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Synthesis of TiO₂ Particles by Self-Hydrolysis Process under the Existence of Additives

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Abstract

TiO₂ nanoparticles were synthesized by self-hydrolysis of TiOCl₂ and the crystalline phase and morphology were controlled by addition of HCl. When 0.1M TiOCl₂ was heated at 100°C for 24h, the XRD peaks of anatase were detected on the precipitate. By addition of 4M HCl, the XRD peaks of anatase disappeared, and brookite and rutile were detected. These results suggest that addition of HCl promotes dissolution- reprecipitation reaction and leads to brookite and rutile formation.

Keywords: Titania, Nanoparticles, Hydrothermal reaction, Additive

1. Introduction

Titania (TiO₂) is used for photocatalyst and many researchers have studied the synthesis method. TiO₂ has three polymorphous which are rutile, anatase and brookite. Each of them have different physical and chemical property, which depends on particle size and morphology. Therefore, there are great demands for control of the crystalline phase and morphology to enhance the performance.

The authors have tried to synthesize TiO₂ particles by self-hydrolysis of TiOCl₂ and proposed the formation mechanism consisting of three steps as follows: (1)deprotonation of [Ti(OH)₂·4H₂O]²⁺ and formation of [Ti(OH)₄·2H₂O], (2)condensation of [Ti(OH)₄·2H₂O] and nucleation of TiO₂ and (3)crystalline growth of TiO₂ by dissolution-reprecipitation^{1), 2)}. In the condensation, TiO₆ octahedra are arranged and form hydrous TiO₂ sol or crystalline nucleus. It was revealed that hydrous TiO₂ sol formed at the early stage of reaction and crystalline growth of rutile occurred with time by dissolution-reprecipitation of hydrous TiO₂ sol.

In this research, we studied the effect of HCl addition to control the crystalline phase by self-hydrolysis process.

2. Experimental Procedure

TiO₂ was synthesized by self-hydrolysis of TiOCl₂. The aqueous solution of TiCl₄ (16-17% Ti) was diluted with deionized water to 2M TiOCl₂, and stored in a refrigerator. The stored solution was further diluted with deionised water, and HCl was added to the solution in an ice-water bath with stirring. The concentration of TiOCl₂ was 0.1M. After 30 minutes stirring, the solution was put into a glass flask(300ml) equipped with a reflux condenser, and heated at 50-100°C for 0.5-24h in an oil bath. The precipitate was separated by centrifugation. The produced powder was washed with deionized water and dried at 50°C for 5h. The products were characterized by XRD and SEM. The change in conversion of TiOCl₂ to TiO₂ was determined from change in conversion of Ti ion in supernatant solution after centrifugation. The supernatant solution was colored by addition of H₂O₂ forming the complex with Ti

ions, and the adsorption spectrum was measured at $\lambda=408.90\text{nm}$.

3. Results and Discussion

3.1 Effect of HCl addition

Crystalline phase of TiO_2 was controlled by the addition of HCl. The 0.6-4M HCl was added to 0.1M TiOCl_2 solution and heated at 100°C for 24h. The XRD patterns and SEM images of the products are shown in Figs.1 and 2, respectively. Without HCl addition, XRD patterns of anatase only were detected, which were assigned to hydrous TiO_2 sol. By addition of 0.6M HCl, intensity of anatase peaks decreased and rutile peaks were detected. Furthermore at 4M HCl, anatase peaks disappeared and brookite peaks were detected with rutile. It was observed on SEM images that agglomerates of nanoparticles grew dispersively by HCl addition. Figure3 shows the change in conversion of TiOCl_2 to TiO_2 at each HCl concentration. Without HCl addition, the conversion became 100% rapidly in about 10min. On the other hand, reaction rate became slow with increase of HCl concentration. In this study, the change in conversion of TiOCl_2 to TiO_2 was determined from change in conversion of Ti ion colored by H_2O_2 addition. The colored ion should be derived from $[\text{Ti}(\text{OH})_2(\text{H}_2\text{O})_2]^{2+}$. From these results, it was suggested that the deprotonation was retarded by HCl addition. As a result, HCl addition retarded the formation of hydrous TiO_2 sol and promoted rutile and brookite formation by dissolution-reprecipitation.

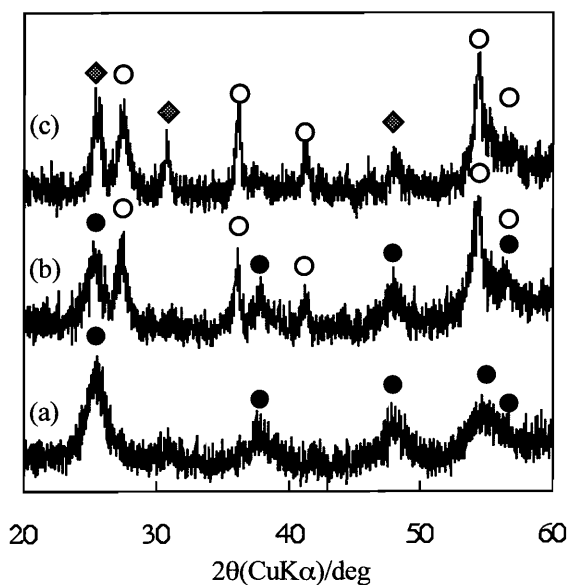


Fig.1 XRD patterns of products synthesized from 0.1M TiOCl_2 for 24h with (a)no addition, (b)0.6M and (c) 4M HCl addition; ○:rutile, ◆:brookite, ●:anatase.

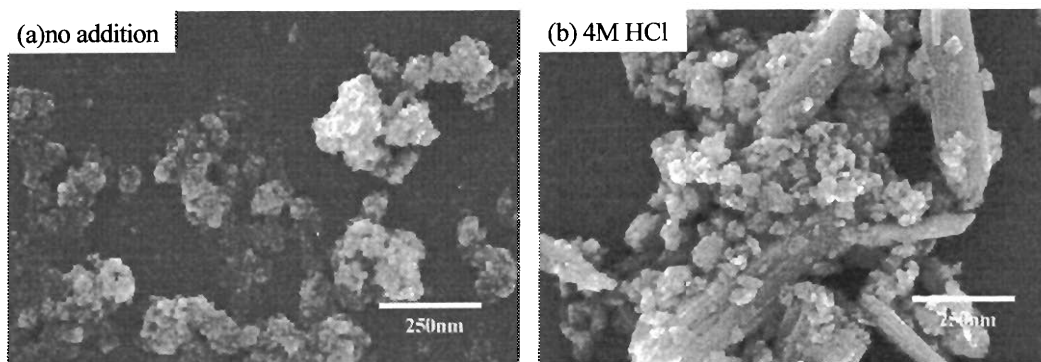


Fig.2 SEM images of products synthesized from 0.1M TiOCl_2 at 24h with (a)no addition and (b) 4M HCl addition.

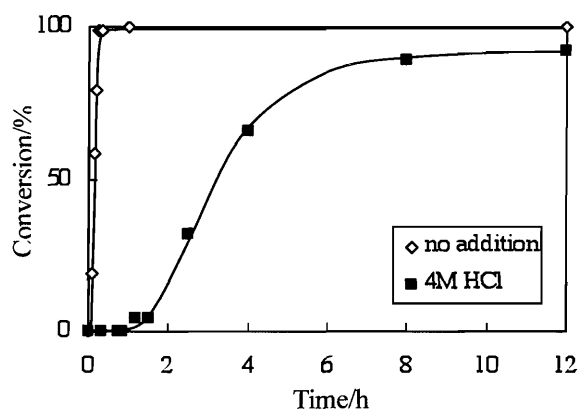


Fig.3 Change in conversion of TiOCl_2 to TiO_2 with no addition and 4MHCl addition.

3.2 Influence of reaction time

The influence of reaction time was investigated when 4M HCl was added. The XRD patterns and SEM images of the products are shown in Figs.4 and 5, respectively. On XRD, anatase and rutile phases appeared at early stage of the reaction. The anatase peaks was assigned to hydrous TiO_2 sol. The intensity of anatase peaks decreased with time and that of brookite peaks increased until 24h. In addition, the intensity of brookite peaks decreased and rutile peaks were rather enhanced at 72h. On SEM images, agglomerate particles were observed at 1h, and fine particles dispersed and acicular particles grew with time. According to the change in XRD patterns, it is found that the fine particles are brookite phase and the acicular particles are rutile phase. These results indicate that crystalline growth occurred with time in order of brookite and rutile.

At the early stage of the reaction, hydrous TiO_2 formed and nucleation of rutile occurred. From change in conversion of TiOCl_2 to TiO_2 (Fig.3), the conversion became constant, leading to ripening stage after 8h. Under the ripening, addition of HCl promoted dissolution of TiO_2 , and hydrous TiO_2 dissolved and reprecipitated slowly. As a result, nucleation and crystal growth of brookite progressed by rearrangement of TiO_6 octahedra. The reason may be that the structure of hydrous TiO_2 is similar to brookite rather than rutile. Moreover, crystalline growth of rutile occurred with time by dissolution-reprecipitation of brookite, because rutile phase is thermodynamically stable.

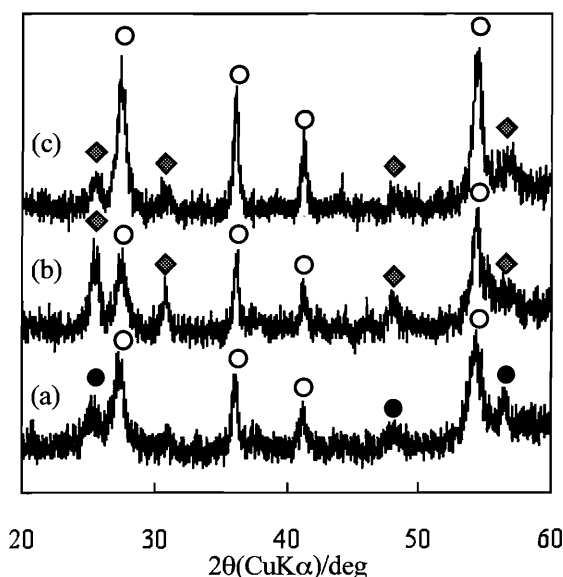


Fig.4 XRD patterns of products synthesized from 0.1M TiOCl_2 by addition of 4M HCl at 100°C for (a) 1h, (b) 24h and (c) 72h; ○:rutile, ◆:brookite, ●:anatase.

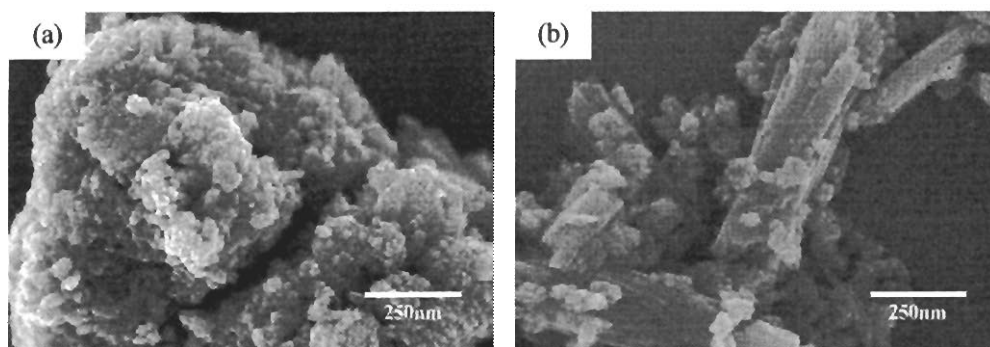


Fig.5 SEM images of products synthesized from 0.1M TiOCl_2 by addition of 4M HCl at 100°C for (a) 1h, (b) 72h.

4. Conclusions

TiO_2 nanoparticles were prepared by self-hydrolysis of TiOCl_2 under the existence of HCl. HCl addition retarded the formation of hydrous TiO_2 sol and promoted the nucleation of rutile, because of slow deprotonation. Moreover when 4M HCl was added, dissolution-reprecipitation of TiO_2 was promoted, which leads to brookite and rutile growth.

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