Preparation of Polyhedral Oligosilsesquioxane-Based Organic-Inorganic Hybrid Porous Nanocomposite by Freeze-Drying Conditions

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Novel organic-inorganic hybrid porous nanocomposites have been obtained by the reaction of octa(aminophenyl)silsesquioxane with formaldehyde under mild conditions by freeze-drying conditions. The structures of the products were characterized by FTIR spectroscopy, N_2 adsorption isotherm and FESEM. The material showed a specific surface area of 340 m^2/g and a pore volume of 0.83 cm^3/g. The material has pore size 3.6-60 nm. The results of FTIR, solid-state ^{13}C and ^{29}Si NMR spectra clearly show that the cage structure of the polyhedral oligosilsesquioxane is retained during the synthesis and the polyhedral oligosilsesquioxane building blocks were successfully woven into the porous structure.

Key Words: Nanocomposites, Organic-inorganic, Freeze-drying, Polyhedral oligosilsesquioxane.

INTRODUCTION

Recently, porous coordination polymers have attracted much attention because of their unique features such as gas storage[1], selective separation[2], catalytic properties[3], electron[4] and proton[5] conductivities and optics devices, *etc*.[6]. Pure inorganic porous materials have their intrinsic limitations lacking both functionalities and mechanical strength[7]. Organic-inorganic hybrid materials have long been known to play a major role in developing high-performance and highly functional materials[8]. The hybrid materials are expected to exhibit both the advantages of organic and inorganic materials. Organically-functionalized porous silicas have received increasing interest from both scientific and technological viewpoints[9].

In the past 2 decades, researchers have shown great interests in polyhedral oligosilsesquioxane (POSS), which was considered as the smallest possible silica particles, are unique three-dimensional nanobuilding blocks with a well-defined cage-like structure made of silicon and oxygen atoms linked together in a cubic form[10]. Typical polyhedral oligosilsesquioxane cages have the empirical formulas $(RSiO_{1.5})^{8,10,12}$, abbreviated as T_8, T_{10} and T_{12}, respectively[11]. Polyhedral oligosilsesquioxane plays an important role as building block for organic-inorganic hybrid materials containing the cage structure of polyhedral oligosilsesquioxane monomers, because of its unique physical and chemical properties[12]. Polyhedral oligosilsesquioxane can serve as a nanobuilding block for

constructing functional materials. Various methods have been developed for preparing polyhedral oligosilsesquioxane-containing organic-inorganic hybrid porous nanocomposites[13]. Octa(aminophenyl)silsesquioxane (OAPS) is easily prepared in two steps[14]. Laine and coworkers[15] reported octa(aminophenyl)-silsesquioxane as a model nanobuilding block for rigid, high-temperature hybrid nanocomposite materials. Octa(aminophenyl)silsesquioxane appears to offer excellent potential as a nanoconstruction site for the preparation of materials ranging from high-temperature nanocomposites to precursors for organic light-emitting diodes to multiarmed stars to templates for high-temperature porous materials and so on[14].

Freeze-drying is known to be one of the most powerful techniques for the preparation of highly homogeneous precursors for ceramic synthesis[16]. Powders obtained by means of this technique are usually characterized by high values of specific surface area, small particle sizes and improving their reactivity in solid-state reactions[17]. The most widely used precursors for freeze-drying are aqueous solutions of certain metal salts, though in some cases colloid solutions or insoluble salts are also used[18]. A number of attempts were undertaken to apply freeze drying to gels[19]. However, apply freeze drying to polyhedral oligosilsesquioxane-based organic-inorganic hybrid porous nanocomposite has not been reported yet. Herein, we report a approach that octa(aminophenyl)silsesquioxane reacted with formaldehyde to produce hybrid porous materials under mild conditions by freeze-drying conditions (Fig. 1).
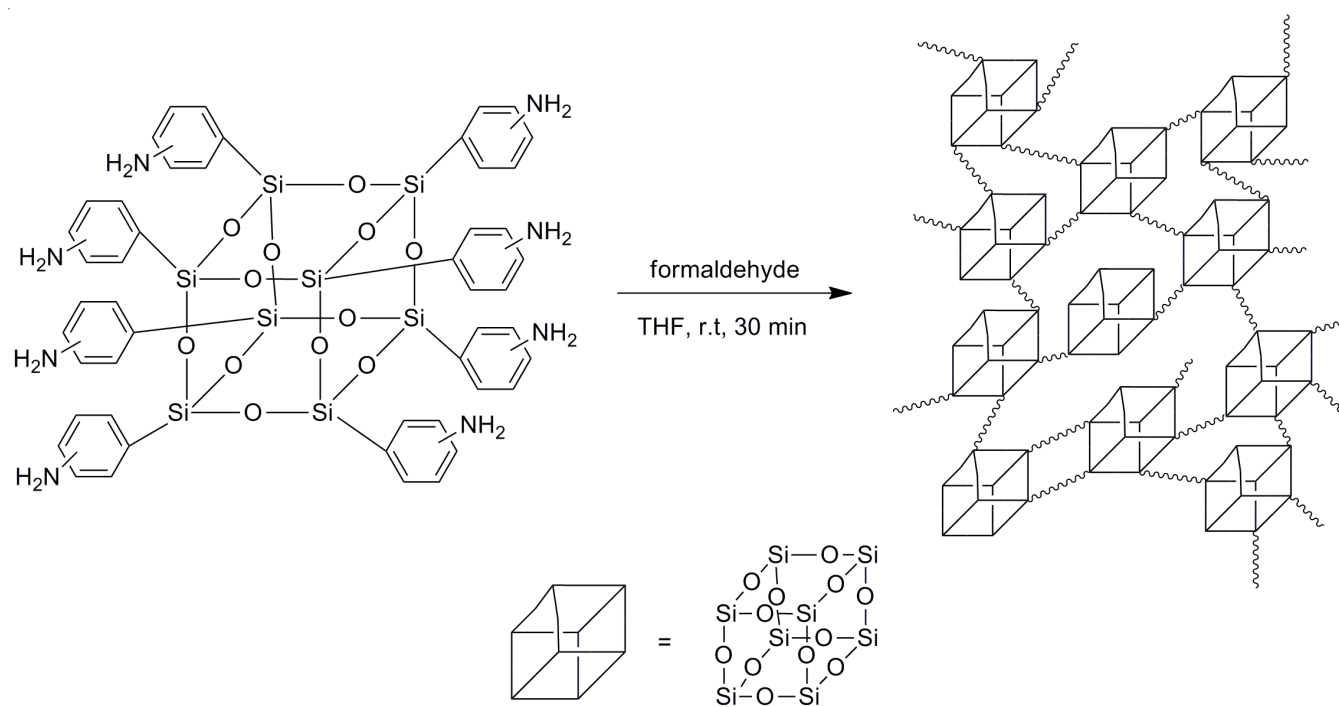
Fig. 1. Synthesis of the porous materials

EXPERIMENTAL

All the solvents were obtained from commercial sources and were used as received. Octa(aminophenyl)silsesquioxane was synthesized by reported procedures[14].

Preparation of the hybrid porous materials (P1): The mixture of OAPS (1.101 g, 0.954 mmol), formaldehyde (0.676 mL, 9.18 mmol) and THF (5 mL) was stirred at room temperature for 0.5 h. Then, the precipitate was isolated by filtration and washed with excess acetone, THF and dichloromethane. The sample was dried in a laboratory freeze-dryer to afford P1.

Detection method: The sample was dried in a laboratory freeze-dryer α 2-4(CHRIST). The pressure during the process was sustained at 3-5 Pa. The temperature of the heating plate was gradually increased from -50 ℃ to 50 ℃ for 24 h. Fourier transform infrared (FTIR) spectra were recorded on an FTIR spectrometer (Nicolet 320) using KBr crystal in the infrared region 4000-400 cm^{-1}. Solid-state NMR analyses were conducted on a Varian Infinity Plus 300WB spectrometer operating at 75.4 MHz for ^{13}C and 59.56 MHz for ^{29}Si. Apparent surface areas were determined by the multi-point Brunauer-Emmitt-Teller (BET) method from nitrogen adsorption measurements at 77 K using a Quadrasorb SI instrument. Samples were degassed for 6 h prior to analysis at a temperature of 423 K whilst under vacuum. The pore size distribution was calculated with the cylindrical BJH method[20] and the BET surface area was calculated from the slope of the isotherm at p/p$_0$ values up to 0.20. Field emission scanning electron microscopy (FESEM) was performed on an FEI Sirion 200.

RESULTS AND DISCUSSION

Structural analysis: The FTIR spectra for OAPS and P1 is shown in Fig. 2. Several distinct peaks were clearly observed. A strong Si-O (cube)[15] peak at about 1120 cm^{-1} and primary
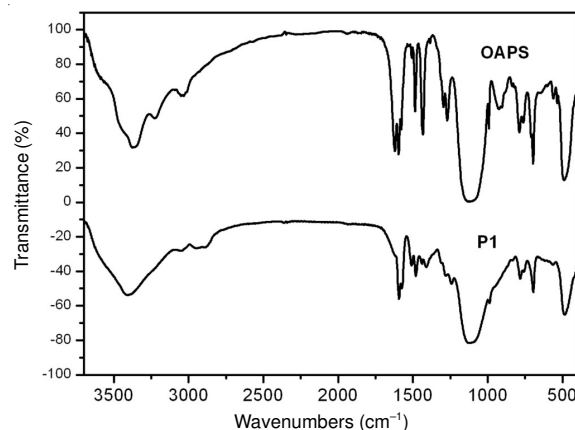

Fig. 2. IR spectra of OAPS and P1

amine groups at 3590 and 3450 (NH$_2$ stretching) and 1600 cm^{-1} (NH$_2$ deformation) were shown in the OAPS spectrum. In the spectra of P1, the primary amine group or the carbonyl function of the aldehydes at about 1725 cm^{-1} (C=O stretching) were absent. Bands that can be attributed to the cage Si-O at about 1120 cm^{-1} and the second amine group at about 3410 (NH stretching) were found in the spectra of P1. Bands that can be attributed to the C-H peak at 3000-2800 cm^{-1} were found in the spectra of P1. A weak C-N stretching band at about 1290 cm^{-1} was exhibited in the spectra of P1.

In Fig. 3, the solid-state ^{13}C and ^{29}Si NMR spectra of OAPS and P1 are shown. Signals for the aromatic carbons of the benzene rings were shown in the ^{13}C NMR spectrum of OAPS and the ^{13}C NMR spectrum of P1 shows signals both for the aromatic carbons of the benzene rings and the carbon atoms of the alkyl groups (Fig. 3a). The ^{29}Si NMR spectrum of OAPS and P1 shows similar signals which fall in the typical range for a polyhedral oligosilsesquioxane cage structure (Fig. 3b)[21]. The results of FTIR, solid-state ^{13}C and ^{29}Si NMR spectra
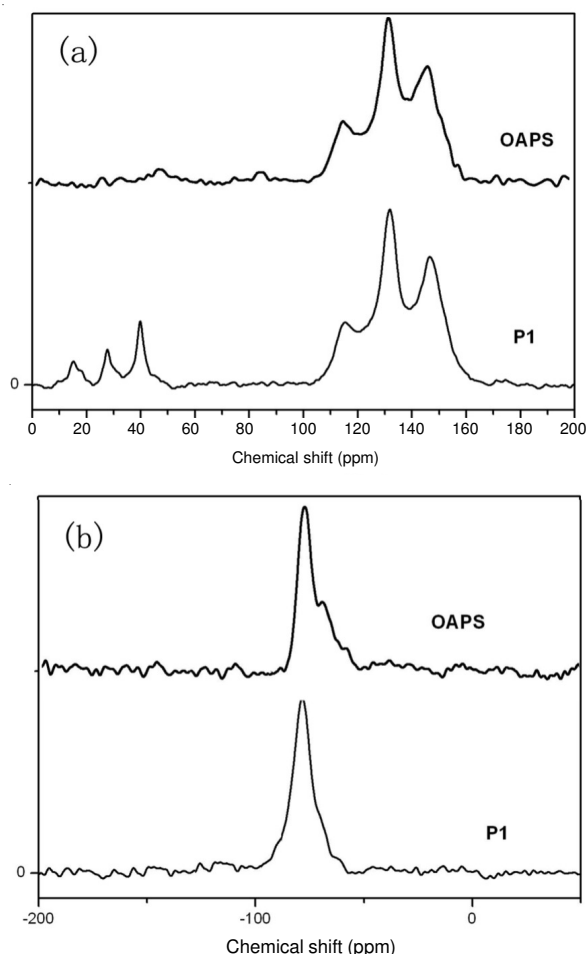
Fig. 3. (a) solid-state ^{13}C NMR and (b) solid-state ^{29}Si NMR spectra of OAPS and P1

Fig. 4. Nitrogen-sorption isotherm and corresponding pore-size-distribution curve of P1

Fig. 5. FESEM image of P1

clearly show that the cage structure of the polyhedral oligosilsesquioxane is retained during the synthesis and the polyhedral oligosilsesquioxane building blocks were successfully woven into the porous structure of the hybrid materials without obvious alteration of the structural characteristics of polyhedral oligosilsesquioxane.

Porous properties of the hybrid material: P1 was subjected to BET measurements to evaluate the porosity of the polymer. Fig. 4 showed that the the nitrogen-sorption isotherms and the corresponding pore-size-distribution curve of P1, respectively. According to the original IUPAC classification, the adsorption isotherm is not the classical type IV normally associated with mesoporous materials. The desorption isotherm does not close and is relatively horizontal even when the relative pressure is decreased to a low ratio. This may suggest the pores obtained are narrow and N_2 molecules are trapped in the pores[22]. According to BET calculation, the polysilsesquioxane network has the specific surface area of 340 m^2/g and pore volume of 0.83 cm^3/g. According to BJH pore size distribution curves, P1 has pores at 3.6-60 nm.

The porous structure of material was further investigated with FESEM. Fig. 5 shows the FESEM image of P1. As shown in Fig. 5, the porous structure of the materials was made from a large number of sizes of 20-40 nm particles, which were composed of pearl chainlike arrays. In the string of pearls with a large number 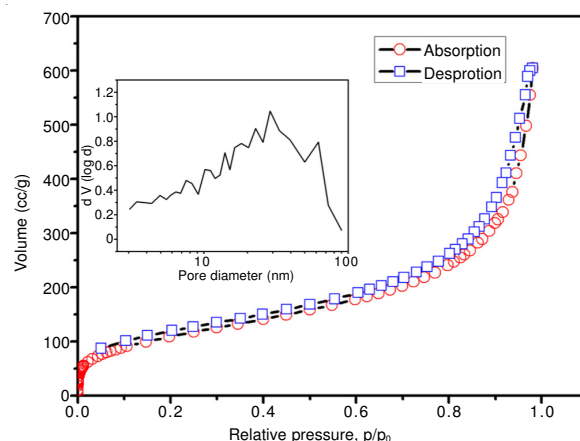of holes between the stacked structure, th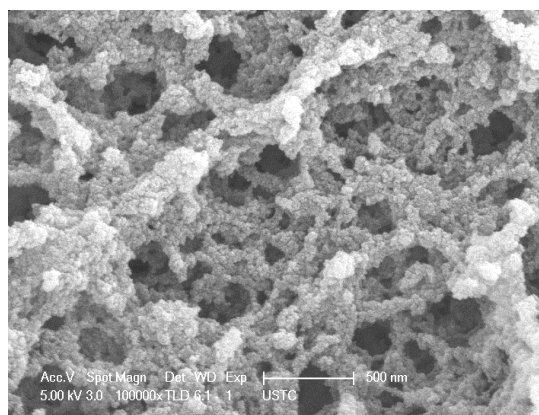e existence of holes could be estimated from the figure and were mainly in the size of 5-60 nm and below, with a few holes of about 100 nm. This observation was consistent with the N_2-sorption measurements.

Conclusion

In summary, we have reported a catalyst-free, one-pot method for preparing a novel covalently bonded polyhedral oligosilsesquioxane-containing organic-inorganic hybrid porous nanocomposite at room temperature by freeze-drying conditions. The structures of the products were characterized by FTIR spectroscopy, N_2 adsorption isotherm and FESEM. The material showed a specific surface area of 340 m^2/g and a pore volume of 0.83 cm^3/g. The material has pores at 3.6-60 nm The results of FTIR, solid-state ^{13}C and ^{29}Si NMR spectra clearly show that the cage structure of the polyhedral oligosilsesquioxane is retained during the synthesis.

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