

Biphenyl-functionalized Ethane-silica Hybrid Materials with Ordered Hexagonal Mesoporous Structure

R. Rivera Virtudazo^{*}, E. Magdaluyo, Jr.^{**}, L. dela Cruz^{***}, E. Castriciones^{****} and H. Mendoza^{*****}

^{*}Ceramic Engineering Department, Mariano Marcos State University, Batac, Ilocos Norte, Philippines, rrvr26@yahoo.com

^{**}Department of Mining, Metallurgical and Materials Engineering, University of the Philippines, Diliman, Quezon City, Philippines, edmagdaluyo@gmail.com

^{***}National Science Research Institute, University of the Philippines, Diliman, Quezon City, Philippines

^{****}Inorganic Synthesis and Computational research Laboratory, Institute of Chemistry, University of the Philippines, Diliman, Quezon City, Philippines, ecastriciones@yahoo.com

^{*****}Department of Mining, Metallurgical and Materials Engineering, University of the Philippines, Diliman, Quezon City, Philippines, herman.mendoza@up.edu.ph

ABSTRACT

An ordered mesoporous hybrid xerogel has been prepared using a sol-gel route involving the co-condensation of 4,4'-bis(triethoxysilyl)biphenyl and 1,2-bis(triethoxysilyl)ethane. Chemical treatment was performed under basic conditions, using cetyltrimethylammonium bromide as a structure-directing agent. The obtained mesoporous organosilica materials were subsequently characterized. FTIR spectra confirmed that the biphenyl moiety is covalently linked in the ethane-silica framework. The interplanar spacing was observed between 8 to 9 nm, surface area from 1196.99 to 1578.57 m²/g, total volume from 1.2 to 0.75 cm³/g and primary pore diameter from 3.54 to 3.56 nm. Particle morphology of the biphenyl-functionalized organosilica produced rod-shaped, wormlike and spherical particles. The TEM images revealed hexagonal array of mesopores and lattice fringes along and perpendicular to the pore axis.

Keywords: biphenyl, organosilica, surfactant-templated

1 INTRODUCTION

Many new developments in the field of hybrid materials have been reported [1-3]. The synthesis to generate ordered hexagonal mesoporous structure is made of inorganic silica incorporating organic moieties in the framework [4]. 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, sensing technology and

nanoelectronics [5-6]. It has been shown that the properties and structure of mesoporous materials can be varied based on the synthesis process and conditions, such as base concentrations, temperatures, and the nature of the organic moiety to be incorporated [7-10].

In this paper, we report the synthesis of novel periodic mesoporous biphenyl-functionalized ethane-silica. The preparation involves 4,4'-bis(triethoxysilyl)biphenyl and 1,2-bis(triethoxysilyl)ethane co-condensation. Investigation was extended on the influence of the surfactant ratio and heat treatment on the properties of the bifunctional hybrid material.

2 METHODS

The 4,4'-bis(triethoxysilyl) biphenyl organosilane precursor was synthesized based on the general procedure described by Shea et al. For the surfactant-templated polymerization of organosilica, the process was done by employing 1:1:8 mole ratio of the organosilica precursor monomer, bis(triethoxysilyl)ethane and tetraethoxysilane (TEOS) respectively. The mixture under basic media (62.0 {H₂O}:0.64 {CTAB}: 0.25 {NaOH} ratio) was stirred for twenty-four hours and placed in an oven at 95–100 °C for three 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. The surfactant ratio and heat treatment were subsequently varied to investigate the effect on the properties of the obtained organosilica materials. All the resulting products were characterized using Fourier Transform Infrared Spectroscopy (FTIR), Powder X-ray Diffraction (XRD), Transmission Electron Microscopy (TEM), and Scanning Electron Microscopy (SEM).

3 RESULTS AND DISCUSSIONS

The success of polymerization and incorporation of biphenyl moiety in the organosilica framework was analyzed using Fourier Transform Infrared Spectroscopy (FTIR). Table 1 summarizes the functional groups present in the obtained mesoporous hybrid material.

Table 1: FTIR peak assignment

Functionality		Wavenumber (cm ⁻¹)
C–H stretch	Phenyl	2930
	Aliphatic	2895
C=C vibration	Phenyl	1633
	Aliphatic	1409
Si–O–Si	Asymmetric	1081
C–H	Aromatic	964
Si–O–Si	Symmetric	974

The intense absorption bands at 1081 and 794 cm⁻¹ are characteristics for the asymmetric and symmetric stretching respectively of the Si–O–Si bonds. The C–H deformation vibrations at 2895 and 1409 cm⁻¹ were observed due to the aliphatic part of the bridging silsesquioxanes incorporated into the structure. The peaks at 2930, 1633 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.

Formation of enhanced rope- and rod-based morphologies, as well as observation of larger particles with gyroid and granular characteristics was observed under SEM when surfactant was varied. With longer heat

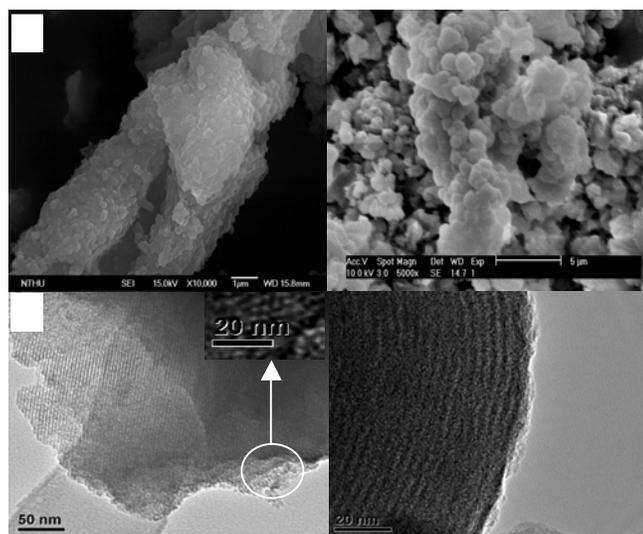


Figure 1: SEM (A) and TEM (B) images of the organosilica

treatment, spherical particles morphology were greatly observed.

Transmission electron microscopy images reveal many lattice fringes with hexagonal array of mesopores. 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 molecules, and between the precursor molecules and surfactant. The hexagonal structure was confirmed by XRD analysis and the pattern showed a two-dimensional *p6mm* space group with interplanar spacing ranges from 8 to 9 nm.

Samples of solvent-extracted mesoporous organosilica under varying surfactant ratio and heat treatment were tested for N₂ adsorption/desorption isotherms as shown in Figure 2. Analyses showed that the materials exhibit type IV isotherms. This is typical for the well ordered mesoporous material with narrow pore size distribution. All the formulations exhibit an H1 hysteresis loop at the range of 0.55-0.80 relative pressure (P/P₀).

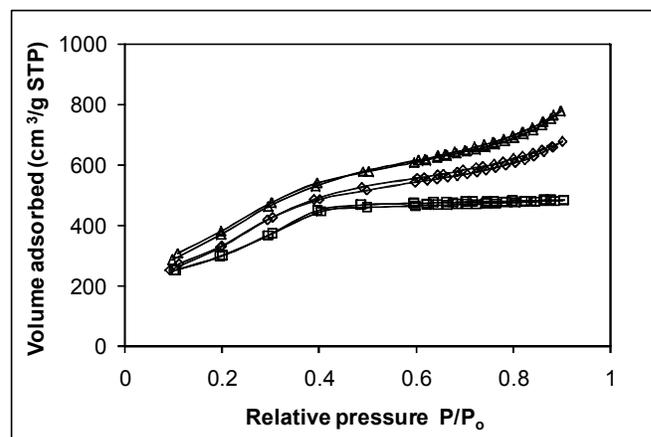


Figure 2: N₂ adsorption /desorption isotherm of the solvent-extracted mesoporous organosilica: Δ surfactant ratio (0.32), heat treatment (3 hrs); \diamond surfactant ratio (0.64), heat treatment (3 hrs); \square surfactant ratio (0.64), heat treatment (9 hrs)

Table 2: Effect of surfactant ratio and heat treatment on the structure of organosilica derived from N₂ isotherms

Surfactant ratio	Heat treatment (hrs)	Surface area (m ² /g)	Pore volume (cm ³ /g)	Pore diameter (nm)
0.32	3	1196.99	0.750	3.56
0.64	3	1578.57	1.205	3.55
0.64	9	1423.07	1.049	3.54

The specific surface area ranges from 1196.99 to 1578.57 m²/g, and the total pore volume from 1.2 to 0.75 cm³/g. Using the BJH desorption method, the primary pore diameter from ranges from 3.54 to 3.56 nm. This indicates that no greater effect on the increasing surfactant concentration and heat treatment in terms of pore diameter.

4 CONCLUSION

Biphenyl-containing mesoporous hybrid organosilica materials have been synthesized and characterized. The organic group was covalently bonded in the framework and formed a two-dimensional hexagonal crystal structure.

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