APPLICATIONS OF CO_2 IN HOMOGENEOUS CATALYSIS

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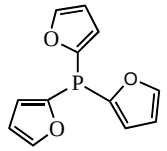
Introduction

Carbon dioxide can serve as a solvent for homogeneous catalysis but it is capable of much more. Over the past 4 years, we and others have shown that it can be used as an extractant for the removal of products from ionic or polymeric liquid solvents after homogeneous catalysis, as a modifier of liquid phase solvent properties, as an agent for accelerating solventless reactions of some solids, and as a trigger for partitioning and miscibility changes. All of these capabilities of CO_2 can be used to modify the selectivity, increase the turnover frequency, or achieve the recycling of homogeneous catalysts. In addition, of course, CO_2 can serve as a reagent. Our recent results in these areas will be presented.

Homogeneous Catalysis in Supercritical CO_2

Homogeneous catalysis has been performed in supercritical CO_2 ($scCO_2$)[1] since Kramer and Leder's isomerization experiments in the 1970's,[2] although most work in this area has been done since the mid 1990's.[3] Examples of increased rates[4,5] or selectivities[6] compared to those in liquid solvents have been observed. In many cases, catalyst solubility in $scCO_2$ was found to be insufficient, especially when triarylphosphine ligands were employed. This problem has been addressed by switching to trialkylphosphines[4] or by putting fluorinated groups on the meta or para positions of the triarylphosphines.[7] New data, obtained in collaboration with Beckman's group, will be presented showing that incorporation of ether or ester groups into the phosphines increases the solubility of the ligand in $scCO_2$. Solubility data comparing PPh_3 with electronically similar ligands containing heteroaromatic rings (e.g. structure **1**) or ester-containing substituents (e.g. structure **2**) will be presented.[8] On a weight fraction basis, both are significantly more soluble than PPh_3, while on a mole fraction basis ligand **1** has by far the greater solubility.



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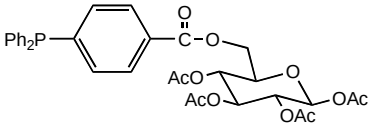

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Biphasic Catalysis

Homogeneous catalysts are too expensive and often too toxic to be allowed to be lost in the product stream. Traditional methods for recovering the catalyst usually involve destroying the catalyst, but newer techniques including biphasic catalysis make it possible to recover the catalyst without damage. Biphasic catalysis involves two mutually immiscible fluids and relies on the catalyst partitioning exclusively into one phase (the catalyst-bearing phase) while the product partitions primarily into the other phase. Many systems of this type suffer from nonexclusive partitioning of the catalyst, leading to catalyst losses, and partial miscibility of the two fluid phases, leading to loss of one solvent in the other.

CO_2/Ionic Liquid Mixtures. Blanchard et al.[9] showed that a common ionic liquid, N,N-butylmethylimidazolium hexafluorophosphate ([bmim]PF_6]) is completely insoluble in $scCO_2$. The Jessop group showed that this fact, combined with the observation that heavy aromatic compounds (in analogy to asymmetric ligands of the BINAP type) partition essentially exclusively into the ionic liquid (IL) phase rather than the $scCO_2$ phase. This was the basis for a catalyst successful recycling scheme,[10] in which homogeneous catalysis was performed in an IL following which product was extracted by $scCO_2$, leaving behind a reusable catalyst solution in IL. The product could thus be obtained free of solvent or catalyst.

CO_2/Liquid Polymer Mixtures. The excellent performance of the CO_2/IL biphasic catalysis method encouraged further research in this area in the Jessop group, but it became obvious that the method could be improved by finding a cheaper replacement for the IL. The ideal replacement would be cheaper, halide-free and entirely nontoxic. PEG (poly(ethylene glycol)) was chosen, even though at room temperature it is a solid. PEG is nontoxic, very inexpensive, and able to dissolve catalyst precursors and organic substrates. The solubility of PEG in $scCO_2$ is very low, especially at molecular weights over 1000 g/mol. The fact that it is a solid at room temperature is less problematic than it sounds because a) the melting point is only 20-40˚C above room temperature, and b) the melting point of PEG is significantly lower in the presence of $scCO_2$. Early tests with a simple homogeneous hydrogenation showed that biphasic catalysis could be performed in the PEG/$scCO_2$ mixture, that the product could be easily extracted by the $scCO_2$, and that the catalyst solution could then be recycled multiple times.[11]

Continued work in this area involves the evaluation of several possible liquid polymers and other nonvolatile solvents. Some, such as glycerol and polyols, have been rejected because they are incapable of dissolving catalyst precursors and substrates. Others such as poly(dimethylsiloxane) and eicosane have been rejected because they are too soluble in $scCO_2$. Liquids that are currently being considered are shown in Figure 1. Their polarities are illustrated in Figure 2.

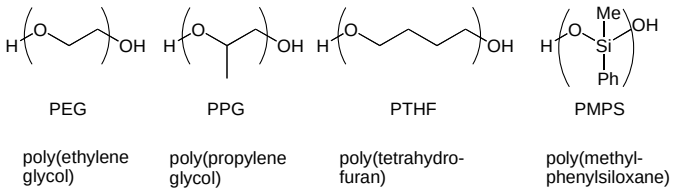

Figure 1. The structures of liquid polymers being considered as potential solvents for biphasic homogeneous catalysis.

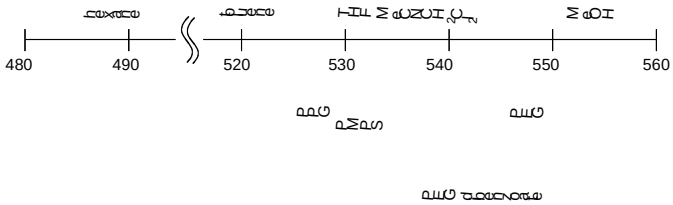

Figure 2. The polarity of liquid polymers compared to traditional liquid solvents, shown on a scale of Nile Red absorption maxima.

Obedient Catalysts and Solvents

Bergbreiter[12] introduced the idea of "smart" ligands or catalysts, meaning ligands or catalysts that change their nature or solubility when circumstances require it, without need for a signal from the human operator. In his work, the ligands formed complexes that had lower solubility at higher temperatures, so that if an exothermic reaction got carried away and the temperature rose as a result, the catalyst would automatically precipitate and thereby slow down the reaction.

In a collaboration between the Jessop group and the Eckert and Liotta groups at Georgia Tech., we have been exploring the possibility of designing "obedient" ligands and solvents, which reversibly change their nature upon receiving a signal or input from the human operator. For example, cyclohexane is fluorophobic (meaning that it can not dissolve highly fluorinated compounds) but cyclohexane with CO_2 dissolved therein (at >30 bar CO_2) is fluorophilic and therefore capable of dissolving fluorinated compounds[13] or being miscible with fluorinated liquids.[14] Thus cyclohexane is a very simple example of an obedient solvent with CO_2 dissolution as the trigger for the change. This fact was used as the basis for a method that causes an "obedient" catalyst to switch back and forth between being homogeneous and being heterogeneous. Powdered fluorous silica with a highly fluorinated catalyst precursor complex adsorbed on its surface is placed in a solution of substrate in cyclohexane. Dissolution of CO_2 into the cyclohexane triggers the extraction into solution of the catalyst from the silica, thereby allowing homogeneous catalysis to take place. After the reaction, the CO_2 pressure is released, triggering the redeposition of the catalyst back onto the silica, so that the catalyst becomes heterogeneous for the purposes of catalyst/product separation.

CO_2 as a Reagent or Substrate

Research by many groups has been directed at increasing the rate of reactions of CO_2 and increasing the range of reactions in which CO_2 acts as a reagent or substrate. Recent results in the Jessop group include the development of a facile method for combinatorial catalyst discovery for CO_2 fixation at high pressure,[15] and new or improved syntheses of formic acid,[15-18] formanilide,[19] carbanilide,[19] tetraalkylureas,[20] and carboxylic acids (in progress).

CO_2 in Other Roles

Carbon dioxide can assist homogeneous catalysis in many other ways. CO_2 dissolved in organic solvents lowers the melting point, viscosity, and polarity of the liquid phase and increases mass transfer rates and the solubility of reagent gases. These changes can directly affect rates and selectivities of catalysis.[16,21-26]

Carbon dioxide can also be used to accelerate solventless reactions of some solids,[27] by taking advantage of the melting-point lowering that occurs in the presence of CO_2. In a similar manner, the final yields of some reactions can be increased.

Carbon dioxide can also serve as an in-situ temporary protecting group, as reported by Leitner.[28]

Concluding Remarks

Although it is considered a waste material, CO_2 can be useful for the promotion of homogeneous catalysis in a wide variety of ways, not all of which have been presented here. In similar ways, CO_2 can promote other kinds of reactions; research in other groups continues along those lines. While it is not claimed that use of CO_2 in this manner will have any significant effect on the global warming problem, it is precisely the fact that CO_2 is a waste product that makes it inexpensive enough to be considered for some of these roles.

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