

# POLYMER SUPPORTED HOMOGENEOUS CATALYSTS FOR REACTIONS IN SUPERCRITICAL CARBON DIOXIDE

A. Akgerman<sup>1\*</sup>, R. Flores<sup>1</sup>, Z. K. Lopez-Castillo<sup>1</sup>, I. Kani<sup>2</sup>, and J. P. Fackler, Jr.<sup>2</sup>

<sup>1</sup> Chemical Engineering Dept., <sup>2</sup>Department of Chemistry  
Texas A&M University, College Station, TX 77843

Email: [a-akgerman@tamu.edu](mailto:a-akgerman@tamu.edu), Fax: (979)-260-9197

## Introduction

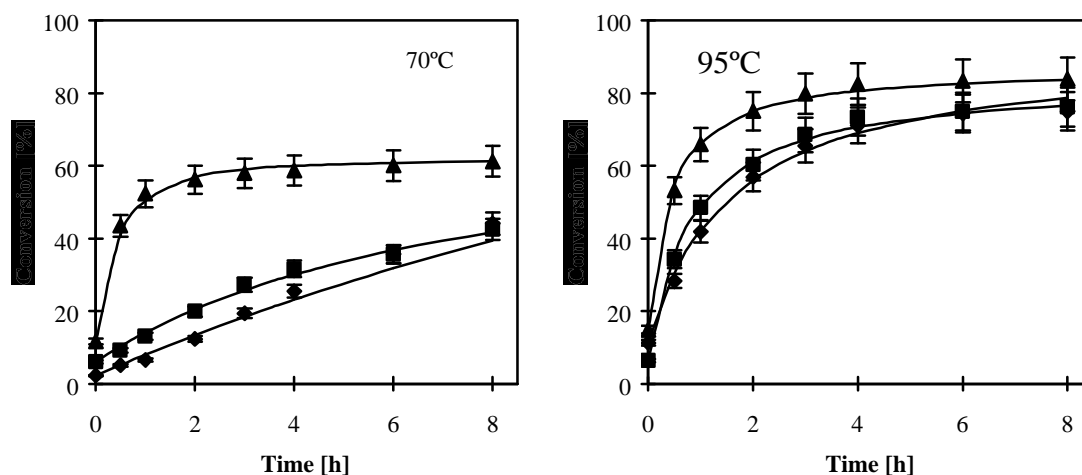
Organometallic catalysts in homogeneous media offer high reactivity, selectivity, and tunability. Supercritical carbon dioxide, near the critical region, is easily tunable by small variation in pressure and/or temperature allowing the possibility of engineering the reaction environment to improve the reactivity and selectivity [1-3]. Limitations of scCO<sub>2</sub> as solvent are associated to its weak solvent strength. Efforts have been directed to the design of catalyst ligands that are soluble in scCO<sub>2</sub> under mild conditions [4-6]. Particularly, fluoroacrylate polymers have been moderately soluble in scCO<sub>2</sub>. Therefore, a new catalyst was synthesized by attaching a homogeneous rhodium catalyst to a fluoroacrylate polymer backbone making it soluble in scCO<sub>2</sub>. The polymer was synthesized from polymerization of 1H,1H,2H,2H-heptadecafluorodecyl acrylate monomer (zonyl TAN) and N-acryloxysuccinimide (NASI), the former increasing the solubility in scCO<sub>2</sub> and the latter providing attachment sites for the catalyst. Diphenylphosphino-propylamine, NH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>PPh<sub>2</sub>, (DPPA) was used to exchange the N-acryloxysuccinimide groups in the polymer, which was then reacted with [RhCl(COD)]<sub>2</sub> to obtain the catalyst. The activity of the catalyst was evaluated in hydrogenation and hydroformylation of different olefins and a kinetic model was proposed for each reaction. In special cases, statistical methods were applied to discriminate among rival models.

## I – Materials and Methods

Organic substances were purchased from Sigma-Aldrich and used as received. Carbon dioxide and hydrogen were bought from Brazos Valley Welding Supply and used as received. The preparation and characterization of the catalyst has been explained in full detail elsewhere [7]. A number of catalysts with various copolymer composition and rhodium to copolymer molar ratio were prepared. The experimental equipments and procedure used for the experimentation have been described elsewhere [8]. A small visual cell reactor with sapphire windows, 8 mL, was used to visually confirm the solubility of the catalyst and a single-phase of the reaction mixture at experimental conditions. A 100 mL batch reactor with sampling on-line was set up for taking samples at different times. Finally, it we also used a 57 mL visual cell reactor with sampling on-line for both taking samples at different times and to confirm one phase of reaction mixture. After each experiment the reactors were carefully washed and blank reaction tests were made to verify total removal of the catalyst. If any conversion was observed during the blank test, the cleaning procedure was repeated until there was no conversion. The samples taken from the reactors were analyzed by gas chromatography (HP-

FID 5890) using a 5% phenyl polyxilosane capillary column. The chromatograph was calibrated using pure samples of the products and reactants.

The hydrogenation of 1-octene was studied in the 100 mL reactor at 70 and 95°C and pressures from 172 to 241 bar. The catalyst employed for this study had a copolymer with a zonyl TAN to NASI molar ratio of 15,  $\text{RhCl}(\text{TAN}_{15}\text{DPPA})_3$ , with 15 % of oxidized phosphines. The initial mole fractions of 1-octene and hydrogen were kept constant in all experiments at 0.001 and 0.033, respectively. The substrate to catalyst molar ratio employed was 800. Figure 1 shows the experimental results obtained at different conditions.



**Figure 1.** Hydrogenation of 1-octene at 70 and 95°C using the catalyst  $\text{RhCl}(\text{TAN}_{15}\text{DPPA})_3$  with 15% of oxidized phosphines. Pressure: (Δ) 172 bar, (◻) 207 bar, (◐) 241 bar, (—) predicted.

The main product was n-octane, and the side products were (E)2-octene and (Z)2-octene in all the experimental conditions. Deactivation of the catalyst was also noticed. Increasing the pressure enhanced the activity of the reaction for both hydrogenation and isomerization. However, increasing the pressure also faster deactivated the catalyst. A reaction mechanism was proposed, which involved the formation of several catalytic complexes [9]. It was assumed that the catalyst first reacts with hydrogen to form mono- and dihydride catalytic species that further promote the isomerization and hydrogenation of the olefin, respectively. Also, it was considered that catalyst was deactivated due to the formation of an unsaturated catalytic olefin complex. The cycle for the generation of isomer must be repeated twice with different rate constants, one for the production of (E)2-octene, and the other for the production of (Z)2-octene.

Many kinetic models were proposed by assuming different rate-controlling steps in the hydrogenation and isomerization cycles. Some models were immediately discarded because of the lack of fitting with the experimental data. The remaining models were discriminated by applying the *Method of Likelihood Ratio as a Discrimination Criterion* and the *Method of Non-Intrinsic Parameters* [10]. Finally, the optimal kinetic model considered the insertion of hydrogen into the olefin as rate-determining step for hydrogenation reaction and the coordination of the olefin to the monohydride catalytic species (steps 6 and 10) for the isomerization reactions. The following kinetic equations are obtained:

$$\frac{dC_P}{dt} = \frac{k_3 K_1 K_2 C_A C_B C_{cat}}{1 + (1 + K_2 C_A) K_1 C_B + K_5^{1/2} C_B^{1/2}} \quad \frac{dC_C}{dt} = \frac{k_6 K_5^{1/2} C_A C_B^{1/2} C_{cat}}{1 + (1 + K_2 C_A) K_1 C_B + K_5^{1/2} C_B^{1/2}}$$

$$\frac{dC_D}{dt} = \frac{k_{10} K_5^{1/2} C_A C_B^{1/2} C_{cat}}{1 + (1 + K_2 C_A) K_1 C_B + K_5^{1/2} C_B^{1/2}} \quad \frac{dC_{cat}}{dt} = \frac{k_{14} C_A C_{cat}}{1 + (1 + K_2 C_A) K_1 C_B + K_5^{1/2} C_B^{1/2}} - k_{14'} C_{dcat}$$

where, A: 1-octene, B: hydrogen, P: n-octane, C: (E)2-octene, D: (Z)2-octene

The value of the parameters at 50 and 70°C and all operating pressures are presented in Table 1 and 2. Figure 1 also presents the comparison of predicted and experimental values for the hydrogenation of 1-octene at all the studied experimental conditions. It can be concluded the kinetic model is consistent with the total conversion of 1-octene.

**Table 1.** Parameter values of the kinetic model for the hydrogenation of 1-octene at 70°C

Parameter	172 bar	207 bar	241 bar
$k_3$ [=] h <sup>-1</sup>	1.29E4 ± 0.26E3	1.47E4 ± 0.86E3	2.83E5 ± 1.09E4
$k_6$ [=] L mole <sup>-1</sup> h <sup>-1</sup>	4240 ± 151.4	4607 ± 281.8	5.66E4 ± 1.33E3
$k_{10}$ [=] L mole <sup>-1</sup> h <sup>-1</sup>	2415 ± 149.6	3079 ± 185.1	3.76E4 ± 0.86E3
$k_{14}$ [=] L mole <sup>-1</sup> h <sup>-1</sup>	0 ± 0	29 ± 10.9	1089 ± 27.5
$k_{14'}$ [=] h <sup>-1</sup>	0	0	0
$K_1$ [=] L mole <sup>-1</sup>	4.90 ± 0.153		
$K_2$ [=] L mole <sup>-1</sup>	0.32 ± 0.009		
$K_5$ [=] L <sup>1/2</sup> mole <sup>-1/2</sup>	7.96 ± 0.079		

**Table 2.** Parameter values of the kinetic model for the hydrogenation of 1-octene at 95°C

Parameter	172 bar	207 bar	241 bar
$k_3$ [=] h <sup>-1</sup>	1.70E5 ± 0.65E4	2.00E5 ± 0.49E4	4.09E5 ± 0.83E4
$k_6$ [=] L mole <sup>-1</sup> h <sup>-1</sup>	4.31E4 ± 1.32E3	5.84E4 ± 1.55E3	1.27E5 ± 0.32E4
$k_{10}$ [=] L mole <sup>-1</sup> h <sup>-1</sup>	2.84E4 ± 1.11E3	3.28E4 ± 1.07E3	7.14E4 ± 1.75E3
$k_{14}$ [=] L mole <sup>-1</sup> h <sup>-1</sup>	1.21E3 ± 0.089E3	2.05E3 ± 0.061E3	4.10E3 ± 0.145E3
$k_{14'}$ [=] h <sup>-1</sup>	0	0	0
$K_1$ [=] L mole <sup>-1</sup>	4.69 ± 0.189		
$K_2$ [=] L mole <sup>-1</sup>	0.44 ± 0.014		
$K_5$ [=] L <sup>1/2</sup> mole <sup>-1/2</sup>	8.38 ± 0.208		

The same kinetic mechanism was also employed to determine the kinetic parameters for the hydrogenation of cyclohexene using the catalyst RhCl(TAN<sub>15</sub>DPPA)<sub>3</sub> with 30% of oxidized phosphines. The temperature range studied was 70-120°C at 172 bar. The substrate to catalyst molar ratio was 400 at 70°C, and 700 at 95 and 120°C. The initial mole fraction of reactants was kept constant in all the experiments at different temperatures. The only product of the reaction was cyclohexane but the formation of monohydride catalytic species is taken into consideration for modeling the reaction. This was done in order to keep the same mechanism. The double bond in cyclohexene may be shifting around, but it did not produce a distinct new isomer. The following kinetic equations are obtained:

$$\frac{dC_P}{dt} = \frac{k_3 K_1 K_2 C_A C_B C_{cat}}{1 + (1 + K_2 C_A) K_1 C_B + K_5^{1/2} C_B^{1/2}} \quad \frac{dC_{cat}}{dt} = \frac{k_{14} C_A C_{cat}}{1 + (1 + K_2 C_A) K_1 C_B + K_5^{1/2} C_B^{1/2}} - k_{14'} C_{dcat}$$

where A is cyclohexene and B is hydrogen.

Table 3 presents the values of the parameters for the hydrogenation of cyclohexene at 172 bar and different temperatures and Figure 2 shows the comparison of predicted and experiments results for these experiments. Once more, the calculated values fit very well the experimental data.

**Table 3.** Parameter values of the kinetic model for the hydrogenation of cyclohexene at 172 bar

Parameter	70°C	95°C	120°C
$k_3$ [=] h <sup>-1</sup>	319 ± 16.9	1.66E4 ± 2.22E3	9.06E4 ± 1.236E4
$k_{14}$ [=] L mole <sup>-1</sup> h <sup>-1</sup>	3.4 ± 1.41	149 ± 27.3	370 ± 58.6
$k_{14'}$ [=] h <sup>-1</sup>	0	0	0
$K_1$ [=] L mole <sup>-1</sup>	2.16 ± 0.107	2.09 ± 0.121	0.70 ± 0.026
$K_2$ [=] L mole <sup>-1</sup>	1.94 ± 0.072	2.00 ± 0.105	3.49 ± 0.125
$K_5$ [=] L <sup>1/2</sup> mole <sup>-1/2</sup>	7.96 ± 0.079	8.38 ± 0.208	8.38 ± 0.208

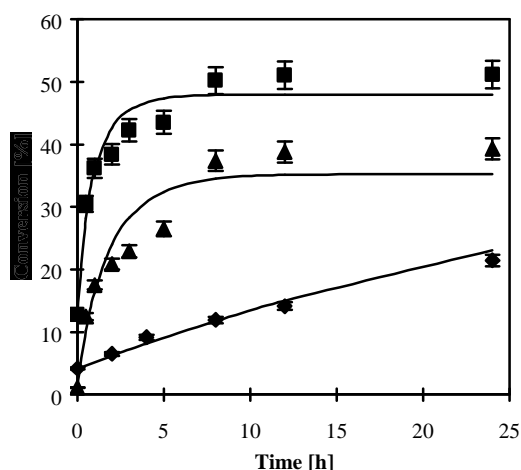
The hydroformylation of 1-octene was studied at 50-75°C and 172-241 bar in the 100 mL batch reactor. The catalyst employed in this study was RhCl(TAN<sub>15</sub>DPPA)<sub>3</sub>, with 15 % of oxidized phosphines. The experimental results are presented in Figure 5. Isomerization and hydroformylation of the substrate, and hydroformylation of the isomers were obtained at all conditions studied. The main product was 2-methyloctanal, and the side products were n-nonanal, isomers of 1-octene, and their respective hydroformylation products. The effect of pressure at 50°C was more evident than at 75°C. The reaction was modeled with a pseudo-first order expression. Table 4 presents the value of the rate constant at different experimental conditions and Figure 3 also shows the fitting of the kinetic model with the experimental data.

**Table 4.** Parameter values of the kinetic model for the hydroformylation of 1-octene

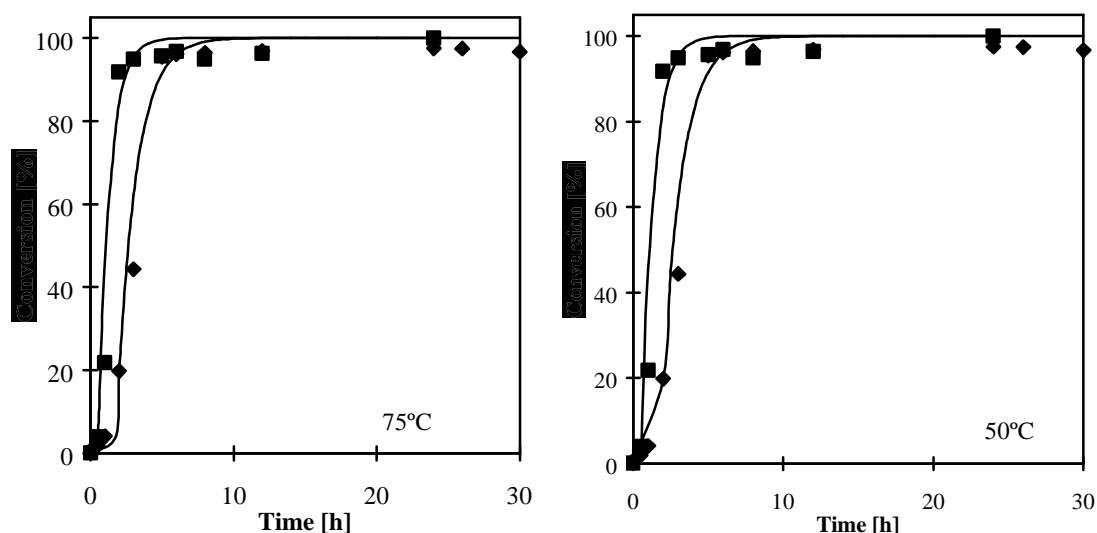
Parameter	172 bar		241 bar	
	50°C	75°C	50°C	75°C
k'	0.15 ± 0.019	0.75 ± 0.004	0.70 ± 0.057	1.21 ± 0.008

The hydroformylation of styrene was studied at 50 and 75°C, and between 172 and 241 bar in the 57 mL visual cell reactor. The catalyst employed in this study was RhCl(TAN<sub>15</sub>DPPA)<sub>3</sub>, with 15 % of oxidized phosphines. The initial mole fractions of styrene, carbon monoxide and hydrogen were 0.0004, 0.06365 and 0.06365, respectively. The substrate to catalyst mole ratio was 200 in all the experiments. The main product was 2-phenylpropionaldehyde with small amounts of 3-phenylpropionaldehyde and traces of ethylbenzene. The experimental results are presented in Figure 4. This reaction was modeled using the dissociative mechanism for hydroformylation of olefins presented by (Cornils and Herrmann, 1996). Before the catalytic cycle, several reactions have to proceed to finally generate the key intermediate HRh(CO)<sub>2</sub>L<sub>2</sub>. Because the great excess of CO and H<sub>2</sub> in the reaction system, the concentration of both compounds are considered constant during the reaction. Therefore, the final kinetic equation was as given below where S is styrene.

$$-\frac{dC_S}{dt} = \frac{kK_{10}C_S C_{cat}}{K_8 + K_9 C_S}$$



**Figure 2.** Hydrogenation of cyclohexene at 142 bar using the catalyst  $\text{RhCl}(\text{TAN}_{15}\text{DPPA})_3$  with 30% of oxidized phosphines. Temperature: (○) 70°C, (△) 95°C, (□) 120°C, (—) predicted.

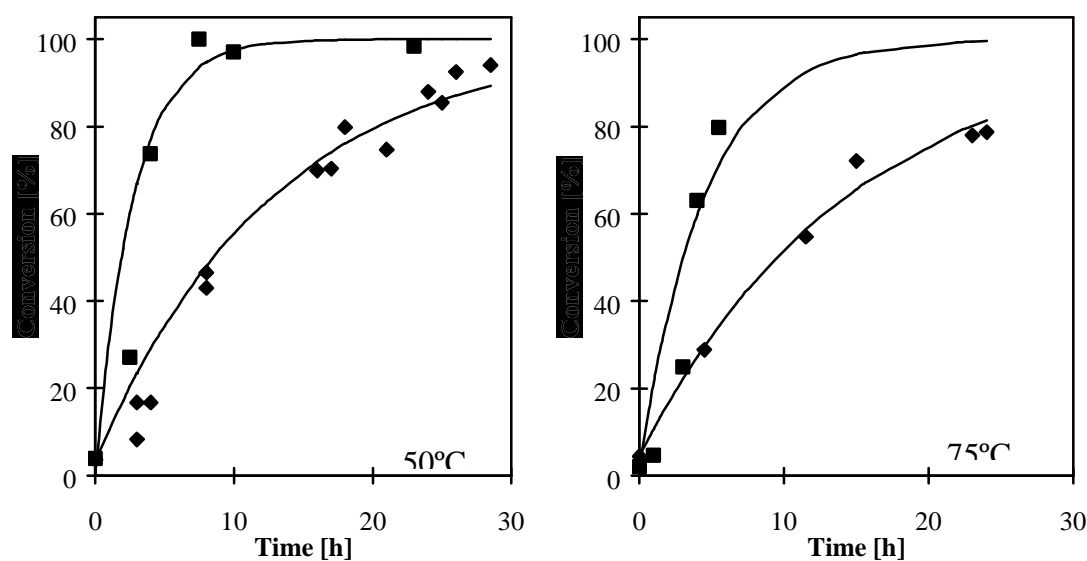


**Figure 3.** Hydroformylation of 1-octene at 50 and 75°C using the catalyst  $\text{RhCl}(\text{TAN}_{15}\text{DPPA})_3$  with 15% of oxidized phosphines. Pressure: (○) 172 bar, (△) 241 bar, (—) predicted.

The values of the parameters for kinetic model are reported in Table 5 and 6. Figure 6 also shows the fitting of the kinetic model with the experimental data. It can be concluded the kinetic model is consistent with the general profile of all the products.

**Table 5.** Parameter values of the kinetic model for the hydroformylation of styrene at 50°C

Parameter	172 bar	207 bar	241 bar
$k$ [=] $\text{L mole}^{-1} \text{h}^{-1}$	$3824 \pm 171$	$7815 \pm 364$	$8540 \pm 1887$
$K_8$ [=]	$3.75 \pm 0.118$		
$K_9$ [=] $\text{L mole}^{-1}$	$2.98 \pm 1.370$		
$K_{10}$ [=]	$2.92 \pm 0.095$		



**Figure 4.** Hydroformylation of styrene at 50 and 75°C using the catalyst  $\text{RhCl}(\text{TAN}_{15}\text{DPPA})_3$  with 15% of oxidized phosphines. Pressure: (◊) 172 bar, (◻) 241 bar, (—) predicted.

**Table 6.** Parameter values of the kinetic model for the hydroformylation of styrene at 75°C

Parameter	172 bar	207 bar	241 bar
$k$ [=] $\text{L mole}^{-1} \text{h}^{-1}$	$3059 \pm 146$	$9321 \pm 495$	$9170 \pm 1134$
$K_8$ [=]		$2.70 \pm 0.092$	
$K_9$ [=] $\text{L mole}^{-1}$		$3.60 \pm 0.526$	
$K_{10}$ [=]		$3.73 \pm 0.127$	

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