Structural Control of Phenylene-bridged Periodic Mesoporous Organosilica with Organic Additives

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The effects of organic additives on the structure of phenylene-bridged periodic mesoporous organosilica have been investigated. The mesostructure and pore size were controlled by adding organic additives, such as 1,3,5-triisopropylbenzene and benzyl alcohol under acidic or basic conditions.

Periodic mesoporous organosilicas (PMOs) synthesized from bridged organosilicon precursors via the surfactant-directed self-assembly route are a new class of ordered porous materials having inorganic–organic hybrid frameworks.[1] Phenylene-bridged PMO is one of the most studied materials because it can be synthesized from a commercially available precursor and has many special features. Most interestingly, Inagaki et al.[2] reported the synthesis of a hierarchically ordered PMO where phenylene groups are regularly arranged to form crystal-like pore walls. The phenylene groups on the pore surface allows postmodification such as sulfonation[3,4] and amination,[5] which is very important for catalytic applications. To further enhance their usefulness, structural diversification of phenylene-bridged PMOs is an important issue. Various mesostructures, including lamellar,[6] hexagonal *p*6*mm*,[7–9] cubic $Pm\bar{3}n$,[10] and cubic $Im\bar{3}m$,[11] have been reported to date depending on the kinds of surfactants as well as on the reaction conditions.

Here we report the structural control of phenylene-bridged PMO formed from 1,4-bis(triethoxysilyl)benzene (BTEB) by the addition of organic molecules. When cetyltrimethylammonium bromide (CTAB) is used as the surfactant template, a hexagonal *p*6*mm* phase with a crystal-like pore wall is formed under basic conditions,[2,12] while a cubic $Pm\bar{3}n$ phase is generally formed under acidic conditions.[10] To these systems, we added several organic molecules such as 1,3,5-triisopropylbenzene (TIPB) and benzyl alcohol (BA). It was found that TIPB acted as a pore expander to increase the pore size in both acidic and basic systems, although the structural orders were decreased to some extent. In contrast, the addition of BA induced the phase change from cubic $Pm\bar{3}n$ to highly ordered hexagonal *p*6*mm* under acidic conditions. This is the first report on the structural control of PMOs with organic additives, despite extensive studies on pure mesoporous silica materials.

The synthesis of phenylene-bridged PMOs under basic conditions was performed by adding BTEB to a basic CTAB solution containing organic additives, followed by stirring the mixture at 95 °C for 20 h.[2,12] The molar composition of the reactants was 1.0BTEB:0.96CTAB:594H_2O:4.0NaOH:0–0.96[organic additives]. The synthesis under acidic conditions was performed by adding BTEB to an acidic CTAB solution containing organic additives, followed by stirring the mixture at room temperature for 24 h. The molar composition of the reactants was 1.0BTEB:1.54CTAB:2000H_2O:140HCl:0–1.54[organic additives]. In both systems, the molar ratio of organic additives/CTAB was 0, 0.5, and 1.0. The resultant white precipitates were collected by filtration, washed with water, and air-dried overnight at 80 °C. These samples were stirred in an ethanol/HCl mixture at 70 °C for 8 h to remove surfactants.

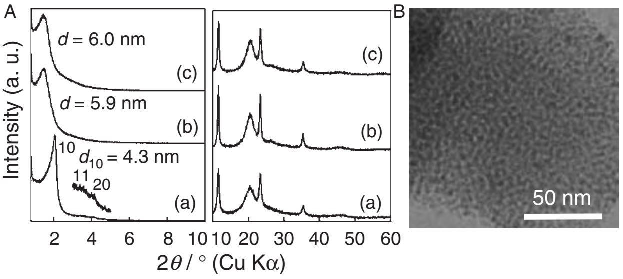

Figure 1. (A) XRD patterns of phenylene-bridged PMOs synthesized under basic conditions at TIPB/CTAB = (a) 0, (b) 0.5, and (c) 1.0, and (B) TEM image of the product synthesized at TIPB/CTAB = 1.0.

The XRD patterns of the products prepared at TIPB/CTAB = 0, 0.5, and 1.0 under basic conditions are shown in Figure 1A. In the absence of TIPB ((a) TIPB/CTAB = 0), a hexagonal *p*6*mm* phase is formed.[2,12] The peaks at higher angle regions (2θ = 10–50°) are attribute to the regular arrangement of phenylene groups in the pore wall. When TIPB was added (TIPB/CTAB = (b) 0.5 and (c) 1.0), single broad peaks with larger *d* spacings are observed, suggesting that wormhole-like mesostructures with increased pore sizes have been formed. The TEM image of the product (TIPB/CTAB = 1.0) indeed shows a wormhole mesostructure (Figure 1B). Interestingly, the diffraction peaks at higher angles are still clearly observed, confirming that the crystal-like pore wall is preserved despite the loss of the hexagonal pore arrangement. The SEM image of this product shows spherical nanoparticles along with larger, irregular particles observed for the product prepared without TIPB.[2,13]

The N_2 adsorption–desorption isotherms of the products exhibit type IV curves characteristic of mesoporous silica.[13] The BET surface areas, pore volumes, and BJH pore sizes are listed in Table 1. By the addition of TIPB, the total pore volume almost doubled and the pore size also increased from 2.5 to 3.9 nm. Further increase in the TIPB amount (TIPB/CTAB > 1.0) resulted in only slight increase of pore size. Thus TIPB acts as a pore expander in this system, although there appears to be an upper limit on the pore size reached by the addition of TIPB. Up to now, increases of the pore size of phenylene-bridged PMO have been only achieved by using surfactants with higher molecular weights such as Brij56 and P123; however, the resulting products have amorphous pore walls.[8,9] Our finding provides a facile method for the synthesis of large-pore phenylene-bridged PMOs while keeping crystal-like pore walls.

Table 1. Structural parameters of the products

Conditions	Mesophase	$A_{\mathrm{BET}}{}^{a}$ /m^2 g^{-1}	$V_{\mathrm{p}}{}^{b}$ /cc g^{-1}	$D_{\mathrm{p}}{}^{c}$ /nm
Basic				
Without additive	Hexagonal *p*6*mm*	656	0.67	2.5
TIPB/CTAB = 1.0	Wormhole-like	600	1.38	3.9
Acidic				
Without additive	Cubic $Pm\bar{3}n$	904	0.71	2.1
TIPB/CTAB = 1.0	Disordered cubic	952	0.81	2.7
BA/CTAB = 1.0	Hexagonal *p*6*mm*	1381	1.18	2.1

$^{a}A_{\mathrm{BET}}$: BET specific surface area. $^{b}V_{\mathrm{p}}$: Total pore volume. $^{c}D_{\mathrm{p}}$: Pore size calculated by the BJH method from the adsorption branch.

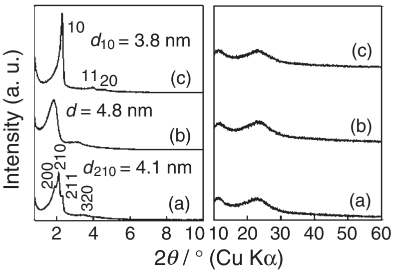

Figure 2. XRD patterns of products synthesized under acidic conditions; (a) without additive, (b) TIPB/CTAB = 1.0, and (c) BA/CTAB = 1.0.

We also examined the addition of TIPB under acidic conditions. In the absence of TIPB (Figure 2a, TIPB/CTAB = 0), a cubic $Pm\bar{3}n$ phase without the molecular-scale periodicity in the pore wall is formed under our experimental conditions.[10] Similar to the results obtained under basic conditions, the addition of TIPB caused the pore size expansion, along with a decrease of structural regularity as confirmed by XRD (Figure 2b, TIPB/CTAB = 1.0) and TEM.[13] All of the products have globular particle morphologies, as confirmed by SEM.[13] The pore size was increased from 2.1 to 2.7 nm by adding TIPB (Table 1). It is expected that the pore size can be controlled by varying the TIPB amount.

Recently, we have reported the structural variation of pure mesoporous silica materials under similar acidic conditions.[14,15] The addition of TIPB induced the phase change from hexagonal *p*6*mm* → cubic $Pm\bar{3}n$ → cubic $Fm\bar{3}m$ with increasing TIPB.[15] However, such structural changes are not observed in the present system using BTEB as the precursor. We speculate that the relatively rigid framework of the phenylene-bridged PMOs inhibits the phase change into the mesophases with higher surface curvature at least under our experimental conditions.

Similar results were obtained when 1,3,5-trimethylbenzene and *n*-octane were used as the additives; however, the addition of BA gave quite different results. When BA was added under the basic conditions, no obvious change in the structure was observed (data not shown). In contrast, under acidic conditions, phase change from cubic $Pm\bar{3}n$ to a highly ordered hexagonal *p*6*mm* occurred when BA/CTAB = 1.0 (Figure 2c). The particle morphology also changed from globular to rod-like with this phase change.[13] To the best of our knowledge, this is the first example of the highly ordered *p*6*mm* phenylene-bridged PMO prepared under acidic conditions using alkyltrimethylammonium surfactant. This product has considerably higher surface area and larger pore volume than the *p*6*mm* material synthesized under basic conditions (Table 1).

The hexagonal *p*6*mm* phase was also formed when *n*-hexanol was added instead of BA. It appears that the OH groups play a crucial role in this structural change. Considering that the OH groups can interact with silanol groups via hydrogen bonds, the location of the alcohol molecules should be different from that of TIPB. They are possibly located between surfactant molecules with their long axis being parallel with that of the surfactant. In such a case, the packing parameter g value is increased,[15] and, therefore, the formation of the mesophase with lower surface curvature, i.e., hexagonal *p*6*mm* phase, should be favored.

In conclusion, variation of the mesostructure and the pore size control of phenylene-bridged PMOs have been achieved by simply adding organic molecules during the synthesis. These findings should be important not only for fundamental research but also for practical applications such as in catalysis and separation.

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