$ can be decreased by changing catalyst, by lowering the temperature or by lowering CO$_2$ or H$_2$ partial pressures. Figures 6.6 and 6.7 show that CO poisoning is negligible at lower temperatures and H$_2$ partial pressures. However, both lower temperature and lower H$_2$ partial pressure lead to a decrease in the PS hydrogenation rate. The catalyst not only can influence $k_1'$, but can also influence $k'$ and $\alpha$, which will affect the overall catalyst activity as shown above. Hence, the activity of different catalysts for the PS hydrogenation, with and without the presence of scCO$_2$, was investigated, as shown in Table 6.3. These catalysts exhibited different activity for PS hydrogenation. Pd and Ni catalysts showed higher activity and Pt and Rh catalysts showed lower activity for PS hydrogenation. The extent of catalyst deactivation was different for different catalysts. 65%Ni/Al$_2$O$_3$/SiO$_2$ showed negligible deactivation which indicated that this catalyst could be used for the PS hydrogenation in the presence of scCO$_2$.

Table 6.3 Catalyst screening

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>T (°C)</th>
<th>t (hr)</th>
<th>HD (%)</th>
<th>DHN</th>
<th>CO$_2$-swollen DHN</th>
</tr>
</thead>
<tbody>
<tr>
<td>65%Ni/Al$_2$O$_3$/SiO$_2$</td>
<td>150</td>
<td>3</td>
<td>98%</td>
<td>100%</td>
<td></td>
</tr>
<tr>
<td>10%Pd/activated carbon</td>
<td>150</td>
<td>7</td>
<td>99%</td>
<td>92%</td>
<td></td>
</tr>
<tr>
<td>10%Pd/alumina</td>
<td>150</td>
<td>10</td>
<td>96%</td>
<td>78%</td>
<td></td>
</tr>
<tr>
<td>5%Pt/alumina</td>
<td>150</td>
<td>10</td>
<td>18%</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>10%Pt/activated carbon</td>
<td>150</td>
<td>10</td>
<td>22%</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>5%Rh/alumina</td>
<td>150</td>
<td>10</td>
<td>27%</td>
<td>---</td>
<td></td>
</tr>
</tbody>
</table>

3wt%PS-DHN, 1 g catalyst/g PS, 2500rpm, 750 psig H$_2$ or 750psig H$_2$ and 2250psig CO$_2$. 

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A continuous hydrogenation process could minimize the influence of CO poisoning on the hydrogenation rate. Arunajatesan et al.\textsuperscript{16} reported that a short residence time might minimize CO poisoning because the continuous gas flow swept CO out of reactor, such that the CO concentration was maintained at very low level. Consequently a low CO concentration led to low adsorption of CO on the catalyst and therefore a negligible loss of catalyst activity.

The removal of CO from the CO\textsubscript{2} and H\textsubscript{2} mixture can also be achieved by catalytic reactions, such as selective oxidation, water gas shift reaction and methanation\textsuperscript{29}. Selective oxidation and water gas shift reaction require the addition of O\textsubscript{2} or H\textsubscript{2}O into the system, which makes the polymer hydrogenation even more complex. In addition, H\textsubscript{2}O can also adsorb on the catalyst and cause a decrease of the active sites available for hydrogenation. As shown in Figure 6.11, the addition of H\textsubscript{2}O into the reaction did not improve the activity of 5\% Pd/BaSO\textsubscript{4} in the presence of CO\textsubscript{2}. Therefore, the selective oxidation and water gas shift reaction may not be viable for removing CO during PS hydrogenation in this work. Hence methanation becomes a more promising alternative.
6.4.6 65%Ni/Al₂O₃/SiO₂

Table 6.4 shows that 65%Ni/Al₂O₃/SiO₂ produced much less CO during a reaction compared to 5%Pd/BaSO₄. The concentration of CO is less than 5 ppm at all temperatures. Moreover, a significant amount of CH₄ was formed when using 65%Ni/Al₂O₃/SiO₂ as the catalyst. Fischer et al. 30 compared methanations catalyzed by various metals and found the following decreasing order of methanation activity: Ru, Ir, Rh, Ni, Co, Os, Pt, Fe, Mo, Pd, Ag. Hence, it is reasonable that 65%Ni/Al₂O₃/SiO₂ can produce significant CH₄ while 5%Pd/BaSO₄ does not catalyze the methanation to any significant extent, as shown in Table 6.1. Table 6.2 demonstrates that methanation has large reaction equilibrium constants, indicating that it is very favorable for the conditions described herein. Thus, even if the
methanation of CO\textsubscript{2} occurs via the intermediate formation of CO, most of the CO will be converted to CH\textsubscript{4} with a good methanation catalyst such as Ni.

### Table 6.4 CO and CH\textsubscript{4} concentration

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>T °C</th>
<th>t hr</th>
<th>CO ppm</th>
<th>CH\textsubscript{4} %</th>
</tr>
</thead>
<tbody>
<tr>
<td>65%Ni/Al\textsubscript{2}O\textsubscript{3}/SiO\textsubscript{2}</td>
<td>120</td>
<td>4</td>
<td>2</td>
<td>0.04</td>
</tr>
<tr>
<td>65%Ni/Al\textsubscript{2}O\textsubscript{3}/SiO\textsubscript{2}</td>
<td>150</td>
<td>3</td>
<td>2</td>
<td>0.23</td>
</tr>
<tr>
<td>65%Ni/Al\textsubscript{2}O\textsubscript{3}/SiO\textsubscript{2}</td>
<td>180</td>
<td>2</td>
<td>3</td>
<td>0.98</td>
</tr>
<tr>
<td>65%Ni/Al\textsubscript{2}O\textsubscript{3}/SiO\textsubscript{2}</td>
<td>150</td>
<td>5</td>
<td>4</td>
<td>0.37</td>
</tr>
</tbody>
</table>

All the reactions were carried out with 0.9% 65% Ni/Al\textsubscript{2}O\textsubscript{3}/SiO\textsubscript{2}, 750 psig H\textsubscript{2} and 2250 psig CO\textsubscript{2}, and 2500 rpm.

Figure 6.12 shows the results of PS hydrogenation using 65%Ni/Al\textsubscript{2}O\textsubscript{3}/SiO\textsubscript{2} as the catalyst. Below 150°C, there is no apparent difference between the hydrogenation in DHN and in CO\textsubscript{2}-swollen DHN. The different results for 5%Pd/BaSO\textsubscript{4} (Figure 6.6) vs. 65%Ni/Al\textsubscript{2}O\textsubscript{3}/SiO\textsubscript{2} (Figure 6.12) at 150°C are attributable to the different CO concentrations during hydrogenation, i.e., 5%Pd/BaSO\textsubscript{4} was poisoned by the presence of about 50 ppm CO. However, a significant decrease in the PS hydrogenation rate was observed at 180°C using 65%Ni/Al\textsubscript{2}O\textsubscript{3}/SiO\textsubscript{2}. The deactivation of 65%Ni/Al\textsubscript{2}O\textsubscript{3}/SiO\textsubscript{2} at 180°C is attributed to the formation of H\textsubscript{2}O. It is known that H\textsubscript{2}O can also adsorb on the active sites of a catalyst and cause a decrease in activity\textsuperscript{31}. According to equation (6.3), two moles of H\textsubscript{2}O will be formed when one mole of CH\textsubscript{4} is formed. Thus about 2% H\textsubscript{2}O, based on the measured concentration of CH\textsubscript{4}, is present when using 65%Ni/Al\textsubscript{2}O\textsubscript{3}/SiO\textsubscript{2} at 180°C. This may explain the decrease in the PS hydrogenation rate.
6.4.7 Bimetallic catalyst system

During the hydrogenation of benzoic acid, Zhang et al.\textsuperscript{32, 33} found that addition of Ni catalyst into the reaction can stabilize the activity of a noble metal catalyst and improve its anti-poisoning ability against CO formed from hydrocracking. Hence, a bimetallic catalyst mixture composed of 5%Pd/BaSO\textsubscript{4} plus 3wt% 65%Ni/Al\textsubscript{2}O\textsubscript{3}/SiO\textsubscript{2} was investigated for PS hydrogenation in the presence of CO\textsubscript{2}. Figure 6.13 shows that the mixture of 5%Pd/BaSO\textsubscript{4} and 65%Ni/Al\textsubscript{2}O\textsubscript{3}/SiO\textsubscript{2} exhibited negligible catalyst deactivation between 120 and 180°C.
The conversion of CO to CH₄, catalyzed by Ni, is one possible explanation for the improved catalyst performance. As shown in Table 6.5, the CO concentrations produced by the mixture of Pd and Ni catalyst are much lower than those from the reaction catalyzed by 5%Pd/BaSO₄ only. The CH₄ concentrations are higher than with 5%Pd/BaSO₄. This suggests that some of the CO produced by the 5%Pd/BaSO₄ is converted to CH₄ by 65%Ni/Al₂O₃/SiO₂. Therefore, the bimetallic catalyst system shows improved anti-poisoning
ability in the presence of CO$_2$. Furthermore, the addition of other well known methanation catalysts, such as Ru, Co, Fe and Mo$^{26}$, may also improve the performance of hydrogenation catalysts in the presence of scCO$_2$. Also, a bimetallic catalyst with a precious metal for hydrogenation and a methanation metal on the same support may show better stability and resistance to CO during hydrogenation in the presence of CO$_2$.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>T (°C)</th>
<th>t (hr)</th>
<th>CO (ppm)</th>
<th>CH$_4$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd &amp; Ni</td>
<td>120</td>
<td>5</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>Pd &amp; Ni</td>
<td>150</td>
<td>5</td>
<td>14</td>
<td>0.018</td>
</tr>
<tr>
<td>Pd &amp; Ni</td>
<td>180</td>
<td>5</td>
<td>22</td>
<td>0.14</td>
</tr>
</tbody>
</table>

3wt% 5%Pd/BaSO$_4$ and 0.09wt% 65%Ni/Al$_2$O$_3$/SiO$_2$, 2500rpm, 750 psig H$_2$ and 2250 psig CO$_2$

6.4.8 Kinetics of PS hydrogenation in the presence of scCO$_2$

It has been shown that the hydrogenation of PS is first order with respect to aromatic ring concentration and essentially zero-order in H$_2$ under high H$_2$ pressure. Therefore, the rate equation, $-\frac{dC_A}{dt} = k'C_{cat}C_A$ and its integrated form $-\ln(1-X) = k'C_{cat}t$, was used here to represent the kinetics of PS hydrogenation in the presence of CO$_2$. In these equations, k' is the reaction rate constant, t is the reaction time, $C_{cat}$ is the catalyst concentration, and X is the conversion of the aromatic rings. Figure 6.14 shows a plot of $-\ln(1-X)$ vs. $C_{cat}$. The slope of the lines is the reaction rate constant. The values of $C_{cat}$ in Figure 6.14 for the CO$_2$-swollen
liquids were calculated taking the estimated volume expansion into account, as described in Chapter Five. Figure 6.14 shows that the reaction rate constants are higher in CO₂-swollen DHN than in pure DHN. The calculated reaction rate constants at each temperature are given in Table 6.6.

Figure 6.14. Hydrogenation of 3wt% PS-DHN
750 psig H₂, or 750 psig H₂ and 2250 psig CO₂, 2500rpm, 1g catalyst /g PS
5%Pd/BaSO₄ plus 3wt% 65%Ni/Al₂O₃/SiO₂

- 120°C, H₂, ◆ 150°C, H₂, – 180°C, H₂
Δ 120°C, H₂ & CO₂, □ 150°C, H₂ & CO₂, ◊ 180°C, H₂ & CO₂
Table 6.6. Reaction rate constants of PS hydrogenation

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Gas</th>
<th>k (ml/g/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>120</td>
<td>H₂</td>
<td>0.00090</td>
</tr>
<tr>
<td></td>
<td>H₂+CO₂</td>
<td>0.0014</td>
</tr>
<tr>
<td>150</td>
<td>H₂</td>
<td>0.0062</td>
</tr>
<tr>
<td></td>
<td>H₂+CO₂</td>
<td>0.0097</td>
</tr>
<tr>
<td>180</td>
<td>H₂</td>
<td>0.015</td>
</tr>
<tr>
<td></td>
<td>H₂+CO₂</td>
<td>0.022</td>
</tr>
</tbody>
</table>

3wt% PS-DHN, 750 psig H₂, or 750 psig H₂ and 2250 psig CO₂, 2500rpm, 1g catalyst /g PS 5%Pd/BaSO₄ plus 3wt% 65%Ni/Al₂O₃/SiO₂

6.5 Conclusions

The hydrogenation of PS in CO₂-swollen DHN was studied over a range of conditions with 5%Pd/BaSO₄ as the catalyst. The 5%Pd/BaSO₄ catalyst was deactivated at temperatures above 150°C when used in CO₂-swollen DHN. The degree of hydrogenation of PS after 10 hours was found to decrease significantly with increasing CO₂ partial pressure until it became independent of CO₂ pressure above about 1200 psig. The analysis of the gas phase at the end of the reaction showed that CO was present, and probably poisoned the catalyst during PS hydrogenation. A catalyst deactivation model based on CO poisoning during hydrogenation was developed. The model predicted a long-time asymptote of less than 100% fractional conversion of aromatic rings for PS hydrogenation. This prediction was consistent with experimental results.

Catalyst screening was conducted to investigate the effect of CO poisoning on different catalysts. It was found 65%Ni/Al₂O₃/SiO₂ showed negligible deactivation below
about 150°C. Moreover, with the 65%Ni/Al₂O₃/SiO₂ catalyst, significant concentrations of CO were not detected during hydrogenation in CO₂-swollen DHN. However, significant concentrations of CH₄ were formed, probably via methanation. Deactivation of 65%Ni/Al₂O₃/SiO₂ occurred at 180°C, which was attributed to the poisoning by H₂O formed in the methanation reactions.

A bimetallic catalyst mixture, 5%Pd/BaSO₄ with 3wt% 65%Ni/Al₂O₃/SiO₂, was tested for PS hydrogenation in the presence and in the absence of scCO₂. This catalyst mixture showed negligible deactivation at temperatures from 120 to 180°C in the presence of CO₂. The analysis of the gas phase suggested that the Ni catalyst in the mixture converted CO to CH₄, which reduced the CO poisoning of the Pd catalyst. Finally, the kinetic study with this bimetallic catalyst mixture showed that hydrogenation in CO₂-swollen DHN had a higher rate constant than the hydrogenation in pure DHN.

References


(18) Pillai, U. R.; Sahle-Demessie, E.; Young, D., Maleic Anhydride Hydrogenation over Pd/Al\textsubscript{2}O\textsubscript{3} Catalyst under Supercritical CO\textsubscript{2} Medium. *Applied Catalysis B: Environmental* **2003**, 43, 131.

(19) Pillai, U. R.; Sahle-Demessie, E., Hydrogenation of 4-Oxoisophorone over a Pd/Al\textsubscript{2}O\textsubscript{3} Catalyst under Supercritical CO\textsubscript{2} Medium. *Ind. Eng. Chem. Res.* **2003**, 42, 6688.


Chapter 7

Start-up Procedures and Polystyrene Adsorption

7.1 Introduction

The start-up procedure can influence the observed catalyst activity for polymer hydrogenations. For example, Gehlsen\(^1\) found that holding catalyst and polymer solution at the reaction temperature for one hour prior to adding H\(_2\) could cause a 30% decrease in the hydrogenation rate constant. The decrease of hydrogenation rate was attributed to the irreversible adsorption of polymer on the catalyst, which reduced the available catalytic sites for polymer hydrogenation.

On the other hand, it has been demonstrated that the adsorption of polystyrene (PS) and the conformational rearrangement of PS on the catalyst surface are the rate-limiting steps in PS hydrogenation. The overall rate constant of PS adsorption and conformational rearrangement on the catalyst should be essentially the same as the hydrogenation rate constant at high H\(_2\) pressure. Thus, the factors that can influence the adsorption and conformational rearrangement of PS can affect the PS hydrogenation as well.

This chapter will cover the effect of start-up procedures on the PS hydrogenations. Studies on the adsorption of PS onto solid catalysts will be discussed in order to explain the influence of start-up procedures and to understand the kinetics of PS hydrogenation. Finally, a kinetic model will be developed to represent the adsorption of PS.
7.2 Background of polymer adsorption

Due to the large dimension and the large number of chain configurations, the adsorption of polymers differs drastically from the adsorption of small molecules. The entropy loss per molecule upon adsorption is greater for flexible polymer chains than for small molecules. The decrease in energy is also much higher for polymers than for small molecules due to the many possible attachments per adsorbed chain. Hence, polymer molecules usually interact very strongly with the solid surface. The adsorption of a polymer chain on a solid will occur whenever its repeating units are attracted sufficiently by the solid surface. The shape and dimension of the adsorbed polymer chains depend on the nature of the polymer, surface and solvent, and on the conditions. Usually, in an adsorbed linear polymer molecule, three types of segment sequence can be distinguished: trains, loops and tails. A train is a series of segments that are all in contact with the surface. A loop consists of segments in contact with the solvent and it is bound by a train on each side. A tail is a series of segments, which is bound to a train only on one end, with the other end dangling in the solvent.

Theoretical models have been established for describing the adsorption of polymers on a solid surface. For example, self-consistent field theory has been used to estimate the distribution of train, loops and tails of an adsorbed polymer chain. Scaling theory is usually used to describe the influence of polymer concentration in the adsorbed layer on the segment density profile and its thickness. Renormalization group theory allows one to describe the excluded volume effects in adsorbed polymer chains. Monte Carlo simulation has been used to calculate the density profile and thickness of the adsorbed layer.
According to the experimental and theoretical study, some general trends can be formulated for polymer adsorption. For example\(^2\), the amount of polymer adsorbed at equilibrium will increase with the polymer concentration until it reaches a plateau. Also, adsorption decreases with increasing solvent quality. Adsorption increases with molecular weight in poor solvents, but is insensitive to molecular weight in good solvents. The adsorption of polymer is a slower process than the adsorption of small molecules, especially if the molecular weight distribution is wide. Temperature can affect the adsorption of polymers in that it can influence the solvent quality and polymer chain motions\(^{14}\). Due to the variety of polymer, solvent and solid, the equilibrium and kinetics of a particular polymer adsorption may not follow the above general trends. In that case, accurate experimental results and theoretical analysis will be necessary to explain the adsorption behaviors.

### 7.3 Materials and procedures

#### 7.3.1 Materials

5\%Pd/BaSO\(_4\) was obtained from Aldrich and was used as received. 65\%Ni/Al\(_2\)O\(_3\)/SiO\(_2\) was obtained from Aldrich and was used as received. The catalysts were characterized by scanning electron microscopy (SEM). The particles have an irregular shape, with an average equivalent spherical diameter of approximately 20 \(\mu\)m for 5\%Pd/BaSO\(_4\) and 10 \(\mu\)m for 65\%Ni/Al\(_2\)O\(_3\)/SiO\(_2\). 5\%Pd/BaSO\(_4\) has a true density of 4.42 g/cm\(^3\), a BET surface area of 4.6 m\(^2\)/g, an average pore diameter of 1.3 \(\mu\)m and a porosity of 71.7\%. CO chemisorption showed a metal dispersion of 0.29\% assuming a Pd/CO ratio of 2.0. 65\%Ni/Al\(_2\)O\(_3\)/SiO\(_2\) has a BET surface area of 142 m\(^2\)/g, an average pore diameter of 0.033 \(\mu\)m and a pore volume of 1.088 cm\(^3\)/g\(^{15}\). The metal dispersion is 7.7\% by CO chemisorption assuming a Ni/CO ratio of 1.0\(^{16}\). Commercial polystyrene with a weight average molecular
weight of approximately 290,000 g/mol was used as received. Decahyronaphthalene (DHN) was obtained from Aldrich and used as received. CO₂ (>99.998%) and H₂ (>99.999%) were supplied by National Welders and used as received.

7.3.2 Procedures and analysis

A. Hydrogenation of PS

Hydrogenation reactions were carried out in a 50 mL batch reactor at 150°C and with H₂ partial pressures of 750 psig (and CO₂ partial pressure of 2250 psig if the reaction was designed to be in the presence of CO₂). Hydrogen was fed periodically during each experiment to maintain the desired total pressure. The agitation rate was 2500 rpm for the all the experiments. Details on the hydrogenation process are provided in previous chapters.

After the reactor was cooled down to room temperature, the pressure was released slowly and the hydrogenated PS solution was filtered to remove the catalyst and was then diluted with DHN. The absorption of the diluted sample was measured at 261.5 nm with a UV-VIS spectrophotometer (Jasco V-550) to determine the concentration of aromatic rings. The degree of hydrogenation (HD), which is equivalent to the conversion of aromatic rings X, was calculated using

\[ HD = X = 1 - \frac{C_A}{C_{A_0}} \]

where the \( C_A \) is the concentration of aromatic rings in the bulk liquid phase after hydrogenation and \( C_{A_0} \) is the initial concentration of aromatic rings.

In a normal start-up procedure for the above hydrogenation, catalyst was loaded into the reactor, then PS solution was loaded into the reactor. The reactor was sealed and purged with N₂ to remove air. After purging the reactor with H₂ to replace N₂ in the reactor, the reactor was heated up under ambient pressure and with agitation. Once the reactor was up to
150°C, it was pressurized with H₂ (and then pressurized with CO₂ if the reaction was supposed to be in the presence of scCO₂) and the hydrogenation was initiated.

In the second start-up procedure, the catalyst was loaded into the reactor first, then the PS solution was loaded. The reactor was sealed and purged with N₂ followed by H₂. Then the reactor was pressurized with 300 psig H₂ and heated up with H₂. Once the reactor was up to 150°C, the pressure was adjusted to the final pressure by injecting more H₂ into the reactor and the hydrogenation was initiated.

In the third start-up procedure, the catalyst was loaded into the reactor, then the PS solution was loaded. The reactor was sealed and purged with N₂ followed by H₂. Then the reactor was heated up under ambient pressure and with agitation. After the reactor was up to 150°C, it was agitated at this temperature for 3 hours and with ambient pressure. Then the reactor was pressurized with H₂ (and then pressurized with CO₂ if the reaction was supposed to be in the presence of CO₂) and the hydrogenation was initiated.

In the fourth start-up procedure, the catalyst was loaded into the reactor, then 10 mL of DHN was loaded into the reactor. The reactor was sealed and purged with N₂ followed by H₂. The reactor was then heated up at ambient pressure and with agitation. PS dissolved in 15 mL DHN was heated up in another vessel at ambient pressure. Once the reactor and the vessel were up to 150°C, the PS solution was purged into the reactor from the vessel by low pressure H₂. After all the PS solution was transferred into the reactor, the reactor was pressurized immediately with H₂ to the final pressure and the hydrogenation was initiated. For comparison, the PS solution in the reactor had the same concentration as the other procedures after adding PS solution from the vessel into the reactor.
B. Adsorption of PS

The adsorption of PS was studied in a similar manner as the hydrogenation reaction. The catalyst was loaded into the reactor first. Then PS solution was loaded into the reactor. The reactor was sealed and purged with N\textsubscript{2} to remove air. Then the reactor was heated up with agitation at ambient pressure. Once the reactor was up to the desired temperature, the stopwatch was started. After a certain time (1 to 25 hour), the adsorption experiment was stopped by stopping the agitation and cooling the reactor with water to room temperature. To be consistent with the hydrogenation reactions, all the adsorption experiments were done with 2500 rpm agitation rate.

The PS solution was filtered to remove catalyst and measured by UV-VIS to determine the PS concentration in the bulk liquid phase $C_{PS}$. The fraction of adsorption $X_{Ad}$ was defined as $X_{Ad} = \frac{C_{PS}^a}{C_{PS}^o} = \frac{C_{PS}^o - C_{PS}}{C_{PS}^o}$. Here, $C_{PS}^a$ is the moles of adsorbed PS per unit volume of the solution. $C_{PS}^o$ is the initial PS concentration.

To investigate the adsorption of PS in the presence of CO\textsubscript{2}, the reactor was pressurized with CO\textsubscript{2} to the desired pressure after it was heated up to the desired temperature. After the reactor was cooled down to room temperature, the pressure was released slowly. The rest of the procedure was the same as the above adsorption experiment at ambient pressure.

7.4 Results and discussion

7.4.1 Start-up procedures
In the heterogeneous hydrogenation of polyisoprene, Gehlsen\textsuperscript{1} observed that the irreversible adsorption of polymer chains on the catalyst surface could cause a lower hydrogenation rate. For example, the hydrogenation that was initiated at $t=0$ minute by adding H\textsubscript{2} into the reactor showed an apparent reaction rate constant that was 30\% higher than the hydrogenation that was initiated after holding the polymer solution with catalyst at 27°C for 60 minutes before adding H\textsubscript{2}. The lower rate in the second reaction was attributed to the irreversible adsorption of polymer chains, which occupied active sites required for polymer to react with H\textsubscript{2}. Weimann\textsuperscript{17} studied the heterogeneous hydrogenation of PS. It was found that heating up the PS solution in the absence of H\textsubscript{2} could cause the fouling of catalyst. Therefore, all the hydrogenations in Weimann's work were done by heating PS solution in the presence of 800 or 350 psi H\textsubscript{2}. However, this procedure could cause some saturation of the polymer during heating of the solution, which might affect the accuracy of the kinetic experiments.

As shown in Figure 7.1, holding PS solution at 150°C for 3 hours before adding H\textsubscript{2} (Startup procedure c) causes the lowest hydrogenation rate. The standard procedure (Startup procedure a) procedures a higher hydrogenation rate. Heating up the PS solution with 300 psi H\textsubscript{2} (Startup procedure b) leads to the next highest rate. Finally, heating up PS solution and catalyst separately prior to adding H\textsubscript{2} (Startup procedure d) shows the highest hydrogenation rate. From these results, it is inferred that contacting PS solution with catalyst in the absence of H\textsubscript{2} prior to hydrogenation leads to low hydrogenation rates. It is known that polymer can adsorb on the solid and form a layer on the surface. Hence, contacting PS solution and catalyst in the absence of H\textsubscript{2} may form a layer of polymer on the catalyst surface, which could reduce the rate at which H\textsubscript{2} reaches the catalytic sites and reacts with aromatic rings. In
the presence of H₂, polymer diffuses into the catalyst and contacts the surface simultaneous with H₂. The surface reaction will then take place, which will convert aromatic rings to cyclohexane rings. Cyclohexane rings are less favorable for adsorbing on the catalyst surface\(^\text{18}\). Thus the hydrogenated PS chain will be likely to desorb from the catalyst surface and leave the catalytic surface available for the fresh PS chains.

![Figure 7.1 Start-up procedures of PS hydrogenation](image)

**Figure 7.1 Start-up procedures of PS hydrogenation**

(6wt% PS-DHN, 3wt% 5%Pd/BaSO4, 0.09wt% 65%Ni/Al2O3/SiO2, 150°C, 750psig H₂, 2500 rpm.)

a - load PS solution and catalyst at room temperature, heat-up and then add H₂
b - heat up the PS solution with 300psi H₂
c - hold the PS solution at 150°C for 3 hour before adding H₂
d - add the PS solution at 150 °C into the reactor which has the catalyst and some solvent at 150 °C
Figure 7.2 shows the effect of start-up procedures on hydrogenations in the presence of CO₂. The results indicate that irreversible adsorption of PS onto catalyst had less influence on the hydrogenation rate in the presence of CO₂. The change of solvent strength in CO₂-swollen DHN can influence the conformation of PS chains in the solution. The change in solvent also can influence the interaction between PS, solvent and catalyst surface, which will influence the adsorption and desorption of PS. Thus, adding CO₂ to DHN can change the effect of irreversible adsorption of PS on the hydrogenation rate.

Figure 7.2 Start-up procedures of PS hydrogenation

(6wt% PS-DHN, 3wt% 5%Pd/BaSO4. 0.09wt% 65%Ni/Al2O3/SiO2, 150°C, 750psig H₂, 2500 rpm,)

Unfilled points - standard startup procedure
Filled points - 3 hr induction, i.e., PS solution was held at 150°C for three hours prior to adding H₂.
7.4.2 Adsorption of PS onto catalyst

Figure 7.3 shows the adsorption of PS onto solid catalysts. The adsorption of PS is a slow process. As shown in Figure 7.3, it takes about ten hours for PS adsorption to approach equilibrium. Moreover, the PS adsorption at higher temperatures is slower in the first hour. After the first hour, the adsorptions at higher temperatures show higher adsorption fractions \( X_{Ad} \) and eventually obtain higher amounts of adsorption at equilibrium. Generally, the adsorption of small molecules is exothermic, therefore higher temperature leads to lower adsorption at equilibrium, which differs from the results in Figure 7.3. The unique behavior of PS adsorption can be attributed to the long-chain properties of PS molecules. The dimension of polymer coil is dependent on the temperature. Whittier\(^{19} \) observed that the hydrodynamic radius of PS in DHN solution increased with increasing temperature. Moreover, it has been suggested that the adsorption of macromolecules is usually controlled by the diffusion at the beginning stage of adsorption\(^{20} \). The smaller dimension of PS coils at lower temperatures may lead to a high diffusion rate inside the pores of the catalyst, especially in the smaller pores, which could lead to a higher adsorption fraction. But diffusion coefficients of PS are higher at higher temperatures\(^{19} \), which should lead to a faster diffusion rate. Hence, the higher fraction of adsorption at low temperatures in the first hour can not be explained by the diffusion rate only.

A polymer chain adsorbed on the solid surface can rearrange its conformation, which allows the free polymer chain to contact the solid surface. The influence of conformational rearrangement becomes more important when the majority of the catalyst surface has been covered by polymers because the possibility for a free chain to find an available area becomes lower. At high temperatures, the conformational rearrangement of PS on the
catalyst surface is faster\textsuperscript{21}, which gives the free polymer chains more possibility to contact the surface. As a result, a higher amount of adsorbed polymer is observed at high temperatures in the stage close to equilibrium. Moreover, the larger dimension of polymer chains at high temperatures may lead to more entanglement between polymer chains near catalyst surface. The entanglement between polymer chains will trap some polymer molecules on the top of the adsorbed polymer layer, which results in a multi-layer adsorption and a higher amount of adsorbed polymer on the surface. On the other hand, the large dimension of a polymer coil at high temperature creates a larger excluded volume, which could reduce the amount of adsorbed polymer. However, the results in Figure 7.3 indicate that the effect of the fast conformational rearrangement dominate the adsorption at these conditions.

![Figure 7.3 Adsorption of PS onto catalyst](image)

Figure 7.3 Adsorption of PS onto catalyst

0.56wt\% PS-DHN solution, 1 g 5\%Pd/BaSO\textsubscript{4} and 0.03 g 65\%Ni/Al\textsubscript{2}O\textsubscript{3}/SiO\textsubscript{2}, 2500 rpm
Figure 7.4 shows the effect of PS concentration on adsorption. All these adsorption experiments lasted for twenty-five hours. As shown in Figure 7.3, the adsorption at 150°C is essentially at equilibrium after about ten hours. Thus, in Figure 7.4, adsorption can be assumed to be at equilibrium. The amount of adsorbed PS increases with increasing PS concentration. However, the fraction of PS adsorbed decreases with increasing PS concentration because the available catalyst surface decreases as more PS chains adsorb on the surface. Hence, it is expected that the amount of adsorbed PS will approach to a plateau if the PS concentration were further increased.

Figure 7.4 Effect of PS concentration on adsorption

150°C, 1 g 5%Pd/BaSO₄ and 0.03 g 65%Ni/Al₂O₃/SiO₂, 25 hr, 2500 rpm
Figure 7.5 shows the adsorption of PS in the presence of CO₂. As a comparison, the adsorption of PS in the absence of CO₂ at the otherwise identical conditions is shown as the solid points in Figure 7.5. PS adsorption in the presence of CO₂ shows a lower rate than in the absence of CO₂. CO₂ is an antisolvent for PS, which will cause a collapse of PS coils. It was observed that the radius of gyration of PS in toluene reduc²²es upon pressurizing the PS solution with high pressure CO₂. The reduced dimension of PS coil might cause a higher adsorption rate at the early stage of adsorption as mentioned above. However, the reduced ability of conformational rearrangement due to the collapse of PS coil will cause a lower adsorption rate over a long period of adsorption. On the other hand, CO₂ can absorb on the catalyst itself. Hence, CO₂ could be assumed as a displacer here. The binding of CO₂ on the catalyst surface can significantly reduce the possibility for free PS molecule to find an available area and therefore decrease the adsorption of PS. Moreover, CO₂ could replace the adsorbed PS on the surface and lead to the desorption of the adsorbed PS chain. Both of these will decrease the rate of PS adsorption in the presence of CO₂.
10 ml 0.56%PS-DHN solution, 1 g 5%Pd/BaSO₄, 0.03 g 65%Ni/Al₂O₃/SiO₂, 2500 rpm, 5 hours, CO₂ mole fraction in the liquid phase is about 55% at all temperatures.

Figure 7.5 Adsorption PS in the presence of CO₂

It has been observed that an induction period, i.e. holding PS solution with catalyst at the reaction temperature without H₂, has less effect on the PS hydrogenation in the presence of CO₂. The influence of an induction period on the hydrogenation rate can be attributed to the irreversible adsorption of PS on the catalyst surface. Hence, the reduced adsorption of PS in the presence of CO₂ should lead to a lower extent of catalyst deactivation by irreversible adsorption of PS, which is consistent with the observed experimental results as shown in Figure 7.2.

Table 7.1 shows that the partially hydrogenated PS produced from CO₂-swollen DHN can be separated into two samples, one has a degree of hydrogenation close to 60%, and the
other one has a low degree of hydrogenation. This could be explained by the 'blocky' hydrogenation mechanism as described in Chapter Three. However, the extracted part of a partially hydrogenated PS produced from DHN shows a degree of hydrogenation close to 80%. According to the 'blocky' mechanism, the adsorbed PS chain will not desorb from the catalyst surface until most of the aromatic rings in this chain have been hydrogenated. The degree of hydrogenation of a PS chain after the first adsorption step depends on the property of solvent, polymer and catalyst. Figure 7.5 shows the adsorption of PS is lower in CO₂-swollen DHN than in DHN. It implies that the CO₂-swollen DHN is unfavorable for PS adsorption on the catalyst. Therefore, in CO₂-swollen DHN, an adsorbed PS chain will desorb after about 60% of the aromatic rings in this chain have been hydrogenated, while an adsorbed PS chain will desorb after about 80% of aromatic rings have been hydrogenated in DHN. Hence, the extracted part of partially hydrogenated PS from DHN shows about 80% degree of hydrogenation while the extracted part of partially hydrogenated PS from CO₂-swollen DHN shows about 60% degree of hydrogenation as shown in Tables 3.1 and 7.1.

<table>
<thead>
<tr>
<th>Overall HD</th>
<th>HD of extracted polymer</th>
<th>HD of undissolved polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>39%</td>
<td>58%</td>
<td>30%</td>
</tr>
<tr>
<td>51%</td>
<td>58%</td>
<td>50%</td>
</tr>
</tbody>
</table>

Table 7.1 Separation of partially hydrogenated PS

Partially hydrogenated PS samples were obtained from hydrogenations in the presence of scCO₂. The polymers were extracted by hexane using the same procedure as described in Chapter Three.

7.4.3 Kinetics of PS adsorption

The rate of PS adsorption onto catalyst can be expressed as$^6, 23, 24$
\[ \frac{dC_{PS}^a}{dt} = k_a(1 - \theta)C_{PS} - k_dC_{PS}^a \]  \hspace{1cm} (7.1)

Here, \( C_{PS}^a \) is the moles of adsorbed PS per unit volume of the solution, \( C_{PS} \) is the concentration of PS in the liquid phase \( C_{PS} = C_{PS}^o - C_{PS}^a \), and \( \theta \) is the fractional surface coverage. \( k_a \) and \( k_d \) are the adsorption and desorption rate constants (1/time). Due to the strong adsorption of polymer molecules on the solid surface\(^3,20\), desorption was neglected in this analysis, i.e. \( k_d = 0 \).

One way\(^24\) to visualize the PS molecules on the surface is as being ellipsoidal in shape with a width \( l \) and a height \( h \), as shown in Figure 7.6. Then the fractional surface coverage \( \theta \) can be defined as

\[ \theta = \frac{C_{PS}^a V N_{AV} a}{S} \]  \hspace{1cm} (7.2)

Where \( V \) is the total volume, \( N_{AV} \) is Avogadro's number, \( a \) is the area of the cross section of the ellipsoid, \( a = \frac{\pi \cdot l^2}{4} \), and \( S \) is the total surface area of catalyst in the solution. Equation (7.2) can be written as

\[ \theta = \frac{C_{PS}^a}{n} \]  with

\[ n = \frac{4 \cdot S}{\pi \cdot V \cdot N_{AV} \cdot l^2} \]

Therefore, the rate of PS adsorption can be re-written as

\[ \frac{dC_{PS}^a}{dt} = k_a(1 - \frac{C_{PS}^a}{n}) \cdot (C_{PS}^o - C_{PS}^a) \]  \hspace{1cm} (7.3)
Integrating equation (7.3) from $t=0$ to $t$ with $C_{PS}^a = 0$ at $t = 0$, gives

$$X_{Ad} = \frac{1 - \exp\left(\frac{C_{PS}^o - n}{n} k_a t\right)}{1 - \frac{C_{PS}^o}{n} \exp\left(\frac{C_{PS}^o - n}{n} k_a t\right)}$$

Equation (7.4)

Here $X_{Ad}$ is the fraction of adsorption. Equation (7.4) can be used to fit the experimental results in Figure 7.3 in order to determine the adsorption rate constant and the dimensions of the adsorbed PS molecules.

![Ellipsoidal shape of adsorbed PS molecule](image)

Figure 7.6 Ellipsoidal shape of adsorbed PS molecule
(The cross-section of the ellipsoid is circular with a diameter $l$)

When adsorption is complete,

$$\frac{dC_{PS}^a}{dt} = k_a \left(1 - \frac{C_{PS}^a}{n}\right) \cdot (C_{PS}^o - C_{PS}^a) = 0$$

Equation (7.5)

Where $C_{PS}^a$ is the final value of the moles of adsorbed PS per unit volume. Equation (7.5) can be equal to zero only when $1 - \frac{C_{Ad}^a}{n} = 0$. Hence, $n = C_{Ad}^a$. As shown in Figure 7.3, the rate of PS adsorption approaches zero after about 10 hours. Hence, the experimental concentration $C_{PS}^a$ at 25 hours can be assumed to be close to $C_{PS}^a$. The value of $C_{PS}^a$ (25 h)}
is taken to be the initial guess for \( n \) when equation (7.4) is fit with the experimental data. The adsorption rate constant and the final value of \( n \) can be determined by fitting Equation (7.4) to the experimental data using KaleidaGraph.

As shown in Figures 7.7 - 7.11, the above model fits the experimental data reasonably well at temperatures from 25 to 150°C. Table 7.2 shows the adsorption rate constant \( k_a \) and the parameter \( n \), which were obtained from the curve fitting. It is found that the adsorption rate constant decreases with increasing temperature from 25 to 90°C. It approximately approaches to a constant between 90 and 120°C and then slightly increases at 150°C. It is known that temperature can affect the solvent quality and polymer chain motion\(^1\). The worse solvent quality at low temperatures can lead to a higher adsorption. But the faster rate of conformational rearrangement at high temperatures will enhance the possibility for free PS molecules to contact the surface, which will increase the adsorption. Thus, the results in Table 7.2 indicate that the solvent quality dominates the PS adsorption rate constant at low temperature range and the polymer conformational rearrangement dominates the adsorption rate constant at high temperatures.

<table>
<thead>
<tr>
<th>( T (°C) )</th>
<th>( k_a (s^{-1}) )</th>
<th>( n (\text{mol/mL}) )</th>
<th>( a (\text{nm}^2) )</th>
<th>( R )</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>1.49×10(^{-4})</td>
<td>2.34×10(^{-9})</td>
<td>628.96</td>
<td>0.994</td>
</tr>
<tr>
<td>60</td>
<td>1.01×10(^{-4})</td>
<td>2.65×10(^{-9})</td>
<td>555.38</td>
<td>0.953</td>
</tr>
<tr>
<td>90</td>
<td>6.14×10(^{-5})</td>
<td>3.78×10(^{-9})</td>
<td>389.35</td>
<td>0.996</td>
</tr>
<tr>
<td>120</td>
<td>6.11×10(^{-5})</td>
<td>4.52×10(^{-9})</td>
<td>325.61</td>
<td>0.988</td>
</tr>
<tr>
<td>150</td>
<td>7.78×10(^{-5})</td>
<td>4.55×10(^{-9})</td>
<td>323.46</td>
<td>0.966</td>
</tr>
</tbody>
</table>

\( R \) - Correlation coefficient

\( k_a \) and \( n \) were obtained by fitting the data; \( a \) was calculated from \( n \).
Figure 7.7 PS adsorption at 150°C

O experiment, — kinetic model

Figure 7.8 PS adsorption at 120°C

O experiment, — kinetic model
Figure 7.9 PS adsorption at 90°C
O experiment, — kinetic model

Figure 7.10 PS adsorption at 60°C
O experiment, — kinetic model
It has been suggested that the difference in the densities of the adsorbed polymer and the polymer in the bulk liquid is nonessential. If so, the dimension of adsorbed PS on the surface can be calculated by the following procedures.

Whittier measured the hydrodynamic radius $R_H$ of PS with a molecular weight of 412000 g/mol in dilute DHN solution using dynamic light scattering at various temperatures. The hydrodynamic radius is known to depend on the polymer molecular weight by the relation $R_H \propto M_w^{0.588}$. Therefore, the average hydrodynamic radius of PS ($M_w \approx 290000$) used in this work can be calculated from Whittier's work and the above relation. Calculated values of $R_H$ are shown in Table 7.3. The volume of a PS coil in solution can be determined from $R_H$. From the value of $a$ obtained in the above kinetic study, as shown in Table 7.2, the length $l$ and the height $h$ of the adsorbed PS coil can be calculated by the following relations.
(7.6) and (7.7), assuming the adsorbed PS coil is ellipsoidal and the volume of the adsorbed PS is the same as the volume of PS dissolved in DHN.

\[
l = 2 \sqrt{\frac{a}{\pi}} \quad (7.6)
\]

\[
h = \frac{8R_h^3}{l^2} \quad (7.7)
\]

Table 7.3 Dimensions of adsorbed PS molecules

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>R_H (nm)</th>
<th>2R_H (nm)</th>
<th>l (nm)</th>
<th>h (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>13.00</td>
<td>26.00</td>
<td>28.30</td>
<td>21.94</td>
</tr>
<tr>
<td>60</td>
<td>13.38</td>
<td>26.76</td>
<td>26.59</td>
<td>27.11</td>
</tr>
<tr>
<td>90</td>
<td>13.83</td>
<td>27.66</td>
<td>22.27</td>
<td>42.68</td>
</tr>
<tr>
<td>120</td>
<td>15.35</td>
<td>30.70</td>
<td>20.36</td>
<td>69.79</td>
</tr>
<tr>
<td>150</td>
<td>16.69</td>
<td>33.38</td>
<td>20.29</td>
<td>90.34</td>
</tr>
</tbody>
</table>

The apparent height of the PS coil increases with increasing temperature. The height \( h \) approximately represents the thickness of the adsorbed PS layer on the catalyst surface. Thus the thickness of the adsorbed PS layer increases with temperature. Comparing the height of the adsorbed PS with the diameter (2R_H) of the PS dissolved in DHN, the height \( h \) is less than 2R_H at 25°C. However, the height \( h \) becomes greater than 2R_H with increasing temperature. These results indicate that the adsorbed PS molecule is compressed on the surface at 25°C. As the temperature increases, the motion of PS chain becomes faster, therefore PS molecule undergo conformational rearrangements to form a stretched ellipsoidal shape, which allows more PS molecules to adsorb on the surface.
After the layer of adsorbed PS molecules is formed on the catalyst surface, it will inhibit the diffusion of H$_2$ molecules to the surface and therefore inhibit the hydrogenation of aromatic rings. As shown by the above kinetic analysis, PS molecules adsorb on the catalyst strongly. The desorption of PS can be assumed as zero at conditions used in this work. Hence, the formed PS layer will remain on the catalyst surface during hydrogenation, which will virtually reduce the catalytic sites and cause a low hydrogenation rate. As shown in Figures 7.1 and 7.2, holding PS solution with catalyst prior to adding H$_2$ will cause a lower hydrogenation rate, which is consistent with the above analysis. On the other hand, the adsorption of PS chain in the presence of H$_2$ will cause the hydrogenation reaction between H$_2$ and aromatic rings on the catalyst surface, which will convert aromatic rings to cyclohexane rings. It has been suggested that saturated aromatic rings do not adsorb on the surface of solid catalyst$^{18}$. The unfavorable interaction between cyclohexane rings and the catalyst surface will cause the desorption of the PS chain. Therefore the surface is re-opened for the free PS molecules and the hydrogenation of PS will continue on the surface. Hence reducing the contact of PS solution with catalyst prior to adding H$_2$ should lead to higher hydrogenation rates, as shown in Figure 7.1.

7.5 Conclusions

It was found that the start-up procedures could greatly influence the rate of PS hydrogenation. Holding PS solution with catalyst at the reaction temperature for a period of time before adding H$_2$ led to the lowest hydrogenation rate. Adding H$_2$ right after mixing PS solution and catalyst at the reaction temperature showed the highest hydrogenation rate. This phenomenon was attributed to the irreversible adsorption of PS on the catalyst surface, which
reduced the available catalytic sites for hydrogenation and therefore caused a lower hydrogenation rate.

The adsorption of PS onto catalyst was studied. It was found the amount of adsorbed PS at the equilibrium increased with increasing temperature. PS adsorption also depended on the polymer concentration. Higher adsorption could be obtained with increasing PS concentration. However, the fraction of adsorption decreased with increasing PS concentration. Moreover, the presence of CO\textsubscript{2} significantly reduced the adsorption of PS.

A kinetic model neglecting PS desorption was developed and was found to fit the experimental data reasonably well at temperatures from 25 to 150\degree C. The adsorption rate constant decreased with temperature at low temperatures and increased with temperature at high temperatures. This behavior was attributed to the influence of temperature on the solvent quality and PS chain motion, i.e., the PS adsorption rate constant was dominated by the solvent quality at low temperatures, and was dominated by the rate of conformational rearrangement of PS chains at high temperatures. The thickness of the adsorbed PS layer on the catalyst surface was calculated according to the kinetic model and was found to increase with temperature. At 150\degree C, the thickness of the adsorbed PS layer was about 90 nm.

References


Chapter 8
Conclusions and Recommendations

8.1 Conclusions

Hydrogenated polystyrene (PS) has some unique properties, such as a higher $T_g$ (147°C) than PS (105°C), plus improved thermal and oxidative stability and excellent optical properties. However, the high viscosity of PS solutions makes catalytic hydrogenation difficult. The rates of mass and heat transfer, and therefore, the rate of the hydrogenation reaction can be low. Carrying out the hydrogenation reaction in a solvent that is expanded with supercritical CO$_2$ (scCO$_2$) may overcome this difficulty. It is known that scCO$_2$ can dramatically reduce the viscosity of polymer solutions, and increase the H$_2$ solubility and polymer diffusion coefficient in the solution.

The heterogeneous hydrogenation of PS (3wt% or less) in decahydronaphthalene (DHN) catalyzed by 5%Pd/BaSO$_4$ was investigated in a batch reactor. The effect of temperature and H$_2$ pressure on PS hydrogenation was studied. The hydrogenation rate increased with temperature but the polymer chain scission became severe at high temperatures. At 150°C, the hydrogenation rates were dependent on H$_2$ pressure below 500 psig, but became independent of H$_2$ pressure above about 500 psig. A partially hydrogenated PS sample could be separated into two fractions, one with about 80% degree of hydrogenation and the other which was lightly hydrogenated. This behavior implies that PS hydrogenation followed a 'blocky' mechanism, i.e. the hydrogenation of an individual PS chain approached about 80% during a single adsorption step, and subsequent adsorption steps
were required to achieve fully hydrogenated PS. Based on the above mechanism, a kinetic model was developed for heterogeneous PS hydrogenation assuming the adsorption and conformational rearrangement of PS on the catalyst are the rate limiting steps. At high H$_2$ pressure, the rate equation can be simplified to a first order rate equation with respect to aromatic ring concentration. The first order rate equation was found to fit the experimental data reasonably well. The apparent activation energy was 59.6 kJ/mol for heterogeneous PS hydrogenation at concentrations of 3wt% or less.

In order to investigate the effect of mass transport in PS hydrogenation, the viscosity and diffusion coefficient of PS solutions were measured at various temperatures. For the hydrogenation of 3wt% PS solution at 150°C, an agitation rate of at least 2000 rpm was required to essentially eliminate the resistance to gas-liquid mass transfer. Moreover, calculations showed that the liquid-solid and pore diffusion resistances also were negligible at PS concentration of 3wt% or less. However, the hydrogenation rate constants for 'concentrated' PS solutions (4.5wt% - 9wt%) were lower than for 'dilute' PS solutions (3wt% or less) at an agitation rat of 2500 rpm. Higher agitation rates were required to increase the rate constants of concentrated PS solutions close to those of dilute PS solutions. This behavior implies that gas-liquid mass transport could influence the PS hydrogenation in concentrated solutions.

Carbon dioxide is an anti-solvent for PS. It can cause PS to precipitate from solution at high pressures. Thus, the phase behavior of PS in different solvents swollen with high pressure CO$_2$ were studied at 120°C. It was found that PS would not precipitate from DHN at 120°C until the CO$_2$ pressure was 3000 psig. Moreover, DHN has a fully saturated structure, which avoids the side reaction of hydrogenation of solvent. Hence, DHN was selected as the
solvent for PS hydrogenation in the presence of scCO\textsubscript{2}. The volume expansions of DHN and PS in DHN solutions were measured at various temperatures and CO\textsubscript{2} pressures. The volume expansions of DHN and PS-DHN solution were calculated from the Peng-Robinson equation of state (PR-EOS) and the Sanchez-Lacombe equation of state (PR-EOS). The calculated volume expansions were consistent with the experimental results. The ternary phase diagrams of DHN-CO\textsubscript{2}-H\textsubscript{2} were generated using the PR-EOS. At 150°C and constant total pressure, the H\textsubscript{2} solubility in CO\textsubscript{2}-swollen DHN increased as the CO\textsubscript{2} pressure was increased only at very high pressures. However, at constant volume (50 cc) and constant H\textsubscript{2} partial pressure (750 psig), the H\textsubscript{2} solubility in CO\textsubscript{2}-swollen DHN with 2250 psig CO\textsubscript{2} pressure was about twice that in pure DHN. At temperatures from 90 to 150°C and CO\textsubscript{2} pressure from about 700 psi to 3000 psi, the viscosity of CO\textsubscript{2}-swollen PS solution could be represent by a linear equation $\eta = A \sum X_i \eta_i$. Here, $\eta_i$ and $X_i$ are the viscosity and mole fraction of PS-DHN solution and CO\textsubscript{2} respectively, and $A$ is a constant.

The heterogeneous hydrogenation of PS in CO\textsubscript{2}-swollen DHN was studied. Deactivation of 5%Pd/BaSO\textsubscript{4} was observed at temperatures above 150°C in the presence of scCO\textsubscript{2}. The degree of hydrogenation of PS after 10 hours was found to decrease significantly with CO\textsubscript{2} partial pressure until it became independent of CO\textsubscript{2} above 1200 psig. The analysis of the gas phase showed that about 50 ppm CO was present at 150°C at the end of a batch reaction. This CO probably was formed via the reverse water gas shift reaction, and probably poisoned the catalyst during hydrogenation. A catalyst deactivation model based on CO poisoning during hydrogenation was developed. The model predicted a long time asymptote.
for PS hydrogenation, which was consistent with experimental results. A 65%Ni/Al$_2$O$_3$/SiO$_2$ catalyst did not produce significant CO during hydrogenation, but formed CH$_4$ via methanation. The deactivation of 65%Ni/Al$_2$O$_3$/SiO$_2$ in PS hydrogenation occurred at 180°C, which was attributed to poisoning of the catalyst by H$_2$O formed from methanation reactions. A bimetallic catalyst system (5%Pd/BaSO$_4$ and 3wt% 65%Ni/Al$_2$O$_3$/SiO$_2$) was tested for PS hydrogenation in CO$_2$-swollen DHN. Negligible deactivation of this bimetallic catalyst system by CO poisoning was demonstrated for PS hydrogenation at temperatures from 120 to 180°C. Analysis of the gas phase showed that CO was converted to CH$_4$ by 65%Ni/Al$_2$O$_3$/SiO$_2$, which avoided CO poisoning.

The effect of start-up procedures on PS hydrogenation was investigated. Contact of PS solution with catalyst prior to adding H$_2$ leads to a lower hydrogenation rate. This phenomenon was attributed to the irreversible adsorption of PS on catalyst surface. The adsorption of PS from DHN onto solid catalyst was studied. It was found that the adsorption of PS was a slow process. The amount of adsorbed PS at equilibrium increased with temperature, which was attributed to fast rate of conformational rearrangement of PS chains at high temperatures. Assuming PS adsorption was irreversible, a kinetic model was developed and was found to fit the experimental results reasonably well at temperatures from 25 to 150°C. The thickness of the adsorbed PS layer on the catalyst surface increased with
increasing temperature and was about 90 nm at 150°C. It also was found that the adsorption of PS was reduced significantly in the presence of high pressure CO₂.

8.2 Recommendations

Hydrogenation in the presence of other supercritical fluids has been reported¹⁻⁵. Propane is the most popular supercritical fluid that has been used as a hydrogenation medium. The solubility of high molecular weight hydrocarbons is higher in supercritical propane than in scCO₂. Propane, H₂ and hydrocarbons can form a homogeneous phase at relatively mild conditions. Therefore, hydrogenation can take place in a one-phase regime, which avoids the resistance to gas-liquid mass transfer. Moreover, catalyst poisoning by CO can be avoided in supercritical propane. Hence, study of the phase behavior of PS solution in the presence of high pressure propane is recommended. Furthermore, the hydrogenation of PS in the presence of supercritical propane could be investigated.

It has been demonstrated that methanation can effectively convert CO to CH₄, which avoids catalyst poisoning by CO. As a result, the bimetallic catalyst system (5%Pd/BaSO₄ and 3wt% 65%Ni/Al₂O₃/SiO₂) showed improved resistance to CO poisoning in this study. Hence, a catalyst with a precious metal for PS hydrogenation and a methanation metal on the same support is expected to show better stability and resistance to CO poisoning. It is recommended that a catalyst with a precious metal (Pd, Pt, Rh and etc.) and a methanation
metal (Ni, Ru, Co, Fe, Mo and etc.) on the same support is synthesized and tested for PS hydrogenation in the presence of CO₂.

The adsorption of PS has been studied. PS adsorption is a slow and apparently irreversible process. The adsorption rate constants at various temperatures have been obtained from the kinetic study. However, the rate of conformational rearrangement of adsorbed PS chains cannot be obtained from the present adsorption study, which makes it difficult to compare the adsorption results with the hydrogenation kinetics. Adsorption of polymers on solid surfaces has been studied using Monte Carlo simulation⁶⁻⁸. Moreover, the heterogeneous catalytic hydrogenation of low molecular weight hydrocarbon also has been studied using Monte Carlo simulation⁹⁻¹². Hence, the Monte Carlo simulation of adsorption, conformational rearrangement, and surface reaction of PS chains on solid catalysts could provide further information about the mechanism and kinetics of polymer hydrogenation.

The high entanglement molecular weight of hydrogenated PS and the resulting brittle, glassy property is one of the major limitations for its applications. It has been suggested that the toughness of hydrogenated PS can be improved by incorporating rubbery saturated diene blocks into hydrogenated PS chain to form a block copolymer¹³, ¹⁴. For example, hydrogenated butadiene-styrene pentablock copolymer has showed significant improvements in toughness¹³, ¹⁴. Hence, hydrogenation of copolymers containing styrene units is recommended to create high performance polymeric materials.
Few continuous processes of heterogeneous polymer hydrogenation have been reported\textsuperscript{15,16}. A continuous process for polymer hydrogenation in CO\textsubscript{2}-swollen solvent has not been published. The reduced viscosity and enhanced H\textsubscript{2} solubility and polymer diffusion coefficient in CO\textsubscript{2}-swollen solvent, and therefore the faster mass transfer rates and hydrogenation rate allow the continuous polymer hydrogenation to be operated at high space time yield and in a smaller reactor. Hence, the development of a continuous process for PS hydrogenation in the presence of scCO\textsubscript{2} is recommended.

References


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Appendix A

Phase Equilibria

A.1 $k_{ij}$ for Peng-Robinson equation of state

1. $k_{\text{CO}_2\text{-DHN}}=0.125$

   ![Figure A.1 Phase equilibrium of Decahydronaphthalene (DHN)-CO$_2$ at 126.6°C](image1)

   Experimental data were taken from Inomata et al.$^{1,2}$

2. $k_{\text{H}_2\text{-CYC}}=0.17$

   ![Figure A.2 Phase equilibrium of H$_2$-Cyclohexane (CYC) at 137.8°C](image2)

   Experimental data were taken from Berty et al.$^3$
3. \( k_{H_2-MeOH} = -0.19 \)

Figure A.3 Phase equilibrium of \( H_2 \)-Methanol (MeOH) at 100.0°C
Experimental data were taken from Brunner et al.\(^4\)

A.2 \( k_{ij} \) for Sanchez-Lacombe equation of state

1. \( k_{CO_2-PS} = 0.066 \)

Figure A.4 Phase equilibrium of \( CO_2 \)-Polystyrene (PS) at 150.0°C
Experimental data were taken from Sato et al.\(^5\)
3. $k_{\text{CO2-DHN}} = 0.057$

![Figure A.5 Volume expansion of DHN-CO$_2$ at 150.0 °C](image)

Experimental data were measured in this work.

4. $k_{\text{PS-DHN}} = -0.06$

![Figure A.6 Volume expansion of 3wt% PS-DHN solution with CO$_2$ at 150.0°C](image)

Experimental data were measured in this work.
Figure A.7 Volume expansion of 3wt% PS-DHN solution with CO₂ at 150.0°С

Experimental data were measured in this work

Figure A.8 Volume expansion of 3wt% PS-DHN solution with CO₂ at 150.0°С

Experimental data were measured in this work
Figure A.9 Volume expansion of 3wt% PS-DHN solution with CO$_2$ at 150.0°C
Experimental data were measured in this work

A.3 Ternary Phase Diagram
1. CYC-H$_2$-CO$_2$

Figure A.10 Ternary phase diagram of CYC-H$_2$-CO$_2$ at 150°C and 3000 psi
Figure A.11 Ternary phase diagram of CYC-H₂-CO₂ at 150°C and 5000 psi

Figure A.12 Ternary phase diagram of CYC-H₂-CO₂ at 150°C and 7000 psi
2. MeOH-H$_2$-CO$_2$

Figure A.13 Ternary phase diagram of MeOH-H$_2$-CO$_2$ at 150°C and 3000 psi

Figure A.14 Ternary phase diagram of MeOH-H$_2$-CO$_2$ at 150°C and 5000 psi
References


Appendix B

Heterogeneous Hydrogenation of Poly(bisphenol A carbonate)

It was reported that 2,2-bis(4-hydroxycyclohexyl)propane-diphenyl carbonate copolymer (hydrogenated poly(bisphenol A carbonate), HPC) exhibited a softening temperature at least 225°C, which was higher than poly(bisphenol A carbonate) (PC)\(^1\). Therefore, HPC might be useful in applications where higher temperatures are encountered. Moreover, HPC shows limited or complete insolubility in usual PC solvents, which allows it to replace PC in some applications requiring resistance to such solvents. Due to these unique properties, HPC has been proposed to be used as coatings, films, electrical insulating materials, wrapping or packaging materials, containers, etc\(^1\).

2,2-bis(4-hydroxycyclohexyl)propane-diphenyl carbonate copolymer has been synthesized by the direct polymerization of saturated bisphenol A (2,2-bis(4-hydroxycyclohexyl) propane) and diphenyl carbonate as shown in Figure B.1\(^1,2\). However, the synthesis of HPC from the hydrogenation of PC has not been investigated. Based on research on the hydrogenation of polystyrene, the heterogeneous hydrogenation of PC was studied, which could be an alternative to the synthesis of HPC from polymerization.

The hydrogenation of PC was conducted in a 50 mL autoclave and by a similar procedure as hydrogenation of polystyrene. 5%Pd/BaSO\(_4\) and 5%Rh/Al\(_2\)O\(_3\) were used as the catalysts. The degree of hydrogenation of aromatic rings was measured by UV-VIS at 265 nm with tetrahydrofuran (THF) as solvent. The hydrogenation of the carbonyl group was
measured by FTIR. Molecular weight of the hydrogenated polymers was measured by GPC with THF as the mobile phase.

Table B.1 lists the solvents or the solvent mixtures, catalyst and reaction conditions with which PC hydrogenation was attempted. PC was insoluble in many solvents at moderate temperatures, so that the hydrogenation had to be conducted at high temperatures (150-180°C) where PC might be soluble. However, side reactions, polymer chain scission and hydrogenation of the carbonyl group in PC, became severe at high temperatures. As shown by a typical FTIR spectrum in Figure B.4, the peak at 1500 cm\(^{-1}\) that represents the aromatic rings reduces significantly, which indicates the saturation of aromatic rings by hydrogenation. However, the peak at 1750 cm\(^{-1}\) that represents the carbonyl group reduces significantly as well and a peak that represents the formed OH group appears at 3350 cm\(^{-1}\), which indicate that hydrogenation of the carbonyl group occurs at the reaction conditions.

Due to the severe chain scission and hydrogenation of carbonyl group, the following two-step process is suggested for synthesis of hydrogenated PC in the future.

a) Selective hydrogenation of aromatic rings in oligomers of PC. The oligomers of PC could be dissolved at moderate temperatures, therefore the hydrogenation might be conducted at moderate temperatures, which will reduce the polymer chain scission during hydrogenation. The oligomers will exhibit high diffusion rate and low viscosity in solution, both of which will reduce the residence time of the oligomers in the pores of catalyst, which could reduce the side reactions, such as chain scission or hydrogenation of carbonyl group.

b). Solid-state polymerization. It is known that the oligomers of PC can be converted to high molecular weight PC using solid-state polymerization.\(^3\)\(^-\)\(^5\) Hence, high molecular
weight HPC might be obtained from the solid-state polymerization of the hydrogenated PC oligomers.

The two-step process will avoid the problems of insolubility of PC and high viscosity and low diffusivity of PC solution. Thus the side reactions can be controlled at an acceptable level.

Figure B.1 Synthesis of 2,2-bis(4-hydroxy-cyclohexyl)propane-diphenyl carbonate copolymer
Figure B.2 Hydrogenation of aromatic rings in PC

\[
\begin{align*}
\left[ \begin{array}{c}
\text{O} \\
\text{CH}_3
\end{array} \right] & \begin{array}{c}
\text{C} \\
\text{CH}_3
\end{array} \begin{array}{c}
\text{O} \\
\text{C}
\end{array} \\
\left[ \begin{array}{c}
\text{CH}_3 \\
\text{O}
\end{array} \right]_{n} + \text{H}_2 \\
\rightarrow \left[ \begin{array}{c}
\text{O} \\
\text{CH}_3
\end{array} \right] & \begin{array}{c}
\text{C} \\
\text{CH}_3
\end{array} \begin{array}{c}
\text{O} \\
\text{C}
\end{array} \\
\left[ \begin{array}{c}
\text{CH}_3 \\
\text{O}
\end{array} \right]_{n}
\end{align*}
\]

Figure B.3 Hydrogenation of the carbonyl group in PC

\[
\begin{align*}
\left[ \begin{array}{c}
\text{O} \\
\text{CH}_3
\end{array} \right] & \begin{array}{c}
\text{C} \\
\text{CH}_3
\end{array} \begin{array}{c}
\text{O} \\
\text{C}
\end{array} \\
\left[ \begin{array}{c}
\text{CH}_3 \\
\text{O}
\end{array} \right]_{n} + \text{H}_2 \\
\rightarrow \left[ \begin{array}{c}
\text{O} \\
\text{CH}_3
\end{array} \right] & \begin{array}{c}
\text{C} \\
\text{CH}_3
\end{array} \begin{array}{c}
\text{O} \\
\text{C}
\end{array} \begin{array}{c}
\text{OH} \\
\text{O}
\end{array} \\
\left[ \begin{array}{c}
\text{CH}_3 \\
\text{O}
\end{array} \right]_{n}
\end{align*}
\]
<table>
<thead>
<tr>
<th>Solvent 1 (Volume)</th>
<th>Solvent 2 (Volume)</th>
<th>Solubility</th>
<th>PC wt%</th>
<th>Catalyst (wt%)</th>
<th>T(°C)</th>
<th>HD</th>
</tr>
</thead>
<tbody>
<tr>
<td>DHN (25mL)</td>
<td></td>
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<td>1wt%</td>
<td>5%Pd/BaSO₄ (1wt%)</td>
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<td>61%</td>
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<tr>
<td>THF (25mL)</td>
<td></td>
<td>Y</td>
<td>1wt%</td>
<td>5%Pd/BaSO₄ (1wt%)</td>
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<td>9%</td>
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<tr>
<td>CHN (25mL)</td>
<td></td>
<td>Y</td>
<td>1wt%</td>
<td>5%Pd/BaSO₄ (1wt%)</td>
<td>180</td>
<td>5%</td>
</tr>
<tr>
<td>DHN (14mL) IPA (11mL)</td>
<td></td>
<td>Y</td>
<td>1wt%</td>
<td>5%Pd/BaSO₄ (1wt%)</td>
<td>180</td>
<td>14%</td>
</tr>
<tr>
<td>DHN (22.5mL) THF (2.5mL)</td>
<td></td>
<td>N</td>
<td>1wt%</td>
<td>5%Pd/BaSO₄ (1wt%)</td>
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<td>60%</td>
</tr>
<tr>
<td>DHN (25mL)</td>
<td></td>
<td>N</td>
<td>1wt%</td>
<td>5%Pd/BaSO₄ (3wt%)</td>
<td>180</td>
<td>90%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>N</td>
<td>3wt%</td>
<td>5%Pd/BaSO₄ (3wt%)</td>
<td>180</td>
<td>20%</td>
</tr>
<tr>
<td>CHO (25mL)</td>
<td></td>
<td>Y</td>
<td>3wt%</td>
<td>5%Pd/BaSO₄ (3wt%)</td>
<td>180</td>
<td>0%</td>
</tr>
<tr>
<td>DHN (14mL) IPA (11mL)</td>
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<td>Y</td>
<td>3wt%</td>
<td>5%Pd/BaSO₄ (3wt%)</td>
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<td>0%</td>
</tr>
<tr>
<td>DHN (20mL) CHO (5mL)</td>
<td></td>
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<td>15%</td>
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<td>3wt%</td>
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<tr>
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<td>5%Rh/Al₂O₃ (1wt%)</td>
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<td>4%</td>
</tr>
<tr>
<td>DHN (15mL) IPA (10mL)</td>
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<td>5%Rh/Al₂O₃ (1wt%)</td>
<td>150</td>
<td>20%</td>
</tr>
</tbody>
</table>

All reactions were conducted with 750 psig H₂ pressure and 2500 rpm. The reaction time was 9 hours.

Solvent: DHN - decahydronaphthalene, THF - tetrahydrofuran, CHN - cyclohexanone, CHO - cyclohexanol, IPA - isopropanol

Solubility: Y - denotes that PC at the indicated concentration can be dissolved by the solvent or solvent mixture at the corresponding reaction temperature.

Solubility: N - denotes that PC at the indicated concentration can not be dissolved completely by the solvent or solvent mixture at the corresponding reaction temperature.

HD: the degree of hydrogenation of aromatic rings in PC

PC with a weight-average molecular weight of approximately 28,800 was obtained from Aldrich. 5%Pd/BaSO₄, DHN, THF and IPA were obtained from Aldrich. CHN and CHO were obtained from Acros Organics. 5%Rh/Al₂O₃ was obtained from Alfa Aesar.
Figure B.4 FTIR spectrum of poly(bisphenol A carbonate)
Figure B.5 FTIR spectrum of hydrogenated poly(bisphenol A carbonate)

References


