Intensification of Catalytic Olefin Hydroformylation in CO_2-Expanded Media

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CO_2-expanded liquids (CXLs) are demonstrated to be effective reaction media for the catalytic hydroformylation of 1-octene. The performance of several rhodium catalysts, Rh(acac)$(CO)_2$, Rh(acac)$[P(OPh)_3]_2$, Rh(acac)(CO)$[P(OAr)_3]$, and two phosphorous ligands, PPh_3 and biphephos, was compared in neat organic solvents and in CXLs wherein more than 50% of the solvent volume is replaced with dense CO_2 at relatively mild temperatures (30–90°C) and pressures (<12 MPa). For all catalysts, enhanced turnover frequencies (TOFs) were observed in CXLs. For the most active catalyst, Rh(acac)$(CO)_2$ modified by biphephos ligand, the selectivity to aldehyde products was improved from approximately 70% in neat solvent to nearly 95% in CXL media. The enhanced rates and selectivity are attributed to increased syngas availability in the CXL phase. In experiments performed without added solvent, a TOF maximum was observed at an optimum CO_2 content. It appears that at higher than optimum CO_2 content, the TOF decreases as a result of dilution of substrate by CO_2, whereas at lower than optimum values the TOF is limited by reduced syngas availability. The observed TOF ($\sim$300 h^{-1}), n/i ratio (>10), and aldehyde selectivity ($\sim$90%) at the optimum CO_2 content were either comparable to or better than values reported with other media and catalysts. Furthermore, the operating pressure (3.8 MPa) and temperature (60°C) for the CXL process are significantly milder than those reported for industrial hydroformylation processes. © 2006 American Institute of Chemical Engineers *AIChE J,* 52: 2575–2581, 2006

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Introduction

Industrial processes for the catalytic hydroformylation of higher olefins (> C_5) face several challenges, including efficient catalyst recovery/recycle and the limited solubilities of the gaseous reactants (H_2 and CO) in the liquid reaction phase.[1] The commercial catalysts used in the lower olefin processes, mostly rhodium-based, are not applied in higher olefin hydroformylation because of their instability at the temperatures required for product separation/distillation. Thus, the less expensive cobalt-based catalysts are used; however, harsher conditions (140–200°C, 5–30 MPa) are often used to activate and stabilize the catalysts. In addition, the catalyst recovery typically involves significant quantities of solvents, acids, and bases in a series of many operating units.[2] An optimized engineered system is desired to achieve process intensification

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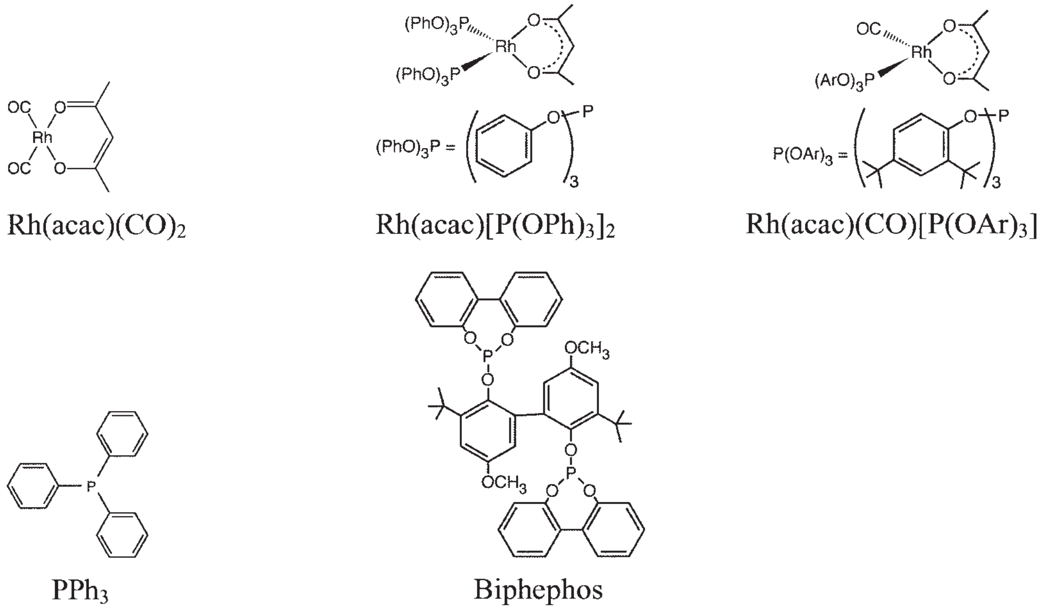

Figure 1. Structures of catalysts and ligands investigated in the present work.

at milder conditions with a highly active catalyst that requires a relatively simpler and environmentally friendlier catalyst recovery method.

Several approaches for catalyst recovery have been reported in the literature:

(1) Immobilizing homogeneous Rh catalysts on various supports, that is, MCM-41,[3] zeolites,[4] nanotubes,[5] SAPC,[6] and polymers.[7,8]

(2) Biphasic media such as water/organic,[9] water/CO_2,[10,11] and room-temperature ionic liquid/CO_2,[12] wherein the catalyst is sequestered in either the water or the ionic liquid phases, whereas the product preferentially separates into the organic phase or the CO_2 phase.

(3) Using a "phase transition switch," whereby reactions are performed homogeneously, following which the catalysts are recovered from the product stream by phase transition triggered by a change in either the system temperature[13,14] or pressure.[15,16]

The use of CO_2-expanded liquids (CXLs) as reaction media has received increased attention. CXLs are a continuum of compressible media generated when various amounts of dense-phase CO_2 are added to an organic solvent. CXLs offer both reaction and environmental benefits. Near-critical CO_2 possesses highly tunable transport properties (ranging from gas-like diffusivities to liquid-like viscosities)[17]; the presence of dense CO_2 imparts similar tunability to CXLs as well. The solubilities of many gaseous reagents (that is, O_2[18,19] and H_2[20-22]) in CXLs are enhanced severalfold relative to the neat liquid phase. Although most transition metal complexes are only sparingly soluble in supercritical CO_2 (*sc*CO_2), the presence of an appropriate amount of the organic liquid in CXLs ensures adequate solubilities of transition metal complexes in a CXL phase for performing homogeneous catalysis. Such solubilities are attained at pressures an order of magnitude lower than those required in *sc*CO_2 medium for solubilizing Rh catalyst complexes with fluorinated ligands.[16] In contrast, an excess amount of CO_2 addition causes the transition metal complex catalyst to precipitate from the CXL phase, which may be exploited for separating the catalyst postreaction. Indeed, catalysts may be designed to take advantage of this highly tunable solubility for recovery and recycle. The significant replacement of volatile organic solvents (VOCs) by dense CO_2 in CXLs results in improved process safety and less exposure to hazardous materials. In addition, the unique heat capacities of near-critical CO_2 may be exploited to effectively curtail the temperature rise of a highly exothermic reaction and thereby to prevent thermal runaway.[23]

Recently, we reported the homogeneous catalytic hydroformylation of 1-octene in CO_2-expanded acetone with an unmodified rhodium catalyst.[24] At 30 and 60°C, the turnover frequencies (TOFs) in CO_2-expanded acetone were up to fourfold greater than those obtained in either neat acetone or compressed CO_2. The enhanced rates in CXLs were realized at significant solvent replacement (up to 80% by volume) and at mild operating pressures (<12 MPa). The regioselectivity toward linear and branched aldehydes (*n*/*i* ratio) remained unaffected by the change in either the solvent medium or the temperature.

In the present work, we examine the performance of several conventional rhodium-based catalysts in CXLs using 1-octene as substrate. The structures of the catalysts investigated, including the unmodified Rh(acac)$(CO)_2$ and those modified by various phosphorous ligands, are summarized in Figure 1. Systematic screening experiments are performed in neat and CO_2-expanded organic solvents over a range of temperatures (30–90°C) and pressures (0.6–12 MPa) to compare the activities and selectivities of the catalysts in these media. Effects of CO_2 addition on catalyst solubility in CXLs are also discussed.

Experimental

Solubility of reactants and catalysts in CO_2-expanded liquids

The miscibility of CO_2 in the reaction mixtures containing dissolved Rh complexes was investigated in a 50-cm^3 Jergu-

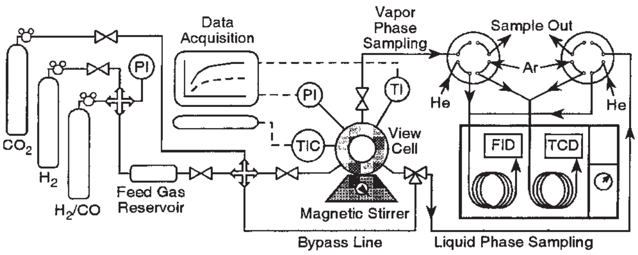

Figure 2. Apparatus for catalyst screening studies.

son® view cell, placed in a constant-temperature water bath. Details of the apparatus are described elsewhere.[24]

The expansion of the liquid mixtures by CO_2 is recorded in terms of the relative increase in the liquid volume from the initial state (CO_2-free, atmospheric pressure, P^0) to the final state (CO_2-expanded, equilibrated pressure, P) at the same temperature, expressed as

$$\frac{V}{V_0} = \frac{V(T, P)}{V(T, P^0)} \tag{1}$$

In a typical experiment, the addition of CO_2 is continued until either the limit of the operating pressure is reached or a phase separation is observed, with or without catalyst precipitation. The liquid volume corresponding to phase separation is termed the *maximum homogeneous expansion level* (MHEL). The *P–T* region below MHEL is used for performing homogeneous hydroformylation in CXLs, whereas the region above MHEL may be exploited for catalyst precipitation postreaction.

Catalyst screening experiments

The catalytic hydroformylation experiments were performed in fixed-time batch studies using a 15-cm^3 316 stainless steel high-pressure view cell. A schematic of the reactor setup is shown in Figure 2. Details of the apparatus are discussed elsewhere.[24] Briefly, the cell is fitted with two sapphire windows, which allow visual observations of the phase behavior and the mixing of the reactor contents. Temperature and pressure are monitored and controlled using a data acquisition system (Camile® TG, Argonaut Technologies, Redwood City, CA). In a typical run in CO_2-expanded solvents, a liquid mixture containing the substrate, the catalyst, and the organic solvent is pre-loaded into the reactor and then heated to the reaction temperature, followed by addition of CO_2 until the desired volume is reached. Syngas is introduced once the system pressure is stabilized, initiating the start of the reaction. The pressure is kept constant for a given run. Samples are withdrawn from the liquid phase during the experiments and analyzed using an inline GC (Varian 3800).

The major products detected are the aldehydes (linear and branched) and the octene isomers, the byproducts of 1-octene isomerization. The chemoselectivity (S_a) is defined as the moles of aldehydes or the octene isomers formed relative to the moles of 1-octene converted, whereas the ratio of the linear to the branched aldehydes (*n*/*i*) in the product represents the regioselectivity. The turnover frequency (TOF) is defined as the number of moles of 1-octene reacted per mole catalyst per hour of batch run time.

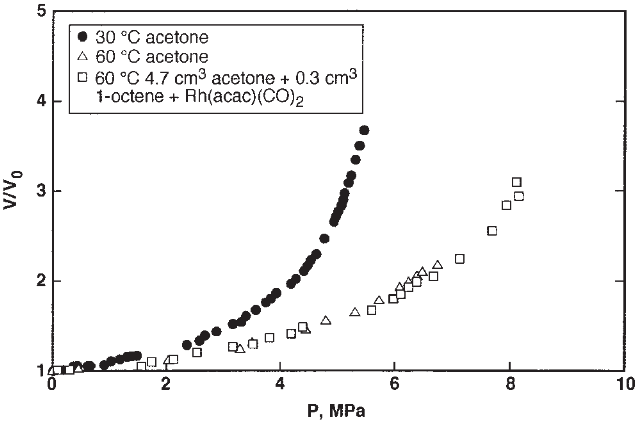

Figure 3. Volumetric expansion of acetone by CO_2 at various temperatures.

Materials

HPLC-grade 1-octene, acetone, and 2-propanol were procured from Aldrich Chemical Co. (Milwaukee, WI), distilled using a Schlenk line to remove water, air, and peroxide impurities, and stored under nitrogen before usage. The unmodified rhodium catalyst $Rh(acac)(CO)_2$ and triphenylphosphine (PPh_3) ligand were procured from Johnson Matthey (London, UK) and Strem Chemicals (Newburyport, MA), respectively. Two other rhodium catalysts, $Rh(acac)[P(OPh)_3]_2$ and $Rh(acac)(CO)[P(OAr)_3]$, and one bidentate ligand (biphephos) were synthesized following reported procedures.[25,26] All catalysts and ligands were stored under nitrogen before usage. Coolant-grade liquid CO_2 and research-grade compressed H_2 were supplied by Air Products and Chemicals (Allentown, PA) in cylinders. Syngas (99.99% purity; molar H_2/CO ratio of 1:1) was provided by Scott Specialty Gases (Plumsteadville, PA).

Results and Discussion

CO_2-expansion experiments

The expansions of acetone and 1-octene at various temperatures, 30–60°C, are presented in Figure 3 and 4, respectively. Both solvents demonstrate good miscibility with CO_2 at mild pressures (<12 MPa). The volumetric expansions of these

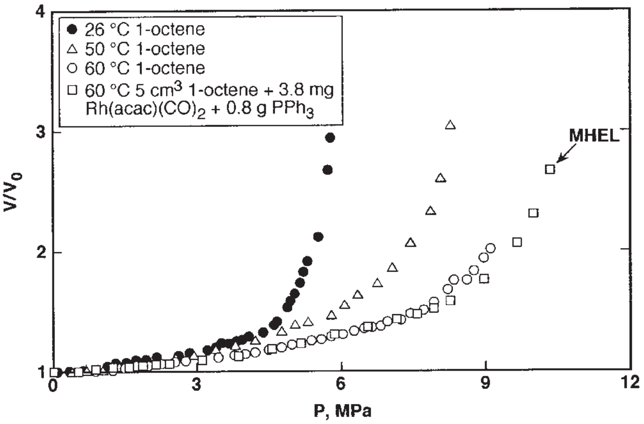

Figure 4. Volumetric expansion of 1-octene by CO_2 at various temperatures.

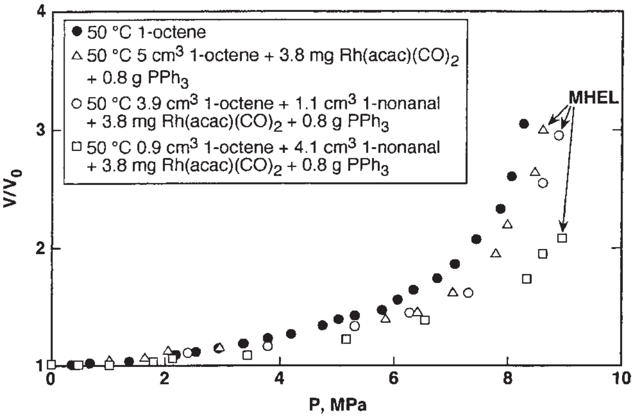

Figure 5. Catalyst solubility in representative hydroformylation reaction mixtures expanded with CO_2.

liquids in the presence of dissolved Rh catalysts are also compared. No significant variations are observed between the expansions with and without catalysts because of the relatively dilute catalyst concentrations (~10^{-3} mol/L). Although the catalysts were soluble in CO_2-expanded acetone in the range of pressures studied, precipitation of the catalyst was observed around 9 MPa in CO_2-expanded 1-octene at 60°C. Unlike 1-octene, the polar acetone functions as an effective cosolvent for dissolving the Rh complex.

The expansions of several hydroformylation mixtures containing 1-octene, dissolved catalyst [$Rh(acac)(CO)_2$ and PPh_3] and nonanals (approximating 0–20% 1-octene conversion to the nonanals) are compared in Figure 5. In all cases, catalyst precipitation was observed around 9 MPa. These results guide the choice of operating conditions (*P*, *T*, and composition) for the catalyst screening studies, including the level of volumetric expansion at each selected pressure and the range of pressures where 1-octene hydroformylation in CXLs can be performed homogeneously. The observation of MHEL (Figure 5) also demonstrates the potential of exploiting CO_2 as an antisolvent for catalyst recovery.

Catalyst screening experiments

Table 1 summarizes the results of 1-octene hydroformylation performed in both neat and CO_2-expanded acetone solvents with four rhodium-based catalysts: $Rh(acac)(CO)_2$, $Rh(acac)[P(OPh)_3]_2$, $Rh(acac)(CO)[P(OAr)_3]$, and a complex formed *in situ* with equivalent amounts of $Rh(acac)(CO)_2$ and the biphephos ligand. Over all four catalysts, 1-octene conversions were greater in CO_2-expanded acetone than in neat acetone. This is consistent with our previous observations.[24] With the most active catalyst, the complex formed by $Rh(acac)(CO)_2$ and biphephos ligand, the selectivity of aldehydes ($n + i$) was improved from nearly 70 to 94% in the presence of CO_2. The enhanced activity is attributed to increased syngas availability in the CO_2-expanded liquid phase, which also promotes hydroformylation over alkene isomerization to internal olefin isomers. It should be noted that the enhanced catalyst performance was achieved with 50% (v/v) replacement of acetone by CO_2.

Table 1. Activity/Selectivity of Various Catalysts in Neat and CO_2-Expanded Acetone*

Media	Catalyst/ Ligand	Time (h)	Conversion (%)	S_a (%)	*n*/*i*
Acetone	1	20	74	91.4	1.2
	2	6	74	94.7	1.8
	3	6	79	97.9	1.8
	1/L1	6	93	69.9	1.7
CXL/Acetone	1	6	73	90.3	1.3
	2	6	91	79.5	2.1
	3	6	97	99.2	1.9
	1/L1	6	97	94.0	1.7

1 = $Rh(acac)(CO)_2$; 2 = $Rh(acac)[P(OPh)_3]_2$; 3 = $Rh(acac)(CO)[P(OAr)_3]$; L1 = biphephos; 1/L1 molar ratio = 1. Conditions: 30°C, 1-octene = 2.7 mmol, total volume = 10 cm^3, volumetric CO_2/acetone ratio (v/v) in CXL/acetone runs = 1, molar syngas/substrate ratio = 5, molar 1-octene/Rh ratio = 209, S_a = selectivity to aldehydes ($n + i$); main byproducts are octene isomers.

When comparing results in each medium, it is observed that catalysts modified by phosphorous ligands always give higher conversions than the unmodified catalyst, $Rh(acac)(CO)_2$. However, with a ligand/Rh (L/Rh) molar ratio of 1, the regioselectivity to the linear aldehyde (*n*/*i* ratio) was still severalfold lower ($n/i < 2$) than the value preferred in industrial hydroformylation ($n/i > 5$). Table 2 presents the results of 1-octene hydroformylation conducted at L/Rh ratios ranging from 103 to 270. A commercial ligand, triphenylphosphine (PPh_3), was used and the data were compared to literature values.[27] The *n*/*i* ratio has a relatively weak dependency on the L/Rh ratio (103–270 range), which is consistent with the literature.[28,29] In sharp contrast, when the substrate (1-octene) itself was used as solvent medium, both the TOF and aldehyde selectivity (S_a) were found to be significantly improved. A more than a fivefold TOF enhancement and an *n*/*i* ratio of 13.8 were achieved in the absence of an added organic solvent such as acetone or toluene. It must also be noted that in the absence of an added solvent, the selectivity toward the octene isomers is ≤3.5%. Although the reduced substrate dilution can partly explain the increased TOF in the runs without added solvent, the reasons for the increased *n*/*i* ratio are not yet clear. This observation is nevertheless significant because it means less separation load during the product isolation step. Clearly, more systematic investigations, including kinetics and reactor modeling, are needed to fully understand these effects.

Figure 6 shows the effects of temperature on 1-octene hydroformylation conducted without an added solvent. The performance of $Rh(acac)(CO)_2$ catalyst, modified by PPh_3 ligand at L/Rh ratios ≅ 200, is compared at temperatures of 30, 60, and 90°C. Increase in temperature led to higher reaction rates and *n*/*i* ratios. These beneficial temperature effects on the linear aldehyde selectivity are consistent with reported temperature

Table 2. Hydroformylation of 1-Octene at Higher Ligand/Rh Molar Ratios

Solvent	Ligand	Ligand/Rh (molar)	TOF (h^{-1})	S_a (%)	*n*/*i*
Toluene[27]	PPh_3	103	n/a	82.0	4.6
Toluene	PPh_3	270	161	72.8	4.7
None	PPh_3	205	887	96.7	13.8

Conditions: 90°C, 135 min, total volume = 7 cm^3, pressure = 0.6 MPa, molar syngas/substrate ratio = 5, molar 1-octene/Rh ratio = 2767 (in toluene), 2139 (in 1-octene), S_a = selectivity to aldehydes ($n + i$); main byproducts are octene isomers.

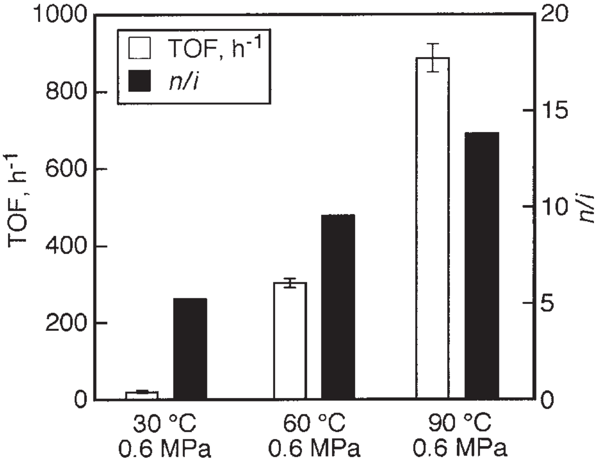

Figure 6. Effect of temperature on activity and product selectivity.

Rh(acac)$(CO)_2$ modified by PPh_3; L/Rh ≅ 200; t = 135 min; no added solvent.

effects.[30] An increase in temperature tends to favor the yield of linear aldehyde over 1-octene isomers. The reduced isomer formation means that the undesired hydroformylation of the octene isomers to form internal aldehydes is also curtailed.

Figure 7 presents the effect of CO_2 addition at 60°C. The experimental conditions were similar to those in Figure 6, except that various amounts of CO_2 were added to the 1-octene solution in each run. A maximum TOF occurred at a volume expansion by 10% ($V/V_0 = 1.1$). This suggests that, although CO_2 addition to 1-octene may enhance the syngas availability in the CXL phase (because of enhanced solubilities and mass transfer rates), the substrate dilution by CO_2 eventually lowers the reaction rates. Measurements of the liquid-phase mole fraction of H_2 showed several-fold solubility enhancement in CO_2-expanded 1-octene relative to neat 1-octene pressurized with pure H_2 at the same pressure (Figure 8). Thus, it may be possible to tune the syngas ratio in the liquid phase.

Remarkably, the CO_2 addition was found to continuously improve the *n*/*i* ratio. Similar to the temperature effect, increased syngas availability in the liquid phase promotes the hydroformylation route over isomerization, resulting in higher yields of linear product. To clarify the CO_2 effect, several conversion and selectivity measurements were performed at fixed initial concentrations of the substrate (1-octene) and the catalyst and the batch run time. The experimental conditions are as follows: (1) an expanded-liquid mixture ($V/V_0 = 1.3$) is subjected to a total pressure of 6.4 MPa, with the partial pressures of syngas and CO_2 being 0.6 and 5.8 MPa, respectively; (2) a liquid mixture with the same volume as in run *a* but under a total pressure of 0.6 MPa, primarily being the syngas, with the CO_2 replaced by a volumetrically equivalent amount of *n*-hexane, a liquid at ambient pressures, and whose polarity is very similar to that of CO_2; the conditions in runs *c* and *d* are similar to those in run *b*, except that the vapor phase is composed of pure syngas (6.4 MPa) in run *c*, and a mixture of syngas and N_2 (partial pressures of syngas and N_2 being 0.6 and 5.8 MPa, respectively) in run *d*. As shown in Figure 9, the TOFs in CO_2-expanded 1-octene at 6.4 MPa (run *a*) is 33% greater than TOF in *n*-hexane at 0.6 MPa (run *b*) with similar *n*/*i* ratios in both runs. The TOFs are reduced by roughly a third and the *n*/*i* ratio is reduced by more than twofold when CO_2 was replaced by either N_2 (run *d*) or syngas (run *c*). Although these results clearly show that the addition of CO_2 has a beneficial effect on the TOF and *n*/*i* ratio, the inhibition effects arising from either N_2 or syngas addition are as yet not fully

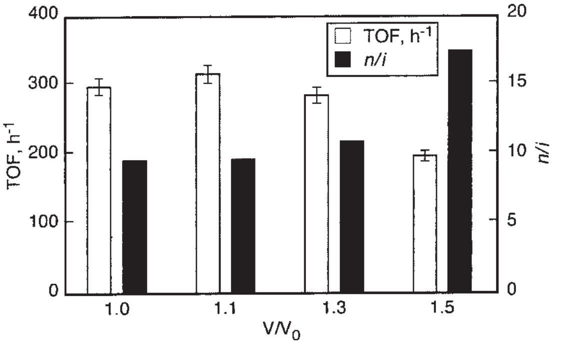

Figure 7. Effects of CO_2 addition on TOF and *n*/*i* ratio without added solvent.

Rh(acac)$(CO)_2$ modified by PPh_3; L/Rh ≅ 200; t = 135 min; T = 60°C.

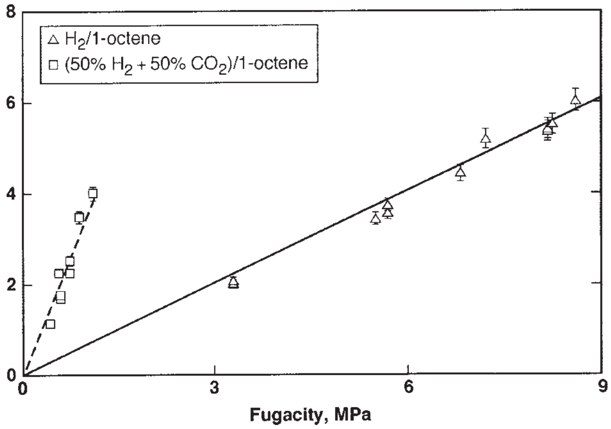

Figure 8. Solubility of H_2 in neat and CO_2-expanded 1-octene at 60°C.

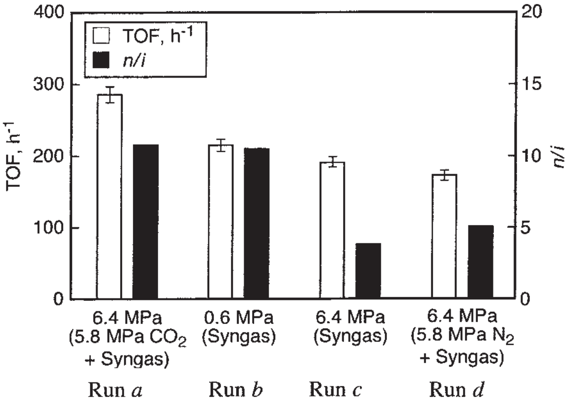

Figure 9. Pressure effects on TOF and *n*/*i* ratio.

The solvents used are liquid CO_2 in run *a* and *n*-hexane in runs *b*–*d*. Rh(acac)$(CO)_2$ modified by PPh_3; L/Rh ≅ 200; t = 135 min; T = 60°C.

Table 3. Comparison with Commercial Processes and Other Reported Work*

Process	BASF (Co)	Shell (Co/P)	SCF-IL (Rh/P)	SCF (Rh/P)	CXL (Rh/P)
Substrate	1-octene	1-octene	1-octene	1-octene	1-octene
P, MPa	30	8	20	12.5	3.8
T, °C	150	200	100	100	60
TOF, h^{-1}	35	20	517	259	316
$S_{n\text{-aldehyde}}$, %	50	80	75	75	89

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understood. Investigations with a high-pressure IR probe are currently under way to monitor the reacting species *in situ* and should provide better mechanistic insights.

Table 3 compares the TOFs, *n*/*i* ratio, and operating conditions (P and T) from the current work with those of some existing industrial processes and recently published work that use supercritical CO_2 and ionic liquids as reaction media.[31] Clearly, hydroformylation in CO_2-expanded octene appears to be promising in terms of both TOF ($\sim$300 h^{-1}) and selectivity ($\sim$90%, *n*/*i* $>$ 10). In addition, the required operating conditions (60°C and 3.8 MPa) are much milder compared to those of other processes. Preliminary economic analysis reveals that demonstrating active and easily recyclable catalysts that function effectively in CO_2-expanded media is the key to developing commercially viable CXL-based hydroformylation. Our current research efforts are aimed at achieving this goal.

Summary

The use of CO_2-expanded liquids (CXLs) as reaction media for the catalytic hydroformylation of 1-octene was investigated in the present work, over a range of temperatures (30–60°C) and pressures (0.6–12 MPa). The performance of several Rh-based catalysts, $Rh(acac)(CO)_2$, $Rh(acac)[P(OPh)_3]_2$, $Rh(acac)(CO)[P(OAr)_3]$, and two phosphorous ligands, PPh_3 and biphephos, was compared in neat solvent media (that is, without CO_2 addition) and in CO_2-expanded media, both in the presence and the absence of added solvents such as acetone. TOFs were higher in CXLs than in neat organic solvents in all catalytic systems studied. With the most efficient catalyst, $Rh(acac)(CO)_2$ modified by biphephos ligand, the presence of CO_2 improved the syngas availability in the liquid phase and enhanced the selectivity to the desired aldehyde products from nearly 70 to 94%. The enhanced rates and selectivities were achieved in CXLs at a 50% reduction in the organic solvent usage.

In experiments performed without an added solvent, the addition of CO_2 enhanced the syngas availability in the CXL phase. However, because of substrate dilution by CO_2 addition, a maximum TOF was found at a CO_2-expanded 1-octene medium with 10% CO_2 by volume. The increased syngas availability in the CXL phase also favors the formation of the linear aldehydes. Observed TOF ($\sim$300 h^{-1}), *n*/*i* ratio ($>$10), and aldehyde selectivity ($\sim$90%) at the optimum were comparable to or better than values reported with other media and catalysts. In addition, the operating pressures ($\sim$4–6 MPa) and temperatures ($\sim$60–90°C) required for this process were significantly lower than those reported for other processes. Preliminary economic analysis shows, as expected, that the key to making the CXL process practically viable is to design easily recyclable Rh-based catalysts through solvent polarity switch. Such a catalyst would significantly simplify the conventional Co-based processes, which involve tedious catalyst separation steps requiring extensive use of acid and alkali for catalyst separation and recycle.

Acknowledgments

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