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Preparation and Physisorption Characterization of D-Glucose-Templated Mesoporous Silica Sol−Gel Materials

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The synthesis of mesoporous silica materials has been achieved with D-glucose as a nonsurfactant pore-forming agent in the sol−gel reactions of tetraethyl orthosilicate under basic or near neutral (pH 6) conditions. Regardless of the pH values of the medium, transparent and monolithic glucose-containing silica gels could be obtained. D-Glucose was removed by water extraction to afford silica materials with high specific surface area of ~800 m^2/g, pore volume of ~0.5 cm^3/g, and narrow pore distribution with BJH pore diameter of 3.2−3.5 nm, indicative of the mesoporosity. As the glucose concentration is increased in the synthesis, these pore parameters generally increase, and the N_2 sorption isotherms gradually transform from reversible type I to type IV-like isotherms with H2 hysteresis. At low glucose concentrations (<36 wt %), both micropores and mesopores contribute to the porosity of the materials. However, at high glucose concentrations (36−64 wt %), mesopores are dominant. The characteristics of pore structures are similar to those for the materials obtained under acid catalysis. The aggregation or assembly of the aggregates of the glucose molecules and their hydrogen-bonding interactions with the silicate species might direct the mesophase formation.

Introduction

The discovery of the M41S family of mesoporous silicate and aluminosilicate molecular sieves using the surfactant templated hydrothermal sol−gel process in 1992[1,2] has drawn great interest because of the potential applications of mesoporous materials as catalyst, catalyst support, separation medium, and host material for inclusion compounds. Numerous mesoporous or nanoporous materials[3−19] have been synthesized, and the pore diameter extended from less than 1.3 nm for conventional zeolites to about 10 nm and lately up to 30 nm.[8] Many synthetic routes and strategies have been developed to yield a wide diversity of materials of various framework chemical compositions and pore structures. In most of the studies, ionic and neutral surfactants have been employed as templates, which direct the mesophase formation based on the electrostatic and hydrogen-bonding interactions, respectively.

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(1) Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature* **1992**, *359*, 710.

(2) Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowcz, M. E.; Kresge, C. T.; Schmitt, K. D.; Chu, C. T.-W.; Olson, D. H.; Sheppard, E. W.; McCullen, S. B.; Higgins, J. B.; Schlenker, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 10834.

(3) During the revision of this article, an excellent review on mesoporous materials was published: Ying, J. Y.; Mehnert, C. P.; Wong, M. S. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 56.

(4) Raman, N. K.; Anderson, M. T.; Brinker, C. J. *Chem. Mater.* **1996**, *8*, 1682.

(5) (a) Davis, M. E. *Nature* **1993**, *364*, 391. (b) Mann, S. *Nature* **1993**, *365*, 499. (c) Huo, Q.; Margolese, D. I.; Ciesla, U.; Feng, P.; Gier, T. E.; Sieger, P.; Leon, R.; Petroff, P. M.; Schüth, F.; Stucky, G. D. *Nature* **1994**, *368*, 317. (d) Huo, Q.; Margolese, D. I.; Ciesla, U.; Feng, P.; Gier, T. E.; Sieger, P.; Leon, R.; Petroff, P. M.; Schüth, F.; Stucky, G. D. *Chem. Mater.* **1994**, *6*, 1176. (e) Wu, C.-G.; Bein, T. *Science* **1994**, *266*, 1013. (f) Stein, A.; Fendorf, M.; Jarvie, T. P.; Mueller, K. T.; Benesi, A. J.; Mallouk, T. E. *Chem. Mater.* **1995**, *7*, 304. (g) Behrens, P. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 515. (h) Tian, Z. R.; Tong, W.; Wang, J. Y.; Duan, N. G.; Krishnan, V. V.; Suib, S. L. *Science* **1997**, *276*, 926. (i) Jones, C. W.; Tsuji, K.; Davis, M. E. *Nature* **1998**, *393*, 52. (j) Zhou, W.; Thomas, J. M.; Shephard, D. S.; Johnson, B. F. G.; Ozkaya, D.; Maschmeyer, T.; Bell, R. G.; Ge, Q. *Science* **1998**, *280*, 705.

(6) Antonelli, D. M.; Ying, J. Y. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 426.

(7) Chen, C.-Y.; Li, H.-X.; Davis, M. E. *Microporous Mater.* **1993**, *2*, 17.

(8) Zhao, D.; Huo, Q.; Feng, J.; Chmelka, B. F.; Stucky, G. D. *J. Am. Chem. Soc.* **1998**, *120*, 6024.

(9) Bagshaw, S. A.; Pinnavaia, T. J. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1102.

(10) Attard, G. S.; Glyde, J. C.; Göltner, C. G. *Nature* **1995**, *378*, 366.

(11) Bagshaw, S. A.; Prouzet, E.; Pinnavaia, T. J. *Science* **1995**, *269*, 1242.

(12) Tanev, P. T.; Pinnavaia, T. J. *Science* **1995**, *267*, 865.

(13) Tanev, P. T.; Pinnavaia, T. J. *Chem. Mater.* **1996**, *8*, 2068.

(14) Whitehurst, D. D. U.S. Pat. 5,143,879, 1992.

(15) Coustel, N.; Renzo, F. D.; Fajula, F. *J. Chem. Soc., Chem. Commun.* **1994**, 967.

(16) Branton, P. J.; Hall, P. G.; Sing, K. S. W. *J. Chem. Soc., Chem. Commun.* **1993**, 1257.

(17) Branton, P. J.; Hall, P. G.; Sing, K. S. W. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 2965.

(18) Schmidt, R.; Stöcker, M.; Hansen, E.; Akporiaye, D.; Ellestad, O. H. *Microporous Mater.* **1995**, *3*, 443.

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The pore size in MCM-41 materials could be controlled from 1.5 to 10 nm by the hydrophobic alkyl chain length of ionic surfactants or with the aid of auxiliary organic compounds as spacers and fillers.[1−4] The ionic templates are usually removed by high-temperature calcination[1,2] or by ion exchange.[14] Strong electrostatic interactions between the ionic surfactants and the inorganic species also result in MCM-41 matrices with limited pore wall thickness of 0.8−1.3 nm[2−4,7,8] that are influenced little by the pH in the synthesis.[15] As a consequence, the materials often have limited thermal stability as evidenced by significant pore contraction or even structure collapse during calcination.

Mesoporous materials prepared with neutral surfactants as the template[8−13] usually have improved stability. With primary amine templates,[12,13] the pore size may be adjusted by changing the hydrophobic tail length of amines. The template can be removed by solvent extraction. The mesoporous materials have greater wall thickness (1.7−3.0 nm) due to the absence of electrostatic or charge-matching effects and thus higher thermal stability than M41S materials. However, the materials exhibit both complementary textural and framework-confined mesoporosity.[12] The toxicity of amines also remains a concern if a large-scale production is intended. The use of neutral PEO surfactants as templates has been demonstrated advantageous in solving the problems of ionic surfactant charge-matching and organic amine toxicity, since the PEO surfactants are neutral, nontoxic, and biodegradable.[9,11] The pore size of the materials (MSU-1)[9,11] can be tuned by varying the size and structure of the surfactant molecules though the channels are largely disordered. Recently, ordered mesoporous (2−30 nm) silicas with large wall thickness values of 3.1−6.4 nm and pore volumes up to 2.5 $cm^3\ g^{-1}$ have been synthesized by using alkyl PEO oligomeric surfactants and poly(alkylene oxide) block copolymers as templates in strongly acidic media.[8]

We have reported a nonsurfactant route to the mesoporous materials.[20] The synthesis of mesoporous silica is achieved by HCl-catalyzed hydrolysis and polycondensation (i.e., sol−gel reactions[21]) of tetraethyl orthosilicate (TEOS) in the presence of nonsurfactant organic compounds, including dibenzoyltartaric acid, D-glucose, and D-maltose, as the pore-forming agents, which can be removed by solvent extraction. The materials have high surface areas of ∼1000 $m^2\ g^{-1}$, pore volumes as large as ∼1.0 $cm^3\ g^{-1}$, and narrowly distributed mesopores of ∼2−6 nm in diameter, adjustable by changing the nonsurfactant concentration.[20] Unlike the M41S but very similar to the MSU-1 (i.e., PEO-templated[9,11]) silicas, the channels are not highly ordered but have good thermal stability.[20,22] It should be emphasized that *we do not yet understand fully how the nonsurfactant compounds lead to (or direct) the formation of mesoporosity*, and hence, both the terms “pore-forming agent” and “template” are used in this article. The use of organic acids such as tartaric acid in the synthesis of mesoporous silicas[23] and alumina[24] has also been reported. Recently, glucosamine molecules were found to direct the formation of novel zinc phosphate phases.[25] Organic compounds have been used as dopants or pore fillers in silicate sol−gel materials for studying pore environment and molecule−matrix interactions.[26] Because of their low concentrations in the materials, these compounds have little effect on silicate framework formation.[26]

As a further study of mesoporous materials via the neutral nonsurfactant pathway, we studied the synthesis of mesoporous silica materials under base catalysis or near neutral conditions in the presence of a nonsurfactant template. It is known that the rate of polycondensation in the sol−gel reactions is very fast at pH ∼7 though the hydrolysis needs acid or base catalyst.[21] We hypothesized that the nonsurfactant templates may also direct the mesophase formation, particularly during the polycondensation and gelation process, under basic or near neutral conditions, similar to that under the acid catalysis. Here we report the preparation of mesostructured silicas from TEOS precursor, by using either NaOH as sole catalyst or HCl as catalyst in the prehydrolysis followed by neutralization with NaOH to pH of 6 for subsequent polycondensation in the presence of D-glucose at various concentrations. Removal of the glucose templates by water extraction affords mesoporous silica materials. The materials before and after the template removal were characterized by means of infrared spectroscopy, thermogravimetric analysis, and nitrogen sorption measurements.

Experimental Section

Materials and Synthesis. Tetraethyl orthosilicate (TEOS) was purchased from Aldrich (Milwaukee, WI). Ethyl alcohol was supplied by Pharmco Products (Brookfield, CT). D-Glucose, NaOH, and HCl were from Fisher Scientific (Fair Lawn, NJ). All chemicals and reagents were used as received without further purification. The preparation of mesoporous silica materials followed the same procedures as previously reported,[20,22] except that NaOH was used as catalyst for the polycondensation or for both the hydrolysis and polycondensation. Thus, in the preparation of one series of samples (denoted as NEG series), HCl was used as the catalyst for the prehydrolysis to afford the TEOS sol, as previously reported.[20,22,28] Then NaOH was added to bring the pH of the HCl-prehydrolyzed TEOS sol to about 6.0 in the presence of various amounts of D-glucose template. In the preparation of another series of samples (denoted as BEG series), HCl was substituted with an equal amount of NaOH to catalyze the hydrolysis of TEOS. To the resultant TEOS sol were added various amounts of a 50 wt % glucose aqueous solution. In both series, the glucose-containing solutions were homogeneous, and the sol−gel reactions (i.e., further hydrolysis and polycondensation) proceeded at room temperature. Upon dry-

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(19) Llewellyn, P. L.; Grillet, Y.; Schüth, F.; Reichert, H.; Unger, K. K. *Microporous Mater.* **1994**, *3*, 345.

(20) Wei, Y.; Jin, D.; Ding, T.; Shih, W.-H.; Liu, X.; Cheng, S. Z. D.; Fu, Q. *Adv. Mater.* **1998**, *3*, 313.

(21) (a) Brinker, C. J.; Scherer, G. W. *Sol−gel Science: The Physics and Chemistry of Sol−Gel Processing*; Academic Press: New York, 1990. (b) Ziegler, J. M., Fearon, F. W., Eds. *Silicon-Based Polymer Science;* Advances in Chemistry Series 224*;* American Chemical Society: Washington, DC, 1990.

(22) Jin, D. Ph.D. Dissertation, Drexel University, 1997.

(23) Vaudry, F.; Khodabandeh, S.; Davis, M. E. *Chem. Mater.* **1996**, *8*, 1451.

(24) Izutsu, H.; Mizukami, F.; Kiyozumi, Y.; Maeda, K. *J. Am. Ceram. Soc.* **1997**, *80*, 2581.

(25) Nenoff, T. M.; Thoma, S. G.; Provencio, P.; Maxwell, R. S. *Chem. Mater.* **1998**, *10*, 3077.

(26) Dunn, B.; Zink, J. I. *Chem. Mater.* **1997**, *9*, 2280.

(27) Sing, K. S. W.; Everett, D. H.; Haul, R. A. W.; Moscou, L.; Pierotti, R. A.; Rouquerol, J.; Siemienieska, T. *Pure Appl. Chem.* **1985**, *57*, 603.

(28) Wei, Y.; Jin, D.; Ding, T. *J. Phys. Chem.* **1997**, *101*, 3318.

Table 1. Compositions of the Sol−Gel Silica Samples Prepared in the Presence of 0−64 wt % D-Glucose Template under NaOH Catalysis (BEG Series) and under HCl Prehydrolysis Followed by NaOH Neutralization (NEG Series) as Well as the Pore Parameters of the Porous Silica Materials after Complete Removal of Glucose by Extraction with Water[a]

sample code	D-glucose content, wt % calcd	D-glucose content, wt % found[b]	surf. area, S_{BET}, cm^2 g^{-1}	pore vol V, cm^3 g^{-1}	BET pore diameter,[c] Å	BJH pore diameter,[d] Å	micropore[e] area, cm^2 g^{-1}	micropore[e] vol, cm^3 g^{-1}
NEG0	0	7.9	378	0.214	22.6	<17	314	0.174
NEG0[f]	0		334	0.197	23.6	<17	285	0.158
NEG15	15	19.1	557	0.311	22.3	<17	295	0.166
NEG26	26	29.1	698	0.402	23.1	<17	49	0.026
NEG36	36	37.0	756	0.483	25.6	<17		
NEG45	45	45.3	772	0.603	31.3	34.0		
NEG58	58	58.3	749	0.629	33.6	34.8		
NEG64	64	62.5	740	0.767	41.5	34.9		
BEG0	0	7.1	389	0.222	22.8	<17	281	0.157
BEG0[f]	0		395	0.227	23.0	<17	308	0.172
BEG15	15	18.8	652	0.369	22.6	<17	164	0.094
BEG26	26	28.1	712	0.394	22.1	<17	103	0.057
BEG36	36	37.1	813	0.482	23.7	<17		
BEG45	45	43.7	837	0.545	26.0	31.5		
BEG52	52	53.2	789	0.540	27.4	31.9		
BEG64	64	62.0	793	0.549	27.6	32.2		

[a] The pore parameters were measured from N_2 adsorption−desorption isotherms. [b] Values from the weight loss of the sample, which represent total contents of volatile compounds, at 750 °C. [c] The simple average pore diameter calculated from $4V/S_{\mathrm{BET}}$ by the BET method. [d] Determined from the maxima of the BJH desorption pore size distribution curve with the Halsey equation. [e] Determined by the *t*-plot method. [f] As-synthesized sample without any solvent extraction prior to the BET measurement.

ing, transparent and monolithic glucose-containing silica gels were obtained as as-synthesized samples. At high concentrations of glucose, the samples sometimes broke into smaller but still transparent and crack-free pieces during the drying process. Control samples were also prepared under identical conditions in the absence of glucose template. To remove the template, the as-synthesized samples were ground into fine powders and extracted with a large amount of distilled water at room temperature. The extent of template removal was monitored by IR spectroscopy and by TGA after extraction.

As a typical procedure, TEOS (0.15 mol), ethanol (0.46 mol), H_2O (0.375 mol), and HCl (2.0 M, 1.5 mmol) were mixed in a flask at room temperature under agitation. After ~15 min the mixture became homogeneous. The solution was then heated to reflux under N_2 for 2 h. Upon cooling to room temperature, such a prehydrolyzed TEOS sol was obtained as a stock solution ready for the subsequent synthesis. For the preparation of a sample containing 45 wt % D-glucose, 4.0 g of the prehydrolyzed TEOS sol (containing 1.01×10^{-2} mol of the precursor TEOS initially) was neutralized with 0.32 mL of 0.25 M NaOH(aq) followed by adding a solution of 0.5 g of D-glucose in 0.5 g of distilled water under stirring. The resultant homogeneous solution was sealed in a cylindrical glass container with paraffin film, which had 10−12 small holes punched with a syringe needle to allow the evaporation of volatile molecules such as ethanol and water. Upon gelation and drying at room temperature for 3−7 days, a transparent and monolithic disk of glucose-containing silica sample was obtained.

To prepare the mesoporous silica material, the glucose-containing sample (0.3−0.9 g, depending on the glucose content) was ground into a fine powder, which was immersed in 15 mL of distilled and deionized water under agitation for 15 min. After centrifugation and decantation, the sample was placed in another 15 mL of water for 3 h under agitation. The mixture was centrifuged, and the sample was soaked in 15 mL of water overnight. In the following 2 days, the sample was washed twice a day in the same manner. After such an extraction with a total of ~100 mL of water in seven portions, the sample was dried in an oven at 115 °C overnight. Both IR and TGA measurements showed the removal of glucose was complete.

Characterization and Instrumentation. The D-glucose concentration in the sol−gel material was determined from the weight loss at 750 °C using thermogravimetric analysis (TGA) on a DuPont 2000 thermal analyzer equipped with a TGA 950 module. The sample was first ground into a fine powder of 100−500 μm in the particle size. Upon drying at 115 °C for 2 h in an oven, the powdered sample was loaded to the TGA sample container and heated from ambient temperature to 800 °C at a heating rate of 10 °C min^{-1} under oxygen atmosphere. The infrared spectra of the samples were measured in the form of KBr powder-pressed pellets on a Perkin-Elmer 1600 FT-IR spectrophotometer (Norwalk, CT) under ambient conditions. Both as-synthesized and water-extracted powder samples were used for the spectral measurements. The N_2 sorption characterization on the powdered samples before and after removing D-glucose template by extraction was conducted on a Micromeritics ASAP 2010 surface area and pore size analyzer (Micromeritics, Inc., Norcross, GA) at −196 °C (liquid nitrogen). The samples were degassed at 200 °C and 10^{-6} Torr overnight prior to N_2 adsorption−desorption measurement. The surface and pore parameters were calculated using the accompanying software from Micromeritics, Inc.

Results and Discussion

Mesoporous silica materials have been prepared via the sol−gel reactions of TEOS in the presence of D-glucose as a nonsurfactant template followed by removal of the template with water extraction under mild ambient conditions. In addition to the acid-catalysis route as previously reported,[20] the synthesis can be accomplished by the sol−gel reactions under basic (i.e., with NaOH as catalyst in both prehydrolysis of TEOS and polycondensation) or near neutral conditions (i.e., HCl-catalyzed prehydrolysis followed by neutralization with NaOH for subsequent polycondensation).

The compositions of the glucose-containing silica materials prepared via the nonsurfactant-templated sol−gel reactions and the pore parameters of the porous silicas upon removal of D-glucose by water extraction are summarized in Table 1. The compositions, as represented by the glucose concentrations in the as-synthesized materials, calculated from the feed stoichiometry are comparable to those determined from TGA experiments. The discrepancies could be attributed to incomplete sol−gel reactions and water molecules tightly bound to the silica matrix, particularly in the cases that the glucose is absent (i.e., NEG0 and BEG0) or at low concentrations. As the glucose content increases, the

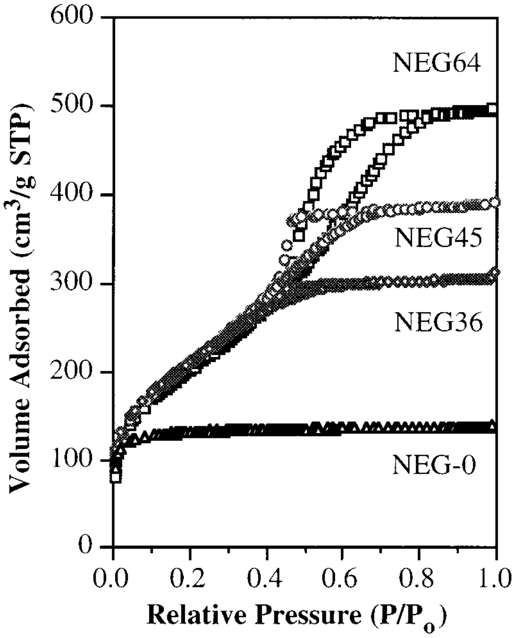

Figure 1. N_2 adsorption−desorption isotherms at −196 °C for the water-extracted samples made from NaOH-neutralized, HCl-hydrolyzed TEOS sol (NEG series) with varied concentrations of D-glucose.

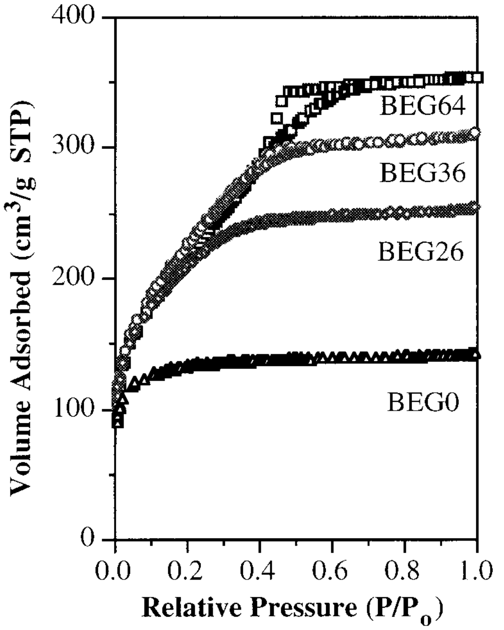

Figure 2. N_2 adsorption−desorption isotherms at −196 °C for the water extracted samples made from NaOH-catalyzed TEOS sol (BEG series) with varied concentrations of D-glucose.

discrepancy becomes smaller and relatively negligible. The results from N_2 adsorption−desorption measurements show that addition of D-glucose as the nonsurfactant template in the sol−gel reactions under basic or near neutral conditions modified the microstructure of silica matrices leading to mesoporosity, similar to that under acid catalyst.[20]

Representative N_2 adsorption−desorption isotherms at −196 °C for the porous silica samples after water extraction are given in Figures 1 and 2. Both the NEG and BEG series show similar isotherm patterns at the same glucose contents. The control samples, i.e., NEG0 and BEG0, exhibit reversible type I isotherms,[27] which are typical of the xerogels with microporous structure.[21] With increasing concentration of glucose, the N_2 sorption isotherms gradually transform from reversible type I to the isotherms that resemble type IV with H2 hysteresis.[27] The H2 hysteresis loop becomes greater in magnitude and shift to higher relative pressures (P/P_0). At the glucose content of 36 wt % or higher, the materials have high surface areas (~800 $m^2\ g^{-1}$) and pore volume (≥0.5 $m^3\ g^{-1}$), indicative of mesoporosity. They also show type IV-like isotherms with H2 hysteresis loops at P/P_0 of ~0.4−0.8 with a sharper step. There is a well-defined plateau following the loop at $P/P_0 >$ 0.8, suggesting the occurrence of pore filling by capillary condensation of nitrogen in the framework-confined mesopores instead of adsorption in the interparticle textural pores.[29] The BET surface areas (Table 1) calculated according to the Kelvin equation[27,29] are found to increase with glucose concentration, up to around 800 $m^2\ g^{-1}$ at 45 wt %, and then remain relatively unchanged. The pore volume obtained at P/P_0 ~ 1 continues to increase with glucose concentration. It is noted that at high glucose concentrations it becomes much harder to obtain homogeneous, crack-free samples. When more than 64 wt % of D-glucose was added, separation of glucose from the gels during drying process was observed.

The as-synthesized samples before removing D-glucose exhibit different types of N_2 isotherms depending on the amount of glucose in the composites. In general, an increase in the amount of glucose up to 45 wt % leads to a decrease in the surface areas and pore volumes. The control samples show similar type I isotherms, surface areas, and pore volumes as those after extraction as listed in Table 1. Apparently, the water-extraction procedures may have little effect on the silica structure. For the samples with increasing glucose content from 15 to 36 wt % or higher, the N_2 sorption isotherms changed from type I to type II with H4 hysteresis, which is typical of nonporous solids.[27,29] The lack of porosity is further evidenced by their very small values of specific surface areas (<5 $m^2\ g^{-1}$) and pore volumes (~0.005 $cm^3\ g^{-1}$). The *t*-plot analysis[30,31] shows that these values, however small, are mainly contributed from exterior surface and voids of the sample powders. These observations indicate that in the as-synthesized samples the silica matrix and glucose molecules form closely contact, intermingled composites without internal pores detectable by the N_2 adsorption method.[29]

The pores or channels in the silica materials after removing glucose by extraction come from the space previously occupied by the templating glucose molecules. In fact, analysis on the net pore volume and BET surface area, which are the differences between the water-extracted and as-synthesized samples, reveals that they are linearly dependent on the glucose concentration up to 45 wt %, with good correlation coefficients

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(29) (a) Gregg, S. J.; Sing, K. S. W. *Adsorption, Surface Area and Porosity*, 2nd ed.; Academic Press: New York, 1982; Chapter 3. (b) ASTM C 1274-95, "Standard Test Method for Advanced Ceramic Specific Surface Area by Physical Adsorption" 402, 1995.

(30) (a) Lippens, B. C.; De Boer, J. H. *J. Catal.* **1964**, *3*, 32. (b) **1965**, *4*, 319.

(31) Dullien, F. A. L. *Porous Media: Fluid Transport and Pore Structure*, 2nd ed.; Academic Press: San Diego, CA, 1992; pp 188−192.

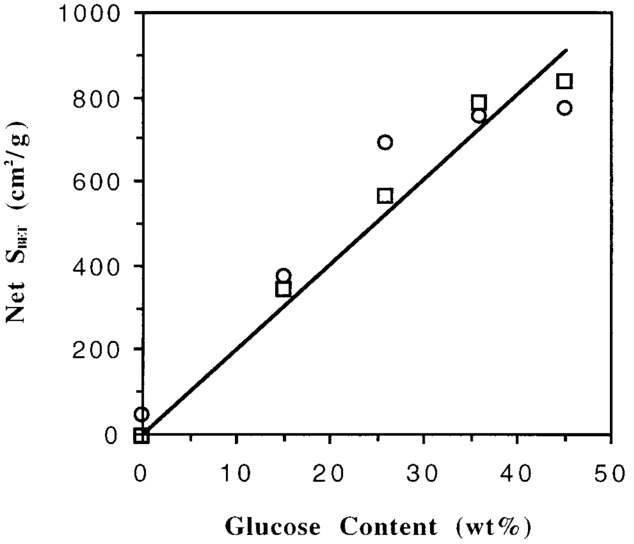

Figure 3. Relationship between the net BET surface area and the found D-glucose content prior to water extraction for both the NEG (circle) and BEG (square) series samples.

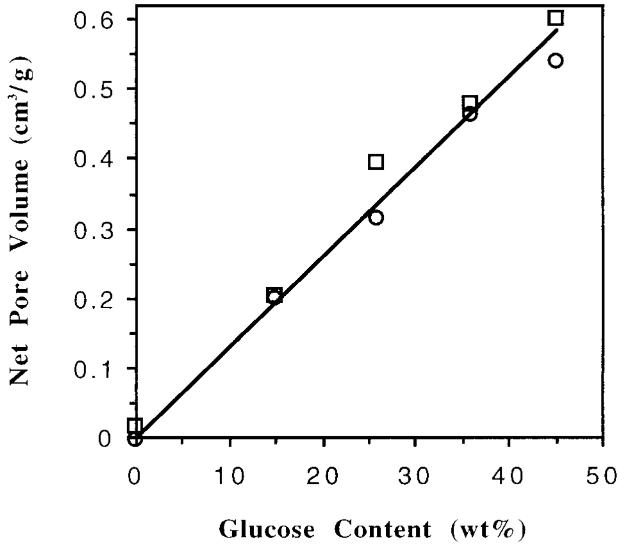

Figure 4. Relationship between the net pore volume and the found D-glucose content prior to water extraction for both the NEG (circle) and BEG (square) samples.

of $R^2 = 0.92-0.99$ (Figures 3 and 4). Hence, the observed total surface areas and pore volumes in the extracted materials (Table 1) are mainly contributed from the internal voids.

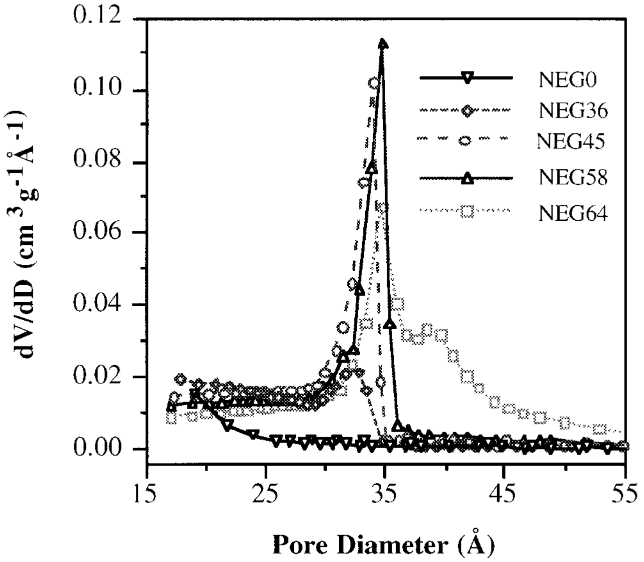

Figure 5. BJH pore size distributions obtained from the N_2 desorption isotherms at −196 °C for the water-extracted samples (NEG series) made with NaOH-hydrolyzed TEOS sol and varied concentrations of D-glucose.

Since the irreversibility of the N_2 isotherm as indicated by the hysteresis loop (e.g., Figures 1 and 2) is quite commonly observed in mesoporous materials, there has been much discussion about its origin and interpretation. It might be caused by one or more of the following factors. First of all, it could be attributed to network effects of interconnecting pores[27,29] generated by the templating molecules such as glucose.[20,22] Second, ink bottle-shaped pore structure or pore size inhomogeneity also leads to the N_2 isotherm with H2 hysteresis.[27,31] Third, the possibility for the system incapable of reaching equilibrium during the acquisition of each data point cannot be excluded. In fact, there have been reports that reversible isotherms for MCM-41 mesoporous molecular sieves in the relative pressure range 0.4−0.6 could be attained by allowing 1 h, instead of 5 s as commonly used, for the system to equilibrate at each desorption point.[16−18] Finally, it is known that the meniscus of condensed nitrogen within the capillary pores becomes instable which leads to the steep region of the desorption branch at the lower closure point at $P/P_0 \sim 0.42$.[19,27] Although it is difficult to differentiate the contributions of one factor from the other to the observed isotherms, the network effect and ink bottle pore structure are considered the major factors for the occurrence of type H2 hysteresis loops. Despite the complexity and uncertainty in using gas adsorption to determine the pore size and distribution of mesoporous solids, this method still gives a good description of pore size distribution for a series of samples.[29] The pore diameter values determined from the BJH method have been found in favorable agreement with those obtained from the TEM image and XRD.[9,20]

Figures 5 and 6 show the pore size distributions, in which differential volume is plotted against pore size for the desorption branches of the N_2 sorption isotherms according to the BJH method with the Halsey equation[32] for multilayer thickness. With the glucose contents of 45−64 wt % in the NaOH-catalyzed system (Figure 6) or of 45−58 wt % in the NaOH-neutralized, HCl-prehydrolyzed system (Figure 5), the extracted silica matrices possess narrowly distributed mesopores centered at about 3.2 or 3.5 nm, respectively. The BJH pore diameters (Table 1) are around 32−35 Å at the glucose concentration of 45 wt % or higher. The BET average pore diameter, derived from $4V/S_{BET}$, increases with glucose concentration. Pore size distributions from the adsorption branches of isotherms also show a similar pattern as in Figures 5 and 6 but with broader distributions. The pore volumes obtained at $P/P_0 \approx 1$ and the mesopore surface areas calculated from the BJH method are found to increase with the glucose content. Both micropores and mesopores in the materials contribute to the observed pore volumes and areas, which could

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(32) Barrett, E. B.; Joyner, L. G.; Halender, P. P. *J. Am. Chem. Soc.* **1951**, *73*, 373.

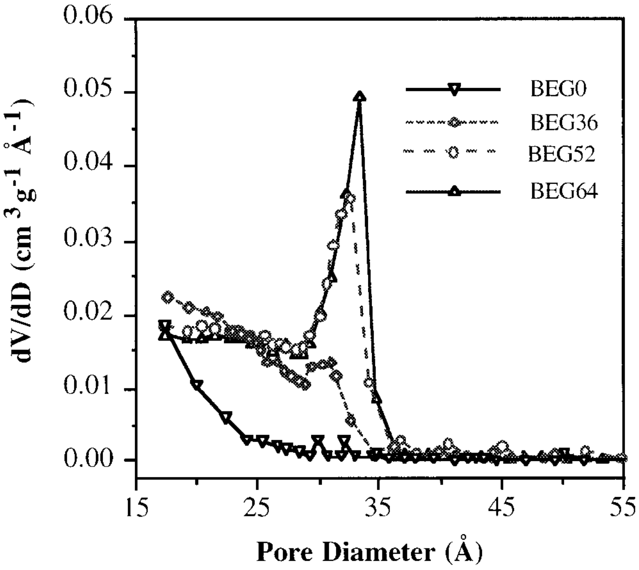

Figure 6. BJH pore size distributions obtained from the N_2 desorption isotherms at −196 °C for the water-extracted samples (BEG series) made with NaOH-neutralized, HCl-hydrolyzed TEOS sol and varied concentrations of D-glucose.

be differentiated approximately by *t*-plot analysis. As the glucose content increases, the contribution from the micropores decreases. At the glucose content of 36 wt % or higher, the contribution from mesopores becomes dominant while that from the micropores is negligible. All these results are quite similar to those obtained in the acid-catalyzed system.[20,22] The pattern of N_2 sorption isotherms closely resembles those of MSU-1 mesoporous silica materials prepared with poly(ethylene oxide) as the neutral surfactant template.[9,11] The transmission electron microscopy images exhibit numerous cylindrical-shaped interconnecting network of pores, similar to the wormlike channel motif in MSU-1 materials.[11]

The infrared spectra of both as-synthesized and water-extracted samples show the major absorption bands associated with network Si−O−Si vibrational modes at ~460, 790, 1080, and 1220 cm^{-1}, along with Si−OH asymmetrical stretching at ~960 cm^{-1} and SiO−H stretching at 3400 cm^{-1}.[21,33] As anticipated, the intensity of the band at 2940 cm^{-1} for C−H stretching of the glucose component in the as-synthesized samples increases with glucose concentration. This band disappeared after water extraction, indicating the removal of the glucose template. The complete removal of glucose is further supported by the fact that the extracted samples showed little or no weight loss upon heating to 800 °C under oxygen in the TGA measurements.

We postulate that, in the nonsurfactant pathway to the organic−inorganic composites and then to mesoporous materials, several factors might govern the generation of the mesostructures without causing macroscopic phase separation in a certain composition range. The nonsurfactant templates, which have been investigated so far, include glucose, maltose, cyclodextrins, tartaric acid derivatives, agarose, and glycerol.[20,22,28,34] They are generally the compounds having high affinity for intermediate silicates, appropriate hydrophilicity and solubility, and low volatility. In our previous communication,[20] we suggested that the aggregates of glucose molecules (not individual molecules) may be responsible for the mesophase formation on the basis of the fact that the dimer of glucose, i.e., D-maltose, gives essentially the same effect as D-glucose though the molecular size is doubled. Furthermore, since the template molecules were used in relatively high concentrations and the pore diameters were found to be much greater than the size of individual template molecules, the templates should be present in forms of aggregates or assembly of the aggregates, whose interactions with the silicate species through hydrogen bonding might play an important role in directing the mesophase formation prior to and/or during the gelation.

The hydrogen bonding between the organic template, e.g., D-glucose, and the intermediate silicate species, $Si(OR)_{4-x}(OH)_x$, brings the two major components together and forms a homogeneous sol without macroscopic particulation of silicates. It may also facilitate the hydrolysis and further condensation of the silanol groups, similar to the case where amine surfactants were used as the templates.[6,12,13] We observed that the sols underwent gelation faster at higher concentrations of D-glucose, suggesting that the presence of glucose promotes condensation. After the gelation and during the subsequent drying process, the affinity of glucose for the silicate species, together with high and increasing viscosity of the system, might keep the inorganic and organic moieties from macroscopic phase separation, while the volatile solvent molecules and reaction byproducts (i.e., alcohol and water) were gradually evaporated from the system. The interactions between the silicates and the template molecules would stabilize silica framework and prevent it from fracture caused by capillary pressure and internal stress buildup during the drying process.[21] As a result, an organic−inorganic composite with bicontinuous networks of silica and the template was obtained as transparent and monolithic solids. Removal of the templates by solvent extraction or by calcination afforded silica materials with interconnecting mesopores.

Summary and Remarks

We have described the synthesis of mesoporous silica materials via the nonsurfactant pathway. D-Glucose was used as the pore-forming agent. The sol−gel reactions of TEOS were carried out with NaOH as catalyst in both prehydrolysis of TEOS and polycondensation of silicate intermediates or with HCl as catalyst in the prehydrolysis followed by neutralization with NaOH to pH of 6 for subsequent polycondensation. Regardless of the pH conditions in the synthesis, transparent and mono-

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(33) Lin, C.; Hemment, P. L. F.; Li, J.; Chan, C. W. M. *Mater. Lett.* **1992**, *15*, 137.

(34) A referee of this paper asked why we decided to use chiral compounds in this study. Our original intent was to make amorphous inorganic materials with “chiral imprints/cavities” upon removal of the chiral organic compounds. It turned out that we were not be able to detect any significant chiral cavity in the sol−gel silica after complete extraction of chiral molecules. However, interestingly the materials were optically rotatory monoliths before the extraction[28] and were mesoporous after the extraction.[20] Achiral compounds such as glycerol worked as well as those chiral ones.

lithic glucose-containing silica gels could be obtained. The glucose template was removed completely by water extraction. The resultant materials, as characterized by N_2 sorption measurements, exhibit high specific surface area, pore volume, and narrow pore distribution with BJH pore diameter of 3.2−3.5 nm, indicative of the mesoporosity. These pore parameters generally increase and the N_2 sorption isotherms gradually transform from reversible type I to type IV-like isotherms with H2 hysteresis as the glucose concentration is increased in the synthesis. At low glucose concentrations (<36 wt %), both micropores and mesopores contribute to the porosity of the materials. However, at high glucose concentrations (36−64 wt %), mesopores are dominant with narrow pore size distributions. The characteristics of pore structures are similar to those observed for the porous silica materials prepared via the nonsurfactant templating pathway under acid catalysis or via the neutral PEO surfactant pathway.

In addition to the low cost, environmental friendliness, and ease in removal under mild conditions, the nonsurfactant templates such as D-glucose offer many advantages, including good compatibility with enzymes. In particular, the achievement of mesoporous materials with the glucose template under nearly neutral conditions provides an interesting opportunity for immobilization by entrapment of enzymes and other biologically active substances in a rigid mesoporous framework with controllable pore diameters. Compared to macroporous materials, the diameters of mesopores are small enough to prevent leakage of enzyme molecules. On the other hand, they are large enough to allow an easier transport of substrates and products in and out of the materials, compared to microporous materials as obtained from conventional sol−gel processing.[35,36] We have been actively exploiting this opportunity in our laboratories.

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(35) Avnir, D.; Braun, S.; Lev, O.; Ottolenghi, M. *Chem. Mater.* **1994**, *6*, 1605.

(36) Dave, B. C.; Dunn, B.; Valentine, J. S.; Zink, J. I. *Anal. Chem.* **1994**, *66*, 1120A.