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Phase-separable catalysis using room temperature ionic liquids and supercritical carbon dioxide

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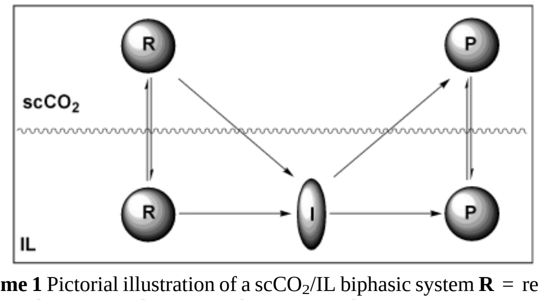
A new phase-separable catalysis concept is demonstrated using supercritical carbon dioxide and the room temperature ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate for hydrogenation of alkenes and carbon dioxide.

There is a continuing interest in developing new concepts for biphasic or phase-separable catalysis where a homogeneous catalyst is immobilized in one liquid phase and the reactants and/or products reside largely in another liquid phase.[1] Brennecke and Beckman[2] have recently reported that the room temperature ionic liquid (IL) 1-butyl-3-methylimidazolium hexafluorophosphate, **1**, ([BMIM][PF_6]), exhibits very interesting phase behavior with supercritical carbon dioxide ($scCO_2$), where CO_2 can dissolve significantly (up to 0.6 mole fraction) into the lower IL phase, but no polar IL dissolves in the upper $scCO_2$ phase. They further illustrated that organics such as naphthalene could be extracted from the IL phase using $scCO_2$. Kazarian *et al.*[3] recently provided corroborating spectroscopic evidence that CO_2 dissolves in **1**. This intriguing discovery of phase behavior suggested that a reaction system comprised of $scCO_2$ and an ionic liquid might offer particular advantages as a new biphasic catalysis system. Herein, such a $scCO_2$/IL biphasic system is demonstrated, where a homogeneous transition metal catalyst is immobilized in an IL phase and products can be isolated from a distinct $scCO_2$ phase.[4]

Room temperature ionic liquids[5] and supercritical carbon dioxide[6] have both been extensively studied as alternative solvents for a wide range of homogeneously catalyzed reactions including hydrogenation, hydroformylation, selective oxidation and carbon–carbon bond formation. We chose to examine the $scCO_2$/IL system through investigations of the hydrogenation of dec-1-ene and cyclohexene using Wilkinson's catalyst $RhCl(PPh_3)_3$, **2**, which is insoluble in $scCO_2$ but soluble in water-stable [BMIM][PF_6], **1**.

All reactions were run in custom-designed, high pressure stainless steel view cells with a sapphire window using magnetic stirring at 50 °C, as described previously.[7]† The hydrogenation of dec-1-ene proceeded in 98% conversion to *n*-decane in 1 h at 48 bar H_2 and a total pressure of 207 bar, which implies a time-averaged reaction turnover frequency (TOF) of 410 h^{-1}. The reaction mixture was biphasic throughout the reaction with a colorless carbon dioxide phase above a yellow ionic liquid phase. Hydrogenation of cyclohexene proceeded more slowly under identical conditions with 82% conversion being observed after 2 h reaction at 50 °C (time-averaged TOF = 220 h^{-1}) and 96% conversion measured after 3 h. Product recovery and catalyst recycling were demonstrated for dec-1-ene using a variable volume reaction vessel to transfer the upper $scCO_2$ phase to a separate receiver under high pressure after reaction.[8] The reaction vessel was then recharged with dec-1-ene, hydrogen and carbon dioxide and allowed to react for 1 h. This process was repeated up to four times and the reaction proceeded to *ca.* 98% conversion each time, thereby demonstrating efficient catalyst recycling through immobilization of the rhodium catalyst in the ionic liquid.



Scheme 1 Pictorial illustration of a $scCO_2$/IL biphasic system **R** = reactant, **P** = product, **I** = polar intermediate (*e.g.* carbamate **4**).

Since many organic compounds are not miscible with imidazolium-based ionic liquids, many of the reported catalytic reactions in ILs can be considered to be organic/IL biphasic systems. Product separation has been demonstrated in a number of cases.[9] In order to benchmark the reactivity of the $scCO_2$/IL system with organic/IL systems, we also examined the above hydrogenation reactions using *n*-hexane in place of carbon dioxide, under otherwise identical conditions.‡ The reaction of dec-1-ene to form *n*-decane proceeded to 99% conversion after 1 h at 50 °C in *n*-hexane/[BMIM][PF_6]. Conversions of cyclohexene to cyclohexane were similar to those measured in the $scCO_2$/[BMIM][PF_6] experiments: 88% after 2 h, 98% after 3 h at 50 °C. These results suggest that there is no reactivity advantage for CO_2 over *n*-hexane for simple hydrogenation reactions.

In order to capitalize on advantages arising from the polar nature of the ionic liquid phase, we sought to examine reactions that proceed through polar intermediates which would be soluble in the IL phase and not in $scCO_2$ (Scheme 1). We studied the hydrogenation of carbon dioxide in the presence of dialkylamines to produce *N*,*N*-dialkylformamides. Noyori *et al.*[10] and Baiker *et al.*[11] have reported elegant studies on the catalytic hydrogenation of CO_2 to formamides in $scCO_2$ using $scCO_2$-soluble $RuCl_2(PMe_3)_4$ and $scCO_2$-insoluble $RuCl_2(dppe)_2$ (dppe = $Ph_2PCH_2CH_2PPh_2$), **3**, respectively. These reactions involve ionic carbamate intermediates, since dialkylamines react with CO_2 reversibly to form dialkylammonium dialkylcarbamates, **4** [eqns (3), (4)].[12]

$$CO_2 + H_2 \overset{[cat]}{\rightleftharpoons} HCO_2H \tag{1}$$

$$HCO_2H + R_3N \rightleftharpoons [HNR_3]^+[HCO_2]^- \tag{2}$$

$$HNR_2 + CO_2 \rightleftharpoons R_2NCO_2H \tag{3}$$

$$R_2NCO_2H + NHR_2 \rightleftharpoons \underset{\mathbf{4}}{[NH_2R_2]^+[O_2CNR_2]^-} \tag{4}$$

$$[NH_2R_2]^+[O_2CNR_2]^- + 2HCO_2H \rightarrow 2HCON(R)_2 + 2H_2O + CO_2 \tag{5}$$

Noyori *et al.* reported that salt **4a** (R = CH_3) separated from the $scCO_2$ phase right from the start of the reaction starting with dimethylamine and rates using **4a** were similar to those using dimethylamine. Very high rates for selective *N*,*N*-dimethylformamide (DMF) formation were reported using either liquid **4a**,[10] or dimethylamine.[10,11] Significantly Noyori *et al.* found that activity and selectivity (*i.e.* formic acid *vs.*

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Table 1 Production of formamides from amines and CO_2 in different solvent systems

Amine	Solvent	Catalyst	T/°C	t/h	Con (%)	Sel (%)	TON[a]	TOF (h^{-1})[b]
$NH(C_2H_5)_2$[c]	$scCO_2$	$RuCl_2(PMe_3)_4$	100	13	38	46[d]	820	63
$NH_2(n\text{-}C_3H_7)$[c]	$scCO_2$	$RuCl_2(PMe_3)_4$	100	5	18	30[d]	260	52
$NH(n\text{-}C_3H_7)_2$	$scCO_2$/IL	$RuCl_2(dppe)_2$	80	5	100	> 99	110	> 22

[a] TON = mol product/mol ruthenium. [b] Time-averaged TOF. [c] Ref. 10. [d] Other product is formic acid.

formamide production) decreased rapidly with longer chain amines (R ≠ CH_3) which lead to solid, $scCO_2$-insoluble carbamate intermediates.[10]

In the $scCO_2$/IL system, catalyst **3** and carbamate **4** are both soluble in the IL phase. Carbamate **4a** could be completely converted to DMF after 4 h at 80 °C using 55 bar hydrogen under a total pressure of 276 bar.§ While this unoptimized reactivity is significantly less than that reported by Baiker for the liquid carbamate,[11]‡ we found that the reactivity and more importantly the selectivity is higher for amines other than dimethylamine in the $scCO_2$/IL biphasic system. Under similar reaction conditions, di-*n*-propylamine¶ led to complete amine conversion and exclusive production of the corresponding *N*,*N*-di-*n*-propylformamide after only 5 h at 80 °C. The activity and selectivity are higher than those reported[10] for less bulky diethylamine and *n*-propylamine in neat $scCO_2$ (Table 1). The increased selectivity in the $scCO_2$/IL biphasic system likely arises from the increased solubility of the solid dialkylcarbamate intermediates in the IL phase or through rate enhancement of amidation of formic acid derived from CO_2 hydrogenation [eqn (5)].

The highly polar formamide products appear to be very soluble in the ionic liquid phase, **1**. Preliminary experiments reveal that they do not partition strongly into the $scCO_2$ phase after only one reaction cycle. Quantitative data on the partitioning of organic compounds between ionic liquids and either organic solvents or $scCO_2$ are just starting to appear in the literature.[13,14] We have demonstrated extraction of DMF from IL **1** in a separate experiment. After stirring 30 mL $scCO_2$ (P_{tot} = 276 bar) over a solution of 1.0 mL ionic liquid **1** and 1.0 mL DMF for 1 h at 80 °C, the upper CO_2 phase was transferred under high pressure to another vessel. Subsequent pressure let-down led to 151 mg of isolated DMF (16% recovery). We have been able to demonstrate effective product recovery for *N*,*N*-di-*n*-propylformamide after several reaction/recovery cycles. The recovery yield in the first cycle was poor (less than 5%), however, the yield in the second cycle improved significantly to 61%. *N*,*N*-di-*n*-propylformamide can be almost quantitatively recovered in the third and fourth cycle, suggesting the IL phase becomes saturated with the product in the first two cycles.[15]

In conclusion, we demonstrate one of the first examples[4] of catalysis in a biphasic system incorporating supercritical carbon dioxide and ionic liquids and more importantly the first example involving CO_2 reaction chemistry. High selectivity, catalyst recycling and product recovery were observed for hydrogenation of CO_2 in the presence of dialkylamines, demonstrating the potential advantages arising from dissolving polar reaction intermediates in the IL phase. We are in the process of investigating other reactions, particular those involving polar intermediates, as well as quantifying the partitioning of reactants (including gases), products and catalyst between the two phases.

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Notes and references

† *Typical experimental procedure for olefin hydrogenation*: 20 mg (21 μmol) of **2** were added to 10.5 mmol of olefin (500 equiv. relative to catalyst **2**) and 1 mL of ionic liquid **1** in the reaction cell which was then pressurized with hydrogen (48 bar) and CO_2 to a total pressure of 207 bar. All the experiments were conducted at 50 °C using *n*-nonane as an internal standard.

‡ While magnetic stirring may not be optimal for these reactions, our preliminary experimental conditions allow for a semi-quantitative comparison.

§ *Typical experimental procedure for CO_2 hydrogenation*: 0.5 mL (4.3 mmol) of **4a** was charged into a 33 mL stainless steel reaction cell with a solution of 10 mg (10 μmol) of **3** in 1 mL of **1**. The cell was heated to 80 °C after being filled with 55 bar H_2, then it was pressurized to a total pressure of 276 bar with CO_2. The start of the reaction was defined as the time of CO_2 gas introduction. The yield and identification of formamide were performed by GC, GC-MS and ^1H NMR.[10]

¶ 0.15 mL (1.1 mmol) of di-*n*-propylamine and 1 mL of **1** were used. Higher concentration of amine (*e.g.* 7.3 mmol di-*n*-propylamine in 1 mL of **1**) led to precipitation of a white solid (carbamate).

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