

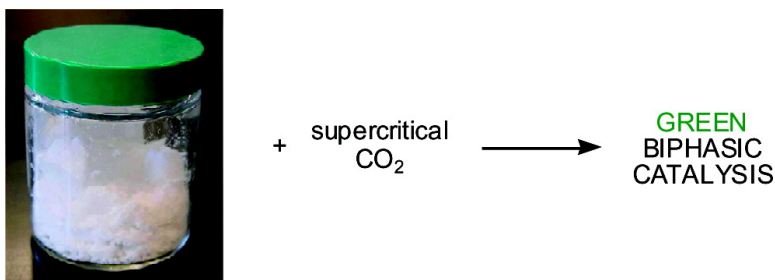
Communication

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## Liquid Poly(ethylene glycol) and Supercritical Carbon Dioxide: A Benign Biphasic Solvent System for Use and Recycling of Homogeneous Catalysts

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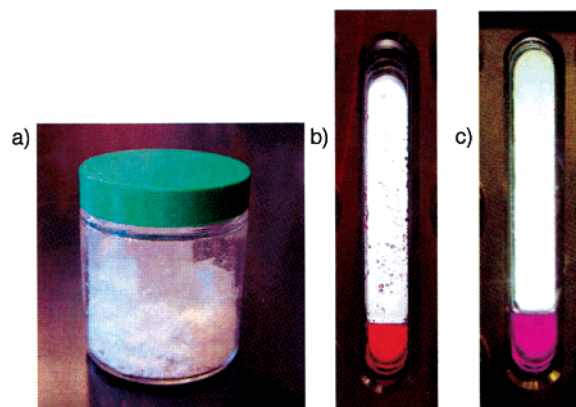
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While environmental considerations may be driving academic interest in replacing solvents that are volatile organic compounds (VOCs) with new alternative solvents (neoteric solvents), the unusual properties of certain neoteric solvents offer the possibility of new homogeneous catalyst immobilization strategies. Homogeneous catalysis is generally preferable to heterogeneous catalysis in terms of activity and selectivity, but homogeneous catalysts suffer from being difficult to separate from the product. Biphasic catalysis, an important immobilization technology for rendering homogeneous catalysts recyclable, involves one solvent, generally polar, that dissolves and retains the catalyst, and another solvent, generally nonpolar, that dissolves the products. The success of such schemes requires that the two liquids be sufficiently different in properties, usually polarity, that the partitioning of the catalyst will be almost exclusively to one phase. The first pairing of non-VOC solvents for biphasic homogeneous catalysis was the combination of liquid water and supercritical CO<sub>2</sub> (scCO<sub>2</sub>). The H<sub>2</sub>O/scCO<sub>2</sub> system is effective for water-soluble catalysts<sup>1–3</sup> but not effective for reactions in which the catalyst, substrate, or reagent is water-insoluble or sensitive to the low pH of the aqueous phase.<sup>4</sup> The recently discovered<sup>5,6</sup> VOC-free combination of ionic liquids (ILs) and scCO<sub>2</sub> (Figure 1c) solves these problems, allowing the use of hydrophobic homogeneous catalysis with catalyst recycling.<sup>7–10</sup> Unfortunately, currently available ILs are moderately to enormously expensive, and knowledge of their environmental impact is still limited. The goal of the current research is to evaluate poly(ethylene glycol) (PEG) as an inexpensive, nonvolatile, and benign alternative for the catalyst-bearing phase in biphasic catalysis with scCO<sub>2</sub>.

That the lower, catalyst-bearing phase in a biphasic solvent system be nonvolatile is preferred because this eliminates evaporative losses and allows the extraction of products from the liquid with scCO<sub>2</sub> without concomitant extraction of the solvent. That the lower phase be lipophilic is preferred because this permits the use of water-insoluble or water-sensitive catalysts and substrates. Although both ILs and PEGs fit these requirements, PEGs are preferred over ILs because they are orders of magnitude less expensive, they are completely nonhalogenated, and their toxicities have been studied and are known to be very low.<sup>11</sup> PEG and CO<sub>2</sub> are so benign that they are approved for use in food<sup>12</sup> and in beverages, respectively.

There is literature precedent for the use of PEG as a solvent for biphasic catalysis. The hydrogenation of 1-hexene by Rh complexes in a biphasic poly(ethylene oxide)/MeOH/heptane system was reported by da Rosa et al.<sup>13</sup> Naughton and Drago<sup>14</sup> reported the use of water-soluble hydroformylation catalysts dissolved in PEG films over inorganic supports in a technique called Supported Homogeneous Film Catalysts. Tundo developed a phase-transfer catalysis method for the high-temperature reaction of organic vapors over PEG as a reagent- or catalyst-bearing lower phase.<sup>15</sup> Halmov and Neumann described a polyoxometalate-catalyzed oxidation of benzyl alcohols to benzaldehydes in PEG, with use of cyclohexane



**Figure 1.** (a) Poly(ethylene glycol) with an average  $M_n$  of 1000. (b) The same poly(ethylene glycol) under scCO<sub>2</sub> at 172 bar and 40 °C. (c) An ionic liquid/scCO<sub>2</sub> biphasic solvent system at 210 bar (the ionic liquid is *N,N*-butylmethylimidazolium hexafluorophosphate). In both biphasic systems, the dye Nile Red can be seen visually to be entirely in the lower (PEG or ionic liquid) phase.

to extract the product.<sup>16</sup> The combination of PEG and scCO<sub>2</sub> for biphasic catalysis has not previously been reported, although Bhanage et al. used ethylene glycol and scCO<sub>2</sub>.<sup>2</sup>

Poly(ethylene glycol)s (Figure 1a,b) are miscible with common organic liquids, able to dissolve common organic solids and metal phosphine complexes, have very poor solubility in scCO<sub>2</sub>, and are expandable with CO<sub>2</sub>. CO<sub>2</sub>-expansion of a liquid is a phenomenon in which application of CO<sub>2</sub> gas pressure over an organic liquid causes the latter to expand up to severalfold.<sup>17–19</sup> Such expansion is accompanied by changes in the physical properties of the liquid phase mixture, including lowered melting points,<sup>20</sup> lowered viscosity, increased gas/liquid diffusion rates,<sup>21</sup> and increased ability to dissolve H<sub>2</sub>.<sup>22</sup> Reactions in liquid solvents are known to be affected by gas-expansion of the solvent,<sup>23–25</sup> probably as a direct result of such physical property changes. The viscosity of liquid PEG is known to drop dramatically (8- to 10-fold) upon expansion by CO<sub>2</sub>,<sup>26</sup> and we have observed lowered melting points of PEG fractions under CO<sub>2</sub> pressure.<sup>27</sup> Whether or not CO<sub>2</sub>-expansion of PEG affects reaction behavior is currently the subject of further experimentation.

We therefore expected that a PEG/scCO<sub>2</sub> biphasic solvent system would allow catalyst recycling and product extraction with minimal loss of catalyst and minimal coextraction of the PEG solvent.

The utility of the method for biphasic catalysis has now been demonstrated with the RhCl(PPh<sub>3</sub>)<sub>3</sub>-catalyzed hydrogenation of styrene to ethyl benzene in PEG ( $M_n$  900) as a test reaction. Five successive hydrogenations were performed in a 160 mL stainless steel bomb containing 10 mL of PEG with 5 μmol of catalyst dissolved therein. Degassed styrene (4.4 mmol) was injected under nitrogen. The vessel contents were stirred for 19 h at 40 °C under 30 bar H<sub>2</sub> and 50 bar CO<sub>2</sub>. Although PEG 900 is a waxy solid at

room temperature, it is a liquid under these conditions. Afterward, the vessel was warmed to 55 °C, and prewarmed scCO<sub>2</sub> was bubbled through the PEG phase for 4 h at 155 bar and 2 mL/min, the gas phase then passing through a back-pressure regulator into a trap of cooled catch solvent (CH<sub>2</sub>Cl<sub>2</sub>, 0 °C). The vessel was then cooled to room temperature, bled to 1 bar, and opened under nitrogen. Fresh styrene was introduced to begin the next cycle. A total of five cycles were performed with the one batch of catalyst/PEG solution, without replenishing either the catalyst or the PEG. Rotary evaporation of the trap contents and NMR spectroscopy of the residue showed the presence of ethyl benzene and small amounts of PEG. Mass recovery of ethylbenzene product (after rotary evaporation of catch solvent) was low in the first cycles but reached 79% in the fifth cycle. The catalyst remained active as >99% conversion was found for all five cycles, as determined by NMR spectroscopy. AA/ICP measurements showed that the Rh content of the ethyl benzene product was too low to be detected (i.e., <1 ppm). The extent of extraction of PPh<sub>3</sub> was measured in a separate experiment, in which 54 μmol of RhCl(PPh<sub>3</sub>)<sub>3</sub> in 10 mL of PEG was similarly washed with scCO<sub>2</sub>; 0.06 equiv of PPh<sub>3</sub> per Rh was extracted.

The amount of PEG extracted by scCO<sub>2</sub> along with the ethylbenzene was also evaluated. Ethylbenzene (340 mg) in PEG-900 (10 mL) in a 160 mL steel vessel at 60 °C was extracted with scCO<sub>2</sub> (155 bar, 2 mL/min, 4 h) as described above. Rotary evaporation of the trap contents and NMR spectroscopy of the residue showed the presence of ethyl benzene (200 mg, 59% mass recovery) and small amounts of PEG and catch solvent. The amount of PEG in the ethylbenzene was determined by complete evaporation of all volatiles, which left 0.9 mg of PEG and water as residue. Thus, the extracted material was <0.5 wt % nonvolatiles.

Conditions are being sought in which the extraction of the PEG is negligible compared to the extent of extraction of the reaction product. For example, the solubility of PEG in scCO<sub>2</sub> can be dramatically reduced by increasing the temperature and by increasing the *M<sub>n</sub>*. Increasing the temperature of the scCO<sub>2</sub> decreases the solubility of the PEG; literature data show that the solubility of PEG-600 in scCO<sub>2</sub> at 204 bar is reduced by 69% by increasing the temperature from 40 to 50 °C.<sup>28,29</sup> In contrast, raising the temperature significantly raises the solubility of typical organic small molecule products.<sup>30</sup> This difference arises because the crossover pressure (the pressure at which the temperature dependence of solubility in scCO<sub>2</sub> reverses) is typically 110–160 bar for small organic molecules but must be very high for PEGs. The other important parameter is the *M<sub>n</sub>* of the PEG solvent. Commercially available PEG fractions with average molecular weights of 300 and 600 are viscous liquids at room temperature but are readily extracted by scCO<sub>2</sub>. PEGs with *M<sub>n</sub>* values of 900 and 1000 are waxy solids. Commercially available PEG-1500 was found to be a waxy solid at room temperature, melting at 48–51 °C, but a liquid at 40 °C if it is under a CO<sub>2</sub> pressure of greater than 90 bar. Thus, PEG-1500 can be used as a solvent at 40 °C or higher. Ethylbenzene extracted from PEG-1500 using the method described above was found to contain significantly less coextracted PEG, by <sup>1</sup>H NMR spectroscopy and by mass of nonvolatiles (0.2 mg, 0.1%), than was the case with the PEG-900. The same experiment but with 7.8 g of ethylbenzene and using PEG-1500 had 97% mass recovery of ethylbenzene.

In conclusion, a new biphasic solvent system consisting of scCO<sub>2</sub> and PEG has been found, suitable for homogeneous catalysis with catalyst recycling without the use of volatile or halogenated solvents.<sup>31</sup> Homogeneously catalyzed hydrogenation can be performed in the molten PEG, followed by extraction of the product by scCO<sub>2</sub>. The catalyst-containing PEG phase which remains in the vessel can be reused repeatedly for hydrogenation without addition of further catalyst or PEG.

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## References

- (1) Bhanage, B. M.; Ikushima, Y.; Shirai, M.; Arai, M. *Chem. Commun.* **1999**, 1277–1278.
- (2) Bhanage, B. M.; Ikushima, Y.; Shirai, M.; Arai, M. *Tetrahedron Lett.* **1999**, *40*, 6427–6430.
- (3) Jacobson, G. B.; Lee, C. T.; Johnston, K. P.; Tumas, W. *J. Am. Chem. Soc.* **1999**, *121*, 11902–11903.
- (4) Bonilla, R. J.; James, B. R.; Jessop, P. G. *Chem. Commun.* **2000**, 941–942.
- (5) Blanchard, L. A.; Hancu, D.; Beckman, E. J.; Brennecke, J. F. *Nature* **1999**, *399*, 28–29.
- (6) Blanchard, L. A.; Brennecke, J. F. *Ind. Eng. Chem. Res.* **2001**, *40*, 287–292.
- (7) Brown, R. A.; Pollet, P.; McKoon, E.; Eckert, C. A.; Liotta, C. L.; Jessop, P. G. *J. Am. Chem. Soc.* **2001**, *123*, 1254–1255.
- (8) Liu, F. C.; Abrams, M. B.; Baker, R. T.; Tumas, W. *Chem. Commun.* **2001**, 433–434.
- (9) Bösmann, A.; Franciò, G.; Janssen, E.; Solinas, M.; Leitner, W.; Wasserscheid, P. *Angew. Chem., Int. Ed.* **2001**, *40*, 2697–2699.
- (10) Sellin, M. F.; Webb, P. B.; Cole-Hamilton, D. J. *Chem. Commun.* **2001**, 781–782.
- (11) "Toxicological Evaluation of Certain Food Additives," World Health Organization, Food Additives Series 14, 1979.
- (12) "Code of Federal Regulations, Title 21, Volume 3, CITE 21CFR172.820," FDA, 2001.
- (13) da Rosa, R. G.; Martinelli, L.; da Silva, L. H. M.; Loh, W. *Chem. Commun.* **2000**, 33–34.
- (14) Naughton, M. J.; Drago, R. S. *J. Catal.* **1995**, *155*, 383–389.
- (15) Tundo, P.; Moraglio, G.; Trotta, F. *Ind. Eng. Chem. Res.* **1989**, *28*, 881–890.
- (16) Haimov, A.; Neumann, R. *Chem. Commun.* **2002**, 876–877.
- (17) Gallagher, P. S.; Coffey, M. P.; Krukons, V. J.; Klasutis, N. In *Supercritical Fluid Science and Technology*; Johnston, K. P., Penninger, J. M. L., Eds.; American Chemical Society: Washington, DC, 1989; Vol. 406, p 334.
- (18) Chang, C. J.; Randolph, A. D. *AIChE J.* **1990**, *36*, 939–942.
- (19) Kordikowski, A.; Schenk, A. P.; Van Nielen, R. M.; Peters, C. J. *J. Supercrit. Fluids* **1995**, *8*, 205–216.
- (20) McHugh, M. A.; Yogan, T. J. *J. Chem. Eng. Data* **1984**, *29*, 112–115.
- (21) Dariva, C.; Coelho, L. A. F.; Oliveira, J. V. *Fluid Phase Equilib.* **1999**, *160*, 1045–1054.
- (22) Freitag, N. P.; Robinson, D. B. *Fluid Phase Equilib.* **1986**, *31*, 183–201.
- (23) Thomas, C. A.; Bonilla, R. J.; Huang, Y.; Jessop, P. G. *Can. J. Chem.* **2001**, *79*, 719–724.
- (24) Liu, J.; Han, B.; Liu, Z.; Wang, J.; Huo, Q. *J. Supercrit. Fluids* **2001**, *20*, 171–176.
- (25) Subramaniam, B.; Busch, D. H. In *Carbon Dioxide Conversion and Utilization*; Song, C., Gaffney, A. F., Fujimoto, K., Eds.; American Chemical Society: Washington, DC, 2002; pp 364–386.
- (26) Gourguillon, D.; Avelino, H.; Fareleira, J.; da Ponte, M. N. *J. Supercrit. Fluids* **1998**, *13*, 177–185.
- (27) Heldebrant, D. J.; Jessop, P. G. 2002, unpublished material.
- (28) Lopes, J. A.; Gourguillon, D.; Pereira, P. J.; Ramos, A. M.; da Ponte, M. N. *J. Supercrit. Fluids* **2000**, *16*, 261–267.
- (29) Daneshvar, M.; Kim, S.; Gulari, E. *J. Phys. Chem.* **1990**, *94*, 2124–2128.
- (30) Bartle, K. D.; Clifford, A. A.; Jafar, S. A.; Shilstone, G. F. *J. Phys. Chem. Ref. Data* **1991**, *20*, 713–756.
- (31) Although a VOC was used as the trap solvent, a larger-scale application of this method would not require a trap solvent.

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