

# Synthesis and Characterization of Alkali-free, Ga-Substituted MCM-41 and Its Performance for n-Hexane Conversion

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Received December 10, 1996; revised November 7, 1997; accepted November 20, 1997

Various kinds of alkali-free Ga-substituted MCM-41 catalysts were synthesized. The BET surface area of all catalysts was over 700 m<sup>2</sup>/g, and the XRD patterns suggested the hexagonal structure. The hexagonal repeat distance was controlled by changing the carbon number of the surfactant. The acid-probe reaction, 2-methyl-2-pentene isomerization, on Ga-MCM-41 and NH<sub>3</sub>-TPD profiles indicated that incorporated Ga produced Brønsted acid sites. <sup>71</sup>Ga NMR demonstrated that Ga was substituted for Si with tetrahedral coordination in the Ga-MCM-41 structure. The Ga-MCM-41 catalyst functioned in the aromatization of n-hexane, and it was confirmed that the framework Ga is the active site for aromatization. The catalytic activity was much improved by the modification of 1 wt% Pt, and n-hexane was converted to benzene with a yield of 78%. © 1998 Academic Press

## INTRODUCTION

MFI-type Ga-silicate has been reported to have an excellent activity for the aromatization of hydrocarbons (1). In this reaction, benzene, toluene, and xylene, BTX, were the main products due to the medium-size pore with ca 5.5 Å diameter consisting of 10-member oxygen ring. On the other hand, Mobil has patented a family of mesoporous molecular sieve materials designated MCM-41 (2-5), while Inagaki *et al.* also have prepared the mesoporous materials from Kanemite (6). Mesoporous silicates gave a possibility for selective conversion of bulky hydrocarbons due to their uniform and relatively large pore diameter ranging from 15 to 100 Å (7). They also gave a possibility of rapid conversion due to low diffusion resistance resulting from larger pore sizes. However, it is still necessary to improve catalytic activity for practical use. Metal incorporation into the framework is expected to provide a new catalytic function, such as acidity, and to introduce redox capacity. For acid catalysts, alkali-free synthesis is preferable, because of the stronger acidity that results relative to alkali-containing materials.

The Mobil method of preparation has advantages because it is easy to substitute the metal for Si and alkali-free synthesis is possible (8). At Yale, the Mobil preparation method has been modified and various kinds of alkali-free metal-substituted MCM-41 such as V-MCM-41, Ti-MCM-41, and Cr-MCM-41 have been prepared (9).

In this study, a new Ga-MCM-41 catalyst, similar to that recently described by Chi-Feng Cheng *et al.* (10), which functions as the aromatization catalyst, was examined. Because the control of the acid strength is one of the most important factors in aromatization, the effect of Ga content on the acidity was examined through characterization of Ga-MCM-41.

## EXPERIMENTAL

### Catalyst Preparation

The Ga-substituted mesoporous silicate, Ga-MCM-41, was prepared according to Beck *et al.*'s report with some modification (8). Ga(NO<sub>3</sub>)<sub>3</sub> was dissolved in 100-g solution of 29 wt% quaternary ammonium surfactants C<sub>n</sub>H<sub>2n+1</sub>(CH<sub>3</sub>)<sub>3</sub>NOH/Br (n = 10, 12, 14, 16). A 50-g portion of tetramethylammonium silicate solution (0.5 TMA/SiO<sub>2</sub>, 10 wt% SiO<sub>2</sub>, from SACHEM, Inc.) and 12.5 g of HiSil-233 (fused silica, from Pittsburgh Plate Glass) were added to the surfactant solution with stirring. The mixture was heated from room temperature (RT) to 150°C for 1 h in an autoclave and was held at 150°C for 48 h. After cooling, the products were collected by filtration, followed by washing with de-ionized water and drying in air at RT. A 3-g portion of the crystals formed was calcined in a stream of ultra-high purity (UHP) He at a flow rate of 15 ml/min from RT to 540°C for 20 h and was held at 540°C for 1 h. UHP He was gradually replaced by UHP oxygen, and the temperature maintained at 540°C for 5 h.

Pt/Ga-MCM-41 was prepared by the incipient wetness impregnation method. The Ga-MCM-41 was impregnated with Pt(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub> solution at 1.0 wt% Pt loading. It was calcined in a stream of UHP oxygen at a heating rate of

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1°C/min from RT to 400°C with a flow rate of 600-mL/min/g-catalyst, and it was held at 400°C for 1 h. After cooling to RT, the Pt-impregnated Ga-MCM-41 was reduced in a stream of UHP hydrogen at a heating rate of 1°C/min from RT to 400°C and held at 400°C for 1 h a flow rate of 100 mL/min/g-catalyst.

### Catalyst Characterization

The catalysts formed were characterized by X-ray diffraction and measurements of BET surface area. The XRD patterns were obtained on a Rigaku Dmax-B diffractometer with Ni-filtered Cu K $\alpha$  radiation at small angle. BET-surface areas were measured on Micromeritics FlowSorb II 2300 by the one-point method from the amount of N<sub>2</sub> adsorbed at liquid N<sub>2</sub> temperature.

The NH<sub>3</sub> temperature-programmed desorption (TPD) profiles were obtained by using Bell Japan, TPD-1-AT with Q-Mass detector. After the sample was treated in a He stream at 100°C, the desorption of NH<sub>3</sub> was measured on mass number 16 by Q-Mass detector with a constant heating rate of 10°C/min at the temperature range from 100 to 600°C.

Particle size distribution of the samples was observed after ultrasonic treatment in water for 10 min. Dynamic light scattering (DLS) spectrophotometer of Photal Otsuka Electronics, ELS-8000SA was used at a 90° angle.

<sup>71</sup>Ga NMR spectra were obtained on a Fourier transform AM-500 spectrometer at 152.53 MHz. A Doty broad-band double-channel 5-mm MAS probe was used. The samples were spun up to ~8 kHz with air as the driving gas. A 4- $\mu$ s pulse width, 40-degree, was used with 50-ms recycle delay, while the number of scans and line broadening factor were changed according to the signal-to-noise ratio and width of the peak. 1 M Ga(NO<sub>3</sub>)<sub>3</sub> were used as external standard shift references for <sup>71</sup>Ga NMR.

### 2-Methyl-2-Pentene Isomerization

2-Methyl-2-pentene, 2M2P, isomerization was carried out by using an atmospheric continuous-flow reactor to estimate the acidity (11, 12). The reaction gas composed of 7% 2M2P diluted with He was passed through 80 mg of catalyst packed in a U tube at 250°C at a flow rate of 25 mL/min. The products were analyzed by gas chromatography.

### n-Hexane Aromatization

The aromatization of n-hexane was carried out by using an atmospheric continuous-flow reactor. The reaction gas composed of 15% n-hexane diluted with He was passed through 300 mg of catalyst packed in a U tube reactor at 550°C with a flow rate of 10 mL/min. The products were analyzed by gas chromatography.

## RESULTS AND DISCUSSION

### Structure of Ga-MCM-41

The XRD patterns for Ga-MCM-41 samples are shown in Fig. 1. Most for Ga-MCM-41 samples have three peaks assigned to [100], [110], and [200] even after calcination, but the patterns for Ga-MCM-41 with low Ga content and small carbon number of surfactant as Si/Ga = 50 with n = 14 was not clear. Since as-synthesized samples had three peaks, it was confirmed that the Ga-MCM-41 has hexagonal structure.

The effect of the carbon number of the surfactant, n in C<sub>n</sub>H<sub>2n+1</sub>(CH<sub>3</sub>)<sub>3</sub>NBr, on the structure of Ga-MCM-41 with Si/Ga of 50 was examined in Fig. 2. The BET-surface area of every Ga-MCM-41 with Si/Ga 50 is over 700 m<sup>2</sup>/g, suggesting a well-ordered structure. In the hexagonal structure, the repeat distance is expected to be 2/ $\sqrt{3}$  times the [100] d-spacing calculated from the observed peak position. Beck *et al.* proposed the following liquid crystal templating mechanism of the formation of MCM-41 (8). The hexagonal MCM-41 structure is consistent with the aggregation of C<sub>n</sub>H<sub>2n+1</sub>(CH<sub>3</sub>)<sub>3</sub>N<sup>+</sup> surfactant micelles into rod shapes. Inorganic silicate present in the reaction mixture could then form around these arrays to produce an inorganic structure, reflecting the hexagonal micellar array. Results obtained here show that the repeat distance increases with an increase in carbon number of surfactant, suggesting the formation of C<sub>n</sub>H<sub>2n+1</sub>(CH<sub>3</sub>)<sub>3</sub>N<sup>+</sup> surfactant micelles. This result is consistent with the mechanism proposed by Beck *et al.* (8), although aggregation into the micellar array after precipitation of the inorganic structure cannot be ruled out.

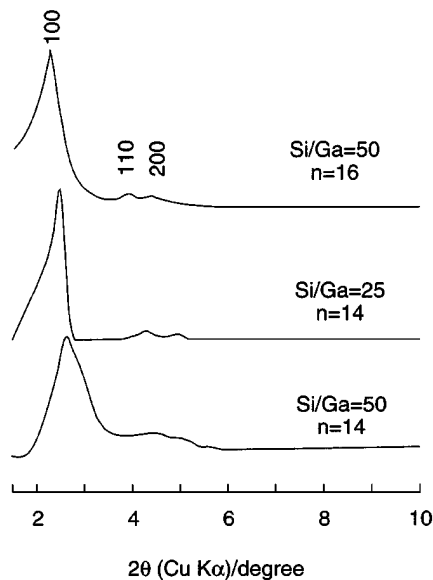


FIG. 1. X-ray diffraction patterns for various Ga-MCM-41.

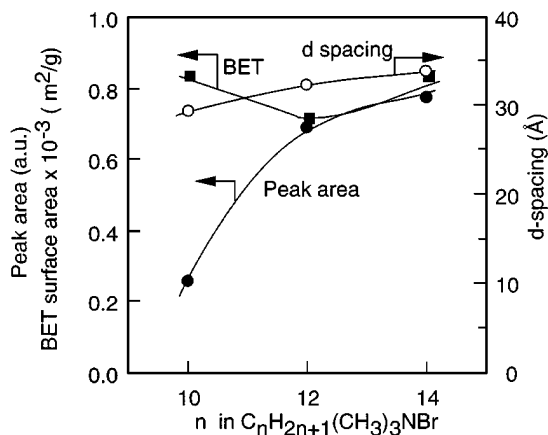


FIG. 2. Effect of carbon number on structure of Ga-MCM-41 with Si/Ga = 50. Peak area = [100] peak area/packing density of  $SiO_2$ ; d-spacing = d-spacing calculated from [100] peak.

The [100] peak area per packing density of  $SiO_2$  is expected to be roughly proportional to regularity of hexagonal structure of the Ga-MCM-41. According to the peak areas, regularity of the structure increased with an increase in the carbon number of the surfactant (see Fig. 2). This suggests that the micellar rods consisting of long chain surfactant aggregate more easily than short-chain surfactant to make well-ordered particles.

Figure 3 shows the effect of the carbon number on the surfactant fraction and yield of Ga-MCM-41 with Si/Ga = 50. The surfactant fraction (S fraction) is defined as the proportion of the surfactant in the as-synthesized Ga-MCM-41. The S fraction increased with an increase in the carbon number of the surfactant. The yield of Ga-MCM-41 increased with an increase in the carbon number of the surfactant. Yields of MCM-41 and S fractions may depend on the formation of the micellar rod.

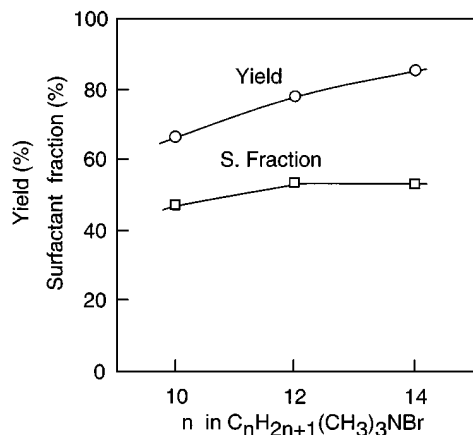


FIG. 3. Effect of carbon number on yield of Ga-MCM-41 with Si/Ga = 50. Yield = [(as syn.)  $\times$  (after calcin.) / (before calcin.)] / [ $SiO_2$  (in  $Hisil + TMA$ ) +  $Ga_2O_3$ ]  $\times 100$ . S Fraction = surfactant / (as syn.)  $\times 100$  = [(before calcin.) - (after calcin.)] / (before calcin.)  $\times 100$ .

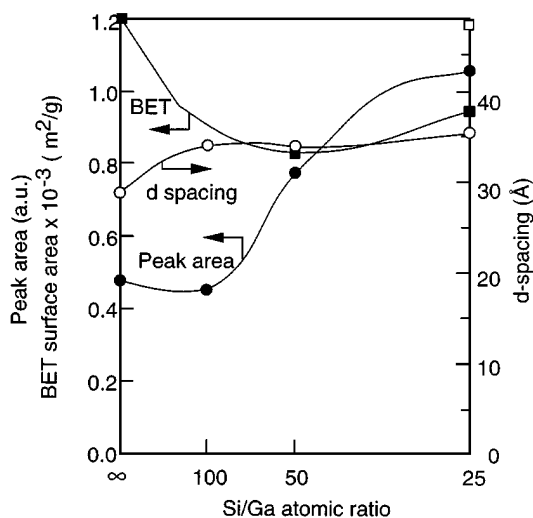


FIG. 4. Effect of Ga content on structure of Ga-MCM-41 prepared by using  $C_{14}H_{29}(CH_3)_3NBr$  as the template. Peak area = [100] peak area/packing density of  $SiO_2$ ; d-spacing = d-spacing calculated from [100] peak.

The effect of Ga content on the structure is shown in Fig. 4. All of BET-surface areas are over  $700 m^2/g$ ; it is suggested that the structure is stable, even with a Ga concentration as high as Si/Ga = 25. Because the bond length of the Ga-O is longer than Si-O, the repeat distance of Ga-MCM-41 is longer than that of pure silica MCM-41, as is expected from the results of Al-MCM-41 (8). However, the repeat distance of Ga-MCM-41 does not increase with increasing Ga content. This may be caused by the fact that the Ga-O-Si bond angle decreases with increasing Ga content. The increase in bond length and the compensating decrease in bond angle, dominating the change in repeat distance, was also observed in Al-MCM-41 (13, 14). On the other hand, XRD peak areas which correspond to the regularity of the hexagonal structure increase with increasing Ga content. Therefore, particle size should affect the XRD peak areas.

Particle size distribution of Ga-MCM-41 was measured by DLS method. The average particle size increases with increasing Ga content as shown in Fig. 5. This tendency was confirmed by SEM observation. This suggests that the surface potential of the gel precursor is reduced by the addition of  $Ga^{3+}$  ion to produce ordered particles.

Figure 6 shows that the S fraction and yield of Ga-MCM-41 are almost independent of the Ga content. This result indicates that micellar rods contain the same amount of surfactant. Yields of MCM-41 only depend on the formation of the micellar rod. The particle sizes depend on the aggregation of the micellar rod. This means that the surface potential of the micellar rod is reduced by the addition of  $Ga^{3+}$  ion and the micellar rod with low surface potential aggregates more easily to produce ordered particles.

The control of the acidic property of the Ga-MCM-41 is one of the most important factors in an acid-catalyzed

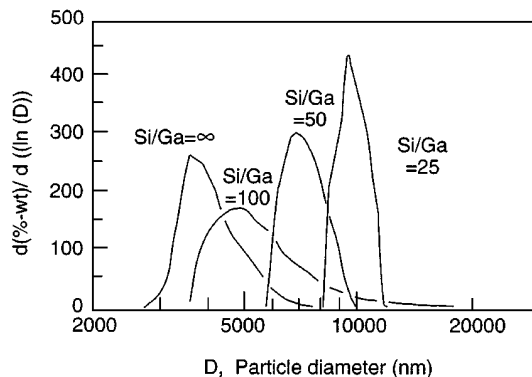


FIG. 5. Effect of Ga content on particle size distribution of Ga-MCM-41 prepared by using  $C_{14}H_{29}(CH_3)_3NBr$  as the template.

reaction. The isomerization of 2-methyl-2-pentene is a useful acid-probe reaction, because it is converted to 4-methyl-2-pentene and 3-methyl-2-pentene via a double-bond shift and a methyl shift, respectively (11, 12). The double-bond shift requires weaker acidity than a methyl shift does. This implies that 4-methyl-2-pentene is formed on less-acidic sites, and 3-methyl-2-pentene is formed on more-acidic sites. The ratio of 3-methyl-2-pentene over 4-methyl-2-pentene (3M2P/4M2P) is an index of the acid strength per acid site, if, to first order, we assume that all acid sites are capable of double bond isomerization (11, 12).

As shown in Fig. 6, the 3M2P/4M2P ratio gradually increased with increasing Ga content, but even pure silica MCM-41 has acidity. The silanol groups may be present as the charge balancing groups associated with the quaternary ammonium ion, and it can be confirmed by the appearance of a large  $Q^3$  peak of  $^{29}Si$  NMR. The MCM-41 structure has a large number of silanol groups which also comprise

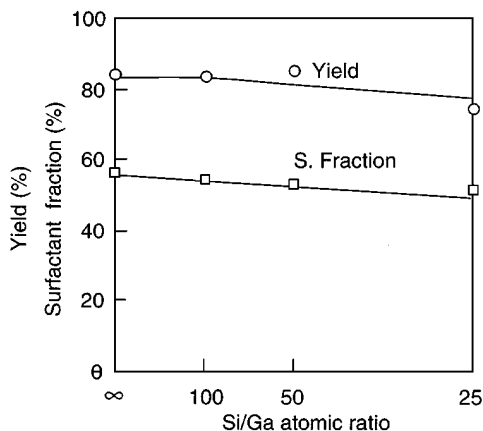


FIG. 6. Effect of Ga content on yield of Ga-MCM-41 prepared by using  $C_{14}H_{29}(CH_3)_3NBr$  as the template. Yield = [(as syn.)  $\times$  (after calcin.)]/(before calcin.)/[ $SiO_2$  (in Hisil+TMA) +  $Ga_2O_3$ ]  $\times$  100. S Fraction = surfactant/(as syn.)  $\times$  100 = [(before calcin.) - (after calcin.)]/(before calcin.)  $\times$  100.

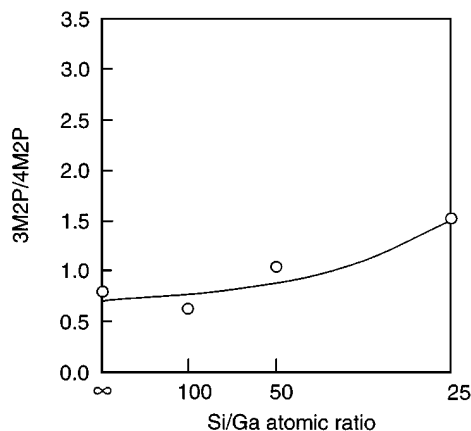


FIG. 7. Effect of Ga content on acidity of Ga-MCM-41 prepared by using  $C_{14}H_{29}(CH_3)_3NBr$  as the template. Ga-MCM-41, 80 mg; 7% 2M2P diluted with He, 25 mL/min; 250°C, after 5 min.

the acid sites. Increase in the 3M2P/4M2P ratio with the increasing Ga content ratio indicate that the Ga in Ga-MCM-41 clearly produced acid sites. This result strongly suggests that Ga is isomorphously substituted for Si to produce acid sites. The acid property is an expected characteristic of Ga-silicate. Note that if the 3M2P/4M2P were only measuring acid strength (acid density being normalized out by the ratios to 2M2P) then all Ga-MCM-41 would be expected to have the higher 3M2P/4M2P ratios than for pure silica MCM-41 (11, 12) (see Fig. 7).

In order to determine the Brønsted site,  $NH_3$  TPD profiles are observed as shown in Fig. 8. Since the pure silica MCM-41 has no peaks, the peak the  $NH_3$  TPD is caused by the Ga in the MCM-41 structure. The amount of acid site is almost proportional to the Ga content until Si/Ga = 50. However, amount of acid sites for Si/Ga = 25 was smaller that expected from the charged ratio. This result also

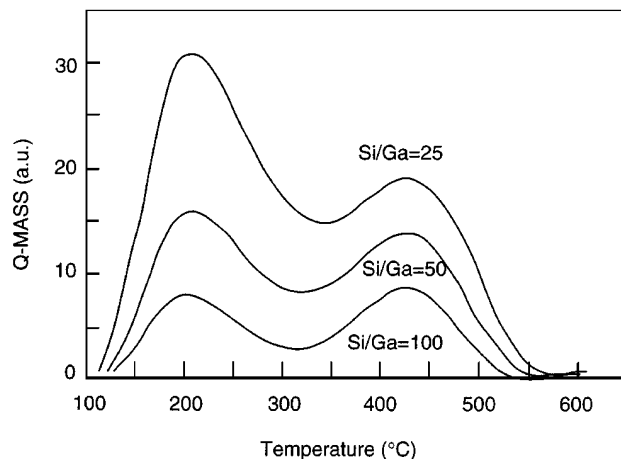


FIG. 8.  $NH_3$  TPD profiles for Ga-MCM-41 prepared by using  $C_{14}H_{29}(CH_3)_3NBr$  as the template.

indicate that Ga is isomorphously substituted for Si to produce Brønsted acid sites.

### $^{71}\text{Ga}$ NMR for Ga-MCM-41

$^{69}\text{Ga}$  and  $^{71}\text{Ga}$  NMR spectra of the Ga-silicate with rigid structures have been recorded by Oldfield *et al.* (15). However, solid-state Ga NMR is expected to be much more difficult than Al. Moreover, the amorphous structure of Ga-MCM-41 should make it more difficult because of the broader line width owing to the wide distribution of Ga-O-Si bond angles. Chi-Feng Cheng *et al.* succeeded in quantitative analysis of Ga in Ga-MCM-41 (10). In order to determine the state of Ga in Ga-MCM-41,  $^{71}\text{Ga}$  NMR spectra were observed for the Ga-MCM-41 prepared by  $\text{C}_{14}$ , as shown in Fig. 9. The number of scans depended on concentration of Ga, and it was sometimes more than  $1.6 \times 10^6$ . Every Ga-MCM-41 has a peak around 150 ppm assigned to Ga with tetrahedral coordination. This confirms that Ga was substituted for Si in as-synthesized MCM-41. Ga with octahedral coordination is not observed for Ga-MCM-41. Therefore, all of Ga atoms are incorporated in the MCM-41 structure after the hydrothermal treatment. However, Ga in Ga-MCM-41 after calcination could not be recorded. The Ga highly dispersed on the surface of MCM-41 may

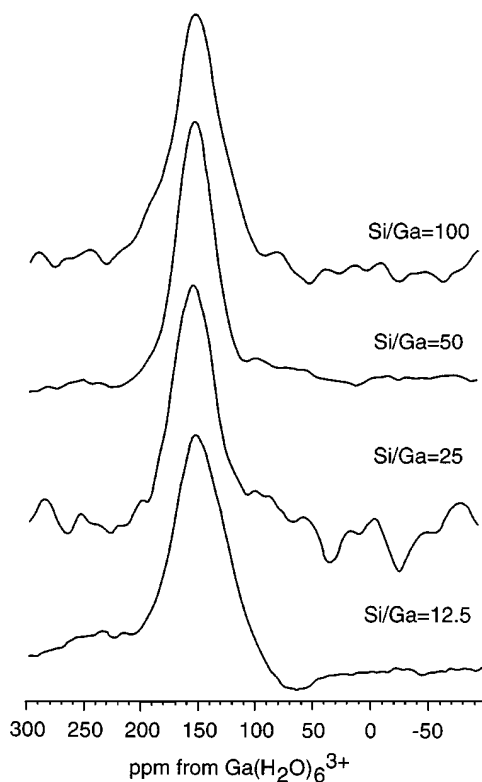


FIG. 9.  $^{71}\text{Ga}$  MAS NMR spectra of as-synthesized Ga-MCM-41 with Si/Ga = 100, 50, 50, and 12.5 prepared by using  $\text{C}_{14}\text{H}_{29}(\text{CH}_3)_3\text{NBr}$  as the template.

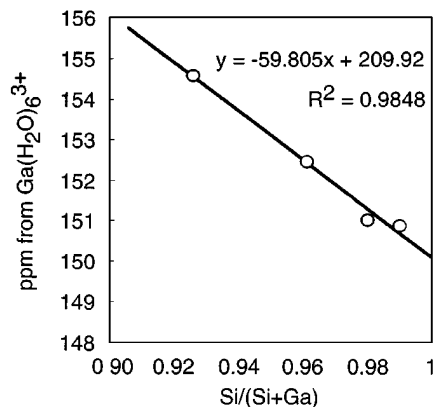


FIG. 10. The dependence of  $^{71}\text{Ga}$  chemical shift on Si/(Si + Ga) for the as-synthesized Ga-MCM-41 with Si/Ga = 100, 50, 25, and 12.5 prepared by using  $\text{C}_{14}\text{H}_{29}(\text{CH}_3)_3\text{NBr}$ .

result in a large electron field gradient, EFG, and as with other quadrupolar nuclei, such as Al, be greatly broadened.

Figure 10 shows the dependence of the  $^{71}\text{Ga}$  chemical shift on the (Si/(Si + Ga)). A linear relation is obtained for  $\text{C}_{14}$  (15), indicating that chemical shift moves upfield with increasing Ga content. This implies that the mean (Si-O-Ga) bond angle,  $\theta$ , and acid strength decrease with increasing Ga content. The same tendency is observed for  $^{27}\text{Al}$  NMR of Al-MCM-41 prepared by  $\text{C}_{12}$  as shown in Fig. 11. This also indicates that the mean (Si-O-Al) bond angle,  $\theta$ , and acid strength decreased with increasing Al content (16).

Compared with other silicate with a rigid crystal structure, the interpretation of mean bond angle is less obvious. Because the wall of Ga-MCM-41 is known to be amorphous, the bond angle distribution is wider than for a rigid framework structure. Thus the incorporation of Ga into the amorphous structure has less effects on the mean bond angle.

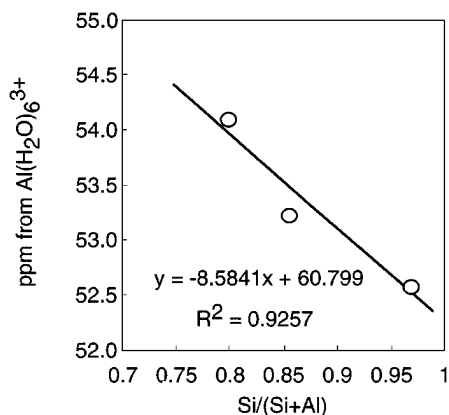
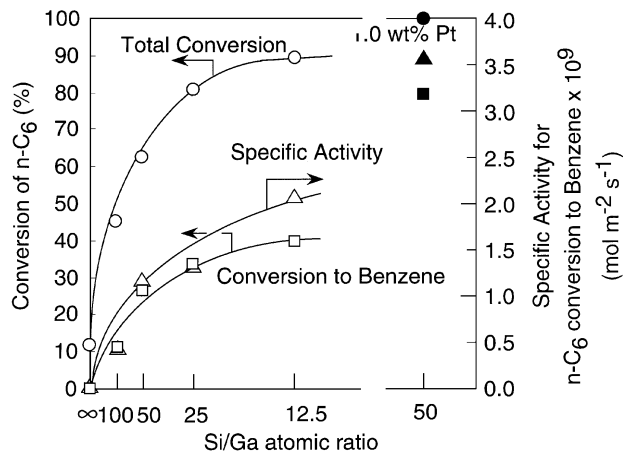


FIG. 11. The dependence of  $^{27}\text{Al}$  chemical shift on Si/(Si + Al) for the as-synthesized Al-MCM-41 prepared by using  $\text{C}_{14}\text{H}_{29}(\text{CH}_3)_3\text{NBr}$  as the template. 130.4 MHz,  $10^\circ$  pulse.



**FIG. 12.** Effect of Ga content upon the conversion of *n*-hexane on (Pt)/Ga-MCM-41 prepared by using  $C_{14}H_{29}(CH_3)_3NBr$  as the template. Open symbols, Ga-MCM-41; closed symbols, 1.0 wt% Pt/Ga-MCM-41 (Si/Ga = 50), 300 mg; 15% *n*-hexane diluted with He, 10 mL/min; 550°C, time on stream, 60 min.

#### *n*-Hexane Aromatization on Ga-MCM-41

The aromatization activity of Ga-MCM-41 was investigated with the *n*-hexane reaction, as shown in Fig. 12. *n*-Hexane total conversion and its conversion to benzene increase with increasing Ga content. A part of Ga is expected to be dispersed on the surface of the Ga-MCM-41 because it is difficult to observe  $^{71}Ga$  NMR after calcination. Ga species of the surface induced electron field gradient, it disturbed the NMR spectra. Therefore, the Ga-MCM-41 may contain both extraframework and framework Ga species. It was reported that extraframework Ga species are active sites for the aromatization of *n*-hexane (17). It was also reported that the extraframework Ga alone is inactive, although it is active with a framework Ga species (18). Inui *et al.* reported that the framework Ga functioned as aromatization site for light paraffin (1). Since Ga incorporation after calcination should be limited, extraframework Ga is expected to increase with increasing Ga content from Si/Ga = 25 to Si/Ga = 12.5. However, *n*-hexane conversion to benzene does not change so much. The amount of acid site, which can be seen in Fig. 8, corresponds to the conversion of *n*-C<sub>6</sub> to benzene. Therefore, it is considered that framework Ga in Ga-MCM-41 may be an active site and the extraframework Ga should then be a promoter. Pt is known to be a strong promoter for the aromatization (1). When Ga-MCM-41 with Si/Ga = 50 is modified by Pt

with 1 wt% loading, yields of benzene increased from 27 to 78%.

## CONCLUSION

Ga was incorporated into an MCM-41 structure and produced acid sites. The number of acid sites increased with increasing Ga content. The incorporated Ga functioned as an aromatization site, but the aromatization activity was much improved by the addition of Pt.

## ACKNOWLEDGMENT

This work was funded by DOE, Office of Basic Energy Science, and partly supported by a Japan Society for the Promotion of Science (JSPS) Fellowship for Research at Center for Excellence Abroad.

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