Fuel effects on properties of alumina nanoparticles synthesized by combustion technique

M Fazli*, M J Tafreshi, F Bustan Afruz & A Rahmani

*Faculty of Chemistry, Semnan University, Semnan, Iran
Faculty of Physics, Semnan University, Semnan, Iran

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Alumina nanopowders have been produced by solution combustion synthesis using aluminum nitrate as oxidizer and urea (U), ammonium acetate (AA) and ammonium nitrate (AN) as fuels. The fuel effects on properties of products have been studied. Enthalpy and adiabatic flame temperature are calculated theoretically for each fuel based on thermodynamic concept to determine its exothermicity. Thermogravimetric (TG) analysis has also been carried out to determine the thermal properties of the metal nitrate and fuels. The prepared samples have been characterized by X-ray diffraction (XRD), N₂ adsorption (BET) and scanning electron microscopy (SEM). The results show that by reducing the exothermicity of reaction, alumina nanopowders with smaller crystallite size, finer agglomerate and higher specific surface area are produced.

Keywords: Solution combustion synthesis, Fuel, Alumina, Thermodynamic calculation

1 Introduction

Among the large number of techniques employed for the synthesis of oxides, solution combustion synthesis is simple, low cost and rapid production process with energy and time savings. This technique has successfully been applied to produce variety of alumina phases such as γ-alumina that is an extremely important material in catalytic surface activity. Various methods such as sol gel, hydrothermal processing and control precipitation have been employed to produce alumina nanopowders. Most of these techniques are quite complicated and need high temperatures and long processing time.

Among the various control parameters in a combustion process, fuel plays an important role in determining the properties of products. It has been reported that characteristics such as particle size, surface area, extent and nature of agglomeration are primarily governed by enthalpy or flame temperature generated and the amount of the gases that escape during combustion. These factors themselves depend on the nature of the fuel. Combustion process has the advantage of choice of a wide variety of fuels. Urea seems to be the most convenient one to be employed in this technique to produce alumina nanostructures, but using urea as fuel directly yields α-alumina powders with high crystallite size, low specific surface area and hard agglomerates, because of the formation of stable polymeric intermediates that prevent the dissipation of heat and thereby sintering the oxides during combustion. So, other fuels have been used in pure form or mixed with urea to reduce energy of reaction and improve size and specific surface area of alumina nanoparticles. These researches have shown that utilization of variety fuels leads to different thermal reactions and production of powders with different properties.

Recently, we reported synthesis of alumina nanoparticles using ammonium carbonate ((NH₄)₂CO₃) and ammonium sulfate ((NH₄)₂SO₄) as two new fuels. These fuels can produce alumina nanoparticles of smaller crystallite size and higher surface area in compared with other fuels. Therefore, fuels containing ammonium are proposed as a new group of fuels to produce alumina nanoparticles of smaller crystallite size and higher surface area. In this paper, we are reporting synthesis of alumina nanoparticles using ammonium acetate, ammonium nitrate and urea to compare the results obtained from utilizing fuels containing ammonium with urea. These two fuels have lower enthalpy and flame temperature compared with urea, so we predict production of better results. In addition, fuel effects and thermodynamic of combustion

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*Corresponding author (E-mail: mfazli@semnan.ac.ir)
synthesis on specific surface area, crystalline size and agglomerate size distribution of the prepared powders are investigated.

2 Experimental Procedure

In all the experiments Merck analytical reagents were used as raw materials. Aluminum nitrate nonahydrate (Al(NO\(_3\))\(_3\)9H\(_2\)O) was used as oxidizing agent. Urea (CO(NH\(_2\))\(_2\)), ammonium acetate (CH\(_3\)COONH\(_4\)) and ammonium nitrate (NH\(_4\)(NO\(_3\))) were used as fuels. Suitable amount of stoichiometric starting materials was dissolved in minimum amount of deionized water. Then, the dish containing as-prepared precursors heated in a pre-heated furnace maintained at 400 °C. The materials foamed, decomposed and generated large volume of gases. Then spontaneous ignition occurred and underwent smoldering combustion with enormous swelling, producing a foamy, voluminous mass. The voluminous foamy mass was easily crushed to the powders. The samples prepared from ammonium acetate and ammonium nitrate were calcined at 700 °C. The alumina powders obtained were named as SU (urea as fuel), SN (ammonium nitrate as fuel) and SA (ammonium acetate as fuel).

The crystallinity and phase identification of synthesized powders were determined by using D4 Bruker X-ray diffractometer with Cu-K\(_\alpha\) as the radiation source and Ni as the filter. To confirm the results obtained from X-ray diffraction regarding phase and nature of products, TG analysis was carried out in air atmosphere with TGA Q50 V6.3 system in the temperature range between 25 °C and 700 °C at a heating rate of 20 °C/min to assess the weight losses due to conversion of precursors. The surface area of synthesized powders was calculated according to the Brunauer-Emmet-Teller (BET) procedure by using the data of adsorption of nitrogen on the samples at 77 K assuming the cross sectional area of 0.16 nm\(^2\) for the nitrogen molecule by adsorption analyzer (BEL Japan, Inc). SEM micrographs of the samples were recorded using XL-30 /TMP electron microscope.

3 Results and Discussion

3.1 Thermodynamic modeling

In combustion synthesis of a fuel-nitrate mixture, an exothermic reaction occurred and mixture underwent a self-propagating and non-explosive reaction. Different types of fuels caused different thermal reactions\(^ {20}\). Combustion reactions occurred following different fuel-to-nitrate mixtures. These reactions are expressed as follows:

\begin{align}
2\text{Al(NO}_3\text{)}_3\cdot9\text{H}_2\text{O} + 5\text{H}_2\text{N}_2\text{CO} &\rightarrow \text{Al}_2\text{O}_3(s) + 5\text{CO}_2(g) + 28\text{H}_2\text{O}(g) + 8\text{N}_2(g) \\
\text{... (1)}
\end{align}

\begin{align}
2\text{Al(NO}_3\text{)}_3\cdot9\text{H}_2\text{O} + 2.73\text{CH}_3\text{COONH}_4 &\rightarrow \text{Al}_2\text{O}_3(s) + 4.36\text{N}_2(s) + 27.55\text{H}_2\text{O}(g) + 5.46\text{CO}_2(g) \\
\text{... (2)}
\end{align}

\begin{align}
2\text{Al(NO}_3\text{)}_3\cdot9\text{H}_2\text{O} + \text{NH}_4\text{NO}_3 &\rightarrow \text{Al}_2\text{O}_3(s) + 10\text{N}_2(s) + 3\text{N}_2\text{O}(g) + 11\text{H}_2\text{O}(g) \\
\text{... (3)}
\end{align}

For comparing exothermicity of different fuels in reaction with the nitrates, enthalpy and adiabatic flame temperature of the reactions between urea, ammonium acetate and ammonium nitrate with aluminium nitrate were calculated in the stoichiometric condition, by the following equations:

\[ \Delta H_f = (\sum n\Delta H_p) - (\sum n\Delta H_f) = \int_{T_0}^{T_f} (\sum nC_p) dT \quad \text{... (4)} \]

and

\[ T_f = T_0 + \frac{\Delta H_f - \Delta H_p}{\sum nC_p} \quad \text{... (5)} \]

where \(\Delta H_p\), \(\Delta H_f\) and \(\Delta H\) are the enthalpies of combustion, products and reactants, respectively; \(T_f\) is the adiabatic flame temperature, \(T_0\) is 298 K and \(C_p\) is the molar heat capacity of products at constant pressure. The thermodynamic data for the various reactants and products are listed in Table 1.

To investigate evolution of energy and flame temperature during combustion, the enthalpies of combustion and adiabatic flame temperature were calculated for each fuel according to Eqs (4) and (5) and presented in Fig. 1. Urea has higher exothermicity due to higher enthalpy of reaction with aluminum nitrate and it shows more flame than AN and AA fuels during combustion reaction, so this enthalpy of combustion and adiabatic flame temperature effects on properties of produced powders.

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\Delta H_f) (kcal/mol)</th>
<th>(C_p) (cal/mol .K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>\text{Al(NO}_3\text{)}_3\cdot9\text{H}_2\text{O}(s)</td>
<td>-857.59</td>
<td>—</td>
</tr>
<tr>
<td>\text{NH}_4\text{NO}_3(s)</td>
<td>-87.40</td>
<td>—</td>
</tr>
<tr>
<td>\text{CH}_3\text{COONH}_4(s)</td>
<td>-147.26</td>
<td>—</td>
</tr>
<tr>
<td>\text{CO(NH}_2\text{)}_2(s)</td>
<td>-56.33</td>
<td>—</td>
</tr>
<tr>
<td>\text{N}_2(g)</td>
<td>0</td>
<td>6.5+0.0010T</td>
</tr>
<tr>
<td>\text{Al}_2\text{O}_3(g)</td>
<td>-399.09</td>
<td>28.062+0.01038T</td>
</tr>
<tr>
<td>\text{H}_2\text{O}(g)</td>
<td>-57.96</td>
<td>7.2+0.0036T</td>
</tr>
<tr>
<td>\text{CO}_2(g)</td>
<td>-94.051</td>
<td>10.34+0.00274T</td>
</tr>
</tbody>
</table>

Table 1—Thermodynamic data for the various reactants and products\(^ {2,13}\)
3.2 Thermal analysis

In order to explain the predilection of aluminum nitrate with respect to different fuels, thermal analysis was carried out. The decomposition rate of aluminum nitrate below 160 °C is much higher than its value above 160 °C, so thermal decomposition of aluminum nitrate takes place at 135 °C. Urea decomposes at 133 °C which lies in the temperature range in which aluminum nitrate decomposes with maximum rate. Overlapping the decomposition temperature of aluminum nitrate and urea triggers an energetic combustion reaction that yields α-alumina powder.

On the other hand, it has been observed that fuels such as glycine and citric acid which decompose at 240 °C and 175 °C, respectively, give smoldering combustion with aluminum nitrate leading to the formation of amorphous powders. Similarly, in this work ammonium acetate decomposes at 165 °C and ammonium nitrate decomposes above 200 °C, so their reaction gives smoldering combustion leading to the formation of amorphous powders and only after annealing they change to crystalline alumina. An elevated adiabatic temperature does not necessarily imply a vigorous combustion reaction. According to different authors, the ignition mechanism of combustion process usually takes place between the gaseous decomposition products of metal nitrite and fuel. Therefore, it can be inferred that a prerequisite for the occurrence of combustion reaction in metal nitrate/fuel systems is the existence of an overlapping temperature interval in which thermal decomposition of metal nitrate and fuel occurs simultaneously.

The thermal behavior of aluminum nitrate mixture with different types of fuels using TG analysis is shown in Fig. 2. Different fuels show different thermal decomposition behaviors. Decomposition starts below 200 °C for all the samples. The reaction of sample SU takes place rapidly. It is very steep, showing that the reaction takes place rapidly. The rapid slope weight loss at 200-260 °C associated with the rapid auto ignition, another crucial factor, is the fast cooling due to the rapid evolution of the gases during auto-ignition. In the SN and SA samples, the slopes were less steep when compared to SU, indicating lesser decomposition in temperature range of 150-250 °C.

3.3 Physico-chemical characterization

The XRD patterns of the samples have been shown in Fig. 3. It shows that sample SU (alumina prepared by urea) is in the alpha phase corresponding to previous which is in consistent with other reports. This figure also shows that the samples SA and SN are in gamma phase and they are pure crystalline in nature. Broadening of the peaks clearly shows the
nano-size nature of crystallites (Fig. 3). The crystallite sizes were calculated using the Scherrer equation.

\[ D = \frac{k\lambda}{\beta \cos \theta} \]

where \( k \) is a constant \( \sim 0.9 \), \( \lambda \) is the wave length of the X-ray, \( \beta \) is the full width of diffraction peak at half maximum (FWHM) intensity and \( \theta \) is Bragg angle. The calculated crystallite sizes were found to be almost 37, 3.5 and 3 nm for samples SU, SN and SA, respectively. These results show that using ammonium group fuels leads to reduction in exothermicity of reaction and production of alumina with smaller crystallite size.

The surface area, pore size distribution and average pore volume data for different samples are given in Table 2. The pore size distribution of prepared powders from BJH method is shown in Fig. 4. Table 2 shows that the samples SN and SA have higher surface area as compared to that of the sample SU, and sample SA has bigger average pore size and pore volume in comparison with other samples which is in consistent with Fig. 4. So, by reduction in exothermicity of reaction between fuel and aluminum nitrate the surface area increases and there is reduction in crystallite size and agglomerate size attributed to decrease in flame temperature. There is a correlation between the increase in crystallite size and the reduction of surface area as a function of type fuel (Table 2). Many authors have already reported this relationship\(^2,18\). A particularly desirable property of \( \gamma \)-alumina is its high specific surface area and the related adsorption characteristics, which can be affected by the raw material and the preparation procedures\(^22\).

The SEM micrographs of the samples are shown in Fig. 5. For all the samples, the micrographs have exhibited foamy agglomerated particles and large voids in their structure, which are attributed to the evolution of a large amount of gas during combustion. As it can be seen, all samples have exhibited flaky

<table>
<thead>
<tr>
<th>Samples</th>
<th>Specific surface area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Average pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SU</td>
<td>18.49</td>
<td>0.34</td>
<td>2.41</td>
</tr>
<tr>
<td>SN</td>
<td>199.32</td>
<td>0.257</td>
<td>2.41</td>
</tr>
<tr>
<td>SA</td>
<td>205.70</td>
<td>0.378</td>
<td>3.12</td>
</tr>
</tbody>
</table>

Table 2—The surface area, pore volume and average pore size for samples synthesized by different fuels

Fig. 4—Pore size distribution of prepared powders obtained from BJH method

Fig. 5—SEM micrograph of the samples
morphology, and samples SA and SN have finer agglomerates.

4 Conclusions
Effects of fuels and thermodynamic of combustion on properties of alumina nanoparticles prepared by combustion reaction were studied. Ammonium acetate, ammonium nitrate and urea were used to produce alumina nanoparticles via solution combustion synthesis. For these three fuels, thermal behavior was predicted by thermodynamic calculation and measured by TG analysis. Due to change in thermal parameters such as enthalpy, adiabatic flame temperature, energy released from reactions and decomposition temperatures, ammonium group fuels resulted in synthesizing high specific surface area (200 m²/g) and fine particle size (3nm) γ-alumina nanoparticles where as these two values were found to be 18.4 m²/g and 37 nm for α-alumina nanoparticles synthesized by urea. Pore size, pore volume and micrograph of the samples were found to be in consistent with our earlier studied results.

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References