

## Physicochemical properties of aluminas obtained from different aluminum salts

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### Abstract

Al<sub>2</sub>O<sub>3</sub> materials were obtained by calcination of boehmite samples of varying crystallinity at 600 °C. Boehmites were obtained from Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·18H<sub>2</sub>O or AlCl<sub>3</sub> under hydrothermal conditions and autogenous pressure at different synthesis temperatures ( $T_s = 40, 140$  and  $180$  °C), and were studied by XRD, IR(Py), DTA and TGA. It was found that  $T_s$  is closely related to the physicochemical properties of boehmites, and thus of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Increased amounts of sulfur were detected in  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> for lower  $T_s$  using aluminum sulfate. Less-crystalline boehmites were obtained when using aluminum sulfate compared to aluminum chloride. While only Lewis acidity was found in  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> materials produced from aluminum chloride, aluminum sulfate produced both Lewis and Brønsted acidity, with the Brønsted/Lewis ratio depending on the crystallite size.

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### 1. Introduction

In recent years, the preparation of different grades of hydrous oxides of aluminum has become an important area of research and development due to their technical importance as precursors for special grades of aluminum oxide, representing a family of materials that can be synthesized from different precursors [1–5] under a wide range of conditions and that may exist under various crystalline phases.

$\gamma$ -Al<sub>2</sub>O<sub>3</sub> is obtained by dehydroxylation of boehmite prepared by precipitation [6,7] from aluminum chloride or nitrate, or by hydrolysis of aluminum alkoxides [6,8].

The crystallinity of the boehmite precursor can be adjusted by controlling the temperature and duration of the hydrothermal treatment [9–13] performed under autogenous pressure. The crystallinity of the subsequent alumina depends on the crystallinity of the boehmite precursor.

Alumina has good thermal stability, high specific surface area and acid–base properties that can be modulated by changing the synthesis conditions [9,14]. Their use as adsorbents and catalysts or catalyst supports and their ease of preparation explains why they are so frequently used in the petrochemical industry [15–17].

The application of transitional alumina is of special interest in fluid catalytic cracking (FCC), which is one of the most important oil-refining processes [18,19]. One of the current approaches in FCC heavy and residue feeds processing is to design cracking catalysts with moderate zeolite contents supported on a matrix such as a transitional alumina, which can have different physicochemical properties.

For structural reasons, surface acidity is of the Lewis type and their properties are well documented [20,21]. There are no Brønsted sites in pure alumina Al<sub>2</sub>O<sub>3</sub>, whatever its origin. The formation of such sites by impregnation of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with sulfuric acid followed by calcination in air at approximately 600 °C has been reported [21–23].

The aim of this work was to study the effect of the aluminum source [AlCl<sub>3</sub> or Al<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>·18H<sub>2</sub>O] on the

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Al(OH)<sub>3</sub> precipitate obtained under identical conditions. The physicochemical properties and the effect of aging under hydrothermal conditions are also reviewed.

## 2. Experimental

### 2.1. Synthesis

Al(OH)<sub>3</sub> was precipitated between pH 7 and 9 at room temperature from solutions of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·18H<sub>2</sub>O or AlCl<sub>3</sub>, using a 28% solution of NH<sub>4</sub>OH.

The precipitate was transferred into a 2-l autoclave, where it was treated at synthesis temperatures of  $T_s = 50, 140$  and  $180$  °C for 18 h. Afterwards, the gel was washed thoroughly with deionized water and dried at  $100$  °C. The solid was then calcined at  $600$  °C for 4 h.

### 2.2. Characterization

#### 2.2.1. X-ray powder diffraction

The X-ray powder diffraction patterns of samples packed in a glass holder were recorded at room temperature with Cu K $\alpha$  radiation in a Bruker Advance D-8,  $\theta$ – $\theta$  diffractometer equipped with a graphite secondary-beam monochromator. The diffraction intensity was measured between  $10^\circ$  and  $110^\circ$ , with a  $2\theta$  step of  $0.02^\circ$  for 8 s per point. The crystalline structure was refined according to the Rietveld technique using DBWS-9411 [24] and FULLPROF-V3.5d [25] programs.

#### 2.2.2. Textural analysis

Specific surface areas and pore size distributions were obtained from nitrogen adsorption–desorption isotherms measured in an automatic Micromeritics ASAP-2100 analyzer. The adsorption was carried out on annealed solids, after outgassing at  $200$  and  $400$  °C, respectively, under a residual pressure of  $10^{-5}$  Torr during 4 h.

#### 2.2.3. Acidity

The Fourier-transform infrared (FTIR)-pyridine adsorption technique was used to determine the type of acid sites on calcined samples. Experiments were carried out in a Nicolet model 170-SX FTIR spectrometer. Prior to pyridine adsorption, the samples were outgassed and then heated up to  $500$  °C at  $20$  °C/min and cooled down to room temperature. After this pretreatment, they were exposed to saturated pyridine vapor for 20 min. After adsorption, infrared spectra were recorded after outgassing at  $50, 100, 200, 300$  and  $400$  °C. The amount of pyridine adsorbed (coordinated or pyridinium ion) was estimated using methods described by Hughes and White [26] and Emeis [27].

#### 2.2.4. Sulfur content

The amount of sulfur in the solids was determined at  $1350$  °C in a Leco model SC-444 analyzer fitted with an infrared detector.

#### 2.2.5. Differential gravimetric analysis

Weight loss and temperatures associated with phase transformations were determined by thermogravimetry and differential thermal analysis using Perkin-Elmer TG-7 and 1700 models, respectively. Samples were heated in a static atmosphere from room temperature up to  $1400$  °C at  $10$  °C/min.

## 3. Results and discussion

Fig. 1A and B shows the XRD patterns of boehmite and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> obtained from an aluminum sulfate or chloride aluminum source, respectively. Increasing  $T_s$  generally resulted in larger and better-crystallized boehmite and alumina. In the solids obtained at low temperature ( $T_s = 50$  and  $140$  °C) from aluminum sulfate, residual ammonium sulfate was observed in the boehmite precursor. Correspondingly, the  $\gamma$ -phase contained residual aluminum sulfate (Fig. 1A). The aluminum sulfate content decreased by approximately 50% for an increase in  $T_s$  from  $50$  to  $140$  °C (Table 1).

In concordance with Fig. 1 and from Tables 2 and 4, it is clearly evident that the evolution of the crystallite size is a function of the aluminum source and the synthesis temperature. In both series, the crystallite size increases as the temperature increases. However, for Bo-S and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, this crystallite size is lower than in samples synthesized from aluminum chloride. The crystallization of boehmite from aluminum sulfate is inhibited by the presence of sulfate anions present in the gel [28].

The specific surface area of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> samples prepared from aluminum chloride (Table 3) is almost constant for  $T_s$  between  $50$  and  $140$  °C. However, it decreases sharply (30%) at  $T_s = 180$  °C. Accordingly, the average pore diameter increases from  $42$  to  $192$  Å in this  $T_s$  interval. In contrast, the specific surface area of the alumina obtained from aluminum sulfate is more variable, with a maximum near  $248$  m<sup>2</sup>/g for  $T_s = 140$  °C (Table 1).

The endothermic and exothermic characteristics in the TGA–DTA analysis reveal a transition temperature for boehmite to  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> ( $380$ – $580$  °C) or for  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> ( $1090$ – $1290$  °C). The evolution of the weight loss with temperature is classical for this type of material. The molar ratio H<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> obeys the expected stoichiometry when the alumina source was aluminum chloride (Table 4). The ratio was greater for the solids obtained from aluminum sulfate (Table 2). This is consistent with the idea that the number of coordinately unsaturated sites is greater for small crystallite size.

The transition temperature for boehmite to  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and the thermal stability increase as the crystallite size increases (Tables 2 and 4). However, this transition is higher in the series prepared from aluminum sulfate. In contrast, the transition temperature for  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> is higher for alumina prepared from aluminum chloride (Table 4).

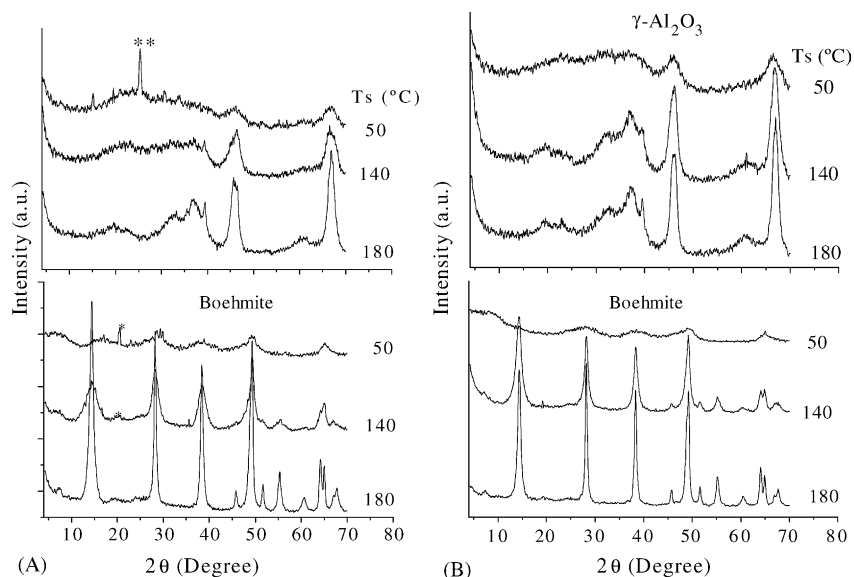


Fig. 1. XRD patterns of the Boehmite precursors and corresponding  $\gamma$ - $\text{Al}_2\text{O}_3$ , obtained from: (A) aluminum sulfate (\*\* ammonium sulfate and \*\*) aluminum sulfate) and (B) aluminum chloride.

In agreement with reference [29], the transition temperature is a function of the surface energy and thus of the specific surface area. Therefore, residual sulfate groups decrease the specific surface energy, and thus the transition temperature to  $\alpha$ - $\text{Al}_2\text{O}_3$  decreases. In contrast, the surface energy for samples prepared from chloride is more homogeneous and the transition temperature to  $\alpha$ - $\text{Al}_2\text{O}_3$  is higher.

The alumina materials obtained at  $T_s = 50^\circ\text{C}$  from aluminum sulfate (Gs-50) and from aluminum chloride (Gcl-50) differ in the nature of their acid sites. The FTIR spectra of adsorbed pyridine are shown in Fig. 2. For Gs-50, both Brönsted ( $1540\text{ cm}^{-1}$ ) and Lewis ( $1450\text{ cm}^{-1}$ ) sites are observed, while for Gcl-50, only Lewis sites were present. Fig. 2 suggests that the Brönsted acidity in Gs-50 sample is weaker, since the band at  $1540\text{ cm}^{-1}$  disappears at  $300^\circ\text{C}$ , whereas the Lewis band at  $1450\text{ cm}^{-1}$  persists up to  $400^\circ\text{C}$ .

The content of Lewis sites characteristic of  $\gamma$ - $\text{Al}_2\text{O}_3$  is a direct function of the crystallite size for the alumina prepared from chloride (Table 3). This relationship is not

observed for the sample obtained from sulfate. Alternatively, in  $\gamma$ - $\text{Al}_2\text{O}_3$  from aluminum sulfate, the surface density of Lewis sites (per unit area) does not seem to be related to the crystallite size, but is greater than in the Gcl series.

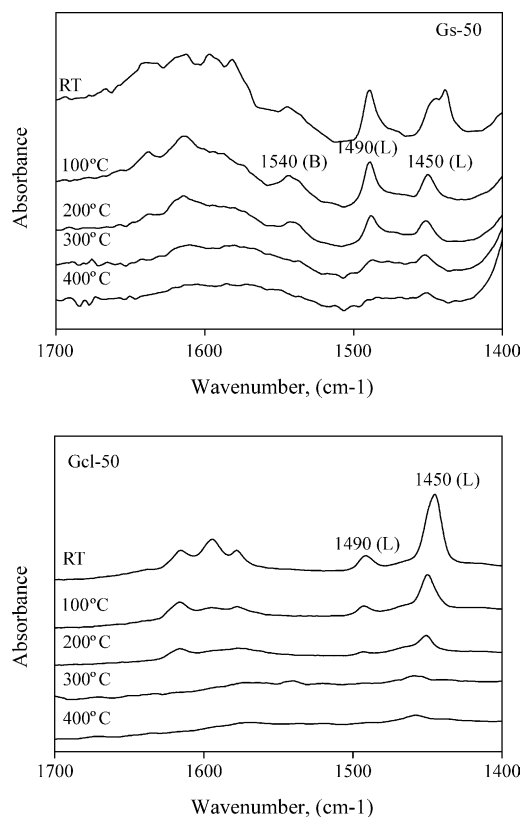


Fig. 2. Pyridine adsorption on  $\gamma$ - $\text{Al}_2\text{O}_3$  synthesized at  $T_s = 50^\circ\text{C}$ , from the sulfate (Gs-50) or from the aluminum chloride (Gcl-50).

Table 1  
Textural and acidic properties of  $\gamma$ - $\text{Al}_2\text{O}_3$  synthesized from aluminum sulfate

$T_s$ ( $^\circ\text{C}$ )	SA <sup>a</sup> ( $\text{m}^2/\text{g}$ )	PV <sup>a</sup> ( $\text{cm}^3/\text{g}$ )	PDS <sup>a</sup> ( $\text{Å}$ )	[S] (wt.%)	Acidity <sup>b</sup> ( $\mu\text{mol}/\text{m}^2$ )	
					BA	LA
50	88	0.09	43	5.86	0.59	2.28
140	248	0.30	49	2.38	0.60	1.39
180	136	0.54	159	0	–	4.15

$T_s$ : synthesis temperature.

<sup>a</sup> Calcined materials at  $600^\circ\text{C}$ .

<sup>b</sup> On  $\gamma$ - $\text{Al}_2\text{O}_3$ , surface density of Brönsted acidity (BA) and Lewis acidity (LA) calculated from pyridine adsorption at  $50^\circ\text{C}$ .

Table 2  
Transition temperature, crystal size and H<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> molar ratio of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> synthesized from aluminum sulfate

$T_s$ (°C)	Molar ratio <sup>a</sup> H <sub>2</sub> O/Al <sub>2</sub> O <sub>3</sub>	Crystal size <sup>b</sup> (Å)		Transition temperature <sup>a</sup> (°C)	
		Bo-S	$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	$\alpha$ -Al <sub>2</sub> O <sub>3</sub>
50	3.51	17	19	388	1095
140	1.40	36	29	509	1161
180	1.11	102	51	520	1205

$T_s$ : synthesis temperature.

<sup>a</sup> From TGA and DTA.

<sup>b</sup> From the Rietveld method.

Table 3  
Textural and acidic properties of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> synthesized from aluminum chloride

$T_s$ (°C)	SA <sup>a</sup> (m <sup>2</sup> /g)	PV <sup>a</sup> (cm <sup>3</sup> /g)	PSD <sup>a</sup> (Å)	Acidity <sup>b</sup> ( $\mu$ mol/m <sup>2</sup> )	
				BA	LA
50	181	0.20	42	–	1.54
140	186	0.52	113	–	1.68
180	114	0.55	192	–	3.66

$T_s$ : synthesis temperature.

<sup>a</sup> Calcined materials at 600 °C.

<sup>b</sup> On  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, surface density of Lewis acidity (LA) calculated from pyridine adsorption at 50 °C.

Table 4  
Transition temperature, crystal size and H<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> molar ratio in  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> synthesized from aluminum chloride

$T_s$ (°C)	Molar ratio <sup>a</sup> H <sub>2</sub> O/Al <sub>2</sub> O <sub>3</sub>	Crystal size <sup>b</sup> (Å)		Transition temperature <sup>a</sup> (°C)	
		Bo-Cl	$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	$\alpha$ -Al <sub>2</sub> O <sub>3</sub>
50	1.34	20	30	413	1203
140	1.13	69	45	471	1249
180	1.07	142	62	508	1289

$T_s$ : synthesis temperature.

<sup>a</sup> From TGA and DTA.

<sup>b</sup> From the Rietveld method.

The presence of Brønsted sites is obviously related to the existence of residual sulfate species on the surface. Possibly, terminal OH groups could be involved in the coordination of HSO<sub>4</sub><sup>-</sup> [20] formed in solution. The residual sulfate could also delay crystallite sintering. On the other hand, an increase in  $T_s$  increases the solubility of aluminum sulfate and would indirectly favor the mobility of aluminum species in solution and the growth of bigger particles.

#### 4. Conclusions

The crystallite size of the boehmite precursor and consequently of the transition alumina increased with the synthesis temperature.

Synthesis from aluminum sulfate produced a smaller crystallite size. Probably, residual sulfates in the surface delayed crystallization compared to samples prepared from chloride, which produced more homogeneous surfaces.

The transition temperature for boehmite to the  $\gamma$ -species was higher for the sulfate series. However, the inverse trend was observed for the transition temperature to the  $\alpha$ -phase.

$\gamma$ -Al<sub>2</sub>O<sub>3</sub> obtained from aluminum sulfate had both Brønsted and Lewis acid sites, whereas material obtained from chloride had Lewis sites only.

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