

Contribution to the Characterization of alumina-based HDT catalysts precursors by Solid State ^{27}Al and ^{17}O NMR

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Abstract: Commercial and synthesized alumina-based HDT precursors have been investigated by X-ray diffraction, thermal analysis, Fourier Transform Infrared spectroscopy, and ^{27}Al and ^{17}O solid state NMR, to evidence the differences and similarities in those supports. Good agreement between the data obtained by X-ray, TG, FTIR and MAS NMR was observed. NMR parameters were obtained by simulation of the Al-O-Al and Al-OH regions in ^{17}O MAS NMR spectra.

Introduction

There are many applications on the active aluminas (γ - and η - Al_2O_3) obtained from two hydroxides, bayerite and pseudoboehmite. The structure of pseudoboehmite is considered traditionally similar to the structure of boehmite because of the correspondence in the peak positions on their diffraction patterns.¹ Bayerite, α - $\text{Al}(\text{OH})_3$, is rarely found in nature.² Pseudoboehmite or poorly crystalline boehmite (γ - AlOOH) is widely used in industrial applications to ceramics,³ sorptive materials,⁴ catalysis,⁵ and nanomaterials⁶ because of its high surface area (between 90 and 410 m^2/g).

The surface area of the pseudoboehmite is important considering that the extent of available surface can be correlated with increased surface reactivity.⁷ In oil refining hydrodesulphurization process (HDS) metal sulfides supported on γ -alumina are still the most used promoters.⁸ According to literature the particle size of the active phase, coordination of metal atoms and their interaction with the support have influence on the performance of these materials.⁹ Recent theoretical research has investigated the morphology and surface properties of boehmite samples and confirmed that the

precursor characteristics were somewhat relevant for the final γ -alumina.¹⁰ In this work X-ray diffraction (XRD), Textural Evaluation, Thermal Analysis (TG), Fourier Transform Infrared spectroscopy (FTIR), and Solid State ^{27}Al and ^{17}O nuclear magnetic resonance: ^{27}Al MAS (magical angle spinning) and ^{17}O MAS NMR are used to the characterization of the structural properties of commercial and synthesized alumina precursors, used as support in industrial hydrotreating promoters in order to show the differences and similarities between the pseudoboehmite samples.

Experimental

One commercial sample of pseudoboehmite from Sasol (USA and Germany) was used for characterization, named "Com", and two synthesized samples named "Synt1" and "Synt2" (the last one was a mesostructured material)^{11,12} were studied. The samples were analyzed as received, and with isotopic enrichment (^{17}O).

Oxygen-17 enriched pseudoboehmite samples were prepared according to Walter et al.¹³ by exchanges between H_2^{17}O (40% in ^{17}O) and were stored in a desiccators with P_2O_5 to minimize the adsorption of atmospheric moisture. Powder X-ray diffraction patterns were collected on a RIGAKU MINIFLEX diffractometer using $\text{Cu K}\alpha$ radiation ($k = 1.54188 \text{ \AA}$), operating at 30 kV and 15 mA using a scanning step of 0.05° for 1s in 2θ range from 4° to 80° . The crystallite sizes were estimated using the Scherrer relation: $D = 0.9 \lambda / \beta \cos\theta$. The Bragg angle and β were calculated using WINPLOTR program version:

February 2008. Samples were dried at $150^\circ\text{C}/24\text{h}$ before the analyses. Nitrogen sorption isotherms were obtained by a MICROMERITICS ASAP 2020 instrument at -196°C to the analysis of specific surface area by BET method¹⁵ (Brunauer-Emmett-Teller), pore volume by single point adsorption total pore volume at $P/P_0 = 0.98$ (where P the pressure and P_0 the saturation vapour pressure) and pore-size distribution for the particles by BJH method (Barrett-Joyner-Halenda). The samples were previously dried at a pressure of 10^{-6} torr (vacuum) and temperature of $150^\circ\text{C}/14\text{h}$. Thermal analyses of commercial samples were conducted on a RIGAKU analyzer model THERMO PLUS TG 8120. For the synthesized samples the equipment used was a SHIMADZU DTG 60 Thermal Analyzer. Analysis conditions: from 25 to 1000°C , $10^\circ\text{C}\cdot\text{min}^{-1}$ in $50 \text{ ml}\cdot\text{min}^{-1}$ of argon. Fourier FTIR spectra was recorded to the powdered samples mixed with potassium bromide (KBr) and pressed to disks on a NICOLET spectrometer model MAGNA-IR 760 with a resolution of 4 cm^{-1} .

For ^{27}Al nuclei solid state nuclear magnetic resonance spectra (MAS NMR) were collected on a Bruker spectrometer AVANCE 300 (7.05 T) operating at 78.2 MHz and equipped with 2.5 mm MAS probe. Approximately 10 mg of each sample were used in a zirconium rotor. The rotational speed was 10 kHz. The recycle time was 0.5 s, and the results were collected by using $\pi/6$ ($P1 = 1.2 \mu\text{s}$) pulses, number of scans 1024 and spectral width 93.9 KHz. The spectra were referenced with $\text{Al}(\text{H}_2\text{O})_6^{3+}(\text{aq})$ standard (0.0 ppm).

For ^{17}O MAS NMR experiments, approximately 80 mg of ^{17}O enriched sample were used in a zirconium rotor and 4 mm MAS probe. ^{17}O spectra (one pulse sequence) were acquired on a Bruker model AVANCE III 500 WB (11.7 T, Bruker Biospin, Germany) operating at 67.8 MHz. The spinning speed was 12 kHz. The results were collected by using $\pi/6$ ($P1=0.8 \mu\text{s}$) pulses, recycle time 1s, spectral width 250 KHz and number of scans 1024. ^{17}O CP MAS spectra were obtained by using $\pi/6$ ($P1=25 \mu\text{s}$) pulses, contact time of 100 μs and 100 KHz of CW proton decoupling during acquisition. The number of scans for sample Com was 2048, and for samples Synt1 and Synt2 were 7904. The 3Q-MQMAS¹⁶ of samples Com and Synt2 were acquired on a Bruker spectrometer model AVANCE III 400. Rotational speed was 12 KHz. $P1=4 \mu\text{s}$ (pulse that creates 3Q coherence), $P2=1.5 \mu\text{s}$ (3Q 0Q conversion pulse) and $P3=54 \mu\text{s}$ (selective pulse). The recycle time was 0.5 s. The spectral width in F2 was 100 KHz. The

spectral width in F1 was 12.5 KHz. Number of scans was 960 and 128 fids were accumulated. All the spectra were referenced with a sample with 10% H_2^{17}O (0.0 ppm).

Results and Discussion

The DRX obtained by the samples that were studied showed a strong line width of diffraction for the three samples. The data were compared with American Mineralogist Database¹⁷ and showed that the diffractograms are in accordance to the boehmite phases, and no extra peaks due to impurities were found.

The diffraction peaks can be indexed to the orthorhombic $\gamma\text{-AlOOH}$ and the 020 diffraction lines showed displacement for lower values of the Bragg angles. The estimated crystallite sizes and interlayer distances d_{020} were determined by the position of the peak of the 020 diffraction line, and are presented in Table 1. It was observed that sample Com shows the largest crystallites, compared with samples Synt1 and Synt2.

Table 1. Crystallite size, D, and the interlayer spacing, d_{020} , of the samples analysed

Sample	Crystallite size D (\AA) ^a			Interlayer spacing d_{020} (\AA)
	from diffraction lines			
	020	031	120	
<i>Com</i>	43	53	50	6.187
<i>Synt1</i>	34	41	40	6.259
	28 ^b			
<i>Synt2</i>	28	39	32	6.162

^a Crystallites size²⁰ estimated with error of 20%; ^b ref. 11

The isotherms obtained from N₂ adsorption-desorption are of type IV. This type of isotherm is found in many mesopores and solid adsorbents.^{18,19} The specific areas measured by BET method, are presented in Table 2. It was observed that the commercial sample showed surface area similar to Synth2.

The crystallite's size shows a correlation with the porosity as well, specially the average pore diameter seems to grow according to the crystal size. The values of porous volume are similar between samples Com and Synt2. The synthesized samples showed the lowest percentage of microporous area.

The results of TG/DTG/DTA analyses were summarized in Table 3. The curves obtained for all the samples studied show three mass loss events, and are related, according to Nguefack et al.²¹ to the loss of physically adsorbed water, to dehydration and transformation of boehmite²² and to continuous dehydroxylation of the surface on the transition alumina thus formed.

These data confirm the X-ray results, where the raise of the diffraction line is directly related to the hydration level of the studied materials. Commercial sample showed almost the same mass loss at the second weight loss process.

Table 2. Surface area, pore volume and average pore diameter of the commercial and synthetic samples.

Sample	Surface area (m ² /g)	Micropore Area (m ² /g)	Pore volume (cm ³ /g)	Av. pore diameter ^c (Å)
<i>Com</i>	248	27	0.37	52.7
<i>Synt1</i>	219 352 ^a	6	0.26	37.1
<i>Synt2</i>	247 452 ^b	8	0.39 0.81 ^b	44.7 50.0 ^b

^a ref.11; ^bref.12^c Estimated using the BJH desorption branch of the isotherm.

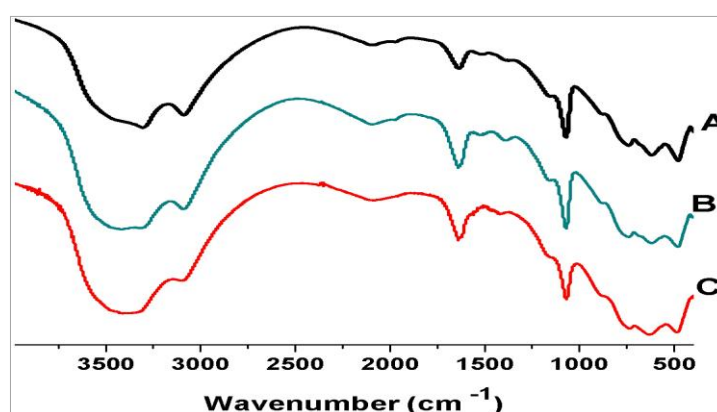
Table 3. TG/TGA results obtained for samples studied

Sample	First Isotherm Peak (°C)	Second Isotherm Peak (°C)	First lost Weight (%)	Second lost Weight (%)	Third lost Weight (%)
Com	68	442	11.69	14.70	1.48
Synt1	70	424	19.24	15.22	3.85
Synt2	74	438	9.79	14.56	4.00

The infrared spectra of boehmite samples (Figure1) can be divided into three main regions: the Al–O octahedron region (200–800 cm^{-1}), the Al–OH bending region (800–1300 cm^{-1}) and the OH stretching region (over 3000 cm^{-1}).²³ The spectra of sample shows that a band centered around 3400 cm^{-1} , OH stretching of adsorbed water⁷ for the sample. This was assigned for stretching mode of adsorbed water.

Wavenumbers around 3300 cm^{-1} and 3090 cm^{-1} were due to OH stretching vibration mode associated with the structural zigzag hydrogen-

bonded chains $\text{OH}\cdots\text{OH}\cdots\text{OH}$ ^{21, 24, 25} absorptions around 2090 cm^{-1} and 1970 cm^{-1} represent combination bands, whereas those at 1150 cm^{-1} and 1070 cm^{-1} represent bending of Al–OH, asymmetric and symmetric, respectively^{24, 25}. The band observed at around 880 cm^{-1} represents O–H vibration in the solid surface.^{7, 26} The O–H torsional mode was observed around 740 cm^{-1} . Some authors consider this band as Al–O stretching.²⁷ The bands observed around 620 cm^{-1} , 570 cm^{-1} and 480 cm^{-1} are related to the stretching modes of AlO_6 .²⁴

**Figure 1.** Infrared spectra of pseudoboehmite samples: A) Sample Com; B) Sample synt1; C) Sample synt2.

Wavenumbers around 1520 cm^{-1} and around 1385 cm^{-1} was assigned as impurities.²⁸ Wavenumber around 1635 cm^{-1} was due to OH bending mode of adsorbed water⁷.

The main information extracted from the infrared spectra was the difference in the water amount between samples, according to the X-ray results and thermal analysis. Figure 2 (left) displays the ^{27}Al MAS NMR spectrum of the sample Com: a single signal with chemical shift with a maximum near 0 ppm, corresponding to octahedral AlO_6 species.^{29,30} The spectrum of sample Synt2, a mesostructured material (Figure 2, right) is the only one that shows also a signal of tetrahedral aluminum³¹ in low intensity at 65 ppm, suggesting that in this sample the distribution of surface Al is slightly different comparing to

sample Com and Synt1, a mesoporous material.

The results of solid state ^{17}O MAS NMR analysis were depicted in Figure 3. The spectra presented a maximum at about 71 ppm, corresponding to coordinated Al-O-Al sites.^{13,32} This signal is relatively narrow, indicating the presence of ordered structures. It was not possible to discern in those spectra any second-order quadrupolar splitting. A second site, described in the literature as Al-OH^{13,32} and with extremely high quadrupole constant (for crystalline boehmite) was also observed with a maximum at about 0 ppm. The spectra were simulated by using DMFIT program³³ version: 20110209, and the results are shown in Table 4.

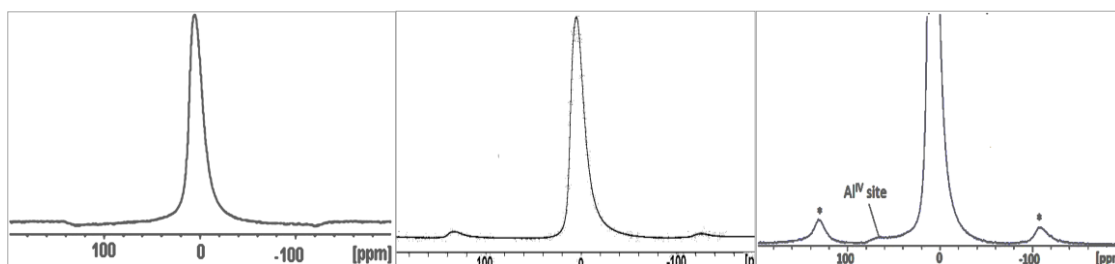


Figure 2. ^{27}Al MAS NMR spectra: (left) sample Com; (center) Synt1; (right) sample Synt2.

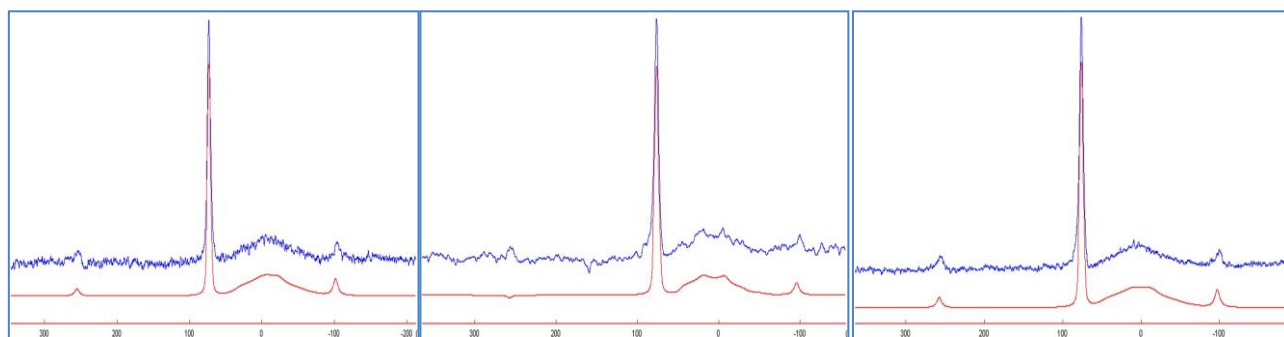


Figure 3. ^{17}O MAS NMR spectra of sample Com (left), Synt1 (center) and Synt2 (right): (up) experimental (up); simulation by using DMFIT program (down).

Table 4. ^{17}O NMR parameters determined for samples Com, Synt1 and Synt2.

parameter	Com		Synt1		Synt2		ref. 13	
	Al-O-Al	AlOH	Al-O-Al	AlOH	Al-O-Al	AlOH	Al-O-Al	AlOH
δ_{max} (ppm)	73,3	5,1	76,4	5,2	76,2	9,2	-	-
δ_{iso} (ppm)	76,8	39,2	80,8	51,4	80,0	52,8	70,0	40,0
C_Q (KHz)	1603	5827	1715	5673	1648	6000	1200	5000
η_Q	0,59	0,62	0,65	0,47	0,61	0,60	0,1	0,5

C_Q : quadrupolar coupling Constant; η_Q : quadrupolar asymmetry parameter

To reveal the presence of multiple oxygen sites in the alumina precursors, 3QMQMAS ^{17}O spectra of the samples Com and Synt2 were recorded (spectrum not shown). Although slightly different spectral characteristics in the two cases could be observed, it was justified by the different disorders's degree of the two samples and the

presence of multiple oxygen sites could not be confirmed. Further experiments must be performed to describe better the MQMAS variations along the samples's series. ^1H - ^{17}O CP MAS NMR spectra of samples Com, Synt1 and Synt2 were performed (Figure 4) and confirmed the presence of the hydroxylated site.

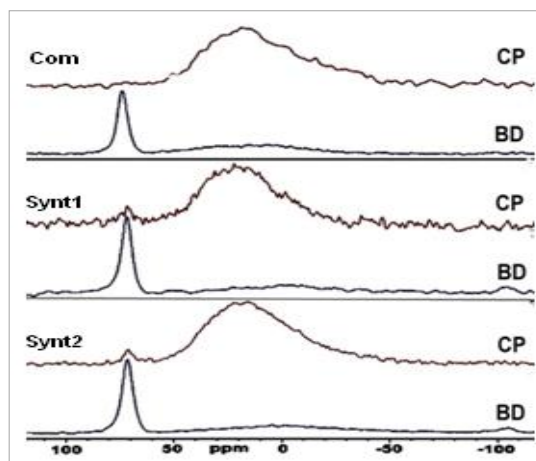


Figure 4. ^{17}O NMR MAS (one pulse sequence) and CPMAS (cross polarization, CP) spectra of the samples Com, Synt1 and Synt2.

It was noteworthy the slight difference CP signals shape, sample Com being the one with the largest half height width. This finding is also an evidence of the different distribution on OH sites in those samples.

4. Conclusions

In this work the alumina-based HDT precursors were analyzed and could be differentiated according to some of their structural features, particularly the crystal size and AlOH sites, as detected by ^{17}O MAS NMR spectra. ^{27}Al NMR analysis confirmed the existence of a single type of aluminum (AlO_6 octahedral) in mesoporous precursors; mesostructured sample (Synt2) showed a minor tetrahedral Al component. The ^{17}O MAS NMR spectra show the existence of at least two types of oxygen in all samples, one of which, assigned to AlOH sites, has a variable relative intensity along the series, roughly proportionally to the crystallite size. The results

seem to indicate that mesostructured alumina precursors present ^{17}O chemical shifts slight more deshielded compared to mesoporous samples. Further experiments will be performed to confirm this tendency.

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