

PREPARATION OF STRONG ACID CATALYSTS BY SULFATE TREATMENT OF CALCINED BOEHMITE

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Solid acid catalysts with acid strength of $-14.52 < H_0 < -8.2$ were prepared by sulfate treatment of the samples of boehmite calcined at 105 – 800 °C. Two preparation methods were used: impregnation of the calcined boehmite with 3.5M H₂SO₄ or mixing of the boehmite samples with anhydrous aluminum sulfate, in both cases followed by calcination in nitrogen at 650 °C. The catalysts were characterized by measurements of surface area, adsorption of pyridine and benzene, acid strength measurements by the indicator method and by catalytic activity tests in the isomerisation of cyclohexene, *p*-xylene and *n*-hexane. Properties of the catalysts prepared by both methods were comparable.

Sulfate treatment of some oxides, e. g. ZrO₂, TiO₂, SnO₂, Fe₂O₃ or HfO₂ can increase significantly their acid strength¹⁻⁶. Usually, the sulfated oxide catalysts has been prepared by impregnation of corresponding hydroxides or amorphous oxides with water solutions of H₂SO₄ (refs¹⁻⁶) or (NH₄)₂SO₄ (refs^{7,8}) and subsequent calcination at 500 – 800 °C (refs^{4,3,8}). The calcination should be performed either in air or in nitrogen, the use of hydrogen is not suitable^{9,10}.

Properties and structure of active centers of sulfated alumina were also studied^{6,7,10-13}, but some discrepancies have been found in the reports. Some authors^{7,12} claimed that the sulfate treatment of alumina changes the number of acid centres but weak or medium acid centres were detected in the resulting materials. However, the superacid catalysts have been prepared from γ -alumina¹¹ and boehmite¹⁵. Arata and Hino¹¹ reported that for the preparation of superacid sulfated alumina, in contrast to other oxides, it is better to use the well crystallized oxide than hydroxide or amorphous oxide. In our own experiments¹⁵, the properties of sulfated alumina prepared from aluminum hydroxide (boehmite) or γ -alumina were found comparable. The aim of this work was to clarify these differences and to test the possibility of sulfate treatment of alumina by aluminum sulfate.

EXPERIMENTAL

Preparation of the Catalysts

Aluminum hydroxide (boehmite) prepared by hydrolysis of AlCl_3 in Chemical Works Litvínov was used for the preparation of sulfated alumina catalysts. Its calcination at the temperatures of 105, 150, 350, 500 or 800 °C, respectively in a tube reactor under flow of nitrogen provided a series of precursors used in further procedures. The properties of the precursors are shown in Table I.

The first method of sulfate treatment consisted of impregnation of calcined precursor with 3.5M H_2SO_4 (1 h, room temperature). In the impregnation 1.6 or 1.2 ml of the acid per 1 g of the precursor were used alternatively. The impregnated samples were dried at 105 °C in air for 2 h. As a result, two series of impregnated materials differing in their sulfur content were obtained. Sulfur content determined in the dried samples was 5.73 and 4.39 mmol g^{-1} , respectively. All samples were then calcined in a tube reactor in a flow of dry nitrogen at 650 °C for 2 h.

The second sulfate treatment consisted of the mechanical mixing of the precursors (whose properties are shown in Table I) with anhydrous aluminum sulfate in three different ratios. Resulting dried mixtures contained 2.92, 4.39 and 7.63 mmol sulfur g^{-1} , respectively. The mixtures were calcined at the same conditions as the impregnated samples. Only two series of the catalysts with lower sulfur content were used for further experiments because all the mixtures with the highest sulfur content melted during calcination.

Characterization of the Catalysts

The surface area of samples was measured by nitrogen adsorption using classical 5-point BET method.

The strength of acid centers was measured by the indicator method¹⁴. The following indicators were used: dicinnamalacetone ($H_0 = -3$), benzalacetophenone ($H_0 = -5.6$), anthraquinone ($H_0 = -8.2$), *p*-nitrochlorobenzene ($H_0 = -12.7$), *m*-nitrochlorobenzene ($H_0 = -13.16$), 2,4-dinitrofluorobenzene ($H_0 = -14.52$).

The amount of chemisorbed pyridine and benzene has been used as a measure of the total number of acid centres and of the number of strong acid centres, respectively. The basicity of pyridine and benzene differs considerably and the strongly basic pyridine can be assumed to be chemisorbed nearly on all the acid centres while the much less basic benzene is chemisorbed on the acid centres with $H_0 \leq -5.6$ only¹⁵. Of course, this number of acid sites can be influenced by nonstoichiometric adsorption of the base or by nonacid-base interactions between the base and the adsorbent. However, for a simple comparison of samples with similar surface properties (which is our case) such approach can be accepted. The following experimental procedure was used: Approximately 0.2 ml of pyridine or benzene was added to 1 g of the catalyst in the glass tube reactor and the tube was sealed after 30 min of stabilization at room temperature by the flow of dry nitrogen at 50 °C. All superfluous (presumably physically bonded) adsorbate was desorbed. The remaining amount of chemisorbed pyridine or benzene was determined gravimetrically.

Catalytic activity was tested using three different hydrocarbons (cyclohexene, *p*-xylene and *n*-hexane). It is known that acid sites with different strength are necessary for isomerisation and cracking reactions of these hydrocarbons. At the not too high reaction temperatures, the weak acid centres can induce transformations of cyclohexene, the strong acid centres are necessary to induce *p*-xylene reactions and the superacid centers catalyze reactions of *n*-hexane. The catalytic activity was measured in a glass tube reactor (i.d. 6 mm) with a pulse arrangement. The amount of the catalyst was 0.4 g, the size of pulse 1 μl , nitrogen flow rate 20 ml/min and reaction temperatures 125 °C, 250 °C and 125 °C were used for cyclohexene, *p*-xylene and *n*-hexane, respectively. The product of cyclohexene reaction was mainly methylcyclopentene, the products of *p*-xylene reaction were *o*-xylene, *m*-xylene and also a small amount of toluene and benzene, and pentane isomers were found as the main products of *n*-hexane reaction.

RESULTS AND DISCUSSION

The properties of starting materials used for sulfate treatment were obtained by calcination of boehmite at different temperatures and are summarized in Table I. Transformation of boehmite to γ -alumina proceeds¹⁶ at temperatures higher than 300 °C and hence, the precursors calcined at 105 and 150 °C (precursors 1 and 2) can be classified as boehmite. The precursor 3 calcined at 350 °C was probably a mixture of γ -alumina and aluminum hydroxide and the precursors 4 and 5 calcined at 500 °C and 800 °C were probably composed of γ -alumina only.

The surface areas of the precursors 1 – 4 were approximately 200 m² g⁻¹, regardless the calcination temperature. Significant decrease of the surface area (approximately to 150 m² g⁻¹) was found after calcination at 800 °C only.

The highest pyridine adsorption was observed with the materials calcined at 350 or 500 °C, the lowest one was found with the sample calcined at 105 °C. The amounts of benzene adsorbed on the samples calcined at 350 – 800 °C (precursors 3 – 5) were 0.22 – 0.25 mmol g⁻¹, while on the precursors 1 and 2 (calcined at 105 and 150 °C) the benzene adsorption was found to be very low (approx. 0.05 mmol g⁻¹). Very likely this finding comports with the absence of acid centres with $H_0 \leq -3$ which was found with the precursors 1 and 2 by the indicator method. The acid centres with $H_0 \leq -3$ were found in the precursor 3 and the centres with $H_0 \leq -5.6$ in the precursors 4 and 5.

The properties of the catalysts sulfated by sulfuric acid are shown in Table II and those prepared using aluminum sulfate are given in Table III.

A part of the sulfur introduced into the catalyst in the sulfate treating step was liberated in the form of sulfuric acid and/or sulfur oxides during the final calcination step. That is why the sulfur content in the calcined catalysts did not depend on the amount of added sulfates only but also on the calcination temperature of the starting aluminum

TABLE I
Properties of calcined aluminum hydroxide

Parameter	Sample				
	1	2	3	4	5
Calcination temperature, °C	105	150	350	500	800
Surface area, m ² g ⁻¹	199	204	212	196	148
Ads. of pyridine, mmol g ⁻¹	0.17	0.26	0.51	0.61	0.30
Ads. of benzene, mmol g ⁻¹	0.03	0.06	0.24	0.25	0.22
Max. acid strength, -H ₀	>3.0	>3.0	≤ 3.0	≤ 5.6	≤ 5.6
Conversion of cyclohexene, %	0	0	0	0 ^a	0 ^a

^a Traces of methylcyclopentene.

TABLE II
Properties of calcined boehmite sulfated with H₂SO₄

Parameter	Catalyst										
	16	17	18	19	20	21	22	23			
Sulfur content in the precursor ^a , mmol g ⁻¹			5.73						4.39		
Calcination temperature of boehmite, °C	150	350	500	800	150	350	500	800			
Surface area, m ² g ⁻¹	135	115	95	93	166	154	131	105			
Sulfur content, mmol g ⁻¹	4.06	3.20	4.07	3.90	1.64	1.36	2.67	1.20			
Adsorbed pyridine, mmol g ⁻¹	0.80	0.64	0.46	0.24	0.76	0.83	0.50	0.22			
Adsorbed benzene, mmol g ⁻¹	0.44	0.16	0.08	0.06	0.47	0.41	0.11	0.08			
Max. acid strength, -H ₀	14.52	12.7	12.7	12.7	14.52	13.2	12.7	12.7			
Conversion of cyclohexene, %	93.1	87.3	68.9	76.8	95.0	93.5	91.2	82.8			
Conversion of p-xylene, %	44.7	38.4	22.4	21.9	81.8	58.4	52.9	28.3			
Conversion of n-hexane, %	3.0	0 ^b	0 ^b	0 ^b	5.9	2.7	0.9	0.7			

^a Before final calcination; ^b traces of pentanes.

TABLE III
Properties of calcined boehmite sulfated with aluminum sulfate

Parameter	Catalyst														
	6	7	8	9	10	11	12	13	14	15					
Sulfur content in the precursor ^a , mmol g ⁻¹			4.39												
Calcination temperature of boehmite, °C	105	150	350	500	800	105	150	350	500	800	105	150	350	500	800
Surface area, m ² g ⁻¹	77	89	97	83	61	101	113	129	116	114	101	113	129	116	114
Sulfur content, mmol g ⁻¹	3.75	2.43	2.14	2.76	1.49	1.41	1.46	1.37	2.69	1.34	1.41	1.46	1.37	2.69	1.34
Adsorbed pyridine, mmol g ⁻¹	0.47	0.48	0.40	0.36	0.26	0.33	0.67	0.60	0.60	0.50	0.33	0.67	0.60	0.60	0.50
Adsorbed benzene, mmol g ⁻¹	0.19	0.33	0.32	0.18	0.09	0.25	0.34	0.29	0.23	0.20	0.25	0.34	0.29	0.23	0.20
Max. acid strength, -H ₀	14.52	14.52	14.52	13.2	12.7	14.52	14.52	13.2	12.7	8.2	14.52	14.52	13.2	12.7	8.2
Conversion of cyclohexene, %	92.0	96.1	91.8	94.4	82.7	91.8	95.3	82.7	87.7	65.1	91.8	95.3	82.7	87.7	65.1
Conversion of <i>p</i> -xylene, %	74.5	91.8	77.4	30.1	4.5	76.5	55.3	37.1	23.1	16.7	76.5	55.3	37.1	23.1	16.7
Conversion of <i>n</i> -hexane, %	1.0	1.9	1.9	0.4	0	0.9	0.9	0.2	0 ^b	0 ^b	0.9	0.9	0.2	0 ^b	0 ^b

^a Before final calcination; ^b traces of pentanes.

hydroxide. Except for the starting material calcined at 500 °C, the final sulfur content of the catalysts was inversely proportional to the calcination temperature. The amount of sulfur remaining in the catalysts was slightly higher when prepared with aluminum sulfate than in the case of impregnation of the precursors by sulfuric acid.

The surface area of the sulfated catalysts was significantly lower than the surface area of the original samples of the calcined boehmite. The higher the sulfur content or the calcination temperature, the lower was the surface area.

The total number of acid centres (the amount of adsorbed pyridine) of the sulfated catalysts increased distinctly when these catalysts were prepared using the precursors calcined at relatively low temperatures (the precursors 1 and 2, 3). This increase was higher when the catalysts were sulfated by sulfuric acid compared to aluminum sulfate treatment. Similar trend was also observed in the amount of adsorbed benzene (the measure of the number of strongly acid centers).

The strength of acid sites was affected very substantially by sulfate treatment. With one exception, all the sulfated catalysts contained acid centres with $H_0 \leq -12.7$ and, therefore, they can be considered solid superacids.

The sulfate treatment increased considerably the catalytic activity of the prepared catalysts. While the unsulfated precursors were practically inactive in all the test reactions, all the sulfated catalysts were active in the reactions of cyclohexene and *p*-xylene. Most of them were also active in the isomerisation of n-hexane. The general pattern of the catalytic activity followed the expected dependence on the strength of acid centres.

From all the factors examined, the strongest influence on the properties of the catalyst showed the temperature of the catalyst precursor calcination. In contrast to the results of Arata et al.¹¹, we found that the lower the calcination temperature of the starting aluminum hydroxide, the higher was the acid strength and catalytic activity of the sulfated catalysts. Our results confirm that the preparation of superacid catalysts is possible from both aluminum hydroxide (boehmite) and γ -alumina. Sulfate treatment of the calcined boehmite with sulfuric acid and aluminum sulfate produced catalysts with similar properties.

REFERENCES

1. Hino M., Arata K.: *J. Chem. Soc., Chem. Commun.* 1980, 851.
2. Hino M., Arata K.: *J. Chem. Soc., Chem. Commun.* 1979, 1148.
3. Hino M., Arata K.: *Chem. Lett.* 1979, 477.
4. Wang G. W., Hattori H., Tanabe K.: *Chem. Lett.* 1983, 277.
5. Matsubashi H., Arata K., Hino M.: *Chem. Lett.* 1988, 1027.
6. Arata K., Hino M.: *React. Kinet. Catal. Lett.* 25, 143 (1984).
7. Jin T., Yamaguchi T., Tanabe K.: *J. Phys. Chem.* 90, 4794 (1986).
8. Tanabe K., Yamaguchi T., Akiyama K., Mitou A., Ivabuchi K., Isogai K.: *Proc. 8th Int. Congr. Catal., Berlin*; Vol. 5, p. 601. Verlag Chemie, Weinheim 1984.

9. Hino M., Arata K.: *Chem. Lett.* 1985, 1483.
10. Yamaguchi T., Jin T., Tanabe K.: *J. Phys. Chem.* 90, 3148 (1986).
11. Arata K., Hino N.: *Appl. Catal.* 59, 197 (1990).
12. Makoto H., Kobayashi S., Arata K.: *J. Am. Chem. Soc.* 101, 6439 (1979).
13. Sauer O., Bensitel M., Saad A. B. M., Lavalley J. C., Tripp C. P., Morrow B. A.: *J. Catal.* 99, 104 (1986).
14. Walling C.: *J. Am. Chem. Soc.* 72, 1164 (1950).
15. Hochmann T.: *Thesis*. Czechoslovak Academy of Sciences, Prague 1990.
16. Linsen B. G.: *Physical and Chemical Aspects of Adsorbents and Catalysts*, p. 188. Academic Press, London 1970.

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