REACTION ENGINEERING, KINETICS, AND CATALYSIS

Enhanced Hydroformylation by Carbon Dioxide-Expanded Media with Soluble Rh Complexes in Nanofiltration Membrane Reactors

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DOI 10.1002/aic.14142

A novel process for continuous hydroformylation in CO_2-expanded liquids (CXLs) is demonstrated using bulky phosphite ligands that are effectively retained in the stirred reactor by a nanofiltration membrane. The reactor is operated at 50°C with a syngas pressure of 0.6 MPa to avoid CO inhibition of reaction rate and selectivity. The nanofiltration pressure is provided by ~3.2 MPa CO_2 that expands the hydroformylation mixture and increases the H_2/CO ratio in the CXL phase resulting in enhanced turnover frequency (~340 h^{-1}), aldehydes selectivity (>90%) and high regioselectivity (n/i ~8) at nearly steady operation. The use of pressurized CO_2 also reduces the viscosity in the CXL phase, thereby improving the mass-transfer properties. Constant permeate flux is maintained during the 50 h run with Rh leakage being less than 0.5 ppm. This technology concept has potential applications in homogeneous catalytic processes to improve resource utilization and catalyst containment for practical viability. © 2013 American Institute of Chemical Engineers *AIChE J*, 59: 4287–4296, 2013

Keywords: hydroformylation, CO_2-expanded liquids, 1-octene, membrane filtration

Introduction

CO_2-expanded liquids (CXLs) have attracted interest as reaction media during the last decade.[1–4] CXLs allow a much lower working pressure than supercritical CO_2 and are inherently safe for oxidation reactions.[3] CXLs also possess enhanced transport properties characterized by decreased viscosity and increased diffusivity.[1] Because of their increased free volume compared to conventional solvents, CXLs allow unique pressure-tunability of the solubilities of reactant gases such as CO, H_2 and O_2,[5–7] which have been exploited to enhance catalyst activity and selectivity. Previously, we reported that for triphenylphosphine (TPP)/rhodium (Rh) catalyzed 1-octene hydroformylation in CXLs, turnover frequency (TOF) and regioselectivity (*n*/*i*) were significantly enhanced and pressure-tunable.[8,9] Since our early studies, other groups have also reported similar results.[10,11]

It is well-known that the concentrations of the syngas components (CO and H_2) in the liquid phase are major determinants of the reaction pathways and therefore the product selectivity. Figure 1 shows a commonly accepted mechanism[12] for Rh-catalyzed hydroformylation. In this mechanism, step 8 is considered to be the rate-limiting step. In this step, hydrogen is inserted to the Rh-acyl complex, which then undergoes the hydride transfer to form aldehydes. Furthermore, the H_2 insertion in step 1 is essential to activate the catalyst and to commence the catalytic cycle. Therefore, an increase in H_2 concentration in the liquid phase favors the overall hydroformylation rate. On the other hand, an increase in CO concentration often leads to reduced reaction rates and aldehyde regioselectivity (*n*/*i*). This effect is manifested in two steps: CO dissociation in step 2, where high CO concentration is known to cause excessive ligand substitution[13] and reduces the regioselectivity; and the CO complexation in step 7, which in the presence of excess CO inhibits the H_2 insertion to form active catalytic intermediate, and thereby lowers the reaction rate.[14–16]

In general, therefore, higher H_2 concentrations and lower CO concentrations in the reaction phase are required to achieve higher rates and linear aldehyde selectivity. Because CO is generally more soluble than hydrogen in most conventional solvents,[17] the resulting H_2/CO ratio in the liquid phase is less than that in the feed syngas. However, when

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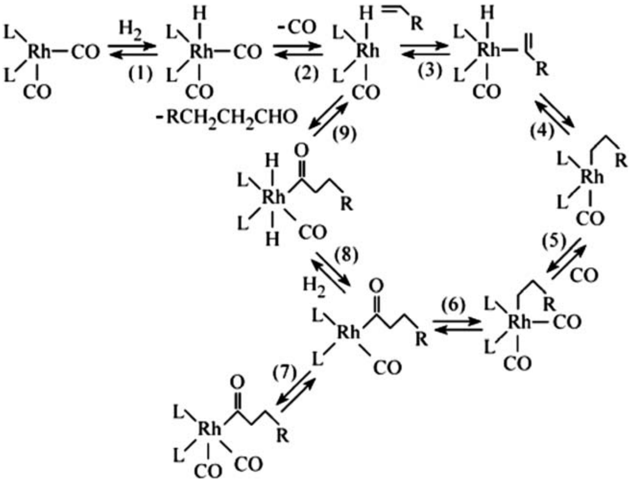

Figure 1. Simplified mechanism for Rh-catalyzed hydroformylation.[12]

CO_2 is added to either 1-olefin or nonanal (to create a CXL), we observe that the enhancement of H_2 solubility is more than CO in the CXLs.[7,9] This means that the H_2/CO ratio in the liquid phase should be greater in CXLs (based on the organic solvent and extent of CO_2 addition) compared to the ratio without adding CO_2. Thus, the observed beneficial effects of CXLs on hydroformylation activity and on selectivity are attributed to the favorable tunability of H_2/CO ratio in the CXL phase. Moreover, by using CXLs, CO inhibition is alleviated and therefore the adverse effect on *n*/*i* ratio is avoided at higher total pressure. This manuscript clarifies these intriguing effects observed with CXLs through a combination of systematic phase equilibrium and reaction studies.

This manuscript also reports on continuous reactor operation with CXLs building on our earlier work,[18] wherein we demonstrated a continuous nanofiltration membrane reactor. The use of soluble, polymer-bound bidentate ligand[19] not only allowed better binding of the Rh center but also facilitated superior Rh retention by the membrane. Rh leaching in the permeate at steady state was on the order of a few tens of ppb which easily meets the economic viability criterion.[20] However, the requirement of relatively high-syngas pressure (3 MPa) to facilitate filtration inhibits the reaction rate and reduces the regioselectivity. This work examines whether the use of CXLs with low syngas partial pressure during continuous reactor operation could overcome the syngas inhibition while also lowering the viscosity of the reaction mixture to improve mixing and nanofiltration rates in the reactor.

Experimental

Materials

The purchased materials are listed in Table 1 and are used as is unless otherwise noted. In addition, the JanaPhos ligand (Figure 2) was synthesized in-house using published methods.[19] The molecular weight of the JanaPhos ligand is centered around 10,000 g/mol with a polydispersity index of 1.3.

Apparatus and methods

Volumetric Expansion and Phase Equilibrium Studies. The equipment and procedures used for volumetric expansion and phase equilibrium studies are described elsewhere.[7,8] For measuring the volumetric expansion of a typical hydroformylation reaction mixture of known composition, a Jerguson® view cell was used. The volumetric expansion ratio was calculated using Eq. 1

$$\frac{V}{V_0}=\frac{V(T,P)}{V(T,P_0)} \tag{1}$$

For measuring the vapor–liquid phase equilibrium of CO_2-expanded hydroformylation mixtures, including the solubilities of CO and H_2 in the CXL phase, a Supercritical Fluid Technologies® variable-volume equilibrium cell equipped with on-line sampling of the vapor and liquid phases was used. Details of this equipment and its operation are provided elsewhere.[7]

Batch Studies of 1-octene Hydroformylation in CXL. The equipment and procedures used for batch reactions are describe elsewhere.[21] The TOF and chemoselectivity are calculated using Eqs. 2 and 3, respectively. The TOF in the batch run is estimated based on the number of moles of syngas converted corresponding to 20% 1-octene conversion (assuming a 1:1 stoichiometry). The number of moles of syngas converted is obtained from the syngas consumed in the external reservoir while maintaining the syngas pressure constant in the reactor.

$$TOF(\mathrm{h}^{-1})=\frac{\text{Moles of syngas consumed corresponding to 20\% 1-octene conversion}}{(\text{Moles of Rh})\ (\text{batch time})} \tag{2}$$

The *chemoselectivity* is defined as the number of moles of aldehydes formed relative to the number of moles of 1-octene reacted at the end of the 6 h batch runs. The *regio selectivity* (*n*/*i*) is estimated as the molar ratio of the linear to branched aldehydes in the product following the 6 h batch runs.

$$Chemoselectivity(\%)=\frac{\text{Moles of aldehyde products formed}}{\text{Moles of 1-octene converted}}\times 100\,\% \tag{3}$$

Measurement of Viscosities of CXLs Containing Dissolved Polymer. The viscosity measurements were performed using ViscoPro 2000 System 4 with SPL-440 high-pressure viscometer and Viscolab software, acquired from Cambridge Viscosity. The details of the viscometer are described elsewhere.[22] Additional details of the viscometer and the

Table 1. Materials used in this Work

Material	Purity	Company	Additional Comments
1-Octene	>98%	Sigma-Aldrich	Purified by passing through molecular sieve to remove water; stored under nitrogen
n-Nonanal	>95%	Sigma-Aldrich	
Toluene	Anhydrous, 99.8%	Sigma-Aldrich	Stored under argon
Triphenylphosphine (TPP)	99%	Sigma-Aldrich	
Acetylacetonatorhodium(I) dicarbonyl [$Rh(CO)_2(acac)$]	99%	Alfa Aesar	Stored under argon
Syngas	49.5% H_2 with balance being CO	Linweld	
CO_2	99.999%	Linweld	

procedure for measuring the viscosity of CXLs are given in the supplementary materials.

Continuous Reactor with Nanofiltration Membrane. The equipment used for performing continuous hydroformylation in CXLs with *in situ* membrane filtration is a modified version of the equipment used previously,[18] capable of maintaining a constant holdup of the CXL phase in the reactor. A schematic of the setup is shown in Figure 3. The polyimide membrane used for retaining the JanaPhos complex was PuraMem 280 (molecular weight cut-off of 280 g/mol), purchased from Evonik. It has a pressure limit of 6 MPa and temperature limit of 50°C. A circular piece 9 cm in diameter is cut to fit into the reactor. Additional details of the membrane reactor and the operating procedure are provided in the supplementary materials.

The turnover frequency during the continuous run (TOF_c) at pseudo steady state is estimated as follows

$$TOF_c(\mathrm{h}^{-1})=\left(\frac{\text{Molar 1-octene feed rate)}\ \text{(1-octene conversion at time } t)}{\text{(Initial moles of Rh in the reactor - cumulative Rh loss till time } t)}\right. \tag{4}$$

The amount of Rh in the reactor at a given time is estimated by subtracting from the initial Rh loading the cumulative Rh loss in the permeate measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

Results and Discussion

Volumetric expansion of 1-octene hydroformylation reaction mixtures

Knowledge of the extent of volume expansion of typical hydroformylation reaction mixtures by compressed CO_2 at the reactor operating conditions (P and T) is essential for rational reactor design and operation. Volumetric expansion studies were performed using model reaction mixtures corresponding to a typical 1-octene hydroformylation experiment at 80% 1-octene conversion using toluene as solvent (0.3 mL 1-octene + 1.4 mL nonanal + 3.5 mL toluene). Three different starting volumes were used in the expansion studies: 5, 10 and 15 mL at 40°C.

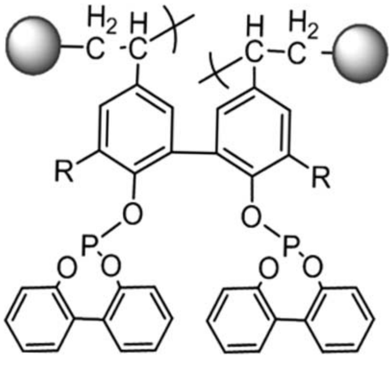

Figure 2. Structure of JanaPhos ligand.[19]

As seen from Figure 4, the volume of the liquid mixture increased exponentially in all cases upon CO_2 pressurization, increasing linearly at lower pressures and exponentially as the pressure approaches the CO_2 critical pressure (7.38 MPa). The expansion ratios (estimated using Eq. 1) were almost identical for the different starting volumes of the mixture dominated by toluene. Such expansion data for specific compositions of hydroformylation reaction mixtures are useful for determining CXL holdup volumes during either batch or continuous reactor operation.

Volumetric expansion studies were also performed at several temperatures (40, 50 and 60°C), with and without 0.6 MPa syngas (H_2/CO ratio = 1) in the gas phase (Figure 5). As expected, the volumetric expansion was greater and more sensitive to pressure at the lower temperature (40°C), as compared to the higher temperatures (50 or 60°C). At a given pressure, the CO_2 density (and, therefore, its solubility) in the CXL phase decreases with an increase in temperature. Also, the pressure dependence of the expansion ratio reflects that of the tunability of CO_2 density with pressure, which is more sensitive closer to its critical temperature (31.1°C). Furthermore, the presence of 0.6 MPa syngas did not have a measurable effect on the overall expansion (which is dominated by CO_2 dissolution) even though the syngas solubility should increase at higher CO_2 pressures. For determining the syngas solubility, separate VLE studies were performed in a variable volume cell as described in the following section. From previous studies[9] and the observations from this work, the Rh/TPP catalyst complex remained soluble in the liquid under current operating conditions. We

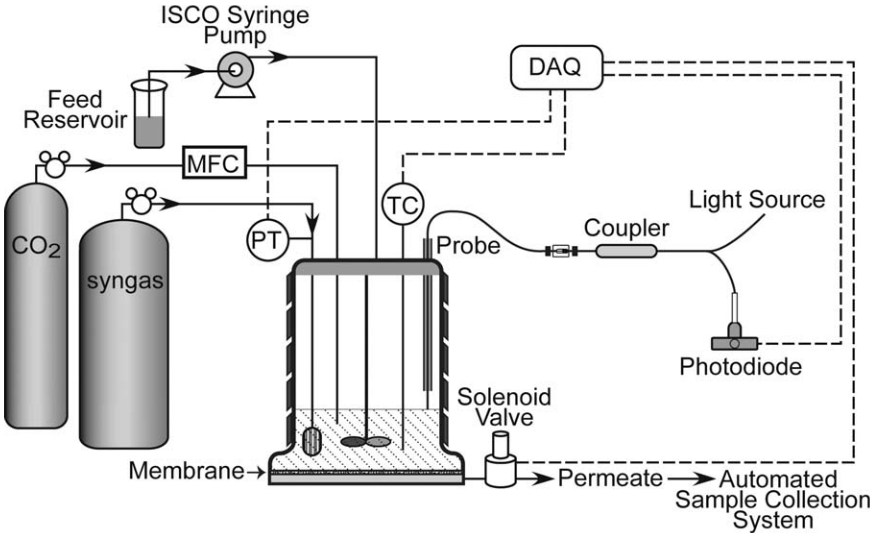

Figure 3. Reactor setup for continuous run with membrane filtration.

have recently modeled such quarternary systems involving CO_2 in order to reliably predict such expansions.[23]

Effect of CXLs on H_2/CO ratio

The equilibrium solubilities of CO and H_2 were measured in a CO_2-expanded liquid mixture consisting initially of 0.3 mL 1-octene, 1.4 mL nonanal and 3.5 mL toluene, same as the initial mixture used in the volumetric expansion studies. The H_2 and CO concentrations in the liquid phase at 50°C with and without CO_2 are shown in Table 2. The standard deviations are less than 5% for all data points.

From Table 2, it is seen that when pressurized with syngas alone, both H_2 and CO concentrations increased with syngas pressure, with the H_2/CO ratio remaining more or less constant (0.59–0.60). This is simply a reflection of the fact that both solubilities follow Henry's law and that the solubility of CO is greater than H_2 in the organic phase. The Henry's law constants for H_2 and CO solubilities in 1-octene were estimated using measured vapor–liquid equilibrium data between 40–60°C and compared with literature data[24] (Table 3). Clearly, the Henry's law constants obtained in this work match well with previously reported values.

In contrast, replacing syngas in excess of 0.6 MPa with CO_2 increased the H_2/CO ratio in the liquid phase. As seen in Table 2, the H_2/CO ratio in the neat reaction mixture is 0.59 with 5.6 MPa syngas but increases to 0.72 with 0.6 MPa syngas + 5 MPa CO_2. Furthermore, the H_2/CO

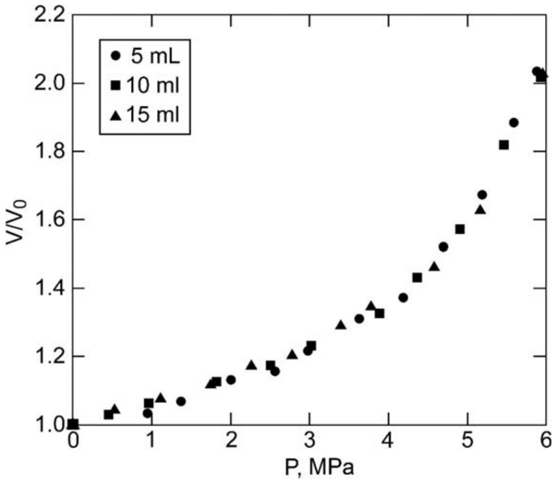

Figure 4. Volumetric expansion of 1-octene hydroformylation reaction mixtures with CO_2, with starting volumes of 5, 10 and 15 mL at 40°C.

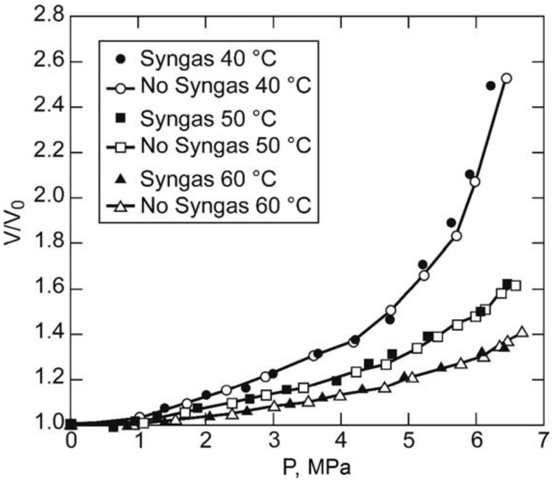

Figure 5. Effects of temperature and syngas partial pressure (0.6 MPa syngas) on the volumetric expansion of 1-octene hydroformylation reaction mixtures.

Table 2. CO and H_2 Mole Fractions (x) in Neat and CXL Reaction Mixtures at 50°C

	Syngas Only			CXL (0.6 MPa syngas + CO_2)		
P, MPa	x, H_2	x, CO	H_2/CO	x, H_2	x, CO	H_2/CO
0.6	0.0011	0.0019	**0.60**	0.0011	0.0019	**0.60**
2.5	0.0048	0.0079	**0.60**	0.0012	0.0019	**0.62**
3.8	0.0073	0.0124	**0.59**	0.0013	0.0021	**0.65**
5.6	0.0105	0.0177	**0.59**	0.0016	0.0022	**0.72**

Standard deviations less than 5% for all data points.

Table 3. Henry's Law Constant (K_H, MPa m^3/kmol) for H_2 and CO in 1-Octene

	This Work[a]			Literature[24]	
Temperature, °C	40	50	60	80	90
H_2	23.65	23.64	23.64	21.58 ± 0.38	21.12 ± 0.47
CO	11.71	11.56	11.38	11.76 ± 0.37	11.42 ± 0.23

[a]The K_H values from this work have an uncertainty of ±5%

enhancement in CXLs is achieved at CO mole fractions that are 4 to 8 times lower compared to pressurization with syngas alone at similar total pressures (see Table 2). In other words, it is possible to achieve similar or higher H_2/CO ratios at much lower CO concentrations in the CXL phase compared to pressurization of the liquid phase with syngas alone. Such a unique and tunable combination of H_2/CO ratio and low CO mole fraction in CXL phases favors hydroformylation as shown in the following section.

Clearly, H_2 is more soluble in the CO_2-expanded reaction mixture than in the mixture pressurized with syngas alone, causing the H_2/CO to increase as more CO_2 is added. At higher pressures, the dense CO_2 dissolves substantially in the liquid phase creating a CXL phase with increased free volume.[25] We therefore hypothesize that the smaller molecular radius of H_2 (74.1 picometer) relative to CO (112.8 picometer)[26] might contribute to the easier accommodation of H_2 in increasingly expanded CXL phases, giving rise to a non-linear increase in the individual gas solubilities that deviates from the ideal Henry's law behavior. This hypothesis has to be confirmed by molecular modeling studies (similar to those given in the work of Houndonougbo et al.[27]).

Effect of CXLs on hydroformylation activity and selectivity with Rh/TPP catalysts

Hydroformylation reactions catalyzed by homogeneous Rh complexes are significantly affected by the concentrations of CO and H_2 in the liquid phase. In general, higher H_2 concentrations favor turnover frequencies (TOFs)[28] while higher CO concentrations inhibit both TOF as well as regioselectivity. It is therefore of interest to investigate how the tunability of H_2 and CO concentrations in CXLs affects the hydroformylation reaction. The catalyst complex employed in this investigation is composed of $Rh(CO)_2(acac)$ and TPP. In all our experimental runs reported here, the molar 1-octene/Rh ratio was 988. A high P/Rh ratio of 205 is used to avoid ligand deficiency and ensure complete utilization of Rh in forming the catalyst complex. Depending on the extent of toluene expansion by CO_2 at the operating pressure (Figure 5), the initial volume of the toluene used was varied to ensure a constant initial liquid volume in all the batch runs. The stirrer speed was maintained at 1000 rpm to eliminate gas-liquid mass transfer limitations.[25] All data were repeatable within experimental error (±5%).

As seen in Table 4, higher syngas pressures are detrimental to both activity (TOF) and regioselectivity. The TOF decreased by 37% and the *n*/*i* ratio decreased by more than two-fold as the syngas pressure was increased from 0.6 to 5.6 MPa. As seen in Table 2, the CO concentration in the liquid phase increases by nearly an order of magnitude in this pressure range. In contrast, when syngas in excess of 0.6 MPa was replaced with CO_2, the TOF increased from ~66 h^{-1} at 0.6 MPa syngas (without CO_2 addition) to ~79 h^{-1} at 3.8 MPa (0.6 MPa syngas + 3.2 MPa CO_2). However, a further increase in total pressure to 5.6 MPa (0.6 MPa syngas + 5 MPa CO_2) caused the TOF to decrease to ~68 h^{-1} as further increases in CO_2 addition might change the density and polarity of the liquid phase. Most notably, the *n*/*i* ratio increased from 7.2 at 0.6 MPa syngas to 10.4 at 5.6 MPa CXL (0.6 MPa syngas + 5 MPa CO_2). Furthermore, at even at a similar H_2/CO ratio (~0.60) in the reaction phases at 2.8 MPa total pressure, the TOF and *n*/*i* ratio in CXLs are greater by approximately 50 and 225%, respectively, compared to pressurization of the liquid phase with syngas alone. These enhancements are attributed to the four-fold lower CO concentration in the CXL phase compared to pressurization with syngas alone (see Table 2).

Indeed, in the liquid phase, the increase in absolute concentration of CO with pressure has a greater impact on the *n*/*i* ratio than does the H_2/CO ratio. This can be seen from Tables 2 and 4. As shown in Table 4, for pure syngas, as pressure increases from 0.6 to 5.6 MPa, the H_2/CO ratio remains fairly constant at 0.60 while the *n*/*i* ratio drops significantly, from 7.2 to 3. The drop in *n*/*i* corresponds to an order-of-magnitude increase in the mole fraction of CO in the liquid phase (0.0019 to 0.0177).

For CXLs, the H_2/CO ratio may play a more significant role in *n*/*i* ratio. Across the same range of pressures, the mole fraction of CO is relatively stable (0.0019 to 0.0022), with a 20% increase in H_2/CO ratio (0.60 to 0.72), as seen in Table 2. Since the partial pressure of syngas in the CXL is maintained at 0.6 MPa, the mole fraction of CO in the CXL phase is comparable to that of pure syngas at 0.6 MPa (0.0019). The stable mole fraction of CO corresponds to a relatively constant *n*/*i* ratio (9.9 to 10.4) as seen in Table 4. Yet, these *n*/*i* ratios in CXLs represent a nearly 40% increase compared to that achieved with pure syngas at 0.6 MPa (7.2) and may be attributed to the simultaneous increase in the H_2/CO ratio in CXLs.

As seen from Table 2, while the CO concentration increases by approximately 15%, the H_2 concentration

Table 4. Effect of CXLs on H_2/CO, TOF and *n*/*i* at 50°C

	TOF, h^{-1}		*n*/*i*		H_2/CO	
Total Pressure, MPa	Syngas Only	CXL (0.6 MPa Syngas + CO_2)	Syngas Only	CXL (0.6 MPa Syngas + CO_2)	Syngas Only	CXL (0.6 MPa Syngas + CO_2)
0.6	65.8	–	7.2	–	0.60	–
2.8	55.4	83.9	4.1	9.9	0.60	0.62
3.8	48.5	78.9	3.5	10.1	0.59	0.65
5.6	41.5	68.2	3	10.4	0.59	0.72

1-octene/Rh = 988; P/Rh = 205; ligand: $-PPh_3$. For CXL runs, total pressure = 0.6 MPa syngas + CO_2 pressures. Solvent: Toluene. Identical liquid volume for neat solvent and CXL runs.

Table 5. Effect of CXLs on TOF and *n*/*i* at 60°C

Total Pressure, MPa	TOF, h^{-1} Syngas Only	TOF, h^{-1} CXL (0.6 MPa Syngas $+CO_2$)	*n*/*i* Syngas Only	*n*/*i* CXL (0.6 MPa Syngas $+CO_2$)
0.6	165.9	–	7.8	–
2.7	140.5	170.6	3.9	9.4
3.8	134.6	150.2	3.7	10.7
5.6	115.6	121.3	3.4	12.9

1-octene/Rh = 988; P/Rh = 205; ligand: -PPh_3. For CXL runs, total pressure: 0.6 MPa syngas + CO_2 pressures. Solvent: Toluene. Identical liquid volume for neat solvent and CXL runs.

increases by nearly 45% in this pressure range, resulting in an increase in the H_2/CO ratio. Remarkably, the increase of H_2/CO ratio in the reaction phase is achieved with syngas of a fixed composition (i.e., without adding extra hydrogen in the gas phase). Thus, CXLs provide a convenient way to enhance the H_2 concentration in the reaction phase without causing CO inhibition. These two effects are known to be beneficial to both the rate and regioselectivity, as seen from the increased TOF and *n*/*i* ratio in the case of CXLs compared to the use of syngas alone (see Table 4).

At 60°C, similar results were observed (Table 5). Both TOF and *n*/*i* decrease when the liquid phase is pressurized only with syngas. When replacing the syngas in excess of 0.6 MPa with CO_2 pressure, the TOF was higher when compared to pressurization with only syngas. The pressure effect on TOF at 60°C was less pronounced than at 50°C, probably because the kinetic rate constant is much higher at 60°C and offsets the reduction in rate caused by the dilution effect. The *n*/*i* ratio increased by more than threefold in CXLs compared to pressurization with syngas alone. These results clearly demonstrate that the injection of CO_2 into the liquid phase (a) increased the H_2/CO ratio in the CXL phase even at relatively low-syngas partial pressures (0.6 MPa), (b) reduced CO inhibition observed when using equivalent pressures of syngas alone, and (c) enhanced the TOF and *n*/*i* ratio.

The generally accepted mechanism for CO inhibition of the regioselectivity during hydroformylation by Rh/TPP complex was proposed by Pruett and Smith (Figure 6).[13] From Figure 6, we infer that in addition to PPh_3, CO is also a ligand for the Rh complex. The progressive substitution of PPh_3 by CO attachment to the Rh center is believed to worsen the regioselectivity. Thus, for a given catalytic system, it is plausible that at certain CO concentrations in the liquid phase the three PPh_3 ligands could all be displaced by CO. Beyond this threshold CO concentration, the beneficial effect of CXLs will no longer be evident. To test this hypothesis, we also carried out experiments using syngas partial pressures of 0.9 and 1.2 MPa.

When syngas partial pressure is increased from 0.6 to 0.9 MPa in the CXL experiments, the enhancement in both TOF and *n*/*i* were similar (Table 6) compared to 0.6 MPa syngas partial pressure at identical CO_2 partial pressures (Table 5). When the syngas partial pressure is further increased to 1.2 MPa, the observed TOFs in CXLs are less compared to the run with only syngas at 1.2 MPa (Table 7). Furthermore, the increases in *n*/*i* ratio with CXLs are moderate, from ~5 with syngas alone to 6.4 at the highest CO_2 pressure of 5 MPa. Thus, the observed increases in the *n*/*i* ratio with CXLs are much less at higher syngas pressures (0.9 and 1.2 MPa) compared to those at a syngas partial pressure of 0.6 MPa (Table 5). The deterioration in the CXL enhancement effect at higher syngas pressure is attributed to the resulting higher CO concentration in the liquid phase, which is detrimental to the regioselectivity. Clearly, the syngas pressure of 0.6 MPa is more suitable for use with CXLs. Lower syngas pressures typically lead to syngas starvation in the liquid phase and loss of selectivity toward isomer formation.

Effect of CXLs on hydroformylation activity and selectivity with Rh/JanaPhos complex

It is well-known that it is difficult to recover and recycle Rh/TPP catalyst complexes from reaction mixtures. In previous work, the bulky polymer-bound JanaPhos ligand was shown to facilitate effective retention of the Rh complex (~20 ppb Rh in the permeate) during a continuous hydroformylation run at 50°C in a stirred reactor equipped with a nanofiltration membrane of 400 molecular weight cutoff (MWCO).[18] A syngas pressure of 3 MPa was required for filtration with the polyimide nanofiltration membrane. Even though steady activity and selectivity were demonstrated, the observed regioselectivity was only 3.3 at this syngas pressure. To improve the regioselectivity, we investigated the concept of CXL media in which the total filtration pressure is made up of dense CO_2 and a lower syngas pressure to enhance the regioselectivity. To test this concept, $Rh(CO)_2(acac)$ complexed with JanaPhos ligand was first tested in CXLs in batch hydroformylation reactions. The

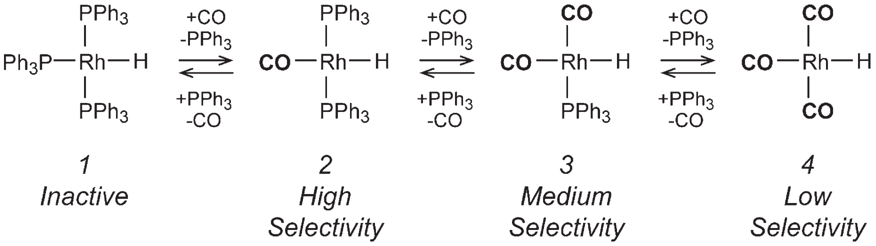

Figure 6. Influence of CO as a Rh/TPP ligand on hydroformylation regioselectivity.[13]

Table 6. Effect of CXLs with 0.9 MPa Syngas Partial Pressure at 60°C

	Total Pressure, MPa	TOF, h^{-1}	*n*/*i*
Syngas Only	0.9	162.1	6
CXL (0.9 MPa	3.0	169.1	6.6
syngas + CO_2)	4.1	156.7	7.3
	5.9	123.3	8.2

1-octene/Rh = 988, P/Rh = 205, ligand: -PPh_3, solvent: toluene. For CXL runs, total pressure: 0.9 MPa syngas + CO_2 pressures. Liquid phase volume maintained constant.

batch experiments were run at 50 and 60°C under 0.6 MPa syngas pressure and 3.2 MPa CO_2. The results are shown in Table 8.

The *n*/*i* ratio observed with the Rh/JanaPhos complex increased to 6.6 (50°C) and 7.7 (60°C) at the lower syngas pressure of 0.6 MPa. However, at both temperatures, the *n*/*i* ratio in CXL media increases by ~10% compared to that observed with syngas alone at 0.6 MPa. These enhancements are relatively less compared to those observed with the Rh/TPP complex (Tables 4 and 5). Furthermore, the TOFs with Rh/JanaPhos complex actually decrease slightly in CXLs compared to neat media (e.g., 484 h^{-1} in CXL vs 494 h^{-1} in non-CXL phase at 50 °C). This is partly due to lower density of the CXL phase and partly because the TOFs with bidentate ligands depend not only on CO dissociation but also on the ligand bite angle.[28] Although the effect of CXLs on TOF and *n*/*i* is more modest in the case of Rh/JanaPhos complex, the CXLs nevertheless provide the necessary pressure (3 MPa minimum) for nanofiltration without introducing CO inhibition that occurs when syngas alone at 3 MPa is employed. Additionally, the significant viscosity reduction obtained with CXLs, discussed in the following section, facilitates the nanofiltration process.

Viscosity reduction in CXLs

The use of CXL should decrease the viscosity of the reaction mixture containing the dissolved polymer ligand. In order to quantify the extent of viscosity reduction, experimental viscosity measurements were undertaken. Figure 7 shows the viscosities measured for the mixture of toluene and JanaPhos ligand at a concentration of 0.7 wt %, at four temperatures and five CO_2 pressures. At these conditions, the polymer ligand stays dissolved in the CXL (i.e., operating conditions are below the cloud point). Such information provides valuable guidance for both the batch as well as continuous hydroformylation studies under homogeneous conditions. From Figure 7, it may be inferred that the viscosities decrease with increasing temperature at the same CO_2 pressure and with increasing CO_2 pressure at the same temperature. When pressurizing with up to 4 MPa CO_2 at temperatures of 30 and 60°C, viscosities decrease by 50 and 30%, respectively. Remarkably, these viscosity reductions are greater in magnitude than those achieved with increases in temperature. For example, negligible change in viscosity with temperature was observed at CO_2 pressure of 4 MPa. Furthermore, the viscosity reduction achieved in the 30–60 °C range with no CO_2 addition is roughly 50% less compared to the viscosity reduction achieved at 30°C by adding 4 MPa CO_2. At the desired operating temperature of 50°C, the viscosity reduction upon adding 3 MPa CO_2 is approximately 33%.

Table 7. Effect of CXLs with 1.2 MPa Syngas Partial Pressure at 60°C

	Total Pressure, MPa	TOF, h^{-1}	*n*/*i*
Syngas Only	1.2	154.5	5.0
CXL (1.2 MPa	3.3	148.8	5.7
syngas + CO_2)	4.4	139.9	5.9
	6.2	125.8	6.4

1-octene/Rh = 988, P/Rh = 205, ligand: -PPh_3, solvent: toluene. For CXL runs, total pressure: 1.2 MPa syngas + CO_2 pressures. Liquid phase volume maintained constant.

Table 8. Effect of CXLs on Hydroformylation with Bidentate Ligands (JanaPhos)

T, °C	50		60	
Pressure, MPa	0.6	3.8 (CXL)	0.6	3.8 (CXL)
Time, h	4	4	1.5	1.5
TOF, hr^{-1}	494	484	987	976
Conversion, %	97.9	97.1	97.0	97.2
S (aldehyde), %	85.6	85.9	80.6	80.2
S (octane), %	6.8	6.5	9.2	9.5
S (isomers), %	7.2	7.3	9.9	10
n/*i*	6.6	7.3	7.7	8.5

1-octene/Rh = 1000, P/Rh = 6, 1-octene/toluene = 3/7 (V/V). For CXL runs, total pressure = 0.6 MPa syngas + CO_2 pressures. Liquid phase volume maintained constant.

Continuous reaction with membrane filtration in CXLs

During continuous runs with conventional liquid phase reaction media, the liquid volume is relatively independent of pressure fluctuations and hence level control was not a major issue.[18] In contrast, when using gas-expanded liquids, stable level control posed more of a challenge compared to conventional liquid phases, due to the significant pressure dependence of the volume of the expanded phase. An optic fiber probe, similar to that demonstrated for measuring volume expansions and phase transitions with supercritical fluids in closed vessels,[29] was used to provide feedback to a solenoid valve located in the permeate stream downstream of a Swagelok® double pattern metering valve (Figure 3). By employing this level control system during the continuous filtration run in CXL media, steady permeate flow rate of

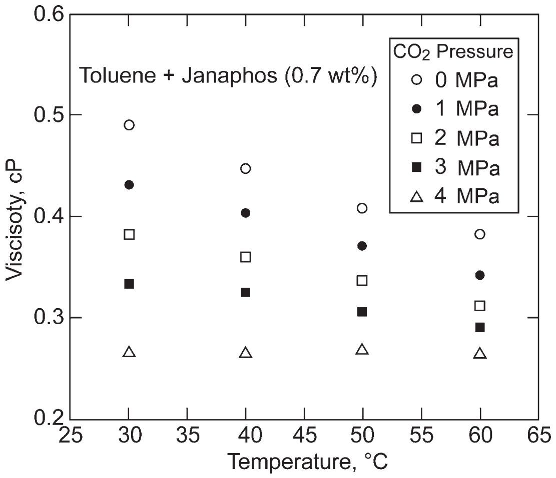

Figure 7. Variation of viscosities with temperature for (toluene + 0.7 wt % JanaPhos) mixtures at different CO_2 pressures.

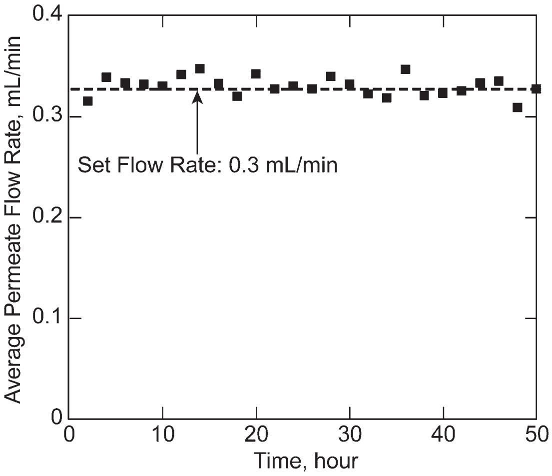

Figure 8. Average permeate flow rate with fiber optics-based level control of CXL phase in the stirred reactor.

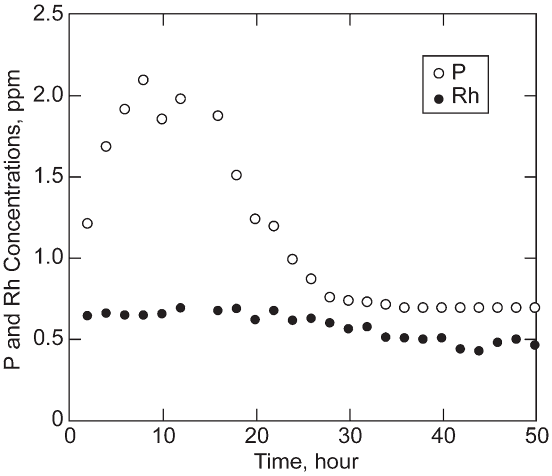

Figure 10. Temporal Rh and P concentrations in permeate of continuous reactor based on ICP analyses (operating conditions same as for run shown in Figure 9).

approximately 0.33 ± 0.01 mL/min was maintained for 50 h (Figure 8), matching the 0.33 mL/min liquid inlet flow rate set at the syringe pump. The pressure and temperature sensors along with control mechanisms were interfaced with a LabVIEW® data acquisition and control system for continuous data monitoring.

Continuous reaction in CXLs with membrane filtration was carried out for 50 h and the results are shown in Figure 9. In our previous continuous reactor studies with syngas only at 3 MPa,[18] the conversion stabilized at 50% and the *n*/*i* was around 3.3 due to syngas inhibition. In contrast, the conversion increased to more than 70% and the *n*/*i* was nearly 8 in the case of the CXL run that utilized 0.6 MPa syngas (to alleviate inhibition of TOF and *n*/*i* ratio) and 3.2 MPa CO_2. Aldehyde selectivity was more than 90%. The conversion appears to stabilize around 70% with a TOF_c value of ~340 h^{-1} (cumulative TON = 17,680 after 50 h). Clearly, the use of a combination of low syngas partial pressure and CO_2 is beneficial to the regioselectivity as well as reaction activity. Furthermore, the nearly steady TOF_c and permeate flow at constant pressure indicate that the membrane pores are not blocked or fouled during the 50 h run.

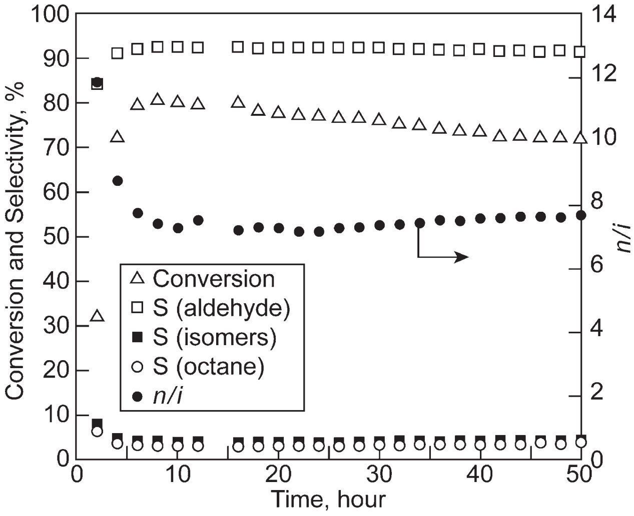

Figure 9. Temporal 1-olefin conversion and product selectivities during continuous Rh/JanaPhos catalyzed homogeneous hydroformylation in CXL media performed in a stirred reactor fitted with a nanofiltration membrane.

Reaction conditions: 1-octene/toluene = 3/7 (V/V), liquid flow rate = 0.33 mL/min; syngas partial pressure = 0.6 MPa (maintained constant); total pressure = 3.8 MPa; CO_2 flow rate = 25 sccm; T = 50°C; initial Rh concentration = 130 ppm.

ICP-AES analysis of the permeate stream showed low Rh and P leaching rates during the CXL runs (Figure 10). The P concentration in the permeate stabilized at 0.5 ppm after 25 h. Rh concentration was less than 0.5 ppm after 25 h. The total leaching of Rh in 50 h was 0.46 mg (5%). Total leaching of P was 0.89 mg (4.6%). At concentrations of a few ppm, the Rh can be effectively recovered by using suitable absorbents,[30–32] thus providing nearly quantitative Rh recovery. It has been shown previously that a CXL-based process concept as demonstrated in this manuscript would be economically competitive with conventional cobalt-based hydroformylation of higher olefins.[20]

Concluding Remarks

Continuous homogeneous hydroformylation was demonstrated in CXL media in a stirred reactor equipped with a nanofiltration membrane to effectively retain the bulky Rh catalyst complex. In CXL media, H_2/CO ratio can be increased at fixed syngas composition, low-syngas partial pressures (thereby avoiding CO inhibition) and mild total pressures (a few MPa). For Rh catalyzed 1-octene hydroformylation, the increased H_2/CO ratio in CXL medium increases both the TOF and regioselectivities compared to neat hydroformylation reaction mixtures. At 0.6 MPa syngas partial pressure and 5 MPa CO_2 pressure, the increase in TOF is up to 64% at 50°C and 21% at 60°C, while the corresponding increases in regioselectivity (*n*/*i*) are 250 and 280%, respectively. At higher syngas partial pressures of 0.9 and 1.2 MPa, the increases in *n*/*i* ratio with CXL media were relatively less than at 0.6 MPa. This ability of tuning H_2/CO ratio in CXL can in general be applied to hydroformylation of other olefinic substrates as well.

The advantages of low syngas pressure and CXL media on TOF and selectivity are particularly well suited for performing continuous reactions with *in situ* nanofiltration, wherein operating pressures of 3–4 MPa are needed to obtain a reasonable transmembrane flux for the 280 MWCO membrane. By maintaining a constant syngas partial pressure of 0.6 MPa and a CO_2 partial pressure of 3.2 MPa in the reactor, we not only avoid syngas inhibition (observed when 3 MPa syngas alone is used as pressurizing gas) but also exploit the resulting CXLs to increase the H_2/CO ratio in the reaction phase and the lower the viscosity. Continuous hydroformylation in such CXL media, using soluble bulky phosphite ligands, was successfully conducted for up to 50 h at 50 °C. The increased H_2/CO ratio in the CXL phase helps to attain nearly steady TOF_c ($\sim$340 $h-^1$) and selectivity ($n/i = 8$, aldehydes $> 90\%$). Constant permeate flux is maintained across the nanofiltration membrane during the 50 h run with low Rh and P leaching ($<$ 1 ppm each in permeate) at steady state. It should be possible to implement the demonstrated CXL-based continuous reactor concept with *in situ* nanofiltration by replacing existing hydroformylation reactors with the proposed system. Furthermore, the concept should also be applicable in general to homogeneously catalyzed reactions where effective catalyst containment is the key for practical viability.

The development of new hydroformylation technology concepts may also find application as an atom economical C—C coupling reaction route utilizing emerging feedstocks such as bioethanol, biosyngas and ethane/propane (from natural gas).[33] For example, the bioethanol may be converted by dehydration to ethylene, which is then hydroformylated to linear propanal that is converted to propanol. The propanol is then dehydrated providing access to C_3 olefins. In this manner, successive hydroformylation, reduction and dehydration steps help increase the chain-length of the olefins.

Acknowledgments

This research was supported with funds from the following sources: the National Science Foundation Engineering Research Centers Grant EEC-0310689; and the United States Department of Agriculture/National Institute of Food and Agriculture (USDA/NIFA) Award 2011–10006-30362.

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Manuscript received Dec. 2, 2012, and revision received Mar. 12, 2013.