

## 具有高机械强度的双孔硅胶的制备

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## Preparation of Bimodal Porous Silica with Excellent Mechanical Strength

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**Abstract:** The macroporous structure was formed in the wet gels by controlling the phase separation process induced by the hydrolysis and polycondensation of alkoxysilane. Further bimodal porous silica with good mechanical strength can be obtained by aging process.

**Key words:** bimodal porous silica; mechanical strength; sol-gel; aging

## 0 Introduction

Porous materials are useful for a variety of applications, for example, heterogeneous catalysis, adsorption and molecular separation<sup>[1-3]</sup>. In addition to conventional mesoporous and microporous materials, multimodal such as bi- or trimodal porous materials have attracted immense interests, and a number of methods have been used to create such pore structures in silica<sup>[4-6]</sup>. Nakanishi et al.<sup>[7,8]</sup> prepared a bimodal porous silica with interconnected macropores and mesopores by fixing transitional structures of phase separation by gelation and the material was applied as monolithic column for high-performance liquid chromatography (HPLC). In the bimodal porous silica, mesopores act as functional surfaces after surface modification, and

macropores serve as high-speed pathway for gas- and liquid-phases molecules to reach the surfaces in mesopores. Because of this advantage in the bimodal porous silica gel, it would have potential applications other than HPLC, such as catalysis, adsorption, and separation and so on<sup>[9-11]</sup>.

As we know, the mechanical strength of the silica materials is an important parameter for their applications in fields such as industrial catalysts and adsorbents, and is of outstanding importance for their manufacturing and packaging, as well as for loading and operation in the reactors. Improved mechanical strength and stiffness are of interest to increase their commercial viability. However, our work has shown that the bimodal porous silica prepared by the method in the reference<sup>[8]</sup> has limited mechanical strength.

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In this work, based on the preparation method as described in the literature<sup>[8]</sup>, we propose a simple and easy procedure to enhance the mechanical strength of the bimodal porous silica gels without changing their structures and decreasing the pore size drastically.

## 1 Experimental

### 1.1 Preparation of bimodal porous silica

The procedure for the preparation was as follows: 28.4 mL of Tetramethoxysilane (TMOS) was added to a solution containing 4.974 g of poly ethylene oxide with an average molecular weight of 10 000 (PEO) and 52 mL of 0.01 mol·L<sup>-1</sup> acetic acid, and the mixture was then stirred at 0 °C for 30 min. The resultant homogeneous solution was cast into Teflon tubes with an inner diameter of 7 mm and kept at 40 °C for 2 h for gelation. The wet gel rods obtained were soaked in 20vol% H<sub>2</sub>O/methanol for 24 h at 60 °C followed by aging in a solution of 70vol% TMOS/methanol for 72 h at 70 °C. The wet gels were further washed in methanol for 24 h at 50 °C and then in n-heptane for 24 h at 50 °C. The gels were heated in air at 700 °C for 2 h to remove organic residues after drying at ambient pressure at 70 °C for 24 h. The samples were denoted as SM.

As a reference, a bimodal porous silica gel was prepared using a procedure described by Ishizuka et al. (denoted as SR)<sup>[8]</sup>. The composition of the reaction mixture (including TMOS, PEO and acetic acid) was the same as above for the silica gels preparation.

### 1.2 Characterization

A scanning electron microscope (SEM: JSM-35C,

Japan) was employed to examine the morphology of samples on a micrometer scale using the flat fractured surfaces of the dried gels. The accelerating voltage was 25 kV. Macropore size was obtained by averaging more than five directly measured values on the SEM photographs. A nitrogen adsorption-desorption isotherm for each silica gel sample was measured at -196 °C on an automatic adsorption-measurement system (AUTOSORB-1, USA) after the sample had been degassed at 150 °C for 30 min under vacuum. The specific surface area was calculated from the adsorption branch according to the Brenauer-Emmett-Teller (BET) method. The pore size distribution was calculated by the BJH method using the desorption branch of the isotherm. The total pore volume was calculated from the amount of N<sub>2</sub> adsorbed at  $P/P_0 > 0.95$ . The crushing strength was determined by using a grain crushing strength tester (Dalian Equipment Diagnose Factory) according to ASTM D-4179. A test piece was required the length of 10 mm and diameter of less than 7 mm. The grain crushing strength,  $\sigma$ , was calculated with,

$$\sigma = F/L$$

where  $F$  is the breaking load of the test pieces,  $L$  is the length of each test piece. Ten test pieces were broken to obtain an average value.

## 2 Results and discussion

SEM images (Fig.1) show the continuous macroporous morphology of SM and SR. The macroporous structure is formed by spinodal decomposition which leads to the formation of continuous micrometer range domains, and it has been essentially completed al-

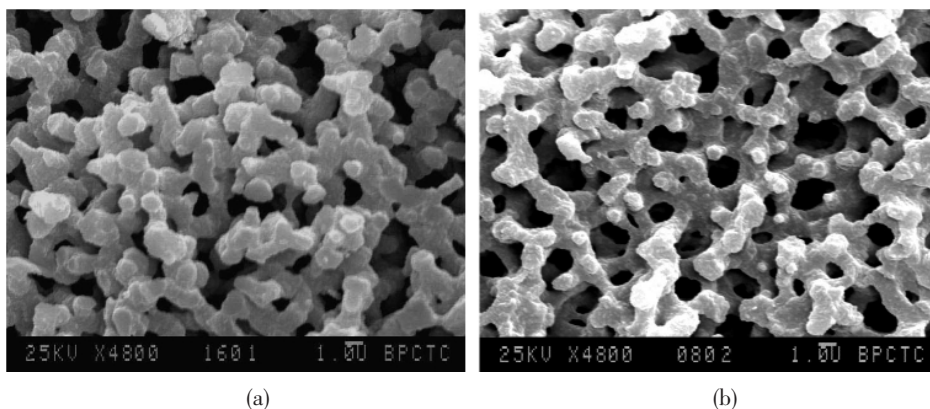


Fig.1 SEM images of the bimodal porous silica gels SM (a) and SR (b)

ready in the wet state after gelation<sup>[8]</sup>. Fig.2 shows adsorption-desorption isotherms and corresponding pore size distribution of the gel samples. SR shows maxima in its pore size distribution at *ca.* 7 nm and SM at *ca.* 4 nm. A comparison of properties between SR and SM

is reported in Table 1. The BET surface area, macropore size and pores volume of the SM gels are smaller than those of the SR gels. The crushing strength is about ten times higher for the SM gels compared to the SR gels.

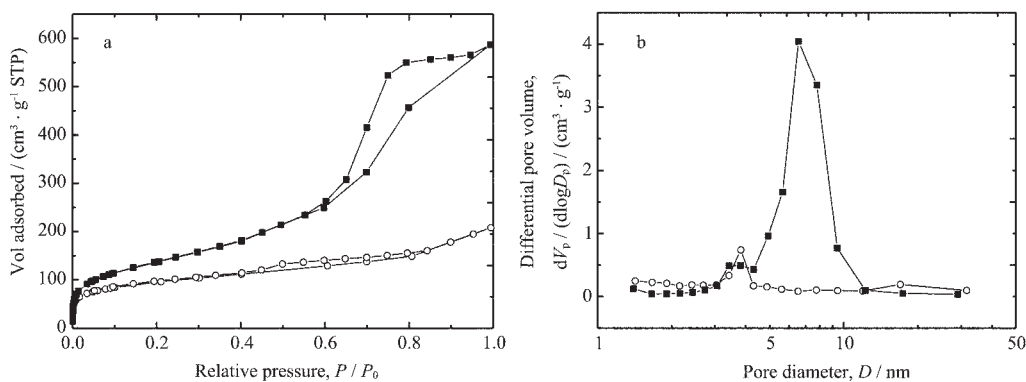


Fig.2 Nitrogen adsorption-desorption isotherms (a) and corresponding pore size distribution (b) of the gel samples  
Open circle: SM. Closed square: SR.

Table 1 Properties of the samples

Sample	SA* / (m²·g⁻¹)	MS** / μm	V*** / (cm³·g⁻¹)	σ / (N·mm⁻¹)
SM	286	1.5	0.27	16
SR	456	1.7	0.83	1.5

\* SA is BET surface area of the samples.

\*\* MS is macropore size.

\*\*\* V is the total pore volume.

Prior to aging in the TMOS solution, all the gels were washed in a 20vol% H<sub>2</sub>O/methanol solution. During washing, gel strength and stiffness increased due to dissolution of silica from the particles (convex surface) and reprecipitation into the necks (concave surface) between the particles<sup>[12]</sup>. This effect of dissolution/precipitation could be observed for SM gels giving a decrease in surface area. However, this increase in strength and stiffness is not sufficient and further aging in TMOS solution is necessary. Aging the wet gels in a solution of TMOS causes silica to precipitate from the aging solution onto the silica network which gives a corresponding strengthening and stiffening of the gel network<sup>[13]</sup>. An increase in crushing strength to 16 N·mm<sup>-1</sup> was obtained and a little decrease in macropore size and total pore volume was observed at the same time. The increased mechanical strength makes the gels easy to sustain higher pressures during loading and operation in the reactors and have a more ex-

tensive application.

In the preparation of SR, wet silica rods were immersed in an aqueous ammonium hydroxide solution in order to tailor mesopore structure after the gelled sample was aged for 24 h at 40 °C, while the preparation of SM had no procedure for tailoring mesopore structure. This is one of the reasons that pore volume of SM is smaller than SR.

In conclusion, bimodal porous silica gels with good mechanical strength can be synthesized utilizing the phase separation in the polymerizing sol-gel system and aging the wet silica gels in a silane solution.

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