EFFECT OF TEMPERATURE OF CALCINING HYDRATED ALUMINIUM OXIDES ON THEIR SORPTION PROPERTIES
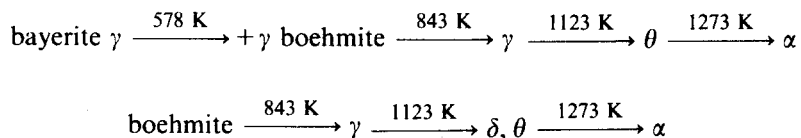
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The effect of the temperature of calcining hydrated aluminium oxides on their sorption properties was investigated.

It was found that the sorption properties and the porous structure of aluminium oxides depend on the type of material calcined and on the conditions under which this process occurs.

As a result of the thermal dehydration of aluminium hydroxides and aluminium oxyhydroxides, also called hydrated aluminium oxides, active aluminium oxides are obtained. These display a developed porous structure and a large number of active centres. The properties of aluminium oxides depend, among other, on the type of material being calcined.

The sorption properties were studied of two hydrated aluminium oxides, UTG–3 and UTG–4, obtained in a pilot plant by leaching sulphates periodically from basic aluminium ammonium sulphate with aqueous ammonia solution at 343 K (UTG–3), or below 343 K (UTG–4). Both samples were dried to constant weight at 378 K in a laboratory drier. By means of X-ray phase analysis, it was found [1] that sample UTG–3 is a mixture of boehmite (AlO(OH)) and bayerite (Al(OH)$_3$), whereas UTG–4 is boehmite. On the basis of thermal and radiographic analyses, the following scheme of thermal decomposition was given for sample UTG–3 in air.

$$\text{bayerite } \gamma \xrightarrow{\text{578 K}} + \gamma \text{ boehmite} \xrightarrow{\text{843 K}} \gamma \xrightarrow{\text{1123 K}} \theta \xrightarrow{\text{1273 K}} \alpha$$

$$\text{boehmite} \xrightarrow{\text{843 K}} \gamma \xrightarrow{\text{1123 K}} \delta, \theta \xrightarrow{\text{1273 K}} \alpha$$

From hydrated aluminium oxides UTG–3 and UTG–4, 6 samples were prepared in the way described in Table 1. The composition of sample UTG–3 was evaluated from the mass loss of sample UTG–3b. It contains about 80% of boehmite and 20% of bayerite. Similarly, from the mass loss for UTG–4b, it can be deduced that

Table 1 Characteristics of samples

Sample	Conditions of preparing samples for measurement	Waste of amount, %
UTG–3a	Degasing in vacuum in temperature 293 K	7.5
UTG–3b	Heating in vacuum in temperature 623 K	26.2
UTG–3c	Baking in temperature 973 K in open air for 5 hours, next moving to apparatus and heating in vacuum in temperature 623 K	12.5
UTG–4a	Degasing in vacuum in temperature 293 K	7.2
UTG–4b	Heating in vacuum in temperature 623 K	33.0
UTG–4c	Baking in temperature 973 K in open air for 5 hours, next moving to apparatus and heating in vacuum in temperature 623 K	10.6

UTG–4a may be a mixture of boehmite and gel. Samples UTG–3c and UTG–4c, previously baked at 973 K in air, can be α-Al_3O_3. For samples prepared in such a way, isotherms of adsorption and desorption of benzene vapour and methanol were determined by the weight method at 293 K from 10^{-3} Pa to the saturated vapour pressure of the adsorbate (p_0). Model isotherms of adsorption for samples of series UTG–3 a4e shown in Figs 1 and 2. The shape of the resulting isotherms is typical for adsorbates containing mainly mesopores.

Isotherms of adsorption of methanol vapour at low relative pressures show the shape of a Langmuir isotherm.

From the isotherms of desorption and sorption of benzene vapour, the following parameters were calculated: the specific surface, S_{BET} [2] the value for the settling surface of the benzene molecule was taken as $\omega = 0.40$ nm² [3]); the volume of pores in which adsorption is reversible, V_0 (this is the adsorption value at the beginning of the hysteresis loop); the volume of pores with radius less than 30 nm, V (equal to the adsorption at $p/p_0 = 0.93$); the volume of micropores, V_m [4]; and the volume of mesopores, V_{mes}, calculated as the difference between V and V_m. From the differential curve the mesopore volume according to their effective radii [5], the radius of the pores prevailing in this sample, r_{mes}, was evaluated. The linear form of Langmuir's equation ($\omega_{CH_3OH} = 0.17$ nm² [6]) was used to determine the specific surface S_L of samples from the isotherms of methanol adsorption. The volume of pores in which methanol adsorption is reversible, V_o, and the total volume of pores with radii less than 30 nm, V (equal to the adsorption of methanol
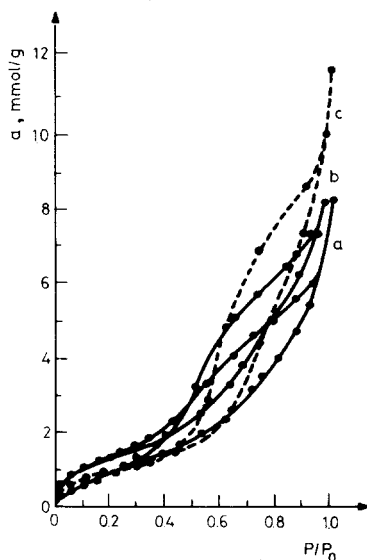
Fig. 1 Isotherms of adsorption and desorption of benzene vapours on UTG–3 (a, b, c)
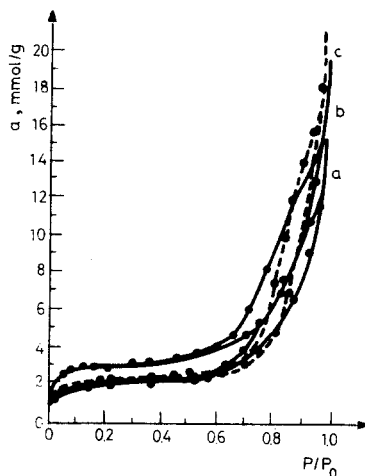

Fig. 2 Isotherms of adsorption and desorption of methanol vapours on UTG–3 (a, b, c)

at $p/p_0 = 0.975$), were also determined. parameters describing the porous structure of the tested aluminium oxides are shown in Table 2. All the values were compared with the amount of hydrous oxide. Analysis of the data in Table 2 leads to the conclusion that calcining at 623 K in vacuum generally does not cause any change in the specific surface of a sample. For sample UTG–3b, the volume of the pores is

Table 2 Parameters of porous structure of aluminium oxides

Size	Unit	UTG–3a	UTG–3b	UTG–3c	UTG–4a	UTG–4b	UTG–4c
		Adsorption of benzene					
S_{BET}	m^2/g	299	289	198	305	325	218
V_0	cm^3/g	0.091	0.111	0.081	0.090	0.131	0.083
V	cm^3/g	0.669	0.658	0.817	0.552	0.713	0.678
V_m	cm^3/g	0.009	0.038	0.005	0.001	0.014	0.001
V_{mez}	cm^3/g	0.660	0.620	0.812	0.551	0.699	0.677
r_{mez}	nm	3.7	3.7	4.3	1.7	1.8	2.6
		Adsorption of methanol					
S_L	m^2/g	261	330	234	294	368	
V_0	cm^3/g	0.092	0.116	0.085	0.104	0.132	
V	cm^3/g	0.667	0.651	0.800	0.579	0.700	

practically unchanged, though the volume of the micropores increases a little at the expense of the volume of the mesopores. The differences in porous structure for oxide UTG–4b are greater than those for UTG–4a. The volume of the pores in which adsorption is reversible is increased by about 50%, and the volume of the mesopores by 25%. The above findings are in agreement with the results of other researchers. Fricke and Jockers [7] found that calcining at temperatures lower than 673 K does not cause any change in the specific surface of aluminium oxide. Boreskov and co-workers [8] observed a lack of change in the porous structure of aluminium oxide up to 873 K. Sample UTG–4a is a mixture of boehmite and gel, dehydration can result in an oxide with a developed porous structure [9].

As a result of calcining at 973 K in open air, the specific surfaces of samples c are much smaller than those of samples a. Similar changes of specific surface are reported in [10]. In our opinion, calcining in open air, i.e. when water vapour is present, leads to the formation of thick-crystalline product. The volume of the tested oxide mesopores increases when their effective radius is increased from 3.7 nm to 4.3 nm for sample UTG–3c, and from 1.7 nm to 2.6 nm for sample UTG–4c. Due to this phenomenon, the specific surfaces of the samples decrease, as the volume of the pores increases considerably.

The use of methanol as an adsorbate to determine the porous structure of aluminium oxides gives results similar to those found with benzene. The specific surfaces S_L and S_{BET} agree within ± 15%, while the volumes of pores in which the process of adsorption is reversible, V_0, and the volumes of pores smaller than 30 nm, V, show resonable agreement with the data for the adsorption of benzene vapour. The results obtained in this study allow us to draw the following conclusions:

1. The sorption properties and porous structure of aluminium oxides depend on the type of material calcined and on the conditions under which this process occurs.

2. The calcining of oxides UTG–3 and UTG–4 in vacuum at 623 K does not cause any change in the specific surfaces of the samples. In the case of oxide UTG–4, calcining results in a pore volume increase of about 30%.

3. The calcining of oxides UTG–3 and UTG–4 at 973 K in open air and 623 K in vacuum causes a decrease in the specific surface and a simultaneous increase in the volume of the mesopores.

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Zusammenfassung — Es wurde der Effekt der Kalzinierungstemperatur von hydratiertem Aluminiumoxid auf dessen Sorptionseigenschaften untersucht. Es wurde festgestellt, daß die Sorptionseigenschaften und die Porenstruktur von Aluminiumoxid von Typ des kalzinierten Materials und von den Bedingungen abhängen, unter denen dieser Prozess abläuft.

Резюме — Исследовано влияние температуры прокаливания гидратированных окислов алюминия на их сорбционные свойства. Установлено, что сорбционные свойства и пористая структура окислов алюминия зависят от типа прокаливаемого вещества и условий прокаливания.