Synthesis of Mesoporous MCM-41 Gallosilicates *via* Shift of Gallosilicate Polymerization Equilibrium

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Recently, mesoporous MCM-41 materials with a hexagonal array of parallel one dimensional channels have been reported by Mobil scientists.[1,2] The novelty in synthesis of the MCM-41 is the use of surfactant micelles, around which silicates polymerize hydrothermally to form the matrix structure. An exciting property of these materials is the possibility to control the pore size in the range between 2 nm and 10 nm by using surfactants with different molecular chain lengths and auxiliary organic species during crystallization process. The large channel diameters and its tailorability provide new opportunity as supports for catalysts, host for the inclusion of compound and nanosize clusters and molecular sieves for large molecules.[3-5]

The incorporation of gallium into a pure silica MCM-41 framework causes a negative charge of the framework that renders an ion-exchange property to the materials. Therefore we expect that gallium containing MCM-41 will possess an ion-exchange capacity by catalytically active transition metal ions as found in zeolites and SAPO-n materials. Such transition metal ion species may offer potential for specially tailored catalytic application of the MCM-41 gallosilicate materials.

In this work, we report for the first time the synthesis of mesoporous MCM-41 gallosilicate materials with uniform hexagonal array of cylindrical pores through shifting gallosilicate polymerization equilibrium by addition of acid during the conversion of gallosiliate and $N(Me)_3(C_{16}H_{33})Cl$ to a MCM-41 phase.

Experimental

Synthesis. A typical mesoporous MCM-41 gallosilicate material has been synthesized based on modification of the procedure described by Ryoo *et al.*[6] A surfactant source was obtained by dissolving 2.40 g of dodecyltrimethylammonium(DTA)bromide(from Aldrich) and 2.08 g of tetrapropylammonium(TPA)bromide(from Aldrich) in a mixture of 40.00 g of 25 wt% aqueous solution of hexadecyltrimethylammonium chloride(HTACl), 0.58 g of 28 wt% aqueous NH_3 solution, and 20.00 g of deionized water. A clear solution of sodium silicate with a Na/Si ratio of 0.50 was prepared by combining 93.80 g of 1.00 M aqueous NaOH solution with 28.60 g of a colloidal silica, Ludox HS40 (39.5 wt% SiO_2, 0.4 wt% Na_2O and 60.1 wt% H_2O, from Aldrich) and heating the resulting gel mixture with stirring for 2 h at 353 K. Gallium source was a solution of 0.29-0.88 g of Ga_2O_3 (from Aldrich) added in a mixture solution prepared by dissolving 0.36-0.75 g of NaOH in 12.2-20.0 g of doubly distrilled water. The resulting sodium gallate solution was heated to boiling with stirring for about 2 h to form a clear solution, and then cooled to 313 K.[7] The silicate solution was dropped to the surfactant source with vigorous stirring at room temperature. Two different procedures are carried out for mixed gel preparation depending upon addition of sodium gallate.

Procedure 1: After a resulting surfactant-silicate gel mixture was stirred for 1 h at room temperature, the sodium gallate solution was dropwise added with vigorous stirring. The resulting surfactant-gallosilicate gel mixture had a bulk molar composition of 6.00 SiO_2: xGa_2O_3: 1.00 HTACl: 0.25 DTABr: 0.25 TPABr: 0.16 $(NH_4)_2O$: 1.70-1.86 Na_2O: 302-315 H_2O where $0.05 < x < 0.15$. The gel mixture was stirred for 30 min more to form a homogeneous mixture before heating in oven at 373 K for 24-48 h. The HTA-gallosilicate mixture was then cooled to room temperature. Subsequently, pH of the reaction mixture was adjusted to 10.2 by dropwise addition of 30 wt% acetic acid with vigorous stirring. The reaction mixture after the pH adjustment to 10.2 was subsequent by heated at 373 K for 24 h. The pH adjustment and subsequent heating was repeated twice more.

Procedure 2: After a surfactant-silicate gel mixture was stirred for 1 h at room temperature, the mixture was directly heated in oven at 373 K for 48 h without gallium source. After the preheated HTA-silicate mixture was cooled to room tempearture, sodium gallate solution was dropwise added with vigorous stirring into the mixture. Subsequently, pH of the reaction mixture was adjusted to 10.2 by dropwise addition of 30 wt% acetic acid with vigorous stirring like in Procedure 1. The reaction mixture after the pH adjustment to 10.2 was subsequent by heated for 24-48 h. The pH adjustment and subsequent heating was repeated twice more. The resulting mixture had the same bulk molar composition as that for Procedure 1.

The precipitated product, MCM-41 gallosilicate with HTA template, was filtered, washed with doubly distilled water, and dried at room temperature. The dried MCM-41 gallosilicate product was stirred in an ethanol-hydrochloric acid mixture (0.1 mol of HCl per L of ethanol) for 1 h under reflux conditions. Subsequently, the product was washed with ethanol at room temperature and dried at room temperature. Calcination of the product was carried out in O_2 flow while the sample was heated to 823 K over 10 h and maintained at this temperature for 10 h.

Analysis. Powder X-ray diffractometer (XRD) measurements were performed with a Philips PW 1840 diffractometer before and after calcination of as-synthesized MCM-41 gallosilicate to confirm that the synthesis product has a MCM-41 structure. Electron spin resonance spectra were measured both at room temperature and 77 K on an ESP 300 Bruker spectrometer. Elemental analysis was performed with inductively coupled plasma (ICP) emission spectroscopy.

Results and Discussion

The idea for addition of acid is that acid addition shifts gallosilicate polymerization equilibrium to a MCM-41phase by removing hydroxide ions in equilibrium as suggested below.[6]

$$\text{gallosilicate} + \text{HTA}^+ \rightleftarrows \text{MCM-41} + \text{OH}^-$$

In procedure 1, a surfactant-gallosilicate gel mixture was prepared before hydrothermal heating. The gallium ions are expected to be distributed homogeneously throughout the resulting gallosilicate MCM-41 framework. However, in procedure 2, a surfactant-silicate gel mixture is heated to synthesize a pure silica MCM-41 phase before addition of gallium source. The gallium solution is then added to the preheated sample, and thus gallium ions may react with surfacial silica of a crystallized pure silica MCM-41 or with remaining unreacted surfactant-silicate. The pre-formed silica MCM-41 crystal may also play as a seed for gallosilicate MCM-41 crystallization. In this case, since gallosilicate polymerization occurs over the outer side of a pure silica MCM-41 core crystal, gallium is expected to be distributed mainly around the pure silica MCM-41 core compared to homogeneous gallium ion distribution in the MCM-41 framework for procedure 1. Thus we can control the distribution of gallium ions in a mesoporous MCM-41 gallosilicate crystal through these synthetic approaches. Analysis for gallium distribution in a mesoporous MCM-41 gallosilicate crystal is in process.

The XRD patterns show at least four singals shown in Figure 1, indicating the existence of a hexagonal MCM-41 phase. Upon calcination, the first intense peak little or slightly shifted to a higher angle (Figure 1a and 1b). The intensity of the signals after calcination increases to more than twice that in as-synthesized MCM-41 gallosilicate. As gallium content increases, the XRD peak intensity decreases and the peak shifted to a higher angle, 2θ=2.00, 2.13, 2.25 and 2.30 for Figure 1f, 1e, 1d and 1c. This shift to a higer angle corresponds to narrower spacing of a main channel due to the incorporation of bulkier gallium ions into a MCM-41 framework. The gallosilicate samples prepared by Procedure 2 showed higher XRD signal intensities than those in Precedure 1 with identical gallium content under identicaltreatment conditions.

Some of pure silica MCM-41 and gallosilicate MCM-41 samples were ion-exchanged with 10 mM $Cu(NO_3)_2$ solution according to procedure described earlier for electron spin resonance spectroscopic analysis.[8] The Cu^{+2} exchanged sample was filtered and washed with hot deionized water several times to remove external excess Cu^{+2} ions. Figure 2 show ESR spectra at room temperature and at 77 K of a hydrated Cu(II)-exchanged MCM-41 gallosilicate with Si/Ga=44.62 prepared in Precedure 1. The fresh hydrated sample measured at 77 K produces an anisotropic ESR signal characteristic of an axial powder spectrum of Cu(II) with spin Hamiltonial parameters of $g_{\parallel}=2.047$, $A_{\parallel}=144\times10^{-4}$ cm^{-1} and $A_{\perp}=2.08$ (Figure 2b). The ESR spectrum measured at room temperature, however, shows an almost isotropic signal at $g_{iso}=2.186$ with $\Delta pp=144$ G as shown in Figure 2a. Such an isotropic ESR signal at room temperature is indicative of mobile species which is rotationally unrestricted on the ESR time scale. This species is assigned to a hexaaquo cupric ion species, $[Cu(H_2O)_6]^{2+}$ based on similar isotropic signals from ESR and pulsed ESR techniques.[9] At 77 K this $[Cu(H_2O)_6]^{2+}$ complex becomes immobilized and gives an asymmetirc spectrum as shown in Figure 2b. Cu (II)-exchanged pure silica MCM-41 also shows a simliar ESR spectrum but with much weaker singal(about 100 times weaker than those in Cu(II)-exchanged MCM-41 gallosilicate) because of neutrality of the pure silica framework. Also Cu(II) ESR intensity was increased as Cu(II) exchange

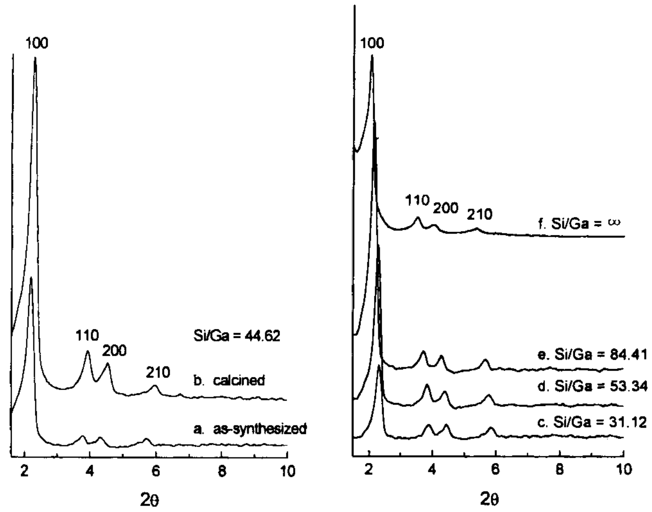

Figure 1. X-ray diffraction patterns of (a) as-synthesized, (b) calcined MCM-41 gallosilicate with Si/Ga=44.62 prepared in Procedure 1 and calcined MCM-41 gallosilicate (c) with Si/Ga=31.12 (d) with Si/Ga=53.34 and (e) with Si/Ga=84.41 prepared in Procedure 2 and (f) a pure silica MCM-41 with no Ga content. The intensity scale of (f) was put in half compared to that of (c), (d) and (e).

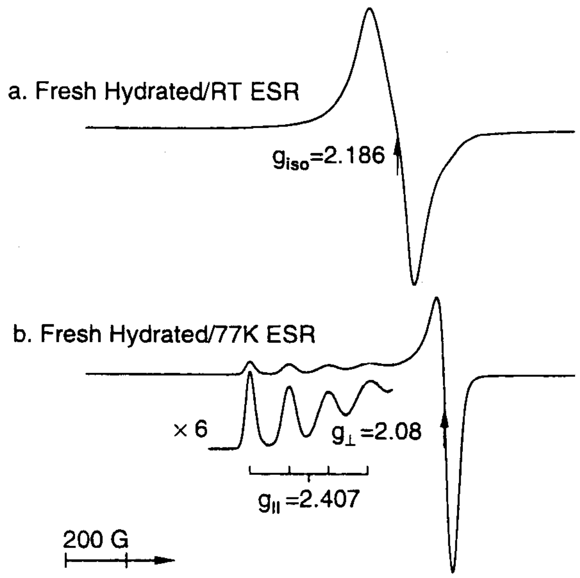

Figure 2. ESR spectra measured (a) at room temperature and (b) at 77 K of hydrated Cu(II)-exchanged MCM-41 gallosilicate with Si/Ga=44.62 prepared in Procedure 1.

Table 1. Ga incorporation and sodium ion exchange on mesoporous MCM-41 gallosilcates prepared in this work

Procedure[a]	Si/Ga[b]	Na/Ga[b]	Procedure[a]	Si/Ga[b]	Na/Ga[b]
1	23.66	0.35	2	31.12	0.49
1	44.62	0.61	2	53.34	0.78
1	68.50	0.90	2	84.41	1.01

[a] See the text for the explanation. [b] Atomic ratios determined by inductively coupled plasma emission spectroscopy. A pure-silica sample gave a Na/Si ratio of 0.0005.

was repeated for Ga containing MCM-41 while no remarkable change was observed for pure silica MCM-41 despite of repeated Cu(II) exchange. Such an ion-exchange property indicates gallium incorporation into MCM-41 framework.

To further investigate an ion-exchange properties of Ga-containing MCM-41, calcined producted was ion-exchanged with 10 mM sodium nitrate solution (100 mL per 1g calcined sample) at room temperature with stirring for 2-3 h. To ensure maximum Na^+ ion exchange, This procedure was repeated 3 times. The Na^+ exchanged sample was filtered and washed with deionized water several times to remove external excess Na^+ ions. There were no significant changes in XRD peak intensity before and after Na^+ ion exchange. Elemental analysis for the Si/Ga ratio and Na^+ content was performed with inductively coupled plasma (ICP) emission spectroscopy and the results are summarized in Table 1. The Na^+/Ga ratio increases as the Si/Ga ratio increases. The Na^+ ion exchange was near 100% for the Si/Ga ratios of 70 and higher. Considering that a pure silica MCM-41 gave little ion-exchange, it is evident that Na^+ ion-exchange capacity of the Ga-containing MCM-41 materials comes from Ga incorporation into the MCM-41 framework.

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References

1. Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Back, J. S. *Nature* **1992**, *392*, 170.
2. Back, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T.; Schmitt, K. D.; Chu, C. T-W.; Olson, D. H.; Sheppard, E. W.; McCullen, S. B.; Higgins, J. B.; Schkenker, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 10834.
3. Hou, Q.; Margolese, D. I.; Ciesla, U.; Feng, P.; Gier, T. E.; Sieger, P.; Leon, R.; Petroff, P. M.; Schuth, F.; Stucky, G. D. *Nature* **1994**, *386*, 317.
4. Coustel, N.; Renzo, F. D.; Fajula, F. *J. Chem. Soc., Chem. Commun.* **1994**, 967.
5. Sayari, A. *Chem. Mater.* **1996**, *8*, 1840.
6. Ryoo, R.; Kim, J. M. *J. Chem. Soc., Chem. Commun.* **1995**, 711.
7. Yu, J. S.; Ryoo, J. W.; Kim, S. J.; Hong, S. B.; Kevan, L. *J. Phys. Chem. Soc.* **1996**, *100*, 12624.
8. Yu, J. S.; Ryoo, J. W.; Kim, S. J.; Hong, S. B.; Kevan, L. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 1225.
9. Yu, J. S.; Kim, S. J.; Hong, S. B.; Kevan, L. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 855.

Oxidation of Pinusolide, *via* an Iodohydrin Intermediate, to 17-Hydroxy-8,13-labdadien-6,15-olid-9-oic Acid Methyl Ester by Treatment with Iodic Acid or Periodic Acid in Aqueous Acetone

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In the course of structure-activity relationship study on pinusolide (8(17),13-labdadien-16,15-olid-19-oic acid methyl ester, **1**), a platelet activating factor antagonist isolated from *Biota orientalis*,[1] we observed that **1** underwent an oxidative transformation to 17-hydroxy-8,13-labdadien-16,15-olid-19-oic acid methyl ester (**4**) on treatment with HIO_3 in aqueous acetone.

Compound (**4**) was first formed as a major product when the reaction condition of oxidation/glycol scission reaction of **1** was changed from $OsO_4/NaIO_4$ (dioxane : H_2O=1 : 1), where **1** was, as expected, oxidized to 17-nor-8-oxo derivative,[2] to OsO_4/H_5IO_6 (acetone : H_2O=5 : 1) in an attempt to increase solubility of **1** in the reaction mixture (Scheme 1). Subsequent studies revealed that **4** was formed in absence of OsO_4 and that use of HIO_3 in place of H_5IO_6 resulted in higher yields.

The structure of **4** was determined by spectroscopic and chemical analyses as 17-hydroxy-8,13-labdadien-16,15-olid-19-oic acid methyl ester. Its molecular weight was 362, 16 mass unit greater than that of **1**. In ^{1}H NMR, two singlet peaks at 4.56 and 4.87 ppm due to the exocyclic methylene protons in **1** were substituted by two oxymethylene doublet peaks at δ 4.11 and 4.24 ppm in **4**. When **4** was subjected to acetylation with acetic anhydride and pyridine, acetyl pro-