

Agglomeration of Barium Titanyl Oxalate Tetrahydrate

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The optimal condition for minimal agglomeration of barium titanyl oxalate tetrahydrate, the precipitate on preparing barium titanate by oxalate process, was investigated. Burette-dropping and dual-nozzle-spraying were used as adding methods. pH of washing water for precipitates was changed, and sodium pyrophosphate solution, methanol, ethanol, and acetone were used as washing agents for precipitates, as well as distilled water. Drying temperature was changed from 50°C to 120°C. Spraying, methanol-washing, and drying at 60°C showed the most dispersed distribution. Below 70°C, the crystalline phases were observed.

Key words : Agglomeration, BT-oxalate, Washing agents, Drying temperature

I. Introduction

Powder preparations by solution technique show compositional homogeneity, fine particle size, narrow particle size distribution, low phase formation temperature, and chemical purity.^{1,2,3)} However, agglomerates are common in powders due to the tendency of fine particles to reduce their surface free energy. An agglomerate with a very open arrangement of crystallites might develop large pores or pore clusters. On the other hand, closely packed agglomerates may undergo preferential intra-agglomerate sintering over interagglomerate sintering and pull away from neighboring agglomerates, leaving large lenticular voids which are difficult to close.^{4,5,6)} So, dispersing fine particles need to be solved in powder preparations.⁷⁾

Oxalate process is a kind of coprecipitation methods.^{8,9)} This process is that the mixed solution containing metallic ions is added into oxalic acid, and then metal-oxalate, the precipitate, is formed. This metal-oxalate is dissoluble in water, and it precipitates. Especially, barium titanate preparation by this method is very widely studied. This method has very simple procedure, and high yielding ratio.^{8,9)}

In preparing barium titanate powders, the agglomeration of precipitates was observed to be retained to the aggregation of barium titanate powders. Hence, above all, precipitated barium titanyl oxalate tetrahydrate [BaTiO(C₂O₄)₂·4H₂O, BT-oxalate] was thought to be dispersed to obtain preferable fine barium titanate powders by this oxalate process. From this point, the synthesis conditions of BT-oxalate were considered on in this experiment. That is, the conditions that may affect agglomeration were varied; adding method, pH of washing water for precipitates, washing agents for precipitates, and drying temperature. Dispersions of BT-ox-

alates from these variations were compared and evaluated, and then dispersed BT-oxalate was obtained.

II. Experimental Procedure

Starting materials are reagent-graded TiCl₄ (SHOWA, 99.5%), BaCl₂·2H₂O (YAKURI, 99.0%), and H₂(C₂O₄)₂·2H₂O (SHINYO, 99.5%). At 2°C, TiCl₄ is dropped into stirred, distilled water with nitrogen atmosphere. From this TiCl₄ solution, exact Ti⁴⁺ content is examined by thermal decomposition. According to this result, 0.5 M Ti⁴⁺ solution is made, and barium-titanium mixed solution is made by adding BaCl₂·2H₂O to this solution in the ratio of Ba²⁺ : Ti⁴⁺ = 1 : 1. 1 M oxalic acid solution is made to 50% excess stoichiometry. Barium-titanium mixed solution is, then, added to this oxalic acid solution. As adding methods, dropping with burette and spraying with dual nozzle are chosen. In spraying, oxygen gas is used as carrier gas. On washing precipitates to eliminate Cl⁻ adsorbed to them, pH's of washing waters are controlled from 1 to 10 using HCl and NH₄OH. And, dispersant (sodium pyrophosphate, Na P.P.) solution, methanol, ethanol, and acetone are used as washing agents as well as distilled water. Washed precipitates are dried at various temperatures from 50°C to 120°C. To evaluate particle size distributions, centrifugal particle size analyzer (SHIMADZU, SA-CP3) is used, and shapes of particles are observed by SEM (JEOL, JSM-5400). XRD (MAC, M 03XHF) is used to examine crystalline phase of precipitates, and TG/DTA (RIGAKU, TG8110) to investigate thermal behavior of precipitates. In Fig. 1, schematic of experimental procedure is shown.

III. Results and Discussion

(a) of Fig. 2 is SEM photograph of agglomerated BT-ox-

alates. (b) is SEM photograph of barium titanate which is thermal decomposed at 600°C for 3 hours. Shapes of agglomerated precipitates in (a) are roughly spherical, and consisted of many primary particles. And these

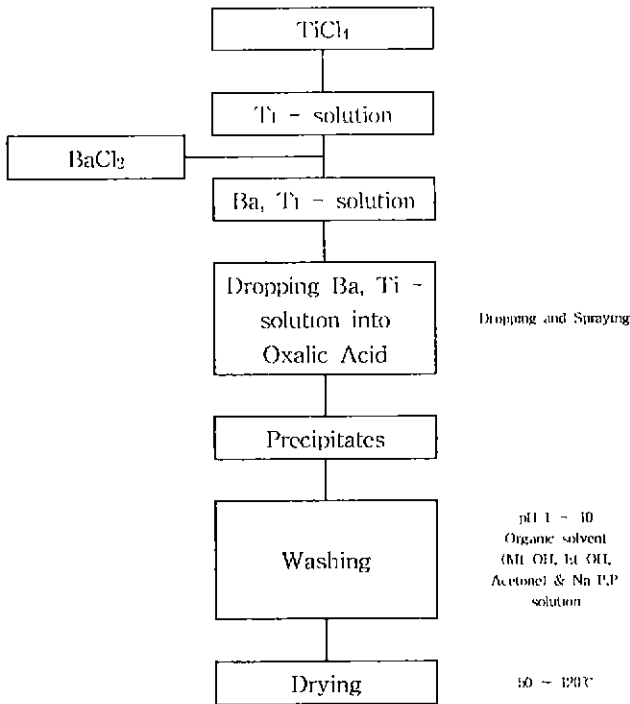


Fig. 1. Experimental procedure.

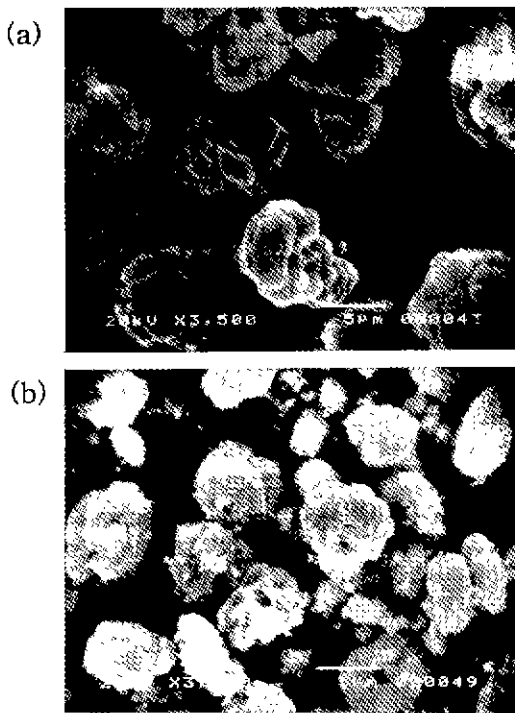


Fig 2. SEM photographs of agglomerated (a) BT-oxalate and (b) BaTiO₃ calcined at 600°C for 3 hrs. Sprayed and dried at 120°C.

shapes are also shown in (b), resultant barium titanates.

Fig. 3 is particle size distributions of BT-oxalates from two adding methods. In Fig. 3, modal sizes are same, between 0.1 μm and 0.2 μm. However, particle size distribution of sprayed BT-oxalates is seen in smaller size region, on the whole. Especially, in the region larger than 0.2 μm, particle size distribution of each methods are pretty different. From this, to obtain uniform precipitates, spraying method has been chosen, assumed that one droplet would form one precipitate.

Fig. 4 is particle size distributions of BT-oxalates before drying with variation of pH of washing water. For pH 1, modal size is larger than those of other pH values a little, but this difference may not be so noticeable. For pH 2, however, change of particle size distribution appears. That is, particle size distribution increases in the region larger than 0.2 μm, where particle size is large

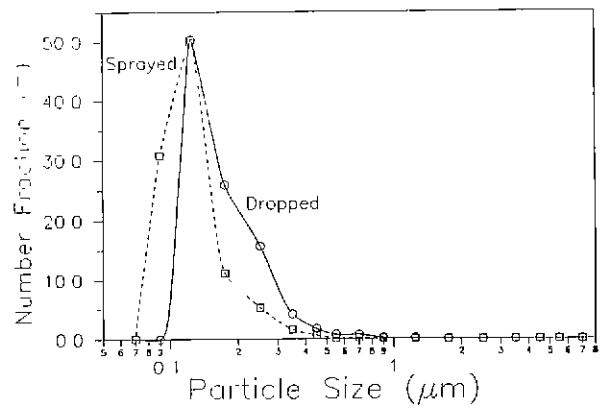


Fig. 3. Particle size distributions of BT-oxalates with two adding methods. Not dried.

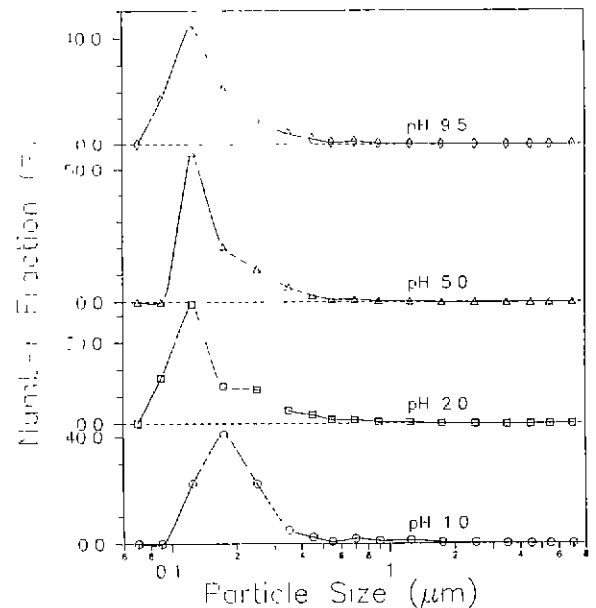


Fig. 4. Particle size distributions of BT-oxalates with variation of pH of washing water (Sprayed and not dried).

enough to be regarded as agglomerated particles. But, in spite of varying pH for wide range, large particle size distribution change are not observed.

Fig. 5 is SEM photographs of BT-oxalates dried at 120°C with variation of pH of washing water. In photographs, agglomerated particles are principally observed, but the sizes of them are relatively uniform, and

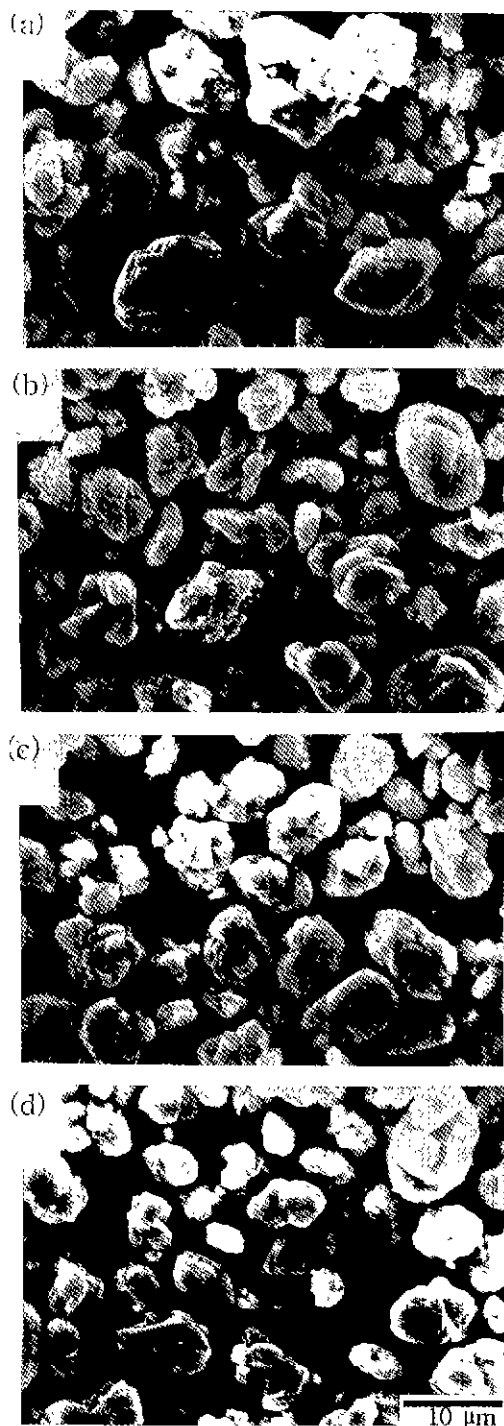


Fig. 5. SEM photographs of BT-oxalates with variation of pH of washing water (Sprayed and dried at 120°C). pH values are (a) 1.0, (b) 2.0, (c) 5.0 and (d) 9.5.

do not show large change for pH changes. So, precipitated BT-oxalates can be known not to improve so much, in spite of change of particle surface charge caused by pH change.

Fig. 6 is particle size distributions of BT-oxalates washed by various washing agents, and dried at different temperatures. Precipitates washed by methanol show superior dispersion to the others. And, in changing drying temperature, the lower temperature, the better dispersion. Dried at 120°C, except (c), there are bimodal particle size distributions before and after particle size of 5 μm or so. Particle size distributions smaller than 5 μm are not agglomerated, or a little, and those larger than 5 μm are significantly agglomerated. Dried at 80°C, trend of particle size distributions is similar to that of 120°C case. When washed by methanol, best dispersion observed. For BT-oxalates washed by organic agents and dried at 60°C, dispersions of them seem to improve, but particle sizes do not become smaller. BT-oxalate washed by ethanol is better than those dried at higher temperature and that washed by acetone shows wide but monodispersed distribution.

Fig. 7 is SEM photographs of BT-oxalates washed by various washing agents and dried at 120°C. Comparing (a) and (b), dispersant affects a little, and among (c), (d), and (e), dispersions seem to change with polarity. And also, comparing (a), (b), and (c), (d), (e), the difference between these groups may be caused by the difference of capillary forces during drying, for the liquid-solid interface energies of them are different from each other. Meanwhile, for precipitates washed by methanol, the acicular particles are thought to be methyl oxalates [$C_2O_4(CH_3)_2$], and for those washed by ethanol, the solution and reprecipitation of BT-oxalates may be occurred by monoethyl oxalate [$HOOC-COOC_2H_5$] or ethyl oxalate [$[(COOC_2H_5)_2]$] which are liquid phases.

Fig. 8 is SEM photographs of BT-oxalates washed by various washing agents and dried at 80°C. Results in Fig. 6 can be approved here. For (a), (b), (d), and (e), they are similar to those in Fig. 7, but for (c) which is for precipitates washed by methanol, dispersion become much better. This seems to be appeared by the difference of drying rate with temperature change. So, considering dispersion change at lower temperature has been needed.

Fig. 9 is SEM photographs of BT-oxalates washed by various washing agents and dried at 60°C. In Fig. 9, for precipitates washed by methanol and ethanol, they are much far dispersed, but those washed by acetone show very coarse particles. But, all of them are smaller than those dried at higher temperature. Compared with cases of 120°C, acicular particles thought to be methyl oxalates do not appear, and solution and reprecipitation might not have occurred.

Fig. 10 is TG/DTA patterns of BT-oxalates washed by water and methanol and dried at 120°C. In DTA patterns, exothermic peaks between 300°C and 400°C are

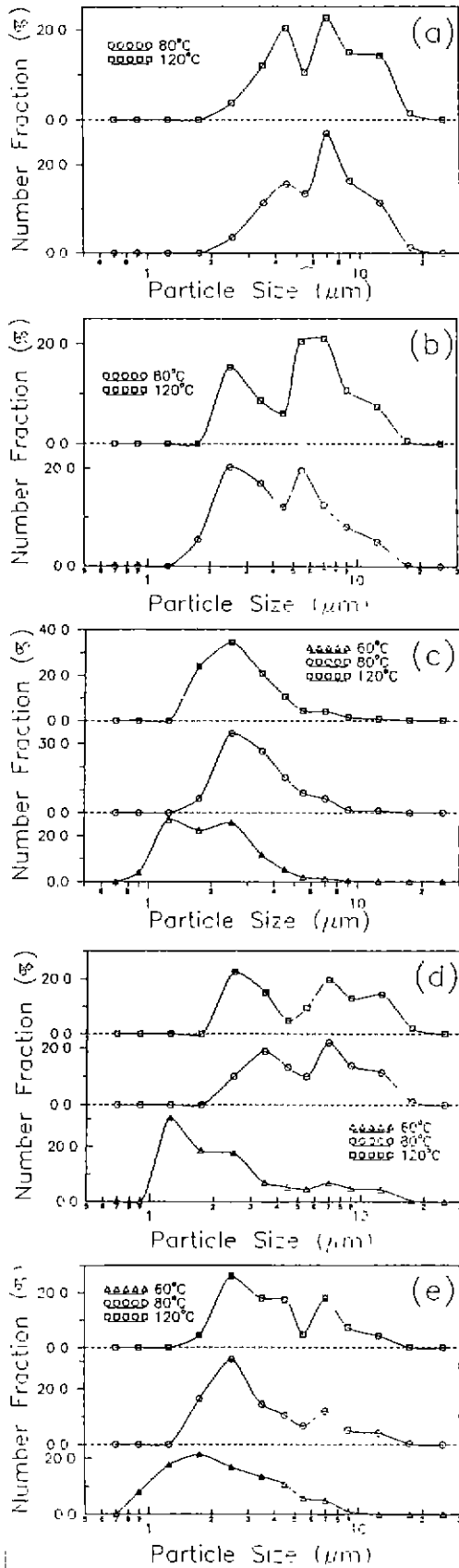


Fig. 6. Particle size distributions of BT-oxalates with various washing agents (Sprayed and dried at 60°C, denoted by '△', 80°C, '○', 120°C, '□'). (a) water, (b) Na P.P. solution, (c) methanol, (d) ethanol and (e) acetone.

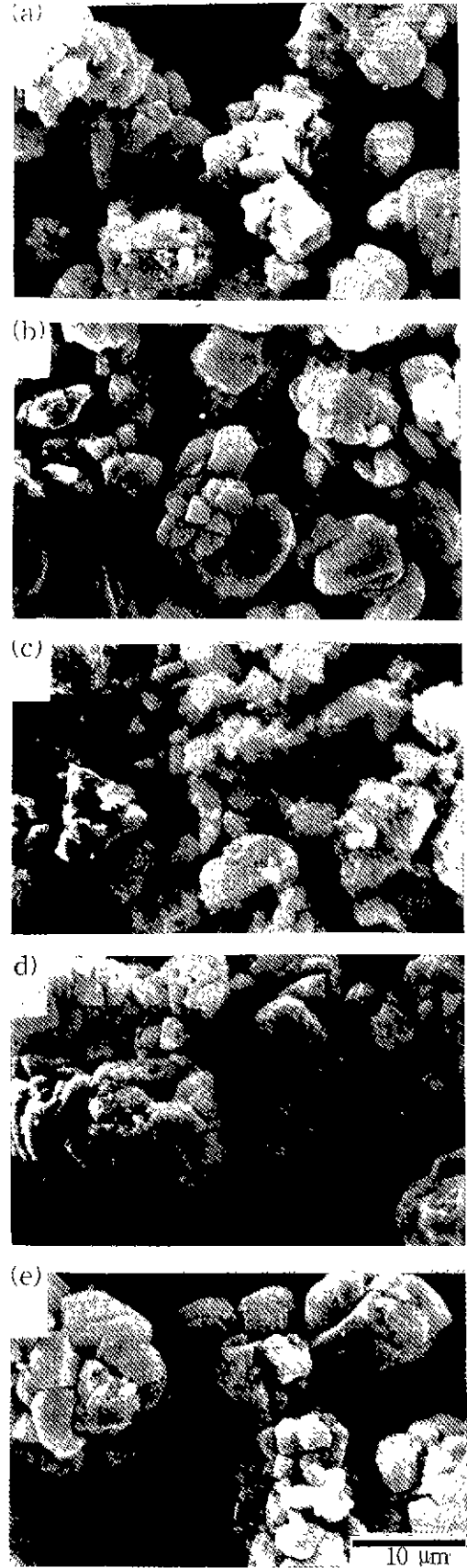


Fig. 7. SEM photographs of BT-oxalates with various washing agents (Sprayed and dried at 120°C). (a) water, (b) Na P.P. solution, (c) methanol, (d) ethanol and (e) acetone.

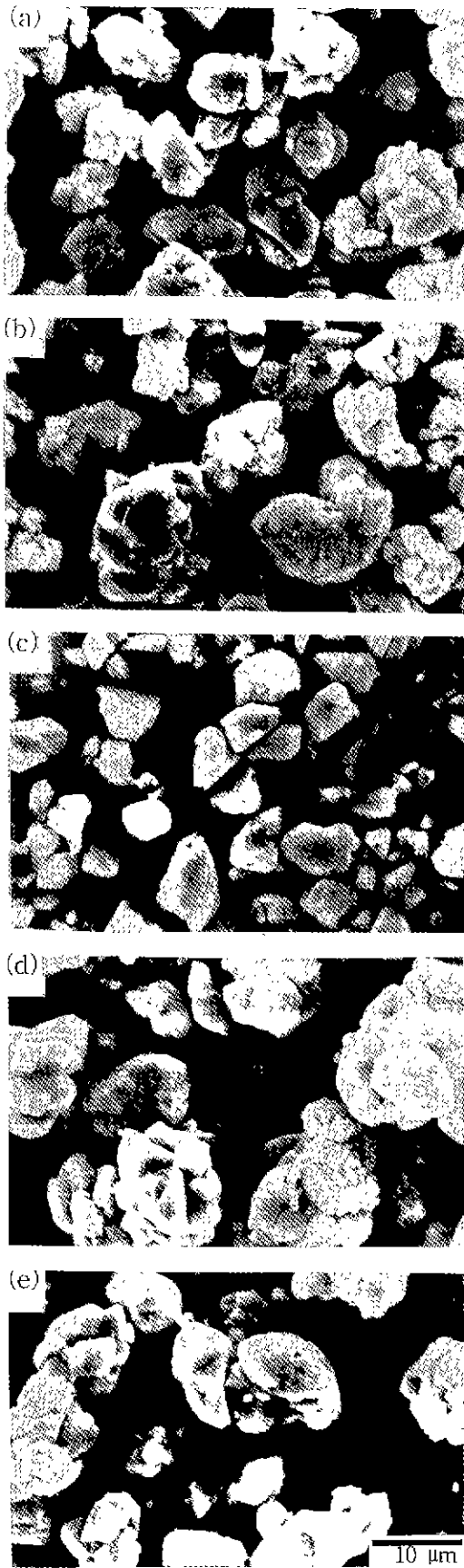


Fig. 8. SEM photographs of BT-oxalates with various washing agents (Sprayed and dried at 80°C). (a) water, (b) Na P. solution, (c) methanol, (d) ethanol and (e) acetone.

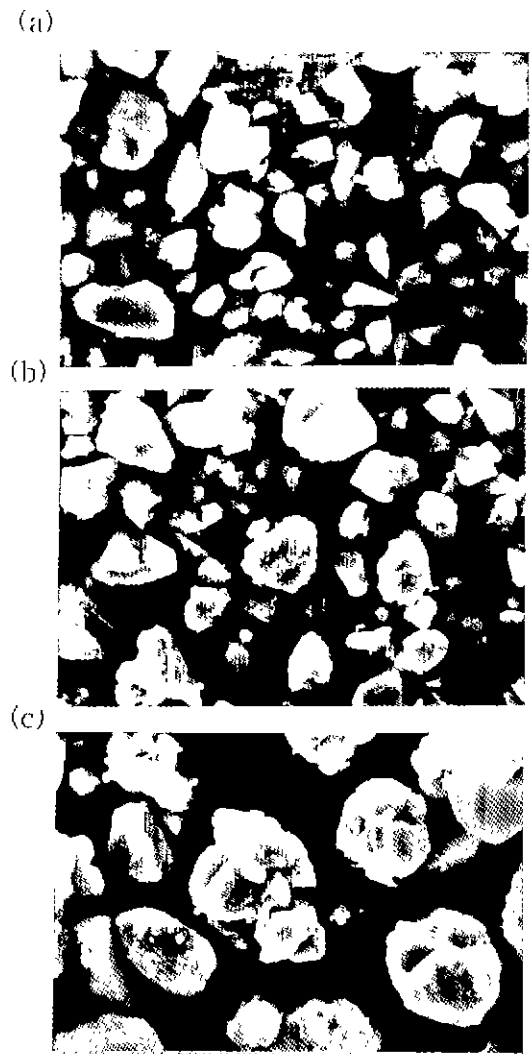


Fig. 9. SEM photographs of BT-oxalates with various washing agents (Sprayed and dried at 60°C). (a) methanol, (b) ethanol and (c) acetone.

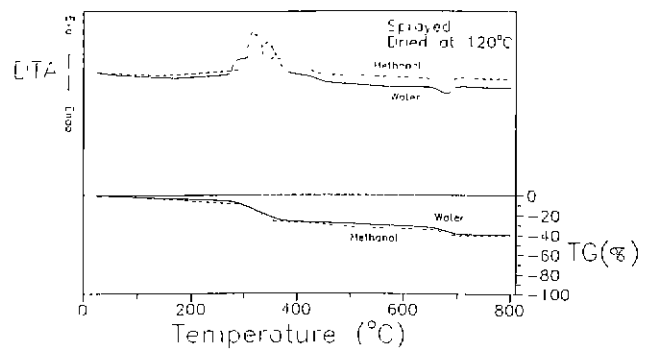


Fig. 10. TG/DTA patterns of BT-oxalates with various washing agents (Sprayed and dried at 120°C).

thought to be appeared by thermal decomposition of oxalic radicals. For cases of water, endothermic peak appeared to be overlapped on exothermic peak between 300°C and 400°C is considered as that by thermal decom-

Table 1. Appearance of Crystalline and Amorphous BT-oxalates Determined by XRD Patterns (Crystalline: ○, Amorphous: ×)

Drying Temperature	Washing Agents				
	D.I. Water	Na P.P. Solution	Methanol	Ethanol	Acetone
120°C	×	×	×	×	×
80°C	×	×	×	×	△*
60°C	○	○	○	○	○

*Crystalline but somewhat ambiguous.

position of remnant oxalic acid, and for case of methanol, endothermic peak after exothermic peak is considered as that by thermal decomposition of methyl oxalate.

Table 1 shows crystalline contents of BT-oxalates washed by various washing agents. Similar to Fang and Lin's study,¹⁰ amorphous phases exist at high temperatures. At 80°C, most of them appeared amorphous, but for acetone, ambiguous but crystalline phase appeared. At 60°C, all of them appeared crystalline. At low temperature, crystalline phases are stable, similar to Fang and Lin's results.

IV. Conclusion

Followings are concluded;

1. BT-oxalates can be most dispersed when washed by methanol.
2. Change of pH of washing water can not affect dispersions of BT-oxalates to large content.
3. At lower temperature, more dispersed BT-oxalates can be obtained.

4. At low temperature, crystalline phases appear, but at higher than 70°C, amorphous phase appear.

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