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Synthesis, Characterization, and Applications of Organic-Inorganic Hybrid Mesoporous Silica

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Abstract−Organic-inorganic hybrid mesoporous materials composed of homogeneously distributed ethane group in a silica framework were prepared by using 1,2 bis(trimethoxysilyl) ethane (BTME) as a precursor and alkyltrimethylammonium-chloride or -bromide surfactant as a structure directing agent with or without the presence of a swelling agent, mesitylene. Characterization of the materials was performed by XRD, TEM/SEM, ^{29}Si-/^{13}C-solid state NMR, and N_2-adsorption. Testing of the hybrid material as a reversed phase HPLC column stationary phase after C18 surface-functionalization demonstrated a promising result, which closely approaches the performance of a commercial product. Mn-salen complex tethering on the hybrid material produced a catalyst with somewhat enhanced performance in liquid phase etherification with tert-butyl hydroperoxide as oxidant.

Key words: Organic-Inorganic Hybrid Material, Mesoporous Organosilica, Chromatography, Catalyst Support

INTRODUCTION

Since the emergence of high surface area mesoporous MCM-41 type silica materials via a surfactant-templated synthesis route by Mobil in 1992 [Kresge et al., 1992], organic modification schemes imparting various functionalities to the inorganic silica surface have received much attention [Kang et al., 2002; Kim et al., 2000]. One approach to surface modification is post-synthetic grafting by means of a condensation reaction between silanol groups on the mesoporous materials with various organosilanes or siloxanes containing amino, thiol, or epoxide groups [Cauvel et al., 1997; Diaz et al., 1997; Liu et al., 1998], and the other is direct synthesis methods, introducing an appropriate organosilane precursor by mixing with a silicone-alkoxide precursor in the synthesis gel mixture [VanRhijn et al., 1998; Macquarrie, 1996; Moller et al., 1999]. For the latter, organic groups are being incorporated into the pore walls, rather than bonded to the pore surface and usually result in materials with stronger bonding between organic and inorganic parts. However, the maximum organic part that can be incorporated is limited to ca. 30 wt% at best, and the hybrid materials obtained generally exhibit poor structural orders than in pure inorganic counterparts.

Recently, Inagaki [Inagaki et al., 1999], Stein [Melde et al., 1999], and Ozin [Asefa et al., 1999] groups independently prepared a new class of hybrid mesoporous materials that incorporate homogeneous distribution of organic components within a silica framework without structural deterioration. By using a double trialkoxysilyl precursor in which bonding between silicon and carbon is established with the assured stoichiometry, periodic ordered mesoporous organosilica (PMO) materials in which ethane or ethylene groups were directly integrated into silica framework were synthesized. In a similar fashion, methylene, acetylene, thiophene, benzene, bithiophene, or ferrocene incorporated materials were reported [Yoshina-Ishii et al., 1999], and cubic hybrid mesoporous material with a uniform decaoctahedral shape [Guan et al., 2000], and SBA-15 version of the hybrid materials prepared in strongly acidic condition [Burleigh et al., 2001; Zhu et al., 2002; Guo et al., 2003] were reported. Asefa et al. [2002] reviewed the developments in the synthesis and chemistry of PMOs.

These new materials have been expected to lead to advanced materials in catalysis, chromatography, membranes, and microelectronics due to the possibility of controlling the kind and loadings of various functional groups by optimizing co-condensation protocol leading to tunable physical properties and uniform distribution of functional groups [Lu et al., 2000; Asefa et al., 2001]. But, despite these high expectations for potential uses, as yet very limited work on the actual applications of the PMO has been reported. Yamamoto et al. prepared a Ti-containing PMO co-condensed with TEOS, and reported that undesirable allylic oxidation was suppressed in cyclohexene epoxidation [Yamamoto et al., 2001]. 1,2-Bis(triethoxysilyl)ethane as a linking group in the direct synthesis of ordered macroporous silica functionalized with polyoxometalate clusters, on the other hand, was rather disappointing in catalytic epoxidation of cyclooctene [Schroden et al., 2001].

In this study, we have prepared an organic-inorganic hybrid mesoporous silica using 1,2 bis(trimethoxysilyl)ethane (BTME) as a precursor based on the recipe by Inagaki et al. [Guan et al., 2000]. After evaluating their physicochemical properties, we examined them as catalyst support in cyclohexene etherification reaction using tert-butyl hydroperoxide (TBHP) and also tested as a packing material for a reversed phase HPLC column.

EXPERIMENTAL

Synthesis of an organic-inorganic hybrid material in cubic structure (PMO-C) was carried out at the substrate molar ratios of 1 BTME: 0.91 CTMACl (cetyltrimethylammonium chloride): 2.28 NaOH: 336 H_2O. First, a mixture was produced by adding CTMACl to NaOH

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[‡] This paper is dedicated to Professor Hyun-Ku Rhee on the occasion of his retirement from Seoul National University.

aqueous solution in a polypropylene bottle and stirred vigorously with mild heating until it became clear. After BTME was added dropwise to this clear solution inside a glove box in N_2 atmosphere, the mixture was stirred for 19 h at 25 °C and subsequently kept stirred at 95 °C for further 21 h. White thick precipitates obtained were filtered, washed with distilled water, and dried at room temperature. After refluxing 1 g sample of as-synthesized mesoporous material in 4 g of 35 wt%HCl in 150 ml ethanol for 6 h at 50 °C to remove the surfactant, we collected product by filtration, washed it with ethanol and dried it in the atmosphere. Changing the surfactant from CTMACl to CTMABr (cetyltrimethylammonium bromide) resulted in a hybrid material in hexagonal pore structure (PMO-H). For pore size expansion of PMO-H, mesitylene was initially mixed with CTMABr in mesitylene/CTMABr ratio(mol) of 0.55 and 1.1 before introducing BTME.

Crystallinity of the samples prepared was measured by X-ray diffraction using Ni-filtered CuKα radiation (Philips, PW-1700), and those with the enlarged pores were measured using WAXD/SAXD (Rigaku DMAX 2500). The morphology of the samples was examined by TEM (Philips, CM 200) and SEM (Hitachi, X-650). The specific surface area and average pore diameters were determined by N_2 physisorption at liquid nitrogen temperature using Micromeritics ASAP 2000.

For evaluation of PMO as a support for catalytic applications, Mn-salen complex anchored on PMO was prepared according to the synthesis schemes of Choudary et al. [2000] and tested in the etherification of cyclohexene by using TBHP as oxidant.

For testing PMOs as a column material, C-18 modification and capping on samples by trimethysilyation were carried out and a micro-column (0.5 mm I.D×300 mm) was packed with the functionalized PMO powders and examined for its chromatographic performance in reversed phase HPLC. C-18 modification and trimethysilyation steps were carried out as follows. One gram of PMO, pyridine 0.6 mL, and xylene 6 mL were put into a small round bottom flask with a reflux condenser, and stirred for 10 seconds, and then 0.4 g of chlorodimethyloctadecylsilane was added and stirred at 100 °C for 5 hours. The product was filtered and washed with toluene, THF, and methanol, and dried. One gram of the dried product, 0.6 mL pyridine, and 6 mL xylene were placed in a small round bottom flask with a reflux condenser, and stirred for 10 seconds, then 0.2 mL chlorotrimethylsilane was added and stirred at 100 °C for 3 hours. The final product was filtered, washed with toluene, THF, and methanol, and dried. Details of preparation of a micro-column and construction of a μLC system can be found elsewhere [Cheong et al., 1997].

RESULTS AND DISCUSSION

1. Synthesis and Characterization

A preliminary investigation of the several reported recipes for PMOs established that the materials prepared by Inagaki et al. [Guan et al., 2000] exhibit the best resolved XRD patterns with crystal-like particle morphologies in relatively uniform size distribution. It was chosen as a standard PMO sample to be tested as a catalyst support and HPLC column packing material after appropriate surface functionalization steps.

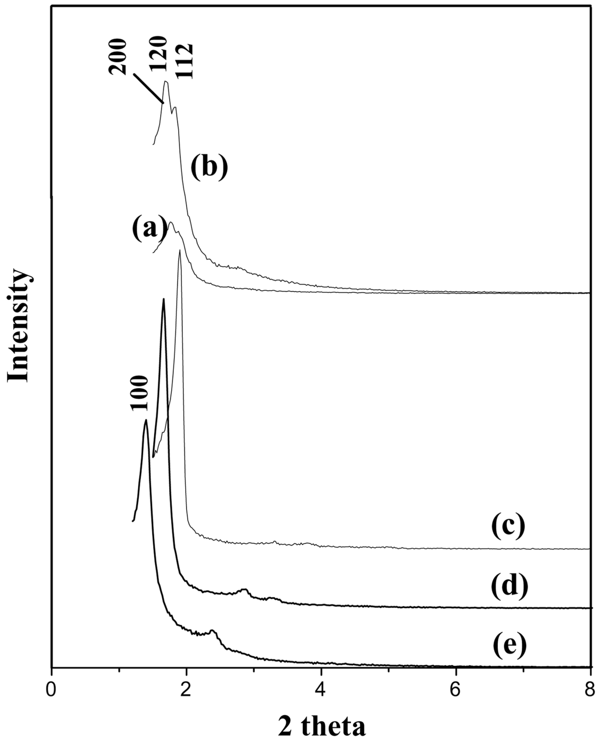
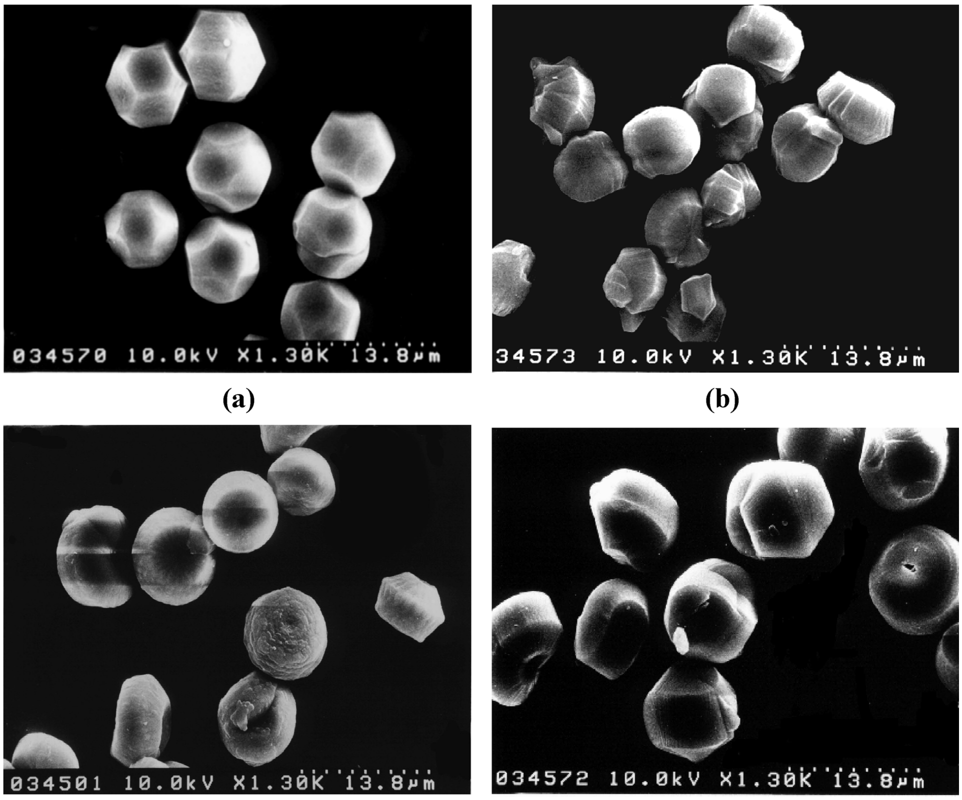


Fig. 1. X-ray diffraction patterns of (a) PMO-C (as-synthesized), (b) PMO-C (solvent extracted), (c) PMO-H ($M/S^*=0$), (d) PMO-H (M/S=0.55), (e) PMO-H (M/S=1.1).
*M/S=mesitylene to surfactant mol ratio

Fig. 1 shows the comparison of XRD patterns of the PMOs prepared. PMO-C has the cubic Pm-3n space group, similar to the silica mesoporous material known as SBA-1. Main peak corresponding to (120) at d=49.5 Å was observed and its intensity increased substantially after surfactant extraction by using ethanol/HCl. The peak remained at the same position, indicating that little structural contraction took place after removing the CTMACl surfactant. Interestingly, simple changing of the surfactant from CTMACl to CTMABr at the same substrate composition produced MCM-41 type PMO with hexagonal structure, PMO-H, which was identified by the characteristic X-ray diffractograms shown in Fig. 1. This phase transition is believed to be a consequence of a change in g factor [Tolbert et al., 2001] such that the larger size of bromide anion compared to chloride makes g factor to increase. Packing parameter, g is defined as V/a_0I , where V is the total volume of surfactant, a_0 represents surfactant head group area, and I, kinetic dimension of surfactant tails. In general, a cubic (*Pm*3*n*) phase is known to be produced at g=1/3, hexagonal (p6m) at 1/2, cubic (*Ia*3*d*) at 1/2-2/3, and lamellar phase at 1, i.e., as the g factor increases, curvature at the micelle interface decreases and transition from cubic to lamellar phase takes place. Pore size enlargement of PMO-H using mesitylene as a swelling agent resulted in lattice parameter increase and the characteristic (100) peak shifted towards the left as the amount of swelling agent added increased.

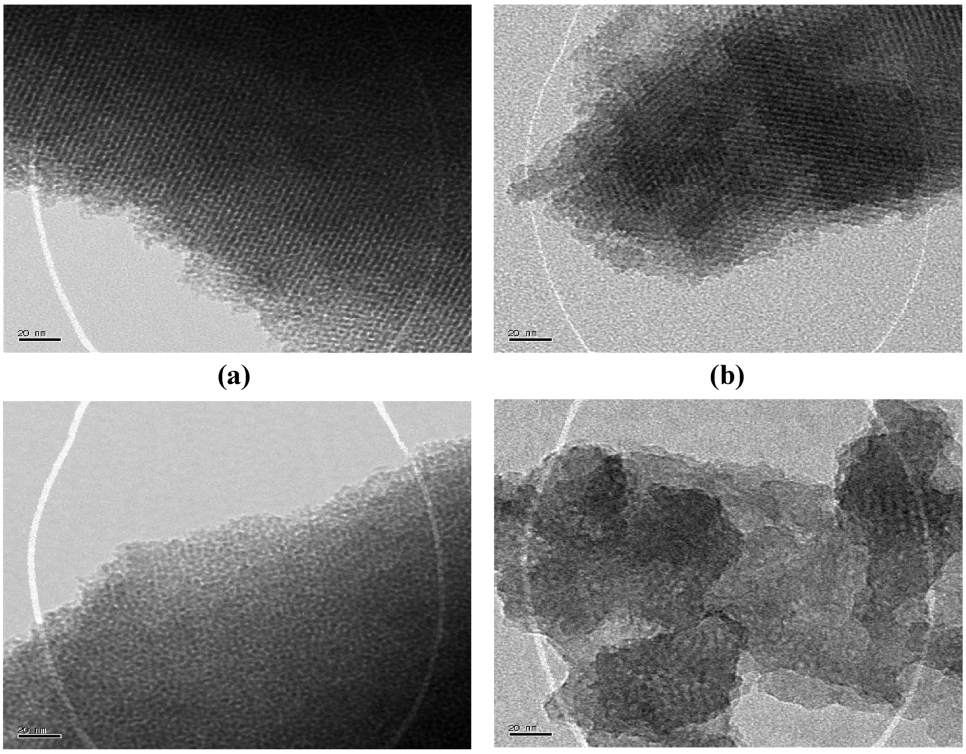
SEM images in Fig. 2 show uniform decaoctahedron shape particles with average size of ca. 8 micron in diameter for PMO-C, while more flat and squashed particles of the similar size were formed for PMO-H. Slight increase in particle size was accompanied by the addition of mesitylene as pore swelling agent. Regular well or-



(a) (b)

(c) (d)

Fig. 2. SEM images of (a) PMO-C, (b) PMO-H (M/S*=0), (c) PMO-H (M/S=0.55), (d) PMO-H (M/S=1.1).
*M/S=mesitylene to surfactant mol ratio



(a) (b)

(c) (d)

Fig. 3. TEM images of (a) PMO-C, (b) PMO-H (M/S*=0), (c) PMO-H (M/S=0.55), (d) PMO-H (M/S=1.1).
*M/S=mesitylene to surfactant mol ratio

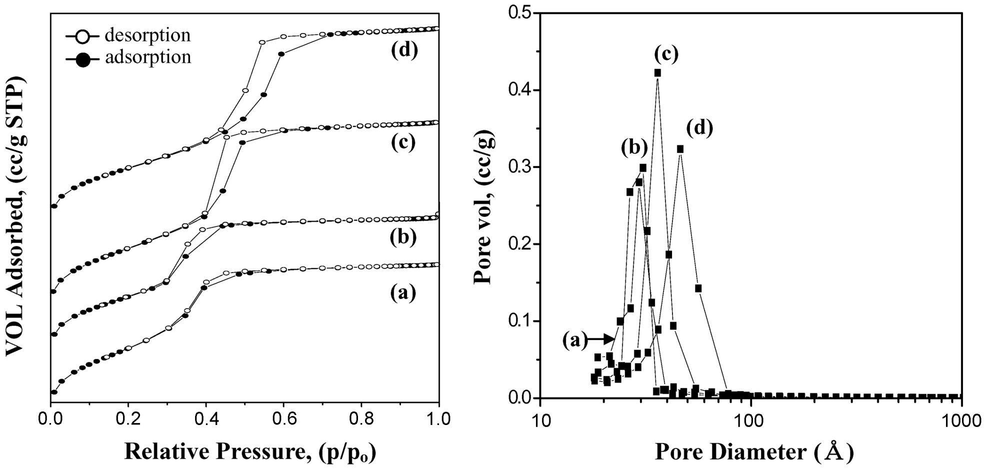


Fig. 4. N_2 adsorption-desorption isotherm and BJH adsorption pore size distribution of (a) PMO-C, (b) PMO-H (M/S*=0), (c) PMO-H (M/S=0.55), (d) PMO-H (M/S=1.1).
*M/S=mesitylene to surfactant mol ratio

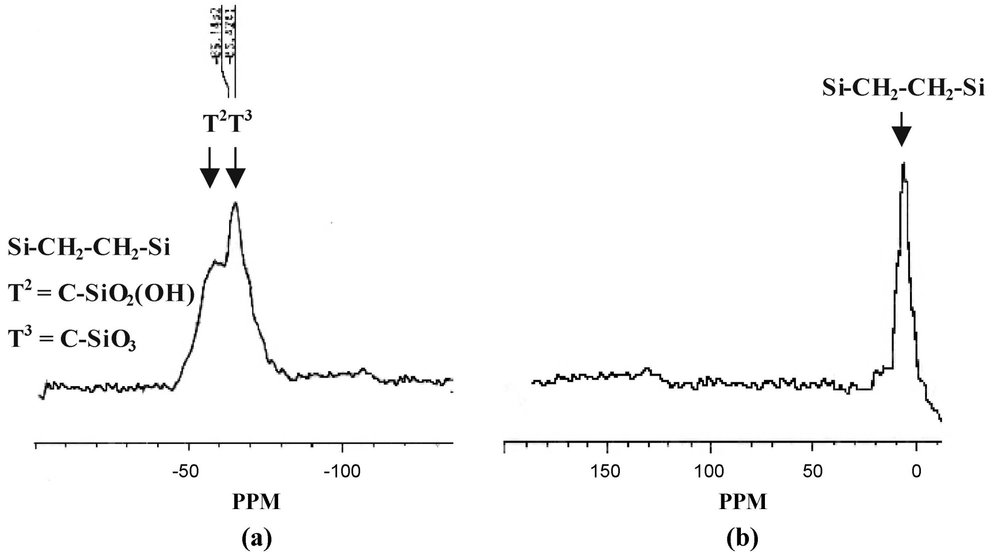
dered channels of the PMOs prepared were confirmed by TEM images in Fig. 3, but PMO-H samples with mesitylene showed increasingly disordered pore arrangement. Average pore diameter of 28 Å with narrow pore size distribution was verified for PMO-C as shown by N_2 adsorption in Fig. 4. Pore size enlargement of PMO-H using mesitylene as a swelling agent resulted in lattice parameter shift (d=46 to 63 Å) and pore size increase [Fig. 4(a)], but narrowness in pore size distribution [Fig. 4(b)] and XRD long range order (Fig. 1) and regularity in pore channels (Fig. 3) deteriorated as mesitylene/CTMABr (mol) ratio was increased from 0 to 1.1. These are all in accordance with the known physical changes accompanied by swelling treatment by mesitylene for inorganic mesoporous silicas [Lindlar et al., 2001]. Primary purpose of swelling for mesoporous materials is for pore size enlargement of mesoporous materials to promote diffusion rate and to increase the accessibility of reactant molecules to active sites inside the pores, but swelling also produced particle size growth as shown in Fig. 2. For a porous material with ordered crystal-like morphology, it is natural to expect such a particle size expansion as a result of hydrophobic core expansion. Textual properties of the PMOs are summarized in Table 1.

^{29}Si-/^{13}C-MAS NMR spectra for PMO-C are shown in Fig. 5.

Table 1. Textual properties of PMOs

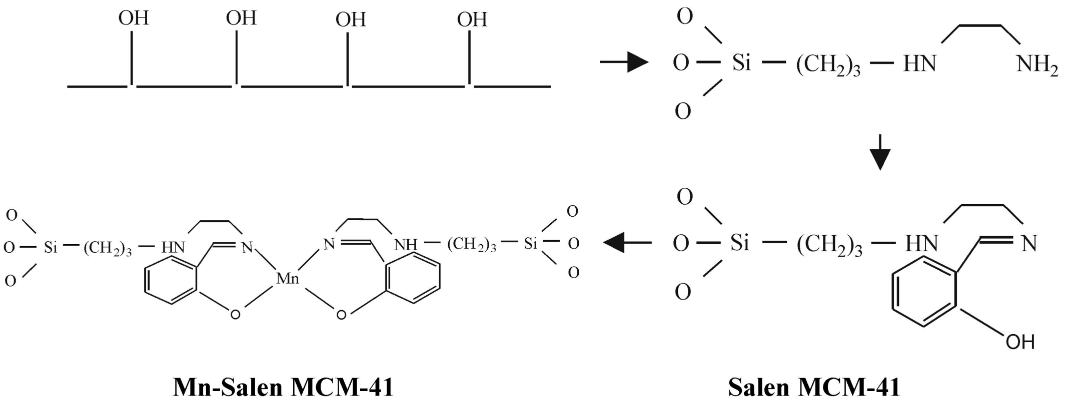
Materials	Pore size (Å)	Pore vol. (cc/g)	Surface area (m^2/g)
PMO-C	28	0.79	799
PMO-H (M/S*: 0)	28	0.74	778
PMO-H (M/S: 0.5)	33	0.96	805
PMO-H (M/S: 1.1)	40	0.97	714

*M/S=mesitylene to surfactant mol ratio.



(a) (b)

Fig. 5. NMR spectra of the PMO-C; (a) ^{29}Si MAS NMR, (b) ^{13}C CP MAS NMR.



Scheme 1. Mn-salen complex tethering steps.

^{29}Si MAS NMR spectra (a) confirm that Si-C covalent bond is the basic unit of framework structure for hybrid mesoporous material. T^2 [SiC(OH)(OSi)$_2$] and T^3 [SiC(OSi)$_3$] resonance appeared at −57 and −65 ppm, while those peaks −90 ppm and −120 ppm corresponding to Q^3 [Si(OH)(OSi)$_3$] and Q^4 [Si(OSi)$_4$] species, respectively, were absent. ^{13}C-NMR data (b) confirmed that the ethane fragments of the precursor were not cracked during hydrolysis process judging by the peak at 5.4 ppm, which is assignable to -CH$_2$-CH$_2$- located in between two Si atoms. These combined NMR results indicate that Si-C-C-Si unit was kept intact during the PMO synthesis and uniformly integrated into the mesoporous structure. Virtually identical spectra were obtained for other PMO-H samples. Decomposition of ethane fragment in the pore wall took place above ca 573 K according to TGA (not shown).

2. Catalysis

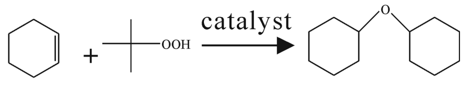
Testing of the PMO-H as a catalyst support for liquid phase oxidation reaction was carried out after immobilization of Mn-salen complex on PMO as shown in Scheme 1. These were applied as catalysts for cyclohexene etherification by using TBHP. The corresponding test reaction result is summarized in Table 2, and a comparison of the catalytic performance with inorganic MCM-41 supported catalysts is also included.

High hydrophobicity of the catalyst has been known to be useful in increasing conversion or selectivity in liquid phase oxidation reactions, but the improvement in catalytic performance by using PMO-H was rather minor; cyclohexene conversion to ether increased from 22.0 to 25.1%. The reaction was repeated twice for data confirmation.

Enhanced hydrophobicity of PMOs compared to MCM-41 is well established [Inagaki et al., 1999; Melde et al., 1999]. This was also confirmed by our experiment in which surface silanol concentration of PMO-H available for (MeO)$_3$Si(CH$_2$)$_3$Cl grafting amounted only to ca. 5% of MCM-41. It can be conjectured that the active metal-ligand species grafted on PMO-H are relatively little affected by the enhanced hydrophobicity of the mesoporous wall surface rather than those created by organic agents attached to the surface by post-synthetic silylation. The latter is expected to be in more close proximity to the active metal species for the catalysts prepared in this work. Further work is planned to test this hypothesis.

Table 2. Catalytic performance of Mn-salen/PMO in cyclohexene oxidation

Material	Cyclohexene converted into ether (%)
Mn-MCM-41	22.0
Mn-PMO-H	25.1



Reaction conditions: 1.26 ml cyclohexene, 1 ml TBHP as an oxidant (5.5 M in decane), 10 ml dichloromethane, 0.25 g catalyst, refluxed at 323 K for 10 h.

3. Chromatographic Separation

Mesoporous materials have been claimed to be useful in separation science, but only limited cases of chromatographic applications have appeared in the literature [Boissiere et al., 2000; Grun et al., 1996; Bruzzoniti et al., 2000; Gallis et al., 1999; Kisler et al., 2001], most of which concerned normal phase liquid chromatography where mesoporous materials were used without chemical modification on the surface. Modification of APMS (acid-prepared mesoporous spheres) with C8 ligand was, however, recently introduced in the literature [Gallis et al., 1999]. It seems that good chromatographic separation of analytes with either bare or ligand-modified mesoporous material has not been reported yet.

As shown by the characterization work mentioned above, the PMOs prepared in this study have high surface area and uniform mesopores. More importantly, enhanced hydrophobicity and well-defined particle morphology are expected to be beneficial to chromatographic separation. Thus, we packed a microcolumn (0.5 mm I.D.×300 mm) with the PMOs and examined its chromatographic performance in comparison with a column packed with a commercial silica packing material (Lichrosopher Si60) using some carefully selected solute components. For reversed phase applications in which non-polar stationary phase and polar mobile phase are employed to resolve the separation of non-polar molecules, we chemically modified the PMOs and commercial silica by attachment of C-18 ligand via reaction with chlorodimethyloctadecylsilane. Further capping by trimethysilylation was carried out for commercial silica, but no capping sequence was conducted for PMOs, since they have little silanol left after C-18 attachment, and capping procedure could adversely result in the removal of the surface attached C18 species instead. The separation results are presented in Figs. 6 and 7. We can see that the C-18 modified PMOs work quite well in separation of nitroaniline isomers (Fig. 6). The relatively narrow

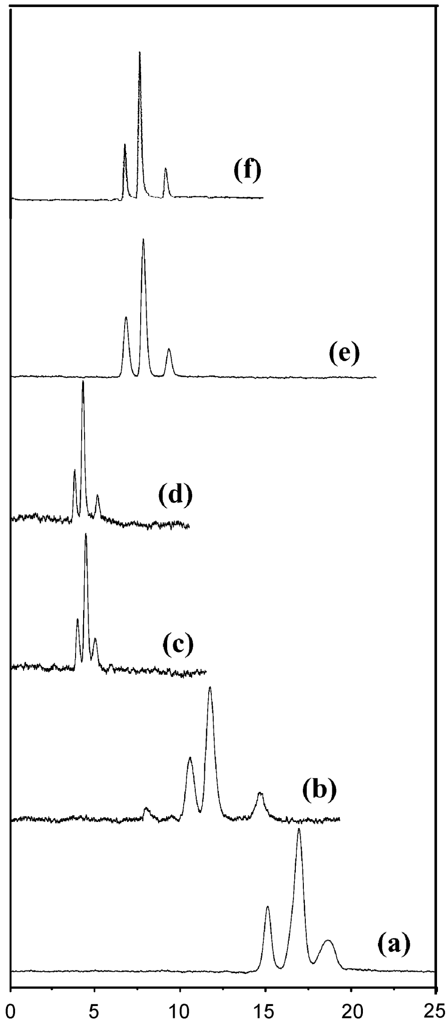


Fig. 6. Chromatograms obtained in 70/30 v/v% MeOH/H_2O at the flow rate of 10 μl/min with different stationary phases.
(a) PMO-H (M/S*=0)+C18, (b) PMO-H (M/S=0.55)+C18, (c) PMO-H (M/S=1.1)+C18, (d) PMO-C+C18, (e) PMO-C (6 μm)+C18, (f) commercial silica+C18+TMCS
*M/S=mesitylene to surfactant mol ratio
Solutes, 1; o-Nitroaniline, 2; m-Nitroaniline, 3; p-Nitroaniline

and long channels in PMO-H retard fast mass transfer and thereby cause band broadening of chromatographic peaks with longer retention time. But as the pore size enlargement is achieved by the introduction of mesitylene, peaks resolved out more quickly and became congested. PMO-C with cubic structure seems to promote solute diffusion inside the pores more than PMO-H with 1-dimensional pores and also resulted in fast peak elution. By controlling the hydrothermal synthesis time from 21 to 16 h, it was possible to make the PMO-C with smaller particle size of ca. 6 micron, and this PMO-C (e) produced excellent separation almost equivalent to the commercial silica due to more compact packing in the micro-column.

Finally, PMO-C(6m) was tested for separation of large nonpolar molecules in Fig. 7. While clean solute separation was achieved, separation of large nonpolar solutes such as acenaphthene, phenanthrene, and anthracene was not quite up to the performance of commercial product. An explanation for the chromatographic performances should be sought from the differences in particle size/shape and pore sizes between the hybrid material and commercial silica packing. The PMO-C is multi-faced decaoctahedron shape while the commercial silica is spherical. Packing quality of decaoctahedron powders in 6 to 8 microns in a column would be inferior to that of spherical powders of ca 3-5 microns, and the quality can deteriorate further if the particle size of the former is bigger, which is the case here. The pore size of the PMO-C is ca 30 Å, while the pore size of the commercial silica is ca. 60 Å. Thus, the flow channels in the PMO-C particles are long and narrow, causing slow mass transfer and diverse spread of analytes along the column depending upon the orientation of channels, while those in the silica are wide and short, securing fast mass transfer and minimized spread of analytes. A uniform 3-dimensional pore system of PMO-C, though, seems to make some compensation. It is therefore recommended to develop methods of producing spherical PMO particles with 3-5 microns and increasing the pore size of the hybrid material. Producing PMO-C in a microwave-heated oven is in progress to secure these proposed features.

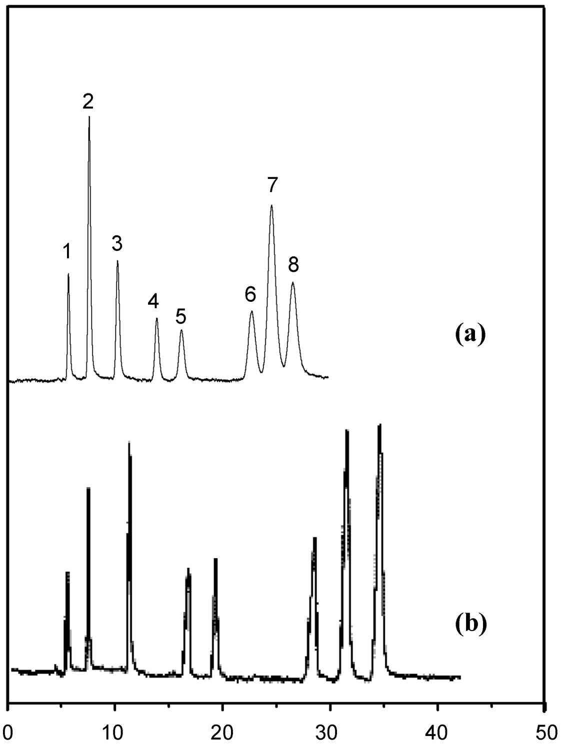


Fig. 7. Chromatograms obtained in 80/20 v/v% MeOH/H_2O at the flow rate of 10 μl/min with different stationary phases.
(a) PMO-C (6 μm)+C18, (b) commercial silica+C18+TMCS
Solutes, 1: 4-Methoxyphenol, 2: Acetophenone, 3: Ethylbenzoate, 4: Ethylbenzene, 5: Acenaphthylene, 6: Acenaphthene, 7: Phenanthrene, 8: Anthracene

CONCLUSIONS

6 to 8 μm decaoctahedron shaped PMOs with uniform size distribution in cubic form could be prepared. PMOs with swelled pores in hexagonal structure could be prepared equally well by changing the surfactant from CTMACl to CTMABr with the aid of mesity-

lene. PMOs demonstrated limited advantage as a catalyst support material, but consistently demonstrated enhanced product yield in cyclohexene etherification using TBHP. PMOs, due largely to the high hydrophobicity and uniform particle morphology, could be implemented as a column material for reversed phase HPLC after C18 functionalization. Further work on optimization of synthesis parameters is necessary to prepare spherical PMO particles with expanded pores.

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REFERENCES

Asefa, T., MacLachlan, M. J., Coombs, N. and Ozin, G. A., "Periodic Mesoporous Organosilicas with Organic Groups Inside the Channel Walls," *Nature*, **402**, 867 (1999).

Asefa, T., Kruk, M. M., MacLachlan, J., Coombs, N., Grondey, H., Jaroniec, M. and Ozin, G. A., "Novel Bifunctional Periodic Mesoporous Organosilicas, BPMOs: Synthesis, Characterization, Properties and in-Situ Selective Hydroboration-Alcoholysis Reactions of Functional Groups," *J. Am. Chem. Soc.*, **123**, 8520 (2001).

Asefa, T., Ozin, G. A., Grondey, H., Kruk, M. and Jaroniec, M., "Recent Developments in the Synthesis and Chemistry of Periodic Mesoporous Organosilicas," *Stud. Surf. Sc. Catal.*, **141**, 1 (2002).

Boissiere, A., Larbot, A. and Prouzet, E., "Preparation of Spherical Micrometric MSU-X Mesoporous Silica Particles for Chromatography Applications," *Stud. Surf. Sc. Catal.*, **129**, 31 (2000).

Bruzzoniti, M. C., Mentasti, E., Sarzanini, C., Onida, B., Bonelli, B. and Garrone, E., "Retention Properties of Mesoporous Silica-based Materials," *Anal. Chim. Acta*, **422**, 231 (2000).

Burleigh, M. C., Markowitz, M. A., Wong, E. M., Lin, J. S. and Gaber, B. P., "Synthesis of Periodic Mesoporous Organosilicas with Block Copolymer Templates," *Chem. Mater.*, **13**, 4411 (2001).

Cauvel, A., Renard, G. and Brunel, D., "Monoglyceride Synthesis by Heterogeneous Catalysis Using MCM-41 Type Silicas Functionalized with Amino Groups," *J. Org. Chem.*, **62**, 749 (1997).

Cheong, W. J., Lee, C. S. and An, H. J., "Improved Glass-Lined Stainless Steel Packed Microcolumns of 0.3 mm I.D.," *Bull. Korean Chem. Soc.*, **18**, 1036 (1997).

Choudary, B. M., Kantam, M. L., Bharathi, B., Sreekanth, P. and Figueras, F., "Epoxidations of Olefins Catalysed by New Mn(II) Salen Immobilized Mesoporous Materials," *J. Mol. Catal. A*, **159**, 417 (2000).

Diaz, J. F., Balkus, K. J., Bedioui, F., Kurshev, V. and Kevan, L., "Synthesis and Characterization of Cobalt-Complex Functionalized MCM-41," *Chem. Mater.*, **9**, 61 (1997).

Gallis, K. W., Araujo, J. T., Duff, K. J., Moore, J. G. and Landry, C. C., "The Use of Mesoporous Silica in Liquid Chromatography," *Adv. Mater.*, **11**, 1452 (1999).

Grun, M., Kruganov, A. A., Schacht, S., Schuth, F. and Unger, K. K., "Comparison of an Ordered Mesoporous Aluminosilicate, Silica, Alumina, Titania and Zirconia in Normal-Phase High-Performance Liquid Chromatography," *J. Chromatogr. A*, **740**, 1 (1996).

Guan, S., Inagaki, S., Ohsuna, T. and Terasaki, O., "Cubic Hybrid Organic-Inorganic Mesoporous Crystal with a Decaoctahedral Shape," *J. Am. Chem. Soc.*, **122**, 5660 (2000).

Guo, W., Park, J. Y., Oh, M. O., Jeong, H. W., Cho, W. J., Kim, I. and Ha, C. S., "Triblock Copolymer Synthesis of Highly Ordered Large-Pore Periodic Mesoporous Organosilicas with the Aid of Inorganic Salts," *Chem. Mater.*, **15**, 2295 (2003).

Inagaki, S., Guan, S., Fukushima, Y., Ohsuna, T. and Terasaki, O., "Novel Mesoporous Materials with a Uniform Distribution of Organic Groups and Inorganic Oxide in Their Frameworks," *J. Am. Chem. Soc.*, **121**, 9611 (1999).

Kang, T., Park, Y., Park, J. C., Cho, Y. S. and Yi, J., "Preparation of Chemically Active Mesoporous Adsorbent for Pt(II) and Pd(II) Adsorption from Aqueous Solutions," *Korean J. Chem. Eng.*, **19**, 685 (2002).

Kim, G. J., Park, D. W. and Ha, J. M., "Synthesis of a Siliceous MCM-41 using C_{22}TMACI Template and Preparation of Heterogenized New Chiral Salen Complexes," *Korean J. Chem. Eng.*, **17**, 337 (2000).

Kisler, J. M., Dahler, A., Stevens, G. W. and O'Connor, A. J., "Separation of Biological Molecules Using Mesoporous Molecular Sieves," *Micropor. Mesopor. Mater.*, **44-45**, 769 (2001).

Kresge, C. T., Leonowicz, M. E., Roth, W. J., Vartuli, J. C. and Beck, J. S., "Ordered Mesoporous Molecular Sieves Synthesized by a Liquid-crystal Template Mechanism," *Nature*, **359**, 710 (1992).

Lindlar, B., Kogelbauer, A., Kooyman, P. J. and Prins, R., "Synthesis of Large Pore Silica with a Narrow Pore Size Distribution," *Micropor. Mesopor. Mater.*, **44-45**, 89 (2001).

Liu, J., Feng, X., Fryxell, G. E., Wang, L. Q. and Kim, A. Y., "Hybrid Mesoporous Materials with Functionalized Monolayers Advanced Materials," *Adv. Mater.*, **10**, 161 (1998).

Lu, Y., Fan, H., Doke, N., Loy, D. A., Assink, R. A., LaVan, D. A. and Brinker, C. J., "Evaporation-Induced Self-Assembly of Hybrid Bridged Silsesquioxane Film and Particulate Mesophases with Integral Organic Functionality," *J. Am. Chem. Soc.*, **122**, 5258 (2000).

Macquarrie, D. J., "Direct Preparation of Organically Modified MCM-type Materials. Preparation and Characterisation of Aminopropyl-MCM and 2-cyanoethyl-MCM," *Chem. Commun.*, 1961 (1996).

Melde, B. J., Holland, B. T., Blanford, C. F. and Stein, A., "Mesoporous Sieves with Unified Hybrid Inorganic/Organic Frameworks," *Chem. Mater.*, **11**, 3302 (1999).

Moller, K., Bein, T. and Fisher, R. X., "Synthesis of Ordered Mesoporous Methacrylate Hybrid Systems: Hosts for Molecular Polymer Composites," *Chem. Mater.*, **11**, 665 (1999).

Schroden, R. C., Blanford, C. F., Melde, B. J., Johnson, B. J. S. and Stein, A., "Direct Synthesis of Ordered Macroporous Silica Materials Functionalized with Polyoxometalate Clusters," *Chem. Mater.*, **13**, 1074 (2001).

Tolbert, S. H., Landry, C. C., Stucky, G. D., Chmelka, B. F., Norby, P., Hanson, J. C. and Monnier, A., "Phase Transitions in Mesostructured Silica/Surfactant Composites: Surfactant Packing and the Role of Charge Density Matching," *Chem. Mater.*, **13**, 2247 (2001).

VanRhijn, W. M., DeVos, D. E., Sels, B. F., Bossaert, W. D. and Jacobs, P. A., "Sulfonic Acid Functionalised Ordered Mesoporous Materials as Catalysts for Condensation and Esterification Reactions," *Chem. Commun.*, 317 (1998).

Yamamoto, K., Nohara, Y. and Tatsumi, T., "Synthesis and Catalysis of

Ti-MCM-41 Materials with Organic-Inorganic Hybrid Network," *Chemistry Letters*, 648 (2001).

Yoshina-Ishii, C., Asefa, T., Coombs, N., MacLachlan, M. J. and Ozin, G. A., "Periodic Mesoporous Organosilicas, PMOs: Fusion of Organic and Inorganic Chemistry 'Inside' the Channel Walls of Hexagonal Mesoporous Silica," *Chem. Commun.*, 2539 (1999).

Zhu, H., Jones, D. J., Zajac, J., Dutartre, R., Rhomari, M. and Roziere, J., "Synthesis of Periodic Large Mesoporous Organosilicas and Functionalization by Incorporation of Ligands into the Framework Wall," *Chem. Mater.*, **14**, 4886 (2002).