POLYSTYRENE HYDROGENATION IN SUPERCRITICAL CARBON DIOXIDE-EXPANDED DECAHYDRONAPHTHALENE

Laura Beth Dong[1], Ruben G. Carbonell[1], Douglas J. Kiserow[1,2], George W. Roberts[1,*]

[1] Department of Chemical and Biomolecular Engineering, North Carolina State University, Campus Box 7905,
Raleigh, NC 27695-7905, USA
[2] United States Army Research Office, P. O. Box 12211, Research Triangle Park, NC 27709-2211, USA

* To whom correspondence should be addressed: groberts@eos.ncsu.edu, Fax: 1 919-515-3465

ABSTRACT

The aromatic rings of polystyrene (PS) were hydrogenated in decahydronaphthalene (DHN) expanded with supercritical carbon dioxide ($scCO_2$). Conducting the hydrogenation in $scCO_2$-DHN offers the benefits of improved transport properties, specifically lower solution viscosity and a higher PS diffusion coefficient. Various Pd catalysts are effective for hydrogenating the aromatic rings of PS at temperatures in the region of 150°C. Typically hydrogen pressure is 800 psig. When 1250 psig CO_2 is added to the Pd-catalyzed PS hydrogenation system, carbon monoxide (CO), a catalyst poison, is formed via the reverse water-gas shift reaction (RWGSR).

Previously, when 5% $Pd/BaSO_4$ was used to hydrogenate PS in $scCO_2$-DHN, aromatic ring hydrogenation still occurred after 5 hours. In contrast, when either 5% Pd/SiO_2 or 5% Pd/Al_2O_3 is used, PS hydrogenation ceased within 15 minutes of the start of the reaction in $scCO_2$-DHN. Compared to the $Pd/BaSO_4$-catalyzed reaction, CO concentrations were on the order of 10-fold greater in the Pd/SiO_2 counterpart and 20-fold larger with the Pd/Al_2O_3 system. The dramatic increases in CO concentrations are believed to be a result of the accessibility of catalytic sites to H_2 and CO_2. In this research, only a fraction of the PS molecules are able to reach the active sites in the interior of the Al_2O_3 and SiO_2-supported catalysts. However, the smaller CO_2 and H_2 molecules can easily diffuse in and out of the catalysts' pores and react to form CO.

CO can be converted to methane using a Ni or Ru catalyst. Bimetallic catalyst systems containing Pd and a methanation catalyst were used to hydrogenate PS in $scCO_2$-expanded DHN. A physical mixture of catalysts reduced CO levels, but no dramatic increases in the degrees of PS hydrogenation were observed. A SiO_2 catalyst co-impregnated with Pd and Ru was effective for both PS hydrogenation in $scCO_2$-DHN and reduction of CO levels.

INTRODUCTION

Carbon dioxide-expanded liquids (CXLs) and supercritical carbon dioxide ($scCO_2$) have been used as reaction media [1, 2, 3]. Oftentimes, chemical reactions in CXLs or $scCO_2$ exhibit higher reaction rates, which are a result of the increased reactant diffusion coefficients and lower solution viscosity. The presence of CO_2 also offers a way to tune reaction conditions. Despite these favorable characteristics, there have been reports of losses of selectivity and catalyst poisoning in reactions in CXLs and $scCO_2$. For example, Minder et al. studied 5% Pt/Al_2O_3-catalyzed ethyl pyruvate hydrogenation at 35°C [4]. They reported the cessation of hydrogen consumption upon CO_2 addition to the reaction mixture. Their

Fourier transform infrared (FTIR) spectroscopy studies showed the formation of carbon monoxide (CO), a known catalyst poison.

Carbon monoxide is believed to be formed from the reverse water gas-shift reaction (RWGSR). Shown in Equation 1, CO_2 and hydrogen (H_2) react to yield water (H_2O) and CO.

$$CO_2 + H_2 \leftrightarrow CO + H_2O \tag{1}$$

A strategy to negate the effect of CO is to employ a methanation catalyst such as Ni or Ru to convert CO to methane (CH_4) through the methanation reaction shown in Equation 2.

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \tag{2}$$

In this research, the aromatic rings of polystyrene (PS) were hydrogenated in $scCO_2$-expanded decahydronaphthalene (DHN) using Al_2O_3 or SiO_2 supported-Pd catalysts. Previous research on PS-CO_2-DHN indicates that the presence of CO_2 results in a reduction in polymer solution viscosity [5] and increased polymer diffusion coefficients [6]. In prior studies, when a non-porous, 5% Pd/$BaSO_4$ catalyst was used to hydrogenate PS in $scCO_2$-DHN, catalyst poisoning occurred [7]. A mixture of 5% Pd/$BaSO_4$ and 65% Ni/SiO_2/Al_2O_3 was employed to successfully hydrogenate PS and convert the CO to CH_4 via the reaction shown in Equation 2. This work explores the use of Ru as part of the bimetallic catalyst system, as well as the effect of the catalyst preparation technique on PS ring saturation in $scCO_2$-expanded DHN.

MATERIALS AND METHODS

Materials.

Used as it was received, the 5% Pd/Al_2O_3 catalyst (Aldrich Chemical) has a BET surface area and pore volume of 89 m^2/g and 0.259 cm^3/g, respectively. Assuming a Pd/H ratio of 1, the dispersion of this catalyst was determined to be 75% by hydrogen chemisorption. The 5% Pd/SiO_2 catalyst was purchased from Strem Chemicals and used as received. Its BET surface area, pore volume, and dispersion were determined to be 233 m^2/g, 1.08 cm^3/g, and 76%. The 5% Ru/Al_2O_3 catalyst, which was purchased from Aldrich Chemical and used as received, has a BET surface area of 86 m^2/g, a pore volume of 0.277 cm^3/g, and a dispersion of 20% (assuming a Pd/H ratio of 1). The 65% Ni/SiO_2/Al_2O_3 was purchased from Aldrich Chemical and used as received.

The PS (Aldrich Chemical), which was used as received, has a weight average molecular weight (M_w) of 336 kDa and a polydispersity index of 1.5. Decahydronaphthalene (mixture of *trans* and *cis* isomers) was purchased from Aldrich Chemical and used as received. Air (zero grade), hydrogen (99.999% purity), nitrogen (99.999% purity), and carbon dioxide (Coleman grade) were supplied by National Welders.

Methods.

Catalyst Preparation A 2.0% Ru/4.9% Pd/SiO_2 catalyst was prepared by using the incipient wetness technique to impregnate the purchased 5% Pd/SiO_2 powder with an acidic, aqueous solution of ruthenium(III) chloride. The impregnated powder was dried overnight at 115°C, calcined in air at 500°C for 3 hours, and reduced for 2 hours at 327°C using H_2. The resulting Ru/Pd/SiO_2 catalyst has a BET surface area of 240 m^2/g and a pore volume of 0.872 cm^3/g.

Hydrogenation A 50 mL batch reactor equipped with vertical baffles and a dip tube was used to hydrogenate PS. After the reactor was loaded with catalyst and polymer solution, N_2 was used to purge the reactor. The reactor was then flushed with H_2 before being heated to the reaction temperature. The reactor was then pressurized with 800 psig H_2 before CO_2 was added to obtain the desired reaction pressure. The reactions were run at 150°C with an agitation rate of 2500 rpm. At the end of the reaction, the reactor was cooled to ambient temperature. The reactor gas was collected and drawn through a CO detection tube (Draeger, CO 10/b) by an accuro bellows pump (Draeger). The CO concentrations obtained with this technique are semi-quantitative since CO concentrations were relatively low. The product polymer solutions were filtered to remove the catalyst and then diluted with DHN. UV-VIS spectroscopy was used to measure the absorbance of the diluted solutions at 261.5 nm. From that information, the concentration of aromatic rings was calculated and used to determine the degree of aromatic ring hydrogenation (x_{PS}).

RESULTS

Figures 1 illustrates the effect of CO_2 on PS hydrogenation catalyzed by 5% Pd/Al_2O_3. High aromatic ring conversions were achieved when there was no CO_2 in the system. When CO_2 was present, hydrogenation appeared to cease after a very short time, and CO concentrations neared 1000 ppm.

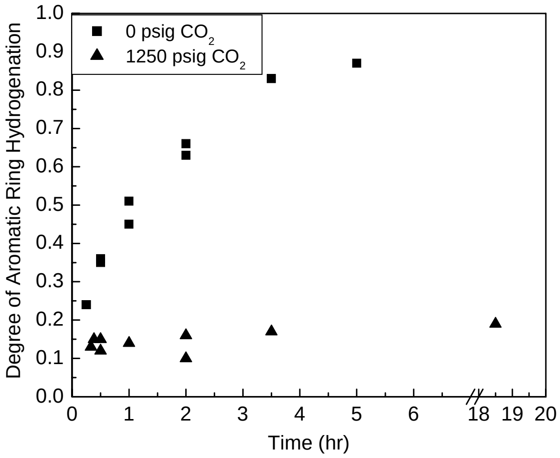

Figure 1: Effect of CO_2 on Pd/Al_2O_3-Catalyzed PS Hydrogenation (T=150°C, 3 wt% PS-DHN, 800 psig H_2, 2500 rpm, 1 g catalyst/g PS)

These results are not surprising in view of previous research. Burgener and co-workers studied the reaction of 1 mol% H_2 with $scCO_2$ over Al_2O_3-supported noble metals [8]. Their attenuated total reflection infrared (ATR-IR) spectroscopy results showed CO peaks when supported Pt, Pd, Ru, or Rh was the catalyst. At 50°C, there appeared to be more CO formation on the Pt and Pd catalysts than on the Ru or Rh counterparts. Arunajatesan et al. used FTIR to monitor the RWGSR under supercritical conditions on neat Al_2O_3 and Al_2O_3-supported Pd, Ru, and Ni at 70°C [9]. They found that CO formed when Pd/Al_2O_3 was in the presence of CO_2 and H_2 (in a molar ratio of CO_2:H_2=19), but no traceable amounts of CO were detected when Ni/Al_2O_3 or Ru/Al_2O_3 was used.

Ideally, a reduction of CO levels by methanation should result in aromatic ring conversions returning to relatively high levels. While Ni and Ru both have aromatic ring hydrogenation abilities, their use also results in significant, undesirable polymer backbone scission. Therefore, like the previous 65% $Ni/SiO_2/Al_2O_3$-5% $Pd/BaSO_4$ studies, 65% $Ni/SiO_2/Al_2O_3$ or 5% Ru/Al_2O_3 was mixed with Pd/Al_2O_3 to hydrogenate PS in a Pd/(Ni or Ru) ratio of 2.5 g/g. Despite the significantly reduced CO levels shown in Table 1, catalyst deactivation still occurred since aromatic ring hydrogenation did not greatly improve. The inability to achieve similar degrees of ring hydrogenation in neat and $scCO_2$-DHN contrasted with the results observed with the 65% $Ni/SiO_2/Al_2O_3$-5% $Pd/BaSO_4$ system.

Table 1: PS Hydrogenation Using 5% Pd/Al_2O_3

Catalyst	CO_2 (psig)	x_{PS}	CO (ppm)
5% Pd/Al_2O_3	0	0.66	---
	1250	0.16	1000
5% Pd/Al_2O_3 + 65%Ni/SiO_2/Al_2O_3	1250	0.21	90
5% Pd/Al_2O_3 + 5% Ru/Al_2O_3	1250	0.43	4

T=150°C, 2 hr., 3 wt% PS-DHN, 800 psig H_2, 2500 rpm, 1 g catalyst/g PS, Pd/(Ni or Ru)=2.5 g/g

One possible explanation for this difference is the contribution of the support material to the RWGSR. Solymosi and co-workers demonstrated that the adsorption of a CO_2/H_2 mixture (1:1) onto Pd/Al_2O_3 was over two-fold greater than the mixture's adsorption onto Pd/SiO_2 at 100°C [10]. As shown in Figure 2, the 5% Pd/SiO_2 catalyst is quite effective for aromatic ring hydrogenation. In fact, if the 0 psig CO_2 data from Figures 1 and 2 are compared, the 5% Pd/SiO_2-catalyzed ring saturation is faster than its 5% Pd/Al_2O_3 counterpart. Like the 5% Pd/Al_2O_3-catalyzed reaction, the presence of CO_2 results in an asymptotic degree of hydrogenation.

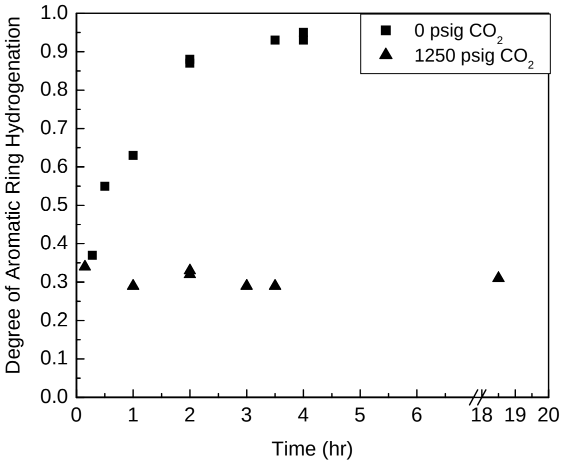

Figure 2: Effect of CO_2 on Pd/SiO_2-Catalyzed PS Hydrogenation (T=150°C, 3 wt% PS-DHN, 800 psig H_2, 2500 rpm, 1 g catalyst/g PS)

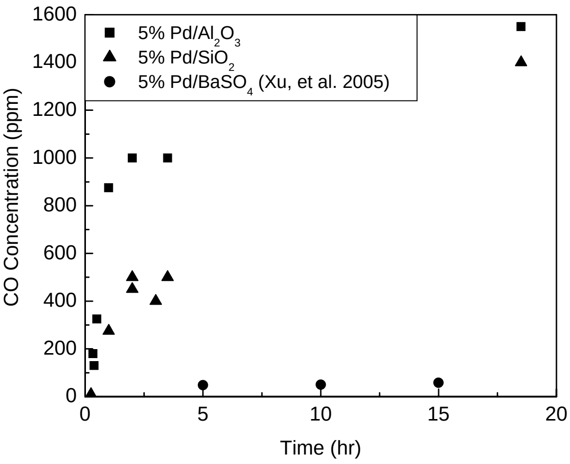

Figure 3: CO Evolution During PS Hydrogenation (T=150°C, 3 wt% PS-DHN, 800 psig H_2+1250 psig CO_2, 2500 rpm, 1 g catalyst/g PS)

Interestingly, as demonstrated in Figure 3, CO concentrations in the 5% Pd/SiO_2 system are between the levels measured in the 5% Pd/Al_2O_3 and 5% Pd/$BaSO_4$ counterparts. CO levels in the reaction catalyzed by 5% Pd/Al_2O_3 are roughly two times greater than the concentrations for the same system catalyzed by 5% Pd/SiO_2. The results shown in Figure 3 support the theory that the RWGSR occurs. The CO concentrations are also reflective of Solymosi et al.'s claim of catalyst support effects on CO_2/H_2 adsorption.

In an effort to lower CO levels and increase PS hydrogenation, supported Ni and Ru catalysts were mixed with 5% Pd/SiO_2 to hydrogenate PS in CO_2-DHN. As shown in Table 2, the addition of 5% Ru/Al_2O_3 was effective in reducing CO concentration, but only a marginal increase in PS hydrogenation was observed. The addition of 65% Ni/SiO_2/ Al_2O_3 catalyst did not appear to have any effect on either the aromatic ring saturation or CO levels. Like the bimetallic systems containing 5% Pd/Al_2O_3, their 5% Pd/SiO_2-containing counterparts were ineffective in hydrogenating PS in the presence of CO_2-DHN.

Table 2: PS Hydrogenation Using 5% Pd/SiO_2

Catalyst	CO_2 (psig)	x_{PS}	CO (ppm)
5% Pd/SiO_2	0	0.88	---
	1250	0.32	500
5% Pd/SiO_2 + 65% Ni/SiO_2/Al_2O_3	1250	0.29	500
5% Pd/SiO_2 + 5% Ru/Al_2O_3	1250	0.36	14

T=150°C, 2 hr., 3 wt% PS-DHN, 800 psig H_2, 2500 rpm, 1 g catalyst/g PS, Pd/(Ni or Ru)=2.5 g/g

One striking difference between the currently studied catalysts and 5% Pd/$BaSO_4$ is the structure of the supports. The $BaSO_4$ is essentially non-porous while the 5% Pd/Al_2O_3 and 5% Pd/SiO_2 have average pore diameters of 25 nm and 18 nm, respectively. Based on dynamic light scattering measurements, the hydrodynamic radius of the PS coils should be in the neighborhood of 18 nm at 150°C. Therefore, their sizes should exclude some of them from the inside of the 5% Pd/Al_2O_3 and 5% Pd/SiO_2 catalysts. This leaves the interiors accessible to CO_2 and H_2, which then react to form CO. The CO then deactivates catalytic sites for ring hydrogenation and diffuses out of the porous catalyst. Carbon monoxide is eventually reduced by the methanation catalyst, but it has already poisoned the Pd sites.

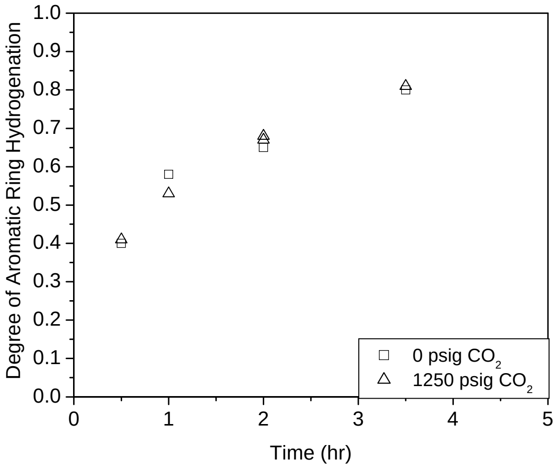

Figure 4: Effect of CO_2 on Ru/Pd/SiO_2-Catalyzed PS Hydrogenation (T=150°C, 3 wt% PS-DHN, 800 psig H_2, 2500 rpm, 1 g catalyst/g PS)

A SiO_2 catalyst co-impregnated with Pd and Ru was synthesized in an effort to prevent the CO poisoning that was not eliminated by the bimetallic physical catalyst mixtures. As shown in Figure 4, the 2% Ru/4.9% Pd/SiO_2 can successfully hydrogenate PS in both neat and CO_2-expanded DHN. In fact, the degrees of ring hydrogenation in the two environments are comparable. No CO was detected. The detrimental affect of the RWGSR reaction appears to be negated by the synergistic effect of Pd and Ru being present on the same support.

CONCLUSIONS

At 150°C, PS hydrogenation catalyzed by 5% Pd/Al_2O_3 or 5% Pd/SiO_2 occurs at reasonable rates. However, the presence of scCO_2 results in the unwanted reverse water-gas shift reaction. The CO product deactivates the catalyst, and hydrogenation ceases after a very short time. CO levels were consistently higher when the 5% Pd/Al_2O_3 catalyst was used. A physical mixture of 65% Ni/SiO_2/Al_2O_3 or 5% Ru/Al_2O_3 with either Pd catalyst reduces CO concentrations, but no drastic improvements in PS hydrogenation were observed. However, when the methanation component is located on the same support as Pd, PS hydrogenation in scCO_2-DHN yields similar degrees of hydrogenation as the reaction in neat DHN. This research demonstrates that PS hydrogenation can benefit from using scCO_2 if a bimetallic catalyst of 2% Ru/4.9% Pd/SiO_2 is used.

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