

Preparation of Metal/Metal Oxide Network Using Organic Polymer Gel

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Inorganic networks of metal/metal oxide (Fe , Fe_xO_y , TiO_2) were prepared using organic polymer gels as a template and/or a reaction field in which the inorganic networks were synthesized. The inorganic networks were obtained by introducing a starting material of metal/metal oxide into the organic polymer gel followed by a stabilization of the starting material and a heat-treatment. The inorganic network was produced during the stabilization and the heat-treatment process. The organic polymer gel was also removed during the heat treatment. Characterization of the produced metal/metal oxide networks was carried out in terms of produced phase, network structure, elemental distribution of the constituents, specific surface area and pore size distribution of the network by means of XRD, SEM with EDX, BET and BJH analysis. The produced network was constituted by chains of particles with several hundreds nanometer to micrometer in diameter. The organic polymer gel was found to be useful as the template and/or reaction field to produce the inorganic network rather simply.

Key words: Organic polymer gel, Template, Metal/Metal oxide network, Synthesis

1. INTRODUCTION

Synthesis of mesoporous inorganic materials has been attracting much attention because of their importance in many engineering fields such as separation, catalysis, and so on. Several synthetic routes to produce the mesoporous inorganic materials simply and rigorously have been reported by many researchers. Porous materials can be classified from a viewpoint of ratio of pore size to wall size as shown in Fig.1. Synthesis using templates such as surfactant and some organic or inorganic nano-particles is general method to create micro and meso pores [1]. In the case of cellular solid with large pores, techniques such as liquid metals forming [2,3] and template method using particles with sub-mm to mm diameter were used. In spite of these a lot of studies, there are few reports that study the synthetic method of porous materials that have a network structure with several hundreds to micrometer size open pores. The porous material with the network structure is considered to be useful in an application such as adsorbent, micro reactor, energy absorber and photoactive agent. Caruso *et al* recently reported the synthesis of the TiO_2 network by means of reverse replication of cellulose based organic polymer gel and showed the effectiveness of the organic polymer gel

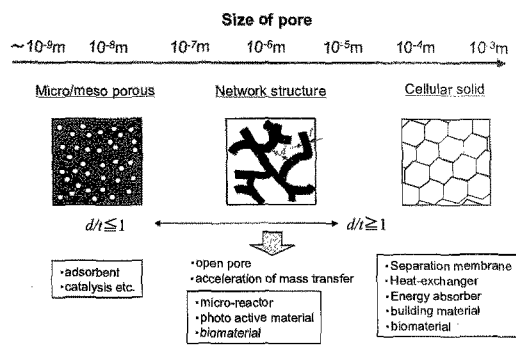


Fig.1 Inorganic Porous materials

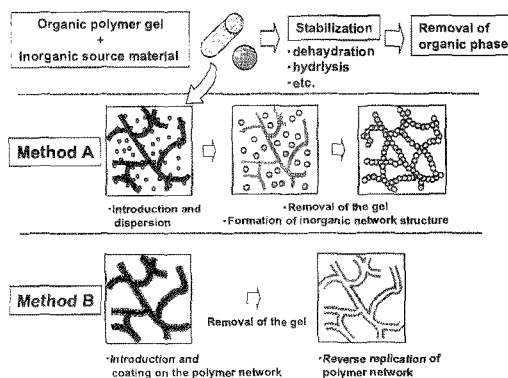


Fig.2 Schematic diagram of the synthetic method

network as a template of reverse replication in the preparation of the inorganic. The crosslinked organic polymer gel is a potential template material for the synthesis of inorganic network with wide range of open pores. The pore size of the inorganic network will depend on the network structure of the template gel. The synthesis using the crosslinked organic polymer gel is also a potential method to produce monolithic inorganic network. There is a possibility of controlling outer shape of the inorganic network by adjusting shape of the crosslinked organic polymer gel.

In the present study, Synthesis of porous inorganic network with micro to macro pores was examined using crosslinked organic polymer gel as the template of the network structure of the inorganic network and/or a reaction field in which the inorganic network was produced.

2. EXPERIMENTAL

2.1 Synthesis performed in this study

Schematic diagram of synthetic method of the inorganic network performed in this study is shown in Figure 2.

Method A: Metal ions were introduced in organic ionic

polymer gel through ion exchange. Using ionic gel, the introduced metal ions were well dispersed and immobilized electrostatically on the network of the gel. The introduced metal ions also separated each other by the polymer network. By those reasons of the immobilization of the metal ions, migration and coagulation of the metal element during the heat-treatment mentioned below will be reduced. The gel with metal ions was washed by a large amount of distilled water, and then was heat-treated at a temperature in an electric furnace under air to produce inorganic network along with removing the organic phase (the gel). The metal ions migrate with oxidation and form particles during first stage of the heat-treatment. The inorganic network will be produced through coagulation and sintering among the particles during the heat-treatment. In this method, the gel is used as a reaction field for the formation of the inorganic network.

Method B: Principle of this method is basically the same as the Caruso's method [4]. Metal alkoxide was filled in network of organic polymer gel to coat the network. Then the gel with metal alkoxide was immersed in an aqueous solvent to hydrolyze the metal alkoxide in the network of the gel. The gel was removed by heat-treatment at a temperature under air to obtain inorganic network. Produced inorganic network will be a reverse replicate of the network of organic polymer gel.

2.2 Sample preparation

Inorganic networks were synthesized based on the methods mentioned above.

Method A: Acrylic type cation exchange resin (IRC76, Organo co. ltd., 500 μm in diameter, pore volume = 0.39 ml/ml-resin) was used as the template and/or reaction field for the synthesis of the inorganic network. Fe ions were introduced in the resin through cation exchange from an aqueous solution of its nitrate salt. The amount of introduced metal ions was adjusted by the concentration of the solution and the solid/liquid (amount of the resin/volume of the solution) ratio during the ion exchange. The ratio of introduced amount of the metal ions to the cation exchange capacity of the resin was adjusted to be 0.3 by equivalent basis. The resins exchanged with Fe ions were then separated by filtration and were washed by distilled water several times to remove residual chemicals. The resins were heat-treated in an electric furnace at 1273 K for 1 h in air. Heating rate in the heat-treatment was 5 K/min. The resin without metal ions originally shows degradation from around 473 K and burns out at around 773 K. Another set of Fe exchanged resin was reduced using hydrazine before the heat-treatment. The resin was heat-treated in hydrogen atmosphere at 973 K for 1 h.

Method B: Titanium propoxide was introduced in the resin by immersing the resin in the solution of Titanium propoxide under an application of ultrasound for 6 h. The resin with Titanium propoxide was collected by filtration and was then immersed in a large amount of 1:1 (wt/wt) mixture of distilled water and propanol to hydrolyze the Titanium propoxide. The slurry was kept for 24 h at room temperature with stirring. The resin was collected by filtration and was heat-treated in the electric furnace at 473 K for 2 h and 773 K for 5 h in air.

2.3 Characterization

The obtained inorganic samples were observed by means of scanning electron microscopy with energy dispersive X-ray microanalysis (SEM/EDX, S-3500N, Hitachi, Co. Ltd.). The resolution of the EDX was 1 μm . Produced phase in the inorganic samples was identified using powder X-ray diffractometer. Adsorption and desorption isotherms of the samples for nitrogen at 77 K were obtained using Autosorb (Quantachrome Co.). Specific surface area, pore volume and pore size distribution of mesopore of the samples were calculated based on the isotherms by BET and Barrett-Joyner-Halenda (BJH) method. Micropore area was also estimated by means of t-plot of the isotherms.

3. RESULTS AND DISCUSSION

Figure 3 shows SEM photographs of the inorganic sample obtained from the Fe exchanged resin prepared by the method A (heat-treated at 1273 K). Monolithic inorganic sample that kept the initial spherical shape of the resin was obtained. Formation of a three-dimensional network structure was observed. The three-dimensional network structure was formed by particles with 500 nm



Fig.3 SEM photographs of the inorganic sample obtained from the Fe exchanged resin prepared by the method A (heat-treated at 1273K)

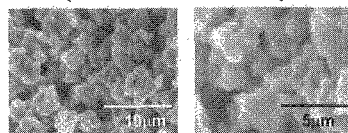


Fig.4 SEM photographs of the Fe_2O_3 sample prepared by the heat-treatment of $\text{Fe}(\text{NO}_3)_3$ in air without the resin

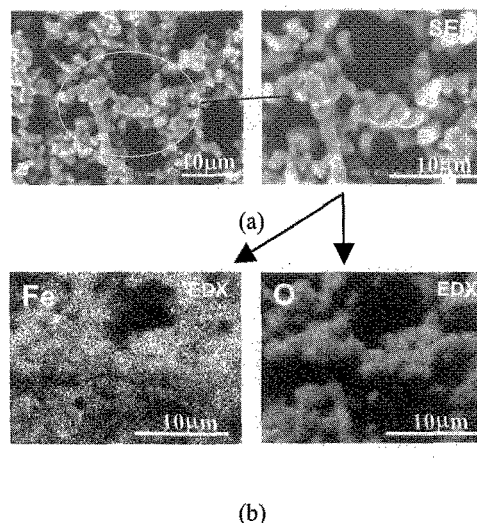


Fig.5 SEM photographs of the sample prepared from the reduced Fe exchanged resin heat-treated in the hydrogen atmosphere (a) and EDX images of the sample in Fig.5(a)

in diameter that connected each other with neighboring ones. The produced phase was assigned to be Fe_2O_3 by XRD analysis. Specific surface area and pore volume of the network were $10 \text{ m}^2/\text{g}$ and 0.7 ml/ml-sample , respectively. The micropore area calculated from the t-plot of the data was almost zero. Figure 4 shows SEM photographs of the Fe_2O_3 sample prepared by heat-treatment of $\text{Fe}(\text{NO}_3)_3$ in air but without using the resin. There was no network structure and the produced particles of Fe_2O_3 were with more than several μm in diameter. By the synthesis using organic polymer gel, the inorganic network structure that was constituted with homogeneous sub-micron particles of the inorganic material can be obtained.

Figure 5(a) shows SEM photographs of the inorganic sample obtained from the reduced Fe exchanged resin that was heat-treated in hydrogen atmosphere at 973 K. Monolithic sample that kept the initial shape of the resin was not obtained in this case although the network structure was produced. Network structure that was constituted with several micron particles was obtained. Figure 5(b) shows EDX pattern of the sample. Existence of Fe and O was confirmed but less than 1% of carbon (data is not shown) so that the obtained sample mainly consisted of both Fe and O and the organic phase was almost removed under the reductive condition of the heat-treatment. The metal iron produced during the heat-treatment worked as a catalyst of carbon oxidation in the hydrogen atmosphere at above 773 K [5]. Produced phases in the sample assigned by the XRD analysis were α -iron, Fe_3O_4 and Fe_2O_3 . Specific surface area and pore volume of the sample was $390 \text{ m}^2/\text{g}$ and $2.67 \text{ ml/ml-sample}$, respectively. Figure 6 shows the adsorption isotherm of the sample along with the t-plot of the isotherm. Type II isotherm of IUPAC classification was obtained. Figure 7 shows the pore size distribution of the sample in the range of mesopore calculated from the isotherm in Fig.6 by the BJH method. Development of meso pores with less than 10 nm in diameter was confirmed. Compared with the particle size of the constituents of the network, the specific surface area of the network ($390 \text{ m}^2/\text{g}$) was much larger than that was expected from the particle size ($\sim 1 \text{ m}^2/\text{g}$). This indicates the formation of micropores in the particles. The micropore area calculated from the t-plot of the data was $130 \text{ m}^2/\text{g}$. Among the prepared inorganic network samples, development of micropore was observed only in this sample prepared from the reduced Fe exchanged resin in the H_2 atmosphere. The organic polymer gel used in this study burns out at 773K under oxidative condition. In the synthesis under the reductive atmosphere, carbonization of the resin occurs first during the heat-treatment and the produced carbon still remains at the high temperature of the synthesis in and/or on the produced metal/metal oxides particles until the carbon is consumed by the reaction catalyzed by metal iron as mentioned above. The existence of the carbon at the high temperature may affect the production of the micropore. The carbons that remain in the final product may also be a source of the micropore. Further study should be done to understand the reason why the micropore is produced in the sample.

Figure 8 shows SEM photographs of the inorganic sample obtained from the Ti introduced resin prepared

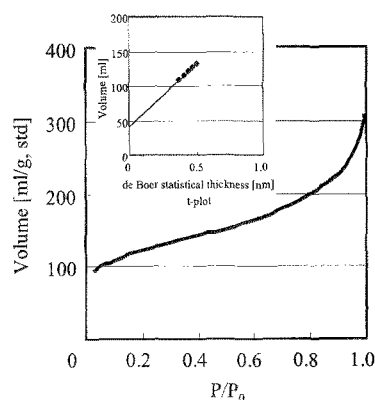


Fig.6 Adsorption isotherm of the sample prepared from the reduced Fe exchanged resin heat-treated in the hydrogen atmosphere

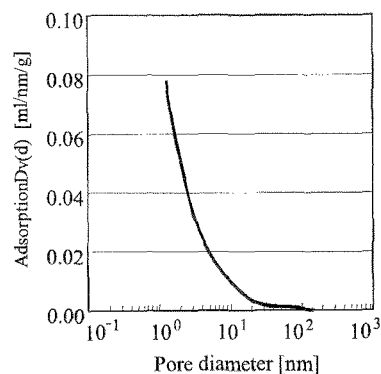


Fig.7 Pore size distribution isotherm of the sample prepared from the reduced Fe exchanged resin heat-treated in the hydrogen atmosphere

by the method B. Monolithic inorganic sample that

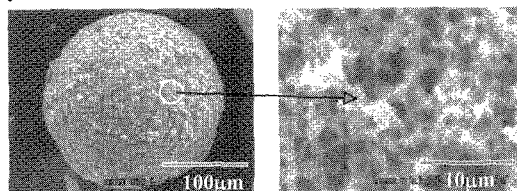


Fig.8 SEM photographs of the inorganic sample obtained from the Ti introduced resin prepared by the method B

keeps the initial spherical shape and the size of the resin with a three dimensional reverse replicated network structure was obtained. The produced phase was identified to be TiO_2 , anatase by the XRD analysis. Figure 9 shows the adsorption and desorption isotherms of the sample. Specific surface area and pore volume of the sample was $47 \text{ m}^2/\text{g}$ and $0.50 \text{ ml/ml-sample}$, respectively. The specific surface area of the sample was larger than that was expected from the size of the constituent of the network and was also larger than that of commercially supplied TiO_2 powder with several ten nm in diameter (Kojundo Kagaku co. Ltd., $8 \text{ m}^2/\text{g}$). The micropore area calculated from the t-plot of the data was almost zero. Figure 10 shows pore size distribution of the sample. Formation of mesopores with 4-6 nm in diameter was found.

4. CONCLUSIONS

Synthesis of metal/metal oxide network using crosslinked acrylic type cation exchange resin was demonstrated.

Synthesis of monolithic metal oxide network is available using the polymer gel as the template and/or reaction field of the synthesis of inorganic network.

Using acrylic acid resin, monolithic iron network constituted by homogeneous particles of metal iron and iron oxides with several hundred nm in diameter can be prepared.

In the case of TiO_2 network synthesized through alkoxide-based process, reverse replication of the organic polymer network can be performed.

The synthesized metal oxide networks showed a large specific surface area with mesopores in spite of the large particles that constitute their networks.

5 References

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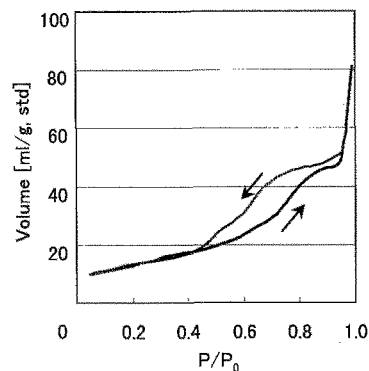


Fig.9 Adsorption isotherm of the TiO_2 network

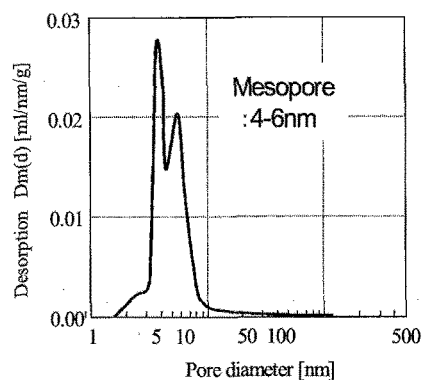


Fig.10 Pore size distribution of the TiO_2 network