Alumina-Titania Nanofibers, Synthesis by a pH-Swing Method

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Introduction

The synthesis of materials with nano-scale dimensions and structure is of great interest and importance in materials science and nanotechnology[1-2]. Particularly, alumina nanofibers have great potential applications as adsorbents, catalysts support, composite materials, and ceramics, among others. In the last years, several studies on alumina nanofibers formation have been reported[3-5].

In an Al_2O_3-TiO_2 mixed oxide system, the incorporation of TiO_2 to alumina is known to increase the acidity of the resulting mixed oxide; depending strongly on the preparation method and the titania concentration[9]. When using TiO_2 as a support of NiMo catalysts, initial catalytic activity in hydrodesulfurization reactions is much higher than that on catalysts based on pure alumina[10]. One of the main inconveniences of using TiO_2 as a catalyst support is its low specific surface area (50-60 m^2/g) and pore volume (~0.3 cm^3/g). One approach to overcome these textural disadvantages is to disperse TiO_2 on a given alumina support. Therefore, the use of alumina-titania as a catalyst support is a good alternative to improve hydrotreating catalysts performance, as long as high TiO_2 dispersions are achieved [11-13]. To our knowledge, studies on fibrillar alumina-titania mixed oxides have not been reported. The importance of fibrillar alumina morphology lies on its inter-fibrillar pores, which favor the diffusion and eventual transformation of huge refractory asphaltene and Ni, V porfirinic molecules contained in oil residua, which represent the most difficult hydrocarbons to transform in oil hydrotreatment reactions, and contribute enormously to deactivation of catalysts active sites[8].

We have found that by implementation of a pH swing method, it is possible to obtain boehmite alumina with fibrillar morphology[14]. This pH swing method was first reported by Ono et al.[15]; and consisted on swinging the pH value from acid to basic pH region which corresponded to the limits of the U-shaped solubility curve of alumina. As a result, Ono et al. disclosed a method to control of pore size and pore size distribution of aluminas, simply by varying the number of times (swings) a pH value was swung. However, these authors overlooked that in certain conditions, pH swing method can afford alumina nanofibers.

In this study, we aimed at obtaining alumina-titania by a pH swing method and combined with three different techniques to incorporate TiO_2 on Al_2O_3 (co-precipitation, deposition and stepwise deposition). The overall purpose was to disclose a method in which TiO_2 was highly dispersed.

Experimental

Both single alumina (A6S5) and TiO_2-Al_2O_3 mixed oxides were synthesized following a modified pH swing method[15]. A general preparation flow diagram is displayed in Figure 1. All preparations were carried out at constant 60 °C temperature. The first pH-swing cycle was as follows: In a glass vessel containing 200 ml of aqueous $Al_2O_3 \cdot NaO_2$ (basic pH), an aqueous $Al_2(SO_4)_3 \cdot 18H_2O$ solution (acid pH) was poured until reaching pH=2. Then the white precipitate was kept for 5 minutes and then aqueous $Al_2O_3 \cdot NaO_2$ solution was added until stable pH=8 stable in the reaction mixture, and aged for 5 min. This stage is the first pH swing cycle, and can be repeated a number of times to affect the textural properties. In this work, we carried out six pH swing cycles in all synthesis, maintaining all other conditions constant.
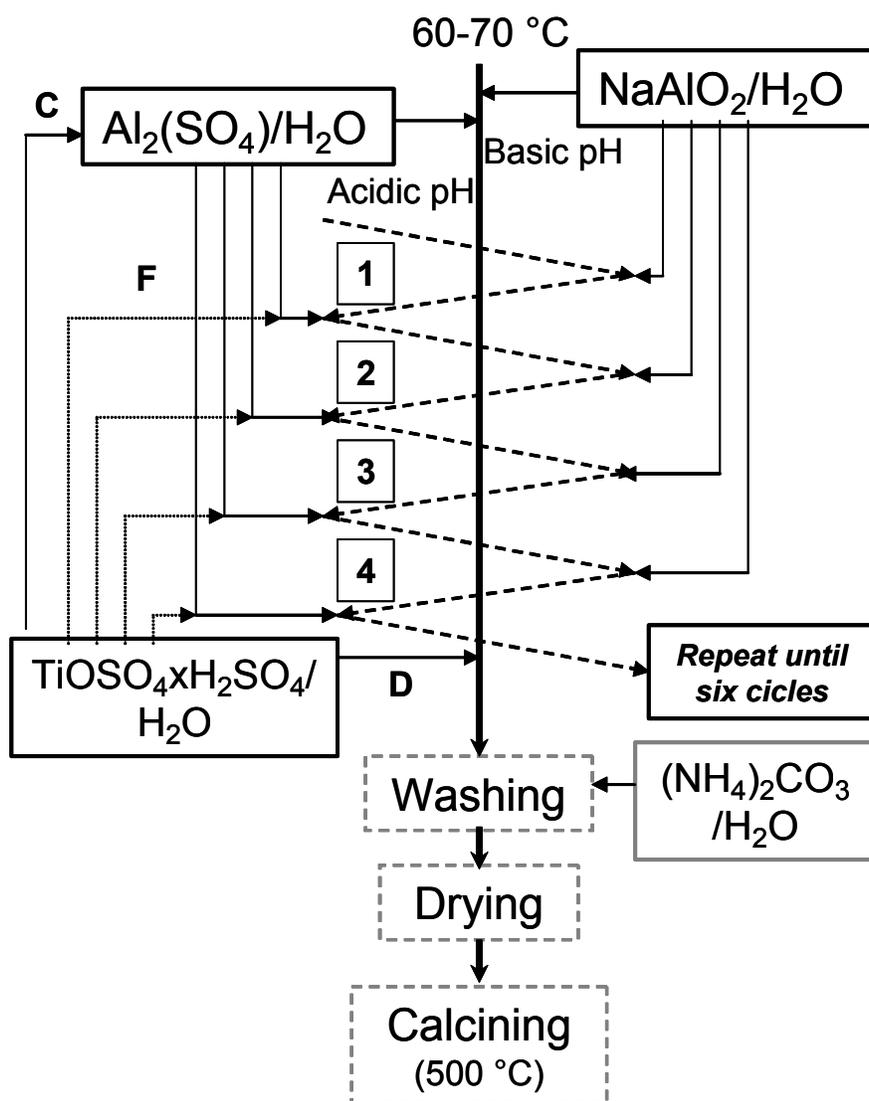
Figure 1. Preparation flow diagram of alumina and alumina-titania by a pH-swing method and the different incorporation techniques of titania. C: coprecipitation, D: deposit, F: step deposit.

Materials characterization

Textural analysis (TA): All textural properties were determined on calcined materials at 500 °C, using a Micromeritics Digisorb ASAP-2405 equipment. Specific surface areas were calculated by a Brunauer-Emmet-Teller equation, based on adsorption isotherm of N2 at -196 °C. Pore size distributions were obtained by a Barret-Joyner-Hallenda method (BJH) on desorption cycle.

X-ray diffraction (XRD): Powdered materials were characterized by XRD using a Siemens D-5005 equipment with a digital record system and CuKα (λ=1.5406 Å) radiation, where Kα2 was eliminated by a Diffract Plus V 1.01. Software. Diffraction intensity was measured in 2θ range between 10 and 80°, with a 0.03° step each 8 seconds for point.

Chemical analysis (CA): Ti content in pH-swing alumina-titania solids was determined by ion-coupled plasma spectroscopy (ICP) in Perkin-Elmer OPTIMA 3200DV equipment. Samples (0.3 g) were dissolved in nitric acid and transferred to the nebulization camera using a peristaltic pump at 1 cm3/minute, using Ar as carrier gas.

Transmition Electronic Microscopy (TEM): TEM analysis was performed using JEOL 2010F Microscopy operating at 200 KV. Samples were pulverized and suspended in isopropanol at ambient temperature with ultrasonic stirring, and then an aliquot was dropped in a 3 mm carbon-copper grid.

Raman spectroscopy (RS): Raman spectra were recorded at ambient temperature on samples calcined at 500 °C, in a Yvon Jobin Horiba T64000 spectrometer equipped with a Olympus BX-41 confocal microscopy, 514.5 nm laser beam and 15 mW power. This spectrometer was equipped with a CCD detector.

UV-visible analysis (UV-v): UV-vis diffuse reflectance spectra were obtained in a Varian Cary-4 UV-v spectrometer with a Harrick-Scientific Praying-Mantis special accessory of diffuse reflectance.

Results

Textural properties of Al_2O_3-TiO_2 and single alumina (A6S5) materials, after calcining at 500°C, are shown in Table 1. The specific surface area of A6S5 was 298 m^2/g, while Al_2O_3-TiO_2 materials showed values between 311-337 m^2/g, indicating a relative increase in specific area values in spite of the different preparation methods and the presence of TiO_2. The highest surface area (337 m^2/g) was obtained in the Cs5 sample, while the lowest one was 311 m^2/g, in Ds5 prepared by deposition.

Table 1. Textural Properties and TiO_2 content of alumina-titania materials and single alumina A6S5 calcined at 500°C.

Sample	Specific area (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)	TiO_2 (%wt)
Cs5	337	0.57	6.8	8.9
Fs5	330	1.05	12.8	10.8
Ds5	311	1.02	13.1	13.7
A6S5	298	0.99	13.3	-

The morphology of A6S5 and Al_2O_3-TiO_2 materials was examined by TEM and their images are shown in Fig. 2. All samples showed clear fibrillar morphologies. The fibrils are mainly disordered and very few bundles were found where fibrils were parallel to each other. In A6S5 fibrils are in average 90 nm long by 6 nm wide. Ds5 and Fs5 showed fibrils with similar dimensions as those in A6S5, but additionally some plaque-like regions (rhombohedral shaped) of about 12 nm were found.
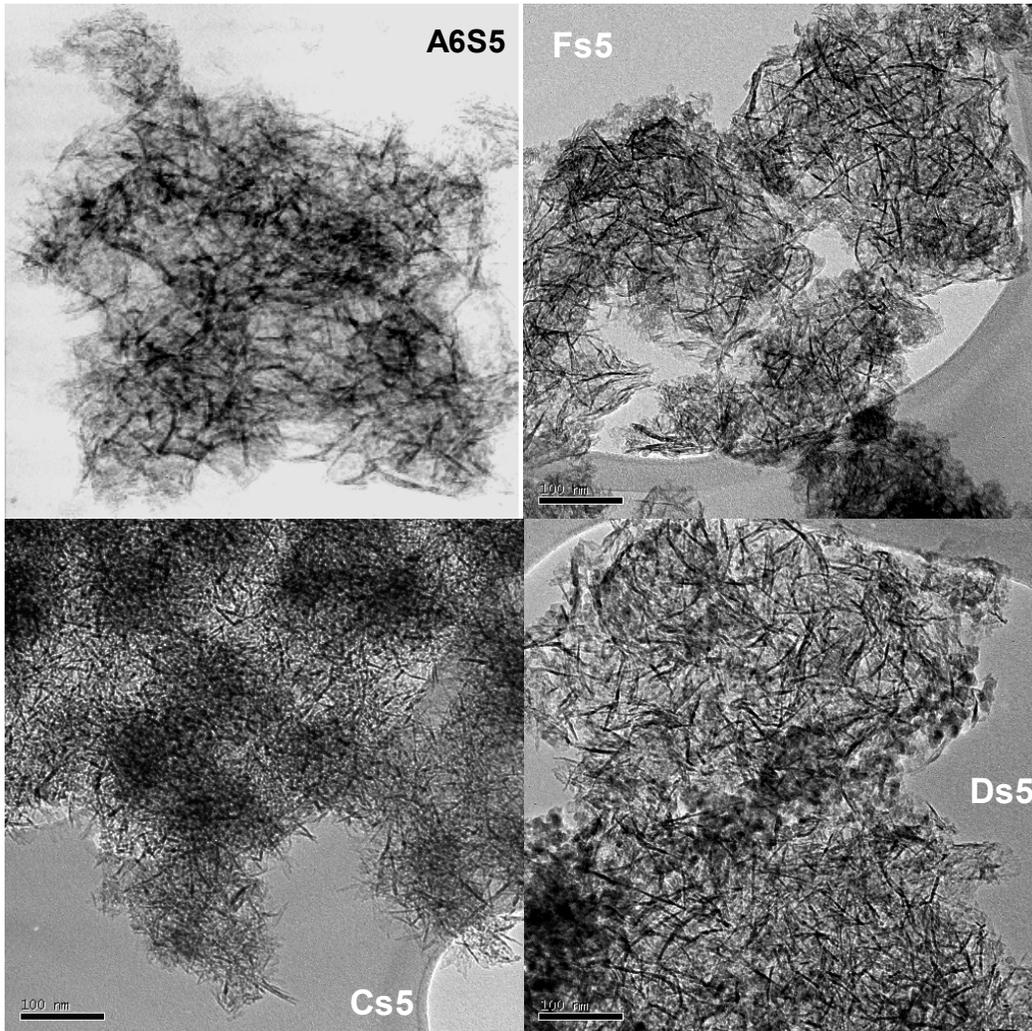
Figure 2. TEM images that show the fibrillar morphology of single alumina A6S5 and alumina-titania materials calcined at 500°C.

X-ray diffraction (XRD) patterns in Fig. 3 showing γ-alumina phase in all samples (specifically 440, 400 and 311 planes), besides of TiO_2 anatase phase in some samples (more intense peak in 101 plane on 25.5° at 2θ axis). Particularly, the material obtained by deposition (Ds5) displayed the highest intensity of the five characteristic peaks of anatase phase (plane 101 is the most intense and representative). Sample Fs5, obtained by stepwise deposition had an intermediate intensity in comparison with those of Cs5 and Ds5 samples and showed XRD patterns with anatase peaks for 101 and 211 planes only. Co-precipitated sample, Cs5, showed an XRD pattern with the least intensity, in which only

a faint 101 peak was observed. The intensity and width difference in the 101 plane for three Al_2O_3-TiO_2 mixed oxides indicate generation of different anatase crystallite sizes. A higher peaks intensity of alumina in Ds5 and Fs5 samples in comparison with those in Cs5 and A6S5 single alumina, suggests a better Al_2O_3 crystallinity in Ds5 and Fs5 samples.
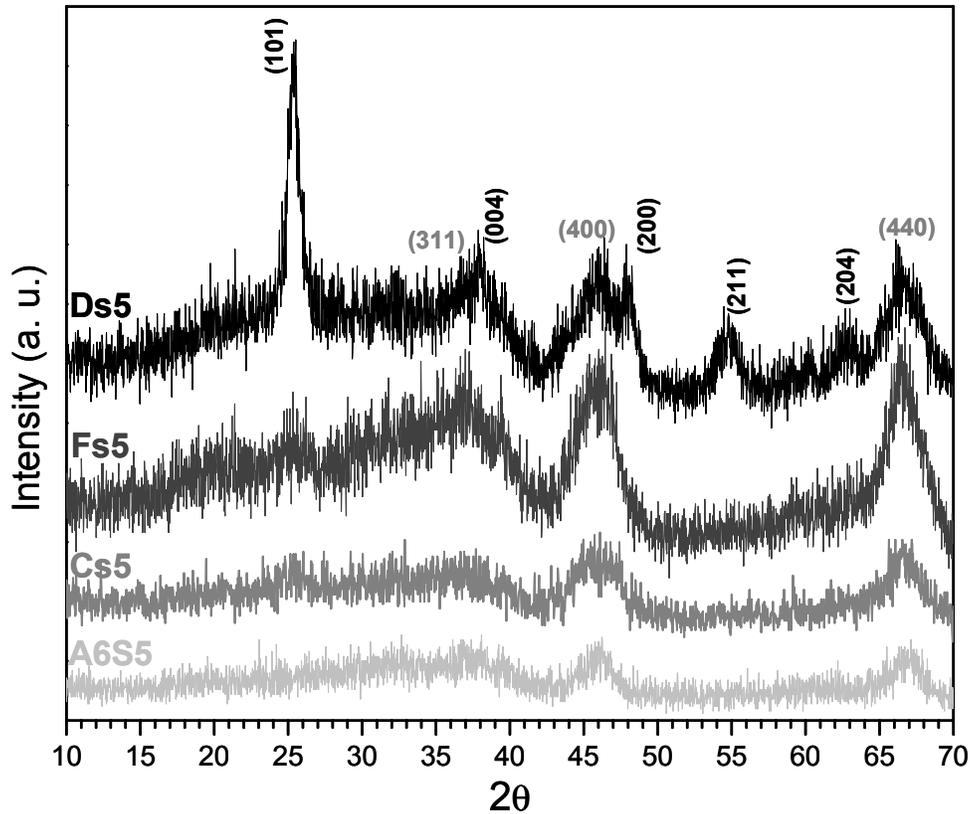
Figure 3. Wide-angle XRD patterns of single alumina A6S5 and alumina-titania materials calcined at 500°C.

Conclusions

The three different ways to incorporate titanium oxysulfate combined with a pH swing method yielded nanofibrillar alumina-titania materials, but with a clear different titania dispersion depending on the incorporation method of the Ti compound.

In the three alumina-titania systems only one TiO_2 phase was detected: anatase. In the end, Al_2O_3-TiO_2 nanofibrillar systems were obtained by a pH swing method, with specific surface areas higher than 300 m2/g, and pore volumes equal or higher than 1 cm^3/g, after calcining at 500 °C; maintaining its fibrillar morphology below this temperature.

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