JOURNALOF

Ceramic Processing Research

Synthesis of γ -Al₂O₃ nanopowder by the sol-gel method: Effect of different acid precursors on the superficial, morphological and structural properties

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The main aim of this investigation is to study the effect of three acid precursors (nitric acid, acetic acid and citric acid) during the synthesis of γ -Al₂O₃ nanopowder by the sol-gel method. The TEM analyses showed that the γ -Al₂O₃ prepared by using the strongest acid were irregular nanofibers with a length of 50 nm and a diameter of 5 nm, while the γ -Al₂O₃ prepared with citric acid showed agglomerates. On the other hand, the SEM analyses showed very similar morphologies. The N₂-physisorption analyses confirmed that there is a relationship between the acidity and the surface area; and between the presence of mesopores and micropores on the surface of the synthesized Al₂O₃. The effect of the acid strength on the surface area was as follows: nitric acid ($347 \text{ m}^2 \cdot \text{g}^{-1}$) > acetic acid ($252 \text{ m}^2 \cdot \text{g}^{-1}$) > citric acid ($164 \text{ m}^2 \cdot \text{g}^{-1}$). In addition, the XRD results confirmed that for all the samples thermally treated at 600 °C, the main phase was γ -Al₂O₃; nevertheless, the thermal analyses showed that the γ -Al₂O₃ synthesized with the weakest acid was not stable above 600 °C.

Key words: γ-Alumina, Sol-Gel Method, nanopowder

Introduction

Since its commercial production at the end of the nineteenth century, alumina (Al₂O₃) has been widely used as a ceramic material in a variety of industrial applications because of its advantageous engineering properties: high mechanical strength and hardness as well as wear, corrosion and heat resistance. Since then, enormous research efforts have been put into understanding the chemical, electric and catalytic properties of Al₂O₃. Panias and Krestou reported that the wide variety of applications of Al₂O₃ is related to both the corundum structural phase (α -alumina) and transition aluminas [1]. In the first phase, the hexagonal microstructure of close-packed oxygen ions shows excellent mechanical, electrical, thermal and optical properties [2-4]. While the transition aluminas, which have a cubic microstructure of close-packed oxygen ions, show high surface area, mesoporosity and surface acidity; and, as a result, they are used as absorbents, catalysts or biotechnology materials [5-6].

An exponential growth of research activities has been seen in nanosciences and nanotechnology in the past decades [7-9]. New physical and chemical properties emerge when the size of the materials become smaller and smaller; right down to the nanometric scale. In the case of transition aluminas, the powder preparation with controlled pore structure, morphology and porosity is of great importance to prove the potential applications of γ -Al₂O₃ powder in catalysis [6, 10].

Although many research studies have been carried out on the production of nanosized γ -Al₂O₃ based on the liquid phase reaction [11-13], gas phase synthesis [14] or hydrothermal treatment at high pressure [15], none of the aforementioned methods is suitable to control all the properties present in these materials. However, the sol-gel method is the most promising to prepare highly pure powders with high surface areas. The disadvantages of this route are the high cost of the precursor and the long gelation time.

The goal of this study was to investigate the effect of the synthesis of Al_2O_3 using different acids (nitric, acetic and citric) on the superficial, textural and structural properties at 600 °C.

Experimental Part

Preparation of samples by the sol-gel method

Three different preparations of γ -alumina by the sol-gel method were carried out under acid conditions. Firstly, a mixture of aluminum isopropoxide (99.99%, Aldrich) and isopropanol (99.00%, Jalmek) was refluxed at 80 °C with vigorous stirring. Then, in a second step, an acid solution (acid/water = 0.02) containing either nitric acid (65%, DEQ), acetic acid (99.7%, DEQ) or citric acid (99.5%, Sigma-Aldrich) was added drop by drop in order to promote and control the hydrolysis step. The reaction mixture was kept at 80 °C for 48 h. The gel obtained

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was washed with 2-propanol (99.9 DEQ); and then dried at 100 °C. Afterwards, the precursors were divided into several portions to perform the thermal treatments at 600 °C/5 h with a heating rate of 2 K.minute⁻¹.

Structural Characterization

The sol-gel powders, were characterized by X-ray powder diffraction (XRD) using a Bruker D8 Advance diffractometer with CuK_{α} radiation. The specific surface area and pore size distribution were determined by nitrogen adsorption and desorption isotherms using a Quantachrome NOVA 2000 apparatus. Simultaneous thermal analyses (TGA/DTA) of the fresh samples were performed in a Q600 TA-Instruments apparatus under nitrogen atmosphere using a heating rate of 10 K.minute⁻¹. The acid sites of the γ -Al₂O₃ compound were determined by Thermo-Programmed Desorption of carbon dioxide (TPD-CO₂); once the NH₃ was chemisorbed at 100 °C, it was desorbed by heating the sample from 100 to 800 °C at 5 K.minute⁻¹. The morphology was determined by Scanning Electron Microscopy in a JEOL 6490LV; and also by Transmission Electron Microscopy in a JEOL 2010.

Results and Discussion

The XRD patterns of the dry samples (100 °C) are shown in Fig. 1. In general, the diffraction patterns of the precursors are related to the boehmite phase, indicating that a crystalline precursor is obtained by the sol-gel method. In addition, all the samples show an amorphous phase; however the intensity of the main peaks increases as follows: acetic acid > nitric acid > citric acid. It has been reported in the literature that boehmite is also a direct parent to obtain highly pure γ -Al₂O₃ with a reasonably high surface area [1, 13].

Figure 2 shows the XRD patterns of the samples prepared in different acid media and calcined at 600 °C. All the characteristic γ -Al₂O₃ peaks can be seen; however, the degree of crystallinity was improved when the γ -Al₂O₃



Fig. 1. X-ray diffraction patterns of the alumina precursor prepared in different acid media: A) acetic acid, B) nitric acid, C) acid citric.



Fig. 2. X-ray diffraction patterns of the g-alumina prepared in different acid media at 600 °C: A) acetic acid, B) nitric acid, C) acid citric.



Fig. 3. Thermal behavior of the alumina precursor synthesized with: A) acetic acid, B) nitric acid, C) citric acid.

was synthesized with both the acetic acid and nitric acid. As for the alumina prepared with the weakest acid, the transformation to γ -Al₂O₃ requires higher temperatures.

The thermal behavior of the as-dried precursor was studied by DTA/TGA; and the experimental curves of the alumina gels are shown in Fig 3. Two major endothermic weight losses were observed in the TGA curves, between 50 and 450 °C. In addition, the sample prepared with citric acid showed a very small weight loss above 500 °C. For the differential analyses, the endothermic peaks are explained as follows: The first endothermic weight loss at 80 °C, is related to a removal of physically adsorbed water/alcohols, while the second weight loss, above 300 °C, is reported as a dehydroxylation process. The wide exothermic peak at 1,050 °C, could be attributed to the transformation from γ -Al₂O₃ to α -Al₂O₃.

A total weight loss ranging from 35 to 50% can be seen during the three-step decomposition process. If the boehmite phase had only been formed, the theoretical weight loss of 50% could have been expected. In our case, only the sample prepared with citric acid is close to this.

The surface area, pore size and pore volume data obtained for the γ -Al₂O₃ at 600 °C are presented in the Table 1 for the sake of comparison. By analyzing the

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Acid Medium	Nitric Acid	Acetic Acid	Citric Acid
BET Area $(m^2 \cdot g^{-1})$	347	252	164
Size Pore (nm)	8	3	9
Pore Volume (cm ³ \cdot g ⁻¹)	0.50	0.97	0.72

Table 1. Effect of the reaction conditions on the textural properties of the g-Al₂O₃ samples

effect of the reaction conditions on the γ -Al₂O₃ sample that was prepared with the strongest acid, it can be seen that it shows the highest surface area (347 m²·g⁻¹), followed by the γ -Al₂O₃ samples prepared in the medium acid (252 m²·g⁻¹); and finally by that prepared with a weak acid (164 m²·g⁻¹). For the same samples, the pore size is a function of the strength of the acid used during the synthesis. On the other hand, the pore volume decreased in the same samples.

The mesoporous character of the materials was also verified by the N₂ adsorption-desorption isotherms; as can be seen in Fig. 4. All the isotherms belong to type IV with different hysteresis-loop sizes, which indicate changes in the pore structure in these materials [16]. In general, the adsorption isotherm at the lowest pressure can be assigned to the monolayer coverage of mesopores and surface particles; the adsorption at medium pressure (P/Po = 0.40-0.85) mainly to capillary condensation of N₂ in mesopores, while that occurring at the highest pressure (P/Po = 0.85-0.99) is mainly contributed to aggregated pores.

Figure 4 shows the N₂ adsorption-desorption isotherms for the samples synthesized and calcined at 500 °C, which look rather similar. At the lowest relative pressure (P/ Po = 0-0.40), type-I-adsorption behavior is observed, with a rapid increment of the amount of adsorption, which is a typical characteristic of microporous materials [17]. However, a type IV isotherm with a H₃ type hysteresis loop appears at the relative pressure range of 0.4-0.99, which is characteristic of mesoporous solids, where the H₃ type hysteresis loop at high relative pressure (P/Po)



Fig. 4. N_2 adsorption-desorption isotherms for the γ -alumina prepared in different acid media at 600 °C: A) acetic acid, B) nitric acid, C) acid citric.



Fig. 5. NH₃-TPD profiles of the g-alumina prepared in different acid media at 600 °C: A) acetic acid, B) nitric acid, C) acid citric.

is often associated with the formation of aggregates with slit-shaped pores, i.e. a loosely coherent group of particles [18].

The NH₃-TPD spectra were carried out to track the acid strength of γ -Al₂O₃. In the NH₃-TPD curves, the peaks are generally distributed into two regions: low-temperature (LT, T < 400 °C) and high-temperature (HT, T > 400 °C) regions [19, 20]. The peaks in the HT region are associated to desorption of NH₃ from strong Brönsted and Lewis type acid sites, while the peaks in the LT region are the result of the desorption of NH₃ from weak acid sites. As shown in Fig. 5, the peaks appear in both temperature regions, which confirm that two types of acid sites are on the surface.

Therefore, these data provide strong evidence of the activity that is expected from the catalyst, as has been reported for the catalytic activity, which shows a close relationship between the total acidic sites and their high number and strength; which causes a direct positive effect on the catalyst activity. Those with a high number of acidic sites, allowed us to obtain a high dispersion when a noble metal is deposited.

As has been seen from the results, the nature of the acid precursor causes an important effect on the microstructural properties as was seen in the results about the surface area.

The γ -Al₂O₃ samples synthesized with different acid precursors were analyzed by Scanning Electron Microscopy (SEM). Figure 5 (5a and 5b) shows the corresponding morphologies of the γ -Al₂O₃ obtained using nitric acid and citric acid, respectively. Nevertheless, we cannot see significant differences. On the other hand, when the same samples were analyzed by TEM, the differences in the morphology of each sample were obvious.

Figure 6B, which corresponds to the γ -Al₂O₃ synthesized with citric acid, shows agglomerates ranging from 7 to 10 nm, in contrast with Figure 6A, which corresponds to the γ -Al₂O₃, which used nitric acid as precursor. The material formed nanofibers with a length of 50 nm and a diameter 5 nm. From this result, we show that the morphologies play an important role in the materials





Fig. 6. SEM micrographs of the γ -Al₂O₃ prepared in different acid media at 600 °C: A) nitric acid; and B) acid citric. The TEM images are respectively inserted.

causing substantial effects on the surface area as was seen by the N_2 physisorption analysis. Until now, the growth of such structures is not well known; and the researchers have stated different points of view [21-23]; as a consequence, it is necessary to study the mechanism variables about the formation of these nanostructures. The importance of understanding the mechanisms present during the synthesis of such structures comes from the fact that very important applications are predicted in catalysis and other areas that need large contact surfaces.

Conclusions

Sol-gel γ -alumina was successfully synthesized using different acid precursors. Firstly, it was shown that the acid conditions causes a strong influence on the Al₂O₃ morphology since the alumina prepared with citric acid showed agglomerates with particle sizes between 7 to 10 nm, while the samples prepared using nitric acid formed nanofibers with a length of 50 nm and a diameter of 5 nm. Then, the XRD also showed that the force/power of the acid has a positive influence on the microcrystalline structure at 600 °C. The same tendency was observed by the N₂ physisorption to obtain surface areas up to 250 m²·g⁻¹. In addition, these materials showed a good thermal stability around 500 °C; except for the γ -Al₂O₃ prepared with

citric acid. On the other hand, the γ -Al₂O₃ developed a high percentage of strong acidic sites. In spite of these good results, we cannot see a clear relationship between the total acidity of the samples and the crystallinity and the morphology. As a consequence, more studies will have to be carried out to draw out the mechanism that favors each reaction.

Acknowledgements

This research was supported by the projects PROMEP/ 103.5/07/2523 and 103.5/07/3578. CONACyT 62370. The authors are grateful to Dra. Leticia M. Torres Guerra, head of the Ecomateriales and Energy department (FIC-UANL); E. López Cuellar (FIME-UANL) and F. Alejandre-Sandoval (FIC-UANL) for their invaluable help with the TEM and SEM analyses.

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