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Preface: Phase separable homogeneous catalysis

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One key challenge in the commercial development of homogeneous catalysis has always been the separation of product from the catalyst. The separation process is often complicated by the air and thermal sensitivity associated with many of these catalysts. In 1984, Ruhrchemie AG commercialized a hydroformylation process utilizing a biphasic system in which the olefin and aldehyde products were contained in a separable organic layer but the catalyst, consisting of a sulfonated triphenylphosphine salt complexed with Rh, was contained in an aqueous phase. At the time of this commercial application, the concept was still new and little chemical, physical, and engineering information was available regarding this type of catalytic process. With the introduction of this unique process, the development of homogeneous biphasic catalysts began in earnest.

Since this initial work, the field has expanded significantly. Improvements in synthetic methodology have allowed chemists to generate a vast array of new water soluble ligands for use in the generation of catalysts. Accompanying the improvements in synthetic methodology, new applications have begun to emerge where phase separable catalysts have been applied to a number of other catalytic processes. The potential for commercializing these new catalyst systems is greatly enhanced by the development of mathematical models which can now be used by chemical engineers in designing plants utilizing these biphasic catalytic processes.

These mathematical models often point to limitations associated, not with ultimate reaction, but with transport phenomena, particularly when applied to reactions of longer (and more insoluble) organic reactants. This has led a number of scientists and engineers to develop techniques that increase mass transport into the aqueous phase, such as the application of cyclodextrins and cyclodextrin bound catalysts to increase the reaction rates. Other approaches have evolved from increased understanding of micelle behavior and applying this knowledge to develop alternative catalysts that take advantage of some of the unique capabilities of micelles to increase transport of the organic substrate.

More recent developments have now begun to diverge from the relatively easily separated water/organic systems to reactions involving systems which are totally miscible under reaction conditions but which are phase separable outside of reaction conditions. The most familiar has been the generation of catalysts with Teflon® 'ponytails' (polyfluorinated portions of the ligands) which take advantage of the fact that fluorocarbons are miscible in most organics when warm, but separate upon cooling. In this case, the fluorocarbon side chain on the catalyst forces the catalyst to separate with the fluorocarbon media. Additional examples of separable polymers have been demonstrated as well. (The discovery of efficient systems that possess this alternating miscible–immiscible behavior prompted us to title the proceedings in this issue from Biphasic Homogeneous Catalysis to Phase Separable Homogeneous Catalysis).

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Lastly, further improvements have been observed with Supported Aqueous Phase (SAP) catalysis. This methodology entails adding a thin film of water over the surface of an inorganic support, generally silica, and dissolving the aqueous soluble catalyst in this thin film. The catalyst is then used under fairly normal conditions in place of the more familiar homogeneous catalyst. Catalyst recovery is accomplished by simple filtration. Two advantages of this technique are that the high selectivity generally associated with homogeneous catalysts is retained but one now gets the ease of separation associated with heterogeneous catalysts.

This technique has the further advantage of addressing the issues of mass transport as well. By dispersing the catalyst over a large surface the amount of catalyst available at the organic/aqueous interface is markedly increased. In systems where the organic substrate is very insoluble and the reaction takes place at the interface rather than in the aqueous phase, this technique serves to markedly increase the availability of catalyst at the aqueous/organic interface by spreading the interface over a large surface. When the film is properly established, essentially all the catalyst is available at the boundary layer.

The rapid development of these multiple approaches to readily phase separable homogeneous catalysts led the editors of this issue to organize a full day symposium on the subject that was held on 11 September 1997 at the 214th National Meeting of the American Chemical Society in Las Vegas, Nevada. The meeting included speakers representing universities and industries from six countries and included examples of all the topics described above. This issue should serve as a highlight of the leading edge technologies being developed in this field.