

# Chemical modification of crystal-like mesoporous phenylene-silica with amino group†

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**Amination of phenylene moieties in crystal-like mesoporous silica hybridized with phenylene is successfully achieved with close to 28% conversion of phenylene by a two-step chemical transformation process while preserving both the ordered meso-structure and crystal-like molecular scale periodicity of the parent material.**

Mesoporous organosilica solids have attracted considerable attention due to the broad range of potential applications of such materials in catalysis, adsorption, sensors, and electrical and optical devices.<sup>1–3</sup> Hybrid mesoporous materials (HMMs) having a periodic arrangement of organic and silica moieties are expected to exhibit unique chemical and physical properties arising from the highly organized organic framework.<sup>2,3</sup> Crystal-like pore-wall structures have been achieved for mesoporous silica hybridized with phenylene (–C<sub>6</sub>H<sub>4</sub>–),<sup>4,5</sup> biphenylene (–C<sub>6</sub>H<sub>4</sub>–C<sub>6</sub>H<sub>4</sub>–),<sup>6</sup> vinylene-phenylene (–CH=CH–C<sub>6</sub>H<sub>4</sub>–CH=CH–),<sup>7,8</sup> and ethenylene (–CH=CH–).<sup>9</sup> In these materials, the organic moieties are strictly assembled in a circle around the pore channels. Fig. 1 shows a model of the pore-wall structure of a crystal-like phenylene-bridged HMM (Ph-HMM). Chemical modification of the framework organic moieties in HMMs is an effective approach to the construction of highly functionalized and controlled chemical environments with uniform and stable mesopore spacing. Such environments provide functionality similar to that of enzymes, with application in selective catalysis and adsorption.

To date there have been only a few reports on the chemical transformation of organic moieties in crystal-like HMMs. The present authors have reported the direct sulfonation of framework phenylene (–C<sub>6</sub>H<sub>4</sub>(SO<sub>3</sub>H)–) by treatment of Ph-HMM with fuming sulfuric acid, although the conversion of phenylene groups was less than 10%.<sup>4</sup> Kamegawa *et al.* reported the formation of arenetricarbonyl complexes (–C<sub>6</sub>H<sub>4</sub>M(CO)<sub>3</sub>–, M = Cr, Mo)<sup>10</sup> by treatment of Ph-HMM with Cr(CO)<sub>6</sub> or Mo(CO)<sub>6</sub> vapor, achieving 15% conversion. The low rates of conversion can be attributed to the low reactivity of covalently bonded phenylene moieties in the siloxane network of

Ph-HMM. Direct bromination,<sup>11</sup> amination,<sup>12,13</sup> hydroxylation,<sup>14</sup> and Diels–Alder reaction<sup>15</sup> of bridged organic moieties have also been reported for the preparation of HMMs, although such approaches have only been applied to mesoporous ethenylene-silica with an amorphous pore-wall structure.

The incorporation of functional amino groups into the framework organics of an HMM is expected to afford highly useful materials, since the amino group can be transformed into various functional groups *via* amide (–NCO–R), imide (–NCH–R), and diazo (–NN–R) bond formation. Amino-functionalized HMMs are also potentially applicable as solid base catalysts. In the present report, the direct amination of framework phenylene moieties of crystal-like Ph-HMM *via* a two-step chemical transformation is demonstrated for the first time (Scheme 1). This route achieves phenylene conversion of close to 28% while preserving both the ordered mesoporous structure and pore-wall crystallinity of the parent Ph-HMM. The structure is maintained even upon treatment with very strong acid solutions of HNO<sub>3</sub>–H<sub>2</sub>SO<sub>4</sub> and SnCl<sub>2</sub>–HCl, demonstrating the high chemical stability of Ph-HMM.

Crystal-like Ph-HMM was synthesized according to the previously reported procedure.<sup>4</sup> A typical modification involves careful treatment of Ph-HMM (0.524 g) with a mixed acid solution of 96% v/v sulfuric acid (15.2 g) and 69% v/v nitric acid (3.47 g). After stirring the reaction mixture at 27 °C for 3 days, the solution was poured into cold distilled water (300 mL). The solid product was isolated by filtration and repeatedly washed with a large amount of distilled water. The nitrated Ph-HMM (NO<sub>2</sub>-Ph-HMM, 0.480 g) was obtained as

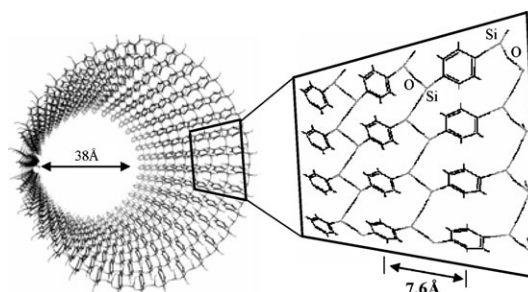
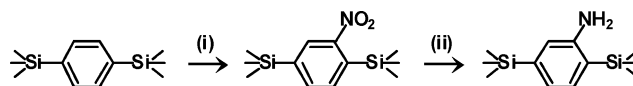


Fig. 1 Structural model of pore walls in crystal-like Ph-HMM.



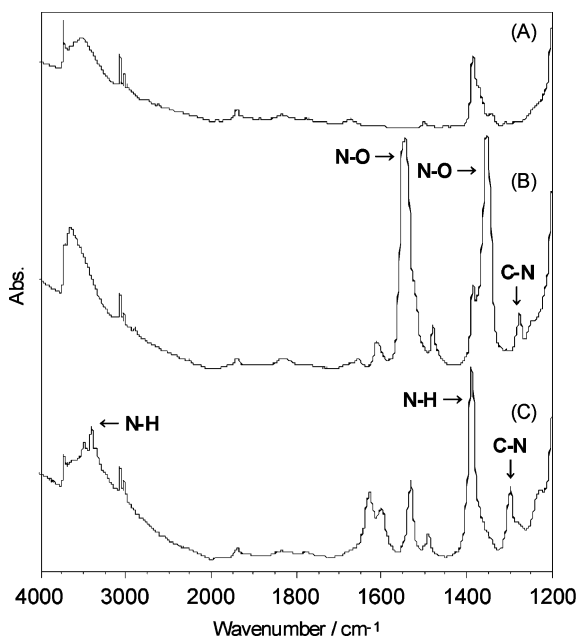
Scheme 1 Amination of phenylene-bridged moiety in crystal-like Ph-HMM: (i) HNO<sub>3</sub>–H<sub>2</sub>SO<sub>4</sub> and (ii) SnCl<sub>2</sub>–HCl.

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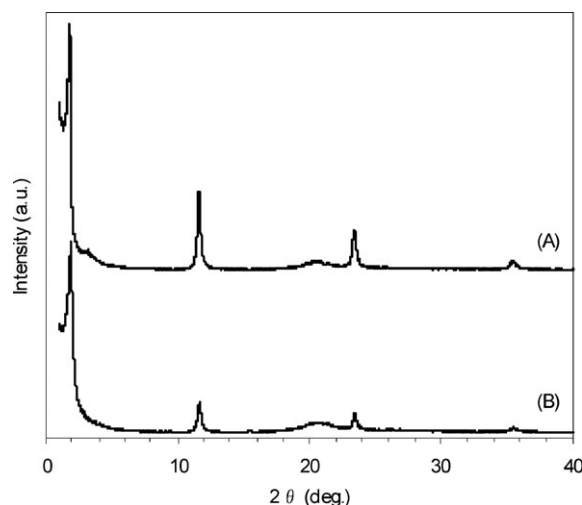


**Fig. 2** FTIR spectra of (A) Ph-HMM, (B) NO<sub>2</sub>-Ph-HMM, and (C) NH<sub>2</sub>-Ph-HMM.

a pale yellow powder after drying to completeness. The NO<sub>2</sub>-Ph-HMM powder (0.480 g) was suspended in 15 mL of 37% v/v HCl solution containing SnCl<sub>2</sub> (1.59 g) and the suspension was stirred continuously at 27 °C for 3 days. After reaction the suspension was poured into distilled water (300 mL) and filtered to collect the products. The obtained material was further washed with a large amount of distilled water, followed by isopropylamine (10 mL) and ethanol (100 mL). Recovered material was finally vacuum-dried to afford aminated Ph-HMM (NH<sub>2</sub>-Ph-HMM, 0.445 g) as a pale pink powder.

The amination of phenylene moieties in Ph-HMM was confirmed by Fourier transform infrared (FTIR) (Fig. 2) and <sup>13</sup>C cross-polarization magic angle spinning (CP/MAS) nuclear magnetic resonance (NMR) analyses (Fig. S1†). Mesoporous powder was pressed into thin self-supporting wafers and placed in a quartz cell for FTIR measurements. The FTIR spectra were recorded in absorbance mode after evacuation at ambient temperature for 30 min. The FTIR spectrum of the parent Ph-HMM displayed absorption bands attributable to the stretching modes of silanol (3200–3800 cm<sup>-1</sup>), C–H species (3010–3060 cm<sup>-1</sup>), and the overtones of benzene ring vibrations (1300–2000 cm<sup>-1</sup>). These responses are similar to those reported previously for dry Ph-HMM.<sup>16</sup> Treatment with H<sub>2</sub>SO<sub>4</sub>–HNO<sub>3</sub> produces two strong bands at 1350 and 1550 cm<sup>-1</sup> assigned to the symmetrical and asymmetrical stretching modes of N–O, respectively. The band at 1277 cm<sup>-1</sup> corresponds to the stretching mode of C–N, indicating the covalent linkage of nitro groups (–NO<sub>2</sub>) to phenylene moieties in the parent Ph-HMM. Upon treatment with SnCl<sub>2</sub>–HCl, the N–O stretching vibrations disappeared completely while new bands emerged at 1628 and 3398–3487 cm<sup>-1</sup> attributable to the bending and stretching modes of N–H.

The <sup>13</sup>C CP/MAS NMR spectra further support the amination of phenylene moieties in Ph-HMM. The parent Ph-HMM displayed a single resonance peak at 135 ppm attributable to a



**Fig. 3** XRD patterns of (A) Ph-HMM and (B) NH<sub>2</sub>-Ph-HMM.

very small difference in chemical shift of two carbon species in the 1,4-substituted phenylene moieties. This peak split into four resonance peaks at 130, 135 (initial), 138, and 150 ppm upon nitration, corresponding to carbon in phenylene linked to nitro groups ( $\equiv\text{Si}-\text{C}_6\text{H}_4(\text{NO}_2)-\text{Si}\equiv$ ) (Fig. S1†). The subsequent reduction of nitro groups to amino groups resulted in slight changes in the spectrum, with resonance peaks assignable to carbon in phenylene linked to amino groups ( $\equiv\text{Si}-\text{C}_6\text{H}_4(\text{NH}_2)-\text{Si}\equiv$ ).

Quantitative reduction of nitro to amino groups was confirmed by the complete disappearance of the N–O and C–NO stretching bands in the FTIR spectrum, and by the resonance of nitrated phenylene moieties in the <sup>13</sup>C CP/MAS NMR spectrum. Elemental analysis of NH<sub>2</sub>-Ph-HMM gives an amino group density of close to 1.2 mmol g<sup>-1</sup>, indicating that nearly 28% of phenylene moieties were linked to amino groups in the parent Ph-HMM. The <sup>29</sup>Si MAS NMR spectrum also indicates that no Si–C bond cleavage occurred during chemical modification (Fig. S2†).

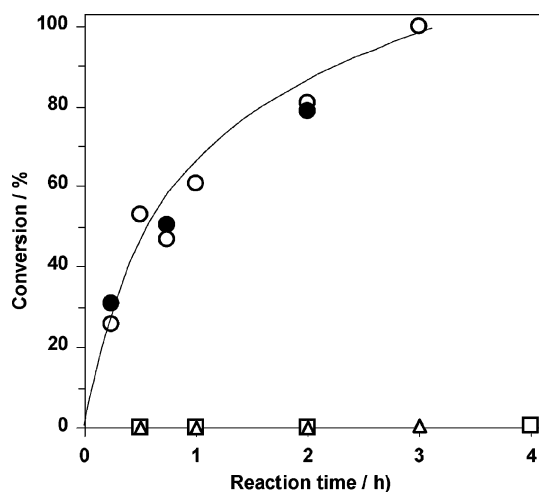
Powder X-ray diffraction (XRD) analysis of the parent Ph-HMM and NH<sub>2</sub>-Ph-HMM (Fig. 3) reveals diffraction peaks at low angles ( $2\theta < 5^\circ$ ) attributable to an ordered arrangement of meso-channels. Three sharp diffractions are apparent at intermediate scattering angles ( $d = 7.6, 3.8, \text{ and } 2.5 \text{ \AA}$ ), attributable to the periodic arrangement of phenylene and silica layers within the pore walls. These results confirm that both the ordered mesoporous structure and the crystal-like molecular-scale periodicity of the pore walls are preserved, even upon treatment with very strong acid and a powerful reduction reagent. Nitrogen adsorption–desorption isotherms also confirmed the complete retention of a uniform pore structure (Fig. S3†). However, the XRD peak intensity of the NH<sub>2</sub>-Ph-HMM material is slightly lower than that of the parent material, indicated by the adsorption–desorption isotherms to be due to a minor loss of surface area and pore volume, as shown in Table 1.

The catalytic performance of NH<sub>2</sub>-Ph-HMM was studied by conducting a typical base-catalyzed reaction, the Knöevenagel condensation reaction. This reaction is an important C–C bond-forming reaction that is widely used in the synthesis of

**Table 1** Textural properties of Ph-HMM and NH<sub>2</sub>-Ph-HMM

	Surface area/ m <sup>2</sup> g <sup>-1</sup>	Pore volume/ cc g <sup>-1</sup>	Pore diameter <sup>a</sup> / nm
Ph-HMM	780	0.48	3.0
NH <sub>2</sub> -Ph-HMM	720	0.44	2.7

<sup>a</sup> By the Barret–Joyner–Halenda method.

**Fig. 4** Knöevenagel condensation reaction of malononitrile with benzaldehyde at 60 °C in toluene solution catalyzed by (□) Ph-HMM, (△) NO<sub>2</sub>-Ph-HMM, (○) NH<sub>2</sub>-Ph-HMM, and (●) recycled NH<sub>2</sub>-Ph-HMM.

chemical intermediates and end products for pharmaceutical products and perfumes.<sup>17</sup> The reaction of benzaldehyde and malononitrile over NH<sub>2</sub>-Ph-HMM proceeded to yield a quantitative amount of 1,1-dicyanophenylethylene (Fig. 4). Under identical conditions, Ph-HMM and NO<sub>2</sub>-Ph-HMM exhibited negligible activity for this reaction. Conversion of close to 80% was achieved after 2 h on stream, and none of the Michael addition byproducts typically associated with the reaction of malononitrile with the double bond of the reaction product (1,1-dicyanophenylethylene) were detected. Further, the reusability of the NH<sub>2</sub>-Ph-HMM was also assessed. After reaction, the catalyst was filtered off and recycled by washing and drying under vacuum for further use. No obvious loss of its initial catalytic activity was monitored upon first recycle.

The results of catalysis further support the successful amination of Ph-HMM and the usefulness of the resultant material as a base catalyst.

In summary, framework phenylene moieties in crystal-like Ph-HMM were successfully modified with covalently linked amino groups at high conversion rates (*ca.* 28%). The highly ordered mesostructure and molecular-scale periodicity of the pore walls of Ph-HMM were completely retained upon modification despite the use of strong acid and a powerful reduction reagent. The resultant NH<sub>2</sub>-Ph-HMM material successfully catalyzed the Knöevenagel condensation reaction as a solid base catalyst, and is expected to be applicable as a precursor material for the design of highly functionalized mesoporous solids with strong shape-selectivity for catalytic and adsorption processes.

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