

Biphasic Homogeneous Catalysis

By Paul J. Dyson, David J. Ellis and Thomas Welton

Department of Chemistry, Imperial College of Science, Technology and Medicine, London

Biphasic catalysis is becoming an area of environmentally responsible catalysis, but its development and use have until recently been somewhat neglected. Here, the basic principles and the design of features going into such systems are explained, and a general overview is presented with the intention of encouraging greater interest in this under utilised technique. Some well-established aqueous-organic regimes are described and there is a discussion of some possible future directions involving ionic-liquid/organic systems.

There are many benefits to be gained by using homogeneous catalysis in place of heterogeneous catalysis in organic synthesis, the most notable being the use of less aggressive reaction conditions and increased selectivity.

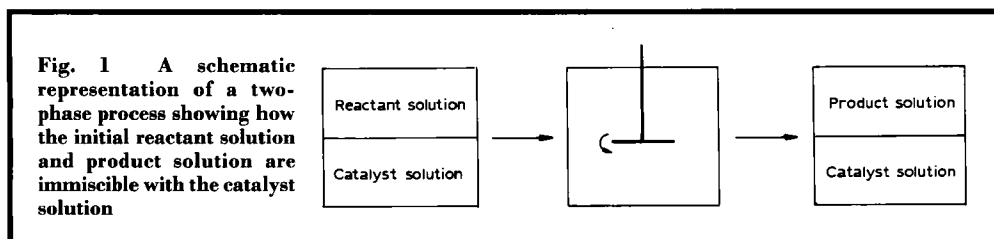
The main disadvantages of traditional organic phase reactions employing homogeneous transition metal catalysts are the difficulties associated with separating the catalyst from the product and solvent. Separation techniques, such as distillation, require an extra expenditure of energy and can, in certain instances, lead to degradation of both the products and the catalyst used. As the catalyst requires extraction before a new reaction run can be performed, the 'turn around time' between runs also becomes a prime factor.

These problems coupled with the inevitable loss of the catalyst species (allowing for some imperfection in the separation techniques employed) tend to redress the balance between heterogeneous and homogeneous catalysis.

One possible solution to these problems is to heterogenise the catalyst and product into two separate and immiscible phases. Reactions may

then be performed as shown in Figure 1. Here the catalyst resides in solution in one of the two phases and the substrate resides in the other phase. During reactions, the two layers are vigorously stirred, thus allowing suitable interaction of catalyst and substrate. Once the reaction has reached the appropriate stage, the stirring is stopped and the mixture of phases separates into two layers, one containing the product and the other containing the catalyst. Separation of the two is then carried out by simple decantation and, in principle, the catalyst solution is available for immediate reuse. Clearly, these biphasic reactions offer a potential answer to the problems mentioned above.

This type of approach was first used commercially for the polymerisation of ethylene (Shell Higher Olefins Process (1)) although in this case the catalyst and substrate are initially in a single phase and the product forms the second, immiscible phase; the principal, however, is the same. Clearly, this approach is not suitable for many other processes and has thus lead to the selection of water as the preferred catalyst solvent for biphasic conditions.



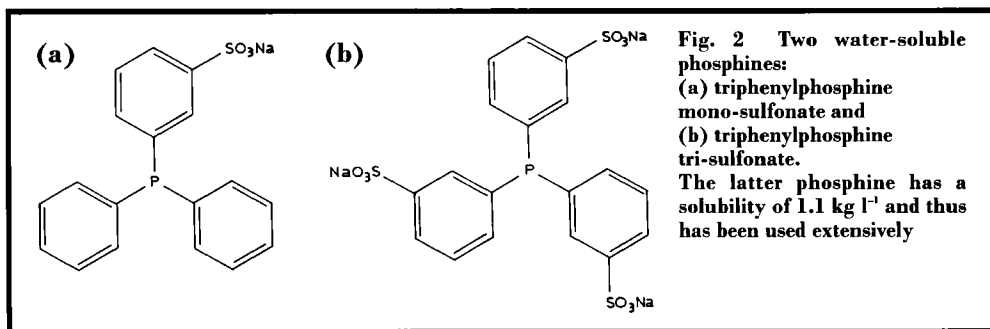


Fig. 2 Two water-soluble phosphines:
(a) triphenylphosphine mono-sulfonate and
(b) triphenylphosphine tri-sulfonate.
 The latter phosphine has a solubility of 1.1 kg l^{-1} and thus has been used extensively

The selection of water is straightforward and offers many benefits. First, wide ranges of organic solvents are immiscible with water; water is cheap, easily purified, and readily obtained and disposed of. However, despite the many advantages offered by aqueous/organic biphasic systems, the level of commercial exploitation is still relatively low. This is probably due, at least in part, to a lack of suitable water-soluble catalysts. However, having said this, interest in fundamental research has escalated rapidly in recent years. There have been a number of reviews published (2–6), for instance, an entire volume of the *Journal of Molecular Catalysis*, with an excellent editorial dedicated to the subject (7), and a recent book, reviewed here on page 145, which examines aqueous phase catalysts from an industrial perspective (8).

Sulfonated Phosphines and Their Industrial Use

The main consideration when attempting to design a water-soluble complex is how to render hydrophilic a typical hydrophobic organometallic complex. In order to do this, an appropriate ligand (or ligands) must be placed around the metal centre (or centres); alternatively, ionic catalysts, such as Dipamp $\text{Rh}(\text{cod})^+$ and (binap)Ru cations, could be used. One class of ligands that are widely used in homogeneous single phase catalysis are phosphines and diphosphines and it is therefore not surprising that the synthesis of water-soluble phosphine derivatives is attractive and has been the focus of much ligand design. Inducing hydrophilicity into a phosphine may be achieved by the introduction of

polar groups onto the phosphine substituent. In this respect, one of the most widely used groups is a sulfate (SO_3^-) group which can be attached to the phenyl rings in PPh₃. These represent, at the current time, the most widely commercially exploited ligand system.

The first of these sulfonated phosphines, triphenylphosphine mono-sulfonate (TPPMS, see Figure 2(a)) was reported as early as 1958 and was produced by the oleum sulfonation of triphenylphosphine (9). Modification of this synthesis led to the production of the tri-sulfonated ligand (TPPTS, see Figure 2(b)) which is now the most common ligand in use (10, 11). The tri-sulfonated ligand has an extremely high water solubility of *ca.* 1.1 kg l^{-1} (2). Formation of the catalyst complex is then carried out by co-ordination of the sulfonated phosphine ligand. Although direct sulfonation of pre-complexed triphenylphosphine ligands should be possible, the extremely acidic conditions needed to effect the change make the process unreliable.

Concentrating for the moment on the tri-sulfonated ligands, a whole range of water-soluble catalysts based on monometallic and cluster compounds has been reported, and a review by Kalck and Monteil includes a comprehensive list of these compounds (3).

Of particular interest here is the rhodium complex which is used in the Ruhrchemie/Rhône-Poulenc process for the biphasic hydroformylation of propene to *n*-butyraldehyde (12), a process which is used to produce about 330,000 tons of *n*-butyraldehyde per year. This process is highly selective and gives a linear aldehyde to branched aldehyde (*n/iso*) ratio of 95/5 with

99 per cent substrate conversion. Side reactions and loss of catalyst are both negligible. Since the use of this process commenced, catalyst development has continued and more active catalysts have been reported, although the selectivity has decreased (13, 14).

Rhône-Poulenc have also expanded the use of their biphasic production facilities into the manufacture of alcohols by hydrogenation and hydrodimerisation (5). A similar process with a rhodium/TPPTS catalyst is also used for the production of valeraldehyde from butene (15), which is the basis of *n*-valeric acid, used in the manufacture of CFC-free refrigerants.

Although the majority of work has concentrated on sulfonated phosphines there are other polar groups that can be used to induce water solubility. These include (in no particular order) hydroxyl, ether, carboxylate and amine groups. Ligands with these water solubilising groups will not be discussed in detail, due to the large number which exist, and in most cases the catalytic properties of complexes with these ligands have not been investigated in detail. The reviews mentioned previously present a more comprehensive and fuller picture of these ligands (2–6).

Metal Clusters as Water-Soluble Catalysts

The use of metal clusters in conventional homogeneous processes has been widely studied because they are considered to have properties intermediate between homogeneous and heterogeneous catalysts. As a cluster consists of several metal atoms, activation of an organic substrate may take place at more than one metal atom and this can have a profound effect on the activity. The number of catalytic processes in which clusters are effective is extensive, although examples where they are used in commercial processes are rare (16). Also, there is often uncertainty as to whether the cluster is broken down into mononuclear fragments during catalytic processes or whether the metal core remains intact.

A new aspect of biphasic catalysis has been the synthesis of water-soluble clusters. There are only a few water-soluble clusters at present and

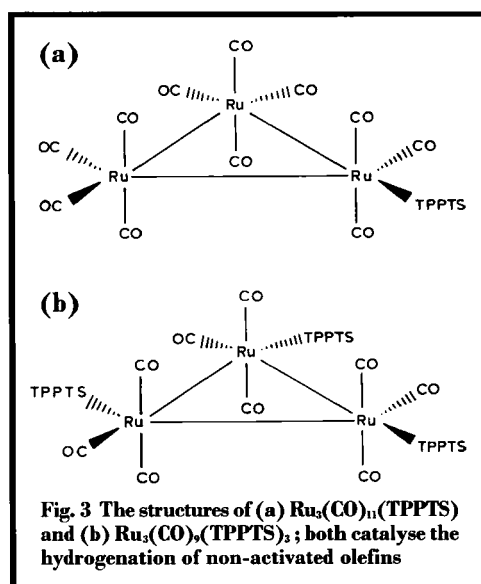
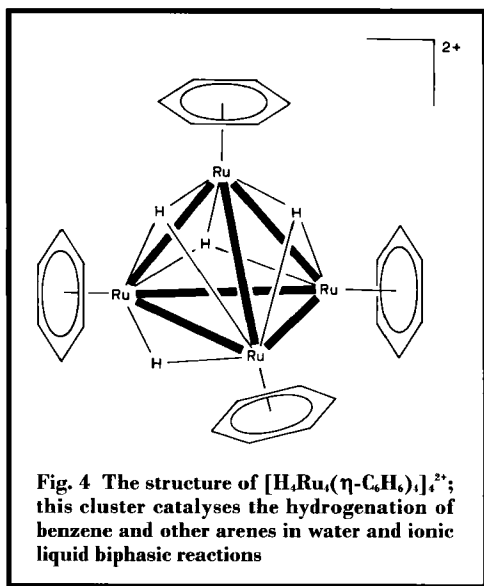


Fig. 3 The structures of (a) $\text{Ru}_3(\text{CO})_9(\text{TPPTS})_2$ and (b) $\text{Ru}_3(\text{CO})_6(\text{TPPTS})_3$; both catalyse the hydrogenation of non-activated olefins

two main types have been reported (17, 18). The first of these is based on TPPTS derivatives, two examples of which are shown in Figure 3. In most cases the synthesis of this type of cluster is simple and is achieved by the replacement of one or more carbonyl ligands with the water-soluble phosphine ligand under reflux in a suitable solvent.

The use of these compounds in the water-gas shift reaction (the reduction of water to hydrogen) has also been examined (19). This is a particularly valuable reaction, as it would potentially allow water to be the source of hydrogen for biphasic hydrogenations. All of the clusters tested were found to catalyse the water-gas shift reaction, although no quantitative measurements were performed, and some changes in the catalysts were found to have taken place during the course of the reaction.

We have since directed our attention to the use of this range of catalysts in both hydroformylation and hydrogenation reactions. Early results for hydrogenations of olefins have proved positive although catalytic turnovers are quite low. A similar change in the catalyst also occurs during hydrogenation and this is now thought to be independent of the catalytic reaction. However, the change in species does not seem



to affect catalytic activity. A detailed analysis of our findings will be published in due course.

An alternative series of water-soluble clusters has also been reported (17). These are not based on phosphine ligands but on cationic tetraruthenium clusters with arene and hydride ligands. Several have been synthesised and characterised and one of the clusters, see Figure 4, has been successfully used to hydrogenate benzene and some simple arenes – which is encouraging from an industrial perspective (20). The clusters are reported to be quite active, especially for the hydrogenation of benzene to cyclohexane, but not unexpectedly the conversion of the arene derivatives showed slightly lower activity and was not particularly selective. Indeed, where the substrate molecules possessed unsaturated side-groups, these were preferentially hydrogenated.

Ionic Liquids – the Future of Biphasic Catalysis?

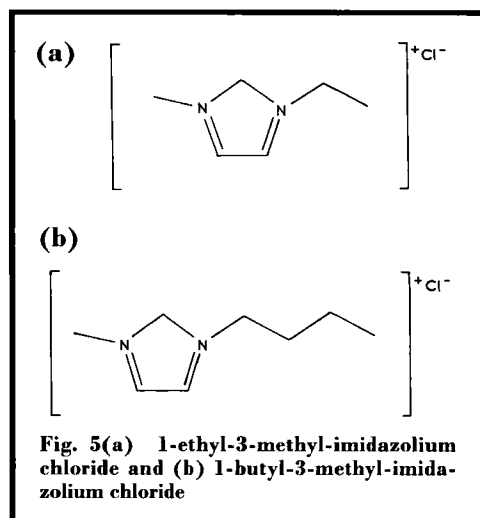
While water has proved to be the most widely used solvent for biphasic reactions there are several problems associated with it. For example, the chemical modifications to the catalyst which are needed to induce water solubility often reduce the catalytic activity, and certain active homogeneous catalysts are unsuited to any type

of conversion. Also, catalysts which are sensitive to moisture (as many are) cannot be used in water. The ideal situation would be an alternative solvent, capable of dissolving a wide range of metal compounds without reacting with the metal centre and so deactivating the catalyst. Even without modification, ionic liquids may represent an alternative solvent.

Ionic liquids are fundamentally molten salts. Molten sodium chloride (m.p. 803°C) is an example of a single component ionic liquid. It is clear to see – from its high melting point – that sodium chloride would not be suitable as a solvent for biphasic catalysis. However, a range of dual-component ionic liquids is available which are molten at and near room temperature (21). The physical properties of these liquids are quite interesting but the main properties of interest here are:

- their immiscibility with a wide range of organic solvents (making them ideal for biphasic systems);
- their polar nature (making them good solvents); and
- the low nucleophilicity of their component ions (preventing deactivation of the catalyst).

The ionic liquids we are interested in using are formed from two chemical components: an organic component (either 1-ethyl-3-methyl-imidazolium chloride, see Figure 5(a), or



1-butyl-3-methyl-imidazolium chloride, see Figure 5(b)) and an inorganic salt (aluminium chloride or sodium tetrafluoroborate).

A number of studies in biphasic catalysis have already been performed using an ionic liquid as the catalyst solvent (22–26). Ionic liquid systems have been used for hydrogenations (with rhodium, ruthenium and cobalt complexes), hydroformylations (with rhodium complexes), Heck coupling (with palladium complexes) and oligomerisations (with nickel complexes).

So far our interest has concentrated on the use of metal clusters in the ionic liquid. We have carried out a preliminary investigation into the effect of the chloroaluminate acid melt (a 2:1 molar ratio of AlCl_3 and 1-butyl-3-methyl-imidazolium chloride) on a range of metal carbonyls. The strongly Lewis acidic environment presented by the ionic liquid causes a change in the metal carbonyls over a period of time, but we have been unable to draw any conclusions at the present time.

Since our preliminary work into the effect of the acidic melt and with the experience of several low-pressure hydrogenation attempts (in which the melt has initiated rapid oligomerisation of the olefins used) we have shifted our attention to ionic liquids based on the tetrafluoroborate ion. These ionic liquids, unlike those based on chloroaluminates, are air stable and are thus much easier to handle. They also do not cause oligomerisation of the olefin substrates. The main disadvantage concerned with the tetrafluoroborate range of ionic liquids is that they exhibit considerably greater viscosity than the chloroaluminate variety and thus very aggressive agitation is required. Another

disadvantage is that uncharged species have decreased solubility in this ionic liquid whereas a wide range of neutral compounds can dissolve in the chloroaluminate melts. The tetrafluoroborate melts are still, however, very strongly polar in character and as such will dissolve charged species easily. We are currently designing new catalysts based on these requirements.

Conclusions

Biphasic catalysis is an under-exploited technique, but with increasingly demanding environmental legislation the opportunity for this technique to become more widespread in industry is quite clear. In addition to those discussed above, other biphasic regimes are also available, for example, a group of perfluorinated ethers which are chemically inert, non-toxic and generally immiscible with other organic solvents, has been reported (27–29). As with aqueous biphasic catalysis, the catalytic species have to be modified to achieve solubility, but in this case, such modifications are based on the replacement of traditional ligands with partially fluorinated or perfluorinated ligands. However, the high cost of both the fluorinated solvent phase and the catalyst systems required has, at the present time, made this type of biphasic system less attractive to industry even though they are environmentally friendly compared to the systems currently available.

The use of biphasic catalysis is gradually becoming increasingly acceptable and it can be expected that the number of processes involving it will continue to grow as the benefits that it offers are shown to be both environmentally sound and cost effective.

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Progress in Dye-Sensitised Photovoltaics

The 12th International Conference on the Conversion of Solar Energy into Photovoltaic Power and Storage, IPS-12, was held in Berlin from 9th to 14th August. This is the principal technical conference on photovoltaics and solar energy storage worldwide, and is held every two years. This year there were over 400 delegates, with most coming from academic institutions. The major surprise of the conference was the growth in activity in dye-sensitised photovoltaics (DSPVs), with over half of the presentations and posters being related to this topic.

The basic science behind dye-sensitised photovoltaic cells is well known (1). Cells are typically constructed from a glass/ITO electrode coated with a thin layer of dyed titania (TiO_2). The TiO_2 is dyed with ruthenium-based compounds, such as $\text{Ru(II)(2,2'-bipyridyl-4,4'-dicarboxylate)}_2(\text{NCS})_2$, and then impregnated with a liquid electrolyte containing the I^-/I_3^- couple as a regenerative redox shuttle between the dye and the counter electrode (platinum-coated glass/ITO). The cell power-conversion efficiency can be remarkably high, with figures of > 10 per cent under AM1.5 conditions being quoted, due to the broad absorption spectrum of the dye (extending into the infrared region for some dyes (2)) and the absence of significant charge recombination in the (*n*-type) semiconducting TiO_2 .

While the complex photophysics and chemistry of this system are still challenging, some consensus emerged as to what makes these cells work as well as they do:

- The more advanced ruthenium-based dyes show evidence for long-term stability, provided that proper sealing of the cell is achieved to prevent ingress of oxygen and water (which initiate free-radical attack of the dye).
- Electrons move primarily through TiO_2 by

diffusive processes, although under some conditions this is likely to be field-assisted.

- The extraordinarily slow time-constants (typically hundreds of ms) of the cell in response to chopped illumination is almost certainly due to extensive trapping of electrons in surface states on the TiO_2 .
- Increased cation (for example Li^+) penetration into the pores of the TiO_2 probably improves the efficiency of the electron transfer process and certainly assists the ionic (iodide) current in the liquid phase. The net benefit is an increase in cell current, although the type of cation also affects the cell open-circuit potential in ways that are not yet clearly understood.
- The electron-hole recombination may be retarded by virtue of the fact that the iodide 'hole-carrier' is negatively charged.
- The electron-injection kinetics (not the efficiency) are relatively insensitive to the dye type and very sensitive to the surface condition of the TiO_2 .

Perhaps the highlight of the conference was a 'live' demonstration of DSPV technology by Dr K. P. Hanke, Institut für Angewandte Photovoltaik, Gelsenkirchen, Germany, who used a prototype module to turn an electric fan, during his lecture on issues involved in cell scale-up.

In summary, the work presented at this conference has shown that dye-sensitised photovoltaic cells are continuing to show promise as practical devices, and may, in the longer term, open up a new market for ruthenium and platinum-based materials.

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