

Evaluation of Polymer-Supported Rhodium Catalysts in 1-Octene Hydroformylation in Supercritical Carbon Dioxide

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Supercritical CO₂ has been used as a benign solvent in the hydroformylation of 1-octene using a Rh-based catalyst. The catalyst is attached to a polymer backbone that has fluoroacrylate branches that make it soluble in supercritical CO₂. Quantitative solubility determinations of catalyst precursors and the catalyst were carried out at 318.15 K and 172.4 bar. The catalyst was evaluated in the hydroformylation reaction of 1-octene at 323.15 and 348.15 K and 172.4 and 241.3 bar. Results showed that the reaction rate is enhanced by pressure at constant temperature. The catalyst was evaluated for intact recovery after reaction using an arlcite filter. Hydrogenation of 1-octene was the model reaction. A total of 20 reaction cycles were performed in the batch mode with no decrease in activity and no Rh leaching.

Introduction

Hydroformylation of olefins is the oldest and largest-volume industrial homogeneous reaction employing organometallic catalysts. Hydroformylation products include linear and branched aldehydes and are formed by the insertion of H₂ and CO to a double bond. Hydroformylation chemistry is used in the production of aldehydes and alcohols. Aldehydes are commercially important products for the fabrication of plasticizers, surfactants, and detergents. Commercial hydroformylation processes involve a homogeneous catalyst soluble in a suitable solvent. Homogeneous catalysts are preferred because of their selectivity, reactivity, and stability.

Hydroformylation (the oxo reaction) is usually carried out in the liquid phase with Co- or Rh-based catalysts. Reaction conditions depend on the catalyst metal. Because of environmental regulatory restrictions, different attempts have been made in order to replace the toxic organic solvents employed in homogeneous catalysis. The most common benign solvent is supercritical carbon dioxide (scCO₂). It is nonflammable, inert, and inexpensive, is readily available at high purity, and has low critical properties. Another advantage of using scCO₂ as a solvent is its complete miscibility with gases such as H₂ and CO, eliminating problems associated with mass-transfer limitations when the reaction is carried in a liquid. There has been an increasing interest in homogeneous catalysis using scCO₂ as an environmentally benign solvent in recent years. Several groups have investigated the homogeneously catalyzed hydroformylation of olefins in scCO₂. The pioneering work of Rathke et al.¹ was on the hydroformylation of propylene using a Co catalyst in scCO₂. Additionally, scCO₂ has been proven to affect reaction rates and selectivity. Guo

and Akgerman^{2,3} showed that selectivity can be doubled at constant temperature by changing the pressure for the hydroformylation of propylene in scCO₂ using a Co catalyst.

Bach and Cole-Hamilton⁴ reported the use of triethylphosphine complexes for the hydroformylation of 1-hexene in scCO₂. A slight improvement in regioselectivity was obtained compared to the reaction carried out in an organic solvent. They also reported traces of isomerized alkenes, and a maximum turnover frequency (TOF) of ca. 50 was obtained. Lin and Akgerman⁵ reported the hydroformylation of styrene in scCO₂ using a Rh-complex catalyst and showed that the reaction rate and regioselectivity can be tuned by changing the pressure at constant temperature. High activity and selectivity were reported in the hydroformylation of 1-hexene in scCO₂ using rhodium complexes prepared in situ.⁶ However, low TOFs were reported along with isomerization and linear-to-branched product ratios of 5. A fluorinated polymeric phosphine and [Rh(acac)(CO)₂] were used in the hydroformylation of acrylates.⁷ This catalyst showed high chemoselectivity to alkyl acrylates compared to olefin, in which hydroformylation was nil. When the reaction was carried out in organic solvents, the reaction was ca. 5 times slower than that in scCO₂. The fluorinated tag demonstrated its effectiveness in the solubility of arylphosphines that are usually sparingly soluble in scCO₂. Extensive work has been reported by Erkey's group on the hydroformylation of 1-octene in scCO₂. Palo and Erkey⁸ reported the synthesis of a fluorinated catalyst of the conventional catalyst *trans*-RhCl(CO)(PPh₃)₂. The new catalyst *trans*-RhCl(CO)-[P(*p*-CF₃C₆H₄)₃]₂ exhibited moderate solubility in scCO₂ of 5.5 mM (*T* = 343 K; *P* = 273 atm; ρ = 0.77 g/mL) and was active for the hydroformylation of 1-octene. Selectivity for nonanal was 2.4, and negligible hydrogenation or isomerization was observed. Later, Palo and Erkey^{9,10} reported the synthesis and evaluation of the complex RhH(CO)[P(*p*-CF₃C₆H₄)₃]₃ in the hydroformylation of 1-octene. This complex exhibited a solubility of 7.6 mM (*T* = 323 K; *P* = 273 atm) and did not produce isomerization or hydrogenation products with an *n*/*iso* ratio of 3.0. By using this Rh complex, the total pressure

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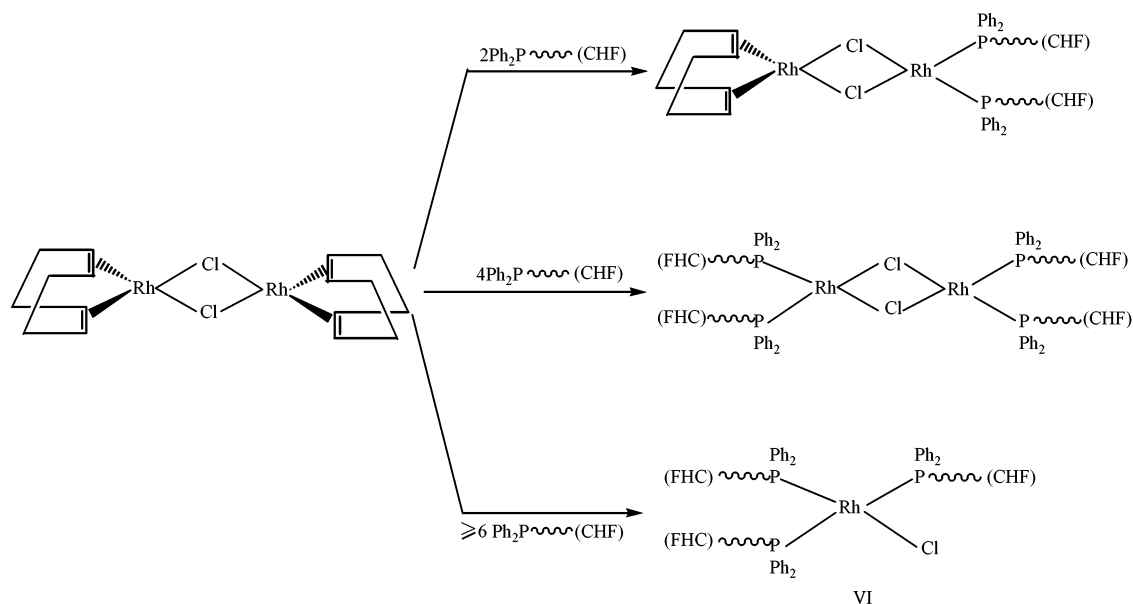


Figure 1. Catalyst structures. Structure VI is the most probable.

did not show any effect on the reaction rate or selectivity at constant initial concentrations, in contrast with the results reported by Guo and Akgerman^{2,3} using a Co catalyst and by Lin and Akgerman⁵ using a Rh catalyst.

Recently, Palo and Erkey¹¹ published their research on the synthesis of fluoroalkyl- and fluoroalkoxy-substituted tertiary arylphosphines in the hydroformylation reaction of 1-octene in scCO_2 . In this study, the *n*/*iso* ratio was 3 for most of the ligands but the activity differed significantly according to the extent and location of the fluoroalkyl or fluoroalkoxy substitution on the phosphines.

Another problem in homogeneous catalysis is the intact recovery of the catalyst after completion of the reaction. Different approaches have been used in order to recover the catalyst intact after completion of the homogeneous reaction. Koch and Leitner¹² used the properties of scCO_2 to selectively extract the hydroformylation products by changing the temperature and pressure. The aldehydes contained less than 1 ppm of rhodium, and the catalyst was reused. Kainz et al.¹³ reported the selective extraction in the hydrogenation of imines in scCO_2 . The metal content in the collected product by atomic absorption spectroscopy was below 5 ppm. For four subsequent experiments, identical hydrogenation results were obtained, although for subsequent cycles, longer reaction times were required to achieve similar enantiomeric excess. Another approach has been to use insoluble catalysts. Sellin and Cole-Hamilton⁶ reported on insoluble rhodium complexes prepared in situ in the hydroformylation reaction of 1-hexene in scCO_2 . By flushing of the reactor with scCO_2 , catalyst-free products were collected and no Rh was detected ($<0.01\%$ of Rh charged). The catalyst activity remained similar in three consecutive runs, and in the two later runs, the linear-to-branched ratio decreased. It was found that the catalyst was hydrolyzed during the reaction.

Attempts have been made in the recovery of the catalyst using heterogeneous catalysts. Rhodium on activated carbon¹⁴ and Rh and Fe on unmodified and modified silica catalysts¹⁵ using scCO_2 as a solvent in the hydroformylation reaction of propylene have been reported. It was found that rhodium supported on

activated carbon was active for the hydroformylation reaction but not selective, and for the second study, the conversion varied from 1.4 to 13% depending on the support and Rh leaching was observed.

In this study, we are using a recoverable soluble rhodium catalyst. The catalyst is attached to a high molecular weight polymer. Because the catalyst is grafted to a fluoroacrylate copolymer backbone, it can be easily recovered by using a membrane reactor. In this work we present the hydroformylation reaction of 1-octene in scCO_2 using this polymer-supported rhodium catalyst. We synthesized a Wilkinson's analogue catalyst. The polymer contains long fluoroacrylates branches, which provide solubility in scCO_2 .

Experimental Section

The catalyst synthesis has been previously reported in the literature.¹⁶ The structure of the catalyst is shown in Figure 1. The dominating structure depends on the proportion of catalyst synthesis reactants. We reported on excellent reproducibility in the synthesis of the catalyst by running hydrogenation of 1-octene in scCO_2 with different batches of the same catalyst.¹⁷ Brazos Valley Welding Supply provided CO_2 at 99.99% minimum purity and hydrogen at 99.8% purity, and an equimolar mixture of H_2/CO was provided by Trigas Industrial Gases. Olefins were purchased from Sigma and used as received.

Hydroformylation was carried out in a 100-mL reactor. The experimental setup has been previously described.¹⁷ Before a typical experiment, blank reactions were performed to ensure complete cleanness of the reactor (no conversion). Experiments were performed at two different pressures and two temperatures, and the mole fraction of the reactants was kept constant in all experiments.

For the intact recovery of the catalyst, several cycles of the hydrogenation of 1-octene were carried out. Hydrogenation was preferred over hydroformylation because it is a simpler reaction with only three products that are well identified. The reaction was studied in a 100-mL reactor depicted in Figure 2. A custom-manufactured filter by Filtros Limited was used to recover

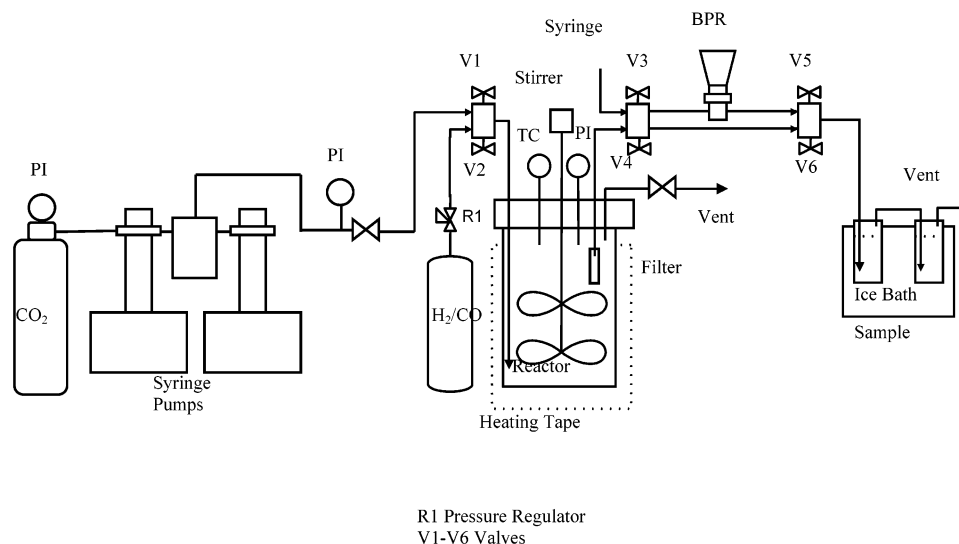


Figure 2. Schematic representation of the experimental setup for the intact recovery of the catalyst in the hydrogenation of 1-octene in scCO_2 .

the catalyst. The filter was a porous arlcite tube of $\frac{1}{4}$ in. length \times $\frac{1}{4}$ in. o.d. \times $\frac{1}{8}$ in. i.d. \times $\frac{1}{8}$ in. depth with one closed end. The probable nominal particle retention is $0.2 \mu\text{m}$, and the maximum pore diameter is $5 \mu\text{m}$. The arlcite tube was attached to a $\frac{1}{8}$ in. stainless steel tubing and located inside the reactor. The reactor was thoroughly cleaned, and a blank run was performed to ensure complete cleanness. The catalyst was weighed and placed in the high-pressure vessel. The reactor was closed and flushed several times with CO_2 and then with H_2 . After several flushes, the reactor was believed to be air-free. The reactor was kept under H_2 overnight at 34.5 bar. The hydrogen was then released, the desired amount of 1-octene was injected into the reactor through one of the openings, and the desired amount of hydrogen was fed to the reactor to get a molar ratio of H_2 /1-octene of 30. Then CO_2 was fed to the reactor using an ISCO model 260 syringe pump up to a pressure below the operating pressure. The temperature was then increased using a heating tape, and stirring was initiated at 1600 rpm. When the temperature was approximately 10 K or less than the desired temperature, additional CO_2 was pumped, and the final adjustment was made when the desired reaction temperature was reached. After 24 h of reaction, the sample was taken using a double-valve system (V4 and V6 in Figure 2). Opening and closing valve V4 trapped the supercritical fluid mixture in a loop of 1 mL (27 cm length \times 3.18 mm o.d.). The pressure was then released slowly by manually opening valve V6, and the effluent was bubbled through two bottles that contained hexane to trap the unreacted 1-octene and products. The sample bottles were immersed in an ice bath. After complete depressurization of the loop, the samples were analyzed in a HP 5890 gas chromatograph with a flame ionization detector. The column 5% phenylpolysiloxane (30 m length \times 0.53 mm i.d. \times 1.50 μm FT) phase ZB5 was used. The amounts of unreacted 1-octene and products were determined, and the reaction conversion was calculated. After taking the sample, the reactor was cooled to room temperature. In this process, the pressure went down to 68.9–75.8 bar. Then, the reactor was depressurized to 34.5 bar, and CO_2 was added to the reactor at a constant flow rate of 50 mL/h controlled by the ISCO 260D pump controller. During this step, the pressure was regulated using a spring-hold backpressure regulator (TESCOM

Table 1. Quantitative Solubility at 318.15 K and 172.4 bar

polymer/catalyst	wt %
TAN ₁₀ NASI	6.8×10^{-3}
TAN ₂₀ NASI	26.5×10^{-3}
1:3 Rh(TAN ₂₀ DPPA)Cl	31.4×10^{-3}

series 26-1700). Samples were taken at different time intervals until no reactant and/or products were detected in the effluent by the gas chromatograph. Typically, the time for complete cleaning of the reactor was around 24 h. When cleaning was complete, the reactor was pressurized with hydrogen to 34.5 bar and kept there overnight. Then, the reactor was depressurized, and fresh 1-octene was charged to the reactor using one of the openings. The next cycle was started by pressurizing and heating the reactor. In this way, different cycles were performed with the same catalyst.

Results and Discussion

Quantitative solubility determinations in scCO_2 were carried out in an experimental setup similar to that developed by Sherman et al.¹⁸ To verify the reliability of the experimental setup, the solubility of phenanthrene in scCO_2 , for which there are much accurate data by different investigators, was determined. Results were satisfactory. In Table 1, the results obtained using this gravimetric technique for the polymers TAN₁₀NASI and TAN₂₀NASI and the catalyst Rh(TAN₂₀DPPA)Cl with a Rh/polymer ratio of 1:3 are shown. As can be seen, the solubility of the polymer with more fluoroacrylate branches, TAN₂₀NASI, is 4 times greater than the solubility of the polymer TAN₁₀NASI as expected. Also, it can be seen that the solubility of the catalyst 1:3 Rh(TAN₂₀DPPA)Cl is similar to that of its precursor, the polymer TAN₂₀NASI. This may look like it is in contrast to the possible cross-linking that Rh is inducing in the catalyst. However, it is quite possible that the Rh is attached to phosphines from different polymer chains. This is more likely when the polymer precursor of the catalyst has a high ratio of fluoroacrylates (TAN) to DPPA, such as in the case of the polymer with a TAN/DPPA ratio of 20:1. Additionally, this quantitative technique relies on the ability of measuring accurate weight differences and is subject to experimental error.

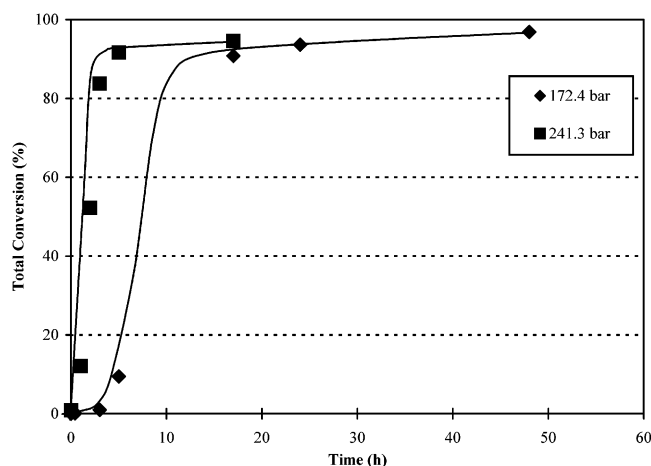


Figure 3. Effect of pressure on the hydroformylation of 1-octene in scCO_2 using catalyst 1 at 323.15 K. 1-Octene initial mole fraction: 1.29×10^{-3} . 1-Octene/Rh molar ratio: 500.

However, Palo and Erkey⁹ reported a solubility value of the same order of magnitude for the catalyst $\text{HRh}(\text{CO})[\text{P}(p\text{-CF}_3\text{C}_6\text{H}_4)_3]_3$ (in the reaction mixture) at higher densities of scCO_2 . This is the most soluble homogeneous catalyst reported to date in pure scCO_2 .

For the evaluation of the catalyst activity in the hydroformylation of 1-octene, a catalyst with a Rh/polymer ($\text{TAN}_{13}\text{DPPA}$) ratio of 1:3 was used. Two different batches were prepared with the Rh content of 3.74 (catalyst 1) and 4.56 mg of Rh/g of catalyst (catalyst 2). The rhodium content was determined by neutron activation analysis at the Center for Chemical Characterization & Analysis at Texas A&M University. Results showed less than 1% error. Catalysts 1 and 2 were evaluated in the hydroformylation of 1-octene in scCO_2 . The effect of pressure at 323.15 K is shown in Figure 3 with catalyst 1. The molar ratio of 1-octene to rhodium was 500 for both experiments. The mole fraction of reactants was kept constant in all experiments to evaluate the pressure effect. Because the reactor was a batch reactor, different amounts of substrate were added in order to keep the mole fraction constant; that is, at higher pressures more substrate was added. As can be seen in Figure 3, faster conversion is obtained at 241.3 bar than at 172.4 bar.

We also studied the reaction at 348.15 K, the results of which are shown in Figure 4. Catalyst 2 was used for this purpose. For the reaction carried out at 172.4 bar, 400 mol of 1-octene/mol of rhodium was used, and for the experiment at 241.3 bar, 500 mol was used. As can be seen again, the reaction is enhanced by pressure. Kainz et al.¹⁹ reported the use of a triphenylphosphate analogue in the hydroformylation reaction of 1-octene in scCO_2 . The absence of side reactions, hydrogenation, or isomeric aldehydes was observed. Figure 5 shows the product distribution at 323.15 K and 241.3 bar; similar distributions were obtained at all conditions.

An empirical expression was used to fit the experimental data of the hydroformylation of 1-octene:²⁰

$$r = k[\text{substrate}][\text{catalyst}] \frac{p(\text{H}_2)}{p(\text{CO})}$$

where k is the rate constant, $[\text{substrate}]$ is the substrate concentration, $[\text{catalyst}]$ is the catalyst concentration, $p(\text{H}_2)$ is the hydrogen partial pressure, and $p(\text{CO})$ is the carbon monoxide partial pressure. This expression

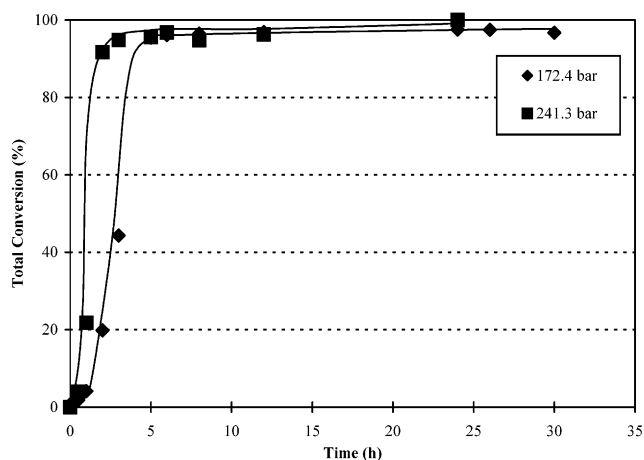


Figure 4. Effect of pressure on the hydroformylation of 1-octene in scCO_2 using catalyst 2 at 348.15 K. 1-Octene initial mole fraction: 1.29×10^{-3} . 1-Octene/Rh molar ratio: 400 at 172.4 bar and 500 at 241.3 bar.

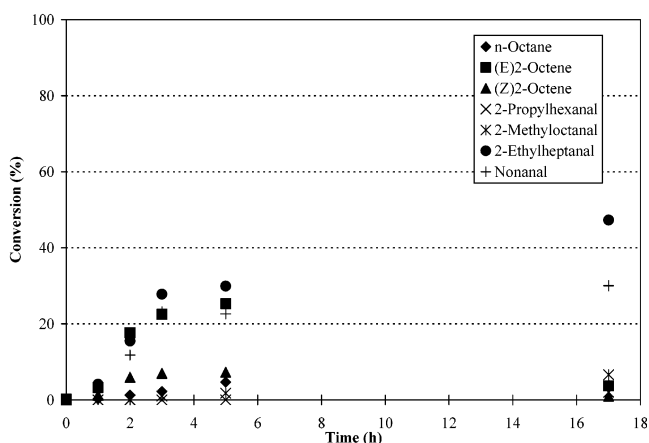


Figure 5. Product distribution at 323.15 K and 241.3 bar.

Table 2. Parameter Estimation in the Hydroformylation Reaction of 1-Octene in ScCO_2 Using SimuSolv

experiment	k'	standard deviation
323.15 K and 172.4 bar	0.15	1.877×10^{-2}
323.15 K and 241.3 bar	0.70	5.709×10^{-2}
348.15 K and 172.4 bar	0.748	4.153×10^{-3}
348.15 K and 241.3 bar	1.211	8.799×10^{-3}

proved to be valid for Co- and Rh-based catalysts.^{3,20} We evaluated this empirical rate expression for the reaction carried out in scCO_2 . Because the ratio of hydrogen and carbon monoxide was 1 in all experiments and the same amount of catalyst was used, the rate of reaction can be rewritten as a pseudo-first-order expression:

$$r = k'[\text{substrate}]$$

where

$$k' = k[\text{catalyst}] \frac{p(\text{H}_2)}{p(\text{CO})}$$

A modeling and simulation software (SimuSolv) was used for parameter estimation of the pseudo-first-order expression. In Table 2, the parameters obtained with SimuSolv that best agree with the experimental data are shown. In Figures 6–9, the experimental data and the prediction using the parameters shown in Table 2

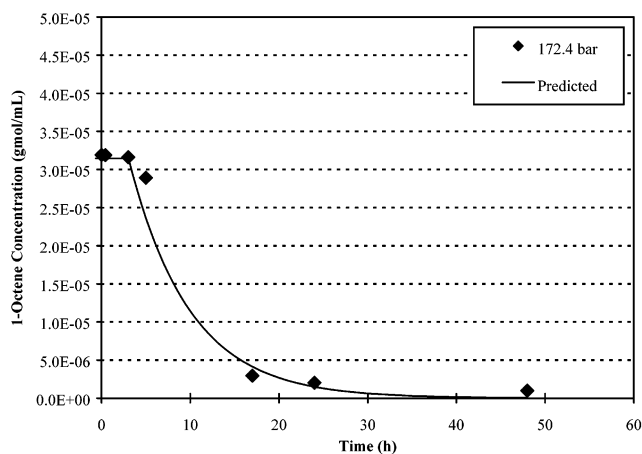


Figure 6. Predicted values in the hydroformylation of 1-octene in scCO_2 at 323.15 K and 172.4 bar.

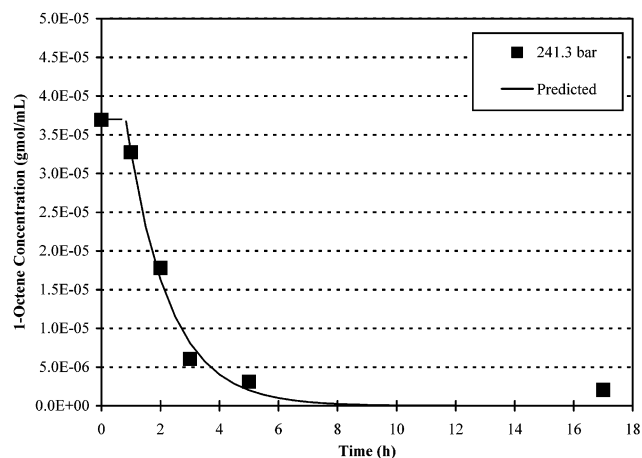


Figure 7. Predicted values in the hydroformylation of 1-octene in scCO_2 at 323.15 K and 241.3 bar.

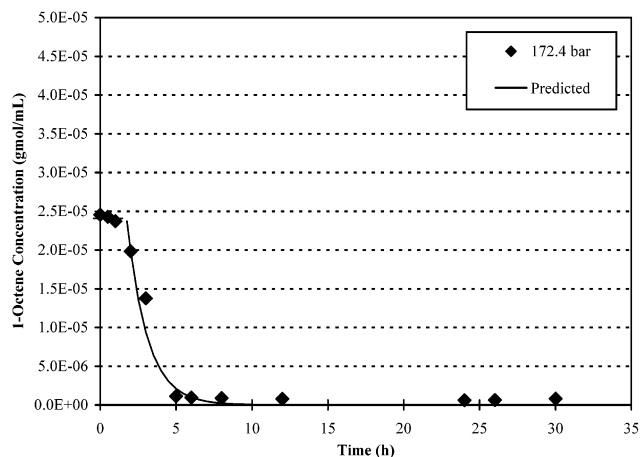


Figure 8. Predicted values in the hydroformylation of 1-octene in scCO_2 at 348.15 K and 172.4 bar.

are shown. As can be seen in the figures, an induction period is observed at most reaction conditions. The induction period is less evident at higher pressures and temperatures. The induction period for the hydroformylation of terminal olefins in conventional solvents using rhodium-based catalysts has been reported.²¹ This substrate inhibition has been attributed to inactive species that form at high substrate/rhodium concentrations.²² In using scCO_2 as a solvent, this behavior has also been reported. Palo and Erkey⁸ reported a significant induction period in the hydroformylation of 1-octene

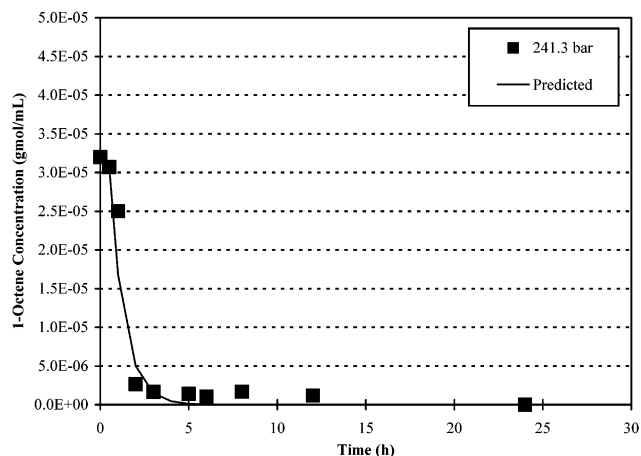


Figure 9. Predicted values in the hydroformylation of 1-octene in scCO_2 at 348.15 K and 241.3 bar.

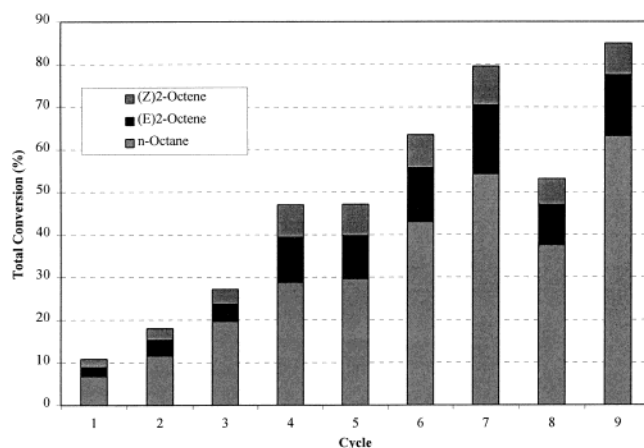


Figure 10. Hydrogenation of 1-octene in scCO_2 at 343.15 K and 172.4 bar using the arlcite filter for the intact recovery of the catalyst. Catalyst: 1:3 $\text{Rh}(\text{TAN}_{20}\text{DPPA})\text{Cl}$ with 2.16 mg of Rh/g of catalyst.

using the catalyst $\text{trans-RhCl}(\text{CO})[\text{P}(p\text{-CF}_3\text{C}_6\text{H}_4)_3]_2$. The rate constants given in Table 2 are fitted by taking this induction period into consideration. Palo and Erkey reported a kinetic expression for a Rh-complex catalyst in the hydroformylation of 1-octene in scCO_2 .⁹ The rate expression determined differs significantly from the rate expressions developed for reactions in organic solvents. The most significant difference was the ~ 0.5 order rate dependence on the hydrogen concentration and the lack of substrate inhibition.

For the intact recovery of the catalyst, 0.1771 g of the catalyst $\text{Rh}(\text{TAN}_{20}\text{DPPA})\text{Cl}$ with a rhodium/polymer ratio of 1:3 (2.16 mg of rhodium/g of catalyst) was used in the first experiment. The hydrogen/1-octene molar ratio was 30, and the substrate/rhodium molar ratio was 400. The cycles of hydrogenation were carried out at 343.15 K and 172.4 bar for 24 h. Figure 10 presents the total conversion of these experiments. The bars represent the total conversion; hydrogenation products and isomerization products were detected and are marked to differentiate them. Nine cycles were performed with no decrease in the activity of the catalyst until cycle number 8. In these experiments, the total conversion increased gradually, and the maximum total conversion achieved was 85% in the 9th cycle.

In Figure 11, the total conversion of the hydrogenation of 1-octene is shown. A total of 0.2024 g of the catalyst 1:3 $\text{Rh}(\text{TAN}_{13}\text{DPPA})\text{Cl}$ with 2.3 mg of rhodi-

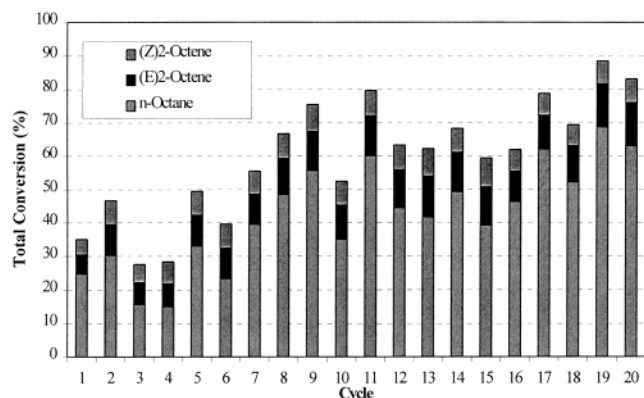


Figure 11. Hydrogenation reaction of 1-octene in scCO_2 at 343.15 K and 172.4 bar using the arlcite filter for the intact recovery of the catalyst. Catalyst: 1:3 Rh(TAN₁₃DPPA)Cl with 2.3 mg of Rh/g of catalyst.

um/g of catalyst was used. A total of 1.7879 mmol of 1-octene was charged to the reactor, and the reactions were carried out at 343.15 K and 172.4 bar. A total of 400 mol of substrate/mol of rhodium and a molar ratio of hydrogen/1-octene of 30 were used. All reactions were performed for 24 h. This catalyst with a different polymer gave a total conversion of 35% in the first cycle. The total conversion increased gradually with the cycles. After the 20th cycle, the reactor was opened and the catalyst recovered using freon. Approximately 0.0288 g of catalyst was recovered (9.33%). This recovery task was difficult to perform in this large-volume reactor with many moving parts. Samples taken in the 1st and 19th cycles were analyzed for rhodium content by neutron activation analysis. No trace of rhodium in the effluent was found.

We had concerns about a possible hydride–iron–phosphine species acting as a catalyst in the hydrogenation of 1-octene in scCO_2 . To test the hypothesis, the polymer containing the phosphine groups was used. Blank reactions were performed. A total of 0.2029 g of the polymer TAN₁₃DPPA was used. The molar ratios of substrate/rhodium and hydrogen/1-octene were the same as those in the previous experiments. A total of 280 μL of 1-octene (1.788 mmol) was injected using a syringe. Then, the reactor was charged with 13.1 bar of hydrogen at room temperature. The reactor was heated and pressurized with CO_2 . The reaction preceded 24 h at 343.15 K and 172.4 bar. Samples were collected using hexane. Gas chromatographic analysis showed a 0.7% total conversion for this first cycle. The cycle was repeated for the second time, and a conversion of $\sim 1\%$ was observed. Negligible conversion was obtained in both cycles using the polymer TAN₁₃DPPA under identical reaction conditions as the catalysts. Therefore, no hydride–iron–phosphine species was active in the hydrogenation reaction of 1-octene. At this point, there is no explanation for the increase in the activity of the catalyst with the number of cycles. It might be possible that some structural modification to the polymer occurs during the exposure to scCO_2 and during expansion and pressurization cycles that makes more active sites accessible to the substrate.

In summary, we have demonstrated that a Rh-polymer bound catalyst was active in the hydroformylation reaction of 1-octene in scCO_2 at the reaction conditions studied. To date, this catalyst is the most soluble used in pure scCO_2 at 318.15 K and 172.4 bar. Also, the polymer bound catalyst was recycled up to 20

times with no loss in activity in the hydrogenation reaction of 1-octene. Activity increased with the number of cycles. We do not have a complete explanation for this behavior but believe that it is possible that during expansion and pressurization processes the catalysts grafted to a polymer undergo some structural modifications that make active sites more accessible. This also might be accomplished by prolonged exposure to scCO_2 .

Acknowledgment

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