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Facile assembly of novel hybrid mesoporous material with phenyl-bridging groups

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Large-pore phenyl-bridged mesoporous material was facilely synthesized by the synergistic effect of $SnCl_4$-KCl salt pair without using any mineral acids in the assembly process. The structural properties were characterized by small angle X-ray scattering (SAXS), nitrogen sorption isotherms, transmission electron microscopy (TEM) and ^{13}C CP/^{29}Si MAS NMR. The ordered material exhibits large uniform mesopores of 7.9 nm in diameter after extraction. The mesoporous phenyl-bridged hybrid product shows an ordered hexagonal structure with space group p6mm and high surface areas (up to 1050 m^2/g), clearly reflecting the effectiveness of the proposed synthesis protocol.

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1. Introduction

In the past few years, periodic mesoporous organosilicas (PMOs) have received much attention in materials science owing to their homogeneous distribution of organic groups in the framework as well as unique surface properties imparted from different functional groups [1], which make them have various potential applications in catalysis [2], adsorption [3], and high-performance liquid chromatography [4], etc.. Following the first template-directing synthesis pathway, a variety of PMOs with different organic bridges have been successfully prepared [5]. In contrast, phenyl-bridged PMOs are much more desirable due to the benzene groups can be further modified through designed chemical reactions [6]. To date, however, most ordered phenyl-bridged PMOs were synthesized under basic conditions with cationic alkyltrimethylammonium as templates [1,5], which may restrict their applications in some fields where large-pore ones are in demand.

As is well known, triblock copolymer like $EO_{20}(PO_{70})EO_{20}$ (P123) has an advantage of preparing hexagonal mesoporous silicas with large-pores and thick-walls [7]. However, most reported cases on phenyl-bridged PMOs templated by P123 were carried out in somewhat critical condition of strong acid [1,8]. Therefore, to find alternative mild synthesis method is an interesting task to the synthesis of ordered phenyl-bridged PMO. In our previous study, it was found that the combination of $SnCl_4$-NaCl could effectively promote the formation of ordered ethane-bridged PMOs without addition of mineral acid [9]; however, using the salt pair of $SnCl_4$-KCl as a promoter to obtain large-pore phenyl-bridged PMO has not been reported. In this paper, we report the synthesis of phenyl-bridged PMO with the proposed synthesis method by using Pluronic P123 as template, and our results show that the salt-assisted method is similarly effective in the formation of phenyl-bridged PMO as those conducted in highly acidic system [1,8].

2. Experimental

In a typical synthesis, 1.5 g P123, 2.2 g KCl and 0.26 g $SnCl_4\cdot 5H_2O$ were dissolved in 50 g of deionized water and stirred for 4 h at a fixed temperature of 40°C. After then, 3.1 ml 1,4-bis(triethoxysily)benzene (BTEB, 90%, Aldrich) was added to the solution and stirred for 24 h at 40°C, and the molar ratio of the system is BTEB/P123/H_2O/KCl/ $SnCl_4\cdot 5H_2O$ = 1: 0.034: 400: 4: 0.1. The solution along with the precipitate was then treated at 80°C for 48 h. The product was filtered and extracted two times with HCl acidified ethanol (v/v, 3/100) at 60°C for 6 h to remove the P123 template.

Small-angle X-ray scattering (SAXS) was performed using synchrotron X-ray source: CoKα (λ = 1.608 Å) radiation with an energy range of 4~16 kev (energy resolution $\Delta E/E = 5\times10^{-4}$, photo flux = 10^{10}~10^{11} ph./s, beam size < 1 mm^2). Transmission electron microscopy (TEM) was obtained by a JEOL2010 electron microscope with an acceleration voltage of 200 kV. Nitrogen sorption was obtained by a Quantachrome's Quadrasorb SI analyzer at -196°C after the treatment at 120°C for 12 h in vacuum. The pore size distribution was calculated by the conventional Barrett-Joyner-Halenda (BJH) method from the desorption branch. ^{13}C and ^{29}Si CP MAS NMR spectra were obtained on a Bruker DSX400 spectrometer at room temperature with a 4 mm zirconia rotor spinning at 6 kHz (resonance frequencies of 79.5 and 100.6 MHz for ^{29}Si and ^{13}C CPMAS NMR, respectively).

3. Results and discussion

Fig. 1 shows the SAXS patterns of the product synthesized with/without salt pair in the aqueous system. The SAXS pattern of the solvent-extracted phenyl-silica prepared with the aid of $SnCl_4$-KCl exhibits three discernible reflections. Following previous studies [8,10], the three basal reflections can be indexed as (100), (110) and (200) plane of a typical hexagonal (*p6mm*) mesoporous materials, and the corresponding unit cell parameter a_0 is calculated to be *ca*. 13.0 nm. In contrast, no distinct reflection peaks can be observed for both samples synthesized without the objective salt pair. The results clearly suggest that both salts can effectively promote the assembly of ordered mesoporous materials.

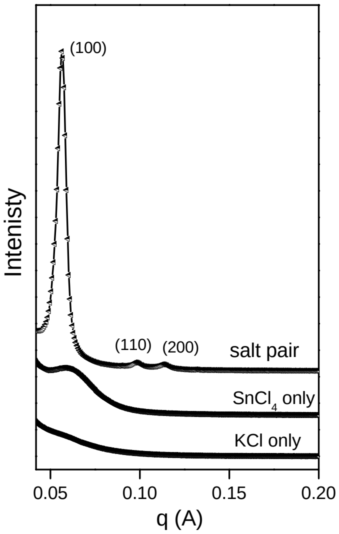

Fig. 1. SAXS patterns of the samples synthesized with/without the salt pair.

As shown in Fig. 2, N_2-adsorption/desorption isotherms of the sample exhibits representative type IV curves with a sharp capillary condensation step at a relative pressure range of 0.7~0.8, indicative of a large uniform mesopores [7]. Besides, a parallel H1-type hysteresis loop is clearly observed, implying a hexagonal mesostructure with perfect cylinder channels, and this is in agreement with the well-resolved SAXS pattern (Fig. 1). The phenyl-bridged mesoporous PMO material has a BET surface area of 1050 m^2/g and a pore volume of 1.19 cm^3/g. The pore diameter is calculated according to the BJH model to be 7.9 nm (Fig. 2, insert).

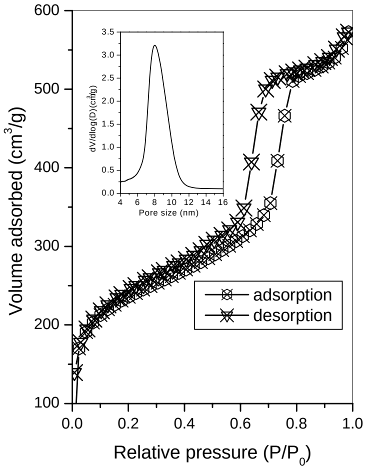

Fig. 2. N_2-adsorption/desorption isotherms and pore-size distribution (inset) of the phenyl-bridged PMO material assisted by the salt-pair of Sn_4Cl-KCl.

A representative TEM image of the salt-promoted mesoporous material shows large domains of ordered hexagonal arrangement, clearly indicating an ordered hexagonal mesostructure with 1-D pore channels (Fig. 3). The unit cell parameter (a_0) is estimated from TEM image to be approximately 13.5 nm, which is in good agreement with the value calculated from the SAXS data. Based on SAXS, N_2 sorption and TEM results, it is clear that highly ordered mesoporous hybrid sample has been facilely prepared using the combination of Sn_4Cl-KCl in the absence of common mineral acids as usually used HCl [7].

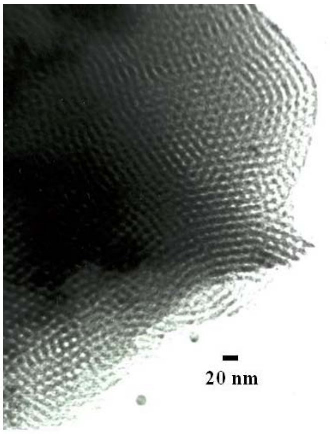

Fig. 3. TEM image of the template-free phenyl-bridged PMO obtained by the salt-assisted pathway.

^{29}Si CP MAS NMR spectrum (Fig. 4a) of the solvent-extracted sample shows three signals at 62.1, 70.7 and 79.3 ppm, which can be assigned to T^1 [C-Si(OH)$_2$(OSi)], T^2 [C-Si(OH)(OSi)$_2$] and T^3[C-Si(OSi)$_3$] sites, respectively. This observation clearly suggests that the phenyl-bridged groups have been incorporated into the pore walls along with the assembly process. Besides this, no distinct resonance can be observed in the range of 90 ~ 120 ppm, usually detectable for the silicate sites as Q^n, clearly suggesting a full incorporation of phenyl-bridged groups in the framework, that is, there is no cleavage of the Si-C bonds occurs during the synthesis and treatment. This result is better than that for phenyl-bridged PMOs prepared from Pluronic surfactants and the hydrothermal approach under highly acidic conditions [7,8].

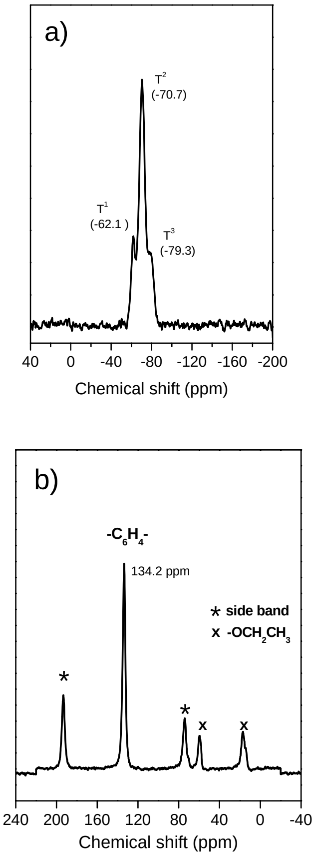

Fig. 4. ^{29}Si /^{13}C CP MAS NMR spectra of the studied phenyl-bridged PMO material.

As shown in Fig. 4(b), the ^{13}C CP MAS NMR spectrum of the sample further reveals that the whole framework is bonded covalently through the phenyl-bridging groups. The occurrence of a strong signal at about 134.2 ppm along with sidebands (denoted with asterisks) is attributed to the carbons in the phenyl group connected to Si atoms [1,7]. Additionally, two signals are observed at 17 and 58 ppm, which may be due to the remaining $-OCH_2CH_3$ groups adsorbed/exchanged on the synthesized phenyl-bridged framework during the template removal process [9].

Clearly, high-quality phenyl-bridged PMO material can be easily prepared employing the promoting effects of Sn_4Cl-KCl salt pair without introducing extra acids in the system. Based on the specific composition of the system and the physicochemical feature of each salt added, a plausible formation mechanism, that is, the hydrolysis and condensation of organosilica precursor can be promoted by the self-generated acidity from the hydrolyzable inorganic salt Sn_4Cl; besides this, another factor need to be considered is the promoting effect of “inert” KCl on the strengthened interaction between the hydrolyzed organosilica species with polymeric micelles [1,9].

4. Conclusion

In conclusion, phenyl-bridged PMO material with ordered hexagonal mesostructures has been facilely synthesized *via* a simple salt-pair promoted approach with Pluronic P123 as template. The obtained organic-functional material shows a high BET surface area (1050 m^2/g) and a large uniform pore size (~7.9 nm). The presence of organic phenyl groups in the framework endows these materials with the interesting hydrophobic property and further possibility of chemical modification through post-functionalization. Furthermore, the study of the state of Tin atom in the hybrid framework and catalytic applications is underway and will be reported elsewhere.

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