Post-Synthetic Incorporation of Ga into Mesoporous Siliceous MCM-41

Jeong Yeon Kim, Seung Jae Lee, and Jong-Sung Yu[*]

Hannam University, Department of Chemistry, Taejon 306-791, Korea
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The recent synthesis of M41S family with large-diameter apertures has greatly expanded the adsorptive and catalytic capabilities of porous materials to mesoporous dimensions.[1-6] Of particular interest is MCM-41 which possesses a regular hexagonal array of parallel one dimensional silica tubes. An exciting property of this material is the possibility to control the tube 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.

However, for this material to be useful for catalytic applications, it is essential to incorporate other metal ions into the siliceous framework to create an ion-exchange capacity. The incorporation of tivalent metal ions such as aluminium or gallium into a pure silica MCM-41 framework causes a negative charge of the framework that renders an ion-exchange property to the material. However, the direct synthesis using mixed gel of the metal-containing MCM-41 has proved to be challenging, requiring specialized synthetic conditions. The incorporation of even small amount of the metal into the MCM-41 framework causes a decrease in hexagonal ordering.[4,6] An alternative synthetic approach is the post-synthetic incorporation/grafting of metal ions into siliceous MCM-41. This is possible due to the presence of high density of silanol groups on the pore surface of the MCM-41 to which guest species may be attached.[6-8] Maschmeyer *et al.*[6] reported modified mesoporous MCM-41 materials obtained by grafting metallocene complexes onto mesoporous silica. Palladium grafted MCM-41 was synthesized by vapor deposition of a volatile palladium complex onto the inside walls of the porous framework.[7] Versatile lanthanide silylamides were also grafted onto mesoporous MCM-41.[8] Hamdan *et al.*[9] and Mokaya *et al.*[10] prepared Al-containing MCM-41 materials by grafting Al onto purely siliceous MCM-41. Mostly recently, Ryoo *et al.*[11] reported a more general route through which various elements such as Al, Sn, Zn and Mn can be incorporated within various mesoporous materials after the synthesis in pure silica forms. These newly prepared metallosilicates exhibited an ion-exchange properties and a high acidity.

There have been only a few reports on direct hydrothermal synthesis of MCM-41 gallosilicate,[12,13] but no report so far has been made on post-synthetic gallium incorporation into MCM-41. The introduction of gallium into silicates or aluminosilicates results in high selectivity to aromatics in the catalytic conversion of olefins and paraffins.[14-17] Gallium sites also exhibit good catalytic activity for alkane dehydrogenation.[17,18] In this work, we report for the first time the synthesis of mesoporous MCM-41 gallosilicate materials through a post-synthetic gallium implantation into a pure silica MCM-41 framework. We expect that such prepared gal-lium containing MCM-41 will possess an ion-exchange capacity as found in zeolites and SAPO-n materials.

Experimental Section

A typical mesoporous siliceous MCM-41 material was hydrothermally synthesized based on modification of the procedures previously reported in the literature[1,2,5,19] The precipitated product, MCM-41 silicate with HTA (hexadecyltrimethylammonium) template, was filtered, washed with doubly distilled water, and dried at room temperature. The dried MCM-41 silicate 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 and dried at room temperature. Such stirring and washing resulted in the removal of more than 95% of the surfactant, which was confirmed by infrared absorption spectroscopy. Some of product was calcined in O_2 flow to remove surfactants with temperature slowly increased to 823 K over 10 h and maintained there for 10 h. The mesoporous MCM-41 silica materials after the removal of surfactant, either by the solvent extraction or calcination, were slurried in absolute alcohol solution containing $Ga(NO_3)_3$ with stirring for 1 h at room temperature. The MCM-41 material was then washed with absolute ethanol, dried and calcined in air/O_2 using a muffle furnace. calcination was carried out at slowly increasing temperature upto 823 K over 10 h where temperature was maintained for 5 h. In order to increase the Ga incorporation into a pure silica MCM-41 framework, the slurry and filtration were repeated several time more before calcination treatment. Such post-synthetic Ga-grafted samples in ethanol are designated as Ga-MCM-PSE1, Ga-MCMPSE2 and Ga-MCMPSE3, respectively. Some sample was slurred in aqueous solution of $Ga(NO_3)_3$ with stirring at room temperature for 1-2 h instead of alcohol solution and then filtered, dried in air and calcined, which are designated as Ga-MCMPSW1 and Ga-MCMPSW2. Ga concentration was 10 mM in either ethanol or water. Since some Ga precipitation was observed in both water and ethanol when Ga solution was left on the benchtop for 12-24 h, Ga solutions were prepared just before use.

Results and Discussion

Powder X-ray diffractometer (XRD) measurements were performed before and after Ga incorporation into a pure silica MCM-41 materials. All mesoporous samples obtained by the present post-synthetic Ga-implantation gave same XRD patterns as those for their parent pure silica with at least four
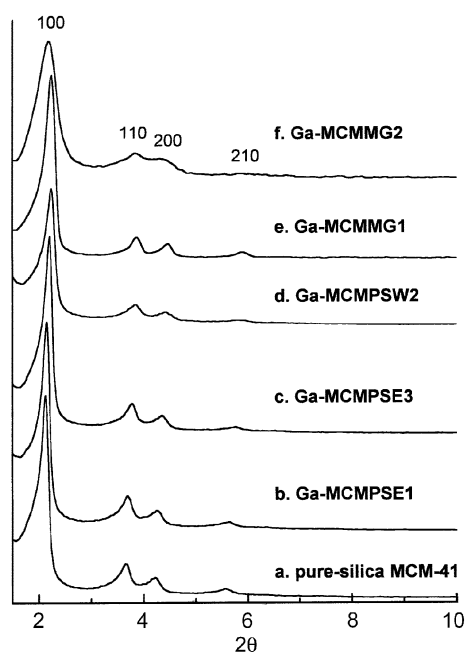
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Figure 1. X-ray diffraction patterns of (a) a pure silica MCM-41, (b) Ga-MCMPSE1, (c) Ga-MCMPSE3, (d) Ga-MCMPSW2, (e) Ga-MCMMG1 and (f) Ga-MCMMMG2.

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

Sample	$\dfrac{Ga}{Si+Ga}$ [a]	$\dfrac{Na}{Si+Ga}$ [a]	d/Å	α/Å[f]	BET surface area,[g] m^2g^{-1}
MCM-41[b]	0	0.0005[e]	44.14	50.97	857.8
Ga-MCMPSE1[c]	0.0141	0.0108	42.04	48.54	792.4
Ga-MCMPSE2[c]	0.0202	0.0123	41.06	47.41	790.8
Ga-MCMPSE3[c]	0.0289	0.0124	40.68	46.97	793.4
Ga-MCMPSW1[c]	0.0163	0.0111	41.56	47.99	798.8
Ga-MCMPSW2[c]	0.0346	0.0116	39.40	45.51	788.4
Ga-MCMMG1[d]	0.0144	0.0129	39.15	45.20	812.9
Ga-MCMMG2[d]	0.0406	0.0142	39.94	46.12	802.2

[a]Atomic ratios determined by inductively coupled plasma emission spectroscopy. [b]A calcined pure siliceous MCM-41. [c]Ga-MCMPSE and Ga-MCMPSW represent MCM-41 samples prepared by post-synthetic Ga implantation in ethanol solution and water, respectively. [d]Ga-MCMMG represents a MCM-41 gallosilicate sample prepared by hydrothermal synthesis of gallosilicate mixed gel. [e]Values in parenthesis indicates Na/Si mole ratios. [f]α=Lattice parameter from XRD data using formula $\alpha=2d/\sqrt{3}$. [g]BET was determined by Argon physisorption.

distinctive signals for a hexagonal phase as shown in Figure 1a, 1b, 1c and 1d. There were no significant changes in the XRD peak intensity and line widths resulting from Ga implantation irrespective of Ga extent and type of Ga solution (ethanol or water). Most of post-synthetic grafting methods of metals into pure silica framework were performed in dry nonaqueous solvents such as ethanol, hexane and chloroform in order to prevent the precipitation of metal hydroxides easily occurring in aqueous solution.[6,8,10,11] In this work, we showed that very similar results are obtained even in aqueous solution. No additional XRD peaks occurred over the 2θ region higher than 10°. Mesoporous MCM-41 gallosilicates, designated as Ga-MCMMG1 and Ga-MCMMG2 were also prepared by hydrothermal synthesis with gallosilicate mixed gel.[13] In this case, XRD peak intensities were decreased and line widths were increased as Ga extent was increased as shown in Figures 1e and 1f. The d spacings and lattice parameters were slightly decreased as Ga contents in the framework increased as shown in Table 1. The similar changes were also observed in Ga-MCM-41 prepared in direct hydrothermal synthesis.[12,13] The BET surface areas also decreased upon Ga incorporation into framework site compared to that of pure silica MCM-41.

A pure silica MCM-41 has a neutral framework and thus shows little ion-exchange properties as shown in Table 1. The ion-exchange capacity can then be used as a means to probe the incorporation of Ga into a silica framework. To investigate an ion-exchange properties of Ga-containing MCM-41, calcined product was ion-exchanged with 10 mM sodium nitrate solution (100 mL per 1 g calcined sample) at room temperature with stirring for 2-3 h. To ensure maximum Na+ ion exchange, exchange 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 ratios and Na+ content were performed with inductively coupled plasma (ICP) emission spectroscopy and summarized in Table 1. There are remarkable increases in Na ion exchange capacities after Ga incorporation compared to that of pure silica MCM-41. Charge balancing Na+ ions do increase, but not much as linearly as Ga content increases. It is unlikely that all the cation sites are ion-exchanged by Na+ ions. Even then, there is still possibility that some of Ga may be extracted from framework sites and located at extra lattice sites especially when Ga content increases. 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.

The incorporation of Ga into the silica framework is also consistent with a remarkable development in the [71]Ga MAS NMR peak intensity for Ga with tetrahedral coordination, upon calcination as shown in Figure 2. The NMR spectrum shows a much weaker peak intensity before calcination while shows predominant development for tetrahedral Ga near ~150 ppm upon calcination. A weak signal is observed near ~0 ppm and maintains its intensity before and after calcination. Ga with octahedral coordination is expected to show resonance near ~0 ppm. A pure silica MCM-41 showed a [71]Ga MAS NMR spectrum similar to that in Figure 2a. Thus the weak signal observed near ~0 ppm is considered as a background signal. Other Ga-containing mesoporous materials and zeolite analogs did not show any resonance near ~0 ppm for octahedral Ga.[12,20-22] A predominant increase of the tetrahedral Ga signal indicates that initially deposited Ga ions on the silica framework become implanted into the silica framework with tetrahedral coordination during calcination. Almost identical [71]Ga MAS NMR results were observed
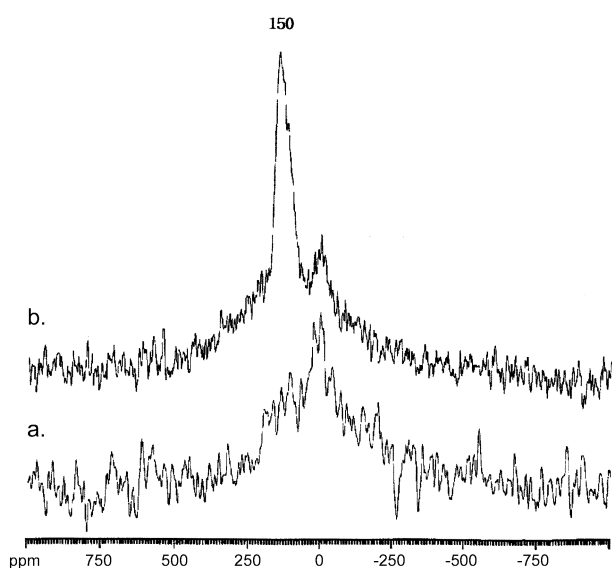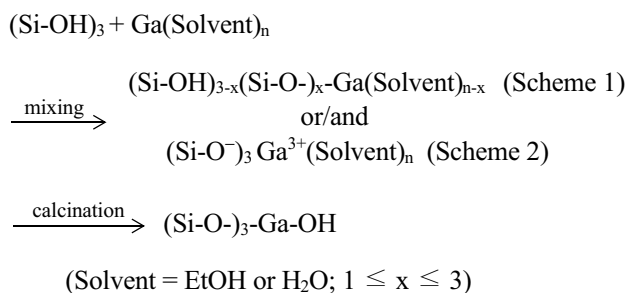
Figure 2. ^{71}Ga MAS NMR spectra of a post-synthetic Ga-grafted MCM-41 sample, Ga-MCMPSE3 (a) before and (b) after calcination.

in Ga-MCMPSW2 prepared in an aqueous solution. When pure silica MCM-41 was slurried in a Ga-containing solution, the Ga species may be attached on the silanol groups in the silica framework and then during calcination, anchored into framework sites, probably initially *via* bonding of solvated Ga to some of framework silicon-oxygen group(s) (Scheme 1)[6] or/and electrostatic interaction between framework silicon-oxygen groups and a solvated Ga cation (Scheme 2) as suggested below.

$(Si\text{-}OH)_3 + Ga(Solvent)_n$

$$\xrightarrow{\text{mixing}}$$

$(Si\text{-}OH)_{3-x}(Si\text{-}O\text{-})_x\text{-}Ga(Solvent)_{n-x}$ (Scheme 1)

or/and

$(Si\text{-}O^-)_3\,Ga^{3+}(Solvent)_n$ (Scheme 2)

$$\xrightarrow{\text{calcination}} (Si\text{-}O\text{-})_3\text{-}Ga\text{-}OH$$

(Solvent = EtOH or H_2O; $1 \leq x \leq 3$)

Mesoporous MCM-41 gallosilicate materials were prepared by post-synthetic Ga implantation into their parent siliceous materials in ethanol or water solution. This post-synthetic incorporation of Ga ions into the framework provides a efficient synthetic approach of gallosilicate mesoporous materials with superior structural integrity, allowing the maintenance of structural order of the parent siliceous materials in the resulting gallosilicates and ion-exchanging capacity.

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