CHAPTER 5 BIPHASIC SYSTEMS: WATER – ORGANIC

ERNST WIEBUS[1], BOY CORNILS[2]
[1] *Celanese Europe GmbH, Werk Ruhrchemie, D-46128 Oberhausen, Germany;*
[2] *D-65719 Hofheim, Germany; e-mail: boy.cornils@t-online.de*

5.1 Introduction

Biphasic techniques for recovery and recycle are among the recent improvements of homogeneous catalysis - and they are the only developments which have been recently and successfully applied in the chemical industry. They are specially introduced into the hydroformylation (or "oxo") reaction, where they form a fourth generation of oxo processes (Figure 5.1 [1]). They are established as the "Ruhrchemie/Rhône-Poulenc process" (RCH/RP) [2]; cf. also Section 5.2.4.1), with annual production rates of approximately 800,000 tonnes y^{-1} (tpy).

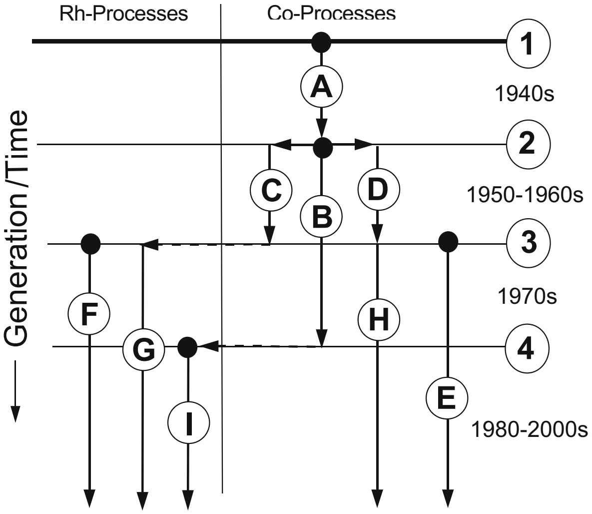


Figure 5.1. The generations of oxo processes [3] (symbolized by full points).A, First generation Ruhrchemie process 1943 (diaden process [4]); B, second generation Ruhrchemie process; C, second generation BASF process; D, second generation Kuhlmann process; E, third generation Shell process; F, third generation LPO (UCC) process; G, third generation BASF process; H, third generation Exxon (Kuhlmann) process; I, fourth generation Ruhrchemie/Rhône-Poulenc process

According to the early scientists developing this process, Manassen/Whitehurst [5a] and

D. J. Cole-Hamilton and R. P. Tooze (eds.), Catalyst Separation, Recovery and Recycling, 105–143.

Joó [5b,c,d], biphasic stands for the use of two immiscible liquid phases, one containing the catalyst and the other containing the unreacted substrate and the reaction products. The tremendous progress in homogeneous catalysis is that both liquids, i.e., phases, can be separated off after the reaction is complete by simply separating the second phase from the catalyst solution, thus making it easy to recirculate the latter without any thermal or chemical stress (which is the case in all classical separation methods, see Chapter 2 and [3]). Therefore, this technique allows full utilization of the inherent advantages of homogeneous catalysis and avoids the costly recycling procedures of traditional homogeneous catalysts. In this respect, biphasic catalysis is the most successful variant of an immobilization technique, i.e., an "anchoring" of the catalyst onto a liquid support [6]. The application of biphasic catalysts simplifies the process of homogeneous catalysis considerably.

Early experimental work on biphasic techniques came up with large scale processes for the above mentioned hydroformylation of alkenes, oligomerization of ethene, telomerization of butadiene, and some small-scale processes for the manufacture of fine chemicals. Whereas the oligomerization proceeds in an organic/organic biphasic system (SHOP process of Shell; [7]), the other reactions use biphasic *aqueous* conditions which offer an especially advantageous mode of operation. Speaking of "Green Chemistry" and "Green Catalysis" and their definitions (Ken Seddon: "Green chemistry is all about reducing the number and amount of harmful chemicals that are used and/or generated in research and industry.... This new field is all about minimizing the amount of waste..."), reacting substrates in aqueous biphasic operation is the most progressive example [8] - far beyond other techniques such ionic liquids where the specialists make encouraging statements such as "You think your process is green, how do you know?" [8c] or "Ionic liquids are not always green!" [8d].

This Chapter will concentrate on the hydroformylation of propene by means of rhodium catalysts, modified by water-soluble ligands such as TPPTS (**tri****p**henyl**p**hosphine *m*-**tris**ulfonate).

5.2 Immobilization with the Help of Liquid Supports

5.2.1 GENERAL

In Chapter 3 about *Supported Catalysts* the numerous unsuccessful attempts to heterogenize oxo-active transition metal complexes are compiled: the difficulty of catalyst/product separation appeared to have been solved. However, it was discovered during long-term tests to verify the utility of the concept (tests which do simulate industrial conditions in terms of uninterupted long runs and numerous catalyst cycles, TONs and TOFs, changes of temperatures, pressures, loads, etc.) all of these essentially supported oxo catalysts, tended to leach out. This means that the active catalyst metal and also the modifying ligand slowly, but steadily, became detached from the heterogeneous support and were carried away after an uneconomically short time: the problem of homogeneous catalysis may have been delayed but has not been solved. Even hybrid techniques such as

SLPC or SAPC (**s**upported **l**iquid [or **a**queous] **p**hase **c**atalysis [9,10,62,64]; see also Section 5.2.5) provide no improvement, probably because of the tremendous stress on the support/transition metal bond during the repeated change between tetrahedral and trigonal-bipyramidal metal carbonyls over the course of a single catalyst cycle. Only recent publications [11,21,26b,28h] report on successful realization of supported homogeneous hydroformylation catalysts, but so far there is no confirmation by practise-soriented tests - not to mention by commercial applications.

5.2.2 BIPHASIC SYSTEMS

Only the biphasic method, specially of *aqueous*-biphasic catalysis, has provided a fundamental remedy to the problem of stress-free and economical recovery and recycle of homogeneous oxo catalysts [12]. The fact that the catalyst, which still acts homogeneously, is dissolved in water, thus in a polar solvent, and remains dissolved, enables it to be separated from the nonpolar products without problems and with minimal effort after reaction.

The decisive step was the development of ligands with two concurrent properties: they are simultaneously water-soluble and they modify the catalytically actice complex [13]. Pioneering work was carried out by Joó (mainly concerning hydrogenations) [5], Kuntz (then with Rhône-Poulenc, [12g,14]), and the former Ruhrchemie AG [12,77,79] - and thus in industry - which led to the first large-scale utilization of the aqueous, homogeneous catalysis technique at the beginning of the 1980s [7,12]. The generally used embodiment of two-phase catalysis (e.g., as practized in Shell's SHOP method [7]; see also Section 5.2.6) was thus joined by *aqueous* two-phase catalysis.

In classical homogenous catalysis, an organic compound, i.e., a real liquid phase (a solvent) dissolves all of the reactants, catalysts, and products. The role of the solvent is underlined by the fact that it has to be separated from the reaction products by an additional and costly step, for example by distillation.

Olivier-Bourbigou and Hugues [15] define the importance of solvents as follows: "The role of the solvent in organic reactions is of the utmost importance [16b]. Its effect can just be limited to a "physical effect" in making possible the solubilization of the reactants, with no direct interaction with the active center. More interesting are the cases in which the solvent interacts through specific forces, such as hydrogen bonds, thus altering the mechanism, the rate, and eventually the selectivity of the reaction in stabilizing certain reaction intermediates. In homogeneous catalysis, the solvent effect is often difficult to explain due to the large number of reaction intermediates involved. However, for catalytic applications involving coordinatively unsaturated cationic metal centers, the "ideal" solvent should be able to solubilize the metal ion, while maintaining its ionic character, and should create weak and labile metal-solvent bonds. It should he highly polar and non-coordinating for the active metal center. Most of the classical organic solvents are covalent and do not satisfy the above requirements." Especially the necessity for a separate and costly separation step is a heavy burden for bulk chemical processes operating with real solvents, diluents, etc.

For aqueous biphasic systems, the "solvent" is water which shows pronounced solvent effects (cf. Section 5.2.3.1) but, on the other hand, does not have to be separated by means involving thermal or other stresses either from the reactants or from the products. Therefore, the water of the aqueous-phase processes has to be regarded as a "supporting fluid" rather than a real solvent although there are many cases known in which water acts as an accelerator for organic and even organometal-catalyzed reactions [17,18]. The key for this behavior is the role of water in both, the influence on activity and selectivity of the desired reaction **and** the suitability to act as phase separating agent [19] - presumably enhanced by its tendency to form micelles, microemulsions, or other surface-based aggregates [51b,51c,52d, 54,58]. Not recognized by all academian scientists [20], the phase-separating power is the decisive advantage of water.

5.2.3 AQUEOUS BIPHASIC CATALYSIS

5.2.3.1 Water as a Solvent

Aqueous biphasic catalysis is a special case of the two-phase processes of homogeneous catalysis. Despite the academic literature's provocative question "Why water?" [18a,18b], the advantages of water as the second phase and the "liquid support" are numerous. On the one hand, the search for the necessary solubility gap is much easier with water than with various organic-phase liquids (Figure 5.2). Additionally, water has many properties which predestine it as a ideal liquid support in homogeneous catalysis (see Table 5.1) [18c,18d].

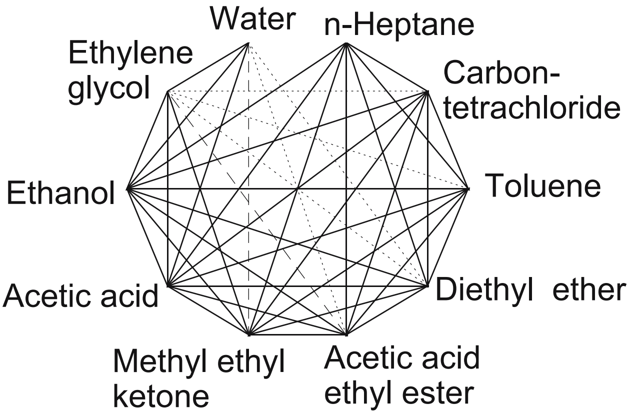


Figure 5.2. Miscibility diagram (and solubility gaps) of water and organic-phase liquids. Solvents not connected by a binding line in Figure 5.2 are immiscible; solvents of unlimited miscibility are connected by a solid line, those of limited miscibility by a dotted line [16]

Water has several anomalous features (e.g., density, being the only nontoxic and liquid "hydride" of the non-metals, melting point varying with pressure, etc.). Of direct importance for the aqueous biphasic process are the physiological (entries 2 and 4 of Table 5.1), economic (1,3,6,9), ecological/safety-related (2,3,4,9), process engineering (1,6,7,9,10,11,12), and chemical and physical properties (1,5,6,8,11,13) of water. The different properties interact and complement each other. Thus water, whose high

Hildebrand parameter and high polarity advantageously influence organic chemical reactions (such as hydroformylation), has sufficiently high polarity and density differences compared to organic (reaction) products to enable separation of the phases after the homogeneously catalyzed reaction is completed [17].

TABLE 5.1. Properties of Water as a Liquid Support [12j]

Entry	Property
1	Water is polar and easy to separate from non-polar solvents or products; its polarity may influence (i.e., improve) reactivity
2	Water is non-flammable and incombustible: A decisive advantage in terms of safety and occupational health
3	Water is ubiquitous and available with suitable quality
4	H_2O is odourless and colourless which makes contamination easily detectable
5	The physical and physico-chemical characteristics (e.g., hexagonal 2D surface structure, tetrahedral 3D molecular network) influence the mutual (in)solubility significantly; chaotropic compounds lower the order by H-bond breaking
6	The Hildebrand parameter as the unit of solubility of non-electrolytes in organic solvents/ reaction products is high
7	Water's density of 1 $g \cdot cm^{-3}$ provides a sufficient difference in density from those of most organic substances
8	The dielectric constant, DK, is very high; the refraction index n_D is low
9	The high thermal conductivity, the high specific heat capacity, and the high evaporation enthalpy of water make it suitable as solvent **and** heat removing fluid
10	Water has a high solubility for gases, especially CO_2
11	Water may form hydrates and solvates
12	Water is highly dispersable; it has a high tendency to support micelle and/or microemulsion formation. These tendencies may be enhanced by additives such as surfactants
13	Water has amphoteric behaviour in a Brønsted sense

Compared with this, the high solvent power for many compounds and gases, in some cases boosted by solvate or hydrate formation or by H-bonding, facilitates reactions in the two-phase system.

The chaotropic properties of many chemical compounds prevent the H_2O cage structures necessary for the formation of solvates and thus facilitate the transfer of nonpolar molecules between nonaqueous and aqueous phases. Water is incombustible and non-flammable, odorless and colorless, and is universally available in any quality: important prerequisites for the solvent of choice in catalytic processes. The DK and n_D can be important in particular reactions and are advantageously used for the analysis and control of substrates and products. The favorable thermal properties of water make it highly suitable for its simultaneous dual function as a mobile support *and* heat transfer fluid, a feature that is utilized in the RCH/RP process (see below).

Compared to the inexpensive and ubiquitous solvent and support, water, with its unique combination of properties, other alternative solvents may well remain unimportant. Others make the same comments using different words (Table 5.2).

TABLE 5.2. Pros and cons of water as a reaction fluid [21]

Advantages	Disadvantages
* Not inflammable	* Large heat of evaporation[1]
* Non-toxic	* Detection in case of leakage[2]
* No smell	* Low solubility of many nonpolar substrates
* Good separation with many organics	* Hard to collect in case of spills[3]
* Cheap	
* Unique fluid properties	* No incineration of bleed streams[4]
* Stabilization of certain organometalic complexes	* Decomposition of water-sensitive compounds[5]

[1] Possibly an advantage within the economics of the heat compound; [2] an advantage since contaminated water smells intensively; by the way the danger occuring in case of spills is severely overestimated. Additionally, it must be underlined that the danger in case of spills is identical with biphasic or with homophasic (conventional) operation; [3] True for all "solvents" and all organic liquids and no specific disadvantage of water; [4] Advantageous when containing the water-soluble catalyst - the system is self-extinguishing; [5] A matter of evaluation: nobody will recommend water in case of decomposition of water-sensitive compounds.

5.2.3.2 Aqueous-phase Catalysis as a Unit Operation

Operating homogeneously catalyzed conversions under aqueous-biphasic conditions is certainly a recently introduced technique but does not necessarily require newly designed apparatuses and exorbitant new sets of reaction conditions. To "do the solubility split" [19], the catalyst should only be soluble in one of the liquids (i.e., water), while the products (and occasionally the reactants) should be mainly soluble in the other - preferentially the phase of the reaction products itself. In this case, the separation of the catalyst from the products can simply be achieved by decantation (or temporarily by other means such as extraction, etc.). In all cases, the reactor design ought to maintain biphasic operation by proper mixing of the reactants. After decantation, the phase containing the catalyst can simply be recycled to the reactor, and the products can be separated and/or purified without the need to consider any stability or reactivity problems for the catalyst or the product. Basically, the flow sheet of an aqueous-biphasically and homogeneously catalyzed oxo process is as simple as shown in Figure 5.3 b) in comparison to the scheme of a classical hydroformylation unit Figre 5.3 a). The comparison gives an impression of the tremendous savings in investment made possible by aqueous biphasic operation.

An important feature of biphasic hydroformylation is the separability due to density differences. Because of the differences in density of the polar compound water (1.0 $g\cdot cm^{-1}$) and the hydrophobic oxo products (average 0.8), no problems occur. Additionally, the hydroformylation products are not sensitive to water. Another important question is to what extent water and the reactants are mixed. Therefore, the reactor in Figure 5.3 b), a continuously stirred tank reactor (CSTR) [22], normally contains usual installations to guarantee excellent mixing. For the lower alkenes with their significant water solubility (propene, butene) this is no problem. In these cases, the hydroformylation reaction takes place at the interfacial region [23].

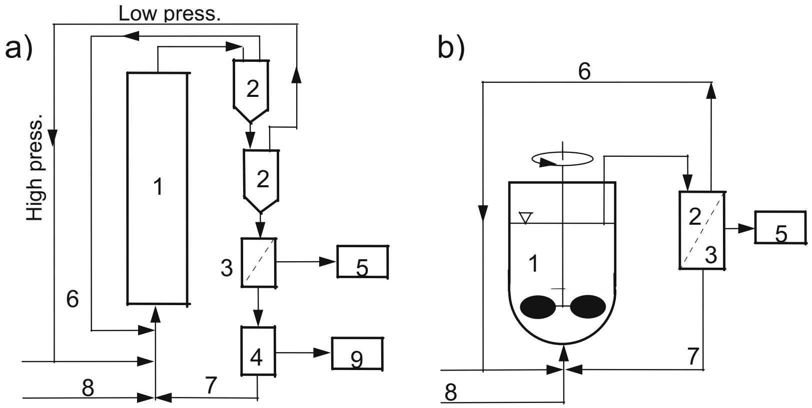


Figure 5.3. Basic flow-sheets of a) a conventional, homogeneously catalyzed process and b) an aqueous-biphasically, homogeneous catalytic process.1, Reactor; 2 Separator(s); 3, Catalyst separator; 4 , Make-up; 5, Further purification and processing;6, Gas recycle(s); 7, Catalyst recycle; 8, Reactant feed; 9, Withdrawal of high boilers

So far only propene and butene are hydroformylated commercially using the RCH/RP process. A reason which has been postulated for this is the decreasing solubility in water with increasing number of C atoms in both the starting alkene and the reaction products (Figure 5.4) and the associated mass-transfer problems in the relatively complicated gas-liquid-liquid, three-phase reaction.

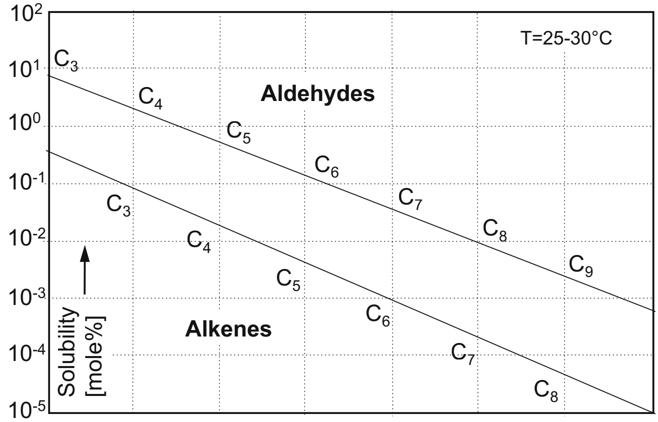


Figure 5.4. Solubility of alkenes and aldehydes in water (calculated. from [24])

Up to now only limited kinetic data and thus rate models (and even mechanistic details) of aqueous phase operation are available. Thus, in many cases only estimates and experimentally found data are at the disposal for reaction engineers' work (e.g.[25]). The state of the art of the hydroformylation of higher alkenes (>C_5) comprises additions of supplementary solvents/diluents or extraction fluids, surface-active agents (detergents), intensity and mode of stirring ([22b], power of agitation (cf. Figure 5.5) operation in micelles [51b,51c,52d,54,56h,58], thermo-regulated systems, etc. [26a,27,54a]. Up to now, it has to be noted that many measures may improve conversion and yield but not sufficiently to cover the additional expenses. The same is true for new and exotic ligands, although this measure would be the ideal solution of the problem when no additional solvents/extracting agents and their costly recycling are permitted [27,28,41e].

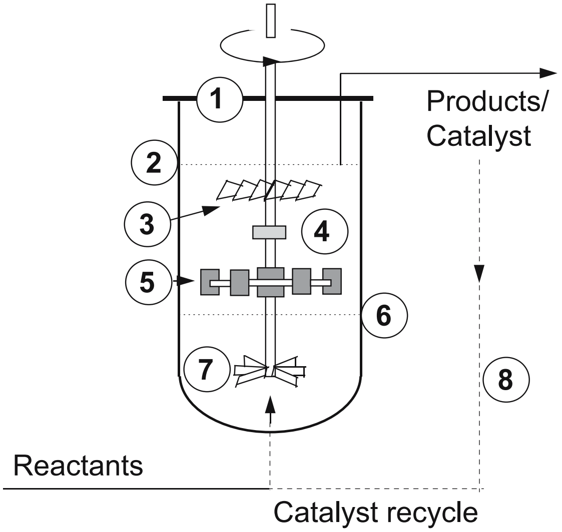


Figure 5.5. Example of a highly sophisticated CTSR [25a; other examples see 25c].
1, CTSR; 2, Interphase gas/liquid; 3, Self-rotating floating baffle; 4, Annulus for position limiting; 5, Rushton disk turbine; 6, Interphase liquid/liquid; 7, Pitched blade turbine upward (mixer/stirrer); 8, Aqueous-phase catalyst recycle

Quite new ideas for the reactor design of aqueous multiphase fluid/fluid reactions have been reported by researchers from Oxeno. In packed tubular reactors and under unconventional reaction conditions they observed very high space-time yields which increased the rate compared with conventional operation by a factor of 10 due to a combination of mass transfer area and kinetics [29]. Thus the old question of aqueous-biphase hydroformylation "Where does the reaction takes place?" - i.e., at the interphase or the bulk of the liquid phase [23,56h] - is again questionable, at least under the conditions (packed tubular reactors, other hydrodynamic conditions, in mini plants, and in the unusual,and costly presence of ethylene glycol) and not in harsh industrial operation. The considerable reduction of the laminar boundary layer in highly loaded packed tubular reactors increases the mass transfer coefficients, thus Oxeno claim the successful hydroformylation of 1-octene [25a,26,29c,49a,49e,58d,58f]. The search for a new reactor design may also include operation in microreactors [59].

The hydroformylation reaction is highly exothermic, which makes temperature control and the use of the reaction heat potentially productive and profitable (e.g, steam generation). The standard installation of Ruhrchemie/Rhône-Poulenc's aqueous-phase processes is heat recovery by heat exchangers done in a way that the reboiler of the distillation column for work-up of the oxo products is a falling film evaporator incorporated in the oxo reactor itself [2,12]. The heat of the oxo reaction is thus recovered as the reboiler heat source. This is a great advantage over the classical (non-aqueous) hydroformylation, which simply discard parts of the oxo reaction heat. The RCH/RP process is a net steam exporter. In the case of the above mentioned Oxeno developments the large catalyst flow is said to serve as a heat transfer medium itself thus making the process nearly isothermal [29g].

There are many proposals for addressing the problem of proper phase separation (and reducing the leaching of the catalyst) of aqueous-phase processes when partial mixing of the two phases occurs (or is necessary because of reaction engineering reasons). In this case the simple, rapid, and perfect phase separation without any leaching as in the RCH/RP process (the losses are of the order of 1 ppb [12e]) needs considerable effort; for example extraction with an appropriate additional solvent which is either added after the catalytic conversion or is already present during reaction [30]. In all cases, the reaction loop has to be completed by additional stages such as extraction devices and separation, recovery, and recycle of the extraction fluid. Two examples are given in Figure 5.6; they should be compared with the simple flowsheet of RCH/RP's oxo process (cf. Section 5.2.4.1) to recognize the expense which ia associateded with those solutions [21,30a,31].

Theoretically, it is possible to control chemical reactions by the different solubilities of the reactants or of special intermediates (e.g., according to their nucleophilicity) in different solvents or various catalyst fluids. The principle has been proven but is not yet used for special applications in industry [32].

The search for new ligands (which in a restricted sense is no unit operation) which would combine various properties such as modification of the central atoms of the complex catalyst, creating modifying and surfactant properties, offering chiral properties, etc. is still going on. There are some results but no ligand better than TPPTS has been developed so far ("better" includes simultaneously water-solubility, activity, selectivity, and price [17h,33]). On the contrary, all proposed new ligands are more expensive and shift the level of their costs close to those of the precious metals such as rhodium, palladium, or platinum. The search for "novel catalysts" for multiphase reactions must be done as an integrated task in close relationship with reactor design [34,48] - colloidal suspensions included [35a].

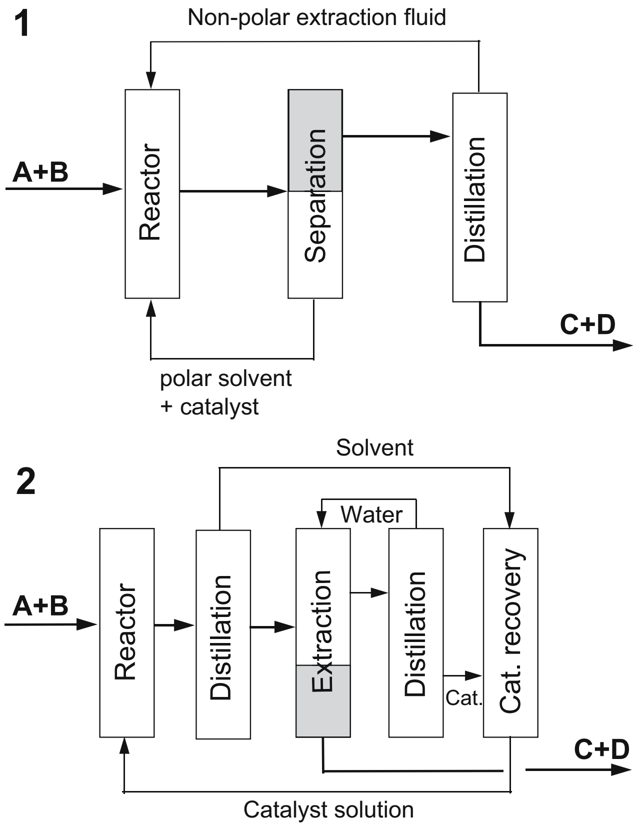
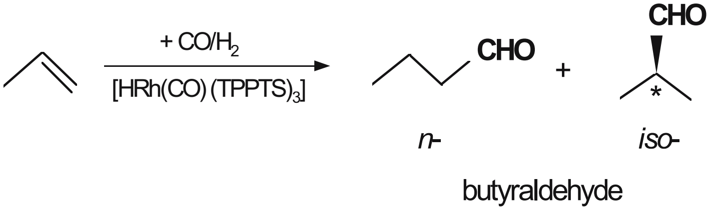


Figure 5.6. Process flowsheets of biphasic reaction A+B → C+D and extraction
1, Simultaneous reaction and extraction within the reactor; 2, Separate reaction and catalyst extraction

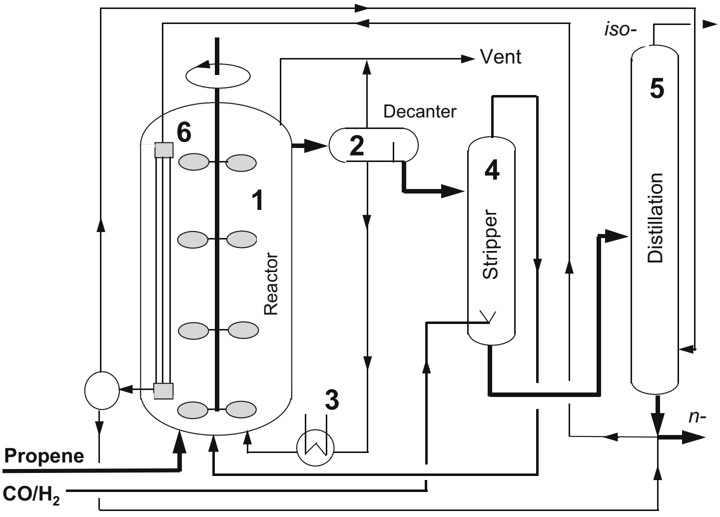
5.2.4 EXAMPLES OF AQUEOUS BIPHASIC CATALYSIS

5.2.4.1 Hydroformylation (Ruhrchemie/Rhône-Poulenc[RCH/RP] process)

The RCH/RP process converts propylene to *n*- and *iso*-butyraldehydes (or butenes to valeraldehydes) in the presence [HRh(CO)(TPPTS)] (with TPPTS = tris[sodium-*m*-sulfonatophenyl]phosphine as water soluble ligand) according to Equation 5.1.



Equation 5.1. Hydroformylation of propylene in the RCH/RP



process

Figure 5.7. Process design for the Ruhrchemie/Rhône-Poulenc oxo process

The process scheme is shown in Figure 5.7. The reactor **1** is stirred and supplied with reactants and the catalyst. The catalyst [HRh(CO)(TPPTS)$_3$] is prepared by mixing a Rh salt and aqueous TPPTS solution (which may partly be recycled; see Section 5.3) in a simple "preforming" step (much simpler than the preforming in other oxo processes [35b-e]). Temperature is controlled *via* the heat recovery system with the reaction heat from the exothermic hydroformylation being used in the reboiler of the distillation column **5**. The reboiler is the internal cooler **6** of the reactor. The cooling medium is the reaction product, *n*-butanal. From the reactor, the reaction products pass through a downstream phase separator (decanter **2)** and stripping column **4**. The major part of the catalyst solution remains in the reactor; only a smaller part is separated in the decanter and returns directly to the reactor. In the phase separator, the crude aldehyde formed is freed of gases and further separated into mutually insoluble phases. This decanter ensures the essentially spontaneous phase separation. The reaction heat that is retained in the catalyst solution is recovered by a heat exchanger **3**, and the catalyst solution, supplemented by an amount of water equivalent to that carried off with the *iso*-butanal (since the *n*-aldehyde is practically anhydrous), is recirculated to the reactor. The crude aldehyde is freed of any unreacted alkene in the stripper **4** by means of syngas flowing countercurrently. It is essential that this stripping is accomplished in the absence of the oxo catalyst and, therefore, no selectivity- and/or yield-reducing secondary reactions of the crude aldehyde occur. Typical for the RCH/RP process are high yields and selectivities (99% butanals with an *n/i* ratio of up to 98:2; selectivity toward C_4 products: >99.5%) under mild conditions (120°C at 5 Mpa) [2,12].

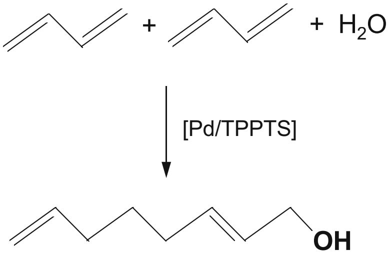
The process is highly effective and, as the process data illustrate, represents an economic advantage as well (cf. Section 5.3.3). In ecological terms, the RCH/RP process also provides a considerable improvement (Section 5.3.4) over conventional methodologies.

Recovery and recycle of the catalyst are described in Section 5.3.

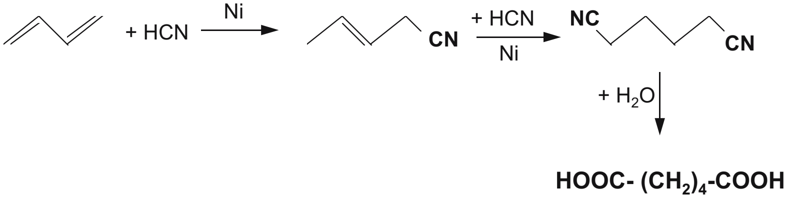
5.2.4.2 Other Industrially Used Aqueous-biphasic Processes

Hydroformylation comprises the state-of-the-art of bulk chemical production via aqueous-biphasic processes. At present five plants produce worldwide some 800,000 tpy of oxo products [1]. Another bulk process - the hydrodimerization of butadiene and water, a variant of telomerization – is run by Kururay with a capacity of 5000 tpy (Equation 5.2 [31b,36]).

The reaction product of telomerization is 2,7-octadiene-1-ol. In subsequent steps this dienol may be converted to 1-octanol by hydrogenation or hydrogenated/dehydrogenated to 1-octenal. This unsaturated aldehyde again can be hydroformylated to yield nonadialdehyde and then hydrogenated to nonadiol.

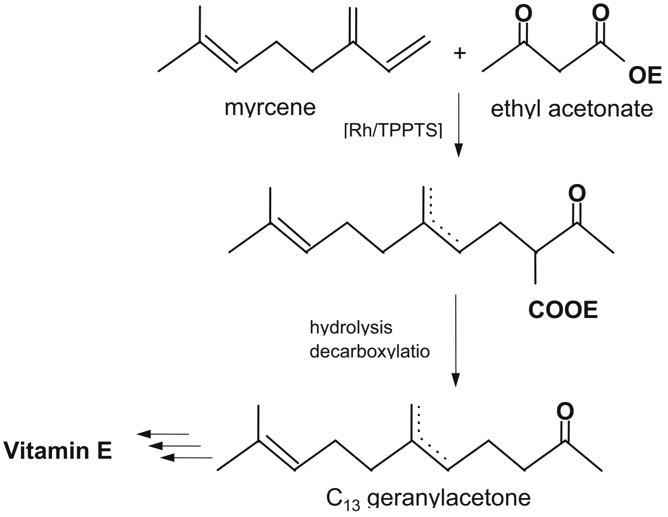


Equation 5.2. Hydrodimerization of butadiene and water

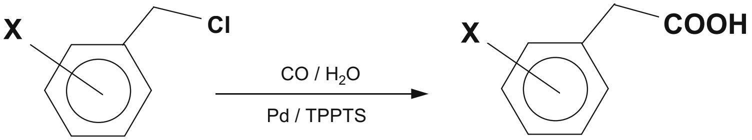


Equation 5.3. Hydrocyanation of butadiene

The remarkably versatile C_1 building block HCN may be used in the aqueous two-phased hydrocyanation, too (Equation 5.3; [37]). Also, some fine chemicals such as intermediates for vitamins, phenyl acetic acid, etc. are manufactured on an industrial scale using this technology (Equations 5.4 and 5.5; [12e,31b,38]).



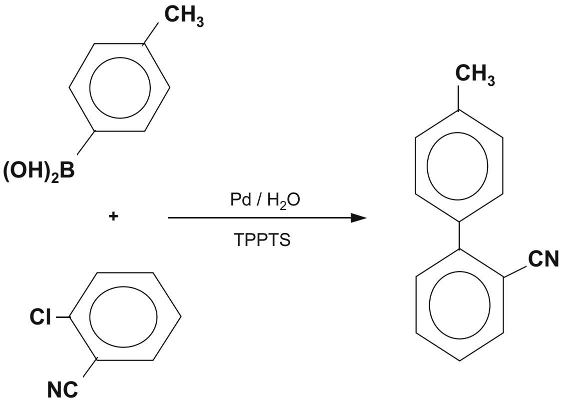
Equation 5.4. Manufacture of vitamin E precursors



Equation 5.5. Manufacture of phenyl acetic acid

Today, the Suzuki cross coupling of aryl halides and arylboronic acids is also carried out in aqueous-biphasic operation starting from chlorinated derivatives instead of their more costly bromo or iodo equivalents (Equation 5.6, [39]).

The commercially applied biphasic processes are compiled in Table 5.3. Tests to produce economically interesting profens or other analgesics by two-phase hydrocarboxylation [40] remain industrially unsuccessful.



Equation 5.6. Suzuki coupling to yield aromatic biphenyls

TABLE 5.3. Commercial biphasic processes

Process/Catalyst	Products	Capacity / [tpy]
Shell SHOP/ Ni-P,O ligand	∟-Olefins and internal olefins	900 000
Ruhrchemie-RP (now Celanese)/Rh-TPPTS	*n*-Butanal	800 000
Kururay Co Ltd / Pd-TPPMS	*n*-Octanol, nonadiol	5 000
Clariant AG/Pd-TPPTS	Substituted biphenyls	<1 000
Rhodia (former Rhône-Poulenc)/Rh-TPPTS	Vitamin precursors	*

* Exact production figures not known

5.2.4.3 Short Overview of Other Reactions

A multitude of other reactions are compiled in (Table 5.4,[12m]). A proper choice of ligands and reaction conditions will make many other reactions available *via* aqueous-biphasic operation.

TABLE 5.4. Recently described examples for aqueous-biphasically operated reactions

Type of reaction/Catalytic metal involved	Refs.
Aldolization/Sc,In,Cu,Ln	[41a-d]
Alkylation/K,Pd, organocatalysts	[41e-g]
Allylation/Ru,Pd	[41d,h]
Alternate copolymerisation of CO-ethylene/Pd	[42]
Carbonylation	[43]
Claisen rearrangement/Al	[41i]
Diels-Alder reaction/Si,Cu	[41d,j,k]
Epoxidation/W,Re,Mn	[41l-p]
Friedel-Crafts reaction/Sc	[41q]
Heck reaction/Pd	[41r-v]
Hydrogenation/Ru,Rh,Pd,Ir,Pt	[5b],[41w-ii]
Hydrosilylation/Pt	[41jj]
Mannich reaction/Zn	[41d,vv]
Metathesis/Ru	[44]
Michael reaction/Ln	[41d,45]
Oxidation/Ru,Pd,Os,W,Mn	[46]
Polymerization/Cu,Ti,Ni,Pd,Rh,Co	[41kk-pp]
Reformatsky reaction/Zn	[57]
Sharpless dihydroxylation/Os	[41qq-ss]
Ullmann reaction/Pd,Rh,Ni	[41tt,uu]

5.2.5 OTHER PROPOSALS FOR WATER - BIPHASIC SYSTEMS

With the RCH/RP process, it is possible to hydroformylate propene up to pentenes with satisfying space time yields. On the other hand, heavier aldehydes such as C_{10} (*iso*-decanal) or higher from the hydroformylation of nonene(s), decenes, etc. can not be separated from the oxo catalysts by conventional means such as distillation due to thermal instability at the required temperatures and thus especially needs the careful aqueous-biphasic separation technique. There are numerous attempts to overcome the problem of low reactivity of higher alkenes which is due to low miscibility of the alkenes in water [26,27b, 50a,58d]. These proposals can briefly be summarized as:

(1) The use of amphiphilic water-soluble ligands which influence the alkene solubility or increase the catalyst concentration at the interface area of the phases [48,49];

(2) The use of co-solvents such as alcohols or detergents to improve interface exchange of the feedstock and the reaction products [11,21,26b,28h,50,51c,56g, 58i];

(3) Substitution of the water-biphasic procedure by supported aqueous phase catalysis (SAPC, see below) [39,10,26b,64];

(4) The separation of the reaction products from the catalyst solution by membrane techniques (Figure 5.8, [52]);

(5) In continuation of Bayer/Schurig's work from 1975/1976 [28a,b], the use of

polymeric water-soluble supports as "smart ligands" (see also the work of Bergbreiter and Mecking [48,53,56m,60,61]);

(6) The addition of surfactants to improve the formation of micelles, microemulsions, etc. [26e, 51,58];

(7) The introduction of specially developed ligands [11,26h,27b,28,33,49a,54a,60,61];

(8) Measures for the controlled switch of the catalyst system from the two-phase system (suitable for the *separation* of products from the catalyst) to a monophasic system which supports the *reaction* itself (Figure 5.9, [27,54]).

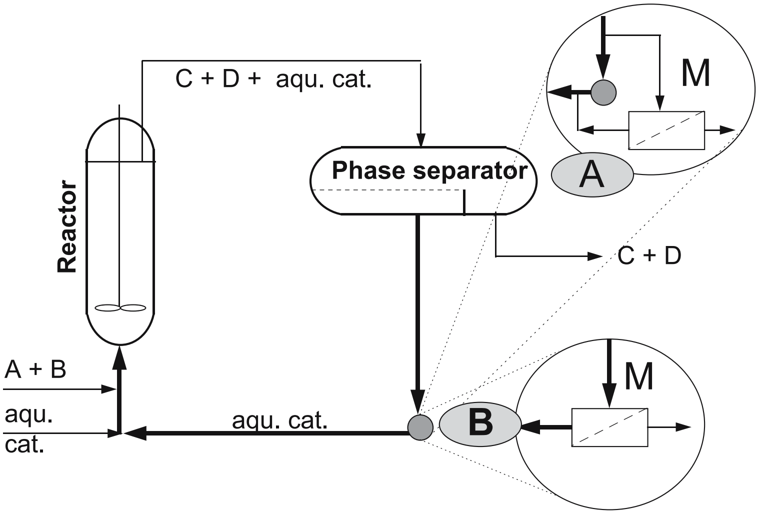


Figure 5.8. Membrane steps as a constituent part of aqueous-biphasic hydroformylation A+B->C+D

The method outlined in 8) above may be applied by the use of thermo-regulating or -separating systems. These take advantage of a temperature-dependent "cloud-point" associated with P-bound poly(alkylene glycol ether) as ligands, i.e., oxo catalysts which combine water solubility together with phase separating properties depending upon temperature. Developments of Fell and Jin based on ethoxylated phosphines give the first pointers to such a procedure.

As shown in Figure 5.9, at the cloud point the ligand (and thus the catalyst complex) loses its hydration shell, just as in the case of other compounds of this type, causing the two-phase reaction mixture, normally obtained when (higher) alkene is added to the catalyst solution, to merge into a single phase, thereby initiating a rapid conversion that is no longer impeded by mass transport problems. Subsequent lowering of the temperature causes the hydration shell to be reversibly restored, inducing the catalyst complex solution once again to separate out as an independent phase, this time from the reaction products, viz. the desired higher aldehydes. The disadvantage of this higher cost technique is the resulting lower linear/branched (*n/iso*) ratio. Jin refined this technique to a highly sophisticated method, including transitions to other variants (e.g., water-soluble polymers, pH-dependent operation, etc.)[55].

The membrane process, incorporated into the catalyst recycle either in the main stream or in the side stream, may also separate the reaction products from the remaining catalyst (Figure 5.8).

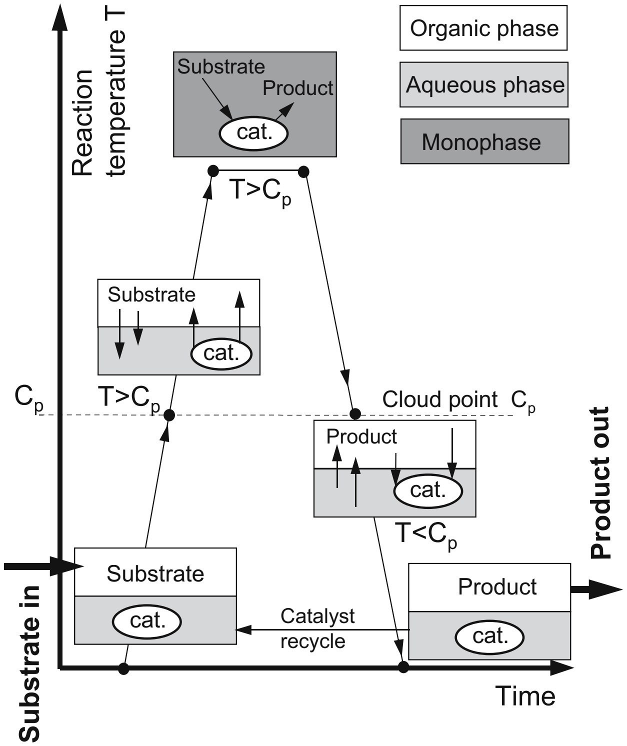


Figure 5.9. Phase change of thermoregulating ligands

As an alternative to the heterogenization of homogenous catalysis, there are some proposals to realize a solid catalyst with an immobilized species in aqueous-organic media. This concept, a continuation of the "**s**upported (or solid)-**l**iquid **p**hase **c**atalysis" (SLPC) has mainly published and highlighted by Scholten et. al [62], consists of a thin film of catalytic material that resides on a high-surface-area support such as controlled-pore glass, silica, zeolites, etc. Thus this concept of a "**s**upported **a**queos-**p**hase **c**atalysis" (SAPC) contains both a hydrophilic liquid and a hydrophilic organometallic catalytic complex on a solid support as shown in Figure 5.10 [63].

Reactions take place at the water film - organic phase interface and are catalyzed by the phase-immobilized complex catalyst which is usually [$HRh(CO)(TPPTS)_3$]. Other hydrophilic solvents, e.g., glycols or suitable liquids, adjusted to the requirements of the respective reaction, can be used instead of water for the formation of the immobilized liquid layer. As in all SPC variants, the catalytic process proceeds homogeneously in the supported film (SLPC) or at the interface (SAPC), thus avoiding the problem of the separation of the reaction products from the catalyst. It is believed that the hydrophilicity of the ligands and the support creates interaction energies suffient to maintain the immobilization.

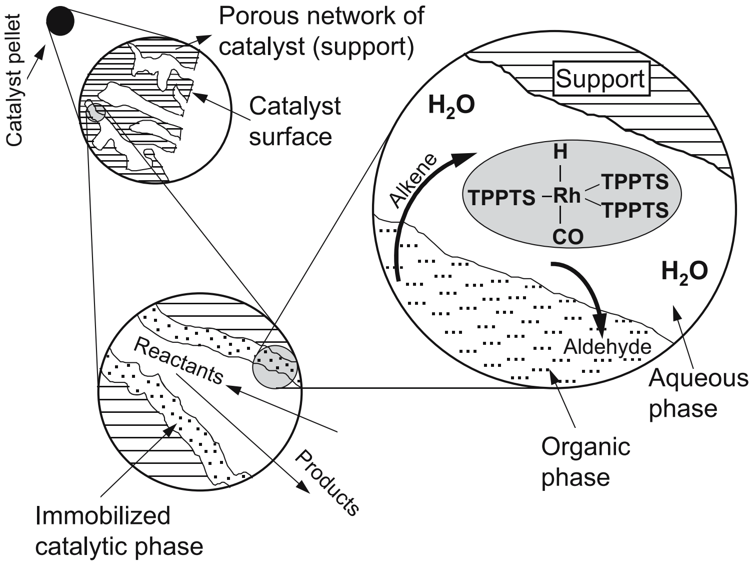


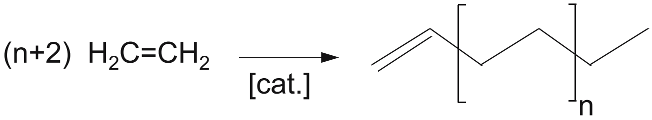
Figure 5.10. Schematic illustration of a supported aqueous-phase catalytic system (SAPC)

So far, various reactions have successfully been accomplished with SAPC such as hydrogenation (including asymmetric hydrogenation), hydroformylation, alkylation, Wacker oxidation, etc.[64]. However, no continous long-term runs nor commercial tests have been carried out. As a process requiring relatively complex processing, the SAPC technique is most likely to find applications in the manufacture of sophisticated and high-priced products (e.g., pharmaceuticals or chiral intermediates). It is likely that rare metals and unusual and specially designed ligands are needed to fully meet the demands of those processes and products. The lifetime of SAPS catalysts under continuous operation and industrial load is as yet unknown.

Advantageously, SAPC as a technique with immobilized catalysts does not need devices for catalyst separation and recycling, since the reactions can in principle be carried out using standard flow reactors commonly used in heterogeneous catalysis. On the other hand, the presumed processes for the work-up of the constituents of the catalyst, the ligand (and - may be - the support) will be demanding and expensive, too.

5.2.6 INTERLUDE - BIPHASIC SYSTEMS: ORGANIC-ORGANIC

The first biphasic process which has been commercialized uses Ziegler's *Aufbaureaktion* ("growing reaction") of ethene yielding oligomeric alkenes (Equation 5.7, [65]).



Equation 5.7. "Aufbaureaktion" according to Ziegler

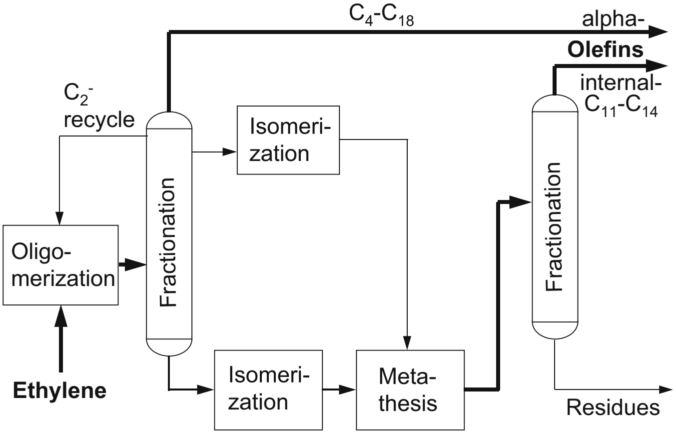


Figure 5.11. Scheme of Shell's SHOP process

Based on this reaction, commercial processes have been developed by different companies such as Chevron, Ethyl, Mitsubishi, Idemitsu, and Shell [66]. The processes use Ziegler-type catalysts (Chevron, Ethyl, Mitsubishi), Zr compounds (Idemitsu), or specially developed, P,O bidentate Ni complexes (Shell). Shell runs the largest capacities with approximately 900,000 tpy of "SHOP" (**S**hell **H**igher **O**lefin **P**rocess) products, consisting of valuable terminal alkenes and of special internal alkenes (see Table 5.3). Combining the oligomerization (Aufbaureaktion) with subsequently operated isomerization and metathesis stages, the overall product range of SHOP plants are linear terminal alkenes C_4-C_{18} *and* internal alkenes C_{11}-C_{14} [67]. The biphasic operation of the process is a consequence of the fact that the chelating catalyst is dissolved in polar 1,4-butandiol and the nonpolar products, the alkenes, are insoluble in the diol. Thus, the catalyst-containing solution can easily be separated from the insoluble products in a decanter. In a series of distillation towers, the various terminal alkene cuts (preferred are C_4-C_{18}) are isolated. The lower and the C_{18+} fractions are combined to be isomerized to internal linear alkenes by catalysts such as Na/K on alumina or MgO in the liquid phase. The resulting linear alkenes are subsequently subject to a metathesis reaction which combines the lower and the higher internal alkenes to give a mixture of alkenes with odd and even carbon chain lengths. The process is depicted in Figure 5.11. The catalytic cycle is shown with Figure 5.12.

Only a small amount of information has been released by Shell about the recovery and recycle of the special P,O bound Ni catalyst. Obviously, the overall operation of the SHOP plants is economical but one has to keep in mind that the non-homogeneously catalyzed parts of Shell's integrated system of processes use inexpensive, heterogeneous catalysts. It is to be expected that a large part of these catalysts can be disposed off without any recycling – neither of the metal content nor of the supports.

According to Figure 5.2 and to chemical experience, the selection of other pairs of non-miscible organic liquids is difficult and yields mainly unusual (not to say, exotic) solvents or pairs of solvents [68] such as fluorous liquids (cf. Chapter 6). This is the reason why no other organic-organic biphasic catalytic processes have yet been commercialised.

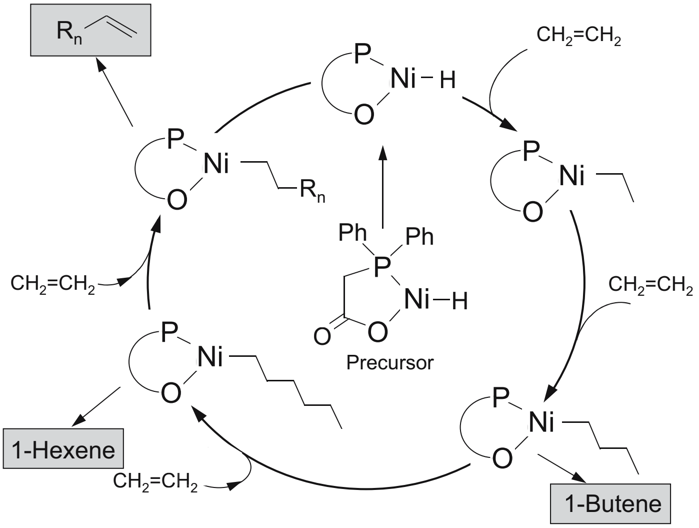


Figure 5.12. Postulated mechanism for ethylene oligomerization according to Shell's SHOP process with a P,O-stabilized catalyst

5.3 Recycle and Recovery of Aqueous Catalysts

Recovery and recycle of homogeneous catalysts are said to be the focal point of any new generation of, for example, hydroformylation technologies. Additionally, the costs of the new process are determined by the losses, which may be a particular problem when using high-price rare metal catalysts such as rhodium or palladium. Obviously this is true because a new mode of recyling charaterizes a new process. But on the other hand, metal losses (and supplementary ligand costs) are only a (minor) part of the overall cost as will be demonstrated in Section 5.3.3.

In recent years, the evaluation of environmentally benign (so-called "green" processes) has been a focal point of oxo developments, according to the definitions and targets of the

OECD Workshop on Sustainable Chemistry (1998) [8c]:

> "Within the broad framework of sustainable development, we should strive to maximize resource efficiency through activities such as energy and non-renewable resource conservation, risk minimization, pollution prevention, minimization of waste at all stages of a product life-cycle, and the development of products that are durable and can be re-used and recycled. Sustainable chemistry strives to accomplish these ends through the design, manufacture and use of efficient and effective, more environmentally benign chemical products and processes".

In this respect, risk minimization and life cycle assessments play a major role.

Figure 5.13. Large-scale oxo plant using the water-soluble Ruhrchemie/Rhône-Poulenc catalyst [$HRh(CO)(TPPTS)_3$]. Note the horizontal decanter in front of the reactor

5.3.1 RECYCLING

As mentioned in Section 5.2.4.1, the part of the aqueous catalyst solution which leaves the oxo reactor accompanying (but not dissolved in) the reaction products passes through a phase separator (decanter **2** in Figure 5.7) which is a characteristic part of the plant shown in Figure 5.13. In this decanter, which ensures essentially spontaneous phase separation, the crude aldehyde formed by hydroformylation according to Equation 5.1 is freed of gases and separated into mutually insoluble phases. The catalyst solution, supplemented by an amount of water equivalent to the water content of the crude aldehyde, is recirculated to the reactor. During its active life, the Rh catalyst is mainly situated in the oxo reactor, it is not moved in bulk and no aliquots are withdrawn as in other processes. For this reason, rhodium losses are low - in the range of parts-per-billion (ppb) - and thus the background for the high economy (see Section 5.3.3) [12e,12l]. Like every technically rused and thus "real" catalyst, the complex [HRh(CO)(TPPTS)$_3$] and the excess ligand TPPTS undergo a degree of decomposition that determines the catalyst's lifetime as measured in years. The catalyst deactivation mechanism has been clarified in detail (Figures 5.14 and 5.15; Equation 5.8) [69].

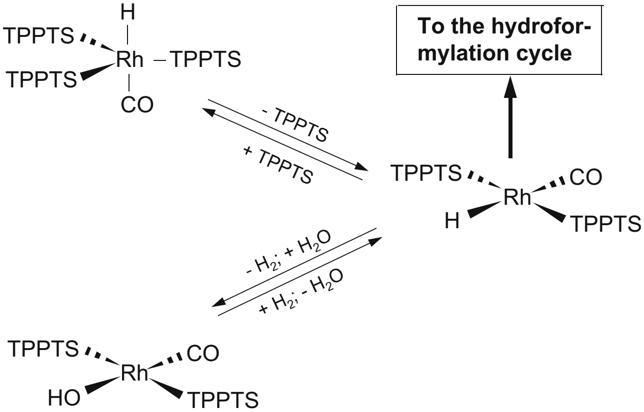
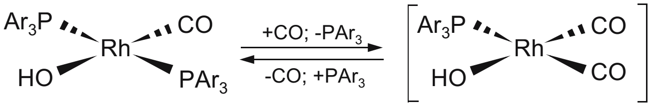


Figure 5.14. From the precatalyst to the oxo-active species

The compound [HRh(CO)(TPPTS)$_3$] is a "precatalyst" and dissociates to the 16e species [HRh(CO)(TPPTS)$_2$]. This oxo-active complex initiates the hydroformylation cycle. Under oxo conditions (presence of CO/H$_2$, H$_2$O, and a surplus of TPPTS) the hydroxo complex [(HO)Rh(CO)(TPPTS)$_2$] may be formed and again reversibly converted to [HRh(CO)(TPPTS)$_3$] (equilibrium lies almost completely towards the hydride). However, higher carbon monoxide partial pressures may cause the displacement of TPPTS by CO according to Equation 5.8.



Equation 5.8. The Influence of CO

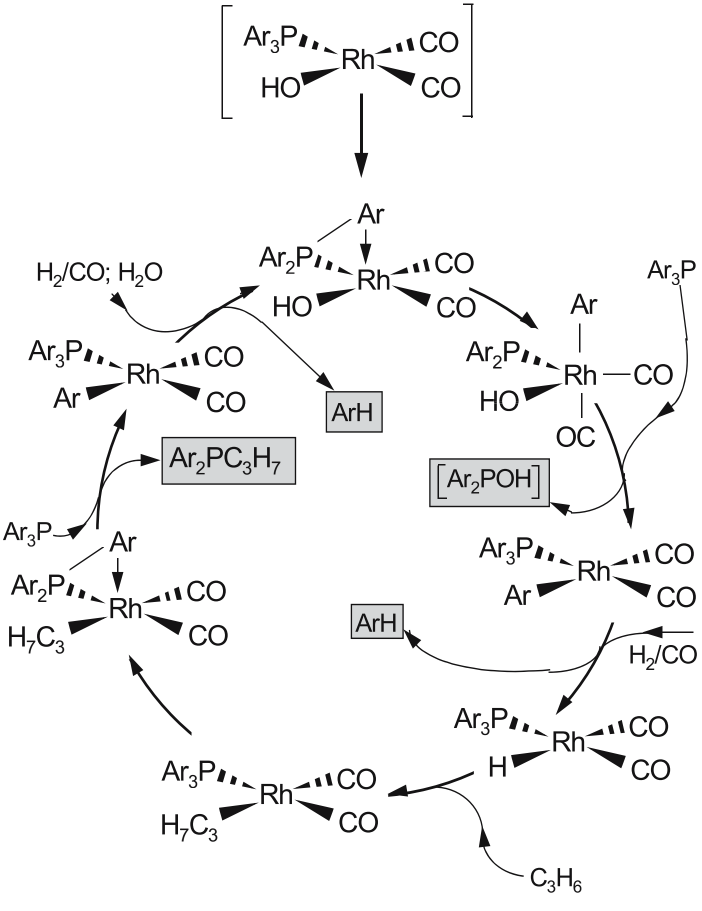


Figure 5.15. Deactivation Mechanism of Rh^1-TPPTS Catalyst (Ar = 3-$C_6H_4SO_3Na$)

The hydroxo complex [(HO)Rh$(CO)_2$TPPTS] starts the deactivation cycle as shown in Figure 5.15 [69] [70a,b]. The single steps will not be discussed here. Other decomposition products such as the reductively eliminated bis(*meta*-sulfophenyl)phosphinous acid Ar_2POH (cf. Figure 5.15) and the phosphine oxides $Ar_2P(OH)(=O)$ and $Ar_2P(=O)(CH[OH]C_3H_7)$ (Ar = 3-$C_6H_4SO_3Na$) have been identified. According to Figure 5.16, the intermittent addition of excess ligands extends the catalyst's lifetime in a saw-tooth curve. This addition of ligand compensates for the system-immanent formation of deactivating substances which are brought into the system by the feedstocks. Most of the gaseous poisons are removed with the heavy ends of the stripper **4** in Figure 5.7. Filters, guard beds, or special precautions to avoid larger sulfur or oxygen inputs and their concentrations (as in other processes, [70c,d]) are not necessary. Additionally, other activity-lowering oxo poisons may be separated with the organic product phase of the decanter and are thus continuously removed at the very point of their formation from the system: any accumulation of activity-decreasing poisons in the catalyst solution is prevented. It might be worth mentioning that the Ruhrchemie plant has been supplied over longer periods with syngas manufactured from coal by the TCGP (Texaco coal gasification process) [12e].

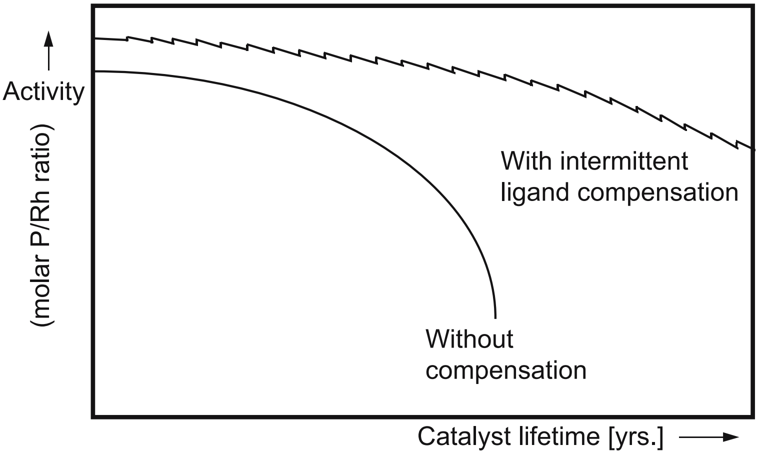


Figure 5.16. The effect of excess ligand on the catalyst's lifetime

Catalyst deactivation includes (among other reactions) the formation of inactive Rh species, ligand decomposition, or P-C cleavage by direct oxidative insertion of the rhodium metal for formation of PDSPP (propyldi[*m*-sulfophenyl]phosphine) acting as strong electron donor reducing the amount of active Rh catalyst. It turned out to be beneficial to control the P^{III}/Rh ratio and the CO partial pressure very carefully.

After years of use catalyst solutions typically contain 20 $mg \cdot L^{-1}$ iron and 0.7 $mg \cdot L^{-1}$ of nickel, thus showing no corrosivity. The Rh content of crude aldehyde is in the ppb range; this corresponds to losses of less than 10^{-9} g kg^{-1} *n*-butanal, totalling some kg rhodium over a twenty-year period and a production of approximately 5 million metric tons of *n*-butanal.

5.3.2 RECOVERY

Eventually, the spent catalyst solution has to leave the oxo loop for work-up. The Ruhrchemie works of Celanese AG in Oberhausen (Germany) operate several rhodium-based oxo processes: besides the well-known Ruhrchemie/Rhône-Poulenc process (RCH/RP, the described low pressure oxo process with TPPTS-modified Rh catalyst), there are the "Ruhrchemie process" with an unmodified Rh catalyst at high pressure (comparable to the late ICI process [76]; this variant is for the benefit of a high *iso/n* ratio in cases where this strange ratio is required), and a high pressure technique using ligand-modified rhodium catalysts. The various processes deliver aldehydes from C_4 up to C_{10} and additionally fine chemical aldehydes, starting from bicyclic alkenes, functionalized alkenes, etc.

The compound of the distinct three oxo processes, all rhodium-based, enables a highly efficient recovery system to be achieved. Figure 5.17 describes the TPPTS manufacture and its use for the preparation of the rhodium catalyst, using either freshly introduced Rh acetate or recycled Rh 2-ethylhexanoate. The recycle technique of the RCH/RP process and its performance is depicted earlier. Spent Rh-TPPTS solutions are worked-up (see Figures 5.18 and 5.19), the resulting TPPTS returns to the RCH/RP process. The rhodium portion passes also a work-up stage and is reformulated as Rh 2-ethylhexanoate. This Rh salt may serve all various oxo processes of the oxo loop and will compensate for possible Rh losses as mentioned earlier.

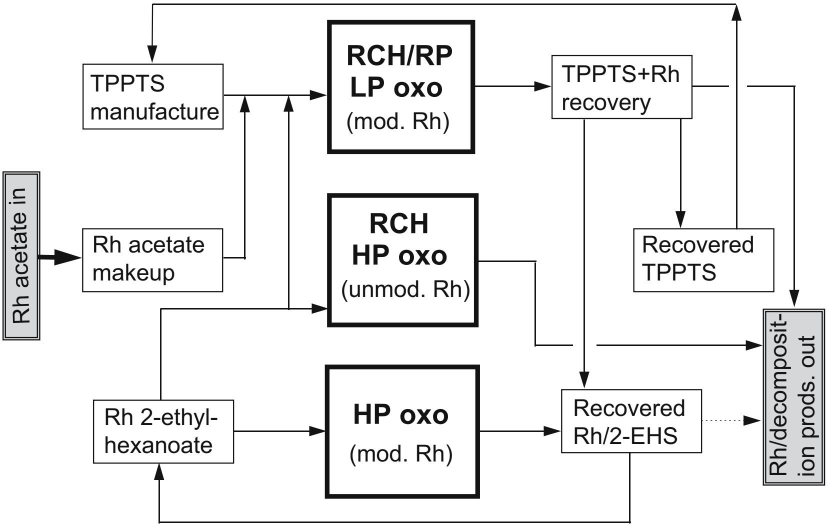


Figure 5.17. Compound of various oxo processes at the Ruhchemie works

According to Figure 5.17, the only external input is rhodium(III)acetate besides TPPTS from its own manufacturing unit. Rhodium compounds which are too difficult to be worked-up (catalyst poisons, metal aggregates, clusters, etc.) together with decomposition products, residues, etc. leave the recovery steps to be processed by external precious-metals refiners. These have their own expertise and trade (and production) secrets as far as the technical know-how is concerned. Depending upon the status and the "quality" of these fractions (if necessary, following a referee's check, various samplings, etc.), the credit for the rhodium is >95% of its content [80].

The work-up scheme as described in Figure 5.17 takes into account the decomposition rate of TPPTS (and thus the ligand losses), the different volume of the consumed Rh streams and their residual activity, and – last but not least – the Rh losses. Advantageously, these losses may be minimized by proper use of the different sources from the various oxo stages. Most steps are covered by patents [77], and the same is true for similar processes developed by competitors [78].

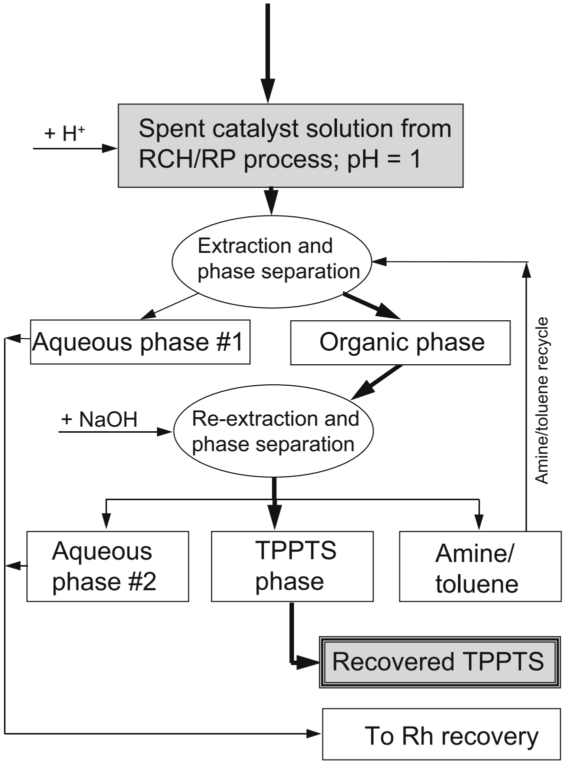


Figure 5.18. TPPTS recovery

The economics of the TPPTS recovery (cf. Figure 5.18) depend on the costs and its relation to the Rh price. Since the procedure of *work-up* is identical with some steps within the *manufacture* of fresh TPPTS [78], existing devices of the TPPTS manufacture unit can be used advantageously. According to Figure 5.18, the work-up of rhodium follows an acidification of the spent catalyst and extraction with a mixture of a tertiary alkylamine and toluene. The resulting two phases (aqueous phase #1, containing rhodium, and the organic phase with amine/toluene and TPPTS) are further processed. The organic phase is reextracted with aqueous NaOH (which purifies existent Rh(III) compounds and TPPTS), yielding three pH-dependent fractions: An aqueous solution #2 of rhodium compounds, the TPPTS fraction (TPPTS as sodium salt, ready for recycle and re-use; recovery rate: approximately 80%), and the amine/toluene phase which is recycled either to the manufacture of fresh TPPTS or to the TPPTS recovery. Both rhodium-containing fractions of the TPPTS recovery (#1 and #2) are subject to the rhodium recovery as depicted in Figure 5.19.

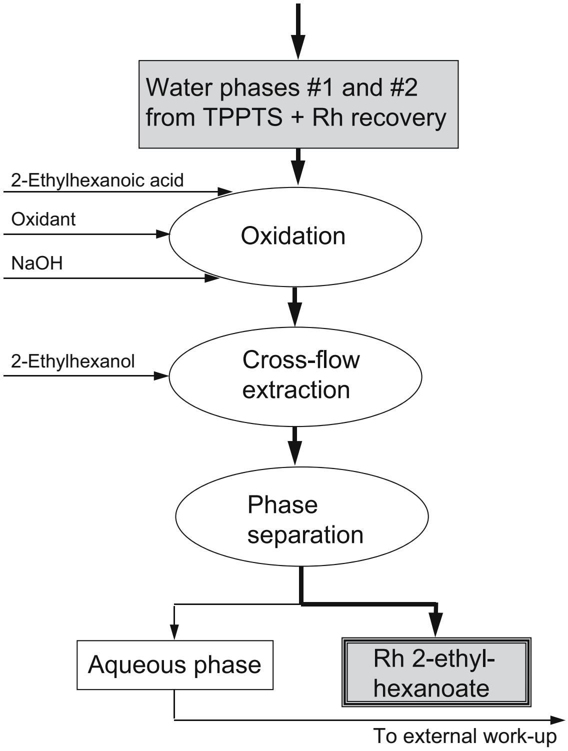


Figure 5.19. Rhodium recovery

These Rh-containing phases are mixed with NaOH and 2-ethylhexanoic acid and subsequently oxidized with air, H_2O_2, or other oxidizing agents. The Rh compounds in phase #1 and #2 are thus converted to Rh 2-ethylhexanoate and are extracted in a cross-flow manner by means of 2-ethylhexanol. The recovery rate of rhodium is 97-98%. The residual water phase ends up in the fraction for external work-up as described above.

It may be expected that higher-valued ligands (which might be used for the conversion of long-chain alkenes) or even co-ligands, co-solvents, modifiers, surfactant promoters,etc. can be processed the same way. There are already small-scale processes employing aqueous-phase catalysis which use “exotic” ligands such as di-, tri-, or multidentate phosphines where the situation demands drastic measures including a high-sophisticated management for rhodium and ligand recycle and recovery (e.g., [73]).

The "real" oxo precatalyst $[HRh(CO)(TPPTS)_3]$ is easily made in the oxo reactor by reacting suitable Rh salts (e.g., rhodium acetate or rhodium 2-ethylhexanoate) with TPPTS – both components freshly prepared or recovered and recycled - without any additional preformation step. The reaction starts after formation of the active species and adjustment of the whole system with water to the desired P/Rh ratio (ensuring the stability of the catalyst and the desired *n/iso* ratio).

5.3.3 ECONOMICS OF THE PROCESS

In comparison to other oxo variants the RCH/RP process is highly economic, *inter alia* reflecting the technological progress of the aqueous-phase operation, better energy management, and the higher selectivities which are a consequence of the TPPTS ligand. Under equal conditions (basing on market prices without internal clearing prices) the RCH/RP process offers clear advantages of approximately 10% over other ligand-modified processes (Table 5.5) [12e].

TABLE 5.5. Manufactering costs of 100 kg *n*-butanal (RCH/RP=100)

Costs	RCH/RP Process	Other rhodium catalysed process
1. Raw materials	88.9	89.0
2. Energy	1.5	9.7
3. Credits (*iso*-butanal, *n*-butanol, others)	-7.7	-11.4
4. Costs for materials (sum 1+2+3)	82.7	87.3
5. Fix cost plus license fee[1)]	17.3	22.1
6. Sum 4+5 = Manufacturing costs[1)]	100.0	109.4

[1)] For updating see the *Chemical Engineering Plant Cost Index* (CEPCI, [12n]).

5.3.4 ENVIRONMENTAL ASPECTS

In addition to their economic advantages (see Section 5.3.3), catalyzed organic reactions in aqueous media have received signifcant attention as a result of environmental considerations [6,15]. The fundamental advance represented by the RCH/RP process in terms of the environment, conservation of resources, and minimization of risks such as enviromental pollution - aiming at sustainable “green” processes - can be demonstrated by various criteria and proved by means of the analysis of *atom economy* (according to Trost [71]) and, more convincingly and constructively, by the *environmental E factor* according to Sheldon [72]. The latter defined the *E* factor as the ratio of the amount of waste ("waste" is everything except the desired product) produced per kilogram of "target" products and he specified the *E* factor for every segment of the chemical industry (Table 5.6; [74]).

TABLE 5.6. The Environmental factor *E*

Industry segment	Product tonnage [tpy]	*E* factor
Oil refining	10^6-10^8	approx. 0.1
Bulk Chemicals	10^4-10^6	<1 - 5
Fine chemicals	10^2-10^4	5 - 50+
Pharmaceuticals	10-10^3	25 - 100+

As expected from Table 5.7, this environmental quotient for conventional oxo processes (basis: Co catalysts) and for the manufacture of the bulk chemical *n*-butanal is actually about 0.6-0.9, depending on the definition of the term "target" product. The range 0.6-0.9

indicates that the by-product *iso*-butanal occuring with conventional oxo processes is further processed by some producers (to *iso*-butyric acid, neopentylglycol, etc.) so that the *iso*-aldehyde thus becomes a target product and the E factor falls from 0.9 to 0.6. Strictly speaking, this observation is included in Sheldon's wider assessment, according to which the E factor is refined and becomes the environmental quotient EQ, depending on the nature of the waste. Since such quotients are "debatable and will vary from one company to another and even from one production to another" (Sheldon) they will not be discussed here. The crucial point is that on the same basis, taking into account all by-products including those produced in ligand manufacture, etc., which exhibit for conventional oxo processesve an *E* factor of 0.6-0.9, this factor falls to below 0.1 in the RCH/RP process: an important pointer to the environmental friendliness of the RCH/RP process (Table 5.7).

TABLE 5.7. *E* factors of different processes for the hydroformylation of propene

	E factor	
	iso-butanal as value product	*iso*-butanal as by-product
Co catalyst	>0.6	>0.9
Rh catalyst (RCH/RP)	<0.04	<0.1

Whereas this important quotient is calculated solely from the product spectrum, process simplifications are a consequence of combining the rhodium catalyst with the special two-phase process. Compared with the conventional oxo process and with other variants (which, for example, include disadvantegeously thermal separation of the oxo reaction products from the catalyst) the procedure is considerably simplified (as shown in several papers, e.g., [2,12]).

The conservation of energy resources with the RCH/RP process is dramatic. Note should be taken of the much milder reaction conditions and of the fact that the RCH/RP process is an energy exporter because of an intelligent, integrated heat network - an unusual occurence for conventional oxo processes, competing processes with PPh_3-modified Rh catalysts included. Furthermore, the steam consumption figures for the older, cobalt-based processes are very much higher than those for the Rh process and power consumption was twice as high as that of the RCH/RP process: both of theses factors represent an environmental burden. The relative compression costs alone for the required syngas are 1.7:1 (Co versus Rh process). The volume of waste water for the RCH/RP process is 70 times lower than that from the cobalt-based high pressure process - convincing evidence of an environmental benign and "green" process and one of the reasons for the advantageous results from the life cycle assesssment. It may be added that the process thus meets the requirements of the "production-integrated environmental protection", sometimes known as "cleaner production" which has the aim of avoiding and reducing residues and using resources carefully [8c,75].

The solvent water reliably averts the risk of fire, which was inherent in the old cobalt-based process as a result of leaking highly flammable, metal carbonyls. The technique with its "built-in extinguishing system" reliably prevents such fires, and the painstaking measuring and monitoring procedure necessitated by the valuable rhodium-based catalyst, accompanied by constant simultaneous balancing of the RCH/RP process, permits any leaks from the aqueous system to be detected much earlier than was ever possible with the expensive mass and liquid balance of the old Co process. This also applies for the cooling system, in which any leak from the falling film evaporator would be noticed immediately. For the other advantages of using water as the solvent, see Section 5.2.3.1.

5.4 Concluding Remarks

Taking all criteria into consideration, aqueous two-phase techniques are very sound methods for homogeneously catalyzed processes such as hydrogenations or hydroformylations. Of the various alternatives to the conventional (and solvent-free) processes most progress in terms of ecological impact and economics has been attained by the aqueous biphasic approach (Figure 5.20).

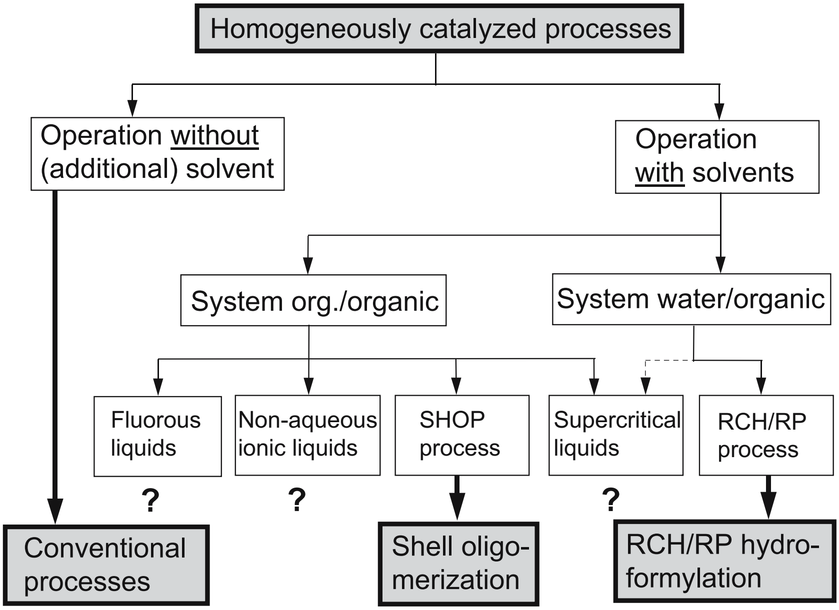


Figure 5.20. The various possibilities for biphasic operation of homogeneous catalysis

So far, only the systems organic/organic and water/organic have produced cost-effective, commercial processes. It is believed that aqueous biphasic systems have larger potential than organic/organic systems because their solubility patterns are more promising. The other possibilities such as fluorous liquids, supercritical fluids and non-aqueous ionic liquids are discussed in detail in later chapters of this book, but none have yet been commercialised They are labeled with a question mark in Figure 5.17 to underline the uncertainty of their development. The same is true for recent work using water-soluble polymers [61]. All of these processes need costly media (fluorous solvents, non-aqueous ionic liquids), high-priced ligands (fluorous processes or processes with supercritical CO_2), and /or additional means such as phase separating fluids, co-solvents, etc.

The aqueous-biphasic processes are easy to handle thus emphasizing their great environmental compatibility. They have significant potential for further development whether in terms of varying the ligand TPPTS (and thus the activity and selectivity of the conversions chosen, e.g., the hydroformylation; [74]) as well as the possibility of achieving asymmetric conversions, or in terms of other feedstocks. The adoption of the aqueous two-phase reaction for hydroformylation in particular (but also for other homogeneously catalyzed conversions in general) shows the striking and unequalled advantages of this special neat type of "immobile" catalyst and its "heterogenization" by the catalyst carrier, water as a result of which it is handled in similar fashion to a heterogeneous catalyst. This affects the costs as well as the enviromental compatibility

The advantages of successful waste management and avoiding by-products are further good points of the process, which ultimately lead to the higher cost-effectiveness as a result of the mentioned advantages together with less downtime: further proof of the likelihood that even in the medium term only environmentally sound processes will remain the most effective. The fact that basicly Sheldon's *E* factor is inversely proportional to a successful life cycle assessment underlines the superior quality of aqueous-organic biphasic systems.

5.5 References

[1] H. -W. Bohnen, B. Cornils, *Adv. Catal.* 2003, **47**, 1.

[2] (a) B. Cornils, C. W. Kohlpaintner, E. Wiebus in J. J. McKetta, G. E. Weismantel (Eds.), *Encyclopedia of Chemical Processing and Design*, Dekker, New York 1999, Vol. 66, p. 273; (b) B. Cornils in I. T. Horváth et al. (Eds.), *Encyclopedia of Catalysis*, Wiley, New York 2003; Vol. 1, p. 805; (c) B. Cornils in P. Knochel (Ed.), *Topics in Current Chemistry*, Vol. 206, Springer, Berlin/Heidelberg 1999, p. 133; (d) B. Cornils, *Ind. Catal. News* 1998, No. 2; (e) R. V. Chaudhari, A. Bhattacharya, B. M. Bhanage, *Catal. Today* 1995, **24**, 123.

[3] J. Falbe(Ed.), *New Syntheses with Carbon Monoxide*, Springer, Berlin 1980.

[4] Field Information Agency, Technical (FIAT) Report No. 1000 (1945), (Reports of the Occupational Forces in Germany).

[5] (a) J. Manassen, in F. Basolo and R. L. Burwell (Eds.), *Catalysis Progress in Research*, Plenum Press, London 1973, p. 183 and YEDA, US 4,415,500 (1983); (b) F. Joó, M. T. Beck, *Magy. Kém. Folyóirat* 1973, **79**, 189; (c) F. Joó, *Aqueous Organometallic Catalysis*, Kluwer, Dordrecht 2001, p. 3; (d) F. Joó, E. Papp, A. Kathó, *Top. Catal.* 1998, **5**, 113.

[6] B. Cornils, W. A. Herrmann (Eds.), *Aqueous-Phase Organometallic Synthesis*, Wiley-VCH, Weinheim 1998; 2nd Ed. 2003,

[7] W. Keim, F. -H. Kowaldt, R. Goddard, C. Krüger, *Angew. Chem.* 1978, **90**, 493.

[8] (a) R. T. Baker, W. Tumas, *Science* 1999, **284**, 1477; (b) S. K. Ritter, *Chem. & Eng. News* 2002, May 20, 38; (c) A. D. Curzons, D. J. C. Constable, D. N. Mortimer, V. L. Cunningham, *Green Chem.* 2001, **3**, 1; (d)

R. P. Swatloski, J. D. Holbrey, R. D. Rogers, *Green Chem.* 2003, **5**, 361; (e) G. Centi, S. Perathoner, *Catal. Today* 2003, **77**, 287.

[9] B. Cornils, W. A. Herrmann, R. Schlögl, C. -H. Wong (Eds.), *Catalysis from A to Z*, Wiley-VCH, Weinheim, 2nd ed. , 2003.

[10] (a) Z. Li, Q. Peng, Y. Yuan, *Appl. Catal. A:* 2003, **239**,79; (b) M. Benaissa, U. J. Jáuregui-Haza, I. Nikov, A. M. Wilhelm, H. Delmas, *Catal. Today* 2003, **79/80**, 419; (c) U. J. Jáuregui-Haza, E. Pardillo-Fontdevila, Ph. Kalck, H. Delmas, *Catal. Today* 2003, **79/80**, 409; (d) A. Riisager, K. M. Eriksen, J. Hjortkjaer, R. Fehrmann, *J. Mol. Catal. A:* 2003, **193**, 259; (e) M. Dessoudeix, U. J. Jáuregui-Haza, M. Heughebaert, A. M. Wilhelm, H. Delmas, A. Lebugle, Ph. Kalck, *Adv. Synth. Catal.* 2002, **344**, 406; (f) Z. Li, Q. Peng, Y. Yuan, *Appl. Catal. A:* 2003, **239**, 79; (g) Y. Yuan, H. Zhang, Y. Yang, Y. Zhang, K. Tsai, *Catal. Today* 2002, **74**, 5; (h) Z. Li, Q. Peng, Y. Yuan, *Appl. Catal. A:* 2003, **239**, 79; (i) G. Fremy, E. Monflier, J. -F. Carpentier, Y. Castanet, A. Mortreux, *Angew. Chem.* 1995, **107**, 1608.

[11] C. Botteghi et al. , *J. Mol. Catal. A:* 2003, **200**, 147.

[12] (a) B. Cornils, J. Falbe, *4th Int. Symp. on Homogeneous Catalysis*, Leningrad, Sept. 1984, Proceedings p. 487; (b) H. Bach, W. Gick, E. Wiebus, B. Cornils, *Int. Symp. High-Pressure Chem. Eng.* , Erlangen/Germany, Sept. 1984, Preprints p. 129; (c) H. Bach, W. Gick, E. Wiebus, B. Cornils, *8th ICC*, Berlin 1984, Preprints Vol. V, p. 417; [C. A. 1987, 106, 198,051; cited also in A. Behr, M. Röper, *Erdgas und Kohle* 1984, **37**, 485]; (d) H. Bach, W. Gick, E. Wiebus, B. Cornils, *1st IUPAC Symp. Org. Chemistry*, Jerusalem 1986, Abstracts p. 295; (e) E. Wiebus, B. Cornils, *Chem. Ing. Techn.* 1994, **66**, 916; (f) B. Cornils, E. Wiebus, *CHEMTECH* 1995, **25**, 33; (g) E. G. Kuntz, *CHEMTECH* 1987, **17**, 570; (h) C. W. Kohlpaintner, R. W. Fischer, B. Cornils, *Appl. Catal. A:* 2001, **221**, 219; (i) B. Cornils, *J. Mol. Catal. A:* 1999, **143**, 1; (j) B. Cornils, *Org. Proc. Res. & Dev.* 1998, **2**, 121; (k) C. -D. Frohning, C. W. Kohlpaintner in [6], p. 294; (l) E. Wiebus, B. Cornils, *Hydrocarb. Proc.* 1996, March, 63; (m) B. Cornils, W. A. Herrmann in [6], Introduction; (n*) Chem. Eng.* 2002, Jan., 62.

[13] (a) P. Kalck, M. Dessoudeix, S. Schwarz, *J. Mol. Catal. A:* 1999, **143**, 41; (b) R. M. Deshpande, S. S. Divekar, B. M. Bhanage, R. V. Chaudhari, *J. Mol. Catal. A:* 1992, **75**, L19.

[14] (a) Rhône-Poulenc Recherche (E. Kuntz), FR 2,314,910 (1975); FR 2,349,562 (1976); FR 2,338,253 (1976); FR 2,366,237 (1976) and other patent applications; (b) B. Cornils, E. G. Kuntz, *J. Organomet. Chem.* 1995, 505, 177.

[15] (a) H. Olivier-Bourbigou, F. Hugues in R. D. Rogers, K. R. Seddon, S. Volkov (Eds.), *Green Industrial Applications of Ionic Liquids*, NATO Science Series, Vol. 92, Kluwer, Dordrecht 2002.

[16] (a) G. Duve, O. Fuchs, H. Overbeck, *Lösemittel Hoechst*, 6th ed. , Hoechst AG, Frankfurt/M. 1976, p. 49; (b) C. Reichardt, *Solvents and Solvent Effects in Organic Chemistry*, 3rd ed. , Wiley-VCH, Weinheim/Germany 2002.

[17] (a) P. A. Grieco (Ed.), *Organic Synthesis in Water*, Blacky Academic, London 1998; (b) H. Fuhrmann, T. Dwars, G. Oehme, *Chem. Unserer Zeit* 2003, **37**, 40; (c) C. J. Li, T. H. Chan, *Organic Reactions in Organic Media*, Wiley, New York 1997; (d) C. J. Li, *Chem. Rev.* 1993, **93**, 2023; (d) C. J. Li, T. H. Chan, *Tetrahedron* 1996, **52**, 5643; (e) M. Groß, *Chem. Unserer Zeit* 2003, **37**, 170; (f) K. Nomura, *J. Mol. Catal. A:* 1998, **130**, 1; (g) N. J. Buurma, M. J. Blandamer, J. B. F. N. Engberts, *Adv. Synth. Catal.* 2002, **344**, 413; (h) F. Reynal, R. Barhdadi, J. Périchon, A. Savall, M. Toupel, *Adv. Synth. Catal.* 2002, **344**, 45; (i) S. Ribe, P. Wipf, *Chem. Commun.* 2001, 299.

[18] (a) A. Lubineau, *Chem. Ind.* 1996, February, 123 (not p. 125, as printed); (b) H. W. Roesky, M. G. Walawalkar, R. Murugavel, *Acc. Chem. Res.* 2001, **34**, 201; K. R. Asmis et al. , *Science* 2003, **299**, 1375 ; T. Köddermann, F. Schulte, M. Huelsekopf, R. Ludwig, *Angew. Chem. Int. Ed.* 2003, **42**, 4904; (c) N. J.

Buurma, M. J. Blandamer, J. B. F. N. Engberts, *Adv. Synth. Catal.* 2002, **344**, 413; (d) K. Itami, T. Nokami, J. Yoshida, *Adv. Synth . Catal.* 2002, **344**, 441.

[19] E. G. Hope, A. M. Stuart, *Chem. &Ind.* 1999, 4 Oct. , 755.

[20] C. C. Tzschucke, C. Markert, W. Bannwarth, S. Roller, A. Hebel, R. Haag, *Angew. Chem. Int. Ed.* 2002, **41**, 3964.

[21] P. W. N. M. van Leeuwen, P. C. J. Kamer, J. N. H. Reek, *Cattech* 1999, **3**, 64.

[22] (a) R. J. Stokes, D. F. Evans, *Fundamentals of Interfacial Engineering*, Wiley-VCH, Mew York/Weinheim 1997; (b) BASF, DE 3,220,858 (1983).

[23] (a) O. Wachsen, K. Himmler, B. Cornils, *Catal. Today* 1998, **42**, 373; (b)E. Lindner, T. Schneller, F. Auer, H. A. Meyer, *Angew. Chem. Int. Ed.* 1999, **38**, 2155; (c) Ph. Kalck, M. Dessoudeix, S. Schwarz, *J. Mol. Catal. A:* 1999, **143**, 41.

[24] (a) R. M. Stephenson, *J. Chem. Eng. Data* 1993, **38**, 630; (b) C. McAuliffe, *J. Phys. Chem.* 1966, **70**, 1267; (c) P. L. Davis, *Gas Chromatogr.* 1968, **6**, 518.

[25] (a) C. Yang, X. Bi, Z. -S. Mao, *J. Mol. Catal. A:* 2002, **187**, 35; (b) Y. Önal, M. Baerns, P. Claus in [6], p. 151; (c) *Chem. Ing. Tech. plus*. 2003, Issue Sept. , 46; (d) Y. Zhang, Z. -S. Mao, J. Chen, *Catal. Today* 2002, **74**, 23; (e) C. Yang, Z. -S. Mao, Y. Wang, J. Chen, *Catal. Today* 2002, **74**, 111.

[26] (a) E. A. Karakhanov, Y. S. Kardesheva, E. A. Runova, V. A. Semermina, *J. Mol. Catal. A:* 1999, **142**, 339; (b) J. N. H. Reek, A. J. Sandee, M. Schreuder Goedheijt, P. C. J. Kamer, P. W. N. M. van Leeuwen, *Erdöl, Erdgas, Kohle* 2001, **117**, 134; (c) H. Chen, Y. Li, R. Li, P. Cheng, X. Li, *J. Mol. Catal. A:* 2003, **198**, 1; (d) U. Ritter, N. Winkhofer, H. -G. Schmidt, H. W. Roesky, *Angew. Chem. Int. Ed.* 1996, **35**, 524; (e) M. Li, Y. Li, H. Chen, Y. He, X. Li, *J. Mol. Catal. A:* 194, **13**; (f) Y. Huang, L. Min, Y. Li, H. Chen, P. Cheng, X. Li, *J. Mol. Catal. A:* 2002, **185**, 41; (g) Y. Zhang, Z. -S. Mao, J. Chen, *Catal. Today* 2002, **74**, 23; (h) H. Chen, Y. Li, J. Chen, P. Cheng, X. Li, *Catal. Today* 2002, **74**, 131; (i) Z. Li, Q. Peng, Y. Yuan, *Appl. Catal. A:* 2003, **239**, 79; (k) F. Monteil, R. Queau, Ph. Kalck, *J. Organomet. Chem.* 1994, **480**, 177; (l) M. Giménez-Pedrós, A. Aghmiz, C. Claver, A. M. Masdeu-Bultó, D. Sinou, *J. Mol. Catal. A:* 2003, **200**, 157; L. Wang, H. Chen, Y. He, Y. Li, M. Li, X. Li, *Appl. Catal. A :* 2003, **242**, 85.

[27] Among a multitude of publications: (a) B. Fell et al. , *J. Prakt. Chem. /Chem. Ztg.* 1996, **338**, 124; *J. Mol. Catal.* 1997; **116**, 55; *Fett/Lipid* 1996, 98, 393; (b) Z. Jin et al. , *J. Mol. Catal. A:* 1999, **147**, 131 and **149**, 113; 2000, **157**, 111 and **159**, 37; 2001, **171**, 85; 2002, **188**, 79; 2003, **195**, 133; 2003, **198**, 23; *Catal. Today* 2002, **74**, 85; *Catal. Commun.* 2003, **4**, 129; (c) E. Paetzold, G. Oehme, C. Fischer, M. Frank, *J. Mol. Catal. A:* 2003, **200**, 95; (d) J. A. Loch, C. Borgmann, R. H. Crabtree, *J. Mol. Catal. A:* 2001, **170**, 75; (e) B. M. Bhanage, M. Shirai, M. Arai, *J. Mol. Catal. A:* 1999, **145**, 69; (f) U. Ritter, N. Winkhofer, H. -G. Schmidt, H. W. Roesky, *Angew. Chem. Int. Ed. Engl.* 1996, **35**, 524.

[28] (a) E. Bayer, V. Schurig, *CHEMTECH* 1976, (March), 212; (b) E. Bayer, V. Schurig, *Angew. Chem. Int. Ed. Engl.* 1975, **14**, 493; (c) M. Giménez-Pedrós, A. Aghmiz, C. Claver, A. M. Masdeu-Bultó, D. Sinou, *J. Mol. Catal . A:*2003, **200**, 157; (d) E. Paetzold, M. Michalik, G. Oehme, *J. Prakt. Chem.* 1997, **339**, 38; (e) A. Kumar, G. Oehme, J. P. Roque, M. Schwarze, R. Selke, *Angew. Chem.* 1994, **106**, 2272; (f) S. Ganguly, J. T. Mague, D. M. Roundhill, *Inorg. Chem.* 1992, **31**, 3500; (g) S. Shimizu, S. Shirakawa, Y. Sasaki, C. Hirai, *Angew. Chem.* 2000, **112**, 1313; (h) M. Schreuder Goedheijt, P. C. J. Kamer, P. W. N. M. van Leeuwen, *J. Mol. Catal. A:* 1998, **134**, 243; (i) K. V. Katti, H. Gall, C. J. Smith, D. E. Berning, *Acc. Chem. Res.* 1999, **32**, 9; (k) M. Beller, J. G. E. Krauter, A. Zapf, S. Bogdanovic, *Catal. Today* 1999, **48**, 279; (l) S. Shimizu, T. Suzuki, S. Shirakawa, Y. Sasaki, C. Hirai, *Adv. Synth. Catal.* 2002, **344**, 370; (m) C. Bertucci, C. Botteghi, D. Giunta, M. Marchetti, S. Paganelli, *Adv. Synth. Catal.* 2002, **344**, 556; (n) E. Monflier, G. Fremy, Y. Castanet, A. Mortreux, *Angew. Chem.* 1995, **107**, 2450; (o) G. T. Baxley, T. J. R. Weakly, W. K.

Miller, D. K. Lyon, D. R. Tyler, *J. Mol. Catal. A:* 1997, **116**, 191; (p) A. Gong, Q. Fan, Y. Chen, H. Liu, C. Chen, F. Xi, *J. Mol. Catal. A:* 2000, **159**, 225; (q) Q. Peng, Y. Yang, C. Wang, X. Liao, Y. Yuan, *Catal. Lett*. 20023, **88**, 219; (r) A. Aghmiz, A. Orejón, M. Diéguez, M. D. Miquel-Serrano, C. Claver, A. M. Masdeu-Bultó, D. Sinou, G. Laurenczy, *J. Mol. Catal. A:* 2003, **195**, 113; (s) X. Z. Liu, F. Kong, X. Zheng, Z. Jin, *Catal. Commun.* 2003, **4**, 129; (t) D. C. Mudalige, G. L. Rempel, *J. Mol. Catal. A:* 1997, **116**, 309; (u) A. Riisager, K. M. Erksen, J. Hjortkaer, R. Fehrmann, *J. Mol. Catal. A:* 2003, **193**, 259; (v) S. Ganguly, J. T. Mague, D. M. Roundhill, *Inorg. Chem.* 1992, **31**, 3500; (w) S. Shimizu, S. Shirakawa, Y. Sasaki, C. Hirai, *Angew. Chem.* 2000, **112**, 1313; (x) R. Amengual, E. Genin, V. Michelet, M. Savignac, *Adv. Synth. Catal.* 2002, **344**, 393 ; (y) E. A. Karakhanov, Y. S. Kardasheva, E. A. Runova, M. V. Terenina, *EuropaCat-VI*, 31,Aug-4, Sept. ,Preprints; (z) F. Chécot, S. Lecommandoux, Y. Gnanou, H-A. Klok, *Angew. Chem. Int. Ed.* 2002, **41**, 1340.

[29] (a) G. Protzmann, K-D. Wiese, *Erdöl,Erdgas,Kohle* 2001, **117**, 235; (b) Oxeno (G. Protzmann, K-D. Wiese, J. Koch, M. Trocha, D. Röttger), DE 199 25 384 (2000); (c) Oxeno (K-D. Wiese, G. Protzmann, J. Koch, D. Röttger, M. Trocha), EP 1,057,524 (2000); (d) Oxeno (G. Protzmann, K-D. Wiese, W. Büschken, D. Röttger), DE 199 57 528 and 199 57 522 (1999); (e) Oxeno (G. Protzmann, K-D. Wiese, W. Büschken), EP 1,057,538 (2001); (f) Oxeno (K-D. Wiese, P. Olbrich, J. Gabriel), DE 199 08 320 (2000); (g) K. -D. Wiese, O. Möller, G. Protzmann, M. Trocha, *Catal. Today* 2003, **79/80**, 97.

[30] (a) B. Driessen-Hölscher, P. Wasserscheid, W. Keim, *Cattech* 1998, June, 47; (b) A. Behr, *Chem. Ing. Tech.* 1998, **70**, 685; (c) A. Behr, C. Fängewisch, *Chem. Ing. Tech.* 2002, **73**, 874.

[31] (a) A. Behr, *Chem. Ing. Tech.* 1998, **70**, 685; (b) B. Auch-Schwelk, C. Kohlpaintner, *Chem. Unserer Zeit* 2001, **35**, 306.

[32] T. Prinz, W. Keim, B. Driessen-Hölscher, *Angew. Chem.* 1996, **108**, 1835.

[33] (a) H. Bahrmann, H. Bach, C. D. Frohning, H. J. Kleiner, P. Lappe, D. Peters, D. Regnat, W. A. Herrmann, *J. Mol. Catal. A:* 1997, **116**, 49; (b) M. Beller, B. Cornils, C. D. Frohning, C. W. Kohlpaintner, *J. Mol. Catal. A:* 1995, **104**, 17; (c) B. Cornils, W. A. Herrmann, R. W. Eckl, *J. Mol. Catal. A:* 1997, **116**, 27; (d) M. Yuan, H. Chen, R. Li, Y. Li, X. Li, *Appl. Catal. A:* 2003, **251**, 181.

[34] G. Centi, S. Perathoner, *Catal. Today* 2003, **79/80**, 3.

[35] (a) C. Larpent, E. Bernard, F. Brisse-le Menn, H. Patin, *J. Mol. Catal. A:* 1997, **116**, 277 ; (b) Davy/McKee (Union Carbide), GB 2,075,857 (1981) and EP 096,987 (1983) ; (c) Union Carbide, EP 055,487 (1982) and EP 068,480 (1082); (d) Daicel, JP 5-8186-443A (1983); (e) BASF EP 053,688 (1982).

[36] (a) Elf Atochem, US 5,345,007 (1994, Monflier); (b) A. Behr, M. Urschey, *J. Mol. Catal. A:* 2003, **197**, 101; (c) N. Yoshimura in [6], p. 408; (d) T. Prinz, W. Keim, B. Driessen-Hölscher, *Angew. Chem.* 1996, **108**, 1835; (e) Kuraray, JP 080642 (1981), JP 5-8131-994° (1982) and JP 58216138 (1984); (f) M. Matsumoto, M. Tamura, *J. Mol. Catal.* 1982, 16, 209; (g) Kuraray, EP 088,955 (1983); IFP (H. Chauvin), US 6,525,228 (2001).

[37] (a) DuPont (W. D. Drinkard et al.), US 3,536,748 (1970), 3,579,560 (1971), 3,676,481 (1972), and 3,739,011 (1973); (b) Rhône-Poulenc (E. G. Kuntz), US 4,087,452 (1978); (c) H. E. Bryndza, J. A. Harrelson in [6], p. 393.

[38] (a) R. Chansarkar, K. Mukhopadhyay, A. A. Kelkar, R. V. Chaudhari, *Catal. Today* 2003, **79/80**, 51; (b) C. W. Kohlpaintner, M. Beller, *J. Mol. Catal. A:* 1997, **116**, 259; (c) A. L. Lapidus, K. B. Petrovskii, I. P. Beletskaya, *Russ. J. Org. Chem.* 1997, **33**, 1083; (d) P. Jayasree, S. P. Gupta, R. V. Chaudhari, *Stud. Surf. Sci. Catal.* 1998, **113**, 875; E. Paetzold, G. Oehme, *J. Mol. Catal. A:* 2000, **152**, 69.

[39] (a) C. Dupuis, K. Adiey, L. Charruault, V. Michelet, M. Savignac, J-P. Gênet, *Tetrahedron Lett.* 2001, **42**, 6523; (b) N. E. Leadbeater, M. Marco, *Angew. Chem. Int. Ed.* 2003, **42**, 1407; (c) E. Paetzold, G. Oehme,

J. Mol. Catal. A: 2000, **152**, 69; (d) S. Haber in [6], p. 440.

[40] F. Bertoux, S. Tilloy, E. Monflier, Y. Castanet, A. Mortreux, *J. Mol. Catal. A:* 1999, **138**, 53.

[41] (a) S. Nagayama, S. Kobayashi, *Angew. Chem. Int. Ed.* 2002, **39**, 567; (b) Y. Mori, K. Manabe, S. Kobayashi, *Angew. Chem.* 2001, **113**, 2898; (c) K. Inoue, T. Ishida, I. Shibata, A. Baba, *Adv. Synth. Catal.* 2002, **344**, 283; (d) K. Manabe, S. Kobayashi, *Chem. Eur. J.* 2002, **8**, 4095; (e) T. Ooi, Y. Uematsu, K. Maruoka, *Adv. Synth Catal.* 2002, **344**, 288; (f) S. Shimizu, T. Suzuki, S. Shirikawa, Y. Sasaki, C. Hirai, *Adv. Synth. Catal.* 2002, **344**, 370; (g) (l) D. Sinou, C. Rabeyrin, C. Nguefack, *Adv. Synth. Catal.* 2003, **345**, 357; (h) S. Sigismondi, D. Sinou, *J. Mol. Catal. A:* 1997, **116**, 289; (i) P. Wipf, S. Rodriguez, *Adv. Synth. Catal.* 2002, **344**, 434; (j) K. Itami, T. Nokami, J. Yoshida, *Adv. Synth. Catal.* 2002, **344**, 441; (k) C. Loncaric, K. Manabe, S. Kobayashi, *Adv. Synth. Catal.* 2003, **345**, 475; (l) Nagoya University, *Bull. SocSoc. Jpn.* 1997, **70**, 905 [ref. in *CHEMTECH* 1997, (Nov.), 5]; (m) I. V. Kozhevnikov, G. P. Mulder, M. C. Steverink-de Zoete, M. G. Oostwal, *J. Mol. Catal. A:* 1998, **134**, 223; (n) H. Rudler, J. Ribeiro Grigorio, B. Denise, J. -M. Bregeault, A. Deloffre, *J. Mol. Catal. A:* 1998, **133**, 255; (o) G. Pozzi, I. Colombani, M. Miglioli, F. Montanari, S. Quici, *Tetrahedron* 1997, **53**, 6145; (p) B. Boyer, A. Hambardzoumian, G. Lamaty, A. Leydet, J. -P. Roque, P. Bouchet, *New J. Chem.* 1996, **20**, 985; (q) K. Manabe, N. Aoyama, S. Kobayashi, *Adv. Synth. Catal.* 2001, **343**, 174;(r) S. Mukhopadhyay, G. Rothenberg, A. Joshi, M. Baidossi, Y. Sasson, *Adv. Synth. Catal.* 2002, **344**, 348; (s) R. Amengual, E. Genin, V. Michelet, M. Savignac, J. -P. Genêt, *Adv. Synth. Catal.* 2002, **344**, 393; (t) B. M. Bhanage, M. Shirai, M. Arai, *J. Mol. Catal. A:* 1999, **145**, 69; (u) M. Beller, J. G. E. Krauter, A. Zapf, S. Bogdanovic, *Catal. Today* 1999, **48**, 279; (v) T. Koike, X. Du, T. Sanada, Y. Danda, A. Mori, *Angew. Chem. Int. Ed.* 2003, **42**, 89; (w) Z. Yang, M. Ebihara, T. Kawamura, *J. Mol. Catal. A:* 2000, **158**, 509; (x) P. J. Baricelli, J. Lopez, E. Lujano, F. Lopez-Linares, *J. Mol. Catal. A:* 2002, **186**, 57; (y) T. Malmström, C. Andersson, *J. Mol. Catal. A:* 2000, **157**, 79; (z) A. Andriollo, J. Carrasquel, J. Marino, F. A. López, D. E. Páez, I. Rojas, N. Valencia, *J. Mol. Catal. A:* 1997, **116**, 157; (aa) G. Süss-Fink, M. Faure, T. R. Ward, *Angew. Chem. Int. Ed.* 2002, **41**, 99 and *J. Mol. Catal. A:* 1998, **132**, 5; (bb) G. Papp, J. Elek, L. Nádasdi, G. Laurenczy, F. Joó, *Adv. Synth. Catal.* 2003, **345**, 172; (cc) G. Laurenczy et al. , *Adv. Synth. Catal.* 2003, **345**, 211,216; (dd) J. A. Loch, C. Borgmann, R. H. Crabtree, *J. Mol. Catal. A:* 2001, **170**, 75; (ee) H. Jiang, Y. Xu, S. Liao, D. Yu, H. Chen, X. Li, *J. Mol. Catal. A:* 1999, **142**, 147; (ff) D. Sinou, *Adv. Synth. Catal.* 2002, **344**, 221; (gg) F. López-Linares, M. G. Gonzalez, D. E. Páez, *J. Mol. Catal. A:* 1999, **145**, 61; (hh) K. Nomura, *J. Mol. Catal. A:* 1998, **130**, 1; (ii) A. W. Heinen, G. Papadogianakis, R. A. Sheldon, J. A. Peters, H. van Bekkum, *J. Mol. Catal. A:* 1999, **142**, 17; (jj) A. Behr, N. Toslu, *Chem. Ing. Tech.* 1999, **71**, 490; (kk) S. Mecking, A. Held, F. M. Bauers, *Angew. Chem. Int. Ed.* 2002, **41**, 545; (ll) B. Manders, L. Sciandrone, G. Hauck, M. O. Kristen, *Angew. Chem. Ind. Ed.* 2001, **40**, 4006; (mm) D. M. Jones, W. T. S. Huck, *Adv. Mater.* 2001, **13**, 1256; (nn) M. A. Zuideveld, F. M. Bauers, R. Thomann, S. Mecking, 36th Meeting of German Catalysis, Weimar 19-21, March, 2003, *Preprints*, p. 385 and *Chem. Commun.* 2000, 301; (oo) A. Held, S. Mecking, *Chem. Eur. J.* 2000, **6**, 4623; (pp) P. Dupau, R. Epple, A. A. Thomas, V. V. Fokin, K. B. Sharpless, *Adv. Synth. Catal.* 2002, **344**, 421; (qq) G. M. Mehltretter, C. Döbler, U. Sundermeier, M. Beller, *Tetrahedron Lett.* 2000, **41**, 8083, *J. Am. Chem. Soc.* 2000, **122**, 10289 and *Angew. Chem. Int. Ed.* 1999, **38**, 3026; (rr) T. Wirth, *Angew. Chem. Int. Ed.* 2000, **39**, 334; (ss) T. Ishida, R. Akiyama, S. Kobayashi, *Adv. Synth. Catal.* 2003, **345**, 576; (tt) S. Venkatraman, T. Huang, C. -J. Li, *Adv. Synth. Catal.* 2002, **344**, 399; (uu) F. Raynal, R. Barhdadi, J. Périchon, A. Savall, M. Troupel, *Adv. Synth. Catal.* 2002, **344**, 45; (vv) T. Akiyama, J. Takaya, H. Kagoshima, *Adv. Synth. Catal.* 2002, **344**, 338.

[42] (a) G. Verspui, F. Schanssema, R. A. Sheldon, *Angew. Chem. Int. Ed.* 2000, **39**, 804; (b) G. Verspui, G. Papadogianakis, R. A. Sheldon, *Chem. Commun.* 1998, 401; (c) Z. Jiang, A. Sen, *Macromol.* 1994, **27**,

7215; (d) A. Sen (Ed.), *Catalytic Synthesis of Alkene-Carbon Monoxide Copolymers and Cooliogomers*, Kluwer, Dordrecht 2003.

[43] (a) R. G. da Rosa, J. D. R. de Campos, R. Buffon, *J. Mol. Catal. A:* 2000, 153, 19; (b) G. Papadogianakis, L. Maart, R. A. Sheldon, *J. Mol. Catal. A:* 1997, **116**, 179; (c) G. Verspui, G. Papadogianakis, R. A. Sheldon, *Catal. Today* 1998, **42**, 449.

[44] (a) R. H. Grubbs et al. , *J. Am. Chem. Soc*. 1998, **120**, 1627, 3187; (b) M. C. Schuster, K. H. Mortell, A. D. Hegeman, L. L. Kiessling, *J. Mol. Catal. A:* 1997, **116**, 209; (c) A. Romerosa, M. Peruzzini, *Organometallics* 2000, **19**, 4005; (d) R. H. Grubbs (Ed.), *Handbook of Metathesis*, Wiley-VCH, Weinheim 2003.

[45] S. Kobayashi et al. , *Tetrahedron Letters* 2000, **418**, 3107.

[46] (a) C. Venturello, M. Gambaro, *J. Org. Chem.* 1991, **56**, 5924; (b) P. L. Mills, R. V. Chaudhari, *Catal. Today* 1999, **48**, 17; (c) G. -J. ten Brink, I. W. C. E. Arends, R. A. Sheldon, *Adv. Synth. Catal.* 2002, **344**, 355 and *Science* 2000, **287**, 1636; (d) Y. Kita, *Angew. Chem. Int. Ed.* , 2000, **39**, 1306; (e) J. Cornely, L. M. Su Ham, D. E. Meade, V. Dragojlovic, *Green Chem.* 2003, **5**, 34; (f) L. Cammarota, S. Campestrini, M. Carrieri, F. Di Furia, P. Ghiotti, *J. Mol. Catal. A:* 1999, **137**, 155; (g) C. Dobler, G. M. Mehltretter, U. Sundermeier, M. Eckert, H. -C. Militzer, M. Beller, *Tetrahedron Lett.* 2001, **42**, 8447; (h) R. A. Sheldon, I. W. C. E. Arends, G. -J. ten Brink, A. Dijksman, *Acc. Chem. Res.* 2002, **35**, 774 and *Adv. Synth. Catal.* 2003, 345, 497; (i) Y. Uozumi, R. Nakao, *Angew. Chem. Int. Ed.* 2003, **42**, 194,; (j) W. Sun, H. Wang, C. Xia, J. Li, P. Zhao, *Angew. Chem. Int. Ed.* 2003, **42**, 1042; (k) G. -J. ten Brink, I. W. C. E. Arends, R. A. Sheldon, *Science* 2000, **287**, 1636; (l) G. J. ten Brink, I. W. C. E. Arends, R. A. Sheldon, *Adv. Synth. Catal.* 2002, **344**, 355; (m) E. Garcia Fidalgo, L. Plasseraud, G. Süss-Fink, *J. Mol. Catal. A*: 1998, **132**, 5; (n) S. Trinkhaus, R. Kadyrov, J. Holz, L. Götze, A. Börner, *J. Mol. Catal. A:* 1999, **144**, 15.

[47] (a) A. Behr, R. Ott, B. Turkowski, *36th Meeting of German Catalysis*, Weimar 2003, Preprints, p. 449.

[48] B. Cornils, W. A. Herrmann, I. T. Horváth, W. Leitner, S. Mecking, H. Olivier-Boubigou, D. Vogt (Eds.), *Multiphase Homogeneous Catalysis*, Wiley-VCH, Weinheim 2004.

[49] (a) A. Buhling, P. C. J. Kamer, P. W. N. M. van Leeuwen, J. W. Elgersma, *J. Mol. Chem. A:* 1997, **116**, 297; (b) A. Buhling, P. C. J. Kamer, P. W. N. M. van Leeuwen, *J. Mol. Catal. A:* 1995, 98, 69; (c) B. E. Hanson, H. Ding, C. W. Kohlpaintner, *Catal. Today* 1998, **42**, 421; (d) F. Robert, G. Oehme, I. Grassert, D. Sinou, *J. Mol . Catal. A:* 2000, **156**, 127; (e) Q. Peng, Y. Yang, C. Wang, X. Liao, Y. Yuan, *Catal. Letters* 2003, **88**, 219; (f) Y. Uozumi, M. Nakazono, *Adv. Synth. Catal.* 2002, **344**, 274.

[50] (a) F. Monteil, R. Queau, P. Kalck, *J. Organomet. Chem.* 1994, **480**, 177; (b) S. Trinkhaus, R. Kadyrov, R. Selke, J. Holz, L. Götze, A. Börner, *J. Mol. Catal. A. :* 1999, **144**, 15; (c) L. Lavenot, A. Roucoux, H,. Patin, *J. Mol. Catal. A:* 1997, **118**, 153; (d) K. C. Tin, N. -B. Wong, R. -X. Li, Y. -Z. Li, X. -J. Li, *J. Mol. Catal. A:* 1999, **137**, 113; (e) B. E. Hanson in [6], p. 181; 2nd edition 2003; (f) R. M Deshpande, Purwanto, H. Delmas, R. V. Chaudhari, *Ind. Eng. Chem. Res.* 1996, **35**, 3927; (g) F. Bertoux, E. Monflier, Y. Castanet, A. Mortreux, *J. Mol. Catal. A:* 1999, **143**, 23; (h) E. Paetzold, M. Michalik, G. Oehme, *J. Prakt. Chem.* 1997, **339**, 38; (i) H. Chen, Y. Li, J. Chen, P. Cheng, X. Li, *Catal. Today* 2002, **74**, 131; (j) M. Deshpande, S. S. Divekar, B. M. Bhanage, R. V. Chaudhari, *J. Mol. Catal.* 1992, **75**, L19; (k) A. Roucoux, J. Schulz, H. Patin, *Adv. Synth. Catal.* 2003, **345**, 222; (l) Ph. Kalck, L. Miquel, M. Dessoudeix, *Catal. Today* 1998, **42**, 431; (m) S. Paganelli, M. Zanchet, M,. Marchetti, G. Mangano, *J. Mol. Catal. A:* 2000, **157**, 1.

[51] (a) L. Wang, H. Chen, Y. He, M. Li, X. Li, *Appl. Catal. A. :* 2003, **242**, 85; (b) A. Riisager, B. E. Hanson, *J. Mol. Catal. A:* 2002, **189**, 195; (c) H. Chen, Y. Li, J. Chen, P. Chen, Y. He, X. Li, *J. Mol. Catal. A:* 1999, **149**,1; (d) A. Roucoux, J. Schulz, H. Patin, *Adv. Synth. Catal.* 2003, **345**, 222; (e) J. Texter, *Reactions and*

Synthesis in Surfactant Systems, Dekker, New York 2001; (f) T. Ooi, Y. Uematsu, K. Maruoka, *Adv. Synth. Catal.* 2002, **344**, 288; (g) J. Texter (Ed.), *Reactions and Synthesis in Surfactant Systems, Marcel* Dekker, New York 2001.

[52] (a) Exxon (J. R. Livingston, E. J. Mozeleski, G. Sartori), US 5,288,818 (1994) and PCT WO 93/04,029 (1993); (b) Th. Müller, H. Bahrmann, *J. Mol. Catal. A:* 1997, **116**, 39; (c) L. W. Gosser, W. H. Knoth, G. W. Parshall, *J. Mol. Catal.* 1977, **2**, 253; (d) T. Dwars, J. Haberland, I. Grassert, G. Oehme, U. Kragl, *J. Mol. Catal. A:* 2001, **168**, 81; (e) H. Fuhrmann, G. Oehme et al. , *Adv. Synth. Catal.* 2003, **345**, 202; (f) X. Liu, M. Jiang, S. Yang, M. Chen, C. Yang, K. Wu, *Angew. Chem. Int. Ed.* 2002, **41**, 2950; (g) A. G. Dixon in J. J. Spivey (ed.), *Catalysis*, Vol. 14, Chapter 2, p. 40, RSC, London 1999; (h) H. Bahrmann, M. Haubs, Th. Müller, N. Schöpper, B. Cornils, *J. Organomet. Chem.* 1997, **545/546**, 139; (i) H. Fuhrmann, T. Dwars, D. Michalik, G. Holzhüter, C. Grüttner, U. Kragl, G. Oehme, *Adv. Synth. Catal.* 2003, **345**, 202.

[53] (a) K. Kuroda, T. Swager, *Chem. Commun.* 2003, 26; (b) M. R. Buchmeiser, *Polymeric Materials in Organic Synthesis and Catalysis*, Wiley-VCH, Weinheim 2003; (c) X. Huang, K. L. Witte, D. E. Bergbreiter, C. -H. Wong, *Adv. Synth. Catal.* 2001, **343**, 675; (d) S. Mecking, A. Held, F. M. Bauers, *Angew. Chem. Int. Ed.* 2002, **41**, 545; (e) D. E. Bergbreiter, *CHEMTECH* 1987, (Nov.), 686; (f) D. E. Bergbreiter, J. G. Franchina, B. L. Case, *Org. Lett.* 2000, **2**, 393; (g) T. Malmström, C. Andersson, *J. Mol. Catal. A:* 2000, **157**, 79 and *Chem. Commun.* 1996, 1135; (h) D. E. Bergbreiter, *Catal. Today* 1998, **42**, 389; (i) T. J. Dickerson, N. N. Reed, K. D. Janda, *Chem. Rev.* 2002, **102**, 3325; (j) Z. Lu, E. Lindner, H. A. Mayer, *Chem. Rev.* 2002, **102**, 3543.

[54] (a) T. Borrmann, H. W. Roesky, U. Ritter, *J. Mol. Catal. A:* 2000, **153**, 31; (b) J. A. Loch, C. Borgmann, R. H. Crabtree, *J. Mol. Catal. A:* 2001, **170**, 75,

[55] E. Paetzold, G. Oehme, C. Fischer, M. Frank, *J. Mol. Catal. A:* 2003, **200**, 95.

[56] (a) P. J. Baricelli, G. Rodríguez, M. Rodríguez, E. Lujano, F. López-Linares, *Appl. Catal. A:* 2003, **239**, 25; (b) D. U. Parmar, S. D. Bhatt, H. C. Bajaj, R. V. Jasra, *J. Mol. Catal. A:* 2003, **202**, 9; (c) F. López-Linares, M. G. Gonzalez, D. E. Páez, *J. Mol. Catal. A:* 1999, **145**, 61; (d) D. C. Mudalige, G. L. Rempel, *J. Mol. Catal. A:* 1997, **116**, 309 and 123, 15; (e) S. Kolaríc, V. Sunjic, *J. Mol. Catal. A:* 1996, **111**, 239; (f) E. Garcia Fidalgo, L. Plasseraud, G. Süss-Fink, *J. Mol. Catal. A:* 1998, **132**, 5; (g) F. Robert, G. Oehme, I. Grassert, D. Sinou, *J. Mol. Catal. A:* 2000, 156, **127**; (h) C. Larpent, E. Bernard, F. Brisse-le Menn, H. Patin, *J. Mol. Catal. A:* 1997, **116**, 277; (i) T. Dwars, G. Oehme, *Adv. Synth. Catal.* 2002, **344**, 239; (j) F. Joó, *Acc. Chem. Res.* 2002, **35**, 738; Jóo, *Aqueous Organometallic Catalys*, Kluwer, Dordrecht 2001; (l) D. Sinou, *Adv. Synth. Catal.* 2002, **344**, 221; (m) Q. -H. Fan, G. -J. Deng, X. -M. Chen, W. -C. Xie, D. -Z. Jiang, D. -S. Liu, A. S. C. Chan, *J. Mol. Catal. A:,* 2000, **159**, 37; (n) T. Malmström, C. Andersson, *J. Mol. Catal. A:* 2000, **157**, 79; (o) Z. Yang, M. Ebihara, T. Kawamura, *J. Mol. Catal. A:* 2000, 158, 509; (p) K. Nomura, *J. Mol. Catal. A:* 1998, **130**, 1; (q) G. Papp, J. Elek, L. Nádashdi, G. Laurenczy, F. Jóo, *Adv. Synth. Catal.* 2003, **345**, 172.

[57] A. Chattopadhyay, A. Salaskar, *Synthesis* 2000, 561.

[58] (a) D. L. Reger, M. M. Habib, *J. Mol. Catal.* 1978, **4**, 315; (b) I. Grassert, J. Kovács, H. Fuhrmann, G. Oehme, *Adv. Synth. Catal.* 2002, **344**, 312; (c) V. Nardello, M. Hervé, P. L. Alsters, J. -M. Aubry, *Adv. Synth. Catal.* 2002, **344**, 184; (d) M. Haumann, H. Yildiz, H. Koch, R. Schomäcker, *Appl. Catal. A:* 2002, **236**, 173; (e) M. Haumann, H. Koch, R. Schomäcker, *Catal. Today* 2003, **79/80**, 43; (f) M. Haumann, H. Koch, P. Hugo, R. Schomäcker, *Appl. Catal. A:* 2002, **225**, 239; (g) M. Giménez-Pedrós, A. Aghmiz, C. Claver, A. M. Masdeu-Bultó, D. Sinou, *J. Mol. Catal. A:* 2003, **200**, 157; (h) X. Liu, M. Jiang, S. Yang, M. Chen, D. Chen, C. Yang, K. Wu, *Angew. Chem. Int. Ed.* . 2002, **41**, 2950; (i) A. Riisager, B. F. Hanson, *J. Mol. Catal. A:* 2002, **189**, 195; (k) H. Chen, Y. Li, J. Chen, P. Cheng, Y. He, X. Li, *J. Mol. Catal. A:* 1999, **149**, 1,

[59] (a) C. de Bellefon, N. Tanchoux, S. Caravieilhes, P. Grenouillet, V. Hessel, *Angew. Chem.* 2000, 112, 3584; (b) R. Hodiamont, W. Leitner, B. Driessen-Hölscher, *36th Meeting of German Catalysis*, Weimar 2003, 19-21, March, Preprints, p. 77.

[60] (a) X. Huang, K. L. Witte, D. E. Bergbreiter, C. -H. Wong, *Adv. Synth. Catal.* 2001, **343**, 675; (b) D. E. Bergbreiter, *CHEMTECH* 1987, Nov. , 686; (c) D. E. Bergbreiter, J. G. Franchina, B. L. Case, *Org. Lett.* 2000, **2**, 393; (d) D. E. Bergbreiter, *Catal. Today* 1998, **42**, 389.

[61] (a) M. A. Zuideveld, F. M. Bauers, R. Thomann, S. Mecking, *36th Meeting of German Catalysis,* Weimar, 19,-21, March 2003, Preprints, p. 385; (b) S. Mecking, A. Held, F. M. Bauers, *Angew. Chem. Int. Ed.* 2002, **41**, 545; (c) B. Xing, M. -. F. Choi, B. Xu, *Chem. Eur. J.* 2002, **8**, 5028.

[62] (a) J. J. F. Scholten, L. A. Gerritsen, J. M. Herman et al. , *J. Mol. Catal.* 1980, 9, special issue; (2) C. D. Frohning, C. W. Kohlpaintner, H. -W. Bohnen in B. Cornils, W. S. Herrmann (Eds.), *Applied Homogeneous Catalysis with Organometallic Compounds*, 2nd ed. , Wiley-VCH, Weinheim 2002, p. 31; W. Strohmeier et al. , *J. Organomet. Chem.* 1981, **221**, 361,

[63] M. E. Davies in B. Cornils, W. A. Herrmann (Eds.), *Aqueous-Phase Organometallic Catalysis*, Wiley-VCH, 1st ed. . ,Weinheim 1998, p. 241; *CHEMTECH* 1992, 498.

[64] (a) Z. Li, Q. Peng, Y. Yuan, *Appl. Catal. A:* 2003, **239**, 79; (b) G. Fremy, E. Monflier, J. -F. Carpentier, Y. Castanet, A. Mortreux, *Angew. Chem.* 1995, **107**, 1608 ; (c) J. N. H. Reek, A. J. Sandee, M. Schreuder Goedheijt, P. C. J. Kamer, P. W. N. M van Leeuwen, *Erdöl,Erdöl,Kohle* 2001, **117**, 134; (d) M. Dessoudeix, U. J. Jáuregui-Haza, M. Heughebaert, A. M. Wilhelm, H. Delmas, A. Lebugle, Ph. Kalck, *Adv. Synth. Catal.* 2002, **344**, 406; (e) J. R. Anderson, E. M. Campi, W. R. Jackson, Z. P. Yang, *J. Mol. Catal. A:* 1997, **116**, 109.

[65] K. Ziegler, H. Gellert, H. Kühlhorn, H. Martin, K. Meyer, K. Nagel, H. Sauer, K. Zosel, *Angew. Chem.* 1952, **64**, 323.

[66] D. Vogt in B. Cornils, W. A. Hermann (Eds.), *Applied Homogeneous Catalysis with Organometallic Compounds*, 2nd ed. , Wiley-VCH, Weinheim 2003, p. 240.

[67] Shell Dev. Corp. (S. R. Baur, H. Chung, P. W. Glockner, W. Keim, H. van Zwet,D. Camel, R. F. Mason), US 3,. 635,937, 3,637,636, 3,644,563, 3,644,564, 3,647,914, 3,647,915, 3,661,803, and 3,686,159 (1972 and 1973); W. Keim, *New J. Chem.* 1987, **11**, 531.

[68] V. Neff, T. E. Müller, J. A. Lercher, *Chem. Commun.* 2002, 906.

[69] W. A. Herrmann, C. W. Kohlpaintner, *Angew. Chem. Int. Ed. Engl.* 1993, **32**, 1524.

[70] (a) W. A. Herrmann, J. A. Kulpe, W. Konkol, H. Bahrmann, *J. Organomet. Chem.* 1990, **389**, 85; (b) W. A. Herrmann, J. A. Kulpe, J. Kellner, H. Riepl, H. Bahrmann, W. Konkol, *Angew. Chem. Int. Ed. Engl.* 1990, **29**, 391; (c) Union Carbide, EP 060,523 (1982); (d) Neftekhim, *Neftekhimija* 1981, **21**, 879.

[71] B. M. Trost , *Science* 1991, **254**, 1471 and *Angew. Chem. Int. Ed. Engl* 1995, **34**, 259.

[72] R. A. Sheldon, *CHEMTECH* 1994, **24**, 38; *Chem. &Ind.* 1992, 903 and 1997, 12; *Green Chem***.** 1999, **1**, G3.

[73] (a) M. McCarthy, H. Stemmer, W. Leitner, *Green Chem.* 2002, **4**, 501; (b) S. Kainz, D. Koch, W. Baumann, W. Leitner, *Angew. Chem.* 1997, **109**, 1699.

[74] B. Cornils, E. Wiebus, *Recl. Trav. Chim. Pays-Bas* 1996, **115**, 211.

[75] C. Christ, *Chem. Ing. Tech.* 2000, **72**, 42.

[76] Information given by F. A. Kirk, Synetix, Billingham UK, on the occasion of the DGMK-Conference “Synthesis Gas Chemistry”, Sep. 27-29, 2000 at Dresden (Germany), Proceedings, p. 131.

[77] (a) Ruhrchemie AG (G. Dämbkes, H. D. Hahn, J. Hibbel, W. Materne), DE 3,347,406 (1983); (b)

Ruhrchemie AG (G. Dämbkes, H. D. Hahn, J. Hibbel, W. Materne), EP 0,147,824 (1984); (c) Ruhrchemie AG (B. Cornils, W. Konkol, H. Bahrmann, H. W. Bach, E. Wiebus), DE 3,411,034 (1984) and EP 0,156,253 (1985); (d) Ruhrchemie AG (H. Bahrmann, W. Konkol, J. Weber, H. W. Bach, L. Bexten), DE 3,534,314 (1985); (e) Ruhr-chemie AG (L. Bexten, D. Kupies), DE 3,626,636 (1986); (f) Hoechst AG (L. Bexten, D. Kupies), EP 0,255,673 (1987); (g) Hoechst AG (G. Diekhaus, H. Kappeser), EP 0,322,661 (1988); (h) Hoechst AG (P. Lappe, L. Bexten, D. Kupies), DE 3,822,037 (1988), EP 0,348,833 (1989) and US 5,294,415 (1994); (i) Hoechst AG (J. Weber, L. Bexten, D. Kupies, P. Lappe, H. Springer), EP 0,367,957 (1989); (j) Hoechst AG (P. Lappe, H. Springer), DE 3,934,824 (1989) and EP 424,736 (1990); (k) Hoechst AG (P. Lappe, H. Springer), DE 4,025,074 (1990) and EP 0,475,036 (1991); (l) Hoechst AG (P. Lappe, H. Springer), EP 0,510,358 (1992); (m) Hoechst AG (I. Förster, K. Mathieu), EP 0,538,723 (1992); (n) Hoechst AG (W. Konkol, H. Bahrmann, W. A. Herrmann, C. W. Kohlpaintner), EP 0,544,091 (1992); (o) Hoechst AG (G. Diekhaus, H. Kappeser), EP 0,584,720 (1993).

[78] Among a multitude of filings: (a) Union Carbide Corp. (E. Billig, D. B. Stanton), EP 0,049,781 (1981) and 0,083,094 (1982); UCC (S. J. Dougherty), US 4,263,218 (1981); (E. Billig, D. B. Stanton), US 4,605,780 (1986); (b) BASF AG (H. -J. Kneuper, A. Aron, F. -M. Korgitzsch, M. Nilles, W. Harder, M. Roeper, R. Paciello), US 5,919,987 (1999), BASF (R. Paciello, H. -J. Kneuper, □ Geissler, M. Roeper), US 6,107,524 (2000), and BASF (B. Geissler, M. Roeper, R. Paciello, J. Decker, H. Voss, N. Mahr(, US 6,310,261 (2001); (c) Montedison SpA (G. Gregorio, G. Montrasi), US 3,968,134 (1976); (d) Elf (G. S. Silverman, P. Mercando), US 5,773,655 (1998); (e) BP (J. L. Carey), US 5,364,822 (1994); (f) UOP Inc. (E. H. Homeier, T. Imrai, D. E. Mackowiak, C. E. Guzolek), US 4,329,521 (1981); UOP (T. Imrai, E. -H. Homeier), US 4,374,287 (1983); UOP (T. Imrai), US 4,298,499 (1980); UOP (H. M. Quick), US 4,388,279 (1981); (g) Eastman-Kodak (R. L. Barnes), US 4,364,907 (1988), Eastman-Kodak (J. L. Cooper), US 4,388,476 (1983), WP 82-03,856 (1982), UOP (J. L. Dawes, T. J. Devon), US 4,400,547 (1981); (h) Mitsubishi (Y. Tsunoda, S. Tomita, C. Miyazawa, Y. Omori), GB 2,085,747 (1982); JP 81-02,994 (1981) [C. A. 1982, 96, 68297q]; (i) Shell (Z. Ali, J. Radder), FR 2,474,333 (1981); (j) Oxeno (K. -D. Wiese, M. Trocha, D. Röttger, W. Toetsch, A. Kaizek, W. Büschken), US 6,500,991 (2002) and Oxeno (D. Gubisch, K. Armbrust, B. Scholz, R. Nehring), US 6,015,928 (2000); (k) Ets. Kuhlmann (C. Demay), US 4,306,086 (1981); (l) ARCO (T. Chang), US 5,290,743 (1994).

[79] (a) Ruhrchemie AG (R. Gärtner, B. Cornils, L. Bexten, D. Kupies), DE 3,235,029 (1982), EP 0,103,845 (1983), and EP 0,107,006 (1983); (b) Ruhrchemie AG (L. Bexten, B. Cornils, D. Kupies), EP 0,175,919 (1985); (c) Ruhrchemie AG (H. Bahrmann, W. Konkol, J. Weber, H. W. Bach, L. Bexten), EP 0,216,315 (1986); (d) Hoechst AG (W. A. Herrmann et al.), EP 0,352,478 (1989).

[80] K. M. Beirne, *Chem. Engng.* 2002, Jan., 87.