

# Acid–Base Surface Properties of Binary Systems Based on Aluminum and Zirconium Oxides

R. G. Romanova and E. V. Petrova

*Kazan State Technological University, Kazan, 420015 Tatarstan, Russia*

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**Abstract**—The formation of a hydroxyl cover and acid–base sites on the surfaces of electrochemically coprecipitated binary aluminum and zirconium oxides is studied. It is found using IR probe spectroscopy that the surface electron-donor and electron-acceptor properties of binary aluminum–zirconium oxide systems depend on the synthesis conditions.

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The effect of supports on the catalytic properties of systems is a key problem in heterogeneous catalysis. Recent studies have demonstrated that the structure and texture characteristics of oxide supports is of importance because they are mainly responsible for the catalytic activity and physicomechanical characteristics of catalysts. Systems based on zirconium dioxide are used as promising heterogeneous catalysts, thermally stable supports, and composite materials. This wide use of zirconium-containing supports is a result of the wide variety of available  $\text{ZrO}_2$  modifications and their structure peculiarities. The composition, texture, and crystal structure of zirconium dioxide are sensitive to preparation conditions; this is reflected in changes in the catalytic properties. Membrane technologies are of theoretical and practical interest for the production of highly efficient supports with predictable properties. Previously, the structure, electron-acceptor properties, and hydroxyl covering of aluminum hydroxides and aluminum oxides synthesized in a membrane electrolyzer were studied [1–4]. It was noted that, in the course of hydroxide structure formation upon precipitation in an electrochemical reactor, the effect of an electric field made a considerable contribution. This effect was responsible for a set of nonequilibrium electrical surface phenomena, which resulted in a change in the qualitative characteristics of a heterogeneous phase. Polynuclear species formed under real conditions were responsible for the structure and surface characteristics of the resulting sparingly soluble hydroxides. Experimental results demonstrated that the structure and acid–base properties of hydroxides precipitated in the anode chamber of an electrolyzer were much different from those of aluminum hydroxides prepared in accordance with traditional technologies.

The aim of this work was to study the surface acid–base properties of aluminum–zirconium oxides prepared by coprecipitation in a membrane electrolyzer.

## EXPERIMENTAL

The surface acid–base properties of aluminum–zirconium oxides were studied by IR spectroscopy. The IR spectra were obtained on a Shimadzu 8300 Fourier spectrophotometer with a resolution of  $4 \text{ cm}^{-1}$  and a number of accumulated spectra of 50. (The measurements were performed at the Boreskov Institute of Catalysis, Siberian Division, Russian Academy of Sciences, Novosibirsk (head of laboratory E.A. Pauksh-tis).) Lewis acid sites (LASs) were determined with the use of carbon monoxide as a probe. The concentration of LASs was determined from the integrated intensities of corresponding absorption bands in the spectrum of adsorbed CO using published integrated absorption coefficients [5]. These integrated absorption coefficients depend on the position of the absorption band of CO complexes ( $\nu(\text{CO})$ ) in accordance with the equation  $A_0 = 0.13 \nu(\text{CO}) (2130)$ . The site detection limit was  $0.2 \mu\text{mol/g}$ . For the determination of base sites, the spectra of a sample before and after  $\text{CDCl}_3$  adsorption at the saturation vapor pressure of deuteriochloroform until the complete saturation of the base sites were measured in the region  $2000$ – $2300 \text{ cm}^{-1}$  at room temperature. The concentration of base sites was determined from the integrated intensity of the bands  $\nu_{\text{CD}}$  of corresponding deuteriochloroform complexes with base sites of different strengths [5]. The strength of base sites was characterized using the scale of proton affinity (PA). The values of PA for the  $i$ th base site were determined from the correlation equation  $\log \Delta\nu(\text{CD}) = 0.0066PA - 4.36$ , where  $\Delta\nu(\text{CD})$  is the shift of the  $i$ th band of CD vibrations from the position  $\nu(\text{CD})$  in a gas phase. The concentration of OH groups in arbitrary units was evaluated from the intensity of absorption bands at corresponding maximums separated after decomposing the spectra into components in the region of OH vibrations.

**Table 1.** Preparation conditions and composition of electrochemically coprecipitated aluminum hydroxide and zirconium hydroxide

Sample no.	Precipitation conditions			$\text{ZrO}_2/\text{Al}_2\text{O}_3/\text{H}_2\text{O}$	$\text{MO}_n/\text{H}_2\text{O}$	$\text{Na}_2\text{O}^*$		
	$T, \text{ K}$	pH	$t_{\text{precipitation}}, \text{ min}$			%	$\mu\text{mol/g}$	$\mu\text{mol/m}^2$
<b>1</b>	303	6	400	1 : 1.53 : 9.81	1 : 3.81	0.226	73	—
<b>2</b>	303	9	415	1 : 1.53 : 10.3	1 : 4.03	0.089	29	0.101
<b>3</b>	323	8	140	1 : 1.31 : 6.73	1 : 2.87	0.088	28	—
<b>4</b>	323	9	255	1 : 1.61 : 8.31	1 : 2.99	0.090	29	0.115
<b>5</b>	343	6	297	1 : 1.31 : 5.93	1 : 2.44	0.155	50	0.158
<b>6</b>	343	9	320	1 : 1.26 : 7.13	1 : 2.99	0.275	89	0.342
<b>7</b>	343	10	220	1 : 1.41 : 7.08	1 : 2.83	0.208	67	0.263

\* The  $\text{Na}_2\text{O}$  content was calculated based on aluminum–zirconium oxide prepared after the calcination of the corresponding hydroxide at 1123 K.

The coprecipitation of aluminum–zirconium hydroxides was performed in the anode chamber of a membrane electrolyzer by continuously supplying sodium aluminate to a solution of  $\text{ZrO}(\text{NO}_3)_2$ . Platinum was used as an anode, and Kh18N9T steel was used as a cathode. An MK-40 cation-selective membrane was used for separating the anode and cathode compartments. The conditions of precipitation were varied over the range of pH 6–10 and the temperature range 303–353 K. After precipitation, the resulting suspension was electrochemically purified for the removal of sodium ions and aged in the mother liquor for 48 h. The concentrations of sodium and aluminum were determined using flame photometry and chelatometry, respectively. The determination of zirconium was performed by X-ray fluorescence analysis on a VRA-20 instrument. The sample was mixed with an inert substrate in a ratio of 1 : 15 and pelletized. Reagent-grade boric acid was used as the inert substrate. Standard samples with known zirconium concentrations were prepared in an analogous manner. Zirconium dioxide of high-purity grade was used for preparing standard samples. The water contents of the samples were determined from the results of calcination at 1123 K (see Table 1 for sample specification).

## RESULTS AND DISCUSSION

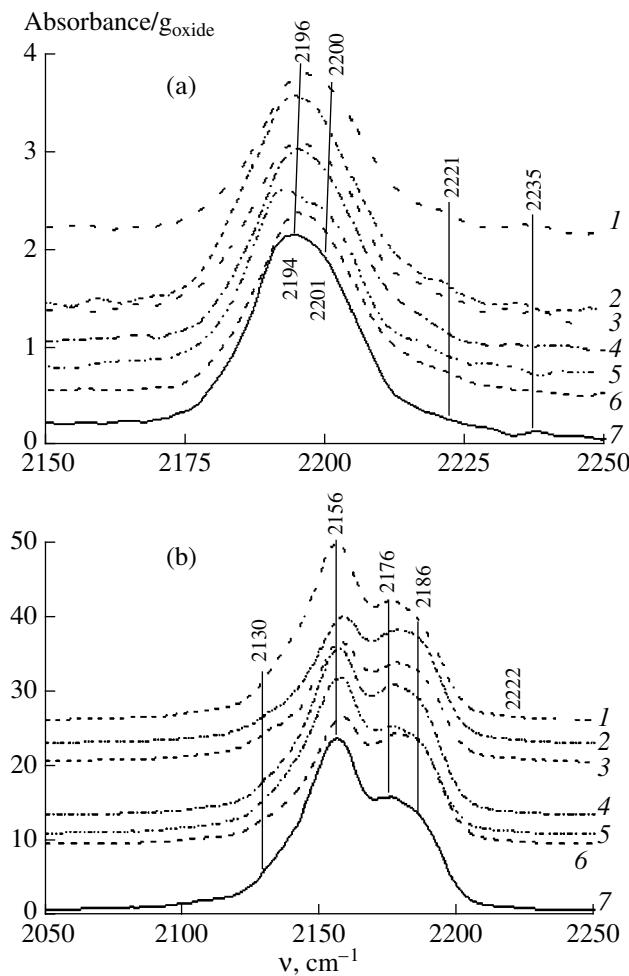
Table 1 summarizes the preparation conditions and characteristics of the synthesized samples. It follows from the data in Table 1 that the composition of aluminum–zirconium hydroxides prepared in the anode chamber of an electrolyzer depends on precipitation conditions. The samples differed in the concentrations of sodium impurity ions, which affect the catalytic properties of oxide systems. In the precipitation of binary aluminum–zirconium hydroxides, the residual concentration of sodium depended on the conditions of

electrolysis and varied over a range from 0.088 to 0.275 wt %. The character of changes in  $\text{Na}_2\text{O}$  concentration, depending on the temperature and pH of precipitation for aluminum–zirconium hydroxides, differed from that for individual oxides. This suggests a more complicated mechanism of the mass transfer of sodium ions from a suspension of binary hydroxides to the cathode chamber. In the samples synthesized at 303 and 323 K, minimum concentrations of  $\text{Na}^+$  ions were found at pH 9 and 8, respectively, whereas sample no. 5 ( $\text{pH}_{\text{precipitation}} 6$ ) corresponded to a lower concentration of impurity ions in aluminum–zirconium hydroxides prepared at 343 K. It is likely that the observed behavior was due to the formation of a heterogeneous phase with a minimum sorption capacity for ions (in this case,  $\text{Na}^+$ ) under these conditions; this is consistent with currently available concepts of the zero-charge point of a surface [6, 7].

Figure 1 shows the IR spectra of carbon monoxide adsorbed on aluminum–zirconium oxide samples at liquid-nitrogen temperature and various pressures. The spectra of CO adsorbed on the samples at ~0.1 Torr (Fig. 1a) allowed us to detect the strongest Lewis sites, which correspond to absorption bands with maximums in the range 2200–2250  $\text{cm}^{-1}$ . Figure 1b shows the spectra obtained at a CO pressure of 10 Torr; in this case, carbon monoxide formed complexes with both weak and strong Lewis sites.

Table 2 characterizes the LASs of aluminum–zirconium oxide samples and individual aluminum oxides.

Several LAS structures can occur on the surface of aluminum oxide [2, 5, 8]. It is believed that the most likely of them are hexacoordinated ( $\text{Al}_6$ ) and pentacoordinated ( $\text{Al}_5$ ) aluminum atoms, in which one coordination site is vacant and the others are occupied by oxygen atoms. Sites of four types have actually been identified [1, 5]. In the spectra of adsorbed CO, absorption



**Fig. 1.** IR spectra of CO adsorbed on the samples of aluminum-zirconium oxides at 77 K and pressures of (a) 0.1 and (b) 10 Torr: (1) sample no. 2, (2) sample no. 1, (3) sample no. 4, (4) sample no. 7, (5) sample no. 6, (6) sample no. 5, and (7) sample no. 3.

bands at 2178–2182, 2185–2195, 2203–2210, and 2235  $\text{cm}^{-1}$  correspond to the first–fourth types, respectively. It is most likely that the first three types of sites belong to the structure of  $\text{Al}_o$ , and differences in the positions of absorption bands are due to differences in the second coordination sphere of aluminum. For example, we can suppose the occurrence of neighboring tetrahedral aluminum or assume the presence of the OH group in the coordination sphere, etc. The absorption bands in the region 2210–2235  $\text{cm}^{-1}$  correspond to “defect” hexacoordinated aluminum atoms  $\text{Al}_o(d)$ , which structurally differed only in the second coordination sphere of aluminum. Previously [5, 8], the occurrence of a much greater number of Lewis site types including tricoordinated, tetracoordinated, and penta-coordinated aluminum atoms and paired Lewis sites (with the possibility of adsorption at two aluminum atoms), which are formed on the removal of the oxygen atom from a bridging position, was considered. The

structure of the  $\text{Al}_p$  type corresponds to a stronger acid site than  $\text{Al}_o$  and  $\text{Al}_o(d)$ , and it can occur at a crystal edge. The concentration of acid sites in aluminum oxides is sufficiently high and varies from 2.6 to 5.2  $\mu\text{mol}/\text{m}^2$  ( $1.5\text{--}3.0 \times 10^{-2}$  site/ $\text{\AA}^2$ ). In this case, the greatest is the fraction of sites of the  $\text{Al}_o$  type.

According to published data [9–11], two types of LASs occur on the surface of zirconium dioxide. Absorption bands at 2204 and 2180  $\text{cm}^{-1}$  in the spectrum of adsorbed carbon monoxide correspond to these LASs. The results of studies performed with other oxides [1–5, 8], in particular,  $\text{Al}_2\text{O}_3$ , demonstrated that the strongest LASs are defects—coordinatively unsaturated cations resulting from the removal of terminal OH groups. A correlation between the intensities of absorption bands due to terminal OH groups and the concentration of LASs was also observed in zirconium dioxide. Thus, an additional amount of zirconium oxide supported on the surface of parent  $\text{ZrO}_2$  by impregnation, that is, surface enrichment in extralattice cations, increased the concentration of terminal OH groups. Simultaneously with this, the concentration of the strongest aprotic sites increased by a factor of ~1.5. The presence of a modifying element noticeably changed the electron-acceptor properties of the surface of  $\text{ZrO}_2$ . For example, the presence of  $\text{La}^{3+}$  cations on the surface significantly decreased the number of the strongest LASs on the  $\text{ZrO}_2$  surface, and sites of the second type ( $\nu(\text{CO}) = 2180 \text{ cm}^{-1}$ ) became predominant. Moreover, new sites appeared, and the adsorption of CO at these sites resulted in a decrease in the vibration frequency of the C–O bond with respect to the frequency in a gas phase: 2111 and 2126  $\text{cm}^{-1}$ . Data obtained for different populations of surface adsorption sites suggest that new adsorption sites were occupied simultaneously with the strongest Lewis sites on the surface of  $\text{ZrO}_2$  [10]. All of the previous publications considered the surface electron-acceptor properties of individual aluminum hydroxides and zirconium hydroxides or those modified with individual elements or metal oxides ( $M = \text{Sc}$ ,  $\text{Y}$ , and  $\text{La}$ ). The surface acid properties of binary aluminum–zirconium systems were not studied previously.

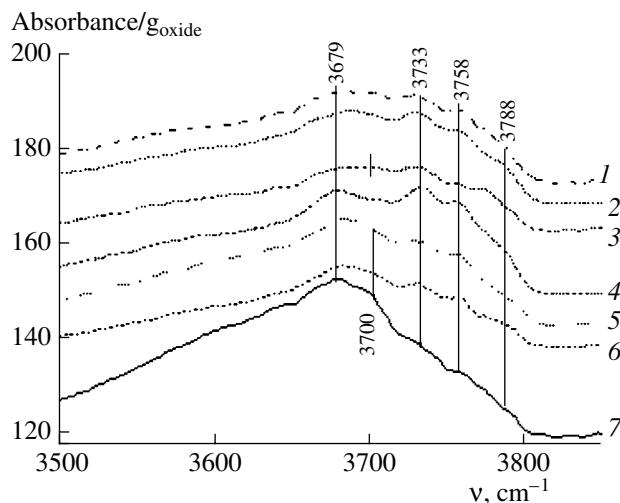
The positions of the absorption bands due to adsorbed CO at 2180–2185 and 2203–2210  $\text{cm}^{-1}$  coincided for individual zirconium dioxide and aluminum oxide, whereas the absorption bands at 2173–2178 and 2185–2195  $\text{cm}^{-1}$  were characteristic of only  $\text{Al}_2\text{O}_3$  [1–5, 8–12]. Consequently, the IR absorption in the former two regions can be due to the presence of various LASs in the individual phases of aluminum and zirconium oxides. However, as follows from reported data, the concentration of LASs in aluminum oxide is higher than that in zirconium dioxide by a factor of 10–50. Therefore, we can conclude that the absorption in the coincident regions of the spectrum primarily characterizes the  $\gamma\text{-Al}_2\text{O}_3$  phase.

All of the test samples exhibited absorption in the region 2173–2178  $\text{cm}^{-1}$ , which corresponds to the first

**Table 2.** Characteristics of Lewis sites in aluminum-zirconium hydroxide samples and individual oxides

Sample	Characteristics of Lewis sites				
	v(CO), cm <sup>-1</sup>	N, μmol/g	ΣN, μmol/g	N, μmol/m <sup>2</sup>	ΣN, μmol/m <sup>2</sup>
<b>1</b>	2217	2.0	444.0	—	—
	2185	348.0			
	2178	94.0			
<b>2</b>	2233	0.3	542.2	0.001	1.893
	2212	8.9		0.031	
	2197	37.0		0.129	
	2186	313.0		1.093	
	2173	183.0		0.639	
<b>3</b>	2241	0.3	442.3	—	—
	2212	11.0			
	2205	2.6			
	2195	40.4			
	2185	284.0			
	2174	104.0			
<b>4</b>	2220	1.6	417.4	0.006	1.653
	2211	7.8		0.031	
	2196	42.0		0.166	
	2186	259.0		1.026	
	2175	107.0		0.424	
<b>5</b>	2216	7.7	588.2	0.024	1.855
	2196	38.5		0.121	
	2179	542.0		1.710	
<b>6</b>	2216	1.2	439.1	0.005	1.687
	2200	23.9		0.092	
	2189	150.0		0.576	
	2177	264.0		1.014	
<b>7</b>	2215	3.0	581.0	0.012	2.282
	2208	21.0		0.082	
	2196	42.0		0.165	
	2185	378.0		1.485	
	2174	137.0		0.538	
Alumina	α [5]	2182	42.0	4.286	4.286
	γ [5]	2178	140.0	1.333	2.666
		2186	140.0	1.333	
	χ [5]	2185	400.0	5.263	5.263
	η [5]	2190	650.0	2.708	2.833
		2235	30.0	0.125	
Alumina [1] (pH 9, T = 323 K)		2207	80.0	0.195	1.918
		2192	708.0	1.723	
Alumina [1] (pH 9, T = 353 K)		2206	93.0	0.296	2.411
		2190	664.0	2.115	
ZrO <sub>2</sub> * [17] (T <sub>calcination</sub> = 773 K)		2200	2.52	0.056	0.239
		2188	8.24	0.183	
ZrO <sub>2</sub> * [17] (T <sub>calcination</sub> = 873 K)		2197	1.02	0.085	0.301
		2185	2.59	0.216	
ZrO <sub>2</sub> * [17] (T <sub>calcination</sub> = 873 K)		2196	1.69	0.141	0.307
		2188	1.99	0.166	

\* The samples of zirconia were prepared by the calcination of commercial zirconium hydroxide of high-purity grade at specified temperatures for 6 h.

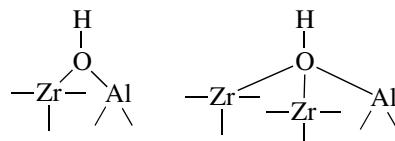


**Fig. 2.** IR spectra of OH groups in the samples of aluminum-zirconium hydroxides: (1) sample no. 2, (2) sample no. 1, (3) sample no. 4, (4) sample no. 7, (5) sample no. 6, (6) sample no. 5, and (7) sample no. 3.

type of aprotic sites in individual  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Note that absorption bands at 2178, 2179, and 2177 cm<sup>-1</sup> were distinguished in the samples synthesized at 303 (pH 6) and 343 K (pH 6 and 9), respectively. In the other samples, the frequency of this absorption band was shifted by 3–5 cm<sup>-1</sup> toward the region 2173–2175 cm<sup>-1</sup>. The absorption at 2185–2195 cm<sup>-1</sup>, which corresponds to the second type of LASs, was also present in the absorption spectra of all of the synthesized aluminum-zirconium hydroxides except for sample no. 6, which was prepared at 343 K and pH 9. Of the aluminum-zirconium hydroxides, only sample nos. 3 and 7 exhibited absorption bands at 2208 and 2205 cm<sup>-1</sup>, respectively, which are characteristic of the third type of LASs. Note that the numbers of sites of this type in the samples were small and different. Thus, in sample no. 7, which was synthesized at 343 K and pH 10, the number of these sites was much greater (21  $\mu$ mol/g) than that in sample no. 3 (2.6  $\mu$ mol/g), which was prepared at a lower temperature (323 K) and pH 8. Note that aluminum-zirconium hydroxides with a minimum set of LASs were formed at pH 6; only three absorption bands were distinguished in the spectra of CO adsorbed on these samples. All of the samples other than sample nos. 1 and 3 exhibited an absorption band in the region 2196–2200 cm<sup>-1</sup>, which is uncharacteristic of individual oxides. Sample no. 3, which was synthesized at 323 K and pH 8, should be emphasized; this sample exhibited the greatest number of absorption bands at 2174, 2185, 2195, 2205, 2212, and 2241 cm<sup>-1</sup>. The amount of strong sites in this sample was much lower than that in the other aluminum-zirconium hydroxides. In this case, it is likely that the synthesis conditions were favorable for the formation of the particles of a heterogeneous phase with an uncharged surface (zero-

charge point); as a result of this, the precipitate rapidly coagulated. In this sample, the rate of precipitation reached a maximum ( $t_{\text{precipitation}} = 140$  min); this facilitated the formation of a heterogeneous structure under these conditions.

The strongest sites were easily detected in sample nos. 1 and 2 by the appearance of an absorption band at 2230–2240 cm<sup>-1</sup>. This band was absent from the spectra of the other samples, or the concentration of sites was very low (Table 2). As can be seen in Table 2, the test binary systems exhibited a number of absorption bands that are uncharacteristic of the individual oxides (2196–2200 cm<sup>-1</sup>). It is likely that these absorption bands belonged to a heteronuclear phase and were due to the following mixed-type electron-acceptor centers:



In general, the test oxides exhibited a decrease in the Lewis acidity, as compared with the samples of individual aluminum oxide and zirconium oxide, in terms of both the amount and the strength of acid sites. It is likely that a decreased acidity of electrochemically coprecipitated aluminum-zirconium hydroxides was due to the removal of defects, which can also exhibit Lewis acidity [5], from the surface of alumina. It is most likely that, in the course of formation of the surface of aluminum-zirconium hydroxides, zirconium ions were incorporated into the defect sites of the crystal lattice of alumina to form an “ideal” structure. Thus, the experimental studies demonstrated that LASs that occurred on the surface of the synthesized alumina-zirconia samples could be formed by both individual oxides and a complex heteronuclear phase.

Figure 2 shows the absorption spectra of surface OH groups in binary aluminum-zirconium oxides prepared upon the calcination of corresponding hydroxides, which were synthesized in a membrane electrolyzer, at 823 K. The complex contour of the spectra suggests that a variety of hydroxyl groups were formed in the electrochemical coprecipitation of aluminum-zirconium hydroxides. The test samples exhibited six absorption bands due to the stretching vibrations of various types of hydroxyl groups (Table 3; Fig. 2).

To identify surface OH groups, we analyzed published data on the IR absorption of individual and binary aluminum and zirconium oxides in the region 3600–3800 cm<sup>-1</sup> of the spectrum and compared them with the experimental results. We found a number of differences by comparing the hydroxyl cover of the synthesized samples with that of electrochemically precipitated alumina [1]. The spectra of the latter exhibited absorption bands with maximums at 3670, 3680, 3700, 3730, 3765, and 3790 cm<sup>-1</sup>. In the binary aluminum-zirconium systems, absorption bands at 3670, 3700, 3730, and 3790 cm<sup>-1</sup> were retained and maximums at

**Table 3.** Intensities (arb. units) of absorption bands due to surface OH groups ( $\nu(\text{OH})$ ,  $\text{cm}^{-1}$ ) in the samples of aluminum-zirconium hydroxides

Sample no.	Absorption band intensity (fraction of corresponding OH groups, %)					
	3670	3700	3730	3758	3775	3790
	$\text{Al}_p\text{OHAl}_t$ $\text{ZrOHZr(Al)}$	$\text{Al}_o\text{OHAl}_p$	$\text{Al}_o\text{OHAl}_o$	$\text{Al}_o\text{OH}$ $\text{ZrOH}$	$\text{Al}_p\text{OH}$ $\text{ZrOH}$	$\text{Al}_t\text{OH}$ $\text{ZrOH}$
1	4.9(13.3)	4.9(13.3)	7.8(21.2)	7.8(21.2)	5.9(16.0)	5.5(15.0)
2	5.2(14.9)	6.2(17.8)	7.2(20.6)	7.2(20.6)	5.2(14.9)	3.9(11.2)
3	10.4(21.8)	11.7(24.6)	8.5(17.8)	7.5(15.8)	5.9(12.4)	3.6(7.6)
4	2.9(9.2)	3.9(12.3)	6.2(19.6)	5.2(16.5)	5.5(17.4)	7.2(25)
5	5.5(19.7)	5.2(18.6)	5.9(21.2)	5.9(21.2)	3.0(10.7)	2.4(8.6)
6	5.9(20.3)	5.2(17.9)	5.9(20.3)	6.8(23.6)	2.9(10.0)	2.3(7.9)
7	5.5(13.4)	4.6(11.2)	9.1(22.2)	10.1(24.7)	6.2(15.1)	5.5(13.4)

3758 and  $3775 \text{ cm}^{-1}$ , which are uncharacteristic of individual aluminum oxides, were also observed. According to Paukshtis [5], high-frequency absorption bands in the region  $3800$ – $3755 \text{ cm}^{-1}$  belong to terminal OH groups, whereas low-frequency absorption bands in the region  $3730$ – $3670 \text{ cm}^{-1}$  belong to bridging hydroxyl groups arranged between two aluminum atoms with different coordination. Hydroxyl groups on the surface of aluminum oxide exhibit various acidities, which are characterized by PA values. Thus, according to Paukshtis [5], OH groups that exhibit absorption at  $\nu = 3700$ – $3670 \text{ cm}^{-1}$  are the most acidic; for these groups,  $\text{PA} = 1380$ – $1410 \text{ kJ/mol}$ . Hydroxyl groups with absorption bands at  $3730$ – $3710 \text{ cm}^{-1}$  exhibited a medium acidity ( $\text{PA} = 1410$ – $1440 \text{ kJ/mol}$ ), whereas hydroxyl groups with  $\nu = 3796$ – $3756 \text{ cm}^{-1}$  exhibited a minimum acidity ( $\text{PA} = 1440$ – $1590 \text{ cm}^{-1}$ ).

In the test samples, the hydroxyl groups that correspond to the absorption band at  $3670 \text{ cm}^{-1}$  can be related to aluminum ions in pentahedral and tetrahedral coordination. At the same time, according to Kharlanov *et al.* [10], the introduction of a modifier like  $\text{M}_2\text{O}_3$  into zirconium dioxide resulted in a shift of the absorption bands at  $3675 \text{ cm}^{-1}$  to a lower frequency region. Therefore, it is believed that, in the aluminum-zirconium hydroxides, the absorption bands at  $3670 \text{ cm}^{-1}$  correspond to OH groups that belong to both zirconium ions and aluminum ions in various coordination environments. Note that the intensity of absorption due to the OH groups of this type is somewhat lower than that in individual aluminum oxide [1].

It is most likely that the absorption band at  $3700 \text{ cm}^{-1}$  belongs to the vibrations of bridging OH groups bound to aluminum ions in octahedral and pentahedral coordination in aluminum oxide. Note that the fraction of hydroxyl groups of the  $\text{Al}_o\text{OHAl}_p$  type in the test samples was lower than that in individual aluminum hydroxides prepared under analogous conditions.

According to published data [1, 5], sites of this type were due to the presence of defects on the surface of aluminum oxides. A decrease in the fraction of sites of this kind in the test samples of aluminum-zirconium hydroxides suggests the formation of a regular crystal structure. This hypothesis was supported by a simultaneous increase in the intensity of the absorption band at  $3730 \text{ cm}^{-1}$ , which is characteristic of hydroxyl groups bound to aluminum ions in octahedral coordination.

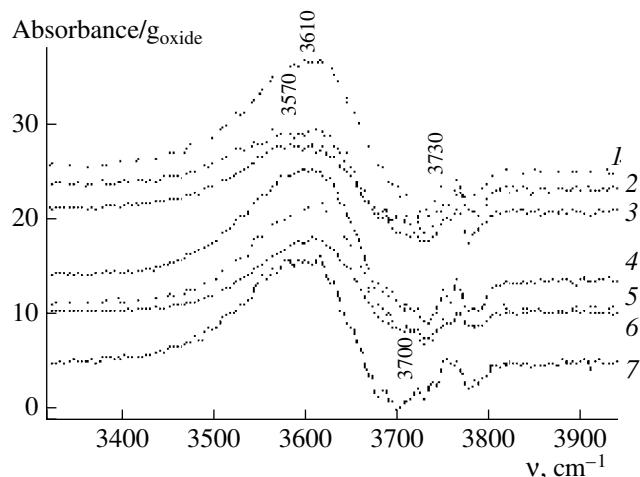
Absorption at  $3775 \text{ cm}^{-1}$  was not detected in electrochemically precipitated aluminum hydroxide [1]. However, Ivanova *et al.* [13] attributed this absorption band to OH groups bound to a pentahedral aluminum ion in boehmite and pseudoboehmite structures. On the other hand, the absorption at  $3775 \text{ cm}^{-1}$  was also characteristic of an individual phase of zirconium dioxide. Analogously, absorption at  $\nu(\text{OH}) = 3790 \text{ cm}^{-1}$  can be attributed to terminal OH groups bound to both the aluminum ion in tetrahedral coordination and zirconium ions. However, in aluminum hydroxides electrochemically prepared under similar conditions [1], the fraction of hydroxyl groups of the  $\text{Al}_t\text{OH}$  type was much lower than that in the test binary systems. Consequently, an increase in the intensity of absorption in this region is indicative of the predominance of terminal OH groups bound to the zirconium ion. In general, the fraction of terminal OH groups in aluminum-zirconium oxides is higher than that in aluminum oxides by a factor of more than 2. In this case, note that the aluminum-zirconium hydroxides examined showed a trend toward an increase in the fraction of terminal hydroxyl groups with pH of precipitation. This behavior was most clearly pronounced in the samples prepared at 323 and 343 K. As noted above, the formation of binary oxide systems by electrochemical precipitation is a complicated process, which can occur toward the crystallization of both individual phases and heteronuclear spinel structures. In this context, the formation of heteronu-

**Table 4.** Characteristics of Brønsted acid sites in aluminum–zirconium hydroxide samples

Sample no.	$\nu(\text{CO})$ , $\text{cm}^{-1}$	Number of sites, $\mu\text{mol/g}$	Number of sites, $\mu\text{mol/m}^2$
1	2159	129	—
2	2156	23	0.080
3	2157	175	—
4	2158	118	0.468
5	2157	63	0.199
6	2157	158	0.607
7	2157	162	0.637

clear structures can be responsible for the increase in the fraction of terminal OH groups in aluminum–zirconium hydroxides.

Bridging hydroxyl groups, which contain an active proton and are Brønsted acid sites (BASs), can form hydrogen bonds with the molecules of weak bases. As a result of this, the absorption spectrum changed in the region 3500–3800  $\text{cm}^{-1}$ . As a rule, various weak bases ( $\text{H}_2$ ,  $\text{N}_2$ ,  $\text{CO}$ , and  $\text{NO}$ ), as well as  $\text{Ar}$ ,  $\text{O}_2$ , and hydrocarbons, have been used as probe molecules for the identification of BASs [5, 14–16]. The use of carbon monoxide, which forms complexes with both LASs and BASs, as a probe molecule is of practical interest for studying the proton-donor ability of oxide systems [5]. Silant'eva *et al.* [16] studied BASs on the surface of aluminum oxide using the adsorption of  $\text{CO}$  molecules, which corresponds to the line at 2155  $\text{cm}^{-1}$  in the IR spectra. It was found that modifier additives practically had no effect on the position of the absorption band at



**Fig. 3.** IR spectra of OH groups in the samples of aluminum–zirconium hydroxides after CO adsorption: (1) sample no. 2, (2) sample no. 1, (3) sample no. 4, (4) sample no. 7, (5) sample no. 6, (6) sample no. 5, and (7) sample no. 3.

~2155  $\text{cm}^{-1}$ ; however, they resulted in noticeable intensity changes.

An absorption band at 2155–2159  $\text{cm}^{-1}$  was observed in the spectra of the test samples of aluminum–zirconium hydroxides in the presence of gaseous  $\text{CO}$  (Fig. 1b). This absorption band characterizes hydrogen-bonded complexes of  $\text{CO}$  with BAS protons on the oxide surface. Table 4 characterizes the BASs of electrochemically precipitated aluminum–zirconium hydroxides. These data indicate that the concentration of BASs increased from 23 to 158  $\mu\text{mol/g}$  in the order of sample nos. 2, 4, and 6, which were synthesized at pH 9, as the precipitation temperature was increased. Note that, in the aluminum–zirconium hydroxides prepared at 303 and 323 K, the concentration of BASs decreased with pH of precipitation, whereas the behavior was reverse in sample nos. 5–7 ( $T_{\text{precipitation}} = 343$  K).

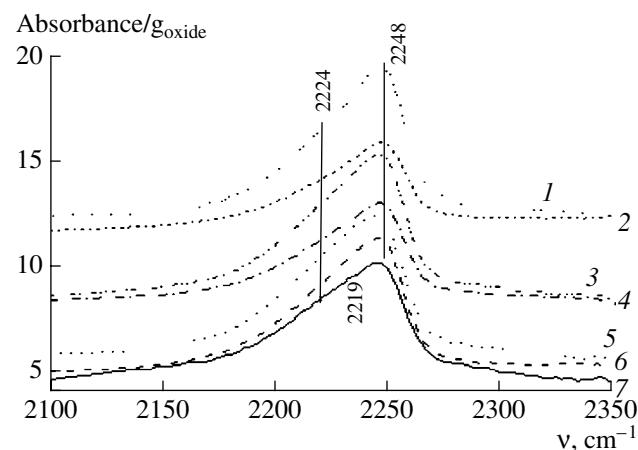
To study the nature and strength of BASs, we analyzed changes in the spectra of aluminum–zirconium hydroxides in the region 3500–3800  $\text{cm}^{-1}$ , which resulted from the formation of hydrogen bonds between surface hydroxyl groups and carbon monoxide. The spectra after  $\text{CO}$  adsorption, which are shown in Fig. 3, exhibit a complex character with broad maximums at 3570 and 3610  $\text{cm}^{-1}$ , which are indicative of a shift of the absorption bands due to bridging hydroxyl groups with  $\nu(\text{OH}) = 3670$ , 3700, and 3730  $\text{cm}^{-1}$  to the low-frequency region. Consequently, the protons of bridging hydroxyl groups with  $\nu(\text{OH}) = 3670$ –3730  $\text{cm}^{-1}$  can be BASs on the surface of aluminum–zirconium hydroxides. It is believed that the shift of the frequency of stretching vibrations of acidic OH groups ( $\Delta\nu(\text{OH})$ ) as a result of their interactions with weak bases characterizes the strength of the resulting hydrogen bond: the greater  $\Delta\nu(\text{OH})$ , the stronger the interaction. In the test aluminum–zirconium oxides, the frequency shift was ~100  $\text{cm}^{-1}$ ; the small shift of the absorption bands of bridging hydroxyl groups suggests that the strength of BASs is small. In all of the samples, absorption at 3758, 3775, and 3790  $\text{cm}^{-1}$ , which corresponds to terminal OH groups with base properties, was retained.

To study base sites, we obtained the IR spectra of deuteriochloroform adsorbed on the surface of the synthesized aluminum–zirconium oxides. The absorption spectra, which are shown in Fig. 4, exhibit a complex contour, which suggests that base sites that form hydrogen bonds with deuteriochloroform are nonuniform. Table 5 summarizes the concentrations and absorption band frequencies of base sites in aluminum–zirconium hydroxides.

Currently available data on base sites are very limited; pyrrole, chloroform, deuteriochloroform, carbon dioxide, and benzoic acid molecules have been used as probes for the IR-spectroscopic identification of base sites [6, 14–19]. Paukshtis [5] detected two types of sites with the use of deuteriochloroform as a probe on the surface of  $\gamma\text{-Al}_2\text{O}_3$ . Strong sites are characterized by

a band with  $\nu(\text{CD}) = 2220\text{--}2225 \text{ cm}^{-1}$ , which corresponds to the calculated value of  $\text{PA} = 900 \text{ kJ/mol}$ . The second type of base sites corresponds to  $\text{PA} = 810 \text{ kJ/mol}$ ,  $\nu(\text{CD}) = 2250 \text{ cm}^{-1}$ . It was hypothesized that practically every oxygen atom acts as a base site; strong sites are due to  $\text{Al}-\text{O}-\text{Al}$  bridging oxygen atoms, whereas weak sites are due to the oxygen atoms of  $\text{OH}$  groups. In the shape analysis of the contour of  $\nu(\text{CD})$  bands due to deuteriochloroform adsorbed on aluminum oxide, a band at  $2240 \text{ cm}^{-1}$  was additionally distinguished [5]. This suggests a more complex heterogeneity of oxide base sites; however, it is difficult to study experimentally because the observed  $\nu(\text{CD})$  bands show a great width. Quantum-chemical calculations demonstrated a potentially wide range of base sites with different properties: these are both oxygen atoms bound to aluminum in an octahedron and tetrahedron and the oxygen atoms of various  $\text{OH}$  groups.

Lamberov *et al.* [1] studied the base properties of aluminum oxides whose precursors were aluminum hydroxides prepared by electrochemical precipitation. In the samples synthesized at pH 11 and 7 and temperatures of 323 and 353 K, respectively, three types of base sites were observed: strong at  $\nu(\text{CD}) = 2200\text{--}2225 \text{ cm}^{-1}$  ( $\text{PA} = 920\text{--}915 \text{ kJ/mol}$ ), medium-strength ( $\nu(\text{CD}) = 2230\text{--}2235 \text{ cm}^{-1}$ ;  $\text{PA} = 880 \text{ kJ/mol}$ ), and weak with



**Fig. 4.** IR spectra of deuteriochloroform adsorbed on the samples of aluminum-zirconium hydroxides: (1) sample no. 2, (2) sample no. 1, (3) sample no. 4, (4) sample no. 7, (5) sample no. 6, (6) sample no. 5, and (7) sample no. 3.

$\nu(\text{CD}) = 2250 \text{ cm}^{-1}$  ( $\text{PA} = 820 \text{ kJ/mol}$ ). In the other samples, medium-strength sites were not distinguished. The predominance of strong base sites in the samples was noted. In aluminum hydroxides prepared at various pH values, the dependence exhibited an extremal char-

**Table 5.** Base properties of aluminum-zirconium hydroxide samples

Sample	$\nu(\text{CD})$ of chloroform-D, $\text{cm}^{-1}$	Number of sites, $\mu\text{mol/g}$	$\Sigma N$ , $\mu\text{mol/g}$	Number of sites, $\mu\text{mol/m}^2$	$\Sigma N$ , $\mu\text{mol/m}^2$
<b>1</b>	2249	124	207	—	—
	2231	83			
<b>2</b>	2248	276	431	0.963	1.504
	2228	155		0.541	
<b>3</b>	2249	117	288	—	—
	2232	171			
<b>4</b>	2248	280	447	1.110	1.772
	2225	167		0.662	
<b>5</b>	2248	152	341	0.480	1.158
	2231	189		0.678	
<b>6</b>	2248	152	367	0.584	1.409
	2231	215		0.825	
<b>7</b>	2249	148	328	0.582	0.936
	2230	90		0.354	
$\gamma\text{-Al}_2\text{O}_3$ [5]	2250	800	1800	3.478	7.826
	2225	1000		4.348	
Alumina [1] (pH 9, $T = 323 \text{ K}$ )	2250	132	293	0.321	0.713
	2225	161		0.392	
Alumina [1] (pH 9, $T = 353 \text{ K}$ )	2250	174	657	0.554	2.092
	2225	483		1.538	

acter with a maximum at pH 9–10. The concentrations of base sites in aluminum oxides synthesized in an electrochemical reactor (61–483 and 60–174  $\mu\text{mol/g}$ ) were much lower than those in aluminum oxides prepared by traditional methods (1000 and 800  $\mu\text{mol/g}$ , respectively).

Published data on the electron-donor properties of the surface of zirconium dioxide are limited. Thus, Fionov *et al.* [15] used diffuse-reflectance IR spectroscopy in order to analyze the surface acid–base properties of individual zirconium dioxide and, for comparison,  $\text{ZrO}_2$  modified with yttrium oxide. It was noted that the accumulation of base sites was observed as the promoter concentration was increased above 0.5 wt %. In this case, absorption bands at 2094–2100, 2110–2114, and 2120  $\text{cm}^{-1}$  appeared in the IR spectrum of adsorbed CO. These absorption bands correspond to CO complexes in which donor–acceptor and dative bonds occur simultaneously [15]. The intensity of absorption bands in this region increased symbatically with promoter concentration; this suggests a relation between these bands and the presence of a modifying element. An absorption band at 2096  $\text{cm}^{-1}$  corresponds to the adsorption of CO in a molecular form with the formation of a complex with the ion pairs  $\text{M}–\text{O}^–\text{M}$ , which consist of valence-unsaturated and coordinatively unsaturated metal (M) and oxygen ( $\text{O}^-$ ) ions. These centers can be formed as a result of the degradation of oxygen-containing surface structures, for example, on the removal of two neighboring terminal hydroxyl groups. It was hypothesized that absorption bands at 2110 and 2120  $\text{cm}^{-1}$  belong to CO adsorbed at adsorption sites like  $\text{M}–\text{O}^–\text{Zr}$ .

The IR spectra of deuterochloroform complexes with the test aluminum–zirconium oxides in the region  $\nu = 2100–2320 \text{ cm}^{-1}$  are somewhat different from the complexes with individual aluminum and zirconium oxides. In this case, a considerable decrease (by a factor of 4–8) in the concentration of base sites was observed. A maximum concentration of base sites was detected in sample no. 4, which was prepared at 323 K and pH 9. This was the only sample that exhibited absorbance at 2225  $\text{cm}^{-1}$ , which characterizes the absorption of strong base sites. Previously, it was noted that the fraction of terminal groups in this sample was much higher and the intensity of absorption bands due to bridging hydroxyl groups was lower than those in the other samples. Note that medium-strength electron-donor sites were predominant in sample nos. 3, 5 ( $T_{\text{precipitation}} = 343 \text{ K}$ ; pH 6 and 9, respectively), and 6 ( $T_{\text{precipitation}} = 323 \text{ K}$ ; pH 8). In this case, the concentration of these sites increased with increasing pH of precipitation. It was also found that the precipitation time affected the amount of base sites formed: the longer the electrochemical coprecipitation process, the more base sites formed on the surface of aluminum–zirconium hydroxides.

According to published data [6], the surface of a heterogeneous phase acquired a zero charge (zero-charge

point) in certain cases of hydroxide precipitation. For zirconia gels prepared based on  $\text{ZrO}(\text{NO}_3)_2$ , the zero-charge point strongly depended on the anionic composition of solution and occurred in the range of pH 8.8–9.3. In the presence of an oriented electric field, the orientation of particles along the external field vector and polarization coagulation made a certain contribution. Ultimately, these factors were responsible for the real values of  $\text{pH}_{\text{zero-charge point}}$  and, correspondingly, for the rate of formation of a heterogeneous phase. Considering sample nos. 2, 4, and 6 precipitated at pH 9, in which a zero-charge surface can be formed, note that the qualitative and quantitative characteristics of base sites at 30 and 50°C coincided (in sample no. 2, an absorption band due to strong sites was shifted by 3  $\text{cm}^{-1}$ ). The concentration of weak base sites in samples synthesized at pH 9 was higher than that in other samples prepared under analogous conditions.

Thus, the surface acid–base properties of aluminum–zirconium oxides and their qualitative and quantitative characteristics mainly depend on synthesis conditions. The hydroxyl covers and electron-donor and electron-acceptor properties of binary systems based on aluminum oxide and zirconium oxide synthesized with the use of membrane technology elements differ from the corresponding individual oxides prepared by traditional precipitation. Differences in the surface properties of binary and individual oxides can be due to the formation of a complex heteronuclear phase along with a phase of individual hydroxides.

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