THE EFFECT OF SILICA ADDED ON LARGE SURFACE AREA
OF NANOCRYSTALLINE TITANIA

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Abstract

Nanocrystalline titania was obtained from the glycothermal reaction of titanium (IV) tetra-tert-butoxide in 1,4-butanediol solution. An appropriate amount of tetraethyl orthosilicate having Si/Ti ratio of 0 to 0.5 was added into the solutions before taking place of the reaction. The crystallization reaction was conducted in an autoclave under nitrogen atmosphere and a reaction temperature of 300°C for 2 hours. The product was then calcined at various temperatures from 300 to 1000°C. The XRD patterns of the titania products obtained revealed that all the products had the anatase structures. This result indicated that addition of small amount of tetraethyl orthosilicate in the titania provided significantly increasing of the BET surface area and reducing the crystallite sizes, and that the peak intensities were not affected by the tetraethylorthosilicate content in the reaction mixture. These results also suggested that addition of silica causes the anatase-rutile phase transformation to shift markedly toward higher temperatures. However, addition of silica over the proper limit will result in the presence of the amorphous phase leading to drastic decrease of thermal stability of the titania product. In this work, the functional group of the product surface was identified using FT-IR spectroscopy in order to observe this effect.

1. Introduction

The preparation of titania [titanium (IV) oxide, TiO_2] has been the subject of considerable interest because this material is widely used as catalyst supports, photocatalysts, pigment, filter, and recently, as membrane and anti-reflection coating. To be used as a catalyst support, materials must have large-surface areas. However, it has been reported that this kind of materials has high tendency towards sintering because of their surface energies.

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Since thermal stability seriously affects the catalyst life, titania having large-surface area with reasonable thermal stability has been sought. Therefore, many studies have been devoted to improve the thermal stability of titania using additives such as Al, Si, La, and others [1-3].

In most of the titania synthesis processes, metal oxides with large-surface areas are obtained from alkoxides which hydrolyzed in an alcoholic solution. However their surface areas are drastically decreased after calcination at the temperatures because corres ponding oxides begin to crystallize.

Recently, Inoue et al.[4-6] have examined the thermal reaction of metal alkoxide in glycols (glyco thermal reaction) or other organic media and demon strated that a number of novel or characteristic cry stalline products can be obtained directly without any bothersome procedures such as purification of the reactants or handling in inert atmosphere. By applying this method[7-9], nanocrystalline titania in anatase phase having extremely large-surface area can be obtained by the proper reaction conditions and careful choice of the titanium source and organic solvent. However, transformation of anatase into rutile taking place in the temperature range of 600-1000 °C results in drastic decrease of the surface area.

In this study, this novel method was employed for the system of silica modified titania in order to investigate the effect of the amount of tetraethyl orthosilicate on the thermal stability of nanosized titania.

2. Experimental

2.1 Crystallization

A portion of 25 g of titanium (IV) tetra-tert -butoxide (TTB) and an appropriate amount of tetraethyl orthosilicate (TEOS, Si/Ti atomic ratio of 0 to 0.5) were dissolved in 100 cm³ of 1,4-butanediol (1,4-BG) in a test tube which was set in anautoclave. An additional 30 cm³ of 1,4-BG was placed in the gap between the test tube and autoclavewall. The autoclave was purged thoroughly with nitrogen, heated to 300°C at a rate of 2.5°Cmin¹, and kept at that temperature for 2 hours. The autonomous pressure during the reaction gradually increased as the temperature was raised. After the autoclave was cooled down to room temperature, the product powders were washed repeatedly with methanol and dried in air. The thus-obtained product was calcined in a box furnace by heating at a rate of 10°Cmin⁻¹ to a desired temperature (600,800 and 1000°C) and kept at that temperature for 1 hour.

2.2 Characterization

X-ray diffraction measurements were car ried out on a SIEMENS XRD D5000 diffractometer using a Ni-filterd Cu Kα radiation. The crystallite size of titania was calculated from the half-height width of the diffraction peak using the Scherrer equation. TEM pictures were obtained on a JEOL TEM-200CX. FT-IR spectra were recorded on a Nicolet Model Impact 400. The specific surface areas (S$_{BET}$) were calculated using the BET single point method.

3. Results and Discussion

3.1 Formation and transformation of pure anatase titania

An XRD pattern of the as-synthesized product obtained from the glycothermal reaction conducted at 300°C for 2 hour is shown in Figure 1. It can be seen that the anatase phase was formed without any
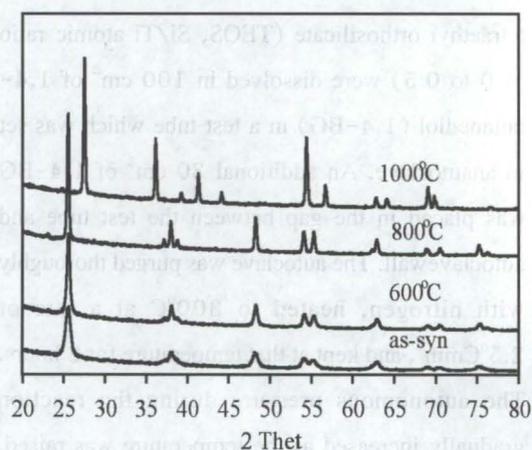
Figure 1 XRD patterns of pure titania before and after calcination at 600, 800 and 1000°C

contamination of any other phases such as rutile or brookite. The crystallite size calculated from the line-broadening of the diffraction peak was 17 nm. The average particle size determined from the transmission electron micrograph (TEM) of the product was 16.7 nm This value is in good agreement with the crystallite size calculated from the diffraction peak. The result suggested that each primary particle observed was a single crystal of anatase. The BET surface area of this product was 89.3 m^2g^{-1}.

The BET surface area and the XRD pattern of the calcined products were investigated from three portions of the product which were calcined at 600, 800 and 1000°C. The BET surface area of the products after calcination at 600°C and 800°C were 38.4 and 16.1 m^2g^{-1}, respectively, respectively, (see Table 1). Their
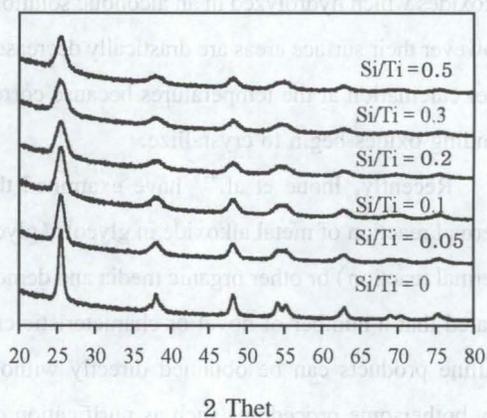
Figure 2 XRD patterns of all Si/Ti ratio of silica modified titania

Table 1 BET surface area and crystallite size of the products

Charged Si/Ti ratio	S_{BET}[a] (m^2/g)				d_{101}[b] (nm)			
	300°C	600°C	800°C	1000°C	300°C	600°C	800°C	1000°C
0.00	89	38	16	3	17 (16.7[c])	37	96	218
0.05	132	120	59	16	9.7 (10)	11	24	71
0.10	155	138	77	29	8.4 (8.3)	8.4	15	49
0.20	177	174	136	42	7.1 (6.7)	7.1	8.7	35
0.30	173	171	144	47	7.0 (6.7)	7.0	8.1	26
0.50	158	147	132	44	8.1 (8.3)	8.1	8.7	28

[a]   BET surface area

[b]   Crystallite size of titania from the 101 and 110 diffraction peak of anatase and rutile phases

[c]   Crystallite size of titania from TEM photograph

XRD patterns were almost identical to that of the as-synthesized product calcined at 300°C except the fact that the peaks were sharper, as seen in Figure 1. As expected from this pattern, these products still have the anatase structure even after calcination at high temperature. The anatase-rutile transformation took place completely at 1000°C. This transformation temperature was much higher than that of the titania prepared by the hydrazine method[10]. It was also found that the transformation temperature is as high as that of titania prepared by the non-hydrous sol-gel method.[11]

3.2 Formation and transformation of silica modified titania

The XRD patterns revealed that all the products had the anatase structure and the peak intensities were not affected by the TEOS content. This resul provides a sharp contrast against those synthesized by another methods.[12-14] The peak intensity of anatase decreased with an increase of the silica content which was resulted from the formation of amorphousphases as can be seen in Figure 2. The BET surface area increased and the crystallite size decreased with an increase of TEOS up to the atomic ratio of Si/Ti of 0.2 and 0.3, respectively. This indicated that the amount of TEOS added to the reaction mixture should have the optimum portions.

The XRD patterns of the titania products after calcination at various temperatures suggested that small amount of TEOS added to the reactionmixture caused the anatase-rutile phase transformation to shift markedly toward higher temperature. The BET surface area decreased while the crystallite size increased with an increase in the TEOS content and the calcination temperature. It is evident that an increase of the TEOS content retarded the grain growth of the anatase. The titania products having Si/Ti ratio more than 0.2 maintained the BET surface area higher than 40 m^2g^{-1} and the crystallite size less than 30 nm although they were calcined at 1000°C for 1 hour. The XRD patterns of the itania products show that the silica modified titania maintain the anatase structure having large surface area even after calcination at all experimental temperature range. The TEM photograph of the silica of the amorphous phase. The presence of Si in the titania lattice seems to contribute to the deceleration of the grain growth in anatase and the suppression of anatase-rutile transformation.

3.3 Effec of an increase int he silica content on the thermal stability of the products

Since X-ray diffraction spectroscopy cannot be employed to distinguish the phase between silica and titania, the Ft-IR spectroscopy was used to corroborate the effect of an increase in the silica content on the thermal stability of products. The spectra of the pure anatase titania, as can be seen in Figure 3, is characterized by a very strong band with two absorbances at 600 and 486 cm^{-1}. For the silica modified titania, all IR bands of pureanatase were found. The IR bands of Si-O-Si bonds were shifted from 1100 cm^{-1} to 1086 cm^{-1}, and The IR bands of Si-O-ti bonds were found at 940 cm^{-1}.

The FT-IR spectra of the TiO_2 products having Si/Ti of 0.5 calcined at various temperatures are illustrated in Figure 4. The spectrum of the product calcined at 1000°C is different from the others because the product completely transformed from anatase to rutile phase.

It is evident that an increase of the silica content in the titania lattice seems to contribute to the dece leration of gain growth of anatase and the suppression

of anatase-rutile transformation because the rearrangement of titania was prevented by the coexistence of silica. However, the grain growth and aggregation of anatase with calcination were notsuppressed by the introduction of silica because of the phase separation. The increase of silica content in the titania product generated Si-O-Ti inter action and these Si-O-Ti bonds are less stable than Ti-O-Ti and Si-O-Si bonds. Therefore, the unstable Si-O-Ti bonds will break while the Ti-O-Ti and Si-O-Si bonds will reform at higher calcination temperature. Thus, the grain growth and aggregation of the anatase particles occurred.
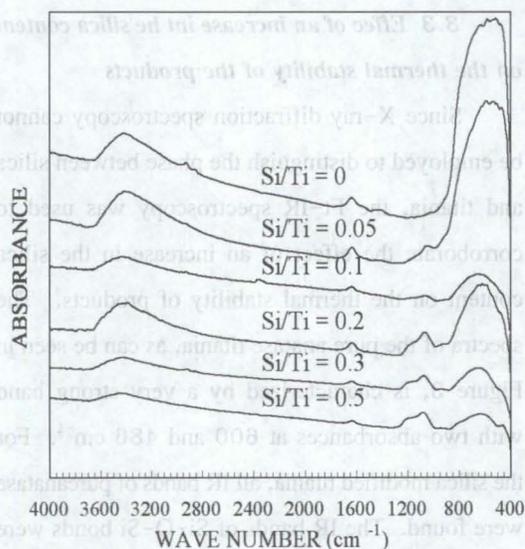
Figure 3 FT-IR spectra of titania and silica modified titania.

4. Conclusions

Addition of small amount of tetraethyl orthosilicate in the titania provided significantly increasing of the BET surface area and reducing the crystallite sizes, Moreover, the silica added also causes the anatase-rutile phase trans-formation to shift mark edly toward higher temperatures. However, an over amount of silica will result in the

presence of the amorphous phase and that the thermal stability of the titania drastically decreased.
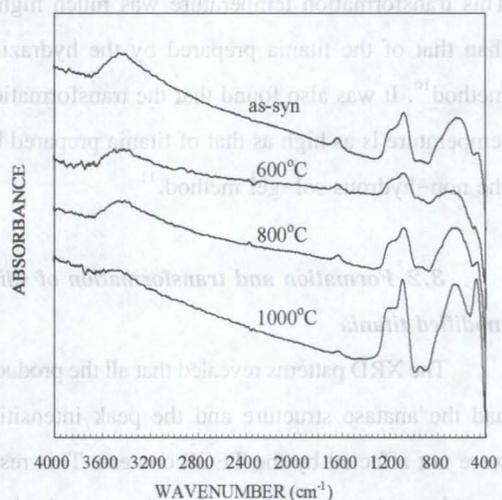
Figure 4 FT-IR spectra of silica modified titania with Si/Ti = 0.5 as- synthesized and after calcined at 600, 800, and 1000°C

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สำเร็จการศึกษาปริญญาตรี และโทวิศวกรรมเคมี และ ปริญญาเอกวิศวกรรมตัวเร่ง ปฏิกิริยา ผ่านการทำงานใน โรงงานผลิตกระดาษพิมพ์เขียน และกองเชื้อเพลิงธรรมชาติกรมทรัพยากรธรณี ก่อนที่จะมาเป็นอาจารย์ที่วิทยาเขตเทคนิค กรุงเทพฯ ผ่านการฝึกอบรมการสอนสาขา วิศวกรรมเคมีจากมหาวิทยาลัยฮิโรชิมา ประเทศ ญี่ปุ่น ฝึกอบรมสาขา Petrochemical Engineering Technology ที่ NALT ประเทศแคนาดา ปัจจุบัน ทำงานวิจัยด้านการเตรียมผลึกโลหะออกไซด์ขนาด นาโนเมตรเพื่อใช้เป็นตัวเร่งในปฏิกิริยาเคมีต่าง ๆ