

ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Homogeneous Stationary Catalysis

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Abstract—Concept of stationary homogeneous catalysis is formulated. According to this concept, a catalyst solution is permanently present within the reactor and the product is removed from the reactor in the form of a gas (vapor) or a stratifying fluid (solution). This technology combines advantages of the homogeneous and heterogeneous catalyses. Some approaches to development of the technology under consideration are presented.

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Owing to their molecular (ionic) nature, homogeneous catalysts exhibit high activity, selectivity, and reproducibility. In a homogeneous system, it is easier to perform heat and mass transfer, which is particularly important when carrying out reactions in industrial apparatus. A fundamental disadvantage of homogeneous catalysts is that they should be separated from the reaction product and regenerated (or newly synthesized) after each conversion.

From this standpoint, heterogeneous catalysts have an apparent advantage. Therefore, much effort is applied and money invested to attempts to create catalysts that would combine advantages of the homogeneous and heterogeneous variants.

The simplest way to heterogenize a homogeneous catalyst is to deposit it onto a support as a film. In this way, the catalyst “Polyphosphoric acid on silica gel” (PPA-S), used for oligomerization of propylene, is manufactured*. However, film-type systems rapidly lose their activity because the catalyst is carried away by the flow of raw materials and products [1]. Therefore, researchers started to fix active groups to the support by chemical bonding. The best known among catalysts of this kind is a copolymer of styrene and divinylbenzene with sulfuric acid groups (KU-2, Amberlyst).

At the end of the last century, researchers spent several decades for heterogenization of metal-complex

catalysts [2–8]. However, complexes “sewn” to a solid support were, as a rule, “washed away” in the course of a reaction [7, 8]. Frequently, systems of this kind combined disadvantages, rather than advantages of both kinds of catalysis.

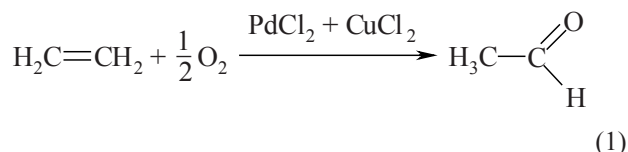
It should be noted that even the best of heterogenized catalysts cannot, in principle, obviate problems associated with hindrances to heat and mass transfer, caused by introduction of a solid phase into the reaction zone. However, several processes have been developed in which the advantages of the heterogeneous and homogeneous catalyses could be fully combined. Some of these processes have been implemented on a large industrial scale. It seems to be of use, for development of studies in this promising area, to consider characteristic examples of processes of this kind with emphasize on the conditions required and ways to create these conditions.

The technology of processes of this kind is very simple: a solution of a homogeneous catalyst is permanently situated within a reactor into which raw materials are fed; the reaction product is discharged in the form of a gas (vapor) or as a fluid (solution) stratifying from the catalyst solution.

We first consider several industrially implemented on a large scale or promising processes with stationary homogeneous catalysts.

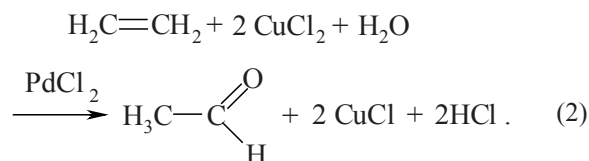
Synthesis of acetaldehyde by oxidation of ethylene and hydration of acetylene. Acetaldehyde is produced by oxidation of ethylene by passing a mixture of ethylene and oxygen through an aqueous solution of the catalyst at 90–130°C and 0.3–1 MPa:

* It should be specified that many catalysts based on phosphoric acid and various modifications of silicon oxide contain no free phosphoric acid and do not belong to the type under consideration [1].

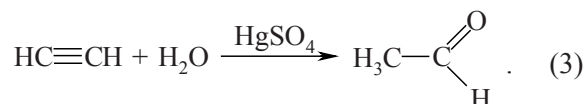


Ethylene is taken in an excess amount (mostly for making the mixture of gases unexplosive). The resulting acetaldehyde is discharged as a vapor together with the remaining ethylene, which is recycled [9]. The catalyst solution is permanently situated within the reactor; this is a typical case of the homogeneous stationary catalysis.

In another variant of ethylene oxidation [9], the synthesis is divided into two stages, each performed in a separate reactor. In the first of these, ethylene is oxidized with CuCl_2 to give acetaldehyde under catalytic action of palladium chloride:



In the second reactor, CuCl is oxidized to give the starting CuCl_2 :

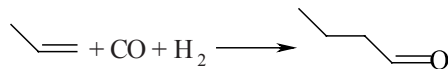


It is easy to verify that combination of reactions (2) and (3) gives reaction (1) and numerous repetition of stages (2) and (3) provides the catalytic reaction (1). Gaseous acetaldehyde is discharged from the first reactor. It is possible to feed air, instead of oxygen, into the second reactor because there is no gas circulation in it. The catalyst solution passes from one reactor into the other, and either oxidizes ethylene or is subjected to oxidation itself. This is a somewhat complicated variant of the homogeneous stationary catalysis. Although the catalyst solution is not permanently situated within a single reactor, it is reasonable to consider a system of two reactors as a single unit from which the catalyst is not removed together with the product.

In both variants of acetaldehyde synthesis, the yields are close to 95% [9]. The process has been developed by Wacker company. At present, a large number of plants are working on the basis of this technology, with a total annual output capacity of several million tons of acetaldehyde.

For similar syntheses of acetone from propylene and of methyl ethyl ketone from butene-1 by oxidation, only a stage-by-stage variant can be used [9].

Before the process of acetaldehyde synthesis by oxidation of ethylene was developed, the main process employed for its manufacture was hydration of acetylene by the Kucherov method:



Here, too, a homogeneous stationary catalyst was used: acetylene was bubbled through an aqueous solution of sulfuric acid and Hg^{2+} and Fe^{3+} sulfates at 80–100°C and 0.1–0.2 MPa, with a conversion of 50–60%. Aldehyde was distilled-off with the excess amount of acetylene [10]. The process failed to withstand competition with ethylene oxidation because of the high cost of acetylene and toxicity of mercury.

Synthesis of aldehydes by hydroformylation of olefins. In the early stage, this reaction was performed exclusively with a cobalt–carbonyl catalyst. Only the discovery of the substantially higher activity of rhodium–carbonyl [11] and rhodium–carbonyl–phosphine [12] complexes and of their nonvolatility laid foundation for development of homogeneous stationary catalytic systems for hydroformylation.

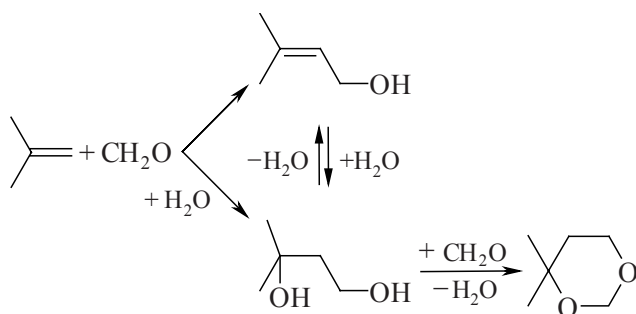
Commonly, the catalytic system permanently situated in the reactor is a solution of the carbonyl–phosphine rhodium complex of the type $\text{HRh}(\text{CO})(\text{PR}_3)_3$ and of an excess amount of phosphine in high-boiling by-products of the reaction. Originally, triphenylphosphine (PPH_3) served as a phosphine; later, phosphines of more complex composition were used, mostly for improving the selectivity [13, 14].

For propylene, the process is performed at a rhodium concentration of 200–300 ppm, phenylphosphine content of 5–10%, temperatures of 90–110°C, and pressures of 1.5–2 MPa. To intensify the vapor-phase discharge of the butyric aldehydes obtained, the starting synthesis-gas is circulated [13, 14].

Processes with the catalytic system under consideration were introduced into industrial practice nearly simultaneously in 1974–1976 by Celanese company and by Union Carbide in conjunction with Davy Powergas and Johnson Matthey. At present, a large number of installations is operating by this method all over the world, with a total annual output capacity of several million tons of n-butyric aldehyde [13, 14].

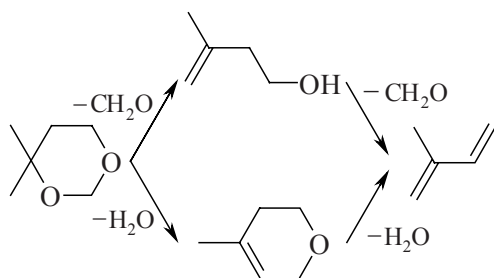
Synthesis of isoprene from isobutene and formaldehyde. Originally, synthesis of isoprene by this method was performed in two stages [15, 16]. In the first stage, isobutene was reacted with formaldehyde by the Prins reaction to give 4,4-dimethyldioxane-1,3 (Scheme 1). The reaction was carried out in the liquid phase at temperatures of 90–100°C and pressures of 1.6–2 MPa with a homogeneous catalyst, sulfuric (concentration of about 1%) or oxalic (2–3%) acid.

Scheme 1. Synthesis of 4,4-dimethyldioxane-1,3 in manufacture of isoprene



In the second stage, dimethyldioxane isolated by rectification was heterogeneously-catalytically cleaved in the gas phase on phosphate catalysts at 350–380°C to give isoprene (scheme 2) [17].

Scheme 2. Gas-phase high-temperature cleavage of 4,4-dimethyldioxane-1,3



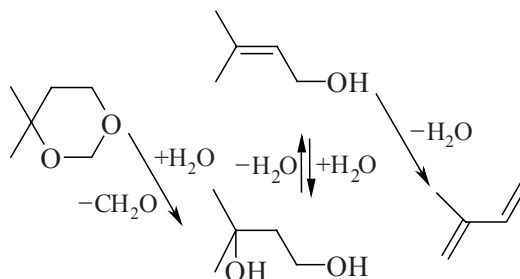
This process was implemented in the USSR in 1964–1965 for the first time in the world.

A weak point of the process is its second stage, and especially necessity for high temperature, gross energy expenditure, and frequent regeneration of the catalyst (not rarely than once in every 3 h).

These shortcomings could be overcome by using the homogeneous stationary catalysis. Dioxane is decomposed in a liquid phase with an aqueous solution of an acid as a catalyst at 150–170°C. Thus, the process

temperature is lowered by 200°C. Dimethyldioxane is delivered into the catalyst solution, the forming isoprene is removed as a vapor, which provides a shift of equilibria in its direction (scheme 3).

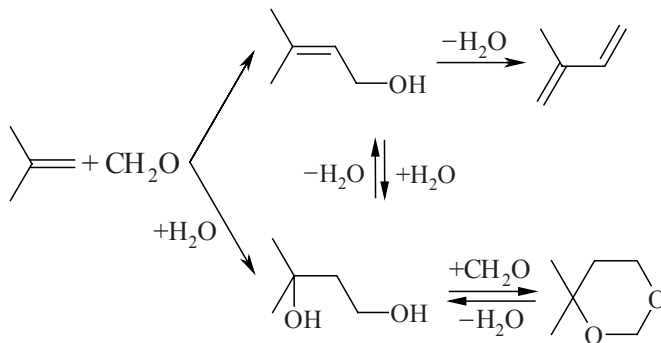
Scheme 3. Liquid-phase low-temperature cleavage of 4,4-dimethyldioxane-1,3 with a homogeneous stationary catalyst



One more molecule of isoprene can be obtained from the forming formaldehyde and isobutene (or its precursor, trimethylcarbinol) additionally introduced into the reaction zone [16].

Application of the stationary homogeneous catalysis also enables a single-stage synthesis of isoprene (Scheme 4).

Scheme 4. Single-stage synthesis of isoprene



Scheme 4 is produced from scheme 1 by inclusion of the reaction of dehydration of an unsaturated alcohol to give isoprene; in Scheme 4, there is no need in intermediate formation of dimethyldioxane.

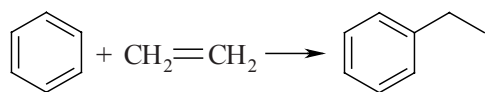
Such a technology has been developed by a Japanese company Kuraray [18] and Russian Eurochim–SPb-Trading Limited-Liability Company and Nizhnekamskneftekhim Open Joint-Stock Company [16], and also by Neftekhimstart (earlier Yarsintez) Limited-Liability Company [19]. An aqueous solution of phosphoric acid (0.5–2.5%) or of its mixture with boric acid (15–30%) with pH 0.5–2.5 is used as a stationary homogeneous

catalyst [18]. Other acids can also be used. The synthesis is performed at temperatures of 150–220°C and pressures of 1–2 MPa. The process was implemented by Kuraray on an installation with an annual output capacity of 30 thousand tons of isoprene [16]. It has been noted that it is advisable to perform the reaction first at 90–110°C (with dimethyldioxane formed) and then at 140–160°C, with discharge of isoprene [19].

It should be noted that application of the stationary homogeneous catalysis in processes performed by schemes 3 and 4 is a necessary condition for the success of the reaction, because it provides a shift of equilibria toward isoprene being removed.

A combined process based on Schemes 1, 3, and 4, developed by Eurochim–SPb-Trading and Nizhnekanskneftekhim [16], was implemented at Nizhnekanskneftekhim in 2006–2007. The annual output capacity of the process exceeded 100 thousand tons.

Synthesis of ethylbenzene, isopropylbenzene, and gasolines by alkylation. Ethylbenzene is produced by alkylation of benzene with ethylene:



The conventional technology consists in that benzene and ethylene are passed through a liquid catalytic complex prepared from aluminum trichloride, polyethylbenzenes (realkylation products), and hydrogen chloride. The process is performed at a temperature of about 100°C and pressures of 0.15–0.20 MPa with a yield of about 95%. The forming ethylbenzene stratifies off and flows out of the reactor, with the liquid catalyst permanently situated in the reactor [20, 21]. In contrast to the above-considered processes with a homogeneous stationary catalyst, the product formed in alkylation reactions is discharged from the reactor as a fluid, rather than as a gas.

Benzene is alkylated with propylene using both the catalytic system described for ethylene and sulfuric acid [21]. In the last case, the process is performed at temperatures of 35–40°C, pressure of 1.2 MPa, and sulfuric acid concentration not exceeding 90% (because, otherwise, the benzene ring is sulfonated).

The described stationary homogeneous-catalytic alkylation techniques experience competition with high-temperature (150–200°C) liquid-phase processes (with dissolved aluminum trichloride used in low

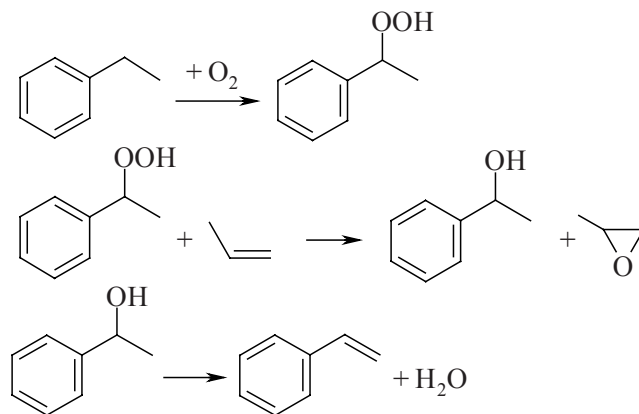
concentrations) and gas-phase (200–400°C) techniques with heterogeneous acid catalysts. On the whole, tens of millions of tons is annually produced in the world.

Alkylation of isobutane with butenes to obtain high-octane components of gasolines is also based on the stationary homogeneous catalysis. Sulfuric acid (88–100%) or anhydrous liquid hydrogen fluoride serve as catalysts. The optimal conditions are 0–10°C and ~0.2 MPa for sulfuric acid and 20–40°C and ~1 MPa for hydrogen fluoride [20, 21]. In alkylation of isoparaffins with olefins, the carbon skeleton undergoes isomerization, which makes stronger the branching and raises the octane number of the products. The annual production of alkylates of this kind in the United States and Western Europe exceeds 50 million tons. This is the largest scale application of the homogeneous catalysis.

Synthesis of styrene by dehydration of 1-phenyl ethyl alcohol. The main part of styrene is produced by dehydrogenation of ethylbenzene on an iron–chromium–potassium oxide catalyst at 600°C with a selectivity of 90%.

A lower, but still measured in millions of tons annually (170 thousand tons a year in Russia) amount of styrene is produced also from ethylbenzene, but via its liquid-phase oxidation to a hydroperoxide. The hydroperoxide and propylene are used to manufacture propylene oxide and 1-phenyl ethanol (Scheme 5).

Scheme 5. Joint production of styrene and propylene oxide



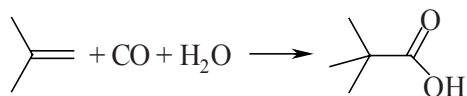
The last stage, dehydrogenation of 1-phenyl ethanol is performed in the industry in the gas phase at temperatures of 280–320°C on γ -aluminum oxide as a catalyst, with a selectivity of 96–97% at a conversion of 90%. The process has been developed by Halcon, ARCO, and Oxirane companies [22].

The R & D activities have been aimed at improving the yield and diminishing the energy expenditure by performing dehydration at lowered temperatures in the liquid phase [23–27]. In the process, 1-phenyl ethanol is continuously delivered into the catalyst solution permanently situated in the reactor, and styrene and water are discharged in the form of vapors. Strong acids serve as catalysts, and the process is performed under normal or lowered pressure.

For the reaction performed at 210°C and 200 mm Hg with the concentration of para-toluenesulfonic acid in the supplied 1-phenyl ethanol equal to 95 ppm, a selectivity of 98% has been reported [24]. For 205°C, atmospheric pressure, and sulfuric acid, a yield of 99.9% at a conversion of 99.95% has been noted in another patent [27].

Acidic stationary homogeneous catalysts can also be used for other dehydration reactions, e.g., trimethylcarbinol into isobutene in purification and concentration of isobutene via its intermediate hydration. In a similar process performed via intermediate formation of methyl-tert-butyl ether, catalysts of this kind must also be effective in decomposition of this ether.

Synthesis of neo acids by hydrocarboxylation of olefins. Hydrocarboxylation of olefins in a strongly acidic medium is used to produce branched acids:



H₃PO₄/BF₃/H₂O or BF₃·H₂O serve as catalysts [29–31], with olefins of cracking fractions C7–C11, and trimers or tetramers of propylene used as raw materials. The process is commonly performed at 40–70°C and 7–10 MPa. The reaction occurs at carbonium ions and is accompanied by strong isomerization, including that of skeletal nature, which yields strongly branched carboxylic acids (neo acids).

Schering company has developed an elegant process for manufacture of neo acids with the use of homogeneous stationary catalysts [30, 32]. The role of catalysts is played by oxonium salts formed by tetrafluoroboric acid with water or methanol: pH₃O⁺[BF₄][–] or [CH₃OH₂]⁺[BF₄][–]. These liquid salts permanently fill the reactor into which an olefin, water, and carbon monoxide are delivered from below. The temperature in the reactor is 40–50°C, and pressure, 15 MPa. The resulting carboxylic acids are insoluble in the catalyst, they stratify-off and are

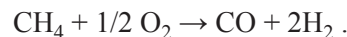
discharged from the upper part of the reactor. The process was perfected on a pilot installation [30, 32], but there is no evidence about its industrial implementation.

Production of hydrogen by water-gas shift reaction. It is particularly easy to perform the stationary homogeneous catalysis in the cases when reaction products are gases. The most demanded of gases is hydrogen, whose world's annual output is 50 million tons [33], and a prognosis to 2010 gives 100 million tons [34]. For a changeover to hydrogen energetics, it is necessary to annually produce 300–400 million tons by the mid-XXI century, and up to 800 million tons, by the end of the century [33, 34].

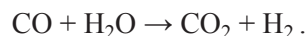
In the most widely used methods for manufacture of hydrogen, natural gas is converted in the first stage with steam at 750–780°C in the presence of nickel on aluminum oxide



or is subjected to incomplete oxidation without a catalyst



In the subsequent stage, carbon monoxide reacts with steam (water gas shift reaction) first at 370–440°C in the presence of an iron–chromium catalyst and then at 230–260°C on a zinc–chromium–copper catalyst:



The water gas shift reaction to give hydrogen can also be performed with carbon monoxide obtained in gasification of fossil coal.

It has been shown that the water gas shift reaction can be carried out in the presence of a homogeneous stationary catalyst, aqueous solution of basic substances (e.g., potassium carbonate). The reaction well proceeds at 250–350°C and pressures of 5–20 MPa [35]. These conditions are rather severe, but a certain hope is instilled by studies aimed at performing the reaction in the presence of metal-complex catalysts at substantially lower temperatures (80–180°C) [35–37].

Advantages and disadvantages of the stationary homogeneous catalysis. The processes considered employ a homogeneous catalyst and take full advantage of its virtues: activity, selectivity, reproducibility and

good heat and mass transfer. At the same time, the catalyst remains within the reactor, as also does the heterogeneous catalyst, and there is no need to separate it from the reaction product and regenerate at the end of every cycle. Also, the loss of the catalyst becomes smaller.

An apparent disadvantage of the stationary homogeneous catalysis consists in additional requirements to reactants, which restrict its applicability fields. For example, in a variant with evaporation of the product, the catalyst should be nonvolatile, and the product, by contrast, volatile. The method of hydroformylation with rhodium–carbonyl–phosphine complexes, considered above, is good for ethylene and propylene, but is not suitable for higher olefins. True, the distillation-off of the product can be intensified by circulation of the gas involved in the reaction (as in the case of propylene hydroformylation and acetylene hydration) or an inert gas (including that in the supercritical state [38, 39]), but this makes higher the power consumption. Another apparent way is to use a vacuum (as in production of styrene [24]).

The variant of the stationary homogeneous catalysis, based on stratification-off of the product, requires that the product or its solution should be well separable from the catalyst solution under the reaction conditions. This problem can be solved by choosing an appropriate solvent for the catalyst and, when necessary, for the product as well. This issue is little understood now and requires extensive studies of general nature.

Approaches to development of homogeneous stationary catalytic systems. Owing to the fact that the possibility of volatilization of the product as a gas (vapor) is supplemented with the possibility of its stratification-off as a fluid (solution), homogeneous stationary catalytic systems can be developed for numerous reactions. However, it is rather difficult to combine the optimal reaction conditions with an effective discharge of the product, and, therefore, some approaches to solution of this problem are to be considered.

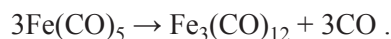
Design of a catalyst. For systems with product discharged in the form of a vapor it is important to provide nonvolatility of the catalyst. This can be done by raising the molecular mass via oligomerization and polymerization, cluster formation, and introduction of “heavy” ligands.

For example, phosphoric acid is converted under heating to pyrophosphoric (diphosphoric) acid:



The subsequent splitting-off of water yields chains, rings, and branched structures. It is these oligomerization and polymerization processes that account for the comparatively long service life of the “Polyphosphoric acid on silica gel” catalyst mentioned at the beginning of this communication.

Similarly to the polymerization of phosphoric acid via splitting-off of water, complex compounds are converted into clusters by splitting-off of ligands:



$\text{Fe}(\text{CO})_5$ is a volatile fluid (bp 102.5°C at 760 mmHg), whereas $\text{Fe}_3(\text{CO})_{12}$ has the form of crystals that can be sublimed only at 0.1 mm Hg.

The advisability of ethylene hydroformylation in the presence of $\text{Rh}_6(\text{CO})_{16}$ can be mentioned as an example of application of clusters in the stationary homogeneous catalysis; the possibility of doing so has been experimentally confirmed by one of the authors.

Introduction of “heavy” ligands is an efficient method for making larger the molecular mass in metal-complex catalysis. For example, if cobalt hydrocarbonyl $\text{HCo}(\text{CO})_4$ boiling at 47°C [4] is used as a catalyst in hydroformylation, it is impossible, with ethylene as a raw material and propionic aldehyde as a product (bp 49°C, to distill-off the aldehyde, with the catalyst remaining in the reactor. At the same time, use of a phosphine-substituted rhodium complex $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ yielded a stationary homogeneous catalyst from which rhodium is not evaporated at all. In this case, the molecular mass was raised from 172 for $\text{HCo}(\text{CO})_4$ to 918 in the case of $\text{HRh}(\text{CO})(\text{PPh}_3)_3$.*

The extreme case of ligand “weighting” are polymeric ligands [41]. These ligands can be obtained [42] by introduction of coordinating groups (phosphine, amine, hydroxy) into polymers, such as polyethylene or polystyrene. In contrast to heterogenization, these polymers with attached complexes should be dissolved in the reaction medium. Use of such designs in a close area has been described: it has been suggested to use

* The stated should not be understood in such a way that purposeful efforts are undertaken to lower the volatility; rhodium–carbonyl–phosphine catalyst was found in an empirical search with emphasis on activity and selectivity.

homogeneous catalysts based on polymeric ligands to enable separation of the homogeneous catalyst from the product of membrane filtration [41, 43, 44]. As far as it is known, polymeric (oligomeric) ligands have not been used so far for lowering the volatility.

The interaction with the reaction medium (solvent) because of the polarity and formation of hydrogen bonds also lowers the volatility of the catalyst, but these factors become even more important in design of stationary homogeneous catalytic systems from which the product is separated by stratification.

In this variant, the distribution of the catalyst among the immiscible liquid phases can be substantially changed by introduction of polar and nonpolar groups into the catalyst molecule. These groups favor or hinder dissolution of substances containing these groups in the corresponding reaction media. Sulfuric acid is widely replaced as a catalyst with toluenesulfonic acid when passing from an aqueous reaction medium to an organic one. Accordingly, the amount of toluenesulfonic acid in the low-polarity phase of a two-phase system will be larger than that of sulfuric acid.

In the metal-organic catalysis, introduction of polar substituents into ligands produces impressive results. A classical example is replacement of triphenylphosphine with sulfonated triphenylphosphine. $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ is well soluble in benzene and insoluble in water, whereas the corresponding $\text{HRh}(\text{CO})[\text{P}(\text{meta-C}_6\text{H}_4\text{SO}_2\text{ONa})_3]_3$ is excellently soluble in water and insoluble in benzene. In the two-layer water–benzene system, the whole amount of the first catalyst is in benzene, and the whole amount of the second, in water [41, 45].

In addition to lowering the volatility and optimizing the polarity, it is important, in development of stationary homogeneous systems, to provide the thermal stability of a catalyst. This problem arises when the product is insufficiently volatile and the reactor temperature is to be raised. It was found that the highest stability is observed for compounds in which the reacting atom is moderately shielded by substituents (ligands); weak shielding favors intermolecular interactions and subsequent conversions, whereas an excessive “closeness” causes cleavage reactions [48]. However, an increase in stability by optimization of the shielding may cause a decrease in the catalytic activity, and, therefore, a balance should be found between the thermal stability and catalytic activity.

When modifying homogeneous catalysts for use in the stationary mode, it is important to preserve their activity and selectivity. Here, the electronic (of donor or acceptor type) influence of substituents (ligands) is highly important. As in the case of thermal stability, steric effects exert a strong influence. For evaluation of the electronic and steric effects of substituents and ligands, it is particularly convenient to use universal (common to all fields of chemistry) constants determined for ligands and substituents of all possible types [49].

Optimization of the reaction medium. In the stationary homogeneous catalysis based on product evaporation, the solvent (reaction medium) should be nonvolatile and thermally stable. The use of triphenylamine enabled experiments on dehydration of 1-phenyl ethanol into styrene at temperatures of up to 330°C [26]. It seems promising to use diphenyl and diphenyl oxide or their mixture, which presently serves as a high-temperature heat-carrying agent (diphenyl mixture, dilyn, Dau-therm A).

However, high-boiling by-products inevitably accumulate in the reaction medium and should be separated in a special unit (by extraction, distillation, or other methods). Therefore, it is more technologically convenient to use as the reaction medium the high-boiling products themselves, because their removal is simplified in this case. High-boiling reaction products have been used as a medium in hydroformylation [13, 14] and have been patented for use in dehydration of 1-phenylethanol into styrene [25].

As regards providing the solubility of a catalyst or reagent, it is useful to keep in mind, if they are electrolytes, that the solubility of many electrolytes increases in proportion to cubed dielectric constant of a solvent [50].

In the stationary homogeneous catalysis based on stratification-off of the product, requirements to the solvent (reaction medium) strongly differ from those in the case of an evaporating product. Here, the ideal reaction medium should well dissolve the raw material, and poorly dissolve the product (or the solvent together with which the product is removed from the reaction zone). For example, hydroformylation of propylene in an aqueous solution of a complex of rhodium with sulfonated triphenylphosphine occurs successfully, but the reaction rate substantially decreases on passing from propylene to hexene-1, which is less soluble in water [45].

It follows from the simplest considerations that, for stratification to occur, the reaction medium and the product should substantially differ in polarity. According to the Hildebrand and Scotch theory, the mutual solubility on nonelectrolytes increases as the difference between their solubility parameters $\delta = (E/V)^{1/2}$, where E is the heat of evaporation and V is the molar volume, becomes smaller [50–52].

For an approximate evaluation of the miscibility of the product and the catalyst solution, the mixotropic series of solvents can be used [53, 54]. In this series, water and lactic acid are at one end of the series, and petroleum ether and paraffin oil, at the other. The farther from each other are solvents in this series, the more probable is their immiscibility.

Of particular interest for the method of homogeneous stationary catalysis are ionic fluids [38, 39, 55, 56]. For typical compounds with ionic bonding, of the type of sodium chloride, melting to give a fluid occurs at 600–1000°C. However, certain organic ions for compounds that are in the liquid state even at room temperature. Nearly a century ago, ethylammonium nitrate $[\text{C}_2\text{H}_5\text{NH}_3]^+\text{NO}_3^-$ melting at 12°C was synthesized. At present, ionic fluids with alkyipyridines and dialkylamidazoles as cations and NO_3^- , SO_4^{2-} , BF_4^- , PF_6^- , AlCl_4^- as anions are widely used in laboratory practice.

It is important for a homogeneous stationary catalysis performed with products discharged in the form of a gas (vapor) that ionic fluids are completely nonvolatile and their upper applicability limits are determined by thermal stability. If, however, it is required that the product or its solution should stratify off, a key role is played by the fact that ionic fluids are immiscible with typical organic (low-polarity) reagents and solvents.

Ionic fluids are incombustible and low-toxic. They well dissolve acidic, basic, and metal-complex catalysts. A monograph devoted to metal-complex catalysis in ionic fluids has even been published [57] and it is frequently mentioned in the monograph that, in these fluids, the catalyst solution stratifies from the product.

Owing to the strong polarizing and solvating effect, ionic fluids can raise the reactivity of substances and activity of catalysts. For example, depolymerization of Nylon-6 into the starting monomer, caprolactam, was performed in ionic fluids at 300°C with a 86% yield in the presence of *N,N*-dimethylaminopyridine as a catalyst, with the monomer distilled-off as it was formed [58]. The

authors performed the process many times in the batch mode, and the optimality of the stationary homogeneous catalysis is apparent here. Reactions of this type are highly topical for utilization of worked-out polymeric articles.

However, promising ionic fluids have a rather complex structure, can be synthesized in multiple stages, and their starting components are expensive. As a result their estimated cost is at the level of 25–50 € per liter [56].* This circumstance hinders their wide use, although just the technique with a stationary catalyst, in which the spreading of the catalyst over the entire technological system is ruled out, is especially favorable for diminishing the loss of the catalyst.

It should be noted that oxonium salts used in synthesis of neo acids seem to be typical ionic fluids. Moreover, they are more easily accessible, but, for some reason, are not mentioned in the relevant monographs and reviews.

Closely related technological solutions. Because the chemical reaction is combined in the homogeneous stationary catalysis with separation of the product, this technique can be classed as a combined process. If the product is released as a new phase (liquid, gaseous), it is suggested to name the combined process reactive-separatory. When the product is removed as a result of distillation, this is a reactive-distillatory (rectifying, evaporative) technique. If the product is discharged with the solvent, we have a reactive-extractive process [59, 60].

To the considered variant of the homogeneous stationary catalysis, in which the product is separated by evaporation from the reactor, is closely related the technique in which the product is evaporated in a separate apparatus after being discharged from the reactor, and the still bottoms are recycled back into the process. This is done if the product is insufficiently volatile and the catalyst is sufficiently thermally stable. For example, in the case of hydroformylation, the stationary homogeneous catalysis is ideally suitable for ethylene, occupies an intermediate position for propylene [14], but is economically inferior to evaporation of the resulting aldehydes in a separate evaporator after the reaction for butylenes [61]. On passing to hydroformylation of higher olefins, the stationary homogeneous catalysis

*Such a value is acceptable. For comparison, let us estimate the cost of 1 kg of a rhodium catalyst in the hydroformylation process considered above. At a rhodium cost of \$4000 for a troy ounce, €/€ = 1.35, and rhodium concentration of 250 ppm, the cost of 1 kg of the catalyst (without the cost of phosphine) is 24 €.

again becomes optimal, but now with stratification of the product in the reactor.

To the variant of homogeneous stationary catalysis, in which the product is separated by stratification in the reactor, is closely related the "biphase catalysis" technique [41, 45]. A catalyst solution is in one liquid phase, and the raw material and the product, in the other; the phases are vigorously agitated in the reactor and then are separated in the separator, from which the catalyst solution is delivered back into the reactor. The biphase catalysis becomes stationary (or, more precisely, biphase stationary) if the catalyst solution and the product can be stratified in the reactor (alkylation, synthesis of neo acids). If, by contrast, it is impossible, when developing a stationary homogeneous catalyst, to separate the product and the catalyst solution without using a separator with conditions differing from the reaction conditions, we have a typical biphase catalysis. Intermediate variants are also possible.

In the biphase catalysis, as also in the homogeneous stationary catalysis, an important role is played by the solubility of raw materials in the catalyst bed; it was already noted that the reaction rate decreases in the case of hydroformylation in a two-phase system on passing from propylene to hexene-1.

The biphase catalysis has been successfully used by Ruhrchemie and Rhone-Poulenc companies for hydroformylation of propylene and butene [14, 15]. An aqueous solution of a rhodium complex with sulfonated triphenylphosphine serves as a catalyst, the technique is employed to annually manufacture several hundred thousand tons of aldehydes. However, this technique is not used as widely all over the world, as Union Carbide, Davy Powergas, and Johnson Matthey processes.

CONCLUSIONS

(1) In the stationary homogeneous catalysis, the catalyst solution permanently remains within the reactor and the product is removed from the reactor as a gas (vapor) or stratifying-off fluid (solution); there are no stages of separation and regeneration of the homogeneous catalyst.

(2) Relationships between the stationary homogeneous catalysis and close technological solutions (biphase catalysis) and more general fields of technology (combined processes) were considered.

(3) Despite the significant advances in industrial implementation of separate processes, no due attention is

presently given to the method of stationary homogeneous catalysis. An important role is played here by difficulties encountered in attempts to combine the reaction and isolation of products from the reaction mixture.

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