

# SYNTHESIS AND PHYSICOCHEMICAL PROPERTIES OF SILICA GELS WITH SMALL ADDITIVES OF ALUMINIUM AND ZIRCONIUM IONS

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## **Abstract**

The method of synthesis of silica gels containing small additives of Al and Zr ions was developed. The porous structure of the synthesized Al,Zr-silica gels has been characterized by the adsorption method. It was found that simultaneous modification of silica gels by aluminium and zirconium ions lead to the formation of micro- and ultramicroporous samples in neutral media of precipitation. The parameters of porous structure of Al,Zr-silica gels are considerably dependent on the modified ions contents. A supposition was made that the formation of porous structure was caused by mutual stabilizing effect of Al and Zr additives on silica gel globules growth at sol-gel stages of synthesis. The nature of surface active sites of the modified silica gels was studied by the diffuse-reflectance IR-spectroscopy with the use of adsorption of deuterioacetonitrile.

## **Introduction**

At present development of the methods for synthesis of new type of adsorbents, catalysts and supports with properties of strong acids and special characteristics of their porous structure is urgent problem. It is known that for many catalytic processes the systems with microporous and ultramicroporous structure are more efficient because of the effect of shape selectivity [1]. In this connection the investigations directed toward the preparation of new micro-, meso- and ultramicroporous materials, exhibiting molecular-sieve selectivity and strong acid surface sites, on the basis of relatively cheap silica gels are of considerable interest. At present, there are only separate data concerning synthesis and study of ultramicroporous silica gels in the scientific literature [2, 3]. The synthesis of such samples may be carried out under conditions of minimum rate of polycondensation (acidic media of gel precipitation and washing), considerable capillary forces (low drying temperature), a stabilizing effect of zirconium ions over a globule sizes. It was earlier shown [4-6] that addition of the small amounts of Al, Ti or Zr ions (up to 5-6 wt.% of oxide) to silica gels at the sol-formation stage would result in increasing of their specific surface area, reducing in pore volume and diameter, and the formation of supermicroporous silica gels in neutral medium of precipitation. This phenomenon can be explained by a stabilizing effect of the above-mentioned ions on the silica gel globules growth at sol-gel stages of the synthesis. It was established that dehydroxylation of the silica gels modified by the Al and Zr ions lead to formation of Lewis acidic sites on their surface [7]. Small additives of these ions were found to improve considerably the silica gel

stability under hydrothermal conditions [8-10]. Thus, the silica gels modification with small additives of one of the mentioned ions can considerably vary both porous structure and nature of the surface active sites. The investigation of the mutual influence of ions of two or several metals on the texture and surface structure of silica gel is of great interest and will result in the development of new materials with unusual combination of molecular-sieve and acid-base properties.

The aim of this work is to elaborate the methods of synthesis of new modified silica gels containing Al and Zr ions simultaneously and investigation of their porous structure and nature of surface active sites.

## Experimental

Al, Zr-silica gels were prepared by the method similar to that described in the works [4, 5]. Sodium silicate, sulfuric acid, aluminium sulfate, and zirconium oxochloride were used as starting reagents. Sols were carried out by interaction of the numbered solutions at pH=7. After setting and syneresis the gels were cut, washed out by distilled water up to absence in washing water of  $\text{SO}_4^{2-}$  ions (test on  $\text{BaCl}_2$ ). The washed gels were dried at 373K or ambient temperature. Samples of one series had the approximately identical content of Al ions and differed in the content of Zr ions. The specific surface areas of the obtained samples were determined from the adsorption isotherms of methanol vapours by the BET method. Volume of sorption pores was designed on amount of adsorption at  $P/P_s = 0.92$ . The investigations of surface active sites of the synthesized silica gels were carried out by diffuse reflectance infrared spectroscopy [7]. Deuterated acetonitrile  $\text{CD}_3\text{CN}$  was used as a test for Lewis acidic sites.

## Results and discussion

Chemical composition and the parameters of the porous structure of obtained samples are given in Table 1. Data presented in this Table show that all samples of series I contain approximately 2.3 wt. %  $\text{Al}_2\text{O}_3$ . Increasing the zirconium ion content in these samples to 6.2 wt. %  $\text{ZrO}_2$  leads to increasing in specific surface area ( $S$ ). Further increasing  $\text{ZrO}_2$  content up to 7.76 wt. % will result in reducing  $S$ . In both cases the pore volume has been gradually decreased. The growth of the zirconium ion content in silica gel samples is accompanied by the following changes in isotherms of adsorption of methanol vapour: at low relative pressures it results in an increase in adsorption values; at high relative pressures the adsorption values decrease; and the hysteresis loop characteristic of the capillary condensation disappears (Fig. 1). Similar regularities were previously observed at Al or Zr ions inclusion into silica gels.

The increase of zirconium ions content in Al,Zr-silica gels containing near 3.5 and 4.7 wt. %  $\text{Al}_2\text{O}_3$  (II and III series of samples, respectively) makes less effect on the parameters of porous structure - specific surface area remains practically constant or slightly reduced and the pore volume tends to diminishing (Table 1). Increase in zirconium ion concentration Al,Zr-silica gels, contained approximately 5.7 wt.% of  $\text{Al}_2\text{O}_3$  (IV series of samples), resulted in reducing of both specific surface area and pore volume (Table 1). The adsorption isotherms of methanol vapour measured for samples of series II-IV are of the 1st type, which is typical for microporous adsorbents [11].

It is known that silica gel represents a porous solid consisting from globules of SiO<sub>2</sub> [12, 13]. The formation and growth of silica gel globules proceed through the reaction of polycondensation of silicic acid, the aggregation of globules formed, and the dissolution-precipitation of silica. The globules finite size and density of their packing depend on the synthesis conditions and define the specific surface area and pore volume of the samples obtained.

The small amounts of Al or Zr ions added into silica gels at the sol-formation stage have a stabilizing effect on the SiO<sub>2</sub> globules sizes, i.e. the presence of these ions during synthesis delays growth of SiO<sub>2</sub> globules [4, 5]. According to [4, 5], the stabilizing effect of Al or Zr ions on the size of SiO<sub>2</sub> globules is due to the following factors: a decreased solubility of SiO<sub>2</sub> in the presence of Al or Zr ions, the isomorphous replacement of silicon ions in the SiO<sub>2</sub> matrix by aluminium ions, and an increase in the hydrophilicity of SiO<sub>2</sub> surface. For silica gels of a series I stabilizing influence of Al ions on the globules probably is not enough for obtaining of samples with the smallest globule sizes. The introduction of zirconium ions into samples of this series renders additional stabilizing influence on the globules SiO<sub>2</sub> that is accompanied by diminution of their sizes and is displayed in increasing of specific surface area.

**Table 1.** Chemical composition and parameters of porous structure of Al, Zr-silica gels\*

Series and sample number	Content, wt. %		S, m <sup>2</sup> /g	V <sub>s</sub> , cm <sup>3</sup> /g
	Al <sub>2</sub> O <sub>3</sub>	ZrO <sub>2</sub>		
I-1	2.24	-	510	0.49
I-2	2.24	1.13	540	0.47
I-3	2.24	2.20	645	0.41
I-4	2.49	3.85	660	0.35
I-5	2.50	6.20	690	0.34
I-6	2.64	7.76	630	0.30
II-1	3.21	-	730	0.37
II-2	3.61	1.04	710	0.33
II-3	3.53	2.05	710	0.33
II-4	3.53	4.10	710	0.29
III-1	4.71	-	790	0.33
III-2	4.71	2.00	730	0.28
III-3	4.72	4.00	620	0.28
IV-1	5.97	-	650	0.28
IV-2	5.76	1.13	640	0.27
IV-3	5.90	4.24	540	0.22
IV-4	5.63	5.64	490	0.22
IV-5	5.48	8.42	520	0.24

\*Samples of series I were prepared by drying of the washed gels at 373K and samples of series II-IV – by drying at 293K.

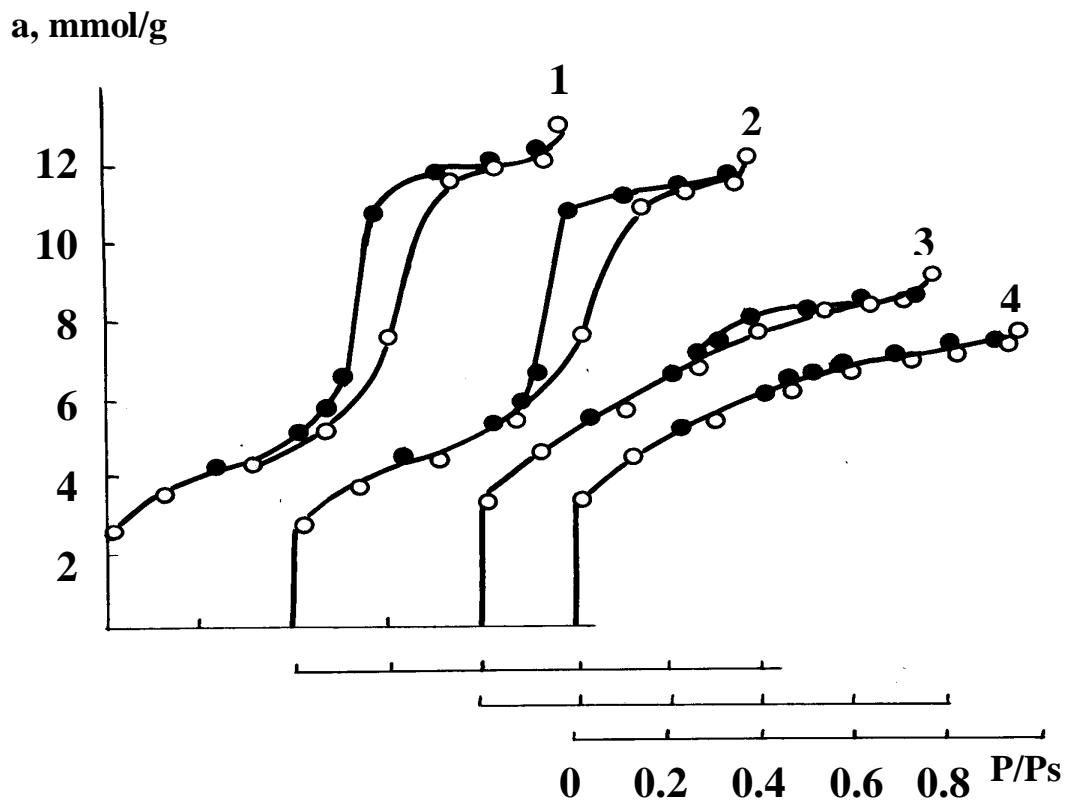
SiO<sub>2</sub> globules, which are smaller on their sizes, are packed more densely at drying that results in diminution of volume of sorption pores (Table 1). The diminution of specific surface area of the sample I-6 can be caused by formation of a part of very fine pores inaccessible for

adsorption of methanol molecules, or by formation of small quantity of a separate phase of zirconium dioxide [7].

For silica gels of series II and III, distinguished by the major content of Al ions, the stabilizing influence of the latter on the globules  $\text{SiO}_2$  is also more that results in preparation of materials with higher specific surface area (samples II-1 and III-1, Table 1). Probably, that is why the influence of Zr ions on the globules of  $\text{SiO}_2$  and parameters of the porous structure of samples of these series is lesser displayed. The silica gels of a series IV contain the greatest quantity of Al ions (Table 1). It results in formation during synthesis fineporous structures, which are accessible only partially for adsorption of methanol vapours. The introduction of Zr ions in these adsorbents results in diminution of specific surface area and volume of pores. The reason of this can be an arrangement of Zr ions on a surface of  $\text{SiO}_2$  globules. It is known that the zirconium ions injected into silica gel at a stage of precipitation are displaced mainly on a surface of  $\text{SiO}_2$  globules [7]. Probably, in Al,Zr-silica gels the Zr ions are also displaced on a surface of globules, blocking thus inlets into the narrowest pores and creating steric hindrances for adsorption of molecules. Thus, in some samples the ultramicropores, which are inaccessible for adsorption of large molecules, can be formed. In order to check such assumption, the adsorption isotherms of carbon tetrachloride vapours were measured on the separate samples. It follows from the data of Table 2 that the porous structure of all samples studied differs in their access for methanol molecules (molecules diameter of 0.34 nm) and to carbon tetrachloride (0.69 nm), i.e. the molecular-sieve selectivity in relation to these adsorbates take place for these adsorbents. However, the molecular-sieve selectivity is the most evidently displayed in the case of samples comprising the greatest amount of Al ions (Fig. 2). For these samples an adsorption of  $\text{CCl}_4$  vapours was not practically observed, i.e. their pores diameter was less than 0.69 nm.

Thus, the simultaneous introduction of the small additives of Al and Zr ions into silica gels leads to the formation of micro- and ultramicroporous samples in a neutral precipitation medium, which is peculiar for the formation of mesoporous samples. It is known that even the smallest inclusions of metal ions can considerably improve adsorptive properties of silica gels and in some cases impart acidic character and catalytic activity to their surfaces. At the same time the attempts to separate acidic OH groups in the samples containing even great amounts of metals were failed [14, 15].

It may be explained by low concentration of acidic OH-groups and by difficulty of their separating against a background of the strong absorption of the terminal  $\equiv\text{SiOH}$  groups. In this work we have attempted to study the Lewis acidic sites of the prepared adsorbents using diffuse-reflectance IR-spectroscopy [16]. Molecules of deuterated acetonitrile were used to test acidic sites. The first series of samples having approximately the same content aluminium ions and differing by zirconium ions content and reference specimen with only aluminium were chosen for the study. Two absorption bands with maxima 2324 and 2270  $\text{cm}^{-1}$  were observed in IR-spectrum of the reference sample (Fig. 3). Evacuation at ambient temperature resulted in a reducing of 2270  $\text{cm}^{-1}$  band intensity and at 373K – to its disappearance in this sample. At the same time the band 2324  $\text{cm}^{-1}$  becomes more intensive and shifts towards high frequencies range.

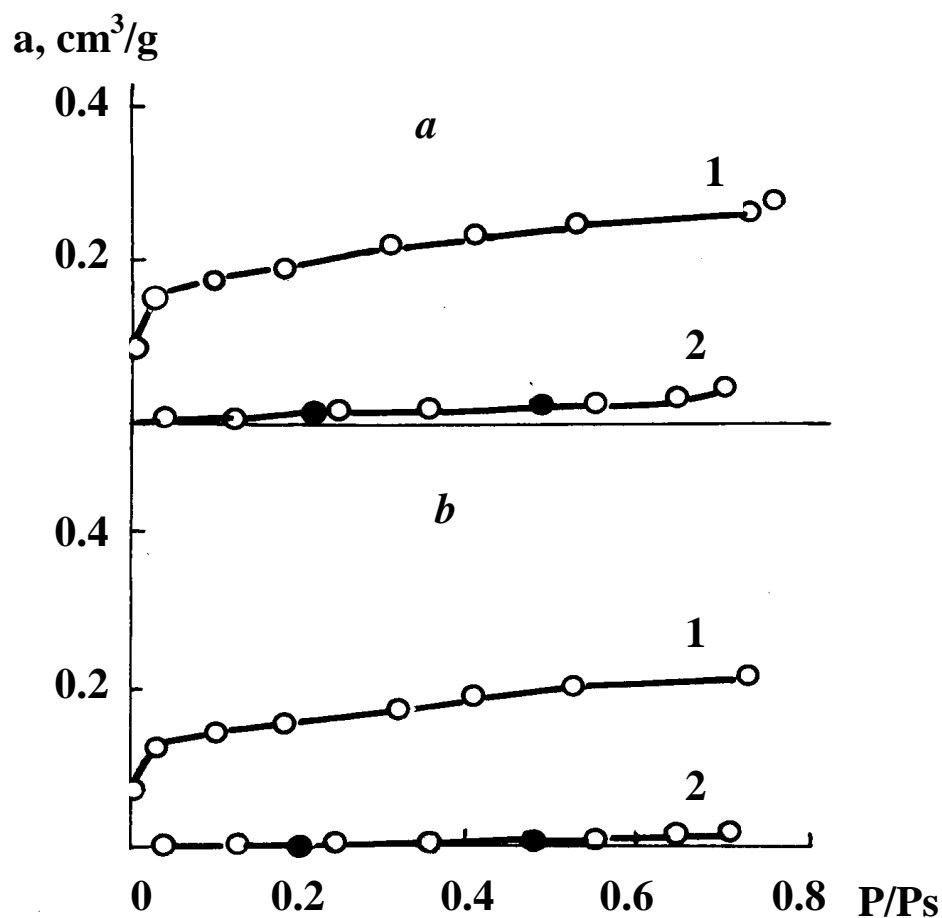


**Fig. 1.** The adsorption isotherms of methanol vapours on Al,Zr-silica gels of series I containing 0 (1), 1.13 (2), 3.85 (3), and 7.76 (4) wt. % ZrO<sub>2</sub>.

**Table 2.** Values of methanol and carbon tetrachloride adsorption by Al,Zr-silica gels\*

Series and sample number	Content, wt. %		CH <sub>3</sub> OH, cm <sup>3</sup> /g	CCl <sub>4</sub> , cm <sup>3</sup> /g
	Al <sub>2</sub> O <sub>3</sub>	ZrO <sub>2</sub>		
II-1	3.21	-	0.33	0.24
II-2	3.61	1.04	0.28	0.20
II-3	3.53	2.05	0.28	0.20
II-4	3.53	4.10	0.26	0.11
IV-1	5.97	-	0.25	0.02
IV-2	5.76	1.13	0.24	0.02
IV-3	5.90	4.24	0.21	0.01
IV-4	5.63	5.64	0.18	0.01
IV-5	5.48	8.42	0.19	0.04

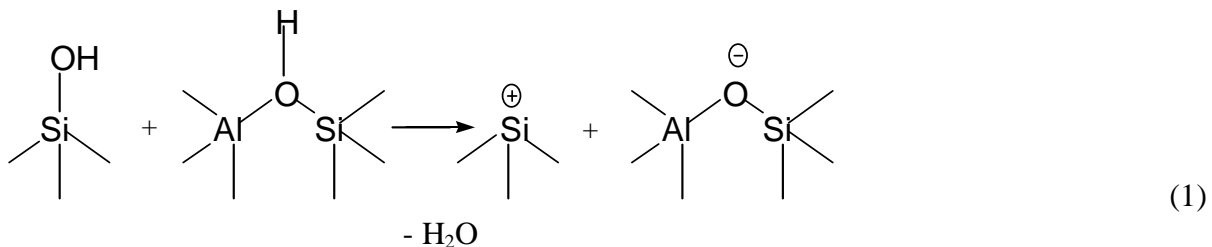
\*Calculated from the isotherms of adsorption at P/P<sub>s</sub>=0.5.

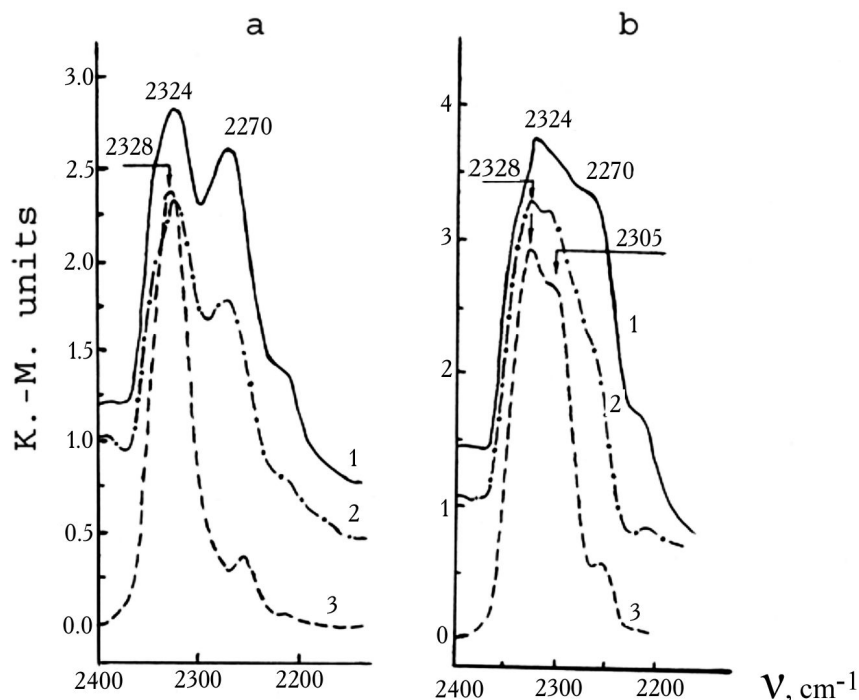


**Fig. 2.** The adsorption isotherms of methanol (1) and carbon tetrachloride (2) vapours on Al,Zr-silica gels of the series IV, containing 0 (a) and 4.24 (b) wt. % ZrO<sub>2</sub>.

As it was reported in the previous work [7], there are two types of active sites on the dehydroxylated at 623K Al-silica gel surface - terminal  $\equiv\text{SiOH}$  groups and three-coordinated silicon ions. As it was shown in that work, an introduction of small additives of Al ions into a skeleton of silica gel proceed through  $\text{Si}^{4+}$  ions isomorphous replacement for  $\text{Al}^{3+}$  and  $\text{Si}(\text{OH})\text{Al}$  acid bridging groups are present on the surface.

In line with the assumption [7], dehydroxylation of silica gels, comprising aluminium ions additives, is performed owing to the removal of a proton of bridging  $\text{Si}(\text{OH})\text{Al}$  group and hydroxyl of the neighbouring terminal  $\equiv\text{SiOH}$  group:





**Fig. 3.** IR-spectra of deuterated acetonitrile on Al,Zr-silica gels of series I containing 0 (a) and 1.13 (b) wt. %  $ZrO_2$  after adsorption (1) and subsequent evacuating at 293K (2) and 393K (3). Samples were previously outgassed at 623K.

One can suppose that the band  $2270\text{ cm}^{-1}$  in IR-spectra (Fig. 3) appertains to molecules of  $CD_3CN$ , physically adsorbed onto terminal  $\equiv SiOH$  surface group. Evacuation of this sample at the ambient temperature and at 373K leads to removal of  $CD_3CN$  molecules from these groups. Other absorption band with the maximum  $2328\text{ cm}^{-1}$  is evidently related with  $CD_3CN$  molecules, retained on the surface Lewis acidic sites - three-coordinated silicon ions.

Inclusion of small amounts of zirconium ions (1.13-3.85 wt. % of  $ZrO_2$ ), equally with aluminium ions, results in changes in IR-spectra. In IR-spectra of the sample with adsorbed deuterated acetonitrile, recorded after degassing at 293 and 393K, along with  $2328\text{ cm}^{-1}$  absorption band a new band at  $2305\text{ cm}^{-1}$  appears. The first band is related to  $CD_3CN$  molecules, interacting with three-coordinated silicon ions, whose formation is evidently proceeding by the same mechanism (1) as for the silica gels with the additives of aluminium ions. Based on these facts, one can assume the similar (like in Al-silica gels) route of isomorphic replacement of  $Al^{3+}$  for  $Si^{4+}$  in Al,Zr-silica gels and the bridging acidic  $Si(OH)Al$  groups are present on the surface of non-dehydroxylated samples. The second band ( $2305\text{ cm}^{-1}$ ) is probably attributed to new Lewis acidic sites - coordinatively-unsaturated zirconium ions [17]. These sites in Al,Zr-silica gels were evidently formed while removing molecules of water from the interior coordination sphere of octahedrally-coordinated zirconium ions:



The mechanism of the Lewis acidic sites formation was earlier proposed for silica gels with the additives of zirconium ions [7].

Thus, dehydroxylation of Al,Zr-silica gels containing 1.13-3.85 wt. % of ZrO<sub>2</sub> is carried out by two mechanisms (1) and (2) simultaneously and lead to the formation on a surface of two types of the Lewis acid sites.

## Conclusions

The obtained in this work experimental data demonstrate that simultaneous modification of silica gel by Al and Zr ions at sol-formation stage of synthesis leads to the preparation of micro- and ultramicroporous adsorbents in a neutral precipitation medium. It is evidently can be attributed to the mutual stabilizing effect of Al and Zr ions on SiO<sub>2</sub> globules growth. Upon Al,Zr-silica gels synthesis the min-sized globules were formed which were closely packed at drying. Dehydroxylation of the prepared Al,Zr-silica gels leads to the formation on the surface of the Lewis acidic sites of two types - coordination-unsaturated ions of Si and Zr. On the analogy with previously derived Al- and Zr-containing samples, one can suppose that in the synthesized Al,Zr-silica gels Al ions are included in SiO<sub>2</sub> structure via isomorphic substitution of Al<sup>3+</sup> for Si<sup>4+</sup> but Zr ions are arranged on globule surface.

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## References

1. Houzvicka J., Hansildaar S., and Ponec V. The shape selectivity in the skeletal isomerization of *n*-butene to isobutene // J. Catal. - 1997. - V.167, N1. - P.273-278.
2. Struzhko V.L., Bondar` L.A., Shamrikov V.M., Slinyakova I.B., and Neimark I.E. Synthesis of silica gels with molecular-sieve properties // Adsorbtsiya i Adsorbenty - 1981. - N9. - P.32-34.
3. Kosenko E.I., Struzhko V.L., Shamrikov V.M., and Malkiman V.I. Influence of conditions of sol formation silicic acid on obtaining silica gels with molecular-sieve properties // Zhurn. Prikl. Khimii. - 1992. - V.65, N2. - P.311-315.
4. Bondar L.A., Struzhko V.L., and Neimark I.E. Geometrical modification of silica gels by small addition of aluminium hydroxides // Kolloidn. Zhurn. - 1984. - V.46, N5. - P.1009-1011.
5. Bondar L.A., Struzhko V.L., Neimark I. E. Malkiman V.I., and Shamrikov V.M. Modification of silica gels by additives of zirconium hydroxides // Ukr. Khim. Zhurn. - 1985. - V.51. N8. - P.814-817.
6. Bondar L.A., Kustov L.M., Beletskii I.P., Stakheev A.Yu., Chuiko A.A., and Kazanskii V.B. Modification of silica gels by small additives of titanium ions // Izv. Akad. Nauk SSSR. Ser. Khim. - 1991. - N10. P.2217-2222.



7. Kustov L.M., Bondar L.A., Borovkov V.Yu., Neimark I.E., and Kazanskii V.B. The state of zirconium and aluminium ions on the surfaces of silica gels modified by small additives of  $\text{Al}_2\text{O}_3$  and  $\text{ZrO}_2$ : IR-spectroscopy in diffuse-reflected light // *Kinetika i Kataliz.* - 1986. – V.27, N6. - P.1392-1397.
8. Bondar L.A. Changes in the texture of ultramicroporous Zr-silica gels under hydrothermal treatment // *Teor. i Eksperim. Khimiya* - 1995. – V.31, N4. - P.259-263.
9. Bondar L.A. and Chuiko A.A. The hydrothermal modification of silica gels, containing small additives of  $\text{TiO}_2$  // *Ukr. Khim. Zhurn.* - 1995. – V.61, N4. - P.12-14.
10. Bondar L.A., Neimark I.E., Malkiman V.I., and Shamrikov V.M. Hydrothermal modification of silica gels, containing small additives of  $\text{Al}_2\text{O}_3$  and  $\text{ZrO}_2$  // *Ukr. Khim. Zhurn.* -1986. – V.52, N2. - P.155-158.
11. Gregg S.J. and Sing K.S.W. Adsorption, Surface Area and Porosity. New York: Academic Press. 1982.
12. Iler R. Chemistry of silica. New York: Wiley. 1979.
13. Neimark I.E. and Sheinfain R.Yu. Silica gels: Preparation, Properties and Application. – Kiev: Naukova Dumka, 1973 (in Russian).
14. Kiselev A.V. and Lygin V. I. Infrared Spectra of Surface Compounds and Adsorbed Substances. Moscow: Nauka, 1972 (in Russian).
15. D`yakonov S.S., Lygin V.I., Shalumov B.Z., Khlopova Z.G., and Shimicheva N.A. Investigation by infrared spectroscopy method of the dehydroxylation of silica alloyed by aluminium oxide // *Kolloid. Zhurn.* - 1985. – V.47, N1. - P.146-149.
16. Kazansky V.B. IR-spectroscopy in diffuse reflectance light and its new possibilities on studying of chemisorbed particles and structure of oxide catalysts // *Izv. Akad. Nauk SSSR. Ser. Khim.* - 1984. – N1. - P.40-51.
17. Paykshtis E.A. and Yurchenko E.N. Application of IR-spectroscopy for investigation of acid-base properties of heterogeneous catalysts // *Uspekhi Khimii.* - 1983. – V.52, N3. - P.426-454.