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Article

Effect of χ -alumina addition on H_2S oxidation properties of pure and modified γ -alumina

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ABSTRACT

The influence of the textural and acidic properties of γ - Al_2O_3 , $(\gamma+\chi)$ - Al_2O_3 , and α - Al_2O_3 on the catalytic activity, selectivity, and stability of direct H_2S oxidation has been studied. A comparison of the H_2S -to-S conversion effectiveness of aluminas with their acidic properties (identified by Fourier transform infrared spectroscopy and temperature programmed desorption of NH_3) shows that H_2S adsorption occurs predominantly on weak Lewis acid sites (LAS). γ -Alumina samples containing a χ -phase and/or modified Mg^{2+} ions have a greater concentration of weak LAS and exhibit greater catalytic activity. When alumina is treated with a sulfuric acid solution, strong LAS appear and the number of LAS decreases significantly. Modification of alumina with hydrochloric acid has a limited effect on LAS strength. Weak LAS are retained and double in number compared to that present in the unmodified alumina, but the treated sample has Al–Cl bonds. Alumina samples modified by sulfate and chloride anions exhibit poor catalytic activity in H_2S oxidation.

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1. Introduction

Low-temperature alumina is widely employed in industrial catalysis as a catalytically active material and as a support for catalytically active components. Its utility is based on the high specific surface area and surface acidity of different crystal modifications of alumina including γ -, η -, and χ - Al_2O_3 . γ - Al_2O_3 has been used most extensively. Pure, activated, and chlorinated γ -aluminas have been applied to the hydroisomerization of C_4 – C_6 hydrocarbons [1–3], alkylation of isobutane by alkenes [4,5], cracking of long-chain alkanes [6], and dehydrochlorination of chloroalkanes [7]. The activity and stability of alumina in these reactions is presumed to depend on surface acidity [2]. In our opinion, χ - Al_2O_3 deserves greater consideration owing to

the greater number of defects in its structure [8] and, consequently, more sites for stabilization of catalytically active components [9].

In this paper, we focus on the use of alumina as a catalyst and as a support for the direct oxidation of hydrogen sulfide. Direct catalytic H_2S oxidation to elemental sulfur selectively removes hydrogen sulfide from natural gas without appreciable conversion of the hydrocarbons [10,11]. The reaction takes place at a comparatively low temperature of 220–280 °C [11]. Although activated carbon [12–14] and zeolites [15] are commonly employed as catalysts for H_2S oxidation, individual oxides of transition metals (e.g., Fe_2O_3 , CuO , MnO_x , CrO_x , and V_2O_5) or their mixtures are more promising [16–32]. Granulated and monolithic aluminas, which are widely used as a support mate-

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rial for this process [17,18,22,25,33], possess a natural activity for direct H₂S oxidation. However, their activity and selectivity are insufficient, because alumina accelerates both the forward and reverse directions of the Claus reaction [34,35].

This work examines the oxidative interaction of hydrogen sulfide with different crystal modifications (γ , χ , and α) of alumina and with cation- and anion-modified aluminas. Fourier transform infrared (FTIR) spectroscopy of adsorbed CO as a probe molecule and temperature-programmed desorption of ammonia (NH₃-TPD) were used to characterize the surface acid properties of aluminas and to explain their catalytic activity in direct H₂S oxidation. The textural properties of aluminas also were used to identify structure-performance relationships.

2. Experimental

2.1. Preparation of Al₂O₃

Five spherical alumina samples, γ -Al₂O₃, (γ +15% χ)-Al₂O₃, (γ +35% χ)-Al₂O₃, (γ +50% χ)-Al₂O₃, and α -Al₂O₃ were prepared by hydrocarbon-ammonia molding [22,36,37]. Samples were treated with an acid peptizer [37] to impart plasticity to the aluminum hydroxide pastes. The acid mole fraction was 0.067 as in [36]. The γ -Al₂O₃ sample was prepared from aluminum hydroxide with a pseudoboehmite structure as in ref. [33]. γ -Al₂O₃ samples containing 15 and 35 wt% χ -Al₂O₃ were prepared from aluminum hydroxide produced by the thermal decomposition of gibbsite in a catalytic heat generator [36,37]. The sample containing 50 wt% γ -Al₂O₃ and χ -Al₂O₃ was produced from a mixture of gibbsite and pseudoboehmite. The χ -Al₂O₃ sample containing trace γ -Al₂O₃ was prepared from gibbsite. The above samples were calcined at 550 °C for 4 h in air. The spherical α -Al₂O₃ sample was prepared by thermal calcination of γ -Al₂O₃ at 1200 °C for 6 h.

MgO/(γ +15% χ)-Al₂O₃ was produced by modifying spherical granules of aluminum hydroxide with magnesium nitrate solution, drying at 110 °C, and heating at 550 °C as described elsewhere [33]. The MgO concentration in the calcined samples was 3.2 wt%. Sulfate-modified alumina samples were prepared by incipient wetness impregnation of spherical granules of (γ +15% χ)-Al₂O₃ with a sulfuric acid solution, drying at 110 °C, and calcining at 500 °C for 4 h. The sulfate content determined by X-ray fluorescence analysis varied from 1 to 10 wt% SO₄²⁻. The chlorinated alumina sample was prepared by impregnating

spherical granules of (γ +15% χ)-Al₂O₃ with a hydrochloric acid solution (0.5 mol/L), drying at 110 °C, and calcining at 500 °C for 4 h. The nominal chlorine concentration was 1 wt% Cl, but the actual Cl content determined by X-ray fluorescence (XRF) analysis was 0.35 wt%.

2.2. Characterization of Al₂O₃

The chemical composition of initial and spent aluminas was examined by XRF spectroscopy using an ARL analyzer with a Rh anode. The physicochemical properties of the samples are given in Table 1. The textural properties of the catalysts including specific surface area (S_{BET}), pore volume (V_{p}), and pore diameter (d) were determined by nitrogen adsorption isotherms at -196 °C using an ASAP2400 automated adsorption analyzer (Micromeritics, United States).

The phase composition of alumina was determined from X-ray diffraction (XRD) patterns recorded for $2\theta = 10^\circ$ – 70° at a scan rate of $1^\circ/\text{min}$ using the crystallographic databases X-ray Powder Diffraction Files JCPDS-ICDD and ICSD-for-WWW (database Fachinformationszentrum (FIZ), Karlsruhe, Germany, 2003-2010). The XRD patterns were obtained on an HZG-4C diffractometer (Freiberger Präzision Mechanik, Germany) using monochromatic Cu K_α radiation. The extent of χ - and γ -modification of the alumina samples was established from XRD data employing calibrating mixtures.

The compositions of spent and sulfated alumina samples were determined by differential thermal and thermogravimetric analysis (DTA-TG) on a NETZSCH STA 449 (Tetzsch-Geratebau GmbH, Germany) instrument. A 100-mg powdered sample was placed in a crucible and heated from 20 to 1000 °C at a rate of 10 °C/min in air (50 cm³/min).

2.3. FTIR experiments

A “BOMEM MB102” FTIR spectrometer was used for spectroscopic studies. Carbon monoxide adsorption was studied in a homemade low-temperature IR reactor/cell equipped with a heating chamber and a chamber with CaF₂ windows. The design allowed us to expose the sample to heat pretreatment under vacuum and then record a spectrum from -196 to 20 °C. Hydrogen sulfide adsorption was examined in a homemade high-temperature spectroscopic reactor/cell, whose design allowed for preheating of the sample under vacuum, adsorption

Table 1
Physicochemical properties of alumina samples.

No	Sample	Modifier (wt%)	$T_{\text{calc.}}$ (°C)	S_{BET} (m ² /g)	Pore volume (cm ³ /g)	XRD phase composition
1	γ -Al ₂ O ₃	–	550	214	0.46	γ -Al ₂ O ₃
2	(γ +15% χ)-Al ₂ O ₃	–	550	167	0.55	85% γ -Al ₂ O ₃ +15% χ -Al ₂ O ₃
3	(γ +35% χ)-Al ₂ O ₃	–	550	160	0.65	65% γ -Al ₂ O ₃ +35% χ -Al ₂ O ₃
4	(γ +50% χ)-Al ₂ O ₃	–	550	160	0.58	50% γ -Al ₂ O ₃ +50% χ -Al ₂ O ₃
5	(γ +90% χ)-Al ₂ O ₃	–	550	166	0.59	10% γ -Al ₂ O ₃ +90% χ -Al ₂ O ₃
6	α -Al ₂ O ₃	–	1200	9.3	0.37	α -Al ₂ O ₃
7	Mg ²⁺ /(γ +15% χ)-Al ₂ O ₃	Mg, 3.2	550	160	0.49	γ^* -Al ₂ O ₃ , $a \sim 7.952 \text{ \AA}$
6	SO ₄ ²⁻ /(γ +15% χ)-Al ₂ O ₃	SO ₄ ²⁻ , 1.25±2.5	500	169	0.53	85% γ -Al ₂ O ₃ +15% χ -Al ₂ O ₃
7	SO ₄ ²⁻ /(γ +15% χ)-Al ₂ O ₃	SO ₄ ²⁻ , 7.5±10	500	120–135	0.40–0.46	85% γ -Al ₂ O ₃ +15% χ -Al ₂ O ₃
8	Cl ⁻ /(γ +15% χ)-Al ₂ O ₃	Cl ⁻ , 1.0	500	165	0.58	85% γ -Al ₂ O ₃ +15% χ -Al ₂ O ₃

γ^* -Al₂O₃ – solid solution Mg²⁺ in γ -Al₂O₃.

of H₂S, and recording of a spectrum at 20–400 °C.

Triturated samples were pressed into 10–20 mg/cm² thick self-supported wafers. A catalyst wafer was placed in the low- or high-temperature spectroscopic reactor/cell and pretreated under vacuum (<10^{−3} mbar) at 400 °C for 4 h. CO or H₂S was then adsorbed on the catalyst.

Pure carbon monoxide was introduced to the spectroscopic reactor/cell at 2.5 mbar. An FTIR spectrum was recorded at room temperature at 1200–4000 cm^{−1} with 4 cm^{−1} resolution and 100 accumulated scans. The sample was cooled to −196 °C with liquid nitrogen to provide maximal CO adsorption on the sample, and a spectrum was recorded. A series of spectra were recorded as the temperature rose from −196 °C to ambient during nitrogen evaporation. This procedure allowed identification of different catalytic sites on the sample surface due to the continuous decrease in CO coverage during a single run. The spectra were normalized by wafer density.

The concentration and strength of Lewis acid sites (LAS) and Brønsted acid sites (BAS) were determined using methods described elsewhere [38,39]. The integrated intensities of absorption bands in the CO vibration regions of 2180–2240 cm^{−1} (LAS) and 2150–2175 cm^{−1} (BAS) were calculated from alumina spectra and were divided by the molar extinction coefficients. The latter quantity (cm/μmol) was assumed to equal 1.23 for the band at 2240–2220 cm^{−1}, 1.1 at 2215–2205 cm^{−1}, 1.0 at 2200 cm^{−1}, 0.9 at 2190–2196 and 2177–2180 cm^{−1} [38,39,40], and 2.6 at 2150–2175 cm^{−1} [40,41]. The BAS content of aluminas was determined using the 3650–3800 cm^{−1} OH vibration region and a molar extinction coefficient of 5.3 cm/μmol [42]. The uncertainty of the quantitative measurements was 20%.

Hydrogen sulfide was added to the spectroscopic reactor/cell, which contained the heat-pretreated sample wafer at a pressure of 40 mbar. Hydrogen sulfide adsorption on alumina was studied at 20 °C, and H₂S transformation was examined at 100, 200, and 300 °C by FTIR spectroscopy. FTIR spectra were recorded at 1000–4000 cm^{−1} with 4 cm^{−1} resolution and 100 accumulated scans.

2.4. NH₃-TPD experiments

The surface acidity of aluminas also was studied by NH₃-TPD. NH₃-TPD experiments were carried out in a flow apparatus equipped with a thermal conductivity detector. A 100-mg sample with a fractional composition of 0.25–0.50 was mixed with 100 mg of quartz of similar granule size. The sample was pretreated in an argon stream (30 cm³/min) at 500 °C for 2 h to remove adsorbed water. It was cooled to 75 °C, and ammonia was adsorbed by flowing a mixture of NH₃ (0.35 vol%) in He over the sample for 1 h. The sample was flushed with helium (30 cm³/min) to remove ammonia from the catalyst pores and cooled to room temperature. The NH₃-TPD curve was recorded by passing helium through the sample at a rate of 30 cm³/min and heating from 25 to 700 °C at a rate of 10 °C/min. The total surface acidity was estimated from the amount of desorbed ammonia (μmol/g) assuming single-site ammonia adsorption.

2.5. Activity tests in the reaction of hydrogen sulfide oxidation

The catalytic activity and stability of the samples was measured in a fixed-bed catalytic reactor at a stoichiometric ratio of reagents (H₂S/O₂ = 2/1) in He. The reactor was positioned vertically so that the sulfur generated in the experiment flowed down to be collected in a glass container. The H₂S concentration in the initial feed was 0.6 vol%. A 1-cm³ alumina sample with a 0.25–0.5 mm granule size was placed in the quartz reactor. The space velocity of the feed was 100 cm³/min, and the gas hour space velocity (GHSV) was 6000 h^{−1}. The catalytic activity of aluminas was studied at 200–400 °C, and the stability of their catalytic behavior was examined at 300 °C over 50 h.

Reagents (H₂S, O₂) and reaction products (SO₂, COS) were analyzed using a “Tsvet-500M” gas chromatograph equipped with a TCD and a Teflon column (3-m length, 3-mm i.d.) with a “Hayesep C” sorbent modified with 0.5% H₃PO₄. The space velocity of the He carrier gas was 30 cm³/min, and the operating temperature of the column was 150 °C.

Experimental data were presented in terms of hydrogen sulfide conversion and sulfur selectivity as a function of temperature. The H₂S conversion (*X*_{H₂S}, %) and selectivity of H₂S oxidation to sulfur (*S*_S, %) were calculated from experimental concentrations of reagents and products using the following equations:

$$X_{\text{H}_2\text{S}} = \frac{C_{\text{H}_2\text{S}}^0 - C_{\text{H}_2\text{S}}}{C_{\text{H}_2\text{S}}^0} \times 100 (\%)$$

$$S_{\text{S}} = \frac{C_{\text{H}_2\text{S}}^0 - C_{\text{H}_2\text{S}} - C_{\text{SO}_2} - C_{\text{COS}}}{C_{\text{H}_2\text{S}}^0} \times 100 (\%)$$

where *C*_{H₂S}⁰ is the concentration of hydrogen sulfide (vol%) in the feed, and *C*_{H₂S}, *C*_{SO₂}, and *C*_{COS} are the concentrations of hydrogen sulfide (vol%), sulfur dioxide (vol%), and COS (vol%) at the reactor outlet. The temperature dependences of H₂S conversion and selectivities of sulfur production were used to compare the catalytic behaviors of aluminas with various crystal modifications.

3. Results and discussion

3.1. Catalytic activity of alumina with different crystal modifications

Fig. 1 displays the catalytic characteristics of aluminas in the direct oxidation of H₂S according to the reaction, H₂S + 1/2O₂ = 1/2S_n + H₂O, where *n* = 6 or 8, at 100–300 °C. The total H₂S conversion and selectivity of H₂S transformation to sulfur are represented. The experimental data show that the crystal modification of alumina significantly affects the catalytic activity. The total H₂S conversion over alumina at 250 °C increases as α-Al₂O₃ < γ-Al₂O₃ < (γ+15%χ)-Al₂O₃ < (γ+35%χ)-Al₂O₃ < (γ+50%χ)-Al₂O₃ ~ (γ+90%χ)-Al₂O₃. Maximum H₂S conversion of 80%–90% occurred over samples containing mixtures of γ-Al₂O₃ with 35–90 wt% χ-Al₂O₃. H₂S conversion over γ-Al₂O₃ and α-Al₂O₃ increased with temperature and achieved a maximum value at 375–400 °C. Maximum H₂S conversion over samples containing χ-Al₂O₃ occurred at temperatures as low as

Fig. 1. Total H₂S conversion (A) and sulfur selectivity (B) in H₂S oxidation on aluminas. (1) γ -Al₂O₃, (2) (γ +15% χ)-Al₂O₃, (3) (γ +35% χ)-Al₂O₃, (4) (γ +50% χ)-Al₂O₃, (5) (γ +90% χ)-Al₂O₃, (6) α -Al₂O₃.

300 °C for 15 wt% χ -Al₂O₃ and 250 °C for 50–90 wt% χ -Al₂O₃. H₂S conversion over samples containing χ -Al₂O₃ diminished slightly at temperatures above 300 °C.

Selectivity with regard to sulfur formation was nearly 100% at 200 °C for alumina samples with different crystal modifications. The main products of H₂S oxidation by O₂ are sulfur and water; SO₂ and COS are not observed under these conditions. At 250 °C, we observed SO₂ among the reaction products and gradually diminished sulfur selectivity due to the reaction, $\text{H}_2\text{S} + 3/2 \text{O}_2 \rightarrow \text{H}_2\text{O} + \text{SO}_2$, and the reverse Claus process, $3\text{S} + 2\text{H}_2\text{O} \leftrightarrow 2\text{H}_2\text{S} + \text{SO}_2$. The phenomenon is more pronounced at higher temperatures, because sulfur oxidation becomes prevalent under these conditions. When the temperature was increased to 400 °C, sulfur selectivity decreased to 90%–92% on γ -Al₂O₃ and α -Al₂O₃ and to 82% on (γ +35% χ)-Al₂O₃. The effect of temperature on the change in sulfur selectivity is enhanced with χ -Al₂O₃. A greater χ -Al₂O₃ content leads to lower sulfur selectivity at 400 °C as shown in Fig. 1(B). Thus, S_s was only 53% for the 90% χ -Al₂O₃ sample.

The results above are in accord with those in the literature [16,21,25]. The same tendencies are observed for catalysts

containing Fe₂O₃ and Cr₂O₃ supported on alumina [16,25], silica [16,21], zirconia [16], and other oxide materials. These catalysts exhibit high selectivity and efficiency of H₂S conversion to elemental sulfur at temperatures close to or slightly above the sulfur dew point, but selectivity diminishes due to SO₂ formation at higher reaction temperatures. For example, Fe₂O₃/ γ -Al₂O₃ provides 92% H₂S conversion and 96% sulfur selectivity at 230 °C [25], although the GHSV was half that of our experiments (3000 versus 6000 h⁻¹). Conversion increased to 98%–99% with increasing temperature, but sulfur selectivity decreased and did not exceed 41% at 350 °C [25]. On the low surface area α -Al₂O₃ modification [16], efficient H₂S conversions (97%–98%) were achieved with Fe₂O₃/ α -Al₂O₃ at 280–400 °C, although sulfur selectivity began to deteriorate (70%–85% at GHSV = 3000–12000 h⁻¹). Thus, 35 wt% χ -Al₂O₃ aluminas are more active and more selective in H₂S → S oxidation at 200–300 °C. Their catalytic behavior is comparable to, and in some cases greater than, that of the supported Fe₂O₃ catalysts mentioned in the literature.

To study the catalytic stability of χ -alumina, we tested it in a H₂S/O₂/He feed at 300 °C for 50 h and compared the results with those for γ -Al₂O₃. The results of the stability test are illustrated in Fig. 2. Both materials catalyzed the oxidation of H₂S to sulfur without deactivation for at least 50 h under a stoichiometric H₂S/O₂ mixture at 300 °C. The (γ +35% χ)-Al₂O₃ catalyst was more active and produced more sulfur compared with γ -Al₂O₃ in the stability tests. The mean sulfur yield over (γ +35% χ)-Al₂O₃ was 78%–82%, which is slightly less than the value allowed by thermodynamics (88%). The mean sulfur yield over γ -Al₂O₃ was nearly 50%. Ceramic supports prone to formation of sulfates (MgO, ZrO₂, TiO₂, and Al₂O₃) are generally believed [16] to exhibit poor characteristics in the oxidation of hydrogen sulfide to sulfur and to be deactivated under the reaction conditions. In contrast to [16], we observed good stability in the catalytic behavior of the (γ +35% χ)-Al₂O₃ catalyst.

Table 2 shows the material balance of H₂S oxidation over γ -Al₂O₃ and (γ +35% χ)-Al₂O₃ following a stability test. The cata-

Fig. 2. Total H₂S conversion (1), sulfur selectivity (2), SO₂ selectivity (3) and sulfur production (4) in H₂S oxidation on aluminas. (A) γ -Al₂O₃, (B) (γ +35% χ)-Al₂O₃. Curve (5) shows sulfur production allowed by thermodynamics.

Table 2Material balance of the H₂S oxidation for sulfur.(a) catalyst: γ -Al₂O₃

Input	g	Output	g
Sulfur introduced to the reactor as H ₂ S for 50h, the feed 100 cm ³ /min and H ₂ S concentration 0.6 vol%	2.560	Sulfur output from the reactor as H ₂ S	1.150
		Sulfur output from the reactor as S	1.240
		Sulfur output from the reactor as SO ₂	0.115
		Sulfur accumulated by the catalyst	0.001
Total	2.560	Total	2.506
Deviation of output and input of sulfur $\Delta = 0.054$ (2%)			

(b) catalyst: (γ +15% χ)-Al₂O₃

Input	g	Output	g
Sulfur introduced to the reactor as H ₂ S for 50h, the feed 100 cm ³ /min and H ₂ S concentration 0.6 vol%	2.560	Sulfur output from the reactor as H ₂ S	0.382
		Sulfur output from the reactor as S	1.900
		Sulfur output from the reactor as SO ₂	0.145
		Sulfur accumulated by the catalyst	0.003
Total	2.560	Total	2.430
Deviation of output and input of sulfur $\Delta = 0.13$ (5%)			

lysts provided average H₂S conversions of 55% and 85%, respectively, at 300 °C (Fig. 2). The main sulfur-containing products were sulfur and sulfur dioxide. The average selectivities for these products were 95% and 4%, respectively, on γ -Al₂O₃ and 92% and 7% on (γ +35% χ)-Al₂O₃. Some sulfur deposited on the catalysts. According to XRF analysis, spent γ -Al₂O₃ and (γ +35% χ)-Al₂O₃ samples accumulated 0.23 and 0.42 wt% sulfur, respectively, during the experiment. The minimum deviation of the sulfur material balance is $\leq 5\%$, which can be attributed to the uncertainty of the measurements.

3.2. Catalytic activity of cation/anion modified aluminas

The catalytic properties of aluminas modified with Mg²⁺ cations or Cl⁻ and SO₄²⁻ anions are shown in Fig. 3. The (γ +15% χ)-Al₂O₃ sample modified with Mg²⁺ produced 82% H₂S conversion at 200–400 °C. This value was 20% greater than that achieved with the unmodified sample at 250 °C and differed by only 5% at 300 °C. Moreover, the sulfur selectivity over Mg²⁺/(γ +15% χ)-Al₂O₃ equaled 93%–94% at 350 °C and above (Fig. 3, curve (2)). The results were superior to those obtained with the unmodified sample.

Modification of (γ +15% χ)-alumina by sulfate ions was ac-

companied by a deterioration in catalytic performance. Hydrogen sulfide conversion was significantly reduced at temperatures below 300 °C and slightly so above 300 °C (Fig. 3(A), curve (3)). The selectivity of sulfur formation was reduced by 5%–10% over the entire temperature range (Fig. 3(B), curve (3)). Modification of (γ +15% χ)-Al₂O₃ with chloride ions resulted in a dramatic decrease in H₂S conversion, although selectivity increased to 100% at temperatures above 350 °C (Fig. 3, curve (4)).

3.3. Surface acidity of aluminas with different crystal modifications

We used NH₃-TPD and FTIR spectroscopy of adsorbed CO as molecular probes of Lewis and Brønsted acid sites to study the surface properties of aluminas. The FTIR spectra of CO adsorbed on alumina with γ , (γ + χ), and α crystal modifications, which are presented in Fig. 4, are discussed first. Absorption bands at 2186, 2210, and 2216 cm⁻¹ in the CO stretching region occur in the spectrum of γ -Al₂O₃ at 20 °C. There also are bands at 2147 and 2156 cm⁻¹ in the -196 °C spectrum. After addition of χ -phase Al₂O₃ to γ -Al₂O₃, new bands appear at 2195–2197 and 2200–2206 cm⁻¹, and the band at 2147 cm⁻¹ vanishes. The frequencies of two absorption bands increase with increasing χ -phase content: 2186 and 2195 cm⁻¹ for (γ +15% χ)-Al₂O₃, 2187 and 2197 cm⁻¹ for (γ +35% χ)-Al₂O₃, and 2189 and 2194 cm⁻¹ for (γ +50% χ)-Al₂O₃ and (γ +90% χ)-Al₂O₃. Also, when the χ -phase content equals or exceeds 50%, the bands at 2210 and 2220 cm⁻¹ reappear in the spectrum. According to published data [20,40,41], the absorption bands at 2140–2155 cm⁻¹ are attributed to CO hydrogen-bonded to hydroxyl groups on the alumina surface. The bands at 2210–2240 and 2180–2200 cm⁻¹ are assigned [38,40–45] to surface LAS that are characterized as unsaturated aluminum cations (Al³⁺) with tetrahedral coordination [41,43,45] at crystallographic defects [46] and with octahedral coordination [44,45] at the regular defects of low-index crystallite faces [45–47], respectively. Shifting of the 2143 cm⁻¹ frequency to greater wavenumbers indicates an

Fig. 3. Total H₂S conversion (A) and sulfur selectivity (B) in H₂S oxidation on aluminas. (1) (γ +15% χ)-Al₂O₃, (2) MgO/(γ +15% χ)-Al₂O₃, (3) SO₄²⁻/(γ +15% χ)-Al₂O₃, (4) Cl⁻/(γ +15% χ)-Al₂O₃.

modified aluminas are shown in Fig. 5(A). The total acid site content estimated by NH_3 -TPD is indicated in Table 3. The $\gamma\text{-Al}_2\text{O}_3$ sample is characterized by ammonia desorption over a wide temperature range with pronounced maxima at 200, 355, and 530 °C and shoulders at 460 and 615 °C. The peaks correspond to ammonia desorption from different acidic sites, which are divided [50] according to the energy of ammonia chemisorption into Lewis acid sites (200–400 °C) and Brønsted acid sites (400–600 °C). The LAS and BAS contributions to the total acidity of the sample are comparable. The proton acid sites have ammonia desorption energies greater than 150 kJ/mol. Moderately strong LAS are characterized by ammonia desorption energies of 85–110 and 110–150 kJ/mol. The $(\gamma+90\%\chi)\text{-Al}_2\text{O}_3$ sample has a broad asymmetric ammonia desorption peak with a maximum at 415 °C and a shoulder at 530 °C. These features correspond to Lewis acid and Brønsted acid sites, respectively. Moderately strong LAS with an NH_3 desorption energy of 110–150 kJ/mol make a greater contribution to the total sample acidity. The BAS content is much lower than in the $\gamma\text{-Al}_2\text{O}_3$ sample. The NH_3 -TPD experiments show that the acidic properties of $(\gamma+15\%\chi)\text{-Al}_2\text{O}_3$ and $(\gamma+35\%\chi)\text{-Al}_2\text{O}_3$ are a superposition of the γ - and χ -phase characteristics. An increase in the χ -phase content leads to an increase in the number of moderately strong LAS with an ammonia desorption energy of 110–150 kJ/mol and a decrease in the BAS and weaker LAS contributions. The total acidity of the two-phase samples, which was calculated from the amount of ammonia desorbed by NH_3 -TPD, is less than that of the pure γ -phase and χ -phase aluminas. For $\gamma\text{-Al}_2\text{O}_3$ and $(\gamma+\chi)\text{-Al}_2\text{O}_3$, the NH_3 -TPD results are consistent with the FTIR data of adsorbed carbon monoxide.

3.4. Surface acidity of cation/anion modified aluminas

Fig. 6 shows spectra of CO adsorbed on the surface of $(\gamma+15\%\chi)\text{-Al}_2\text{O}_3$ modified with Mg^{2+} , SO_4^{2-} , and Cl^- ions. CO adsorption on the MgO -modified sample yields an absorption band at 2154 cm^{-1} , which corresponds to the vibration of CO adsorbed at acidic OH sites [38,43,49], and a band at 2181–2193 cm^{-1} belonging to the vibration of CO adsorbed on

Fig. 6. FT-IR spectra of CO adsorbed on $(\gamma+15\%\chi)\text{-Al}_2\text{O}_3$ samples modified by MgO , SO_4^{2-} and Cl^- at different coverage of the surface with CO. The upper spectra were recorded at temperature -196°C and the lower spectra—at room temperature, other spectra—at increasing of temperature up to ambient.

LAS [38,40,41,43]. The frequency shifts from 2187 to 2181 cm^{-1} and from 2197 to 2193 cm^{-1} indicate a decrease in LAS strength [41,43]. This is accompanied by a twofold increase in the concentration of Al^{3+} LAS. The strengths and concentrations of LAS and BAS sites on the surface of modified alumina samples are given in Table 3.

CO adsorption on (10%)sulfate-modified $(\gamma+15\%\chi)\text{-Al}_2\text{O}_3$ produces absorption bands at 2210 cm^{-1} and 2199 cm^{-1} , which are attributed to CO adsorbed on intermediate and weak Al^{3+} LAS [40,43], respectively. The LAS strength of the 2210 cm^{-1} band is 35%–45% greater than that of the sites of the original $(\gamma+15\%\chi)$ -alumina. However, the number of LAS decreases significantly. There also is a band at 2168 cm^{-1} , which is assigned to CO H-bonded to hydroxyl groups on the catalyst surface [38,43,49]. Their concentration changes little compared to unmodified $(\gamma+15\%\chi)$ -alumina, but their proton acidity increases markedly.

FTIR spectra of CO adsorbed on Cl^- -modified $(\gamma+15\%\chi)\text{-Al}_2\text{O}_3$ exhibit two types of LAS on the catalyst surface. These are characterized by absorption bands at 2191 and 2198 cm^{-1} . Their strength is slightly greater (by 10%–15%)

Fig. 5. NH_3 -TPD spectra for different Al_2O_3 samples. (A) the unmodified ones with crystal phase γ (1), $(\gamma+15\%\chi)$ (2), $(\gamma+35\%\chi)$ (3), and $(\gamma+90\%\chi)$ (4); (B) samples of $(\gamma+15\%\chi)\text{-Al}_2\text{O}_3$ (1) modified by MgO (2), SO_4^{2-} (3) and Cl^- (4).

than that of unmodified alumina. The Cl-modified sample has twice as many Lewis acid ($\nu_{\text{LO}} = 2195\text{--}2198\text{ cm}^{-1}$) and Brønsted acid ($\nu_{\text{LO}} = 2154\text{ cm}^{-1}$) sites, while the number of LAS with $\nu_{\text{LO}} = 2186\text{--}2191\text{ cm}^{-1}$ is comparable to that of the unmodified sample. This occurs, because interaction of HCl with an $>\text{Al-O-Al}<$ fragment [2] forms terminal $>\text{Al-OH}$ (band at 2154 cm^{-1}) and $>\text{Al-Cl}$ (band at 2198 cm^{-1}) groups. The chloride ion content of the calcined $\text{Cl}/(\gamma+15\%\chi)\text{-Al}_2\text{O}_3$ sample was less than of the sample impregnated with hydrochloric acid and dried in air, because chloride ions are partially removed as AlCl_3 or HCl during thermal treatment at $500\text{ }^\circ\text{C}$ [51].

The NH_3 -TPD profiles of modified aluminas are shown in Fig. 5(B). Ammonia desorption from MgO- and Cl-modified samples begins at lower temperatures (200 and $250\text{ }^\circ\text{C}$) than from unmodified $(\gamma+15\%\chi)\text{-Al}_2\text{O}_3$ ($400\text{ }^\circ\text{C}$) and continues to $600\text{ }^\circ\text{C}$. The majority of NH_3 desorbs from $\text{Cl}/(\gamma+15\%\chi)\text{-Al}_2\text{O}_3$ and $\text{MgO}/(\gamma+15\%\chi)\text{-Al}_2\text{O}_3$ at temperatures of $295\text{ }^\circ\text{C}$ ($85\text{--}110\text{ kJ/mol}$) and $415\text{--}430\text{ }^\circ\text{C}$ ($110\text{--}150\text{ kJ/mol}$), respectively, which indicates the presence of weaker LAS sites with lower ammonia desorption energies than in the unmodified sample. NH_3 amount from unmodified and MgO-modified $(\gamma+15\%\chi)\text{-Al}_2\text{O}_3$ at $500\text{--}700\text{ }^\circ\text{C}$ are the same indicating similar BAS concentrations in these samples. The BAS content is somewhat less in $\text{Cl}/(\gamma+15\%\chi)\text{-Al}_2\text{O}_3$. Sulfate(5%)-modified and unmodified $(\gamma+15\%\chi)\text{-Al}_2\text{O}_3$ desorb ammonia over the same temperature range ($400\text{--}700\text{ }^\circ\text{C}$), but the intensity of NH_3 desorption from the modified sample is greater. Because this peak can be a superposition of ammonia and sulfur dioxide desorptions, the BAS concentration (Table 3) determined in this temperature range can be overestimated. SO_2 evolution during NH_3 -TPD experiments was previously reported for sulfated alumina samples and was attributed to a redox reaction between sulfate groups and adsorbed NH_3 [52].

Modification of alumina with Cl^- and Mg^{2+} ions alters surface acidity primarily by formation of more Lewis acid sites, whereas sulfate ions increase the BAS content. Chlorination of $(\gamma+15\%\chi)\text{-alumina}$ significantly changes the strength of the LAS

notably by decreasing the ammonia desorption energy from $110\text{--}150$ to $85\text{--}100\text{ kJ/mol}$. The trends of increasing concentration of protonated and deprotonated sites, which we observe for $(\gamma+15\%\chi)\text{-alumina}$ modified by Mg^{2+} or sulfate/chloride ions, respectively, are consistent with the data published in [41] for modified $\gamma\text{-Al}_2\text{O}_3$ samples.

3.5. Textural properties of aluminas with different crystal modifications

The textural properties of aluminas with γ , $(\gamma+15\%\chi)$, and $(\gamma+35\%\chi)$ crystal modifications, including alumina modified by Mg^{2+} cations, have been described in detail by Ismagilov et al. [33,36,37]. Some of these data are discussed below. The isotherms of low temperature nitrogen adsorption on aluminas with γ , $\gamma+\chi$, and α crystal morphologies and aluminas modified by Mg^{2+} or sulfate/chloride ions are shown in Fig. 7. It is known [53,54] that a phase transition from $\gamma\text{-Al}_2\text{O}_3$ to $\alpha\text{-Al}_2\text{O}_3$, which are low- and high-temperature modifications of alumina, respectively, leads to a sharp change in textural characteristics (Fig. 7, curves (1) and (7)). Modification of $\gamma\text{-Al}_2\text{O}_3$ by addition of the low-temperature χ -form up to $35\text{ wt}\%$ does not lead to a significant change in texture. Low-temperature nitrogen adsorption isotherms of $\gamma\text{-Al}_2\text{O}_3$ and $(\gamma+15\%\chi)\text{-Al}_2\text{O}_3$ are type IV, which is characteristic of 2- to 50-nm microporous or mesoporous materials having some pores filled with capillary condensed nitrogen as the saturation vapor pressure is approached. A hysteresis loop is present in the adsorption isotherms of $\gamma\text{-Al}_2\text{O}_3$ and its mixture with $\chi\text{-Al}_2\text{O}_3$. In the low-temperature nitrogen adsorption isotherms (Fig. 7(a)), there are tendencies for increased nitrogen adsorption with increasing χ -alumina content and for saturation of the pores at somewhat greater relative pressures. This trend usually indicates a change in the pore size and shape of porous materials, which we observe in pore-size distribution curves (Fig. 7(b)). The samples based on $\gamma\text{-Al}_2\text{O}_3$ and $(\gamma+15\text{--}35\%\chi)\text{-Al}_2\text{O}_3$ are biporous, and the fraction of $\leq 4\text{-nm}$ pores decreases while that

Fig. 7. Nitrogen adsorption isotherms (a) and pore size distribution (b) for aluminas with γ (1), $(\gamma+15\%\chi)$ (2), $(\gamma+35\%\chi)$ (3), and α (7) crystal phases, and $(\gamma+15\%\chi)\text{-Al}_2\text{O}_3$ modified by MgO (4), SO_4^{2-} (5) and Cl^- (6).

of 7- to 20-nm pores increases with increasing χ -phase content. The prevailing pore size also increases from 7 nm for γ -Al₂O₃ to 11–12 nm for $(\gamma+15\%\chi)$ -Al₂O₃ and to 14–15 nm for $(\gamma+35\%\chi)$ -Al₂O₃. In addition, the specific surface areas calculated by Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) for low-temperature alumina samples differ by approximately 30%. This means that the pore-size distribution curves indicate ~70% of the material to be mesoporous. The remaining pores are less than 3-nm in size and are not represented in the distribution curves (Fig. 7(b)). The pore-size distribution of α -Al₂O₃ is markedly heterogeneous. The distribution maximum occurs at 4 nm, and larger 5-, 8-, and 40-nm pores also are present. However, the contribution of micropores and mesopores is insignificant, because the ratio of micro/mesopore to macropore volumes is about 0.07. The α -Al₂O₃ sample possesses a very small surface area (9.3 m²/g).

The low-temperature nitrogen adsorption isotherms for modified $(\gamma+15\%\chi)$ -Al₂O₃ shown in Fig. 7(a) (curves (4)–(6)) are type IV, as are the isotherms of the unmodified sample. However, at the same relative adsorbate pressure, the Mg²⁺- and Cl⁻-modified samples bind less adsorbate and reach saturation at lower pressures relative to the unmodified sample. The textural characteristics of modified MgO/ $(\gamma+15\%\chi)$ -Al₂O₃ and Cl/ $(\gamma+15\%\chi)$ -Al₂O₃ are close to those of the unmodified sample. The specific surface area is about 150–165 m²/g, and the micro/mesopore volume is about 0.49–0.58 cm³/g. These values indicate a homogeneous distribution of modifying ions over the alumina surface. A comparison of nitrogen adsorption isotherms of MgO/ $(\gamma+15\%\chi)$ -Al₂O₃, Cl/ $(\gamma+15\%\chi)$ -Al₂O₃, and $(\gamma+15\%\chi)$ -Al₂O₃ reveals a slight increase in the fraction of fine (3- to 4-nm) pores and a decrease in size (from 11–12 to 9 nm) of large pores, which indicates near-surface localization of the modifying ions.

The textural characteristics of $(\gamma+15\%\chi)$ -Al₂O₃ modified with sulfate ions depend on the sulfate ion content. For example, the sample texture changes slightly when 1–2.5 wt% of the modifier is added. This amount corresponds no more than ¼ of that required for monolayer coverage of sulfate ions on the $(\gamma+15\%\chi)$ -Al₂O₃ surface. An increase in sulfate ion loading (up to 7.5–10 wt%) leads to creation of a uniformly porous sample with a large pore size (14–15 nm instead of 11–12 nm; Fig. 7(b), curve (5)), but with a small specific surface area (120–135 versus 167 m²/g) and a reduced pore volume (0.40–0.46 versus 0.55 cm³/g) relative to the unmodified sample. These changes may be due to the surface dissolution of alumina to aluminum sulfate during impregnation with sulfuric acid and to precipitation of Al₂(SO₄)₃ into the larger pores upon calcination. Some mesopores may be transformed into ≤3-nm micropores and not observed in the pore-size distribution curves. This possibility is suggested by the difference in the BET and BJH specific surface areas by a factor of 1.25–1.40. The data obtained on the texture of modified alumina samples are in good agreement with the results of [41,52] from one perspective. However, a monolayer coating by four sulfate groups per nm² [55] usually is achieved at concentrations of 10–12.5 wt% depending on the specific Al₂O₃ surface [52]. A monolayer

coating was achieved at 5 wt% SO₄²⁻ with our $(\gamma+15\%\chi)$ -Al₂O₃ sample. The apparent contradiction can be explained by the presence of NO₃⁻ groups in the initial alumina sample, which decreases the number of centers for sulfate ion stabilization. A decrease in BAS concentration and an increase in LAS concentration were observed for γ -Al₂O₃ obtained by peptizing pseudoboehmite with nitric acid [56]. We used pastes peptized with nitric acid to obtain granular samples of γ -Al₂O₃, $(\gamma+15\%\chi)$ -Al₂O₃, and $(\gamma+35\%\chi)$ -Al₂O₃.

3.6. Discussion

3.6.1. Correlation between surface acid properties and catalytic behaviors of aluminas

Many aluminas are used as a catalyst support for the selective oxidation of hydrogen sulfide [18,34,35]. Thus, it is interesting to note that alumina also contributes to the activity and selectivity of the overlying catalyst. Hydrogen sulfide oxidation data for aluminas with different crystal modifications indicate that samples containing a mixture of γ -Al₂O₃ with 35–90 wt% χ -Al₂O₃ exhibit the greatest catalytic activity. These samples provide 94%–99% selective sulfur formation at temperatures below 300 °C, but differ in their selectivity above 300 °C. Differences in sulfur selectivity can be explained by both the textural (surface area, pore volume, and pore-size distribution) and acidic properties of the aluminas. Pure γ -Al₂O₃ and samples modified with χ -Al₂O₃ are characterized by large specific surface areas of 214 and 160–166 m²/g, respectively. Although these values differ by 25%, the disparity does not clarify the differences in catalytic behavior. Greater H₂S conversion and sulfur selectivity occur with small specific surface area of low-temperature crystal modifications of alumina. The effect of textural properties on sulfur selectivity is more pronounced for α -Al₂O₃, whose textural characteristics differ greatly from those of low-temperature modifications of alumina. Unlike the low-temperature examples of γ -Al₂O₃ and $(\gamma+\chi)$ -Al₂O₃, the sample of α -Al₂O₃ is a wide-pore material with a small surface area. Thus, sulfur selectivity over α -Al₂O₃ decreases from 100% to 90% even at 250 °C. The effect of catalyst pore structure on the selectivity of hydrogen sulfide oxidation is known [57–59] to be associated with the capillary condensation of sulfur vapor in narrow pores. Capillary condensation was observed in zeolites and on activated carbon [16,60], where H₂S is oxidized primarily to elemental sulfur. The latter is effective in the selective oxidation of hydrogen sulfide [61].

According to literature data [62], adsorption of hydrogen sulfide on BAS does not activate H₂S, but Lewis acid and basic sites activate and decompose H₂S to SH and H groups. Thus, we decided to investigate the correlation between LAS content and the catalytic oxidation of H₂S by aluminas. Fig. 8(a) displays hydrogen sulfide conversion as a function of the weak LAS content that is characterized by heats of CO adsorption of 32–35 kJ/mol and FTIR bands at 2186–2195 cm⁻¹. These LAS prevail in low-temperature aluminas. The concentration of weak LAS on the alumina surface unambiguously influences hydrogen sulfide oxidation activity. H₂S conversion increases linearly with the weak LAS content at 200 °C. H₂S conversion

Fig. 8. H₂S conversion on the aluminas vs. content of LAS of weak strength (a.b. 2186 cm⁻¹) (a) and BAS (a.b. 2155–2161 cm⁻¹) (b). There are also presented data for the sulfate-modified alumina (circle symbols, a.b. 2199–2210 cm⁻¹), the chloride-modified alumina (triangle symbols, a.b. 2191 cm⁻¹) and the MgO-modified alumina (rhombus symbols, a.b. 2181 cm⁻¹).

also increases with LAS content at 250 and 300 °C, reaches a maximum at 800–830 μmol/g, and changes only slightly thereafter. Modification of (γ-15%χ)-Al₂O₃ with MgO confirms this supposition by increasing H₂S conversion from 50% to 62% at 200–250 °C accompanied by an increase (from 630 to 1250 μmol/g) in the concentration of LAS. At 300 °C, the difference between the activity of the MgO-modified and unmodified samples (γ-15%χ)-Al₂O₃ becomes inconsequential. Surface modification of (γ+15%χ)-Al₂O₃ with sulfate ion (~10 wt%) completely suppresses the formation of weak LAS based on FTIR evidence. Thus, the activity of the sulfate-treated sample is diminished relative to that of the unmodified sample at temperatures below 250 °C. When the temperature is greater than 300 °C, the effect of sulfate ion on H₂S conversion and sulfur selectivity becomes less pronounced.

Addition of Cl⁻ (1 wt%) to (γ+15%χ)-Al₂O₃ significantly deactivates the catalyst. The maximum H₂S conversion is only 35%. According to FTIR spectroscopy, the acidic properties of the alumina surface change relative to those of the unmodified sample. The number of weak LAS increases some and their strength increases slightly (10%–15%), whereas the intermediate LAS content (38 kJ/mol) doubles. Chlorination of γ-alumina by hydrochloric acid is known [2,41] to enhance the Brønsted acidity of the surface, whereas Al³⁺ LAS become bound by chloride anions [2,4,5]. On the one hand, correlation between the surface acidic properties of Cl⁻-modified alumina and its diminished catalytic activity does not support our hypothesis of the key role of LAS in H₂S oxidation. On the other hand, the decrease in catalytic activity is likely caused by the negative effect of Cl⁻ ion plus the increased concentration of BAS. The presence of chloride ions on the alumina surface and their interaction with Al³⁺ inhibit adsorption of hydrogen sulfide, because the latter is a weaker acid than HCl. BAS do not activate H₂S during adsorption [62].

Fig. 8(b) illustrates the relationship between hydrogen sulfide conversion and BAS content in aluminas. A threefold increase in BAS content (from 60 to 160 μmol/g) on the surface

of low-temperature aluminas has no practical effect on the catalytic oxidation of hydrogen sulfide at 250–300 °C. Although an increase in BAS content of only 6% in (γ+15%χ)-Al₂O₃ is critical for H₂S conversion at 250 °C, it does not influence conversion at 300 °C. The large BAS content in γ-alumina and its small content in α-Al₂O₃ both lead to a decrease in catalytic activity. The properties of modified (γ+15%χ)-Al₂O₃ cannot be described using this acidity-performance relationship.

No correlation was established between the ability of aluminas to oxidize hydrogen sulfide and the total concentration of acid sites determined by NH₃-TPD. This is explicable, because intermediate and strong LAS and proton sites are NH₃-TPD visible, whereas weak LAS are NH₃-TPD silent due to weak bond formation with NH₃ [50]. According to FTIR, the latter sites are active in the selective oxidation of hydrogen sulfide to sulfur.

3.6.2. Correlation between the acidic and catalytic properties of sulfate-modified aluminas

To strengthen our hypothesis concerning the effect of weak LAS on low-temperature aluminas on their selective catalytic oxidation of H₂S, a series of the sulfate-modified (γ+15%χ)-Al₂O₃ samples were prepared and characterized by FTIR spectroscopy. The sulfate content was varied from 1.25 to 10 wt%. Assuming that four sulfate groups can be stabilized on 1 nm² of alumina, the 10 wt% SO₄²⁻ concentrations should be close at monolayer coverage.

According to FTIR data (Table 3 and Fig. 4), two types of weak Al³⁺-LAS (bands at 2195 and 2186 cm⁻¹) are observed for unmodified (γ+15%χ)-Al₂O₃. The LAS detected in sulfate-modified samples (Fig. 6) can be classified into three groups. The first are weak LAS, which are characterized by a heat of CO adsorption less than 38 kJ/mol (ν_{CO} = 2180–2198 cm⁻¹). The second are those with a heat of CO adsorption close to 39 kJ/mol (ν_{CO} = 2199–2200 cm⁻¹), and the third are intermediate sites with a heat of adsorption greater than 40 kJ/mol (ν_{CO} = 2205–2216 cm⁻¹).

Fig. 9. Concentration of LAS vs. loading of sulfate ions in the modified alumina.

The FTIR-detected concentrations of weak and intermediate LAS on aluminas as a function of sulfate loading are shown in Fig. 9. An increase in SO_4^{2-} loading of modified $(\gamma+15\%\chi)\text{-Al}_2\text{O}_3$ results in a sharp decrease in the concentration of weak LAS ($\nu = 2180\text{--}2198\text{ cm}^{-1}$). At the same time, the number of intermediate LAS ($\nu = 2199$ and 2210 cm^{-1}) increases and reaches a maximum value when the SO_4^{2-} content is near 5 wt%. Compared to the unmodified material, the total concentration of LAS sites decreases significantly in $10\%\text{SO}_4^{2-}/(\gamma+15\%\chi)\text{-Al}_2\text{O}_3$. The SO_4^{2-} coverage on the alumina surface (θ_{SO_4}) was evaluated to explain this phenomenon. θ_{SO_4} was calculated on the assumption that an SO_4^{2-} anion occupies an area of $7 \times 7\text{ \AA}$. Fig. 9 shows that the maximum concentrations of intermediate LAS ($\nu = 2199$ and 2210 cm^{-1}) are observed at θ_{SO_4} near 1.0–1.1 monolayer. Prior to reaching monolayer coverage, sulfate ions on an alumina surface have been shown [55,63,64] to exist as isolated, multicentered, and bridging groups. Note that the monolayer on our $(\gamma+15\%\chi)\text{-Al}_2\text{O}_3$, unlike $\gamma\text{-Al}_2\text{O}_3$ [63,64], is achieved when the sulfate ion content is about 5 wt%. Polymeric sulfate species, which form at sulfate loadings above 5 wt% [64], predominate in multilayers [63,64]. There could be

trace amounts of $\text{Al}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$ crystallites, which can be identified by XRD [52,64]. We have not detected a crystalline aluminum sulfate phase by XRD even in $10\%\text{SO}_4^{2-}/(\gamma+15\%\chi)\text{-Al}_2\text{O}_3$, although the aluminum sulfate particles could be amorphous. Therefore, the decrease in concentration of deprotonated surface sites with increasing SO_4^{2-} can be accounted for by a blocking of the surface sites by sulfate anions via formation of polymeric sulfate species and amorphous aluminum sulfate. This conclusion is consistent with Yang's results [63]. Their analysis showed that the acidity of sulfate species on an alumina surface decreases as surface sulfates > multilayer sulfates > aluminum sulfate. Surface sulfates possess greater acidity due to the induction of Lewis superacid sites, multilayer sulfates have weaker acidity due to the increased concentration of Brønsted acid sites, and crystallized aluminum sulfate is neutral [63].

We next seek to find a relationship between H_2S conversion and the concentration of LAS sites of different strength. Fig. 10 shows that the correlation between H_2S conversion and the concentration of weak LAS ($\nu = 2186\text{ cm}^{-1}$) is similar to that obtained for alumina with different crystal modifications (Fig. 8). Activity increases with weak LAS content and reaches an optimum value near $250\text{--}300\text{ }\mu\text{mol/g}$ at $200\text{ }^\circ\text{C}$ and $400\text{--}500\text{ }\mu\text{mol/g}$ at $250\text{ }^\circ\text{C}$ (Fig. 10(A)). Further increase in the weak LAS concentration does not result in a noticeable change in catalytic activity. Nonlinear trends are observed for intermediate LAS characterized by $\nu = 2199$ and 2210 cm^{-1} (Fig. 10(B), and (C)). H_2S conversion decreases linearly at first with increasing LAS concentration, but then reaches a minimum and begins to grow with increasing LAS content. Careful analysis of these dependences (Fig. 10(B), and (C)) shows that the minimum values of H_2S conversion correspond to modified aluminas with a sulfate content of 7.5 wt% and above. This sulfate coverage amounts to more than a monolayer. If these points are removed from the experimental curves and only 1.25–5 wt% sulfate concentrations are considered, H_2S conversion is practically independent of the intermediate LAS concentration at $200\text{ }^\circ\text{C}$ and changes only slightly at $250\text{ }^\circ\text{C}$. Therefore, we assume that the low activity of highly concentrated (7.5–10 wt%) SO_4^{2-} -modified alumina samples is connected with a change in phase composition, specifically formation of a multilayer sulfate film and highly

Fig. 10. Conversion of hydrogen sulfide at $200\text{ }^\circ\text{C}$ (close symbols) and $250\text{ }^\circ\text{C}$ (open symbols) vs. the concentration of LAS Al^{3+} characterized by absorption bands at 2186 cm^{-1} (A), 2199 cm^{-1} (B) and 2210 cm^{-1} (C) assigned to adsorbed CO. The content (wt%) of sulfate ions in the alumina sample is indicated by the numbers. Area, where the sample properties alter due to change of its phase composition, is marked by the rectangle.

dispersed X-ray amorphous aluminum sulfate. The latter has no acidity [63].

The experimental data confirm that weak LAS enable the catalytic oxidation of H₂S by unmodified aluminas with different crystal modifications (γ , χ , α) and aluminas modified by Mg²⁺, Cl⁻, and SO₄²⁻ ions. The effect depends strongly on temperature with the greatest effect observed below 300 °C.

3.6.3. Study of hydrogen sulfide adsorption

In the catalytic reactions of hydrogen sulfide oxidation [12,18,20] and decomposition [65], adsorption of H₂S on the catalyst surface is thought to be necessary for H₂S activation and its transformation to sulfide or sulfite/sulfate complexes [62,66]. Although H₂S adsorption on γ -Al₂O₃ has been studied in detail [62,66–68], there are debates concerning the nature of the sites involved in H₂S adsorption. H₂S adsorbs in molecular form on proton sites of γ -Al₂O₃ [62,67]. It adsorbs dissociatively on basic sites such surface oxygen [67,69]. H₂S also is thought to adsorb both dissociatively and in molecular form on strong LAS. Physical adsorption of hydrogen sulfide on the surface of oxide catalysts can be accompanied by its oxidation to surface sulfite/sulfate complexes [22,24,70]. The bridging lattice oxygen of the catalyst or oxygen adsorbed on the surface is consumed in H₂S oxidation [71]. However, oxidation on γ -Al₂O₃ is hindered by the low mobility of surface oxygen [68].

Fig. 11 displays FTIR spectra of H₂S adsorbed on the surface of the aluminas. The results of the experiments are summarized in Table 4. The spectra of H₂S-treated aluminas at 20 °C exhibit absorption bands at 1330–1333, 1557–1575, and 2555–2588 cm⁻¹ (the last is not shown in Fig. 11). Free H₂S has three vibrations in the IR region: 2722 (ν_1), 1215 (ν_2), and 2739 (ν_3) cm⁻¹ [72]. These shift due to interaction with the surface of a heterogeneous catalyst [68–75]. The bands at 1330–1333 and 2555–2588 cm⁻¹ are the bending and stretching vibrations of physically adsorbed hydrogen sulfide or chemisorbed HS, respectively [68–71,73–75]. The band at 2588 cm⁻¹ in the spectrum of α -Al₂O₃ treated with H₂S indicates that the broad band at 1330–1368 cm⁻¹ belongs to vibrations of physically ad-

sorbed hydrogen sulfide. The band at 1557–1575 cm⁻¹ is not unambiguously assigned to a specific vibration of any S-containing species, and its origin is still hotly debated [68,71–73]. We repeated the H₂S adsorption experiment several times and always observed the band at 1557–1575 cm⁻¹ in the FTIR spectra of H₂S-treated aluminas at 20 °C. The band decreases in intensity or disappears with increasing temperature. The band at 1550–1568 cm⁻¹ accompanied by 1341, 1625, 2556, and 3400 cm⁻¹ bands was observed early in the spectra of γ -Al₂O₃ [73], MoS₂/ γ -Al₂O₃ [73], and Cu-ZSM-5 [75] exposed to H₂S at room temperature. Dalla Lana et al. [71] reported bands at 1330 and 1568 cm⁻¹ in the spectra of γ -Al₂O₃ pretreated with H₂S or SO₂ and heated at 400 °C. The FTIR spectra of oxidized and reduced aluminas exhibited bands at 2560, 1568, and 1345 cm⁻¹ after alumina treatment by H₂S [69]. Bands at 1330 and 1565 cm⁻¹ were assigned in [69,71] to the S–O vibration of chemisorbed sulfur atoms, which formed SO₂-like species with oxide ions of the alumina lattice. Slager and Amberg [73] assigned a band at 1568–1575 cm⁻¹ to Al–O vibrations, whose frequency changed upon adsorption of different molecules (H₂S, CO, HCOOH, and C₂H₆). Saur et al. criticized both points of view [68] in assigning the 1570 cm⁻¹ band to a carbonate mode [76]. It should be noted that the FTIR spectra in [76] did not display a 1570 cm⁻¹ band for CO₂-treated alumina, but did show this feature after H₂S adsorption on CO₂-treated alumina. Despite disagreement as to the origin of the 1565–1575 cm⁻¹ band, most authors have reached the conclusion [68–76] that surface structures with a coordination bond between Al and S are formed during treatment of alumina with H₂S, CH₃SH, and (CH₃)₂S. Saur et al. [68,76] have suggested that strong and weak Lewis acid-base couples can break the H–S bond in H₂S and that dissociative adsorption of H₂S on the former and latter leads to formation of Al–S and O–H bonds. The reactivity of weak Lewis acid-base couples predominates [68] when the adsorbate has acid properties. Thus, the bands at 1330–1333, 1557–1575, and 2555–2588 cm⁻¹ are assigned to H-bonded and chemisorbed H₂S.

In addition to the features at 1330, 1557, and 2550 cm⁻¹, the

Table 4

FTIR experiment data for the different samples of aluminas treated by H₂S and heated.

Observed frequencies (cm ⁻¹)	Assignment	Ref.	Temperature of H ₂ S-treated aluminas heating, that results in the band observation				
			γ -Al ₂ O ₃	(γ +15% χ)-Al ₂ O ₃	(γ +35% χ)-Al ₂ O ₃	Mg ²⁺ /(γ +15% χ)-Al ₂ O ₃	α -Al ₂ O ₃
1330–1333; 2555–2588	the bending (ν_2) and stretching vibrations of the physically adsorbed (H-bonded) H ₂ S or chemisorbed HS	[68–71]; [73–75]	20	20; 100	20; 100	20; 100	20
1557–1575	See discussion in the text	[68,71,73]	20	20; 100	20; 100	20; 100	20
1120; 1350	ν_s and ν_{as} of S–O bonds in a multicentered sulfate ion (AlO) ₃ SO	[20,55,64,70,77]	20; 200–300	–	200–300	200–300	100–300
1180; 1250–1262	ν_s and ν_{as} of surface inorganic bridging sulfates (AlO) ₂ SO ₂	[55,70,77]	20; 200–300	–	–	–	100–300
1160–1180; 1310–1315	ν_s and ν_{as} stretching vibrations of inorganic chelating bidentate sulfates Al(O) ₂ SO ₂	[77]	200–300	200–300	200–300	200–300	100–300
1230–1237; 1405–1445	polynuclear sulfate complexes	[78]	200–300	100–300	100–300	100–300	100–300
1620–1650	the bending (ν_2) of H ₂ O	[71]	300; evac.	100–300; evacuated	100–300; evacuated	100–300; evacuated	300; evac.

Fig. 11. FTIR spectra of alumina samples evacuated at 400 °C (1) and interacted with hydrogen sulfide at: 20 °C (2), 100 °C (3), 200 °C (4), 300 °C (5), evacuation (6) to 10^{-3} torr at 20 °C after 2–5 steps of H₂S adsorption.

spectrum of H₂S-treated γ -Al₂O₃ at 20 °C shows absorption bands at 1120, 1180, 1262, and 1350 cm⁻¹. These bands correspond to the vibrations of sulfite/sulfate surface complexes and indicate that partial oxidation of H₂S adsorbed on γ -Al₂O₃ occurs at temperatures as low as 20 °C. The absorption bands at 1120 and 1350 cm⁻¹ are attributed to the symmetric and anti-symmetric vibrations of S=O bonds in a multicentered sulfate-containing structure (AlO)₃SO [20,55,64,70,77]. The bands at 1180 and 1260 cm⁻¹ are attributed to the symmetric and antisymmetric vibrations of bridging surface sulfur atoms within (AlO)₂SO₂ centers [55,70,77] that contain free SO₂ unperturbed by hydrogen bonds. Other aluminas do not show bands at 1120/1350 and 1180/1262 cm⁻¹ in their FTIR spectra after H₂S adsorption. Monomeric bi- and tridentate sulfates

(1120/1350 cm⁻¹) form on the surface of χ -modified aluminas after heating at 200–300 °C, whereas inorganic bridging sulfate (1180/1262 cm⁻¹) is not observed even after thermal treatment at 300 °C.

As the H₂S-treated aluminas were heated at 100 °C, the 1332 and 1557 cm⁻¹ bands vanished from the spectra of γ -Al₂O₃ and α -Al₂O₃, whereas these bands did not disappear completely in the case of χ -modified samples. For example, the 1332 cm⁻¹ band diminished in intensity by a factor of 10 after heating H₂S-treated (γ +35% χ)-Al₂O₃ and MgO/(γ +15% χ)-Al₂O₃ at 100 °C, but the band was still observed in the spectra of these samples after heating at 300 °C. The disappearance or decrease in intensity of the 1332 and 1557 cm⁻¹ bands may indicate the oxidation of physically adsorbed hydrogen sulfide and for-

mation of sulfur and water via the reaction, $\text{H}_2\text{S} + [\text{O}] \rightarrow \text{S}_n + \text{H}_2\text{O}$. As discussed below, water was found in the FTIR spectra (as a band at 1650 cm^{-1} [71]) of $\gamma\text{-Al}_2\text{O}_3$ and χ -modified samples after heating at 300 and $100\text{ }^\circ\text{C}$, respectively.

The intensity of the bands at 1350 and 1262 cm^{-1} become more intense in the spectrum of H_2S -treated $\gamma\text{-Al}_2\text{O}_3$ after heating at $200\text{ }^\circ\text{C}$. The bands become stronger at higher temperatures indicating an increase in the amount of multicentered and bidentate sulfate species, respectively. We have identified two new pairs of bands in these spectra. The first pair at $1160\text{--}1170$ and $1315\text{--}1320\text{ cm}^{-1}$ is characterized by asymmetric band shapes. Their frequencies are assigned to symmetric and asymmetric stretching vibrations of a second type of bridging sulfur [77]. The second pair is located at 1232 and $1430\text{--}1445\text{ cm}^{-1}$. Bensitel and co-authors [78] suggested that bands with $\nu(\text{S}=\text{O}) \geq 1400\text{ cm}^{-1}$ are typical of a polynuclear sulfate complex such as $\text{S}_2\text{O}_7^{2-}$. The FTIR spectrum of sulfated zirconia is characterized by a band at $1400\text{--}1405\text{ cm}^{-1}$ at high sulfate loading [78]. However, the spectrum of SO_2 adsorbed on alumina was found by Bensitel et al. [79] to display $\nu(\text{S}=\text{O})$ near 1390 cm^{-1} . Polymeric sulfate species, which are characterized by absorptions at 1538 and 1488 cm^{-1} , were found by Mekhemer [64] in alumina containing $10\text{ wt}\%$ sulfate. We assume that polynuclear sulfate complexes exhibit characteristic absorption bands at $1405\text{--}1445$ and $1230\text{--}1237\text{ cm}^{-1}$ and that their formation is possible during heating of alumina with adsorbed hydrogen sulfide at $200\text{ }^\circ\text{C}$.

Polynuclear sulfate complexes characterized by bands at 1230 and $1405\text{--}1450\text{ cm}^{-1}$ were observed on heating χ -modified aluminas at a lower temperature ($100\text{ }^\circ\text{C}$) than $\gamma\text{-Al}_2\text{O}_3$ ($200\text{ }^\circ\text{C}$). The polynuclear sulfate content in $\alpha\text{-Al}_2\text{O}_3$ was smaller than that in other crystal modifications of alumina. This may be due to differences in the exposed crystal facets of the $\gamma\text{-Al}_2\text{O}_3$ and $\chi\text{-Al}_2\text{O}_3$ structures, which influence the adsorption/desorption pathways of H_2S . Morterra et al. [82] showed in sulfated zirconia that species with $\nu(\text{S}=\text{O})$ equal to $1350\text{--}1375\text{ cm}^{-1}$ are localized at crystallographic defects (edges), whereas those with $\nu(\text{S}=\text{O})$ at $1380\text{--}1400\text{ cm}^{-1}$ are located mainly on regular patches of low-index crystal planes. This result can be extended to aluminas. $\gamma\text{-Al}_2\text{O}_3$ is known [45–47] to contain tetrahedrally coordinated Al^{3+} at crystallographic de-

fect sites as well as octahedrally coordinated Al^{3+} ions at regular defects on low-index crystal faces. Based on FTIR data, these tetrahedral and octahedral Al^{3+} configurations are LAS, which are characterized by high- ($2210\text{--}2240\text{ cm}^{-1}$) and low-frequency ($2180\text{--}2205\text{ cm}^{-1}$) bands, respectively, in the spectra of CO adsorbed on alumina [38,40–45]. According to Table 3, tetrahedrally coordinated Al^{3+} ions belong to $\gamma\text{-Al}_2\text{O}_3$, while octahedrally coordinated Al^{3+} predominates in both $\gamma\text{-Al}_2\text{O}_3$ and samples modified with $15\text{--}35\text{ wt}\%$ $\chi\text{-Al}_2\text{O}_3$. Thus, formation of polynuclear sulfate species ($1405\text{--}1445\text{ cm}^{-1}$) during heating of H_2S -treated aluminas is promoted by weak LAS, which are octahedrally coordinated Al^{3+} ions.

A further increase in temperature to $300\text{ }^\circ\text{C}$ did not result in significant changes in sulfur-containing species in H_2S -treated aluminas. There are different types of isolated sulfate groups and polynuclear sulfate complexes as well as tridentate surface SO_x compounds ($1160\text{--}1180/1350\text{ cm}^{-1}$). A greater polynuclear sulfate content ($1230/1445\text{ cm}^{-1}$) is observed at higher heating temperatures. The spectrum of $(\gamma+35\%\chi)\text{-Al}_2\text{O}_3$ is characterized by an unstructured absorption in the low frequency region ($1100\text{--}1200\text{ cm}^{-1}$), which is associated with the vibration of surface sulfate complexes.

The spectra of H_2S -treated $\gamma\text{-Al}_2\text{O}_3$ samples evacuated at room temperature illustrate the behavior of bands connected with sulfate groups and water. The results show that the sulfate complexes formed over H_2S -treated aluminas during heating at $100\text{--}300\text{ }^\circ\text{C}$ are stable. A broadening of the vibrational frequencies of SO_x surface compounds (1159 cm^{-1}) and inorganic sulfate complexes (1170 and 1260 cm^{-1}) in the $\alpha\text{-Al}_2\text{O}_3$ spectrum can be caused by water adsorption that accompanies a decrease in temperature.

We conclude that physically adsorbed hydrogen sulfide is oxidized on alumina surfaces to stable surface sulfate groups including multicentered SO_x compounds (bands at $1120/1350\text{ cm}^{-1}$), isolated inorganic sulfates ($1180/1260$ and $1160/1314\text{ cm}^{-1}$), and polynuclear sulfates ($1230\text{--}1237/1405\text{--}1445\text{ cm}^{-1}$) at elevated temperatures ($>100\text{ }^\circ\text{C}$). In contrast to the χ -modified samples, oxidation of hydrogen sulfide over $\gamma\text{-Al}_2\text{O}_3$ involving formation of surface SO_x compounds begins at room temperature. Physically adsorbed SO_2 has been postulated by Prette [80] and Steijns [81] to be an intermediate in H_2S oxida-

Fig. 12. TG (1), DTA (2) and DTG (3) curves in air for the spent sample $(\gamma+35\%\chi)\text{-Al}_2\text{O}_3$ after stability test at $300\text{ }^\circ\text{C}$ during 50 h (a) and the initial sample $10\%\text{SO}_4/(\gamma+15\%\chi)\text{-Al}_2\text{O}_3$ (b).

tion on γ - Al_2O_3 at 100 °C. Moreover, H_2S oxidation to adsorbed SO_2 proceeds slowly on γ - Al_2O_3 even when H_2S is oxidized by molecular oxygen. Although further recovery of adsorbed SO_2 with H_2S is rapid, the products are elemental sulfur and water. Water forms preferentially at 300 °C.

H_2S oxidation on γ - Al_2O_3 and α - Al_2O_3 results in two types of isolated inorganic sulfates with different bridging structures, which can be assigned to intermediate and weak strength LAS on the alumina surface. For 15%–35% χ -containing samples, H_2S adsorption leads to formation of a single type of inorganic bridging sulfate probably due to weak LAS. The χ -modified samples are more active, because polynuclear sulfates form on their surface at only 100 °C, and the intensity of absorption bands is greater than is true for γ - Al_2O_3 and α - Al_2O_3 . The presence of polynuclear surface sulfates also was detected by DTA as a mass loss at 920–960 °C in the TG/DTG curves of spent (γ +35% χ)- Al_2O_3 tested for H_2S oxidation at 300 °C for 50 h (Fig. 12(a)). Polynuclear surface sulfates were found by Yang [63] to decompose at 950 °C unlike crystallized aluminum sulfate (800–860 °C) and multilayer sulfate (630 °C). The latter species are typical of (γ +15% χ)- Al_2O_3 modified by 10 wt% sulfate (Fig. 12(b)). Surface sulfates are characterized by a wide peak near 950 °C, which broadens at lower temperatures. It is due to different interactions between polynuclear sulfate and the alumina surface.

4. Conclusions

The phase composition of alumina samples (α , γ , and (γ + χ)- Al_2O_3) strongly influences their activity in hydrogen sulfide oxidation. The catalytic activity of γ - Al_2O_3 , including samples modified with Mg^{2+} , increases in the presence of χ - Al_2O_3 .

The acidic properties of α - Al_2O_3 , γ - Al_2O_3 , and (γ + χ)- Al_2O_3 surfaces were studied by FTIR spectroscopy with CO adsorption and NH_3 -TPD. For α - and γ - Al_2O_3 samples, FTIR spectra reveal the presence of weak and intermediate strength LAS with CO vibrational frequencies greater than 2186 and 2200 cm^{-1} , respectively. Only weak LAS characterized by an absorption band at 2186–2200 cm^{-1} are found on (γ + χ)- Al_2O_3 . Introduction of MgO into (γ +15% χ)- Al_2O_3 reduces the strength of the weak LAS, as observed by a band shift from 2186 to 2181 cm^{-1} , but significantly increases their number.

Interaction of hydrogen sulfide with α , γ , and γ + χ crystal modifications of Al_2O_3 at 100–400 °C results in the appearance of surface SO_x compounds (1120/1350 cm^{-1} absorption bands), inorganic sulfates (1160–1180 and 1260–1314 cm^{-1} bands), and polynuclear sulfates (1230–1237 and 1400–1445 cm^{-1} bands). For α - Al_2O_3 and γ - Al_2O_3 , which possess weak and intermediate LAS, additional inorganic sulfate species with high frequency bands at 1265 and 1300–1315 cm^{-1} are observed.

Based on data from FTIR spectroscopy and a comparison of the catalytic activity and selectivity of alumina samples, we suggest that hydrogen sulfide is adsorbed predominantly on weak LAS. Alumina samples containing χ -phase Al_2O_3 and/or modified with Mg^{2+} are characterized by a large concentration of weak LAS and exhibit enhanced catalytic activity in H_2S oxidation. When alumina is treated with a solution of sulfuric acid,

strong LAS appear and the LAS population decreases significantly. Modification of alumina with hydrochloric acid has a limited effect on LAS strength. Weak LAS are retained and double in number relative to unmodified material, but the chloride-treated sample has Al–Cl rather than Al–O(OH) bonds. Alumina samples modified by sulfate and chloride anions exhibit poor catalytic activity in hydrogen sulfide oxidation.

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Graphical Abstract

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Effect of χ -alumina addition on H_2S oxidation properties of pure and modified γ -alumina

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The activity of aluminas in direct H_2S oxidation depends on their acidic properties. Weak Lewis acid sites (LAS) are more active than other LAS or Brønsted acid sites (BAS). Greater concentrations of weak LAS produce greater catalytic activity.

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χ -氧化铝的添加对纯的和修饰的 γ -氧化铝上 H_2S 氧化反应性能的影响

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摘要: 考察了 $\gamma\text{-Al}_2\text{O}_3$, $(\gamma+\chi)\text{-Al}_2\text{O}_3$ 和 $\alpha\text{-Al}_2\text{O}_3$ 的结构性质和酸性对其催化 H_2S 直接氧化反应性能(活性、选择性和稳定性)的影响。采用红外光谱(FTIR)与氨-程序升温脱附($\text{NH}_3\text{-TPD}$)方法对氧化铝作用下 H_2S 转化为S的反应性能与其酸性进行了比较。结果显示, H_2S 吸附主要发生在弱Lewis酸位。含有 χ 相和/或 Mg^{2+} 修饰的 $\gamma\text{-Al}_2\text{O}_3$ 样品具有更高浓度的弱Lewis酸位,并表现出更高的催化活性。当氧化铝样品用硫酸溶液处理后,表现出强Lewis酸位性质,且Lewis酸位点数量显著下降。而当用HCl对氧化铝进行修饰时,其对Lewis酸位强度的影响很小,保持着弱Lewis酸位的性质,且其Lewis酸位数量与未修饰的样品相比增加了二倍,但处理过的样品中含有Al-Cl键。用硫酸盐和氯离子修饰过的氧化铝样品在 H_2S 氧化反应中的催化性能均较低。

关键词: 氧化铝; $\chi\text{-Al}_2\text{O}_3$; 硫化氢氧化; 酸性质; 路易斯酸位; 红外光谱; 氨-程序升温脱附

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