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Ligand-Enhanced Biphasic Rhodium Catalyst System

Heterogeneous catalysis has a distinct advantage over catalysis in homogeneous media, in that the catalysts are easily separated from the products. Homogeneous systems with two liquid phases were developed for soluble catalysts in order to overcome this separation problem, but the catalysed reaction relies on the transfer of organic substrates into an aqueous layer, and as a result the reaction rates are much lower than those for conventional homogeneous catalysis. Two-phase, or biphasic, catalysis is used commercially in the Ruhrchemie-Rhône Poulenc process for the hydroformylation of propylene to butyraldehyde using a water-soluble rhodium complex catalyst containing triphenylphosphine trisulphonate (TPPTS).

This is an interesting variation of the hydroformylation process developed by Johnson Matthey/Davy McKee/Union Carbide in the 1970s, which uses a single phase organic reaction medium. In 1986, it was reported that 5.9 million tonnes of oxo alcohols were produced annually using homogeneous catalysis; the largest scale use of such catalysts.

However, work is now reported which highlights an interesting and useful variation of the approaches that can be used in biphasic catalysis to improve the performance of the catalyst, ("Enhancement of Interfacial Catalysis in a Biphasic System Using Catalyst-Binding Ligands", R. V. Chaudhari, B. M. Bhanage, R. M. Deshpande and H. Delmas, *Nature*, 1995, **373**, (6514), 501–503).

The authors describe research which shows that catalysis at the interface between phases in a biphasic aqueous/organic system can be enhanced by using a 'promoter ligand'. This ligand is soluble in the organic phase and insoluble in the aqueous phase, but will bind to the water-soluble organometallic catalyst, thus functioning as an enabling agent. Using this technique, the catalyst concentration is increased at the interface between the phases and promotes

a significant enhancement in the reaction rate.

The ligand, which is in addition to those in the rhodium TPPTS catalyst, is insoluble in the aqueous (catalyst) phase, but has a strong affinity for the metal complex catalyst. Since the catalytic complex is insoluble in the organic medium, the reaction of the ligand, such as triphenylphosphine, with the $[\text{Rh}(\text{COD})\text{Cl}]_2/\text{TPPTS}$ (I) catalyst, (where COD is 1,5-cyclo-octadiene) will essentially occur at the liquid-liquid interface, and enhance the concentration of catalytic species there. Thus, they can access the reactants present in the organic phase in much higher concentrations than when the triphenylphosphine is not present. This can result in a dramatic increase in the rate of the biphasic catalytic reaction.

The authors demonstrate this new approach using the hydroformylation of 1-octene in the presence of the rhodium catalyst system (I). Here the hydroformylation proceeds at a turnover frequency in the range 10 to 50 times faster when triphenylphosphine is added.

Recent work described here and elsewhere indicates that modifications of the homogeneous technique could increase and broaden its potential. Papers which support this view include one by K. T. Wan and M. E. Davis (*Nature*, 1994, **370**, (6489), 449–450) (with comments by J. M. Brown and S. G. Davies (*ibid.*, 418–419)) where heterogeneous analogues of homogeneous catalysts are reported, involving interfacial transfer and a catalyst supported on glass microbeads. The potential for high enantiomeric excess in stereospecific synthesis is demonstrated by combining advantages of homogeneous and heterogeneous catalyst systems. These papers are an important development from earlier work on phase transfer catalysis, and with the new approaches are likely to lead in due course to more commercial applications for soluble catalyst systems based upon the platinum group metals.

D.T.T.