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Biphasic Catalysis in Petrochemical Processes

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Abstract—Main features of the concept of homogeneous metal complex biphasic catalysis are considered. Different techniques for immobilization of metal complexes in water, ionic liquids, supercritical carbon dioxide, and fluorous solvents are discussed. The use of discussed approaches in petrochemical processes is analyzed.

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INTRODUCTION

At present the concept of sustainable development determines, to great extent, new trends in chemical industry [1, 2]. The key target in the development of new technologies is to find more highly selective processes that occur in mild conditions, involve less auxiliary stages (separation, purification), and produce less wastes and by-products [3, 4]. The modern petrochemistry makes use mostly of heterogeneous catalysts. The latter are not infrequently fairly inactive and nonselective, and the corresponding reactions are energy-consuming.

Homogeneous metal complex catalytic systems offer advantages of high activity and selectivity and mild reaction conditions. These systems have found application in such large-scale processes as the production of acetic acid by carbonylation of methanol, of acetaldehyde from ethylene, of propylene oxide by epoxidation, and of butanal and higher aldehydes by hydroformylation of alkenes [5].

Wide use of homogeneous metal complex catalysts is restricted first of all by the high cost of separation of catalysts from reaction products, which prevents catalyst recycling [6–8]. The common approach is distillation of solvent and reaction products, and this process frequently destroys the catalyst. High energy expenses for distillation and high probability of environmental pollution, too, form disadvantages of the mentioned technology.

A possible approach to go around these problems consists in immobilization of active metal complex on an organic or inorganic support. A series of highly efficient catalysts have been suggested for such processes as carbonylation, hydroformylation, hydrogenation, and epoxidation [7–9]. At the same time, there are certain problems associated with certain problems, specifically a much restricted mobility of catalysts, which strongly affects their properties, aggregation processes, and washing out of metal from catalyst. Only one industrial technology is known: CHIODIA has developed a methanol carbonylation technology (ACETICA) with rhodium complexes immobilized on cation-exchange resins as catalysts [10].

An alternative to immobilization of catalysts on heterogeneous supports is biphasic catalysis (Fig. 1) [11, 12]. The idea was suggested as far back as early 1970s for water-soluble catalysts and metal complex catalysis in salt melts [13–15]. After reaction in a biphasic system, catalyst should stay in one, whereas reaction products and starting materials in the other. As a result, metal complex is readily separated and can be recycled. The vary procedure of creating such a catalytic system was given the name catalyst immobilization in the liquid phase. This technology was used in hydroformylation of unsaturated compounds on cobalt carbonyls, when the catalyst was extracted into an alkaline medium and separated from reaction products. Further example of catalyst separation in a biphasic system is provided by oligomerization of ethylene on nickel-containing catalysts (SHOP) [5, 6]. The reaction is performed in butan-1,4-diol which

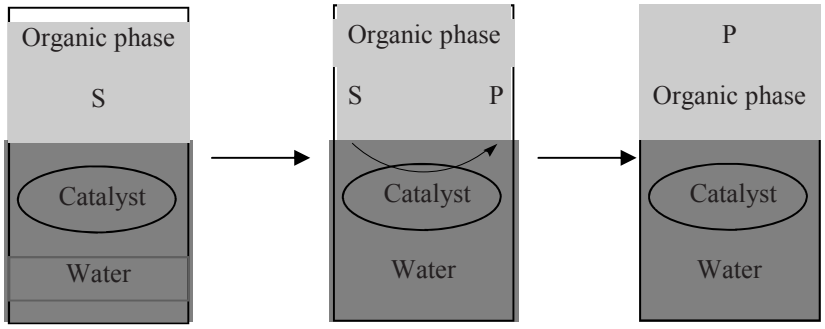


Fig. 1. Scheme of biphasic catalysis. Here and in further figures: *S* is substrate and *P* is product.

dissolves the active catalyst and does not mix with the resulting products.

The first example of large-scale application of water as the reaction medium in biphasic catalysis is the technology of hydroformylation of propylene to butanal, suggested by RuhrChemie and Rhone-Poulenc in 1984 [16–18]. At present a number of technological processes involving biphasic catalyst have been realized (Table 1) [5, 11, 12].

From the viewpoint of green chemistry, of particular interest is the choice of phase for catalyst immobilization, viz. an alternative reaction medium which could be separated and recycled together with catalyst. Biphasic catalyst suggests a minimum of auxiliary substances and use of ecologically friendly solvents. This minimizes the number of problems associated with catalyst regeneration and waste cleaning, which makes new catalytic systems attractive for industrial application.

Over the past two decades abundant experimental evidence has been accumulated in the field of biphasic catalyst, which made it possible to recognize an independent branch of research (called "multiphase" catalyst) [19]. Along with water, ionic liquids, supercritical carbon dioxide, and fluorous solvents are used. The present review considers principal features of several approaches to immobilization of homogeneous metal complex catalysts in biphasic systems.

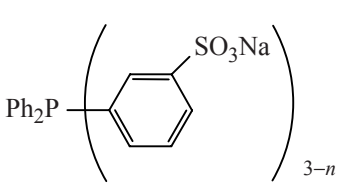
Biphasic Metal Complex Catalysis with Water

Water is the most suitable solvent from the ecological viewpoint, and it offers a number of advantages as the reaction medium [5, 16]. Because of the high polarity, water is easy to separate from most substrates and nonpolar organic solvents. Water is an accessible, nonflammable, and nontoxic solvent; it is colorless and odorless, and, therefore, its contamination is readily evident. The advantages of water include its ability to dissolve many gases, possibility of forming micelles and emulsions, and high dielectric constant, heat conductivity, heat capacity, and heat of vaporization.

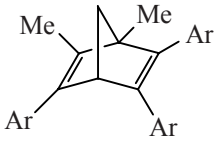
Since traditional organometallic compounds are poorly soluble in water, the main task to solve when developing water-soluble metal complex catalysts is to chose ligands ensuring immobilization in the aqueous phase. To this end, polar groups advantageous in terms of activity and selectivity and sharply enhancing water

Table 1. Biphasic catalysis in inrustry

Process	Company	Active metal	Solvent
Oligomerization of ethylene (SHOP)	Shell	Ni	Butane-1,4-diol
Hydroformylation of propylene and butylene	RuhrChemie/Rhone-Poulenc	Rh	Water
Hydrogenation of unsaturates aldehydes	Rhone-Poulenc	Ru	Water
Telomerization of butadiene	Kuraray	Pd	Water /Sulfolane
Dimerization of propylene	IFP	Ni	Ionic liquids
Oligomerization of ethylene (Linear-1TM)	UOP	Ni	Sulfolane

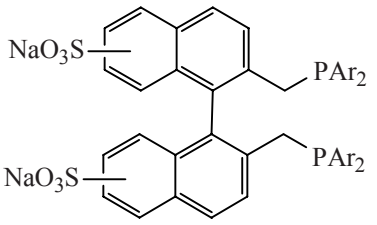


I $n = 0$ (TPPTS)
II $n = 2$ (TPPMS)
III $n = 3$ (TPPDS)



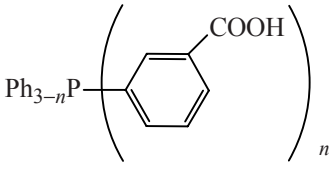
Ar = 4-$SO_3NaC_6H_4$

IV

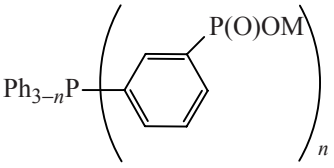


Ar = 4-$SO_3NaC_6H_4$

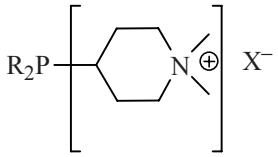
V



VI

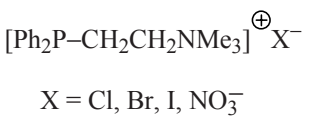


VII



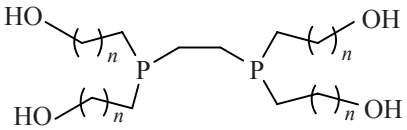
R = Cy, *t*-Bu; X = Cl, I

VIII



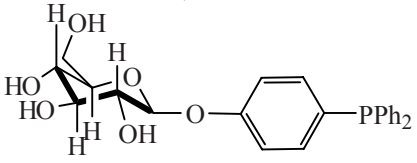
X = Cl, Br, I, NO_3^-

IX

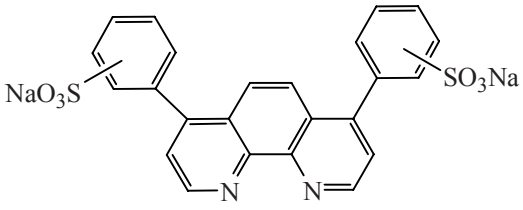


$n = 0, 2, 3$

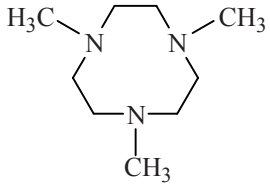
X



XI



XII



XIII

Table 2. Petrochemical processes involving aqueous phase catalysis

Reaction	Active metal	Ligand	Reference
Hydroformylation	Rh	**I–VII, IX–XI**	[20–31]
Hydrogenation	Rh, Ru, Ir	**I–III, V, VI, IX**	[32–43]
Carbonylation	Pd	**I–III**	[44–46]
Waker oxidation	Pd	**XII**	[47]
Dimerization of butadiene	Pd	**I, II**	[48]
Hydrocyanation	Ni	**I**	[49–50]
Metathesis	Ru	**VIII**	[51]
Epoxidation	Mn	**XIII**	[52]

solubility and preventing catalyst transfer to the organic phase after the reaction has been complete are introduced into the structure of catalytic complexes.

The most commonly used polar groups are the ionogenic carboxy, phosphonate, sulfo, quaternary ammonium, and hydroxy groups **I–XIII**. The number of ligands suggested as a result of active research over the past two decades is over the past two-decade research is quite large.

Complexes of such ligands with transition metals have been actively studied in hydroformylation, carbonylation, and hydrogenation of unsaturated compounds, hydrocyanation, oxidation, polymerization, metathesis, and other petrochemical processes (Table 2).

The best studied reaction is hydroformylation of propylene on a rhodium catalyst on the basis of sodium

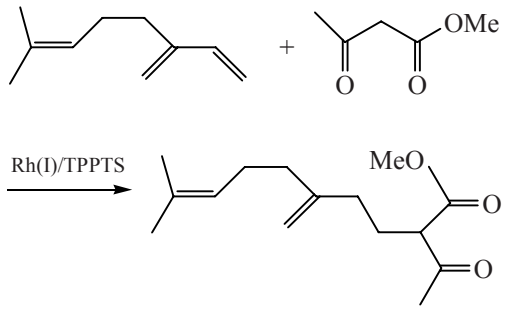
Table 3. Comparison of industrial hydroformylation processes of different companies [5, 11]

Process parameters	RuhrChemie	Shell	UCC	RuhrChemie/Rhone-Poulenc
Catalyst	$HCo(CO)_4$	$Co(CO)_3PR_3$	$HRh(CO)(PPh_3)_3$	$HRh(CO)(TPPTS)_3$
Pressure, MPa	20–30	4–8	1.5–2.0	4–6
Temperature, °C	140–180	160–200	85–115	110–130
Propylene conversion, %			85–89	85–99
n-Butanal/*iso*-butanal selectivity	80/20	88/12	92/8	94/6
Expenses for catalyst separation	High	High	High	Low

tris(3-sulfophenyl)phosphine (TPPTS **I**), realized in industry (600 thsd. ton butanal per year) [5].

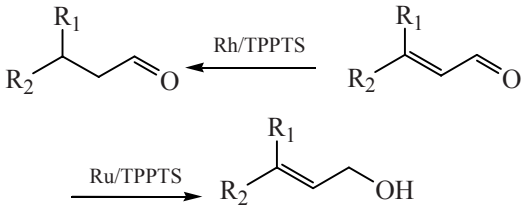
This process offers much advantages over hydroformylation on traditional rhodium or cobalt catalysts (Table 3). Even though the process occurs at slightly higher pressures and temperatures than homogeneous rhodium-catalyzed hydroformylation, its selectivity with respect to normal aldehyde is higher, and the catalyst can be easily separated and recycled. As a consequence, this process in total is much less (by about 10% compared to the UCC process by 40% compared the RurhChemie process) expensive and more effective in terms of the use of raw materials and energy. The *E* factor (the ratio of the weight of generated waste to the total weight of the end product) which is a measure of the waste level of a process is less than 0.04, implying a high environmental efficiency of the technology [2, 4, 11, 21–24].

Complexes with TPPTS are presently used in some other industrial processes. Thus water-soluble rhodium complexes catalyze one of the stages of the synthesis of geranylacetone, an intermediate product of the synthesis of vitamin A from myrcene (7-methyl-3-methylene-octa-1,6-diene) and methyl acetoacetate [53, 54].

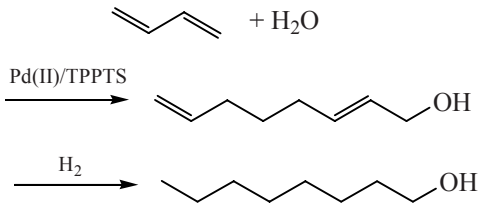


The solubility of complexes in water allows not only easy separation of the catalyst and its recycling, but also ensures a much higher selectivity in the target product.

Unsaturated aldehydes are selectively hydrogenated to alcohols in the presence of ruthenium TPPTS complexes; this technology is realized in industry. It should be noted that the regioselectivity of hydrogenation reactions is controlled by the active metal: With rhodium complexes, hydrogenation involves double bonds, while with ruthenium complexes, the carbonyl group [34].



The Kuraray Company has developed a technology for biphasic telomerization of butadiene [5, 48]:



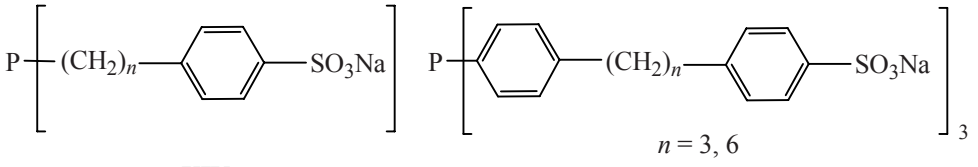
The reaction occurs under CO_2 pressures of up to 2 MPa in the presence of a palladium TPPMS complex with a 50-fold excess of the triethylammonium hydrocarbonate ligand and sulfolane. The selectivity in the target octa-2,7-dien-1-ol is higher than 93%. The subsequent hydrogenation gives octan-1-ol (total production capacity 5000 ton/year).

It should be noted that the rates of reactions with nonpolar substrates in a biphasic system with water-soluble metal complexes are fairly low, which is primarily explained by the poor solubility of such substrates. As a result, special approaches are required to drive the reactions. Among such approaches we can

mention the use of surfactants or soluble polymers as components of the catalytic system. In this case, the reactions occur in surfactant micelles or polymeric aggregates and are much accelerated. Thus, the use of cetyltrimethylammonium bromide together with Rh/TPPTS in hydroformylation accelerated formation of aldehydes from higher alkenes due to solubilization of substrates in micelle nuclei and concentration of active complex in micelle surface layer. Importantly, anionic surfactants, dodecyl sulfonate, or dodecyl benzosulfonate had almost no rate effect [55–58]. Surfactant water-soluble polymers, such as poly(ethylene glycol) or cationic polymers, can also be used as additives [59, 60].

Substrate transfer to the aqueous phase is facilitated by compounds forming host–guest complexes, specifically modified cyclodextrins or calixarenes. This approach was realized in Waker oxidation [61, 62], oxidation of alkylaromatic compounds [59], hydroxylation of aromatic compounds [63], hydrogenation [64], hydroformylation [65], carbonylation [66], and oxidative dimerization of β-naphthols [67]. In this case, substrate is transferred to the aqueous phase as an inclusion complex, which affects not only catalyst activity, but also makes it possible to control process selectivity. Thus, in the Waker oxidation of 1-alkenes in the presence of calix[4]arenes, the maximum yield of methyl ketone was obtained in the case of hex-1-ene, and in the presence of calix[6]arenes, in the case of oct-1-ene [68, 69].

One more approach to enhance catalyst activity in reactions with nonpolar substrates is to apply ligands capable of solubilizing substrates. In this case, an ionogenic group with a linear alkyl residue is introduced in the ligand molecule; as a result, a single molecule combines the properties of a surfactant and a metal complex [70–73]. As a result, the active center is fixed inside micelles, which strongly enhances catalytic activity. Thus, rhodium complexes with ligands **XIV**–**XVIII** catalyze biphasic hydroformylation of higher alkenes [74–80], whereas complexes with ligands **XIX**–**XX** effectively catalyze hydrogenation of a series of unsaturated compounds [81, 82].



XIV

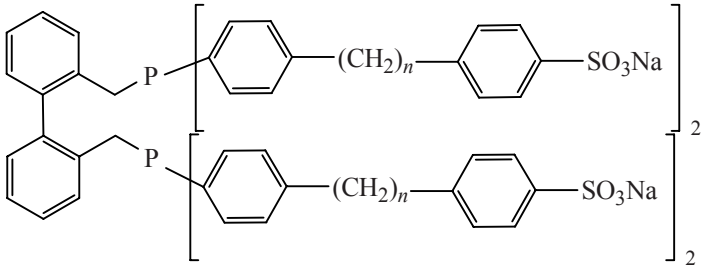
$n = 3, 6$

XV

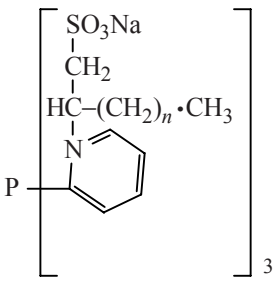
$[Ph_2P–CH_2CH_2NMe_2R]^{\oplus}X^-$

XVI

$R = C_mH_{2m+1}$, $m = 8, 12, 16$; X = Cl, Br



XVII



XVIII

$Ph_2P(CH_2)_nCOOH$
$n = 1–11$

XIX

$Ph_2P(CH_2)_nPO_3Na_2$

XX

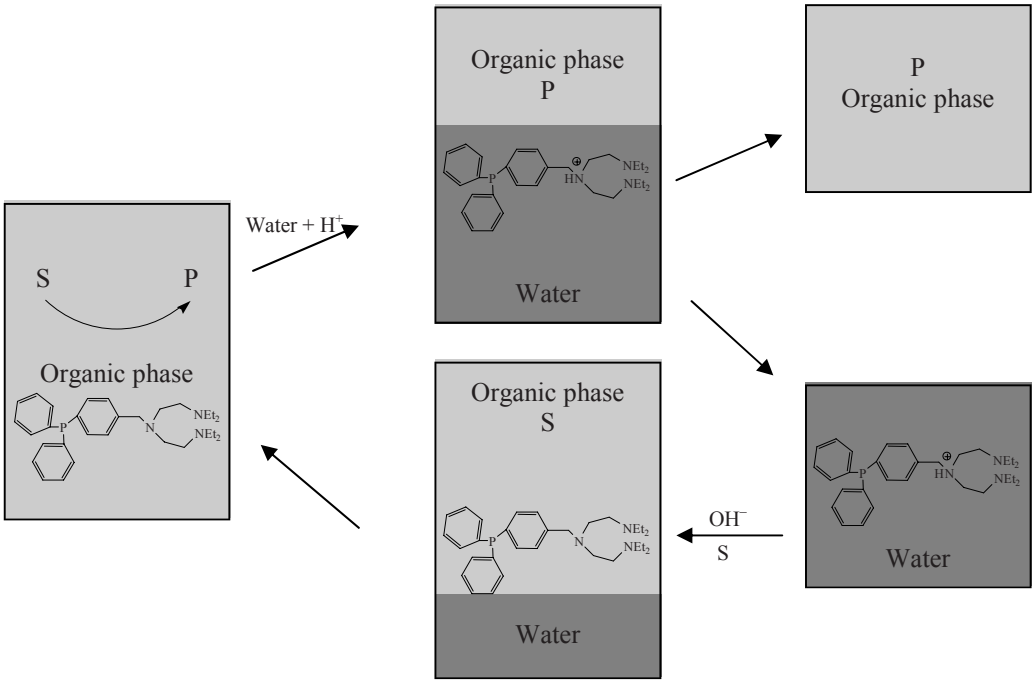
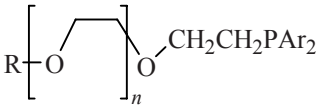


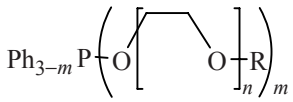
Fig. 2. Biphasic catalysis with use of amine ligands.

Of particular interest in terms of catalyst separation and subsequent recycling are ligands containing amino groups. In this case, the solubility of a complex in the aqueous phase can be controlled by varied pH of the medium. In a neutral medium, such catalysts are readily soluble in apolar solvents or substrates. When the reaction is complete, an acid is added, the ligand is quaternized, and the catalyst almost completely passes to the aqueous phase and thus readily separated from reaction products. To return the catalyst to the organic phase for recycling, to adjust pH to neutral would suffice (Fig. 2) [83–85].

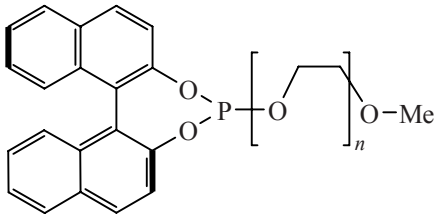
Apart from introduction of ionogenic or hydroxy groups, the water solubility of ligands can be enhanced via fixing complexing groups on water-soluble polymers and oligomers, such as polyethylene oxide, polycarboxylates, and polymers on the basis of alkylated acrylamides (ligands **XXI**–**XXXIII**). Catalysts with such ligands have found application in hydroformylation of higher olefins, carbonylation, hydrogenation of multiple bonds, metathesis, cross coupling, and oxidation of aromatic compounds and alkanes [86–94].



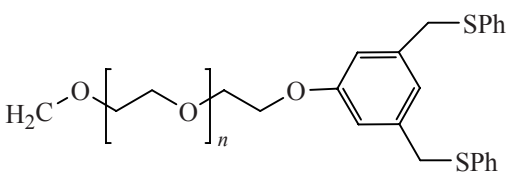
Ar = Ph (**XXI**); Ar = O-2-*iso*-Pr-5-MePh (**XXII**)



XXIII, n = 10–120, m = 1, 2



XXIV, n = 16–17



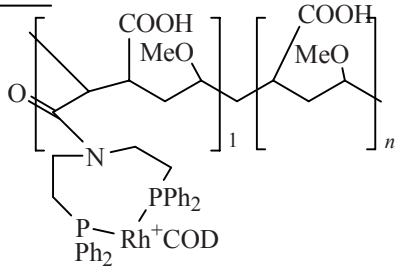
XXV, n = 20–40

For example, in [89, 90] we have studied the use in hydroformylation as catalysts of rhodium complexes on the basis of poly(ethylene oxides) **XXI–XXXIII** modified by terminal phosphorus-containing groups with various electron density on the phosphorus atom. Using such metal complexes, we obtained, in high yields, aldehydes from dec-1-ene, dodec-1-ene, styrene, propenylphenol, and allylphenol under biphasic hydroformylation conditions.

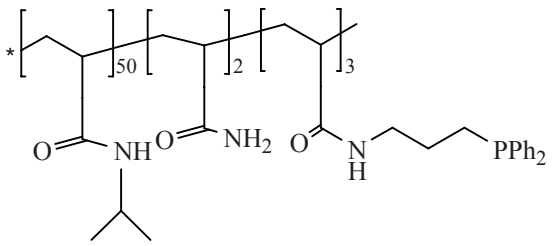
For metal complexes on the basis of modified poly(ethylene oxides) **XXI–XXXIV,** whose water solubility is temperature-dependent, one more elegant approach was suggested and given the name temperature-controlled phase-transfer catalysis [5, 87, 88]. In the water–organic solvent biphasic system at high temperatures, macromolecular metal complexes with phosphine-containing ligands fixed on ethylene oxide oligomers almost completely pass to the organic phase (where the reaction occurs) and then return to the aqueous phase on cooling. As a result, the catalyst can be readily separated from nonpolar products and recycled. The advantages of this approach for hydroformylation and hydrogenation of unsaturated and nitroaromatic compounds were demonstrated on an example of a series of macromolecular complexes of rhodium with various phosphine and phosphite ligands.

Polyacids and polyamides (for example, **XXVI** and **XXVII)** offer broad possibilities for the design of water-soluble ligands. Polar groups incorporated in the polymer chain enhance solubility of such molecules in various polar media, which allows the molecular structure to be fairly ready modified via introduction of various ligands. Modification of acid or amide groups in the chain affects such properties of the polymer as its ability to transfer nonpolar substrates into the aqueous phase, temperature dependence of solubility, etc. [93–96]. Such catalysts were used in hydrogenation, cross coupling, and hydroformylation.

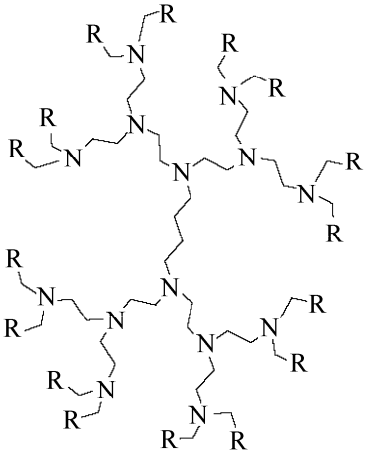
Complexes of dendimers **XXVIII** and **XXIX** form one more type of metal complex catalysts that have been actively used in biphasic hydroformylation, carbonylation, hydrogenation, metathesis, oxidation, etc. [97–100]. The interest in dendrimers is explained by the fact that they are fairly readily separated from reaction products in biphasic systems or be means of

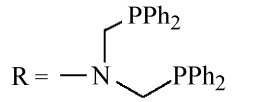


XXVI, n = 4–10

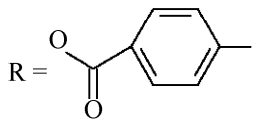


XXVII

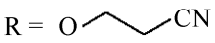




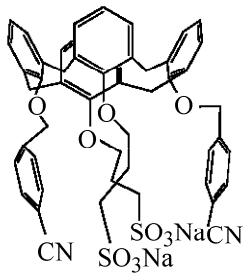
XXX



XXXI



XXXII



XXXIII

XXVIII, R = PPh_2
XXIX, R = CH_2CN

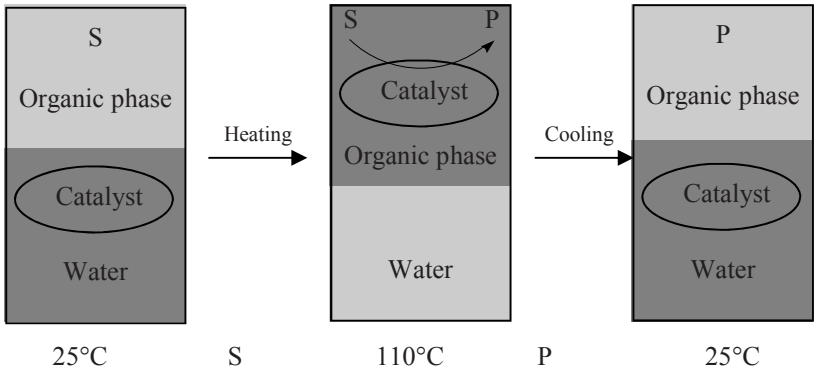


Fig. 3. General scheme of temperature-controlled phase-transfer catalysis with use of ligands **XXI—XXIV.**

membrane filtration. Due to the roughly equal size of dendrimer catalyst molecules, the losses of metal turn to be negligible, and the catalyst itself almost does not loose activity. Second, the presence of catalytically active groups on the outer surface makes it possible to prepare catalysts with a high content of active metal which, due to the dendrimer structure, is substrate-accessible. By introducing active centers into the internal chains or nucleus of dendrimers one can control the selectivity of the catalyst due to the formation of a regular structure around the catalytic center. Third, dendrimers, primarily water-soluble, can immobilize hydrophobic molecules inside, like molecular micelles [100–104].

It should be underlined that catalysts on the basis of dendrimers can exhibit an unusual selectivity. For example, in the Waker oxidation of alk-1-enes, catalyzed by a bimetallic complex of dendrimer **XXIX** with Pd(II) and Cu(II), a high selectivity in the oxidation of terminal double bonds was observed. This phenomenon was explained in terms of a negative dendrite effect with respect to internal double bonds of unsaturated compounds. Catalysts on the basis of palladium dendrimer complexes allowed selective hydrogenation of one double bond in dienes [100].

Of particular interest in biphasic catalysis are ligands that combine, in a single molecule, the properties of metal complexes and the ability for molecular recognition and substrate phase transfer. As a rule, these are water-soluble receptor molecules with complexing groups, such as cyclodextrins (ligands **XXX**–**XXXII**) and calixarenes (ligand **XXXIII**) [105–107]. Catalysts with such ligands offer the advantages of a much higher activity compared to corresponding mixtures and high reaction selectivity [107].

The reactions can be accelerated not only by modifying ligands, but also by using biphasic systems with partial temperature-dependent solubility. At low temperatures such systems comprise immiscible water-containing and nonpolar phases (for example, aqueous ethanol–hexane). As the temperature increases, phase separation disappears. If a catalyst is soluble in the polar phase and almost insoluble in the nonpolar phase, the reaction at an elevated temperature occurs in homogeneous conditions. After cooling, the second phase forms, and the metal complex catalyst is readily separated (Fig. 3). The potential of this approach was exemplified by hydroformylation and hydrogenation [94].

Another approach that has been applied in hydroformylation of higher olefins is based on a sharp decrease of the mutual solubility of an organic solvent and water in the presence of dissolved carbon dioxide (Organic-Aqueous Tunable Solvents, OATS). Thus, water–THF phase separation is attained at CO_2 pressures above 2 MPa, which makes it possible to separate and recycle a water-soluble rhodium catalyst (Rh/TPPTS) [108, 109].

Immobilization of Metal Complex Catalysts in Other Solvents

The activity of biphasic catalytic systems in reactions with nonpolar substrates can be enhanced by using alternative solvents which, on the one hand, meet green chemistry requirements , and, on the other, serve to extend the range of substrates and processes suitable for biphasic catalysis. Such solvents include fluorinated hydrocarbons, ionic liquids, and supercritical CO_2 [7, 11]. Of interest are polar oligomers, in particular oligoethylene oxides, as one of the phases [58, 110].

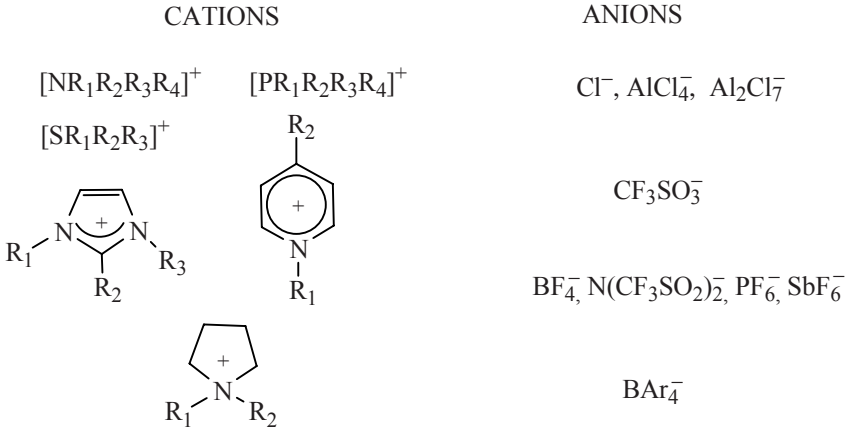
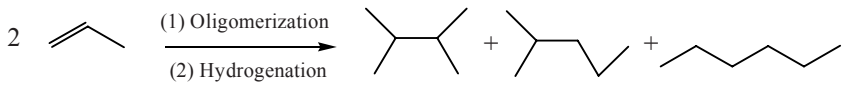


Fig. 4. Ionic liquids used as solvents in catalysis.

Ionic liquids are ionic organic compounds that are liquid at room temperature (Fig. 4). They are stable, low-volatile, and readily modifiable by varying the structure of the anion or cation [111, 112].

Ionic liquids are highly polar and can be used for immobilization of polar complexes. In this case, nonpolar reaction products are isolated via simple phase separation, which was abundantly exemplified. Ionic liquids are actively used as a medium for such reaction as hydroformylation of unsaturated compounds, hydrogenation of dienes to monoenes, hydrogenation of aromatic compounds, oxidation, cross coupling, metathesis, etc. [113, 114].

At present the French Oil Institute has developed a technology for dimerization of propylenes to isomeric hexenes (Difasol process), catalyzed by nickel complexes in imidazole-based chloroaluminate ionic liquids [115, 116]:

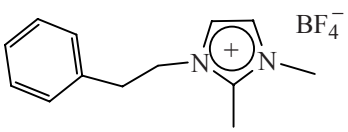


The nickel-containing cationic catalyst is generated directly in the ionic liquid, and chloroaluminate anions act as co-catalysts. The investments in this case are much lower than for the traditional homogeneous Dimersol process. The catalyst is readily separated from nonpolar reaction products.

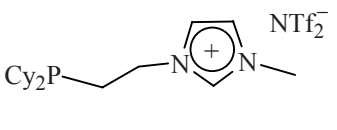
To immobilize metal complexes in ionic liquids, ligands comprising a complex-forming group and the cationic fragment of an ionic liquid are used (ligands **XXXIV**–**XXXVIII**).

Such approach allows a much more effective immobilization and reduction of possible metal losses. For example, ligand **XXXIV** was used in ruthenium-catalyzed hydrogenation of double bonds, ligand **XXXV** in metathesis, ligand **XXXVI** in cross coupling, and ligands **XXXVII** and **XXXVIII** in hydroformylation [117–122].

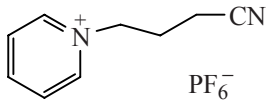
The feasibility of supercritical carbon dioxide for immobilizing metal complexes is explained by reduced diffusion constraints in this solvent and simplified



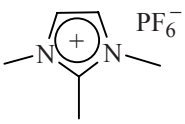
XXXIV



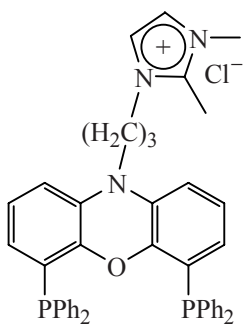
XXXV



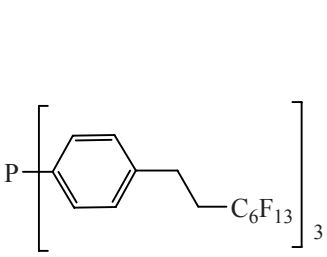
XXXVI



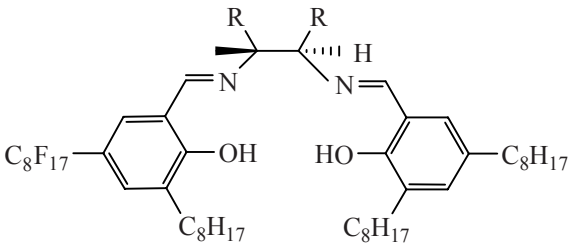
XXXVII



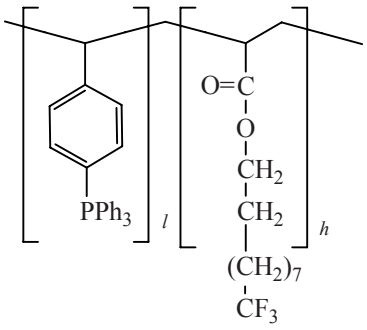
XXXVIII



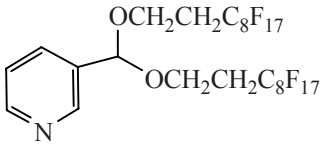
XXXIX



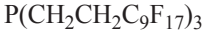
XL



XLI



XLII



XLIII

catalyst separation from reaction products [123–125]. In this case, the process can be accomplished by two schemes (Fig. 5) [5, 124, 125]:

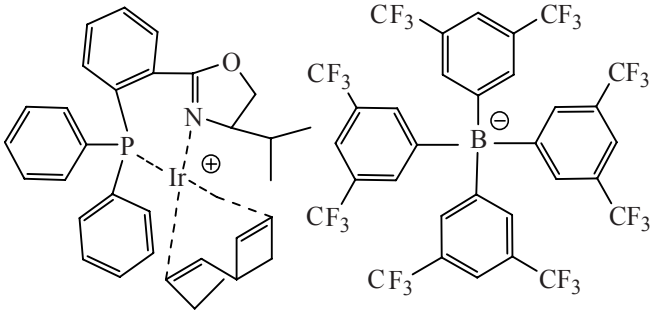
– the reaction is performed in biphasic conditions and products are extracted into supercritical carbon dioxide;

– the reaction is performed in a homogeneous system in the presence of a catalyst that is soluble in supercritical CO_2 and insoluble in reaction products.

The first scheme suggests the use of co-solvents, such as ionic liquids or liquid oligoethylene glycols. The efficiency of this scheme was exemplified by hydroformylation, hydrovilylation, and hydrogenation [124–128]. In the second case, special modification of ligands with perfluorinated groups is generally required to enhance catalyst solubility in supercritical CO_2 [129, 130]. For example, rhodium complxes with ligands **XXXIX** and **XLIII** proved to be active in hydroformylation, hydrogenation, and cross coupling [129–132] and those with ligand **XLI** in hydrogenation [133].

Another approach to immobilization involves synthesis of ionic complexes whose solubility is provided by the counterion (see below) [134].

This approach was applied, in particular, in the development of hydrogenation catalysts [125, 134].



Finally, broad possibilities for separation of metal complex catalysts are opened up by fluorous solvents, such as perfluorohexane, perfluorooctane, perfluoromethylcyclohexane, etc. [135–137]. These quite low-polarity substances do not mix even with nonpolar organic solvents, such as hidrocarbons. They are inert and resistant to oxidation, exhibit a low toxicity, inflammable, and readily dissolve gases.

An advantage of fluorous solvents in that their ability to dissolve nonpolar hydrocarbons is temperature-dependent. This allows reactions with metal complex catalysts soluble in the fluorous solvent to be accomplished at elevated temperatures in homogeneous conditions. After cooling, the phase with the catalyst can be easily separated from reaction products (Fig. 6).

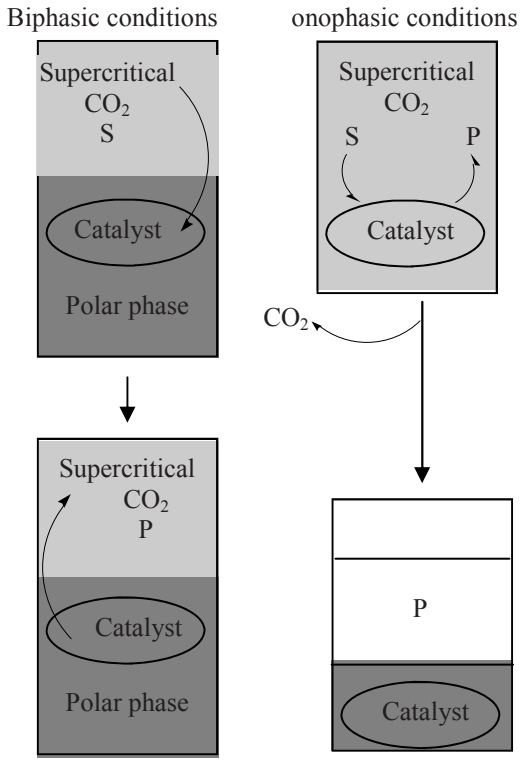


Fig. 5. Possible schemes of use of supercritical CO_2 in metal complex catalysis.

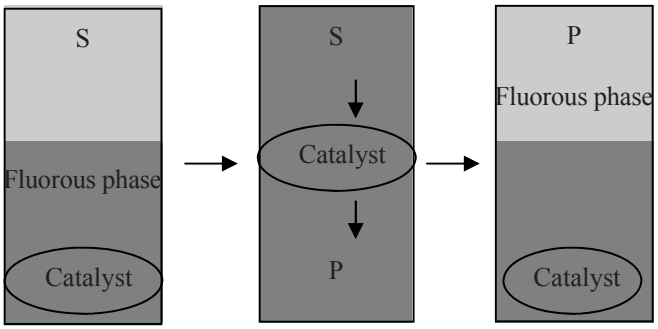


Fig. 6. Scheme of a catalytic process involving fluorous solvents.

Such catalysts are synthesized, like in the case of supercritical CO_2, by introducing fluorine-containing fragments in a ligand [135–142] or fluorine-containing conterions in a complex (for example, $[CF_3(CF_2)_7(CH_2)_3]_3CH_3N^+$ for heteropolyacids) [143]. Catalysts of this type were found to effectively catalyze hydroformylation [135, 138, 139], cross coupling [140], oxidation, epoxidation, etc. [141–143].

Research in biphasic catalysis has outlined a new field in the chemistry of homogeneous metal complex catalysts, which meets the requirements of green chemisty. The diversity of possible approaches in the development of novel biphasic catalytic systems offers broad opportunities for their practical application, and more and more enhancing environmental requirements to petrochemical processes are without doubt simulating of further research in this field.

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