

STUDIES FOR THE CHARACTER OF THE POROUS SILICA CONTAINING THE NANO-SIZED TiO_2 PARTICLE IN THE PORE.

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Key word: Silica, Titanate, Pore size, Specific surface area, and Titanium alkoxide solution.

Abstract

In order to lower porosity of the porous silica, titanium alkoxide solution was filled in the pore of silica in the heating-vacuum condition. The specific surface area of modified samples was decreased effectively from $900 \text{ m}^2/\text{g}$ to $100 \text{ m}^2/\text{g}$. (The aggregation phenomena in modified samples were improved fairly.) Samples were heated at 600°C , and then the titanium alkoxide in the pore was decomposed completely to titanium oxide from TGA-DTA measurement. From SEM result, it was evident that titanium oxide did not coat the surface of the silica. The modified samples were analyzed using SEM, DTA-TGA, BET, and UV-visible spectrometer.

Introduction

Silica has high porosity and high specific surface area because of diffusion of organics or H_2O in the process of drying and heat treatment after synthesis by sol-gel method.¹⁾ The porous silicate is very reactive both with the atmosphere²⁾ and with liquids, especially water, directly after synthesis. The surface of silicate has the hydrophobic and hydrophilic property with environment condition. And the sintered silicate shows the stronger adsorption of polar and non-polar species with environmental condition.

The porous silicate can be highly dispersed because porous silicate has the lower density than that of non-porous type. But the organic materials such as surfactants or dispersion reagents are adsorbed on the surface of silicate and are condensed in the pore of porous silicate, the adsorbed surfactants on the surface of silicate aggregate. The morphology of the adsorbed surfactant is nuclear, but the adsorbed surfactant forms a micelle-like bilayer of sufficiently high coverages.³⁻⁸⁾ And then the other organic materials in the solution can be partitioned into the hydrophobic and hydrophilic environment of the hydrocarbon chains of the adsorbed surfactant aggregates by adsolubilization phenomena. The definition of adsolubilization is the incorporation of compound into surfactant surface aggregates, which compound would not be in excess at the interface without surfactant.⁹⁾

In the cosmetic field, silicate and titanate have been used as white pigment and for protection of ultraviolet region of light. In the case of O/W cosmetics the organic materials such as sebum and in the case of W/O cosmetics salty water such as perspiration from the human skin are absorbed on the surface or condensed in the pore of porous silicate, mono-dispersed silicate is aggregated by adsolubilization phenomena. In order to protect the aggregation phenomena, silicate has to be the morphology of the low porosity.

In this study, to lower porosity of silicate, titanate was filled up in the pore of porous silicate under the heating-vacuum condition. After treatment, the particle size of silicate was same as that of non-treated silicate, only specific surface area was lowered. Our choice of titanate is based on several factors. The titanate has been one of the most frequently studied as topical materials in cosmetic and material science field.

The samples were analyzed using a) SEM (Scanning Electron Microscopy) for particle morphology, b) DTA (Differential Thermal Analysis)-TGA (Thermal Gravimetric Analysis) for the removal of organic contaminants and heat treatment condition, c) BET for specific surface area and pore size distribution measurement, d) UV-visible spectrometer for ultraviolet protection effect and band edge measurement of titanate after heat treatment.

Experiment

Model No. H-51, H-52, H-121 silicate samples were obtained from Asai glass co., Ltd. The surface area, pore size, and particle size of samples are showed in Table 1. The samples were sonicated in ethanol 100ml with sample 5g, were filtered and then were dried in vacuo at 110 °C. The pretreated samples were evacuated under the high vacuum condition at 200 °C for 2hr. In this condition, absorbed organics and water were desorbed, especially air and water condensed in the pore were completely eliminated. After heating-evacuation, samples were contacted with the prepared solution in vacuo at room temperature. The solution is prepared with titanium isopropoxide 15mL, propionic acid 10mL, ethanol 5mL, and 0.1mL surfactant. After treatment, the modified samples were filtered and washed with n-propanol and then were dried in vacuo at 150 °C for 3hr. The modified samples were washed in order to prevent titanate from coating on the surface of silicate until the yellow color of the solution disappears completely. When samples were washed with n-propanol, it was sucked rapidly.

The modified samples were analyzed using SEM for the particle morphology and DTA (Differential Thermal Analysis)-TGA (Thermal Gravimetric Analysis) for the removal of organic materials and heat treatment condition. The X-ray diffraction has been also used to analyze particle structure, but the line intensity of titanate was not detected because the pore size is about 60~120 Å. In this study, the absorbance of ultraviolet region and absorbance band edge of titanate after heat treatment at 600 nm was measured using UV-visible spectrometer. The BET plot method from N₂ absorption isotherm has been used to measure the specific surface area.¹⁰⁾

Results and Discussion

The morphology of the modified samples was obtained from SEM picture. Pictures of all samples are not shown here, we explain only for H-121 sample. But we got the good results for all samples. Figure 1,2 show the particle morphology of non-modified and modified samples respectively. Both show the same morphology, it is evident that titanate did not coat on the surface of the silica. Figure 3,4 are TGA-DTA results of the non-modified (call H-121S) and the modified (call H-121) samples respectively. The TGA curve of H-121S sample decreases rapidly from 25 to 100 . This rapidly decreased section is the desorption region of physisorbed species such as water and organic materials. From 100 to 600 , the TGA curve do not show the variation. The modified sample shows slower decrement than that of H-121S sample because of thermal decomposition of titanium alkoxide in the pore. The organic materials is oxidized at about 300 ~400 region completely. But it is decomposed completely at fairly high temperature, 600 because the titanium alkoxide in the pore is decomposed by oxygen diffusion from the surface.

The specific surface area of samples shows in Table 2. The pore size of H-51, H-52, and H-121 samples are 60 , 250 , and 60 respectively. The rate of the decrement of the specific surface area in the sample with smaller pore size is comparatively larger than that in the sample with larger pore size. In the sample with large pore, titanium oxide was not filled up entirely in the pore because the experiment is performed in the equal concentration of titanium alkoxide solution.

The XRD line intensity of titanium oxide was not detected. In this study, the absorbance of UV region of titanium oxide after heat treatment at 600 was measured using UV-visible spectrometer. Figure 5 is the absorbance spectrum obtained from UV-Visible measurement. The temperature, 600 is determined from TGA-DTA measurement. After heat treatment at 600 , the titanate in the pore is to be nano-sized particle. The absorbance of nano-sized particle shifts to higher energy than that of bulk, because the bandgap of nano-sized particle is larger than that of bulk material.¹¹⁾ In this study, the absorbance peak shift to higher energy, short wavelength.

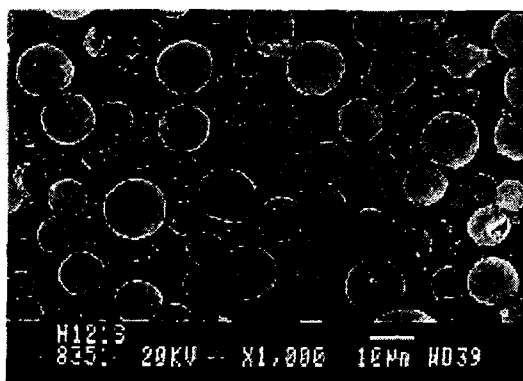
The aggregation phenomena in the modified samples were improved fairly. Those modified samples are being applied for cosmetics now, and the physico-chemical properties of the cosmetic goods are being studied with the modified samples. This method is applied for the synthesis of nano-sized particle such as metal and metal oxide.

Conclusion

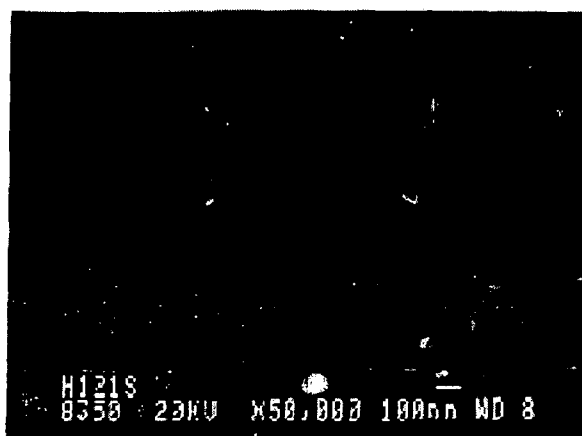
The specific surface area of porous silica contacted with titanium alkoxide was decreased effectively from 900 m²/g to 100 m²/g, so silica showed the character of the low porosity. Also the aggregation phenomena in the modified samples was improved fairly. Titanium oxide filled in the pore of silica is to be the nano-sized particle of cylindrical type, this method is applied for the synthesis of nano-sized particle. The UV-Visible measurement for the analysis of nano-sized amorphous titanium oxide in the micropore is more effective than XRD.

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(A)



(B)

Fig.1 SEM results of the non-modified H-121 Silica.

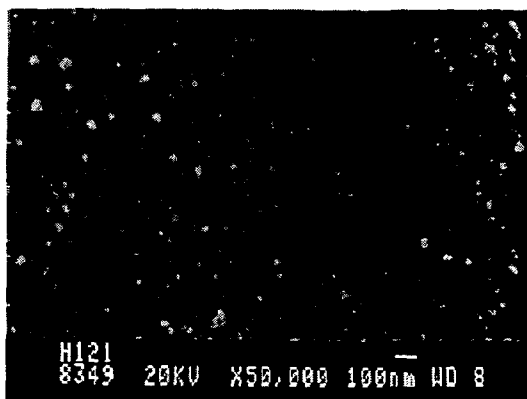


Fig.2 SEM result of the modified H-121 Silica.

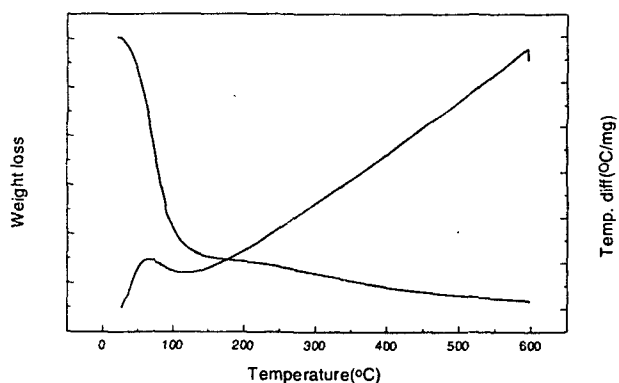


Fig.3 TGA-DTA curves of the non-modified H-121 Silica sample.

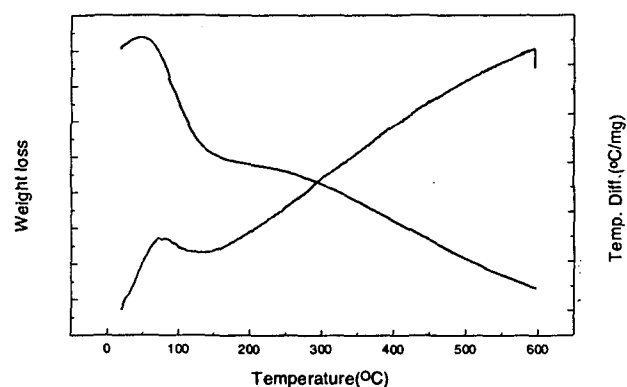


Fig.4 TGA-DTA curves of the modified H-121 Silica sample.

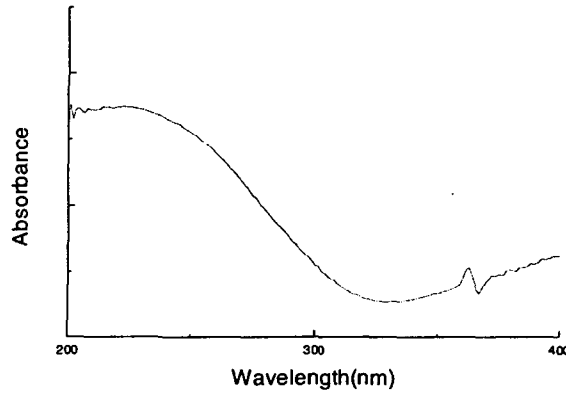


Fig. 5 UV-Visible spectrum of the modified H-121 sample

sample	H-51	H-52	H-121
Particle size (μm)	5	5	12
specific surface area (m^2/g)	900	900	900
Pore size (\AA)	60	250	60
Pore volume (mL/g)	1.0	2.0	1.0

Table 1. The character of samples.

Sample	N_2 BET Surface Area (m^2/g)
H51S	935
H51	125
H52S	792
H52	155
H121S	793
H121	97

H51S is non-modified silica sample.
 H51 is modified silica sample.

Table 2. The specific surface area of samples from BET method.