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Stability of hybrid organosilica materials incorporating a biphenyl moiety

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Quezon City, PhilippinesThe stability of biphenyl-functionalized ethane-silica hybrid materials was investigated by a calcination process, a hydrothermal test and exposure to UV to determine the integrity of its composition, structure, and morphology. The organosilicas were prepared via surfactant-mediated polymerization of 4,4'-bis(triethoxysilyl)biphenyl organosilane monomer and crosslinked with 1,2-bis(triethoxysilyl)ethane and tetraethoxysilane. Infrared spectroscopic and gravimetric analyses showed that the material was thermally stable below 700 °C. Its hydrothermal stability could be accounted for by the strong covalent integration of the bifunctional organic bridging groups in the silica framework. No significant change was observed in the functional groups when the material was exposed to ultra-violet radiation. Post heat treatment of the materials did not significantly change the interplanar spacing of the (100) plane, but enhanced the spherical particle morphology.

Key words: organosilica, Surfactant-mediated polymerization, Biphenyl moiety.

Introduction

solid materials with well-ordered structures such as organosilicas are of great interest because of their broadened applications ranging from catalysis, adsorption, separation, sensing technology to nanoelectronics [1-4]. They can be developed into organic-inorganic nanocomposites, whereby the organic groups are functionalized in the framework structure of the inorganic porous hosts [5]. Various precursors and synthetic routes have been used in the preparation of hybrid materials [6-8].

The molecular structuring of periodic mesoporous organosilicas (PMOs) involves bridging organosilsesquio-xanes with different structures of organic moiety embedded homogeneously inside the channel walls as bridges between silicon centers [9-10]. This leaves the pore channels vacant for further modifications and inclusions of guest species [11-12]. The use of organosilane with a specific organic bridging group can be designed to generate hybrid materials with the desired physical and chemical framework properties. Numerous bridging groups have been incor- porated to develop more functionality of PMOs, ranging from simple alkane, aromatic groups, and to very large organometallic complexes [13-17].

Because of their various potential uses, it is of vital importance to understand the stability of these hybrid organosilica materials. The incorporation of biphenyl moiety in a silica framework provides a general route to multicomponent inorganic-organic hybrid materials and allows possible inclusion of transition metal centers and chirality that are highly tunable for specialized applications. In this paper, we report the stability studies done on a hybrid periodic mesoporous organosilica materials incorporating a biphenyl moiety previously synthesized in our laboratories [18]. The hybrid material obtained was calcined and subsequently characterized to determine its thermal stability as well as the compositional, structural and morphological changes. The hydrothermal stability of the materials in boiling water and UV resistance were also investigated as important requirements for their long-term performance.

Experimental

The surfactant-mediated polymerization was done by employing 1 : 1 : 8 molar ratio of 4,4'-bis(triethoxysilyl) biphenyl precursor, 1,2-bis(triethoxysilyl)ethane and tetraethoxysilane respectively. The mixture in a basic media (62.0{H_2O} : 0.64{CTAB} : 0.25{NaOH} ratio) was stirred for twenty-four hours and placed in an oven at 95 °C for three hours. The products were then filtered, washed and dried. The excess surfactant was removed under reflux, and the white solid was then filtered, washed again with ethanol to a neutral pH and dried in a vacuum.

To investigate the thermal stability of the synthesized organosilica, samples were calcined at 400, 700, and 900 °C

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for three hours under an argon environment. The hydrothermal stability was estimated by refluxing the material in deionized water at 100 °C for five days. After boiling, the sample was filtered and dried in an oven at 60 °C. For an investigation of the stability under UV radiation, the sample was exposed to 15-Watt GE UV germicidal lamp emitting 254 nm wavelength for ten hours.

Powder X-ray diffraction (XRD) measurements were carried out in a Bede Scientific at 30-40 kV and 30 mA using Cu-Kα radiation (wavelength $\lambda = 1.5406$ Å). Scanning electron microscopy (SEM) images for particle morphology were obtained using a LEICA S440 and Philips XL30 FEG-SEM. Transmission electron microscopy (TEM) with a JOEL 2000 FX operating at an accelerating voltage of 160 kV was used to characterize the internal structure. Fourier-transform infrared spectroscopy (FT-IR) with a Nicolet Magna-IR Spectrometer 550 was employed to study the vibration of chemical bonds present at various frequencies and a simultaneous differential thermal-thermogravimetric analyzer (SDT-TGA) TA Instrument SDT-2960 was used for the determination of the thermal stability of the organosilica material.

Results and Discussion

The approach of this surfactant-mediated polymerization is to generate biphenyl-functionalized hybrid materials by inserting organic spacers into the ethane-silica framework as shown in Fig. 1.

The thermal stability of the organosilica material obtained was analyzed using SDT-TGA. Fig. 2 shows the thermogram of the air-dried organosilica Fmaterial taken under a nitrogen environment at a heating rate of 10 Kminute^{-1} up to 1100 °C. A weight loss at around 150 °C was observed due to the removal of absorbed residues and water formed by condensation of residual and neighboring terminal hydroxyl groups. The removal of excess surfactant and organic fragments arises at 400 °C. The subsequent weight loss at 700 °C, which is accompanied by evolution of heat, was assigned to the decomposition of the biphenyl group.

Following from the thermogravimetric analysis, the loss of functional groups is confirmed as seen in the spectroscopy analyses when calcination was employed.

The integrity and preservation of the organic functional groups in the organosilica framework was evaluated using FT-IR spectroscopy. Fig. 3 shows the absorption band characteristics of the hybrid material obtained. The peaks for –CH stretching in the phenyl and aliphatic groups at 2923 and 2853 cm^{-1} [19], aromatic ring vibrations at 1633 and 1479 cm^{-1} [20-21], as well as the bending of alkyl –CH at 1416 cm^{-1} [13], and aromatic –CH at 956 cm^{-1} [19] were observed. This confirms the covalent linking of the biphenyl-bridged moiety in the channels of the hybrid organosilica material. The intense absorption bands at 1078 and 797 cm^{-1} are characteristics for the asymmetric and symmetric stretching respectively of the Si–O–Si bonds of the silica framework resulting from the hydrolysis and

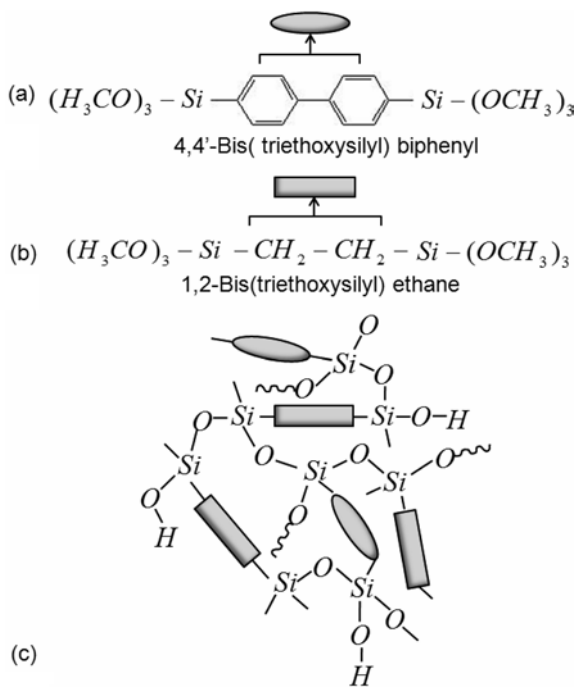

Fig. 1. Representative precursors (a and b) and probable structural framework of hybrid poly(silsesquioxane) with organic bridging group (c).

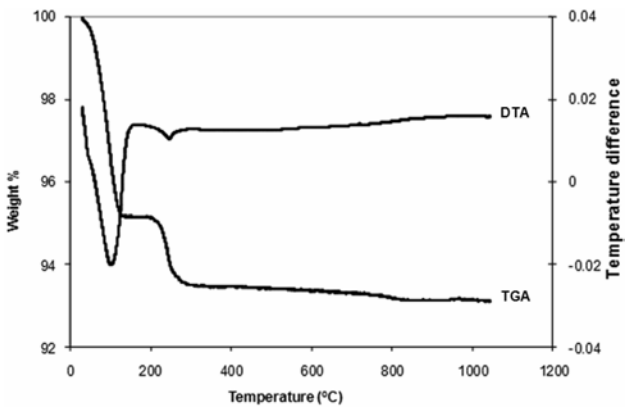

Fig. 2. SDT-TGA thermogram of the organosilica hybrid materials incorporating a biphenyl moiety.

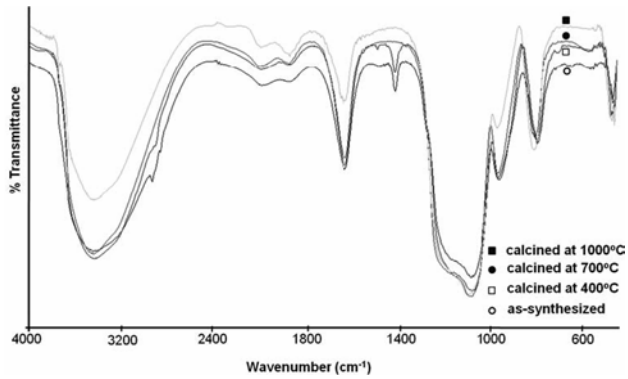

Fig. 3. FTIR spectra of as-synthesized organosilica and hybrid materials calcined at 400 °C, 700 °C, and 1000 °C.

condensation of the silsesquioxane monomers.

However, when the organosilica material was subjected to high temperature calcination from 400 to 1000 °C, the intensities of the organic functional groups diminished. This indicates a decomposition reaction of the organic functional groups in the framework structure of the orga- nosilica. There was a cleaving of the –CH stretching for the aliphatic and aromatic groups. These functional groups were no longer visible in the IR spectra after calcination at 700 °C. The intensity of the –OH group at 3430 cm^{-1} decreased significantly when calcined to 1000 °C. This suggests that condensation of the silanol group was enhanced and converted into Si–O–Si. Elemental analyses through energy dispersive X-ray spectroscopy confirmed a significant loss of carbon with the calcination process at high tem- perature and no observable change for the oxygen-to-silicon ratio.

The structure of the synthesized organosilica was investigated by XRD and TEM. The XRD patterns for all samples as shown in Fig. 4 exhibit one characteristic peak of the hexagonal structure of the mesopores in the low angle region, which can be assigned to the (100) peak of the two-dimensional *p6mm* space group [20]. The absence of resolved secondary features and the broader diffraction peak behaviour indicates no long-range order in the structure of the periodic mesoporous organosilica [21]. Table 1 shows the interplanar d-spacing and lattice constants of the organosilica obtained and samples calcined at 400, 700, and 1000 °C.

The peak intensity and resolution did not change significantly with the calcination process, indicating that the mesostructural order of the material is stable and intact. It is interesting to note that the organic component of such organic-inorganic materials can be removed by calcination, while preserving the structure of the silica network. Therefore, calcination up to 1000 °C produced no significant

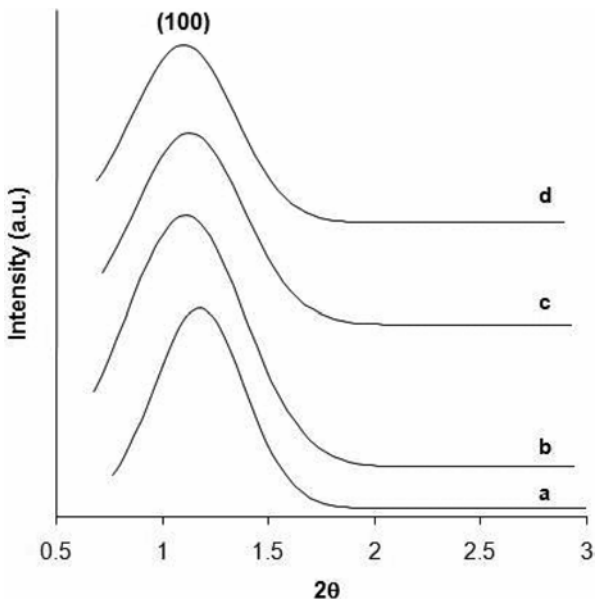

Fig. 4. XRD patterns of as-synthesized organosilica (a) and hybrid materials calcined at 400 °C (b), 700 °C (c), and 1000 °C (d).

Table 1. Structural parameters derived from XRD analyses

	2θ	θ	d_{100} (Å)	a_o (Å)
as-synthesized	1.178	0.589	74.93	86.52
calcined at 400 °C	1.178	0.589	74.93	86.52
calcined at 700 °C	1.187	0.593	74.39	85.90
calcined at 1000 °C	1.187	0.593	74.39	85.90

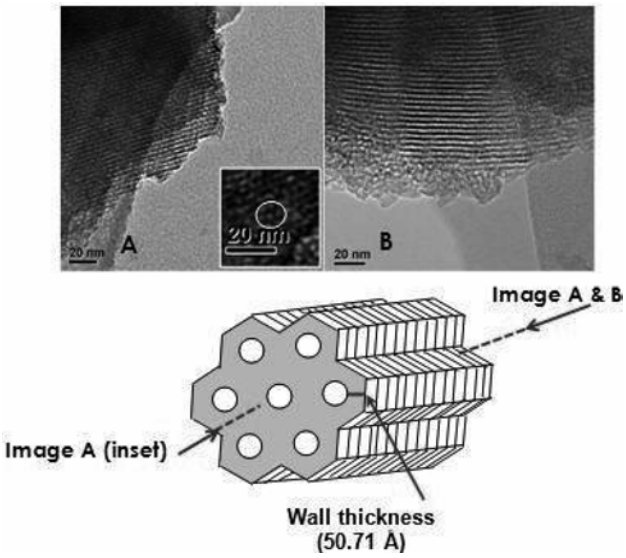

Fig. 5. TEM images showing lattice fringes and ordered mesopores packed in an hexagonal array and a schematic model derived from TEM results.

change in the unit cell parameter a_o, with only a very small decrease in d_{100}. The unit cell parameter of hexagonally-ordered organosilica was derived from the interplanar spacing of the (100) plane.

TEM images of a representative sample of synthesized organosilica in Fig. 5 are consistent with the X-ray diffraction results showing hexagonal symmetry mesopores. The lattice fringes exhibit structural periodicity, wherein the periodic pore structure is due to the alternating hydrophilic and hydrophobic layers of silica and bi-functional organic moieties respectively. Such a network is formed as a result of structure directing interactions between the biphenyl-bridged organosilane monomer to other silsesquioxane molecules brought about by the surfactant as a structure-directing agent.

A varied particle morphology was observed in the organosilica obtained. Highly clustered particles as shown in Fig. 6 led to the formation of a rope- and rod-like morphology [22], as well as aggregates of spherical particles. When calcination was applied, the effect on the morphology of organosilica led to the formation of enhanced micro-spherical particles. Fig. 7 shows the morphology of the calcined organosilica materials. There is no significant difference in the particle characteristics when calcination was done at 700 and 1000 °C. Some rope-like characteristics of the morphology were still evident after heat treatment at 400 °C.

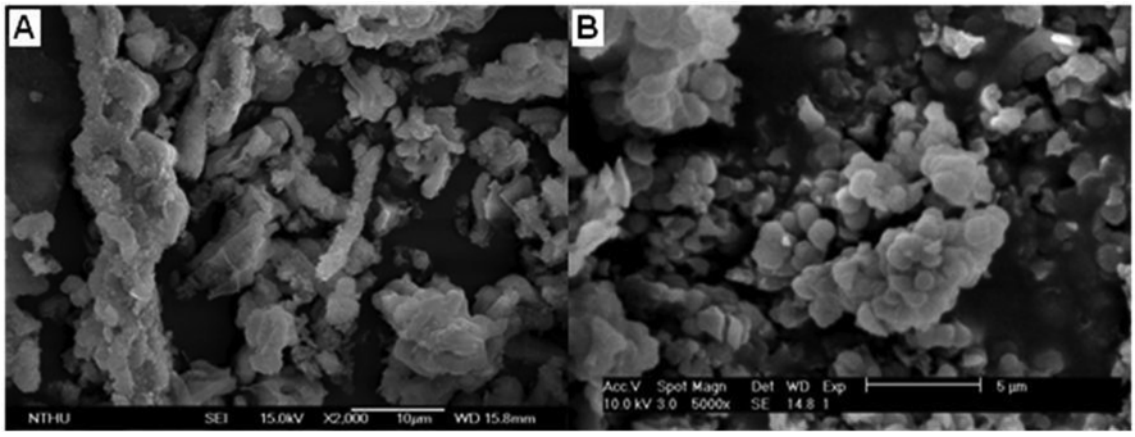

Fig. 6. SEM images of as-synthesized mesoporous organosilica showing rope- and rod-like (A) and spherical morphology (B).

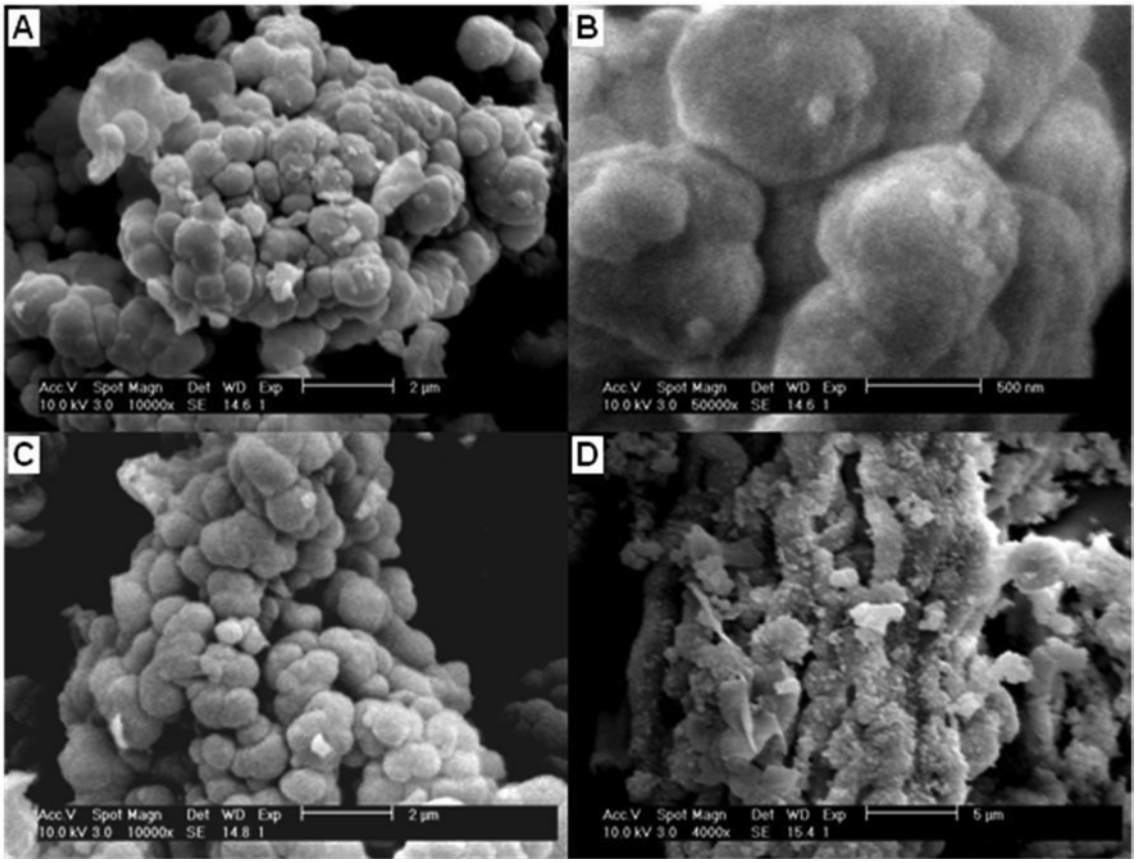

Fig. 7. SEM images of mesoporous organosilica calcined at 1000 °C (A) & (B), 700 °C (C) and 400 °C (D).

The calcination process resulted in the removal of water and organic parts as confirmed by the infrared spectroscopic and thermogravimetric analyses. The enhanced particle shape is brought about by the breakdown of the attractive forces such as hydrogen bonding. Upon release of the solvents, the aggregated powder may separate and eventually initiate grain growth.

The FT-IR spectra of the biphenyl functionalized materials after the hydrothermal treatment revealed that the finger print regions for the organic moieties and Si–O–Si bonds were preserved. Its hydrothermal stability is associated to the highly hydrophobic surface nature of the organosilica framework due to the organic moieties. The thick channel pore wall of the structure is also a contributing factor that will prevent any possible collapse.

The work of Guo *et al*. [23] on the hydrothermal stability of ethane functionalized organosilica (PMO-SBA-15) concluded that the hydrolysis of Si-O-Si bonds into Si–OH bonds to a great extent leads to the remarkable degradation of structural ordering of the hybrid materials to

long-time boiling treatment. For the organosilica obtained, the hydrothermal stability is noticeably observed due to the bifunctional organic components (biphenyl and ethane-bridged) in the silica framework. This provides a protection against water attack during the hydrothermal treatment. It has also been established that the PMO-SBA-15 is hydrothermally stable having a channel wall thickness of 50.8 Å [23]. This only further suggests that the organosilica materials obtained incorporated with biphenyl moiety having an average channel wall thickness of 50.71 Å are also hydrothermally stable.

The average wall thickness of the mesopores was calculated from the difference between average a_o and the average mesopore diameter at around 35.5 Å, which was derived from a Barret-Joyner-Halenda (BJH) calculation scheme.

When the material was exposed to UV light (254 nm), no significant difference in the IR spectra was seen. The exposure up to ten hours showed similar organic functional groups and no diminish in the moiety was observed.

Conclusions

Mesopotous hybrid organosilica materials incorporating a biphenyl moiety were obtained and their stability was investigated through calcination processing, hydrothermal test and exposure to UV. High temperature calcination of the hybrid materials resulted in the release of organic groups in the framework as confirmed by the FT-IR spectra and thermogravimetric analyses, which suggests a relative thermal stability below 700 °C. Structural characterization via X-ray diffraction analyses showed that the two-dimensional hexagonal crystallographic unit was preserved even after the removal of the organic moieties. The hybrid organosilica materials were also found to be hydrothermally stable. There was no significant change in the integrity of the functional groups when exposed to ultraviolet radiation.

Acknowledgments

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References

1. M. Burleigh, M. Markowitz, S. Jayasundera, S. Spector, C. Thomas and B. Gaber, J. Phys. Chem. B. 107 (2003) 12628-12634.
2. T. Asefa, M. Machlachlan, N. Coombs and G. Ozin, Nature 402 (1999) 867-871.
3. M. Davis, Nature 417 (2000) 813-821.
4. P. Wight and M. Davis, Chem. Rev. 102 (2002) 3589-3614.
5. K. Yamamoto, Y. Sakata, Y. Nohara, Y. Takahashi and T. Tatsumi, Science 300 (2003) 470-472.
6. A. Sayari and S. Hamoudi, Chem. Mater. 13 (2001) 3151-3168.
7. T. Salesch, S. Bachmann, S. Brugger, R. Rabelo-Schaefer, K. Albert, S. Steinbrecher, E. Plies, A. Mehdi, C. Reyé, R. Corriu and E. Lindner, Adv. Funct. Mater. 12 (2002) 134-142.
8. B. Park, W. Guo, X. Cui, J. Park and C. Ha, Microporous Mater. 66 (2003) 229-238.
9. D. Joy and K. Shea, Chem. Rev. 95 (1995) 1431-1442.
10. B. Novak, Adv. Mater. 5 (1993) 422-433.
11. L. Zhang, Q. Yang, W. Zhang, Y. Li, J. Yang, D. Jiang, G. Zhua and C. Li, J. Mater. Chem. 15 (2005) 2562-2568.
12. B. Melde, B. T. Holland, C. Blanford and A. Stein, Chem. Mater. 11 (1999) 3302-3308.
13. S. Inagaki, S. Guan, Y. Fukushima, T. Ohsuna and O. Terasaki, J. Am. Chem. Soc. 121 (1999) 9611-9614.
14. C. Baleizao, B. Gigante, D. Das, M. Alvaro, H. Garcia and C. Corma, Chem. Commun.15 (2003)1860-1861.
15. T. Asefa, M. Kruk, M. Machlachlan, N. Coombs, H. Grondey, M. Jaroniec and G. Ozin, J. Am. Chem. Soc.123 (2001) 8520-8530.
16. M. Kuroki, T. Asefa, W. Whitnall, M. Kruk, C. Yoshina-ishii, M. Jaroniec and G. Ozin, J. Am. Chem. Soc. 124 (2002) 13886-13895.
17. G. Temtsin, T. Asefa, S. Bittner and G. Ozin, J. Mater. Chem. 11 (2001) 3202-3206.
18. E. Magdaluyo, R. Rivera Virtudazo, L. dela Cruz, E. Castriciones and H. Mendoza, Philipp. J. Sci. 138,1 (2009) 5-11.
19. S. Grin, A. Kovalenko, S. Alekseev and V. Il'in, Theor. Exp. Chem. 40 (2004) 389-395.
20. W. Guo, J. Park, H. Jeong, M. Oh, W. Cho, I. Kim and C. Ha, Chem. Mater. 15 (2003) 2295-2298.
21. T. Ren, X. Zhang and J. Suo, Microporous Mater. 54 (2002) 139-144.
22. Y. Xiao and X. Zhao, J. Phys. Chem. B 109 (2005) 10727-10736.
23. W. Guo, X. Li and X. Zhao, Microporous Mater. 93 (2006) 285-293.