

Synthesis of Nanoporous Carbon as a Gas Adsorbent by Reverse Replication Process of Silica Template

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ABSTRACT

Porous carbon with high surface area and pore volume was prepared by a reverse replication process and its toluene equilibrium adsorption behavior was investigated. The preparation process of the porous carbon was composed of following sub-processes in series: synthesis and template preparation of silica gel, impregnation and polymerization of DVB monomer in silica template, carbonization of DVB polymer in a silica-polymer composite, and HF-assisted selective etching of silica in carbon-silica composite. The prepared porous carbon was nano porous and had ultrahigh specific surface area (2007 m²/g) and large pore volume (3.07 cm³/g). The nanoporous carbon showed rapid toluene adsorption rate and good toluene adsorption capacity, compared with a commercial Y-type zeolite. In the present study, a reverse replication process to prepare nanoporous carbons will be introduced and its application potential as a gas adsorbent will be discussed.

Key words : Nanoporous carbon, Silica template, Reverse replication process, Toluene equilibrium adsorption

1. Introduction

Since W. Stöber, A. Fink and E. Bohn¹⁾ have developed a silica synthesis process, called later as SFB or Stöber process, synthesis of spherical silica gels in micron size range was industrially out of interest. Silica gels with narrow size distribution have been researched as a model system in sol-gel science²⁾ and commercially applied to a standard for particle size measurement. The SFB process was a NH₃-catalyzed hydrolysis and condensation reactions of tetraethylorthosilicate in a mixed solvent of water and ethyl alcohol.¹⁾ In recent years, synthesis of spherical silica gels with narrow size distribution attracts attentions, because they can apply to CMP (Chemical and Mechanical Polishing) processes to flatten silicon wafer in semiconductor industry, to light guide and illuminating materials (colloidal crystals) in optical fields,³⁻⁷⁾ and to templates for preparing adsorbent materials with highly tuned pore structure.^{8,9)} But, there was no remarkable advance in the synthesis of spherical, silica gels with narrow size distribution, since the pioneers' work in 1968.

Recently, there were a few research reports in which closely packed silica gels have used as templates to prepare three dimensional porous carbon replicas.^{8,9)} Spherical silica gels with narrow size distribution were used as a precursor

to prepare silica templates, which were used for following reverse replication process to synthesize porous carbons with uniform pore size distribution. Silica template resembles to natural opal structure in which spherical silica gels closely pack together and has twelve coordinated neighbors. Synthesis of ordered nanoporous materials are technically important because of their industrial applications in adsorption and concentration processes of large molecular gases such as volatile organic compound, and so on.⁹⁾ Therefore, for the preparation of ordered silica templates, it is important to synthesize spherical silica gels with extremely narrow size distribution and to closely pack them together.

Opal-like silica templates have been prepared by very slow processes such as gravity sedimentation and evaporation processes.³⁾ Therefore, it is also necessary to develop a new making process of silica templates with a high preparation rate.

In the present study, silica templates were rapidly prepared by a centrifugation process with the spherical silica gels prepared by a modified SFB process, and applied to prepare nanoporous carbons with high specific surface area and pore volume. Finally, an industrial potential of the nanoporous carbon as a gas adsorbent was investigated by evaluating its toluene adsorption behavior.

2. Experimental Procedure

2.1. Synthesis and Close Packing of Monodisperse Spherical Silica Gels

Silica gels were synthesized by a modified SFB process and then were forced to closely pack together in a simple

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centrifugation process.

In the modified SFB process to prepare silica gels, tetraethylorthosilicate (TEOS, 99.9%, Aldrich Chemical Co. Ltd., USA), NH_3 aqueous solution (30%, Junsei Chemical Co. Ltd., Japan) and anhydrous ethyl alcohol (EtOH, 99.9%, Hayman Chemical Co. Ltd., England) were used as a silica source material, a base-catalyst and a solvent, respectively. In some cases, mixed solutions made of EtOH and DI water were used as solvents. In all cases, total volume of solvent was 500 ml.

To improve monodispersity of silica gels, mixing sequence of raw materials adopted in the conventional SFB process were modified in the present study. Firstly, 500 ml of mixed solvent was prepared by mixing EtOH and DI water in stirring process for 30 min. In the present study, volume ratio of H_2O to EtOH was controlled to be 0 to 1.5. Secondly, the NH_3 aqueous solution was introduced to and homogenized with the mixed solvent in stirring process for 1 h. The volume ratio of NH_3 aqueous solution to mixed solvent was controlled to be 0.02 to 0.12. Finally, TEOS, a silica source material, was rapidly mixed with the NH_3 -containing mixed solvent in stirring process. In all cases, the volume ratio of TEOS to mixed solvent was 0.01. When TEOS was added in the NH_3 -containing mixed solvent, formation (hydrolysis and condensation) reaction of silica gel began immediately, even though there was some difference in formation rate. In all cases, the reaction time was 24 h. After the reaction completed, the synthesized silica gels were separated from the strong basic mother liquor in a centrifuge (Supra 22 K, Hanil Science Co. Ltd., Korea), washed at three times in 500 ml of DI water, and then applied to prepare ordered silica templates without any introduction of drying process.

Silica templates were prepared by close package of silica gels in repeated centrifugal processes. Rotation speed of the centrifuge was changed to be 4000 to 15,000 rpm and depended on diameters of silica gels. The wet silica templates were naturally dried in air and then applied as templates to prepare porous carbons.

2.2. Preparation of Porous Carbon

Divinylbenzene (DVB, 80%, Aldrich Chemical Co. Ltd., USA) monomer was used as a carbon precursor, and 2,2-

azobisisobutyronitrile (AIBN, 98%, Junsei Chemical Co. Ltd., Japan) was applied as a free radical initiator for DVB polymerization. Firstly, to prepare polymer precursor solution of DVB and AIBN, AIBN was dissolved in DVB in an ultrasonic cleaner. In the polymer precursor solution, the molar ratio of DVB to AIBN was 10.

The polymer precursor solution was impregnated into the dried silica template in an aspirator (ASP-13, Asahi Technologies, Japan). After the impregnation of the polymer precursor solution, residual moisture in the silica template was freeze dried at 3 times with using liquid nitrogen gas. The DVB monomer impregnated silica template was polymerized at 70°C for 12 h in vacuum to produce polymer-silica composites.

The polymer in the polymer-silica composite was carbonized at 800°C for 12 h in Ar atmosphere to produce carbon-silica templates. The silica in the carbon-silica composites was leached out by aqueous HF (50%, Duksan Chemical Co. Ltd., Korea)-assisted etching process. The prepared porous carbon was water washed at three times and then dried at 120°C for 24 h.

2.3. Characterization

Microstructure and pore structure were characterized by SEM (XL30, Phillips, Holland) and BET (ASAP2400, Micromeritics, USA) analysis, respectively. Average diameter of silica gels were measured by a laser scattering system (ELS-8000, Otsuka, Japan).

Toluene adsorption of the prepared porous carbon was investigated at 30°C in a mass equilibrium adsorption measurement system with a magnetic suspension balance (30G500P, Rubotherm, Germany), and then compared with that of a commercial Y-type zeolite (Hisiv-1000, UOP, USA). Before the toluene equilibrium adsorption test, porous carbon and zeolite were dried at 200°C for 1 h.

3. Results and Discussion

Generally, in the SFB process, diameter of silica gels has been affected by processing parameters such as temperature and time of reaction, TEOS and NH_3 concentrations,

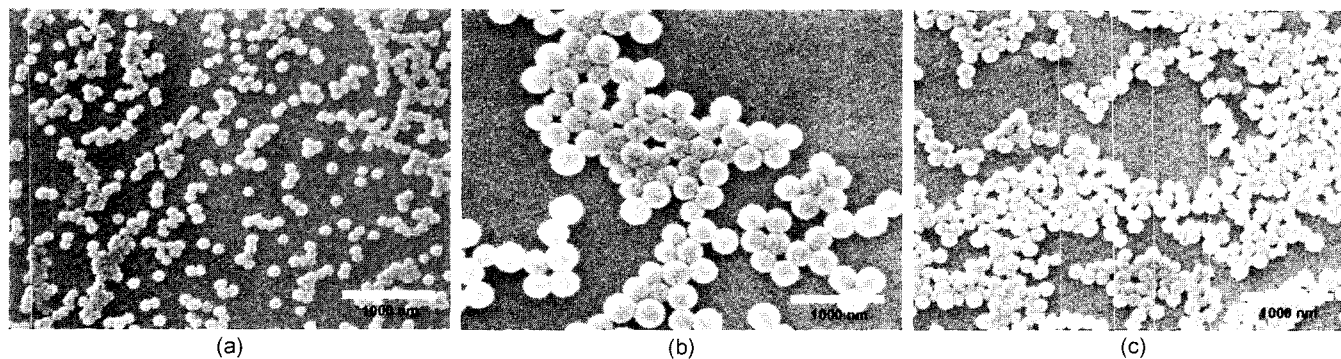


Fig. 1. SEM images of silica gels synthesized in the mixed solvents with volume ratios of H_2O to EtOH of (a) 0, (b) 0.25, and (c) 0.67; in all cases, the volume ratios of TEOS and NH_3 to the mixed solvent were constant to be 0.01 and 0.06, respectively.

volume ratio of H_2O to EtOH and *etc.*^{1,11-13)} In the present study, diameter of silica gels was controlled by changing the volume ratio of H_2O to EtOH and NH_3 concentration without any variation of other parameters.

Fig. 1(a) to (c) represented SEM images of silica gels synthesized in the mixed solvents with volume ratios of H_2O to EtOH of (a) 0, (b) 0.25, and (c) 0.67, respectively. In all cases, volume ratios of TEOS and NH_3 to the mixed solvent were 0.01 and 0.06, respectively. All the prepared silica gels were monodispersed and spherical, even though there was a considerable difference in the particle monodispersity. It will be noted that diameter of silica gels goes through a maximum as H_2O concentration in the mixed solvent is raised in all NH_3 concentrations. In the present study, regardless of NH_3 concentrations, maximum diameter of silica gels was shown when the volume ratio of H_2O to EtOH was 0.1 more or less.

Fig. 2(a) to (d) represented SEM images of silica gels prepared with different NH_3 concentrations; the volume ratios of NH_3 to the mixed solvent were of (a) 0.12, (b) 0.06, (c) 0.05, and (d) 0.04. In all cases, volume ratios of TEOS and H_2O to the mixed solvent were 0.01 and 0, respectively. In Fig. 2, it was clearly shown that the diameter of silica gels increased, as NH_3 concentration increased.

Fig. 3 summarized the variations of gel diameter as functions of H_2O and NH_3 concentrations. The diameter of silica gels went through a maximum as H_2O concentration in the mixed solvent was raised and increased as NH_3 concentra-

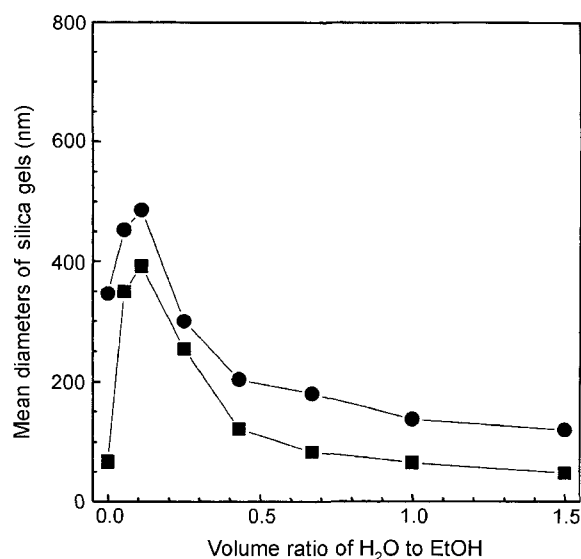


Fig. 3. Mean diameters of silica gel prepared in mixed solvents with different volume ratios of H_2O to EtOH; volume ratios of NH_3 to the mixed solvent were (■) 0.06 and (●) 0.12.

tion increased. In the present study, the diameter of silica gel could be controlled to be 50 to 500 nm by the variation of H_2O and NH_3 concentrations.

G. H. Bogush *et al.*¹¹⁾ have reported the same results

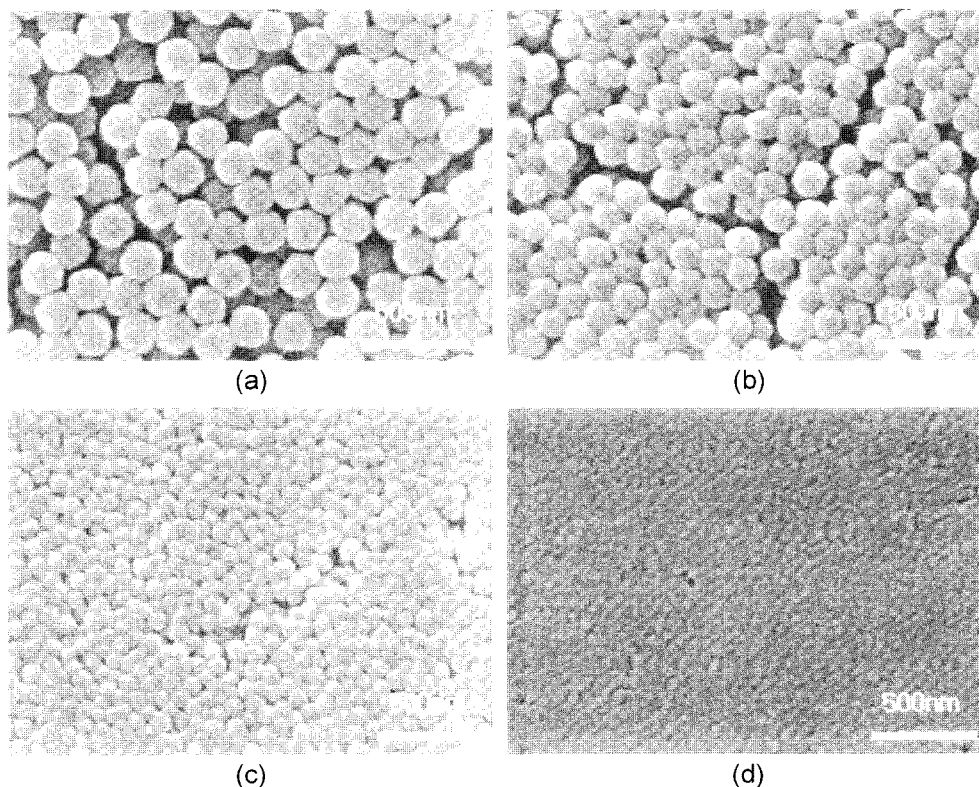


Fig. 2. SEM images of silica gels prepared with different NH_3 concentrations; the volume ratios of NH_3 to the mixed solvent were of (a) 0.12, (b) 0.06, (c) 0.05, and (d) 0.04, and in all cases, the volume ratios of TEOS and H_2O to the mixed solvent were 0.01 and 0, respectively.

shown in Fig. 3, but didn't explain where the dependency of gel diameter on H_2O and NH_3 concentrations was from. Also, G. H. Bogush *et al.*^{14,15} have suggested that the growth of silica gel in the SFB process should be governed by an aggregative growth model. This model states that the growth of spherical gel occurs due to an aggregation of primary nanogels that were nucleated in a mixed solvent supersaturated with silica. Nowadays the aggregation model is competing with the solution and precipitation growth model (Ostwald ripening) suggested by V. K. LaMer and R. H. Dinegar.¹⁶ If the growth of silica gels is governed by the agglomeration model, it is expected that silica gels should have high specific surface area, because silica gels are composed of primary nanogels.

The pore structure of silica gel as shown in Fig. 1(b) was analyzed by BET method. Its specific surface area was 30 m^2/g and was well consistent with that calculated with its mean diameter. In the silica gel, there was no pore except a considerable amount of diffuse mesopores with diameter of 10 to 200 nm. These diffuse mesopores were originated in random packing between silica gels. It will be noted that the silica gel was so dense and there was no considerable micropore. It can be concluded that the growth behavior of silica gel was governed by the solution-precipitation model.

The conclusion for the growth mechanism of silica gels was supported by the fact reported by R. K. Iler.¹⁷ R. K. Iler has systematically summarized the dependence of solubility of amorphous silica on pH.¹⁷ As pH increases, the solubility

of amorphous silica gently decreases at the lower pH, reaches a minimum at pH 7–8, and shows a steep increasing behavior above pH 8. In the SFB process, pH of mixed solvent in which silica gels nucleated and grew was above 10.

Therefore, the dependency of gel diameter on H_2O and NH_3 concentrations, as shown in Fig. 3, could be explained by the combined effect of H_2O and NH_3 on reactant concentration and silica solubility. In the SFB process, H_2O plays two kinds of roles: one does a part of a reactant and the other does a part of a solvent. As H_2O concentration increased, hydrolysis and condensation rates of TEOS increased because concentration of one reactant (H_2O) increased. On the other hand, in high H_2O concentrations, H_2O mainly serves as a solvent. Therefore, as H_2O concentration increased, the diameter of silica gel decreased, because silica solubility decreased, as H_2O concentration was raised.

Fig. 4(a) to (d) represented SEM images of (a) silica template made of silica gels with mean diameter of 250 nm, (b) polymer-silica composite, (c) carbon-silica composite and (d) porous carbon, respectively. As shown in Fig. 4(d), the prepared porous carbon had ordered macropores with average diameter of 150 nm, and the thickness of carbon wall was 50 nm more or less. The mean diameter of macropores in the porous carbon was less than that of silica gels. Rather, the average diameter of silica gels was equal to the sum of the mean macropore diameter and twice of carbon thickness.

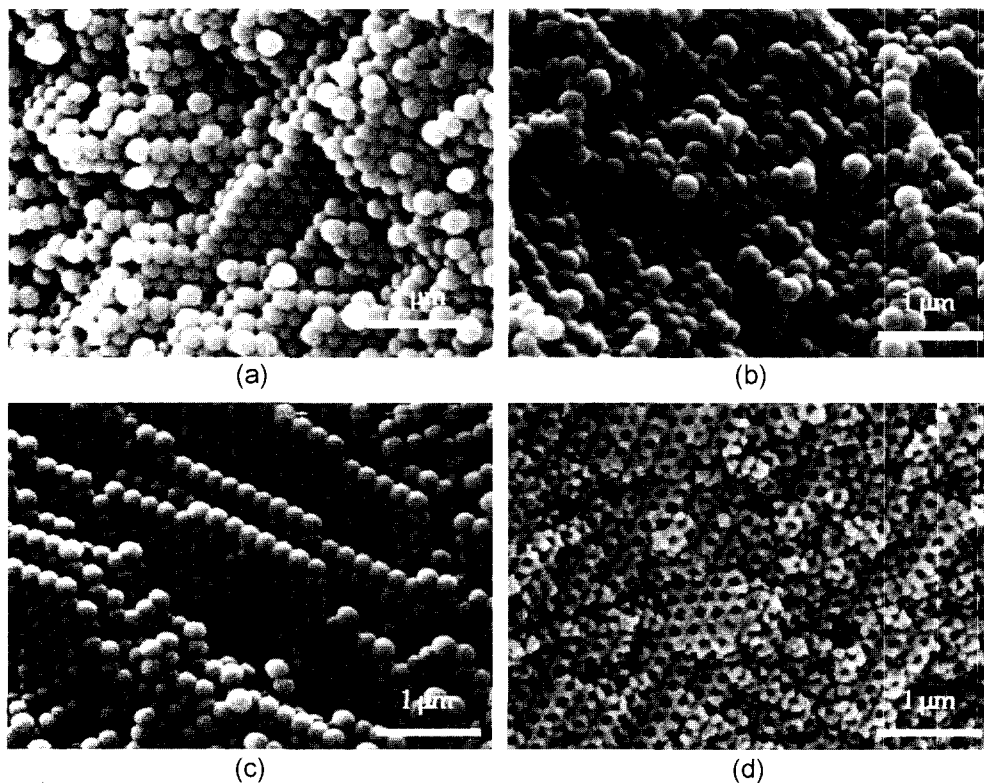
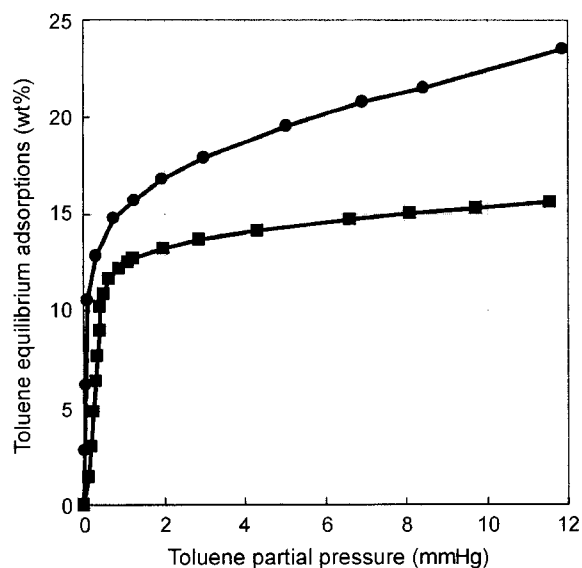


Fig. 4. SEM images of (a) silica template, (b) polymer-silica composite, (c) carbon-silica composite, and (d) porous carbon; the silica template was prepared by closely packing the silica gels with average diameter of 250 nm.

Table 1. Specific Surface Areas and Pore Volumes of Silica Template, Polymer-silica Composite, Carbon-silica Composite and Porous Carbon

	Silica template	Polymer-silica	Carbon-silica	Porous carbon
Specific surface area (m^2/g)	29.7	16.5	34.9	2007
Total pore volume (cm^3/g)	0.06	0.01	0.06	3.07

**Fig. 5.** Toluene equilibrium adsorptions of (●) nanoporous carbon and (■) commercial zeolite as a function of toluene partial pressure.

Specific surface areas and pore volumes of silica template, polymer-silica composite, carbon-silica composite and porous carbon were summarized in Table 1. As expected in Fig. 4, there was a significant change of pore structure before and after the HF-assisted silica etching process to prepare the porous carbon. The porous carbon had $2007 \text{ m}^2/\text{g}$ of specific surface area and $3.07 \text{ cm}^3/\text{g}$ of pore volume. Where the ultrahigh specific surface area of the porous carbon is from is very interesting. If the carbon wall was dense, the specific surface area should be so small. This means that there is a strong possibility of nanopores (micropores and/or mesopores) existence in the carbon wall. In BET analysis of the porous carbon as shown in Fig. 4(d), the average pore diameter of adsorption pores was 61.2 \AA . This indicated that the carbon wall was microporous. Therefore, the ultrahigh specific surface area originated from the micropores in the carbon walls.

Gas adsorption behavior of the nanoporous carbon is also interesting. Fig. 5 represented toluene equilibrium adsorptions of (a) the nanoporous carbon and (b) a commercial Y-type zeolite, as a function of toluene partial pressure. At 12 mmHg of toluene partial pressure, toluene equilibrium adsorptions of the nanoporous carbon and commercial zeolite were 23.57 and 15.71 wt%, respectively. The nanoporous carbon showed higher toluene adsorption rate and

better toluene adsorption capacity than the commercial zeolite. Therefore, it is concluded that in a viewpoint of adsorption characteristics, the nanoporous carbon prepared in the reverse replication process has a high potential as a gas adsorbent.

4. Conclusions

A reverse replication process was introduced to prepare nanoporous carbons with high specific surface area and pore volume. The nanoporous carbon had ultrahigh specific surface area ($2007 \text{ m}^2/\text{g}$) and pore volume ($3.07 \text{ cm}^3/\text{g}$), and showed higher toluene adsorption rate and better toluene adsorption capacity than the commercial Y-type zeolite. For successful applications of the nanoporous carbon in industrial gas adsorption and concentration systems, it is necessary to surmount two hard obstacles: one is the high synthesis cost of monodisperse spherical silica gels and the other is the difficulty in preparing ordered silica templates. If two problems are solved, nanoporous carbons prepared in the reverse replication process have a high application potential to industrial gas adsorption systems.

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