

Photoactivity of Calcium Carbonate Prepared by Surface Modification

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Nanoscale surface design to control surface activity is an important technology for developing functional materials. This technique is also interesting in many industrial processes such as adjusting the interface in composites, the reaction control of catalysis, and improvement of powder dispersions. In this study, we propose a new process to introduce photoactive sites on a material's surface. The forte of the process is that an independent atomic site is able to be introduced onto a surface using an easy technique. The process consists of three steps, which include a chemical surface modification with a titanate-based coupling agent, surface oxidation modifiers and surface hydroxylation. The amount of active sites introduced onto a surface was increased with the repeated application of this process and concentration of the modification reagent. The surface density of the modifiers was evaluated from the weight loss after the combustion of the alkyl group in the modifier, and the specific surface area of the sample. The surface density of the modifiers of about 1nm^{-2} was introduced per one cycle of this process. The process could quantitatively introduce new active sites. The change in the surface acidity was investigated using the temperature programmed desorption (TPD) method. Pyridine was used as probe molecule. Surface acidity increased in proportion to the number of process cycles. The value with increasing number of repeated times approached the acid strength of titanium oxide. The sample prepared having eleven repetitions become photoactive as a catalyst.

Key words: photoactivity, photocatalyst, surface modification, calcium carbonate, titanate-based coupling agent

1. INTRODUCTION

Photocatalyst in the solid state such as provided by titania has recently attracted much attention[1,2]. Especially, applied research concerning the decomposition and the removal from soil using titania is quite active[3,4]. This includes the states of the titania in these investigations using thin films generated on a solid surface, the dispersion of liquid of the particle and so on. The deposition on the surface of the solid can have a wide range of applications, because it is possible to have various states of use. One important technology is titania as a photocatalyst. The easiest method of producing the titania film is dipping into a liquid dispersion of fine particles. However, an internal particle is hidden by particles on the surface by deposition in this method. As a result, the efficiency of the catalyst versus the amount of the titania is low. In addition, there is no mechanical strength. Therefore, the development of a method of making a thin film of titania on the surface of the solid is desired. Up to now, two main methods have been proposed in a report concerning the thin film production of the titania. One is film production by the sol-gel

method[5]. In this case, a titanium based alkoxide such as titanium iso-propoxide ($\text{Ti}[(\text{CH}_3)_2\text{CHO}]_4$) is used. The other method is the titanium tetrachloride (TiCl_4) reaction on the solid surface[6]. It is necessary to add an acid or base as the catalyst to control the hydrolysis of alkoxide in the sol-gel method. On the other hand, hydrogen chloride (HCl) is generated as a byproduct in the method using titanium tetrachloride (TiCl_4). Therefore, the photocatalyst activity cannot be produced on the surface of the solid which is dissolved in acid or base by these methods. As for the method which uses the titanate based coupling agent, the deposition is chemically possible with very mild conditions[7]. In addition, a very thin film can be made, because one titanium atom layer is made by this method. Therefore, an improvement in the catalytic activity and activation by visible radiation can be expected according to the quantum size effect. In this study, the production of a titania thin film was attempted on the surface of calcium carbonate where producing photocatalyst activity was difficult in a past method for the above-mentioned reasons. Moreover, the relation between the basic

deposition mechanism and the appearance of the photocatalyst activity is discussed.

2. EXPERIMENTAL

2.1 SAMPLE AND REAGENT

The colloidal calcium carbonate was supplied by the Nittetsu Mining Co., Ltd. The original and modified samples were observed by TEM (2000FX; JEOL). The crystal structures of these samples were measured by XRD (Mac Science Co., Ltd.; MPX-50). The surface modification reagent of $(\text{CH}_3)_2\text{CHOTi}(\text{OCOC}_{17}\text{H}_{33})_3$ (Ken-react; KR-TTS) was obtained from Ajinomoto Co., Ltd.

2.2 SURFACE MODIFICATION

The procedure for the surface modification consists of three steps. (1) Chemical surface modification using the Ti-based coupling reagent, (2) Oxidation of surface modifiers, (3) Hydroxylation with water vapor. The chemical surface modification is carried out by a chemical reaction between the surface active sites and Ti-based coupling reagent using a reflux method for 1 hour in normal hexane solvent. The solution containing the sample powder was filtered, washed with n-hexane and then dried under reduced pressure. The oxidation of the surface modifiers was performed at 300°C in an electric furnace in which oxygen gas flowed through. After the last surface hydroxylation was done, the sample was kept in a desiccator adjusted to 85%rh for about 10 hours.

2.3 CHARACTERIZATION OF SAMPLE SURFACE

Surface density of the modifier was determined from the specific surface area and weight loss of the samples by combustion of the modifier. The specific surface area was measured by N_2 adsorption using BET method and the weight loss was calculated from the TG-DTA curves. The Surface density of Ti was regarded as the same as the surface density of the modifier. The effect of the introduced sites on surface acidity was investigated by Temperature Programmed Desorption (TPD). Pyridine molecules were used as the basic probe. Two instruments were used to measure the TPD. One had a thermal conductive detector (Pulse Chemisorbe 2700; Micromeritics Co., Ltd.). The other had a mass spectrometer (Thermo Plus; Rigaku Co., Ltd.).

2.4. EVALUATION OF PHOTOACTIVITY

A photoactivity was evaluated by degradation of methylene blue. Ultraviolet irradiation was done using black light (6Wx2). The change in the methylene blue content with degradation was measured by a UV-VIS spectrometer (Hitach Co., Ltd.; U-3210).

3 RESULTS AND DISCUSSION

3.1 INFLUENCE OF SURFACE MODIFICATION ON PROPERTIES OF BASE MATERIAL

Fig. 1 shows the TEM image of colloidal calcium carbonate. The shape of the colloidal calcium carbonate particle was rhombohedral, and the length of one edge was about 60nm. After the surface modification, no remarkable change was observed in the size and shape. Fig. 2 shows the XRD pattern of the colloidal calcium carbonate. It was understood that colloidal calcium

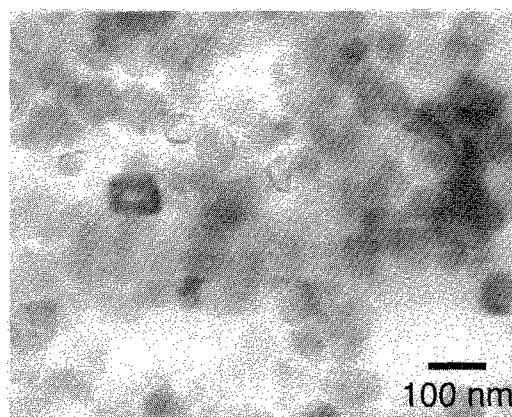


Fig. 1 TEM image of original colloidal calcium carbonate.

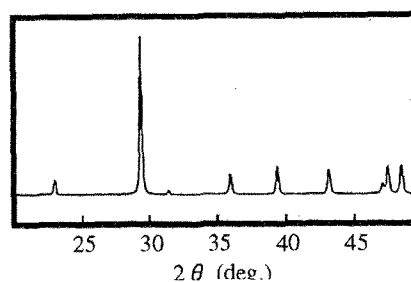


Fig. 2 XRD pattern of original colloidal calcium carbonate. (Cu K α)

carbonate is a calcite. The crystal structure did not change after the surface modification. Moreover, the BET specific surface areas of the original and modified samples showed the same value of $22.5 \pm 0.5 \text{ m}^2/\text{g}$ though the surface modification was repeated. Therefore, it was understood that the physical properties such as the bulk of the colloidal calcium carbonate, which is the base material, do not change after the surface modification.

3.2 SURFACE MODIFICATION

Fig. 3 shows the relation between the surface density of Ti introduced onto the surface and the concentration of the modification reagent. The surface density of Ti at a low concentration rose corresponding to the increase in the concentration of the modification reagent. Therefore, one is able to control the surface density of Ti by the concentration of the modification reagent in this region. On the other hand, the surface density of Ti showed about an almost constant value of 0.95 nm^{-2} , when the concentration of the modification reagent was about $0.3 \text{ mol} \cdot \text{g}^{-1}$ or greater. The reason for this is the steric hindrance among the modification groups. Moreover, this value is the saturation surface density of Ti which can be introduced by a one-time surface modification. Therefore, Ti with the surface density of about 1 nm^{-2} per each reaction can be introduced onto the surface of calcium carbonate by repeated surface modification with a modification reagent concentration of about $0.3 \text{ mol} \cdot \text{g}^{-1}$ or greater. Fig. 4 shows the results of the sample which had repeated surface modifications at a modification reagent concentration of about $0.6 \text{ mol} \cdot \text{g}^{-1}$. The surface density of Ti increased almost proportionally to the repetition

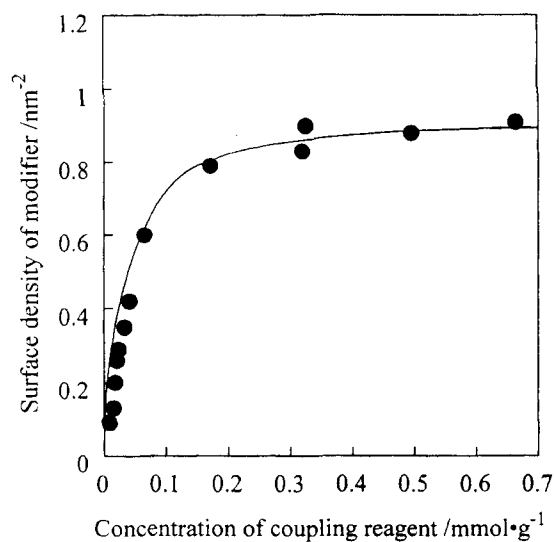


Fig.3 The relationship between concentration of modification agent and surface density of modifier.

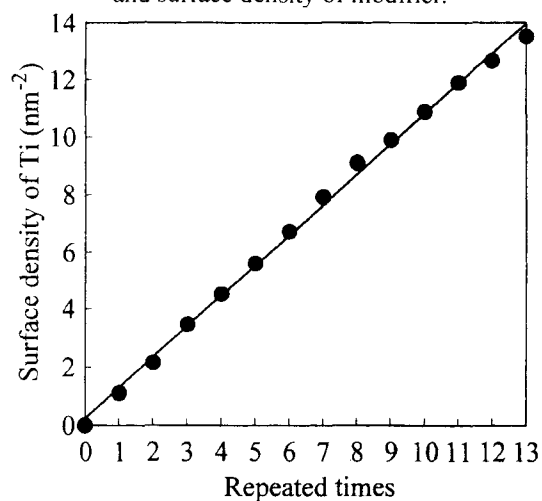


Fig.4 Relationship between repeated times and surface density of Ti on the modified sample surface.

frequency of the surface modification. It was shown that surface density of Ti can be quantitatively increased by repeatedly doing the surface modification based on the above-mentioned results.

3.3 PROPERTIES OF MODIFIED SURFACE

To characterize the surface property of the sample which been modified below the saturated surface density of Ti, the TPD was measured using pyridine as a probe molecule. Fig. 5 shows the result of the TPD measurement. Two peaks existed in the measurement result of the original calcium carbonate. From our previous results[8], the low temperature peak corresponds to the desorption of the physisorbed pyridine, and the high temperature peak corresponds to the desorption of the pyridine strongly adsorbed by a chemical interaction. An increase in the amount of the desorption at 500°C was observed in the TPD curve of the modified sample as the surface density of Ti increased. This is a result of an increase in the acid sites

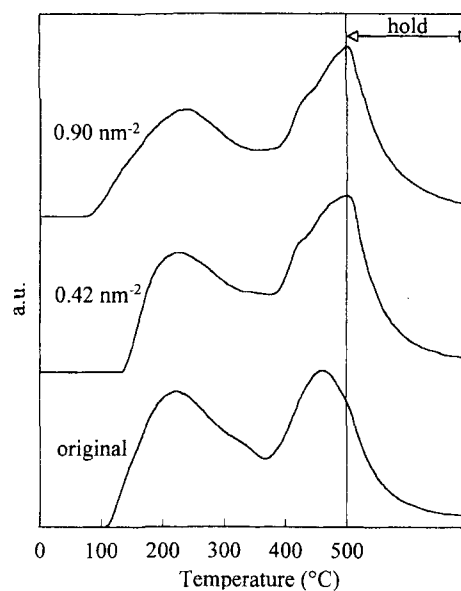


Fig.5 TPD curves of Pyridine adsorbed on original and modified calcium carbonate.

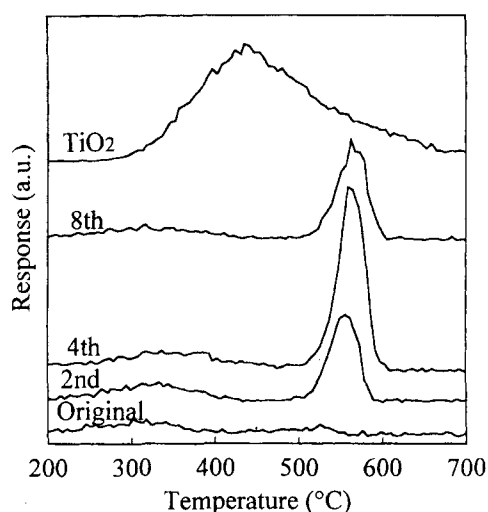


Fig.6 TPD spectra of pyridine adsorbed on original calcium carbonate, the modified samples and TiO₂. The surface density of Ti on the 2nd, 4th and 8th modified samples were 2.15nm², 4.52nm² and 9.10nm², respectively.

on the surface of the modified calcium carbonate due to the introduction of the acid site of Ti onto the basic surface of the original calcium carbonate. It has been understood that the acid site quantitatively increases as the modification reagent concentration increases based on the TPD measurement result. On the other hand, the change in the surface properties of the sample, which was done by the modification at a concentration of 0.6 mol·g⁻¹ to obtain the saturated surface density of Ti, was evaluated using the TPD measurement. The peak at 560°C, which appeared due to one the surface modification was focused on. Fig. 6 shows the TPD curves of the repeated modified samples. The acid

strength increased to about 4.5nm^{-2} in relation to the surface density of Ti. However, the acid strength decreased when the surface density of Ti exceeded 4.5nm^{-2} . A broad peak appeared in the low temperature part corresponding to this decrease. The peak position approached the acid strength distribution of the anatase type TiO_2 . From these results, direct introduction of Ti onto the surface of calcium carbonate ends by repeating the surface modification up to 4.5nm^{-2} . Also, the modification reaction occurs on the acid sites which relates to the previously introduced Ti with a surface density above 4.5nm^{-2} . Therefore, it seems that the surface acidity did not change too much. It is suspected that this is a result of the generation of a site similar to TiO_2 . This consideration is supported by the decrease in the amount of desorbed gas at high temperature, and the observation of a new desorption in the low temperature region.

3.4 PHOTOACTIVITY OF MODIFIED CALCIUM CARBONATE

To investigate the photocatalytic ability of the modified calcium carbonate, the decomposition ability of methylene blue was measured. Fig. 7 shows the decomposition amount of methylene blue versus irradiation time by ultraviolet rays. A clear photocatalytic ability was confirmed for a Ti surface density of about 11.9nm^{-2} (11 repetitions). From the evaluation results of the modified surface, the appearance of photocatalytic ability would relate to the generation of partial TiO_2 -like phase on the surface. In this experiment, three reasons are postulated for the absorbance decrease in the methylene blue solution besides the decomposition of the methylene blue by the photocatalyst. The absorbance decrease might occur due

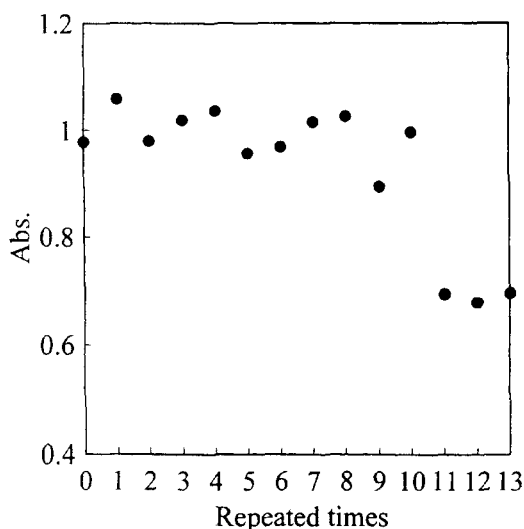


Fig.7 Photocatalytic degradation of methylene blue solution on the modified sample. UV was irradiated for six hours. Absorbance of M.B. solution after photocatalytic degradation is plotted as ordinate and repeated times of modification as abscissa.

to the immediate decomposition of the methylene blue molecule and the methylene blue molecule adsorption on the surface of the particle. To confirm these amounts, a blank experiment was done. The direct decomposition by UV of the methylene blue molecule was very low. The absorbed amount of methylene blue on the particle increased only slightly. It was understood that the absorbed amount of methylene blue increased with basicity, because the modified surface became acidic with the increasing surface density of Ti. However, the amount was only several percent of the entire decomposition amount. The appearance of the photocatalyst ability of the sample, which was prepared by the actual experiment, was confirmed in the above-mentioned results.

4. CONCLUSION

The photocatalyst ability of calcium carbonate by its surface modification was discussed. The following conclusions were obtained as a result.

- (1) It has been understood that photocatalyst ability can be given to a weak material to the acid or the base by using this method.
- (2) Repeating the modification and concentration of the modification reagent could quantitatively control the surface density of Ti.
- (3) It was suggested that a partial TiO_2 like phase is generated at the surface Ti density of more than 2.2nm^{-2} .
- (4) It was confirmed that the ability of the photocatalyst appeared at the above surface density.

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