

Formation of the Monolithic Silica Gel Column with Bimodal Pore Structure

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A biporous monolithic silica gel column possessing both micrometer sized through-pores and nanometer sized mesopores located in the silica skeletons was prepared and the high concentration porogen (e.g., 2 mol/L ammonium hydroxide solution) was used for increasing mesopore size in this work. The mechanism for the preparation of the monolithic column was investigated in detail. Moreover, the effect of the polyethylene glycol concentration in the starting solution was studied and it was found that a lower concentration range was also suitable for forming the interconnected porous structure for the monolithic silica gel column. At lower concentrations, however, the phase separation mechanisms and experimental results were different.

Key Words: Monolithic silica gel column, Phase separation, Sol-gel transition, Pore structure.

Introduction

High performance liquid chromatography (HPLC) has become one of the most commonly used methods due to the need for rapid development in life science, environmental science and the pharmaceutical industry. However, a conventional column packed with microparticulate porous silica or other bead packing has some inherent disadvantages in HPLC¹, such as very high pressure (sometimes up to 250 bars), a lengthy flushing or equilibration time between runs, and limitations on the flow rate or on the length of separation column, in particular on the sample throughput because of resistance in the columns. Therefore operation at high speed is not compatible with high efficiency in the case of particle-packed columns.

In recent years, a novel type, the monolithic silica column^{2,3}, has been developed to overcome these disadvantages. Takahashi et al.⁴⁻⁶ reported that gels with interconnected porous morphology in micrometer range could be prepared in an alkoxide based silica sol-gel system when an organic polymer was incorporated. The method yields rods made of a single piece of porous silica with a well-defined pore structure exhibiting

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both macropores and mesopores. The main feature of the silica monoliths prepared with this method is their high total porosity, approximately 15% higher than that of conventional HPLC columns. The resulting hydraulic resistance of the column is therefore much lower, allowing their operation at higher flowrates or permitting the operation of a long series of columns.

Generally, the homogeneous reaction solution separates into phases. One is rich in organic polymer and the other is rich in silica because of entropy decrease caused by the polymerization of the silica oligomers. However, when polyethylene oxide (or polyethylene glycol) is added, 1 of the 2 phases is rich in solvent and the other in polyethylene oxide (or polyethylene glycol) and silica⁶.

We investigated the formation of biporous monolithic silica gel prepared from a solution containing polyethylene glycol under acetic acid as the catalyst and ammonium hydroxide solution as a porogen solvent. The mechanism for preparation of the monolithic silica gel column, and the effect of polyethylene glycol concentration on the structure of the rods were discussed. Furthermore, we successfully solved the crack and deformation problems involved in preparing the column by adopting improved sol-gel technology, and the dry time was shortened greatly.

Experimental

Reagents and Instruments

Tetramethoxysilane (TMOS) (Wuhan Neomaterial Development Co. Inc. Hubei, China. It was used after purification), was used as a silica source. Polyethylene glycol (PEG) ($M_w=10000$, Japan) was used as a polymer component. Acetic acid (0.01 mol/L), ammonium hydroxide and N,N-dimethylformamide were used as a catalyst for hydrolysis, a porogen solvent of mesopores and a drying control reagent, respectively, during the preparation of the monoliths.

The morphological structures of the rods were observed by scanning electron microscopy (SEM, KYKY-1000B, China).

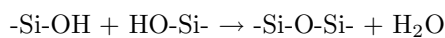
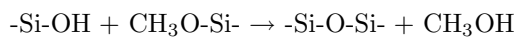
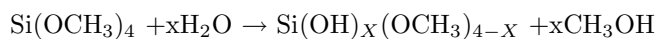
Procedures

The monolithic silica gel columns were prepared by the following procedures: TMOS, PEG and 0.01 mol/L acetic acid (52 mL) were mixed and stirred at 0 °C for 30 min. The mixture (pH3) was then poured into a polytetrafluoroethylene tube and kept at 40 °C for 24 h. During this process, sol-gel transition took place. Then the monolithic silica gel was washed with distilled water, and treated with aqueous ammonium hydroxide solution (0.01-2.0 mol/L) at 120 °C for 9 h to obtain appropriate nanometer-size mesopores. After the treatment in 0.1 mol/L aqueous nitric acid solution, water and N,N-dimethylformamide solution, the wet gel samples were dried with N,N-dimethylformamide at 60 °C for 10 h. The monolithic silica gel was finally heated at 700 °C for 2 h.

Results and Discussion

Inducing spinodal phase separation

In the sol-gel technology, the most important physical chemistry process is hydrolysis and polycondensation. The hydrolysis and polycondensation reactions of TMOS are as follows:



Turbidity occurs when the sol turns to gel. The turbidity implies that the system undergoes phase separation. By spinodal phase separation, the system performs sol-gel transition and gel with micrometer sized inter-pores can be formed under the existence of acid catalyst and PEG.

It is assumed that 2 pathways⁴ can induce spinodal phase separation and fix the inter-pore morphologies:

(1) The incompatibility between polymers is increased by the solvent extraction while limiting the motion of polymers by concentrating the system.

(2) Phase separation is induced by the temperature jump method. The structure depends on the chemical cross-linking reaction.

The first is regarded as a “physical” process because neither the formation nor the breakage of chemical bonds is included. The second is a “chemical” process; the method of inducing phase separation is also termed “chemical cooling” (or “quenching”), and it induces phase separation by promoting a chemical reaction that rapidly modifies the interaction among constituents. In the present sol-gel system containing silica, organic polymer PEG and solvent, the phase separation behavior apparently involves “chemical quenching”.

“Chemical quenching” initiating phase separation thrusts a single-phase mixture into a 2-phase region of the phase diagram rapidly enough to prevent a nucleation growth (NG) process^{5,7}. The NG process is favored in a metastable region; the starting composition and temperature have to pass through the region during the polymerization. Because NG is a relatively slow process incorporated with a diffusion of second-phase components, polymerization makes solution viscosity increase, which leads to restrained NG.

In the present system, PEG is an additive used for inducing phase separation and affecting the phase separation kinetics. It forms strong hydrogen bonds with silanols. This interaction makes the interface between the solvent and adsorbed PEG unstable, which results in phase separation.

Formation of monolithic gel with micrometer sized silica skeletons and through-pores

In the present system, the solution undergoes phase separation during the gel formation. Time-consuming NG is inhibited due to an increasing viscosity and spinodal phase separation dominates. The coarsening degree determines the domain size (a combined size of through-pore and skeleton), which can grow in the crosslinking network. Through gel formation, a transient structure being developed by spinodal phase separation can be fixed as a gel structure. Thus initially the fluid reaction system turns into a continuous solid gel phase with fluid filling interstices in the gel structure. After the fluid is removed, open pores are left.

In the sol-gel process, PEG plays an important role. It controls the size and volume of macropores in the gels. The domain size increases with increasing PEG content in the system.

In order to obtain monolithic columns of different structure, different compositions of the reaction mixture were investigated. Table 1 illustrates the effect of different TMOS/PEG ratios on monolithic silica gel structures. Figure 1 shows several typical examples of the morphology resulting from different TMOS/PEG ratios. Figure 1 and Table 1 show that the domain and through-pore size decrease with increasing TMOS/PEG ratio. However, when the TMOS/PEG ratio was very low and high, aggregates of

gel particles with low connectivity and a monolithic gel matrix without detectable micrometer sized pores were formed, respectively, which are not suitable for chromatographic columns for HPLC.

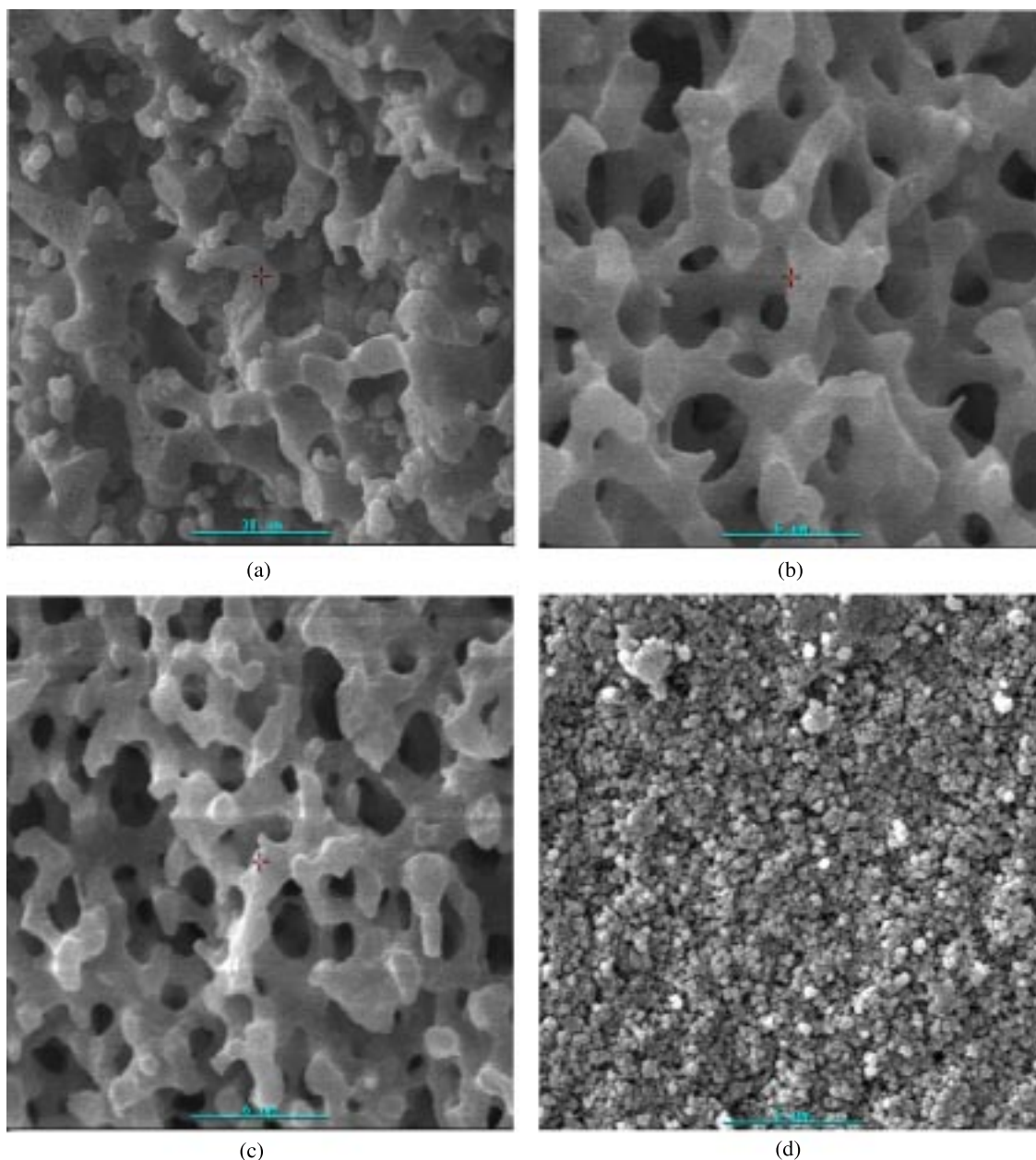


Figure 1. SEM photography of monolithic silica gel samples Samples a-d were prepared from TMOS/PEG ratios of 7.1, 7.6, 8.0 and 8.7 in Table 1, respectively.

The domain size frozen in the gel depends on how far the coarsening of the domains can proceed until the domains are frozen-in by the sol-gel transition⁸. In the present case, the increase in PEG concentration in the reactive solution leads to a stronger hydrogen bond interaction between PEG and silica oligomer, which makes the interface between the solvent and adsorbed PEG more unstable. Thus phase separation takes place at early stages in the growth of silica, which leads to a shallow quench and long coarsening. Large domain size is produced accordingly. This experimental result is contrary to those reported previously^{8,9}.

The reason may be that it is different for the ranges of PEG concentration required in the 2 different systems while interconnected porous structures were formed. When the starting solution is at a relatively low PEG concentration ($4.1 \times 10^{-3} \sim 5.0 \times 10^{-3}$ mol/L), as described above, it dominates for the interaction between PEG and silica oligomer, which results in early phase separation due to the increase in PEG concentration. Under a high PEG concentration ($6.5 \times 10^{-3} \sim 8.3 \times 10^{-3}$ mol/L), in contrast, Ishizuka et al.^{8,9} reported that the increasing PEO or PEG concentration in the starting composition led to retardance of phase separation relative to the sol-gel transition. Thus the phase domains were frozen in the earlier stage of the coarsening, and finer domains were observed in gelled samples. Because in the 2 different systems it is different for the ranges of PEG concentration required while interconnected porous structures were formed, the phase separation mechanisms and experimental results were also different.

Table 1. The effect of the different TMOS/PEG ratio on the monolithic silica samples.

TMOS/PEG ratio	7.1	7.2	7.4	7.6	7.8	8.0	8.2	8.4	8.7
Skeleton size (μm)	a	2.5	2.0	1.5	1.2	0.9	0.6	0.3	b
Through-pore size (μm)	a	4.3	3.0	2.5	2.0	1.2	0.8	0.4	b
Linear shrinkage ratio (%)	25.8	25.9	26.6	27.0	27.9	27.2	26.2	24.6	crack

The contents of TMOS and 0.01 mol/L HAc are respectively 28.4 mL and 52 mL. Mesopores were not fabricated in the batch experiment.

a—Aggregates of gel particles

b—Gel matrix

Fabricating nanometer sized mesopores in the wet continuous gel skeletons

Aqueous ammonium hydroxide was used as a porogen for forming mesopores. The mesopore in the wet gel skeleton was made by alternating the fluid phase with an external solution (ammonium hydroxide solution). As was pointed out, the mesopore size depends mainly on the temperature and pH of the exchanged solution⁸. When $\text{pH} > 8$ in the external solution, initially microporous gel skeletons became reorganized into skeletons with mesopores with the median size above 5nm¹⁰. Table 2 lists the variation of the mesopore size with the porogen concentration. The data in Table 2 indicate that the mesopore size increased with the increase in the porogen concentration when the temperature was at 120 °C, while the micrometer sized structure of the gel skeleton and the through-pores were not obviously affected by the external solution treatments. However, the network structure of the monolithic gels could be destroyed if the porogen concentration were too high. Figure 2 shows the morphological structure treated by 2 mol/L ammonium hydroxide solution. Finally, the chemically and mechanically stabilized bimodal pore structure was obtained through subsequent drying and heattreatment.

Table 2. The effect of the porogen concentration on the structure of monolithic silica samples.

Concentration of porogen (mol/L)	2 ^a	1 ^b	0.1 ^b	0.01 ^b	0 ^b
pH of porogen	12.62	12.11	11.12	10.17	6.90
Skeleton size (μm)	0.9	2.0	1.8	1.5	1.5
Through-pore size (μm)	1.0	2.2	2.0	2.0	2.0
Mesopore size (nm)	28	25	18	14	micropores

a, b used the experimental conditions of TMOS/PEG ratios of 8.2 and 7.8, respectively.

The experimental temperature was 120 °C.

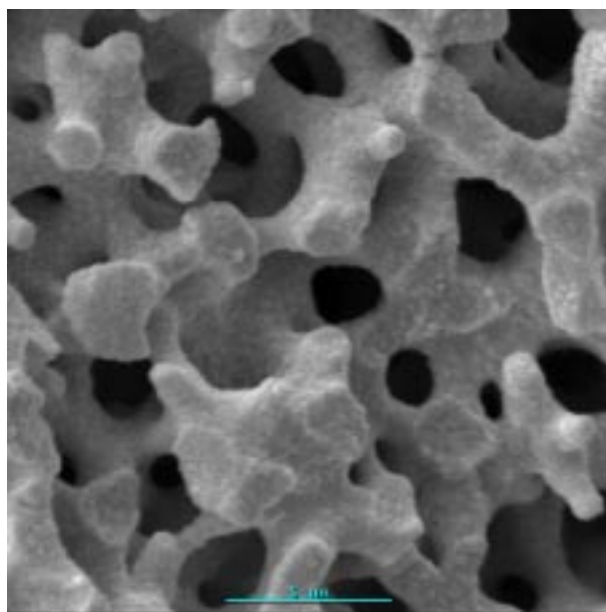


Figure 2. SEM photograph of cross-section of monolithic silica gel sample treated by 2 mol/L ammonium hydroxide solution. The sample was prepared from a TMOS/PEG ratio of 8.2.

Column crack is another frequent problem when directly drying the wet gel column because water with high surface tension can easily cause the gel column to crack. In order to solve this problem, N,N-dimethylformamide with low volatility and surface tension was used as a drying control agent. After the column was treated with N,N-dimethylformamide, water evaporated earlier than N,N-dimethylformamide during the drying of the wet column treated. Thus the drying rate was controlled well, the crack problem of the gel column was solved accordingly, and drying time was shortened from 3 days to 10 h in comparison with that reported ^{2,3}.

The problem of deformation in preparing the column was solved by a heat treatment procedure, i.e. the wet gel column was treated in water at 120 °C for 6 h before it was dried. During the procedure, the skeleton strength of the gel column increased greatly. Thus the column did not tend to deform during subsequent drying at 60 °C and heattreatment at 700 °C.

Conclusion

Gels with continuous micrometer sized silica skeletons and through-pores were obtained by hydrolyzing alkoxy silane with acid as catalyst and the existence of PEG. The morphology, connectivity and pore size of the macroporous gels were controlled by changing the TMOS/PEG ratio when temperature was fixed, which could be explained by the spinodal phase separation mechanism. The reorganization behavior of nanometer sized silica was achieved by alternation of the fluid phase with an external solution, and the mesopore size was controlled by changing the porogen concentration. The monolithic silica column prepared by such a method has good prospects for application.

Acknowledgments

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