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Prospects in the application of alkoxo-technology in heterogeneous catalysis

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Abstract. The main principles, characteristic features, advantages, and disadvantages, of the application of alkoxo-technology† for the preparation of heterogeneous oxide catalysts and carriers are examined. The bibliography includes 293 references.

I. Introduction

The traditional technologies for the preparation of inorganic oxide materials, including carriers and heterogeneous catalysts, which are based on the use of inorganic acid salts, oxides, and hydroxides as precursors, have to a large extent exhausted their possibilities. The probability that a qualitative jump in the development of this field can be achieved and that the characteristics of materials, can be appreciably improved on their basis in extremely small. One of the promising approaches to the overcoming of many disadvantages of the traditional technology and to the creation of new materials and the improvement of the quality of those already known involves the application as starting materials (precursors) of the alkoxides of various chemical elements (metal alkoxides and alkyl esters of ortho-acids). This method has been called alkoxo-technology. Abroad, alkoxo-technology, which is one of the variants of sol-gel technology, made it possible to initiate the manufacture of a series of advanced materials for microelectronic, optic fibre, aerospace, and other branches of engineering.[1–3] The number of publications on this topic throughout the world runs into thousands, but in the Russian scientific and patent literature they are represented by few examples and are either of a purely academic character or are concerned with simple variants of alkoxo-technology associated with the employment of only silicon alkoxides or their mixtures with inorganic salts. This situation has led to an underestimate of the possibilities of the use of alkoxo-technology in heterogeneous catalysis. Furthermore, it was evident from the very beginning that the most promising aspect of its practical application involves the preparation of catalysts and carriers for the latter.[4]

The reviews[5–11] concerning the application of alkoxo-technology in heterogeneous catalysis are relatively inaccessible and are limited to the consideration of a narrow range of problems. The aim of the present review is to survey the most important advances in the field of alkoxo-technology (mainly during the last decade) and also to assess the potential possibilities of its use for the preparation of oxide catalysts and carriers.

† Alkoxide sol–gel methods (Translator).

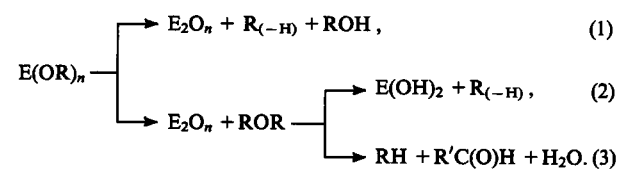
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II. The mechanisms of the conversion of alkoxides into oxides

Alkoxides are converted into oxides in thermal and thermooxidative degradation and hydrolytic processes and in the interaction with the surface OH groups and hydroxides.

In the synthesis of oxide powders by spray pyrolysis in an inert medium, in the chemical vapour-phase deposition of coatings, and in the preparation of coatings and bulky materials from solutions of alkoxides or the products of their partial hydrolysis, the alkoxides undergo thermal decomposition. A schematic illustration of this process, proposed by Tishchenko as early as the past century,[12] can be represented as follows:



(1) (2) (3)

Here the symbol E designates the fundamental element. The composition of the organic product of the thermal degradation (ethers ROR, alkenes $R_{(-H)}$, alkanes RH, aldehydes R'CHO, and alcohols ROH) is determined mainly by the nature of the alkyl group and of the chemical element and also by the process temperature. For example, alkaline earth metal oxides are capable of dehydrating ethers and the decomposition of their alkoxides proceeds predominantly via path (2). Alkoxides with

secondary and tertiary alkyl groups decompose most readily via path (1) (since the heterolytic dissociation of the R—O bond and the abstraction of a proton from the carbonium ion are facilitated under these conditions).[13] For catalytic purposes, it is desirable to employ the alkoxides derived from higher alochols, since in this case the oxides formed have the most extensive porous structure. Products of the thermal decomposition of alkoxides are usually nonstoichiometric oxides E_2O_{n-x} and this factor may be used deliberately for the preparation of a series of catalysts. The thermal decomposition conditions are chosen in such a way that certain catalytically active substances are segregated not in the oxide but in the metallic form (the reduction is effected by the organic thermal degradation products). This mechanism can be achieved also in a mixture of an alkoxide (precursor of the porous carrier) and of the salt undergoing thermal decomposition (precursor of the metal catalyst).

The thermal decomposition of alkoxides for the preparation of catalysts and adsorbents is usually carried out under thermooxidative conditions in the presence of O_2. Together with reaction (1)–(3), the alkyl groups of the alkoxide and of the organic degradation products are oxidised. The compounds formed may interact with the alkoxide: the water evolved in the thermal oxidation hydrolyses the alkoxide, as a result of which the decomposition is sharply accelerated and assumes a chain character.

Not only the final process temperature but also the rate of its increase exert a definite influence on the course of the thermooxidative degradation, which is associated with the sintering of the elementoxane skeleton at high temperatures, decrease in the oxidation surface, and hindrance to the diffusion of oxygen and volatile products. Although all this leads to a sharp fall in the rate of decomposition of alkoxides, nevertheless it is not always taken into account in practice.

Alkoxides are usually converted into oxides by hydrolysis in which the following reactions take place:[14,15]

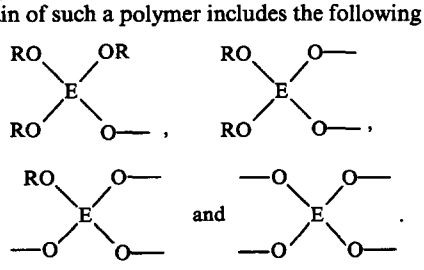
$$E(OR)_n + H_2O \longrightarrow (RO)_{n-1}EOH + ROH, \quad (4)$$

$$(RO)_{n-1}EOH + E(OR)_n \longrightarrow (RO)_{n-1}EOE(OR)_{n-1} + ROH, \quad (5)$$

$$2(RO)_{n-1}EOH \longrightarrow (RO)_{n-1}EOE(OR)_{n-1} + H_2O. \quad (6)$$

The hydrolysis [reaction (4)] of the majority of alkoxides proceeds at a high rate and the overall rate of hydrolysis is determined by diffusional and not kinetic factors. In order to complete the condensation with formation of ROH or H_2O [reactions (5) and (6)], an increased temperature and/or the presence of acidic or basic catalysts is usually required. The dimers formed on condensation enter into further reactions with H_2O and alkoxide hydroxides. The composition and structure of the final hydrolysis (hydropolycondensation) product depend mainly on the nature of the chemical element and the alkyl group, the pH of the reaction medium, and the ratio of the alkoxide and water.

If water has been added in an amount theoretically insufficient for the complete elimination of the RO groups via reactions (4)–(6), for example less than 2 moles of H_2O per mole of the alkoxide of a tetravalent element, then alkoxyelementoxane polymers (oligomers) of different structure are formed. The chain of such a polymer includes the following units:



By selecting the reaction conditions, it is possible to regulate the ratio of such units and the ways in which they are joined together and to synthesise polyalkoxyelementoxanes having a predominantly linear or branched structure, which makes it possible to control the porous structure of the oxides formed on their decomposition.

If the hydrolysis of the alkoxides proceeds in an excess of H_2O, then, depending on the nature of the element, the oxides E_2O_n, the hydroxides $E(OH)_n$, or the oxide hydroxides $EO_x(OH)_{n-2x}$, containing residual RO groups, are formed. This is associated with the reversibility of the reactions and the formation of three-dimensional elementoxane skeletons with sterically 'frozen' RO groups incapable of further hydrolysis or condensation with OH groups.

Complete hydrolysis is usually carried out in aqueous alcoholic media with a 10–20-fold excess of H_2O (relative to the theoretical amount). The hydrolysis products are isolated in the first stage in the form of nanometer-sized particles, so that the reaction medium remains optically transparent. Such a solution, called a sol, may be stabilised by special additives and may be used in the deposition of catalytic coatings and as a binder for carriers. Partly chelated alkoxides, for example $Ti(OR)_2(acac)_2$, are often used for the preparation of sols from the readily hydrolysable aluminium, titanium, or zirconium alkoxides, since this ensures a quieter course of hydrolysis (without the formation of powders or gels) and the stabilisation of the sol formed.

If the sol is not stabilised, the shape and size of the primary particles change during its ageing and gradually combine into various associated species. The sol loses its fluidity and is converted into a gel. The sol–gel transition may be regulated by selecting the solvent and the catalysis and by altering the temperature. An important factor is that this process is fairly controllable and that it does not entail, in contrast to the preparation of a sol from inorganic salts, the laborious washing away of extraneous ions and an increased purity of the product is attained. Although the SiO_2 carriers obtained, for example, from sodium silicates, are cheaper than those obtained from ethyl silicates, they retain 1% of Na_2O even after prolonged washing,[16] which lowers their thermal stability and interferes with a series of catalytic processes.

Water and organic solvents are removed from gels by drying in air at different temperatures or by treatment in an autoclave at temperatures and pressures above the critical values for the solvent being removed (super-critical or hypercritical conditions). Xerogels and aerogels are then obtained respectively. The specific surface (S_{sp}) and the pore volume of the aerogels are somewhat greater than those of the xerogels, but the latter are cheaper and therefore have found more extensive application. Owing to the difference between the capillary tensions in pores with different diameters, large specimens crack and disintegrate during the drying of the xerogels, which, however, does not preclude their application, since the xerogels are usually employed only at starting materials for the preparation of various forms of catalysts and carriers (with the aid of comminution, moulding with a binder, and sintering). In recent years, methods have been developed for the drying of the gels under the usual conditions without cracking.[17] For this purpose, chemical additives, for example formamide, which control the drying process, are introduced into the solutions being hydrolysed.

In most cases only one oxide is insufficient for the preparation of a carrier or catalyst with the optimum combination of properties. Mixed oxides are frequently used in heterogeneous catalysis. When alkoxo-technology is employed, they are obtained by the joint hydrolysis of two and more alkoxides or by the hydrolysis of an alkoxide in the presence of inorganic compounds with subsequent drying and partial sintering. The main problem in the hydrolysis of a mixture of alkoxides is that of the generation of mixed elementoxane fragments E–O–E′, which ensures the homogeneity of the system at the atomic (molecular) level and ultimately makes it possible to reduce sharply the crystallisation

and sintering temperatures or, conversely, to increase the temperatures of undesirable phase transitions.

The homogeneity of the distribution of the components, including small amounts of modifying additives, is the principal advantage of alkoxo-technology. Thus a microheterogeneous mixture of SiO_2 and TiO_2 is formed in the $SiCl_4-TiCl_4$ system on deposition,[18] whereas the joint hydrolysis of $Si(OR)_4$ and $Ti(OR)_4$ leads to the formation of a homogeneous titanosilica gel.[19] When aqueous solutions of aluminium and magnesium salts are made alkaline, mixed hydroxide and oxide hydroxides with a homogeneous distribution of the metals are not formed owing to the difference between their precipitation pH values.[20] In contrast, on dissolution of alkoxides in organic solvents, complex formation takes place and the alkoxo-salt $Mg[Al(OR_4)]_2$ is formed, partial hydrolysis generating the Al–O–Mg fragment. Homogeneity is also retained on subsequent conversion into oxide hydroxides and oxides.[21] Mixed E–O–E′ fragments are formed mainly on condensation of the RO and OH groups attached to different elements:

$$\sim EOH + ROE' \sim \longrightarrow \sim EOE' \sim + ROH,$$

$$\sim EOR + HOE' \sim \longrightarrow \sim EOE' \sim + ROH.$$

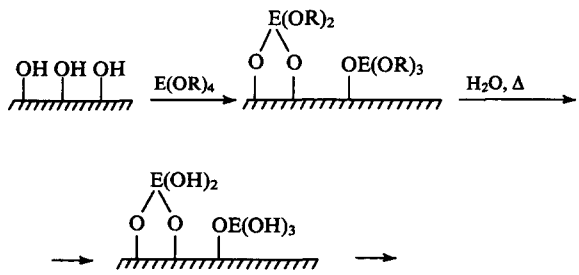
It is noteworthy that the rates of hydrolysis and condensation of alkoxides differ significantly. This complicates the task of achieving atomic homogeneity (simple addition of water to a solution of a mixture of alkoxides usually results in the formation of a heterogeneous mixture of oxide and/or oxide hydroxide particles of nanometer size). A series of methods for the solution of the problem have been developed: slow hydrolysis by atmospheric moisture, selection of RO groups, the use of presynthesised mixed alkoxides, the introduction of organometallic catalysts, and preliminary partial hydrolysis of one of the alkoxides. The last method has received the greatest attention.[22–24] Thus in the manufacture of highly porous 'SiO_2-ZrO_2' carriers, $Si(OEt)_4$ is initially partially hydrolysed, after which $Zr(OPr)_4$ is added, and then the final hydrolysis is carried out:[25]

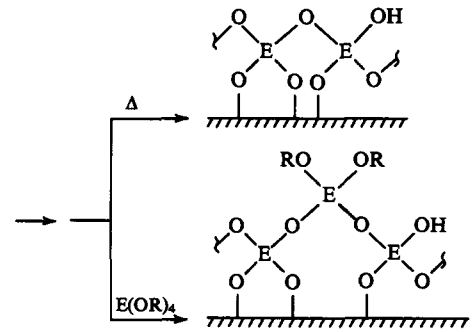
$$Si(OEt)_4 + H_2O \longrightarrow Si(OEt)_3OH + EtOH,$$

$$Si(OEt)_3OH + Zr(OPr)_4 \longrightarrow (EtO)_3SiOZr(OPr)_3 + PrOH,$$

$$(EtO)_3SiOZr(OPr)_3 + nH_2O \longrightarrow SiO_2-ZrO_2.$$

The high chemical reactivity of the RO groups of alkoxides is manifested also when alkoxides come into contact with the OH groups of surfaces and hydroxides. This feature has been used successfully in the modification of the surfaces of catalysts and carriers. The sequence of reactions occurring under these conditions and the structure of the films (monolayer or bilayer in the initial stage of their formation), which are produced when a hydroxylated surface is treated with an alkoxide of a tetravalent element, can be represented as follows:





A similar modification of the surface may be achieved with the aid of anhydrous halides, which are virtually the only alternative to alkoxides. However, this does not afford any significant advantages, whereas the disadvantages of this procedure (among which difficulties in the storage and use of the product and the evolution of hydrogen halides during hydrolysis may be included) are fairly considerable.

The processes in which the precursors of oxide carriers and catalysts are inorganic compounds is of great interest. Alkoxides are then formed or R–O–E fragments are generated. Such processes are based on familiar reactions involving the formation of alkoxides from hydroxy-compounds, on the one hand, and oxides, hydroxides, and the salts of volatile acids (acetic, carbonic, and nitric), on the other.[26–27] For example, the alkoxide (glycolate) was obtained directly in the reaction mixture in the synthesis of the $Ni-SiO_2$ catalyst:[28]

$$Ni(OH)_2 + HOCH_2CH_2OH \longrightarrow \overbrace{NiOCH_2CH_2O} + 2H_2O.$$

Until recently, attention has been devoted to the specific synthesis of alkoxides from cheap inorganic compounds directly during the preparation of carriers and catalysts, i.e. to the attainment of the chain of reactions inorganic compound → alkoxide → oxide within the framework of alkoxo-technology.

III. Principal aspects, advantages, and disadvantages of the application of alkoxo-technology in heterogeneous catalysis

The chemical properties of alkoxide and the products of their hydrolysis described above as well as the mechanism of their conversion into oxides provide alkoxo-technology with the following important advantages:

– high purity of the final products (other elements can be fairly readily eliminated from alkoxides even at the synthesis stage or on distillation, and the preparation of powders does not require a milling stage in which the product might be contaminated);

– structural and chemical homogeneity of multicomponent mixtures;

– an appreciable decrease in the phase formation and sintering temperatures;

– simplicity of deposition of coatings with a controllable porosity and thickness on carriers of any shape;

– the possibility of synthesising new crystalline and amorphous compounds, the preparation of which by traditional methods is difficult or impossible;

– high quality of the intermediate products obtained when hydrolysed alkoxides are used as binders for large articles;

– the possibility of obtaining products in the form of fibres and microspheres;

– ecological cleanliness of the processes.

In modern chemical engineering, ecological advantages have assumed particular importance. Firstly, when alkoxides are employed, problems of the purification of waste waters do not arise. Secondly, the alcohols and organic compounds formed when alkoxides are converted into oxides may be fairly readily trapped, reused, or combusted further to CO_2. This is significantly simpler than neutralisation of nitrogen and sulfur oxides as well as hydrogen halides, which are frequently present in the effluent gases in the synthesis of catalysts from inorganic precursors.

The main disadvantages of alkoxo-technology are as follows:

– the use of organic compounds as solvents;

– the considerable shrinkage in the preparation of dense materials;

– the higher cost of alkoxides compared with inorganic compounds.

The handling of organic compounds (solvents, alcohols, and decomposition products) requires the use of explosion-proof apparatus. However, this is not a significant obstacle to the employment of alkoxo-technology in catalysis, because the manufacture of catalysts is in general distinguished by a high degree of technological sophistication. Similar problems arise (are solved) also in the handling of ammonia, ammonium salts, and acetates.

The appreciable shrinkage during sintering is known to have a negative effect on the preparation of dense, and bulky ceramic materials.[29] In heterogeneous catalysis, alkoxides and their hydrolysis products are usually employed for the deposition of thin coatings or as binders in the preparation of bulky carriers and catalysts. In such cases, the problem of shrinkage is not so significant, particularly since the heat treatment is carried out at temperatures such that only partial sintering of the oxide skeleton generated from the alkoxide takes place and the optimum ratio of porosity to strength is ensured (porosity reduces sharply the strength of oxide materials).

The higher cost of alkoxides compared with inorganic compounds is undoubtedly the most important disadvantage of alkoxo-technology. Nevertheless, both in Russia and abroad silicon alkoxides are widely used in the casting of metals in accordance with smeltable models. The world prices of silicon, titanium, and aluminium alkoxides are comparable and are respectively about 3.5, and 3 U.S. dollars per kilogram.[30] The reasons why foreign investigators and practicianers in the field of the sol-gel process have turned to its alkoxide version are not discussed in the Russian literature,[31] so that the hypotheses concerning the use of cheaper inorganic precursors are insufficiently convincing. It is striking that abroad it is regarded economically justified to employ for the preparation of a series of oxide materials not only alkoxides but also even acetylacetonates,[32,33] the cost of which is higher by a factor of tens.

The application of the mixed alkoxoacetylacetonates $E(OR)_x(acac)_{n-x}$, also of the acetylacetonates $E(acac)_n$, is considered in this review, since the latter represent a special kind of alkoxide with an intramolecular coordinate bond and a conjugation system, which are formed with participation of acetylacetone in the enolic form.

Not so much the high cost as the lack of a wide-scale industrial manufacture of aluminium and zirconium alkoxides, which together with silicon and titanium alkoxides are the principal reagents in alkoxo-technology, is a more realistic obstacle to the introduction of the latter in Russia. Their manufacture is now being initiated, but an electrochemical procedure is used for this purpose,[34] which differs from the industrial methods of alkoxide synthesis generally adopted in world practice.[35]

Figure 1 presents schematically the principal aspects of alkoxide use in the technology of heterogeneous catalyst synthesis. This scheme embraces silicon, aluminium, and titanium alkoxides. Sometimes the oxide formed from one alkoxide is catalytically inactive or is insufficiently active. Such an oxide may function as a cocatalyst, a carrier, or an inorganic carrier,

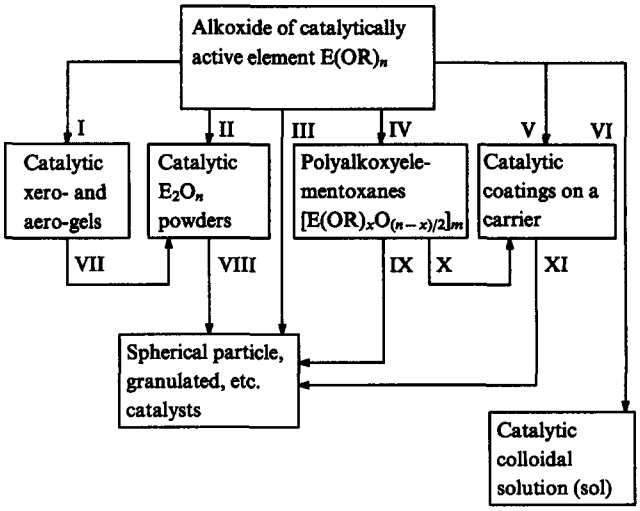


Figure 1. Principal operations in the preparation of intermediate products and catalytic materials from the alkoxides of catalytically active elements.

while the active component may be added to it, for example, in the course of, or after, joint hydrolysis.

There are several ways of synthesising heterogeneous catalysts, including the following operations (Fig. 1): I and II — total hydrolysis and drying, III — hydrolysis accompanied by the introduction of a filler and moulding, IV — partial hydrolysis; V — treatment of the carrier with a liquid or gaseous alkoxide; VI — total hydrolysis with stabilisation of the sol; VII — dispersion; VIII — introduction of inorganic binders (including their introduction via alkoxides) and moulding; IX — preparation of the solution, introduction of the filler, and moulding; X — treatment of the carrier with a polymer solution; XI — introduction of binders and moulding (preparation of fibrous and powdered carriers). The concluding operation in procedures I, III, V and VIII — XI is heat treatment. Specific ways of implementing individual variants of this general scheme will be examined below.

IV. Regulation of the chemical and phase compositions of oxide systems

The purity of the alkoxides, the uniformity of the distribution of the components in their joint hydrolysis mixtures, and the increased reactivity of the oxides formed after the removal of the organic component favour the specific regulation of the chemical and phase compositions of catalyst materials and hence exert a definite influence on their characteristics.[36]

One of the commonest carriers and also catalysts or cocatalysts in many reactions is porous γ-Al_2O_3. In its preparation, it is necessary to solve a whole series of problems: the formation and stabilisation of a large surface area, the attainment of definite acid — base characteristics, and the retardation (shifts towards higher temperatures) of the $\gamma \rightarrow \alpha$ transition. The last problem is especially important in high-temperature catalysis, since the $\gamma \rightarrow \alpha$ transition is accompanied by an increase in grain size and in the density of the carriers and catalysts, which leads to a sharp decrease in their specific surfaces (S_{sp}) and strength up to disintegration. The use of alkoxo-technology made it possible to achieve significant advances in all these aspects. Thus γ-Al_2O_3 obtained from an alkoxide is distinguished by an increased thermal stability:[37,38] after heat treatment at 800 °C, the specific surfaces of the alkoxide and nitrate γ-Al_2O_3 are respectively 150 and 50 $m^2\ g^{-1}$.

The thermal stability of γ-Al_2O_3 increases significantly after the introduction of certain elements in the $Al(OR)_3$ hydrolysis stage:[39] the specific surfaces of γ-Al_2O_3 without additives and following the addition of 4% of ThO_2, ZrO_2, and SiO_2 were 80, 99, 88, and 150 $m^2\ g^{-1}$ respectively after they had been maintained at 1000 °C for 24 h, while the specimens containing 7% of SiO_2 had S_{sp} = 116, 98.4, and 84.9 $m^2\ g^{-1}$ after heat treatment at 1100 °C for 30, 100, and 400 h respectively. The increase in thermal stability is due to the uniform distribution of the additives in the alumina matrix, which hinders the conversion of the low-temperature modifications of alumina into the thermostable α-form and shifts it into the region of higher temperatures.

Alkali and alkaline earth metal hexa-, undeca-, and dodecaaluminates have a greater ability than γ-Al_2O_3 to retain an extensive specific surface at temperatures above 900 °C. They can be most conveniently synthesised by employing alkoxides or mixtures of alkoxides with acetylacetonates and hydroxides.[40-44] Thus barium hexaaluminate, obtained by the traditional solid-phase synthesis from $BaCO_3$ and Al_2O_3, had S_{sp} = 6.3 $m^2\ g^{-1}$ after heat treatment at 1300 °C, while the specimen obtained by the alkoxide method had S_{sp} = 20.2 $m^2\ g^{-1}$.[42]

It is of interest to compare the alkoxide method with other procedures for the preparation of aluminates. For example, the traditional method of preparation of hexaaluminates as carriers for final-combustion catalysts includes the following principal technological operations: fusion of Al_2O_3, B_2O_3, and alkaline earth metal oxides at temperatures exceeding 1500 °C, maintenance at 750–850 °C, comminution, leaching with acids (for example, with acetic acid), washing, and drying.[45] This process is distinguished by high energy consumption, is laborious, and generates a series of ecological problems. When alkoxo-technology is employed, water is simply added to alkoxides and the powders are separated and heat-treated (up to 900 °C). Such simplification of the technology combined with an increased heat resistance of the products justifies the view that the alkoxide method is an economically more acceptable procedure for the preparation of aluminate carriers for high-temperature catalysts.[43] All these advantages outweigh the disadvantages associated with the increased cost of the alkoxide precursors.

The use of alkoxo-technology makes it possible to regulate the degree of homogeneity in the distribution of the components in multicomponent systems.

Thus, depending on the conditions in the joint hydrolysis of $Al(OR)_3$ and $Si(OR)_4$, powders having the mullite composition ($3Al_2O_3 \cdot 2SiO_2$) could have a specific surface of either 6.8 or 38 $m^2\ g^{-1}$ after heating at 1500 °C.[46] The degree of homogeneity of the former did not then attain the atomic level (nanocomposite) and that of the latter corresponded to the atomic or nearly atomic level of distribution of the components. In the latter case, the mullite microcrystals were formed at 900–1000 °C and the vitreous aluminosilicate phase, through which recrystallisation accompanied by a decrease in S_{sp} in fact largely occurs, was then absent from the system.

The aluminomagnesium alkoxide spinel — a promising chemically inert carrier — also has an enhanced thermal stability.[47] Its specific surface at 1100 °C is 30 $m^2\ g^{-1}$.[47]

Depending on the alkoxide decomposition conditions (the effect of water or atmospheric moisture, thermal decomposition), γ-Al_2O_3 powders with different acidities, which affect their catalytic properties, are formed.[48] Thus, in the dehydration of ethanol on one of such powders, the yields of C_2H_4 and Et_2O were 73% and 8% respectively for a conversion of 82%, whereas on γ-Al_2O_3 obtained from inorganic precursors the yields were 2.6% and 10% respectively.

Modification of the chemical composition of the γ-Al_2O_3 surface by treating the latter with $Si(OR)_4$ and subsequent deposition of palladium or platinum made it possible to obtain a thermostable catalyst capable of ensuring the flame-free combustion of hydrocarbons, diminishing thereby the evolution of CO and NO_x during catalytic combustion.[49]

A special program for the preparation of artificial clays is being developed in Japan. Its aim is to improve the quality and to attain the stability and reproducibility of the properties of promising ceramic materials.[50] Such clays are used, for example, in the manufacture of ceramic cellular carriers for catalytic converters in internal combustion engines. The possibility of using alkoxides as oxide precursors is being investigated, which is not surprising since Japan is the leader in the introduction of alkoxo-technology. Treatment of natural clays with alkoxides makes it possible to obtain secondary clays with increased interlayer distances and greater specific surfaces,[51] which ensures the creation of a comparatively cheap heat-resistant and strong ceramics.

Studies carried out by the Nissan Motor Company and the National Chemical Laboratory of Japan have shown that, depending on the structure of the added low-molecular-mass polyether, anatase or rutile may be obtained from $Ti(OPr^i)_4$ after hydrolysis and heat treatment.[52] This is important, since different modifications of TiO_2 have significantly different catalytic properties. For example, anatase is preferable in the selective catalytic reduction of NO_x. The thermal decomposition of $Fe(NO_3)_3$ on surfaces modified with organic compounds, for example with ethylene glycol, has also been investigated.[53] As noted above, ROE fragments are generated in such systems on heating. Depending on the structure of the modifying agent, coatings having the Fe_2O_3 composition with a spinel or corundum structure are obtained.

The influence of the reaction conditions on the structure and properties of TiO_2 powders, obtained by the thermal decomposition of $Ti(OPr^i)_4$ and $TiO(acac)_2$ at 200–300 °C, has been studied.[54] Rutile was obtained from the latter in the presence of ethylene glycol, whereas anatase with S_{sp} = 200 $m^2 g^{-1}$ was produced in the presence of toluene, the specific surface not diminishing on heating to 550 °C.

Mixed crystalline oxides with the perovskite structure are active catalysts and promising carriers.[55,56] The catalytic activities of a series of perovskites are comparable with those of noble metals. The inclusion of noble metals in the perovskite lattice increases the chemical and thermal stabilities of mixed catalysts and prevents the volatilisation of the noble metals in the form of oxides, for example, Ru_2O_3 or RuO_3. The principal obstacle to the wide-scale introduction of catalysts with the perovskite structure is the high temperature of their synthesis (~900 °C). This greatly hinders their preparation by the impregnation method. At the same time, the solid-phase synthesis with subsequent dispersion does not ensure the formation of a sufficiently large surface. Even on an inert carrier such as $MgAl_2O_4$, only insignificant amounts of a mixed perovskite are formed from a mixture of copper, cobalt, and lanthanum nitrates. Their reaction with the support generates mainly spinels.[57] The optimum support for the synthesis of a perovskite might be ZrO_2, but, since this carrier is expensive and has a low S_{sp}, it has not found a wide-scale application.

Low temperature methods of synthesis of perovskites at reduced temperatures (400–700 °C) employing alkoxo-technology have been developed in recent years.[58-59] It is to be expected that this will provide a fresh stimulus to the employment of perovskites in heterogeneous catalysis. This is of particularly great current interest for Russia, where chromium-containing catalysts or catalysts based on noble metals are mainly used for the purification of effluent gases.[56,60] It is noteworthy that abroad the manufacture of the former has been curtailed owing to the high biological activity of chromium(VI) compounds[61] and that of the latter has been reduced because of their high cost.

One of the most important advantages of alkoxo-technology is the possibility of obtaining new crystalline and amorphous phases, the synthesis of which by the traditional methods is difficult or impossible. This is caused mainly by the need to carry out the solid-phase synthesis at high temperatures,[62] the formation of phases stable in the low-temperature region being impossible under such conditions. Furthermore, in solid-phase synthesis

it is extremely difficult to ensure the homogeneity of multicomponent systems, particularly when small amounts of additives are introduced. On the other hand, when alkoxo-technology is employed, atomic (molecular) homogeneity is already attained at the hydrolysis stage and heat treatment leads mainly to the densification of the oxide skeleton. This results in a decrease in the formation temperature of the crystalline phases and eliminates the liquation phenomenon — heterogeneous separation in glass melts (when amorphous oxides are obtained). Naturally, the transition from the theoretical consideration of the possibility of using alkoxo-technology to its practical implementation requires much effort. Nevertheless, considerable advances have already been achieved on these lines: barium titanates with the ratio $BaO:TiO_2 = 1:2$ and $1:5$,[63] previously regarded as metastable, the previously unknown compound $5La_2O_3 \cdot 2Al_2O_3$,[64] $LiNbO_3$ films,[65] and other materials have been obtained. Even though there is as yet no information about the use in heterogeneous catalysis of new crystalline compounds obtained with the aid of alkoxo-technology, data concerning the application of new amorphous materials (for example, in the manufacture of SiO_2-ZrO_2 porous glasses with an increased ZrO_2 content)[25] are already available.

V. Preparation of coatings and thin films

Catalysts obtained by deposition from solutions of catalytically active compounds onto a highly porous carrier with subsequent heat treatment are usually employed in many catalytic reactions, particularly in the external diffusion region. A carrier with a high surface area (primary carrier), treated with solution or suspensions, from which highly porous coatings (secondary carrier) are obtained on heat treatment, is also used as a support. In such cases, aqueous solutions of inorganic salts which can be decomposed by heat treatment (the cheapest and most readily available compounds) are traditionally employed for the introduction of catalytically active elements. However, the thermal decomposition of inorganic salts is usually accompanied by the evolution of corrosive and toxic gases and in addition the nitrates most frequently used are explosive. However, the main disadvantage of this technology is the crystallisation of inorganic salts on evaporation of water, which ultimately rules out the possibility of obtaining a uniform coating (a 'patchy' oxide coating is formed), reduced S_{sp}, and increases the consumption of catalytically active elements.

In multicomponent systems, the situation is aggravated by the occurrence of separate (fractional) crystallisation, since the probability of isomorphism or of the formation of complex salts is low. As a result, heat treatment gives rise to the formation of a microheterogeneous mixture of oxides, the homogenisation of which with formation of a mixed crystalline oxide having the specified structure requires an increased temperature and this leads to sintering accompanied by a decrease in S_{sp}, the formation of relatively inactive phases with participation of the carrier, and the alteration of the component ratio.

The application of alkoxo-technology makes it possible to overcome fairly readily these disadvantages of the traditional technology. The principal advantages of alkoxo-technology are ability of the products of the hydrolysis of alkoxides to form films and the establishment of homogeneity in the hydrolysis stage. The hydrolysis of alkoxides results in the formation of predominantly linear or branched polymers as well as oxide or oxide hydroxide particles of controllable size. The latter are produced either immediately in the form of a sol or (after peptisation) in the form of gels and powders.

Solutions of the hydrolysis products, deposited on supports by immersion, impregnation, or sputtering methods, give rise to uniform organic-inorganic coatings. After drying and moderate heat treatment at temperatures of 400–800 °C, ensuring the elimination of the organic component and the partial sintering of the coatings with retention of their high porosity, such coatings

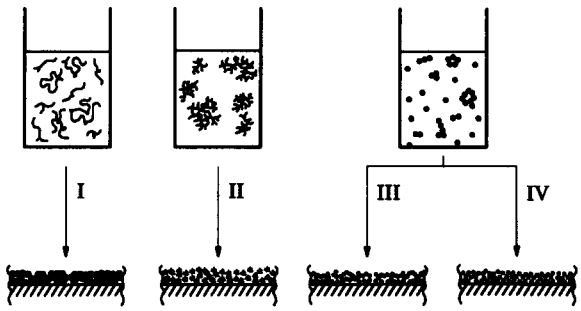


Figure 2. The structure of oxide coatings formed from different hydrolysed alkoxides.

are converted into oxide ones. Their structure is illustrated conventionally in Fig. 2.

Type I coatings are characterised by a low open porosity and have no special importance in catalysis, but they can be used as an oxide binder, which sinters at a low temperature, for example in the preparation of ceramic honeycomb carriers. Type II–IV oxide coatings (films), which have a high open porosity and a large contact surface, are used as carriers and catalysts. The structure of the oxides formed from the alkoxide hydrolysis products obtained under various conditions has been examined in detail.[66,67]

For the deposition of coatings, one may use either liquid alkoxides directly or solutions of liquid and solid alkoxides in organic solvents with subsequent hydrolysis by atmospheric moisture and/or heat treatment. However, this method has not found extensive application, because it is fairly difficult to regulate the structure of an oxide coating having an appreciable thickness (>0.1 μm). It is more convenient to deposit monolayer and multilayer coatings from dilute solutions of alkoxides. The properties of such coatings, especially monolayer ones, differ significantly from those of bulk-phase materials owing to their anomalous structure (distortion of bond angles and changes in bond lengths and in the electronic state of their atoms), which is particularly important for catalysis. For example, Fe_2O_3 in a surface layer deposited from $Fe(acac)_3$ on TiO_2 has a lower activity in the oxidation of CO than bulk-phase Fe_2O_3.[68] This can be explained by the fact that a monolayer coating of this kind (obtained as a result of interaction with the support) is chemically closer to iron silicate rather than to Fe_2O_3.

However, monolayer coatings exhibit much more frequently a higher catalytic activity than multilayer ones. Thus the dehydration of ethanol to C_2H_4 on the Nb_2O_5/SiO_2 monolayer catalyst obtained from $Nb(OEt)_5$ proceeds to an extent of 99%–100%, whereas on the analogous impregnation catalyst considerable amounts of Et_2O are formed together with C_2H_4.[69] The rate of the esterification reaction between AcOH and EtOH on a monolayer catalyst of this kind is 20 times greater than on massive Nb_2O_5.[70] When platinum or nickel is deposited on it, the effect of the strong metal–carrier interaction is not manifested, in contrast to the deposition of the same metals on 'pure' Nb_2O_5. The dispersity of copper in the Cu/SiO_2 monolayer catalyst obtained by deposition from $Cu(acac)_2$ solution does not change even after 10 oxidation-reduction cycles, whereas in a multilayer catalyst it is lower immediately after preparation and falls to a particularly large extent after five such cycles have been performed.[71]

The surface monolayers obtained by depositing $Nb(OR)_5$ or its mixture with $Al(OR)_3$ do not crystallise with formation of Nb_2O_5 or aluminium niobates even after heating at 900 °C.[72]

V_2O_5 coatings, for the deposition of which one may employ vanadium and vanadyl alkoxides[73–80] or acetylacetonates,[81–87] have acquired practical importance. They are used for the selective catalytic reduction of NO_x in effluent gases. Monolayer catalysts containing 2%–4% of V_2O_5 have activities in this reaction comparable to those of catalysts obtained by impregnating the

carrier with NH_4VO_3 solutions or deposited from $V_2(SO_4)_3$ solutions containing 20%–24% of V_2O_5.[86] Thus the activity of the alkoxide catalyst referred to unit mass of V_2O_5 is almost ten times greater than that of a traditional catalyst obtained from inorganic precursors.

For low surface coverages of the SiO_2, TiO_2, Nb_2O_5, Al_2O_3, or ZrO_2 carriers by V_2O_5 films obtained from $VO(OR)_3$, vanadate forms containing one terminal V–O bond and three VO–carrier bridge bonds are formed on the surface.[75] It has been suggested that vanadium oxide catalysts for the reduction of NO_x be obtained by impregnating cellular carriers with solutions of partly hydrolysed alkoxide-based mixtures, for example, a mixture of $Ti(OBu)_4$, $VO(OBu)_3$, and WCl_6.[80]

The method involving the chemical vapour-phase deposition (CVPD) of the $B(OEt)_3$, $Si(OEt)_4$, $P(OMe)_3$, and $Ti(OPr^i)_4$ alkoxides has been used to obtain the B_2O_3/SiO_2,[88–90] B_2O_3/Al_2O_3,[91] SiO_2/Al_2O_3,[92–95] TiO_2/carrier,[96] SiO_2/aluminosilicate,[97] and BPO_4/SiO_2[98] catalysts. The supported catalysts obtained from alkoxides by the CVPD method have a higher activity: thus boron oxide is uniformly distributed on the carrier surface even when its content is more than 30% (in the usual impregnation deposition, large B_2O_3 crystals are formed in this case).[89–90] This promotes a high activity and selectivity (95%–96%) of the catalyst in the rearrangement of cyclohexanone oxime to caprolactam. The SiO_2/Al_2O_3 alkoxide catalyst, which has a lower S_{sp} than the industrial catalyst having a similar composition (177 and 360 $m^2\ g^{-1}$ respectively) has a catalytic activity in the cracking of cresol comparable to that of the latter. This is apparently associated with the fact that it contains a larger number of acid centres.[92] The fixation of the first layer on deposition of SiO_2 formed from $Si(OEt)_4$ on Al_2O_3 takes place as a result of the interaction between the HOAl and EtOSi groups with formation of Al–O–Si fragments. In a nitrogen atmosphere, the residual EtO groups do not decompose, whilst in the presence of oxygen they are oxidised with formation of acetaldehyde and the regeneration of OH groups.[93]

The formation of catalytic oxide coatings from alkoxides by the CVPD method has also been investigated in other studies.[99–108] Silicon dioxide, obtained from $Si(OEt)_4$, covers only the outer surface of zeolites. This alters the dimensions of the inlet pores with retention of the inner structure of the zeolites and increases sharply the selectivity of the latter in relation to the volume of the reacting molecules, which is indicated, for example, by the results of a study of the cracking of octane isomers.[101] Coatings in the form of SiO_2, deposited from the vapour phase, exhibit a higher chemical reactivity even on an inert carrier such as ZrO_2. At 550 °C, they partially coalesce with formation of clusters and partly dissolve in the carrier.[107]

The method involving the deposition of coatings by treating the carrier with an alkoxide under thermal decomposition conditions is close to CVPD. The SiO_2/Al_2O_3 catalyst has been obtained by this procedure.[109] It is assumed that the deposition takes place via the interaction of the EtO groups in $Si(OEt)_4$ with Lewis acid centres on the Al_2O_3 surface. However, this explanation cannot be extended to the formation of the second and subsequent layers (the overall increment in the mass of SiO_2 reaches 20%).

A comparative study of several Pd/Al_2O_3 impregnation catalysts showed[110] that highly disperse palladium particles are formed from $PdCl_2$ and $Pd(acac)_2$. On reduction, they are converted into a finely disperse metallic phase, whereas the decomposition of $Pd(NO_3)_2$ leads to the formation of large particles.

Aluminium, tantalum, and titanium alkoxides have been used for the modification of the surfaces of porous carriers before deposition of catalytically active metals on the latter.[111–113] For a comparatively slight increase in the specific surface of the specimens (for example, from 100 $m^2\ g^{-1}$ for the initial γ-Al_2O_3 to 120 $m^2\ g^{-1}$ for the modified oxide), this made it possible to increase sharply their activity and to obtain effective catalysts for a series of reactions. Thus the degree of conversion of carbon monoxide into methane on a modified $Ru/Al_2O_3/\gamma$-Al_2O_3 catalyst was 99% for selectivity of 100%, whereas on the usual Ru/γ-Al_2O_3 catalyst it was 62% with a selectivity of 99%. A similar approach has been used to obtain active Pd/TiO_2/spherical glass bead hydrogenation catalysts[114,115] and for the deposition of Al_2O_3 coatings on highly porous SiO_2 carriers.[116] It is important to note that this procedure makes it possible to attain a significant catalytic effect for a low consumption of alkoxides.

A modified copper/zeolite catalyst, obtained by ion exchange followed by treatment in a $Ti(OMe)_4$ solution, has been developed for the catalytic conversion of moist exhaust gases.[117] Different additives have different effects on the modification of γ-Al_2O_3 (S_{sp} = 13.7 $m^2\ g^{-1}$) with $Ti(OPr^i)_4$ or $Si(OEt)_4$ solutions in hexane.[118] Best coatings with S_{sp} up to 29.4 $m^2\ g^{-1}$ are formed in the presence of EtOH, PrOH, and Pr^iOH, whereas added surfactants exhibit a negative effect.

A process involving the fixation on honeycomb ceramic carriers of secondary γ-Al_2O_3 carriers, formed from sols obtained by the hydrolysis of $Al(OR)_3$ and the peptisation of the gels produced, has been patented.[119] A disadvantage of the traditional technology for the fixation of secondary carriers from suspension is the accumulation of γ-Al_2O_3 particles in corners of the channels within the honeycomb carrier, which reduces the effectiveness of the catalyst and increases its aerodynamic resistance. The proposed method is free from this disadvantage. In addition, 14.7% of Al_2O_3, and not 33% as in the formation of a suspension coating, is sufficient for the attainment of S_{sp} = 25–30 $m^2\ g^{-1}$.

A process has been developed for the deposition of alumina coatings on barium aluminate.[120] A catalyst obtained from platinum salts and a mixture of $Ti(OEt)_4$ and $Al(OPr^i)_3$ has been designed for use in automobile converters. The mixture of alkoxides is subjected to joint hydrolysis, deposited on a honeycomb carrier, dried, and maintained at 500 °C. The degree of conversion of CO on this catalyst reaches 94% at 250 °C and falls to 81 % after being used for 1000 h at 800 °C (for the usual catalyst, the corresponding conversions are 88% and 75%).[121]

VI. The use of alkoxides for the preparation of carriers and catalysts

In studies[6,41,122–144] on the use of alkoxides for the preparation of carriers and catalysts and of their physicochemical and catalytic properties, attention was concentrated on the chemical mixing method. It has been shown for mixtures of silicon and aluminium alkoxides with aluminium, ruthenium, and copper chlorides that the process should consist of four stages:

(1) the formation of complexes of the alkoxides and chlorides with organic polydentate ligands;

(2) hydrolysis with formation of a sol and gel;

(3) drying and dispersion;

(4) sintering and reduction in a stream of hydrogen (when copper and ruthenium salts are used).

The introduction of polydentate ligands such as aliphatic diols and low-molecular-mass polyethers makes it possible to monitor the course of the hydrolysis and polycondensation (by virtue of their coordination to the RO groups of the alkoxides or their substitution, the ligands lowering the rates of these reactions), ensures the binding of the metal ions to the elementoxane chains, and regulates the shape and size of the pores as well as S_{sp}. Thus, in the hydrolysis of $Al(OR)_3$ in the presence of the polyether $Me(OCH_2CH_2)_nOMe$, micropores with an average diameter of 10 nm predominated in the γ-Al_2O_3 obtained for n = 2, whereas for n = 3 or 4 a wide size distribution of the pores was observed (from 10 to more than 100 nm).[132] In the joint hydrolysis of $Si(OR)_4$ and $Al(OR)_3$ in the presence of ethylene glycol, 2-methylpentane-1,2-diol, or hexane-1,6-diol, aluminosilicates (3.3% of Al_2O_3) with an average pore diameter of 0.55–0.65 nm were obtained.[140] The structure of the diol introduced has a decisive influence on the specific surfaces of such aluminosilicates (Table 1).

Table 1. The influence of the nature of the ligand on the specific surfaces of the 3.3% $Al_2O_3-SiO_2$ carriers obtained from alkoxides by the chemical mixing method.[141]

Ligand	S_{sp}/m^2 g^{-1}
Ethane-1,2-diol	399
Propane-1,2-diol	170
Butane-2,3-diol	179
2-Methylpropane-1,2-diol	308
Butane-1,2-diol	315
Pinacol	319
Pentane-1,2-diol	483
Propane-1,3-diol	210
Butane-1,3-diol	222
2-Methylbutane-1,3-diol	545
2-Methylpentane-2,4-diol	486
Butane-1,4-diol	5
Pentane-1,5-diol	365
Hexane-1,6-diol	595
Decane-1,10-diol	734
Dodecane-1,12-diol	637

The homogeneities in the distribution of the components were compared on $TiO_2-Al_2O_3$ specimens synthesised in different ways: by sintering TiO_2 and Al_2O_3 powders, by precipitating mixtures of oxide hydroxides from aqueous solutions of salts with ammonia or urea, and by chemical mixing.[140]

In the last case, the crystallisation of TiO_2 was not noted after heating for 5 h at 550 °C. The specimen remained X-ray-amorphous, which confirmed the high degree of homogeneity attainable when the chemical mixing method is employed. In a number of instances, this is of practical importance.

The catalysts synthesised were tested in reactions involving the partial hydrogenation of benzene, the alkylation of naphthalene, and the conversion of methanol. Data on the partial hydrogenation of benzene to cyclohexene on the $Ru-SiO_2$ and $Ru-Al_2O_3$ catalyst obtained by the chemical mixing method and on impregnation catalysts employed for comparison are presented in Table 2.

Chemical mixing was used also in the study of the influence of added metal oxides (10%) on the S_{sp} of alumina.[41] The introduction of SrO, BaO, La_2O_3, and ZrO_2 suppressed the sintering of Al_2O_3 in the range 1000–1200 °C. After heating the $BaO-Al_2O_3$ mixture for 100 h at 1000 °C, a high specific surface of alumina

Table 2. Partial hydrogenation of benzene to cyclohexene on different ruthenium catalysts.[134]

Method of preparation	Ligand	Catalyst composition	Conversion of benzene (%)	Yield of cyclohexene (mol %)
Chemical mixing (TEOS–$AlCl_3$)	ethylene glycol	2%Ru–SiO_2	86.8	27.0
	ethylene glycol	(2%Ru + 0.2%Cu) SiO_2	83.3	31.4
	pinacol	(2%Ru + 0.2%Cu) SiO_2	42.7	14.2
	hexylene glycol	(2%Ru + 0.2%Cu) Al_2O_3	53.1	24.5
Impregnation		2%Ru–SiO_2	64.3	8.6
		2%Ru–Al_2O_3	54.5	5.3

Note. Reaction temperature 453 K, H_2 pressure 7 MPa, benzene : water = 1.6 : 1.

(139 m^2 g^{-1}) was retained, whilst after heating for 3 h at 1200 °C S_{sp} diminished to 96 m^2 g^{-1}. The addition of CaO, MgO, and CeO_2 accelerated the sintering and reduced the S_{sp} of alumina.

The chemical mixing method was also applied in other studies.[145–151] It was shown in relation to the selective reduction of NO_x that mixed $V_2O_5-TiO_2$ catalysts exhibit an enhanced catalytic activity compared with impregnation catalysts.[149]

The average rhodium particle size in the Rh/SiO_2 catalyst synthesised using the $Rh(NO_3)_3-Si(OEt)_4-HOC_2H_4OH$ systems increased from 1 to 5.6 nm with increase in the rhodium content from 0.34% to 6.89%. The activity of this catalyst in the PrOH decomposition reaction increased sharply for particle sizes of 1–2 nm, when the fraction of metal atoms at the corners and on the edges of microcrystallites was a maximum.[151] A similar dependence of the selectivity in the hydrogenation of propionaldehyde on the nickel particle size has been observed on the Ni/SiO_2 catalyst, in which the metal particle size increased from 4 to 12 nm with increase in the nickel content from 2% to 26%.[150] It was shown by IR spectroscopy that the metal particles are retained on the support as a result of the formation of the Ni–O–Si linkage. The cobalt particle size in the Co/TiO_2 catalyst increased from 10 to 40 nm with increase in the reduction temperature to 600 °C, but at ~700 °C, where the anatase–rutile transition takes place, it again decreased to 10–15 nm.[147] The redispersion effect, characteristic solely of catalysts obtained by chemical mixing but not of impregnation catalysts, is apparently due to a strong metal–carrier interaction.

Catalyst powders obtained as a result of the operation of the reaction chain alkoxide → xerogel → powder (Fig. 1, operations I and VII modified by the introduction of inorganic salts and ligands) were considered above. In industry, powders are rarely employed as the finished form of the catalysts, serving mainly as the starting material for the preparation of various bulk-phase catalysts.

Boehmite (AlOOH) powders synthesised via alkoxides have found the greatest practical application.[116] Previously they were obtained as side products in the synthesis of higher alcohols by the Ziegler method, but subsequently a number of companies, for example Conoco and Vista,[152] set up a special industrial process. The alkoxide obtained by the reaction of metallic aluminium with an alcohol was hydrolysed, after which boehmite was separated and dried, while the alcohol was regenerated. The process has satisfactory ecological characteristics and the powders synthesised have a high purity and dispersity. They can be readily made to undergo a transition to the sol state by adding water and small amount of acid (in certain cases the addition of acid is not required). The employment of such powders for the deposition of secondary γ-Al_2O_3 coatings on honeycomb carriers made it possible to create Pt/γ-Al_2O_3/honeycomb carrier catalysts, which, whilst having the same activity as the industrial analogues, contain 10 times less platinum.[153]

The Al_2O_3,[154–158] SiO_2-TiO_2,[159–161] TiO_2,[162–166] $SiO_2-Al_2O_3$,[167,168] TiO_2-ZrO_2,[169] SiO_2,[28] $V_2O_5-Al_2O_3$,[170] etc. catalytic powders have been obtained with the aid of alkoxo-technology. By selecting the method of synthesis and the reaction conditions, it is possible to regulate S_{sp} and the size and volume of the pores. For example, in the thermolysis of $Al(OR)_3$ solutions in secondary and tertiary alcohols, where water is generated *in situ* as a result of the thermal degradation of the alcohols, γ-Al_2O_3 powders with $S_{sp} \approx 500$ m^2 g^{-1} are produced.[158] Gels were obtained by preliminary partial hydrolysis of $Si(OR)_4$ in the $Si(OR)_4-Ti(OR)_4$ system and were then dried, comminuted, impregnated with chromium salts, and sintered.[159] The uniform distribution of the components promoted an increase in the thermal stability of the resulting 1% Cr/SiO_2-TiO_2 catalytic powders; after heat treatment for 3 h at 850 °C, their specific surface was 404 m^2 g^{-1} with a porosity of 2.19 cm^2 g^{-1}.

By virtue of the high specific surface of alkoxide powders, they may be pelleted without a binder.[171] A powder catalyst of the Fisher–Tropsch process has been obtained by the joint hydrolysis of $Ti(OPr^i)_4$ and $Zr(OPr^i)_4$ in the presence of $Fe(OAc)_3$.[169]

A spherical shape of the catalytic powder particles is preferred, since this diminishes wear due to abrasion. Porous microspheres 1–100 μm in diameter and with pore dimensions of 10–40 nm were obtained by heating the products of the hydrolysis of $Si(OR)_4$ at $Ti(OR)_4$ at 400–900 °C.[172] Microspheres having the composition 3% Y_2O_3–ZrO_2 with an average diameter of 40–50 μm are formed when products of the joint hydrolysis of the corresponding alkoxides are mixed with alkyl phthalates, the mixture being subsequently forced through a draw plate into high-boiling organic liquids.[173] The formation of an emulsion in the region of immiscibility of the alkoxide–ethanol–water ternary system was used to obtain SiO_2–TiO_2 powders having spherical particles with $S_{sp} \leqslant 375\ m^2\ g^{-1}$ and a controllable diameter from 0.05 μm to 1 mm.[161] Alkoxide TiO_2 and Al_2O_3–TiO_2 microsphere powders, activated by the addition of V_2O_5 and CuO, have found a practical application in the purification of the effluent gases from various industries, while TiO_2 microsphere powders are used in the photochemical decomposition of organic compounds in waste waters.[174,175]

Stable TiO_2 or ZrO_2 spherical particle powders, designed for use as carriers and catalysts, with an average diameter of 1–100 μm, pore dimensions of 1–500 nm, and a porosity of 0.1–1 $cm^3\ g^{-1}$ have been obtained by the hydrolysis of alkoxides, spray drying of the resulting sols, and heat treatment at 500 °C.[176] The TiO_2 spherical particle powder for the promotion of photochemical reactions has been synthesised by the hydrolysis of $Ti(OR)_4$ in the presence of HCl.[177] SiO_2–Al_2O_3 microspheres have been obtained similarly.[167]

Porous spherical particle powders may be obtained also without the use of alkoxides, but in most cases the alkoxide procedure is preferred. For example, a high quality SiO_2 microsphere powder with S_{sp} up to 300 $m^2\ g^{-1}$ and a porosity of 1.3 $cm^2\ g^{-1}$ is obtained by the Vycor process.[178] In terms of resistance to wear, this powder is superior to alkoxide powders. However, the Vycor process consumes a large amount of energy, takes a long time, and, what is most important, is designed mainly for the preparation of high-silica microspheres, whereas alkoxo-technology has virtually unlimited possibilities for the selection of components.

SiO_2–Al_2O_3,[179,180] SiO_2–ZrO_2,[181–183] SiO_2–TiO_2,[184] SiO_2,[185] ZrO_2,[186] and SiO_2–B_2O_3[187] xerogels have been obtained for use in heterogeneous catalysis. Studies[187–192] on the joint hydrolysis of $Si(OR)_4$ and $Zr(OR)_4$ are of great interest. These investigations have served as a basis for the establishment of the industrial manufacture of highly porous glasses with an increased thermal stability and resistance to alkalies.[25] Thus 30% ZrO_2–SiO_2 glasses have specific surfaces of 392, 350, 250, and 119 $m^2\ g^{-1}$ at 300, 500, 800 and 900 °C respectively and lose their porosity completely as a result of sintering only on attainment of 950 °C. After heat treatment at 800 °C, $Ti(OBu)_4$ xerogels contained 30% of anatase and 70% of rutile; when 5% of Cr_2O_3 was introduced with the aid of $Cr(acac)_3$, the anatase content increased to 90%.[193] The addition of different amounts of $R_4N^+ \cdot OH^-$ to a mixture of silicon and aluminium alkoxides made it possible to obtain porous aluminosilicates with a molar ratio $SiO_2 : Al_2O_3$ from 30 : 1 to 500 : 1, S_{sp} = 50–1000 $m^2\ g^{-1}$, a porosity of 0.3–0.6 $cm^2\ g^{-1}$, and a pore diameter of 1 nm. They contained no pores with diameters > 3 nm.[168] In order to regulate porosity, it has been suggested that a proportion of 0.03–0.4 of an organic polymer relative to the alkoxide be introduced: on formation of a gel, the latter is segregated as a separate phase, which ensures, after burning it off and sintering, the creation of a highly porous oxide structure.[179]

The anomalously high porosities and specific surfaces of alkoxide aerogels are especially valuable in heterogeneous catalysis.[194–207] Thus the Fe_2O_3–$SiO_2(Al_2O_3)$ aerogel catalysts obtained from $Si(OMe)_4$ or $Al(OBu)_3$ and $Fe(acac)_3$ are more active in the Fischer–Tropsch reaction by 2–3 orders of magnitude than the usual iron-containing catalysts and, what is no less important, do not become saturated with coke, in contrast to the latter.[196] Catalysts with S_{sp} = 20–700 $m^2\ g^{-1}$, a porosity of 1.5–12 $cm^3\ g^{-1}$, and an apparent density of 0.003–0.5 g cm^{-3} have been obtained by the joint hydrolysis of $Al(OBu^s)_3$ and $Pd(OAc)_2$ [or $Ni(OAc)_2$]. They are distinguished by a uniform distribution of the components and the absence of clusters. They are designed for the reduction of nitro-compounds and hydrodesulfurisation.[195] The traditional catalysts based on tin and antimony or molybdenum and bismuth oxides are incapable of accelerating the synthesis of nitriles from unsaturated hydrocarbons and NO, whereas the Ni–Al_2O_3 (SiO_2) aerogel catalyst is highly active and selective in this reaction.[201,202]

The γ-Al_2O_3-based porous ceramic obtained via an aerogel is used as a carrier, retaining S_{sp} = 72 $m^2\ g^{-1}$ after heating for 5 h at 1200 °C.[208] Alkoxo-technology is formally not used in the synthesis of aerogel from Cr_2O_3,[205] but since CrO_3 and MeOH are used as the starting compounds, it follows that in this process too there is a possibility of the generation and subsequent decomposition of chromium(III) and chromium(IV) methoxides because instances of the formation of alkoxides from CrO_3 and alcohols are known.[209] Products analogous to aerogels are formed in the glycothermal synthesis, which involves the treatment of a mixture of $Al(OPr^i)_3$ with glycols in an autoclave at 300 °C for 2 h and subsequent heat treatment at ~ 600 °C.[157] The dominant pore diameters in the γ-Al_2O_3 obtained using ethylene glycol, propane-1,3-diol and butane-1,4-diol were respectively 7, 16, and 70 nm, while S_{sp} varied from 184 to 354 $m^2\ g^{-1}$. γ-Al_2O_3 modified by the addition of SiO_2 in order to increase its thermal stability has been synthesised by a similar method.[210]

Catalysts with a honeycomb structure, which exhibit low aerodynamic and hydrodynamic resistances and make it possible to perform catalytic processes in liquids and gaseous media in the presence of heterogeneous admixtures, have come to be widely used abroad during recent years. A porous ceramic with a cordierite ($2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$) composition, a low coefficient of thermal expansion, and a resistance to temperature gradients is most often employed as a carrier for honeycomb catalysts. The Corning Company, which has devoted a considerable amount of attention to alkoxo-technology,[37,39,213–218] is the pioneer and recognised leader in the development and introduction of ceramic honeycomb carriers.[211,212] For example, it developed a new type of monolithic honeycomb catalysts with porous catalytic coatings, which are not on the walls (washcoat), as in the traditional catalyst, but within them (washcoat-in-the-wall), which reduces the consumption of expensive metals per unit volume of the catalyst and improves its operating characteristics.[217] It may be postulated that alkoxo-technology has found an application in the manufacture of a new honeycomb catalyst with an increased operating lifetime.[219]

A cordierite ceramic has been obtained in Japan with the aid of alkoxo-technology.[220–222] For this purpose, a mixture of ethyl silicates with magnesium and aluminium salts was spray pyrolysed, which resulted in the formation of porous cordierite microsphere powders, which were heat-treated in the temperature range 950–1450 °C. The resulting ceramic has a high porosity (48%–92%) and is promising material for honeycomb carriers. The purity of the alkoxide cordierite powders is important, since impurities significantly increase the coefficient of thermal expansion of cordierite[212] and reduce the heat resistance of the finished product.

In Russia, the large-scale industrial manufacture of ceramic cordierite carriers has not been initiated (mainly owing to the difficulties arising during heat treatment, associated with achieving a compatible combination of the stages involving the synthesis of cordierite and sintering within a narrow process temperature range). Carriers based on glass or polycrystalline fibres (paper, cardboard, fabric, etc.) may serve as an alternative.

The deposition of porous coatings on these materials from aqueous solutions of inorganic salts is difficult because such solutions have no film-forming properties and when they are dried crystallisation takes place. The employment of alkoxides and the products of their hydrolysis makes it possible to overcome these difficulties easily. For example, the carrier and the catalyst may be obtained by impregnating various fabrics having specified mesh dimensions with suspensions based on aqueous alcoholic solutions and silicon, aluminium, and/or titanium alkoxides and oxide powders of the same elements.[223]

A convenient procedure for the creation of a heat-resistant fibrous oxide structure is the method involving the burning away of a matrix. A fibrous organic material is impregnated with a hydrolysed solution of an alkoxide (in one step or with periodic intermediate drying) and is heat-treated under conditions ensuring the burning away of the organic matrix and the sintering of the oxide coating generated.[224-226] It has been suggested that heat-resistant highly porous carriers be obtained by the cyclic impregnation of foam-carbon articles with a chelated alkoxide and intervening heat treatment.[227]

Elements of alkoxo-technology and ion exchange have been used in a novel method of preparation of catalysts.[228,229] According to this method, soluble substitution products are obtained initially by the interaction of titanium, zirconium, or tantalum alkoxides with a methanol solution of NaOH, this being followed by hydrolysis and ion exchange with nickel, palladium, or molybdenum salts.

$$Ti(OPr)_4 + NaOH \xrightarrow{\text{methanol}} \text{soluble products} \xrightarrow{\text{acetone, water}}$$

$$\longrightarrow (NaTi_2O_5H)_x \xrightarrow{Ni^{2+}} [Ni(Ti_2O_5H)_2]_x .$$

The catalysts synthesised have a high specific surface (150–300 $m^2 g^{-1}$) and an increased catalytic activity: for a 1% content of the catalytically active metal, they are just as effective in the liquefaction of coal as industrial catalysts with a 15% content of this metal.

Interesting procedures for the employment of alkoxo-technology in the preparation of phosphorus vanadium oxide catalysts for the synthesis of maleic anhydride by the selective oxidation of C_4 hydrocarbons have been proposed. Here the alkoxide $VO(OR)_3$ may be used as one of the starting compounds in the synthesis of the catalyst,[230] vanadium(IV) and vanadium(III) alkoxides may be formed and segregated in one of the technological stages,[231] and, finally, the alkoxides may be formed *in situ* from V_2O_5 and ROH and react with H_3PO_4.[232-234] The use of alkoxides has a dual purpose. Firstly, they are the most convenient vanadium compounds suitable for interaction with H_3PO_4 (vanadates or vanadium chlorides are unsuitable for this purpose and the synthesis of vanadium catalysts from a mixture of V_2O_5 powders with P_2O_5 or H_3PO_4 is also impossible). Secondly, alcohols reduce vanadium(V) to vanadium(III) and vanadium(IV), which promotes the attainment of a high activity and selectivity. Another alkoxide, $Si(OEt)_4$, is also used in these synthesis, its role consisting mainly in the binding of the water evolved, which facilitates the formation of a cryptocrystalline catalytic powder.

$$V_2O_5 + 2H_3PO_4 + RCH_2OH \longrightarrow$$

$$\longrightarrow (VO)_2H_4P_2O_9 + RC(O)H + 2H_2O ,$$

$$Si(OEt)_4 + 4H_2O \longrightarrow Si(OH)_4 + 4EtOH .$$

Large foreign companies, for example Union Carbide, Mobil Oil, Chevron, etc., have devoted much attention during the last decade to the use of alkoxides for the preparation of synthetic molecular sieves having the compositions $(Si_xAl_yP_z)O_2$,[235,236] $(M_qSi_xAl_yP_z)O_2$ (M = Mg, Fe, or Ti),[237-240] $(Ti_xAl_ySi_z)O_2$,[241-243] $Al_2O_3-P_2O_5$,[244] etc.,[245-248] which is associated with increased reactivity of the oxides and oxide hydroxides formed on hydrolysis of alkoxides. The use of $Ti(OR)_4$ and of its modified analogues, formed when a proportion of the RO groups are replaced by chelating groups, made it possible to achieve the homogeneous insertion of TiO_2 into the aluminosilicate framework, which could not be achieved when other titanium compounds were employed.[243] The molecular sieves were synthesised by the hydrothermal treatment of a mixture of compounds of the corresponding elements, at least one of which is an alkoxide or a product of its hydrolysis, in the presence of an organic structure-forming agent (alkylamine, pyridine, tetraalkylammonium hydroxide) with subsequent heat treatment in air at 200–700 °C for the complete or partial removal of the structure-forming agent. For example, SAPO-11 aluminosilicon phosphate molecular sieves have been obtained in this way and the 0.5% Pd/SAPO-11 catalyst was prepared from them. The yield of neutral distillates in hydrocracking on this catalyst reaches 75.4%, whereas in the presence of the traditional catalyst having a similar composition it is 64.7%.[235] Evidently in the presence of this effect the question of the increased cost of the precursor alkoxide does not arise. An unusual method of synthesis of molecular sieves has been proposed[249] in which $Si(OR)_4$ serves as the cross-linking agent for alkali metal silicates, titanates, and mixed titanates swollen in the reaction medium.

Many specialists in the field of catalysts manufacture believe (see, for example, Ref. 250) that the main problem nowadays is the creation of carriers with a definite set of characteristics ensuring their functioning under specified conditions rather than the choice of catalytically active elements and their introduction into the catalyst. For example, the widely used γ-Al_2O_3 carriers disintegrate when acted upon by the acid reagents (HCl, SO_3) present in contaminated air or formed during its purification. The replacement of γ-Al_2O_3 by SiO_2, TiO_2, ZrO_2, and their mixtures is the most promising procedure. The choice of inorganic precursors for such carriers is limited and their application does not ensure the attainment of a high porosity and S_{sp} and gives rise to significant ecological problems.

These deficiencies are overcome when alkoxides are employed. Thus, among the available TiO_2 precursors, $Ti(OR)_4$ is most preferred. It is employed for the preparation of an aqueous TiO_2 sol (a catalyst of photochemical reactions),[251] microspheres or fibres,[252] powders,[253] extruded materials,[254] carriers with effective ion-exchange properties [for this purpose, $Ti(OR)_4$ is hydrolysed in the presence of NaOH or KOH],[166] and also as an organic binder with catalytic properties.[255] In most cases, such materials possess a high catalytic activity. For example, the catalysts obtained by depositing the active component on alkoxide-derived TiO_2 powder are more effective in the reduction of NO_x than those obtained by deposition on powdered aerosil, rutile, anatase, or rutile–anatase mixtures.[253]

The authors of the present review initiated comprehensive studies on the chemical foundations of alkoxo-technology and its application in heterogeneous catalysis.[256-259] A method for the joint hydrolysis of two and more alkoxides, ensuring the formation of a large number of mixed elementoxane bonds and affording significant practical advantages (the consumption of organic solvents is reduced, the effectiveness of the process is increased, and the use of inorganic acids and expensive chelating agents is eliminated) has been developed. A method of synthesis of vanadium-containing alkoxide joint hydrolysis products, envisaging the replacement of the usually employed scarce and expensive vanadium alkoxides as precursors by V_2O_5 powder, which is heated jointly with $E(OR)_n$ (E = Si, Ti, Zr, P, Al) and ROH, has been proposed. The synthesis of oligomeric products by heating one or several metal acetates with high-boiling di- and tri-hydroxy organic compounds has been achieved. This procedure is free from the disadvantages associated with the use of mixtures of acetates (fractional crystallisation, low solubility in water, lack of film-forming properties). Furthermore, the application of the self-

propagating high temperature synthesis weakens significantly the interaction of the deposited catalytic coating with the carrier.

It has been suggested that the heat resistance of the aluminosilicate carrier obtained from $Al(OR)_3$ and $Si(OH)_4$ be increased by introducing 0.5% of La_2O_3.[260] For the ratio $Al_2O_3:SiO_2$ = 99.5:0.5, the specific surfaces after heat treatment at 550 °C (3 h) and 1100 °C (24 h) are 242 and 42 $m^2\ g^{-1}$ in the absence of La_2O_3 and 245 and 72 $m^2\ g^{-1}$ respectively in its presence. This process has been patented by the Conoco Company on Russian territory.

In recent years, comprehensive studies on the use of alkoxo-technology in heterogeneous catalysis have been initiated in Mexico. Carriers and catalysts with the composition $Pt-Sn/Al_2O_3$ [produced by the joint hydrolysis of $Al(OBu)_3$ and $SnBu_4$],[261] $Ru-SiO_2(Al_2O_3)$,[262] $SiO_2-Al_2O_3$,[263] Al_2O_3,[180,264] and $Pt(Pd)/SiO_2$ [265] have been obtained.

VII. Achievements of alkoxo-technology in the manufacture of materials structurally similar to carriers and catalysts

The oxide materials obtained with the aid of alkoxo-technology may be employed in a wide variety of fields. For example, SiO_2-TiO_2 coatings possess simultaneously catalytic, light reflecting, abrasion-resistant, and electrically insulating properties. The procedures for the preparation of alkoxide materials, developed for use in a specific field, may be employed also in other fields, naturally taking into account the specific requirements as regards some of their properties. It is therefore of interest to examine also the advances of alkoxo-technology in the manufacture of oxide materials structurally similar to carriers and catalysts but having a different functional purpose.

High-temperature superconducting ceramics occupy a special place among such 'related' materials. The main task of alkoxo-technology in this field is the low-temperature synthesis of thin layer multicomponent oxide coatings with a perovskite structure on different supports. The same problem is also faced by heterogeneous catalysis. The fact that many perovskites used nowadays as high-temperature superconductors possess also catalytic properties brings these two aspects even closer together. For example, the high temperature superconducting $YBa_2Cu_3O_7$ perovskite actively catalyses the oxidation of CO and hydrocarbons.[266]

The low-temperature synthesis of perovskites with the aim of obtaining coatings makes it possible to diminish their chemical interaction with the support and helps to overcome the negative phenomena associated with this factor. During several years of studies (the high-temperature superconductivity of oxide ceramics was not discovered until 1986),[267] it has been possible to develop with the aid of alkoxo-technology procedures for the synthesis of superconducting perovskites at temperatures of about 400 °C[268] or 650–700 °C,[269] whereas the traditional synthesis requires heating above 950 °C. Evidently further advances of alkoxo-technology in the preparation of high-temperature superconducting ceramics still remain in the future. The task of specialists in catalysis is a critical analysis and purposeful employment of these developments.

The principal difference in the requirements which must be met by the oxide materials used as superconductors and catalysts (carriers) concerns the size and distribution of pores. Superconductors and catalysts must have respectively minimum and maximum porosities. In this respect, specialists in catalysis are in the best position, since, owing to the high content of the organic component in the initial mixture and the sharp increase in density on passing from organometallic to inorganic oxide materials, it is much simpler to obtain porous coatings from alkoxides than dense nonporous ones.

Another field close to heterogeneous catalysis is the electronics industry, where the employment of alkoxo-technology for the synthesis of powders with the aim of depositing coatings has been vigorously investigated and introduced.[270] For example, $NiFe_2O_4$ powders with S_{sp} = 221 $m^2\ g^{-1}$ have been obtained from alkoxides.[271] Evidently these and similar powders can be used also as catalysts for a series of reactions. A review on the preparation of powders for electronics, including their preparation with the aid of alkoxo-technology, has been published.[272]

There are no fundamental differences in the structures of the porous oxide coatings used in ultrafiltration or membrane separation and in catalysis. The principal difference concerns the form of the primary carrier and the operating conditions. The employment of alkoxides in the technology for the manufacture of inorganic (ceramic) membranes is the most promising method, since it ensures the possibility of a fine regulation of the pore dimensions within wide limits.[273,274] Like high-temperature catalysis, the filtration of hot gases or the purification of liquids with subsequent burning away of organic impurities gives rise to the problem of increasing the heat resistance, which is solved, for example, by synthesising aluminate-based membranes by means of alkoxo-technology.[44] Filtering coatings based on γ-Al_2O_3 and the products of its hydrolysis are most often employed.[275–278] TiO_2-SiO_2 membranes with an average pore size of 4 nm and S_{sp} = 324 $m^2\ g^{-1}$ have been obtained from the products of the joint hydrolysis of alkoxides.[279] Aluminosilicate membranes, the specific surfaces of which were 217, 384, 456, and 472 $m^2\ g^{-1}$ with pore radii of 2.21, 2.15, 2.15, and 1.72 nm for the ratios $Al_2O_3:SiO_2$ = 5.6:1, 4.4:1, 4.2:1, and 1.5:1 respectively have been obtained by the separate hydrolysis of $Si(OMe)_4$ and $Al(OBu^s)_3$ with formation of sols and subsequent mixing and heat treatment.[280] It has been recommended that these membranes be used also in heterogeneous catalysis.

Separating ZrO_2 layers are used in catalysts with metallic carriers, which are employed in the high-temperature purification of gases, for improving the resistance of the metal to oxidation and for increasing the adhesion of the metal to the porous γ-Al_2O_3 carrier.[281] Such layers, 0.1 μm thick and obtained from $Zr(acac)_4$, retained their continuity and did not peel off on heating to 1000 °C.[282]

Oxide coatings synthesised from various alkoxides and their mixtures prevent the high-temperature oxidation of metals.[283–286] They also prevent chemical corrosion and increase the resistance of materials to abrasion. The chemical compositions of the coatings (SiO_2, TiO_2, Al_2O_3, ZrO_2) suggest their possible use in catalysis not only for the creation of separating layers but also directly as acid–base catalysts or carriers. Here one must take into account the difference between the requirements as regards the porosities of protective and catalytic coatings. Special procedures and methods are used to increase the porosity, for example, additives which are burnt off with formation of pores are introduced.

In systems for the catalytic purification of exhaust gases in automobile transport, oxygen sensors prepared from $Zr(OR)_4$ and ZrO_2 powder are employed.[287] After their deposition on a suitable support and the introduction of catalytically active metals, such materials may also function as high-temperature catalysts, for example, in the same systems for the purification of exhaust gases.

It is believed [288] that alkoxo-technology will play an important role in the creation of sensors in the future.

One of the most significant advances in modern ceramic technology is the use of the products of the hydrolysis of alkoxides as binders in the preparation of bulky ceramic materials.[289] Such binders make it possible to reduce or to eliminate completely the cracking occurring during moulding, drying, and heat treatment (sintering) of the ceramic, improving its strength. This approach has a great future in the manufacture of porous ceramic glass and composite materials,[290,291] which may be employed also as carriers for heterogeneous catalysts.

VIII. Conclusion

The alkoxides of various chemical elements (as precursors of oxides) have come to be widely used nowadays for the preparation of heterogeneous catalysts and carriers. Large chemical companies of the USA and Japan have shown special interest in alkoxo-technology. Although a considerable proportion of the publications in this field are in the nature of advertisements and many details of the process are not specified, nevertheless there have evidently been significant advances associated principally with the creation of catalytic materials having a high specific surface and porosity and a controllable pore size. The use of alkoxo-technology also makes it possible to obtain heat-resistant carriers and catalysts with a high activity and selectivity combined with a reduced (by an order of magnitude and more) consumption of catalytically active elements. A series of alkoxide catalysts possess unique properties which traditional catalysts lack. The ecological cleanliness of the process involving the preparation of catalysts and carriers by the alkoxo-technological method is very important.

At the same time, the use of alkoxo-technology in heterogeneous catalysis is still at the development stage. Among the numerous possibilities provided by alkoxo-technology, only a small proportion have been realised. For example, possibilities for the low-temperature synthesis of known and especially new crystalline and amorphous compounds are only beginning to be realised. Alkoxo-technology is also used in the preparation of a series of oxide materials structurally similar to catalytic substances but having a different functional purpose. The approaches to the appropriate modifications developed in this connection may be used also in the technology for the manufacture of heterogeneous catalysts and carriers.

In Russia and the Commonwealth of Independent States, adequate attention has not so far been devoted to the application of alkoxo-technology in heterogeneous catalysis. At the same time, some investigations have led to the development of a series of approaches (for example, the synthesis of catalysts via metal resinates),[292,293] which, although they have no direct bearing on alkoxo-technology, can nevertheless find partial applications in the preparation of heterogeneous catalysts by this method.

Studies on alkoxo-technology have been initiated in recent years at the Faculty of Chemistry of the Moscow State University, at the State Institute of the Chemistry and Technology of Organoelement Compounds, at the Institute of Petrochemical Synthesis of the Russian Academy of Sciences, and in certain other scientific establishments. The practical introduction of alkoxo-technology has also begun. Thus the synthesis of boehmite has been implemented in the undertakings of Yaroslavl' and Ufa (the Condea chemie Company).

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