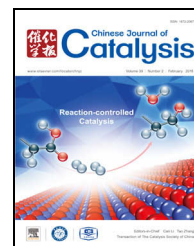


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## Article

# Effect of $\chi$ -alumina addition on H<sub>2</sub>S oxidation properties of pure and modified $\gamma$ -alumina

Svetlana A. Yashnik<sup>a,\*</sup>, Vadim V. Kuznetsov<sup>a</sup>, Zinifer R. Ismagilov<sup>a,b</sup><sup>a</sup> Borekov Institute of Catalysis SB RAS, Lavrentieva, 5, Novosibirsk 630090, Russia<sup>b</sup> Institute of Coal Chemistry and Materials Science FRC CCC, SB RAS, Sovetskii, 18, Kemerovo 650000, Russia

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## ABSTRACT

The influence of the textural and acidic properties of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, ( $\gamma+\chi$ )-Al<sub>2</sub>O<sub>3</sub>, and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> on the catalytic activity, selectivity, and stability of direct H<sub>2</sub>S oxidation has been studied. A comparison of the H<sub>2</sub>S-to-S conversion effectiveness of aluminas with their acidic properties (identified by Fourier transform infrared spectroscopy and temperature programmed desorption of NH<sub>3</sub>) shows that H<sub>2</sub>S adsorption occurs predominantly on weak Lewis acid sites (LAS).  $\gamma$ -Alumina samples containing a  $\chi$ -phase and/or modified Mg<sup>2+</sup> 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<sub>2</sub>S 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  $\gamma$ -,  $\eta$ -, and  $\chi$ -Al<sub>2</sub>O<sub>3</sub>.  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> has been used most extensively. Pure, activated, and chlorinated  $\gamma$ -aluminas have been applied to the hydroisomerization of C<sub>4</sub>–C<sub>6</sub> 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,  $\chi$ -Al<sub>2</sub>O<sub>3</sub> 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<sub>2</sub>S 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<sub>2</sub>S oxidation, individual oxides of transition metals (e.g., Fe<sub>2</sub>O<sub>3</sub>, CuO, MnO<sub>x</sub>, CrO<sub>x</sub>, and V<sub>2</sub>O<sub>5</sub>) or their mixtures are more promising [16–32]. Granulated and monolithic aluminas, which are widely used as a support mate-

\* Corresponding author. Tel: 8(383)3306681; Fax: 8(383)3306219; E-mail: yashnik@catalysis.ru

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rial for this process [17,18,22,25,33], possess a natural activity for direct H<sub>2</sub>S 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 ( $\gamma$ ,  $\chi$ , and  $\alpha$ ) 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 (NH<sub>3</sub>-TPD) were used to characterize the surface acid properties of aluminas and to explain their catalytic activity in direct H<sub>2</sub>S oxidation. The textural properties of aluminas also were used to identify structure-performance relationships.

## 2. Experimental

### 2.1. Preparation of Al<sub>2</sub>O<sub>3</sub>

Five spherical alumina samples,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, ( $\gamma$ +15% $\chi$ )-Al<sub>2</sub>O<sub>3</sub>, ( $\gamma$ +35% $\chi$ )-Al<sub>2</sub>O<sub>3</sub>, ( $\gamma$ +50% $\chi$ )-Al<sub>2</sub>O<sub>3</sub>, and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> 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  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> sample was prepared from aluminum hydroxide with a pseudoboehmite structure as in ref. [33].  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> samples containing 15 and 35 wt%  $\chi$ -Al<sub>2</sub>O<sub>3</sub> were prepared from aluminum hydroxide produced by the thermal decomposition of gibbsite in a catalytic heat generator [36,37]. The sample containing 50 wt%  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and  $\chi$ -Al<sub>2</sub>O<sub>3</sub> was produced from a mixture of gibbsite and pseudoboehmite. The  $\chi$ -Al<sub>2</sub>O<sub>3</sub> sample containing trace  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was prepared from gibbsite. The above samples were calcined at 550 °C for 4 h in air. The spherical  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> sample was prepared by thermal calcination of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at 1200 °C for 6 h.

MgO/( $\gamma$ +15% $\chi$ )-Al<sub>2</sub>O<sub>3</sub> 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 ( $\gamma$ +15% $\chi$ )-Al<sub>2</sub>O<sub>3</sub> 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% SO<sub>4</sub><sup>2-</sup>. The chlorinated alumina sample was prepared by impregnating

spherical granules of ( $\gamma$ +15% $\chi$ )-Al<sub>2</sub>O<sub>3</sub> 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 Al<sub>2</sub>O<sub>3</sub>

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 ( $S_{\text{BET}}$ ), pore volume ( $V_{\text{p}}$ ), 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  $2\theta = 10^\circ$ – $70^\circ$  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  $K_{\alpha}$  radiation. The extent of  $\chi$ - and  $\gamma$ -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  $10^\circ\text{C}/\text{min}$  in air ( $50\text{ cm}^3/\text{min}$ ).

### 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 CaF<sub>2</sub> 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)	$S_{\text{BET}}$ (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	XRD phase composition
1	$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	–	550	214	0.46	$\gamma$ -Al <sub>2</sub> O <sub>3</sub>
2	( $\gamma$ +15% $\chi$ )-Al <sub>2</sub> O <sub>3</sub>	–	550	167	0.55	85% $\gamma$ -Al <sub>2</sub> O <sub>3</sub> +15% $\chi$ -Al <sub>2</sub> O <sub>3</sub>
3	( $\gamma$ +35% $\chi$ )-Al <sub>2</sub> O <sub>3</sub>	–	550	160	0.65	65% $\gamma$ -Al <sub>2</sub> O <sub>3</sub> +35% $\chi$ -Al <sub>2</sub> O <sub>3</sub>
4	( $\gamma$ +50% $\chi$ )-Al <sub>2</sub> O <sub>3</sub>	–	550	160	0.58	50% $\gamma$ -Al <sub>2</sub> O <sub>3</sub> +50% $\chi$ -Al <sub>2</sub> O <sub>3</sub>
5	( $\gamma$ +90% $\chi$ )-Al <sub>2</sub> O <sub>3</sub>	–	550	166	0.59	10% $\gamma$ -Al <sub>2</sub> O <sub>3</sub> +90% $\chi$ -Al <sub>2</sub> O <sub>3</sub>
6	$\alpha$ -Al <sub>2</sub> O <sub>3</sub>	–	1200	9.3	0.37	$\alpha$ -Al <sub>2</sub> O <sub>3</sub>
7	Mg <sup>2+</sup> /( $\gamma$ +15% $\chi$ )-Al <sub>2</sub> O <sub>3</sub>	Mg, 3.2	550	160	0.49	$\gamma^*$ -Al <sub>2</sub> O <sub>3</sub> , a~7.952Å
6	SO <sub>4</sub> <sup>2-</sup> /( $\gamma$ +15% $\chi$ )-Al <sub>2</sub> O <sub>3</sub>	SO <sub>4</sub> <sup>2-</sup> , 1.25÷2.5	500	169	0.53	85% $\gamma$ -Al <sub>2</sub> O <sub>3</sub> +15% $\chi$ -Al <sub>2</sub> O <sub>3</sub>
7	SO <sub>4</sub> <sup>2-</sup> /( $\gamma$ +15% $\chi$ )-Al <sub>2</sub> O <sub>3</sub>	SO <sub>4</sub> <sup>2-</sup> , 7.5÷10	500	120–135	0.40–0.46	85% $\gamma$ -Al <sub>2</sub> O <sub>3</sub> +15% $\chi$ -Al <sub>2</sub> O <sub>3</sub>
8	Cl <sup>-</sup> /( $\gamma$ +15% $\chi$ )-Al <sub>2</sub> O <sub>3</sub>	Cl <sup>-</sup> , 1.0	500	165	0.58	85% $\gamma$ -Al <sub>2</sub> O <sub>3</sub> +15% $\chi$ -Al <sub>2</sub> O <sub>3</sub>

$\gamma^*$ -Al<sub>2</sub>O<sub>3</sub> – solid solution Mg<sup>2+</sup> in  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

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