

Review

Industrial aspects of aqueous catalysis

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Abstract

In recent years aqueous two-phase catalysis has conquered its own field of homogeneously catalysed processes and has already achieved industrial-scale importance in hydroformylation. Because it has a number of advantages (ease of separation of catalyst and product, catalysts can be matched very precisely to the particular problem and thus tailor-made, use of special properties and effects of water as a solvent and reaction solvent, environmentally benign process) its importance and application will grow further. So far, scientific research has mainly concentrated on the preparation of water-soluble ligands and their metal complexes, but the outstanding features and effects of water-based catalysts in different types of reactions need to be rationalised with regard to their special mechanistic and kinetic aspects.

Keywords: Aqueous-phase homogeneous catalysis; Hydroformylation

1. State of the art and industrial implementations

The history of aqueous, two-phase, homogeneous catalysis is short but impressive: the initial observations by Manassen [1] were followed in 1975–1979 by corresponding research work (especially imaginative basic work by Kuntz [2,3] and Cornils and Kuntz [4]) and from 1984 onwards by the first industrial use, the hydroformylation (oxo-synthesis) of propylene in the plants of Ruhrchemie AG (now a part of Hoechst AG) [4–7].

The crucial advantages of aqueous two-phase

catalysis are the fact that it overcomes the inherent stumbling block of homogeneous catalysis systems, namely separation of the product from the catalyst homogeneously dissolved in it: the presence of the catalyst in the aqueous phase without any leaching and thus practically without loss enables catalyst and product to be separated by simple phase separation. Only in this case it is possible to utilise the great advantage of homogeneous over heterogeneous catalysis: the comparatively mild reaction conditions on using sterically and electronically easily variable, because molecularly defined, catalysts, the chemistry of which can readily be geared to the active metal centre. Associated with this is an exemplary understanding of the mechanisms that can be reproduced under actual conditions, which provides the basis for tailor-made homo-

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geneous catalysts. The contributions to this issue provide a wealth of examples.

In economic and ecological respects, too, this possibility of 'immobilizing' the homogeneous catalyst-heterogenisation by means of the mobile carrier water-leads to substantial advantages (e.g., [5,6,8]). This is specially true if the aqueous-phase procedure is compared with the more expensive phase transfer catalysis with which it is often confused [9].

The development of the aqueous two-phase process was completely untypical: initial research work by Rhône-Poulenc was soon followed by development work by the former Ruhrchemie AG, which led in 1984 to the commissioning of the first oxo-plant using the two-phase process (Ruhrchemie/Rhône-Poulenc [RCH/RP] process). Only after this industrial-scale implementation, in fact only after some considerable time had elapsed, did further fundamental academic work follow, and so this is a unique instance of continuing and fundamental work only being commenced after the outstanding suitability of the method was demonstrated on the industrial scale. The reasons for this, as evidenced by many discussions, would seem to have been in equal measure ignorance of Manassen's claims, doubts about the practicability of the method, and lack of interest in new techniques of homogeneous catalysis.

For the sake of completeness, it should be mentioned that the successful development work of Ruhrchemie AG making the process an industrial one was based on a scale-up factor of 1:24 000: a further indication of the low-risk

adaptation of homogeneously catalysed processes and a major advantage over heterogeneously catalysed reactions, which are frequently subjected to limitations of mass transfer. For details of the development cf. [4].

Aqueous two-phase catalysis, which is simply a special instance of homogeneous two-phase catalysis (see the SHOP two-phase process of Shell for the manufacture of higher olefins, [10]), suffered particularly from widespread scepticism, which virtually ruled out the possibility of organometal complex catalysts being linked to aqueous solvents. Confinement to only a few study groups gave the impression that the process was also restricted in geographical terms for many years. Furthermore, in view of the well-known reservations in particular of academic research scientists about patent literature the fact that advances in this field were published almost exclusively in patents contributed greatly to its academic neglect.

Water was the obvious second medium in any application of the two-phase method in hydroformylation because it was likely that the organic reaction products of oxo-synthesis would be easy to separate if the homogeneous hydroformylation catalyst could be made water-soluble and left in the aqueous phase for re-use. The special properties of water as a solvent, its extremely small molecular volume, its tetrahedral molecular network formed by hydrogen bridges, its isothermal compressibility, etc., makes it ideal for reactions where the hydrophilic and hydrophobic effects (as with all biological processes) are important. Water

Table 1
Industrial aqueous biphasic catalyses

| Process/products | Catalyst | Capacity (ton/y) | Operated by |
|---|----------------------|----------------------|---------------------------|
| Hydrodimerisation (Butadiene → octadienol → octanol/nonanediol) | Ru/TPPMS | 5000 | Kuraray |
| Selective hydrogenation (→ unsaturated alcohols) | Ru/TPPTS | No data | Rhône-Poulenc |
| C–C-bond formation (→ geranyl acetone) | Rh/TPPTS | > 1000 | Rhône-Poulenc |
| Hydroformylation (→ n-butanol and pentanals) (→ n-butanol) (Ref. [17]) | Rh/TPPTS Rh/TPPMS | > 300 000 No data | Hoechst AG Union Carb. |



Fig. 1. Aqueous biphasic hydroformylation: Plant of Hoechst AG/Ruhrchemie.

therefore has a special effect even in chemical reactions [11–13]. The ubiquitousness, lack of odour and non-flammability of water makes it suitable for environmental and safety reasons as a reaction solvent for industrial applications [8].

Aqueous, two-phase, homogeneous catalysis and the associated chemistry has now become a separate (even intimate) field of research with

its own conferences [14] and is already the subject of comprehensive reports because of its fundamental importance [15,16]. On the industrial level, homogeneously catalysed systems of aqueous two-phase catalysis are used with reactions listed in Table 1 [4–8,17–19].

Hydroformylation predominates with an annual capacity of over 300 000 metric tonnes (see

Table 2

Environmentally important data of the RCH/RP's oxo-process as compared to the Co technology [8]

| | Old Co high pressure process | RCH/RP Rh low pressure process |
|--------------------------------------|------------------------------|--------------------------------|
| Selectivities | | |
| Towards C ₄ products (%) | 93 | > 99 |
| Towards C ₄ aldehydes (%) | 86 | 99 |
| Products other than n-butanol (%) | 31 | < 5 |
| n/i-ratio | 80:20 | 93–97:7–3 |
| Manufacturing costs | 140 | 100 |
| Capital expenditure costs | > 1.9 | 1 |
| Waste water volume | 70 | 1 |
| Energy consumption figures | | |
| Steam | 82 | – 6.5 (steam exporter) |
| Power | > 2 | 1 |
| Syngas compression | 1.7 | 1 |
| Reaction conditions | | |
| Pressure (bar) | 300 | < 50 |
| Temperature (°C) | 150 | 120 |
| E factor [22] | 0.6–0.9 | 0.04– < 0.1 |

Fig. 1); the other industrial applications are still in the test stage or are being developed into bulk processes. Successful fundamental work however does make it probable that aqueous two-phase catalysis will be extended to a whole range of other organic syntheses (e.g., hydrocyanation, hydrosilylation, metatheses, Heck reactions [20]). In all commercial applications

"...the biphasic approach, a unique immobilisation technique, offers several advantages over other schemes of anchoring ligands to solid carriers. Most biphasic catalyst systems are mobile and cause only small changes in reaction mechanisms, they allow countercurrent extraction, facile separation of products, and easy catalyst reprocessing..." [21].

The fact that commercialisation of the homogeneously catalysed two-phase processes satisfies vital economic interests has been proved for over 12 years by the Ruhrchemie/Rhône-Poulenc process for propylene hydroformylation. By comparing the environmental process data (RCH/RP versus a classical Co-based process, see Table 2) and the profitability data (RCH/RP versus another modern Rh-based process, see Table 3) the superiority of the two-phase process in the harsh world of economic competition is confirmed.

The technology of aqueous two-phase catalysis has also proved superior in the case of the other processes mentioned in Table 1, either because only with the aqueous catalysts is an economic procedure possible (C–C link to geranyl acetone) or practically with high selectivity

(hydrogenation of unsaturated aldehydes) or because cheap raw materials can be used only with catalysis in water (e.g., butadiene for hydrodimerisation, [20]).

The potential of aqueous two-phase catalysis is far from being exhausted, as the many starting points for further development demonstrate (cf. Section 2).

2. What to do in future?

More than ten years after the unrivalled introduction of TPPTS as a water-soluble ligand and several other auspicious realisations of aqueous catalysis in industry as compiled in Table 1, this subject is now established as one of the most promising areas in homogeneous catalysis.

Despite all its merits a bundle of questions remains. The development of water-soluble ligands, mechanistic and kinetic models, asymmetric syntheses, or other techniques to apply aqueous catalysts to more hydrophobic substrates should be mentioned.

To this day the main contributions from science were first and foremost preparatory as has been reviewed recently [15,16]. The development of new classes of water-soluble ligands such as chelating diphosphines [23,24], cationic [25], non-ionic [26] and surface active [27] phosphines continues and completes the arsenal of biphasic catalysis, but on the other hand there is a lack of knowledge on what is really going on in two-phase catalytic processes. Indeed, there is no sufficient treatise on the different mechanisms and kinetics to explain the observed changes in activity and selectivity when water-soluble catalysts are applied.

High-pressure NMR-study of Horváth et al. [28] and results from Darensbourg et al. with in-situ CIR-infrared spectroscopy [29] revealed a strong difference in substitution and dissociation reactivity between TPPTS and non-sulfonated PPh₃. These observations ought to be confirmed by a kinetic analysis of the RCH/RP-system under catalytic conditions (ob-

Table 3
Manufacturing costs of different oxo-processes for 100 kg n-butanal (%) [6,7]

| Manufacturing costs | RCH/RP process | Other modern processes |
|---|----------------|------------------------|
| 1 Raw materials | 88.9 | 89.0 |
| 2 Energy costs | 1.5 | 9.7 |
| 3 Credits (<i>i</i> -butanal, <i>i</i> -butanol, etc.) | -7.7 | -11.4 |
| 4 Cost of materials (sum 1 + 2 + 3) | 82.7 | 87.3 |
| 5 Fixed costs + license fee | 17.3 | 22.1 |
| 6 Sum 4 + 5 = Manufacturing costs | 100.0 | 109.4 |

tained in the regime where mass and phase transfer are negligible). Sufficient data for the homogeneous rhodium/triphenylphosphine system are available for substrates like e.g., propylene [30], 1-hexene [31], and 1-decene [32]. A recent study of styrene hydroformylation with Rh/phosphole-catalysts [33] illustrates the high value of kinetic measurements in uncovering mechanistic details.

Those investigations of aqueous biphasic reactions should include a closer examination of some special inherent phenomena, like the role of salt effects [34], micelle forming agents [35] and co-solvents. The advent of computer-technology will help to understand the unique role of water [36] and allow calculations of catalytic cycles [37].

Concerted academic and industrial research will again prove to be symbiotic in solving these tasks. The long-term partnership of the academic research group at the Technical University of Munich with Hoechst AG (Ruhchemie) lead to an understanding of the chemistry of TPPTS first (i.e., purification and preparation of the ligand and its catalytic relevant transition metal complexes [38,39]) and the development of new tailored water-soluble phosphines for propylene hydroformylation. The latest peak in activity and selectivity was reached with BINAS-Na as depicted in Fig. 2 [40]. The considerably higher performance and lower activation energy found for this catalyst system in direct comparison with BISBIS-Na, a bisphosphine very similar in bite-angle and electronic proper-

ties, again raises the question about the mechanistic details in hydroformylation.

Thus, the development of water-based catalysts shows to keep in touch with progress made in general homogeneous catalysis [41].

Unquestionably, a major problem associated with aqueous catalysis is the limited and often very low solubility of certain organic substrates in water. Although the Rh/TPPTS-system was very recently applied to valeraldehyde production (14 000 metric tons) by Hoechst AG/Ruhrchemie [42] and its use in the hydroformylation of functionalized olefins was demonstrated for methylacrylate [43], the restriction towards more hydrophobic substrates is still valid. In this context the use of PPh_3 as a 'promotor-ligand' to yield complexes $\text{HRh}(\text{CO})(\text{TPPTS})_{3-x}(\text{PPh}_3)_x$ for the two-phase hydroformylation of olefins such as 1-octene deserves attention [44]. As stated by the authors, leaching of rhodium into the organic phase is insignificant after addition of the 'foreign substance'. Another elegant solution seems to be the additional immobilisation of aqueous catalysts by means of SAP-catalysis [45]. In case of the above mentioned methyl acrylate hydroformylation, fixation of the $\text{HRh}(\text{CO})(\text{TPPTS})_3$ -catalyst on 'controlled pore glass' increased the activity by a factor of 220 as compared to the Rh/ PPh_3 -system. The application of this variant also proved fruitful in case of asymmetric biphasic catalysis. Enantioselective hydrogenation of 2-(6'-methoxy-2'-naphthyl)-acrylic acid with a tetrasulfonated BINAP/Ru-catalyst fixed on SiO_2 gave (*S*)-naproxene in yields up to 96% ee [46].

In connection with enantioselective transformations aqueous catalyses enter a new dimension, since industrial applications of catalytic asymmetric syntheses are usually not only hampered by expensive transition metals but even more by the cost of valuable chiral ligands. Enantio-pure sulfonated diphosphines were successfully employed in hydrogenation reactions by Amrani et al. [47] and later on Ding et al. achieved high enantiomeric excesses using a

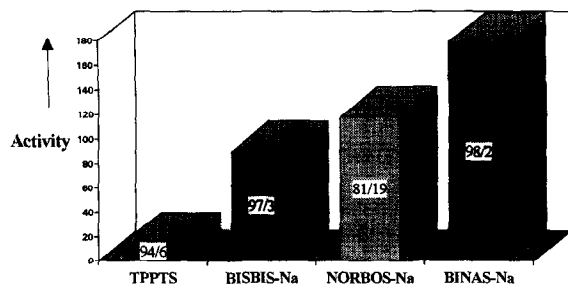
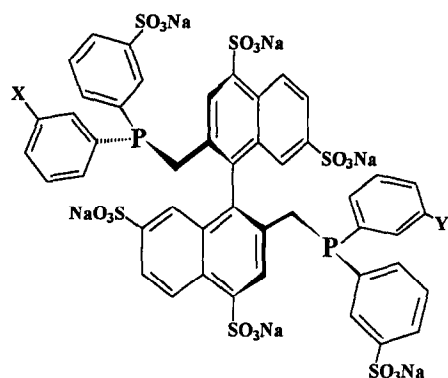


Fig. 2. The performance of new water soluble ligands in propylene-hydroformylation and their linear/branched selectivity.



BINAS 6: X = Y = H

BINAS 7: X = H, Y = SO₃Na

BINAS 8: X = Y = SO₃Na

Fig. 3. Structure of different BINAS-Na-isomers.

chiral surface active bisphosphine based on *R,R*-2,4-pentanediol [48]. Mechanistic studies by Joó et al. revealed a monohydric mechanism [49] for aqueous–organic hydrogenations which could explain the lowering or loss of enantioselectivity observed in most cases.

The work on asymmetric hydroformylation, a major challenge in homogeneous catalysis for more than 25 years [50], was reinforced after the breakthrough in 1993 by Takaya and co-workers [51]. In case of water-soluble catalysts, only racemic aldehydes were obtained in the hydroformylation of styrene when a chiral monophosphine [52] was employed. Preliminary results from our own laboratories indicate enantiomeric excesses near 20% in the same reaction by using atropisomeric pure BINAS-Na [53] (Fig. 3) and a very high selectivity towards hydratropaldehyde formation ($\geq 95\%$).

Mainly due to racemic switches on the pharmaceutical and agricultural sector, the demand for optical pure building-blocks is believed to increase significantly in the next years [54] and thus elaboration of asymmetric syntheses using water-based catalysts is of utmost importance.

In addition, the potential of organic reactions compatible with or even promoted [12] by water is not exploited in full yet. Scientific and industrial research will also focus on reactions like

hydrocyanation, C–C-coupling, isomerisations, oligomerisations and polymerisations. Especially in the field of Pd-catalysed organic reactions, the use of water-soluble ligands will play a dominant role in future [55,56].

The advance in biphasic non-aqueous catalysis is amazing, too. The fluorinated biphasic system (FBS) of Horváth and Rabai [57] and the approach of Chauvin and Olivier-Bourbigou with non-aqueous ionic liquids [58] may find applications in industry, but as the ‘environmental-quotient’ [22] of products is becoming more and more important, water-based catalysts will become so either.

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