^{71}Ga NMR characterization of MFI-type Ga-silicate synthesized by the rapid crystallization method

Tatsuya Takeguchi [a], Koji Kagawa [a], Jim-Bae Kim [a], Tomoyuki Inui [a,*], Di Wei [b] and Gary L. Haller [b]

[a] *Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto 606-01, Japan*

[b] *Department of Chemical Engineering, Yale University, New Haven, CT 06520-8286, USA*

Received 13 December 1996; accepted 22 April 1997

MFI-type Ga-silicate was synthesized by the rapid crystallization method. A peak of ^{71}Ga MAS NMR around 160 ppm proved that Ga was isomorphously substituted for Si with tetrahedral coordination. Less than 5% of the incorporated Ga was moved to extraframework with octahedral coordination by ion-exchange treatment to transform the Ga-silicate to the H-form, as could be seen by the appearance of the −7 ppm peak. High stability of Ga incorporated into the framework of MFI structure by the rapid crystallization method was confirmed.

Keywords: MFI-type Ga-silicate, rapid crystallization method, Ga MAS NMR, isomorphous substitution, tetrahedral coordination

1. Introduction

Various MFI-type metallosilicate catalysts have attracted considerable attention because of their significant and unique catalytic functions for the selective syntheses of valuable hydrocarbons from less-valuable light hydrocarbons. For example, protonated Al-silicate, i.e. H-ZSM-5, functions for the selective synthesis of aromatic-rich gasoline from methanol [1], while Ti-silicate, TS-1, is known for the hydroxylation of aromatics and epoxidation of olefins [2]. Many attempts had been made to synthesize novel metallosilicate catalysts in which a transition metal element was substituted for Al in ZSM-5. Inui et al. developed the rapid-crystallization method to synthesize stable metallosilicate catalysts [3]. Utilizing this method, many transition metals could be incorporated into the MFI structure. It was confirmed that Fe was incorporated in the framework of the structure and produced weak acid sites [4]. The acid strength, which is milder than that of H-ZSM-5, prevented the formation of aromatics which were easily converted to the precursor of aromatic coke. These catalysts could convert light olefins almost quantitatively to a gasoline fraction without deactivation [5].

On the other hand, it was reported that Zn- and Ga-ion-exchanged H-ZSM-5 function as aromatization catalysts for light paraffins [6]. However, they are easily deactivated owing to the evaporation of the Zn- and even Ga-components because of their high vapor pressure. It was reported that MFI-type Ga-silicate prepared by the rapid crystallization method had an excellent activity for aromatization of light paraffins. Moreover, the catalytic activity of Ga-silicate was maintained more than 2000 h during the reaction including a short period of regeneration [7]. To characterize metallosilicates, many kinds of analyses such as NMR, NH_3-TPD, XRD and IR techniques were adopted. NMR spectroscopy was useful to assess the coordination state of the metals. Gallium has two isotopes, ^{69}Ga and ^{71}Ga, and they have a strong quadrupolar moment because the nuclear spin number is greater than 1/2 ($I = 3/2$). Since Ga has lower sensitivity and broader line width than Al, Ga NMR is much more difficult than Al NMR. Compared with Al NMR, smaller number of papers for Ga NMR have been reported. Oldfield et al. reported that Ga had a peak around 169–184 ppm from 1 M $Ga(NO_3)_3$ in Ga NMR spectra and that Ga was incorporated into the framework with tetrahedral coordination for several different zeolite structures [8]. Gabelica succeeded in quantitative analysis of Ga of MFI silicate [9,10].

In this study, the state of Ga in Ga-silicate catalysts was examined, and the stability of the catalysts was tested under severe reaction conditions. The relation between the catalytic activity and the NMR spectra was examined for MFI-type Ga-silicate prepared by the rapid crystallization method.

2. Experimental

2.1. Catalyst preparation

Ga-silicate catalysts with Si/Ga atomic ratios 3200, 400, 100, 20 and 12 were prepared by the rapid crystallization method [3]. A $Ga_2(SO_4)_3$ solution was used as the source of Ga at the stage of gel formation in the rapid

* To whom correspondence should be addressed.

crystallization method. Tetrapropylammonium bromide was used as the template solution. The Si-to-Ga atomic ratio was held constant and the pH of the solution was maintained at 10 during the gel formation. The temperature was programmed during the hydrothermal treatment to the gel mixture. The crystals produced were washed with distilled water and calcined in an air stream at 540°C for 3.5 h. The calcined crystals were ion-exchanged by 1 M NH_4NO_3 solution at 80°C for 1 h, followed by drying and calcination at 540°C for 3 h.

The methanol synthesis catalyst was prepared by using the uniform gelation method [11]. The catalyst composition was Cu 38.1, ZnO 29.4, Cr_2O_3 1.6 and Al_2O_3 30.9 wt%. A concentrated solution of mixed metal nitrates was treated with a vapor of NH_3 until the pH of the mixture became 6.5–7 to form a gel. The gel was dried at 120°C over night and calcined at 350°C for 3 h. The resulting material was mixed with Pd/Al_2O_3 and Pd loading in the composite catalyst was 5 wt%.

2.2. MAS NMR

^{29}Si and ^{71}Ga NMR spectra were obtained on a Fourier transform AM-500 spectrometer at 99.36 and 152.53 MHz, respectively. A Doty broad-band double-channel 5 mm MAS probe was used. The samples were spun up to $\sim$ 8 kHz with air as the driving gas. A 4 μs pulse width, 40°, was used with 20 s and 50 ms recycle delay for solid ^{29}Si- and ^{71}Ga-samples, respectively, while the number of scans and line-broadening factor were changed according to the signal-to-noise ratio and width of the peak. TMS and 1 M $Ga(NO_3)_3$ were used as external standard shift references for ^{29}Si and ^{71}Ga NMR.

2.3. Test reaction using Ga-silicate catalysts

In order to examine the stability of the Ga-silicate, methanol conversion activity was examined in the presence of H_2 and H_2O. Gasoline synthesis reaction from CO_2 was carried out using a two-stage series reactor. Reaction gas containing 22% CO_2, 3% CO and 75% H_2 was passed over the methanol-synthesis catalyst at 8.0 MPa and 250°C. The Ga-silicate was packed in the second reactor connected in series. The first-stage product gas composed of methanol, H_2O, CO, CO_2 and H_2 was allowed to flow through the second-stage reactor to synthesize hydrocarbons at 1.5 MPa total pressure. The activity of the H–Ga-silicate catalyst for methanol conversion was examined.

3. Results and discussion

3.1. Properties of Ga-silicate catalyst

Both atomic absorption analysis and EPMA results showed that the Si-to-Ga ratio was almost equal to that of the synthesis set ratio, suggesting that all of Ga components existed in the crystal particles. XRD patterns of H–Ga-silicate were the same as the pattern of H-ZSM-5 only, and their BET surface areas were more than 300 m^2/g [12]. SEM observation showed that Ga-silicate has fine cubic particles, which are typical of MFI silicate structures.

The ^{29}Si NMR spectrum for the Ga-silicate catalyst with Si/Ga = 20 after ion-exchange treatment is shown in figure 1. It coud be seperated into two peaks, a large peak and a small peak at −109.2 and −102.5 ppm, respectively, with the intensity ratio of 5.2. These are assigned to Q^4(4Si, 0Ga) and Q^4(3Si, 1Ga), respectively; therefore, the Si/Ga ratio in the framework is calculated to be 22 ($= 4 \times 5.2 + 1$). This value does not include the Ga atoms located in the extraframework. This value is in good agreement with the Si/Ga ratio of 20. It was difficult to determine the Q^4(3Si, 1Ga) peak for the Ga-silicate with low Ga concentration. Next, it is necessary to investigate the coordination state of the Ga in the framework and extraframework if it exists.

The ^{71}Ga NMR spectra for as-synthesized Ga-silicate are shown in figure 2. They exhibit peaks around 160 ppm, suggesting that Ga is present in tetrahedral coordination [8]. Although ^{71}Ga NMR spectra of Ga-silicate with Si/Ga = 400 and 3200 were not clear due to the low concentration of Ga, the signals are expected to be almost the same as for the other samples. Combined with the data of ^{29}Si NMR in figure 1, it can reasonably be assumed that Ga was incorporated into the framework of the MFI structure with tetrahedral coordination, and all of Ga was isomorphously substituted for Si.

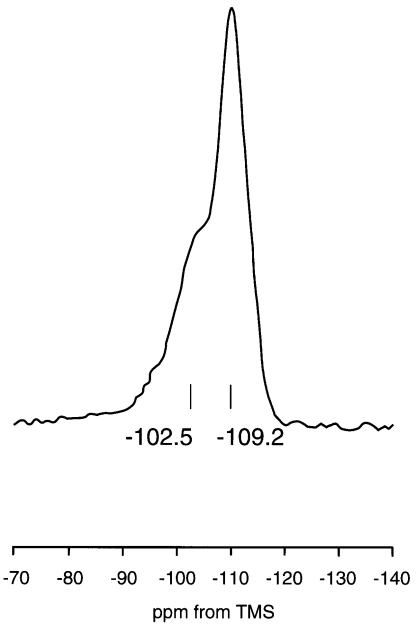

Figure 1. ^{29}Si MAS NMR spectrum of Ga-silicate with Si/Ga = 20 after ion-exchange treatment to form H-type Ga-silicate.

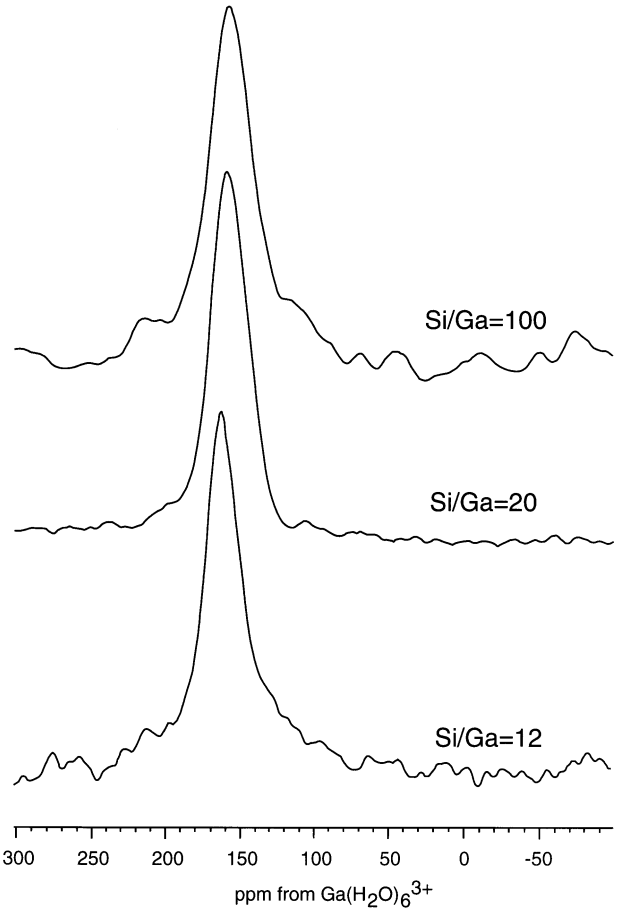

Figure 2. ^{71}Ga MAS NMR spectra of as-synthesized Ga-silicates with Si/Ga = 100, 20 and 12.

The relation between the shifts of ^{71}Ga peaks and concentration is shown in figure 3. The shifts are correlated by the following equation:

$$\delta(^{71}\mathrm{Ga}) = -74.2[\mathrm{Si}/(\mathrm{Ga}+\mathrm{Si})] + 228.5, \quad R = 0.993\,. \tag{1}$$

This equation is almost the same as that given by Timken and Oldfield [8], which is as follows:

$$\delta(^{71}\mathrm{Ga}) = -74.2[\mathrm{Si}/(\mathrm{Ga}+\mathrm{Si})] + 222.2, \quad R = 0.91\,. \tag{2}$$

For ^{27}Al NMR, it was reported that the mean bond angle, θ, had an effect on the chemical shift [13],

$$\delta(^{27}\mathrm{Al}) = -0.50\theta + 132, \quad R = 0.95\,. \tag{3}$$

Therefore, for the MFI-type Ga-silicate, the mean (Si–O–Ga) bond angle, θ, decreased with increasing Ga content. It is considered that the acid strength decreases with decreasing mean bond angle [13]. Bradley et al. [14] showed a good correlation between the ^{71}Ga chemical shift and the ^{27}Al chemical shift expressed as follows:

$$\delta(^{71}\mathrm{Ga}) = 2.83\delta(^{27}\mathrm{Al}) - 4.50, \quad R = 0.9943\,. \tag{4}$$

Therefore, mean bond angles (Si–O–Ga), θ, are expected

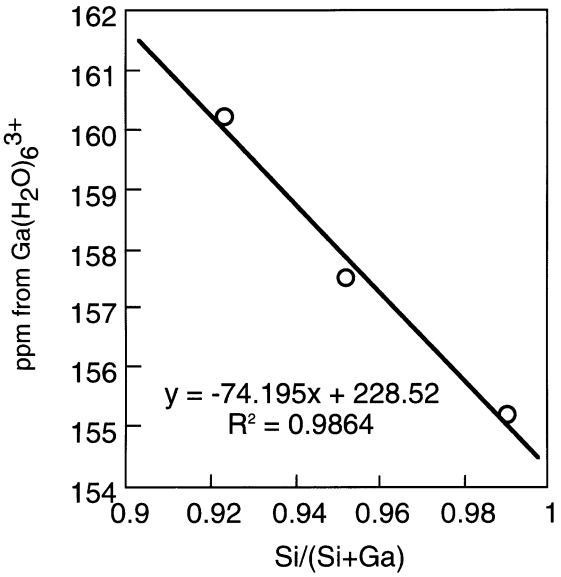

Figure 3. The dependence of the shift of ^{71}Ga peaks on Si/(Si + Ga) for the as-synthesized Ga-silicate with Si/Ga = 100, 20 and 12.

to be 148° (160 ppm for Si/Ga 12), 149° (157 ppm for Si/Ga 20) and 151° (155 ppm for Si/Ga 100) from eqs. (1), (3) and (4). This shows that the mean bond angle (Si–O–Ga) and the acid strength decreased with increasing Ga content. The Ga-silicate with lower concentration of Ga has a smaller number of acid sites, but its acid strength should be high due to the greater angle of Si–O–Ga.

Only tetrahedral Ga species in MFI-type Ga-silicate for ^{71}Ga NMR were observed in this study. Timken and Oldfield [8] also observed only Ga with tetrahedral coordination in various kinds of Ga-silicate. They suggested that extraframework Ga may be present, but not in octahedral coordination.

In order to determine the extraframework Ga, the effect of the ion-exchange was examined. The as-synthesized catalyst was calcined at 540°C and ion-exchanged by 1 M NH_4NO_3 solution twice at 80°C, followed by calcination at 540°C to form H-type silicate. Figure 4 shows that most of the Ga is present in tetrahedral coordination, even at higher Ga concentration. However, a small peak appeared at −7 ppm, which is assigned to extraframework Ga with octahedral coordination. Compared with figure 4, the absence of Ga with octahedral coordination in figure 2 shows that all of the Ga components are incorporated into the framework of the as-synthesized Ga-silicate, and only a small part of Ga was moved to extraframework, suggesting the good stability of the MFI structure of Ga-silicate.

3.2. Catalytic performance of Ga-silicate catalysts

Inui et al. [7] previously reported that the Pt-ion-exchanged H–Ga-silicate catalyst (Si/Ga = 21) prepared by the rapid crystallization method exhibited a high performance for propane conversion to aromatics

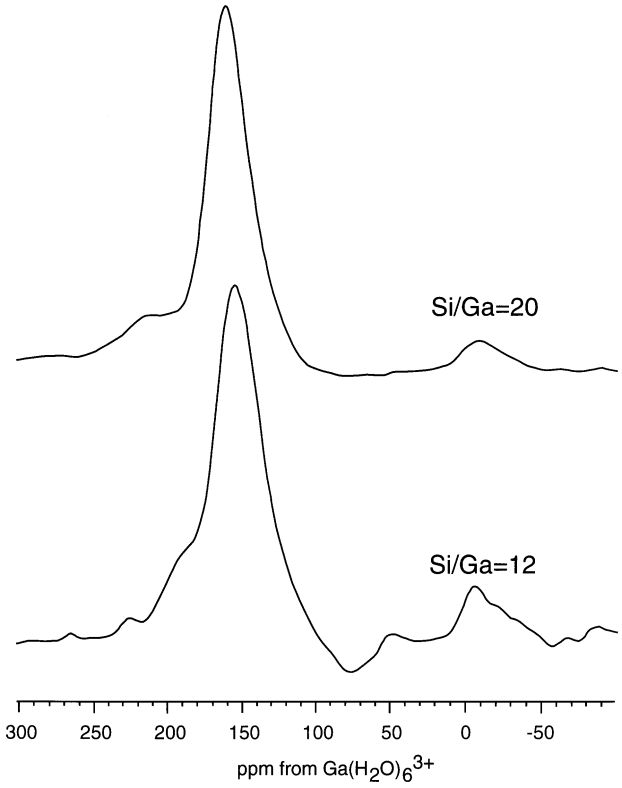

Figure 4. ^{71}Ga MAS NMR spectra of Ga-silicate with Si/Ga = 20 and 12 after ion-exchange treatment to form H-type Ga-silicate.

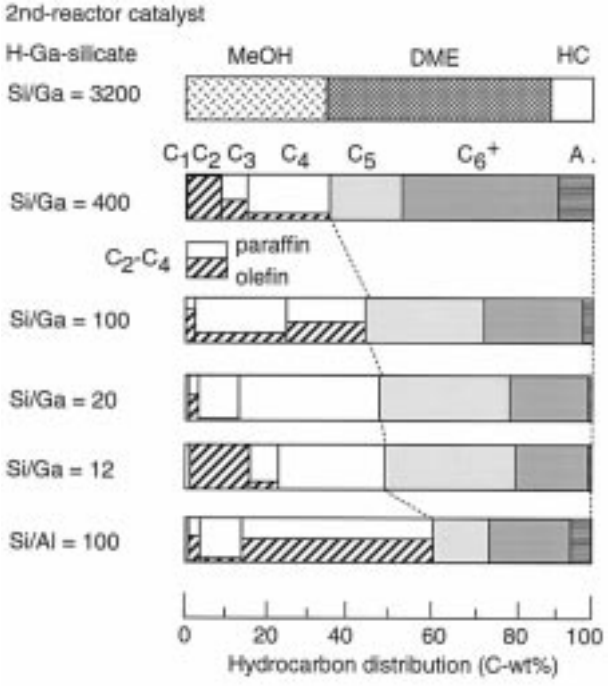

Figure 5. Gasoline synthesis from CO_2 and H_2 using Ga-silicate catalyst in the second reactor of the series reactor. First reactor: Pd-modified Cu 38.1–ZnO 29.4–Cr_2O_3 1.6–Al_2O_3 30.9 wt% catalyst; 22% CO_2–3% CO–75% H_2, 8.0 MPa, 270°C, 18 800 h^{-1}, CO_2 conversion to MeOH 17.4%. Second reactor: Ga-silicate catalyst with Si/Ga 12, 20 and 100 after ion-exchange treatment to H type, 1.5 MPa, 300°C, MeOH formed in the first reactor was totally converted to hydrocarbons (except for Si/Ga = 3200). CO_2 conversion to hydrocarbon is 17.4% in the series reactor (except for Si/Ga = 3200).

even at times on stream of 2000 h with reaction–regeneration recycles, while propane conversion was more than 80% and selectivity to aromatics was more than 60%. Ga-ion-exchanged H-ZSM-5 did not show such stability. This indicates that the Ga with tetrahedral coordination has a high performance for aromatization. The Ga-silicate with Si/Ga = 20 also showed a high performance for methanol conversion to an aromatic-rich gasoline fraction with a yield of 73% [12]. This would be due to the Ga with tetrahedral coordination.

In this study, methanol conversion over Ga-silicates with various Ga contents was examined. Mixed gas composed of CO_2, CO and H_2 was converted to methanol, CO and H_2O in the first reactor. The product gas, composed of methanol, CO and H_2O, was passed through the second reactor with unreacted reaction gas of CO_2, CO and H_2. The second reactor was connected in series and operated at 1.5 MPa total pressure. Methanol was converted on the Ga-silicate catalyst in the presence of H_2 and H_2O. Figure 5 shows the results of this series reaction. Methanol is not totally converted to hydrocarbons but partly to dimethyl ether on the Ga-silicate having Si/Ga ratio of 3200. It is assumed that the number of acid sites is so small that water vapor would be adsorbed on most acid sites. Therefore, it could not convert methanol to hydrocarbon. On the other hand, methanol is totally converted to hydrocarbons on Ga-silicates having Si/Ga ratios of 400, 100, 20 and 12. These results show that Ga of the Ga-silicate is stable even in the presence of H_2 and H_2O at the high pressure of 1.5 MPa. The selectivity to aromatics and C_{5+} hydrocarbons increases with decreasing Ga content. In general, both the number of acid sites and acid strength have an effect on the product selectivity. For example, acid strength of protonated Al-silicate, i.e. H-ZSM-5, was so high that it is not optimum for the gasoline synthesis from methanol in the presence of H_2 [11]. On the other hand, the acid strength of H–Ga-silicate is mild, and it is appropriate for the selective synthesis of gasoline fraction from methanol. It can be seen from the ^{71}Ga NMR spectra in figure 3 that the acid strength and acid site density are controlled by changing the Ga content, and the H–Ga-silicates with lower Ga content are expected to have a little higher acid strength than those with higher content. Since effective contact time at 1.5 MPa is about 15 times as long as that at atmospheric pressure, the acid site number did not have a large effect on the selectivity. The acid strength had a larger effect on the selectivities under these reaction conditions. The selectivity to aromatics and hydrocarbons increased with a little increase of the acid strength and Si–O–Ga bond angle.

4. Conclusion

The as-synthesized Ga-silicate prepared by the rapid crystallization method contains Ga with only tetrahedral coordination. Most of the Ga was maintained in tetrahedral coordination after the calcination and ion-exchange treatment. The tetrahedral Ga is stable against the H_2O and H_2 pressure at reaction temperature. The framework Ga has activity for aromatization. Acid strength, that is the Ga–O–Si angle, was changed with Ga content.

Acknowledgement

This work was partly supported by a Japan Society for the Promotion of Science (JSPS) Fellowship for Research at Center of Excellence Abroad.

References

[1] C.D. Chan, W.H. Lang and A.J. Silvestri, J. Catal. 56 (1979) 268.
[2] B. Notari, Catal. Today 18 (1993) 163.
[3] T. Inui, Am. Chem. Soc. Symp. Ser. 398 (1989) 479.
[4] T. Inui, H. Nagata, T. Takeguchi, S. Iwamoto, H. Matsuda and M. Inoue, J. Catal. 139 (1993) 482.
[5] T. Inui, F. Okazumi, J. Tarumoto, O. Yamase, H. Matsuda, H. Nagata, N. Daito and A. Miyamoto, J. Jpn. Petrol. Inst. 30 (1987) 249.
[6] T. Mole, J.R. Anderson and G. Creer, Appl. Catal. 17 (1985) 141.
[7] T. Inui, Y. Makino, F. Okazumi, S. Nagase and A. Miyamoto, Ind. Eng. Chem. Res. 26 (1987) 647.
[8] H.K.C. Timken and E. Oldfield, J. Am. Chem. Soc. 109 (1987) 7669.
[9] Z. Gabelica, C. Mayanez, R. Monque, R. Galiasso and G. Giannetto, in: *Miropores Materials*, eds. M.L. Ocelli and H.E. Robson (Van Nostrand Reinhold, New York, 1992) p. 15.
[10] G. Giannetto, F.D. Santos, R. Monque, R. Galiasso and Z. Gabelica, Zeolites 15 (1995) 719.
[11] T. Inui, T. Takeguchi, A. Kohama and K. Kitagawa, Energy Convers. Mgmt. 33 (1992) 513.
[12] T. Inui, H. Matsuda, T. Takeguchi and M. Chaisupakitsin, in: *Proc. 2nd Jpn.–Korea Symp. Catal.* (1989) p. 19.
[13] E. Lippmaa, A. Samoson and M. Mägi, J. Am. Chem. Soc. 108 (1986) 1730.
[14] S.M. Bradley, R.F. Howe and R.A. Kydd, Magn. Reson. Chem. 31 (1993) 883.