

Acid–Base Properties of Single-Phase Aluminum Oxides

E. V. Kul'ko, A. S. Ivanova, A. A. Budneva, and E. A. Paukshtis

Boreskov Institute of Catalysis, Siberian Division, Russian Academy of Sciences, Novosibirsk, 630090 Russia

Received November 27, 2003

Abstract—It was found that the surface of single-phase aluminum oxides contains terminal, bridging, and hydrogen-bonded hydroxyl groups, which differ in both concentration and position of related absorption bands. A transition from η - Al_2O_3 to θ - Al_2O_3 does not change the number of absorption bands, but the intensities of these bands decrease. The total concentration of Lewis acid sites in single-phase oxides increases from 2.5 to 5.34 $\mu\text{mol}/\text{m}^2$ for γ - Al_2O_3 and θ - Al_2O_3 , respectively. As distinct from other species, η - Al_2O_3 contains strong Lewis acid sites ($\nu(\text{CO}) = 2238 \text{ cm}^{-1}$). The total concentration of basic sites in aluminum oxides prepared by boehmite dehydration at 600, 800, and 1000°C decreases from 4.86 to 3.72 $\mu\text{mol}/\text{m}^2$.

INTRODUCTION

Aluminum oxides are widely used as acid–base catalyst supports and components.

It was found [1] that the acid–base properties of Al_2O_3 strongly affect the efficiency of catalysts in reforming processes. A great number of publications have been devoted to studies of the acid–base properties of aluminum oxides [2–6]. However, they contain no data on the phase purity of Al_2O_3 or the effect of another phase on the acid–base properties. Meanwhile, aluminum oxides prepared by thermal decomposition of hydroxides are, as a rule, mixtures of related species [7]. According to Sato [8], either pure η - Al_2O_3 and χ - Al_2O_3 or $\eta(\chi) + \gamma$ - Al_2O_3 mixtures can be prepared depending on the particle size of parent trihydroxides (bayerite and gibbsite, respectively). Previously [9], we found conditions for the preparation of single-phase η -, θ -, and χ - Al_2O_3 .

The aim of this work was to study the surface acid–base properties of single-phase aluminum oxides.

EXPERIMENTAL

Aluminum oxides were prepared by thermal decomposition of aluminum hydroxides: pseudoboehmite, boehmite, bayerite, and gibbsite. Pseudoboehmite and boehmite were prepared in accordance with published procedures [10]. Pseudoboehmite was precipitated from a solution of aluminum nitrate (high-purity grade) with an aqueous ammonia solution (high-purity grade) at constant pH and temperature. Boehmite was prepared by hydrothermal treatment of bayerite at 300°C with aging under isothermal conditions for 18 h. Bayerite was precipitated from a solution of aluminum

nitrate (high-purity grade) with a concentrated aqueous ammonia solution (high-purity grade) at constant pH and temperature followed by keeping the suspension (aging) at room temperature for 10 days [9].

The resulting suspensions were filtered, and the precipitates were washed with distilled water until there was an absence of nitrates from the filtrate.

Gibbsite was taken as powder prepared by grinding commercial alumina hydrate, which contained particles of size $<45 \mu\text{m}$, on a planetary mill for 280 min at a rate of 2.5 rps.

All the hydroxide samples were dried at 110°C for a day and calcined under isothermal conditions at different temperatures to obtain corresponding single-phase oxides.

The acid–base properties of the Al_2O_3 samples were studied by IR spectroscopy of adsorbed carbon monoxide and deuteriochloroform molecules. CO forms complexes with Lewis and Brønsted acid sites (LASs and BASs, respectively), and an increase in the frequency of its stretching vibrations depends on the strength of sites. Deuterated chloroform forms hydrogen bonds with surface basic sites. As the strength of the sites increases, the frequency of observed absorption bands due to the C–D bond decreases [11].

IR spectra were measured on a Shimadzu 8300 Fourier transform spectrometer with a resolution of 4 cm^{-1} and a number of accumulated spectra equal to 50. The samples were pressed as pellets without binders with a density of $(8\text{--}20) \times 10^{-3} \text{ g}/\text{cm}^2$ and pumped in an IR cell for 2 h at 500°C and a residual pressure of $<10^{-4}$ Torr. The IR spectra of adsorbed CO molecules were recorded in the range 1200–4000 cm^{-1} ; adsorption of CO was performed at liquid nitrogen temperature (-196°C) over the pressure range 0.1–10 Torr. The determination limit of LASs was 0.2 $\mu\text{mol}/\text{g}$. Deuteriochloroform was adsorbed at 0°C (at saturated vapor pressure). The spectra presented were treated using the

Table 1. Main characteristics of single-phase aluminum oxides

Parent hydroxide	Concentration, wt %			$\text{H}_2\text{O}/\text{Al}_2\text{O}_3$, mol/mol	S_{sp} , m^2/g	T^* , $^{\circ}\text{C}$	Phase	S_{sp} , m^2/g
	Na	Fe	Si					
Pseudoboehmite	<0.001	0.001	0.02	1.52	420	600	$\gamma_1\text{-Al}_2\text{O}_3$	220
						800	$\gamma_2\text{-Al}_2\text{O}_3$	160
Boehmite	<0.001	0.024	0.57	1.06	2	600	$\gamma_b\text{-Al}_2\text{O}_3$	90
Bayerite	<0.001	<0.001	0.08	2.99	38	600	$\eta\text{-Al}_2\text{O}_3$	300
						1000	$\theta\text{-Al}_2\text{O}_3$	106
Gibbsite	0.18	0.02	–	2.92	16	600	$\chi\text{-Al}_2\text{O}_3$	260

* Calcination temperature.

Table 2. Absorption band positions (cm^{-1}) and concentrations of hydroxyl groups

Sample	3795–3788 (Al_tOH)	3776 (Al_pOH)	3758 (Al_oOH)	3735–3730 (Al_oOHAl_o)	3710 (Al_pOHAl_o)	3700–3685 (Al_oOHAl_t)	3680–3670 (Al_pOHAl_t)	3590*
	Concentration of OH groups, $\mu\text{mol/g}$							
$\gamma\text{-Al}_2\text{O}_3$ (pseudoboehmite, 600°C)	24	36	53	80	73	80	67	2
$\gamma\text{-Al}_2\text{O}_3$ (boehmite, 600°C)	2	15	24	53	42	–	63	34
$\chi\text{-Al}_2\text{O}_3$ (gibbsite, 600°C)	42	–	93	29	–	56	67	–
$\eta\text{-Al}_2\text{O}_3$ (bayerite, 600°C)	4	53	–	32	–	58	70	–
$\theta\text{-Al}_2\text{O}_3$ (bayerite, 1000°C)	6	11	–	24	–	20	20	–

Note: Al_t , Al_o , and Al_p refer to tetrahedral, octahedral, and pentacoordinated Al atoms, respectively.

* Belongs to OH groups that form hydrogen bonds.

ORIGIN program package. The concentrations of sites were calculated from the integrated absorption band intensities of corresponding OH groups or LASs ($\nu(\text{CO}) = 2170\text{--}2240\text{ cm}^{-1}$) and basic sites ($\nu(\text{CD}) = 2180\text{--}2260\text{ cm}^{-1}$). The accuracy of quantitative measurements was $\pm 25\%$.

The specific surface area of samples was determined by thermal desorption of argon [12]; experimental error was $\pm 10\%$.

RESULTS AND DISCUSSION

Hydroxyl groups. Table 1 summarizes conditions for the formation of single-phase aluminum oxides and the main characteristics of these oxides. It can be seen that, depending on the nature of the parent hydroxide and on the temperature of treatment, they are different not only in crystal structure but also in specific surface area.

Figure 1 compares the diffraction patterns of low-temperature aluminum oxides prepared by thermal

treatment of corresponding hydroxides at 600°C for 4 h. The positions of corresponding lines in the diffraction patterns of γ - and η - Al_2O_3 are almost the same because of structural similarity (defect spinel structures), whereas the positions of χ - Al_2O_3 lines are significantly different.

The IR-spectroscopic study demonstrated (Fig. 2, Table 2) that the spectra of hydroxyl covers of Al_2O_3 samples contain different numbers of absorption bands. The bands observed correspond to terminal, bridging, and hydrogen-bonded OH groups.

Al_2O_3	χ -	>	γ -	>	η -	>	γ_b -	>	θ -
$\mu\text{mol/g}$	135	>	113	>	57	>	41	>	17

The total concentration of bridging OH groups (absorption bands at 3735–3670 cm^{-1}) decreases in the following order:

Al_2O_3	γ -	>	η -	>	γ_b -	>	χ -	>	θ -
$\mu\text{mol/g}$	300	>	160	\approx	158	>	152	>	64

An increase in treatment temperature to 1000°C, which is accompanied by the transition η - \rightarrow θ - Al_2O_3 , resulted only in a decrease in the concentration of OH groups, rather than changing the nature of these groups. This can be explained by the fact that the degree of oxide surface dehydroxylation increases with calcination temperature. Hydrogen-bonded OH groups occur only in γ - and γ_b - Al_2O_3 , and the concentration of these groups is low (Table 2).

It is well known that bridging OH groups are stronger BASs than terminal hydroxyls. Consequently, it is believed that, among the test aluminum oxides, γ - Al_2O_3 is characterized by the greatest amount of BASs; however, the concentration of these sites on a specific sur-

The first three bands, starting with the high-frequency band, belong to terminal OH groups, which are bound to one aluminum cation in different coordinations. Low-frequency bands belong to bridging OH groups, which are located between aluminum ions with different coordinations. According to current concepts [11], these bands correspond to the structures given in Table 2.

From data given in Table 2, it follows that the total concentration of terminal OH groups (absorption bands at 3795–3758 cm^{-1}) decreases in the following order:

face area basis is insignificant. According to Chukin and coauthors [5, 13], only OH groups with $\nu(\text{OH}) = 3690 \text{ cm}^{-1}$ belong to BASs. From this standpoint, γ - Al_2O_3 is also the most acidic (Table 2).

Lewis acid sites. Aluminum oxides are typical solid Lewis acids. Figures 3 and 4 show the IR spectra of adsorbed CO, and Table 3 summarizes the results of an analysis of these spectra.

It can be seen (Figs. 3, 4) that LASs of various types occurred on the surface of test oxides (absorption bands at 2180–2200, 2220, and 2238 cm^{-1} in Table 3). These bands characterize surface coordinatively unsaturated aluminum cations. A band with $\nu(\text{CO}) = 2158 \text{ cm}^{-1}$ (Figs. 3, 4) corresponds to CO adsorption at OH groups

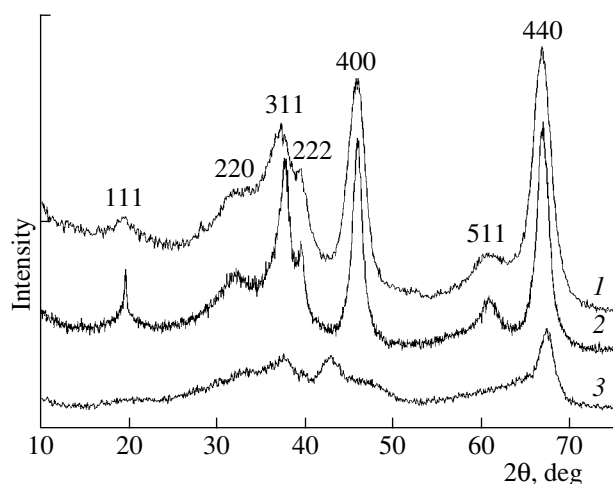


Fig. 1. Diffraction patterns of (1) γ - Al_2O_3 (600°C), (2) η - Al_2O_3 (600°C), and (3) χ - Al_2O_3 (600°C).

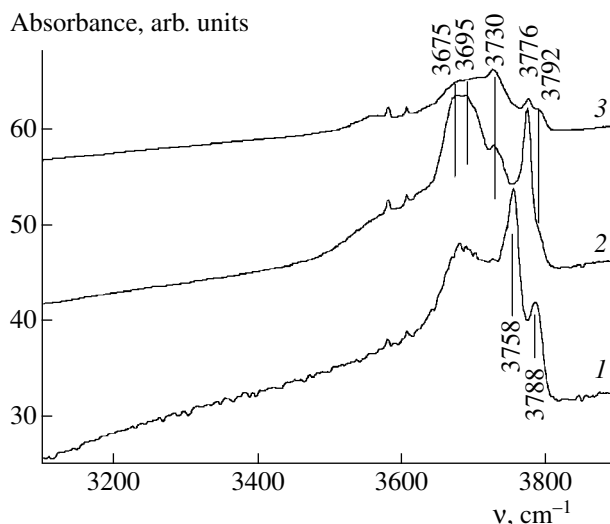


Fig. 2. IR spectra of hydroxyl groups in samples after evacuation at 500°C: (1) γ - Al_2O_3 (600°C), (2) η - Al_2O_3 (600°C), and (3) θ - Al_2O_3 (1000°C).

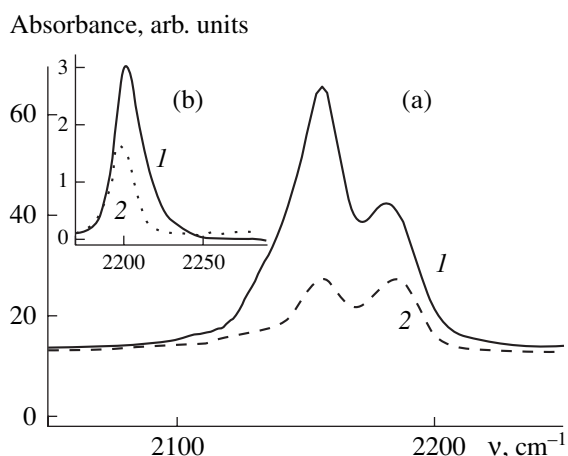


Fig. 3. IR spectra of CO adsorbed on samples from the pseudoboehmite series: (1) γ - Al_2O_3 (600°C) and (2) γ - Al_2O_3 (800°C) at (a) 10 and (b) 0.1 Torr.

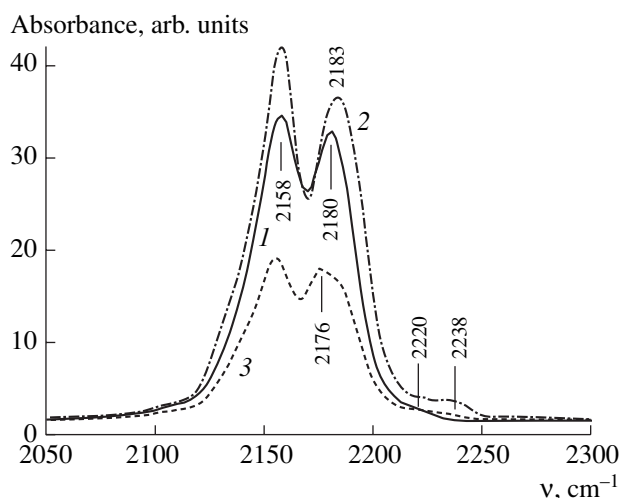


Fig. 4. IR spectra of CO adsorbed at $P = 10$ Torr and $T = -173$ K on the following samples: (1) χ - Al_2O_3 (600°C), (2) η - Al_2O_3 (600°C), and (3) θ - Al_2O_3 (1000°C).

whose oxygen atoms are coordinated to aluminum atoms.

Hypothetically, the nature of the observed sites can be related to the presence of the following surface structures: 2180–2200 cm^{-1} , the structural type Al_o ; 2238 cm^{-1} , this band most likely belongs to the Al_p -type site (in this case, the aluminum atom is bound to four oxygen atoms). This structure can occur at the crystallite edge. Senchenya *et al.* [14] believed that a strong LAS is a truncated tetrahedron, Al_t . According to published data [15, 16], this Lewis site structure is unstable and cannot occur under real conditions.

The total concentration of LASs (ΣLAS) on a specific surface area basis increased from 2.25 to 5.34 $\mu\text{mol}/\text{m}^2$ in the order γ - < γ_b - < χ - < η - < θ - Al_2O_3 . As distinct from the other species, η - Al_2O_3 contains

strong acid sites (absorption band at 2238 cm^{-1}); however, their concentration is low.

The surface concentration of LASs ($\mu\text{mol}/\text{g}$) in aluminum oxides decreases with treatment temperature (Table 3) without changes in the site-strength distribution. Thus, the study demonstrated the occurrence of weak and strong LASs on the surface of aluminum oxides.

Basic sites of alumina. The surface dehydration and dehydroxylation of corresponding aluminum hydroxides resulted in the appearance of coordinatively unsaturated atoms of not only aluminum but also oxygen, which are surface basic sites. Two absorption bands characteristic of basic sites can be distinguished in the spectra of deuteriochloroform adsorbed on the surface of alumina that was prepared by thermal treat-

Table 3. Absorption band positions and concentrations of adsorbed CO

Sample	Acid site concentration (N), $\mu\text{mol}/\text{g}$ ($\mu\text{mol}/\text{m}^2$)			
	2180–2200 cm^{-1}	2220 cm^{-1}	2238 cm^{-1}	ΣLAS
γ - Al_2O_3 (600°C)	495 (2.25)	—	—	495 (2.25)
γ - Al_2O_3 (800°C)	410 (2.56)	—	—	410 (2.56)
γ_b - Al_2O_3 (600°C)	225 (2.50)	—	—	225 (2.50)
χ - Al_2O_3 (600°C)	900 (3.46)	12 (0.045)	—	912 (3.51)
η - Al_2O_3 (600°C)	1125 (3.56)	20 (0.063)	24 (0.076)	1169 (3.70)
θ - Al_2O_3 (1000°C)	550 (5.19)	8 (0.075)	8 (0.075)	566 (5.34)

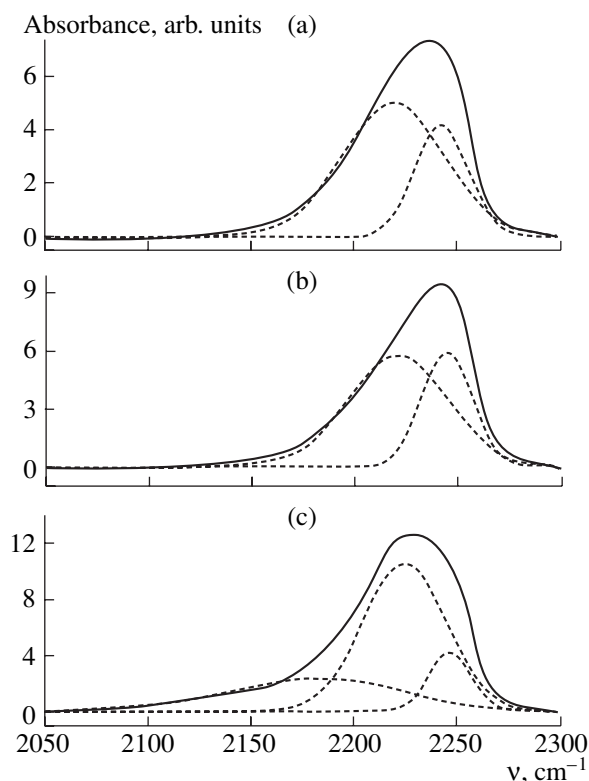


Fig. 5. IR spectra of deuteriochloroform adsorbed on samples from the pseudoboehmite series calcined at (a) 600, (b) 800, or (c) 1000°C.

ment of pseudoboehmite at 600 and 800°C (Fig. 5). A band at 2219–2221 cm^{-1} corresponds to medium-strength sites, whereas a band at 2242–2244 cm^{-1} corresponds to weak sites. Paukshtis [11] hypothesized that the medium-strength basic sites are bridging oxygen atoms (Al–O–Al), whereas the weak sites are oxy-

gen atoms of OH groups (Al–OH). An additional band at 2183 cm^{-1} , which corresponds to very strong basic sites of unknown nature, appeared in the spectrum of Al_2O_3 prepared by calcination at 1000°C. As the treatment temperature was increased, the concentration and strength of basic sites decreased; however, new very strong sites appeared at 1000°C (Table 4).

A comparison between the results of this work and published data [11] suggests that single-phase η - and χ -aluminas are characterized by higher total Lewis acidities:

	η -	χ -	θ -	
ΣLAS , $\mu\text{mol}/\text{m}^2$	3.70	3.51	5.34	[This work]
	2.83	3.05	2.33	[11]

The lower total acidities of aluminum oxides reported in [11] may be attributed to the fact that the aluminum oxides were phase mixtures, for example, γ - + η - Al_2O_3 or γ - + χ - Al_2O_3 . This hypothesis is supported by the fact that γ - Al_2O_3 synthesized from either pseudoboehmite or boehmite exhibited a lower total acidity, as compared with single-phase η - or χ - Al_2O_3 . Therefore, the presence of a particular amount of γ - Al_2O_3 in the preparation of η - or χ - Al_2O_3 will facilitate a decrease in the total concentration of LASs.

The total concentration of basic sites in aluminum oxides prepared by the dehydration of pseudoboehmite at 600, 800, and 1000°C decreased from 4.86 to 3.72 $\mu\text{mol}/\text{m}^2$. The total concentration of basic sites in magnesium oxide prepared by dehydration of hydroxide at 450°C was found in a preliminary experiment to be equal to 5.19 $\mu\text{mol}/\text{m}^2$. Taking into account this value, we can state that aluminum oxide calcined at 600°C is comparable to magnesium oxide in concentration of basic sites.

Table 4. Positions of C–D bands due to adsorbed CDCl_3 and the concentrations of basic sites on the surface of Al_2O_3 after calcination at 600–1000°C

Sample	ν , cm^{-1}	N , $\mu\text{mol}/\text{g}$	Total concentration of sites, $\mu\text{mol}/\text{g}$ ($\mu\text{mol}/\text{m}^2$)
$\text{Al}_2\text{O}_3/600^\circ\text{C}$	2242	460	1070 (4.86)
	2219	610	
$\text{Al}_2\text{O}_3/800^\circ\text{C}$	2244	300	650 (4.06)
	2221	350	
$\text{Al}_2\text{O}_3/1000^\circ\text{C}$	2247	96	466 (3.72)
	2224	270	
	2183	100	

REFERENCES

1. Bitter, J.H., Seshan, K., and Lercher, J.A., *J. Catal.*, 1998, vol. 176, p. 93.
2. Knözinger, H. and Ratnasamy, P., *Catal. Rev.*, 1978, vol. 17, no. 1, p. 31.
3. Geits, B., Kettsir, Dzh., and Shuit, G., *Khimiya kataliticheskikh protsessov* (Chemistry of Catalytic Processes), Moscow, 1981.
4. Oleshko, V.P., Lunina, E.V., Golubev, V.B., *et al.*, *Zh. Fiz. Khim.*, 1981, vol. 55, no. 5, p. 1160.
5. Chukin, G.D., *Zh. Strukt. Khim.*, 1976, vol. 17, no. 1, p. 122.
6. Peri, J., *J. Phys. Chem.*, 1965, vol. 69, no. 1, p. 220.
7. *Physical and Chemical Aspects of Adsorbents and Catalysts*, Linsen, B.G., Ed., London: Academic, 1970.
8. Sato, T., *Thermochim. Acta*, 1985, vol. 88, no. 1, p. 69.
9. Kul'ko, E.V., Ivanova, A.S., Litvak, G.S., Tsybulya, S.V., and Kryukova, G.N., *Kinet. Katal.*, 2004, vol. 45, no. 5, p. 754.

10. Ivanova, A.S., Litvak, G.S., Kryukova, G.N., Tsybulya, S.V., and Paukshtis, E.A., *Kinet. Katal.*, 2000, vol. 41, no. 1, p. 137.
11. Paukshtis, E.A., *Infrakrasnaya spektroskopiya v geterogennom kislotno-osnovnom katalize* (Infrared Spectroscopy in Heterogeneous Acid-Base Catalysis), Novosibirsk: Nauka, 1992.
12. Buyanova, N.E., Karnaukhov, A.P., and Alabuzhev, Yu.A., *Opredelenie poverkhnosti dispersnykh i poristyykh materialov* (Determination of the Surface Area of Disperse Porous Materials), Novosibirsk: Inst. Kataliza, 1978.
13. Chukin, G.D., Sergienko, S.A., Seleznev, Yu.L., Malevich, V.I., and Radchenko, E.D., *Zh. Prikl. Spektrosk.*, 1987, vol. 47, no. 3, p. 427.
14. Senchenya, I.N., Chuvylkin, N.D., and Kazanskii, V.B., *Kinet. Katal.*, 1986, vol. 27, no. 3, p. 608.
15. Danyushevskii, V.G., *Konformatsionnyi analiz organicheskikh molekul* (Conformation Analysis of Organic Molecules), Moscow: Khimiya, 1982.
16. Bokii, G.B., *Kristallokhimiya* (Crystal Chemistry), Moscow: Nauka, 1971.