Mesoporous Hybrid Organosilica Materials Functionalized with Biphenyl Moiety

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The synthesis of well-defined structures of inorganic silica framework systems functionalized with organic moiety renders these systems versatile in designing new materials. We have obtained in our laboratories a mesoporous hybrid organosilica material incorporating a biphenyl moiety from the condensation of 4,4’-bis(triethoxysilyl) biphenyl monomer with tetraethoxysilane and 1,2-bis(triethoxysilyl)ethane in basic medium. The polymerization was carried out via surfactant–templated method. Infrared spectroscopic analyses showed that the biphenyl moiety was covalently integrated in the polymeric organosilica structure, and X-ray diffraction investigation confirmed the reflection of two-dimensional hexagonal symmetry lattice. The incorporation of this organic moiety is limited by the proportion of 1,2-bis(triethoxysilyl)ethane. The interplanar spacing was decreased with increasing amount of organosilane incorporation. Morphology of the hybrid xerogel material was in the form of agglomerated particles composed of rope-like orientation. Our results indicated that by manipulating the synthesis conditions, it is possible to tailor and tune the structural and textural properties of the obtained mesoporous hybrid material, allowing some possible flexibility in their design for specific applications.

Key Words: surfactant-templated, polymerization, organic-inorganic, synthesis

INTRODUCTION

The new developments in the field of hybrid materials include the synthesis of well-ordered structures of inorganic silica incorporating an organic moiety in the framework. The mesoporous organosilica with pore diameters from 20 to 500 Å have a distinct advantage over other mesoporous silica materials (Inagaki 2003; Yamamoto et al. 2003; Hatton et al. 2005). The integration of organic functionality within the inorganic porous hosts expanded their applications. The functionalization represents a useful tool to fine-tune hybrid materials for specific physical, chemical, and surface properties as well as better thermal and hydrothermal stabilities for a wider range of applications in catalysis, adsorption, separation science, sensing technology, and nanoelectronics (Asefa et al. 1999; Davis 2000; Burleigh et al. 2001; 2003; Baleizao et al. 2003).

The synthesis of periodic mesoporous organosilica (PMOs) involves bridging organosilsesquioxanes of the type (EtO)\textsubscript{3}Si–R–Si(OEt)\textsubscript{3}. This silsesquioxane could have different structures of organic moiety within the channel walls, which could be made vacant for further modifications.
and inclusions of guest molecules (Melde et al. 1999; Zhang et al. 2005). The hybrid materials with desired physical and chemical properties can be designed using organosilane with specific organic bridging groups. There are several bridging groups that have been incorporated to increase functionality of PMO’s. These included simple alkanes (Inagaki et al. 1999), unsaturated or aromatic groups (Ishii et al. 1999; Temtsin et al. 2001) and organometallic complexes (Asefa et al. 2001). To date, organic functional moieties have also been incorporated such as the biphenyl moiety (Kuroki et al. 2002; Burleigh et al. 2003). The biphenyl moiety in the silica framework provides a general route to multi-component inorganic-organic hybrid materials. Having good channel reactivity and structural stability, a biphenyl moiety once functionalized or activated, could allow the inclusion of various transition metal centers that could yield catalytic organometallic sites, which are highly tunable. To develop such function-specific materials, it is vital to study the effect of various processing parameters on the morphology and structural properties of hybrid organosilica.

This work deals with the synthesis and characterization of mesoporous hybrid organosilica materials incorporating a biphenyl moiety. Investigation was extended to the compositional and structural properties of the hybrid material when varying amounts of 1,2-bis(triethoxysilyl)ethane and cetyltrimethylammonium bromide (CTAB) for the surfactant concentration were employed during surfactant-templated polymerization.

**MATERIALS AND METHODS**

**Synthesis of the Precursor**

The 4,4’-bis(triethoxysilyl)biphenyl organosilane precursor was prepared by Barbier-Grignard reaction from the aryl dibromide and tetraethoxysilane (Shea et al 1992). A solution of 4,4’-dibromobiphenyl in tetrahydrofuran (THF) and tetraethoxysilane (TEOS) was added to magnesium turnings. The resulting mixture was kept at 75 °C for 5 days under reflux, producing a grey-green solution. The solution was then cooled at room temperature and dried under vacuum to remove the THF. Elimination of the residual magnesium turnings was carried out by adding hexane to the mixture and filtering under nitrogen environment to afford viscous brown oil. Removal of hexane was done in vacuum and remaining TEOS was distilled off, leaving clear colorless oil. Shown below is the scheme for monomer synthesis.

**Surfactant-templated Polymerization**

The surfactant-templated polymerization of organosilica was done by employing 1:n:8 mole ratio of the organosilane precursor, 1,2-bis(triethoxysilyl)ethane (n = 1, 2, 3) and tetraethoxysilane (TEOS), respectively. The mixture under basic media (62.0 [H2O]:0.64 [CTAB]: 0.25 [NaOH] ratio) was stirred for 24 hours and placed in an oven at 95 °C – 100 °C for 3 hours. The products were then filtered, washed, and dried. Removal of excess surfactant from the product was done by reflux, and the white xerogel again filtered out, washed with ethanol to neutral pH, and dried in a vacuum oven.

Varying CTAB concentrations, lower (0.32 [CTAB]), and higher (0.96 [CTAB]) concentrations relative to the original value were employed. Only 1:1:8 mole ratio of the organosilane precursor, 1,2-bis(triethoxysilyl)ethane and tetraethoxysilane was utilized for this particular investigation. All resulting products were subsequently characterized using Fourier Transform Infrared Spectroscopy (FTIR), Powder X-ray Diffraction (XRD), Transmission Electron Microscopy (TEM), and Scanning Electron Microscopy (SEM).

**RESULTS AND DISCUSSIONS**

The success of polymerization and incorporation of biphenyl moiety in the organosilica framework was analyzed using FTIR spectroscopy. Figure 1 shows the absorption band characteristics present in the obtained mesoporous organosilica. Considering the hybrid material at 1:1:8 biphenyl precursor:BTE:TEOS ratio, the intense absorption bands at 1081 and 794 cm⁻¹ (Jeong et al. 2004) are characteristics for the asymmetric and symmetric stretching, respectively, of the Si–O–Si bonds. The C–H deformation vibrations at 2895 (Grin et al. 2004), and 1409 cm⁻¹ (Fukuoka et al. 2001) were observed due to the aliphatic part of the bridging silsesquioxanes incorporated into the structure. The peaks at 2930 (Grin et al. 2004), 1,633 (Llusar et al. 2003), which is assigned to the C=C vibration of the aromatic structure, and 964 cm⁻¹ were indicative of the biphenyl moiety. This confirms that the synthesized biphenyl-bridged organosilane monomer was covalently linked in the channels of the hybrid organosilica material.

![Scheme 1. General reaction for monomer synthesis](image-url)
The incorporation of different proportions of 1,2-bis(triethoxysilyl)ethane to the biphenyl-bridged precursor and tetraethoxysilane was also investigated. The relative intensity of the aromatic ring group and C–H stretch based on the spectroscopic analyses decreased, as the proportions of 1,2-bis(triethoxysilyl)ethane increased during surfactant-templated polymerization. The result suggests that there is lesser tendency of the biphenyl moiety to integrate and crosslink in the framework probably due to the change of hydrolysis and condensation rate of the biphenyl-bridged monomer under varying amounts of 1,2-bis(triethoxysilyl)ethane (Bao et al. 2004).

The reaction mechanism for the formation of the mesoporous organosilica involves the nucleophilic attack of the hydroxyl anion at the silicon center, which results to the hydrolysis of the ethoxysilyl groups to silanols (Baney et al. 1995). The condensation reactions of 4,4’-bis(triethoxysilyl)biphenyl with tetraethoxysilane and 1,2-bis(triethoxysilyl)ethane together with the co-assembly of surfactant micelles to form hexagonal packing formation of the channels, give rise to a solution of growing polysilsesquioxane network. Branching and cross-linking in the solution continue until the network is sufficiently large for gel transition. In the subsequent steps where the gel was allowed to age and solvent extraction was done, the removal of the surfactant to afford a polysilsesquioxane xerogel resulted in the formation of a very fine, white hybrid material.

Particle morphology of the obtained hybrid material is somehow dependent on the preparation for SEM analyses. When the xerogels were viewed in the SEM without ultrasonication, aggregates and angular-shaped particle were observed as shown in Figure 2. The individual particles were not apparent due to very high agglomeration. It is believed that ultrasonication of the particles in solution helps break up the agglomerates, which could be brought about mainly by hydrophobic interactions due to the sticky texture of the remaining surfactant adsorbed on the particle surfaces (Hampsey et al. 2004).

The fine powder particles of the synthesized hybrid material after sonication still appeared to be aggregated, but generally showed the characteristic sub-micrometer spherical morphology as seen in Figure 3. Detailed orientation and closed features of the morphology were affected by the varying amounts of 1,2-bis(triethoxysilyl)ethane. The higher the amount of added organosilane, the better was the observed resolution of the spherical particle morphology. From literature, some described this as rod- and rope-like particles randomly aggregated into large particles (Park et al. 2001).
To enhance the rod-type structures of the synthesized organosilica, different CTAB concentrations were added to the precursors during surfactant-mediated polymerization. The same white solid product was obtained when the reaction mixture contained a lower concentration of CTAB under the same reaction conditions. No product was obtained when the reaction mixture contained a higher CTAB concentration. The mixture turned to a very viscous...
solution at this surfactant concentration. Stirring proved to be very difficult.

Formation of enhanced rope- and rod-based morphologies, as well as observation of larger particles with gyroid and granular characteristics occurred when the type of surfactant was varied. Similar features were observed on other studies of the morphology of mesoporous organosilica (Xiao et al. 2005).

The morphology of the mesoporous organosilica depends strongly on the silica source, as well as the self-assembly of the different organosilanes and surfactant. The particle morphology is formed through hexagonal packing of the self-assembled rod-like organosilicate micelles. This begins with nucleation of the organosilica-surfactant interactions (Wahab et al. 2005; Xiao et al. 2005). The hydrophobic organosilanes with their nonpolar groups and the hydrophobic tails of the surfactant molecules favor and stabilize the formation of the rod-type micelles by intercalating their hydrophobic groups within the micelles-water interface. Formation of large number of rod-like micelles results to aggregation process.

Aggregation of these particles is enhanced by different types of interactions such as electrostatic attraction, hydrogen bonding from the silanol group, hydrophobic interactions between the organosilane and surfactant molecules and the physical friction between the particles (Ishizaki et al. 1998).

The surface structure of the organosilica material may result from alternating hydrophilic and hydrophobic layers composed of silica-biphenyl-silica-ethane functionality, respectively. This material is formed as a result of structure directing interactions between the biphenyl-bridged organosilane monomer to the other silsesquioxane (BTE and TEOS) molecules, and between the precursor molecules and surfactant (Inagaki et al. 2002).

Only 1 characteristic peak was reflected on the powder X-ray diffraction (XRD) patterns for all organosilica samples as shown in Figure 4. This pattern can be indexed as (100) plane according to the two-dimensional $p6mm$ space group. The maximum lattice constant evaluated on the basis of the d-spacing of (100) reflection was approximately 84 Å. No significant change was observed

![Figure 4](image-url)  
*Figure 4. XRD patterns of the mesoporous organosilica at (a) 1:1:8 (b) 1:2:8 (c) 1:3:8 biphenyl precursor:BTE:TEOS ratio*
on the interplanar spacing when the surfactant was varied. Transmission electron microscopy image as shown in Figure 5 reveals many lattice fringes with hexagonal array of mesopores.

The observable change on the interplanar d-spacing and lattice constant is shown in Table 1. As the proportion of 1,2-bis(triethoxysilyl)ethane increased, lattice parameter decreased. This confirms the result earlier given in the FTIR spectroscopic analyses regarding the integration of the biphenyl moiety in the organosilica framework. The biphenyl-bridged moiety has overall longer bond length than the ethane-bridged in 1,2-bis(triethoxysilyl)ethane. A decrease in the incorporation of larger biphenyl moiety in the framework will decrease the unit crystal structure, resulting in the observed decrease on the interplanar spacing and lattice parameter.

Table 1. Structural parameters derived from XRD patterns

<table>
<thead>
<tr>
<th>Biphenyl precursor: BTE: TEOS ratio</th>
<th>d_{100} (Å)</th>
<th>a (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1:8</td>
<td>1.214</td>
<td>72.71</td>
</tr>
<tr>
<td>1:2:8</td>
<td>1.270</td>
<td>69.51</td>
</tr>
<tr>
<td>1:3:8</td>
<td>1.316</td>
<td>67.08</td>
</tr>
</tbody>
</table>

CONCLUSION

Mesoporous hybrid organosilica materials with biphenyl moiety incorporated at the molecular level in the ethane-silica framework has been synthesized. The amount of 1,2-bis(triethoxysilyl)ethane influenced the degree of incorporation of the biphenyl moiety. Diffraction analyses showed that the mesoporous material exhibits hexagonal arrays of mesopores. Solid-state MAS NMR analyses may be conducted to fully ascertain the structure of the organosilica framework.

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REFERENCES


