Easy and efficient processes for catalyst recycling and product recovery in organic biphase systems tested in the hydrogenation of hex-1-ene

Ricardo G. da Rosa,[a] Laura Martinelli,[a] Luís H. M. da Silva[b] and Watson Loh*[b]

[a] *Instituto de Química, Universidade Federal do Rio Grande do Sul, Caixa Postal 15003, Porto Alegre, RS, 91501-970, Brazil*

[b] *Instituto de Química, Universidade Estadual de Campinas, Caixa Postal 6154, 13083-970, Campinas, SP, Brazil. E-mail: wloh@iqm.unicamp.br*

Received (in Cambridge, UK) 17th November 1999, Accepted 26th November 1999

Two organic liquid biphase systems containg poly(ethylene oxide), heptane and either CH_2Cl_2 or methanol have been tested in the catalytic hydrogenation of hex-1-ene using, respectively, Wilkinson's catalyst and a cationic rhodium complex, both leading to high yields and selectivity, with the latter showing a better performance and enabling easy and efficient product separation and catalyst recycling.

Liquid biphase systems have been the focus of great attention in catalysis recently as media for alternative less polluting and more efficient catalytic processes, providing an easier separation between products and catalyst. Among the strategies studied so far, examples include the use of aqueous/organic biphase systems with water soluble catalysts,[1] fluorous biphase systems, where the use of fluorinated ligands leads to catalyst solubility in the perfluorinated phase,[2] functionalised thermosensitive polymers as supports for traditional organometallic homogeneous catalysts [3] and the application of molten salts as ionic liquids.[4] All these procedures present some advantages and disadvantages. Among the latter, is the need for specially prepared catalysts, occurrence of catalyst leaching, or the somewhat difficult handling of the biphase system.

We have recently described[5] an organic biphase system containing poly(ethylene oxide) (PEO), CH_2Cl_2 and heptane which shows a strong segregation between the polar polymer and the hydrocarbon solvent, the polymer being concentrated in the bottom phase. Further studies[6] revealed that this phenomenon is also observed in mixtures containing other polar solvents such as methanol, chloroform and acetonitrile. Because of its characteristics, this ternary mixture may be interchanged between homogeneous and biphasic regions by either composition or temperature changes. These features suggest a variety of applications in different separation processes where the absence of water is desirable including catalysis.

This communication describes studies on the application of these biphase systems in the hydrogenation of hex-1-ene catalysed by Wilkinson's complex, $RhCl(PPh_3)_3$, and by the cationic complex $[Rh(cod)(dppe)]PF_6$, cod = cycloocta-1,5-diene, dppe = 1,2-bis(diphenylphosphine)ethane].† Hydrogenation was chosen as a test reaction because of its technological importance and hex-1-ene was used as substrate owing to its easy product characterisation. The rhodium complexes used were selected considering their well established hydrogenation catalytic behaviour and poor solubility in apolar solvents. Therefore, ideally, this reaction may be conducted in a homogenous system and, after induced phase separation, the catalyst may be selectively separated from the products, allowing for their removal and recycling. In a similar procedure Bianchini *et al.*[7] performed two catalytic reactions in a mixture of methanol and hydrocarbons that was homogeneous at high temperatures and formed a biphase system at room temperature, using a rhodium complex with a chosen ligand that ensured the complex solubility only in the alcohol-rich phase.

The phase diagram for the ternary system PEO 3350–CH_2Cl_2–heptane has been previously reported[5] and that for the ternary system PEO 3350–MeOH–heptane (not shown) is similar, though with a larger biphase area. Additional experiments have shown that in both systems there are only small changes when the polymer molecular weight is varied from 200 to 10 000, provided the polymer content is expressed on a monomer basis. There are, however, some important changes of the phase boundaries with temperature, with the biphase region increasing as the temperature decreases.[6]

Of relevance to this investigation, there are some compositions at which the system may be moved from a biphasic to a homogeneous region by temperature increase, for instance, with 19.5% of PEO 3350, 51.6% of CH_2Cl_2 and 28.9% heptane [compositions expressed on the basis of mol% (for PEO this refers to mol of monomer units)], this transition occurs at 9 °C. However, a significant rhodium loss was spectrophotometrically detected to the upper phase (*ca.* 15%) for this and other compositions which presented temperature-driven phase separation, causing poor recycling properties.

For this reason, we developed another procedure to improve the selectivity of catalyst partitioning. As temperature decreases, these polymer solutions show phase separation of UCST (upper critical solution temperature) type. For PEO solutions in CH_2Cl_2, these phase separation temperatures range from -80 to -40 °C, for PEO 3350 concentrations between 1 and 60% (w/w). As the polymer phase separates, we have verified that most of the catalyst is also removed from the solution phase. Therefore, by cooling the reaction system with liquid N_2, it is possible to selectively separate the catalyst and the reaction products. The striking feature is that, probably owing to large density differences, this biphase system is kinetically stable for a long time (even hours) even at temperatures close to room temperature, allowing easy separation of the liquid phases. Although this system is not in thermodynamic equilibrium, this procedure has provided an easy way of catalyst recycling.

This procedure was employed using Wilkinson's catalyst in the hydrogenation of hex-1-ene,‡ allowing product recovery with no apparent catalyst leaching to the apolar phase (verified spectrophotometrically) and efficient and selective substrate conversion. However, a marked decrease in the catalytic activity was observed after the third recycle. This could be related to the recycling process, which may induce a continuous loss of the triphenylphosphine free ligand in equilibrium with the rhodium complex, as revealed by ^{31}P NMR spectra, generating inactive species.

In order to overcome this problem, a cationic rhodium complex containing a chelating phosphine, $[Rh(cod)(dppe)]PF_6$, was tested as a catalytic precursor. This complex showed poor catalytic activity using the ternary mixture containing CH_2Cl_2. On the other hand, as suggested by other catalytic hydrogenation studies,[8] its performance using methanol as the polar component of the ternary mixture was clearly enhanced. With this second ternary system, the procedure of inducing phase separation by cooling was not effective since the volume of the upper phase was too small thus impeding the product separation. This reaction was then conducted in a homogenous system containing 14 mL of MeOH, 3.6 g of PEO, 0.0335 mmol of Rh complex and 8.01 mmol of hex-1-ene, at room temperature and under H_2 flow. This system requires an activation period of *ca.* 2.5 h to reach its maximum activity. The reaction products were analysed by GC§ 30 min after this period and during eight cycles, producing a 54 ± 5% conversion associated with 90 ± 10% selectivity to hydrogenation. Under these conditions, the estimated turnover frequency was 4 min^{-1}. Maintaining the reaction for 1 h, the substrate was completely and selectively converted to *n*-hexane, suggesting that the isomerisation reaction is faster than hydrogenation and that the isomers produced are reactive towards the catalyst being slowly, but continuously, converted to *n*-hexane. The product was then extracted by heptane addition, with three extractions with 4 mL heptane aliquots yielding 75% of product recovery. In the biphase system then formed, the extent of rhodium leaching was determined by ICP-atomic emission analyses of the upper phase,¶ revealing losses of only 0.083% of metal. Such a low rhodium loss qualifies this procedure as an efficient catalyst recycling.

This reaction is efficient even when performed under biphase conditions as, for instance, using a system composed of MeOH (14 mL), PEO (3.6 g) and *n*-heptane (14 mL), the same rhodium and olefin content as above, with 10 bar of H_2. Under these conditions five runs were made with complete conversion of the substrate to the hydrogenation product and no loss of catalytic activity or selectivity was noted. A kinetic study of this system allowed the determination of an activation time of 50 min. After this time, GC analysis revealed a complete conversion of hex-1-ene to *n*-hexane in 15 min, allowing determination of a turnover frequency of *ca.* 16 min^{-1}. This system can be recycled, at least eight times, with no changes in activity or selectivity.

In conclusion, this set of results, comprising experiments performed with two catalysts under different conditions, have proved the great potential for use of these organic biphase systems as reaction media that enable an easy product separation and efficient catalyst recycling. Furthermore, this procedure allows the use of common catalysts in homogeneous catalysis, requiring, therefore, no special reagents. These biphase systems also display advantages over binary solvent mixtures in that, owing to the presence of the polar polymer, the phase compositions are more different, increasing the partitioning selectivity, without the need of special ligands for the catalyst. The only requirement for their application is the selective partitioning of catalyst and of the desired product, however, this procedure is flexible enough to allow modifications (changing solvents, composition or temperature) that may suit a wide range of catalytic reactions and products.

R. G. da Rosa and L. Martinelli thank FAPERGS for financial support, L. H. M. da S. thanks CAPES-PICDT for a doctoral scholarship, and Universidade Federal de Viçosa for a leave of absence. The authors are grateful to R. F. de Souza and the Laboratório de Reatividade e Catálise - UFRGS for access to their facilities, and to M. Spitzer for providing phase equilibria data for some of the systems used.

Notes and references

† Wilkinson's catalyst was prepared according to the procedure described: J. A. Osborn and G. Wilkinson, *Inorg. Synth.*, 1967, **10**, 68 while [Rh(cod)(dppe)]PF_6 was prepared and characterised following R. R. Schrock and J. A. Osborn, *J. Am. Chem. Soc.*, 1971, **93**, 2397.

‡ In all the catalytic tests, the reactor, a 100 mL stainless steel autoclave, was previously purged by vacuum–argon cycles, then pressurised with hydrogen (99.999%). CH_2Cl_2, methanol and *n*-heptane were distilled prior to use, under argon from P_2O_5, activated molecular sieves (3 Å) and Na/benzophenone respectively. Hex-1-ene (Alpha, 99.9%) was stored over activated molecular sieves (3 Å) under argon. PEO 3350 (Sigma), was dried over P_2O_5. All reactions were conducted at room temperature under magnetic stirring.

§ The chromatographic analyses were performed using a Varian Star 3400 CX Chromatograph, equipped with a 30 m × 0.25 mm LM-1 capillary column, at 50 °C and 1 mL min^{-1} (10 psi) of H_2 as carrier gas.

¶ Rhodium analyses were performed by ICP-atomic emission spectrometry with a segmented-array charge coupled device detector (Optima 3000, Perkin Elmer, Newark, CT). Operating conditions: auxiliary argon flow 0.5 L min^{-1}, plasma argon flow 15 L min^{-1}, nebulizer argon flow 0.8 L min^{-1}, variable incident power (0.75–1.5 kW), cross-flow nebulizer and axial observation. Duplicate aliquots of the upper phase were digested with *aqua regia* for 12 h and then adjusted to produce concentrations close to 0.1 ppm. The final rhodium loss was determined as (0.083 ± 0.001)%.

1 O. Wachsen, K. Himmler and B. Cornils, *Catal. Today*, 1998, **42**, 373.
2 I. T. Horvath, *Acc. Chem. Res.*, 1998, **31**, 641.
3 D. E. Bergbreiter, *Catal. Today*, 1998, **42**, 389.
4 P. A. Z. Suarez, J. E. L. Dullius, S. Einloft, R. F. de Souza and J. Dupont, *Inorg. Chim. Acta*, 1997, **255**, 207; A. L. Monteiro, F. K. Zinn, R. F. de Souza and J. Dupont, *Tetrahedron: Asymmetry*, 1997, **8**, 177.
5 L. H. M. da Silva and W. Loh, *Chem. Commun.*, 1998, 787.
6 M. Spitzer, L. H. M. da Silva and W. Loh, unpublished work.
7 C. Bianchini, P. Frediani and V. Sernau, *Organometallics*, 1995, **14**, 5458.
8 B. D. Vineyard, W. S. Knowles, M. J. Sabacky, G. L. Bachman and D. J. Weinkauff, *J. Am. Chem. Soc.*, 1977, **99**, 5946.

Communication a909101g