

EFFECT OF STEAMING ON PHYSICAL PROPERTIES OF ALUMINIUM HYDROXIDE AND ALUMINIUM OXIDE

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The effect of partial pressure of water vapour (50–750 kPa) in air on physical properties of calcinated aluminium hydroxide AlOOH and aluminium oxide Al₂O₃ was examined. For both materials it was found that increasing pressure of water vapour leads to a decrease in the specific surface area and to an increase in the diameter of their mesopores. However, changes in the surface properties have not been identical: the total acidity of Al₂O₃ decreased whereas the acidity of calcinated AlOOH passed through a maximum. The total basicity of Al₂O₃ increased while that of AlOOH decreased.

Thermal treatment represents the common operation in producing of catalysts and their supports. The action of heat results in the decomposition of support or catalyst precursors and in the formation of the surface containing hydroxyl groups and coordinately unsaturated atoms which act as active sites in the course of the reaction or in the deposition of active components. In preparing the most common catalyst support, aluminium oxide, heating of the hydroxide releases water¹ and the acid sites of different strength and type are formed². At the same time, however, aprotic basic centres³ which are the bridge-bonded oxygens of Al—O—Al are formed on the surface. In dependence on temperature and conditions of annealing, the part of the hydroxyl groups remains bonded to the surface and acts as protic acidic or basic sites, depending on the kind of neighbouring atoms and strength of bonds⁴.

The aim of the present work was to compare the behaviour of boehmitic aluminium hydroxide and aluminium oxide in the course of their thermal treatment by a stream of air with variable amount of water vapour, especially with respect to the porous structure and acid-base properties.

EXPERIMENTAL

Preparation of catalysts. Aluminium oxide Pural SB (Condea Chemie, F.R.G.) of boehmitic structure was kneaded with acetic acid and appropriate amount of water for 1 h, until a paste had

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been formed. This was then extruded through 3 mm-holes, the extrudates were dried at room temperature for 20 h and then at 120°C for 3 h (the designation AlOOH). The half of the sample was annealed at 600°C for 4 h in a crucible furnace (the designation Al₂O₃).

Steam treatment. A sample of about 10 ml of the catalyst was placed into a flow reactor through which dry air was passed by a rate of 35 ml min⁻¹. The air was continuously feeded with different amount of water (0.1–4.5 ml h⁻¹). Treatment conditions: 600°C, 9 h.

Physical properties. The specific surface area was determined by one-point BET method and the texture properties were then examined by high-pressure porosimeter AutoPore 9 260, Micromeritics, U.S.A. Total acidities and basicities were determined by the Benesi method described earlier⁵, using 1-butylamine and benzoic acid as titrating agents and Methyl Red and phenolphthalein as indicators. Prior to measurements, the samples were dried at 120°C for 1 h in a crucible furnace. Temperature-programmed desorption of cyclohexylamine⁶ and trichloromethane⁷ was used to characterize the acid and basic sites of the aluminas in detail. The sample of the catalyst (50 mg) was dried before measurement in hydrogen stream at 120°C for 2 h and after cooling to ambient temperature, 10 µl of cyclohexylamine or trichloromethane was injected and desorbed until zero line has been established. Then, at the same temperature 1 µl of titrating agent was fed for calibration and finally the desorption proper was realized at the rate of temperature increase 15 K s⁻¹. Changes in gas composition were detected by means of a thermal conductivity detector. Based on the areas of TPD curves, the total amount of acid and basic sites was determined; after dividing the area by dropping a perpendicular line in the minimum of the desorption curves on the areas corresponding to the separate peaks, also the amount of the weaker and stronger acid and basic sites was obtained.

RESULTS AND DISCUSSION

Changes in surface area and porosity. Heating of aluminium oxide and aluminium hydroxide at 600°C in the presence of increasing partial pressure of water in air resulted in a gradual decrease of their specific surface area. In general, the decrease of the surface area of porous materials on increasing temperature can proceed⁸ either via mechanism of surface diffusion of mobile particles which operates at temperatures up to 600°C or by mechanism of bulk diffusion which is important at temperatures above 700°C. In our case (600°C) mass transfer has been most likely realized by diffusion over the surface of the elemental solid particles which form the skeleton of porous support to the vicinity of their contact point. The water vapour present in air during calcination of aluminium oxide accelerates mass transfer as formation of coordinated hydrogen bonds⁹ with the bridge-bonded oxygen leads to the formation of aluminium hydroxide which acts likely as the mobile particle. Higher concentration of the surface OH groups in the starting aluminium hydroxide increases obviously the mobility of these particles, and therefore, the observed decrease in the specific surface area with the increasing water vapour partial pressure could be more pronounced with aluminium hydroxide than with aluminium oxide (Fig. 1). In general, decrease in the specific surface area, S , of solid substances on increasing water vapour pressure, p_w , at constant temperature and time of annealing

can be described by the following equation

$$S = S_0 - p_w(a - bp_w)^{-1}, \quad (1)$$

where S_0 denotes the specific surface area of the substance subjected to annealing in the absence of water and a , b are the constants that are functions of the temperature of annealing, of the concentration of mobile particles, of the size of elemental solid particles of porous material, etc. The dependence of the specific surface area of aluminium oxide, S ($\text{m}^2 \text{g}^{-1}$), on the partial pressure of water, p_w (kPa), found in this work is described by the equation

$$S = 175.9 - p_w(44.3 - 0.0247p_w)^{-1}. \quad (2)$$

In accordance with the decrease of the surface area of the aluminium oxide and aluminium hydroxide calcinated in the presence of water vapour were also the irreversible changes in porous structure. In both the hydroxide and the oxide the portion of the pores smaller than 4 nm decreased while the volume of the larger pores increased (Fig. 2). This shift toward the larger pores was again greater for aluminium hydroxide compared to the oxide. However, the total volume of pores has been essentially unchanged by steaming (Table 1). On increasing partial pressure of water, both apparent density and helium density have increased, obviously as the result of the

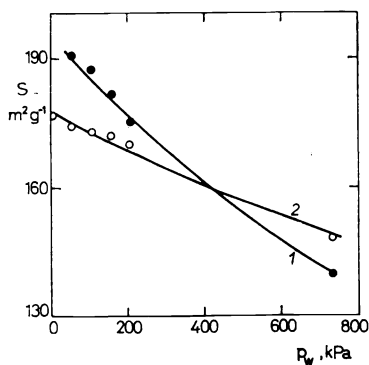


FIG. 1

Dependence of specific surface area of aluminium hydroxide (curve 1) and aluminum oxide (curve 2) on partial pressure of water in air

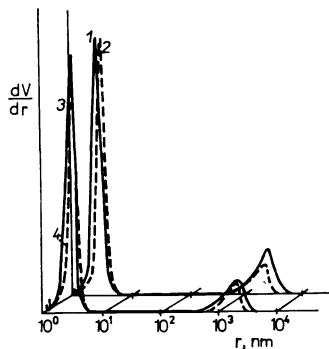


FIG. 2

Comparison of pore size distributions for aluminium hydroxide (curves 1, 2) and aluminium oxide (curves 3, 4) calcinated at partial pressure of water 202.5 kPa (solid lines) and 740.7 kPa (broken lines)

extinction of small pores and of the enlargement of the greater pores. That is why the porosity of samples ε defined as $\varepsilon = (\rho_S - \rho_B) \rho_S^{-1}$ remained constant. This phenomenon caused by action of water vapour was observed also by other authors¹⁰ on annealing boehmite and bayerite.

Changes of surface properties. Desorption curves of cyclohexylamine showed for all the samples of the aluminas annealed at different partial pressures of water vapour the desorption spectrum with two temperature maxima. Koubek et al.¹¹ in the study of adsorption of amines on alumina ascribed the low-temperature desorption peak to the weaker acid sites (which are most likely hydroxy groups) and the other peak, a high-temperature one, to the products which are desorbed from the sites different from those from which the amines were desorbed in the first peak. The second peak should correspond to the desorption from the sites of higher acidity, which is possible also in the form of the products of decomposition reaction. Hence, the desorption of amines need not characterize accurately the relative distribution of the weak and strong acid sites. Nevertheless, in the series of analogous samples this method provides valuable information on the presence of acid sites of different strength. Fig. 3 shows that the total amount of acid sites of the aluminium oxide calcinated in the presence of water vapour decreases with its increasing pressure, while in the case of aluminium hydroxide it passes through a maximum, although not much distinct. This finding can be explained by hydration of the low-temperature aluminium oxide (gamma or eta form) in the presence of a medium containing water vapour. This leads to the formation of hydrogen bonds with the bridge-bonded oxygen and to the simultaneous decrease of the number of the aprotic acid sites, coordinately unsaturated aluminium atoms.

Aluminium hydroxide shows low total acidity. After its exposure to temperatures above 100°C, water bounded in the crystal lattice begins to be gradually released to form the bridge-bonded oxygen atoms and coordinately unsaturated aluminium

TABLE I

Pore volume (V , $\text{cm}^3 \text{g}^{-1}$), bulk density (ρ_B , g cm^{-3}), true density (ρ_{He} , $\text{cm}^3 \text{g}^{-1}$) and porosity ε of aluminium hydroxide and oxide calcinated in presence of various amounts of H_2O in the air (p_W , kPa)

Sample	Al_2O_3		AlOOH		
	p_W	202.5	740.7	202.5	740.7
V		0.684	0.689	0.684	0.680
ρ_B		0.987	1.067	0.989	1.041
ρ_{He}		3.146	3.182	3.013	3.197
ε		0.686	0.665	0.672	0.674

atoms. However, these are hydrated in the presence of water vapour. In the region of low partial pressures of water, its concentration is not necessarily high enough to cause the total hydration of coordinately unsaturated aluminium atoms and thus the acidity can increase above the starting total acidity. At higher partial water pressures the surface is fully hydrated and the total acidity decreases such as in the case of aluminium oxide. The equilibrium amount of hydroxyl groups in crystal lattice depends on temperature of annealing as well as on the concentration of water vapour in the annealing medium¹².

As to the basicity, both materials showed different course of dependences on the partial pressure of water. The total basicity of aluminium hydroxide decreased with increasing p_w while the basicity of aluminium oxide increased (Fig. 3). The increased basicity of aluminium oxide on increasing p_w can be expected since steaming leads to the increase of the number of the surface OH groups. On the other hand, aluminium hydroxide contains a great number of OH groups in the initial state, which are transformed into aprotic basic centres by annealing with the low content of steam. Dependence of the total basicity on p_w is thus the complex result of the decrease of the number of OH groups, of the increase of the number of the bonded oxygen by the effect of calcination and of simultaneous decrease of their number by hydration.

The total number of acid and basic sites includes sites of different strength, i.e. weaker and stronger ones. Their changes on steaming during calcination are seen in more detail in Fig. 4. The figure demonstrates that for both the oxide and the hydroxide, the amount of weak acid centres decreases with increasing p_w . However, this decrease is greater for the oxide than for the hydroxide. In the case of aluminium oxide, the number of strong acid centres decreased exponentially while for aluminium hydroxide it passed through an indistinct maximum, obviously due to formation of the coordinately unsaturated aluminium in the dehydroxylation of aluminium hydroxide. At higher partial pressures of water vapour, the number of the strong centres of aluminium oxide decreased more than that of the weak centres. This agrees with

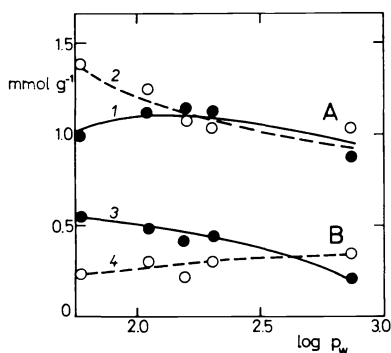


FIG. 3
Total acidity (*A*, mmol g⁻¹; curves 1, 2) and basicity (*B*, mmol g⁻¹; curves 3, 4) of aluminium hydroxide (solid lines) and aluminium oxide (broken lines) in dependence on partial pressure of water in air

data reported in literature¹³, according to which the action of water vapour leads to the decrease of aprotic acidity and to the increase of protic acidity of aluminosilicates and of the catalysts $\text{WO}_3/\text{Al}_2\text{O}_3$.

The more pronounced difference in the surface properties of both materials caused by the presence of water vapour during calcination has been observed for the basicity (Fig. 4). As to aluminium oxide, the number of strong basic sites did not change distinctly with increasing p_w , while the number of weak basic sites was increasing mildly. With aluminium hydroxide, the number of both strong and weak basic sites decreased with increasing p_w , the extinction of the strong centres being more significant.

The position of the desorption peak maximum characterizes the strength of the centres. Fig. 5 shows that in the case of aluminium oxide, neither the strength of acid sites nor that of basic ones changes significantly with the degree of hydration. In the case of the aluminium hydroxide calcinated in the presence of steam, the strength of

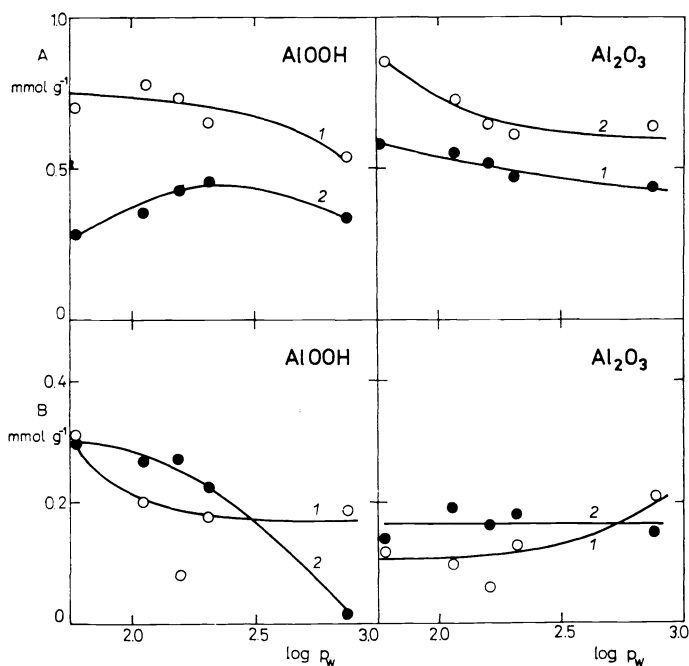


FIG. 4

Dependence of amount (mmol g^{-1}) of acid sites *A* and basic sites *B* of aluminium hydroxide (AlOOH) and aluminium oxide (Al_2O_3) on partial pressure of water in annealing medium (p_w , kPa). Curves 1 weaker sites, curves 2 stronger sites

centres of both types decreased with increasing p_w , the more pronounced decrease being observed for basic sites.

The total number of acid and basic sites of the aluminium oxide and hydroxide calcinated at different partial pressures of water vapour was determined by Benesi titration method. Data on total acidities and basicities obtained by both techniques

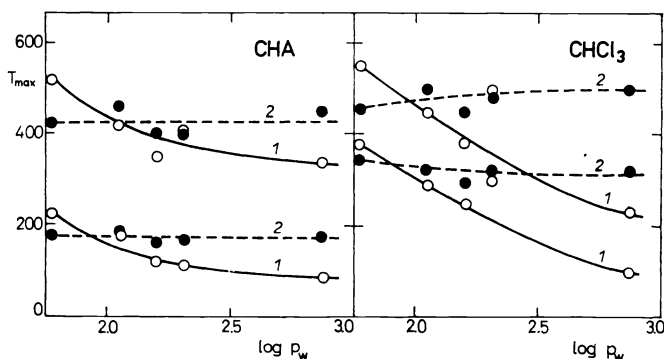


FIG. 5

Temperatures of desorption peak maxima (T_{max} , °C) of cyclohexylamine (CHA) and chloroform (CHCl_3) from aluminium hydroxide (curves 1) and aluminium oxide (curves 2) in dependence of partial pressure of water in annealing medium. Calcination conditions: 600°C, 9 h

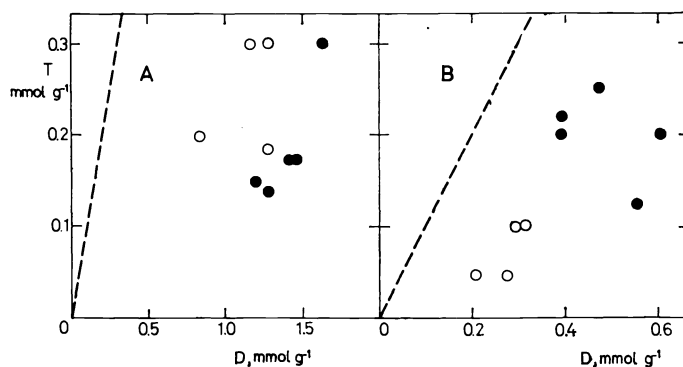


FIG. 6

Relation of surface characteristics of acidities *A* and basicities *B* of aluminium hydroxide (●) and aluminium oxide (○) determined by Benesi titration (T , mmol g^{-1}) and by temperature-programmed desorption (D , mmol g^{-1}) of cyclohexylamine or chloroform

applied i.e. by Benesi titration and by temperature-programmed desorption are compared in Fig. 6. The values of the acidities and basicities determined by Benesi titration are three to five times lower than data obtained by temperature-programmed desorption. The reason seems to be somewhat different procedure for activating the samples prior to measurements, the competitive sorption of the solvent (toluene) on the catalyst surface in Benesi method or the different concentration of the titrating agent – 1-butylamine and cyclohexylamine. Trend in the values obtained by both methods is analogous however, which demonstrates that both procedures can be applied with success for purposes of relative comparison of acidities and basicities in the series of similar samples.

Findings discussed in this work contribute to optimization of the properties of the catalyst support, aluminium oxide. Its production should ensure to the everincreasing extent such physical and surface properties which are tailored with respect to the catalyst for a given catalytic reaction. Depending on the required properties of the product of annealing of aluminium hydroxide, one has to choose specific calcination conditions, e.g. by suitable equipment or by modification of annealing procedure (by intentional addition of water vapour or, on the other hand, by the effective removal of water vapour by calcination). Information concerning the behaviour of aluminium oxide in the presence of water vapour is useful for such processes in which aluminium oxide is exposed to long-termed action of water vapour either as the catalyst or as its support, i.e. in those reactions in which water is reaction component or reaction product.

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