Carbon-TiO₂ Hybrid Spherical Microbeads with Photocatalytic Activity Prepared using Cellulose-Inorganic Hybrid-sphering Technique

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Cellulose/TiO₂ hybrid spherical microbeads were made by a one-step phase-separation method using viscose and an aqueous solution containing sodium polyacrylate. We also report our findings regarding the relationships between cellulose xanthate and the electronic characteristics of TiO₂ particles used in the inorganic hybrid-sphering process. It was suggested that the distribution of TiO₂ particles on the hybrid spherical microbeads be related to electric repulsion between the CSS⁻ group and TiO₂. The narrower the zeta potential distribution of TiO₂ particles, the more TiO₂ particles were driven out from the cellulose xanthate domain. The removal of acetaldehyde was confirmed to depend on the extent of the appearance of TiO₂ particles on the surface of cellulose. The carbon/TiO₂ hybrid spherical microbeads, prepared by carbonization of the cellulose/TiO₂ composite, were also developed and used as the photocatalyst. The removal efficiency of acetaldehyde was increased by carbonization of the microbeads. In addition, it was not only the photodecomposition reaction induced by TiO₂ that contributed to the efficiency of acetaldehyde removal but also the adsorption properties of the carbon matrix. Key words: Cellulose, TiO₂, Zeta Potential, Spherical Microbeads, Viscose Phase Separation

1. INTRODUCTION

To perform rapid and efficient decomposition of the pollutant under low ppm levels such as those found under dilute conditions and to avoid photodegradation by active TiO₂ particles for the other organic materials of the TiO₂-composite, TiO₂ has often been used hybridized with $Al_2O_3^{1, 2, 3}$, SiO_2^{1} , ⁴ apatite⁵, and activated carbon^{6, 7, 8} etc.. Minero et al. have examined the effects of the addition of Al_2O_3 and SiO₂ as inert supports to the TiO₂ photocatalyst suspension for the photodecomposition of several kinds of organic compounds.¹

On the other hand, Taoda et al. have developed hybrid silica microbeads coated sparsely with TiO₂.⁴ Nonami et al. have developed an adsorbent that partially modifies the surface of the TiO₂ particle with apatite.⁵ The contact area of TiO₂ particles with organic material in the TiO2composite is reduced in order to avoid the composite's photo-degradation by active TiO₂ particles. Yamashita et al. have developed a deodorant fiber that hybridizes sparsely photocatalytic TiO₂ particles to cellulose fiber. sparsely They tried to avoid photo-degradation of cellulose fiber by active TiO₂ particles using modified TiO₂. Therefore, it is important for the photoassistedcatalytic adsorbent using cellulose as a matrix that TiO₂ particles be controlled on the surface of cellulose microbeads. We have succeeded in carbon/TiO₂ hybrid spherical preparing microbeads by means of carbonization of cellulose hybrid spherical microbeads prepared by "viscose phase-separation method" a and confirmed their enhancement for removal of

acetaldehyde in aqueous solution as a photoassisted-catalysis.⁹

In the present study, we prepared various types of cellulose/TiO₂ hybrid spherical microbeads using several kinds of TiO₂ particles with the objective of controlling the appearance of the TiO₂ component. Differences relative to the composition of TiO₂ particles were observed in the distribution of TiO₂ contained in hybrid spherical microbeads. Therefore, the relationships between hybrid spherical microbeads and the composition of the TiO₂ particles used were examined, and the mechanism of the hybridsphering process is discussed. We also developed carbon/TiO₂ hybrid spherical microbeads by means of carbonization and discuss herein their assistive effect in photodecomposition.

2. EXPERIMENTAL

2.1 Cellulose/TiO₂ hybrid spherical microbeads

Cellulose/TiO₂ hybrid spherical microbeads were prepared by a one-step phase-separation method using cellulose xanthate aqueous solution and sodium polyacrylate aqueous solution.⁹ The hybrid spherical microbeads prepared by this

Table I Abbeviations and elemental analysis

of hybrid spherical microbeads

wt%a)		TiO2content(wt%)	
TiO2-1	TiO2-2	Calcd.	Found
29.6	_	29.6	27.7
15.0	-	15.0	14.7
-	29.6	29.6	23.9
68.7	-	-	-
40.1	-	-	-
	wt TiO ₂ -1 29.6 15.0 68.7 40.1	wt% ^a TiO ₂ -1 TiO ₂ -2 29.6 - 15.0 - - 29.6 68.7 - 40.1 -	wt% ^a) TiO ₂ control TiO ₂ -1 TiO ₂ -2 Calcd. 29.6 - 29.6 15.0 - 15.0 - 29.6 68.7 - 40.1 - - -

a) weight percent for cellulose containing in viscose

"viscose phase-separation method" are summarized in Table I. The dispersion of various kinds of TiO₂ powder in a cellulose xanthate aqueous solution (Cellulose Content, 9.5 wt%, RENGO Co. Ltd, Osaka, Japan) (325 g) was carried out by stirring successively at 5000 rpm homogenizer (PROCESS using HOMOGENIZER PH91, SMT Company). The dispersion-solution was mixed with 30 wt% aqueous solution (1320 g) of sodium polyacrylate (Aquaric DL-453, Mw: 50000, Nippon Shokubai Co., Ltd., Osaka, Japan) containing NaOH (48 g), and suspended by stirring at 120 rpm at 80 °C for h. After heating and congealing, the 1 cellulose/TiO2 hybrid spherical microbeads were washed with hydrochloric acid aqueous solution and water.

2.2 Carbon/TiO₂ hybrid spherical microbeads

Carbon/TiO₂ microsphere composites, prepared from cellulose/TiO₂ microsphere composites by the following method^{10, 11}: (1) Freeze-drying process, (2) Dehydration: the dehydrated hybrid spherical microbeads was carried out by heating at 300 °C *in vacuo* for 5 h. (3) Carbonization: the carbonized microspheres were heated to 600 °C for over 5 h and then allowed to stand for 4 h.

2.3 Measurement

The zeta potentials of TiO₂ powder were measured by electrophoresis using the Laser method Doppler (Zetasizernano, Sysmex Corporation, Kobe, Japan). Electron micrographs of the hybrid spherical microbeads were obtained using a field emission scanning electron microscope (FE-SEM) (Hitachi S-4000, Hitachi, Ltd., Tokyo, Japan), and electron probe micro analysis (EPMA) was carried out using a JEOL JXA-8900 WD/ED (JEOL, Tokyo, Japan). Since only Ti was detected as a component element of the particles, Ti was performed by EPMA. The cutting of a spherical microbead was carried out with a ultra microtoam (ULTRACUT S, Leica Microsystems). The catalytic evaluation was carried out by the gas-bag method. A given amount of photocatalyst powder (naked TiO2 and the obtained hybrid spherical microbeads) that was set in a shared culture made from polytetrafluoroethylene plate was left in a 5 l bag packed with 85 ppm of acetaldehyde gas. The bag was then illuminated with two 20 W black lights (TOSHIBA FL20BLB: 300-400 nm). After a given time of illumination, the concentrations of acetaldehyde were monitored using an acetaldehyde gas detector tube.

3. RESULTS AND DISCUSSION

We obtained three types of hybrid spherical microbeads with hybridized cellulose and two kinds of TiO_2 powders (TiO_2 -1 and TiO_2 -2) by the viscose phase-separation method. The amount of TiO_2 appearing on the surface of the spherical microbeads was found to depend on the type of TiO_2 powder used. Figure 1(a) and (b) shows the SEM and EPMA images of the hybrid spherical

microbeads. Despite equal weights (30 wt% for cellulose) of the two kinds of TiO_2 powders being respectively mixed into viscose in the process of sphering, it was confirmed that the distributions



Figure 1. SEM (upper) and EPMA element map images (lower) for Ti of hybrid spherical microbeads. a) CT-1-30, b) CT-2-30, magnification: SEM; X 1000 (upper), EPMA; X 2500 (lower).



Figure 2. Cross sectional SEM images of cellulose/TiO₂ hybrid spherical microbeads.
a) CT-1-30, b) cellulose, c) CT-2-30, d) CT-1-15





a) TiO₂ particles possessing homogeneous potential

b) TiO₂ particles possessing inhomogeneous potential

of TiO₂ particles containing in hybrid spherical microbeads depend on the specific type of TiO₂. The number of TiO₂ particles appearing on the surface of the microbeads was on the order of CT-1-30 > CT-2-30. Figure 2 (a) shows an SEM image of a section of CT-1-30. As a reference, an SEM image of a section of cellulose microbead is shown in Fig. 2(b). In the scanning electron micrograph, TiO₂ particles are brightly visible due to their electrostatic charge. Obviously, the SEM image of cellulose microbeads shows no TiO₂ particles. As expected, it was confirmed that the TiO₂-1 particles contained in CT-1-30 were located tightly around the outline of the circle shape rather than inside the circle. In addition, it was confirmed that the hybrid spherical microbeads (stand for CT-1-15) in which the content of TiO₂-1 was 15 wt% had TiO₂-1 particles only on the surface of sphere, because the section of CT-1-15 indicated that the TiO₂-1 particles were located tightly around the outline of the circle shape, as shown in Figure 2(d). In contrast, as shown in section CT-2-30 of Figure 2(c), TiO₂-2 particles contained in CT-2-30 were situated to some extent around the outline of the circle shape, but also in the interior of the circle shape, thus indicating that the CT-2-30 hybrid microbeads involve TiO₂ particles internally. In particular, the SEM image for the section of CT-2-30 indicated the presence of a phase-separation phenomenon between the TiO_2 and viscose domains; as a result, their interface formed wide pores in the conversion from viscose droplets to cellulose microbeads. To examine the mechanism of hybridization of TiO₂ and cellulose, the zeta potentials of the TiO_2 used were respectively measured by electrophoresis using the Laser

Doppler method in pH 13 aqueous solution. The zeta potentials of TiO₂-1 and TiO₂-2 had minus potentials, respectively. However, the zeta potential distributions of TiO₂-1 were much narrower than those of TiO₂-2, indicating that the surface electric potentials of TiO₂-1 particles are comparatively homogeneous. The distribution of TiO₂ particles on the hybrid spherical microbeads must be related to electric repulsion between the CSS⁻ group and TiO₂. Therefore, TiO₂-1 particles are localized at the interface between the cellulose xanthate phase and the PAA aqueous solution phase, as shown in Figure 3(a). On the other hand, TiO₂-2 particles were located within the cellulose xanthate phase because of the diffusion to the plus electric potential (around +60 mV) of its zeta potential (Figure 3 (b)). Figure 4 shows the removal behavior of acetaldehyde gas using CT-1-30 and CT-2-30. Although the TiO₂ contents for CT-1-30 and CT-2-30, respectively, were approximately equivalent, the efficiency for the removal of acetaldehyde of CT-1-30 was much higher than that of CT-2-30, indicating that TiO_2 in CT-1-30 appeared more on the surface of the cellulose microbeads than that in CT-2-30. The CT-1-30 was able to remove acetaldehyde gas for 450 min. In contrast, CT-2-30 did hardly have the removal property for acetaldehyde.

The TiO₂-1 was adopted for TiO₂ particles used for the preparation of $carbon/TiO_2$ hybrid spherical microbeads from spherical cellulose because TiO₂-1 densified on the surface. The TiO₂ crystal phase in the cellulose/TiO₂ hybrid microbeads and the microsphere composite, carbonized in a stream of nitrogen at 600°C, were both found to have the anatase-form, as revealed by the X-ray diffraction pattern. Figure 5 (a) shows the removal behavior of acetaldehyde gas using carbonized-CT-1-15 and carbonized-CT-1-30. The carbonized-CT-1-15 and carbonized-CT-1-30, respectively, were able to completely remove acetaldehyde gas for 120 min. As compared with the removal behavior of



Figure 4. Removal behavior of acetaldehyde using cellulose/TiO₂ hybrid spherical microbeads.
O: CT-1-30 •: CT-2-30 ;O: CT-1-15

acetaldehyde for CT-1-30 of Figure 4, the effects of carbonization on the cellulose/TiO₂ hybrid spherical microbeads for the removal property of acetaldehyde were evident. The increase in the removal efficiency can be attributed to exposing of TiO₂ particles on the surface by carbonization. The removal efficiency of carbonized-CT-1-15 was equal to that of carbonized-CT-1-30.

addition, the removal efficiency Ĭn of acetaldehyde was evaluated, adjusting the amount of carbonized-CT-1-15 and carbonized-CT-1-30, with the decrease to 30 wt% for TiO₂ content of above-mentioned evaluation, as shown in Figure 5(b). Although amount of the TiO_2 in these experiments were equal, the removal efficiency of CT-1-15 was higher than that of CT-1-30. These results indicate that the photodecomposition reaction was induced by TiO₂ not only contributes to the removal efficiency of acetaldehyde but also the adsorption properties of the carbon matrix. The result indicates that the carbon surface was more than adsorptive than cellulose surface, and so carbon support enables the organic substances concentrate around to the loaded TiO₂ These photocatalysts. suggested that the acetaldehyde supplied to the active centers of the



Figure 5. Removal behavior of acetaldehyde using Carbon/TiO₂ hybrid spherical microbeads.

O: Carbonized-CT-1-30, •: Carbonized-CT-1-15

a) TiO₂ weight contained in microbeads: 165 mg

b) TiO2 weight contained in microbeads: 48 mg

surface of the TiO_2 photocatalyst by the surface diffusion efficiently.

4. CONCLUSION

Cellulose/TiO₂ hybrid spherical microbeads were prepared by a one-step phase separation method using a cellulose xanthate aqueous solution and a sodium polyacrylate aqueous solution. The distribution of TiO₂ particles on the hybrid spherical microbeads was found to be related to the electric repulsion between the CSS⁻ group and TiO_2 . The narrower the zeta potential distribution of TiO_2 particles, the more TiO_2 particles were driven out from the cellulose xanthate domain. The removal of acetaldehyde was confirmed to depend on the degree of appearance of TiO₂ particles on the surface of cellulose. In addition, the removal efficiency of acetaldehyde with hybrid spherical microbeads increased with their carbonization. The evaluations of the removal of acetaldehyde using the number of hybrid spherical microbeads corresponding to the TiO₂ content confirmed that the efficiency of the removal of acetaldehyde depends not only on the photodecomposition reaction induced by TiO₂ but also by the adsorption properties of the carbon matrix.

ACKNOWLEDGMENTS

The authors are grateful to the following individuals: Kohei Shiba of the Sysmex Corporation for providing Zeta-potential data and information on the particles used in these experiments; and Hiromi Kubo of Kumamoto University for his capable assistance.

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(Received December 23, 2004; Accepted September 15, 2005)