

Review

Bulk and fine chemicals via aqueous biphasic catalysis

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Abstract

Homogeneous aqueous biphasic catalysis becomes more and more attractive for both bulk and fine chemical manufacture. Hydroformylations, carbonylations, hydrogenations, allylic substitutions, hydrodimerizations, or Suzuki couplings are practised on an economical basis. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

In 1998 the 60th anniversary of the discovery of oxosynthesis (hydroformylation, hydrocarbonylation) by Otto Roelen in the labs of Ruhrchemie will be celebrated [1] (as to the history of the invention cf. Refs. [2,3]). The importance of this best known and most relevant variant of hydrogenative carbonylation—mutual addition of carbon monoxide and hydrogen, the constituents of syngas—is unanimously recognized: production figures of more than 6 millions tonnes per annum are convincing [4,5]. Although the bulk production of *n*-butyraldehyde is dominant a growing palette of fine chemicals manufactured by addition of CO/H₂ to special olefins or functionalized intermediates becomes more and more important [4,6]. All processes of hydroformylation and carbonylation mark the transition from organometallic or coordinative chemistry science to the economical application of homogeneous catalysis [7,8].

Regarding specially the rapid succession of economical hydroformylation processes their importance becomes understandable. So far 60 years of oxo synthesis saw at least five quantum transitions of development—‘Diaden process’ with heterogeneous cobalt catalysts [9], high pressure processes with homogeneous cobalt catalysts [4,10], the introduction of Rh as the central atom of complex catalysts [11] or of ligand modified Rh or Co catalysts [12], and the two-phase catalysis with aqueous catalysts [13–15].

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For carbonylation reactions (as for all homogeneously catalyzed conversions) the problem of separating the—according to definition—homogeneously dissolved catalyst is immanently disadvantageous. So far the difficult separation between the catalyst and the reaction products after reaction could only be overcome by complicated recycle processes. Introducing the aqueous, homogeneous two-phase technique [16] the active catalyst for the reaction is (and remains) dissolved in water, so that the reactants and reaction products, which are ideally organic and relatively nonpolar, can be separated off after the conversion is complete by simply separating the second phase from the catalyst solution, thus making it easy to recirculate the latter [17,18]. This considerable progress represents the reduction of the high sophisticated recycle technique of oxosynthesis to a process low in investment and easy to handle. This 4th generation of oxosynthesis is now under introduction for hydroformylation and increasingly, for other reactions aiming at fine chemicals.

2. Technique of aqueous biphasic catalysis

Aqueous biphasic catalysis is a special case of the two-phase process of homogeneous catalysis whose development began according to proposals of Manassen [19] with Shell's SHOP process by Keim et al. [20,21]. In all two-phase processes the homogeneous catalyst is dissolved in a liquid phase different from the phase of reaction products and reactants [16,22]. With organic liquids the search for solubility gaps is not easy (Fig. 1).

The special case of *aqueous* two-phase variants is quite simpler: from the homogeneous catalyst which is and remains dissolved in water, organic reactants with other hydrophilic or hydrophobic properties can easily be separated by simple mechanical decantation (phase separation, cf. Fig. 2). Thus, activity or selectivity damaging process steps—so far the disadvantage of homogeneous catalysis—can be avoided.

Although the advantages of the aqueous variant of two-phase homogeneous catalysis are obvious, the influence of industry was needed to cross the border from the idea and the early work of Joó [25]

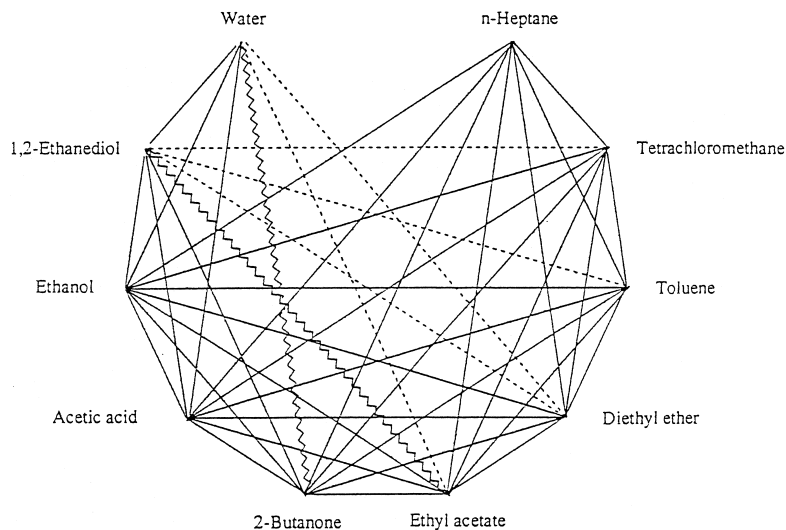


Fig. 1. Miscibility diagram [23,24]. Solvents not connected by a binding line are immiscible; solvents of unlimited miscibility are connected by a solid line, those of limited miscibility by a sawtooth line, and those of low miscibility by a dotted line.

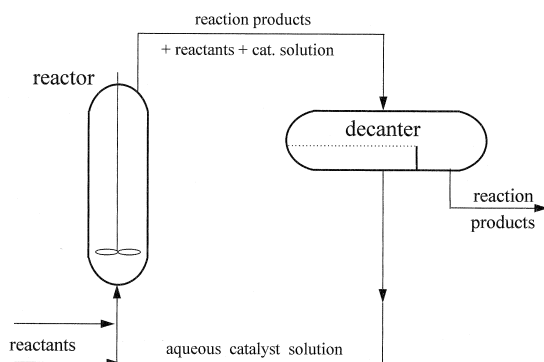
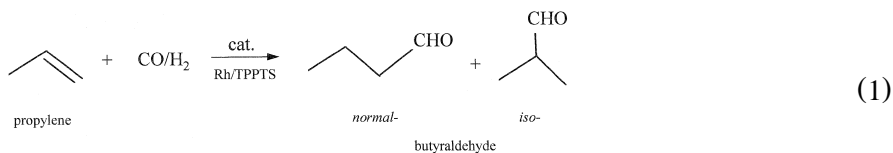


Fig. 2. Principle of aqueous biphasic homogeneous catalysis.

and Kuntz [26] to a real process. One of the focal points of development was the search for appropriate water soluble ligands thus converting the normal phosphine modified catalyst systems to water soluble species (as for the standard ligand TPPTS, the trisulfonated triphenylphosphine, cf. [27–29]). Taking the hydroformylation and thus the production of bulk chemicals into account the aqueous variant is now an established process (Ruhchemie/Rhône-Poulenc process, cf. Section 2.1, [8,13–18]). The manufacture of fine chemicals was originally the domain of Rhône-Poulenc and Kuraray (Section 2.2). It was not until the last years that researchers from academia and industry developed new processes for an increasing amount of fine chemicals thus using the advantages of homogeneous catalysis as well (Table 1).

2.1. Production of bulk chemicals

The state-of-the-art of bulk chemical production via biphasic hydroformylation and of the manufacture of *n*-butyraldehyde is defined by the RCH/RP-process (Eq. (1), [13–16,27–29]).



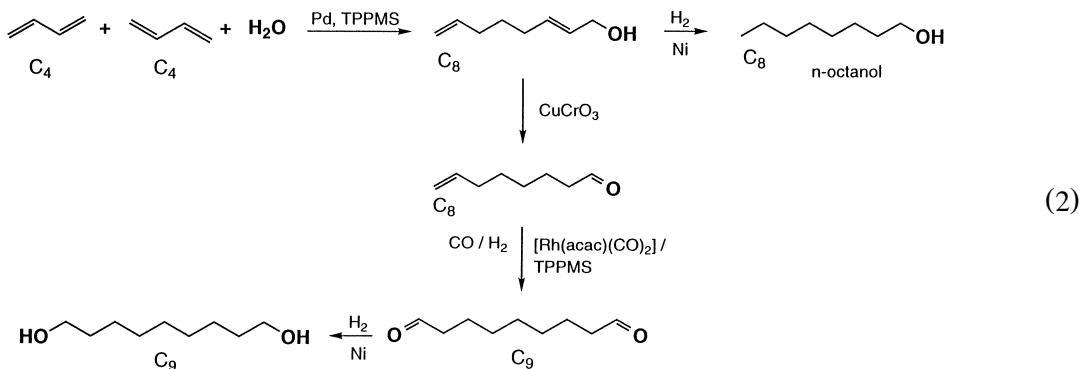
At present four plants produce worldwide 450.000 tonnes per annum of oxo products. The advantages of chemical engineering simplicity, low investment, higher yield via improved selectivity,

Table 1
Homogeneous versus heterogeneous catalysis

	Homogeneous catalysis	Heterogeneous catalysis
Activity (relative to metal content)	High	Variable
Selectivity	High	Variable
Reaction conditions	Mild	Harsh
Service life of catalysts	Variable	Long
Sensitivity toward catalyst poisons	Low	High
Diffusion problems	None	May be important
Catalyst recycling	Expensive	Not necessary
Variability of steric and electronic properties of catalysts	Possible	Not possible
Mechanistic understanding	Plausible under random conditions	More or less impossible

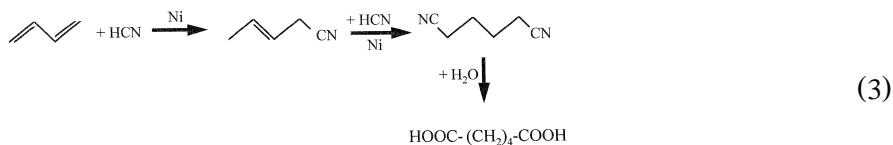
and environmental benign procedure are acknowledged by the community. For all that, research activities go on and comprise first of all the conversion of higher olefins and the search for cheaper and more effective ligands besides basic research for better insight the process [29]. The advantages of that combination of aqueous media and organometallic homogeneous catalysts are undisputed although unimaginable in former times.

Aqueous, two-phase catalysis is utilized in another bulk process apart from hydroformylation. The *hydrodimerization* of butadiene and water, a telomerization variant (Eq. (2)), is carried out in a capacity of 5000 t/annum by Kuraray in Japan [30].



Doing this, the aqueous biphasic procedure is first used to manufacture 2,7-octadien-1-ol, which can be easily hydrogenated to the desired 1-octanol, a valuable plasticizer alcohol. The catalyst used is palladium modified with the Li salt of TPPMS (the monosulfonated triphenylphosphine). Octanol is not the only valuable product. The intermediate octadienol can be dehydrogenated/hydrogenated internally to 7-octenal and this may be hydroformylated to yield nonadienal and then hydrogenated to nonadiol. An interesting feature is the use of CO_2 as coreactant which stabilizes the phosphonium salt of the catalyst as a hydrocarbonate. So far the market success and some internal details of the process are uncertain, and the small current production figures of 1-octanol by Kuraray do not reflect the importance of this bulk chemical. Similar process proposals have been published by BASF, ElfAtochem, and others [31–33].

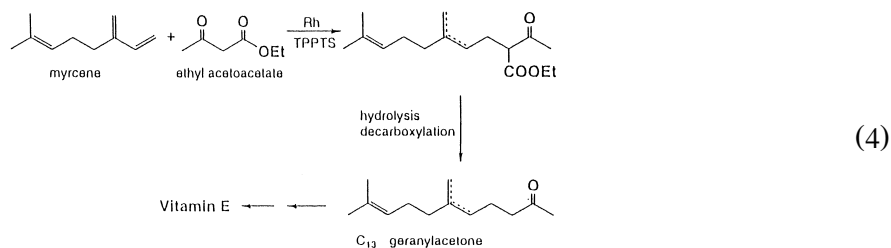
The remarkably versatile C_1 building block hydrogen cyanide may be used in the aqueous two-phased *hydrocyanation*, too. Under the influence of water soluble Ni^0 catalysts HCN is added to unactivated $\text{C}=\text{C}$ double bonds such as in butadiene, yielding 3-pentene nitrile and—on adding another molecule of HCN—adiponitrile, the precursor of adipic acid [34–36] (Eq. (3)):



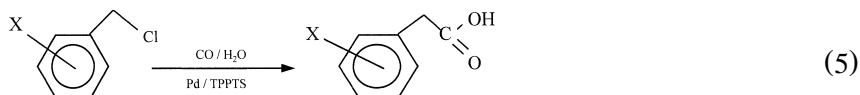
2.2. Manufacture of fine chemicals

Since nearly a decade Rhône-Poulenc is operating some two-phase, aqueous, homogeneously catalyzed C–C coupling processes using TPPTS modified Rh complexes for small-scale productions

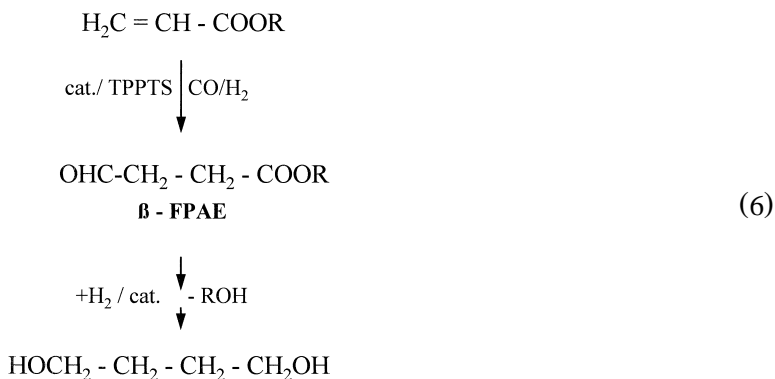
of various vitamin precursors [37,38]. According to Eq. (4) the route to geranyl acetone as a precursor of vitamin E starts from myrcene and ethyl acetoacetate.



The homogeneous, aqueous biphasic catalysis has also acquired industrial significance for the production of phenylacetic acid (PAA). The classical process—benzyl chloride → benzyl cyanide → PAA—suffered from large amounts of salts (1400 kg/kg of PAA) [39]. The new biphasic *carbonylation* method reduces the amount of salt by 60% and benefits from the great cost difference between –CN (approx. \$1.4/kg) and –CO (< \$0.2/kg) (Eq. (5)). As to other homogeneous catalyzed biphasic carbonylations cf. Ref. [40].



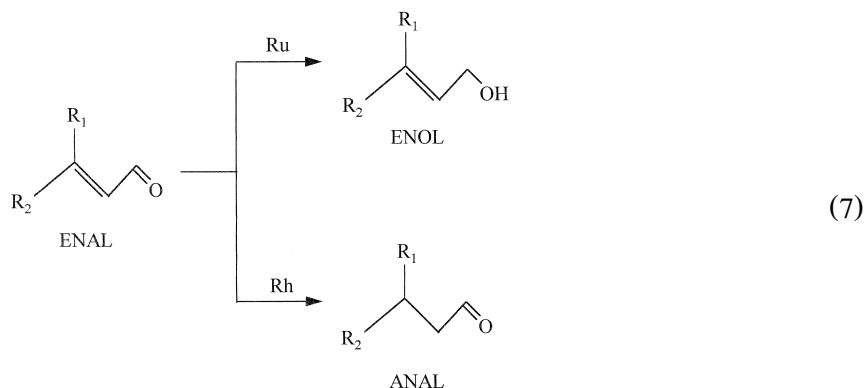
In a wider sense other hydroformylations belong to the biphasic, homogeneous catalyzed carbonylation reactions, such as the conversions of allyl alcohol [41] or acrylic acid esters [42,47] which yield (via the fine chemical β -formylpropionic acid esters [β -FPAE]) eventually bulk chemicals such as butanediol (BDO, Eq. (6)). The aqueous procedure ensures the desired high β : α ratio ([42], Eq. (6)).



Fell and Behr recommended aqueous biphasic processes for the manufacture of oleochemicals, e.g., via hydroformylation of ω -alkene carboxylic esters [48,49]. Other hydroformylations have been described on using the SAPC technique (see below).

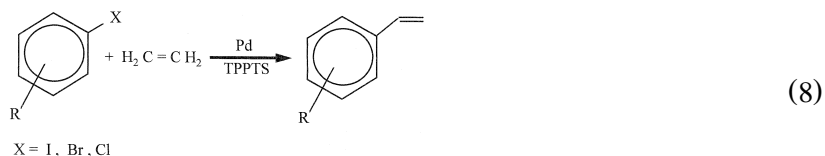
Apart from carbonylations aqueous-phase catalyzed *hydrogenations* for fine chemicals may increase in importance although heterogeneously catalyzed hydrogenations reached a high level state-of-the-art [50–53]. More important are partial or selective hydrogenations which belong to the field of activity of the early pioneer of this catalysis, Ferenc Joó. An excellent example is the partial

hydrogenation of unsaturated aldehydes to either unsaturated (allylic) alcohols or saturated aldehydes (Eq. (7), [54–56]).

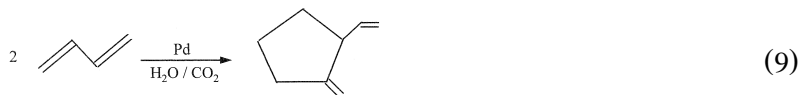


Starting from water/ α,β -unsaturated aldehyde (ENAL) biphasic mixtures unsaturated alcohols (ENOLs) may be obtained with Ru based catalysts, saturated aldehydes (ANALs) with Rh catalysts [54–60]. This sequence may be important for the manufacture of the interesting fine chemicals 2-ethylhexenol and 2-ethylhexenoic acid. Hydrogenating *trans*-cinnamaldehyde it could be proven that the pH serves as a selectivity switch [61] to either cinnamyl alcohol or dihydrocinnamaldehyde. Unsaturated acids are available, too [25,62]. Even for the important asymmetric hydrogenation the aqueous biphasic procedure using chiral sulfonated phosphines offers advantages [63–65].

Both, inter- or intramolecular Heck-type reactions to fine chemicals, may proceed via Pd catalyzed biphasic conversions [66–68], e.g., a Heck arylation of ethylene (Eq. (8)):

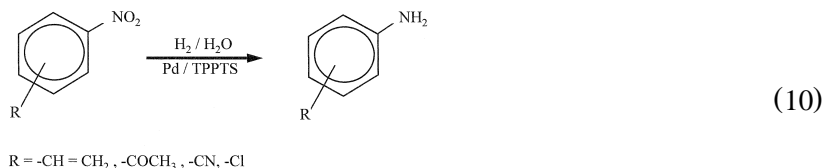


Oligomerizations and similar reactions are also accessible by water soluble catalysts. Some model hydrophilic and lipophilic terminal alkynes such as phenylacetylene have been converted to diphenylbut-1-en-3-yne [69]. Via cyclodimerization 1,3-butadiene is converted to 2-vinylmethylene cyclopentane in a partially aqueous system (Eq. (9) [70]).



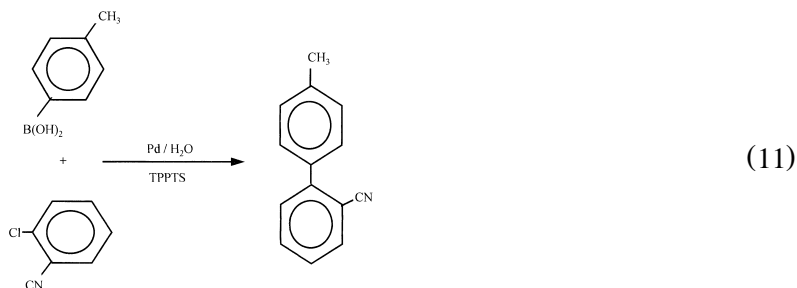
TPPTS has even been used (although not biphased) for the catalytic oligomerization of ethylene [71]. Alternating co- and terpolymerisates from carbon monoxide and ethylene or propylene resp. in an aqueous mode were described by Sen et al. [72,73].

With aqueous biphasic catalyses there are two routes to amines: *aliphatic* amines, e.g., via telomerization of butadienes and ammonia [74], *aromatic amines* preferably by reduction of nitro to amino aromatics (Eq. (10), [75–77]).



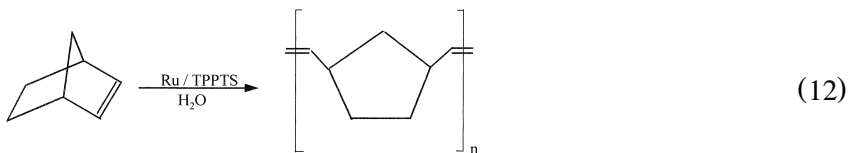
The latter is a very careful access to sensible aromatic amines.

The catalytic *hydration* using hydroxy-bridged dipalladium complexes and water soluble ligands yields hydroxy substituted compounds (e.g., diethyl malate from diethyl maleate) which may be important as fine chemicals [78]. This is also true for the *Suzuki cross coupling* of aryl halides and arylboronic acids [79–81]. The earlier lab-scale methods starting from expensive brominated or iodinated aromatics, only homogeneous and monophasic Pd catalysts could be used; the cheaper chlorinated derivatives require very much more basic phosphines for the catalyst modification. Nowadays, the chlorinated aromatics and catalysts basing on Pd/TPPTS are used in an aqueous procedure on a commercial scale by Clariant (Eq. (11)).



In contrast to monophasic procedures Pd catalyzed allylations are feasible in highly regioselective reactions using aqueous DMSO/TPPTS mixtures [82–84].

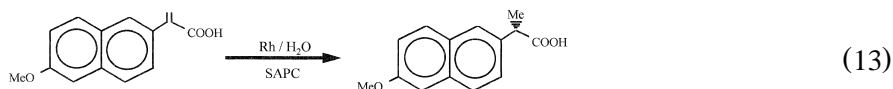
As far as *metathesis* is concerned the aqueous biphasic catalysis is especially important for ring opening metathesis polymerization (ROMP) of cyclic olefins [85–87], e.g., Eq. (12).



Finally, *formic acid syntheses* by hydrogenation of carbon dioxide [88,89] and *Wacker-type* conversions [90] are described under aqueous-biphasic catalytic conditions. Since the process accepts technical grade CO₂ the HCOOH synthesis may become important—and even continuing from fine to bulk chemicals—provided the TONs and TOFs may be increased considerably. Even the economi-

cally important *hydrodesulfurization* process (HDS) receives homogeneous [91] and even aqueous-biphasic catalytical roots [92].

As mentioned earlier the *SAPC variant* of the aqueous biphasic homogeneous catalysis (called ‘supported aqueous phase catalysis—a new class of heterogeneous catalysts’ (!), [93]) finds attention for special reactions such as hydrogenations or hydroformylations [43–46]. Especially for asymmetric hydrogenations such as Eq. (13) SAPC is said to be best suited.



So far the potential of this special kind of heterogenized homogeneous catalysts is unclear, and it is unknown if the expensive technique eventually pays the cost.

3. Conclusions

There is a bright future for fine and bulk chemical production using aqueous biphasic homogeneous catalysis. This overview about important industrial and potential processes and chemicals does not even include the possibilities of other two-phase techniques such as the SHOP process (with two immiscible organic phases, [20,21]), nonaqueous ionic liquids (‘NAILS’, [94]), fluoruous phases [95], or polymer based ‘liquid supports’ [96], not to mention phase-transfer, inverse, or counter phase-transfer catalysis (which require costly additional co-reactants) [97]. About the development of new variants of homogeneous aqueous biphasic catalyses is reported elsewhere [27].

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