Enhanced Catalyst Reactivity and Separations Using Water/Carbon Dioxide Emulsions

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The difficulty of catalyst separation and recovery continues to create economic and environmental barriers to the broader industrial application of homogeneous catalysts for chemical transformations, despite the remarkable activity and selectivity attainable through sophisticated ligand design in these systems. A number of approaches termed biphasic catalysis have been advanced where a soluble catalyst is immobilized in one liquid phase (often aqueous) and the substrates and products are isolated in a separate immiscible phase.[1] We wish to report a new aqueous biphasic homogeneous catalysis system that uses only water and environmentally benign supercritical carbon dioxide[2] (CO_2) along with water-soluble catalysts and emulsion-forming surfactants which are active at the water/CO_2 (w/c) interface.[3] After reaction, the emulsion can be broken by simply decreasing the pressure to effect product separation and catalyst recycle. We demonstrate drastic improvements in reaction rates relative to conventional biphasic water/organic (or water/CO_2)[2] systems for the hydrogenation of alkenes catalyzed by water-soluble rhodium−phosphine complexes. The high reaction rates likely arise from a combination of higher hydrogen concentration due to miscibility in the CO_2 phase and increased interfacial surface area by emulsion formation.

The concept of aqueous biphasic catalysis was advanced over 20 years ago[4] and a number of reactions and water-soluble catalysts have been reported.[5] While rates can be high for volatile or slightly water-soluble reactants (i.e. the commercially practiced hydroformylation of propene[6]), these systems have found limited use for more hydrophobic (i.e. most organic) substrates, because of lower reaction rates due to mass transfer limitations across the interface. Water/organic solvent emulsions can lead to increased reactivity but create problems with breaking the emulsion after reaction. Newer biphasic systems involving fluorous phase[7] or thermomorphic[8] systems have been advanced for a wide range of catalytic reactions, which show considerable promise; however, broad application could be limited by the relatively high cost of these solvents and catalysts. Supercritical CO_2 has been used as a replacement solvent for a number of homogeneous reactions.[9] In some cases improvements in catalyst activity or selectivity have been observed and catalyst recovery has recently been demonstrated.[10] Bhanage et al. have recently reported a simple H_2O/CO_2 biphasic catalysis system (i.e. no emulsions) for hydrogenation of cinnamaldehyde using a water-soluble ruthenium catalyst where higher conversions were observed relative to toluene/water biphasic mixtures.[2]

To demonstrate the advantages of these surfactant-stabilized emulsions for biphasic homogeneous catalysis we chose to study the hydrogenation of alkenes using the water-soluble catalyst RhCl(tppds)$_3$ (tppds[11] = tris(3,5-disulfonatophenyl)phosphine). Three different surfactants were used that we have found to form water in CO_2 (w/c) or CO_2 in water (c/w) emulsions: (1) anionic perfluoropolyether ammonium carboxylate (PFPE COO$^-$NH$_4^+$, MW = 740 and 2500 g/mol), (2) cationic Lodyne 106A ($C_6F_{13}(CH_2)_2SCH_2CH(OH)CH_2N^+(CH_3)_3Cl^-$, MW = 531.5 g/mol), and (3) nonionic poly(butylene oxide)-*b*-poly(ethylene oxide) (PBO-PEO, MW = 860-*b*-660 g/mol).[12] These recently discovered surfactants[3] form emulsions with droplet diameters of 0.5−15 μm and surface areas up to 10^5 m^2/L. They also offer a distinct advantage over common water/oil (w/o) emulsions in that they can be easily broken by simply decreasing the pressure. The low interfacial tension, γ, between water and CO_2 (17 mNm^{-1} at pressures above 70 bar vs 30−60 mNm^{-1} for water−alkenes)[13] facilitates formation of emulsions with only 0.1−2.0 wt % surfactant. These emulsions have been shown to solubilize both hydrophobic and hydrophilic substrates, and have been applied to simple organic reactions.[13,14] Conductivity measurements reveal that the hydrophilic PBO-PEO (400 μS/cm) and Lodyne 106A (800 μS/cm) form c/w emulsions, whereas the water-insoluble PFPE surfactant forms c/w emulsions when the MW = 740 (100 μS/cm) and w/c emulsions when the MW = 2500 (0.1 μS/cm). Using optical microscopy, we measured the PBO-PEO and PFPE emulsion droplets to be 3−5 μm while the Lodyne 106A was found to be 10−15 μm. The pH of the aqueous phase for water/CO_2 mixtures has been measured to be ca. 3 due to formation and dissociation of carbonic acid.[15]

The time profile of ethyl benzene formation in the hydrogenation of styrene is illustrated in Figure 1 for two-phase water/toluene and water/CO_2 systems (i.e. no added surfactant) and for four water−carbon dioxide emulsions stabilized by surfactants.[16] While simple solvent replacement of toluene with carbon dioxide leads to some rate enhancement in our and the Bhanage[2] systems, likely due to higher hydrogen solubility[17] in the CO_2 system, it is clear that this activity is still not practical for most nonpolar, nonvolatile substrates. As shown in Figure 1, the reaction rate

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(1) A recent issue of *Catalysis Today* (**1998** *42* (2)) was devoted to biphasic homogeneous catalysis. Also see: Baker, R. T.; Tumas, W. *Science* **284**, 1477−1479 1999.
(2) (a) Bhanage, B. M.; Ikushima, Y.; Shirai, M.; Arai, M. *Chem. Commun.* **1999**, 1277−1278. (b) Bhanage, B. M.; Ikushima, Y.; Shirai, M.; Arai, M. *Tetrahedron Lett.* **1999**, *40*, 6427−6430.
(3) (a) Johnston, K. P. et al. *Science* **1996**, *271*, 624−626. (b) Clarke, M. J.; Harrison, K. L.; Johnston, K. P.; Howdle, S. M. *J. Am. Chem. Soc.* **1997**, *119*, 6399−6406.
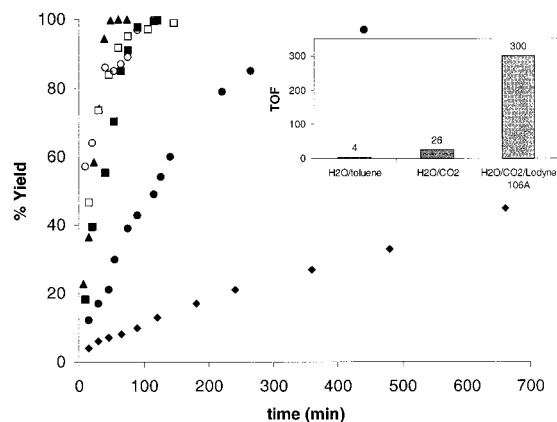(4) Herrmann, W. A.; Kohlpaintner, C. W. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1524−1544.
(5) Cornils, B.; Herrmann, W. A. *Aqueous-Phase Organometallic Catalysis*; Wiley-VCH: Weinheim, Germany, 1998.
(6) Kuntz, E. G. *CHEMTECH* **1987**, *17*, 570−575.
(7) Horvath, I. T. *Acc. Chem. Res.* **1998**, *31*, 641−650.
(8) Bergbreiter, D. E.; Liu, Y.-S.; Osburn, P. L. *J. Am. Chem. Soc.* **1998**, *120*, 4250−4251.
(9) Jessop, P. G.; Ikariya, T.; Noyori, R. *Chem. Rev.* **1999**, *99*, 475−493.
(10) Kaintz, S.; Brinkmann, A.; Leitner, W.; Pfaltz, A. *J. Am. Chem. Soc.* **1999**, *121*, 6421−6429.
(11) We found that the analogous trisulfonated ligand TPPTS also works in this system.
(12) PFPE was synthesized according to published procedures;[19] Lodyne 106A was purchased from CIBA and PBO-*b*-PEO from PPG Industries.
(13) Jacobson, G. B.; Lee, C. T.; daRocha, S. R. P.; Johnston, K. P. *J. Org. Chem.* **1999**, *64*, 1207−1210.
(14) Jacobson, G. B.; Lee, C. T., Jr.; Johnston, K. P. *J. Org. Chem.* **1999**, *64*, 1201−1206.
(15) Holmes, J. D.; Ziegler, K. J.; Audriani, M.; Lee, C. T., Jr.; Bhargava, P. A.; Steytler, D. C.; Johnston, K. P. *J. Phys. Chem. B* **1999**, *103* (27), 5703−5711.
(16) All reactions were performed in custom-designed variable-volume view cells[13] equipped with a six-port high-pressure sampling valve to allow for reagent addition and sample analysis (via gas chromatography). Emulsions were formed from shear across a 762 μm diameter capillary tube created by a recirculating pump and the system was magnetically stirred with a stirbar kept at constant rpm for all reactions. Work investigating the effect of stirring rate is in progress. All reactions were run at 40 °C and 4000 psi with a ligand/Rh/substrate ratio of 6/1/100.
(17) Halpern, J. *Inorg. Chim. Acta* **1981**, *50*, 11−19.

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Figure 1. Time profile of formation of ethylbenzene from hydrogenation of styrene performed in biphasic water/toluene (◆), biphasic water/CO$_2$ (●), and in w/c or c/w emulsions using PFPE MW = 2500 (▲), PFPE MW = 740 (■), Lodyne 106A (○), or PBO-PEO (□) as surfactants. Reaction conditions: 50/50 wt % water/CO$_2$ (4.75 g each), 1.5 wt % surfactant, 80 mM styrene, 1 mol % catalyst to substrate, Rh/L = 1/6, 40 °C, 4000 psi. TOF values at 50% conversion are given as a comparison for biphasic H$_2$O/toluene, H$_2$O/CO$_2$, and H$_2$O/CO$_2$ emulsion systems.

for styrene hydrogenation increases significantly upon addition of surfactant and emulsion formation. The time profiles in Figure 1 suggest the reaction is nearly zero order for at least the first half of the reaction. The initial catalytic activity can be quantified in terms of turnover frequency (TOF), here defined as the moles of substrate transformed per mole of catalyst per hour at 50% conversion. For styrene, the TOF was found to be 4 h^{-1} in toluene/water, 26 h^{-1} in CO$_2$/water, and 150–300 h^{-1} for the emulsions formed from three different surfactants. Significantly, the rate for the emulsions is considerably larger than conventional biphasic water/organic solvent systems[18] and is comparable to the rates of the single phase homogeneous reaction in organic solvents using Wilkinson's catalyst (RhCl(PPh$_3$)$_3$).[19] In an effort to ascertain whether the reaction is occurring in the water phase or at the interface we examined a series of hydrophobic 1-alkenes. The TOF at 50% conversion for 1-octene, 1-decene, and 1-eicosene was measured to be 140, 110, and 30 h^{-1}, respectively. If the initial zero order kinetic dependence on substrate concentration arises from a steady-state concentration of substrate in the aqueous phase (i.e. the water solubility of the substrate), one would expect the relative rates to correlate with the relative solubility in water for these olefins, since the homogeneous reaction rate is known to be independent of chain length.[20] The solubility of 1-octene in water at 25 °C is 2.7 mg/L of water, and the solubility of higher olefins decreases exponentially with molar volume.[21] The observation that 1-eicosene is only about four times slower than 1-octene, despite its markedly lower (orders of magnitude) water solubility, indicates that the reaction could be occurring at the interface where the relative concentrations may be much closer, rather than in bulk water.

(18) Larpent, C.; Dabard, R.; Patin, H. *Terahedron Lett.* **1987**, *28*, 2507–2510.
(19) Jardine, F. H.; Osborn, J. A.; Wilkinson, G. *J. Chem. Soc. (A)* **1967**, 1574–1578.
(20) James, B. R. *Homogeneous Hydrogenation*; John Wiley & Sons: Toronto, 1973.
(21) (a) Tanford, C. *The Hydrophobic Effect: Formation of Micelles and Biological Membranes*; Wiley-Interscience: New York, 1980. (b) McAuliffe, C. *J. Phys. Chem.* **1966**, *70*, 1267–1275.
(22) There is a significant literature on rhodium colloids catalyzing hydrogenations in aqueous biphasic systems: Larpent, C.; Bernard, E.; Menn, F. B.; Patin, H. *J. Mol. Catal.: A* **1997**, *116*, 277–288. ^{31}P NMR analysis of the catalyst solutions before and after reaction demonstrated that the catalyst retains its molecular integrity with only traces of oxidized phosphine observed.
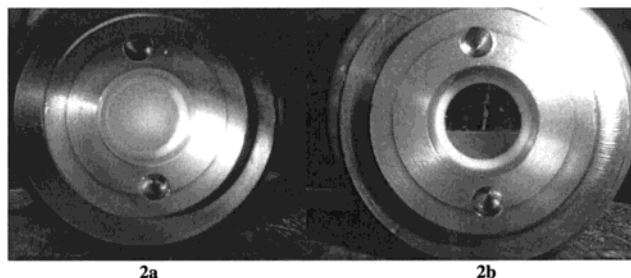
Figure 2. A c/w emulsion using 1 wt % PBO-PEO surfactant (40 °C, 4000 psi) is shown in part a. After decreasing the pressure to 1000 psi a biphasic water–CO$_2$ system is formed, part b.

Phase separation and catalyst recycle are illustrated pictorially in Figure 2 for the PBO-PEO c/w emulsion. During the reaction at 4000 psi, the system is a milky white emulsion (Figure 2a). When the reaction is complete, the pressure is decreased (e.g. from 4000 to 1000 psi) and the pump and magnetic stirring are stopped. After the mixture stands for ca. 10 min complete phase separation occurs (Figure 2b) with supercritical CO$_2$ above the aqueous catalyst phase. The product, which is soluble in CO$_2$ above certain pressures, can be recovered by transfer and subsequent pressure letdown, also allowing for CO$_2$ recycle. The lower aqueous phase contains the rhodium, ligand, and water-soluble surfactant, in the case of PBO-PEO or Lodyne 106A. For the water-insoluble PFPE surfactant, a third phase is formed below both the CO$_2$ and aqueous phases due to the high density of the surfactant (1.8 g/mL). Catalyst recycle was demonstrated by transferring the product-containing CO$_2$ phase under pressure to a separate high-pressure reactor and then charging the aqueous phase, still containing the catalyst and surfactant, with more H$_2$, CO$_2$, and alkene. Repressurization and recirculation leads to emulsion formation. For styrene, we have found that the catalyst activity remains essentially constant for at least three cycles, i.e., complete conversion after 3 h for each cycle, demonstrating efficient catalyst recycle.[22]

In summary, we have found a new biphasic catalysis system that capitalizes on the unique and controllable phase properties of water/supercritical CO$_2$ emulsions and allows for both catalyst recycle and enhanced reaction rates. Supercritical CO$_2$ is unique in allowing for emulsion formation followed by efficient phase separation at lower pressures. Activity for even highly hydrophobic substrates is significantly higher than conventional aqueous biphasic systems. This concept should be applicable to a wide range of catalytic processes, particularly those involving gaseous reagents (e.g. H$_2$, CO, and O$_2$), including hydroformylation and other carbonylations, oxidations, and reductions. We believe the key advantages of our system are (1) high interfacial surface area due to emulsion formation, (2) the ability to break emulsions by pressure decrease for efficient phase separation, (3) miscibility of gaseous reactants, e.g. H$_2$, and (4) low interfacial tension between water and CO$_2$. Preliminary results on hydrophobic alkenes may suggest that the reaction occurs at the interface rather than in the bulk water phase. In addition to exploring other catalytic reactions, we are in the process of studying the detailed kinetics of the hydrogenation system as well as using high-pressure NMR and other spectroscopic techniques to further understand this reaction.