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Current Trends in the Improvement and Development of Catalyst Preparation Methods

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Abstract—The state of the art in the scientific foundations of catalyst preparation is analyzed. New lines and trends in the development of conventional catalyst preparation methods that have appeared in the last 10–15 years are discussed. The theoretical and experimental foundations of the syntheses of porous materials by the sol–gel processing of alkoxides are considered. The synthesis of fine MgO aerogel, which is a unique destructive sorbent and catalyst, is described as one of the numerous examples of the use of this method in combination with supercritical drying. The synthesis of complex oxide and supported metallic catalysts by the sol–gel method is analyzed. Some new approaches to active catalyst deposition are considered, including the deposition–precipitation method. Unconventional methods of catalyst preparation are classified. Tasks are formulated for the development of the scientific basis of these methods.

The 20th century was marked by a swift development of numerous industrial catalytic processes. This became possible due to a variety of newly developed catalysts. Three well-known basic problems appear in the development of modern catalysts: search for highly efficient, catalytically active compositions; their structuring; and ensuring the maximum possible efficiency, stability, and lifetime. In the middle of the last century, these three problems gave birth to three areas in catalysis science:

scientific foundations of predicting the catalytic effect,

scientific foundations of the preparation and manufacture of catalysts, and

problems of the deactivation and stability of catalysts.

The following questions should be considered when discussing catalyst preparation:

(1) What are the optimum structure and texture ensuring the most efficient use of each particular catalyst? It is necessary to know the set of main characteristics of the catalysts [1–3].

(2) What preparation method should be chosen and how should its main and auxiliary steps be carried out to achieve the best characteristics of the resulting catalyst?

It should be noted that sometimes the optimization of each particular parameter or characteristic of a catalyst is an independent problem and necessitates large expenses. Sometimes even a well-known active composition is not commercialized for the reason that it cannot be shaped into an appropriate structure, for example, simple pellets. The preparation of catalysts was initially an art of cookery based on the empirical and intuitive selection of conditions and methods; it was transformed into science upon the development of physical methods of investigation. These methods enable one to monitor the changes in the properties of a catalyst at the initial, intermediate, and final stages of preparation. As our understanding of the mechanisms of catalytic system formation deepened, the methods of preparation were improved and became more complicated. As a result, the terminology of catalyst preparation contains such terms as *conventional* and *new* methods of catalyst preparation. Some researchers believe that conventional methods cannot be further improved and only new, unconventional approaches to catalyst synthesis can result in a breakthrough in the development of catalytic systems with radically new properties. However, the concept of conventional methods should not be viewed as some forever established complex of operations. Considering the current pace of the development of science, these methods can be dynamically enriched with new ideas and radically improved and thus regain significance.

In this review, we analyze, in very general terms, the current status the scientific foundations of catalyst preparation and estimate the new directions and tendencies that have appeared in this area in the last 10–15 years. Of course, one article cannot consider all ideas capable of giving a second wind to the conventional methods of catalyst preparation. Therefore, we will illustrate, using the most striking examples based on in-depth fundamental studies, the possibility of understanding the essence of phenomena and finding a new, promising solution in situations in which all potentialities have seemingly been exhausted. In the second part of the review, we attempt to classify the unconventional methods of catalyst preparation and formulate problems to be solved in the scientific substantiation of these methods.

1. CONVENTIONAL METHODS OF CATALYST PREPARATION

All finely divided systems, including most solid catalysts, can be synthesized by two main methods, namely, condensation and dispersion [4]. Condensation implies the formation of a heterogeneous dispersed system from a homogeneous system by the association of molecules, atoms, or ions into aggregates. Dispersed solids can be obtained by condensation from either a liquid or a gaseous phase. Dispersion is the crushing or powdering of macroscopic phases to microsizes (in some cases, to colloidal sizes). Dispersion can be carried out by mechanical treatment, by causing phase transitions, and by the removal of part of the nonporous material using chemical or thermal treatment. Note that all known conventional and new methods of catalyst preparation are based on these two approaches. However, catalyst preparation, from the preparation of starting substances to the production of a commercial product of a certain shape and size, is a multistep process. A catalyst preparation procedure receives its name from the key step that determines, to a considerable extent, the main parameters of the resulting catalyst. The methods that have found wide use (including industrial use) are usually called conventional. The conventional methods of catalyst preparation can be divided into six main groups [3, 5].

(1) Precipitation from solutions (or coprecipitation from multicomponent systems) includes gel or precipitate formation followed by washing, drying, and thermal treatment. These methods should be viewed as a particular case of condensation methods producing powders and suspensions.

(2) Deposition methods are based on the introduction of a starting substance (a precursor of the active component) into a porous support followed by the deposition of the active component on the surface. These methods are also classified as condensation procedures. Deposition can be carried out from either a gaseous or a liquid phase. The latter variant has found the widest practical use.

(3) Methods based on mechanical mixing of components are used as an alternative to coprecipitation and deposition. Their advantage is that they produce little, if any, wastewater or emissions. The key stage of the method is the dispersion and homogenization of the starting components followed by drying or calcination. A specific feature of this group of methods is that they are satisfied by less favorable solid-phase synthesis conditions than the coprecipitation or calcination of heteronuclear complexes.

(4) Thermal decomposition is the most important step in most preparation methods. Only those thermal decomposition procedures should be united in a distinct group of methods that are essentially different from the thermal decomposition steps involved in methods 1–3. The difference may be in the procedure that affords substances with new properties or in starting substances. The first variant is exemplified by the pulse decomposition or thermochemical activation of gibbsite, which affords a finely divided amorphous product with a high reactivity [6]. An example of the second variant is the decomposition of simple or complex salts (carbonates, formates, oxalates, citrates, etc.) resulting in finely divided oxides [7].

(5) The preparation of porous, spongy bodies by chemical treatment of reagents on a coarse-pore or nonporous solid (leaching of alloys, thermolysis producing active carbons, etc.) has found less wide use. However, this method is employed in the preparation of a variety of very important commercial catalysts and adsorbents.

(6) Chemical vapor deposition methods are based on the pyrolysis of organic and inorganic volatiles in the absence or presence of oxidizing agents. For instance, the pyrolysis of hydrocarbons is used to produce carbon black, technical carbon, and carbon-containing composite supports of the Sibunit family [8]. The vapor-phase hydrolysis or oxidation of volatile chloride $MeCl_4$ is used to prepare dispersed powders of SiO_2, TiO_2, etc. [9]. The decomposition of metal carbonyls, for example, nickel tetracarbonyl, makes it possible to obtain metal particles smaller than 4 nm.

This classification of catalyst preparation methods is provisional, even though it is rather convenient, as it allows the principles of catalyst formation to be considered in the framework of one method. This is due to the fact that the final product (catalyst) is prepared through a series of successive steps proceeding via their own mechanisms and obeying their own laws. This classification ignores catalyst shaping, which is the most important procedure resulting in the preparation of a commercial catalyst [3]. Furthermore, a combination of different preparation methods is often used in the development of an industrial catalyst technology.

Below, using the precipitation and deposition methods as examples, we illustrate the synthesis control and property prediction opportunities that are available for conventional methods if the mechanisms and laws of formation of a variety of catalytic systems produced by these methods are known.

2. DEVELOPMENT OF PRECIPITATION METHODS

Precipitation from solutions is a popular method for producing catalysts, because it allows the chemical and phase compositions, particle size, and morphology of intermediates to be controlled rather reliably. These intermediate products are hydroxides (which are most often used) or salts from which the desired catalytic systems are obtained by subsequent thermal treatments.

The precipitation method is rather universal and is applicable to both one-component and multicomponent catalytic systems, including those classified as supported catalysts. The notorious disadvantages of this method are that it requires aggressive chemicals (acids and bases) and produces much wastewater and harmful emissions to be treated.

The properties (phase composition, particle size and morphology, and porosity) of resulting precipitates depend on a wide variety of precipitation and aging parameters. The main precipitation parameters are precipitation and aging pH, the concentration and composition of the initial solution, the nature of the precipitating anion, the nature of the precipitating agent and solvent, the precipitation technique (precipitation from a homogeneous medium at a variable or constant pH in a batch or continuous apparatus), the nature of additions (surfactants and templates), etc. [10]. The greatest progress in precipitation control was achieved in the 1970–1980s, when the mechanisms of precipitate formation, from the early stages on, were elucidated. Russian scientists have made a great contribution to the development of precipitation theory. The main achievements in this area include the establishment of a uniform stage mechanism of hydroxide formation, the classification of hydroxides according to their ability to crystallize [11], the discovery of the mechanisms of amorphous silica gel aging [12], and the creation of a theory of crystallization of low-solubility hydroxides via the oriented growth mechanism [13].

In the last two decades, the greatest progress has been made in the sol–gel preparation of dispersed single-component and multicomponent systems by the hydrolysis of solutions of metal alkoxides and in the synthesis of new, so-called mesophase mesoporous materials, especially in western countries. Here we consider only the sol–gel method, while the synthesis of mesophase mesoporous materials is described in [14].

2.1. Sol–Gel Method

For the sake of historical justice, it should be noted that the sol–gel method dates not from the end of the 20th century but from the synthesis of silica gel by precipitation from sodium silicate solutions with acids, for example, sulfuric acid. The specific features and regularities of this process are considered in Iler's monograph [15, 16], which has already become a classic. Silica gel and other hydrogels can be synthesized by the sol–gel method using the water hydrolysis of tetrachlorides of various metals (MCl_4), for example, $SiCl_4$, $TiCl_4$, and $ZrCl_4$. These chlorides are known to fume strongly in air, and the resulting gels are heavily contaminated with chlorine ions. The sol–gel method received a new impetus when alkoxides of various metals (Si, Zr, Al, Ti, Mg, Ca, etc.), including tetramethoxysilane (TMOS), tetraethoxysilane (TEOS), tetraisopropoxytitanium, zirconium isopropoxide, aluminum tri-*tert*-butoxide (TBOA), and magnesium methoxide, were employed as starting chemicals. In these techniques, the hydrolyzing agent is water and the solvent is an alcohol (as a rule, the alcohol is related to the alkyl group of the alkoxide).

Alkoxides have the following advantages over inorganic precursors [17–20]:

high purity of the precursor and final products;

reliable control of the process parameters determining the final structure of the alkogel and its properties;

uniformity of the chemical, physical, and morphological properties of the product;

mixing of the components at the molecular level;

possibility of preparing samples at low temperatures;

possibility of introducing a variety of components in one step; and

possibility of controlling the reaction kinetics and stabilizing metastable systems.

Since the sol–gel method is considered in detail in several reviews [17–20], only the main principles and the chemistry of this method will be described below. The method is based on the following fundamental principles established while studying hydroxide formation:

(1) Hydroxides form via the following stepped mechanism [11]: hydrolysis $\longrightarrow$ polymerization of hydrolysis products $\longrightarrow$ polycondensation and formation of primary sol particles $\longrightarrow$ aggregation of primary sol particles (coagulation) and gel or sol formation $\longrightarrow$ precipitate aging.

(2) The properties of the final precipitate and the resulting catalyst depend on the ratio of step rates, which, in turn, depends on the precipitation conditions and parameters [17, 20].

In light of these principles, it seems important to reveal the precipitation conditions driving the process via either gel formation or precipitate (coagel) formation. The formation of the gel and coagel is schematized in Fig. 1 [16]. Whether a gel or a coagel will be formed is determined by the differences between the hydrolysis rate V_h and the coagulation rate V_{coag}.

For $V_h \gg V_{coag}$, hydrolysis, sol formation, and gel formation occur in sequence. A necessary condition for gel formation is the use of a strong hydrolyzing agent and a weak coagulator as the precipitating agent. Gel formation is the bonding of individual particles into branched chains completely filling the sol volume. Therefore, the concentration of solid particles in any chosen macroscopic region of the system does not increase. Instead, all of the medium becomes viscous and then solidifies to form a network consisting of bonded particles. The network of bonded particles can retain a liquid owing to its capillary structure. Interparticle bonds in gels are often chemical (usually due to

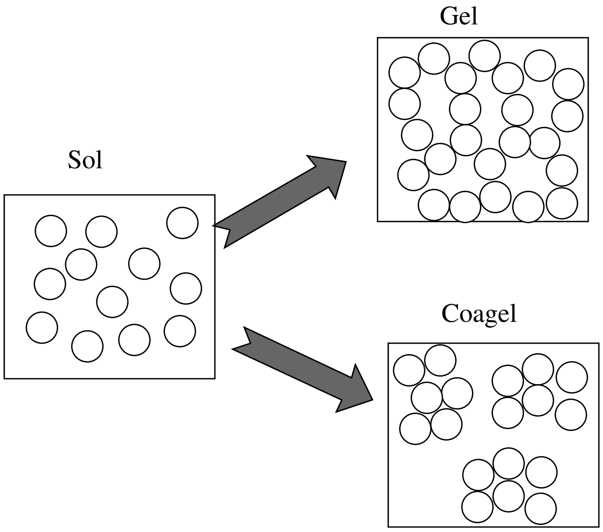


Fig. 1. Formation of a gel and a coagel from a sol.

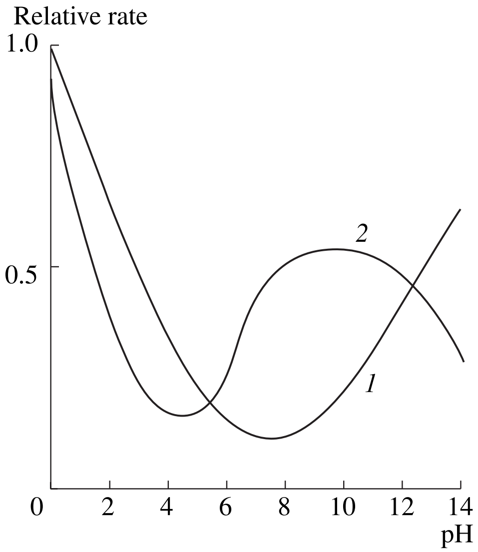


Fig. 2. Ratios between the (*1*) hydrolysis and (*2*) polycondensation rates of TEOS at different pH values.

condensation) and do not cleave when a peptizing agent is introduced into the precipitate [15].

For $V_{\mathrm{coag}} \geq V_{\mathrm{g}}$, sol formation and coagulation occur simultaneously. The best conditions for coagel formation are the use of a weak hydrolyzing agent and a strong coagulator as the precipitating agent. Coagel formation is accompanied by the aggregation of primary particles. The concentration of solid substance is higher in the aggregates than in the starting sols. The packed density of primary particles in the aggregates can vary substantially, depending on the nature of the precipitate and preparation conditions. However, as a whole, the coagulation forces between particles in the aggregates are weak and are usually van der Waals forces. For this reason, the precipitate can transform into a sol again upon mechanical treatment or addition of a peptizing agent.

The use of metal alkoxides as starting reactants and water as the hydrolyzing agent is the most favorable for the process to proceed via gel formation. The conventional treatment of an aqueous solution of an inorganic salt with an alkali or an acid results, as a rule, in a precipitate (coagel). Coagels can be formed under less stringently controlled conditions than gels. Therefore, sol–gel processing has several obvious and promising advantages over precipitation (a moe stringent control over the texture, composition, homogeneity, and structural properties of the final solid product).

This technology, beginning with a step involving the starting reactant (precursor) and ending in the formation of a product, consists of four main steps: (1) hydrogel formation, (2) hydrogel aging, (3) solvent removal (drying), and (4) heat treatment. The versatility of this preparation method is determined by the number of parameters that can be controlled at each of these stages [20].

The chemistry of the gel formation stage is described by the acid- or base-catalyzed nucleophilic addition or substitution reactions (hydrolysis (I) and condensation (II))

$$\text{–M–OR} + \mathrm{H_2O} \longrightarrow \text{–M–OH} + \text{R–OH}, \qquad \text{(I)}$$

$$\text{–M–OH} + \text{XO–M–} \longrightarrow \text{–M–O–M–} + \text{X–OH}, \qquad \text{(II)}$$

where M is a metal cation and X is $\mathrm{H^+}$ or an alkyl group (R).

The key factor determining the properties of the resulting gel is the ratio of the hydrolysis and condensation rates [17, 20]. The critical parameters influencing the hydrolysis or condensation rate are the following:

pH of the process, which is controlled by adding an acid or a base;

water-to-alkoxide molar ratio (*m*);

composition of the alkyl group (R) of the metal alkoxide;

alkoxide concentration;

process temperature; and

stirring vigor.

Since the values of these parameters in each particular process are specific and depend on the chemical nature of the gel to be precipitated, the influence of some of them (pH, *m*, and R) on the structural characteristics of the resulting gel will be illustrated by the example of silica gel synthesis. The hydrolysis and condensation rates of TEOS versus the pH of the medium are presented in Fig. 2.

The highest hydrolysis rate is observed at low and high pH values, whereas the lowest rate is observed for neutral media. In an acidic medium, the alkoxide group is protonated to form a readily leaving group ROH:

$$\equiv\text{Si–OR} + \text{H}^+ \longleftrightarrow \equiv\text{Si–(HOR)}^+,$$

$$\equiv\text{Si–(HOR)}^+ + \text{H}_2\text{O} \longleftrightarrow \equiv\text{Si–(HOH)}^+ + \text{ROH},$$

$$\equiv\text{Si–(HOH)}^+ \longleftrightarrow \equiv\text{Si–OH} + \text{H}^+.$$

Under alkaline conditions, the solution contains the strong nucleophile OH^-, which can attack the alkoxysilane group:

$$\equiv\text{Si–OR} + \text{OH}^- \longleftrightarrow \equiv\text{SiO}^- + \text{ROH},$$

$$\equiv\text{SiO}^- + \text{H}_2\text{O} \longleftrightarrow \equiv\text{Si–OH} + \text{OH}^-.$$

The hydrolysis rate decreases with an increase in the alkyl group size [18, 20]:

$$\text{TMOS} > \text{TEOS} > \text{TPOS} > \text{TBOS},$$

where TPOS and TBOS are tetrapropoxysilane and tetrabutoxysilane, respectively.

The extent of hydrolysis can be controlled by varying the molar ratio of water to alkoxysilane. For complete hydrolysis, this ratio is 4–20. When this ratio is 1 : 1, partially hydrolyzed species are formed, which can be stored for a long time in an acidic solution, undergoing no polycondensation.

Polycondensation leads to the formation of siloxane bonds and by-products (alcohol and water) and can be described by the following equations:

(a) dimer formation,

$$\text{(HO)}_3\text{Si – OH} + \text{HO– Si(OH)}_3$$

$$\longleftrightarrow \text{(HO)}_3\text{Si–O–Si(OH)}_3 + \text{HOH},$$

$$\text{(RO)}_3\text{Si–OR} + \text{HO–Si(OR)}_3$$

$$\longleftrightarrow \text{(RO)}_3\text{Si–O–Si(OR)}_3 + \text{ROH},$$

$$\text{(RO)}_3\text{Si–OH} + \text{HO–Si(OR)}_3$$

$$\longleftrightarrow \text{(RO)}_3\text{Si–O–Si(OR)}_3 + \text{HOH};$$

(b) the formation of linear trimers and tetramers,

$$\text{(HO)}_3\text{Si–O–Si(OH)}_3 + \text{HO–Si(OH)}_3$$

$$\longleftrightarrow \text{trimer} \longleftrightarrow \text{tetramer},$$

$$\text{(RO)}_3\text{Si–O–Si(OR)}_3 + \text{HO–Si (OH)}_3$$

$$\longleftrightarrow \text{trimer} \longleftrightarrow \text{tetramer};$$

(c) the closure of tetramer rings;

(d) the addition of monomers to high-molecular compounds, yielding primary sol particles.

Condensation competes with hydrolysis and is also pH-dependent. It is much more difficult to describe the condensation reaction. Figure 2 (curve *2*) shows that the condensation reaction can be accelerated under both acidic and alkaline conditions. Hydrolysis and polycondensation usually occur almost simultaneously, and the final state of the system is determined by the ratio between the hydrolysis and polycondensation rates.

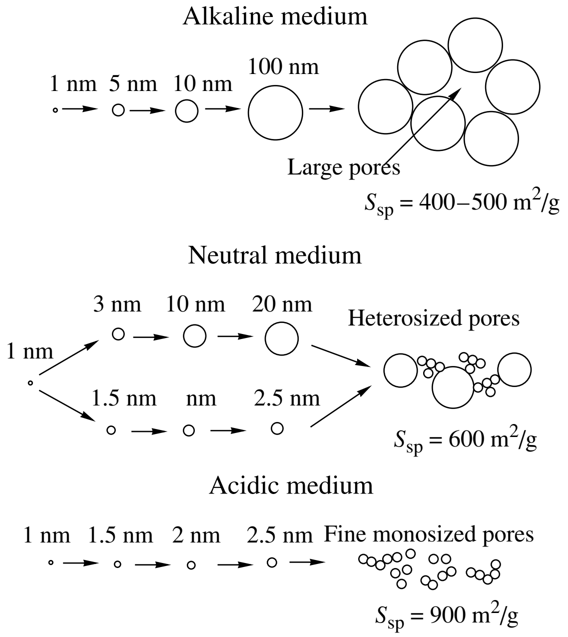


Fig. 3. Influence of the pH of the colloidal solution on the formation of the SiO_2 gel.

In acidic solutions, the hydrolysis rate exceeds the polycondensation rate. Hydrolysis proceeds rapidly to form a large amount of monosilicic acid, resulting in intensive nucleation. Polycondensation is slower and affords many fine sol particles 2–3 nm in size. A homogeneous microporous xerogel with a specific surface area of 800–1000 m^2/g results from gelation followed by drying (Fig. 3).

In alkaline solutions, the polycondensation rate exceeds the hydrolysis rate. No supersaturation necessary for intensive nucleation is observed in the system, and, therefore, only the existing nuclei grow, resulting in sol particles as large as tens of nanometers. The resulting gel is extensively branched and contains colloidal aggregates. In general, gel formation in an alkaline medium is similar to silica gel precipitation as a coagel [12, 14]. The dried xerogel has a specific surface area of 400–500 m^2/g and a coarse-pore structure.

In neutral mesia, both coarse and fine particles form, resulting in a silica gel with a nonuniform pore-size distribution (Fig. 3).

The porous structure of a dried silica gel depends substantially on the drying conditions [21]. As silica gels are dried in air in a standard way, meniscuses appear over the perimeter of the gel network and a solid–liquid–gas interface forms. This leads to the appearance of a force tending to compress the gel network. This force is proportional to the capillary pressure determined from the Laplace equation and reduces

Influence of the preparation method and of drying and calcination conditions on the specific surfaces area of $Mg(OH)_2$ and MgO

No.	Method	Reagents	Solvent	$Mg(OH)_2$		MgO				Reference
				drying conditions	S_{BET}, m^2/g	calcination conditions	T, °C	S_{BET}, m^2/g	material	
1	Precipitation	$Mg(NO_3)_2$, KOH	Water	Air flow	84	Air flow	600	124	Porous oxide	[30]
2	Sol–gel	$Mg(OC_2H_5)_2$, H_2O	Ethanol	″	107	″	600	40	″	[30]
3	″	″	Methanol	Supercritical	581	Dynamic vacuum	500	250	Aerogel	[31]
4*	″	″	Methanol + toluene	″	1011	″	500	522	″	[25]
5*	″	″	″	″	641	″	500 550	475 412	″	[29]

* These procedures differ in the toluene content of the solvent.

the pore volume dramatically. In high-temperature drying under supercritical conditions, an alkogel and an organic solvent are placed into an autoclave and the autoclave temperature and pressure are raised to supercritical values for the solvent. The solvent turns to a fluid that can leave the gel structure without destroying it.

Solvent removal by supercritical drying is widely used in aerogel preparation. Aerogels are transparent monoliths with a porosity of up to 99.8%. These materials are of considerable interest due to their special thermal, acoustic, and optical properties. The texture properties specific to aerogels are promissing for several catalytic processes. Numerous works in this area were analyzed in an earlier review [21]. Here, we will briefly consider the synthesis of MgO aerogel nanoparticles [22], which possess properties of a unique destructive sorbent for toxic substances [23], including poisons [24]. This material was prepared by the sol–gel method in combination with supercritical drying [25]. It has recently been shown that the magnesium oxide aerogel is a promising catalyst for the hydrodechlorination of chlorinated hydrocarbons [26] and for the selective chlorination of methane [27, 28].

What are the specific features of magnesium oxide obtained by this method as compared to MgO prepared by conventional precipitation from an inorganic solution? The sol–gel preparation of magnesium hydroxide is carried out by the hydrolysis of magnesium methoxide with water in methanol according to the reaction [22, 25]

$$Mg(OCH_3)_2 + 2H_2O \longrightarrow Mg(OH)_2 + 2CH_3OH.$$

However, even a stoichiometric amount of water added results in incomplete hydrolysis, yielding products containing unhydrolyzed OCH_3 groups:

$$Mg(OCH_3)_2 + H_2O \longrightarrow Mg(OH)(OCH_3) + CH_3OH,$$

$$Mg(OH)(OCH_3) + H_2O \longleftrightarrow Mg(OH)_2 + CH_3OH.$$

Employing an organometallic compound as the starting substance instead of an inorganic salt, conducting the process in a nonaqueous medium, and performing hydrolysis in water rather than in an alkali markedly slows down both hydrolysis and coagulation, the decrease in the coagulation rate being greater. These conditions favor the formation of a polymeric gel. Furthermore, organic ligands retained by gel particles prevent crystallization and secondary crystal formation. The chemical analysis of the gels shows that the ratio of $OH^- + OCH_3$ to Mg is below stoichiometric. Therefore, the following reactions between the hydrolyzed products occur during gel formation:

$$–Mg–OCH_3 + HO–Mg– \longrightarrow –Mg–O–Mg– + CH_3OH,$$

$$–Mg–OH + HO–Mg– \longrightarrow –Mg–O–Mg– + H_2O.$$

However, the possibility of the formation of less stable hydrogen (H…O) or Mg…O bonds between the $Mg(OH)(OCH_3)$ and $Mg(OH)_2$ molecules in the gels cannot be excluded.

Thus, the hydrolysis of magnesium methoxide includes successive reactions of hydrolysis, polycondensation yielding a sol, and gelation [25]. In the hydroxide precipitation from inorganic salt solutions with an alkali, no polynuclear magnesium hydroxo complexes form and, as consequence, coarse magnesium oxide crystals precipitate immediately [11]. The specific surface area of $Mg(OH)_2$ aerogel dried under supercritical conditions is determined by the sol particle size or the extent of polycondensation. The ratio of the gelation and polycondensation rates depends on the water-to-magnesium methoxide ratio in the reaction mixture. If this ratio is larger than 5, polycondensation is accelerated and the particle size increases. If this ratio is between 2 and 5, the hydrolysis rate is higher than the polycondensation rate and the particle size is minimum. Hydrolysis and gelation are accelerated to the greatest extent in the presence of toluene. By controlling the above-listed parameters, it is possible to vary the specific surface area of the dry product between 500 (in the absence of toluene) to 1010 m^2/g [25] (see the table). A large specific surface area persists as magnesium hydroxide is converted to magnesium oxide [25, 29]. For instance, when calcination is carried out above 500°C, the resulting MgO has a specific surface area of about 400–500 m^2/g, which decreases only slightly upon calcination at 700°C. These specific surface area data for magnesium hydroxide and oxide are remarkable, because they far exceed the corresponding values for the precipitates obtained by standard methods from inorganic salts [11, 30] or by the sol–gel method without supercritical drying [30].

Concluding the consideration of the physicochemical features of the sol–gel method, we can state that the great interest attracted by this technology is due to the fact that it allows the composition and microtexture of the resulting porous body, which are interrelated parameters, to be mutually controlled at the molecular level. This method makes it possible to obtain powders, fibers, thin films, granules of various sizes and shapes, and monoliths. The latter have found use as catalysts and supports, as well as ceramics and materials for microelectronics, atomic industry, pharmacology, cosmetology, etc. In spite of the several obvious technological disadvantages of this method—the high cost of the reagents, fire hazard, and the inevitable incorporation of organic residues—this method is widely used in the synthesis of various porous catalysts and supports. Besides the aforementioned silica gel and MgO, the following finely divided binary oxides have been synthesized: TiO_2 [19], CaO [22], ZrO_2 [32], Al_2O_3 [33], and Fe_2O_3 [17]. The SASOL Company uses this technology to produce high-purity alumina powders, which are employed as supports for reforming, isomerization, and dehydrogenation catalysts [34].

2.2. Chemical Processes in the Sol–Gel Preparation of Mixed Oxides

Undoubtedly, the sol–gel method is of interest for the synthesis of both one-component and multicomponent systems. As in the classical coprecipitation method, two cases can ultimately be distinguished in the preparation of these materials. The first case is the synthesis of mixed oxides, whose components can interact to form stoichiometric and nonstoichiometric compounds at the thermal treatment stage. The second case is the synthesis of supported oxides or metals. Evidently, the approaches to the sol–gel synthesis of these systems will differ.

The sol–gel method was initially used to prepare mixed oxide systems for producing glasses, coatings, and ceramic materials [17]. The first reviews on the subject were published as early as two decades ago [35]. Below we discuss some earlier reported multicomponent systems that are of interest for catalysis and have been prepared by the sol–gel method, including the binary systems $SiO_2–Al_2O_3$, $SiO_2–TiO_2$, $SiO_2–ZrO_2$, $SiO_2–Fe_2O_3$, $Al_2O_3–TiO_2$, $Al_2O_3–ZrO_2$, and $Al_2O_3–MgO$ and the ternary and multicomponent systems $SiO_2–Al_2O_3–TiO_2$, $SiO_2–Al_2O_3–MgO$, $SiO_2–Al_2O_3–La_2O_3$, and $SiO_2–TiO_2–ZrO_2$.

Although the desired properties of the final sol–gel products vary widely (from dense ceramics to porous catalytic materials), the synthesis of both glasses and catalytic materials by this method is based on the same strategies.

An important feature of the synthesis of a multicomponent system is that two or more precursors can be hydrolyzed to different extents, resulting in a dramatic increase in the number of possible hydrolysis and condensation reactions. The control of the hydrolysis and condensation rates in multicomponent systems retains its importance here, and it is complicated by the difference between the reactivities of the precursors. The relative reactivities of the precursors are the key parameters for mixed oxide systems, because they can be used to control the homogeneity of the system [17, 36]. It is natural to expect (at the qualitative level) that the more reactive precursor will be the first to undergo hydrolysis. The less reactive precursor will begin to react later, thus encapsulating or coating the condensation products of the first precursor to form a segregated (separated) product. When the reactivities of the precursors are similar, one can expect the development of a network of homogeneous gel. In this case, heteroatomic bonds M–O–M' can be formed at low temperatures, ensuring the formation of a well-homogenized sample. However, it is important to take into account the fact that homogenization is not always desirable in the sol–gel preparation of multicomponent catalytic systems. Evidently, homogenization is necessary for the preparation of catalysts, which should appear as stoichiometric complex oxides or solid solutions after thermal treatment. To prepare supported oxide catalysts, interaction is not always necessary at the hydrolysis and condensation stages. However, the difference between the precursor reactivities can have an effect on the texture of the resulting support and on the particle size of the supported oxide.

Oxide catalyst pairs, which are most interesting from the standpoint of their acidic properties, are often difficult to mix in order to obtain a homogeneous system. A large difference in electronegativity between the cations is desirable for the formation of the M–O–M' bond. At the same time, if the cations differ in terms of electronegativity, their alkoxides will have different reactivities in hydrolysis and condensation.

However, sol–gel chemistry luckily provides several chemical approaches that enable one to overcome the difficulties arising from the different reactivities of the precursors and to ensure component mixing at a near-molecular level. For the sake of brevity, we will not detail the synthesis of such systems or present experimental proofs for the formation of heteroatomic bonds in multicomponent gels. We will only enumerate these approaches [17], which can be grouped as follows:

(1) At least two alkoxide precursors exist for most metals. Depending on the alkyl group structure and length, hydrolyzability may vary substantially. Differences in hydrolysis rate were mentioned above (in section 2.1) for silicon alkoxides. Therefore, choosing an appropriate alkoxide for each of the metals to be combined, it is possible to considerably reduce the mismatch between the reactivities.

(2) The less reactive precursor (usually silicon alkoxide) should preliminarily be hydrolyzed. In this case, a certain amount of water is added to this component to perform its partial hydrolysis, and then an alkoxide of the second component is added for final gelation. The properties of the resulting product depend strongly on prehydrolysis conditions: the alkoxide concentration, the pH of the solution, the amount of water added, and temperature. For this reason, the conditions are optimized for each particular mixture.

(3) The hydrolysis rate of the more reactive precursor can be decreased by the replacement of alkoxy groups with other ligands. This procedure is known as chemical modification [37]. This approach is used especially widely to control the kinetics of preparation of one-component oxides. Acetic acid and acetylacetone are conventional modifiers.

(4) The rates of all reactions can be decreased by varying some synthesis conditions. This can be achieved by the very slow addition of zing water or by reducing the synthesis temperature.

2.3. Sol–Gel Preparation of Supported Metallic Catalysts

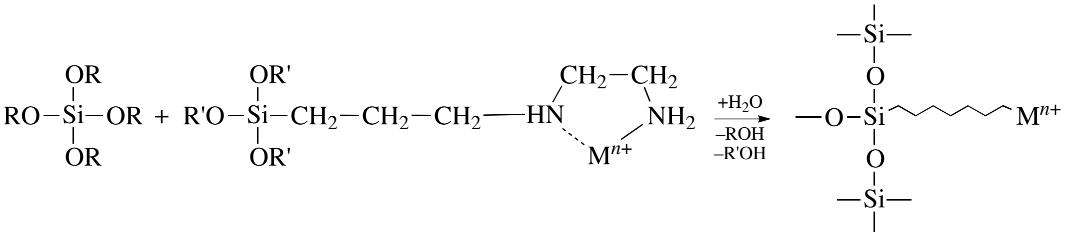
In recent years, researchers working in sol–gel chemistry have taken interest in an area that is unusual for this method, namely, the synthesis of supported metallic catalysts, such as Pt/SiO_2, Pd/SiO_2, Ru/SiO_2, Pt/Al_2O_3, $Pt\text{-}Sn/A_2O_3$, and Pt/TiO_2 [18]. As distinct from standard routes for the preparation of these catalysts, which often include two procedures (support synthesis followed by the deposition of an active metal by some method), the sol–gel technology makes it possible to synthesize the support and to deposit the metal precursor in a single step. Some researchers emphasize that the sol–gel synthesis of such catalysts affords finely divided metals on gels with a stringently controllable texture.

Two distinct approaches to the sol–gel preparation of supported metals can be distinguished. The first combines the sol–gel synthesis of a support from an organic alkoxide, such as TEOS for SiO_2 and TBOA for Al_2O_3, with the simultaneous introduction of metal precursors as inorganic salts conventionally used in deposition methods (H_2PtCl_6, $PdCl_2$, $Pd(CH_3CO_2)_2$, $RuCl_3$, etc.) [18, 33]. The second approach, suggested in the last decade, is to fix a metallic precursor at the early stages of system formation, specifically, at the stage preceding the hydrolysis of the alkoxide [38–43].

Let us briefly consider the main steps of the preparation of metallic catalysts in the framework of these approaches. The technological value of the first approach can be estimated by an analysis of three different methods for the synthesis of the Pt/SiO_2 catalyst. In the first method, the alkoxide (TEOS), the solvent (ethanol), water, and the starting metal compound are mixed to obtain a reaction mixture for gel formation (aqueous ammonia is added to increase pH). In the second method, TEOS is added dropwise to an aqueous solution of the starting metal compound. The third method is the addition of an aqueous solution of the metal compound to a freshly prepared gel [44]. The texture of the resulting xerogel depends on the parameters of the process (pH, m, T, t), as in the case of one-component systems, and the particle size of the resulting metal depends strongly on the nature of the metal precursor. For instance, when H_2PtCl_6 is used as the precursor (pH 1.4) and the H_2O/TEOS ratio (m) is 6, the dispersity of platinum in the catalyst reduced at 400°C is only 18% and the resulting silica gel is microporous (with a pore radius $r < 2$ nm) and has a large specific surface area (653 m^2/g) and a low porosity (0.28 cm^3/g) [45]. For the same platinum content and $m = 6$, the platinum dispersity reaches 80% when $Pt(NH_3)_4(NO_3)_2$ is used as the precursor (pH 4). In this case, the specific surface area of the resulting support is smaller (480 cm^2/g) and the pore size is a little larger ($r =$ 4 nm). The specimen obtained with the use of $Pt(C_5H_7O_2)_2$ has a higher specific surface area (632 m^2/g) and a medium dispersity of the metal (48%). These dispersity data agree well with the fact that, according to the results obtained by conventional deposition methods, the above compounds show different abilities to adsorb on the silica gel surface.

Now it is rather difficult to estimate the advantages of the above approach to the synthesis of supported metallic catalysts over the conventional methods of impregnation and sorption. Note that one of the possible advantages of this method is clearly manifested in the synthesis of metallic systems supported on fine-particle xerogels and aerogels prepared by the sol–gel method. Standard methods of deposition from aqueous solutions are less appropriate, because the aerogel or xerogel structure is dramatically densified in the presence of an impregnating solution, resulting in a decrease in the pore volume and specific surface area [33, 44, 45]. For Pt/Al_2O_3 catalysts prepared by a single-step sol–gel procedure, the following advantages are emphasized: a very large specific surface area of the support (up to 450 m^2/g) after all thermal treatments, a small particle size of the supported platinum, and a high resistance to deactivation by coke deposits [33].

Now let us consider the second, new approach to the synthesis of supported metallic catalysts. This method is often called cogelation [41]. $(RO)_3Si–X–A$ modified alkoxides [40–43] whose organic functional group A is capable of chelating a metal cation (palladium, platinum, nickel, silver, copper, etc.) are used in this approach. This chelate is linked to the silyl group $(RO)_3Si$ through the group X, which is inert and stable to hydrolysis. The co-condensation of these molecules with the gel-forming component $Si(OC_2H_5)_4$ produces a material in which the metal is fixed in the SiO_2 matrix [43]:



These catalysts are synthesized by the following method. An organometallic precursor (e.g., palladium acetylacetonate ($Pd[CH_3C(O)CH{=}C(O^-)CH_3]_2$), silver acetate ($AgCH_3COO^-$), and copper acetate ($Cu(CH_3COO^-)_2$)) and a modified gel-forming alkoxide ($NH_2–CH_2–CH_2–NH–(CH_2)_3–Si(OCH_3)_3$ (EDAS)) are mixed in a certain molar ratio in alcohol. The resulting viscous liquid mixture is stirred at room temperature until a colored solution of the complex is formed [41]. Next, a standard alkoxide, for example, TEOS, is added to the mixture, followed by the addition of an aqueous–alcoholic solution of ammonia. Ammonia is used to maintain a certain pH level of the mixture. The mixture is thoroughly stirred, and the vessel is sealed, heated to 70°C, and kept at this temperature for 3 days to carry out the gelation and aging processes. After that, the gel is dried *in vacuo*, calcined, and reduced at 350–400°C. The metal complex bonded to EDAS acts as a nucleating agent when silica particles are formed [41, 43]. A complex of adsorption and catalytic methods showed that the resulting catalyst consisted largely of small metallic particles (the diameter of Pd particles was about 3 nm), which were readily accessible for the gas phase and located inside the primary silica particles. This accessibility was due to the microporosity of these particles, which had an average pore diameter of about 0.8 nm. Primary silica gel particles form larger aggregates. Some coarse metal particles can exist on the external surface of these aggregates (this is particularly typical of Ag and, to a lesser extent, of Pd and Cu). A model of this structure is shown in Fig. 4.

A specific feature of supported systems obtained by cogelation is that the ultrafine metal particles are very stable to agglomeration because they are "entrapped" in microporous silica gel particles and, therefore, their rearrangement and migration over the surface are strongly obstructed [43]. However, these advantages can hardly compensate for the obvious disadvantages associated with the use of rather rare and expensive organometallic compounds.

3. DEVELOPMENT OF DEPOSITION METHODS

In the 1970–1980s, the main trends in the scientific foundations of the preparation of supported catalysts were the following:

development of the theory of electrostatic adsorption (and ion exchange) for the deposition of precursor cations and anions onto the oxide support surface from aqueous solutions of electrolytes [46–49],

development of the theoretical and practical principles of the deposition of organometallic precursors through chemical interaction with surface functional groups of the support [50, 51], and

development of the foundations of the synthesis of various supported bimetallic catalysts [52–55].

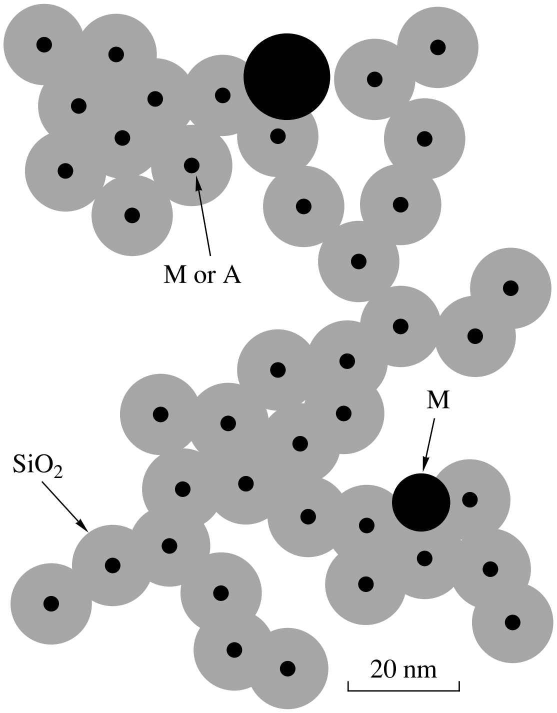


Fig. 4. Model structures of the supported metallic catalyst obtained by cogelation. M is a metal (Pd, Ag, Cu), and A is the Pd–Ag alloy [41].

Among the relatively new trends in this area, the deposition–precipitation (DP) method and use of microemulsions (water in oil) as impregnating solutions should be mentioned. It is reported that, owing to the smaller particle size of platinum, the Pt/Al_2O_3 catalyst prepared by the last method is more active in toluene oxidation than the catalyst obtained by platinum deposition from aqueous solutions of chloroplatinic acid [56]. However, since the studies in the application of microemulsions to the synthesis of supported catalysts are scarce, the mechanisms of formation of these catalysts and the potential of this method remain unclear.

Another distinct trend is the extension of the area of application of the chemical vapor deposition (CVD) method [57]. The chemical processes occurring on the surface during CVD are essential similar to chemical deposition from solutions [50, 51] and differ from the latter only in synthetic procedure [57].

The foundations of the DP method were laid as early as the mid-1980s, but the rapid advancement of this method dates back to the last 10–15 years [58, 59]. As its name indicates, the method is based on the use of precipitation combined with deposition from a liquid medium. The method combines all the achievements of the precipitation method related to the purposeful control of the state of precipitated particles and their size and size distribution. The DP method can be used in the supporting of precursors as metal sols [60], polynuclear hydroxo complexes (PHC) of metals [61], sols, or hydroxide precipitates [58, 59].

The DP method produces dispersed particles (of size 4 nm and below) with a narrow size distribution. Therefore, one of the main reasons for using this method is that some metal compounds have only a weak, if any, capacity for adsorption on support surfaces, as is usually the case in the deposition of inorganic Fe(III) salts on SiO_2 or Al_2O_3. The second reason is that the adsorption of some chloro complexes of noble metals results in the contamination of the surface of dispersed metallic particles with chloride ions, which are catalytic poisons in many reactions. This situation is observed, for instance, in the synthesis of gold catalysts for CO oxidation by the adsorption of $[AuCl_4]^-$ on the surface of various oxide supports [62]. When a gold precursor is deposited as hydroxide particles, the poisoning effect of the chlorine atoms is much weaker. Since the discovery of the surprising activity of supported gold particles of size <5 nm in low-temperature CO oxidation in 1987, the number of publications on these systems has been steadily increasing. Presently, at least 40–50 articles are annually published on ultrafine gold-containing catalysts active in a wide variety of catalytic reactions. The main method of the preparation of this system is DP, because it is the most favorable for producing fine gold particles [63, 64].

A series of reasons for using the DP method follows from the consideration of palladium deposition on carbon supports [65]. When colloidal $[Pd(OH)_2]_n$ (where $n \simeq 100$) particles with a size of 2.0–2.4 nm are formed during deposition, their penetration into fine pores of the carbon support can be prevented and the formation of large amounts of very fine (but inaccessible for reacting gases) metal particles can be ruled out. The fact that palladium hydroxide is reducible at lower temperatures than palladium chloro complexes is another technological advantage of this method of Pd/C catalyst synthesis [65].

The DP method involving the formation of PHCs and hydroxide precipitates uses the same starting reagents as conventional deposition and precipitation methods. For instance, Pd/C catalysts are prepared using the water-soluble compound H_2PdCl_4 or Na_2PdCl_4, while chloroplatinic and chloroauric acids are used to prepare the Au- and Pr-containing catalysts. Precipitation is usually carried out using NaOH, Na_2CO_3, or urea. The DP method is applicable to all oxide and carbon supports.

DP can be carried out by the following three procedures [65]:

(1) A precipitating agent is added to a support suspended in a solution of a precursor of an active component.

(2) A solution of a precursor is added to a suspension of a support in an alkali solution.

(3) A solution of a precursor is mixed with an alkaline agent to obtain colloidal compounds of the precursor as PHC or sols, and then this solution is brought into contact with a support.

The third method is the most convenient for deposition on granular supports. However, colloidal particles should specially be stabilized to avoid their coagulation in the bulk until the solution penetrates into the support pores. The first method is the most widespread. Although the very essence of this method is understood, the mechanism of its separater steps involved in precipitation on the surface remains unclear. The process consists of two steps [48, 59]: (1) precipitation from the bulk of a solution both in the support pores and over the support and (2) the interaction of the precipitate with the support surface. The amount of salt necessary to compose the starting solution is calculated from the amount of substance to be precipitated on the support surface. However, since this method uses a very large volume of impregnating solution as compared to the volume of the support pores, the amount of solute over the support considerably exceeds the amount of solute in the pore space. For this reason, if precipitation is carried out incorrectly, a considerable proportion of the precipitate will be formed in the solution bulk above the support and not inside the pores. Of course, this undesirable phenomenon should be avoided.

A fine and homogeneous active phase can be obtained by involving the surface OH groups of the support in the precipitation process [59]. This precipitation process is spontaneously initiated upon contact between the support and a solution of a readily hydrolyzable salt. In our earlier work [66], surface precipitation was observed on alumina, zinc aluminate spinel, and magnesium aluminate spinel surfaces in contact with aqueous solutions of Cu(II) and In(III) salts. However, since the concentration of OH groups on the surface is limited, extra alkaline precipitating agent should be introduced to increase the ampunt of precipitate. In this case, precipitation strongly depends on the salt concentration in the solution, pH, precipitation time and temperature, and the rate at which the precipitating agent is added. Usually precipitation is carried out from very dilute solutions by adding a precipitating agent at a slow rate. The optimum precipitation pH and temperature are determined by the nature of the precipitated hydroxide. For a given hydroxide, they depend on the nature of the support. The support surface acts as a nucleating agent [62, 63]. In other words, it facilitates the nucleation of the new solid phase on which hydroxide particles are to be formed. Perhaps, hydroxyl groups play an important role in this process. For instance, for gold precipitation on TiO_2 with an alkali (NaOH), the maximum Au content is achieved at pH 6 (the pH of the isoelectric point of TiO_2), that is, when the surface is uncharged [67]. It is believed that the following reaction initially occurs on the surface:

$$3OH^- + AuCl_4^- + H^+ \longrightarrow HAu(OH)_3Cl + 3Cl^-.$$

Next, once the pH of the solution reaches the pH of the isoelectric point of the support, the surface complexes $Au(OH)_3Cl^-$ begin to act as $Au(OH)_3$ nucleation centers.

As mentioned above, the most important point in this method of catalyst preparation is to prevent precipitation far from the support surface. The homogeneous precipitation–deposition method using urea ($CO(NH_2)_2$) as the precipitating agent [58, 59] makes it possible to avoid local pH rises and metal hydroxide precipitation in the solution bulk. Urea is added to the support along with a solution of the starting salt. Under slow heating, the OH^- ions precipitate slowly throughout the solution bulk owing to the hydrolysis of urea:

$$CO(NH_2)_2 + 3H_2O \longrightarrow 2NH_4^+ + CO_2 + 2OH^-.$$

This strong effect of urea is well illustrated by the preparation of an Au/TiO_2 catalyst. If precipitation is carried out with NaOH, at most 3 wt % Au can be deposited as ultrafine particles 2–3 nm in size, while the nominal gold content of the solution is 13 wt %. Attempts to deposit a greater amount of gold result in much larger particles or in bulk precipitation. Deposition in the presence of urea enables one to obtain a material containing up to 8 wt % of the same ultrafine Au particles, to achieve a nearly complete gold extraction, and to prevent bulk precipitation [63]. The gold particles thus obtained are rather resistant to agglomeration at a reduction temperature of 500°C [64].

Thus, in addition to having the above-listed advantages, the DP method using urea as the precipitating agent is the most suitable for the preparation of ultrafine supported catalysts containing 10–20 wt % active component [64].

It can be predicted that the further development of the DP method will be associated with the sol–gel synthesis of supported catalysts. Nowadays, this technology is finding increasing use in the preparation of various film coatings.

4. NEW, UNCONVENTIONAL METHODS FOR CATALYST PREPARATION

There are so many new, unconventional methods for catalyst preparation that it seems impossible to review their principles in one publication and, the more so, to consider their specific features and estimate their potentials for each particular catalytic system described in the literature. Some of these methods are at the research stage. Not all of them will be found to be worth promoting, but it is important that many are either at the early investigation stages or are being tested.

In light of the aforesaid, the following question arises: To what extent is the concept of the scientific foundations of catalyst preparation applicable to new, unconventional methods? To answer this question, we tried to classify all methods known from the literature, dividing them into two groups.

The first group is to include methods using operations of conventional methods in a new combination or engineering modification. These are layering of different ions on the support surface by a series of chemisorption cycles, the pyrolysis of volatile metal compounds on a hot surface, various hydrothermal syntheses, the decomposition of colloidal dispersions of salts of higher acids in alcohol on the support surface, etc. Some steps of conventional methods are well studied. This facilitates, to a considerable extent, understanding of the processes that occur when these steps are used in a new way. However, this group of methods can open up new possibilities.

An interesting example of using conventional hydrothermal treatment in a new way is the synthesis of Al_2O_3/Al, $MO_x/Al_2O_3/Al$, and $M^1/M^2O_x/Al_2O_3/Al$ cermets (where M^1 and M^2 are cations of catalytically active metals), a new class of materials [68]. The synthesis of these materials is based on the partial oxidation of aluminum powder with water in a closed space by hydrothermal treatment with water or steam. The transfer processes at the particle contact sites and the increase in the volume of the solid phase result in the consolidation of the powder into a mechanically strong composite with a macroporous structure. The thermal decomposition of the hydroxo compounds in air yields a composite in which metal particles are relatively uniformly distributed in the alumina matrix with a developed microporous structure. Such composites are very promising for the production of a variety of supports and efficient catalysts. The physicochemical foundations of this method and outlooks for catalytic applications of these materials are considered in [68].

The second group consists of methods that are relatively new in catalyst preparation but that have long been used in the preparation of various disperse materials widely used in the synthesis of chemicals, ceramics, glasses, films, powders, etc. These methods are based on either condensation or dispersion, and, therefore, they can be divided into two large subgroups, namely, chemical (physicochemical) and physical methods [69].

Electrochemical methods for producing substances that can be used as precursors of supports and catalysts should be assigned to the second group [70, 71]. In some cases, the use of these methods revealed their specific features that make it possible to prepare catalysts with improved properties. For instance, electrochemical synthesis at an industrial ac frequency has been reported to afford, under essentially nonequilibrium conditions, aluminum hydroxide with a pseudoboehmite structure, a developed surface, and a high thermal stability [70]. It is also stated in that work that the resulting pore structure is superior in many respects to the pore structure achieved by the conventional synthesis of aluminum hydroxide (continuous precipitation from a salt solution with an alkali). Electrochemical technologies using ion-selective membranes offer new approaches to technical, economical, and environmental problems [71]. The most important of these are the synthesis of metal oxides in an electrolyzer chamber, the electrosynthesis of complex catalytic systems that are usually obtained by coprecipitation, the modification of surface and bulk properties of supports and catalysts by electrochemical treatment, the preparation of supports with desired structural and acid–base properties, the modification of the acid–base properties of zeolites and zeolite-containing catalysts, the electrosynthesis of silica gels and sols of silicic acid, etc.

In our opinion, a prominent example of the use of technologies from related areas of materials science is the application of the Pechini method (the method of ester polymeric precursors) to catalyst synthesis. We will consider this method in greater detail. The method has long been used in the preparation of ceramic powders [72–74] and thin films [75–77]. Of late, it has been used in the synthesis of catalytic systems based on the Ce–Zr–O solid solutions [78] and perovskites [79], both bulky and supported as thin films on monoliths.

In the Pechini method, an α-hydroxycarboxylic acid, for example, citric acid, is used to obtain complexes of cation precursors [72]. These complexes are reacted with a polyatomic alcohol, for instance, ethylene glycol, to produce organic esters and water. This process is schematized in Fig. 5. The heating of this mixture in the solution causes polyesterification, resulting in a homogeneous solution in which metal ions are uniformly distributed throughout the organic matrix [74]. Next, the solution is heated to remove the excess solvent, resulting in a solid resin as an intermediate. This resin can adhere tightly to inert monolith supports [79]. Owing to the high viscosity of the resin and to the strong interactions due to complex formation, the metal ions “freeze” into the solid polymer network and remain uniformly distributed in this network [75]. Next, the solid resin is heated to remove the organic residues. The metal precursors are chemically bound by the resin and, upon pyrolysis, form the desired stoichiometric compounds.

A distinctive feature of this method is that it is possible to perform homogeneous mixing of multicomponent systems at the molecular level [75] and thus obtain complex multicomponent systems with the desired stoichiometry. An advantage of this method is that the citric acid : ethylene glycol ratio can be varied to control the size and morphology of the resulting particles or the thickness of the deposited film [80, 81].

The order of reagent mixing, the ratio of the reactants (water : citric acid : ethylene glycol), and the nature of the metal salt play an important role in sol preparation: it is preferable to use nitrates, which can easily be removed by calcination.

The resulting polymeric structure prevents the segregation of metal cations, particularly in multicomponent systems [73]. Another advantage of this preparation method is the fact that the crystalline phase forms at a low temperature, favoring the formation of smaller and more reactive particles [74]. Due to the organics burning out during the synthesis, the resulting oxide has a high porosity.

Thus, the Pechini method is a combination of conventional catalyst preparation techniques, specifically, the thermal decomposition of a salt mixture and chemical treatment (oxidation) of a nonporous organic matrix.

The disadvantages of this method are large weight losses and the formation of large agglomerates during high-temperature calcination. The decomposition of the organic matrix during calcination may be accompanied by additional heat release, resulting in the formation of partially sintered agglomerates.

The method of mechanochemical activation, which has recently found wide use in catalyst preparation, is worth special consideration. The principles of this method and areas of its application were described in detail in an earlier review [82]. However, it is unclear whether the mechanochemical activation can be assigned to new methods of catalyst preparation. If a substantial particle comminution and, as a consequence, an increase in reactivity are achieved by an intense mechanical treatment of the solid, mechanochemical activation should apparently be considered as an auxiliary stage of a conventional method, for instance, the dispersion of salts and oxides for preparing various solutions and the dispersion and homogenization of the components in the mechanical mixing method. The situation is different when the mecha-

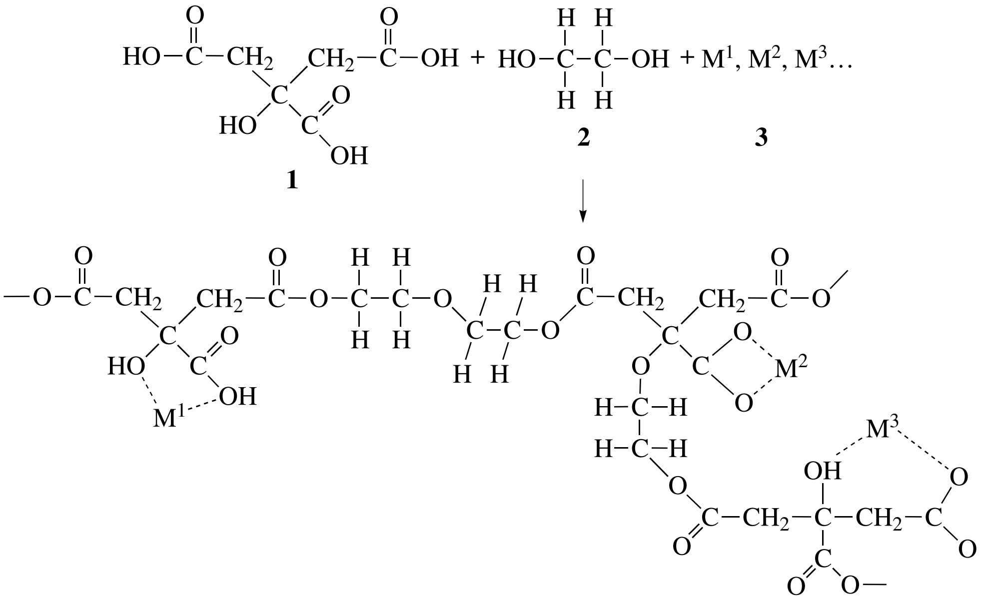


Fig. 5. Formation of the ester of (**1**) citric acid and (**2**) ethylene glycol in the presence of (**3**) metal cations.

nochemical activation affords a substance whose synthesis by conventional methods is impossible, requires very high temperatures, or proceeds via other routes. In this case, this method can be considered as a new, independent method for catalyst preparation. It is sometimes called mechanochemical synthesis [83]. An example of the mechanochemical synthesis of catalysts is the synthesis of new Ni–Mg intermetallide hydrides [82], perovskites [84], and fine-particle solid solutions with a cubic structure (ZrO_2–CaO and ZrO_2–Y_2O_3) [85].

The following physical methods can be considered to be new methods for catalyst preparation: plasma chemical techniques, ultrasonic methods (sonochemistry), electron- and ion-beam methods, laser and cathode evaporation followed by metal condensation, the microarc oxidation of alloys to obtain active oxides, and syntheses in the subcritical and supercritical water [86]. Some of these methods are not used in pure form for catalyst preparation. Sometimes they are applied in combination with conventional approaches to catalyst preparation and their role is limited to an additional activation of the catalytic material. This is true, for example, for plasma chemical treatment [87] as a method for the modification of cobalt Fischer–Tropsch catalysts. The action of the oxygen-containing plasma in a plasma gas flow provides a new approach to the thermolysis of the supported cobalt salt (establishment of oxidative conditions and quick removal of the resulting products with a flowing inert gas). The specific features of plasma chemical treatment (which depend on the power input) are the following: (1) The primary salt distribution on the support surface is conserved due to the rapid plasma thermolysis and to the quenching of the products by the inert gas. (2) The rate of capillary salt removal changes due to the substantially lower effective temperature of the sample. (3) The diffusion of cobalt ions into the support lattice and particle agglomeration are suppressed. (4) New sites of metal-containing component fixation appear on the support surface being dehydroxylated, which can favor the secondary dispersion of the component. (5) The support surface undergoes destruction at high plasma energies. (6) Cobalt oxides are oxidized after nitrate decomposition [87].

The methods based on the cathode or laser evaporation of a substance followed by its condensation as a powder or onto an inert support have found wide use in the preparation of metal nanoparticles. These methods were detailed in a recent monograph [69].

Concluding the discussion of new, unconventional methods of catalyst preparation, we would mention that the development of the scientific foundations of these methods should be based on the mechanisms and regularities known for conventional preparation methods or, more generally, on the physicochemical principles of the preparation of dispersed systems. In the latter case, one should always understand that the fundamental aspect of the problem of the creation of scientific foundations for catalyst preparation implies solving the following interrelated and equally significant problems:

(1) control of the synthesis procedure to obtain a catalyst with the desired chemical and phase compositions and active surface structure and

(2) control of the texture (specific surface area and porous structure), mechanical strength, shape, and size of catalyst grains.

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