

Investigation of acid–base sites on the surface of electrochemically synthesized aluminum oxides

A.A. Lamberov^{*}, R.G. Romanova, I.Kh. Gibadullin

Kazan State Technological University, K. Marx St., 68, 420015 Kazan, Russia

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1. Introduction

Many catalytic processes are carried out on the alumina surface. The chemical nature of the alumina surface affects its catalytic and adsorption properties. Therefore, the investigation of the surface acid–base properties is very important. It is known that aluminum hydroxide synthesis conditions have a significant effect on many characteristics of alumina. Previously, we have elaborated a new electrochemical precipitation method for preparation of aluminum hydroxide [1]. This paper discusses the effect of electrochemical synthesis on alumina acid–base properties.

2. Experimental

Aluminum hydroxides were obtained in the anode chamber of a membrane double-chamber electrolyzer [1]. The acid–base properties were studied by IR spectroscopy on a UR-20 spectrometer. Alumina samples were pressed into pellets (density: 7–17 mg/cm²) and heated in

the air at 732 K for 1 h. They were then evacuated in a vacuum IR cell at 10^{−4} Torr. Afterwards, the samples were cooled by liquid nitrogen under vacuum down to $T = 163$ K. Carbon monoxide and deuteriochloroform were used as probes for testing acid and basic sites. The spectra of cooled samples were recorded in the ranges of 2000–2300 and 3000–3900 cm^{−1}. Then, the CO adsorption was carried out to full saturation of acid sites at $T = 163$ K. The spectra of samples with adsorbed CO were recorded after the adsorption. The concentration of Lewis (L-) acid sites was determined from the integral intensity of corresponding bands in the IR spectrum with adsorbed CO. Integral absorbance factors were taken from Ref. [2]. The strength of L-sites was characterized by $Q_{\text{CO-CO}}$ adsorption heat determined from the equation [2]: $Q_{\text{CO}} = 10.5 + 0.5(\nu_{\text{CO}_i} - 2143)$, where ν_{CO_i} is the vibration frequency of CO adsorbed on L-sites. Before studying the basic sites, a spectrum of the sample treated at room temperature was recorded in the ranges of 2000–2300 and 3000–3900 cm^{−1}. The CDCl₃ adsorption was then carried out at room temperature and saturated vapor pressure until saturation of the basic sites. The concentration of basic sites was determined

^{*} Corresponding author. Fax: +7-8432-36-58-92.
E-mail address: kataliz@cmit.ksu.rus.ru (A.A. Lamberov).

from the integral intensity of ν_{CD} bands of CDCl_3 complexes with basic sites of different strength. Absorbance factors were taken from Ref. [2]. The strength of basic sites was characterized in the PA scale (kJ/mol). PA were calculated from equation $\lg \Delta \nu_{\text{CD}} = 0.0066 \text{ PA} - 4.36$, where ν_{CD} is the shift of CD-bands from the ν_{CD} position in the gas phase.

The sodium concentrations in alumina were determined by flame photometry on a FLAPHO-4 instrument. X-ray spectra were recorded with a DRON-2 diffractometer [3]. The specific surface area was determined by the argon thermal desorption on an ASAP-2400 device. The adsorption isotherms were obtained at 77 K with evacuation at 773 K.

3. Results and discussion

Acid and base sites on the alumina surface were studied. The samples were prepared from aluminum hydroxide electrochemically synthesized under controlled conditions. The characteristics and regimes used are presented in Table 1.

The alumina surface is a combination of aluminum and oxygen atoms, which is covered at room temperature with OH groups or water molecules [2,4]. The dehydration and dehydroxylation lead to appearance of low-coordinated oxygen (L-base) and aluminum (L-acid) atoms. Also, there are bridge and terminal OH-groups (Brönsted acid sites) on the alumina surface. The CO adsorption on L-sites is characterized by intensive bands in the range of 2186–2194 cm^{-1} , which are typical for γ -alumina [2,4,5]. The data presented in Table 2 show that there are three types of L-sites on the alumina surface studied: strong ($Q_{\text{CO}} = 49\text{--}52$ kJ/mol); of medium strength ($Q_{\text{CO}} = 40.5\text{--}42.5$ kJ/mol) and weak ($Q_{\text{CO}} = 34\text{--}35$ kJ/mol). It should be noted that strong acid sites were not abundant. Furthermore, there were practically no strong L-sites in samples 1, 3, 4, 8–10.

According to Ref. [5], several possible L-sites can exist on the alumina surface. Five- and six-coordinated aluminum atoms (Al_p , Al_o) with one vacant coordination site are most probable. The other coordination sites are occupied by oxygen atoms. The absorption bands of CO-complexes with 5- and 6-coordinated Al-atoms

Table 1
The effect of synthesis conditions on the properties of aluminum hydroxides

Sample	Synthesis conditions		Properties of initial aluminum hydroxides					
	pH	T, K	Na_2O , %	S, m^2/g	ΣV , cm^3/g	d_{med} , μm	Morphology ^a	ACD ^b , Å
1	7	293	0.060	350	0.396	> 200	57.1:40.9:1.4	26
2	8	293	0.029	342	0.361	> 200	76.8:22.6:0.5	22
3	11	293	0.030	329	0.346	> 200	86.2:13.6:0.2	26
4	9	323	0.015	411	0.630	12.15	76.0:23.2:0.2	22
5	10	323	0.018	415	0.599	8.63	86.2:13.0:0.8	22
6	11	323	0.027	378	0.774	9.48	80.2:18.4:1.4	22
7	7	353	0.017	378	0.600	8.00	81.2:18.1:0.6	22
8	8	353	0.011	352	0.756	10.81	88.1:11.5:0.3	22
9	9	353	0.016	314	0.592	9.99	87.0:9.3:0.3	22
10	11	353	0.074	432	0.442	14.23	60.0:29.6:9.6	26
11 ^c	9–9.5	363	0.012	260	0.61	12.00	80.2:18.4:1.4	46
12 ^d	9	353	0.032	327	0.588	11.80	87.0:9.3:0.3	32
13 ^e	7	353	1.5	380	0.800	> 200	83.2:16.1:0.6	23

^aPseudoboemite:amorphous phase:bayerite.

^bArea of coherent dissipation.

^cCommercial sample.

^dSample precipitated on commercial electrolyzer.

^eAluminum hydroxide without treatment.

Table 2
Acid properties of aluminum oxides

Sample	L-sites			
	Q_{CO} , kJ/mol	N , $\mu\text{mol/g}$	ΣN , $\mu\text{mol/g}$ ($\mu\text{mol/cm}^2$)	$\text{Al}_{\text{p}}:\text{Al}_{\text{od}}:\text{Al}_{\text{o}}$
1	–	–	270 (0.77)	0:0:100
	–	–		
	36	270		
2	49.5	3	393 (1.15)	1:20:79
	38.5	80		
	33.5	310		
3	–	–	270 (0.84)	0:0:100
	–	–		
	35	270		
4	–	–	788 (1.92)	0:10:90
	42.5	80		
	35	708		
5	50	10	751 (1.81)	1:16:83
	40	117		
	34	624		
6	50	25	769 (2.03)	3:12:85
	40.5	97		
	35	677		
7	49	31	1080 (2.86)	3:7:90
	42.5	73		
	34	976		
8	–	–	730 (2.07)	0:12:88
	41.5	88		
	33	642		
9	–	–	757 (2.41)	0:12:88
	42	93		
	34	664		
10	–	–	604 (1.40)	0:8:92
	41.5	50		
	35.5	554		
11	48	40	610 (1.42)	7:0:93
	35	400		
	29	170		
12	48	25	480 (1.47)	5:13:82
	41.5	60		
	35	300		
13	–	–	250	0:0:100
	–	–		
	32	250		

are in the regions of $\nu_{\text{CO}} = 2210\text{--}2180$ and 2235 cm^{-1} , respectively. In fact, four types of absorption bands were identified. The absorption bands in region $2210\text{--}2235\text{ cm}^{-1}$ have been associated [2,4,5] with defective 6-coordinated Al-atoms (Al_{od}) that have distinction only in the second coordination sphere. The structure of 5-coordinated Al-atoms corresponds to acid sites of greater strength than that of 6-coordi-

nated ones. Unfortunately, direct identification of these bands was not possible since it was difficult to perform quantum-chemical calculations. Therefore, such identification was relative. We used it for comparing the strength of acid sites. More than 83% acid sites present on the surface of investigated alumina samples were weak, in contrast to more than 93% weak sites on industrial samples.

Table 2 shows the effect of preparation conditions on the surface acidity of aluminum hydroxide. The samples precipitated at 353 K were the most acidic (samples 7–11). Alumina precipitated at 293 K had the minimal number of acid sites. The effect of pH at different precipitation temperatures was ambiguous. At 293 K, there was a maximum on this dependence. At 323 K, the number of acid sites practically did not depend on the precipitation pH. The acidity reduction with pH rising was observed at 353 K. In comparison with published data [2,4–8], electrochemically synthesized alumina had higher acidity. Industrial alumina samples have broader bands in the region of $\nu_{\text{CO}} = 2180\text{--}2235\text{ cm}^{-1}$ due to their irregular surface. Perhaps, this fact is connected with changing of the water-aluminate module on transition from laboratory to industrial electrolyzer. It is necessary to note a satisfactory coincidence of the concentration of acid sites measured on industrial samples with previously published data [8]. Hence, the number of L-sites

on electrochemically precipitated alumina depends on the synthesis conditions and following treatment.

An estimation of the basic properties of synthesized alumina was carried out by adsorbing CDCl_3 . Table 3 presents the strength and concentrations of different basic sites. There were three types of basic sites on samples synthesized at $\text{pH} = 11$ ($T = 323\text{ K}$) and $\text{pH} = 7$ ($T = 353\text{ K}$) (samples 6 and 7): strong ($\nu_{\text{CD}} = 2200\text{--}2225\text{ cm}^{-1}$; $\text{PA} = 920\text{--}915\text{ kJ/mol}$) [2]; of medium strength ($\nu_{\text{CD}} = 2230\text{--}2235\text{ cm}^{-1}$; $\text{PA} = 880\text{ kJ/mol}$) and weak ($\nu_{\text{CD}} = 2250\text{ cm}^{-1}$; $\text{PA} = 820\text{ kJ/mol}$). There were no sites of medium strength on the other samples. It has been suggested [2] that bridge oxygen atoms are the strong basic sites while oxygen atoms of OH-groups are the weak ones. There were some other bands in the region of $\nu_{\text{CD}} = 2230\text{--}2235\text{ cm}^{-1}$ corresponding to a variety of basic sites connected with octahedral, tetrahedral and other aluminum atoms. However, the identification of these bands is practically impossible at present.

Table 3
The effect of synthesis conditions on basic properties of aluminum oxides

Sample	Basic properties of aluminum oxides			
	PA, kJ/mol	N , $\mu\text{mol/g}$	Ratio of sites 1(strong):2(medium):3(weak)	ΣN , $\mu\text{mol/g}$ ($\mu\text{mol/cm}^2$)
4	910	161	55:0:45	293 (0.71)
	–	–		
5	820	132	64:0:36	304 (0.73)
	915	196		
6	–	–	59:23:18	466 (1.23)
	820	108		
	915	276		
	880	106		
7	820	84	63:16:21	292 (0.77)
	920	184		
	880	48		
8	820	60	59:0:41	351 (0.99)
	910	207		
	–	–		
9	820	144	74:0:26	657 (2.09)
	910	483		
10	–	–	71:0:29	390 (0.90)
	820	174		
	910	276		
	820	114		

It is necessary to note that the concentration of strong basic sites in the samples studied was much higher than that of the weak ones. For aluminum hydroxides synthesized at different pH, this dependence had a maximum at pH = 9–10. With the use of data published in Ref. [8], the concentrations of strong and weak base sites were estimated to be 1000 and 800 $\mu\text{mol/g}$, respectively. Their concentrations in electrochemically synthesized alumina were 161–483 and 60–174 $\mu\text{mol/g}$, respectively. This fact is important for application of electrochemically synthesized alumina since basic sites participate in the coke formation on the alumina surface. A comparison of the CO and CDCl_3 sorption data shows that total number of L-sites was much higher in the samples studied than the number of the basic sites.

4. Conclusions

We have shown that qualitative and quantitative acid–base properties of electrochemically

precipitated aluminum hydroxide differ from published data. This is caused by the synthesis conditions and the following processing. Our results may be useful for development of catalysts with controlled surface parameters.

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