Fabrication of bimodal (meso/macro) porous alumina materials using yeast cells as templates*

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Bimodal (meso/macro) porous alumina materials were synthesized using yeast cells as bio-templates. Aluminium isopropoxide (AIP) modified with triethanolamine (TEA) was first hydrolyzed by water containing the dispersed yeast cells. This resulted in the formation of slurry consisting of hydrolyzed sol and yeast cells. After centrifuging the solution, the obtained cake which is packed with hydrated sol and yeast cells was subjected to heat treatment. The sample after heat treatment contained finely dispersed bimodal (meso/macro) pores ranging in size from 1.5 to 2.0 µm and several nm. Under the present experimental conditions, the thickness of alumina wall was also controlled by changing the ratio of yeast cells to AIP. It was also observed that with an increase in the thickness of the wall, the size of the pores decreased. [DOI: 10.1380/ejssnt.2005.405]

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I. INTRODUCTION

The development of porous ceramic materials presents a new challenge, because porous ceramics are more durable in severe environments and their surface characteristics permit them to satisfy very specific requirements. The growing demand for porous ceramics, both in scientific research as well as in technological development, has resulted in novel porous ceramic materials through new synthesis routes and improved processing. By tailoring properties like pore structure and pore size, porous ceramics are considered for use in a vast range of applications which include catalysis (e.g. methane combustion [1], catalytic converters [2]), filtration [3] and separation, and sensing [4].

Polystyrene beads and silica gel have been successfully employed as physical templates for obtaining macropores [5]. Monodispersed particle arrays with regular pores have also been fabricated by using a colloidal matrix with windows as lithographic mask [6]. In order to fabricate the nano size and to keep the highest specific surface area, the phase transformation temperature of γ alumina (to α alumina) was raised remarkably by the addition of silica to γ alumina [7]. The surface properties were also changed by modifying the surface of the carrier [8].

In recent years, synthesis and design of various new materials are carried out using natural models as original hierarchial structure and this technique is referred as "Biotemplating". For example, bacteria [9], plant cell [10], starch gel [11] and DNA [12] are used as templates to fabricate various inorganic compounds. Out of the natural models, the yeast cells which are used for brewing and leaven are highly interesting material to act as templates. This is due to that yeast cells are composed of a comparatively solid cell wall [13], with enough hardness that fulfills the function of acting as a template. In addition, they also have the flexibility to soften. This property is very important in order to influence a change in volume of porous materials when they are subjected to sintering.

Exploiting these potential advantages of yeast cells, in the present investigation, a new approach has been developed for the preparation of bimodal (micro/macro) porous alumina materials using the sol-gel method and by using yeast cells as template. It has been observed that by carefully controlling the preparation conditions, it is possible to control the size of pores as well as the thickness of the material.

II. EXPERIMENTAL

Yeast cells used for templating were alive bread yeast (Saccharomyces cerevisiae, Oriental Yeast Co., Ltd.) and were washed several times with water. Aluminum isopropoxide (Nacalai Tesque, Inc.) was used as a source of aluminum oxide and triethanolamine (TEA) (Nacalai Tesque, Inc.) was used as a stabilizer.

The preparation process of porous alumina material using yeast cells was accomplished as follows. At first, solution A was prepared by mixing TEA with AIP at a

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fixed rate and was stirred at room temperature for 12 h. After that, water was added with continuous stirring. Separately, solution B was prepared by adding yeast cells to water and was dispersed for sometime. Solutions A and B were then mixed and stirred for 60 h in order to complete the hydrolysis as well as the deposition of the hydrolysis products on the surface of yeast cells. The slurry with yeast cells and aluminum hydroxide were then washed with ethanol and water, followed by centrifuging the resulting solution. The yeast cells were then removed by heat treatment in between 500–1000°C that resulted in the crystallization of alumina together with thermal decomposition of organic matter.

The crystalline phase analysis of synthesized aluminum oxide powders was performed using X-ray diffractometry (XRD; Model RINT-2550/PC, Rigaku Co., Japan) with CuKα radiation. Thermogravimetric analysis (TG) and differential thermal analysis (DTA) were performed using a simultaneous micro-DTA/TG apparatus (Model 2020S MK12, MAC Science) to study the dehydration or combustion. Samples were accurately weighed to five decimal places in a platinum crucible and weight losses were recorded from 25–1200°C in air atm at a heating rate of 10°C/min and by using α-alumina as a reference. Powder morphology was determined by using a JEOL JM-5600N scanning electron microscopy (SEM) and by using a JEOL JEM-2010 transmission electron microscopy (TEM) operating at 200 kV. Energy dispersive X-ray spectroscopy (EDS) was used for compositional analyses. N₂ adsorption/desorption experiments were carried out using OMNISORP360 apparatus from Coulter. The pore size distributions were calculated using the Barret-Joyner-Hallenda (BJH) model on the desorption branch. Surface areas were calculated using conventional Brunauer, Emmett and Teller (BET) method.

III. RESULTS AND DISCUSSION

A. Effect of TEA addition

TEA has aminoethanolic groups, the alcoholic group of which reacts easily with AIP to form the aminoalcoholate, a chelate compound and thereby stabilizes AIP. After forming the chelate compound, it was then hydrolyzed and heat treated. To understand the effect of TEA addition, AIP without TEA was similarly hydrolysed and subjected to heat treatment.

The advantage of TEA addition during the preparation of as-prepared sample obtained after hydrolysis was investigated by the thermal analysis (Fig. 1) and SEM observations (Fig. 2). The sample obtained without TEA shows an endothermic reaction at 280°C in DTA. This peak could be considered to be due to the dehydroxylation of aluminum hydroxide [4]. This is further supported by TG which shows a weight loss of 35% corresponding to the water weight loss of 35% as represented by the following equation, 2Al(OH)₃ → Al₂O₃ + 3H₂O. Whereas, in the case of sample obtained with TEA, no such endothermic peak has been observed. Surprisingly, presence of exothermic peaks could be observed at 383°C and 492°C in DTA. These peaks could be assumed to be due to the combustion of unreacted products of TEA, because TEA ignites at 324°C. In addition, from TG analysis, it can be observed that for the samples obtained without TEA, the weight loss completes at 300°C. Alternatively, for the samples obtained with TEA the weight loss continues at 500°C also. This maybe due to that the synthesized hydroxide sol is stable even at this high temperature.

From Fig. 2(a), it can be observed that, in the absence of TEA, macropores were not formed, but with the addition of TEA, it forms several m sized pores and the walls are very well separated from them (Fig. 2(b)). The process that leads to the formation of as-prepared product is associated with the synthesis and the combustion of the aluminum hydroxide sol, the dispersion and arrangement of yeast cells and packing of sol. The yeast cells are getting dispersed sufficiently during stirring because of the hydrophilic surface. The aluminum hydroxide sol was then synthesized on the surface of the yeast cells and in the solution after addition of the modified AIP in water.
FIG. 2: SEM photographs of the samples heated at 1000°C for 3h in air: (a) without TEA and (b) with TEA.

The yeast cells and aluminum hydroxide sol are considered to be coexisting in the solution. Thus, by centrifuging, formation of cake without any deformation and separation of the yeast cells and the aluminum hydroxide sol could be obtained. The cake when subjected to heat treatment then leads to the formation of porous materials homogeneously dispersed with macropores.

In the crystal extraction of the biomembrane, it is known that the lipid, the sugar chain, and the film protein on the biomembrane act as the place for the heterogeneous nuclear generation [15]. It is thought that phosphoric acid, sugar or the protein of the lipid similarly contributes to an initial, nuclear generation as for this yeast cell. Therefore, the aluminum hydroxide synthesized by the hydrolysis reaction separate out from the surface of yeast, and sol is mixed enough with the yeast cell. Moreover, it cannot be easy to do the space between yeast and sol. Also, shape and the size of yeasts can be imitated.

B. Effect of heat treatment on the microporous structure

The SEM photograph of the composite of yeast cells and sol obtained after drying the dispersion has been shown in Fig. 3. The sol is covered on the surface of yeasts and nonuniform cohesion between the sols was not found. Also, aggregation of yeasts could not be found.

Figure 4 shows the TG and DTA curves of the yeast cells and the composite consisted of aluminum hydroxide and yeast cells. In DTA, generation of peaks or signals observed at 310°C and 480°C are due to exothermic reaction corresponding to the decomposition of yeast. In TG and DTA, yeast cells were subjected to heat treatment in presence of N₂. It can be observed that the exothermic reaction was small, but it resulted in the formation of 2 µm pores with the trace of the yeast bud remained in the pore. Looking at this, we have confirmed that the pores should have been formed by the burnout of yeast cells. Due to heat treatment the sample contracts and hence the pores and this is the reason for the difference between the size of yeast cells and pores that have been observed.

FIG. 3: SEM photograph of the sample before heat treatment.

FIG. 4: TG-DTA curves of the samples: (a) yeast cells (b) composite consisted of aluminum hydroxide and yeast cells.
FIG. 5: SEM photographs of the sample at different annealing temperatures (a) 1100°C and (b) 1200°C for 3h in air.

The broken face was smooth and grain boundary was not found for the samples heat treated at 1100°C for 3h (Fig. 5(a)). It could be observed that the maximum size of macropores was 2 µm, with the pores dispersed continuously. The TEM photograph of the sample heat treated at 1000°C as shown in Fig. 6 shows that the wall consists of nano particles of γ alumina. In the case of sample obtained by heat treatment at 1200°C for 3 h, as shown in Fig. 5(b), we can observe that the matrix of particles grew from wall up to 5 µm size needle like particles and surround the macropores. The wall of matrix particles are also connected with each other, with distorted shapes in macropores.

The X-ray diffractions of samples obtained at different annealing temperature have been shown in Fig. 7. In the case of as-prepared sample, it shows an amorphous nature, but with heat treatment at 900°C, peaks of γ alumina could be observed. Increasing the annealing temperature further to 1100°C results in an increase in the intensity of γ alumina peak. Whereas, the sample obtained at 1200°C shows the sharp peak of α alumina with the complete disappearance of γ alumina peak. Also, the peak of aluminum phosphate could be observed at 20° which results due to the reaction of phosphorous from the yeasts with alumina.

X-ray diffraction along with SEM observations confirms that γ alumina formation occurs at 1100°C and there is no change in volume. But by subjecting it to heat treatment at 1200°C, the crystal change occurs from γ to α alumina which can be observed from X-ray diffraction studies. Whereas, from SEM, it can be observed that at 1200°C formation of needle like particles occurs and this results in a large change in the volume. Normally, α alumina has a sphere shape, but, the formation of parti-
In order to investigate the effect of heat treatment on the formation of porous structure, the specific surface area and pore distribution were measured at different temperatures. Figure 8 shows the specific surface area obtained as a function of heat treatment temperature. The specific surface area of the sample obtained at 900°C is 205.1 m²/g, which gradually decreases with an increase in temperature, and thus results in the specific surface area of 38.4 m²/g at 1200°C. There are two reasons that results in a decrease in surface area with an increase in temperature. At first, growth of alumina particles occurs with an increase in temperature and secondly, at 600°C formation of mesopores occurs by the release of TEA which decreases with an increase in temperature.

Figure 9 shows the pore size distribution obtained under 2 nm as a function of heat treatment temperature. The peak value of pore size distribution was 0.5 nm at 900°C as well as at 1000°C, which further increased to 0.6 nm at 1100°C, and completely disappeared at 1200°C. The mesopore volume also decreased with increasing the heat treatment temperature.

Figure 10 shows the pore size distribution obtained over 2 nm as a function of heat treatment temperatures. The peak value of pore size distribution was 6.7 nm at 900°C, 8.8 nm at 1000°C, 10.8 nm at 1100°C, and completely disappeared at 1200°C. The largest volume obtained at 900°C, which decreased with increasing heat treatment temperatures. The narrow pore size distribution was found at 900°C with the observation of largest pore was 10 nm, at 1000°C the largest pore was 12 nm, whereas at 1100°C the largest pore was 15 nm. In addition, it was also observed that narrow pore size distribution decreased with an increase in heat treatment temperatures.

C. Control of the microporous structure

In the slurry obtained after centrifuging the mixed solution containing the yeast cells and aluminum hydrate, separation among yeast cells and aluminum hydrate could not be observed. So the ratio of pore volume formed by the disappearance of yeast cells and alumina volume could be changed by changing the ratio of yeast cells to AIP.
FIG. 11: BET specific surface area of the sample obtained with different ratio of yeasts to AIP.

FIG. 12: Pore size distribution over 2 nm obtained from the desorption branch as a function of the ratio of yeast to AIP.

FIG. 13: Pore size distribution under 2 nm obtained from differential HK volume as a function of the ratio of yeast to AIP.

The thickness of wall could also be changed by controlling those ratios. From SEM observation it can be seen that the thickness of wall is in submicrometer and this thin wall is united with the pores. It is predicted that this structure continues to all of the bulk in three-dimensions. With an increase in the ratio, the thickness of wall was also in submicrometer, but a decrease in the number of pores could be observed.

The resultant effect of change in specific surface area of the sample with a change in the ratio of yeasts to AIP has been shown in Fig. 11. The thickness of wall as estimated from SEM varies from 0.1 to 0.2 µm. The wall is so thin that the contents of the yeasts, for example, phosphorus, permeates to the wall during the heat treatment. The particles of the wall with the yeast cells grow rather than the usual alumina particles. Thus, the size of particles increased that result in a decrease in specific surface area. The specific surface area of the sample which has a wall with the width of 0.3 to 0.5 µm was 118.8 m²/g and for the sample which had the wall thickness of 1 µm, the surface area decreased to 49.4 m²/g, and further decreased to 39.7 m²/g with an increase in the thickness of wall. The specific surface area of porous alumina material prepared without using the yeast cells was 29.6 m²/g.

Figure 12 shows the pore size distribution during the desorption process. The peak value of pore size distribution changed from 7.5 to 9.5 nm. With an increase in pore size, its distribution becomes wider and the peak pore volume decreased with the wall getting thin. The peak of pore size distribution for the sample obtained without using the yeast cells was 7.5 nm and has very narrow distribution and had the highest peak pore volume. The isotherms suggest that the pore volume decreased from 205 cc/g to 190 cc/g with an increase in the thickness of wall. The sample obtained without using the yeast cells has the least pore volume of 150 cc/g.

The micropore distributions have been shown in Fig. 13. In the case of micropores, the peak value of distribution of all the samples were 0.5 nm and the distribution shapes also remain same for all the samples. The macropores formed by the disappearance of yeast cells which were used as templates and have been proved to be effective for the porous properties. When the material had the macropores and thin wall, N₂ gas could penetrate inside the wall as well as getting adsorbed on the surface of nano particle. But without macropores, the volume also decreased. In the case of material with too thick wall, N₂ gas could not penetrate through the wall. In addition, N₂ gas could also not be adsorbed by some particles.
and this is the reason that the specific surface area of samples with too thick a wall is smaller than that of the samples having appropriate thickness regardless of both having the same particle size. Another reason could be that a difference in thermal stress to nano particles occurred with a difference in the wall thickness. In the case of thin wall, there is a horizontal tensile stress and the distance between the particles becomes wide. This results in a slow sintering. Whereas, in the case of thick wall, due to the vertical thermal stresses, the contact surface area between the particles is large and thereby sintering becomes so easy.

IV. CONCLUSIONS

The porous alumina materials were prepared by using the yeast cells as bio-templates. In the water solution dispersed with yeast cells, the aluminum hydroxide sols were synthesized by hydrolysis of AIP modified by TEA. The slurry mixed with yeast cells and aluminum hydroxide was then obtained. The composite with yeast cells and aluminum hydroxide were formed by centrifuging this slurry. The porous alumina materials had the bimodal (macro/meso) pores from 1.5 to 2 µm and from 2 to 20 nm homogeneously after the disappearance of yeast cells and the dehydration and sintering of AIP by heat treatment. The ratio of pore to wall, namely the thickness of the wall, was also possible to change by controlling the ratio of yeast to aluminum hydroxide. The highest specific surface area was obtained with 0.4 AIP / yeast ratio and this value decreased with an increase in the ratio of AIP to yeast. The peak of the pore size distribution decreased with an increase in the thickness of wall.

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