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BRIEF COMMUNICATIONS

Study of Acidity of the Modified Alumosilicate Sorbents Prepared by the Method of Destructive Epitaxial Precipitation

E. V. Belik, A. V. Brykalov, F. A. Bostanova and E. M. Golovkina

Stavropol' State Agrarian University, Stavropol, Russia

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Abstract—Acid properties of the surface of copper-, cobalt- and iron-containing alumosilicate sorbents prepared by the method of destructive epitaxial precipitation we investigated. Concentration and strength of the proton acid centers of the samples is studied in comparison with the parent natural alumosilicate sorbent based on the opokas of the Prikaspii lowland of Astrakhan' region.

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The directions of development of the modern material science are connected with the elaboration of technology for the preparation of solid state catalysts and effective sorbents [1]. It is known that adsorption properties of solid substances including silicate and alumosilicate sorbents are essentially defined by the acid properties of their surfaces [1, 2]. Mixed oxides, in particular, alumosilicates possess stronger surface acid properties than isolated oxides [2].

It has been shown [3] earlier that silochrom C-120 containing on its surface titanium oxide monolayers prepared by the method of molecular layer deposition possesses stronger acid properties that the parent siliceous carrier.

Now a direction is actively developed connected with the application of sorption purification of water from various sources and applications from toxic compounds like phenols, pesticides, heavy metals and surfactants. Traditionally for this purpose was used active carbon. However, features of their structure restrict their application to the purification of sewages and natural water from the organic compounds present together with the micellar components (surfactants, humus-like substances) [4]. Use of active carbon in the system of industrial water treatment is acceptable economically only at multiple regeneration, which is quite expensive.

The natural alumosilicate sorbents that are cheap enough are promising for the application to the industrial water treatment due to their high absorprion activity toward toxic substances, and they are effective at the water purification from the micellar components [4]. Therefore it is actual to search for effective sorbents providing purification of sewages from the toxicants of different nature.

The proton-donor ability of alumosilicate sorbents prepared by the method of destructive epitaxial precipitation [5] was investigated in this work.

EXPERIMENTAL

The Brønstedt acid centers were studied on the samples of alumosilicates based on the opokas of Prikaspii lowland of the Astrakhan' region with the following chemical composition (wt %): SiO_2 87, Al_2O_3 4.2. These natural sorbents contain inclusions of iron, magnesium and calcium oxides [6]. Specific surface of the alumosilicate sorbents was 730 $m^2 g^{-1}$, pores volume 0.9 $cm^3 g^{-1}$, fraction size 0.2–0.5 mm. The specific surface of the sorbents was measured by the method based on low temperature nitrogen sorption [7], pores volume by the method of mercury intrusion porosimetry [8]. For the chemical modification of the alumosilicate samples surface was used the method of destructive epitaxial precipitation [5].

For the elucidation of the Brønstedt acid centers on the modified composite sorbent was applied

Results of calculations of Brønstedt acid centers concentration and equilibrium constants K_{av} for the sorbents

Sorbent sample weight, g	$[NH_4^{bound}] \times 10^{-3}$, mmol g^{-1}	$[H^+] \times 10^{-3}$, mmol l^{-1}	$[H^{bound}] \times 10^{-3}$, mmol g^{-1}	$[NH_4^+] \times 10^{-3}$, mmol l^{-1}	$B_0 \times 10^{-3}$, mg-equiv mol^{-2}	$K_{av} \times 10^{-5}$
Natural alumosilicate						
0.1030	0.75	1.96	0.13	129.3	0.31	0.15
0.3000	0.20	1.05	1.45	129.8		
0.5020	0.11	1.06	3.0	129.5		
1.0010	0.10	0.72	–	129.5		
Destructive epitaxial precipitation – Cu						
0.1030	0.50	1.05	0.10	129.8	0.2	0.4
0.3020	0.75	1.91	0.10	129.0		
0.5020	1.00	2.00	0.75	129.5		
1.0030	1.25	3.54	–	129.3		
Destructive epitaxial precipitation –Co						
0.1010	0.50	1.05	0.10	129.0	0.2	0.7
0.3030	0.25	1.60	0.75	129.1		
0.5020	0.10	1.05	0.90	129.0		
1.0030	0.10	1.04	–	129.0		
Destructive epitaxial precipitation –Fe						
0.1020	0.88	1.91	0.20		0.38	0.65
0.3020	0.92	1.97	0.78			
0.5030	0.97	2.00	2.63			
1.0010	0.97	2.00				

the method of ion exchange absorption in aqueous solution [2].

A chemical substance serving as a test probe for measuring acid properties was titrated 0.13 M solution of ammonium acetate which enters into ionic exchange with the surface along the scheme:

$$H^{bound} + NH_4^+ \rightleftharpoons H^+ + NH_4^{bound},$$

where H^+ and NH_4^+ are the ions in solutions, H^{bound} and NH_4^{bound} the ions bound by the sorbent surface centers.

For the investigations, a series of weighted 0.1; 0.3; 0.5 and 1.0 g samples of the sorbents were placed to flat bottom 50 ml flasks, and to each was added 25 ml of 0.13 M solution of CH_3COONH_4, each flask was stoppered tightly with a plug and left for 24 h at the temperature 24°C. Then solution over the precipitate was decanted and its pH was measured on a universal ionometer EV-74. Concentration of the Brønsted acid centers B0 was calculated by the formula:

$$B_0 = \frac{c_x 25}{PS},$$

where c_x is concentration of the acetic acid formed in the reaction of ammonium acetate with the sorbent acid centers (mg-equiv ml^{-1}); P is the sample weight (g), S is the sample specific surface ($m^2\ g^{-1}$).

Concentration of acetic acid was measured in correspondence with the procedure in [3] using precalibrated plot of pH of the 25 ml of 0.13 M CH_3COONH_4 solution at the adding aliquot potrions 0.1 to 3.0 ml of 0.1 M CH_3COOH.

As far as the ions H^+ and NH_4^+ in solution are in dynamic equilibrium with the ions H^{bound} and NH_4^{bound} adsorbed on the surface, we calculated the equilibrium constants K_{av} that allow estimation of the relative strength of the acid centers

$$K_{av} = \frac{[H^+][NH_4^{bound}]}{[H^{bound}][NH_4^+]}. \quad (1)$$

In the relation (1) the concentration of $[H^+]$ ions corresponds to the value of the measured pH of the ammonium acetate solution containing a studied sorbent sample; $[H^{bound}]$ is the difference between the total concentration of the acid centers and $[NH_4^{bound}]$; $[NH_4^+]$ is defined as a difference of the concentrations of $[NH_4^+]$ ions in the initial ammonium acetate solution and $[NH_4^{bound}]$, where $[NH_4^{bound}]$ corresponds to the concentration of acetic acid formed after the reaction of ammonium acetate

with the sorbent.

The table contains data on the concentration of acid centers and equilibrium constants K_{av} for the samples of copper-, cobalt- and iron-containing sorbents synthesized by the method of destructive epitaxial precipitation.

The phenol sorption capacity of a sorbent synthesized by destructive epitaxial precipitation in comparison with that of the natural alumosilicate was measured according to the procedure in [9]. For the natural alumosilicate the value obtained equals 10.3 mg g^{-1} while for the metal-containing sorbents epitaxial-Fe, epitaxial-Cu and epitaxial-Co it equals 14.2, 8.5 and 8.7 mg g^{-1}, respectively.

For measuring sorption characteristics we used model aqueous solutions of phenol with the initial concentrations 180 and 250 mg l^{-1}. The equilibrium at the adsorption of phenol by the developed sorbents established after 25 min contact with the toxicant solution. For active carbon KAD under such conditions the equilibrium was attained in 1 h and the specific sorption capacity was equal to 70 mg l^{-1}[4].

The silica surface is known to possess weak proton donor property (pK_a 6–8) [10]. Its isoelectric point corresponds to pH 2–4, and below this point the silica surface is charged positively. At the pH increase to the value from 2 to 6 the negative charges concentration grows slowly. Unlike the silica that possess only amphoteric silanol groups, for the mixed oxides the presence of surface active Brønstedt and Lewis centers [2] is characteristic.

The data in the table show that the synthesis of the element-containing sorbents by the method of destructive epitaxial precipitation gives rise to the control over the properties of the surface centers, in particular, by changing concentration of the Brønstedt acid centers ant their equilibrium constant K_{av}. Introduction to the surface layer of the iron-containing structural units provides considerable increase in the sorbent acid properties as compared with the parent alumosilicate sorbent based on the opokas of the Prikaspii lowland of Astrakhan' region. The decrease in the values characterizing acid properties of the sorbents containing cobalt and copper as compared with the iron-containing sorbent is explainable probably by the decrease in the electronegativity difference of the elements forming the surface functional groups: $\Delta = \lambda_{Si} - \lambda_{Fe} = 1.8 - 1.6 = 0.2$, as compared with $\Delta = \lambda_{Si} - \lambda_{Co} = 1.8 - 1.7 = 0.1$ and $\Delta = \lambda_{Si} - \lambda_{Cu} = 1.8 - 1.8 = 0$.

The larger difference in the electonegativity favors increase in charge shift of the proton-donor groups and increase of the sorbent acidity.

By the experimental investigations it was established that increase in the acidity of the sorbent surface, in particular, of the iron-containing sorbents, promotes increase in the sorbent maximal sorption capacity of phenol, pointing to the acid-base mechanism of the interaction of sorbents with the adsorbate.

At the destructive epitaxial precipitation in the process of the sorbent synthesis a complicated process proceeds of the formation of amorphous-corpuscular structure on account of the condensation processes involving the silica hydroxy groups and precipitation on the surface of iron, copper and cobalt silicates. The increase in the acid properties of the surface of the sorbents samples can be explained by the increase in the concentration of the Brønstedt centers due to the formation of new proton-containing groups that are accessible for the coordination sorption of water involved into the process of ion exchange.

The physico-chemical properties of sorbents are defined by the structure of the reaction centers at their surfaces, concentration and mutual location of the groups of acid and base type, and by coordination-unsaturated centers.

CONCLUSIONS

It is established that concentration and strength of acidic centers on the surface of iron-containing alumosilicate sorbents synthesized by the method of destructive epitaxial precipitation is higher than those of cobalt- and copper-containing samples and of the parent natural sorbent.

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