Synthesis of Porous SiO₂ Spherical Particles by Sol-Gel Methods in W/O Emulsion

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Dispersed porous spherical silica particles were prepared by a sol-gel process from solutions of tetramethoxysilane (TMOS), polyethyleneglycol (PEG), H₂O and organic solvent in W/O (water in oil phase) emulsions. The interconnected pores can be made by eliminating PEG from gel bodies. Such PEG originates by phase separation between the PEG and the polymerizing silica in common solvents. Microstructures of the particles are affected by the compositions of the starting solutions. The pore diameter increases with an increase in molecular weight of PEG when the molar ratio of PEG as monomer unit to TMOS is fixed to 0.3. The pore diameter decreases and specific surface area increases with an increase in the content of PEG having molecular weight of 50000 when the [PEG]/[TMOS] molar ratio is greater than 0.3. The pore diameter decreases by use of basic solvents such as *N,N*-dimethylformamide (DMF) and formamide (FA) instead of methanol.

Keywords Porous silica, sol-gel method, high-performance liquid chromatography, packing material, W/O emulsion

Surface modified silica gel particles have been used as packing materials for the high-performance liquid chromatography (HPLC). The control of pore sizes and particle sizes of the gels is one of the important problems in this field. Generally, pores of commercial particles consist of interstices of secondary silica particles. For better chemical stability and mechanical strength, however, glasses of interconnected pore structure are preferred. In a previous paper¹, we developed a new type of porous silica particles by thermal and successive acid treatments of sodium borosilicate glasses prepared by the sol-gel process. Although the spherical porous glasses of interconnected pore structure were obtained, it required two steps: first thermal, then acid treatment.

Nakanishi *et al.*²⁻⁵ reported methods for preparing monolithic porous silica gels by the sol-gel process; thus, porous silica gels were prepared from solutions of tetraethoxysilane (TEOS) containing polymers such as polyacrylic acid (PAA). They differentiated the type of morphology and average domain size in terms of the concentration, molecular weight of PAA and solubility parameter of the chemical additives. Ota *et al.*⁶ synthesized organic-inorganic composite gels from tetraethoxysilane-polyethyleneglycol (PEG)-H₂O-methanol (MeOH). Uo *et al.*⁷ succeeded in preparing porous silica gels from solutions of tetramethoxysilane (TMOS)-PEG-H₂O-MeOH. The pore diameters decreased with increases of concentration and molecular weight of PEG. In the initial solution, immiscibility can not be observed. However, progress of polymerization of TMOS shifts the critical solution temperature to a

higher temperature and the solutions are brought into a two-phase region, *i.e.* one phase of PEG+solvent and another phase of polymerizing silica+solvent. This type of phase separation differs from that seen when the temperature of the solution is lowered below the critical solution temperature. The type (spinodal or nucleation and growth) and the degree of phase separation depend on when sol-gel transition occurs. Thus, the factors which determine the morphology of pore structure are mutual solubility of PEG and some organic solvent, molecular weight of PEG and rates of hydrolysis and condensation of TMOS. In this paper, a procedure to prepare spherical silica particles of interconnected pore structure by using the sol-gel reaction in W/O emulsion is developed and the optimum conditions are examined.

Experimental

Syntheses of porous silica particles in W/O emulsions

The compositions of starting solutions are shown in Table 1. Here, the molar ratios of PEG are expressed by monomer units. The particles made using PEG with molecular weights of 50000 and 20000 are denoted hereafter as SiO₂-5 and SiO₂-2, respectively. PEG having molecular weights of 2000000, 500000, 2000 and 200 were also used. Hydrochloric acid was used as a catalyst for hydrolysis. Distilled water containing PEG and hydrochloric acid was spouted slowly through a glass capillary into 2.5 g TMOS diluted with MeOH at room temperature during 45 min. The mixed solution was stirred vigorously during an additional 45 min to 3 h in a beaker

Table 1 Composition of starting solutions

	Molar ratio				
	TMOS	H ₂ O	HCl	CH ₃ OH	PEG
Series A	1	20	0.01	9	0.1–1.0
Series B	1	20	0.01	9	0.1–1.0
Series C	1	20	0.01	0–12	0.3

PEG molecular weights of series A, B and C are 50000, 20000 and 50000 respectively.

Fig. 1 Preparation of porous SiO₂ spherical particles.

covered with aluminum foil, as shown in Fig. 1. Then the sol solution was poured into a 100 ml Teflon beaker containing 26.1 g of kerosene and 30 wt% of surfactants (the weight ratio of sorbitan monooleate:sorbitan monostearate is 3:1). The resulting solution was agitated uniformly using a homogenizer (Tokushu Kika Kogyo Co., Homomixer M) at a rate of 2000 rpm at 45°C; thus, the hydrolysis and condensation reaction is as shown in Eqs. (1)–(3),

were again continued in the water phase of W/O emulsion. After gelation (usually 30 min after emulsifying), particles precipitated at the bottom. These wet particles were filtrated, washed with hexane and acetone, and dried for 3 d in an oven at 40°C. A preliminary thermal analysis of the particles by DTA showed an exothermic

Fig. 2 FT-IR spectra of SiO₂ particles. Heat treatment temperature: A, 40°C; B, 200°C; C, 500°C.

peak around 370°C due to burning of the residual organic solvents, including PEG. FT-IR spectra of particles heated at various temperatures are shown in Fig. 2. Here an absorption band at around 3400 cm⁻¹ is assigned to Si–OH stretching vibration. An absorption around 2900 cm⁻¹ band assigned to PEG (–CH₂CH₂– stretching vibration) disappeared at 500°C. Thus, the temperature was raised to 200°C at a rate of 5°C/h and kept at this temperature for 5 h. Finally the temperature was raised to 500°C at a rate of 50°C/h and was kept for 12 h in an electric furnace.

Characterization of the particles

The specific surface area and pore size distribution were measured using an analyzer (Shibata Co., SA-1100) and a poresizer (Micromeritics Co., 9303), respectively. The particle shape and particle size distribution were determined from images of a scanning electron microscope (Hitachi Co., S-510).

Results and Discussion

Effect of molecular weight and concentration of PEG on morphology of the particles

When PEG of molecular weights of 200 and 2000 were used, the interconnected pore structure did not form; thus, the particles consisted of aggregations of secondary particles of SiO₂. The pore diameter and specific surface area were 4 nm and 500 m²/g; such values are seen in silica gels prepared by the usual sol-gel method without any organic macromolecules. On the other hand, when PEG having molecular weights of 500000 and 2000000 were used, it was difficult to make spherical particles in W/O emulsion due to the high viscosity of the solutions. Figure 3 shows a typical particle size distribution of SiO₂-5 under the present experimental conditions. They are well dispersed and the average particle diameter was about 15 μm. Dependences of the pore size (central values of pore size distribution curves) and specific surface area of SiO₂-5 and SiO₂-2 particles on the

Fig. 3 Typical particle size distribution of SiO₂-5. Fig. 4 Dependences of pore size on the concentration of PEG. $\diamond$: PEG-200; $\blacklozenge$: PEG-2000; $\circ$: PEG-20000; $\bullet$: PEG-50000.

concentration of PEG are shown in Figs. 4 and 5, respectively. The pore size decreased with an increase in the concentration of PEG in SiO₂-5 and SiO₂-2 particles when the molar ratio of PEG to TMOS was greater than 0.3 or 0.4, respectively. This tendencies are similar to the results of monolithic gels made by Uo *et al.*⁷ The specific surface area increased with an increase of the concentration of PEG, when the molar ratio of PEG to TMOS is also greater than 0.3 or 0.4. Figure 6 represent morphologies of SiO₂-5 particles when the [PEG]/[TMOS] ratios are 0.2, 0.3 and 0.8. The specific surface area of interconnected structure increased with an increase of molecular weight of PEG when the molar ratio of [PEG] to [TMOS] is fixed at 0.3. The large pores were observed in particles when PEG of lower molecular weight were used. On the other hand, when

Fig. 5 Dependence of specific surface area on the concentration of PEG; symbols are the same as in Fig. 4.

the [PEG]/[TMOS] ratio is lower than 0.2, the particles consist of aggregations of small secondary particles, so that the specific surface area increases due to the interstices of these secondary particles.

Effect of solvents on morphology of the particles

Figure 7 shows an SEM image of the SiO₂-5 particle when the molar ratio of PEG to TMOS is fixed to 0.3 and that of MeOH to TMOS is 6 or 12. Generally, an isolated pore structure was seen when the [MeOH]/[TMOS] molar ratio is smaller than 6, which contrasts to that seen when this ratio is 9 (Fig. 6). On the other hand aggregation of silica secondary particles was seen in particles when the [MeOH]/[TMOS] ratio is 12. Additions of various organic solvents other than MeOH lead to the changes of the pore diameter of the resultant particles. In Table 2 the specific surface area and pore diameter of the SiO₂-5 particles are listed; here ethyleneglycol (EG), trimethyleneglycol (TMG), *N,N*-dimethyl formamide (DMF) and formamide (FA), whose mole ratio to TMOS was fixed to 9, were used. Nakanishi *et al.*⁴ reported that the average domain size decreased with an increase of solubility parameter. Solubility parameters of EG, DMF and FA are 14.6, 12.1 and 19.2, so that a clear relation of pore sizes to solubility parameters cannot be seen. Rather, DMF and FA, which are classified as Lewis bases, seem to affect the diameters and pore sizes of the particles. The pore diameter obtained by using DMF seems larger than that obtained by FA. FA makes large pores in gels due to the formation of large primary-particles compared with those of DMF.⁸ The primary-particles distribute uniformly over the bulk gel. Therefore, the degree of coalescence among the particles is less than that obtained by using DMF in the hydrolysis and polymerization reactions of TMOS.¹

Fig. 6 Morphologies of SiO₂-5 particles. [PEG]/[TMOS] ratio: A, 0.2; B, 0.3; C, 0.8.

Fig. 7 SEM image of the SiO₂-5 particles. [PEG]/[TMOS] ratio is 0.3. [MeOH]/[PEG] ratio: A, 6; B, 12.

Table 2 Effect of solvents on specific surface area and pore diameter of SiO₂ particles

Solvent	Specific surface area/m ² g ⁻¹	Pore diameter/nm
Ethylene glycol	112	590
Methanol	113	590
Trimethylene glycol	234	320
<i>N,N</i> -Dimethyl formamide	360	86
Formamide	377	60

TMOS : solvent : H₂O : HCl : PEG(50000)=1 : 9 : 20 : 0.01 : 0.3.

Time of hydrolysis

In the present experiment, hydrolysis was pursued at room temperature between 45 min and 3 h after mixing of TMOS solution with PEG and then the temperature was changed to 45°C in W/O emulsions; here gelations occurred in comparatively short times (30 min). The pore sizes decreased with an increase in times of hydrolysis before emulsifying. For example, pore sizes

are 590 nm and 300 nm when hydrolyses were performed for 45 min or for 90 min or more, respectively. With an increase in the hydrolysis time, the polymerization in W/O emulsion may proceed faster and PEG was removed out from the network of silica+PEG system in an emulsion to oil phase. The pore sizes decrease due to large volume fractions of the silica phase. DMF and FA may accelerate the rate of hydrolysis as catalysts.

Mechanism of phase separation

As shown in the literature⁵, schematic phase diagrams for the present system are also shown in Fig. 8. Before the start of the polymerization of TMOS, the solution consists of one phase under a common solvent such as methanol, shown in Fig. 8 (A); here the starting composition is denoted by an open circle. With progress of polymerization of hydrolyzed silica, the compatibility between silica and PEG in the presence of methanol is lowered and the upper critical solution temperature should shift to higher temperature (Fig. 8 (B)). The solution is brought into a two-phase region. When

Fig. 8 Schematic shift of the binodal line (solid lines) and spinodal line (broken lines) with polymerization of TMOS. Starting composition is indicated by a small open circle. The polymerization of TMOS proceeds successively to (A), (B) and (C) (see text⁵).

gelation proceeds in a one-phase region, the resultant particles consist of aggregations of secondary particles of SiO_2 , as seen in Fig. 6(A), where the concentration of PEG is low and that of methanol is high. The polymerization proceeds in a similar way to that seen in an absence of PEG. On the other hand, when the concentration of methanol is low, PEG was included in a silica network, so that SiO_2 particles with isolated pores were formed, due to elimination of PEG from the silica network by thermal treatment (Fig. 7(B)).

When gelation occurs in a two-phase region, the phase separation proceeds by a spinodal decomposition mechanism. The interconnected pore structure can be seen in Figs. 6(B) and 6(C). The pore size increased with an increase in the concentration of PEG. The relationship⁹ between pore diameter or structural period (Λ_m) and

spinodal temperature (T_s) is expressed by Eq. (4):

$$\Lambda_m \propto K(T_s - T_1)^{-1/2} \quad (4)$$

where K and T_1 are a proportional constant and the experimental temperature, respectively. T_1 is kept constant in the present experiment. When gelation occurs at the state of Fig. 8(B), a comparatively large pore structure can be seen (Fig. 7(B)). With an increase of the concentration of PEG, the gelation rate decreased compared with the rate of increase of upper critical solution temperature, and the pore size decreased according to Fig. 8(C) and Eq. (4).

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References

1. H. Mori, H. Yamashita, K. Nakamura and T. Maekawa, *J. Ceram. Soc. Jpn.*, **101**, 1180 (1993).
2. H. Komura, K. Nakanishi and N. Soga, Proceedings of Fall Meeting, The Ceramic Society of Japan (1989), p. 238.
3. K. Nakanishi and N. Soga, *J. Non-Cryst. Solids*, **139**, 1(1992).
4. K. Nakanishi and N. Soga, *J. Non-Cryst. Solids*, **142**, 45 (1992).
5. H. Kaji, K. Nakanishi and N. Soga, *J. Sol-Gel Sci. Technol.*, **1**, 35 (1993).
6. R. Ota, A. Watanabe, J. Fukunaga and N. Yoshida, *J. Ceram. Soc. Jpn.*, **97**, 213 (1989).
7. M. Uo, K. Yamashita, M. Suzuki, E. Tamiya, I. Karube and A. Makishima, *J. Ceram. Soc. Jpn.*, **100**, 426 (1992).
8. T. Katagiri and T. Maekawa, *J. Non-Cryst. Solids*, **134**, 183 (1991).
9. J. W. Cahn, *Acta Metall.*, **9**, 795 (1961).

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