

Analysis of the phase transformation of aluminum formate $\text{Al}(\text{O}_2\text{CH})_3$ to α -alumina by Raman and infrared spectroscopy

Simón Yobanny Reyes-López^{a,*}, Rosa Saucedo Acuña^a, Rigoberto López-Juárez^b and Juan Serrato Rodríguez^c

^aDepartamento de Ciencias Químico Biológicas, Instituto de Ciencias Biomédicas, Universidad Autónoma de Ciudad Juárez. Anillo Envolvente del PRONAF y Estocolmo s/n, C.P. 32300, Cd. Juárez Chih, México

^bInstituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Ciudad Universitaria, A.P. 70-360, C.P. 04510, México D.F, México

^cInstituto de Investigaciones Metalúrgicas, Universidad Michoacana de San Nicolás de Hidalgo, Santiago Tapia 403, C.P. 58000, Morelia, Mich, México

A new simplified route to prepare crystalline α -alumina powders is proposed from the decomposition of aluminum formate $\text{Al}(\text{O}_2\text{CH})_3$ precursor following a process of gelation of $\text{Al}(\text{O}_2\text{CH})_3$ in an aqueous medium. Heat treated powders were characterized by XRD, Raman and infrared spectroscopy showing the presence of η - Al_2O_3 at 1000 °C and the transformation to α - Al_2O_3 at 1100 °C, where SEM images of α - Al_2O_3 revealed an size of 1-2 μm by the aggregated particles, and TEM images confirm a particles size of 200-300 nm. By other hand BET study showed that the specific surface area of η - Al_2O_3 and the α - Al_2O_3 obtained is higher than the specific surface area reported for these materials (until 118 m^2/g), ratify that this new route process at low temperature promote to obtain the powers with an excellent superficial area.

Key words: α -alumina, Aluminum formate, Raman, Infrared spectroscopy.

Introduction

The more important polymorphs of alumina are γ - AlOOH , η - Al_2O_3 and α - Al_2O_3 , which γ - Al_2O_3 and α - Al_2O_3 are commonly used as adsorbents, catalysts and catalyst supports. The main difference between the phases can be explained by the distribution of oxygen sublattice into the interstitial sites. The α - Al_2O_3 is particularly stable thanks to the selective position of oxygen sublattice in octahedral sites instead of being in both tetrahedral and octahedral sites as in the case of the metastable phases [1-3].

Conventional processes for synthesizing α - Al_2O_3 involve different inconvenient: mechanical milling requires extensive milling time where is easy introduces impurities [4], vapor phase reaction demands high temperature up to 1200 °C [5], spray drying and spray pyrolysis, and precipitation methods are complicated and need long time of reaction [6-9], hydrothermal and combustion methods needs high temperatures and pressures, while combustion method obtains hard aggregated powder [10, 11]. For these reasons, actually the efforts are being made to develop new processing routes to produce high quality alumina as sol-gel based on molecular precursors and polymer precursor methods.

The disadvantage of this sol-gel method is that the metal alkoxide raw material is expensive and the gelation period is so long [12], while in the case of chemical synthesis, the process is particularly simple, safe and rapid, where the main advantages are energy and time savings. This quick, straightforward process can be used to synthesize oxide ceramic powders showing high purity and crystallinity in a broad range of particle size [7]. The present study describes a simple and innovative approach for the synthesis of crystalline α -alumina powders involving the use of the metal organic precursor aluminum formate $\text{Al}(\text{O}_2\text{CH})_3$, the advantage of this organometallic precursor is that its gelation property permit to obtain fragile agglomerates and its presence reduces the temperature of α -alumina formation [7]. Decomposition of the aluminum formate precursor, phase transformations and morphology of the synthesized alumina powders obtained were analyzed by the several methods of XRD, MET, SEM, Raman and IR spectroscopy techniques to show clearly the alumina phase transitions.

Material and Methods

Aluminum formate $\text{Al}(\text{O}_2\text{CH})_3$ was synthesized by chemical synthesis described by Reyes et. al, involving a mixture of aluminum with formic acid using mercuric chloride as catalyst to obtain the aluminum formate solution which was spray dried to produce fine granulated metal-organic precursor [7]. The route for

*Corresponding author:

Tel : + 52(656)688-2100 Ext. 1989

Fax: +52(656)688-1864

E-mail: simon.reyes@uacj.mx; yobannyr@yahoo.com.mx

the synthesis of crystalline α -alumina involves the dissolution of the precursor aluminum formate in water using a magnetic stirrer. After it, the final solution was keeping stirred until it was heated to obtain a white gel. This gel was transferred to a closed platinum crucible to put in a furnace up to 1100 °C at rate of 5 Kminute⁻¹, obtaining a blackish voluminous fluffy solid product. Finally, this product was calcined at 900 °C for 2 hrs to form a white powder.

To the follow the phase transformation of the precursor, 10 mg of sample was run on a thermal analysis instrument (Q600, DSC/TGA, TA Instruments), the heating rate was 10 Kminute⁻¹ up to 1400 °C, with a nitrogen gas flow of 100 cm³/min. Precursor and the powders obtained were analyzed using an attenuated total reflection (ATR) technique fitted with a Fourier transform (The TENSOR™ 27 series FT-IR spectrometer, ZnSe crystal, Bruker Optics Inc.), and a Raman Spectra (LabRam, Horiba) with an emission line of 633 nm from He-Ne laser.

The specific surface area of calcined samples was determined by nitrogen sorption according to single point BET method using a Quantacrome apparatus. Microstructure of the calcined powders was studied by transmission electron microscopy (TEM, Phillips TECNAI F20 super Twin, at 200 kV) and SEM (Jeol JSM-6400 SEM, at 15 kV coupled with EDS detector Bruker AXS Inc. XFlash 4010).

Results and Discussion

Thermal behavior of the gel conforming by aluminum formate and water is shown in Fig. 1, where the TGA line corresponding to the gel decomposition exhibit a total ceramic yield of 31.20 % w, where this result corresponds to the total of Al₂O₃ formed, with the transformation process to α -alumina. The rest 67.80%w correspond to the water and carbon dioxide lost. The DTA line in Fig. 1 corresponding to the gel decomposition shows a similar curve to the decomposition of the precursor alone reported by Reyes *et al* [7]. This DTA line reveals too the presence of three endotherm peaks (68, 236 and 333 °C), corresponding to evaporation

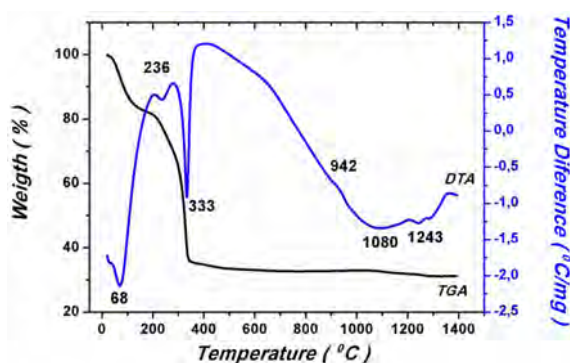
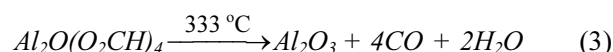
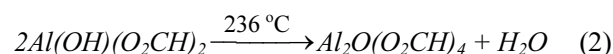
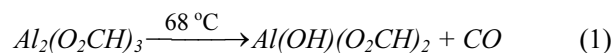


Fig. 1. Thermal analysis: TG and DTA for aluminum formate gel.

of absorbed water and the removal of organics according with the reactions (1), (2) and (3) respectively. At 942 °C the line exhibits an exothermic peak corresponding to the crystallization process of η -alumina, other endothermic peak at 1080 °C refers the formation of α -alumina, and finally the exothermic signal at 1261 °C is related with the crystallization of α -alumina.



The XRD patterns of gel decomposition are shown in Fig. 2. At 25 °C, the material remains exhibit a poor crystallinity, however it is possible to observe in the

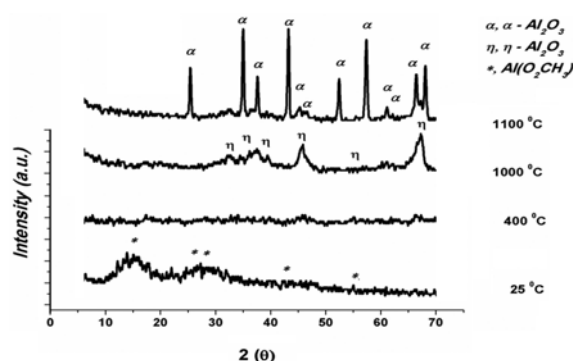


Fig. 2. DRX of Al(O₂CH₃) gel at several temperatures.

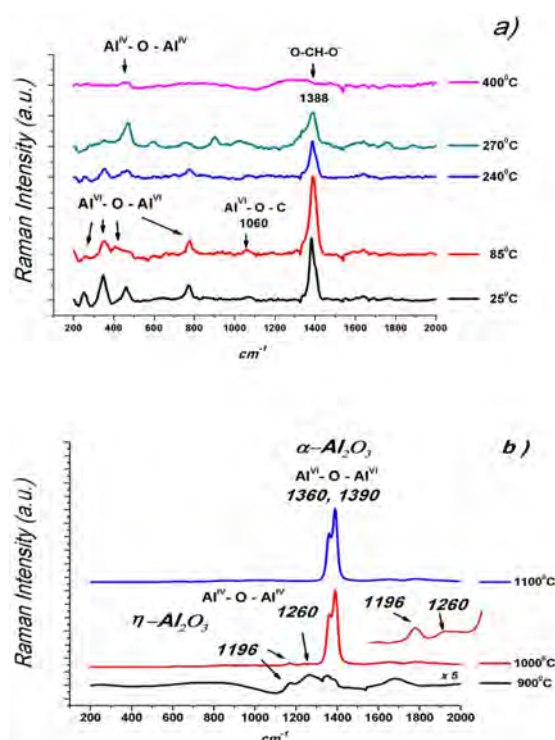


Fig. 3. Raman spectra of gels heated at different temperatures; (a) carboxilate desomposition and (b) transition to α -Al₂O₃.

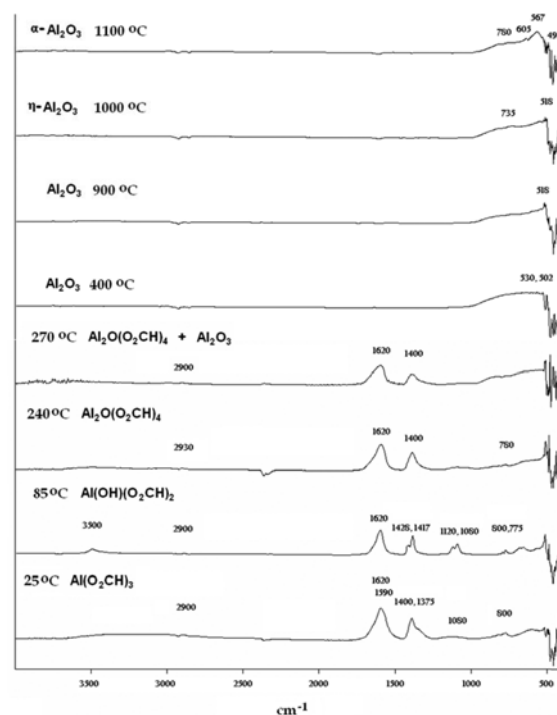
Table 1. IR Bands of $\text{Al}(\text{O}_2\text{CH})_3$, $\text{AlOH}(\text{O}_2\text{CH})_2$ and $\text{Al}_2\text{O}(\text{O}_2\text{CH})_4$ precursors.

Sample	ν (O-H)	ν (C-H)	ν_{as} (OCO)	$\nu_{\text{as,def}}$ (OCO)	ν_{s} (OCO)	ν_{def} (C-H)	$\nu_{\text{s,def}}$ (OCO)
$\text{Al}(\text{O}_2\text{CH})_3$	3600-2300	2900	1620	1400	1375	1080	800
$\text{AlOH}(\text{O}_2\text{CH})_2$	3500	2930	1630, 1605	1428, 1417	1400, 1390	1120, 1080	800, 775
$\text{Al}_2\text{O}(\text{O}_2\text{CH})_4$	—	2900	1620-1590	1400	1380	1080	780

diffraction pattern the matches corresponding to the precursor ($\text{Al}(\text{O}_2\text{CH})_3$). The material becomes lost its structure when it is heated at 400 °C. Until 1000 °C, the powder pattern shows low intensity peaks, which is related with the partial crystallization of η - Al_2O_3 , to turn in α - Al_2O_3 at 1100 °C. Finally at 1261 °C, the α - Al_2O_3 begins to crystallize. This information is confirmed by Raman and infrared spectroscopies (Figs. 3 and 4), where Raman spectrum of gel treated at several temperatures in Fig. 3(a) show the characteristic bands of aluminum formate remain unchanged up to 270 °C, where at 1388 cm^{-1} band corresponds to stretching modes of the formate group (HCOO^{-1}) bonded with aluminum, at 1060 and 780 cm^{-1} the presence of two bands might be due to the vibrations of Al-O-C groups, this assumption is confirmed by the decomposition of aluminum formate at 400 °C, while the bands observed at frequencies lower than 600 cm^{-1} are related to the vibrations of aluminum ions coordinated with six oxygen atoms as occurs in carboxylates and alkoxides compounds [14-16]. By other side, at 400 °C the formate group bands disappear, this phenomenon corroborates the formation of amorphous Al_2O_3 discussed in the XRD results.

In the temperature range of 400-900 °C, Raman spectra shows three bands at 460, 1196 and 1260 cm^{-1} attributed to the vibrations of aluminum with oxygen atoms forming a tetrahedral Al_2O_3 phase, confirming the absence of α - Al_2O_3 (hexagonal symmetry). This conclusion is agree with XRD results, where the peak at 460 cm^{-1} in Fig. 2 was attributed to the vibrations of aluminum atoms coordinated with four oxygen atoms. Fig. 3(b) shows Raman spectra since 900 to 1100 °C, where the transformation of pure alumina into the single α - Al_2O_3 phase was observed started at 1000 °C with the presence of additional bands at 1360 and 1390 cm^{-1} , to finally end at 1100 °C, when all η - Al_2O_3 is converted to α - Al_2O_3 . In the case of Raman a sharp peaks refers a well-dened long-range order in corundum, which is related with the collapse of the porous structure characteristic of the low-temperature phases. All this information is according with the XRD results showed and discussed in Fig. 2.

Fig. 4 and table 1 show the IR spectrums and the peak bands of gel treated at several temperatures. According with them, the O-H stretching, C-H stretching, and C-H bending vibration are related with the presence of carboxylate ions. In this figure bands at 1620 and 1580 cm^{-1} were assigned to the antisymmetric

**Fig. 4.** Infrared spectra of gels heated at different temperatures.

COO^{-} stretching mode for a bridge-type complex. Clearly these peaks decreased its intensity at 270 °C, phenomena that is related with the gradual peaks lost of water and carboxylate groups, while the wide band appearing between 500 and 1000 cm^{-1} corresponds to the vibrational frequencies of coordinated O-Al-O bonds, and this last band begins to take importance between 270-400 °C.

At 400 °C the pyrolysis process continues as it is demonstrated by the strong intensity decreasing of the carboxylate anions, therefore the band ranged at about 500-1000 cm^{-1} keeps gaining intensity. The wide band, corresponding to the Al-O bonds, develops into two small bands (735 and 575 cm^{-1} , respectively) as temperature increases up to 950 °C. These are the characteristic frequencies of AlO_4 tetrahedra, or more specifically, its can be assigned to some stretching lattice vibrations of interlinked AlO_4 tetrahedra, as it occurs in transition alumina. For 500 cm^{-1} region, vibrations may be due to some bending motion of the AlO_4 lattice, it is in agreement with the presence of η -alumina diffractions denoted observed in the XRD pattern from 1000 °C.

In Fig. 4 at 1100 °C, the strong and well dened IR

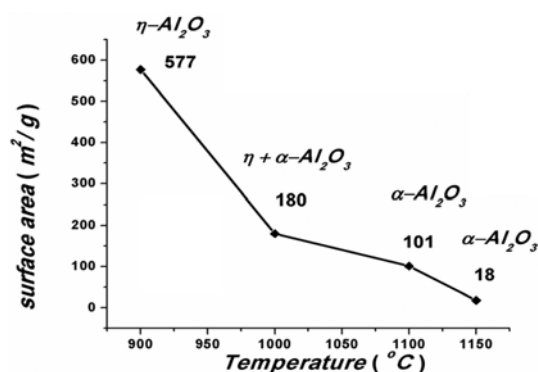


Fig. 5. Variation of surface area of metal-organic precursor as a function of calcination temperature.

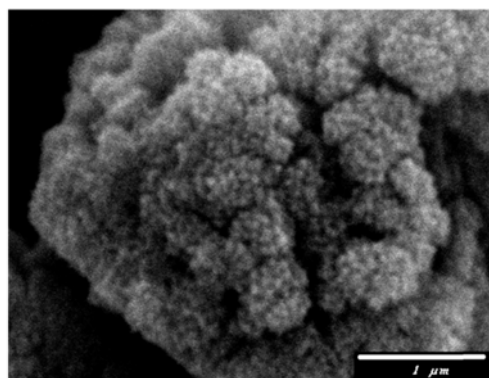


Fig. 6. SEM micrograph of α -alumina powders calcined at 1100 °C.

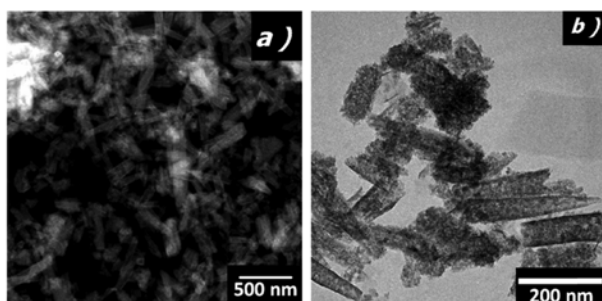


Fig. 7. TEM micrographs of the $\alpha\text{-Al}_2\text{O}_3$ nanocrystalline particles showing the acicular morphology: (a) low amplification (dark field) and (b) higher resolution (bright field).

bands observed for Al-O bondings must be explained taking into account the pure XRD reactions of α -alumina observed. In the case of a corundum structure, it is built up only on octahedral AlO_6 and the most characteristic IR feature is the occurrence of two strong bands near 605, 567 and 495 cm^{-1} together with some others bands of less intensity around 450 and 780 cm^{-1} .

Fig. 5 shows the variation of surface area as a function of calcination temperature for alumina powders. As the surface area of the powder is influenced by content in η and α alumina phase, the samples derived from aluminum formate precursor at various temperatures have been characterized for their surface area and $\alpha\text{-Al}_2\text{O}_3$ phase content. The sample calcined at 900 °C has the highest surface area ($577\text{ m}^2/\text{g}$). This

figure shows too, the effects of calcination temperature in the surface area, where it is significantly reduced when temperature increases showing $101\text{ m}^2/\text{g}$ at 1100 °C, and $11\text{ m}^2/\text{g}$ at 1150 °C. As the calcination temperature increases from 1000 to 1100 °C, the percentage of $\alpha\text{-Al}_2\text{O}_3$ increases, then when the $\alpha\text{-Al}_2\text{O}_3$ phase is formed at 1100 °C, the alumina crystal size increases and the surface area decreases dramatically.

A SEM image of the powders calcined at 1100 °C is shown in Fig. 6. It reveals the presence of submicrometric aggregates, and primary individual particles with diameter of $\sim 100\text{ nm}$. The morphology and particle size of $\alpha\text{-Al}_2\text{O}_3$ crystalline are observed by TEM in Fig. 7. It is clearly seen that the microstructure consists of acicular particles with average size around 200 to 250 nm.

Conclusions

Combining techniques such as DRX, IR and Raman is very useful for obtaining a detailed understanding of the phase transition of alumina. The gel formed by water-soluble precursor upon heat treatment, gives rise to ultrafine crystalline alumina particles. The aluminum formate produces η -alumina which transform to α -alumina above 1000 °C and the transformation is completed below 1100 °C. These results suggest that these carboxylates are useful precursors to produce α -alumina powders at relatively low temperature. The surface area of the resultant η and α -alumina powders is in the range of 577 to $18\text{ m}^2/\text{g}$ and depending on the calcination temperature. In this study, alumina particles with crystallite sizes of 200 to 250 nm could be produced by heat treatment of the gelled mass at 1100 °C, therefore the use of this precursor simplifies the process and provides another alternative process for economical synthesis of crystalline alumina.

References

1. P.P. Pramanik, Pinsa. 67 [1] (2001) 47-70.
2. K. Wefers, C. Misra, Alcoa Laboratories (1987) 32-33.
3. R. Roy Science. 238 [4834] (1987) 1664-1669.
4. M. Panchula, J. Ying, Nanostruct. Mater. 9 [1-8] (1997) 161-164.
5. T. Chou, T. Nieh, J. Am. Ceram. Soc. 74 [9] (1991) 2270-2279.
6. H. Varma, T. Mani, A. Damodran, J. Am. Ceram. Soc. 77 [6] (1994) 1597-1600.
7. S. Reyes, J. Serrato, S. Sugita, Adv. Tech. of Mat. and Mat. 8 (2006) 55-62.
8. B. Jun, S. Lee, G. Messing, Key Engineering Materials. 317-318 (2006) 207-210.
9. J. Li, X. Sun, Acta Mater. 48 [12] (2000) 3103-3112.
10. A. Fanelli, J. Burlew, J. Am. Ceram. Soc. 69 [8] (1986) 174-175.
11. J. Kingsley, K. Patil, Mater. Lett. 6 (1988) 427-432.
12. E. Ponthieu, E. Payen, J. Grimblot, J. Non-Cryst. Solids. 147-148 (1992) 598-605.
13. Liu, Z. Zhang, B. King, J. Halloran, R. Laine, J. Am.

- Ceram. Soc. 79 (1996) 385-394.
14. T. Assih, A. Ayral, M. Abenoza, J. Phalippou, Journal of Materials Science. 23 (1988) 3326-3331.
15. F. Touati, N. Gharbi, P. Colomban, Journal of Materials Science. 35 (2000) 1565-1570.
16. F. Mirjalili, L. Chuah and H. Mohamad, Journal of Ceramic Processing Research. 12 [6] (2011) 738-741.