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Functionalization of Aerogels with Coordination Compounds

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Abstract—Aerogels are unique solid-phase materials characterized by very high open porosity and specific surface area. Owing to these features, aerogels are widely used as heat and sound insulators, gas filters, sorbents, and others. In addition, aerogels are promising matrices for manufacturing selective catalysts, gas sensors, luminophores, etc. Methods and approaches of coordination chemistry provide new possibilities for designing novel hybrid materials characterized by a combination of practically important physicochemical properties inherent in aerogels and metal complexes. The modification of aerogels with coordination compounds gives polyfunctional materials characterized by high porosity and specific surface area along with excellent catalytic, photocatalytic, magnetic, luminescence, and other properties. The approaches of coordination chemistry providing the chemical binding of coordination compounds with the aerogel matrix to form aerogels with new functional properties are generalized and examined for the first time. The known examples for the successful accomplishment of these approaches, including those proposed earlier by the authors, are considered. The data on the practical use of thus prepared materials are presented.

Keywords: sol–gel synthesis, highly porous materials, immobilization, metal complexes, photocatalysts, luminescent materials, catalysts, supports, sensors

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INTRODUCTION

Aerogels are highly porous solid-phase materials with the pore size predominantly from 2 to 50 nm. As a rule, their structures are formed by the linked isotropic (with the size less than 10 nm) or anisotropic nanoparticles or polymer molecules [1]. Since the preparation of the first aerogel in 1931 by Kistler [2], numerous aerogels of various types based on both inorganic compounds [3, 4] and polymers [5–7] have been synthesized and studied.

Aerogels based on metal oxides are traditionally used as structural materials. However, they can also act as supports for the production of functional materials due to high thermal stability and significant open porosity. Recently special attention is paid to hybrid organo–inorganic aerogel-based materials [8]. Coordination compounds with a broad range of practically significant properties play a special role among the modifiers appropriate for the functionalization of aerogels. Modified aerogels can be used as catalysts, gas sensors, Cherenkov detectors, and scintillators [1]. The catalytically active metal complexes immobilized in the aerogel matrix combine advantages of homogeneous and heterogeneous catalysts [9].

The most popular approach to the preparation of metal-oxide aerogels modified with coordination compounds is the physical binding of metal complexes with the matrix due to capturing them by the formed gel or their insertion into the network of the already formed gel. In spite of the simple accomplishment, this approach has several drawbacks, such as a nonuniform distribution of the complex over the material volume, blocking of the matrix pores, the partial decomposition of the porous gel structure because of capillary forces, and others. The listed problems can be solved to a significant extent using approaches based on the chemical (covalent) binding of coordination compounds with the aerogel matrix. The successful accomplishment of these approaches has been demonstrated to the moment for a fairly wide range of systems, but the development of new efficient approaches to the preparation of functional materials based on aerogels chemically modified with coordination compounds remains urgent and requires using methods of coordination and inorganic chemistry, as well as inorganic materials science.

The main approaches to the preparation of functionalized metal-oxide aerogels using methods of coordination chemistry are considered in the present review.

USE OF METHODS OF COORDINATION CHEMISTRY FOR THE PREPARATION OF FUNCTIONAL MATERIALS BASED ON AEROGELS

Methods for the Preparation of Aerogels

The procedure of aerogel preparation usually includes three stages: sol formation, lyogel formation due to the sol–gel transition, and subsequent removal of the liquid from the lyogel pores usually conducted using supercritical drying.

Sodium silicate (hydrolysis of which in the presence of hydrochloric acid afforded hydrogel of hydrated silicon dioxide) was a precursor in the classical method used for the first time in 1931 for the synthesis of the SiO_2 aerogels [10]. Washing of soluble inorganic salts from the lyogel and replacement of water with aliphatic alcohol followed by supercritical (SC) drying made it possible to obtain monolithic aerogels based on SiO_2. Aerogels cannot be prepared by drying in supercritical water ($T_{cr} = 374°C$, $P_{cr} = 22.1$ MPa) because of its high reactivity that caused complete gel peptization under these conditions [11].

One of the main reasons (for which interest in aerogel-based materials was low during a long time, about 30 years) was that the Kistler method required a significant time of synthesis (about 7 days). The use of metal and metalloid alkoxides as precursors made it possible to shorten considerably the synthesis time due to the elimination of the solvent replacement stage [12].

Two main methods are presently used for the preparation of aerogels from metal oxides: the alkoxide method including the synthesis of lyogels by the hydrolysis and polycondensation of the corresponding alkoxides [4] and the epoxide method consisting of the synthesis of lyogels by the hydrolysis of metal salts in the presence of organic epoxides [13]. Note that the approaches of coordination chemistry are rather widely applied in the sol–gel technology. For instance, such ligands as ethylenediaminetetraacetic acid, citric acid, and others are used to suppress hydrolysis and prevent the precipitation of metal hydroxides (hydrated oxides) instead of gelation. The Pechini method is also known well in which the citrate metal complexes exist in the bound form in the polymer formed due to the polycondensation of ethylene glycol and citric acid molecules with the formation of a polymeric covalent network over which the metal ions are uniformly distributed [14].

The most traditional approach in the sol–gel technology is the synthesis of aerogels using alkoxides. The method is based on the hydrolysis of metal or metalloid alkoxides in the presence of acids or bases followed by the condensation of the formed hydroxo compounds and cross-linking of the formed clusters to form sol particles [14, 15]. The sol particles would further be joined together to form a three-dimensional network of lyogel [4, 16].

The lyogel structure depends significantly on the ratio of the rates of alkoxide hydrolysis and condensation of their hydroxo derivatives. Owing to the fast corresponding reactions, the hydrolysis in an acidic medium gives simultaneously numerous hydroxo derivatives in the form of monomeric particles or short-chain oligomers, which further form a lyogel with the polymer-like structure. In an alkaline medium, on the contrary, the formed three-dimensional structure is characterized by large particles and pore sizes due to the fast condensation rate and relatively slow hydrolysis [15].

To prepare the aerogels based on SiO_2 and $Si(OCH_3)_4$ (TMOS) [17] or $Si(OC_2H_5)_4$ (TEOS) [18] are used most frequently. In some cases, other alkoxides, such as polyethoxydisiloxane [19] and methyltrimethoxysilane [20, 21] are applied as precursors. The use of various precursors enlarges the range of properties of the prepared SiO_2-based aerogels. In particular, the use of methyltrimethoxysilane provides the formation of elastic and hydrophobic aerogels [22].

The majority of metal alkoxides is more prone to hydrolysis compared to silicon alkoxides ($Si(OR)_4$). The hydrolysis rate constant of $Ti(OEt)_4$ ($k_h = 10^{-3}$ mol^{-1} s^{-1}) is by five orders of magnitude higher that the hydrolysis rate constant of $Si(OEt)_4$ ($k_h = 5 \times 10^{-9}$ mol^{-1} s^{-1}) [23]. This is due to two main factors. First, the electronegativity of metals is lower than that of Si resulting in a higher partial charge (δ_M) on the metal atom. Second, the coordination number of metals in alkoxides is unsaturated [24]. The hydrolysis rate for many metal alkoxides is so high that their interaction with water results in immediate precipitation. The main approach to decreasing the hydrolysis rate of metal alkoxides is the introduction of ligands in the reaction mixture that coordinate the metal and thus increase its coordination number. Acetic acid (acetate anion) or acetylacetone is often used as such ligands [25]. Particularly, the reaction of $Ti(O\textit{i}Pr)_4$ with acetylacetone can afford complex $[Ti(O\textit{i}Pr)_3acac]$, whereas the reaction with acetic acid gives $[Ti(O\textit{i}Pr)_3(OAc)]_2$ [24].

The described approach makes it possible to prepare lyogels based on both individual metal oxides and mixed (binary and ternary) oxides. The examples of the metal-oxide aerogels based on both individual and mixed oxides synthesized using alkoxides as precursors [26–42] are given in Table 1.

In spite of numerous advantages of alkoxides, they are fairly expensive precursors and the necessity of an additional chemical modification finally increases the cost of the obtained aerogels, which restricts practical use of the precursors. Another substantial drawback of the alkoxide method is that the corresponding alkoxides cannot be obtained for all metals. Therefore, alternative approaches to the preparation of the sol–gel materials were developed [43]. Among them, the

Table 1. Examples of the aerogels based on individual and mixed oxides prepared using alkoxides as precursors

Aerogel	Precursors	Literature
Individual		
Al_2O_3	$Al(OBu^s)_3$ + Etac	[26]
Fe_2O_3	$Fe(acac)_3$	[27]
TiO_2	$Ti(O\textit{i}Pr)_4$	[35]
SnO_2	$[Sn(OBu^n)_4]$ + acac	[36]
ZrO_2	$Zr(O\textit{i}Pr)_4$ + acac	[37]
V_2O_5	$VO(O\textit{i}Pr)_3$	[38]
Nb_2O_5	$Nb(OEt)_5$	[39]
Mixed		
TiO_2–SiO_2	$Ti(O\textit{i}Pr)_4 + Si(OEt)_4$	[40]
Al_2O_3–SiO_2	$Al(OBu^s)_3 + Si(OMe)_4$	[41]
V_2O_5–MgO	$VO(O\textit{i}Pr)_3 + Mg(OMe)_2$	[28, 42]
PbO–Al_2O_3	$Al(OBu^s)_3 + Pb(OAc)_2$	[29]
PbO–ZrO_2	$Zr(O\textit{i}Pr)_4 + Pb(OAc)_2$	[30]
BaO–Al_2O_3	$Ba[Al(OBu^s)_4]_2 + Al(OBu^s)_3$	[31]
$PbTiO_3$	$Ti(O\textit{i}Pr)_4 + Pb(OAc)_2$	[32]
Li_2O–B_2O_3–Al_2O_3	LiOMe + $B(OBu^n)_3 + Al(OBu^n)_3$	[33]
MgO–Al_2O_3–SiO_2	$Al(OBu^s)_3 + Si(OEt)_4 + Mg(OAc)_2$	[34]

use of solutions of inorganic metal salts and organic epoxides (acting as gelating agents) turned out to be most successful [13].

In 1993, Itoh and coauthors proposed to use organic epoxides in the sol–gel technology [44]. However, the method became popular due to the article by Gash and coauthors [13]. A substantial advantage of the epoxide method is a possibility to use solutions of inorganic metal salts in water, alcohol, or other polar protic solvents as precursors.

Organic epoxides act in the epoxide-induced gelation as initiators of hydrolysis and condensation by binding protons in the sol–gel system [45]. The process includes the protonation of the oxygen atom in epoxide followed by epoxide ring opening via the nucleophilic attack from the conjugated base. For example, the introduction of epoxide in a solution containing aqua ions $[Fe(H_2O)_6]^{3+}$ results in the formation of the iron aquahydroxo complex, and the irreversible capture of protons by epoxide increases the pH of the solution [46]. Unlike other bases (OH^-, CO_3^{2-}, or NH_3), the use of epoxides leads to a relatively slow increase in the pH in the system due to which stable sols of metal oxides and, finally, monolytic oxide lyogel are formed.

In the epoxide sol–gel method, such parameters as the epoxide type, solvent nature, and type of the anion in the metal salt significantly affect the structure and properties of the formed aerogel [46, 47]. The duration of gelation during the sol–gel transition can be changed in wide ranges (up to four orders of magnitude) by the variation of the epoxide nature [48].

The epoxide-induced sol–gel method was used for the preparation of aerogels based on various metal oxides [47], for example, tin dioxide, whose surface is characterized by superacidic properties due to which this material is promising for the catalytic conversion of hydrocarbons [49]. One of the key advantages of the epoxide sol–gel approach is that it provides a universal and rather simple method for the preparation of mixed (binary or ternary) oxides, including SiO_2, rare-earth element (REE) oxides, etc. [50]. This approach is also used widely for the preparation of composite aerogels, for instance, containing metal particles [51, 52]. Some examples of the preparation of the aerogels based on both individual and mixed metal oxides by the epoxide sol–gel method [13, 53–69] are listed in Table 2. The epoxide approach is unique because makes it possible to obtain aerogels based on oxides of double-charge cations, including mixed oxides.

The method of SC drying is used most frequently to obtain aerogels from lyogels. However, other methods (sublimation dehydration and drying under atmospheric pressure) are also popular [70, 71]. Strictly speaking, the materials produced by these two meth-

Table 2. Examples of the aerogels based on individual and mixed metal oxides prepared using the epoxide method

Aerogel	Precursors			Literature
	salt	epoxide	solvent	
Individual oxides				
Al_2O_3	$AlCl_3·6H_2O$, $Al(NO_3)_3·9H_2O$	PO*	EtOH	[53]
SnO_2	$SnCl_4·5H_2O$	PO	H_2O	[62]
Ga_2O_3	$Ga(NO_3)_3·xH_2O$	PO	EtOH	[13]
In_2O_3	$In(NO_3)_3·5H_2O$	PO	EtOH	[13]
Fe_2O_3	$FeCl_3·6H_2O$	Epichlorohydrin	EtOH	[63]
Cr_2O_3	$Cr(NO_3)_3·9H_2O$	PO	EtOH	[13]
Ru_2O_3	$RuCl_3·xH_2O$	PO, 1,2-epoxybutane	EtOH, MeOH	[64]
TiO_2	$TiCl_4$	PO	EtOH	[65]
ZrO_2	$ZrOCl_2$	PO	EtOH	[66]
CuO	$CuCl_2·2H_2O$	PO	*i*PrOH	[67]
ZnO	$Zn(NO_3)_2·6H_2O$	PO	MeOH, EtOH, *i*PrOH, acetone	[68]
NiO	$NiCl_2·6H_2O$	PO	EtOH	[69]
CoO	$CoCl_2·6H_2O$, $Co(NO_3)_2·6H_2O$	PO	MeOH	[54]
Ce_2O_3	$CeCl_3·6H_2O$	PO	MeOH	[55]
Gd_2O_3	$GdCl_3·6H_2O$, $Gd(NO_3)_3·6H_2O$	PO	EtOH	[56]
UO_3	$UO_2(NO_3)_2·6H_2O$	PO	EtOH, acetone	[57]
Mixed oxides				
CuO/NiO	$CuCl_2·2H_2O + NiCl_2·6H_2O$	PO	MeOH	[58]
Yttrium-stabilized zirconium oxide (YSZ)	$ZrCl_4 + YCl_3·6H_2O$	PO	H_2O	[59]
$ZnFe_2O_4$	$Zn(NO_3)_2·6H_2O + Fe(NO_3)_3·9H_2O$	PO	*i*PrOH	[60]
$CuO/ZnO/Al_2O_3$	$Cu(NO_3)_2·3H_2O + Zn(NO_3)_2·6H_2O + Al(NO_3)_3·9H_2O$	PO	EtOH	[61]

* PO is propylene oxide.

ods (cryogels and ambigels, respectively) are not aerogels in the classical sense and should be assigned to aerogel-like materials.

Organic solvents (as a rule, lower aliphatic alcohols) and CO_2 are often used for SC drying of lyogels [72]. The critical parameters for the most frequently used solvents (data on H_2O are presented for comparison) [72] are given in Table 3. Taking into account differences in critical temperatures, so-called "low-temperature" (in CO_2) and "high-temperature" (in organic solvents) SC dryings are distinguished [73].

The influence of the solvent used for drying under SC conditions on the composition and properties of aerogels is a new area of research, and studies in this field have just been started [73–75]. In the cycle of articles published by the research groups from the Kurnakov Institute of General and Inorganic Chemistry (Russian Academy of Sciences) and Institute of Physiologically Active Substances (Russian Academy of Sciences), the whole series of new solvents for SC drying characterized by a broad range of critical parameters was proposed: hexafluoroisopropanol, trifluoroethanol, methyl *tert*-butyl and diethyl ethers, ethyl acetate, hexane, acetone, and others [76–81]. As a rule, drying in alcohols leads to the alkoxylation of the aerogel surface due to the interaction of alcohol with the surface OH groups. As a result, the aerogel surface gains hydrophobic properties [80]. Hydrophobic aerogels based on SiO_2 can be prepared by drying in hexafluoroisopropanol or due to using hexafluoroacetone as a cosolvent for the preparation of lyogels [80, 82]. A comparative analysis of the characteristics of the SiO_2, Al_2O_3, and ZrO_2 aerogels obtained by SC drying in media of ethers and fluorinated alcohols shows that both the composition and texture charac-

Table 3. Critical parameters of some solvents applied for SC drying [72]

Solvent	T_{cr}, °C	P_{cr}, bar
Water	374.1	220.5
Methanol	239.4	81
Ethanol	243.0	63.8
Isopropanol	235.1	47.6
Acetone	235.0	46.0
Carbon dioxide	31.0	73.8
tert-Butanol	233	39.7
Trifluoroethanol	226	48.4
Hexafluoroisopropanol	182	30.2
Diethyl ether	193.4	36.1
Methyl *tert*-butyl ether	224.1	34.3
Ethyl acetate	250	38.8
Pentane	196.6	34.0

teristics of the formed aerogels substantially depend on the nature of the applied SC solvent [78].

Several relatively recent studies are devoted to a comparative analysis of the structures of the aerogels prepared by drying in alcohols at the temperatures from 85 to 265°C under the supercritical and subcritical conditions [83, 84]. Remarkably, drying in the whole studied temperature range results in the production of materials characterized by a high specific surface area (~1000 m^2/g), and an increase in the drying temperature is accompanied by a monotonic increase in the average size and specific volume of the pores. At the same time, the drying temperature substantially affects the character of aggregation of individual SiO_2 particles, which is observed as a decrease in the fractal dimension of nanoparticle clusters (from 2.6 at 85°C to 2.1 at 265°C).

Application of Approaches of Coordination Chemistry for the Preparation of Multicomponent Aerogels (for a SiO_2–TiO_2 System as an Example)

The approaches of coordination chemistry are widely used for the production of aerogels, xerogels, glasses, and ceramics based on mixed metal oxides [85–87]. Interest in multicomponent aerogels is caused by a combination of several practically important characteristics in these materials: high specific surface area, porosity, catalytic and photocatalytic activity, and others [88].

Among mixed-oxide aerogels, the materials based on SiO_2–TiO_2 are studied in more detail owing to their high practical significance from the viewpoint of using in the catalytic or photocatalytic systems [89–96]. Therefore, available published data concerning the synthesis of the SiO_2–TiO_2-based aerogels, primarily using the coordination chemistry approaches, will be considered.

Silicon and titanium alkoxides are usually used as precursors in the synthesis of the aerogels based on SiO_2–TiO_2, and TMOS [74, 97], TEOS [98, 99], and even liquid glass (solutions of sodium silicates) mainly serve as silicon sources [100, 101].

Titanium tetraisopropoxide $Ti(O\textit{i}Pr)_4$ (TIP) [97, 102], titanium tetrabutoxide $Ti(O\textit{n}C_4H_9)_4$ [89, 93], or more accessible titanium tetrachloride [103] or titanium oxochloride [104] are applied as titanium sources.

The necessary conditions for the production of multicomponent aerogels and xerogels by the sol–gel method is the achievement of a high degree of cross polymerization during the hydrolysis and polycondensation of various alkoxides [105, 106]. In the simplest method, alkoxides are hydrolyzed in an organic solvent to obtain two-component gels (based on SiO_2 and metal oxide (M)). Heterosiloxane groups (Si–O–M) should be formed after alkoxide hydrolysis. In practice, the hydrolysis and polycondensation rates of different alkoxides differ strongly to result in the independent polycondensation of individual components of the system and phase separation. Various approaches are used for the production of chemically homogeneous materials [89, 107–109], and none of them is universal. The following synthetic procedures are applied, as a rule, for the preparation of mixed SiO_2–TiO_2 aerogels.

(1) Preliminary hydrolysis of one of the components [89, 90, 110]. Alkoxide characterized by a lower affinity to hydrolysis (usually this is $Si(OR)_4$) is prehydrolyzed using a minimum amount of water, and then the second alkoxide characterized by a higher affinity to hydrolysis is added to the reaction system. Since the system contains no free water, reactive alkoxide would

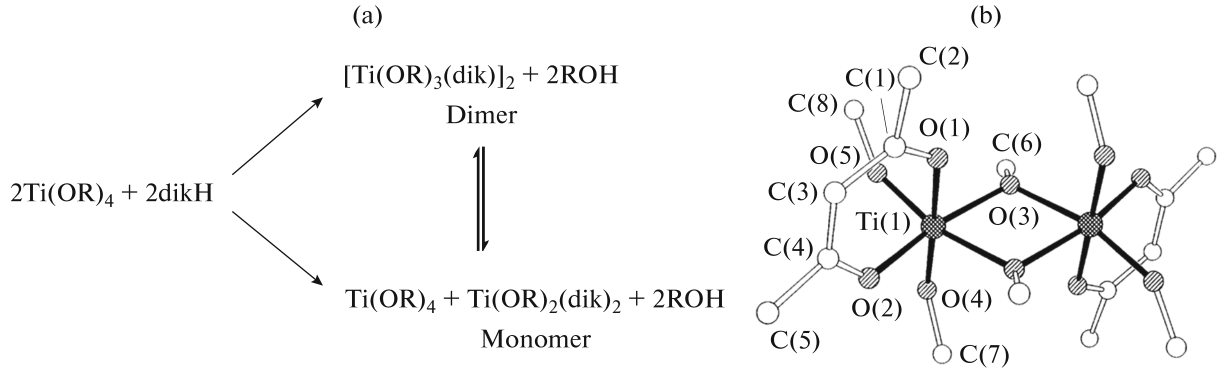
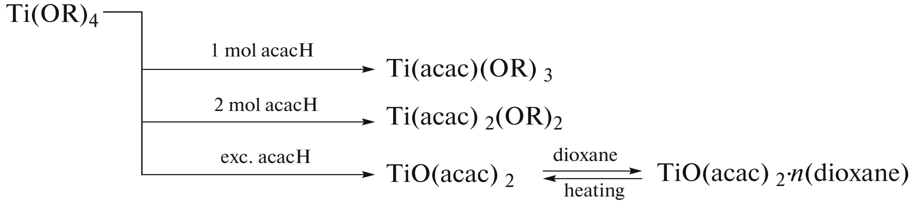


Fig. 1. (a) Rearrangement of the [Ti(iPrO)$_2$(acac)$_2$] complex to the dimeric form and (b) the molecular structure of this form [116].

enter into condensation with ≡Si–OH groups to form Si–O–M bonds.

(2) Chelation of rapidly hydrolyzed alkoxide [88, 90, 91, 93, 111]. A chelating ligand is added to more reactive alkoxide to form a complex relatively resistant to hydrolysis. As a result, the hydrolysis and condensation rates of alkoxides are equalized favoring a high degree of cross polymerization of the components and formation of materials with a high content of heterosiloxane groups. A known example for this approach is the use of acetylacetone (acacH) or acetic acid (AcOH) for the preparation of the mixed-oxide SiO_2–TiO_2 aerogels.

Two titanium complexes with acetylacetone can be formed depending on the molar ratio (Scheme 1). Apparently, they are characterized by different reactivities, and the hydrolysis of these complexes proceeds primarily at the isopropoxyl groups and does not involve the acetylacetonate ligands, which are retained even at a 20-fold water excess in the reaction mixture [112]. The products formed upon the addition of different amounts of acetylacetone to TIP [113] are shown in Scheme 1.



Scheme 1.

Thus, three groups in the Ti(acac)(OR)$_3$ complex are capable of hydrolyzing to form a three-dimensional network of the gel, whereas in the Ti(acac)$_2$(OR)$_2$ complex [113] only two groups are hydrolyzed with the formation of a chain polymer. There are data on the possibility of forming complex [O=Ti(acac)$_2$] in an acetylacetone excess, but no information about the properties of this complex was found.

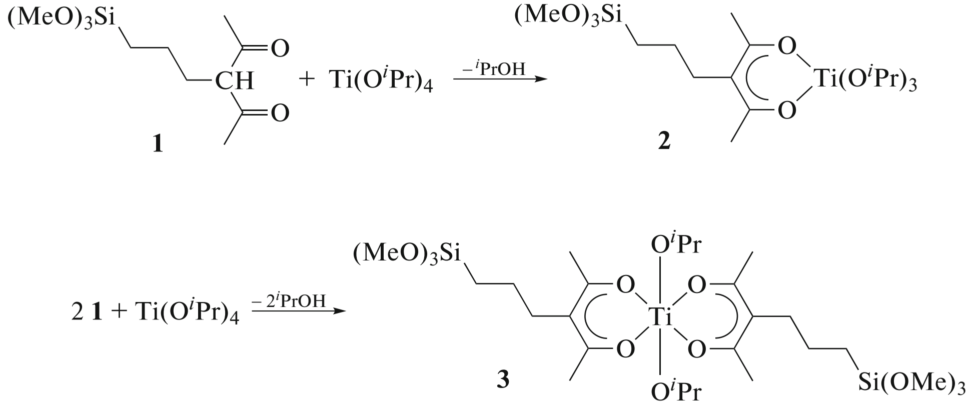
The composition of the complex formed in equimolar mixtures of TIP and acacH was studied in detail by ^{1}H and ^{13}C NMR [114]. The formation of pentacoordinate tris(isopropoxy)acetylacetonatotitanium [Ti(acac)(iPrO)$_3$] was shown. The oxygen atoms in the acetylacetate ligand (due to keto–enol tautomerization) and isopropoxide groups are nonequivalent. It should be emphasized that the isopropoxide complex exists only in the form of monomers unlike similar ethoxide titanium complexes.

The bis(acetylacetonato)bis(isopropoxy)titanium complex [Ti(acac)$_2$(iPrO)$_2$] was studied [115]. Then this complex was shown to transform into the dimeric form [116] with the bridging isopropoxide ligands (Fig. 1). The synthesis of disperse materials based on SiO_2–TiO_2 using this complex was described [117].

There were almost no attempts of systematic analysis of the influence of the amount of acetylacetone introduced in the reaction mixture on the properties of the formed titanium-containing oxide aerogels. The regularities of the synthesis of the photocatalysts based on TiO_2 by the hydrolysis of titanium alkoxides in the presence of various amounts of acetylacetone were studied [118]. The powders obtained in the absence of acetylacetone consisted of isotropic nanoparticles only, whereas TiO_2 nanofibers formed in the presence of acacH. When the acacH : TIP molar ratio was 1 : 2, the fibers formed were longer and thinner than those formed at a ratio of 1 : 1. Similar results were obtained by Sadeghzadeh and coauthors [119]. Attempts to obtain oxide materials of a complicated composition using the titanium acetylacetonate complexes were made only in a few works [120].

Ethylene glycol, its monoalkyl ethers (methyl and ethyl cellosolves), and glycerol are used along with acetylacetone as chelating agents in the sol–gel synthesis [121–123]. The reactions of these compounds with titanium alkoxides are accompanied by the replacement of some monodentate alkoxide ligands with the bidentate derivatives of polyatomic alcohols. The hydrolysis of titanium alcoholates chelated by cellosolves followed by the SC drying of lyogels gave optically transparent monolithic aerogels of titanium dioxide [121].

The approaches based on using heteronuclear coordination compounds, for example, diethoxysiloxane ethyl titanate ($[Si(OEt)_2OTi(OEt)_2O]$) [124] and titanium isopropoxide complexes $Ti(OiPr)_4$ with 3-(propyltrimethoxysilyl)acetylacetone as precursors (Scheme 2, compounds **1** and **2**) seem to be rather promising [125]. The strictly fixed stoichiometry of the complexes and relatively high cost of the precursors are drawbacks of these approaches. The synthesis of the heteronuclear precursors for the preparation of the aerogels based on $SiO_2–TiO_2$ is shown in Scheme 2 [125].



Scheme 2.

Functionalization of Aerogels Using Approaches of Coordination Chemistry

A broad diversity of the functional properties of coordination compounds makes them attractive for the use as modifiers in aerogel modification. The immobilized metal complexes have intensively been studied since the 1960s [126]. The immobilization of isolated and uniformly distributed molecules of the complex over the aerogel surface provides materials combining specific properties of the matrix (strength, porosity, high specific surface area, etc.) with the functional properties of the molecular complex [9, 127, 128]. The use of low-temperature SC drying in CO_2 (T_{cr} = 31°C) allows one to introduce molecules unstable at high temperatures in the aerogel matrix [129].

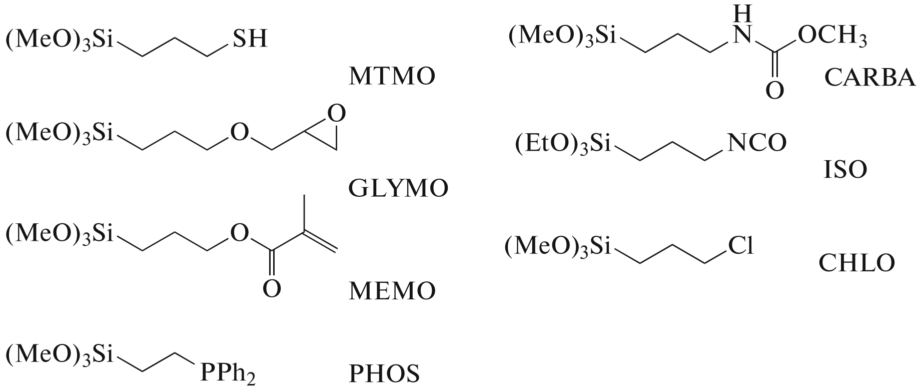
The immobilization of metal complexes in the aerogel matrix provides the heterogenization of homogeneous catalysts; i.e., catalysts combining the activity of a homogeneous catalyst with all advantages of a heterogeneous catalyst can be obtained [9, 130–137]. The immobilization of luminescent complexes in aerogel and xerogel matrices produces materials applied as sensors [129], and in manufacturing displays [138], scintillators [139], lasers [140], and Cherenkov detectors [141].

Both organic polymers [142, 143] and inorganic compounds, primarily oxides [144] synthesized using the sol–gel technology are used as porous material-supports. Oxide supports are applied more frequently due to a higher thermal stability (which is especially necessary for the use in catalysis) [145]. In turn, silicon dioxide and aluminum oxide are most abundant among oxides [1, 9, 146], because the materials based on these oxides retain high porosity at high temperatures. In addition, the sol–gel chemistry of SiO_2 and Al_2O_3 is studied in rather detail [1, 3, 147].

The functionalization of the porous oxide supports is performed by two main methods: at the sol–gel synthesis stage [9, 137] or during the postsynthetic treatment of the preliminarily obtained oxide material [148, 149]. Such approaches as ion exchange, impregnation, and precipitation from the liquid and gas phases are postsynthetic procedures [150]. In spite of a seeming simplicity of postmodification, this procedure is characterized by a number of substantial drawbacks: a complicated control of the amount of the inserted modifier, pore blocking, partial decomposition of the porous structure, multistage character of the process, etc. [150, 151]. The listed difficulties are partially or completely eliminated by the functionalization of the oxide material during the sol–gel transition, for example, during cogelation.

The approach of the chemical modification of the modifier in the support matrix seems to be most promising. This approach has substantial advantages over more traditional ones. Among these advantages are the uniform distribution of the modifier, no aggregation and washing of the modifier, retention of stability, high and controlled loading, and others [150].

Modification of the SiO_2-based aerogels: the main synthetic approaches. Precursors of the $(RO)_nSi–X–A$ type (where A is the functional organic group, and X is the hydrolytically stable spacer (usually hydrocarbon) binding A and alkoxyl fragment $(RO)_nSi$) are used for the chemical immobilization of various molecules and groups in the SiO_2 matrix (Scheme 3) [152]. It should be mentioned that the key point making it possible to considerably enlarge the range of synthesized hybrid organo-inorganic functional materials based on SiO_2 is that silicon forms a stable Si–C bond. Owing to this, diverse methods of organic chemistry can be used for the preparation of functionalized sol–gel materials. Alkoxy groups allow the synthesized molecules to be easily immobilized on oxide supports thus forming a hybrid material with the required functional properties. Examples of organosubstituted alkoxysilanes used in the sol–gel technology [152] are shown in Scheme 3.



Scheme 3.

Precursors of the $(RO)_3Si(CH_2)_nL$ type (L is the donor group) can act as ligands for the synthesis of coordination compounds. The $[(RO)_3Si(CH_2)_nL]_n$-MX_m complexes derived from the precursors can be immobilized in the SiO_2 matrix by the post-treatment of SiO_2 or cogelation with silicon tetraalkoxides $Si(OR)_4$. The following groups usually act as the L group for the coordination of metal cations: $–NH_2$, $–NHCH_2CH_2NH_2$, –CN, –SH, $CH(COMe)_2$, and others [153].

As a whole, the chemical immobilization of metal complexes in the SiO_2 matrix can be performed using one of the four main methods (Scheme 4) [154].

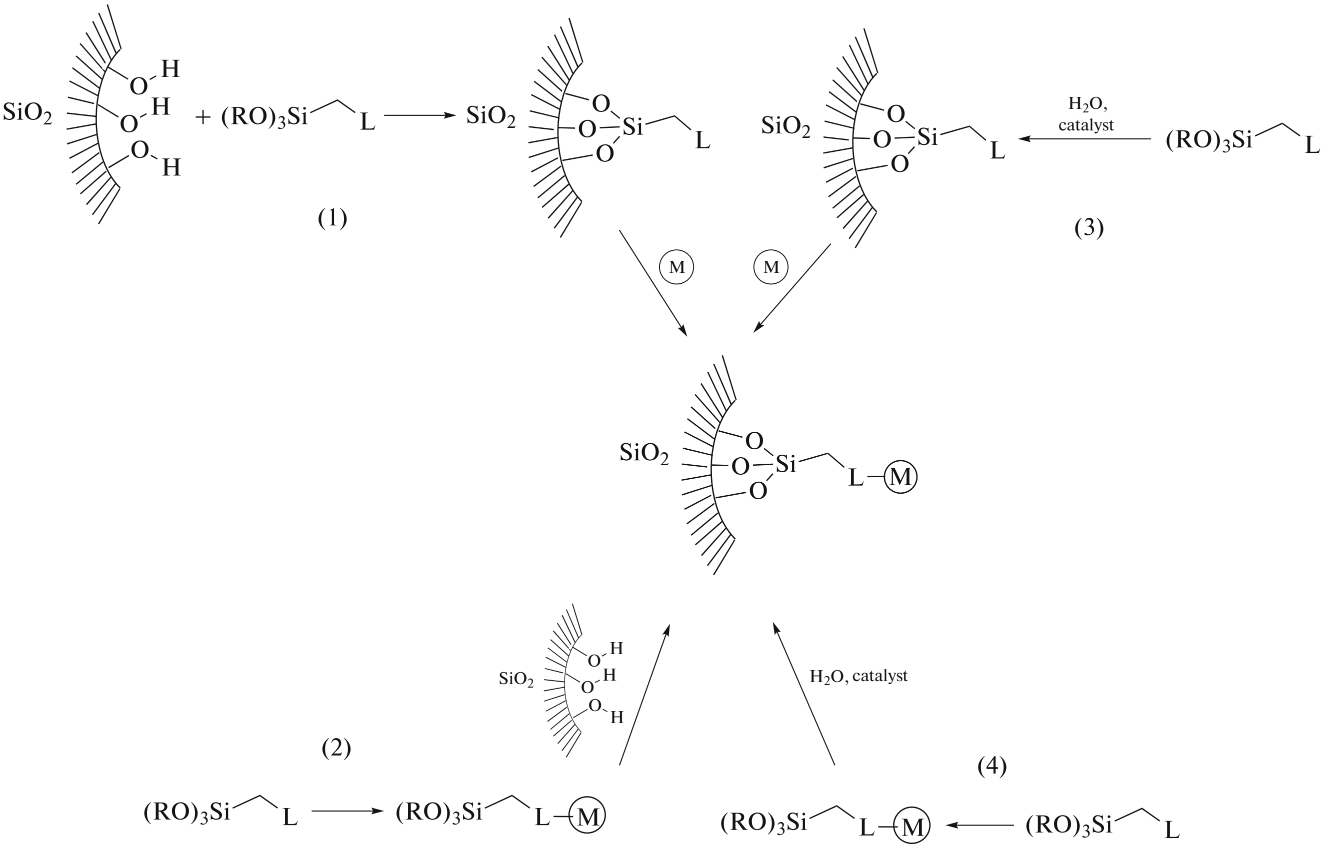
(1) The ligand functionalized with alkoxysilane is first immobilized on the hydrated SiO_2 surface. Then the modified SiO_2 reacts with the metal-containing precursor (usually metal salts) to immobilize the complex on the SiO_2 surface [155–159].

(2) The metal complex with the alkoxysilane-containing ligand is first synthesized and then mixed with the preliminarily prepared SiO_2 thus providing the covalent binding of the complex with the surface Si–OH groups [9, 160, 161].

(3) The alkoxysilane-containing ligand cogelates with tetraalkoxysilane $Si(OR)_4$ due to which the ligand is uniformly distributed over the whole material volume, and then the metal-containing precursor is added in order to bind the latter with the surface ligands [160, 162].

(4) The approach is a modified analog of method (2), where the presynthesized metal complex with the alkoxysilane-containing ligand cogelate with $Si(OR)_4$ [131, 133, 134, 163–168]. This approach is used most frequently for the synthesis of hybrid aerogels based on SiO_2. Note that approach (4) can be realized in practice using two variants. The first one is the primary isolation of complex $[(R'O)_3Si–X–A]_yML_m$ followed by its cogelation with $Si(OR)_4$. The second variant is the simultaneous cogelation of a mixture of ligand $(R'O)_3Si–X–A$ and a solution of M^{n+} and $Si(OR)_4$. The first procedure was applied in [166], and the second procedure was used in [165, 167].

Four main methods for the immobilization of metal complexes in the SiO_2 matrix [154] are shown in Scheme 4.



Scheme 4.

Methods (1) and (2) are classical for the immobilization of metal complexes on the material surface, whereas methods (3) and (4) are examples for using the sol–gel technology to prepare materials containing metal complexes uniformly distributed over the whole volume of the SiO_2 matrix.

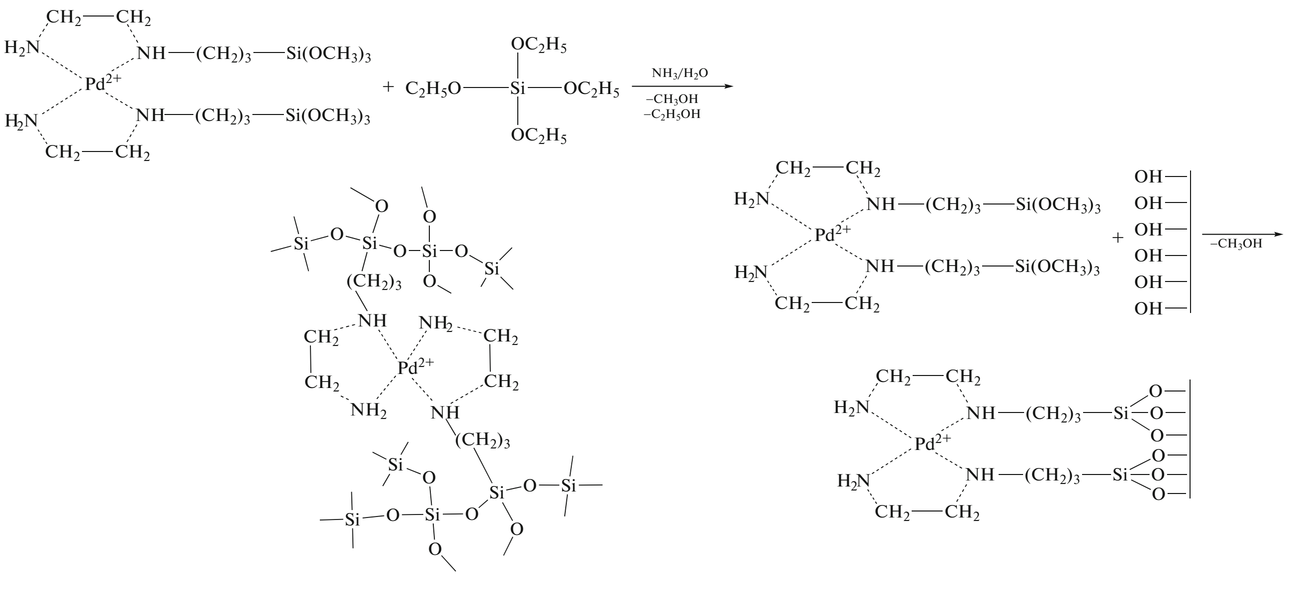
The choice of the modification method exerts a significant effect on the stability and functional properties of the produced hybrid materials. In particular, the use of method (4) was shown to provide catalytic materials (including the rhodium complexes immobilized in the SiO_2 matrix) with a higher activity than that of the catalysts prepared using other methods [169, 170]. On the contrary, it was shown [171] that the catalysts obtained by the immobilization of the rhodium complex in the SiO_2 matrix via method (4) turned out to be less active than those prepared using method (2). The observed effect is presumably caused by the inaccessibility of some catalytically active sites in the materials prepared by method (4).

The synthesis and purification of the alkoxysilane-containing ligand and corresponding metal complex are the most complicated and labor-consuming stages in the immobilization of metal complexes using organosubstituted alkoxysilanes. It should be mentioned that single crystals of the $[(R'O)_3Si{-}X{-}A]_yML_m$ complex cannot always be obtained to characterize its structure in detail. Similar complexes do not often crystalize at all and can be isolated as oily liquids [172]. The subsequent sol–gel synthesis with the formation of the metal complex immobilized in the SiO_2 matrix is rather trivial. Nevertheless, the sol–gel synthesis conditions should thoroughly be selected, because the formed porous structure of the final material that depends on the synthesis parameters determine the functional properties of the modified aerogel.

The sol–gel technologies provide precursor homogenization at the molecular level. However, although at the beginning of the reaction the reactants are really distributed uniformly, a heterogeneous material can be the result of the synthesis if differences in the polycondensation rates of the precursors are rather high. This phase separation will apparently affect substantially the final properties of the material [152].

Aerogels play a special role among the SiO_2-based materials used as matrices for metal complex immobilization. High mesoporosity and specific surface area characteristic of the SiO_2 aerogels make it possible to prepare materials in which the metal complex molecules are stochastically distributed over the matrix volume, isolated from each other in the open porous structure, and thus easily accessible [134, 166, 167].

The SiO_2-based aerogels containing chemically immobilized complexes have first been prepared in 1997 [168]. The corresponding xerogels were also synthesized for comparison. The schemes of the reactions that occur during the immobilization of the Pd(II) complex in the SiO_2 aerogel matrix ((a) cogelation and (b) postmodification [168]) are shown in Scheme 5 (see also Scheme 4, methods (2) and (4)). A powder of $Pd(acac)_2$ was suspended in ethanol, and 3-(2-aminoethyl)aminopropyltrimethoxysilane was added. The suspension was stirred at room temperature until the formation of a transparent yellow solution (color characteristic of the palladium complex with amines). Then the obtained solution of the complex was cogelated with $Si(OC_2H_5)_4$ (Scheme 5a). Lyogels were dried in SC ethanol at 327°C and 12 MPa.



(a) (b)

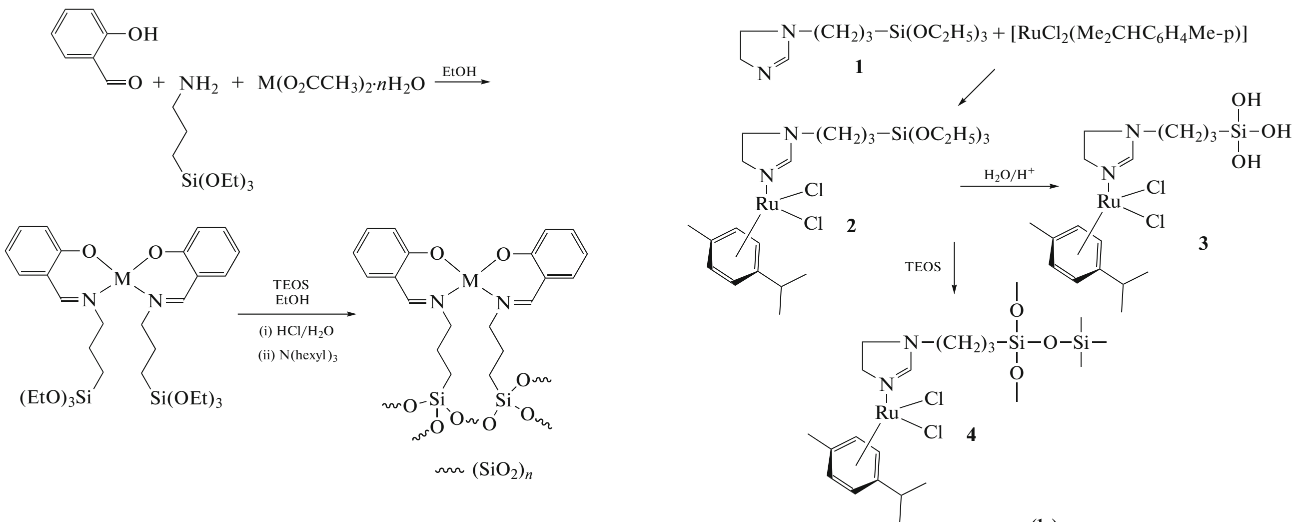
Scheme 5.

To carry out postmodification, the SiO_2 aerogel was synthesized and annealed at 400°C in air. Then the annealed aerogel was placed in a solution of the complex (Scheme 5b). After impregnation, the aerogel was dried again at 300°C in air. The SC drying in ethanol resulted in the reduction of Pd^{2+} to Pd^0 with a particle size of ~2.2 nm. During annealing the Pd crystallites in the samples obtained by cogelation aggregate to a less extent. Note that the reduction of the metal complex during SC drying in alcohols was observed in other studies as well [173].

N-Donor ligands, such as (3-aminopropyl)trimethoxysilane (APTMS) and 3-(2-aminoethyl)aminopropyltrimethoxysilane (EDTMS), are applied most frequently for the coordination of transition metals, since these metals form strong complexes with APTMS and RDTMS. For instance, Ni^{2+} and Pd^{2+} [174], Pt^{2+} [163], and Fe^{3+} [131] ions were successfully immobilized in the SiO_2 matrix using EDTMS as the ligand.

A similar approach based on the cogelation of $Si(OCH_3)_4$ and the complex synthesized by the reaction of copper(II) pivalate with APTMS was used for the production of the copper-containing aerogels [175]. Drying in SC-CO_2 made it possible to synthesize the aerogels containing the chemically immobilized copper(II) complex, and drying in supercritical alcohols (isopropanol, methanol) led to the reduction of divalent copper to the metallic state.

New ligands and related complexes with required characteristics can be synthesized using the modification of aminosubstituted alkoxysilanes. For example, the reaction of salicylaldehyde with (3-aminopropyl)triethoxysilane in a solution of Co(II) and Cu(II) salts was carried out [167] to immobilize the Co(II) and Cu(II) complexes with *N*,*N*'-ethylenebis(salicylidenimines) (Salen, Schiff bases) in the gels. The subsequent cogelation with TEOS afforded the hybrid lyogel. The synthesis and immobilization of the [M(Salen)] complexes in the SiO_2 aerogel matrix (M = Co(II), Cu(II) (a) [167], the synthesis of the new ligand (**1**) and corresponding ruthenium complex (**2**), and the immobilization of the latter in the SiO_2 aerogel (b) [166], are shown in Scheme 6.



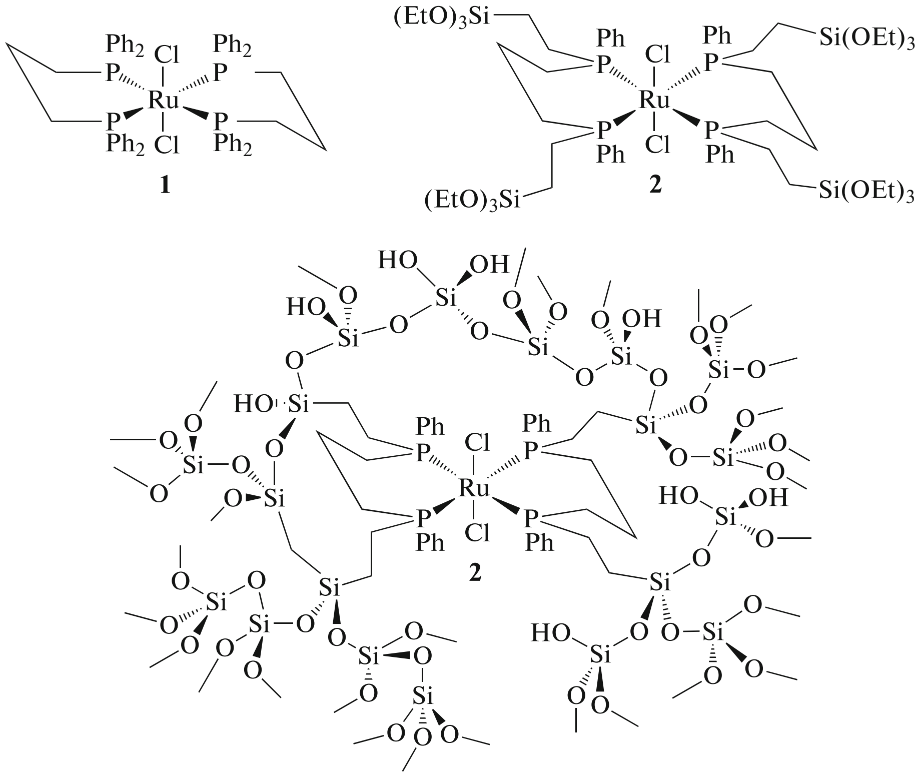
(a)

(b)

Scheme 6.

3-(4,5-Dihydroimidazol-1-yl)propyltriethoxysilane was first synthesized from 3-(2-aminoethyl)aminopropyltriethoxysilane (**1** in Scheme 6b) to prepare the aerogel with the immobilized metal complex [166]. The further reaction of ligand **1** with the ruthenium complex [$RuCl_2$(*p*-$Me_2CHC_6H_4Me$)] afforded complex **2** (see Scheme 6b). The hydrolysis and cogelation of complex **2** with TEOS resulted in the immobilization of the complex in the aerogel matrix (**4** in Scheme 6b).

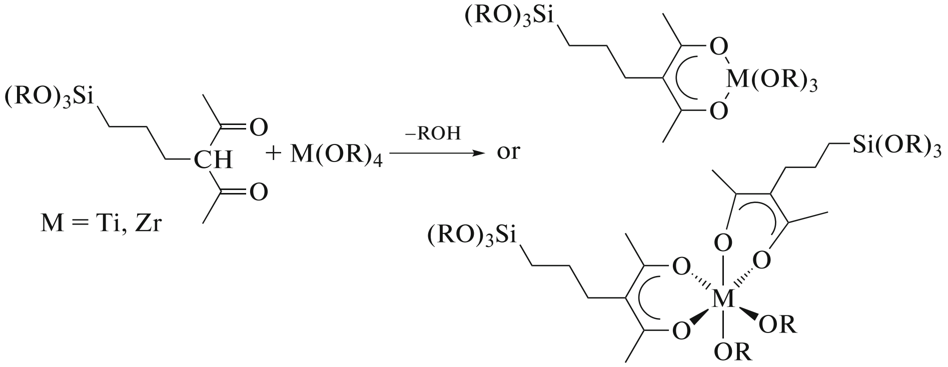
There are studies where the metal complex is premodified with the ligands bearing silanol groups and then cogelated with TEOS before the immobilization in the SiO_2 matrix [133, 134]. The starting ruthenium phosphine complex (**1**), complex modified with organotrialkoxysilane (**2**), and aerogel with the immobilized complex (**3a**) are shown in Scheme 7 [134].



3a, Aerogel
Scheme 7.

The postsynthetic treatment of the immobilized metal complexes provides oxide or metallic nanoparticles uniformly distributed over the aerogel surface (Fig. 2) [174].

O-Donor ligands are widely used along with N-donor ligands for the modification of the silica aerogels. For instance, the precursors based on β-diketone-substituted alkoxysilanes were used to immobilize the transition metal (Ti and Zr) compounds in the aerogel matrix [163]. The synthesis of these precursors for the preparation of the SiO_2-based functionalized aerogels is presented in Scheme 8.



Scheme 8.

Thus, the variation of ligand L and metal M in the coordination compounds $[(RO)_3Si(CH_2)_nL]_nMX_m$ makes it possible to immobilize complexes of nearly any metal in the SiO_2 matrix, including in the form of aerogel. A combination of possibilities of the sol–gel technology and coordination chemistry allows one to vary the synthetic parameters in wide ranges and thus prepare both hybrid aerogels based on SiO_2 with immobilized metal complexes and mixed-oxide aerogels with diverse functional properties.

Chemical modification of the Al_2O_3-based aerogels: the main synthetic approaches. The main described procedures for the modification of the Al_2O_3 aerogels are the cogelation of the aluminum hydroxo complexes with a solution/suspension of the modifier and impregnation of lyogel or aerogel of hydrated alumine with a solution or vapors of the modifier. Selected available synthetic approaches to the modification of the Al_2O_3-aerogels [31, 146, 176–236] are listed in Table 4.

Approaches of coordination chemistry are widely used for the modification of the Al_2O_3-based aerogels. The Al_2O_3 aerogel was prepared using an aqueous solution of $AlCl_3$ and propylene oxide as the initiator of gelation [191]. Polyvinyl alcohol chemically modified with acetoacetic ester (acac–PVA) was also used in the synthesis (Fig. 3a). The latter interacts with the Al^{3+} ions and surface of sol particles of nanodisperse hydrated alumina and thus performs functions of the template (dispersing and complexing agent) (Fig. 3b). The Al_2O_3 aerogels obtained using acac–PVA were characterized by high mechanical strength and mesopore content.

The chelation of aluminum alkoxides with a decrease in their reactivity is widely used in the synthesis of the Al_2O_3-based aerogels. The use of chelating agents is especially urgent when aerogels based on mixed oxides are needed to be prepared (in order to equalize the hydrolysis–polycondensation rates). Aluminum *sec*-butoxide $Al(OBu^{sec})_3$ or aluminum isopropoxide $A1(OPr^i)_3$ is usually used as the starting compound for the preparation of the Al_2O_3-aerogels, and acetylacetone or acetoacetic ester is applied as the chelating agent.

It should be mentioned that the concentration of a chelating agent can determine, to a significant extent, the composition and structure of the final product (Al_2O_3 aerogel). For example, the influence of the molar ratio (*C*) of aluminum *sec*-butoxide to the chelating agent on the sol–gel transition regularities and properties of the formed Al_2O_3 aerogels was studied [232]. Butane-1,3-diol and acetylacetone were chosen as chelating agents. The use of acetylacetone led to the formation of crystalline $Al(acac)_3$ in the whole studied

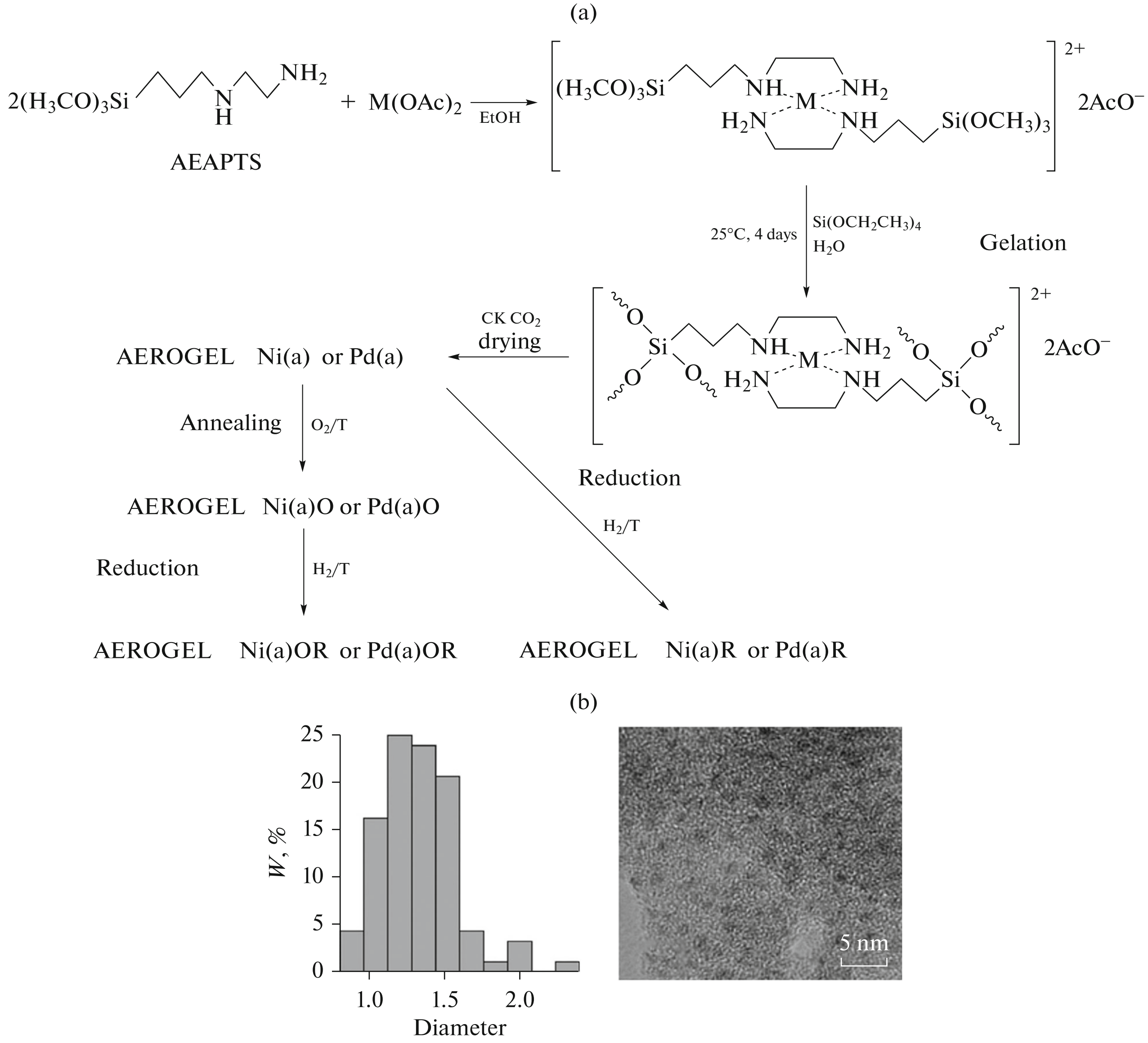


Fig. 2. (a) Scheme of the immobilization of the Ni(II) or Pd(II) complexes in the SiO_2 aerogel matrix and the postsynthetic treatment of the obtained samples and (b) the Pd nanoparticle size distribution according to the transmission electron microscopy data [174].

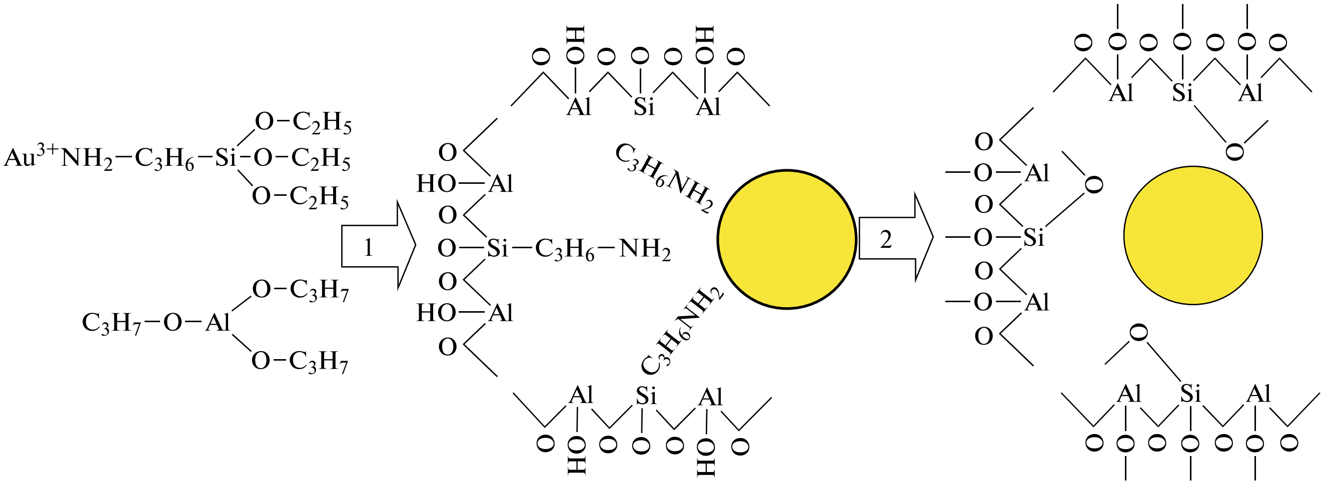
range of parameter C (1–3). In the case of $C = 2$ and 3, $Al(acac)_3$ precipitated and no gel formed, whereas at lower C crystalline aluminum acetylacetonate was observed in the final products of the synthesis (aerogels). On the contrary, when butane-1,3-diol is used, highly porous aerogels based on Al_2O_3 were obtained at all values of parameter C.

Organosubstituted silicon alkoxides are widely used for the immobilization of complexes in the matrices of the Al_2O_3 aerogels. The following approach was applied to immobilize gold nanoparticles in the Al_2O_3 aerogel [177]. A solution of chlorauric acid in heptane was added to a solution of aluminum isopropoxide in anhydrous *i*PrOH. Then (3-aminopropyl)triethoxysilane (APTES) was added to the obtained solution to form an Au(III) complex with APTES. The resulting solution was stirred for 1 h, and a solution of sodium borohydride in isopropanol was added in order to reduce Au^{3+} to Au^0. The mechanisms of formation of the Al_2O_3 aerogel with immobilized gold nanoparticles (sol–gel transition and reduction of gold (1); annealing at 500°C for 5 h (2)) is shown in Scheme 9 [177].

Table 4. Selected synthetic approaches used for the modifications of the Al_2O_3 aerogels

Approach	Starting compounds of aluminum and modifier*	Literature
Modification during lyogel formation	Aluminum alkoxide and modifier salt	[176–180, 186, 197, 208, 219, 230, 234–236]
	Auminum salt and modifier salt	[181–185, 187–191]
	Aluminum alkoxide and modifier alkoxide	[192–196, 198]
	Mixed aluminum and modifier alkoxide	[31, 199, 200]
	Sol of hydrated aluminum oxide and sol of hydrated modifier oxide	[201–206]
	Sol of hydrated aluminum oxide and modifier salt	[196, 198, 202, 207, 209–218]
Impregnation of lyogel or aerogel of hydrated aluminum oxide	Lyogel of hydrated aluminum oxide and solution of modifier compound	[146, 194, 220–222]
	Aerogel of hydrated aluminum oxide and solution of modifier compound	[184, 186, 196, 198, 212, 214, 218, 223–226, 230, 235]
	Aerogel of hydrated aluminum oxide and gaseous modifier compound	[227, 228]
Introduction of chelating ligands to coordination aluminum compounds (including alkoxides) to control hydrolysis and polycondensation rates		[31, 179, 186, 193, 197, 207, 221, 229, 231–233, 235]
Modification of lyogel of hydrated aluminum oxide during supercritical drying		[75, 228]

* As a rule, the modifier is a metal.



Scheme 9.

Gold nanoparticles distributed in the Al_2O_3 aerogel matrix demonstrated an excellent resistance to annealing (500°C, 5 h). The formed $Au/SiO_2@Al_2O_3$ aerogels have a significantly higher catalytic activity in the aerobic oxidation of benzyl alcohol compared to that of the reference catalyst obtained by the traditional method (impregnation).

The ligands containing the carboxyl group can be used for the chemical immobilization of metal complexes in the Al_2O_3 matrix [176, 202, 215, 236]. The following procedure was developed for the immobilization of the REE complexes in the Al_2O_3 matrix [176]. The europium complex with thenoyltrifluoroacetone (TTA) $Na[Eu(TTA)_4]$ was synthesized first. Then 3-(2-carboxypropyl)-1-methylimidazolium bromide (IM^+Br^-) was added to an ethanolic solution of $Na[Eu(TTA)_4]$. As a result, the $[Eu(TTA)_4]^-IM^+$ complex was isolated and then cogelated with aluminum isopropoxide in the molar ratio Eu : Al = 1 : 10 (Fig. 4). The approach developed made it possible to

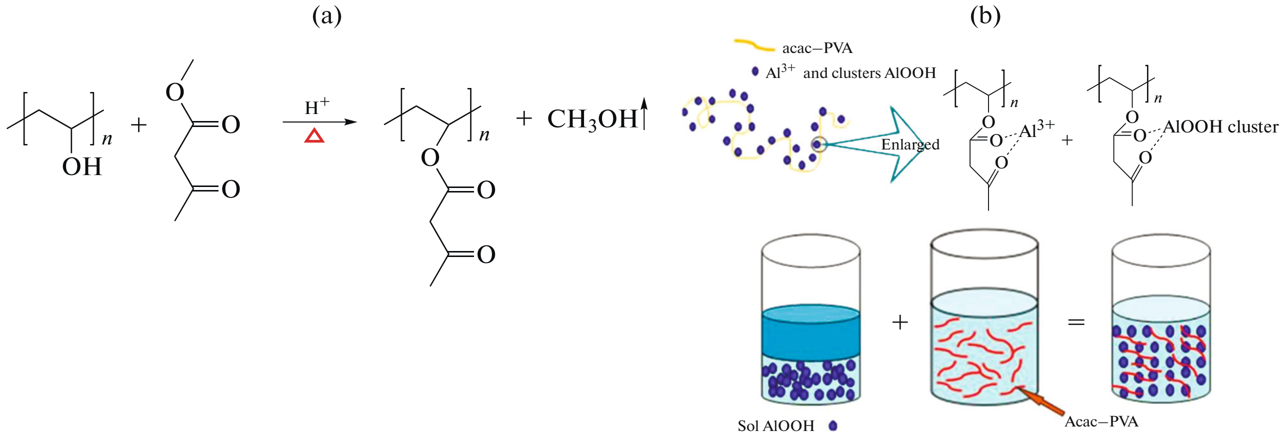


Fig. 3. (a) Esterification of polyvinyl alcohol and methyl acetoacetate with the formation of acac–PVA and (b) the mechanism of gel formation from Al_2O_3 in the presence of acac–PVA [191].

prepare hybrid porous materials demonstrating intense luminescence. A similar approach was used by the authors in other works [215, 236].

As many other metal alkoxides, aluminum alkoxides are highly prone to hydrolysis and, hence, the method based on the epoxide-induced sol–gel transition is preferable for producing aerogels based on Al_2O_3. The use of epoxides for the gelation of solutions containing coordination aluminum compounds can form a basis for the preparation of the Al_2O_3 aerogels containing chemically immobilized metal complexes. The Al_2O_3 aerogels modified with luminescent aluminum 8-oxyquinolinate were obtained using this approach [237]. Note that the gels are formed in the system containing stable aluminum complexes with 8-oxyquinoline within a substantially longer time than in the absence of 8-oxyquinoline (about 100 and 20 h, respectively).

The method of chemical modification of preliminarily produced highly porous materials based on Al_2O_3 was proposed to prepare superlight luminescent Al_2O_3-based materials [238]. The aerogel-like material obtained by the oxidation of metallic aluminum under the controlled wetness conditions through an aluminum amalgam layer was chosen as a matrix for the immobilization of luminescent aluminum 8-oxyquinolinate [239–243]. The chemical modification of the matrix with 8-oxyquinoline was carried out through the gas phase. The material gained superhydrophobic properties (angle of wetting with water reached 153°) due to this modification. Note that a substantial advantage of the chemical modification of aerogels and aerogel-like materials using gaseous reagents is the retention of the structure of the initial matrix, which is very important for the production of highly porous catalytic systems. In particular, the modification of the aerogels based on tin oxide with gaseous sulfuryl chloride and other sulfating agents provided materials characterized by a high catalytic activity in the isomerization and oligomerization of olefins [49, 244].

The chemical modification of the aerogel-like materials based on Al_2O_3 by the introduction of metal or metal oxide nanoparticles in the structure also leads to the formation of efficient catalysts for the skeletal isomerization of hexanes and hexenes [245–249]. The immobilized nanoparticles can serve as catalysts for the formation of carbon nanotubes using chemical vapor deposition (CVD) [240].

FUNCTIONAL PROPERTIES OF AEROGELS MODIFIED USING APPROACHES OF COORDINATION CHEMISTRY

The possibilities of preparing functional materials based on aerogels with catalytic, photocatalytic, and luminescence properties can significantly be extended combining approaches of the sol–gel technology and coordination chemistry.

Catalytic properties of the aerogels based on SiO_2 and Al_2O_3. More than 90% processes in the modern petrochemical and food industries are catalytic, and more than 90% catalysts used are heterogeneous [150]. Heterogeneous catalysts are convenient in use, since they can easily be separated from the reaction mixture and regenerated. However, usually they are strongly inferior to homogeneous catalysts in catalytic activity. In turn, the main drawback of homogeneous processes is a complicated separation of the catalyst from the reaction mixture and regeneration, as well as the prevention of a possible contamination of the final product with the catalyst.

The solid-phase supports with chemically immobilized coordination metal compounds were proposed as catalytic materials in the 1970s [137]. According to Hartley's classification [137], heterogeneous catalysts are catalysts of the first generation, homogeneous catalysts are of the second generation, and catalytic sys-

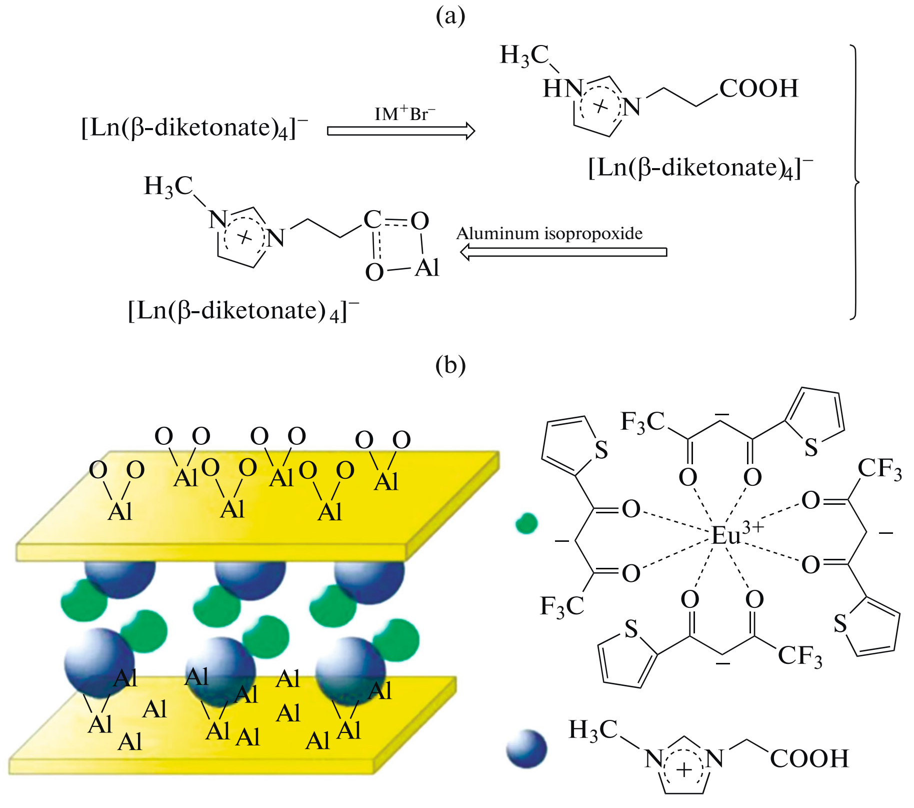


Fig. 4. (a) Synthesis of the hybrid Al_2O_3 xerogel modified with the $[Eu(L)_4]^-IM^+$ complex and (b) the structure of the prepared material [176].

tems containing immobilized metal complexes can be assigned to catalysts of the third generation.

The accomplishment of the concept of metal complex immobilization for catalytic applications assumes the solution of a number of problems related to the design of metal complexes and supports providing a high concentration of active sites and a possibility of isolating the catalyst from the system and regeneration. The solution of these problems implies the transition from the empirical to scientifically substantiated selection of catalysts and prediction of their catalytic effect [126].

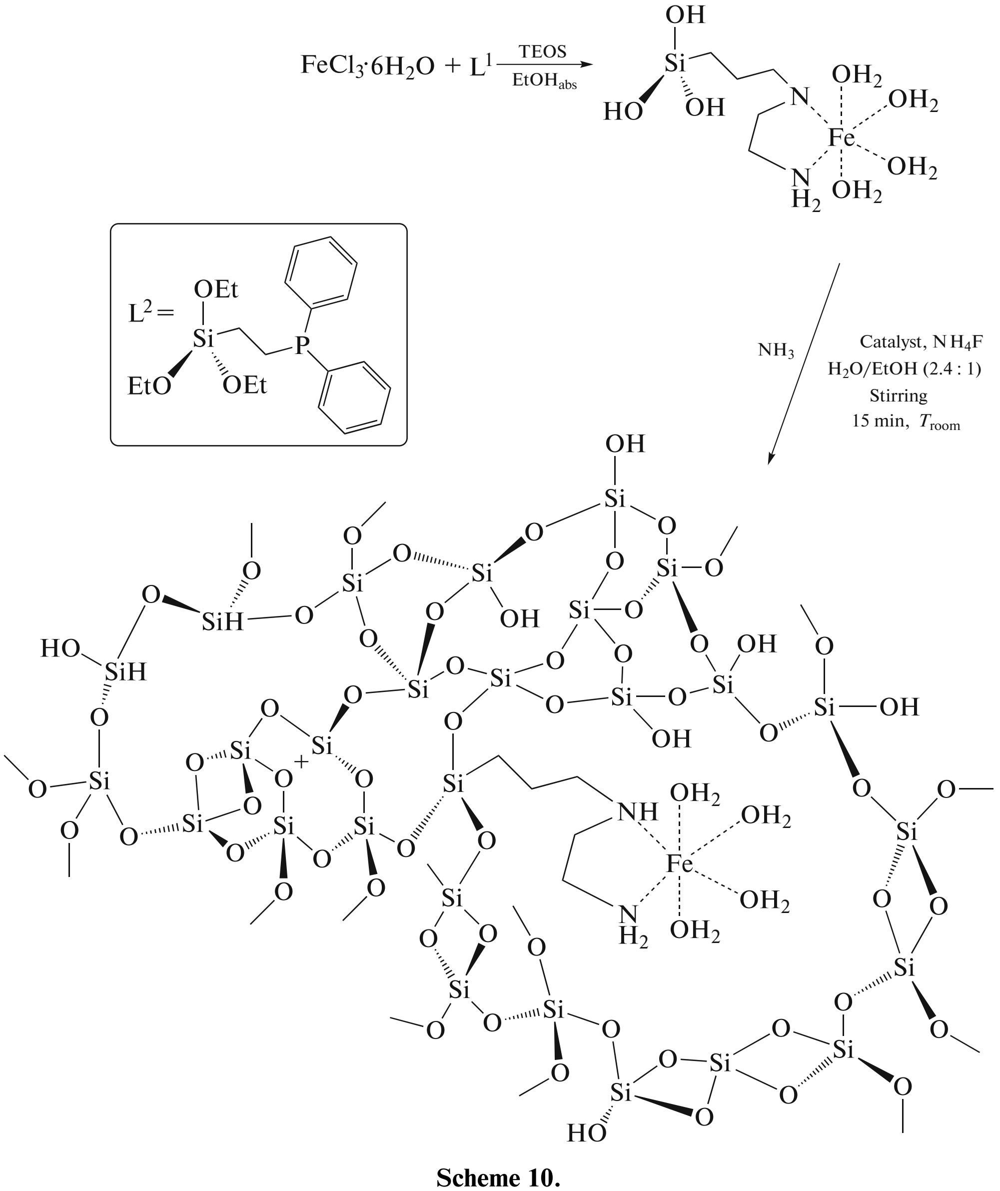
The general strategy for the heterogenization of a homogeneous catalyst is the deposition of catalytically active compounds on solid-phase (inorganic) supports with a high specific surface area, for example, on the metal-oxide aerogels or other highly porous oxide materials prepared by the sol–gel method [150, 250]. Among sol–gel materials, the aerogels based on SiO_2 and Al_2O_3 with high porosity and thermal stability are used most frequently as supports.

For instance, the catalytically active SiO_2 aerogels and xerogels with the immobilized ruthenium complex $RuCl_2[Ph_2P(CH_2)_3PPh_2]_2$ (Scheme 7) were synthesized [134]. The produced hybrid materials were used as heterogeneous catalysts in the synthesis of *N*,*N*-diethylformamide from CO_2, H_2, and diethylamine. The activity of the aerogel (TOF = 18400 h^{-1}) is significantly higher than that of the xerogel (TOF = 2210 h^{-1}) under the same experimental conditions, which is associated with the improved texture characteristics of the aerogel, particularly, containing a high number of mesopores, which eliminates diffusional restraints of the process and provides high accessibility of active sites. Moreover, the catalytic activity of the aerogel turned out to be even higher than the intrinsic activity of the starting complex when using as the homogeneous catalyst. The authors assume that this behavior is related to the influence of the matrix on the electronic structure of the complex. The catalytic activity of the complexes increased over the corresponding homogeneous catalysts after their immobilization in the aerogel matrix [131, 155].

The question about washing of the active phase from the support surface during catalytic reactions is important for the development of heterogeneous catalysts. The covalent immobilization of a metal complex in the aerogel matrix makes it possible to minimize this phenomenon. The stability of a metal complex under the catalytic conditions is also an important factor. It was shown [167] that the storage of the SiO_2 aerogels with the immobilized Cu(Salen) or Co(Salen) complex (see Scheme 6a) in a medium of

DMSO–DMF or ethylbenzene at 110°C for 24 h did not decompose the complex, indicating a high stability of the immobilized complexes under relatively harsh reaction conditions. The obtained materials exhibited the catalytic activity in ethylbenzene oxidation, and the high selectivity to acetophenone and quantitative conversion of ethylbenzene were achieved [251].

The possibility of strong binding of the catalytically active metal complexes with the aerogel surface was also demonstrated for other examples [131, 155]. In particular, the aerogels with the immobilized Fe(III) complex containing 3-(2-aminoethylamino)propyltrimethoxysilane (EDTMS, L^1) and 2-(diphenylphosphino)ethyltriethoxysilane (L^2) (Scheme 10) were prepared [131].



Scheme 10.

The prepared composite aerogels were used as heterogeneous catalysts for the amination of allyl alcohols in an aqueous medium. The activity of the heterogeneous catalyst was shown to exceed that of the homogeneous catalyst $FeCl_3·6H_2O$. The catalysts retained a high catalytic activity within at least six reaction cycles.

The SiO_2 aerogels modified with metallic or oxide Ni and Pd nanoparticles, which were prepared by the postsynthetic treatment of the corresponding covalently bound metal complexes (Fig. 2), demonstrated the high stability in the Mizoroki–Heck reaction [174].

Thus, the oxide aerogels (primarily based on SiO_2) with immobilized coordination compounds are of doubtless practical interest for the development of highly efficient catalytic systems.

Luminescence properties of the SiO_2-based aerogels. Luminescent materials based on aerogels are prepared most frequently by the introduction of luminescent centers in the aerogel matrix. The following compounds usually act as luminescent centers:

- organic luminophores [129, 138, 252];
- oxides [253–256], REE and transition metal salts [138, 257, 258], and metal complexes [259];
- nanoparticles [260–262], including quantum dots [263], fullerenes [264], and silicon nanocrystals [265, 266].

It should be mentioned that individual aerogels based on SiO_2 also demonstrate the luminescence properties in the blue spectral range induced by UV irradiation (365 nm), which is caused by the presence of oxygen vacancies in the SiO_2 matrix [267, 268].

The luminescent aerogels can be used for sensor design [129] and manufacturing displays [138], scintillators [139], lasers [140], etc. Among the complexes used in the preparation of luminescent aerogels, coordination REE compounds containing organic ligands that act as “antennas” play a special role [127, 269, 270]. Compared to metal salts or metal oxides, organometallic REE complexes have a higher extinction coefficients resulting in a more efficient luminescence of lanthanide ions.

The studies describing the immobilization of REE complexes in the matrix of the SiO_2 aerogels are rather fragmented. The luminescent aerogels were synthesized [258] from individual oxide Y_2O_3 and mixed oxides Y_2O_3–SiO_2 doped with Eu^{3+} ions. The luminescence intensity was shown to increase with an increase in the Eu^{3+} concentration in the aerogel. The luminescence intensity of the Y_2O_3-based aerogels was by 50% (on the average) higher than that of the aerogels based on mixed Y_2O_3–SiO_2 oxides. This result is presumably due to a low transparency of the mixed aerogel and the presence of $Y(OH)_3$ in it.

The luminescent aerogel based on SiO_2 and modified with the terbium(III) complex with *N*-hydroxysuccinimide was synthesized [270]. The complex in the aerogel matrix is characterized by a higher stability indicating that the complex interacts with the SiO_2 matrix. At the same time, a comparison of the excitation and luminescence spectra of the free complex and the complex immobilized in the aerogel matrix showed that the aerogel matrix exerted nearly no effect on the photophysical characteristics only decreasing the total photoluminescence intensity. Apparently, this is due to a decrease in the penetration depth of the excitation radiation into the aerogel volume because of light absorption and scattering. Nevertheless, the introduction of the complex in the structure of the SiO_2 aerogel provides a number of advantages, such as the long-term retention of the functional characteristics of the complex on contact with the environment (the free complex is sensitive to moisture) [271].

All methods described for the synthesis of the luminescent aerogels based on the REE complexes considered above are based on the combined gelation of the modifier and alkoxysilane/SiO_2 sol during the sol–gel transition or postmodification of the preliminarily obtained aerogel.

The synthetic approach based on the covalent binding of the REE complexes in the matrix of the SiO_2 aerogels (Fig. 5) was first described by us [272]. It should be emphasized that the aerogel-based materials are characterized, as a rule, by low luminescence characteristics, which is related to luminescence quenching due to the interaction of the luminescent centers with the OH groups present in the aerogels. To solve this problem, we propose to immobilize in the aerogel matrix the bimetallic luminescent complex bearing the luminescent center (europium ion) and nonluminescent linker ion (zinc ion) providing the chemical binding of the complex with the aerogel matrix that shields the europium ion from the hydroxyl groups present on the aerogel surface [272].

The prepared materials are characterized by intense luminescence upon UV irradiation typical of the coordination europium compounds (see Fig. 5b) retaining high specific surface area and porosity inherent in aerogels.

Sensor properties of the aerogels modified with coordination compounds. The detection of chemical substances in air, water, and other media is highly significant for a broad range of applications, including environmental monitoring of dangerous chemicals, medicine, criminalistics, and others. Aerogels are especially attractive for applications in sensor science due to the high specific surface area, high porosity, and low density [273].

The majority of studies on the development of sensor systems based on sol–gel materials, including those modified with coordination compounds of metals, fell on xerogels up to the present time [274]. Silica (SiO_2) is usually used as a matrix for the development of sensors based on aerogels due to its high transparency in the UV and visible ranges, which is important for the design of optical sensors [154].

The SiO_2 aerogel modified with ruthenium(II) tris(1,10-phenanthrolinate) and ruthenium complexes **1** and **2** bearing the electron-withdrawing ligands (Fig. 6a) were used for manufacturing sensors to oxygen [275]. The aerogel with complex **1** (Figs. 6b, 6c) demonstrated the best sensor properties. Interestingly, the luminescence characteristics of the complexes in the aerogel were analogous to the characteristics of a frozen solution of the complex. The luminescence intensity of the complex increased on cooling, and a hypsochromic shift is observed.

A comparative analysis of the sensor characteristics of the ruthenium(II) complexes in the aerogels and xerogels based on SiO_2 was carried out [276]. The response time of the modified aerogel was shown to be by ~5 times lower than that of the corresponding xerogel, which is evidently related to a higher gas permeability of the aerogel compared to the xerogel.

Aerogels modified with nanoparticles of noble metals are used for the detection of organic molecules due to the enhancement of the Raman scattering signal of the corresponding molecules [277–279]. Approaches of coordination chemistry are widely applied to improve the uniformity of the nanoparticle distribution over the aerogel matrix [151].

Photocatalytic and photoprotective materials based on the aerogels. The development of highly efficient photocatalytic systems is very urgent at present, since these systems are widely demanded for water and air decontamination from organic and biogenic contaminators and for the photoelectrochemical decomposition of water [280–282].

The SiO_2 aerogels modified with TiO_2 are used most frequently for the preparation of photocatalysts based on the aerogels [94, 103, 104, 110, 185, 283–289]. The SiO_2 matrix provides high specific surface area and porosity, and TiO_2 imparts a photocatalytic activity (PCA) to the composite aerogel. The presence and uniform distribution of the TiO_2 crystalline phase (anatase) as a photocatalyst combined with a high permeability of the matrix is important for the synthesis of the SiO_2–TiO_2-based aerogels. The choice of SC drying of binary aerogels exerts a substantial effect on the PCA. The aerogels prepared by drying in organic solvents manifest a noticeable PCA, whereas the aerogels prepared using SC-CO_2 have no photocatalytic activity [285, 289]. This is due to the formation of nanocrystalline anatase in the first case and amorphous titanium dioxide in the second case.

In some cases, the dependence of the PCA on the TiO_2 content in the binary aerogels is nonmonotonic. For instance, it was shown [110] that in the range of the TiO_2 concentrations from 20 to 50 mol % the PCA decreases with an increase in the titanium dioxide content due to a decrease in the porosity and transparency of the composite material for UV radiation.

In order to improve the PCA of the SiO_2–TiO_2 aerogels, they are often annealed to crystallize titanium dioxide and form nanocrystalline anatase. The low-temperature annealing (<500°C), due to which organic compounds are removed, favor an increase in the specific surface area and porosity of the aerogels and results in the formation of anatase nanoparticles and an increase in the PCA [284, 289, 290]. The annealing at higher temperatures (650°C and higher) leads, as a rule, to a decrease in the porosity and PCA [290].

Almost no studies devoted to the systematic analysis of the influence of the content of a chelating agent controlling the relative hydrolysis rate of titanium and silicon alkoxides on the structure and photocatalytic properties of the SiO_2–TiO_2 aerogels are known to the moment. The influence of the type of the used supercritical fluid on the physicochemical properties of the aerogels based on SiO_2–TiO_2 remains poorly studied.

Therefore, we discussed for the first time the influence of the SC drying conditions (type of the SC solvent) on the physicochemical characteristics of the binary SiO_2–TiO_2 aerogels with the titanium dioxide content up to 50 mol % [291, 292]. It was shown that in diverse supercritical media both the amorphous SiO_2–TiO_2 aerogels with the homogeneous distribution of the components (CO_2 drying) and composite aerogels containing nanocrystalline anatase (drying in isopropanol and methyl *tert*-butyl ether) characterized by the high specific surface area (about 1000 m^2/g) can be obtained. An important characteristic of the obtained materials is their high thermal stability: annealing at temperatures up to 600°C did not result in a significant decomposition of the porous structure of the aerogels, and they retained high specific surface areas (>400 m^2/g).

The aerogels based on SiO_2 (first of all, SiO_2–TiO_2) are perspective as components of cosmetic products. The successful use of the hydrophobic SiO_2-based aerogel as a matting component of the cream for disguising greasy facial skin was reported in 2018 [293]. The concentration of the aerogel in the cream at a level of 1–2 wt % was shown to efficiently prevent the appearance of greasy shimmer within at least 6 h. The aerogel turned out to be a little more efficient than other mineral additives traditionally used in matting cosmetic products: perlite and talc.

The aerogels based on SiO_2–TiO_2 can be promising as components of sunscreen cosmetic products. It is known that titanium dioxide is a traditional component of sunblock remedies [294, 295]. However, TiO_2 has pronounced photocatalytic properties and, hence, induces skin damages by active oxygen species formed upon UV irradiation [296]. In the composite aerogels, the inert SiO_2 matrix diminished the photocytotoxicity of TiO_2 nanoparticles blocking their surface. The SiO_2 matrix also serves as a physical barrier between titania nanoparticles and components of the cream and/or sebum (cutaneous grease) preventing skin damage by active oxygen species. At the same time, titania in the composite retains the UV filter function.

We pioneered [297] in examining the photoprotective properties of the SiO_2–TiO_2 aerogels synthesized from titanium alcoholates chelated by acetylacetone using the standard ISO 24443 method. The phase composition of the aerogels was shown to substantially

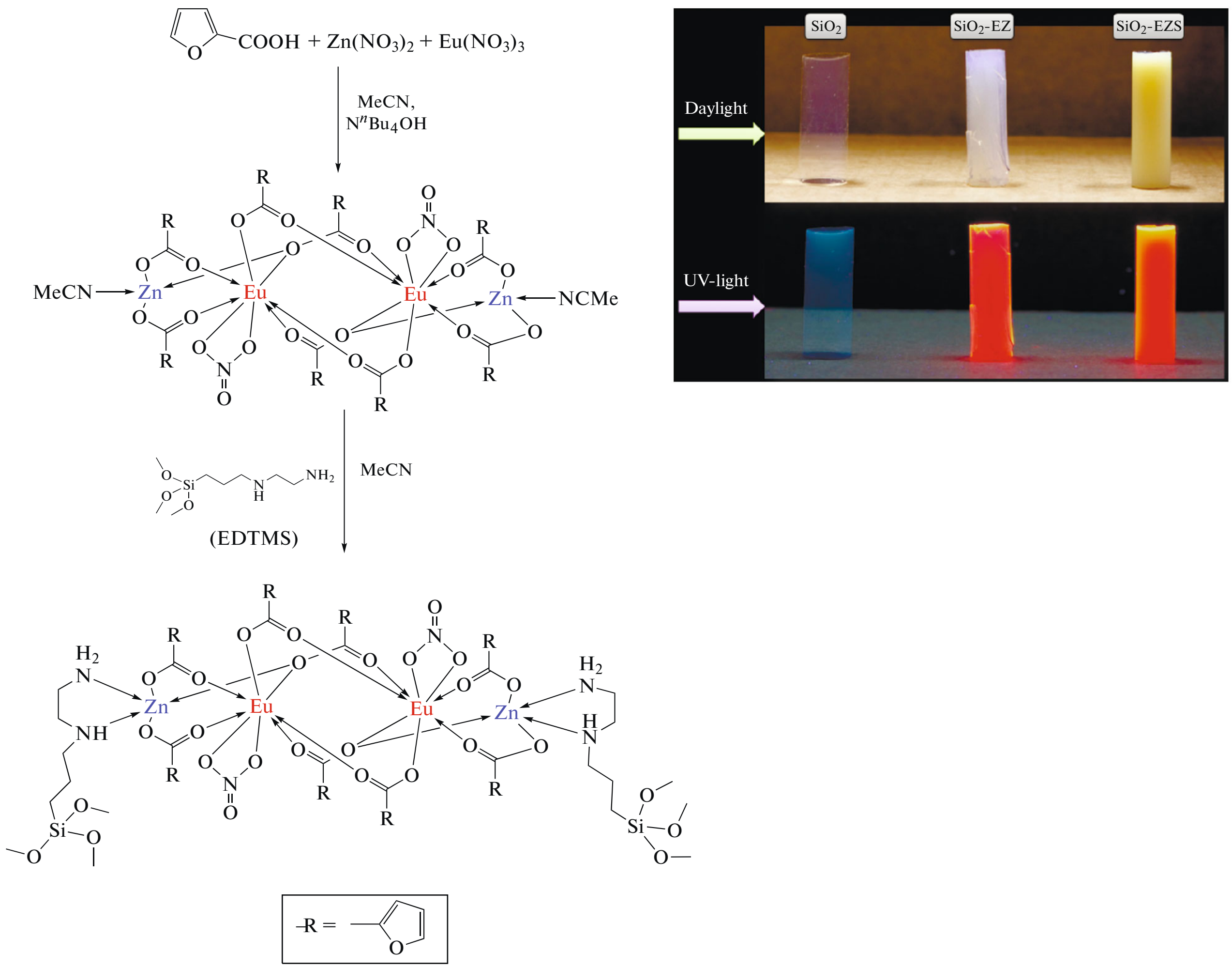


Fig. 5. (a) Scheme of the synthesis and (b) the external view of the luminescent SiO_2 aerogel with the immobilized heterometallic zinc and europium complex [272].

determine their photoprotective characteristics, and the phase composition can purposefully be specified by choosing the solvent used at the stage of SC drying of the material (CO_2, isopropanol, methyl *tert*-butyl ether, hexafluoroisopropanol). The SC drying at the temperatures lower than 200°C (in CO_2 or hexafluoroisopropanol) gave materials amorphous to X-rays, whereas nanocrystalline anatase is formed at higher temperatures of 240–250°C (in isopropanol or methyl *tert*-butyl ether). The prepared aerogels had a low PCA, good matting properties, and rather high photoprotector characteristics in the UVA range. Note that we also showed that the PCA of the TiO_2-based materials traditionally used in photoprotective cosmetic products can exceed that of commercial photocatalysts.

To conclude, the use of the approaches of coordination chemistry in the sol–gel technology considerably extends the range of functional properties and application areas of the complexes themselves and aerogels. In particular, the modification of the aerogels with coordination compounds makes it possible to obtain new polyfunctional materials combining excellent catalytic, photocatalytic, optical, and other properties with high porosity and specific surface area.

The most popular method for the preparation of the hybrid aerogels modified with coordination compounds is the physical binding of the complex with the gel matrix due to capturing molecules of the complex during gelation or due to the insertion of complex molecules into the already formed gel/aerogel. In spite of the simplicity, this approach have a number of substantial drawbacks, including the nonuniform distribution of the complex in the matrix, pore blocking, partial decomposition of the porous structure of the matrix because of capillary forces, and others. The listed problems can be solved to a considerable extent using the approaches based on the chemical immobilization of coordination compounds in the aerogel matrix.

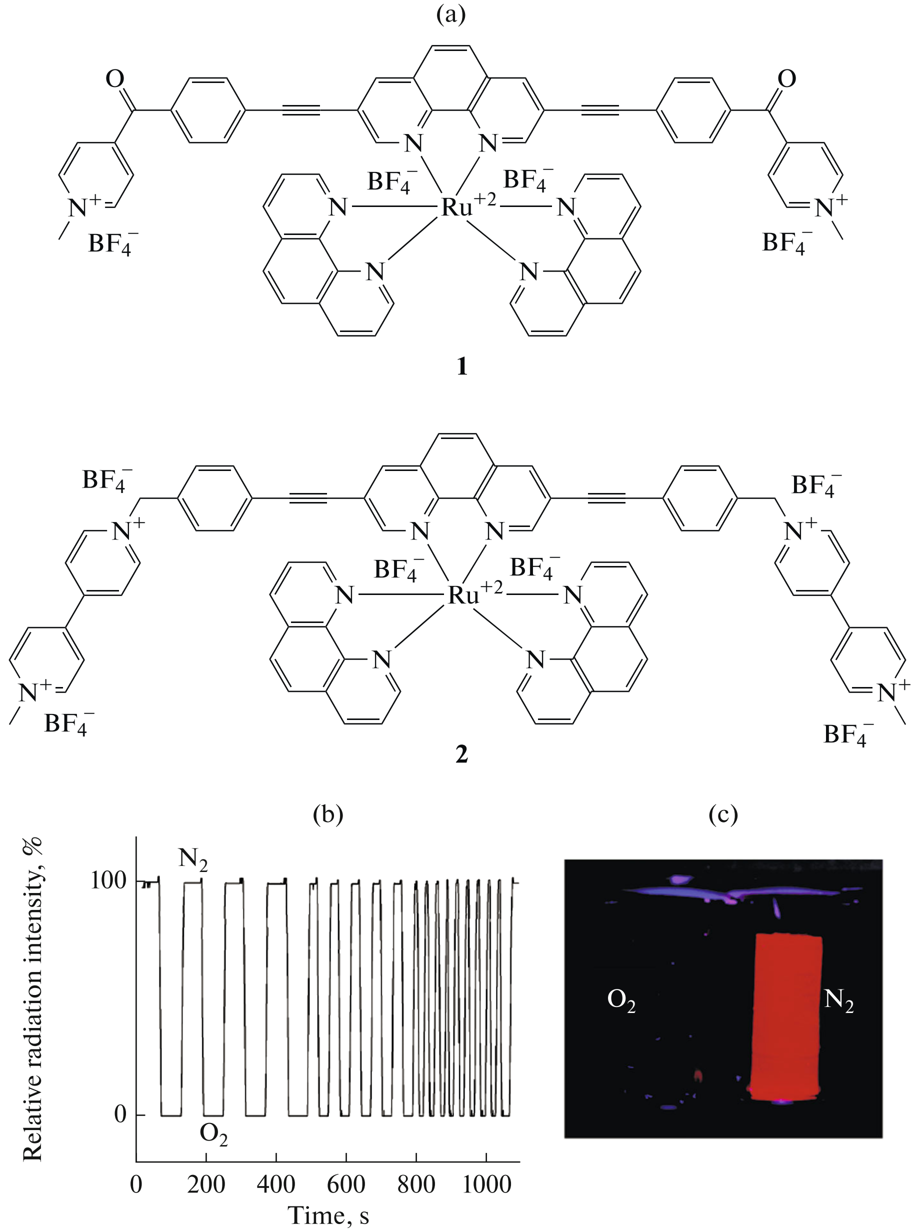


Fig. 6. (a) Structural formulas of the ruthenium(II) complexes with bis(1,10-phenanthroline)mono(3,8-bis(*N*-methyl-4-(4-ethinylbenzoyl)pyridine)-1,10-phenanthroline) tetra(tetrafluoroborate) monohydrate (**1**) and bis(1,10-phenanthroline)mono[3,8-bis(*N*-(4-ethinylbenzyl)-*N*-methyl-4,4'-bipyridine)-1,10-phenanthroline)]ruthenium(II) hexa(tetrafluoroborate) complex (**2**), (b) the sensor response of the SiO_2 aerogel modified with complex **1** at room temperature with alternating N_2 and O_2 flows, and (c) luminescence quenching in an O_2 atmosphere for the aerogel modified with complex **1** [275].

The known approaches of the chemical immobilization of coordination compounds on the matrix surface of metal-oxide aerogels can be divided into two groups.

The first group of approaches is based on the direct binding of the $(RO)_xML_y$ complex (where RO is the alkoxide group, M is the metal, and L is the ligand) with the metal-oxide matrix due to the interaction with the surface OH groups. This approach is used most frequently for the preparation of mixed-oxide aerogels (particularly, aerogels based on SiO_2–TiO_2). The preliminarily chelated metal alkoxide acts as the complex, since its reactivity is considerably lower than that of the starting alkoxide, which is important for the preparation of the aerogels with the uniform distribution of the components in the matrix.

The second group of approaches is based on the immobilization of complexes via a chemically inert (hydrocarbon) fragment using the preliminarily synthesized compound $[(RO)_3Si(CH_2)_nL]_nMX_m$ (where

L is the donor group, e.g., $-NH_2$, $-SH$, etc.; X is the counterion or ligand) due to the condensation of the Si–OR fragments with the surface OH groups of the metal-oxide matrix. The synthesized complex is immobilized at different stages of aerogel synthesis. The most efficient method is the cogelation of the complex with the sol of hydrated metal oxide or with alkoxide of the matrix-forming element. In this approach, the synthesis and purification of the alkoxysilane-containing ligand and the corresponding metal complex are the most complicated and labor-consuming stages. In addition, single crystals of the silane-containing complex cannot be isolated in the most cases, which impedes an unambiguous identification of the synthesized complexes both in the individual state and as a component of the aerogel matrix. The second group of approaches is mainly used for the immobilization of transition metal complexes. Note, by now, the problem of REE complex immobilization in SiO_2 aerogel matrix remains virtually untouched. The available approaches to the synthesis of the aerogels modified with the REE complexes are based on the combined gelation of the modifier and alkoxysilane/SiO_2 sol during the sol–gel transition or post-modification of the preliminarily prepared aerogel.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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