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Nanocrystalline Aerogels of Metal Oxides as Destructive Sorbents and Catalysts

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Abstract

The procedure of the synthesis of aerogels Al_2O_3 and VO_x/MgO with the particle size of several nanometres was developed. The specific surface of materials obtained after drying under supercritical conditions exceeded $1000 \text{ m}^2/\text{g}$. The possibility to govern the properties of aerogels through modification with acids and β -diketones of the solutions of alkoxides used as initial substances was revealed. The high activity of modified aerogel of Al_2O_3 in the processes of destructive sorption and catalytic dehydrohalogenation was demonstrated. It was shown that the aerogel VO_x/MgO exhibits high activity in the reaction of decomposition of Freon CF_2Cl_2 .

Key words: aerogel, Al_2O_3 , VO_x/MgO , destructive sorption, nanoparticles

INTRODUCTION

Aerogel materials are obtained by drying gel under supercritical conditions when surface tension is absent. This technology allows one to avoid the destruction of pore structure and to obtain materials with the small size of nanoparticles, highly developed surface, low density and a large number of surface defects. Due to this fact, these materials can be used as adsorbents and catalysts. Adsorption and chemical properties of very small metal oxide crystals strongly depend on their size. Various nanocrystalline oxides synthesized using the aerogel procedure were extensively studied as destructive sorbents for the decomposition of hazardous organic substances [1–4], neutralization of bacteria and spores [5], and also in various catalytic processes [6–9].

However, till recently, data on the methods to control their properties during synthesis, especially for two-component systems, have been almost completely absent. In the present work we briefly describe general approaches to the preparation of metal oxide aerogels and consider their reactivity. We thoroughly studied the effect of various organic and acidic modifying additives, such as acids, β -diketo-

nates, aromatic alcohols *etc.*, on the properties of resulting nanocrystalline aluminium oxide, in particular modified with carbon and sulphate groups. The results of the detailed investigation into the effect of modifying agents and reaction conditions on the properties of nanosized oxides allowed us to monitor these properties better and to obtain materials with higher specific surface and smaller size of nanoparticles. We also describe an example of the synthesis of two-component aerogel VO_x/MgO and their use for the destructive sorption of Freon 12.

EXPERIMENTAL

In order to prepare modified Al_2O_3 aerogel samples, we dissolved aluminium isopropoxide (Aldrich) in calculated amounts of ethanol and/or another solvent. The modifying agent for hydrolysis was dissolved in 10 mL of the same solvent. Then the solution with the modifying agent was rapidly poured into the main vessel with the solution of aluminium isopropoxide; intense mixing was carried out for 10 min. Then the solution containing stoichiometric amount of water in the chosen solvent was added. The gel formed after the addition of water was stirred with a magnetic mixer for about 15 h.

The resulting gel was placed into the autoclave (Parr Instruments) equipped with a mixer, and heated in the atmosphere of nitrogen to 260 °C at a rate of 1.3 °C/min. The final pressure and temperature were varied to study the effect of these parameters on the texture characteristics of the resulting aerogel. The product materials were calcined at a temperature of 500 °C in the air or in vacuum (in the case of non-modified Al₂O₃ aerogel). Calcination of modified C/Al₂O₃ aerogel was carried out in vacuum at the same temperature. The samples of sulphated Al₂O₃ were calcined at a temperature of 600 °C.

To synthesize the oxide system VO_x/MgO, we used the aerogel procedure described in [10]. At the first stage, aerogel of the joint hydroxide VMg(OH)_x was synthesized by means of hydrolysis of a mixture of V and Mg organic precursors, followed by drying under supercritical conditions. The samples of nanocrystalline oxides VO_x/MgO were obtained by annealing aerogel hydroxides VMg(OH)_x in the air under programmable temperature mode up to $T = 550$ °C.

Specific surface of the samples was determined with the help of the comparative method with a Quantachrome NOVA-1200 instrument using nitrogen adsorption at a temperature of 77 K. The reference was the isotherm of nitrogen adsorption on non-porous sample as reported previously by the authors of [11].

Dehydrochlorination of 1-chlorobutane was carried out in a flow reactor. In the experiments, we used 1-chlorobutane 99 % (Aldrich); it was introduced into the reactor by saturating the argon flow at room temperature. Flow rate was about 2 L/h, the mass of catalyst loaded was 0.02 g. The composition of products after the reactor was analyzed by means of gas chromatography. Before experiment, the catalyst was activated in argon flow at a temperature of 500 °C for 1 h.

To study the destructive sorption of CF₂Cl₂, we took VO_x/MgO samples with vanadium content 2, 10, 15 and 25 % (for V₂O₅). The kinetics of the reaction of nanocrystalline VO_x/MgO oxides with Freon CF₂Cl₂ was studied using the TEOM 1500 PMA (Tapered Element Oscillating Microbalance). The principle that is realized in this device involves mass measurement on the basis of the interconnection between the fre-

quency of oscillations of microreactor pendulum and the mass of the sample under investigation. Analysis of the composition of gases at the outlet of TEOM microanalyzer was carried out with a QMS-200 quadrupole mass spectrometer. Identification of reaction products was performed according to the reference database of the National Institute of Standards and Technology (USA).

PREPARATION AND PROPERTIES OF Al₂O₃ AEROGEL

In the most general understanding, the sol-gel process involves the formation of a disordered branched network (gel) from the solution of a precursor through a system of colloid particles (sol) [12]. To obtain aerogel, one usually uses a procedure based on such organometallic compounds as alkoxides (most frequently), metal β-diketonates and carboxylates. This allows one to reject the use of water as a solvent; at the same time, a number of parameters having a substantial impact on the properties of resulting gels remain to provide control over the process.

A general scheme of the sol-gel process using alkoxides is shown in Fig. 1. The first stage of the process includes homogeneous dissolution or heterogeneous dispersion of metal alkoxides in alcohol or another organic solvent. Subsequent coordination stabilization involves oligomerization, solvation with the substitution of alcohol groups, trans-esterification and possible chemical modification of the coordination sphere by ligands that change the reactivity. Stabilization and modification of the precursor solution corresponds to changes in the coordination sphere due to the reactions of ligands promoting changes of functionality and the number of hydrolyzed alkoxy groups, as well as the reactivity of the complex. Therefore, the nature of precursor solution has a substantial effect on the rates of hydrolysis and condensation.

In the present work we used aluminium isopropoxide as the initial alkoxide. Isopropanol was used as a solvent. Aerogel obtained after supercritical drying of this gel (Al-12) possessed high specific surface – about 1000 m²/g (Table 1). This value is much higher than the specific surface of Al₂O₃ samples used as cata-

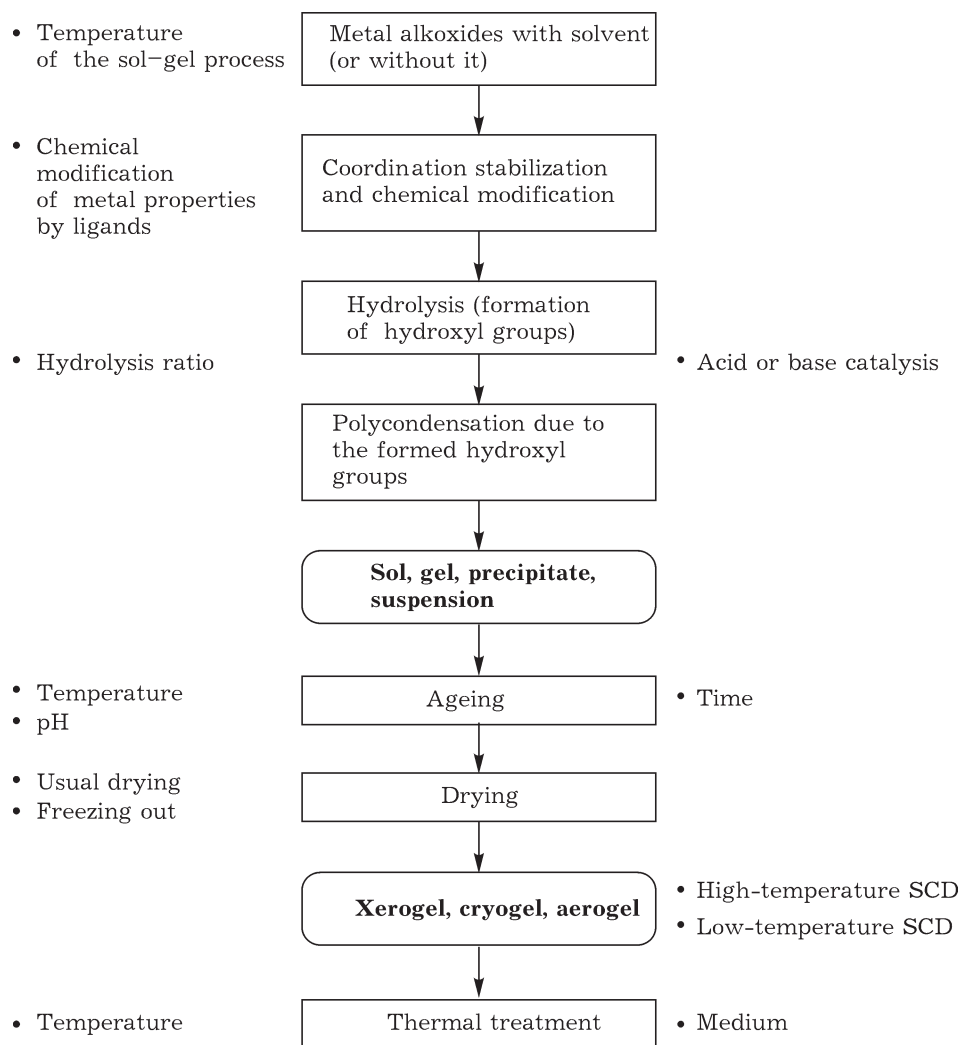


Fig. 1. General scheme of the sol-gel process based on metal alkoxides.

lyst supports, which is usually about 200–300 m²/g after baking. In our case, after baking at a temperature of 500 °C, the specific surface of this sample exceeded 600 m²/g.

Investigation of aerogel samples by means of X-ray diffraction, both directly after drying in autoclave and after baking at a temperature of 500–600 °C, did not reveal the presence of any crystal phases. Only after baking at a temperature of 700 °C we observed the appearance of nanoparticles of γ -Al₂O₃ in the case of non-modified aerogel. It is likely that below this temperature the samples are in disordered X-ray amorphous state. Investigation by means of thermogravimetry revealed substantial mass loss (mainly water) within temperature range 250–350 °C, which is connect-

ed with dehydration of aerogel nanoparticles. For this reason, the material obtained directly after drying in autoclave will be called hydrated aluminium oxide, while the material after calcination will be called aluminium oxide, in spite of the absence of definite crystal phases.

We studied the effect if different additives on the properties of resulting Al₂O₃ aerogel samples. Substitution of isopropanol by ethanol caused some increase in specific surface of aerogel obtained either with individual solvent or with a mixture of alcohol with toluene (see Table 1, samples Al-11 and Al-22, Al-12 and Al-24). After that, we used ethanol as the solvent.

It was shown previously that the addition of toluene or another aromatic solvent causes a substantial (by a factor of 2–2.5) increase in

TABLE 1

Effect of synthesis conditions of texture properties of the aerogel of hydrated aluminium oxide

Samples	Solvent/modifying agent	S_{sp} , m ² /g	Pore volume, cm ³ /g
Al-11	Isopropanol/toluene	1180	1.89
Al-22	Ethanol/toluene	1290	1.99
Al-12	Isopropanol	980	0.88
Al-24	Ethanol	1000	4.46
Al-25	Ethanol/0.5 mol MAA/mol Al	1090	2.80
Al-28	Ethanol/1.0 mol MAA/mol Al	1040	1.75
Al-27	Ethanol/1.5 mol MAA/mol Al	990	1.08
Al-S51	Ethanol/15 mass % H ₂ SO ₄	1050	1.58

Note. MAA is methacryloxy acetylacetone.

the specific surface of aerogel of magnesium hydroxide [4]. In the case of aerogel of hydrated aluminium oxide, the addition of toluene to the alcohol also had a positive effect on the specific surface of aerogel but the effect was noticeably lower: only about 15–20 % (see Table 1, samples Al-11 and Al-12, Al-22 and Al-24). In general, higher specific surface value (about 1200 m²/g) exceeding typical specific surface of the samples of aluminium oxide/hydroxide by a factor of 4–5, was achieved for aerogel of hydrated aluminium oxide prepared using a mixture of ethanol and toluene at a ratio of 1 : 3. Most probably, an increase in specific surface of aerogel in the case when toluene was used is connected with substantially higher solubility of aluminium isopropoxide in the mixture of alcohol and toluene.

MODIFICATION OF Al₂O₃ AEROGEL

Reagents used to modify metal alkoxides in sol-gel processes can play a dual part. They are often used to vary the rates of reactions thus determining the degree of homogeneity and microstructure of resulting gel samples. In this case, modifying agents are completely removed during subsequent calcination, which leads to the synthesis of the corresponding oxides. However, the same reagents can be used to obtain materials containing functional groups or another phase. Thus, they can find application for the synthesis of oxide nanoparticles with carbon coating on the surface. An advantage of this approach is that organic groups are already present on the surface of oxide nanoparticles,

and their comparatively uniform distribution can promote a larger number of nuclei during pyrolysis and therefore the formation of very small carbon nanoparticles.

To prepare aerogel of aluminium oxide with carbon coating, in the present work we used various organic modifying agents, such as acetylacetone, resorcin, methacryloxy acetylacetone (MAA) *etc.* As example, let us consider the effect of MAA on the texture properties of aerogel samples. This modifying agent has a β -diketonate group that provides reliable binding with the surface of oxide nanoparticles, which is able to be conserved after hydrolysis and drying in autoclave. In addition, this reagent possesses a double bond which is able to enter polymerization; it is also characterized by larger number of carbon atoms in comparison with acetylacetone. Adding MAA in the amount not more than 1.5 mol/mol Al(*i*-OC₃H₇) we succeeded in preparing aerogels of hydrated aluminium oxide containing substantial number of organic groups on the surface with the conservation of the high specific surface (see Table 1).

After activation in vacuum at a temperature of 500 °C, the specific surface of Al₂O₃ aerogel samples containing no modifying agents was 600–700 m²/g. In general, the higher is specific surface of initial hydrated aerogel samples, the higher is the specific surface of calcined samples. A drop of specific surface during activation turned out to be lower than in the case of MgO, where the specific surface decreased by a factor of 2–2.5 [4], or ZrO₂, the specific surface of which decreased by a factor of 4–5 [6]. According to the data of elec-

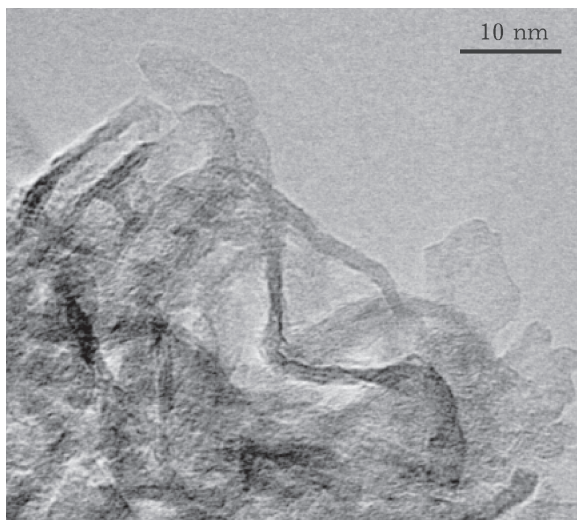


Fig. 2. High-resolution electron microscopic image of aluminium oxide aerogel.

tron microscopy (Fig. 2), calcined aluminium oxide aerogel samples are composed of thin rounded plates about 2 nm thick and about 10 nm in diameter.

Aerogel of sulphated aluminium oxide was synthesized using a similar procedure, with sulphuric acid as a modifying agent. Previously this approach was used to synthesize aerogel of sulphated zirconium oxide exhibiting activity in the reaction of butane isomerisation [6]. It turned out that the addition of sulphuric acid before the hydrolysis of aluminium isopropoxide causes a substantial decrease in the pore volume in aerogel, while specific surface changes only insignificantly. After calcination at a temperature of 600 °C, which is necessary for active acid centres to be formed, the specific surface of sulphated aluminium oxide samples with initial sulphate content 15–30 % is about 600 m²/g. According to our data, this value is 2–3 times higher than the known literature data for the specific surface of sulphated Al₂O₃ catalysts.

DEHYDROCHLORINATION OF 1-CHLOROBUTANE ON AEROGEL Al₂O₃ AND C/Al₂O₃

The catalytic properties of synthesized aerogel were studied in dehydrochlorination of 1-chlorobutane. The progress of this reaction was previously studied in detail on MgO [8] and C/MgO aerogel [4]. It was demonstrated for magnesium oxide that the reactions starts from

the temperature of about 350 °C and accelerates noticeably while magnesium oxide is transformed into chloride, in spite of its not very high specific surface [8]. In this situation, the high specific surface and small particle size of MgO aerogel promoted a substantial acceleration of the process in comparison with materials prepared using traditional methods.

Investigation of the regularities of dehydrochlorination of 1-chlorobutane on aluminium oxide aerogel showed that the process runs at much lower temperatures than in the case of MgO aerogel. The reaction proceeds rather efficiently even at a temperature of 250 °C, when on magnesium oxide the reaction is practically not observed yet (Fig. 3). The high selectivity with respect to butanes is conserved (98 %). Unlike for magnesium oxide, the reactivity of carbonized aluminium oxide turned out to be somewhat lower than the reactivity of pure aluminium oxide. This is connected mainly with somewhat lower specific surface. Nevertheless, also in this system the introduction of porous carbon coating did not prevent dehydrochlorination, and the oxide surface turned out to be accessible for 1-chlorobutane molecules.

It is likely that substantially higher activity of aluminium oxide aerogel is due to a successful combination of high acidity and high specific surface. We did not observe the appearance of other crystal phases after the reaction. The presence of sufficiently strong acid centres on the surface of aluminium oxide is reliably registered using the physical methods. It

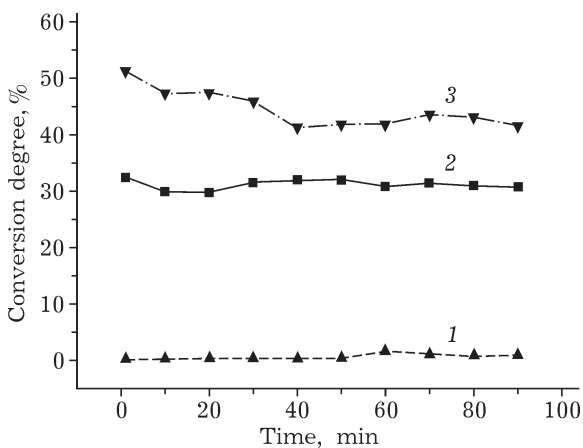


Fig. 3. Degree of 1-chlorobutane conversion on aerogel samples: MgO (1), Al₂O₃ (2) and SO₄²⁻/Al₂O₃ (3) at a temperature of 250 °C.

is evident that dehydrochlorination proceeds much more efficiently on the catalysts possessing acid centres (Al_2O_3 , MgCl_2) than on magnesium oxide which contains mainly basic centres. Even higher activity was observed on aerogel of sulphated aluminium oxide possessing superacid properties (see Fig. 3).

DESTRUCTIVE SORPTION OF CF_2Cl_2 ON VO_x/MgO AEROGEL

The application of aerogel synthesis procedure allows us to achieve the uniform distribution of vanadium in the structure of MgO with in a broad range of V/MgO ratios. The synthesized samples of aerogel hydroxides $\text{VMg}(\text{OH})_x$, similarly to the previous case, are characterized by very high specific surface (about $1200 \text{ m}^2/\text{g}$). After dehydration of hydroxides, the aerogel oxide system VO_x/MgO was obtained in the form of cubic small crystals about 5 nm in size (Fig. 4).

A characteristic feature of the behaviour of oxide nanocrystals in the reaction with Freon-12 is the presence of a clearly exhibited induction period (Fig. 5), which was discovered for the first time for aerogel MgO [13]. As a result of the interaction with CF_2Cl_2 , magnesium oxide is transformed into MgF_2 , therewith an increase in sample mass is observed. As follows from the data shown in Fig. 5, the introduction of 2% vanadium into the structure of MgO aerogel causes a substantial decrease in the induction

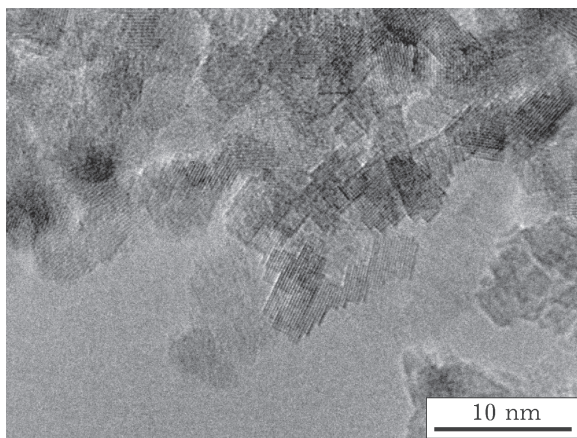


Fig. 4. Structure of aerogel 10% VO_x/MgO according to the data of high-resolution transmission electron microscopy.

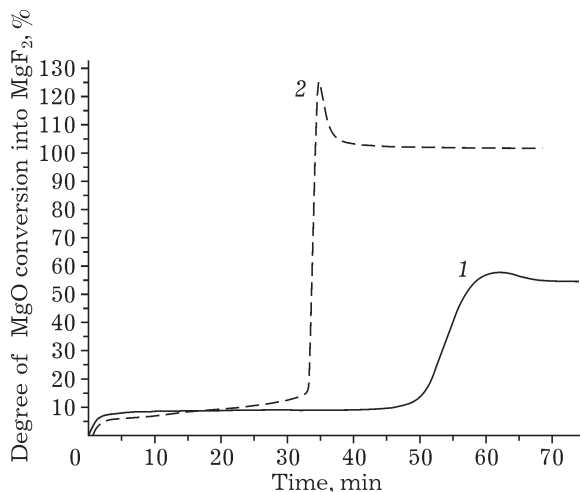


Fig. 5. Effect of vanadium additive on the kinetics of interaction of aerogel magnesium oxide with Freon-12 (CF_2Cl_2) at 340°C : 1 – MgO aerogel, 2 – 2% VO_x/MgO aerogel.

period of the reaction, and also leads to an increase in the degree of MgO transformation by a factor of 1.5. After the induction period is over, the reaction proceeds very rapidly, then a small decrease in the mass of vanadium-magnesium aerogel is observed (see Fig. 5, curve 2). The observed jump in the region of the maximum can be explained by the fact that volatile oxy- and chloro oxy compounds of vanadium are formed, which is confirmed by the data of chemical analysis.

As one can see in Table 2, with a decrease in interaction temperature we observe a substantial increase in the duration of induction period. With further decrease in temperature it becomes impossible to distinguish induction period strictly, the mass of the weighed portion increases gradually, and the curve of mass accumulation acquires S-like appearance which is characteristic of many topochemical reactions. For MgO aerogel, this transition is observed even at 325°C [14], while for the sample with low vanadium content (2 mass % for V_2O_5) at 300°C . With further increase in vanadium concentration in aerogel sample VO_x/MgO , the induction period of the reaction almost disappears (see Table 2).

The authors of [15] put forward a hypothesis for destructive sorption of CCl_4 concerning the promoting action of vanadium: CCl_4 is attached by VO_x group forming VCl_x and CO_2 .

TABLE 2

Effect of vanadium concentration on the duration of induction period in the reaction of aerogel VO_x/MgO oxides with CF₂Cl₂

Mass concentration of vanadium in VO _x /MgO sample, % (for V ₂ O ₅)	Temperature, °C	Duration of induction period, min
0	325	Not revealed
0	340	~180
0	350	15
2	300	Not revealed
2	320	~100
2	340	35
2	350	11
10	350	2
15	350	0.8
25	350	0.5

Then VCl₂ exchanges Cl⁻/O²⁻ getting reduced back to VO_x in MgO nanocrystals. Thus, vanadium oxide acts as a mediator in solid-phase ion exchange passing at the same time Cl⁻ ions to magnesium oxide and O²⁻ ions to CCl₄, which results in the formation of carbon dioxide. The key fact in the explanation of this effect is that VX_n particles (X = O²⁻, Cl⁻) are mobile and allow rapid transfer of electrons in the course of catalytic process.

So, modification of aerogel magnesium oxide by vanadium allows one to enhance the reactivity of MgO in the reactions of destructive sorption. Vanadium distributed uniformly in the structure of magnesium oxide causes a substantial acceleration of the reaction with Freon, and also promotes an increase in the degree of transformation of magnesium oxide almost to 100 %.

CONCLUSION

The possibility of efficient control of texture parameters of aluminium oxide aerogel by choosing solvent and modifying agents was demonstrated. Aerogel of aluminium oxide containing a porous carbon coating on the surface of nanoparticles was prepared by adding modifying agents containing voluminous organic groups, before gel formation, followed by calcination in vacuum. The highest value of the specific surface of hydrated aluminium oxide

aerogel (about 1200 m²/g) exceeding typical values of specific surface for aluminium oxide/hydroxide samples by a factor of 4–5 was obtained for the sample prepared using a mixture of ethanol and toluene at a ratio of 1 : 3. Typical size of aluminium oxide particles after calcination at a temperature of 500–600 °C was several nanometres. It was shown that aerogel of Al₂O₃ and sulphated Al₂O₃ exhibit high activity in dehydrochlorination of 1-chlorobutane. The reaction starts at a temperature lower by approximately 100 °C than that for the case of magnesium oxide aerogel, while high selectivity to butanes (more than 98 %) is conserved.

The aerogel procedure demonstrated its efficiency in the synthesis of nanocrystalline VO_x/MgO systems in which vanadium is uniformly distributed in the structure of magnesium oxide. The introduction of even a small amount of vanadium causes a substantial acceleration of the reaction and promotes an increase in the degree of conversion of magnesium oxide into MgF₂. It was shown that doping of aerogel MgO with vanadium causes a substantial acceleration of the solid-phase exchange between O²⁻ and Cl⁻ ions.

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