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Preparation of Porous Inorganic Oxides Capsules Utilizing the Interfacial Gelling Reaction. III

— Porous Titania Hollow Capsule —

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Abstract

Porous titania hollow capsules were prepared by making organic/inorganic hybrid gel membranes first and then sintering them, and the preparation conditions and the properties of the capsules were investigated. Use of the interfacial gelling reaction of N-lauroyl-L-glutamic acid- α,γ -di-n-butylamide (LGBA), an oil gelling agent, enabled us to prepare porous titania hollow capsules. Addition of drying control chemical additive (DCCA) to water was found to effectively prevent crack formation in the products. When ethylene glycol was used as DCCA, it retarded the hydrolysis and polycondensation of the metal alkoxide in the presence of base catalyst. It was also found that the crystal-form composition of porous titania hollow capsules changes with the temperature of heat treatment, namely, anatase-type of the titania is obtained at 600°C, but its rutile-type is obtained at 1000°C.

Key-words: *Interfacial gelling reactions, Porous titania hollow capsule, Nonaqueous gelling agent, Drying control chemical additive (DCCA), Hydrolysis of alkoxide*

1. Introduction

In recent years, the photocatalytic reactions of semiconductors have increasingly been studied. As a result, titania has been found to possess a remarkable catalytic activity. Titania, like silica and alumina, has also been

widely used as a carrier of various catalysts. Many investigations have been done to improve the efficiency of the metal oxide as a catalyst and carrier by increasing its specific surface area through pore-formation and micropulverization. On the other hand, Heller et al. have reported photochemical decomposition of sea pollution oil with hollow titania capsules, prepared by coating hollow glass beads with titania.¹⁾

We have prepared porous silica²⁾ and alumina³⁾ hollow capsules by use of oil gelling agent.^{4,5)} This technique allows to prepare hollow capsules simply by adding water

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dropwise to a four-component mixed solution consisting of N-lauroyl-L-glutamic acid- α, γ -di-n-butylamide (LGBA) derived from the amino acid (as the oil gelling agent), ethanol or other lower alcohol (as a good solvent for LGBA), tetraalkoxysilane or aluminumalkoxide (as an inorganic wall material), and oil. Although ethanol itself prevents the oil from gelling through binding to LGBA, it can move (dissolve) into water droplet which is added to the four component solution; thereby causing the oil to gel only in the vicinity of the water droplets. As gelling of the oil goes on, the hydrolysis and polycondensation of the metal alkoxide proceeds and the metal oxide formed is trapped in three-dimensional net work structures of the organogel. Porous metal oxide hollow capsules were prepared with heat treatment of the organogel yields.

In this report, titania was taken up as the wall material and the method to prepare porous as well as hollow titania microparticles was studied. The structure of capsule wall and the relation between the hydrolytic reaction rate of the metal alkoxide and the preparation conditions of capsules were also investigated.

2. Experimental

2.1 Methods

2.1.1 Materials

Titanium tetrakisopropoxide (TTIP, purity 99.999%, Kojundo Chemical Laboratory Co., Ltd.) was used as the starting compound of titania capsule wall. The oil, n-tetradecane (reagent grade, Tokyo Kasei Kogyo Co., Ltd.), was used without further purification. N-lauroyl-L-glutamic acid- α, γ -di-n-butylamide (LGBA, Ajinomoto Co., Ltd.) was employed as the oil gelling agent. LGBA can solidify organic solvents to produce gels because it forms molecular aggregates making a fibrous structure in the solvents through hydrogen bonding between the amide groups⁶⁾. The chemical structure of LGBA is shown in Fig. 1.

Fig. 1 Chemical structure of N-lauroyl-L-glutamic acid- α, γ -di-n-butylamide (LGBA).

Reagent grade isopropanol (Wako Pure Chemicals Industries, Ltd.) was used as supplied. Water (Japanese Pharmacopoeia distilled water for injection, pH 5.7, Otsuka Pharmaceutical Co.) was used as purchased.

Ethylene glycol, diethylene glycol, formamide, 1,3-butanediol, and glycerin (reagent grade, Tokyo Kasei Kogyo Co., Ltd.) as drying control chemical additives (DCCA) were employed without further purification. The pH of the water was adjusted by adding hydrochloric acid (reagent grade, Wako Pure Chemicals Ltd.) or 25% ammonia solution (reagent grade, Wako Pure Chemical Industries, Ltd.).

2.1.2 Preparation of porous titania hollow capsules

The procedures for preparing porous titania hollow capsules are shown in Scheme 1. To 1.8 g solution consisting of 1.6 g of n-tetradecane and 0.2 g of TTIP was added 0.01 g of LGBA and the mixture was allowed to gel by the heat-dissolving method.⁴⁾ Water containing a given amount of each of the DCCAs was added dropwise (5 μ l) with a microsyringe to four-component mixed solution A (n-tetradecane: TTIP: LGBA: isopropanol = 80: 10: 0.5: 9.5 (wt%)), which was prepared by adding 0.19 g of isopropanol to the gel obtained above to dissolve it. The system was permitted to stand for 1-720 min at 25°C. After washing the product obtained with hexane, it was collected by decantation and heat-treated to yield porous titania hollow capsules under air atmosphere at the high temperatures over 600°C with an electric furnace of Sanyo Rikagaku-Kikai Seisakusho (TYPE SYK-450-T).

2.1.3 Measurement of Powder X-ray Diffra-

Scheme 1 Preparation method of porous titania capsule with a cavity.

ction

Analysis of the crystal structure of capsule wall was done with an X-ray diffraction apparatus(Rigaku Denki KK, $\text{FeK}\alpha$ line). The samples were prepared by grinding the products made according to the procedures described in 2.1.2 in a mortar.

2.1.4 Observations with Scanning electron microscope (SEM)

Observations of the capsule surface were conducted with a scanning electron microscope (JXA-50A, JEOL).

2.1.5 Measurement of IR spectra

The IR spectra of the samples prepared according to the procedures in 2.1.2 were taken with a Fourier Transformation IR spectrophotometer (JIR-5300, JEOL) by use of the KBr method.

3. Results and Discussion

3.1 Effect of water on capsule formation

3.1.1 Effect of pH

In cases of silica hollow capsules²⁾ and

alumina hollow capsules³⁾, formation of the capsule was significantly affected by the pH of water trapped in the core of the capsule. So, in this work, capsule formation was also carried out using HCl solutions (pH 1.4 and 2.5), distilled water for injection (pH 5.7), and ammonia solutions (pH 9.3 and 12.5) to check the effect of pH of the water. No hollow capsule formation was observed irrespective of pH, because the product wall collapsed at the time of product collection from the four-component solution (mixed solution A in Scheme 1) or during air-drying process after product collection. The reason for this will be as follows. The alcohol and unreacted water still remain in the products and the former evaporates faster during the drying process because of its lower boiling point, which brings about increase in the water content and in the surface tension of the liquid (aqueous solution without the alcohol) in the product. This will make it easy for the product to break down through crack formation.⁷⁾

3.1.2 Effect of DCCA

DCCA prevents crack formation caused by the increase in surface tension of the aqueous solution involved since it remains longer in the product than water in the drying process.⁷⁾ Several DCCAs were tested to know how effective they were in preventing crack formation in the product when they were added to water. They should be soluble in water but not in oil and have a boiling point lower than that of water and a low surface tension. Capsule preparation was conducted using aqueous solutions (pH 5.7) containing each of the five DCCAs shown in **Table 1**. The reaction temperature was 25°C and the reaction time was 10 min. **Table 2** shows the states of reaction products with the DCCAs. Diethylene glycol and ethylene glycol were effective for the production of titania hollow capsules under all mixing ratios of water and DCCA. With formamide, the hollow capsule of titania was

Table 1 Surface tension and boiling point of DCCA⁸⁾ and Water⁹⁾

Liquid	Formula	Surface tension γ (mN/m)	bp (°C)
Formamide	HCONH ₂	58.35(20°C)	210.5
Ethylene glycol	HOCH ₂ CH ₂ OH	46.49(20°C)	197.85
Diethylene glycol	HOCH ₂ CH ₂ OCH ₂ CH ₂ OH	48.5(20°C)	244.8
1,3-butanediol	CH ₃ CHCH ₂ CH ₂ OH OH	37.8(25°C)	207.5
Glycerin	CH ₂ OH CHOH CH ₂ OH	63.3(20°C)	290.0
Water	H ₂ O	72.76(20°C)	100

Table 2 States of reaction products with various DCCAs.

DCCA	Water:DCCA(Weight ratio)						
	1:10	1:8	1:6	1:4	1:2	1:1	2:1
Formamide	○	○	○	○	×	×	×
Glycerin	—	—	—	—	○	○	×
1,3-Butanediol	—	—	—	—	○	○	×
Diethylene glycol	○	○	○	○	○	○	○
Ethylene glycol	○	○	○	○	○	○	○

○: The product has a cavity.

×: The product cannot be isolated.

—: The water drop is not spheric.

prepared in the range of mixing ratio from 1:10 to 1:4. For glycerin and 1,3-butanediol, it was prepared at both mixing ratios of 1:2 and 1:1, but no hollow capsule formation was observed at any mixing in the range of 1:10 to 1:4 because the water drops were broken. It should be noted that, for diethylene glycol and ethylene glycol, the hollow capsule of titania formed irrespective of mixing ratio. These results indicate that formation of hollow capsule depends on structure of DCCAs and mixing ratio of DCCA and water. Namely, when DCCA content involved is too low, the product must be broken.

Next, capsule preparation was carried out by use of the water at different pH and containing DCCA to study the effect of pH on

capsule formation in the presence of the additive. The DCCAs employed were ethylene glycol that allows hollow capsule formation at its mixing ratios to water in a wide range and formamide, which was used to prepare hollow alumina capsules³⁾. The results are shown in **Table 3**. With ethylene glycol, the water content to ethylene glycol which results in the capsule formation increased with an increase in pH except for pH 5.7, while with formamide, the pH did not depend on the mixing ratio of DCCA to water for the capsule formation.

Moreover, the effect on capsule formation of the standing time after adding water containing DCCA was investigated. Ethylene glycol and formamide were used as DCCAs at their weight ratio to water of 4:1. **Table 4** shows that no appreciable effect of standing time is observed on capsule formation at any pH after 2.5 or 5 min reaction when formamide is used. On the other hand, capsule formation generally needed longer standing time at higher pH in the presence of ethylene glycol. Thus, while capsule formation was observed after 2.5 or 5 min reaction at pH 1.4–5.7, it needed 10 min at pH 9.3 and 30 min or more at pH 12.5 because the products were otherwise broken down.

Table 3 States of reaction products under various pH dropped solutions.

DCCA	Water	Water : DCCA(Weight ratio)											
	pH	1:16	1:14	1:12	1:10	1:8	1:6	1:4	1:2	1:1	2:1	4:1	
Ethylene glycol	1.4	×	○	○	○	○	○	○	—	—	—	—	
	2.5	×	×	×	×	×	○	○	○	×	×	×	
	5.7	×	○	○	○	○	○	○	○	○	○	×	
	9.3	×	×	×	×	×	×	○	○	○	○	×	
	12.5	×	×	×	×	×	×	×	×	○	○	○	
Formamide	1.4	×	○	○	○	○	○	○	○	×	×	×	
	2.5	×	○	○	○	○	○	○	○	×	×	×	
	5.7	×	×	×	○	○	○	○	×	×	×	×	
	9.3	×	×	○	○	○	○	○	×	×	×	×	
	12.5	×	×	×	×	○	○	○	○	×	×	×	

Table 4 States of reaction products for various reaction times.

Water drop		Standing Time/min						
DCCA	pH	1	2.5	5	10	30	120	720
Ethylene glycol	1.4	×	○	○	○	○	○	○
	2.5	×	×	○	○	○	○	○
	5.7	×	○	○	○	○	○	○
	9.3	×	×	×	○	○	○	○
	12.5	×	×	×	×	○	○	○
Formamide	1.4	×	○	○	○	○	○	○
	2.5	×	○	○	○	○	○	○
	5.7	×	○	○	○	○	○	○
	9.3	×	×	○	○	○	○	○
	12.5	×	×	○	○	○	○	○

○: The product has a cavity.

×: The product cannot be isolated.

The reason for this will be the following. Glycols and metal alkoxides are known to react with each other as shown in **Scheme 2**.¹⁰⁾ According to the Partial-Charge model by Livage et al.¹¹⁾, while the polycondensation of metal alkoxides occurs preferentially at the terminals of polymer chains in the presence of acid catalyst, the reaction proceeds at the middle part of polymer chains if base catalyst is present. Hence, when hollow capsules are prepared by use of ethylene glycol as DCCA, the reaction at the middle of polymer chains will be hampered by a steric hindrance if basic water is employed since the OPr^{I} radicals of TTIP are replaced by bulky ethylene glycol molecules. That is, no strong capsule walls

could have been obtained unless smaller ratios of DCCA to water or longer standing times were used because the hydrolysis and polycondensation reaction of TTIP are retarded.

Figure 2 is typical SEM pictures of a porous titania hollow capsule prepared by use of formamide-water mixture (mixing ratio is 4: 1, pH 5.7), the standing time of 10 min. The capsule kept its spherical shape with a diameter of about 1.5 μm without breaking down in the air (**Fig. 2(a)**) and was proved to be a hollow particle when it was cut down by an external force (**Fig. 2(b)**).

3.2. Effect of heat treatment on the capsule properties

Scheme 2 Reactions of metal alkoxides with glycols. **Fig. 2** SEM photographs of titania capsule with a cavity.

3.2.1 Structure change of capsule wall

Figure 3 shows the XRD patterns before heat treatment and after heat-treated for 2 hr in the air at 600°C, 700°C, and 1000°C, respectively, of the hollow capsules obtained. The diffraction patterns indicate that the capsule wall before heat treatment is amorphous form and the sample heat-treated for 2 hr at 600°C is anatase (TiO_2). It is also shown that the capsule became a mixture of anatase and rutile TiO_2 after heating for 2 hr at 700°C and changed into 100% rutile TiO_2 after heating for 2 hr at 1000°C.

Figure 4 illustrates the IR spectra of the hollow capsules obtained by heat treatment at different temperatures. Absorption bands were observed at 1620 cm^{-1} and 1575 cm^{-1} are attributable to the amide groups (amide I and II)¹²⁾ of LGBA.

By heat-treatment of the hollow capsule at 600°C, these bands disappeared, then a broad peak and a sharp peak were observed at 900–

500 cm^{-1} and 358 cm^{-1} , respectively. These peaks are due to the lattice vibrations of crystalline TiO_2 .¹³⁾ The spectrum of the capsule heat-treated at 700°C and 1000°C were observed at near 412 cm^{-1} , in addition to that at 358 cm^{-1} . The bands probably are due to a new lattice vibration of O defects. It is considered that the number of existing O defects in TiO_2 crystal tends to increase when the sample acquires energy through UV light irradiation.¹⁴⁾

3.2.2 Surface structure change of capsule wall

Figure 5 is SEM photographs of the TiO_2 hollow capsule surface and the one heat-treated at 600°C and 1000°C. Tiny spherical particles and many pores were seen on the capsule surface after heating though they were not observed before heating. This would be caused by burning down of the organogel trapping TiO_2 particles in its inside during heat treatment, in view of the change in IR spectrum appeared after heating shown in Fig. 4. It was

Fig. 3 X-ray diffraction patterns of titania capsule heated at various temperatures. A, anatase; R, rutile.

Fig. 4 IR spectra of titania capsule with a cavity heated at various temperatures.

Fig. 5 SEM photographs of hollow TiO_2 capsule surface and the heat-treated one.

also observed that heat treatment at 1000°C produced large particles on the capsule surface, compared with the treatment at 600°C, showing an effect of sintering at high temperature.

4. Conclusions

Porous hollow titania capsules were prepared by the interfacial gelling reaction of LGBA added as the oil gelling agent. This technique should be very simple only by adding water dropwise including drying control chemical additive (DCCA) to a four-component mixed solution consisting of oil gelling agent/lower alcohol/oil/titanium tetraisopropoxide. Addition of DCCA to water was found effective in preventing crack formation in the product in the drying process. However, the formation of hollow titania capsule depended on structure of DCCA. Especially, diethylene glycol and ethylene glycol as DCCA gave us the porous hollow capsule of titania at any mixing ratio

of DCCA and water. This may be attributed the fact that the use of glycol retards the hydrolysis and polycondensation of alkoxides in the presence of base catalyst. From XRD patterns and IR spectra, the crystal-form composition of porous titania hollow capsules was found to change with the temperature of heat treatment, namely, anatase-type of the titania is obtained at 600°C, but its rutile-type is obtained at 1000°C.

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界面ゲル化反応法による多孔質無機酸化物カプセルの調製 (第3報) —多孔質酸化チタンカプセル—

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要 旨

界面ゲル化反応法を用いて作製した有機物/チタニアハイブリッドゲル膜を焼成することにより多孔質チタニア中空カプセルの作製を試み、その調製条件および物性を検討した。

油ゲル化剤 LGBA の界面ゲル化反応を利用して、酸化チタン壁膜を有する多孔質中空カプセルを作製することができた。また、乾燥操作による生成物表面の亀裂生成を防ぐためには滴水への乾燥制御剤の添加が有効であり、とくにエチレングリコールを制御剤として用いた場合、塩基触媒下で金属アルコキシドの加水分解および重縮合反応が抑制されることが分かった。さらに、熱処理温度によって酸化チタン中空カプセルの結晶型の組成が変化すること、すなわち、処理温度が 600°C ではアナターゼ型 TiO₂、1000°C ではルチル型 TiO₂ が得られることがわかった。