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Use and recovery of a homogeneous catalyst with carbon dioxide as a solubility switch†

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A method for fluorous biphasic catalysis is described, in which the fluorous liquid is replaced by fluorinated silica, the fluorous catalyst is induced to dissolve in the organic solvent by the presence of CO_2, and the recovery of the catalyst after the reaction is achieved by release of the CO_2 pressure.

Fluorous biphasic catalysis is an elegant new method for performing homogeneous catalysis with post-reaction catalyst recovery and re-use. As first published by Horváth and Rábai,[1] the method involves an immiscible mixture of a “fluorous” (perfluorinated) solvent and a traditional organic solvent. A highly fluorinated§ catalyst precursor dissolves in the fluorous phase while the organic starting materials partition into the organic phase. The catalysis can proceed across the phase boundary but usually the temperature of the reaction mixture is raised in order to make the two liquid phases become miscible.[2,3] After the reaction, the temperature is lowered and the organic product-bearing phase is removed from the catalyst-containing fluorous phase, which is re-used. The method constituted an advance over the earlier aqueous–organic biphasic catalysis[4] because it allows reactions of water-sensitive or water-insoluble catalysts and reagents.

Further refinements of fluorous biphasic catalysis are sought because of a number of difficulties encountered with early versions of the method. First, the fluorous solvents most commonly used (such as perfluoro(methylcyclohexane) and perfluorohexane) are volatile, persistent, and potent greenhouse gases.[5] Secondly, many of these solvents have substantial solubility in the organic phase, so that a portion of the fluorous solvent is lost after each cycle. Thirdly, the use of heat to cause the miscibility of the phases will in some cases cause lower selectivity or even loss of heat-sensitive catalysts. The first two problems can be resolved by dispensing with the fluorous phase entirely[6,7] or using a fluorinated polymer or fluorous silica[8,9] as a replacement for the fluorous phase. The third problem can be solved by using another trigger, other than heat, to induce the fluorous catalyst to enter the organic phase.

We recently reported that expansion of an organic solvent by the application of gaseous (subcritical) CO_2 pressure increases the fluorophilicity of the solvent to such an extent that the solvent is able to dissolve highly fluorinated complexes.[10] This phenomenon made it possible to recrystallize such complexes for the purposes of purification or X-ray crystallography. We have now found that the phenomenon can also be used as a miscibility trigger, instead of heat, in fluorous biphasic catalysis with a fluorous liquid, a fluorous polymer or silica, or with no fluorous phase.

For example, the green highly fluorinated complex $Rh_2(O_2C(CF_2)_9F)_4$ was found to be insoluble in cyclohexane but was soluble in cyclohexane when 40 to 60 bar of CO_2 gas was present.[10] The CO_2 pressure resulted in a marked increase in the volume of the liquid phase and complete dissolution of the coloured complex. Note that CO_2 under these conditions is not supercritical and in the absence of the cyclohexane would be gaseous. The upper phase was gaseous and showed no discoloration, indicating that the complex was not dissolved therein. When the CO_2 pressure was released, the liquid phase returned to its original volume and the complex precipitated, leaving a colourless cyclohexane phase. The amount of nonvolatile material remaining dissolved in the liquid phase was only 0.1 mg, showing that greater than 99% of the solute had precipitated upon release of the CO_2.

Attempts to perform repeated cycles of catalytic cyclopropanation (of styrene with ethyl diazoacetate) using $Rh_2(O_2C(CF_2)_9F)_4$ as the catalyst precursor were frustrated by the fact that the catalyst resting state is far more soluble in cyclohexane than is the catalyst precursor. We therefore turned our attention to other reactions and to the use of fluorous silica gel to capture the catalyst upon release of the CO_2. It was necessary to first demonstrate that fluorinated compounds or complexes could be impregnated into the fluorous support and that they could be reversibly drawn out of the support upon the expansion of the solvent with CO_2.

Fluorinated complexes were deposited onto fluorous silica gel by two methods. For the purple fluorinated complex $Co(O_2CR_f)_2$ (complex **1**, where R_f is a perfluoropolyether tail), deposition onto the fluorous silica was achieved by placing the fluorous silica gel into a solution of the complex in perfluorotributylamine. Over time, the absorbance in the solution decreased significantly, until the solution was clear and the gel purple. In contrast, deposition of the yellow/brown complex $[RhCl\{P(C_6H_4\text{-}p\text{-}CH_2CH_2(CF_2)_6F)_3\}_3]$, (complex **2**) was achieved by CO_2-expansion (at 65 bar and 40 °C) of a 0.2 mL cyclohexane suspension of the complex (8.5 mg) in the presence of 50 mg of fluorous silica. Before the expansion, the complex was insoluble in the cyclohexane. Afterwards, the complex was found to be deposited onto the silica as shown by the change in color of the silica (which went from white to light brown) and the lack of colour in the liquid phase.

The reversible extraction from fluorous silica was monitored in a high pressure UV cell.[11] In the absence of CO_2, complex **1** was completely insoluble in cyclohexane, to the detection limit of the UV–vis spectrometer (approximately 0.005 g mL^{-1} for this compound). In the presence of CO_2, the concentration increased until approximately 100% of the complex (concentration 0.061 g mL^{-1}) was dissolved in the expanded liquid phase at 37 bar. After depressurization, the complex re-deposited on the surface of the silica and was once again undetectable in the liquid phase. Thus the partition coefficient (mass dissolved in liquid/mass deposited on silica) in cyclohexane could only be estimated to change from less than 0.01 in the absence of CO_2 to more than 100 in the presence of CO_2. The process was repeated with similar results for each cycle. Partition coefficients were also obtained for a fluorinated model compound (1,4-bis(perfluorooctyl)benzene) *via* UV–vis spectroscopy. The

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† Electronic supplementary information (ESI) available: methods of preparation of fluorous silica and complexes **1** and **2**. See http://www.rsc.org/suppdata/cc/b3/b311146f/

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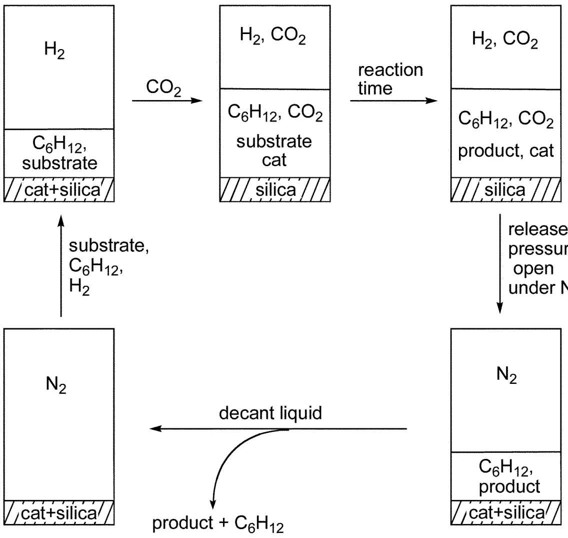
compound was deposited on the surface of the fluorinated silica using the first method detailed above. Partitioning of the bis(perfluorooctyl)benzene between the fluorinated silica surface and organic liquids was examined both in the presence and absence of CO_2 pressure. For the organic solvent methanol, the partition coefficient changed from 0.13 in the absence of CO_2 to 46 in the presence of 43 bar CO_2. In acetonitrile, the partition coefficient changed from 0.12 to 45 when 27 bar of CO_2 was added. It should be noted that bis(perfluorooctyl)benzene is far more soluble in organic solvents than the Co complex due to the use of straight-chain fluorous tails rather than perfluoropolyether tails.[12] Partitioning of complex **2** was monitored in the solvents cyclohexane and methanol. 2 mg of complex **2** was deposited on 11 mg of fluorous silica from gas-expanded cyclohexane or methanol (at 65 bar and 25 °C). In cyclohexane, the partition coefficient changed from 0.024 at 1 bar to 40.84 at 28.6 bar CO_2. In methanol, the partition coefficient was 0.012 at 1 bar to 68.07 at 28.6 bar CO_2. All partitioning experiments were performed at 25 °C. Although partitioning data for catalyst precursors may not be accurate predictors of partitioning behaviour for the true catalytically active species, it seems clear that highly fluorinated species of this type do reversibly transfer into and out of solution upon application and withdrawal of CO_2 gas.

Hydrogenation of styrene using a fluorous version of Wilkinson's catalyst was selected as the reaction for demonstration of catalyst recycling. Conventional fluorous biphasic catalytic hydrogenation by such complexes has been reported previously.[13–15] The hydrogenation was performed in the following manner (Scheme 1). A microstir bar, catalyst precursor **2** (10 mg), degassed styrene (0.080 mL, 280/1 mole ratio to catalyst), degassed cyclohexane (to a total volume of 0.2 mL), and fluorous silica (45 mg) were added, in that order, to a glass vial fixed in an upright position in a pressure vessel under an inert atmosphere. The vessel was allowed to temperature equilibrate in a water bath to 40 °C and was flushed repeatedly with H_2. Hydrogen (30 bar) and then CO_2 (60 bar) were added. The reaction was allowed to proceed overnight, with stirring. The vessel was slowly vented and then opened inside an inert gas glove box, by which time the catalyst had deposited onto the silica (as indicated by the light brown/orange colour of the silica and the lack of colour in the liquid). The liquid was removed by pipette in such a manner as to least disrupt the silica phase, which was then washed three times with cyclohexane. The cyclohexane fractions were combined and analyzed by gas chromatography. Fresh styrene (0.080 mL) and cyclohexane (to bring the total volume to 0.2 mL) were added to the catalyst. The vessel was closed and the cycle repeated. The hydrogenation of styrene to ethylbenzene was performed in this manner five times, using only the initial batch of Rh catalyst. Chromatographic analysis showed that the hydrogenation was complete after each cycle, except for a trace of styrene detected after the fourth (but not fifth) cycle. The Rh content of the washes was found to be too low to be detectable by ICP/AA (< 20 ppm). A similar sequence of 5 cycles but with only 1 h reaction time and a substrate/catalyst ratio of 590 had conversions of 47, 61, 72, 58, and 46% for the 5 cycles, showing that the catalyst is not undergoing drastic changes in activity between runs.¶ These observations demonstrate that the catalyst can be reused repeatedly.



Scheme 1 Hydrogenation and catalyst recycling using CO_2 as a solubility switch and fluorous silica as a catalyst reservoir. The hatched area represents the fluorous silica phase.

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Notes and references

§ The word "fluorinated" is used here to mean a group or molecule containing high fluorine content by mass, and is not meant to imply that the group or molecule was prepared by direct fluorination.

¶ Conversion of the catalyst to Rh metal, if it occurred, was not observable by either a grey discoloration in the silica or a drastic change in catalytic activity between cycles. Further studies are now under way to more definitively rule out Rh metal formation.

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