Effect of Stirring and Heating Rate on the Formation of TiO_2 Powders Using Supercritical Fluid

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The crystalline TiO_2 powders were prepared by highly reactive supercritical fluid with unique properties of both liquid and vapor phases. In this research, the effects of stirring and heating rates on the crystallization behavior of the TiO_2 powders were investigated. The crystalline size of the TiO_2 powders decreased from 90 to 60 nm as the stirring rate increased from 0 up to 150 rpm but increased to 160 nm with a further increase of the stirring rate to 400 rpm. The TiO_2 crystals tend to develop into spherical shape at a stirring rate below 50 rpm. The morphology of the TiO_2 particles changed from spherical to platelet shape as the stirring rate increased from 400 to 600 rpm. The particle size of the TiO_2 powders increased from 200 to 400 nm as the heating rate increased from 3 to 12 °C/min, but the shape of the TiO_2 powder became more spherical.

Introduction

Titanium(IV) oxide has been used for a paint pigment and a photoconductor. Recently, TiO_2 has widely been studied in photocatalysis using the characteristics of a semiconductor. The physical properties of ceramic materials required for practical applications depend on the inherent characteristics of the initial powders. The requirements of ideal characteristics for powders are the high chemical purity and homogeneity, the high density and low agglomerate of the primary particles, the fine spherical morphology of particles, and the narrow range of particle size distribution.[1,2] To satisfy these, several technical processes have been improved to manufacture the fine TiO_2 powders. A wet chemical technique that easily controls the composition by additives and hydrolysis has been studied as a materials processing technique to manufacture titanium(IV) oxide, and the valuable results have been obtained so far.

One of the most popular wet chemical techniques is the sol−gel processing technique, which has produced the TiO_2 powders using a starting raw material of precursor titanium(IV) ethoxide [$Ti(OC_2H_5)_4$]. The hydrolyzed and polymerized alkoxide raw material results in a continuous reaction in the following sequence: the nuclei (2−10 nm), the primary particles (50−100 nm), the agglomerate particles (0.3−1 μm), and then the condensed matter (>10 μm).[3]

This manufacturing process provides the possibility of mixing at the molecular level and thus has the advantages of the ease of composition control and the manufacture of fine particles. The fine pores, however, remained with the shrinkage during the manufacturing process. The inhomogeneous sedimentation occurs because of the method difference of water addition. The obtained powder is amorphous, and the heat treatment is thus required for crystallization, which causes the problems of grain growth and partial sintering. To solve these problems, the manufacturing method for fine ceramic powders might be developed by using another kind of supercritical fluid, which is different from the processes used so far. The supercritical fluid has the advantage of not only liquid and vapor phase reactions but also the direct manufacture of fine ceramic powders by excellent reactivity.[4]

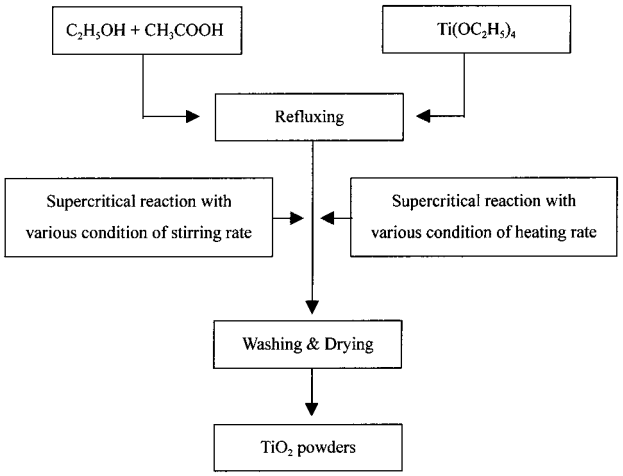

Figure 1. Experimental process to prepare TiO_2 powders.

The objective of this work is to synthesize the fine anatase crystalline TiO_2 powders in supercritical conditions with dense and low viscous properties, which influence chemical reactivity. Also, the effect of stirring and heating rates on the various physical properties of synthesized TiO_2 powders was investigated under the supercritical fluid: particle size and morphology, grain size distribution, and crystallization.

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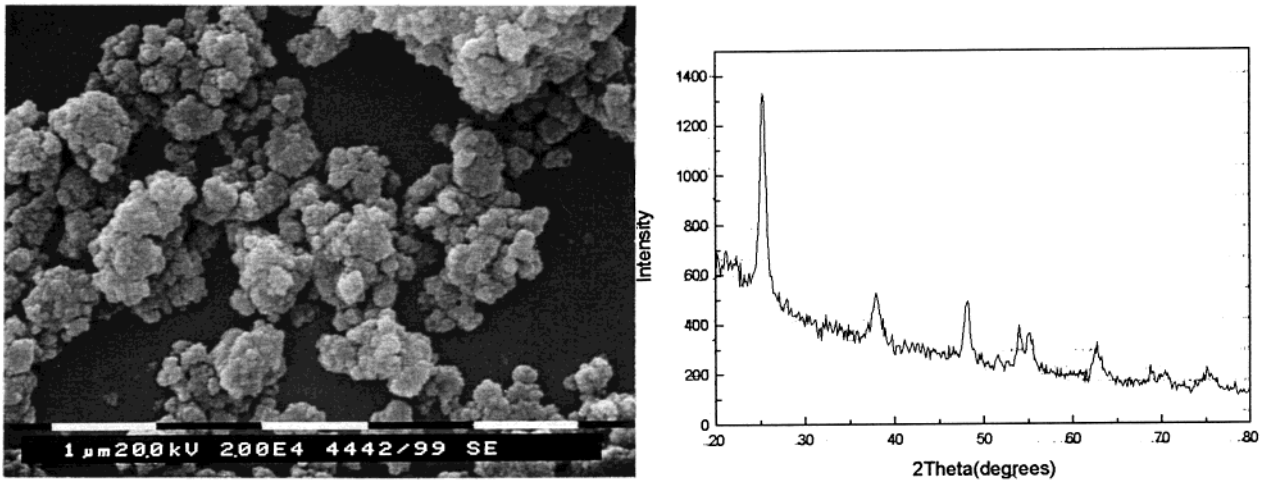


Figure 2. (a) SEM microphotographs and (b) XRD patterns of TiO_2 powders which were obtained using supercritical fluid at 265 °C and 7 MPa for 2 h.

Experimental Procedure

The process to prepare TiO_2 powder using supercritical fluid is schematically illustrated on Figure 1.

The crystalline TiO_2 powders using the supercritical fluid were synthesized by hydrolysis of titanium(IV) ethoxide in water, which was formed by the decomposition of ethanol under the supercritical condition above the critical point of ethanol. The reaction media was prepared by dispersion of titanium(IV) ethoxide into ethanol and then by addition of the reaction catalyst acetic acid (CH_3COOH). The experiment was conducted in N_2 gas with moisture less than 20% in a glovebox because titanium(IV) ethoxide is very sensitive to moisture in the air.

Two types of stainless steel autoclaves with high pressure and a temperature limit up to the critical point of water, 374 °C, were used. One is a 1-L stainless steel pressure vessel equipped with a stirred head and an applied pressure of up to 40 MPa. The other is a pipe type of autoclave with an inner volume of 4.656 cm^3. The resulting reaction media was placed in an autoclave. The autoclave was then heated to the desired temperature at a rate of 3−12 °C/min. The reaction time at the desired temperature was 2 h. After supercritical treatment, the vessel was cooled to room temperature, with any resident pressure relieved via a pressure-release valve. The crystalline phase and size of synthesized TiO_2 powders were characterized by an X-ray diffractometer over the 2θ range from 20 to 80° at a scan rate of 2°/min (Shimazu D1w XRD, Cu Kα radiation). The shape and size of powders was observed using a scanning electron microscope (Topcon ABT-32 SEM).

Results and Discussion

Formation Mechanism of TiO_2 Powders in Supercritical Condition. The ethanol has been known as not only a useful solvent to disperse titanium(IV) ethoxide but also a common solvent for hydrolysis and polymerization of titanium(IV) ethoxide. The decomposition of ethanol in supercritical condition forms diethyl ether and water. The decomposition process of ethanol is as follows:

$$2C_2H_5OH \rightarrow C_2H_5OC_2H_5 + H_2O \qquad (1)$$

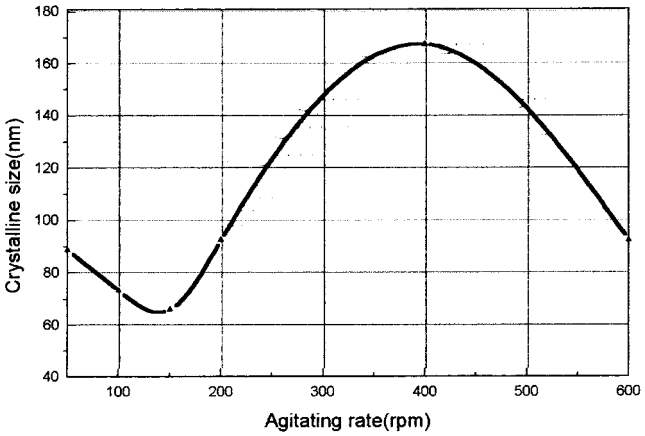


Figure 3. Effect of the stirring rate on the crystalline size of TiO_2.

The amount of water formed from decomposition of ethanol was about 2.6 wt % by the Karl Fischer method, which is enough to hydrolyze titanium(IV) ethoxide in the supercritical state. Titanium oxide was prepared by hydrolysis and polymerization of titanium(IV) ethoxide using H_2O obtained above the critical temperature of ethanol. The main chemical reactions are as follows:[5]

$$2C_2H_5OH \rightarrow C_2H_5OC_2H_5 + H_2O$$

decomposition of ethanol

$$Ti(OC_2H_5)_4 + 4H_2O \rightarrow Ti(OH)_4 + 4C_2H_5OH$$

hydrolysis of titanium ethoxide

$$Ti(OH)_4 \rightarrow TiO_2 + 2H_2O$$

condensation of titanium hydroxide

The reaction was completed in 2 h under the supercritical condition (265 °C and 7 MPa). The crystalline morphology and phase of the synthesized TiO_2 powders were shown in Figure 2. The size of the TiO_2 powders was about 20−30 nm with the structure of anatase, which is the same as the low-temperature TiO_2 phase. The TiO_2 powders were likely to be slightly agglomerated, as shown in Figure 2a.

Effect of the Stirring Rate on the Formation of TiO_2 Powders. Figure 3 shows the effect of the stirring rate on the crystalline size of the TiO_2 powders synthe-

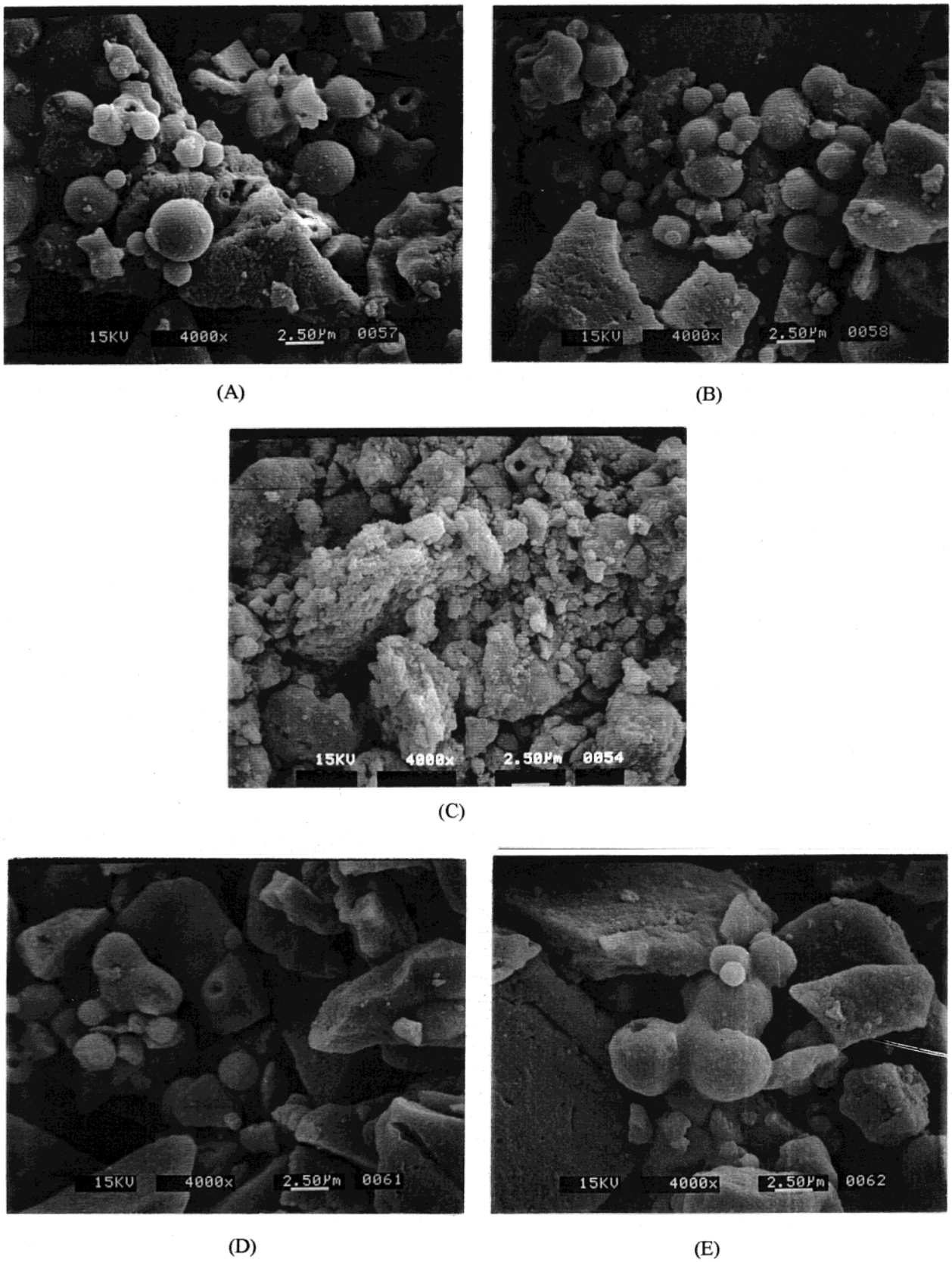
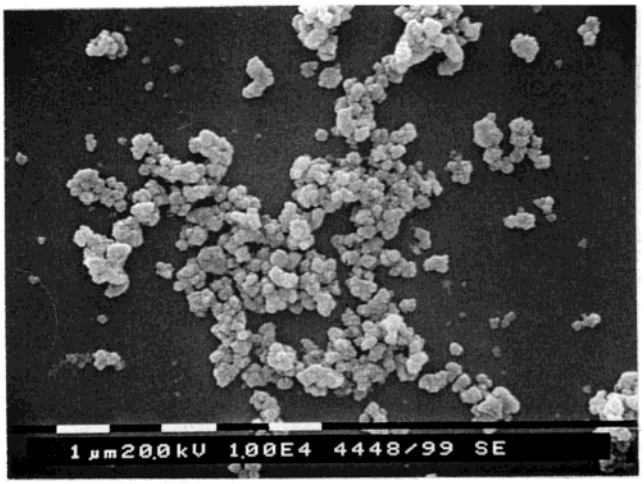


Figure 4. SEM microphotographs of TiO_2 powders at various stirring rates (rpm): (a) 50, (b) 100, (c) 200, (d) 400, (e) 600.

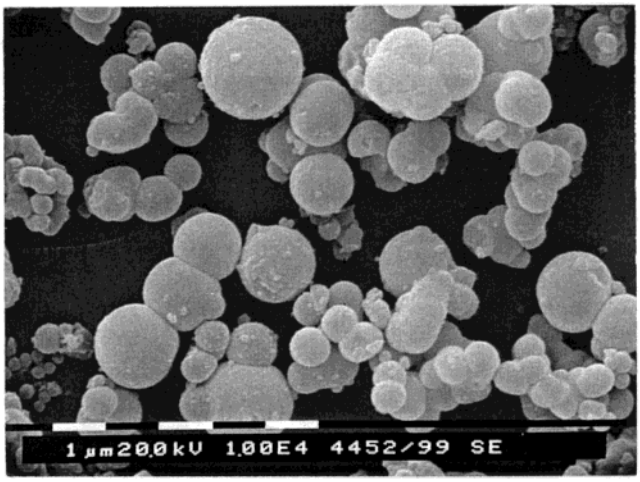
sized via the supercritical reaction. The crystalline size of the synthesized TiO_2 powders was determined from the Scherrer equation. The crystalline size decreased from 90 to 60 nm in the range of low stirring rate between 50 and 150 rpm. This result indicates that the nucleation rate become faster than the growth rate of nuclei because the degree of molecular mobility increases with the stirring rate in the low stirring range.

The crystalline size increased from 60 to 160 nm in the range of media stirring rate between 160 and 400 rpm. In the media stirring range, the particles with size less than the critical nucleus suspended and collided to



(A)

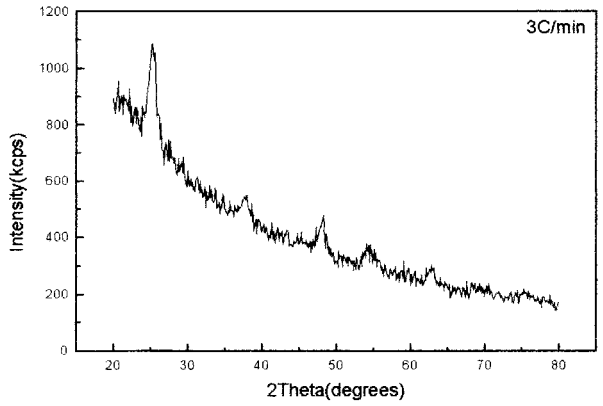
(B)



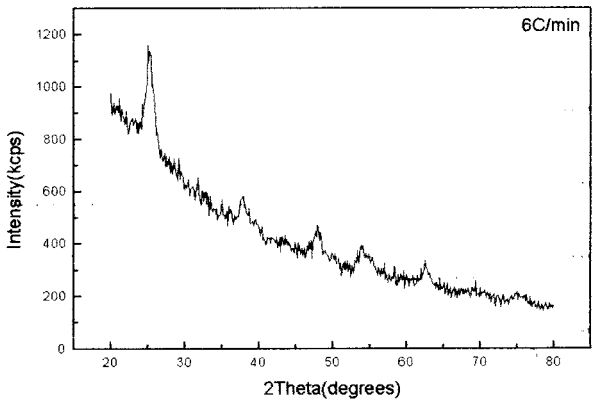
(C)

Figure 5. SEM microphotographs of TiO_2 powders at various heating rates (°C/min) of (a) 3, (b) 6, and (c) 12.

make new nuclei and increased the particle size up to 160 nm by their growth. At the high stirring rate of 600 rpm, the fine particles were dispersed by collision, instead of their growth. Therefore, the number of nucleation sites increased, and the particle size became finer again in the high stirring rate.



(A)



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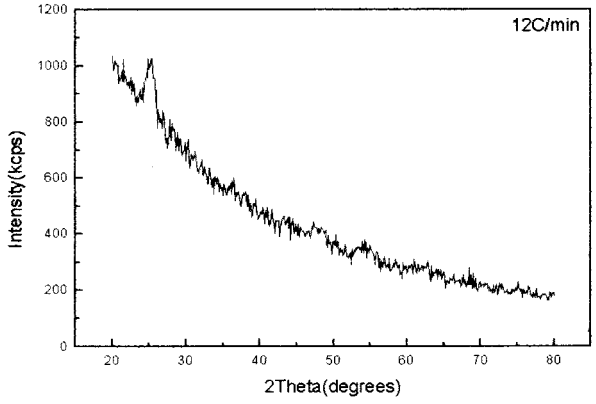

(C)

Figure 6. XRD patterns of TiO_2 powders obtained at heating rates (°C/min) of (a) 3, (b) 6, and (c) 12.

Figure 4 shows the morphology of the agglomerate powders at the various stirring rates. At the stirring rate between 50 and 100 rpm, the morphology of the TiO_2 powders was spherical and the same as that of agglomerate powders prepared without stirring at the supercritical state. The condensed matters collided and their size became finer at 200 rpm. The shape of powders changed from sphere to platelet with directional orientation as the stirring rate increase from 200 to 400 rpm. At the higher agitating rate of 600 rpm, the agglomerate powders showed the well-developed platelet shape with directional orientation. Therefore,

it is clear that the morphology and size of the crystalline TiO_2 powders can be controlled by the stirring rates.

Effect of the Heating Rate on the Formation of TiO_2 Powders. Figures 5 and 6 show the SEM micrographs and XRD data of the TiO_2 powders synthesized in the supercritical state at various heating rates. The morphology of the TiO_2 powders developed into spherical shape and the size of the agglomerated particles became larger as the heating rate increased from 3 to 12 °C/min. This result indicates that the heating rate has a great effect on the formation and growth of particles. At a low heating rate, it took a long time for the reaction to take place in a liquid state. The number of nucleation sites increased, and thus the particle size was small. However, at a high heating rate, it took a short time for the formation reaction to occur in a liquid state. Therefore, the fine powders prepared from the supercritical fluid were condensed and their particle size became bigger under the condition of insufficient numbers of nucleation sites. The powders synthesized from the supercritical fluid in the range of heating rate from 3 to 12 °C/min were identified as the crystalline TiO_2 anatase, as shown in Figure 6.

Conclusions

The results obtained from the supercritical synthesis of TiO_2 powders (265 °C and 7 MPa) at various stirring and heating rates were as follows.

1. The TiO_2 powders synthesized under supercritical condition were weakly agglomerated with primary particles and directly crystallized as anatase.

2. The primary particle size of the TiO_2 powders decreased from 90 to 60 nm as the stirring rate increased from 50 to 150 rpm and increased to 160 nm at 400 rpm. The shape of the powders changed from sphere to platelet with an increase of the stirring rate from 400 to 600 rpm.

3. The size of the agglomerated powders increased from 160 to 400 nm, and the shape became more spherical with an increase of the heating rate from 3 to 12 °C/min.

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