Influences of Temperature on the Conversion of Ammonium Tungstate Pentahydrate to Tungsten Oxide Particles with Controllable Sizes, Crystallinities, and Physical Properties

Asep Bayu Dani Nandiyanto[1,*], Heli Siti Halimatul Munawaroh[1], Tedi Kurniawan[2], and Ahmad Mudzakir[1]

[1]*Department of Chemistry, Universitas Pendidikan Indonesia, Jl. Dr. Setiabudhi No. 229 Bandung 40154, West Java, Indonesia*

[2]*Department of Mechanical Engineering, Universiti Malaysia Pahang, FKM UMP Pekan 26600, Pahang, Malaysia*

Received November 26, 2015; Accepted March 1, 2016

ABSTRACT

The purpose of this study was to investigate influences of temperature on the conversion of ammonium tungstate pentahydrate (ATP) powder to tungsten trioxide (WO_3) particles with controllable sizes, crystallinities, and physicochemical properties. In this study, we used a simple thermal decomposition method. In the experimental procedure, we explored the effect of temperature on the physicochemical properties of ATP by testing various heating temperatures (from 100 to 900 °C). The heated ATP samples were then characterized by a physical observation (i.e. color) and various analysis methods (i.e. a thermal gravimetric and differential thermal analysis, infrared spectroscopy, an X-ray diffraction, and a scanning electron microscope). Experimental results showed that increases in temperature had an impact to the decreases in particle size, the change in material crystallinity, and the change in physical properties (e.g. change of color from white, orange, to yellowish green). The relationships between the reaction temperatures and the physicochemical properties of the ATP were also investigated in detail along with the theoretical consideration and the proposal of the WO_3 particle formation mechanism. In simplification, the phenomena can be described into three zones of temperatures: (1) Below 250 °C (release of water molecules and some ammonium ions); (2) At 250-400 °C (release of water molecules and ammonium ions, restructurization of tungsten and oxygen elements, and formation of amorphous tungsten trioxide); and (3) At higher than 400 °C (crystallization of tungsten trioxide). Since ATP possessed reactivity on temperature, its physicochemical properties changing could be observed easily, and the experimental procedure could be done easily. The present study will benefit not only for "chemistry and material science" but also potentially to be used as a model material for explaining the thermal behavior of material to undergraduate students (suitable used for a class and laboratory experiment and demonstration).

Keywords: *tungsten oxide; ammonium tungsten pentahydrate; thermal decomposition; material science; powder processing*

ABSTRAK

Tujuan penelitian ini adalah untuk melakukan investigasi efek-efek dari suhu pada proses konversi/reaksi ammonium tungstate pentahydrate (ATP) menjadi partikel tungsten trioxide (WO_3) dengan berbagai macam ukuran, kristalinitas, dan sifat fisika-kimia. Pada penelitian ini, kami menggunakan metode dekomposisi termal sederhana. Pada prosedur eksperimen, kami mengeksplorasi efek-efek dari suhu pada sifat fisika dan kimia dari ATP dengan melakukan testing pada berbagai macam suhu pemanasan (dari 100 sampai 900 °C). Sample ATP yang dipanaskan kemudian dianalisa dengan observasi fisik (perubahan warna) dan beberapa metode analisis. Hasil eksperimen menunjukkan bahwa peningkatan suhu memiliki dampak pada penurunan ukuran partikel, perubahan kristanilitas material, dan perubahan sifat fisika (perubahan warna dari putih, oranye, sampai kuning kehijauan). Hubungan antara suhu reaksi dan sifat fisika kimia dari ATP juga diinvestigasi secara detil dan dibandingkan dengan teori yang ada dan kami juga mengusulkan proposal mekanisme bagaimana partikel WO_3 terbentuk. Secara sederhananya, fenomena yang terjadi dapat dijelaskan menjadi 3 zona: (1) di bawah 250 °C (pelepasan molekul air dan sebagian ion amonium); (2) antara 250 dan 400 °C (pelepasan molekul air dan ion amonium, restrukturisasi dari elemen tungsten dan oksigen, dan pembentukan tungsten trioxide yang amorf); dan (3) lebih tinggi dari 400 °C (kristalisasi WO3). Karena ATP memiliki reaktifitas tinggi terhadap suhu, perubahan sifat fisika dan kimia dapat dilihat secara langsung, dan system prosedur eksperimen dapat dilakukan dengan mudah, penelitian yang diajukan ini akan memiliki keuntungan, bukan hanya untuk bidang "ilmu kimia dan material" tapi juga berpotensi untuk

* Corresponding author. Tel/Fax : +62-22-2000579
Email address : nandiyanto@upi.edu

digunakan sebagai model material untuk menjelaskan thermal behavior material untuk mahasiswa S1 (cocok untuk digunakan di kelas dan eksperimen di laboratorium).

Kata Kunci: *tungsten oxide; ammonium tungsten pentahidrat, dekomposisi termal, ilmu material, proses produksi powder*

INTRODUCTION

Recently, the tungsten-related material has been focused by many researchers because it has been widely used in industrial applications (i.e. electrocatalysts, sensors, photochromic devices, and photocatalysts). This material is used in many applications due to its attributes: relative harmlessness, chemical and thermal stability, excellent photostability, and chemical and biological inertness [1]. Therefore, understanding thermal behavior of tungsten-related raw materials that relates to the physicochemical properties (*e.g.,* crystallinity, catalytic active site, material strength) has been increasing attention tremendously.

Several scientific papers have reported the thermal behavior of tungsten-related material [2-10]. For example, Hunyadi et al. [6] reported the thermal behavior of "ammonium metatungstate", and Van put [10] reported "ammonium paratungstate." Although current papers describe well information about experimental results and analysis, fundamental reason behind the change of physicochemical properties (including size, crystallinity, and physical properties) during the thermal decomposition process is still lacking. In fact, this fundamental reason provides significant information toward producing better tungsten products in practical uses. Further, while current papers have reported the thermal behavior of various tungsten-related materials, reports on "ammonium tungstate pentahydrate" (ATP) are virtually non-existent. Also, the name of "ammonium metatungstate" and "ammonium paratungstate", as well as ATP, seems to be similar. However, the chemical structures of these materials are different (see Table 1). Indeed, various chemical structures would result in the different thermal activities and other properties of the chemical itself.

In our previous studies, we successfully produced inorganic oxide particles with controllable sizes, morphologies, and crystallinities [1,11-15]. In the case of WO_3, the WO_3 particles were prepared from various ammonium tungstate raw materials.

Here, the purpose of this study was to investigate influences of temperature on the physicochemical properties of ATP and tungsten oxide product (including size, crystallinity, and physical properties (i.e. color)). Although the release of the ammonium and water molecules from ATP can be predicted theoretically, there is no information regarding the confirmation of the release of these molecules with their characterization analyses. In fact, exact information about the influences of temperature on the physicochemical properties during the thermal decomposition process is important because it will give benefit, specifically relating to the further development and production of tungsten-related materials using a thermal decomposition process.

The relationships between the reaction temperatures and the physicochemical properties of the ATP were also investigated in detail along with the theoretical consideration and the proposal of the WO_3 particle formation mechanism. Although Van Put reported the proposal chemical formulation reaction during heat treatment, the paper did not report the possibility of the change of particle properties, such as particle size and morphology [10].

In addition, ATP is selected as a model of tungsten-related material because ATP is one of the prospective tungsten raw materials for producing tungsten oxides, tungsten carbides, and tungsten metal in the industry [6]. Further, ATP possesses reactivity on temperature, and its physicochemical properties changing can be observed easily. Therefore, this study will benefit for not only "chemistry and material science" but also potentially to be used as a model material for explaining the thermal behavior of material to undergraduate students as a simple laboratory experiment.

EXPERIMENTAL METHOD

In the experimental procedure, 2 g of ATP powder (Kanto Chemical Co., Inc., Japan) was heated using an electrical furnace. The heating process was conducted in the atmospheric condition under a fixed condition: a heating rate of 50 °C/min and a holding time at a specific

Table 1. Comparison chemical structure among "ammonium metatungstate", "ammonium paratungstate", and ATP

Chemical name	Molecular formula
Ammonium metatungstate	$(NH_4)_6[H_2W_{12}O_{40}].4H_2O$
Ammonium paratungstate	$(NH_4)_{10}[H_2W_{12}O_{42}].4H_2O$
Ammonium tungstate pentahydrate (ATP)	$(NH_4)_{10}[W_{12}O_{41}].5H_2O$
Tungsten trioxide	WO_3

Table 2. Theoretical calculation and experimental TG/DTA result of thermal decomposition of ATP

Sample	Molecular formula (molecular weight)	Mass (wt%)	
		Theoretical calculation	TG/DTA result
Initial ATP	$(NH_4)_{10}[W_{12}O_{41}].5H_2O$ (3132.63)	100.00	100.00
ATP after removal of water molecules	$(NH_4)_{10}[W_{12}O_{41}]$ (3042.56)	97.12	96.60
ATP after decomposing into WO_3	WO_3 (231.84)	88.81	89.06

temperature for 30 min. To confirm the influences of temperature on the physicochemical properties of ATP, heating temperatures were varied from 150 to 800 °C.

Several analyses were used to characterize the physicochemical properties of ATP sample. Thermal Gravimetry (TG) and Differential Thermal Analysis (DTA) (DTG-60A, Shimadzu, Japan) were used to analyze the mass degradation at a heating rate of 5 °C/min, a holding time at a specific temperature for 10 min, and a flow of air (200 mL/min). Fourier Transform Infrared Spectroscopy (FTIR; FTIR-8400, Shimadzu, Japan was used to analyze the chemical composition). X-ray diffraction (XRD; Rigaku Miniflex 2, Rigaku Denki Co. Ltd., Japan; operated using Cu-Kα was used to characterize the crystal phase and pattern). Scanning Electron Microscope (SEM; Zeiss Evo 50, Carl Zeiss NTS GmbH Oberkochen, Germany was used to characterize the particle morphology).

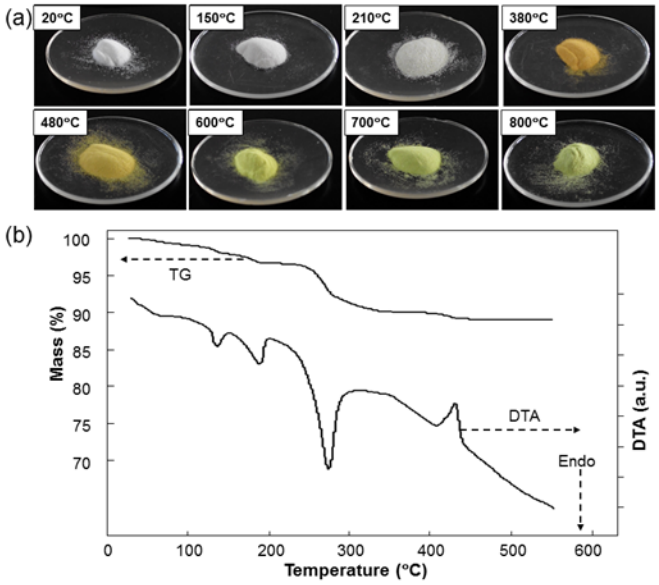

Fig 1. The photograph image (a) and TG-DTA analysis (b) results of samples heated at various temperatures

RESULT AND DISCUSSION

Photograph images (Fig. 1a) showed the change in physical properties (i.e. color) of ATP when ATP was heated at various temperatures. The initial color of ATP was white, and the color changed to orange (at 380 °C) and yellowish green (at higher than 600 °C). These changing colors confirm the temperature influences the physical properties of materials. In addition, since a direct visual observation can obtain the result, the present experiment is suitable for a class demonstration. However, indeed, applying the current study for a class demonstration needs further studies and safety consideration, in which this will be done in our future work.

The TG-DTA analysis (Fig. 1b) detects loss of mass in several steps with increasing temperature. Decreases in mass were found at temperatures of "lower than 150 °C," "between 250 and 300 °C", and "between 420 and 440 °C." The decreases were which matched well with the theoretical approximation (shown in Table 2) for the release of water molecules, the release of ammonium ions, and the decomposition into tungsten trioxide (WO_3), respectively. The results were strengthened by the DTA analysis that detected either an endothermic or an exothermic process at temperatures of 120, 190, 280, and 420 °C.

Fig. 2a shows the FTIR analysis results. The FTIR detected water molecules (at the band of about 1600 and 3600 cm^{-1}), N-H bond (at the band of about 1400 and 3200 cm^{-1}), and tungstate-related bond (in the range below 1000 cm^{-1}) in the initial sample. The intensity of the FTIR peaks decreased when heating samples at 150 and 210 °C. Adsorption peaks of water molecules and N-H bond did not appear in the samples heated at 380, 480, 600, 700, and 800 °C, indicating the removal of water and ammonium molecules from ATP after the ATP samples were heated to temperatures of more than 380 °C.

Fig. 2b shows the XRD results along with the reference pattern for monoclinic WO_3 (Joint Committee on Powder Diffraction Standards (JCPDS) No. 72-1465). The spectra of initial sample were in good agreement with that of pure ATP. By heating ATP at 150 °C, the disappearance of peaks in the range of 20, 30-40, and higher than 50° was identified. The XRD pattern of the sample heated at 210 °C was amorphous. The pattern changed into a monoclinic

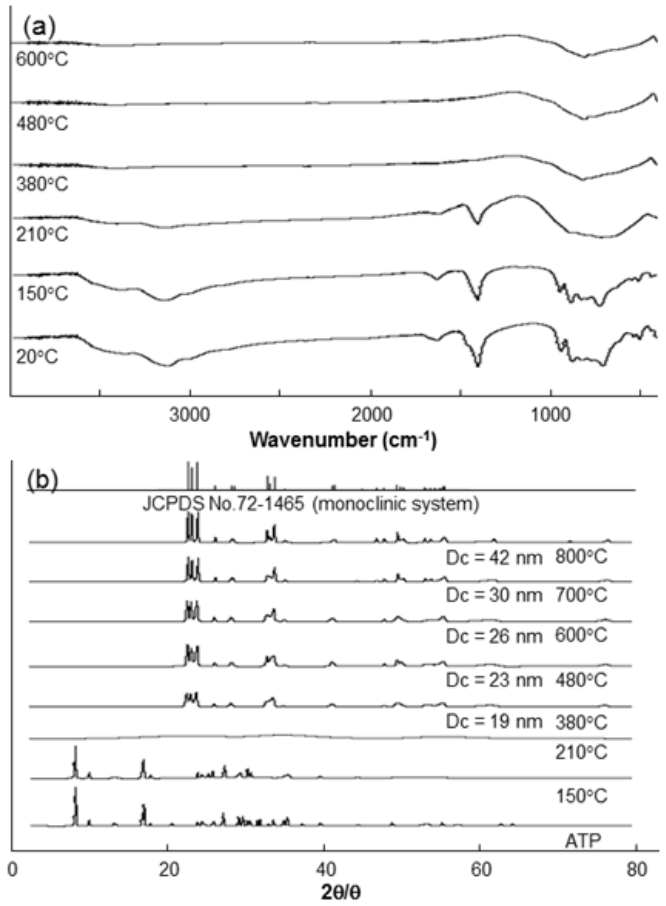

Fig 2. The FTIR (a) and the XRD (b) analysis results of samples heated at various temperatures

phase for the samples heated at more than 380 °C. For the ATP samples heated in the range of 380 to 800 °C, XRD crystal pattern and peak positions were identical, but the intensities of the XRD peaks were different. The Scherer sizes (*Dc*) of the samples heated at 380, 480, 600, 700, and 800 °C were 19, 23, 26, 30, and 42 nm, respectively. The FTIR and XRD results confirm that by adding a heating process to the ATP, water and ammonium molecules begin to release from 150 °C. Then, the release of water and ammonium molecules causes the collapse of tungstate structure, leading the change of ATP molecular structure and forming amorphous WO_3. Further heating process (temperatures of more than 380 °C) has an impact to the crystallization of amorphous to monoclinic WO_3 and the change of crystal sizes (shown by the change of Scherer sizes from 19 to 42 nm).

Fig. 3 shows the SEM images of ATP samples heated to various temperatures. Heating process causes to the change of particle size (see Fig. 3a, d, g, and j). The mean size of initial ATP sample was 101 μm. The average size of ATP heated at 210, 600, and 800 °C were 101, 58, 60 μm, respectively. The high-magnified SEM images (Fig. 3b, e, h, and k) show the change in particle surface morphology with increasing temperature. At 210 °C, some cracks in the surface were found (Fig. 3e). The crack enlarged with increasing temperature (Fig. 3h). Finally, the higher temperature leads to producing rough morphology (Fig. 3k).

According to the results, when heat is added, the release of water and ammonium molecules leaves holes/cracks and breaks the originated particle. This fact verifies that the temperature has a correlation to the change of particle size. In the case of the sample heated at 800 °C, the change in the surface roughness is due to the change in crystallinity.[13]

Based on the results, phenomena happening during the heating process are illustrated in Fig. 4. The phenomena are mainly divided into three zones based on the heating temperature: (1) below 250 °C; (2) 250-400 °C; and (3) higher than 400 °C. Detailed explanations about the zones (shown in Fig. 4) are described in the following:

Below 250 °C. In this zone, the heating process causes to the removal of water and some ammonium molecules. The release of water and ammonium molecules is confirmed by the change of mass in the TG-DTA analysis (Fig. 1b) and the appearance of some cracks in the SEM analysis (shown in Fig. 3e).

The release of water and ammonium molecules leads to the collapse of tungstate structure. Indeed, a new structure is created by changing position and orientation of tungsten (W) and oxygen (O) elements. The re-orientation of W and O elements is shown by the formation of an intermediate amorphous phase in the XRD result (Fig. 2b). The re-orientation of W and O elements are confirmed by the FTIR analysis results (Fig. 2a), as well as the detection of two endothermic heat peaks in the DTA analysis (Fig. 1b).

Between 250 and 380 °C. Phenomena in the temperature zone ranging between 250 and 380 °C are described in the following. When temperature increases into more than 210 °C, all water and ammonium molecules are removed from tungstate structure. The removal of water and ammonium molecules is shown by the decreases in the mass of up to 5 wt% in the TG analysis (Fig. 1b) and the disappearance of peaks in the range of between 2800 and 3800 cm^{-1} in the FTIR analysis (Fig. 2a). Further, an endothermic peak shown in DTA result at 280 °C (Fig. 1b) verifies the existence of chemical reaction phenomena in this step. The phenomena are also confirmed by the change of color from white to orange in the visual observation in Fig. 1a.

When all water and ammonium molecules are removed, the sample consists of W and O elements

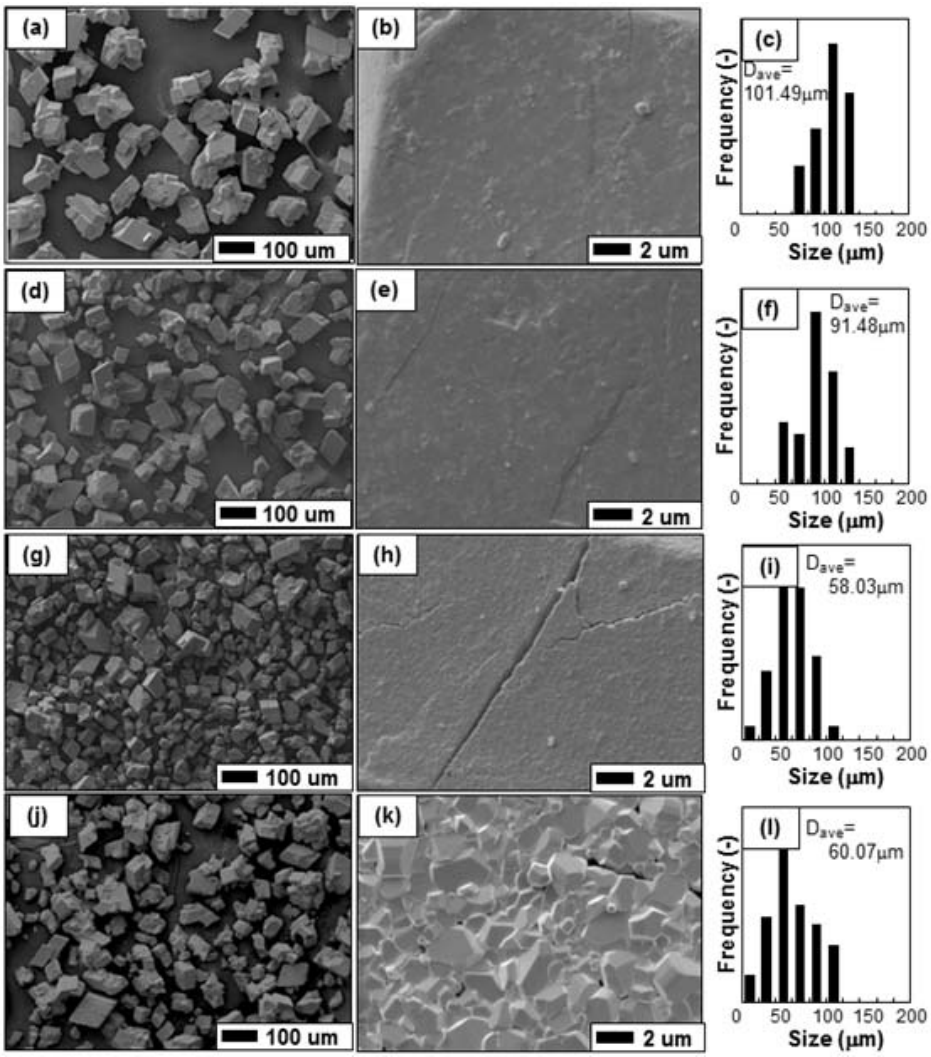

Fig 3. The SEM images of ATP samples heated at "no heat treatment" (a and b), 210 (d and e), 600 (g and h), and 800°C (j and k). Fig. (a), (d), (g), and (j) are the low magnification of SEM images, whereas Fig. (b), (e), (h), and (k) are the high magnification of SEM images. Fig. (c), (f), (i), and (l) are the Ferret analysis result of ATP samples heated at "no heat treatment", 210, 600, and 800°C samples, respectively.

only. The available free spaces abandoned by water and ammonium molecules lead to the re-assembly of tungstate structure into stable condition. Indeed, this makes W and O elements to get connected each other and do further atomic orientation, resulting in the formation of WO_3 material. Further additional heat treatment (heating at 380 °C) causes this material to crystallize by an exothermic heat effect, shown by the formation of WO_3 monoclinic phase system in the XRD analysis result of the ATP sample heated at 380 °C in Fig. 2b.

Higher than 380 °C. In this zone, WO_3 phase transformation occurs. The temperature has almost no impact on the further release of element/component from the sample. This result is strengthened by the obtainment of equal TG mass (Fig. 1b) and the detection of identical peaks and intensities in the FTIR analysis (Fig. 2a).

An exothermic peak at 420 °C is detected in the DTA analysis (Fig. 1b), and the change in physical properties of the sample (i.e. color changed from orange to yellowish green) is found (Fig. 1a). These results imply the occurrence of phenomena during the heating process in this zone.

The XRD analysis in Fig. 2b shows the identical crystal pattern and peak position for samples in the range of 380 to 800 °C. The different results are found only in the intensity of the peaks. Thus, we can conclude that the increases in temperature cause the

change of material crystallinity and crystal size (shown by the change of Scherer size).

The final mass of the sample heated at 800 °C in TG analysis (Fig. 1b) was 89.06 wt%. This result matches well the theoretical values for the decomposition of ATP into WO_3 (Table 1).

CONCLUSION

In this study, we have studied the influences of temperature on the physicochemical properties of ATP and tungsten oxide product, as well as the mechanism occurring during the thermal decomposition process. The experimental results showed that the temperature affected the physicochemical properties of the sample, including particle size, crystallinity, and physical appearance. During the heating process, several phenomena happen: (1) Below 250 °C (the release of water molecules and some ammonium ions); (2) At 250-400 °C (the release of water molecules and ammonium ions, the restructurization of tungsten and oxygen elements, and the formation of amorphous tungsten trioxide); and (3) At higher than 400 °C (the crystallization of tungsten trioxide). Based on this study, chemical reaction accompanying the thermal decomposition at various temperatures is possibly formulated. However, in this study, we focused on the change of physicochemical properties only. Therefore, further analysis and studies regarding the chemical formula and reaction will be discussed in our future work. In addition, since the experiment is simple and direct observation can be conducted, the present study is suitable for a class demonstration. However, indeed, applying the current study for a class demonstration needs further studies and safety consideration, in which this will be done in our future work.

ACKNOWLEDGEMENT

This research was partly supported by a Grant-in-Aid from the Directorate General of Higher Education of Indonesia (*Skim Program Unggulan Perguruan Tinggi Negeri*).

REFERENCES

1. Arutanti, O., Nandiyanto, A.B.D., Ogi, T., Kim, T.O., and Okuyama, K., 2015, *ACS Appl. Mater. Interfaces*, 7 (5), 3009–3017.
2. Basu, A.K., and Sale, F.R., 1977, *J. Mater. Sci.*, 12 (6), 1115–1124.
3. Fouad, N.E., Nohman, A.K., Mohamed, M.A., and Zaki, M.I., 2000, *J. Anal. Appl. Pyrolysis*, 56 (1), 23–31.
4. French, G.J., and Sale, F.R., 1981, *J. Mater. Sci.*, 16 (12), 3427–3436.
5. Gotić, M., Ivanda, M., Popović, S., and Musić, S., 2000, *Mater. Sci. Eng.*, B 77, 193–201.
6. Hunyadi, D., Sajó, I., and Szilágyi, I.M., 2014, *J. Therm. Anal. Calorim.*, 116, 329–337.
7. Magnusson, M.H., Deppert, K., and Malm, J.O., 2000, *J. Mater. Res.*, 15, 1564–1569.
8. Szilágyi, I., Madarász, J., Pokol, G., Hange, F., Szalontai, G., Varga-Josepovits, K., and Tóth, A.L., 2009, *J. Therm. Anal. Calorim.*, 97, 11–18.
9. Szilágyi, I.M., Sajó, I., Király, P., Tárkányi, G., Tóth, A.L., Szabó, A., Varga-Josepovits, K., Madarász, J., and Pokol, G., 2009, *J. Therm. Anal. Calorim.*, 98 (3), 707–716.
10. van Put, J.W., 1995, *Int. J. Refract. Met. Hard Mater.*, 13 (1-3), 61–76.
11. Nandiyanto, A.B.D., and Okuyama, K., 2011, *Adv. Powder Technol.*, 22 (1), 1–19.
12. Nandiyanto, A.B.D., Arutanti, O., Ogi, T., Iskandar, F., Kim, T.O., and Okuyama, K., 2013, *Chem. Eng. Sci.*, 101, 523–532.
13. Arutanti, O., Nandiyanto, A.B.D., Ogi, T., Iskandar, F., Kim, T.O., Okuyama, K., 2014, *J. Alloys Compd.*, 591, 121–126.
14. Arutanti, O., Ogi, T., Nandiyanto, A.B.D., Iskandar, F., and Okuyama, K., 2014, *AIChE J.*, 60 (1), 41–49.
15. Nandiyanto, A.B.D., Suhendi, A., Ogi, T., Umemoto, R., and Okuyama, K., 2014, *Chem. Eng. J.*, 256, 421–430.