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PHYSICOCHEMICAL PROCESSES _____ AT THE INTERFACES ____

Sulfation of Aluminum Oxide and Its Structure and Adsorption Characteristics

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Abstract—Aluminum oxide was modified by sulfuric acid using the adsorption method under static and dynamic conditions, as well as through impregnation. The areas occupied by a molecule in a saturated monolayer on hydro- and dehydroxylated aluminum oxide were equal to 0.44 and 0.36 nm², respectively. The dependence of the surface and adsorption properties and porosity characteristics of aluminum oxide on its thermal treatment and the modifying sulfo-groups content has been demonstrated. On aluminum oxide with a sulfo-group content close to that of the monolayer, the pyridine sorption proceeds on both Lewis and Brøn-sted acid sites. The increase of the contribution of specific interactions on the sulfated aluminum oxide was shown using the adsorption of saturated and aromatic hydrocarbons.

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INTRODUCTION

Sulfated aluminum oxide is a superacid catalyst and a precursor of bifunctional catalysts [1-5]. The catalyst activity is determined by its structural characteristics, modifying sulfo-group content, and character of surface acid sites. The objective of the present work was to investigate modification of aluminum oxide by sulfuric-acid aqueous solutions under static and dynamic conditions. The following problems have been considered: 1) the effect of preliminary annealing of aluminum oxide on sulfuric-acid adsorption, 2) its limiting adsorption, 3) the effect of annealing of the sulfated aluminum oxide on the content of acid sites and their adsorption activity with respect to pyridine and aromatic hydrocarbons, and the 4) effect of modification by sulfuric acid on the aluminum-oxide porous structure.

EXPERIMENTAL

Materials and Methods

AOK-63-11 aluminum γ -oxide (grade A) with a particle diameter of 0.2–0.8 mm manufactured by JSC SKTB Katalizator (Russia) was used in the study. Its specific surface area determined by the method of low-temperature nitrogen adsorption was equal to 200 m²/g. Samples dried at 130°C and annealed at 500°C were used.

For aluminum-oxide modification, titrated solutions of sulfuric acid of concentrations from 0.1 to 1.0 N were prepared.

For titration of supernatant solutions of sulfuric acid after its adsorption on aluminum oxide, titrated solutions of sodium hydroxide were used. Methyl Red was used as an indicator.

Surface Acidic-Group Content

The contents of acidic groups on the surface of the initial and sulfated samples of aluminum oxide were determined by the method of back titration. For this purpose, samples were held for a day in 0.05 N solution of sodium hydroxide. The supernatant aliquot was titrated by 0.01 N solution of hydrochloric acid with the Methyl Red indicator.

Adsorption of Sulfuric Acid under Dynamic Conditions

The effect of sulfuric-acid concentration on its adsorption on aluminum oxide annealed at 500°C under dynamic conditions was investigated. For this purpose, 200 mL of the acid solution was fed through holders, each containing 2 g of aluminum oxide. The acid concentrations were 0.9, 3.8, and 6.3 N; the flow rate was 14 mL/h. The sulfuric-acid content in the eluate was determined though its titration by sodium hydroxide solutions.

Adsorption of Sulfuric Acid under Static Conditions

The kinetics of sulfuric acid sorption on aluminum oxide was investigated. For this purpose, dried and annealed samples (2 g each) were added with 20 mL of

 Table 1. Effect of the concentration of sulfuric-acid solution on its adsorption under dynamic conditions

Concentration of H ₂ SO ₄ , N	0.008	0.04	0.086
A, mmol/g	0.055	0.37	0.60

0.1 N of H_2SO_4 , and, upon stirring, 1 mL of solution was taken for acid concentration determination.

The isotherms of adsorption of sulfuric acid on dried and annealed samples of aluminum oxide were built. Samples (2 g each) were held for a day in 10 mL of sulfuric-acid solutions with concentrations from 0.1 to 1.0 N. Thereafter, the sulfuric-acid concentration was determined in supernatant solutions using titration by sodium hydroxide.

Supernatant solutions were removed by decantation. Sulfated samples were dried at 130°C and annealed at 500°C for 4 h.

Aluminum-Oxide Impregnation with Sulfuric-Acid Solutions

The impregnation method was used to deposit a quantity of sulfuric acid larger than during its adsorption on the surface. Aluminum-oxide samples were impregnated with acid solutions, dried, and annealed at 500° C for 4 h. The acid content in modified samples was determined by the method of back titration.

Determination of Acidic-Group Content in Sulfated Samples

To determine the acid content in samples, the method of back titration was used. For this purpose, samples were held in 0.05 N solution of sodium hydroxide for 4 h. The sodium hydroxide concentration was determined through titration by hydrochloric acid solutions. Methyl Red was used as an indicator.

Aluminum Oxide Specific Surface Area and Pore Volume

To determine the specific surface area and pore volume, the initial and sulfated samples of aluminum oxide were used upon their titration by sodium hydroxide, washing with water, and drying at 130°C. The specific surface area was determined by the method of thermal nitrogen desorption. The initial aluminum oxide with a specific surface area of $200 \text{ m}^2/\text{g}$ determined by the method of low-temperature nitrogen adsorption was used as a reference. The pore volume was found from capillary condensation of saturated water vapor. For this purpose, aluminum-oxide samples were put, while placed inside the preliminarily weighed box, into a dessicator with a cup of distilled water on its bottom. For 5 days, weighing bottles with adsorbents were periodically weighed, and the specific pore volume was determined from the quantity of equilibrium sorbed water.

Adsorption of Pyridine

To determine the pyridine adsorption, samples (20 mg each) of initial and modified samples of aluminum oxide (dried and annealed) were held for a day in 5 mL of pyridine solutions in octane of a concentration of 6.84 mmol/L. Octane was preliminarily dried over NaA zeolite. The pyridine concentration in solutions upon adsorption was determined by spectrophotometry from the optical density in the UV range at a wavelength of 250 nm.

IR Spectroscopy

Diffuse-reflectance IR spectra of the initial sample of aluminum oxide annealed at 500°C, the sulfated sample, and that containing the adsorbed pyridine were obtained using a Prestige-21 Fourier-transform IR spectrometer with a DRS-8000 diffuse-reflectance accessory.

Gas Chromatography

The adsorption properties were also investigated by the method of dynamic sorption using a Kristallux-4000 M chromatograph equipped with a katharometer as a detector. Helium was used as a carrier gas; its feed rate was 30 mL/min. The size of glass columns was 20×0.2 cm. Chromatographic measurements were performed at temperatures from 100 to 170°C with preliminary samples conditioning in the carrier gas flow at 200°C for 3 h. The volume of the adsorbate sample introduced using a microsyringe was varied from 0.5 to 10 µL. At low and intermediate surfacefilling degrees for normal (C_6-C_8) and aromatic $(C_6H_6, C_6H_5CH_3, C_6H_5C_2H_5)$ hydrocarbons, in the above temperature range, the specific retention volumes and adsorption isotherms were measured and isosteric adsorption heat values were calculated according to the technique of [6] for the initial and sulfated aluminum oxide.

RESULTS AND DISCUSSION

The data on the sulfuric-acid adsorption on aluminum oxide preliminarily annealed at 500° C under dynamic conditions are shown in Fig. 1 and Table 1. Aluminum oxide saturation by sulfuric acid was attained approximately within 4–6 h upon elution of about 50–100 mL of solutions. As seen from Table 1, the increase in acid-solution concentration resulted in a proportional increase of acid adsorption at saturation.

As seen from the data of the sulfuric-acid adsorption on aluminum oxide under static conditions, the adsorption equilibrium was achieved, just like under dynamic conditions, within approximately 4-6 h of periodic stirring. The sulfuric-acid-adsorption isotherms are shown in Fig. 2. The H₂SO₄ adsorption was



Fig. 1. Adsorption (A, mmol/g) of sulfuric acid on aluminum oxide under dynamic conditions. Concentrations of sulfuric-acid solutions: (I) 0.086, (2) 0.04, and (3) 0.008 N. Aluminum-oxide sample 2 g, flow rate 14 mL/ h.

somewhat higher on the preliminarily dehydroxylated at 500°C aluminum oxide than on the hydroxylated one.

The limit values of adsorption $(A_m, mmol/g)$ calculated using the Langmuir equation and the single molecule area in the monomolecular layer (ω_m, nm^2) are shown in Table 2.

Further annealing at 500°C of the sulfated aluminum oxide dried at 130°C does not affect the content of acidic groups in samples with a group content of 0.61 meq/g and lower, whereas, for the samples with a higher content (from 0.72 to 0.82 meq/g), an insignificant (about 10%) decrease was observed in them.

The effect of sulfation on the characteristics of the porous structure of aluminum oxide was studied. Table 3 shows the pore volume and the specific surface area of the initial and sulfated samples obtained by the method of sulfuric-acid adsorption. As can be seen from the table, the samples' specific surface area and pore volume undergo virtually no changes. Therefore, no noticeable destruction of the porous structure occurred for the sulfated aluminum oxide with a sulfuric-acid content lower than that for the monolayer adsorption.

On the other hand, a substantial dissolution of aluminum oxide took place at deposition of the sulfuric acid quantity larger than the monolayer one. This was manifested in the emergence of an expressed turbidity in supernatant solutions during their titration by

Table 2. Limiting value of adsorption of sulfuric acid (A_m , mmol/g) and the molecule (ω_m , cm²) on hydroxylated and dehydroxylated aluminum oxide

γ -Al ₂ O ₃	A _m , mmol/g	$\omega_{\rm m},{\rm nm}^2$
Hydroxylated	0.75	0.44
Dehydroxylated	0.85	0.36



Fig. 2. Isotherms of adsorption of sulfuric acid on aluminum oxide: (1) dried at 130° C, (2) annealed at 500° C. Aluminum-oxide sample 2 g, concentrations of initial solutions from 0.1 to 1.0 N, solutions volumes 10 mL, adsorption times 12 h.

sodium hydroxide as a result of transformation of the solved sulfate into aluminum hydroxide. The specific pore volume of such sulfated samples started to decrease. For example, at a triple increase of the H_2SO_4 content up to 2.4 mmol/g, the pore volume decreased 1.5-fold (Fig. 3).

Pyridine is most often used to study surface adsorption sites of aluminum oxide and as a spectral probe [2, 7, 8]. A comparison of pyridine adsorption on dried and annealed sulfated samples was performed (Fig. 4). One can see that the pyridine adsorption on the initial and sulfated samples dried at 130°C is equal to about 0.4 mmol/g and does not depend on the sulfuric-acid content on the surface. The pyridine adsorption increases approximately 1.5-fold (up to 0.6 mmol/g) as a result of annealing of the initial aluminum oxide at 500°C. The pyridine adsorption increases along with the increase of the sulfuric-acid content on a series of annealed sulfated samples. Near the monolayer sulfo-groups, the adsorption increases and is equal to about 1.2 mmol/g. Therefore, drying sulfated aluminum oxide is insufficient to remove sulfo-groups-bonded water hampering the pyridine adsorption. Only annealing develops the adsorption activity of the sulfated aluminum oxide.

The IR spectrum of the initial aluminum oxide contains broad absorption bands in the range $3580-3800 \text{ cm}^{-1}$, as well as around $2200-2400 \text{ cm}^{-1}$. These

Table 3. Sulfuric-acid contents (*A*, mmol/g) in aluminumoxide samples annealed at 500°C, specific pore volume (*V*, cm³/g), and specific surface area (*S*, m²/g)

A, mmol/g	0	0.23	0.5	0.61	0.68	0.75	0.75
V, cm ³ /g	0.52	0.50	0.49	0.49	0.51	—	0.50
$S, m^2/g$	184	192	184	195	—	—	198

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Fig. 3. Specific pore volume $(V, \text{ cm}^3/\text{g})$ of sulfated aluminum-oxide samples obtained by the impregnation method.



Fig. 4. Pyridine adsorption on initial and sulfated aluminum-oxide samples: (*1*) dried at 130°C, (*2*) annealed at 500°C.

bands correspond both to hydroxyl groups present on the surface of aluminum oxide and to different organic compounds molecularly adsorbed from air. The absorption range $900-1700 \text{ cm}^{-1}$ corresponds to the presence of vibrations characteristic of aluminum γ -oxide and inorganic impurities: water and carbon dioxide adsorbed on the surface of Al_2O_3 [8, 9]. The sample annealing at 500°C results in a significant absorption decrease in the ranges 2200-2400 and $900-1700 \text{ cm}^{-1}$, which is due to a partial removal of impurities from the oxide surface (Fig. 5, curve 1). Modification of the Al₂O₃ surface by sulfuric acid results in the emergence of broad bands with maxima characteristic of sulfate ions (1145 cm⁻¹) and covalently bonded sulfate groups (1445 and 1080 cm⁻¹) (Fig. 5, curve 2) [10, 11]. In the spectra of the annealed aluminum oxide containing 0.6 mmol/g of pyridine (Fig. 5, curve 3), one observes the bands of absorption of the molecularly adsorbed pyridine (v_{cc} 1615 and 1600 cm^{-1}) [6]. The absorption maxima for pyridine



Fig. 5. Diffuse reflectance spectra of aluminum oxide: (1) annealed at 500°C; (2) annealed and containing 0.75 mmol/g of sulfuric acid, (3) annealed and containing 0.6 mmol/g of pyridine, and (4) annealed and containing 0.75 mmol/g of sulfuric acid and 1.2 mmol/g of pyridine.

C–H vibrations are in the absorption range of the surface bonded O–H groups and cannot be discerned in the obtained spectrum. Upon adsorption of 1.2 mmol/g of pyridine on the surface of Al_2O_3 modified with sulfuric acid, the absorption bands at 1640, 1540, 1490, and 1450 cm⁻¹ emerge in addition to those of the molecularly adsorbed pyridine in the spectrum (Fig. 5, curve 4) and may be the result of the interaction of pyridine molecules with as Brønsted as Lewis surface sites [6]. The formation of such sites under sulfuric-acid interaction with the aluminum-oxide surface is possible only due to interaction of the acid proton with the oxygen atom of the hydroxyl group (Brønsted) and the sulfo-group with aluminum atoms (Lewis), which is in good agreement with the scheme suggested in [12].

The effect of the aluminum-oxide-surface sulfation was also studied by the method of gas chromatography on the example of aluminum oxide with the sulfuric-acid content of 0.6 mmol/g that is close to the monolayer filling value. Aromatic compounds characterized with electron-donor properties can serve as test molecules for studying the aluminum oxide sulfated surface under gas chromatography conditions. The isotherms of adsorption of normal (C_6-C_8) and aromatic (C₆H₆, C₆H₅CH₃, and C₆H₅C₂H₅) hydrocarbons were measured in the temperature range 100-170°C. The adsorption isotherms calculations were carried out by the Glückauf method. All the isotherms are convex to the direction of the adsorption axis (Fig. 6) and, under the same equilibrium pressures, the adsorption of all adsorbates on both initial and sulfated γ -Al₂O₃ decreases along with the temperature increase.

Isosteric adsorption heats (Q_{st}) for the above adsorbates in the area of small filling values ($a = 30 \,\mu \text{mol/g}$)



Fig. 6. Isotherms of adsorption of (a) $n-C_6H_{14}$ and (b) C_6H_6 at 100°C on γ -Al₂O₃ and 0.6 mmol/g of SO₄/ γ -Al₂O₃.

were calculated from adsorption isotherms (set of Langmuir isotherms) (Table 4). The $Q_{\rm st}$ values for normal hydrocarbons at low degrees of filling on the sulfated aluminum γ -oxide decrease in comparison with those of the initial aluminum oxide, which indicates reduction of the surface adsorption potential due to sulfation. In spite of the decrease of the contribution of dispersive interactions into total energy of adsorption on the surface of the sulfated oxide, the $Q_{\rm st}$ values for aromatic hydrocarbons on the modified sample are higher than on the initial oxide by 5-6 kJ/mol. The values of initial heats of adsorption of aromatic compounds on both initial and sulfated aluminum oxide exceed respective values for *n*-hydrocarbons with the same number of carbon atoms in the molecule due to interaction of π electrons of arene molecules with the surface active sites. However, the $\Delta Q_{\text{spec}} (Q_{\text{arene}} - Q_{n-\text{alkane}})$ values characterizing the contribution of the energy of specific interactions of the π -electron system of arene molecules into total adsorption energy by 0.6 mmol/g SO_4/γ -Al₂O₃ is substantially higher than that for the initial γ -Al₂O₃. For instance, the values of the ΔQ_{spec} contribution of arenes at adsorption on the unmodified aluminum

oxide are in the range 6–15 kJ/mol, while on the sulfated sample the ΔQ_{spec} values for these compounds increase and become equal to 19–20 kJ/mol. The observed substantial increase of the adsorption of aromatic compounds occurs due to extra interaction with the surface sulfo-groups.

CONCLUSIONS

The limiting value of the sulfuric-acid adsorption and the single molecule area in the monolayer on aluminum γ -oxide have been determined. No destruction of the porous structure (specific surface area and pore volume) at the sulfuric-acid content on the surface corresponding to the monolayer filling and lower was observed. The pyridine adsorption on a series of samples with different sulfo-groups contents showed that the sulfated aluminum oxide annealing at 500°C is required to develop its adsorption activity. For the aluminum oxide with the sulfo-groups content similar to that in the monolayer, the pyridine adsorption occurs on both Lewis and Brønsted acidic sites. As was found from the difference of heats of adsorption of saturated

Adsorbates	γ-Al ₂ O ₃		$0.6 \text{ mmol/g SO}_4/\gamma$ -Al ₂ O ₃		
	Q	$\Delta Q_{ m spec}$	Q	$\Delta Q_{ m spec}$	
<i>n</i> -Hexane	42		43		
<i>n</i> -Heptane	50		45		
<i>n</i> -Octane	60		53		
Benzene	57	15	62	19	
Toluene	59	9	65	20	
Ethylbenzene	66	6	72	19	

Table 4. Values of isosteric adsorption heats Q_{st} (kJ/mol) and contributions of specific interactions ΔQ_{spec} ($Q_{arene} - Q_{n-alkane}$), kJ/mol at $a = 30 \,\mu\text{mol/g}$

and aromatic hydrocarbons, sulfation resulted in the increase of the contribution of specific interactions.

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