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Production of granular boron oxide by calcination of ammonium tetraborate tetrahydrate

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Abstract

In this paper, the thermal calcinations of ammonium tetraborate tetrahydrate (ATT) to boron oxide investigated in fluidized bed calcinatory. Single step calcinations of ATT in pure state gives a puffed product with very low bulk density and the calcination is incomplete since ATT particles completely agglomerate at temperature higher than 350 °C. Effect of the temperature on the bulk density and particle size distribution product obtained at the end of single step is given and compared with theoretical calculation. In order to restrict agglomeration at temperature higher than 300 °C, the surface of ATT has been covered with a material with a higher melting point than boric oxide. In order to obtain this high melting cover, a mixture of ammonium tetraborate tetrahydrate and $Ca(OH)_2$ has been calcined in fluidized bed calcinatory. During this calcinations process, quantities such as the bulk density value, particle size distribution and B_2O_3 content of product have been determined as a function of temperature. It was found that the boron oxide can be obtained by calcinations of ATT particle covered with $Ca(OH)_2$ in 90 min time intervals at a temperature range of 450 and 500 °C. As a result, puffed granular boron oxide of 99% purity with bulk density about $0.30\,\mathrm{g\,cm^{-3}}$ has been produced using single step calcination by this new method.

Keywords: Boron oxide; Ammonium tetraborate tetrahydrate; Fluid bed calcinatory; Calcium hydroxide

1. Introduction

Boron and its compounds have a wide field application in industry. Particularly, boric oxide finds many uses in industry, especially in applications in which a high boric oxide content material, containing little or not oxides of alkaline earth metals, is desired. Boric oxide has the advantage of low heat expansion and high refractive index. Because of these natures, boron oxide is used widely in glass ceramic composition since it doped on the ceramic system enhance conductivity and structural stability [1,2]. Also boron oxide utilized in the production of enamels and alloys; in the preparation of fluxes; and as catalyst in organic reactions [3–6].

The production methods of boric oxide can be classified in four main groups depends on the starting materials. These are:

(a) by fusing refined boric acid or under vacuum conditions at a temperature not exceeding 425 K [7–9];
(b) from metal borates given a boron oxide product with a maximum purity of 93–94% [10,11];
(c) from direct reaction of boron with oxygen [12];
(d) by calcinations of ammonium pentaborate octahydrate [13,14].

The main disadvantages in some of these methods are: corrosive nature of molten boric oxide, obtained boron oxide at the end of process containing impurities, working in vacuum condition need complicated equipment and long calcinations periods, hard product obtained required crushing, grinding and sieving before being use.

Production of boron oxide without fusion is very attractive with respect to energy consumption and corrosion. Thus, the attempts have mostly been in dehydration both boric acid and ammonium pentaborate in a fluidized bed [13,15]. Fluidized bed calcinations technique, which allows uniform temperatures, high heat transfer rate between the particles and continuously controlled dehydration operation, has many advantages. Production of boron oxide without melting is very attractive with respect to energy consumption and corrosion. Also, heat input

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of the system is lower compared to the former method and the post-processing of the product, such as crushing and grinding is not needed. Earlier workers are obtained anhydrous form of some borates in powdered or granular form with this technique by using constant temperature and multi-stage calcinations [15–17,20–22]. The main disadvantage of fluidized bed is the puffing or agglomeration of the particles during remove of crystal or structural water.

Thus, a considerable number of attempts have been made to investigate the thermal calcinations behavior of ATT and develop a new method for production boron oxide from ammonium tetraborate tetrahydrate (ATT) without agglomeration. The calcinations of ATT cannot be continued above agglomeration temperature of 300 °C, the amorphous ATT particles which soften readily adhere strongly to each other since ATT particle dissolved in their water. The agglomeration problem has been solved in our system by covering the particles of ATT with a material that has a higher melting point than the final agglomeration temperature. For this propose, the surface of ATT was covered with $Ca(OH)_2$ layer in a solid state media. The presence of $Ca(OH)_2$ in calcinations media prevent the agglomeration of ATT up to 500 °C, since the desired anhydrous calcium borate cover can be formed on the surface of boric oxide particles by interaction forces between the boric acid and $Ca(OH)_2$ particles. Separation of excess $Ca(OH)_2$ particles from the product was achieved by changing air velocity. Using this method ATT can be converted to puffed boron oxide containing 98.9% B_2O_3 in a 90 min interval.

Although many studies have been done on the dehydration of alkali borates [16–24]. We have not found any studies on the dehydration of ATT in fluidized bed.

Thus the main aim of this work is oriented toward determining the optimal calcinations temperature to prevent sintering of ATT to boron oxide in fluidized bed dryer. Therefore, the bulk density, B_2O_3 content, sieve analysis of the product obtained at the end of constant temperature has been investigated under thermal decomposition condition.

2. Experimental

Calcination experiments of ammonium tetraborate tetrahydrate were carried out using the system shown in Fig. 1. In order to observe the process visually, a heat resistance glass column (30 mm-ID, 600 mm high) has been used. The other surface of the glasses column was insulated with 50 mm thick ceramic wool. Fluidization air was fed through a pressure regulator, a calibrated rotameter and an electrical heater unit controlled by a PID type temperature controlling system. The temperature of fluidization air (inlet air) was measured and controlled by means of NiCr–Ni thermocouple, which was fixed at the bottom of the distribution plate. A humidity meter placed before hating unit measured the moisture content of fluidization air. At constant temperature experiments, 15 g ammonium tetraborate tetrahydrate particles were fed at the top of fluidized bed calcinatory (FBC), which had been at thermal equilibrium at the experimental temperature. During all the experiments the flow rate of fluidization air was kept constant at 400 l h^{-1}. At predetermined time intervals, samples were with drown using a vacuum sampling tube.

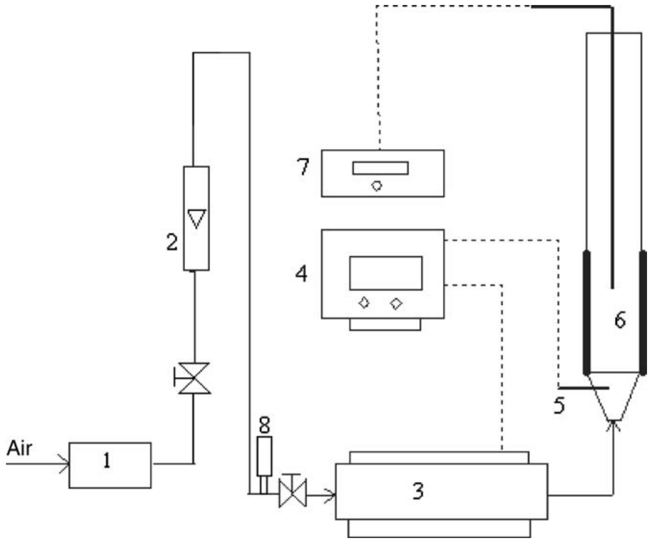

Fig. 1. Experimental set-up: (1) pressure regulator; (2) rotameter; (3) heating furnace; (4) temperature controller; (5) thermocouple; (6) fluidized bed; (7) bed temperature; (8) humiditymeter.

Titrimetric method was used to determine the B_2O_3 [25] content of samples. Bulk density was measured by a standard method [26]. The particles size of ammonium tetraborate tetrahydrate used in the all experiments was chosen with the range 500–710 μm except the effect of particle size in calcinations.

3. Results and discussion

In this step of experimental work, simultaneous TG, DTG and DTA curves for ATT (ammonium tetraborate tetrahydrate) were performed under nitrogen atmosphere at 5 °C/min. Fig. 2 shows the results of TG-DTG–DTA analysis. It can be seen in Fig. 2 that the thermal decomposition of ATT occurs at three different steps. In the literature, the thermal decomposition of many boron compounds shows step-wise dehydration from one hydrated step to another [27–34] since the structure of many boron compounds contain crystal water, structure water or ammonia (NH_3) groups.

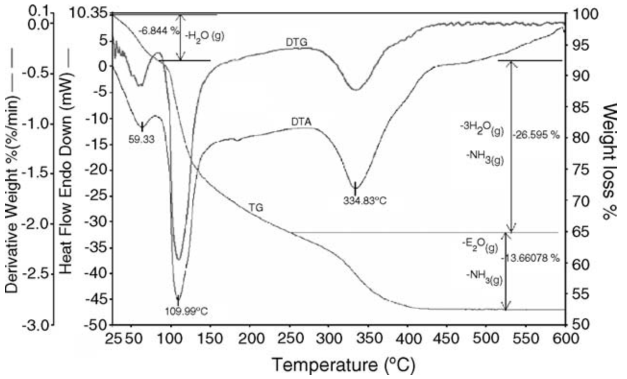

Fig. 2. TG-DTG and DTA curves for the thermal decomposition of ATT with heating rate of 5 °C/min.

It is well known that the crystal structure of ammonium tetraborate tetrahydrate (ATT) also known as diammonium tetraborate tetrahydrate and ammonium biborate tetrahydrate can be described by the formula $(NH_4)_2B_4O_5(OH)_4{\cdot}2H_2O$ [35–37]. Thus, it is expected that NH_4, OH and H_2O groups in the structure of ATT may decompose with thermal effect. From Fig. 2, total weight-loss was calculated as 47.12% in the temperature range 25–450 °C. After this temperature all ammonium tetraborate decompose to boron oxide according to the reaction of

$$(NH_4)_2B_4O_5(OH)_4{\cdot}2H_2O_{(s)} \rightarrow 2B_2O_{3(s)} + 5H_2O_{(g)} + 2NH_{3(g)} \tag{1}$$

The TG curve in Fig. 2 represent a gradually weight loss starting at 25 °C and ending at 70.6 °C with a DTA peak at 59.3 °C. The total loss up to 70.6 °C is related to the loss of 1 mol of crystal water. One sharpen peak is observed in the range from 70.6 to 250 °C, with a peak at 109.99 °C. It corresponds to the separation of 1 mol ammonium and 3 mol of water. At the end of decomposition, one broad endothermic peak is observed in the temperature range from 250 to 450 °C, with a peak at 334.83 °C. The remaining 1 mol of water and 1 mol of ammonium formed from the decomposition of (OH) and NH_4 groups in the structure of ATT is loss continuously up to about 450 °C.

The DTA curve is identical to TG curve. In the light of TG and DTA curves and dehydration of ammonium pentaborates [28,32–34], the thermal decomposition steps of ATT may be illustrated as follows:

$$(NH_4)_2B_4O_5(OH)_4 \cdot 2H_2O_{(s)} \xrightarrow{70.6\,^{\circ}C} (NH_4)_2B_4O_5(OH)_4 \cdot H_2O_{(s)} + H_2O_{(g)} \tag{2}$$

$$(NH_4)_2B_4O_5(OH)_4 \cdot H_2O_{(s)} \xrightarrow{250\,^{\circ}C} (NH_4)B_4O_6(OH)_{(s)} + NH_{3(g)} + 3H_2O_{(g)} \tag{3}$$

$$(NH_4)B_4O_6(OH)_{(s)} \xrightarrow{450\,^{\circ}C} 2B_2O_{3(s)} + NH_{3(g)} + H_2O_{(g)} \tag{4}$$

As seen in the above reaction steps, the thermal calcination of ATT can be subdivided into three stages; dehydration, decomposition and deamination. At the next two stages of the thermal decomposition of ATT comprising the temperature range 250–450 °C, ammonia and remaining amounts of water are lose from the structure of ATT as observed in thermal decomposition of larderellite [32]. It is not known which step or steps control the final physical properties of boron oxide. Therefore dehydration, deamination and decomposition steps should be checked experimentally in fluidized bed calcinatory (FBC) with respect to bulk density, boron oxide content of calcines and sieve analysis.

The calcinations process of ATT carried out in a FBC at the initial fluidization air temperature of 120, 150, 200, 250, 300 and 350 °C during 120 min interval cannot be run over 300 °C, since sintering effect was started at 350 °C. The obtained results shows that the higher the bed temperature, the higher dehydration rate and shorter the dehydration time will be to reach any specified content of B_2O_3, since drying of solid involves the simultaneous transfer of heat to evaporate the liquid and transfer of moisture or other groups as liquid or vapor within the solid and vapor from the surface, into a hot carries gas. The warning up and constant rate period was not observed in thermal decomposition of ATT, since the temperature of particle surface does not remain constant. Thus, it can be said that the thermal decomposition of ATT is controlled by falling rate period include internal moisture movements which are caused by mechanism such as diffusion, capillary flow and flow due to shrinkage and pressure gradients. In porous materials, drying may even take place evaporation inside the solid instead of at the surface. These phenomena can be explained by investigating the changes of bulk density and sieve analysis.

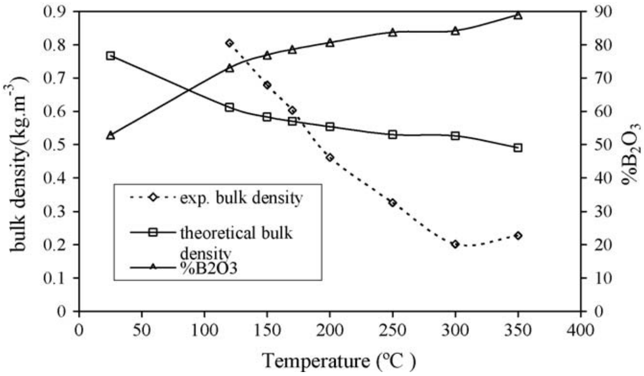

Fig. 3. Effect of constant temperature on the bulk density and % B_2O_3 contents of ATT calcinations.

The effect of dehydration done at different constant temperatures on bulk density and B_2O_3% levels for the samples taken from the fluidized bed at the end of 120 min is given in Fig. 3. In the same figure theoretical values of bulk density calculated from the original bulk density of ATT assuming that particles keep their dimension and shape during calcinations are also given for compression, in order to observe shape changing. In the calculation of theoretical bulk density, water or ammonium loss determined experimentally is taken into account. As can be seen in Fig. 3, experimental bulk density values are higher than theoretical values at temperature up to approximately 170 °C which is related to dehydration of crystal water and removal of ammonium groups in ATT particles. Whereas it becomes lower than theoretical values at temperatures higher than 170 °C, which is corresponding to the beginning of decomposition of structure water and ammonia represented by reaction (4). This behavior of ATT can be explained by two different but competitive physical phenomena, one is shrinking and the other is puffing. Also, it is well known that, the drying rate of such solids are controlled by five interrelated physical mechanism: (1) phase equilibrium between gaseous, liquid and solid phases; (2) diffusion in the gaseous phase; (3) diffusion in the liquid phase; (4) capillary transport of moisture; (5) heat transfer.

The influence of vapor liquid equilibrium and gas-phase diffusion on the one hand and the influence of capillary transport and liquid-phase diffusion on the other hand act together [38].

At low temperature, rate of water and ammonia are slow and thus, capillary flow realized in ATT particle. Therefore they

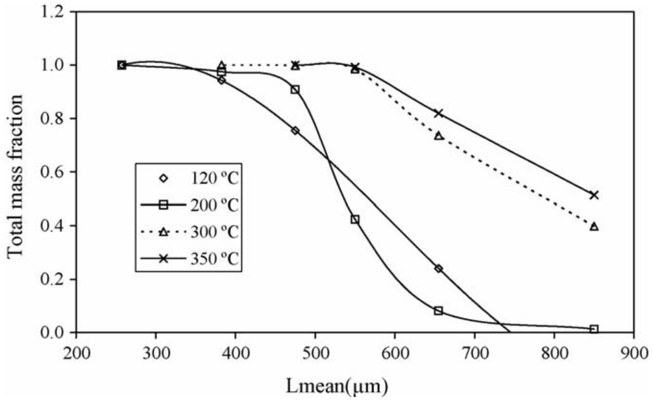

Fig. 4. Particle size distribution obtained at different initial constant temperatures.

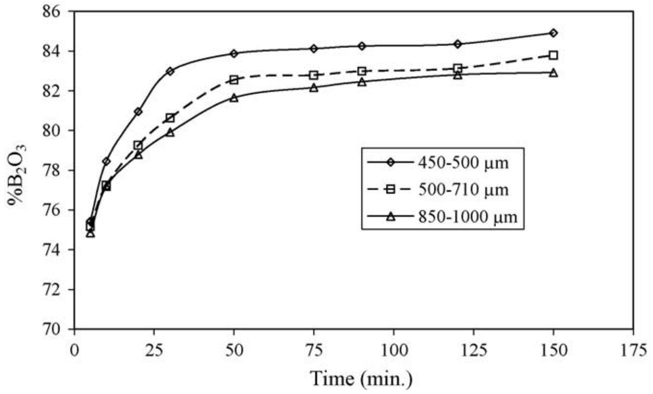

Fig. 5. Changes of ATT calcinations with time for different initial particle sizes.

shrink. At higher temperature than 170 °C, fast lose of crystal water, ammonia and structure water cause the particle to puff.

Fig. 4 shows the changes of total mass fraction with mean particle size for the ATT particles having a initial particle size of 500–710 μm. Same figure illustrated that the particle size distribution calcined at 300 and 350 °C have a puffing with respect to calcined at 200 and 120 °C. As a result, in the case of puffing capillary transport and liquid-phase diffusion realize quickly since reaction rates of Eqs. (2)–(4) proceed together with increasing temperature at the values of higher than 250 °C.

Fig. 5 shows the effect of particle size on the drying rate. The experiments were all performed at the same gas fluidization conditions at the constant temperature of 250 °C. As can be seen in this figure, with increasing the particle size range, the B_2O_3 content of ATT was decreased, since the proportion of the gas in the bulk phase in the bulk of the bed have been considerably greater with the small particles than with the large particles. Also, capillary transports of moisture and heat transfer proceed very quickly at small particles with respect to large particles. As a result of these phenomena, the conversion of small particles increased.

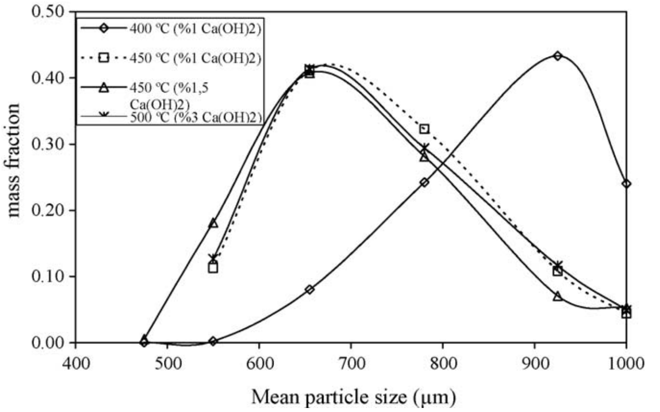

Fig. 6. Changes of particle size distribution with temperature and ATT–$Ca(OH)_2$ mixture.

In the second step of this study, the commercial boron oxide aimed to produce from ATT by step-wise calcinations, coating with $Ca(OH)_2$ in aqueous media and mixture $Ca(OH)_2$ with ATT particle in solid state, since sintering effect was observed from ATT particles at temperature higher than 300 °C. Thus, first of all, the step-wise calcinations were carried out in FBC. But, three different parts of ATT particles calcined at 120, 150 and 170 °C during 90 min and then this pre-calcined ATT particles were fed into FBC preheated at 450 °C, separately. The results of these experiments show that the sintering effect of ATT particles cannot be prevented by step-wise calcinations. In the second group of experimental, the surface of ATT particles were coated with $Ca(OH)_2$ in aqueous solution with predetermined $Ca(OH)_2$ concentration during 5 min. Then the covered particles were dried at ambient temperature. This covered ATT particles were feed into FBC at the temperature of 450 °C. The result obtained at this group study shows that the same portions of ATT particles were sintered.

In the third group of experimental, a mixture containing ATT and 1, 1.5, 3 and 15 wt.% $Ca(OH)_2$ were fed into the calcinator at the different temperatures. In this study the sintering of ATT was prevented by ATT–$Ca(OH)_2$ mixture in solid state. In the experimental results done with $Ca(OH)_2$ is given in Table 1. In the first and second experimental of this group, mixture contain-

Table 1
Effect of different ATT–$Ca(OH)_2$ mixture on the calcinations of ATT particles at different initial constant temperature

	Temperature (°C)							
	350	350	400	400	450	450	450	500
Calcination time (min)	120	120	90	30	90	90	90	120
B_2O_3 (%)	88.947	87.820	88.240	91.866	96.98	96.980	98.973	98.945
Bulk density ($kg\,m^{-3}$)	0.2276	0.160	0.136	0.130	0.305	0.316	0.255	0.2966
$Ca(OH)_2$ initial value	–	15	15	1	1	3	1.5	3
Last product	Little sintering	Granular	Granular	Granular	Little sintering	Granular	Granular	Granular

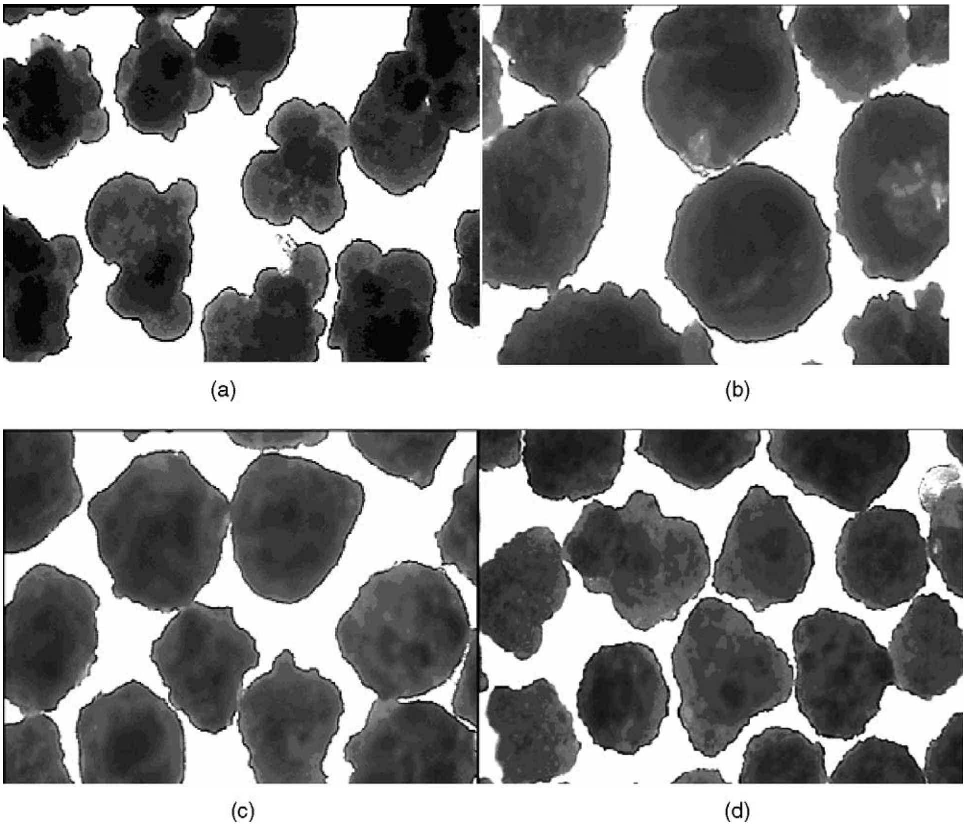

Fig. 7. Microscopic photographs of ammonium tetraborate tetrahydrate: (a) pure (calcined at 250 °C); (b) pure (calcined at 350 °C); (c) 1.5 wt.% $Ca(OH)_2$ at initial condition (calcined at 450 °C); (d) 3 wt.% $Ca(OH)_2$ at initial condition (calcined at 500 °C).

ing ATT and 15 wt.% $Ca(OH)_2$ were fed into the batch FBC for 120 and 90 min at the temperature of 350 and 400 °C, respectively. At the end of these calcinations the granular particle with 88% B_2O_3 content was obtained. After these positive results, the $Ca(OH)_2$ content of mixture were reduced. The mixture containing ATT and 3, 1.5 and 3 wt.% $Ca(OH)_2$ were calcined in FBC for 90 min at the temperature range of 450–500 °C. As can be seen in Table 1, the last two experiments done at 450 and 500 °C give a product containing approximately 99% B_2O_3. Also, the last experimental with 3 wt.% $Ca(OH)_2$ in Table 1, shows that the $Ca(OH)_2$ content of ATT was decreased with increasing temperature and B_2O_3 content of calcines.

As a result of all these, it can be concluded that the ATT particle surface can be covered by $Ca(OH)_2$ particles at high temperature and it may be formed on the surface of boron oxide particle by interaction forces between ATT and $Ca(OH)_2$ particles. Fig. 6 shows the changes of mass fraction with mean particle size, for the last four experiments given in Table 1. As can be seen in Fig. 6, the particle size distribution is approximately same at the temperature higher than 400 °C, since the particle of boron oxide is shrinking. Whereas the particles of ATT are puffing at temperature of 400 °C. Thus, the particle size distribution is increased.

Fig. 7 shows the microscopic photographs of ATT calcined both in pure and containing $Ca(OH)_2$ state at temperature of 250, 350, 450 and 500 °C. In pure state, the ATT particle is puffed at 350 °C, whereas the ATT particle mixture with $Ca(OH)_2$ is shrinking at 500 °C.

4. Conclusion

In order to produce boron oxide with low bulk density by calcinations of ammonium tetraborate tetrahydrate (ATT) in a fluidized bed calcinator, particular attention is paid to cover ATT surface with $Ca(OH)_2$ layer at high temperatures. Also, the dehydration of ATT is presented and conditions of calcinations are determined in fluidized bed calcinatory. The main problem in this process is changes of physical properties of calcines such as particle size, bulk density and boron oxide content due to heating conditions. The results obtained by calcinations of ATT both in pure and presence of $Ca(OH)_2$ in fluidized bed calcinator can be given as following:

- The calcinations of ATT with single stage cannot be carried out at temperature higher than 300 °C and a product contains about 82% B_2O_3, since sintering effect is started. The calcinations of ATT at temperature of higher than 170 °C gives a product with low bulk density with respect to theoretical value, because of puffing.
- Boron oxide can be produced from ammonium tetraborate tetrahydrate without sintering by mixing $Ca(OH)_2$ with ATT in solid state at temperature range 450–500 °C. At this temperature range, the bulk density of boron oxide is increased. In this case, the initial content of $Ca(OH)_2$ in ATT must be higher than 1.4%. In this kind of operation, the ATT particle surface covered with a thin layer of $Ca(OH)_2$ to control the transport rate of liberated gases from inside ATT

particles to air. By this new method, the content of last product is about 99% B_2O_3 which is available in technical use.

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