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PROPERTIES OF ALUMINIUM OXIDES OBTAINED BY CALCINATION OF THE PRODUCTS OF REDUCTIVE ROASTING OF BASIC ALUMINIUM-POTASSIUM SULFATE

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Abstract

The influence of calcination conditions on changes in phase composition and porous structure was studied for hydrous aluminium oxide, obtained by leaching out potassium salts from the products of roasting basic aluminium-potassium sulfate in hydrogen atmosphere at 600°C. The product of calcination at 350°C in vacuum has the most developed porous structure with most pores of internal radius within 10–60 Å. Calcination in air atmosphere at temperatures 700, 800, 900, or 1000°C resulted in decrease of specific surface of aluminium oxide and increase of the share of pores with internal radius above 60 Å in the overall porosity of the samples. The reconstruction of the porous structure proceeds mainly as a result of coalescent sintering.

Keywords: calcination

Introduction

The demand of special sorts of aluminium oxide, used in numerous branches of industry, such as electronics, radio engineering, electrical engineering, chemistry etc. have increased rapidly in the recent years. The use of aluminium oxide of special purposes determines some specific properties of this material, such as particle size, phase composition, purity, texture, sorption capacity, chemical properties at the surface, etc.

The properties can be modified by proper selection of the raw materials and conditions of manufacture of the final product. In earlier works [1, 2] we have studied the physicochemical properties of aluminium oxides obtained by thermal decomposition of basic aluminium-potassium sulfate under reducing conditions in the presence of carbon and water vapour, as well as in hydrogen atmosphere. The product obtained by removal of sulfur linked with aluminium in basic aluminium-potassium sulfate were γ-Al_2O_3 and K_2SO_4. To obtain pure oxides the products of thermal decomposition were leached with water for removal of potassium compounds.

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It has been found that aluminium oxide obtained by decomposition of the basic salt at temperature 600°C in hydrogen atmosphere has the most developed porous structure and good sorptive capacity.

The aim of the present work was to study the effect of calcination conditions on its phase composition and porous structure.

Experimental

The object of the physicochemical studies was the material obtained in decomposition of basic aluminium-potassium sulfate at 600°C in hydrogen atmosphere by a method described in earlier paper [2]. This product was a hydrated aluminium oxide containing X-ray distinguishable phases of γ-Al_2O_3 and pseudoboehmite.

The studies were performed with hydrated aluminium oxide and products of its calcination for 2 h at 350°C in vacuum and in air at temperatures 700, 800, 900 and 1000°C. Roasting in air was effected in Derivatograph-C thermoanalyser, with heating rate of 10 deg·min^{-1}.

Table 1 Sample symbols

No. of sample	Sample symbols	Conditions of preparation
1	P/600/H_2/W	Basic aluminium-potassium sulfate roasted at 600°C in hydrogen atmosphere after leaching of K_2SO_4
2	P/600/H_2/W/350	Sample 1 calcined for 2 h in vacuum at 350°C
3	P/600/H_2/W/700	Sample 1 calcined for 2 h in air at 700°C
4	P/600/H_2/W/800	Sample 1 calcined for 2 h in air at 800°C
5	P/600/H_2/W/900	Sample 1 calcined for 2 h in air at 900°C
6	P/600/H_2/W/1000	Sample 1 calcined for 2 h in air at 1000°C

For the samples denoted by the symbols listed in Table 1 the following determinations have been performed:

– phase composition by means of X-ray phase analysis; the X-ray diffraction patterns were recorded in a HZG-4C diffractometer produced by Carl Zeiss, Jena, using radiation CoK_α.

– specific surface S_{BET} and distribution of pore surface and volume with respect to pore radii, basing on low-temperature nitrogen adsorption isotherms; the results of adsorption measurements were calculated per 1 g of anhydrous Al_2O_3. Samples to be used for adsorption studies were heated for 2 h at 350°C under reduced pressure of 10^{-4} hPa.

Besides, the IR absorption spectra of the samples under study were recorded using a Specord 75 IR spectrophotometer and samples pressed in KBr tablets.

Results and discussion

The results of the studies have been presented in Figs 1–5 and in Table 2. Heating the samples $P/600/H_2/W$ at 350°C in vacuum results in decomposition of pseudoboehmite and partial dehydration of γ-Al_2O_3 with partial amorphisation of the crystalline structure (Fig. 1). In the IR spectrum of the sample the bands characteristic for pseudoboehmite (3100 and 1073 cm^{-1}) practically disappear. The absorption band within 400–1000 cm^{-1} corresponds to γ-Al_2O_3 (Fig. 2).

Heating the sample $P/600/H_2/W$ in air at temperatures 700, 800, 900 and 1000°C results in development of the crystalline structure (Fig. 1). Analysis of X-ray diffraction patterns of the obtained samples shows, that calcination of the samples at temperatures 700–900°C does not alter the crystallographic form of γ-Al_2O_3. In the sample calcined at 900°C one may observe besides to reflexes

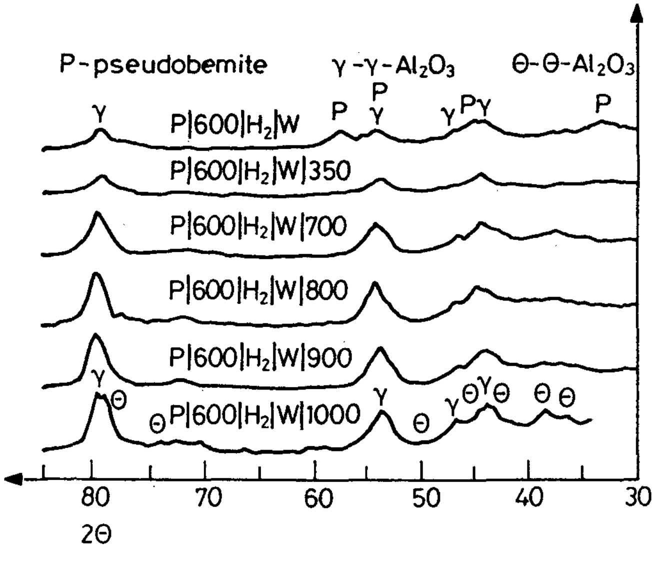


Fig. 1 X-ray diffraction patterns of aluminium oxides calcined under different conditions

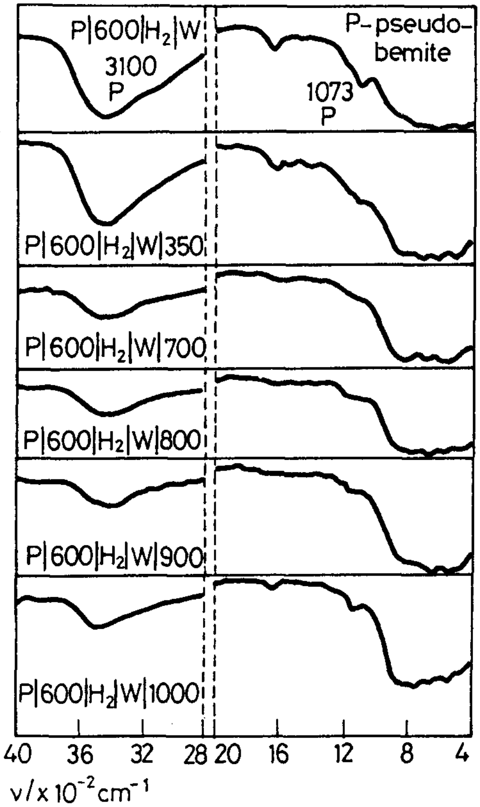


Fig. 2 Infrared adsorption spectra of aluminium oxides calcined under different conditions

characteristic for γ-Al_2O_3, also weak reflexes due to θ-Al_2O_3 (d = 1.40 Å and d = 2.73 Å).

X-ray diffraction pattern of the sample calcined at 1000°C in air contains distinct reflexes both due to γ-Al_2O_3 and θ-Al_2O_3. The results of these studies confirm the scheme of thermal transformations of pseudoboehmite proposed by Lippens and Steggerda [3]. According to these authors the decomposition of pseudoboehmite proceeds as follows:

$$\text{pseudoboehmite} \xrightarrow{300^{\circ}\text{C}} \gamma - \xrightarrow{900^{\circ}\text{C}} \delta - \xrightarrow{1000^{\circ}\text{C}} \theta + \alpha -$$

$$\xrightarrow{1200^{\circ}\text{C}} \alpha\text{-}Al_2O_3$$

The authors have stressed also, that the occurrence of the δ-Al_2O_3 is not always observed.

Table 2 Parameters of porous structure of aluminium oxides

No.*	Volume of pores [cm^3/g] having the radius r/Å within					$V^{**}_{0.92}$ /
	V_{100-60}	V_{60-30}	V_{30-16}	V_{16-10}	$V^{***}_{>100}$	cm^3·g^{-1}
2	0.115	0.199	0.126	0.058	0.002	0.500
3	0.146	0.091	0.033	0.009	0.042	0.321
4	0.174	0.106	0.025	0.013	0.044	0.365
5	0.137	0.065	0.025	0.014	0.080	0.321
6	0.102	0.042	0.023	0.006	0.070	0.243

No.*	Specific surface of pores [m^2/g] having the radius r/Å within					S_{BET}/
	S_{100-60}	S_{60-30}	S_{30-16}	S_{16-10}	S_{100-10}	m^2·g^{-1}
2	30.4	95.4	114.1	87.0	326.9	333.0
3	37.9	40.0	30.1	13.7	121.7	116.0
4	45.1	45.7	26.0	17.9	134.7	134.0
5	34.2	29.1	22.0	20.7	106.0	105.5
6	24.8	18.4	21.9	8.9	74.0	72.6

* number of sample (Table 1)

** volume of pores filled with liquid nitrogen under relative pressure p/p_o = 0.92

*** $V_{0.92} - V_{100-10}$

The observed changes in crystallinity and phase composition of the samples is accompanied by modification of their porous structure. The adsorption isotherm of aluminium oxide obtained by heating in vaccum at 350°C shows that increasing pressure of the adsorbate is accompanied by linear and steep increase of the amount of nitrogen sorbed and a wide hysteresis loop. Such a shape may be accounted for a developed mesopore structure of the sample material. Adsorption isotherms of samples calcined in air are more flat in the range of relative pressures 0.05–0.7; a more rapid increase of adsorption is observed at relative pressures above 0.7.

The hysteresis loop becomes more narrow (Fig. 3 sample P/600/H_2/W/1000) which evidences the presence of mostly wider pores in the sample materials.

Analysis of the pore volume distribution with respect to their radii (Fig. 4) shows that it is advisable to distinguish 4 groups of pores having the radii in the ranges: 10–16 Å, 16–30 Å, 30–60 Å and 60–100 Å.

Table 2 and histograms represented in Fig. 5 provide the comparison of specific surface S_{BET} and pore volume and surface in those ranges of the radii.

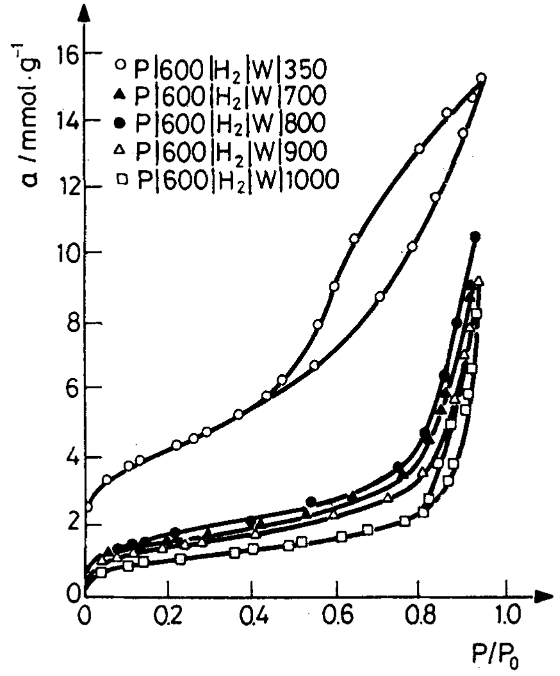


Fig. 3 Isotherms of nitrogen adsorption and desorption

The presented data enable to state that:

– aluminium oxide obtained by calcination in vacuum has higher specific surface S_{BET} and pore surface and volume in the range 10–60 Å than corresponding samples calcined in air. For samples calcined in air the corresponding values fall within 10–45% of the values calculated for samples calcined in vacuum. Only the volume of mesopores having radii >60 Å was smaller for samples calcined in vacuum than for those calcined in air.

The highest contribution to total pore volume and surface area of samples calcined in vacuum was brought by the pores with radii in the range 16–60 Å, whereas in samples calcined in air most pore volume was due to pores with radii greater than 30 Å.

– increase of temperature of calcination in air from 700 to 800°C resulted in small increase of S_{BET} and of volume and surface pores having the radii within 30–100 Å and 10–16 Å.

– further increase of calcination temperature on heating in air to 900 and 1000°C gave the decrease of S_{BET} and of the surface and volume of the pores with radii within 30–100 Å, whereas the volume of pores having radii within 16–30 Å remained practically unchanged. The volume and the surface of pores with radii from the range 10–16 Å increased slightly at calcination temperatures within 700–900°C and then attained a minimum for the sample calcined at 1000°C; the volume of pores with the radii above 100 Å increased with increase of calcination temperature to 900°C, then decreased slightly at higher temperatures.

– the curves of pore volume distribution for samples calcined in air show that increase of calcination temperature has the greater impact on the pores with radii within 30–100 Å. For samples calcined at 700 and 800°C the curves have maxima correspondent to pore radius about 60 Å. Increase of calcination temperature to 900 and 1000°C results, first of all, in disappearence of pores with radii ranging 30–60 Å. As a consequence, it becomes possible to distinguish, on the distribution curves, pores with radii greater than 60 Å. The reconstruction of the porous structure, leading to decrease of the volume of pores with radii within 30–100 Å, gives an increase of the volume of pores with radii exceeding 100 Å.

The distribution of the volume of such pores can be determined by means of porosimetric studies. On using this method Fjedorov *et al.* [4] have noticed that

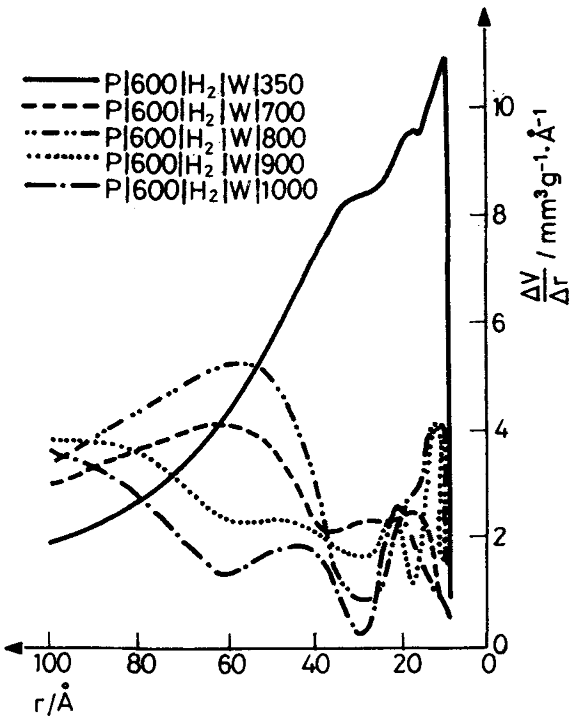


Fig. 4 Distribution of pore volume with respect to their radii

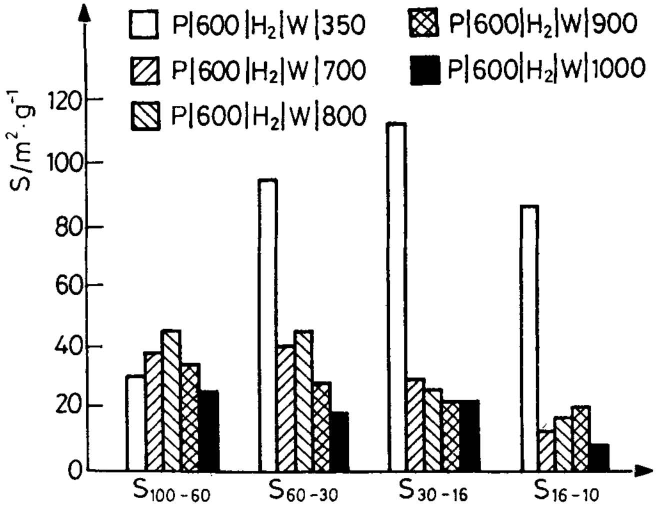


Fig. 5a Distribution of pore surface with respect to their radii

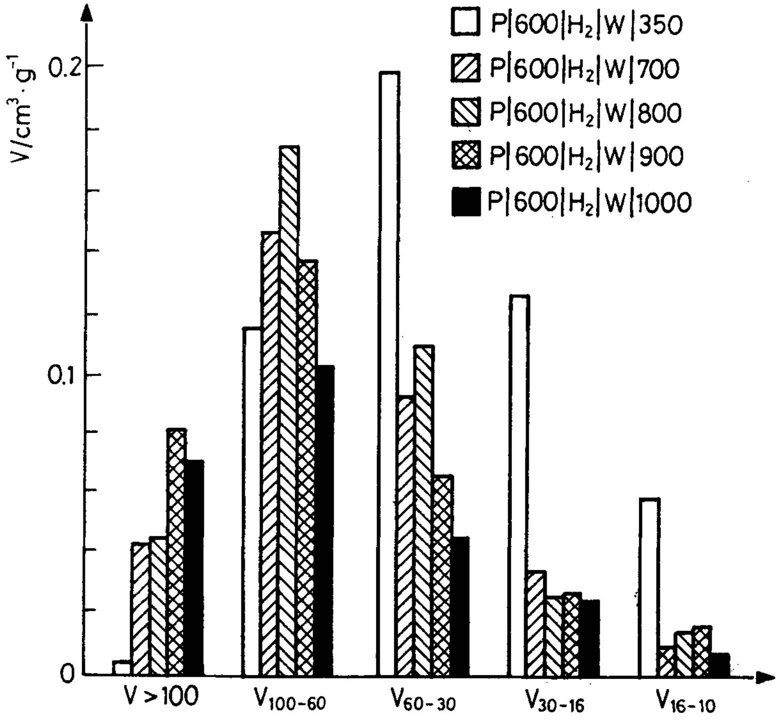
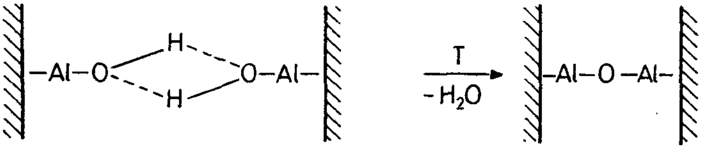


Fig. 5b Distribution of pore volume with respect to their radii

the maximum on distribution curves shifts slowly with increasing pore radius from 80 Å to 120 Å as the temperature of calcination in air atmosphere rises from 550 to 1000°C. The observed changes in the pore structure of aluminium oxide on ignition at various temperatures may be accounted for sintering processes. In temperature range from 550 to 1000°C the process may be due to dehydroxylation of the primary crystallite surface according to the scheme:



leading to formation of Al–O–Al bonds between the crystallites and as a consequence of mass transfer by the way of surface and bulk diffusion.

The surface diffusion consists in mass transfer from naked surface of primary crystallites to the points of their contact. As a consequence the radius of circles inscribed in the narrowest pore cross-sections increases (it is equivalent to increase of the effective pore radius) and the places of contact between neighbouring grains become grown over. As a result there is a slight decrease of pore volume and of specific surface of the sample.

According to the model proposed by Chukin and Seleznev [5, 6] it is possible to distinguish in γ-Al_2O_3 grains, obtained by decomposition of boehmite, two groups of pores: one group having pore radius smaller than 25 Å is formed in consequence of crackings in primary crystallites (the so-called primary pores), and another group of greater dimensions is formed during coalescence of primary crystallites into aggregates (secondary pores).

The increase of the radius of pores in the range of 30–100 Å during calcination of aluminium oxide in air, observed in the present work, may be due to the surface diffusion. This kind of pores might be classified to the group of secondary pores. One may suppose, that in the pores having radius within 10–30 Å are both primary and secondary pores. The primary pores should reduce their radius and volume in the course of the bulk diffusion. The very small changes in the volume of these pores, observed in the present work, result probably from superposition of bulk and surface diffusion.

* * *

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Zusammenfassung — Für Aluminiumoxid, hergestellt durch Auslaugen von Kaliumsalzen aus den Produkten des Röstens von basischem Aluminiumkaliumsulfat in Wasserstoffatmosphäre bei 600°C, wurde der Einfluß der Kalzinationsbedingungen auf Veränderungen der Phasenzusammensetzung und der Porenstruktur untersucht. Das Produkt der Kalzination bei 350°C in Vakuum besitzt die meist ausgeprägteste Porenstruktur, wobei die meisten Poren einen Innenradius zwischen 10 und 60 Å besitzen. Kalzination in Luft bei Temperaturen von 700, 800, 900 oder 1000°C hat eine Reduzierung der spezifischen Oberfläche des Aluminiumoxides zur Folge und erhöht den Porenanteil mit einem Innenradius über 60 Å, bezogen auf die Gesamtporösität der Proben. Der Wiederaufbau der Porenstruktur verläuft hauptsächlich als Ergebnis koaleszenten Sinterns.