

## New Method for Preparation of Nano Alumina Powder Using Aluminum(III) Complexes by Combustion Synthesis Without Fuel

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### Article history:

Received 25/10/2014

Accepted 27/11/2014

Published online 21/12/2014

### Keywords:

Combustion Method

Nanomaterials

Alumina, complex

FESEM

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### Abstract

Alumina nanomaterials were synthesized via a solution combustion technique using tris-(acetylacetonato) aluminum(III) complex (**1**) and tris-(2-formylphenolate) aluminum(III) complex (**2**) at 600, and 1000 °C for 3h. The obtained data showed that the procedure without using fuel resulted in a better phase and morphology. To investigate the phase formation, powder X-ray diffraction technique was used. Also, FESEM micrographs were used to investigate the morphology of the obtained materials. It showed that the morphology of the obtained materials was in the form of different types of porous and particle materials. The optical properties of the obtained materials were studied by FTIR spectra. According to the data, it was found that with annealing at 600 °C, the phase formation of the obtained materials showed cubic crystal structures with cell parameter  $a = 3.14 \text{ \AA}$  for gamma phase. With increasing the annealing temperature to 1000 °C, the obtained material was found to be in a mixture of orthorhombic and hexagonal crystal structures.

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## 1. Introduction

$\text{Al}_2\text{O}_3$  is an important industrial material, which can be widely used as adsorbents [1], catalysts [2], catalyst supports [3,4], functional ceramics [5,6], and reinforcements for composite materials abrasives [7]. It is due to its low cost, good thermal stability and high specific surface area [8, 9]. Aluminium oxide (or alumina), is used in various industrial applications such as ceramic materials, imitation jewellery [10,11], sorbents and catalysts

[12], dosimeters [13] or as an ingredient for preparation of complex oxides possessing promising luminescent [14], thermo-luminescent [15] and scintillation [16] properties. Several methods have been reported for the synthesis of different alumina nanomaterials phases such as precipitation [17], spray pyrolysis [18], sol-gel reactions [19], methods utilizing different surfactants as a template [20], formation of solid precursors aluminium hydroxides or oxyhydroxides

with various composition and crystallinity [21]. The aim of the present article is the investigation of preparation of nano alumina by a novel solution combustion method using a complex without using fuel. We herein use using tris-(acetylacetonato) aluminum(III) complex (1) and tris-(2-formylphenolate) aluminum(III) complex (2). To comparing the synthesis procedure, we used two different reaction temperatures of 600 and 1000°C. So, to our best of knowledge, the method for synthesis of nano-sized  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> particles in a single step using aluminum(III) complexes is being reported for the first time.

## 2. Experimental procedure

### 2.1. Synthesis of complexes (1) and (2)

In a typical experiment, aluminum sulphate, acetylacetone, salicylaldehyde and ammonia solution (5 M) were used as raw materials. 1 mmol acetylacetone or salicylaldehyde was poured in a 100 mL beaker and 4 mL of distilled water added to it. Then 1.8 mL of the ammonia solution was added to the obtained solution (solution A). Afterwards, 3 mmole of aluminum sulphate dissolved in 1 mL distilled water (solution B). Finally, solution A was added to solution B and the pH value was increased with ammonia solution (5M) until the solution became basic. The obtained solution was kept aside for 15 min, filtered and dried in room temperature. The obtained precipitate that is the desired complex is cream like powder.

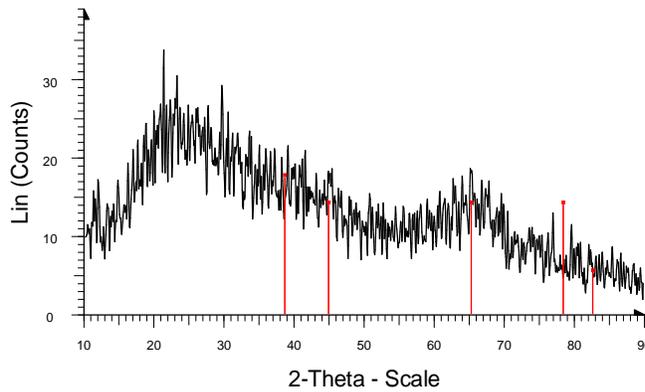
### 2.2. Synthesis procedure of alumina nanomaterial from (1) and (2)

Certain amount of the synthesized complexes (1) or (2) was powdered and transferred into a 25 mL crucible. Then the crucible was transferred into a preheated oven at 600 or 1000 °C and annealed for 3h. After the reaction completed, the crucible was cooled to the room temperature normally. The obtained powder was collected for further analyses.

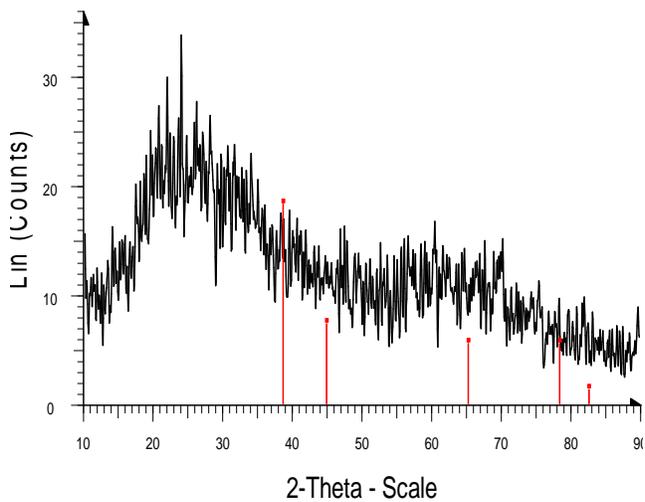
## 3. Results and discussion

### 3.1. XRD analysis

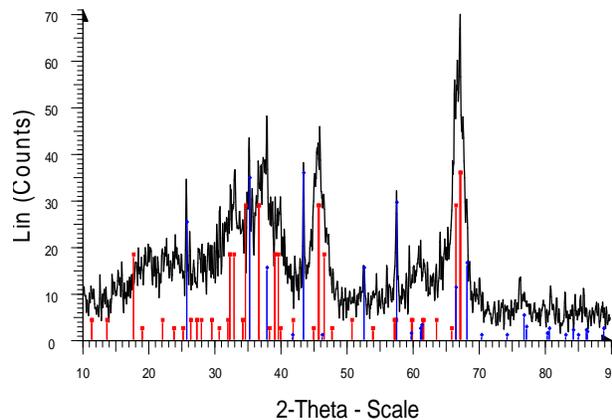
Fig.1 to 4 show the PXRD patterns of the synthesized nanomaterials via a combustion method at different reaction temperatures using two kinds of raw materials acetylacetonato and 2-formylphenolate. Fig. 1 and 2 show that the obtained nanomaterials annealed at 600 °C for 3 h crystallize in a cubic crystal structure with cell parameters of  $a = b = c = 4.0406$  and  $4.03900$  (JCPDS 03-0932), respectively. So the figures show a nearly pure phase for the obtained nanomaterials annealed at 600 °C for 3h. However, fig. 3 and 4 show the PXRD patterns of the synthesized nanomaterials annealed at 1000 °C for 3h. It is clear that the synthesized nanomaterials have been crystallized in multi phase crystal structures. Fig. 3 shows that the synthesized nanomaterials have been crystallized in a mixture of orthorhombic (JCPDS 46-1215) and hexagonal (JCPDS 42-1568) crystal structures. Fig. 4 shows that the synthesized nanomaterial has been crystallized in multi phases of tetragonal (JCPDS 46-1131) and hexagonal (JCPDS 42-1568) crystal structures. It is clear that the crystallization process for samples 1 and 2 are nearly incomplete compared to samples 3 and 4. However, according to the XRD pattern, the phase purity for samples 1 and 2 is higher than those for samples 3 and 4. But it is clear that the hexagonal phase ratio is higher than that for sample 4 compared to the sample 3.



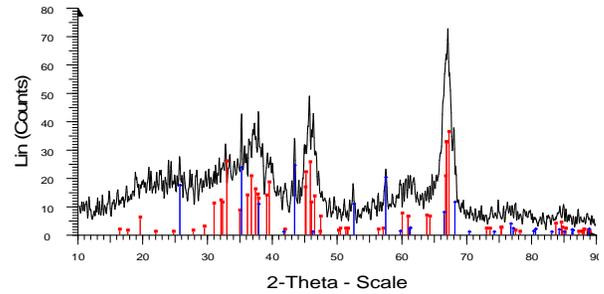
**Fig. 1.** PXRD pattern of the synthesized nano-alumina annealed at 600 °C for 3 h.



**Fig. 2.** PXRD pattern of the synthesized nano-alumina annealed at 600 °C for 3 h.



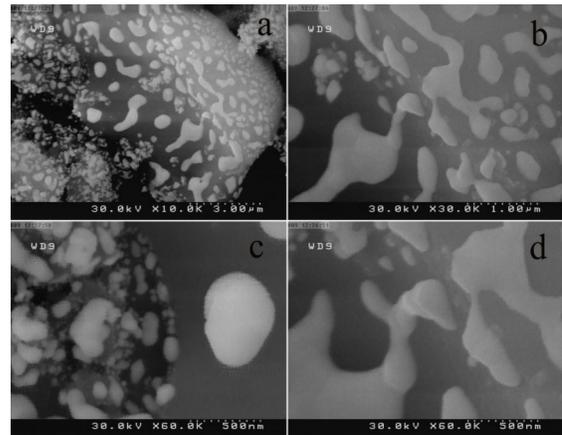
**Fig. 3.** PXRD pattern of the synthesized nano-alumina annealed at 1000 °C for 3 h.



**Fig. 4.** PXRD pattern of the synthesized nano-alumina annealed at 1000 °C for 3 h.

### 3.2. Morphology analysis

Fig. 5 to 8 show the FESEM images of the synthesized nanomaterials at different reaction temperatures for 3 h. Fig. 5 shows the FESEM images of the synthesized nano-alumina using tris-(2-formylphenolate) aluminum(III) as raw material. Figure 5a and Figure 5b show that the synthesized material is composed of a substrate form with some particles as uncus that has been grown on it. Figure 5c and Figure 5d show the high magnification of the synthesized Nanomaterial. It is clear that the uncus particles with small sizes are in a range of about 30-70 nm and with larger sizes are about 200-400 nm.



**Fig. 5.** FESEM images of S1.

Fig. 6 shows the FESEM image of the synthesized Nanomaterial annealed at 600 °C for 3h using tris-(acetylacetonato) aluminum (III) as raw material. Fig.6a and 6b show that the synthesized nanomaterials have porous structures.

The structures have certain multigonal cross sections. Besides, Fig.6c and d show that the length size of each side is in about 250–500 nm and the particles sizes are in about 50–70 nm.

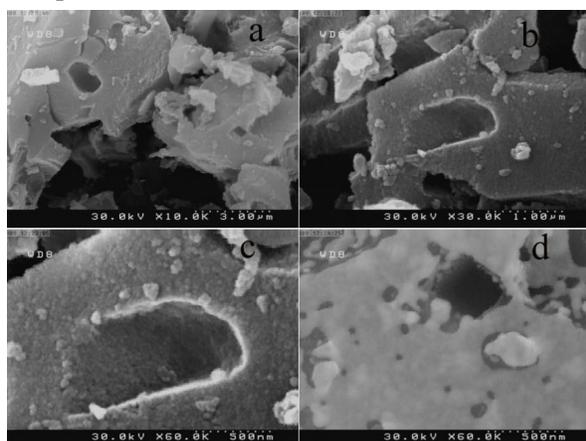


Fig. 6. FESEM images of S<sub>2</sub>.

Fig.7 shows the FESEM image of the synthesized nanomaterial annealed at 1000 °C for 3h using tris-(2-formylphenolate) aluminum (III) as raw material. It is clear that the obtained nanomaterials are in porous structures with highly uniform porosity in size and shape. Fig.7a and 7b show the porosity structures with pore diameter size of about 100–200 nm. Fig.7c and d show that the porous structures have been composed of small particles with the diameter sizes of about 40–60 nm.

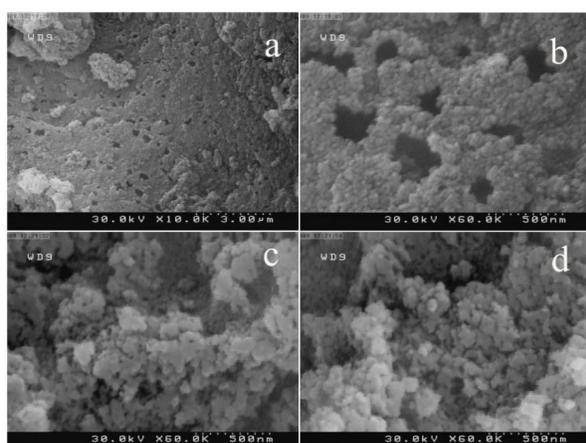


Fig. 7. FESEM images of S<sub>3</sub>.

Fig.8 shows the FESEM images of the synthesized nanomaterials annealed at 1000 °C for 3 h using tris-(acetylacetonato) aluminum(III) as raw material. Fig.8a and 8b show that the obtained nanomaterials have porous structures with the pore cross section of nearly in a circle form. The circle diameter is about 1 μm. Fig.8c and 8d show that there are small particles on the surface of the structures with the sizes of about 30–50 nm for small particles and 100–250 nm for larger particles.

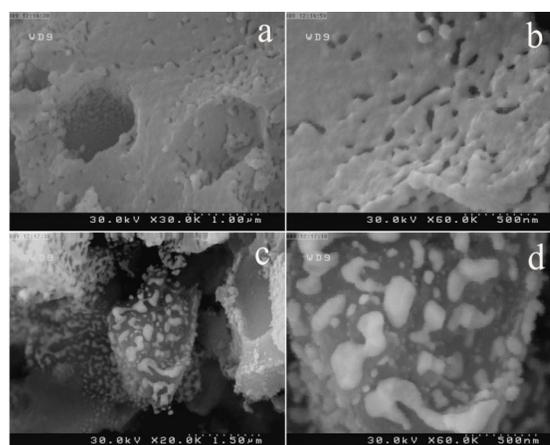
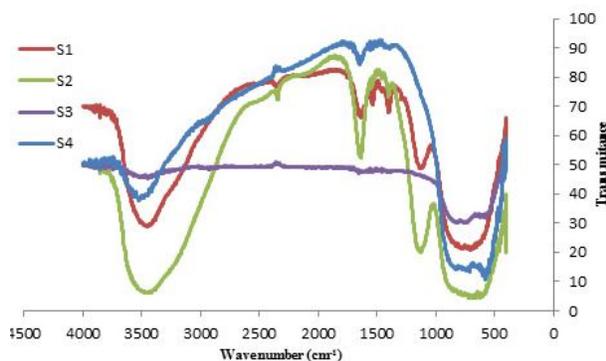


Fig. 8. FESEM images of S<sub>4</sub>.

Fig.9 shows the FTIR spectra of the synthesized nanomaterials via a combustion method at different conditions. The FTIR spectra of the synthesized nanomaterial annealed at 600 and 1000 °C is shown in fig. 9. The peaks at 1625–1650 cm<sup>-1</sup> are assigned to the bending vibrations of hydroxide. The weak peak at 1508 and 2340 cm<sup>-1</sup> are assigned to nitrate and carbonate. The peaks at 400 to 900 cm<sup>-1</sup>, are assigned to Al-O vibrations [22]. The peaks at 500–570 cm<sup>-1</sup> are assigned to AlO<sub>6</sub> and the peaks at 675–775 cm<sup>-1</sup> are assigned to AlO<sub>4</sub>. Also, the peaks at 1635 cm<sup>-1</sup> are assigned to the bending vibrations of hydroxide vibrational

mode and the peak around  $3480\text{ cm}^{-1}$  is assigned to the stretching vibration of hydroxide.



**Fig. 9.** FTIR spectra of the synthesized nano-alumina annealed at different reaction temperatures.

#### 4. Conclusion

Synthesis of nano-alumina with different conditions was performed successfully. PXRD data showed that the obtained nanomaterials were crystallized in different crystal structures with changing the reaction conditions. FESEM images showed that the synthesized nanomaterials were in different morphology that was dependent to the synthesis conditions. It showed that the morphology of the obtained materials was in the form of different types of porous and particle materials. FTIR spectra of the nano alumina were investigated in different synthesis conditions.

#### Acknowledgment

The financial support of this work by Research Council of University of Semnan (Grant number: 8107004/NP/01) is gratefully acknowledged.

#### Reference

- [1] M. E. Mahmoud, M. M. Osman, O. F. Hafez, E. J. Elmelegy, *Colloid Interface Sci.* 349 (2010) 307–313.
- [2] S. F. Gong, A. Shinozaki, M. L. Shi, E. W. Qian, *Energy Fuels.* 26 (2012) 2394–2399.
- [3] J. R. Gaudet, A. Riva, E. J. Peterson, T. Bolin, A.K. Datye, *Am. Chem. Soc. Catal.* 3 (2013) 846–855.
- [4] H. Puroh, J. L. Pinilla, C. Berruero, J. A. Fuente, M. Millan, *Energy Fuels.* 27 (2013) 3952–3960.
- [5] X. He, X. G. Zhou, B. Su, *Mater. Lett.* 63 (2009) 830–832.
- [6] Y. E. Qi, Y. S. Zhang, Y. Fang, L. T. Hu, *Composite: Part B.* 47 (2013) 145–149.
- [7] Z. F. Zhu, H. Liu, H. J. Sun, D. Yang, *Microporous Mesoporous Mater.* 123 (2009) 39–44.
- [8] K. Das, S. S. Ray, S. Chapple, Wesley-Smith, J. *Ind. Eng. Chem. Res.* 52 (2013) 6083–6091.
- [9] N. K. Renuka, A.V. Shijina, A. K. Praveen, *Mater. Lett.* 82 (2012) 42–44.
- [10] M. Furukawa, *Am. Ceram. Soc. Bull.* 62 (1983) 1384–1387.
- [11] D. R. Uhlmann, G. J. Teowee, *Sol–Gel Sci. Technol.* 13 (1998) 153–162.
- [12] J. Cejka, P.J. Kooyman, L. Vesela, J. Rathousky, A. Zukal, *Phys. Chem. Chem. Phys.* 4 (2002) 4823–4829.
- [13] J. Cejka, *Appl. Catal. A.* 254, (2003) 327–338.
- [14] K. P. Muthe, M. S. Kulkarni, N. S. Rawat, D. R. Mishra, B. C. Bhatt, A. Singh, S. K. Gupta, *J. Lumin.* 128 (2008) 445–450.
- [15] C. H. Peng, C.C. Hwang, C.S. Hsiao, *J. Alloys Compd.* 491 (2010) 29–32.
- [16] B. A. Henaish, A. M. El-Agrami, W. I. Abdel-Fattah, W.G. Osiris, *Radiat. Phys. Chem.* 44 (1994) 73–77.
- [17] H. Ogino, A. Yoshikawa, M. Nikl, A. Krasnikov, K. Kamada, T. Fukuda, *J. Cryst. Growth.* 287 (2006) 335–338.
- [18] J. H. Kim, K. Y. Jung, K. Y. Park, S. B. Cho, *Microporous Mesoporous Mater.* 128 (2010) 85–90.
- [19] V. Jayaraman, T. Gnanasekaran, G. Periaswami, *Mater. Lett.* 30 (1997) 157–162.
- [20] J. Aguado, J.M. Escola, M.C. Castro, *Microporous Mesoporous Mater.* 128 (2010) 48–55.

- [21] X. Zhang, M. Honkanen, E. Leva`nen, T. Ma`ntyla, *J. Cryst. Growth.* 310 (2008) 3674–3679.
- [22] K. R. Nemade, S. A. Waghuley, *Ceramics International.* 40 (2014) 6109–6113.