

# Evaluation of the Modified Reduction/Expansion Synthesis in the Production of Nanoparticulate Alumina

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## Abstract

This study aims to probe the feasibility of a modified reduction/expansion synthesis (M-RES) to generate alumina nanoparticles from nitrate precursors. 1/1 weight ratio mixtures of aluminum nitrate and urea exposed to fast heating at three temperatures (350, 650, 950 °C, under oxidize atmosphere), in order to create the kinetic and thermodynamic conditions to promote chemical reactions and phase transformations leading to the formation of alumina nanoparticles. Crystallographic, morphological and textural properties were evaluated via X-ray diffraction, scanning electron microscopy and nitrogen adsorptions isotherms. X-ray revealed little crystallographic development at 350 °C (composed mainly of pseudo boehmite); samples synthesized at 650 and 950 °C presented a well-developed crystallographic structure (delta alumina and gamma alumina, respectively). SEM pictures show the transition from amorphous micron aggregates from the 350 °C sample to a more faceted structure material, characteristic of highly crystalline alumina, at 950 °C. M-RES procedure generates powder material with low total surface area and pore volume. Synthesis temperature showed a direct correlation with the development of total surface area and volume pore, the highest values were obtained for the 950 °C synthesized sample ( $29.5 \text{ m}^2/\text{g}$  and  $1698 \times 10^{-2} \text{ mL/g}$ ), while the 350 °C temperature generated the lowest values ( $4.9 \text{ m}^2/\text{g}$  and  $3,142 \times 10^{-3} \text{ mL/g}$ ). M-RES procedure proved to be a suitable procedure to obtain oxidized nanoparticles of sizes ranging from 50 to 200 nm. The M-RES technical simplicity could become a scalable and efficient process for the synthesis of nanoparticles.

**Keywords:** alumina nanoparticles, reductive/expansion synthesis, nitrate decomposition, urea decomposition

## 1. Introduction

Metal oxides nanoparticles synthesis have been widely investigated in recent years, mainly due to the large and important fields of application such materials could have (catalysts, semiconductors, sensors, medical science and devices, energy storage and batteries). Among the several studied methodologies alkoxides synthesis [1-5], sol-gel [6, 7], plasma torch [8, 9] are the most used. However many of these methodologies generally involve the use of multiple reaction/separation stages, often using expensive equipment and reagents that could be hazardous. The study of simple methods for the production of particulate oxides with high thermal resistance like alumina and alumina based ceramics oxides has aroused great interest recently; in particular, aluminum oxides are of great interest given their important physical characteristics such as high hardness, high stability, high insulation, and transparency. An interesting alternative for the production of metallic particles was proposed by Zea et al [10], involving economic reagents and using simple equipment; this versatile reductive/expansion synthesis (RES) approach not only allows the generation of metallic material but also by tuning the reaction atmosphere allows the formation of oxides. Under this approach (M-RES, modified reductive/expansion synthesis), an initial reductive condition coupled with an oxidant atmosphere and thermal treatment generates aluminum oxides with different crystallographic phases. In the production of alumina, the reactions can be divided into three stages. The first is the formation of aluminum hydroxide, which may be crystalline or amorphous, the most common phases of these aluminum hydroxides are gibbsite, bayerite, nordstrandite and boehmite, the second stage involves the thermal decomposition of the oxide-hydroxide accompanied by evolution of water and the third stage is the reorganization and crystalline stabilization of the remaining aluminum oxide structures. Alumina exists either in metastable or stable forms, of the different forms of alumina ( $\alpha$ ,  $\theta$ ,  $\eta$ ,  $\delta$ ,  $\kappa$ ,  $\beta$ ), all are in the metastable forms except for the  $\alpha$ -alumina. Most industrial and commercial processes produce alumina as a particulate material with average particle size ranging from 50 microns to several centimeters. In order to produce alumina as a particulate material with particle diameters in the sub-micron and nano size additional stages of size reduction such as ball mills, laser ablation or cathodic spraying are required.

## 2. Materials and Methods

The M-RES synthesis process used in this document includes three fundamental steps: the first one involves the physical mixing of aluminum nitrate with urea until an homogeneous paste is formed, the second is a rapid heating process of the obtained paste and the third one is an extended heat treatment under controlled atmosphere, the last two under a permanent flow of synthetic air. The amount of raw materials used during the paste preparation was set to produced a1/1 by

weight ratio of  $\text{CH}_4\text{N}_2\text{O}$  (urea, Aldrich 99.9%) and  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (Aluminum nitrate nonahydrate, Aldrich 99.997%). Once a homogeneous paste of the components was obtained, they were transferred to a refractory vessel of about  $5 \text{ cm}^3$  and evenly distributed therein with a spatula. The refractory vessel was placed in the center of a quartz tube (2.5 cm of outside diameter and 30 cm in length), through which synthetic air (400 ml / m) was passed through. The quartz tube was rapidly transferred into a preheated furnace preheated accordingly to the experimental conditions studied (350, 650, 950 ° C), after approximately 10s, since the moment the quartz tube was placed in the furnace, a white smoke was observed in the quartz tube outlet stream; this time the is required for the mixture to reach the decomposition temperature, then the tube was left inside the furnace for 2 hrs., to be finally removed from the furnace and placed in supports to allow its natural cooling at room temperature, under constant flow of synthetic air. Once the tube has cooled down to room temperature the refractory vessel was withdrawn from the quartz tube and the solids contained therein were recovered. XRD of powdered samples was performed in an Ultima III Rigaku X-ray diffractometer using  $\text{Cu K}\alpha$  radiation of 40 kV. Nitrogen isotherms were conducted at 77 K on an Accelerated Surface and Porosimetry (Micromeritics ASAP-2010 system). Morphological characterization of the synthesized samples were performed in a Scanning Electron Microscope (SEM) JEOL (JSM 6490), at 5 kV of acceleration voltage and a working distance between 3 to 5 mm.

### 3. Results and Discussion

The sample recovered from the refractory vessel was a white granular powder, the granules were easily disintegrated by contact with the spatula. Figure 1 presents the X-ray diffraction profiles of samples synthesized at 350 °C (profile a), 650 °C (profile b) and 950 °C (profile c). The sample synthesized at 350 °C presents little crystallographic development, in which some wide angle low intensity peaks characteristic of the pseudo boehmite (23.2, 26.9, 31.5 and 42, 6), indicating that the reaction/thermal decomposition of the paste raw material initially led to the formation of aluminum oxide-hydroxide species [11-13]. The sample synthesized at 650 °C shows characteristic peaks corresponding to the delta phase (31.03, 34.89, 37.23, 45.33, 46.56 and 50.89°), some indeterminate peaks at  $2\theta$  values of 36.4 and 41.5° are also observed and do not correspond to none of the characteristic phases reported for the alumina transitions, these indeterminate peaks are characterized by having a large amplitude in terms of values of  $2\theta$ , which would indicate with they are the result of the overlapping of phase peaks in transition state [6, 11-14]. The diffraction profile for the sample at 950 °C shows the characteristic peaks for the alpha alumina phase at  $2\theta$  values of 25.57, 35.14, 37.76, 43.33 and 52.53°. The unmatched peaks observed in the sample synthesized at 650 °C are not observed in the profile of the sample synthesized at 950 °C, which would indicate that, the transition process has been completed.

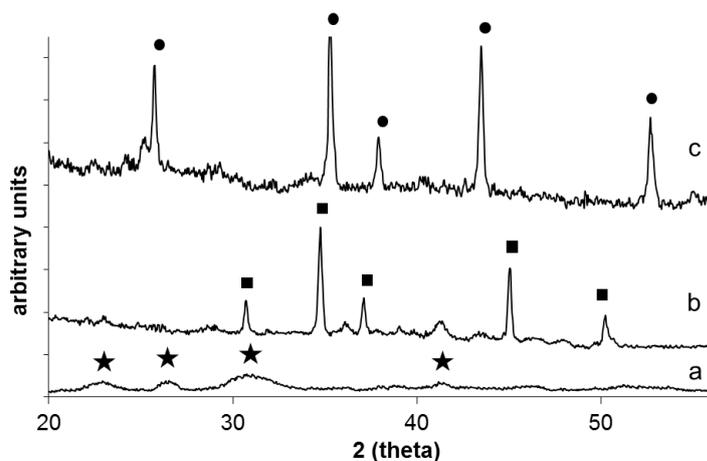


Figure 1. X-ray diffraction profiles of samples synthesized at different temperatures, a) 350 °C, b) 650 °C and c) 950 °C

Figure 2 presents the N<sub>2</sub> adsorption isotherm for the samples synthesized at 350 °C (isotherm a), 650 °C (isotherm b) and 950 °C (isotherm c). The isotherms for the samples synthesized at 350 °C and 650 °C show low volume increases of N<sub>2</sub> adsorbed at P / P<sub>0</sub> values below 0.2, for values of P / P<sub>0</sub> above 0.3 these isotherms develop wide hysteresis. In contrast, for the N<sub>2</sub> adsorption isotherm for the sample synthesized at 950 °C, the adsorbed N<sub>2</sub> values increase rapidly for P / P<sub>0</sub> values below 0.1 also developing a wide hysteresis for P/P values greater than 0.1.

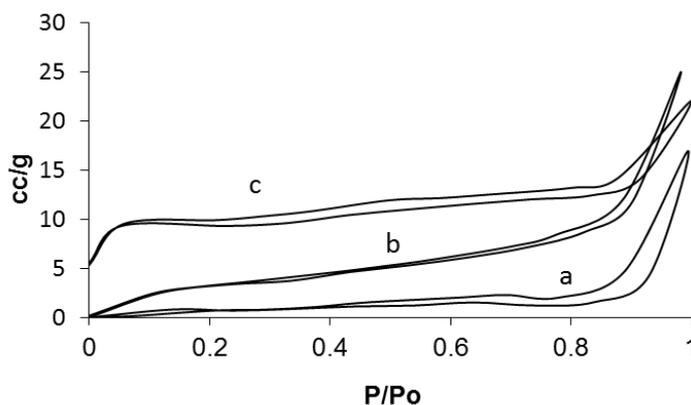


Figure 2. Nitrogen adsorption isotherms of samples synthesized at different temperatures, a) 350 °C, b) 650 °C and c) 950 °C

Total surface area and the micro pore volume are reported in Table 1. According to these values there is an apparent relationship between the synthesis temperatures of the samples and their respective surface areas and micro pore volumes; The sample at higher temperature (950 °C) reports the highest values of surface area and micro pore volume (29.5 m<sup>2</sup>/g and 16.98 μL/g, respectively), while

the sample synthesized at 350 °C reports the lowest values of surface area and micro pore volume (4.9 m<sup>2</sup>/g and 3.142 μL/g, respectively).

Table 1. Total surface area and the micro pore volume of samples reared at 350, 650 and 950 °C

Synthesis temperature (°C)	Total surface area (m <sup>2</sup> /g)	Pore volume (μL/g)
350	4.9	3.142
650	13.2	13.29
950	29.5	16.98

Figure 3 shows the SEM photographs of the representative material obtained at 350 °C (Figure 3a) and 950 °C (Figure 3b). Figure 3a shows material consisting of agglomerated particles that form clusters of about 2 to 3 microns, the morphology of the particles that form the aggregates is not well defined and their average size oscillates between 50 and 100 nm. Figure 3b shows a higher magnification of the particles after the treatment at 950 °C, in which it can be observed that the micron size amorphous aggregates obtained at 350 °C evolved into more faceted structures, characteristic of the crystalline structure of alumina. The faceted structures are made of particles that have an average particle sizes between 50 and 150 nm.

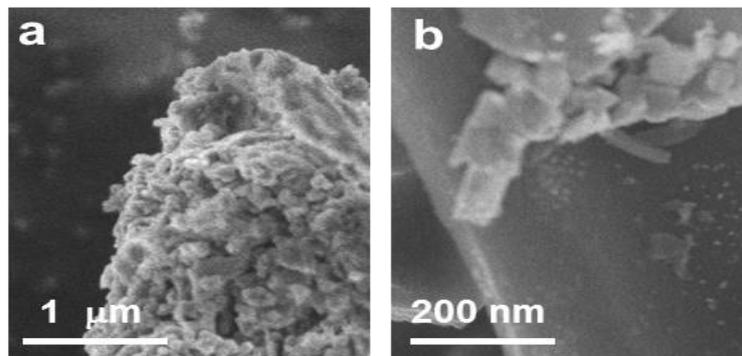


Figure 3. SEM pictures of the samples synthesized at: a) 350 °C and b) 950 °C.

Transferring the mixed paste of aluminum nitrate and urea from room temperature to a preheated oven involves an extremely fast heating of the mixture, leading to a thermal decomposition of the mixture in a temperature range between 160 to 250 °C, depending of the paste composition [7, 12, 13, 15, 16]. Aluminum nitrate decomposition has been reported to start at temperatures as low as 150 °C [15], meanwhile urea decomposes in a first stage between 180 – 250 °C to form ammonium and isocyanic acid followed by a further decomposition of the isocyanic acid to a gaseous mixture of ammonium and carbon dioxide at temperatures above 350 °C [10, 12]. In the case of the aluminum nitrate, the initial stage of decomposition below 170 °C, comprises a series of simultaneous

reactions such as dehydration, hydrolysis, and destruction of nitrate groups sharing comparable reaction mechanism to processes such as dehydroxylation of hydroxy salts, that also could be formed during the thermal decomposition of hydrolytic processes that take place at temperatures above 170 °C. Therefore, stoichiometric and thermodynamics conditions of the mix at the initial moment of decomposition may lead to the formation of an initial hydroxyl compound of the type  $Al_x(OH)_y(NO_3)$ , the nitrate molecules decomposes rapidly due to the thermodynamic favorable reaction to the formation of ammonium in the presence of urea. The remaining  $Al_x(OH)_y$  structures are denominated as aluminum oxide-hydroxide, being trihydrate (Gibbsite) the most stable phase of the aluminum oxide-hydroxide at the initial decomposition temperature; however, if the relevant reaction conditions lead to rapid depletion of oxidative species in the oxidant atmosphere, it could lead to the formation of less stable and poorly crystallized phase as pseudo boehmite, as in this case [3, 11, 13, 16, 17]. The evolution of the alumina crystalline structure due to the effect of thermal transformation have been extensively discussed [2, 5, 9, 11, 13]; initially the dehydration of pseudo boehmite and boehmite phases (from 250 up to 400 °C) via thermal decomposition inducing the formation of surface aluminum oxide phase such as gamma and delta alumina. Evolution of alumina phases is known to be highly dependent of the initial seeding in the crystal formation process, the rapid heating and cooling and the singular chemical condition present during the RES process, limits the variability in the seeding formation, facilitating the transition between phases. Once the thermal decomposition of the mixture begins, two simultaneous processes are carried out. Initially, the nitrates decompose to form submicron oxides. Subsequently, the gas created by the decomposition of urea, quickly chemically reduces the oxide particles formed in the first step. In addition, the rapid generation of gases generated during the decomposition of urea and nitrates is believed to "break" any aggregates, leaving only small, easily separable and highly reactive, metal metallic particles.

The modified RES proved to be a suitable procedure to obtain oxidized nanoparticles of sizes ranging from 50 to 200 nm. Only the temperature effect was considered, so it would be interesting to evaluate the effects that other process variables such as precursors weight ratio and thermal treatment time may have on the distribution of particle size and the predominant phase in the synthesized material. In addition the ease and simplicity of the developed procedure indicates that it may be a scalable and efficient process for the synthesis of nanoparticles.

#### 4. Conclusions

M-RES procedure was proved to be feasible procedure for the synthesis of alumina nanoparticles from the thermal decomposition of nitrates compounds. Characterization results allow concluding the important effect processing temperature has in the evolution of the particle size and phase transition of the generated particles. Only the 650 and 950 °C generated well developed crystallographic alumina samples, composed mainly of delta and alpha alumina

for the 650 and 950 °C, respectively. On the contrary, the 350 °C synthesized sample showed low crystalline pseudo boehmite. SEM microphotographs show the transition from amorphous micron aggregates from the 350 °C sample to a more faceted structure material, characteristic of highly crystalline alumina, at 950 °C. Total surface area and pore volume showed a direct correlation to the synthesis temperature, concluding that the M-RES procedure generates powder material with low total surface area and pore volume. The important temperature effect on the M-RES procedure is due the dominant role it has in establishing the proper kinetic and thermodynamic conditions, responsible of a highly convoluted series of thermally driven chemical decomposition and phase transformation.

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