

Enzyme Catalyzed Preparation of Hollow Alumina Precursor Using Emulsion Template

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エマルジョンテンプレートを利用した酵素法アルミナ前駆体中空粒子の作製

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Hollow alumina precursor was prepared by the enzyme-inspired precipitation onto o/w emulsion using urease. Decomposition of urea by urease increased the pH of the solution to hydrolyze aluminum sulfate. The advantages of the enzymatic reaction are that the apparent precipitation rate could be controlled by the enzyme concentration of urease, and that the precipitation could take place without the destruction of emulsion. Hollow particles were obtained at enzyme concentrations ranging between 10 and 50 mg/l. The destruction of the emulsion occurred at enzyme concentrations < 10 mg/l while nucleation took place spontaneously in the solution at enzyme concentrations > 50 mg/l. Hollow powders with the phase of pseudo-boehmite, maintained their apparent shape after transformation into α -alumina at 1300°C.

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1. Introduction

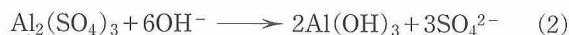
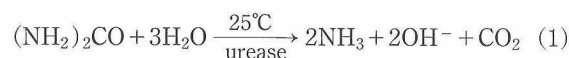
Ceramic hollow particles have a potential as catalyst media because of their high surface area and light weight. Some liquid phase synthesis techniques have been developed to produce hollow particles using an emulsion as a template. The interfacial reaction method^{1)–4)} utilizes precipitation on the oil–water interface by the reaction between hydrophobic component in the oil phase and hydrophilic one in the water phase. Therefore this technique requires effort to find the suitable combination of hydrophilic and hydrophobic components.⁵⁾ Numerous papers used w/o emulsion as a template, and spherical or hollow particles could be obtained by precipitation within the spherical water phase. However, there are few reports on o/w emulsion system although this system is preferred in the aspect of industrial applications.^{6),7)}

The sol-gel process using metal alcoxide is often employed for produce precipitation onto the emulsion,⁸⁾ nevertheless the byproduct alcohol may destroy the emulsion because of its tendency to mix both oil and water.⁹⁾ Hydrolysis of metal salt by thermal decomposition of urea is an alternative and typical precipitation technique without formation of alcohol. However, heating of the solution up to 90°C will also destroy the emulsion. In the previous works,^{10),11)} we demonstrated that homogeneous precipitation at room temperature could be carried out by enzymatic reactions. Another advantage of the enzyme catalyzed precipitation is that the apparent precipitation rate could be controlled by the enzyme concentration. In this work, we described the precipitation of alumina precursor onto the o/w emulsion by the decomposition of urea using urease.

2. Experimental procedure

The starting materials were aluminum sulfate, urea and polyoxyethylene(20) sorbitan monolaurate (Tween20, HLB=16.7, Wako Pure Chemical Ind., Ltd., Osaka). Urease (Nagapsin, derived from *Lactobacillus fermentum*, 2000 active units/g) was supplied by Nagase Biochemicals, Kyoto. Equations (1) and (2) show preparation of alumina

precursor via hydrolysis of aluminum sulfate by enzymatic decomposition of urea.



Decomposition of urea by urease increases the pH of the solution (Eq. 1). Subsequently aluminum hydroxide is formed by hydrolysis of aluminum sulfate (Eq. 2). The composition of the starting solutions are shown in Table 1. After aluminum sulfate, urea, and Tween20 were dissolved and mixed in a aqueous solution, chloroform was added as an oil phase. Urease was added after emulsification in order to prevent the deactivation of the enzyme. Resulting precipitates were filtered and washed by water and ethanol for several times before freeze-drying. Characterizations of the products were performed by scanning electron microscopy (SEM; JSM-6100, JEOL, Tokyo), thermogravimetry and differential thermal analysis (TG-DTA; Model TGDTA2000, Mac Science, Yokohama), and X-ray diffraction (XRD; Model RINT 1000, Rigaku, Tokyo).

3. Results and discussion

Figure 1 shows SEM micrographs of the precipitates. The precipitate (a) H-3 was obtained by usual homogeneous precipitation¹⁰⁾ that means the absence of emulsion template. Hollow particles were obtained from the solutions (c) E-10, (d) E-30 and (e) E-50. In the solutions (b) E-3 and (f) E-90 homogeneous nucleation occurred in the same way as in the case of (a) H-3. The destruction of the emulsion proceeded in the (b) E-3 solution before precipitation because the precipitation occurs very slowly under such a low concentration of enzyme. On the other hand, homogeneous nucleation not on the o/w interface but in the solution might preferably take place in the (f) E-90 solution with a high concentration of enzyme. The effect of enzyme concentration on the precipitation is schematically illustrated in Fig. 2.

Table 1. Composition of the Starting Solutions

Solution	$\text{Al}_2(\text{SO}_4)_3$	$(\text{NH}_2)_2\text{CO}$	Urease	Tween20	CHCl_3
	mmol/l		mg/l	mass%	vol%
H-3	4.38	41.6	3	0	0
E-1	4.38	41.6	1	0.1	1.0
E-3	4.38	41.6	3	0.1	1.0
E-10	4.38	41.6	10	0.1	1.0
E-30	4.38	41.6	30	0.1	1.0
E-50	4.38	41.6	50	0.1	1.0
E-90	4.38	41.6	90	0.1	1.0

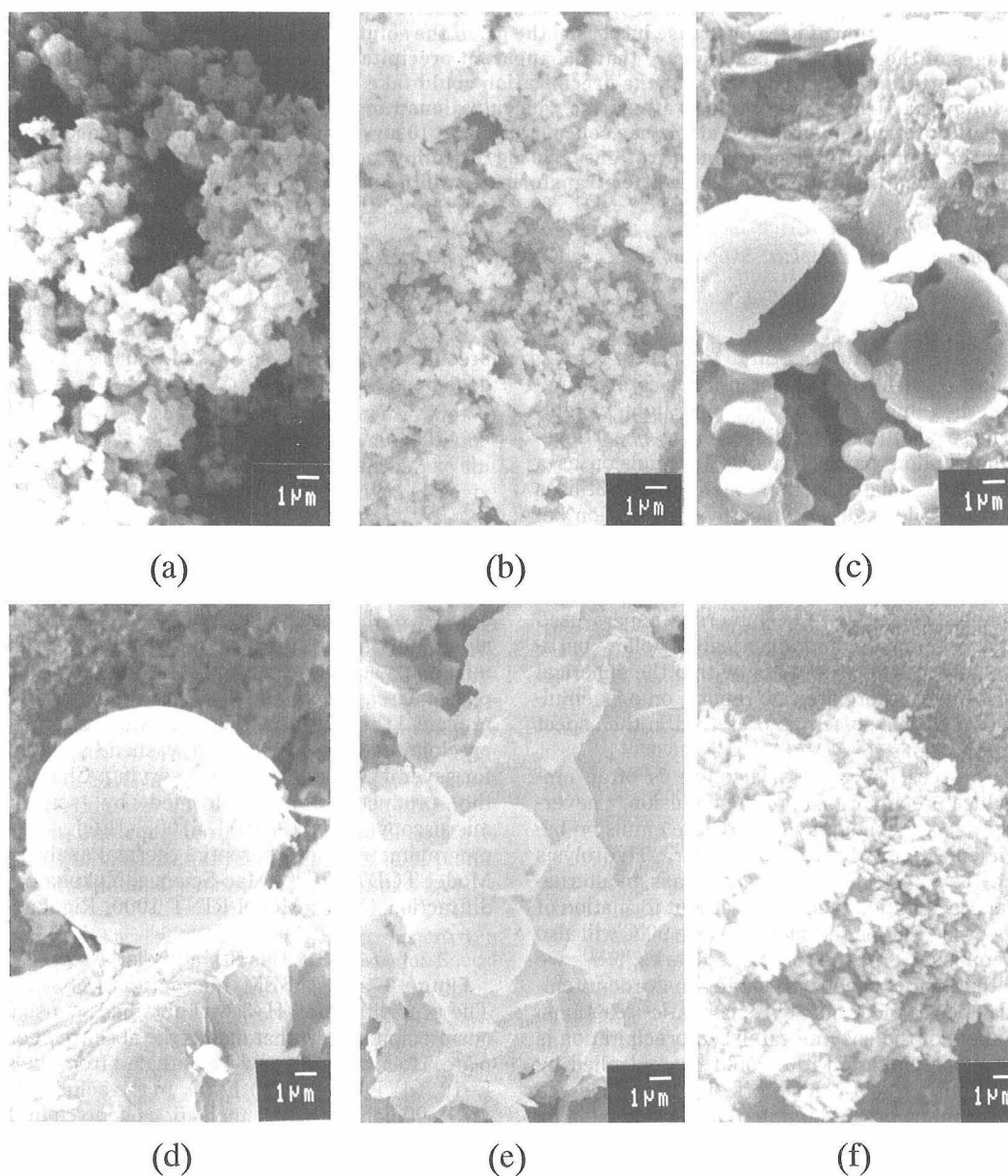


Fig. 1. SEM micrographs of alumina precursor obtained from the solutions (a) H-3, (b) E-3, (c) E-10, (d) E-30, (e) E-50 and (f) E-90.

Figure 3 shows the TG-DTA curves of the E-30 hollow precipitate. The continuous endothermic weight loss up to

400°C results from dehydration that is inherent to pseudo-boehmite. The sharp endothermic weight loss observed at

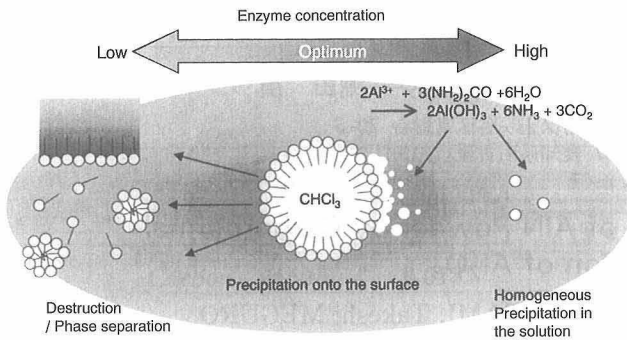


Fig. 2. Schematic representation of the effect of enzyme concentration on precipitation behavior.

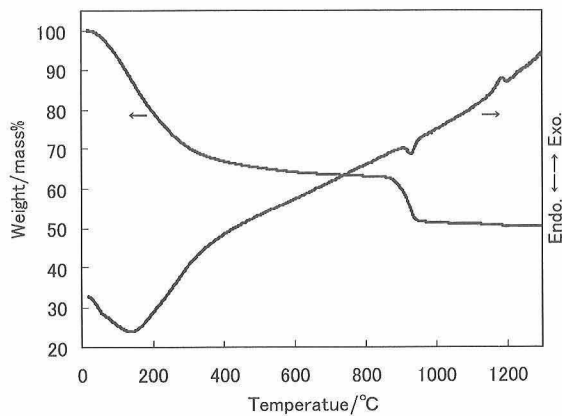


Fig. 3. TG-DTA profiles of hollow alumina precursor obtained from solution E-30 on heating rate 5°C/min.

900°C could be attributed to the decomposition of sulfate ions. The final exothermic peak around 1200°C without weight loss is attributed to the transformation into α -alumina. The results of thermalgravimetric analysis are almost identical to those of the homogeneous precipitation of alumina precursor using urease.¹⁰⁾

Figure 4 shows the XRD patterns of the precipitates. The hollow alumina precursor E-30 showed a fair crystallinity, compared with the non-hollow precipitates E-3 and H-3. One of the possible reasons is that the ordered hydrophilic groups of the surfactant affected on the precipitation process as similarly as the stearic acid mono layers control the crystal growth of CaCO_3 from the solution.¹²⁾ Figure 5 shows that the hollow precursors preserved its original shape after calcination at 1300°C. The shell of calcined hollow particles exhibited a porous and vermicular structure.

4. Conclusions

Hollow alumina precursors were precipitated from the o/w emulsion system at room temperature, using enzymatic decomposition of urea. The apparent precipitation rate could be controlled by the enzyme concentration. Resultantly, hollow particles could be obtained at enzyme concentrations ranging between 10 and 50 mg/l. The destruction of emulsion occurred at enzyme concentrations of < 10 mg/l while spontaneous nucleation in the solution took place at enzyme concentrations > 50 mg/l. The original phase of hollow particles was pseudo-boehmite and their apparent

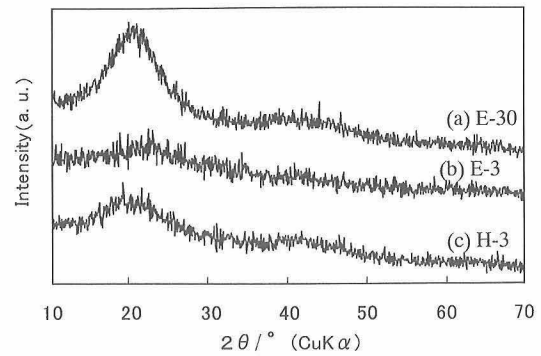


Fig. 4. XRD patterns of the alumina precursors obtained from solutions (a) E-30, (b) E-3 and (c) H-3.

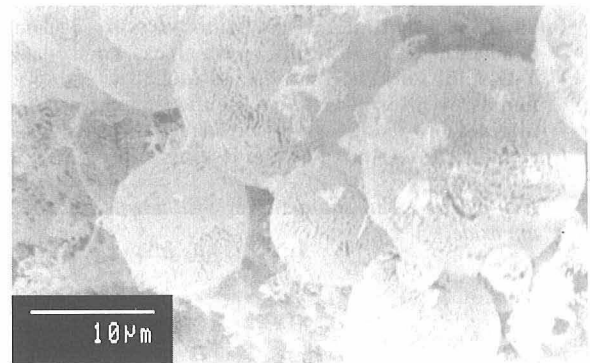


Fig. 5. SEM micrographs of hollow alumina after calcination at 1300°C of E-30.

shape was preserved even after transformation to α -alumina at 1300°C. This study demonstrated that precipitation onto the o/w emulsion using enzymatic reaction can be an innovative process to produce hollow ceramic particles.

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