

SYNTHESIS OF γ -ALUMINA FROM ALUMINUM CANS

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Abstract: In order to take advantage of the residues of Al cans, in this work gamma-alumina ($\gamma\text{-Al}_2\text{O}_3$) was obtained from a boehmite gel ($\text{AlO}(\text{OH})$) obtained from the precipitation of AlCl_3 with NH_4OH . The precursor, $\text{AlO}(\text{OH})$, was aged, washed and characterized. The AlCl_3 was obtained from the reaction between Al cans and industrial hydrochloric acid. For its part, the TGA analysis of $\text{AlO}(\text{OH})$ to $\gamma\text{-Al}_2\text{O}_3$ showed that the transition temperature was between 400 and 500°C and by XRD the typical reflections of a $\gamma\text{-Al}_2\text{O}_3$ were found. The obtained AlCl_3 solution was analyzed by atomic absorption spectroscopy (AA) to find the other metals in the cans. We find small amounts of metals in the following order: $\text{Cu} > \text{Fe} > \text{Hg} > \text{Pb} > \text{Ni} > \text{Zn}$. The alumina obtained from $\text{AlO}(\text{OH})$, was identified by X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Energy Dispersion Spectrometry (EDS), Physisorption of N_2 and H_2O in order to know its characteristics morphological, impurities, BET area and H_2O adsorption capacity. This alumina reached a BET area of 298 m^2/g and a pore diameter of 36 Å, typical of a mesoporous material.

Keywords: Aluminum cans, $\gamma\text{-Al}_2\text{O}_3$, catalyst, boehmite.

INTRODUCTION

Currently in Mexico around 80 thousand 640 tons of aluminum cans are discarded annually from the consumption of packaged beverages. The aluminum in these cans is of high purity, so it can be reused to obtain higher value-added materials such as activated alumina ($\gamma\text{-Al}_2\text{O}_3$). Within the chemical industry, the $\gamma\text{-Al}_2\text{O}_3$ mainly has been used as catalytic support in numerous industrial processes such as: Claus process, Hydrodesulfurization process, Alkenes production from alcohols, steam reforming of natural gas, Catalytic nafta reforming to produce gasoline, Drying gases,

drying liquids, Catalytic cracking, Hydrocracking Isomerization of paraffins and others [Contreras, et al. (2015)].

The alumina used in chemical processes is activated alumina (also γ - Al_2O_3), because in this phase the alumina is highly porous, with a specific area between 100 to 400 m^2/g , with a stable structure in a wide range of temperatures and with a high affinity for water [Contreras, et al,(2015), Schoonover, (1982)].

The shape, texture and size of the particles in the supports vary with respect to the techniques and materials used in their elaboration [Contreras et al.,(2015)] and that is why the best combination of both is sought for a better use of the active compounds [Ramli and Saleh, (2009)]. The magnitude of the specific area depends on the preparation method and the degree of activation, for which there are different preparation methodologies that provide physical qualities and sometimes result in improvements such as raising the specific surface, pore volume and catalytic activity [Contreras et al.(2015), Hartmann et. al., (2012)].

Currently, the aim is to improve the manufacturing process and improve its specific properties such as crystalline structure, catalytic activity, acidity, mechanical and thermal resistance, and specific area, through the preparation variables (concentration of reagents and surfactants, temperature, pH, among others) that intervene during its synthesis.

METHODOLOGY.

PRETREATMENT OF ALUMINUM CANS

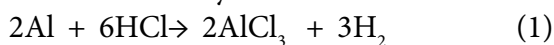
The aluminum cans collected from municipal waste (Figure 1(a)), underwent a cleaning and grinding process to carry out digestion with hydrochloric acid in order to obtain the aluminum chloride salt.

The waste aluminum cans were shredded in

an industrial shredder (SAISA-1)(Figure 1(b)) with stainless steel blades, which allow tearing and do not jam the cans during shredding.

CHEMICAL REACTION OF AL CANS

After the previous stage, the fragments of the cans with an average diameter of 1 cm were washed, dried and weighed with a weight of 10 g of Al, to introduce them into the reactor. The stoichiometry of the global reaction to obtain aluminum chloride (AlCl_3) from the acid attack on aluminum can (Eq.1) involved the formation of hydrogen and AlCl_3 as observed in the stoichiometry of the reaction:



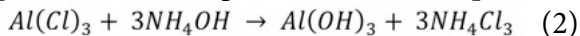
During the reaction with hydrochloric acid HCl (38% J.t. Baker), at 60°C, the formation of H_2 bubbles and foam formation were observed, which corresponded to approximately a volume equal to that of the liquid phase and the aluminum surface turned dark gray, in addition a yellowish color was observed in the liquid solution.

The reaction was carried out in a three necked 2 liter glass flask, without stirring. A condenser was used to recycle the acid vapors at a mouth. In another mouth the acid was fed through a separation funnel with a valve. In the other mouth a glass thermometer with a range of 0-300°C was placed. The Al was added by a mouth directly by weighing it. A stopwatch and titration system was set up with a 1M NaOH solution. To start the reaction, all of the stoichiometric HCl acid was added to the flask. In this reaction, heating was started with the blanket until the reactor was maintained at 60°C. At the end, a filtering of the obtained solution was carried out to remove the remains of the coating varnish layer that the can has adhered.

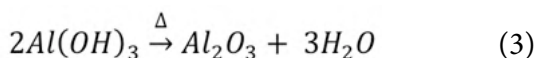
OBTAINING THE BOEHMITE GEL (AL(OH))

Synthesis of the boehmite gel was carried

out from the aluminum chloride solution by precipitation with NH_4OH until reaching a pH of 7, according to the reaction (Eq. 2).



Once the precipitate was obtained, it was left to stand at 25°C without stirring for a period of 72 h (aging time) to allow the formation of boehmite crystals. Afterwards, washings were carried out (in a centrifuge) using deionized water until the gel reached a pH equal to 7 and it was allowed to stand for 48 h. Next, the boehmite ($\text{AlO}(\text{OH})$) gel was dried in a laboratory oven at a temperature range between 100 and 120°C for 24 h. Finally, the boehmite (Eq. 3) was calcined in a temperature range between 200 and 550°C in order to obtain the $\gamma\text{-Al}_2\text{O}_3$ phase [Contreras et al (2015)] and characterize it.



CHARACTERIZATION OF MATERIALS.

ATOMIC ABSORPTION SPECTROSCOPY (AA)

An analysis was carried out by means of AA spectroscopy in an Analyst 400 equipment, (Perkin Elmer). Reference lamps of the elements: Al, Cu, Fe, Hg, Pb, Ni, Zn and As were used.

ULTRAVIOLET-VIS SPECTROSCOPY (UV-VIS)

In order to observe the behavior of chloride (Cl^-) and aluminum (Al^{3+}) ions, the salt obtained was analyzed by UV-vis spectroscopy, for which the equipment was used. Cary Series Uv-vis Spectrophotometer (Agilent Technologies).

GRAVIMETRIC THERMAL ANALYSIS. (TGA)

The thermogravimetric analysis was

recorded in a controlled atmosphere of air flow. The temperature variation was from 25°C to 1000°C . The thermal study (TGA) was performed on an SDT Q600 V20.9 Build 20 equipment, with a heating rate of $10^\circ\text{C}/\text{min}$. and with an air flow of $10 \text{ ml}/\text{min}$, the amount of sample was 3 mg. Its total weight capacity was 350 mg including the sample holder.

X-RAY DIFFRACTION

The diffractograms of the alumina calcined at 550°C were obtained with a Rigaku diffractometer (Phillips Xpert), equipped with a Cu anode tube (30 kV , 20 mA), using $\text{CuK}\alpha$ radiation. Scanning was performed in the range of $2\theta \sim 10\text{-}100^\circ$, with a count time of $2^\circ/\text{min}$. Crystalline phases of $\gamma\text{-Al}_2\text{O}_3$ were identified using the corresponding diffraction data cards JCPDS 10-0425 for Al_2O_3 .

SCANNING ELECTRON MICROSCOPY (SEM) AND EDS

Microstructure images of $\gamma\text{-Al}_2\text{O}_3$ oxides were taken by high-resolution field emission scanning electron microscopy (SEM) in a Jeol microscope (model JFM-6701-F, Japan) using secondary electrons. The preparation of the sample was done by placing it on top of a graphite tape to make the sample conductive and to be able to carry out the analysis.

EVALUATION OF THE H_2O ADSORPTION ISOTHERM

A sample of 24.1613 g of Al_2O_3 was placed in a glass chamber with air saturated with water at 25°C , covered by a hood. The weight of the sample was measured on an analytical balance (Mettler-Toledo) at defined times until completing 5700 min .

N_2 ADSORPTION (BET AREA)

N_2 adsorption-desorption isotherms of $\gamma\text{-Al}_2\text{O}_3$ were determined in a Micromeritics equipment (ASAP-2460, USA) using N_2

physisorption at -196°C . Before adsorption, the samples received a degassing pretreatment at 300°C for 2 h under a vacuum of 1×10^{-4} torr. These results determined the BET specific area, pore volume, and pore diameter distribution by applying the standard BET model [Lippens and Boer (1965)]. To quantify the pore volume (V_p) of the samples, the T-plot method [Barrett, et al. (1951)]. Pore diameter distributions were obtained from the BJH model [Prasad, et al. (1978)], using the desorption isotherm and assuming a cylindrical pore geometry.

RESULTS

REACTION KINETICS OF AL WITH HCL

Figure 2 shows the variation in the concentration of hydrochloric acid (HCl) during the reaction with the waste Al cans, to obtain AlCl_3 , at 60°C . Clearly, a yellow solution and the formation of H_2 bubbles are forming, which show the progress of the reaction. Doing the corresponding calculations, a reaction order of 1 was found.

METAL IMPURITIES BY AA

The metallic impurities of atomic absorption spectroscopy (AA) present in the liquid obtained after the acid attack to the aluminum cans and to a pure Al shot that was chosen as a reference (Labessa-Mexico) are shown in Table 1.

It was observed that after the acid attacks of the shot and the aluminum cans, there was a higher concentration of Cu and Fe in both samples compared to the other elements. In general, higher concentrations of Hg, Pb, Ni and Zn are observed in the case of cans than with shot, and an absence of As is observed in both samples. It was also observed that the order of contaminants was as follows: $\text{Cu} > \text{Fe} > \text{Hg} > \text{Pb} > \text{Ni} > \text{Zn} > \text{As}$.

ULTRAVIOLET-VIS SPECTROSCOPY (UV-VIS)

In the UV-vis spectrum of Figure 3, a band at 220 nm can be observed which is attributed to an electronic transition on the Al^{3+} ion. A charge transfer band between 310 nm and 340 nm was observed as a result of electronic transitions from the metal (Al^{3+} ion) to the ligand (Cl^- ion), respectively.

TGA ANALYSIS OF (BOEHMITE- $\gamma\text{-Al}_2\text{O}_3$)

The experimental curve of the thermal gravimetric analysis (TGA) for the sample in an interval from 25°C to 1000°C is shown in Figure 4. From the analysis the presence of endothermic reactions is observed, the first between $25\text{-}50^{\circ}\text{C}$ due to the loss of physisorbed water on the surface of the sample [Peri, J.B, (1965)].

The second endothermic decomposition is observed between $70\text{-}100^{\circ}\text{C}$ due to the loss of water that is adsorbed on the boehmite surface. The third decomposition is between $400\text{-}500^{\circ}\text{C}$ due to the transformation of boehmite to gamma alumina ($\gamma\text{-Al}_2\text{O}_3$) that occurs after the partial dehydroxylation of the material.

The fourth decomposition was between 500 and 600°C and was due to the elimination of water during dehydroxylation [Liu, et al.(2007)]. The fifth decomposition was between 650 and 700°C due to the phase change of gamma-alumina and the elimination of water by dehydroxylation. Finally, the reaction between 800 and 1000°C is due to the combustion of the remains of impurities, such as sulfur [Nam and Gavalas, (1991)].

X-RAY DIFFRACTION

Figure 5 shows the diffractogram corresponding to $\gamma\text{-Al}_2\text{O}_3$, calcined at 550°C , where the diffractions at 36 , 47 and 66° corresponding to $\gamma\text{-Al}_2\text{O}_3$ (JCPDS:10-0425)



Figure 1(a). Collected cans of juices, soft drinks and packaged foods (b) shredder blades (SAISA-1).

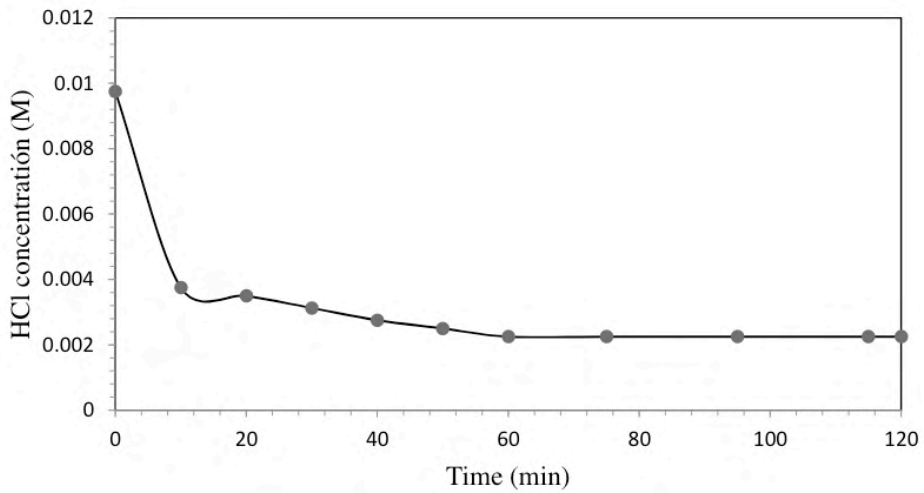


Figure 2. Concentration of hydrochloric acid (HCl) during the reaction with Al from waste cans, to obtain $AlCl_3$, at 60°C.

Sustrato	Hg (mg/L)	Cu (mg/L)	As (mg/L)	Pb (mg/L)	Ni (mg/L)	Fe (mg/L)	Zn (mg/L)
Waste cans	7.949	21.13	0	4.39	3.64	12.13	0.039
Aluminum shot	5.464	20.23	0	0.863	1.782	11.06	0.004

Table 1. Metal concentration after the reaction of HCl and Al.

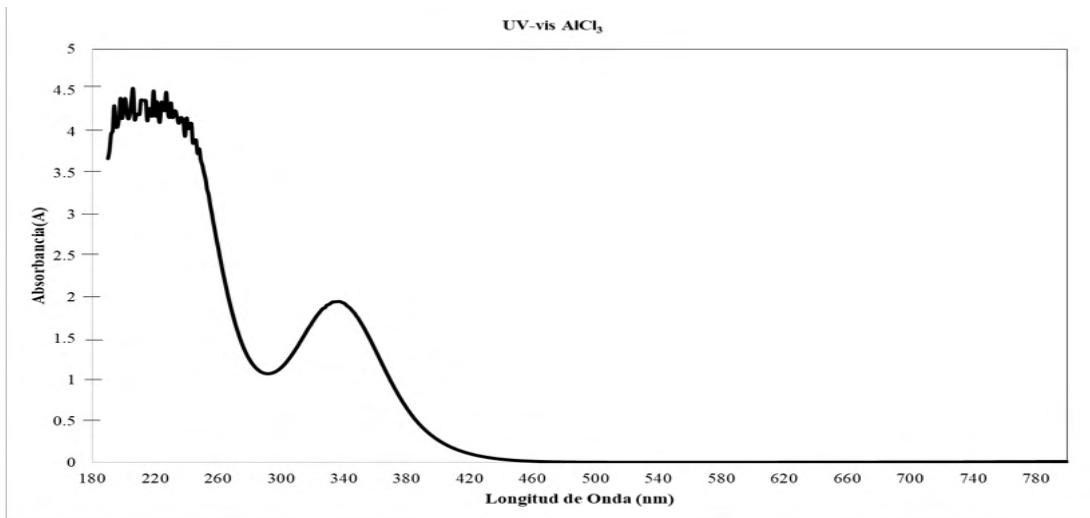


Figure 3. UV-vis spectrum of the AlCl₃ solution obtained after the reaction with HCl and Al cans.

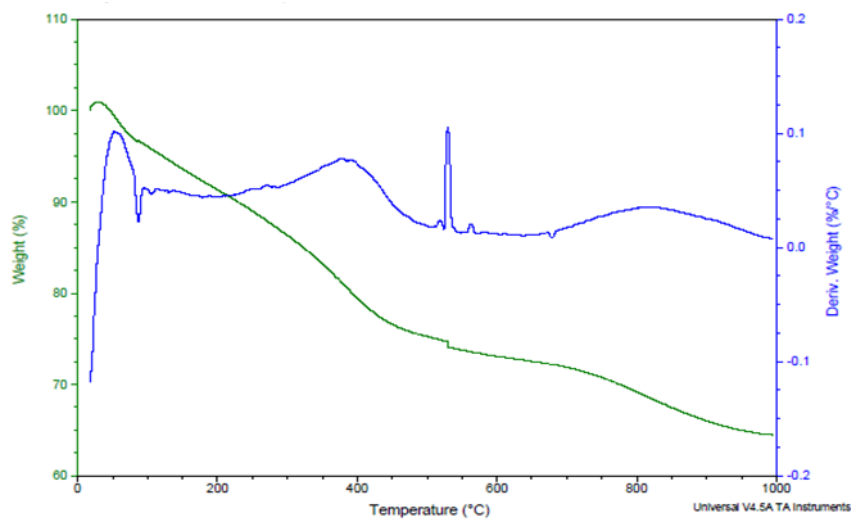


Figure 4. TGA of the boehmite- γ - Al₂O₃ sample in air flow,

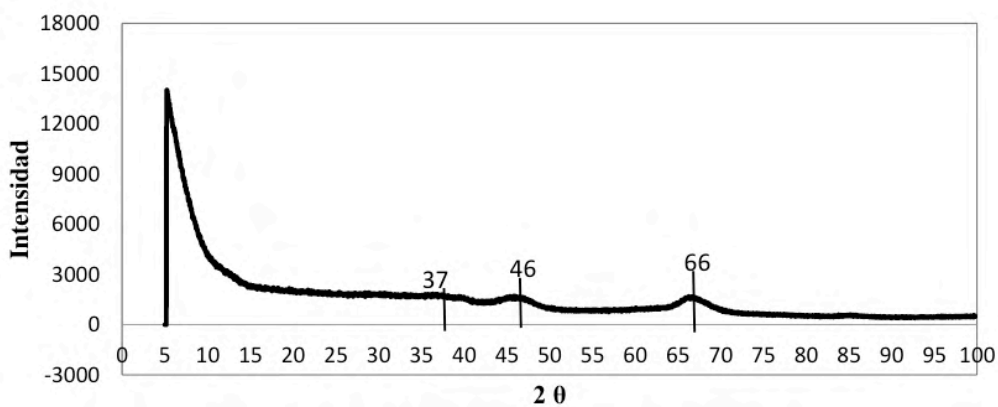


Figure 5. Diffractogram of γ - Al₂O₃ according to the letter: JCPDS 10-0425

are observed. No diffraction peaks were observed for CuO or FeO. These metals were the main contaminants previously detected by atomic absorption spectroscopy,

SEM OF BOEHMITE (AL(OH))

Various morphologies of boehmite nanostructures were observed, such as: nanosheets (Figure 6(a)) and nanoparticles (Figure 6(b)) with three-dimensional flower-shaped nanoarchitectures (Figure 6(c)). The morphologies of boehmite nanosheets have been observed in other investigations [Ram, S. (2001)], as well as the presence of nanoparticles. [Kanti Naskar and Chatterjee, (2005)]

Finally, Zhang et al. (2006) have observed three-dimensional flower-like nanoarchitectures of boehmite. This boehmite preparation showed nanosheets assembled with nanoparticles in the absence of surfactants at a reaction temperature lower than 333 K. Other authors have found nanosheets when boehmite samples of their preparation reached a pH close to 7 [Zhang, et al., (2006)]. The porosity properties produced by the boehmite nanosheets obtained showed that the material can be used as an adsorbent to separate mixtures of paraffinic hydrocarbons [Contreras, et al.(2019)].

SEM of γ -Al₂O₃

In the panoramic micrograph of Figure 7(a) with a X250 resolution, γ -Al₂O₃ particles of different sizes are observed, where between 30-40% have a diameter of 50 μ m with flat and rough surfaces. In the micrograph of Figure 7(b) with a X2000 resolution, a particle with an approximate size of 45 μ m in diameter with a porous surface and overlapping layers were observed.

In the micrograph of Figure 7(c) with a resolution X10,000 a porous surface with ordered multilayer sheets is observed and

finally in the micrograph of Figure 7(d), with a resolution X50,000 sub-particles are observed with a flake morphology.

These flake-like particles are not similar to some worm-shaped particles in aluminas prepared by the sol-gel method using the cationic surfactant hexadecyl trimethylammonium bromide [Ray, et al., (2007)], which come from uncontrolled coalescence of aluminum species that form the walls of the pores, during calcination [Baldovino-Medrano, et al., (2008)].

Figure 8 shows the EDS spectrum of γ -Al₂O₃ obtained from AlCl₃, in which the presence of aluminum and oxygen (Al, O) can be observed. The presence of carbon (C) is also observed, which is present because the samples were placed on a graphite tape to make the sample conductive and to be able to perform the analysis. It is not possible to see the signals of the contaminants that were analyzed by AA spectroscopy (Cu > Fe > Hg > Pb > Ni > Zn > As).

ADSORPTION OF H₂O

Figure 9 shows the percentage of water absorbed by the alumina sample obtained in a period of approximately 24 h, however, it can be seen that the greatest amount of water is absorbed around the first 5 h. This adsorption capacity of 0.3 g_{H₂O}/g_{solido} was lower than the adsorption of commercial alumina (0.4 g_{H₂O}/g_{solido}) [Perez Cabrera, (2017)]. However it is assumed that this alumina may also contain SiO₂.

NITROGEN ADSORPTION (BET AREA)

The γ -Al₂O₃ samples exhibited a type IV isotherm with a hysteresis loop H2 (Figure 10) that is characteristic of mesoporous solids [Brunauer, S. (1944)] and that have bottleneck pores. The loop or loop is attributed to slit-shaped pores with parallel walls, wide pores

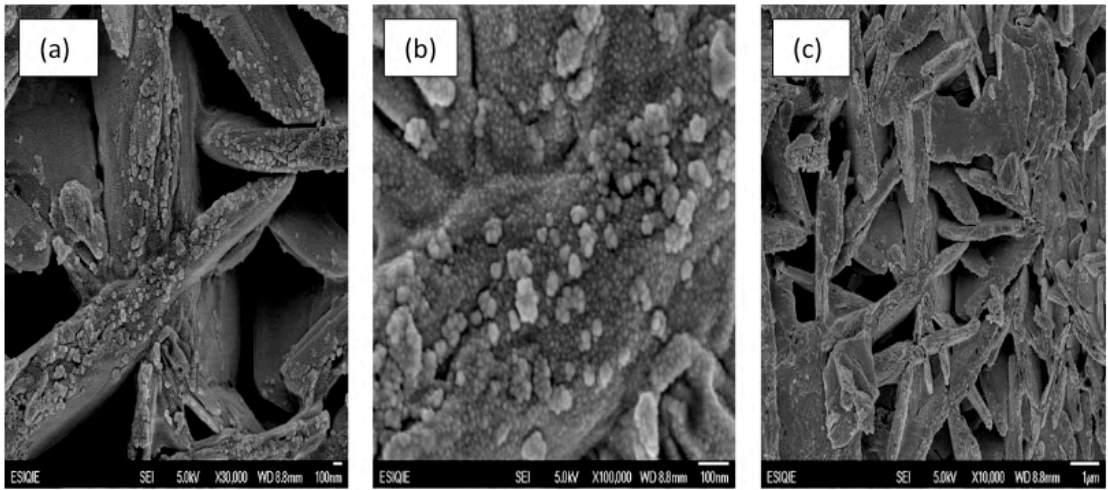


Figure 6 (a) Nanosheets of boehmite ($\text{AlO}(\text{OH})$), (b) nanoparticles of boehmite, (c) three-dimensional nanoarchitectures of flower-shaped boehmite.

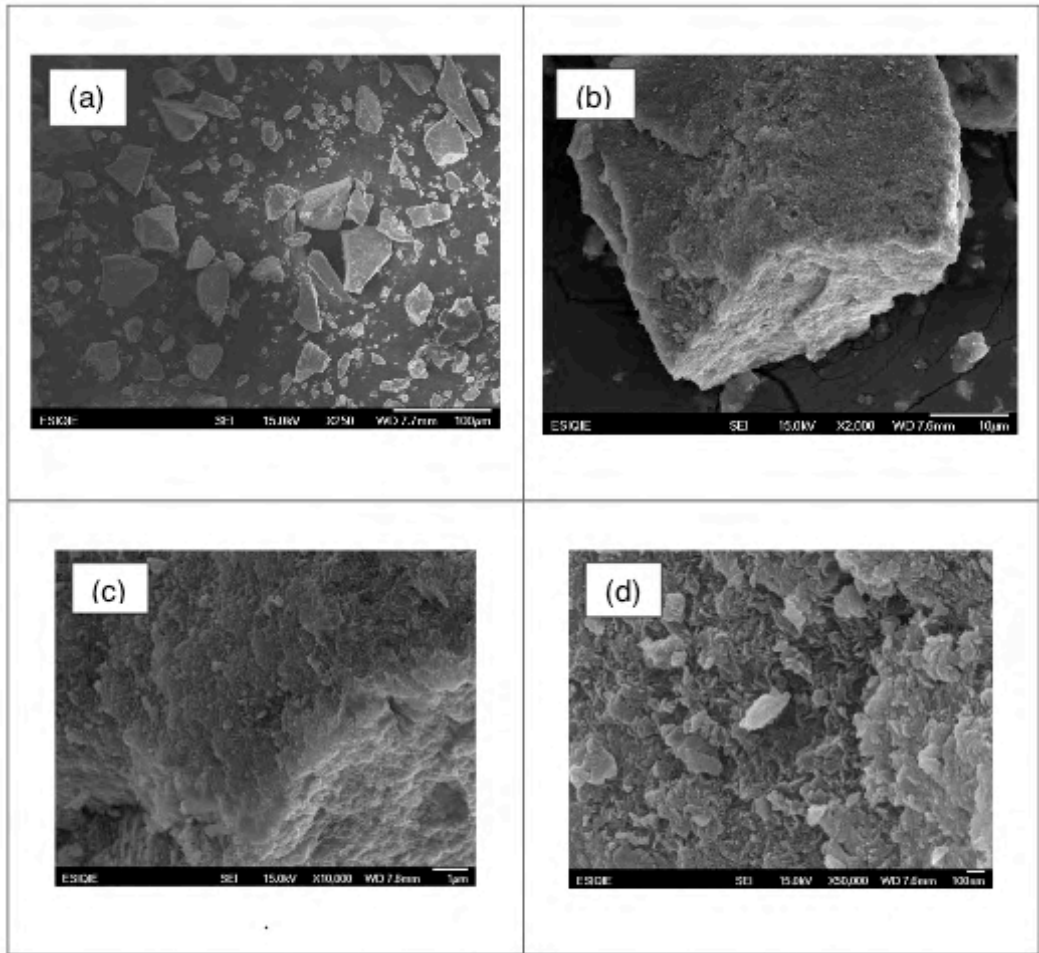


Figure 7(a), Microphotograph of $\gamma\text{-Al}_2\text{O}_3$ with X250 resolution. (b) photomicrograph with X2000 resolution, (c) microphotograph with X10000 resolution, and (d) (b) microphotograph with X50000 resolution.

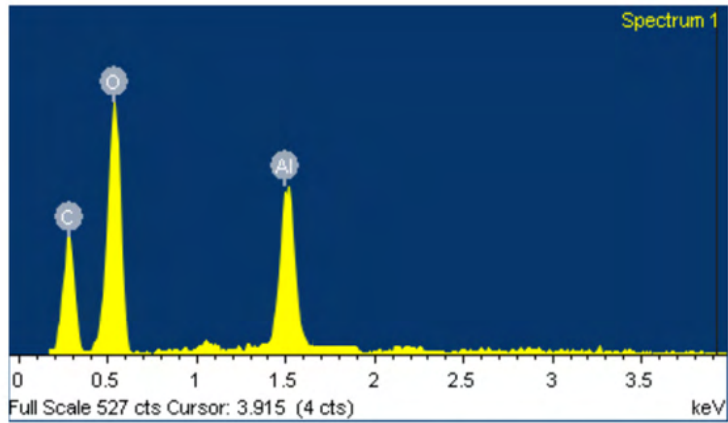


Figure 8. EDS of the $\gamma\text{-Al}_2\text{O}_3$ obtained, showing the signals of aluminum (Al), oxygen (O) and carbon (C). No signs of contaminants can be seen.

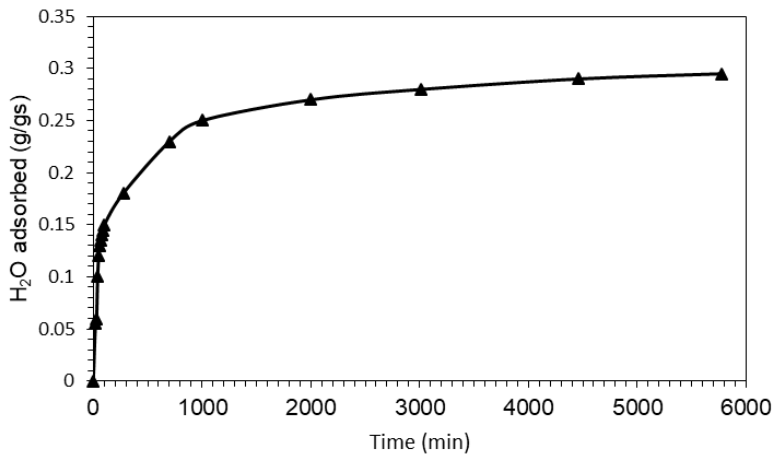


Figure 9. Adsorption isotherm of H_2O on $\gamma\text{-Al}_2\text{O}_3$ at 25°C .

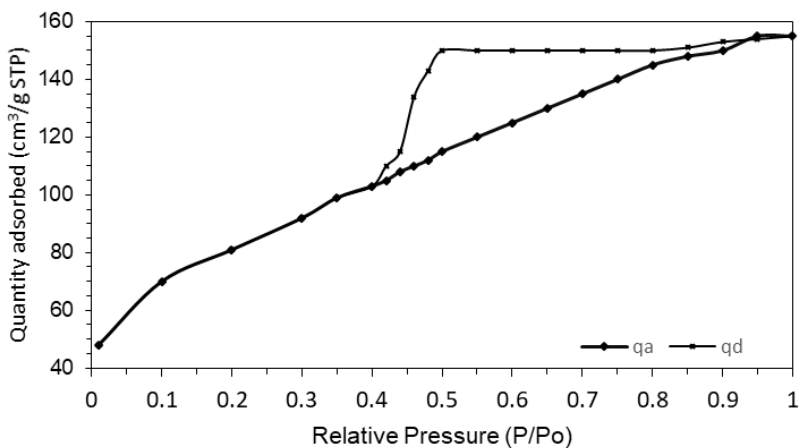


Figure 10. N_2 adsorption isotherm (at 77 K) for $\gamma\text{-Al}_2\text{O}_3$ prepared using waste aluminum cans.

with short, narrow openings. The BET specific area was 298.4 m²/g, the average pore diameter was 36 Å. (BET area considering the accumulated pore adsorption was 226.4 m²/g).

CONCLUSIONS

In this study, it is shown that waste aluminum cans can be used to produce γ -Al₂O₃ as catalyst support or as H₂O adsorbent. During the acid attack of 10 g of Al cans with HCl, some metals were found in solution in small quantities (< 22 mg/L), the concentration of which varied according to the following order: Cu > Fe > Hg > Pb > Ni > Zn and As was not found.

During the UV-vis spectroscopic analysis of the AlCl₃ solution, no bands due to contaminating metals were observed. For its part, the TGA analysis showed that the transition temperature of AlO(OH) to γ -Al₂O₃ is between 400 and 500°C and by XRD the typical reflections of a γ -Al₂O₃ were found.

By SEM, the formation of typical boehmite crystals was found, as well as the formation of crystals in the formation of flakes for the sample calcined at 550°C, while by EDS no significant signs of contaminating metals were found, mainly Cu and Fe.

Finally, through this treatment, specific BET areas of 298 m²/g and an average pore diameter of 36 Å (mesoporous material) were obtained. However the alumina in this study did not reach the water adsorption capacity of a commercial alumina, perhaps because it could contain SiO₂.

ACKNOWLEDGMENTS

The authors thank the Autonomous Metropolitan University of Azcapotzalco and the ESQIE of the National Polytechnic Institute for the facilities of both human resources and laboratory equipment for our research. Jennipner Pérez C. appreciates the scholarship for postgraduate studies granted by CONACYT of Mexico.

REFERENCES

- Baldovino-Medrano V.G., Giraldo S.A., Centeno A., (2008) The functionalities of Pt/ γ -Al₂O₃ catalysts in simultaneous HDS and HDA reactions, *Fuel* 87, 1917–1926.
- Barrett, E.P.; Joyner, L.G.; Halenda, P.P. (1951) The Determination of Pore Volume and Area Distributions in Porous Substances. I. Computations from Nitrogen Isotherms. *J. Am. Chem. Soc.*, 73, 373–380.
- Brunauer, S. (1944), *The Adsorption of Gases and Vapors*, Book 1, Princeton University Press.
- Contreras, J.L, Gomez, G., Zeifert B., Salmenes J., (2015) Book Chapter No.1: Synthesis of mesoporous alumina for catalítica applications, *Book: Comprehensive Guide for Mesoporous Materials*, Mahmood Aliofkhaezai, Nova Science Publishers Inc. New York, p.1-26.
- Hartmann S., Sachse A., Galarneau A., (2012) Challenges and Strategies in the Synthesis of Mesoporous Alumina Powders and Hierarchical Alumina Monoliths p.336-337.
- José L. Contreras-Larios, Antonia Infantes-Molina, Luís A. Negrete-Melo, Juan M. Labadie-Suárez, Hernani T. Yee-Madeira, Miguel A. Autie-Pérez and Enrique Rodríguez-Castellón, (2019) Separation of N-C₅H₁₂-C₉H₂₀ Parafins Using Boehmite by Inverse Gas Chromatography, *Appl. Sci.* 9, 1810; doi:10.3390/app9091810.
- Kanti Naskar, M. Chatterjee, M. (2005), Boehmite Nanoparticles by the Two-Reverse Emulsion Technique. *J. Am. Ceramic Soc.*, 88, 3322–3326.

Lippens, B.C.; Boer, J.H. (1965), Studies on Pore Systems in Catalysts: V. The t Method. *J. Catal.* 4, 319–323.

Liu Qian, Wang Aiqin, Wang Xiaodong, Zhang Tao, (March 2007) Morphologically controlled synthesis of mesoporous alumina, *Microporous and Mesoporous Materials*, V. 100, Issues 1–3, 23 p. 35-44.

Nam S.W., Gavalas G.R. (1991), *Appl. Catal.* 74 (1) 53–64.

Perez Cabrera Jennipher., M.S. Thesis (2022). Obtaining spherical particles of γ -Al₂O₃ from waste aluminum cans to be used as a catalyst support. Universidad Autonoma Metropolitana, Azcapotzalco. Posgrado de Ingenieria de Procesos.

Peri, J.B. (1965), Infrared and Gravimetric Study of the Surface Hydration of γ -Alumina *J. Phys. Chem.* , American Chem. Society, 69, 1, 211–219 doi.org/10.1021/j100885a032.

Prasad, J. Murthy, K.R.; Menon, P.G. (1978) The Stoichiometry of Hydrogen-Oxygen Titrations on Supported Platinum Catalysts. *J. Catal.* 52, 515–520.

Ram, S. (2001) Infrared spectral study of molecular vibrations in amorphous, nanocrystalline and AlO(OH) α -H₂O bulk crystals. *Infrared Phys. Technol.* 42, 547–560.

Ramli Z, Saleh R. (2009) The Effect of Synthesis Routes on the Development of Ordered Mesoporous Alumina by Precipitation Method, *American Institute of Physics*, p. 26.

Ray J.C., You K.S., Ahn J.W. (2007), Mesoporous alumina (I): Comparison of synthesis schemes using anionic, cationic, and non-ionic surfactants, *Microporous Mesoporous Mater.* 100 183–190.

Schoonover M.W., (1982) Manufacture of alumina particles, U.S. Patent 4,318,896, p.1-4, 5-18

Zhang, J., Liu, S., Lin, J.; Song, H., Luo, J., Elssfah, E.M., Ammar, E., Huang, Y., Ding, X., Gao, J., Qi, S., Tang, C. (2006), Self-Assembly of Flowerlike AlO(OH) (Boehmite) 3D Nanoarchitectures. *J. Phys. Chem.*, 110,14249–14252.