The Role of Gallium in the Catalytic Activity of Zeolite [Si,Ga]–ZSM-5 for Methanol Conversion

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The transformation of methanol over a series of aluminum-free [Si,Ga]–ZSM-5 zeolitic catalysts with Ga/(Ga + Si) ratios of 0.015, 0.019, 0.032, 0.039, and 0.054 (corresponding to Si/Ga ratios of 65.7, 51.6, 30.3, 24.6, and 17.5, respectively) has been studied in the 150–450 °C temperature range. There is strong dependence of selectivity and activity on the concentration of Ga for the formation of dimethyl ether at 150–300 °C and for the conversion of alkanes into aromatics at 300–450 °C. The curves describing the yield of dimethyl ether and aromatics rise steadily with the content of Ga, but the curve of the dependence for the yield of olefins is bell-shaped. Framework gallium in Al-free [Si,Ga]–ZSM-5 does generate Brønsted acidity, and the sequence of steps in the reaction of MeOH is the same over [Si,Ga]–ZSM-5 and [Si,Al]–ZSM-5. The role of gallium in the transformation of olefins into aromatics is discussed.

Introduction

The introduction of gallium into aluminosilicate zeolites results in high selectivity to aromatics in the catalytic conversion of olefins and paraffins.[1-18] The Cyclar process, in which C_3–C_5 alkanes are transformed into aromatics, proceeds over zeolite [Si,Ga]–ZSM-5.[2,6] Although it is evident that catalytic activity and selectivity are linked to the elemental composition of the zeolitic framework, we do not know why gallium directs the reaction toward aromatics, while over conventional [Si,Al]–zeolites mainly paraffins are produced.

We know that aluminum is responsible for the Brønsted and Lewis acidity of zeolites. In order to establish whether gallium also generates acidity, one needs to examine the properties of aluminum-free [Si,Ga]–catalysts. There is very little published work concerning such systems,[4,19] in contrast to the profusion of papers on [Si,Al,Ga]–zeolites. However, even nominally Al-free catalysts, for example zeolitic borosilicates, often contain aluminum impurities. Possessing chemical properties similar to those of Al, but with different atomic sizes, B and Ga can be incorporated into zeolitic frameworks. The substitution of B instead of Al results in the contraction[20] and the substitution of Ga in the expansion[21,22] of the unit cell. Although the enhancement of the selectivity to aromatics over [Si,B]–zeolites has been studied, careful experiments have revealed very poor activity of Al-free borosilicates. The conclusion is that aluminum impurities rather than boron are responsible for the conversion.[20]

Studies of aluminum-free [Si,Ga]–catalysts[4,19] suggest that gallium itself is catalytically active. This agrees with the results of temperature-programmed desorption (TPD) of ammonia,[19,23] 2-propanol, and 2-propanamine,[19] which reveal that zeolites [Si,Ga]–ZSM-5 and [Si,Al]–ZSM-5 are much stronger Brønsted acids than [Si,B]–ZSM-5. Unlike gallosilicates,[1a,24,25a] borosilicates are inactive for MeOH conversion.[26] The question remains whether the activity is generated by Ga or by Al impurities.

Since enhanced aromatization may be associated with framework or nonframework gallium,[12,27,28] it is important to distinguish between mechanisms involving framework or nonframework activity and to choose the right catalytic reaction for the purpose. Since Lewis acidity is known to be associated with both framework and nonframework species, it is clearly preferable to choose a reaction relying solely on Brønsted acidity, which involves only the zeolite framework.[29] We have chosen the conversion of methanol (MeOH) to hydrocarbons. The first step in this reaction, the catalytic condensation of MeOH to dimethylether (DME), involves weakly bonded protons. This is the only process occurring below ca. 300 °C, so the yield of DME at low temperatures is a measure of Brønsted acidity. Although dominant at low temperatures, DME is not the only product of diagnostic value. Further steps of the MeOH reaction network give rise to the same products as the cracking and the Cyclar processes, so they can

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also be of use in the study of enhanced aromatization.

The series of aluminum-free [Si,Ga]–ZSM-5 zeolites (with different amounts of Ga, so as to eliminate the influence of the "Al impurity factor") was subjected to catalytic testing for the conversion of MeOH, and the results were plotted as a function of gallium content. In order to establish the origin of the catalytic activity of our samples and compare the results with the behavior of ZSM-5 containing nonframework gallium, Ga-impregnated aluminum-free silicalite was also investigated. Experiments were carried out in a pulse microreactor, enabling a quick comparison of activity within a series of samples to be made. As a nonsteady-state device, the pulse reactor requires that maximum reproducibility of reaction parameters be maintained. We were able to meet this condition because all the catalysts had approximately the same surface area (ca. 400 m^2/g).

Experimental Section

Catalytic Tests. Calcined samples of 0.05 g of catalyst (30–60 mesh) were used. The catalyst bed was first activated in the microreactor for 4 h at 450 °C in helium flow (50 cm^3/min). The same flow rate of helium was used in all catalytic experiments. The volume of a MeOH pulse was 5 μL (125 μmol). Products were separated and analyzed with a gas chromatograph on line with the microreactor. Pulses introduced into the chromatograph at each temperature were repeated several times. Excellent reproducibility of all results indicates that there was no deactivation of the catalysts during the experiments. Each point on the plots represents an average of three or four pulses.

Catalyst Preparation. [Si,Ga]–ZSM-5 was prepared from the following solutions: solution 1, 0.15–1.2 g of Ga_2O_3 was added to 25 mL of NaOH solution; solution 2, 3.0 g of H_2SO_4 was added to 4.0 g of TPABr in 100 g of H_2O; solution 3, 22.5 g of colloidal silica (40 wt %) in 25 g of H_2O.

Solutions 1 and 2 were mixed, and solution 3 was then added with continuous stirring. The mixture was heated at 170 °C for 6 days in PTFE-lined autoclaves. The product was filtered, washed with distilled water, and dried at 60 °C. The gallium content in the final product was determined by the concentration of Ga_2O_3 in solution 1. Five such solutions were prepared, each with a different amount of gallium. In order to maintain maximum reproducibility, autoclaves with different preparations were heated simultaneously in the same oven. The samples were calcined at 550 °C for 5 h, ion-exchanged with NH^{4+}, and calcined again at 500 °C for 3 h in order to obtain the H form. The ratio $X = Ga/(Ga + Si)$ for the samples in this series was 0.015, 0.019, 0.032, 0.039, and 0.054 (by atomic absorption). The level of Al impurity was about 100 ppm. The samples were designated as Ga-X.

In order to prepare Ga-impregnated silicalite, the purely silicous ZSM-5 (Al impurity level about 100 ppm) was mixed with an aqueous solution of $Ga(NO_3)_3$, evaporated, and heated at 500 °C in the flow of oxygen for 6 h. The Ga/(Ga+Si) ratio for this sample was 0.048 (corresponding to Si/Ga = 19.8).

Characterization. Samples for SEM investigations were crushed in an ultrasonic bath for 1 h and placed on a carbon film on a copper grid from an acetone suspension. FTIR spectra were recorded using a Nicolet MX-1 spectrophotometer. The specimen was pressed in a KBr disk. Powder XRD patterns were collected with a Philips PW-1060 diffractometer equipped with a vertical goniometer using Ni-filtered Cu Kα radiation. ^{69}Ga and ^{71}Ga magic-angle-spinning (MAS) NMR spectra were measured on a Bruker MSL-400 multinuclear spectrometer at 96.04 and 122.03 MHz, respectively, with short (0.6 μs equivalent to 9°) and powerful radio frequency pulses and a 0.3-μs recycle delay. Samples were spun in air at ca. 10 kHz.

Results

TEM demonstrates that all samples consist of irregular aggregates of crystals. The average crystal size is the same, but the degree of crystallinity decreases with the content of gallium. This is seen more clearly in the SEM images of samples treated in an ultrasonic bath for 1 h, given in Figure 1a–e. In samples of lower gallium content (samples Ga-0.015 and Ga-0.019 in Figure 1a and b, respectively), single crystals are present. The amount of amorphous material increases with the concentration of Ga, but well-shaped crystals are still present in Ga-0.032 (Figure 1c). Amorphous particles dominate in samples Ga-0.039 and Ga-0.054 (Figure 1d and e, respectively), in agreement with XRD measurements. The same trend was reported for [Si,Ga]–ZSM-5[25b] and [Si,Al]–ZSM-5.[30]

IR spectra are consistent with those reported in the literature.[31] The shift of the band representing asymmetric external vibrations (~1250 cm^{-1}) is small but systematic, and the difference in frequencies between samples at the extremes of the gallium content is only 15 cm^{-1}. There are no differences between the spectra of samples before and after the catalytic reaction.

XRD results are typical of ZSM-5.[32,33] Crystallinity of our gallosilicates decreases with the concentration of gallium, in agreement with Handreck and Smith.[25b] There is clearly a systematic influence of gallium content: increasing the concentration of gallium results in the general decrease in peak intensity (corresponding to decreasing crystallinity) and in the change of the relative intensity of the two dominant reflections: (101) at 7.92° 2θ, and (501) at 23.1°. Figure 2 shows a nearly linear increase of the $h(501)/[h(501) + h(101)]$ peak height ratio as a function of Ga/(Ga + Si).

^{71}Ga MAS NMR spectra have been recorded for all the catalysts, and for sample Ga-0.054, a ^{69}Ga spectrum has also been measured. Only 4-coordinated gallium was detected in all cases, which indicates that gallium is part of the zeolite framework. The ^{71}Ga chemical shift decreases from 158–159 ppm for Ga-0.015 to 154 ppm for Ga-0.054, in agreement with literature reports.[24,28,34,35] Figure 3 shows ^{69}Ga and ^{71}Ga MAS NMR spectra for the sample Ga-0.054.

Figure 4 shows the temperature dependence of the yield of DME from MeOH. There is a clear relationship between the amount of Ga and the production of DME in the 150–300 °C region, in which the yield of DME reflects the Brønsted activity. Note the very low activity of Ga-impregnated silicalite. The degree of MeOH conversion and the yield of DME, both as a function of Ga/(Ga + Si) at 250 °C, are shown in Figure 5. Above 300 °C, the yield of DME decreases dramatically for all the samples, as the consecutive reactions leading to olefins and aromatics begin to occur. Only a small amount of paraffinic hydrocarbons is detected, because their production requires a longer residence time than that usually used in the pulse microreactor. Propylene dominates among the olefins formed in the DME transformation, in agreement with earlier work.[36,37] An additional reason for the decrease in the yield of DME may be the temperature-dependent shift of the equilibrium from Brønsted toward Lewis acidity.

Figure 6 shows the selectivity toward aromatic hydrocarbons, and Figures 7 and 8 show the selectivity toward aromatics and olefins at different temperatures plotted as a function of Ga/(Ga + Si). Selectivity for olefins reaches a maximum at $X = 0.032$ after which it no longer increases with the concentration of Ga, while the formation of aromatics increases over the entire concentration range. Sample Ga-0.039 differs from the others: here the yield of DME is relatively higher (Figure 5), while the selectivity toward aromatics is lower than expected from the behavior of other samples (Figures 6, 7, and 9). While we cannot explain this effect at present, we suggest that it is related to a changed

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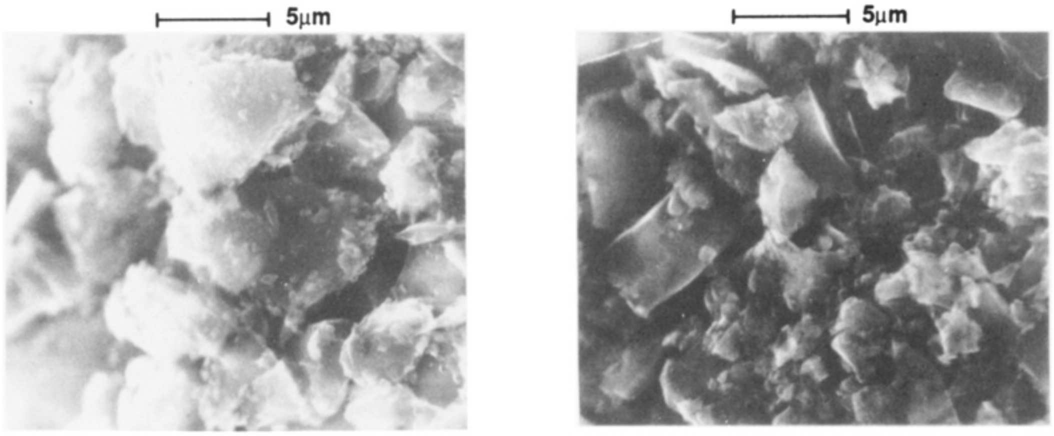
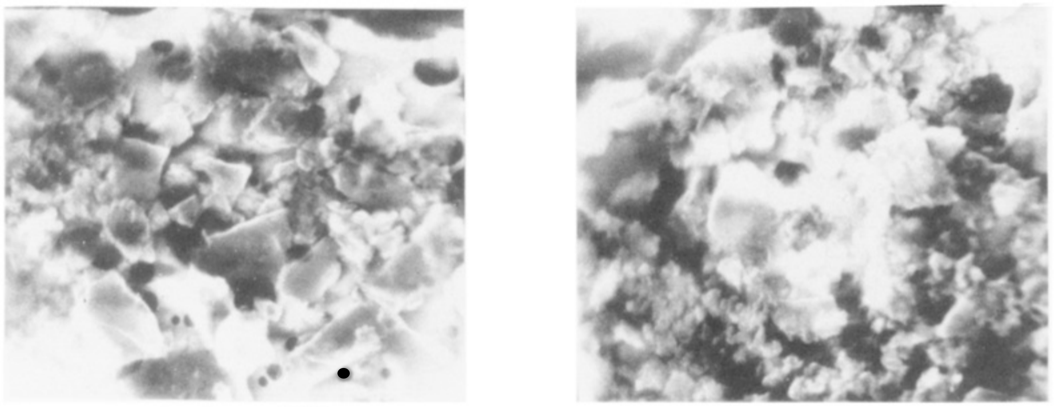


(a) Ga - 0.015

(b) Ga - 0.019



(c) Ga - 0.032

(d) Ga - 0.039

(e) Ga - 0.054

Figure 1. Scanning electron micrographs of [Si,Ga]–ZSM-5: (a) Ga-0.015; (b) Ga-0.019; (c) Ga-0.032; (d) Ga-0.039; (e) Ga-0.054.

distribution of framework gallium at increased Ga contents.

Discussion

Figures 4 and 5 show that the introduction of gallium into ZSM-5 generates catalytic activity. The close correlation between the yield of DME and the Ga/(Ga + Si) ratio clearly indicates that the catalysis over [Si,Ga]–ZSM-5 is brought about by framework Ga and not by Al impurities. Since condensation of MeOH to DME requires Brønsted acidity, we conclude that framework Ga generates Brønsted acidity involving the so-called "bridging" hydroxyl groups. Note that silicalite, the purely silicious member of the ZSM-5 substitutional series, is inactive for MeOH conversion and so is Ga-impregnated silicalite containing nonframework gallium.

DME is subsequently transformed into olefins, mainly propylene, which, in turn, undergo the conversion to aromatics. Two explanations of enhanced aromatization over [Si,Ga]–ZSM-5 have been proposed, both involving nonframework Ga. According to one, gallium accelerates the removal of hydrogen from the reaction site.[14] Hydrogenous species are released during aromatization of olefins and paraffins, and gallium is thought to facilitate the spillover of these from the zeolite to the surface of the gallium-containing cocatalyst, thereby shifting the equilibrium toward aromatics. However, this explanation leaves one question unanswered. Since, according to this, gallium does not catalyze aromatization, but only the subsequent reaction of the hydrogenous species with the cocatalyst, the latter would soon saturate unless a regeneration mechanism was present. However, no such mechanism has been suggested. The second theory, by Khodakov et al.,[12] attempts to explain the catalytic activity of [Si,G]–ZSM-5 in terms of Lewis sites associated with extra-framework gallium formed during thermal treatment.

Although most authors attribute the enhanced aromatization to nonframework gallium,[4,6,12,14,27] it is possible to rationalize our results exclusively in terms of framework Ga. Figure 9 shows that the yield of aromatics and olefins strongly depends on the concentration of Ga. The curve describing the formation of olefins is bell-shaped with a maximum at $X = 0.032$, while that for

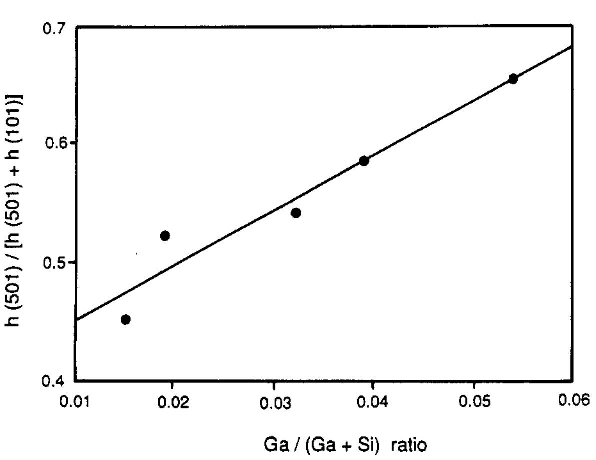


Figure 2. Relative intensity of the (501) XRD peak defined as *h*(501)/(*h*(501) + *h*(101)) versus the Ga/(Ga + Si) ratio, where *h*(*hkl*) denotes the intensity of the (*hkl*) reflection.

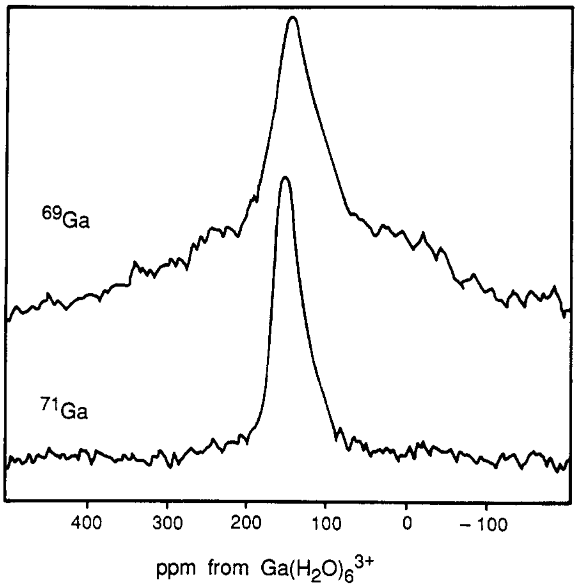


Figure 3. ^{69}Ga and ^{71}Ga MAS NMR spectra.

aromatization rises continuously with the concentration of gallium. After passing through the maximum, further increases in the gallium concentration suppress the production of olefins and enhance aromatization. Such behavior indicates that aromatics are produced from olefins. In other words, the higher the concentration of Ga, the faster the consumption of olefins. This is in agreement with the sequence of steps proposed for the Cyclar process where the formation of aromatics is considered to be a secondary reaction using olefins produced by the dehydration of propane.[2,3,6a] In these circumstances, the reduced yield of unsaturated hydrocarbons (Figure 9) over more and more active (Ga richer) catalysts is expected and may be a simple consequence of the increasing content of framework Ga.

All the same, the involvement of the extra-framework Ga in samples richer in gallium cannot be ruled out, since 6-coordinated gallous species can be expected to be formed during thermal treatment.[12,27,28] It may be argued that [Si,Ga]-ZSM-5 has two kinds of activity. The first, at relatively low Ga content and due to the Brønsted acidity associated with framework gallium, is responsible for the production of DME. The second begins to operate at higher Ga concentrations and results in enhanced aromatization and the fall of the yield of olefins. Since aromatization involves Lewis acidity, we can identify the second kind of activity as a Lewis acidity associated with extra-framework gallium.[12]

We have examined this possibility using MAS NMR spectroscopy. ^{71}Ga MAS NMR spectroscopy detects no 6-coordinated gallium in the calcined samples. Six-coordinated Ga was detected

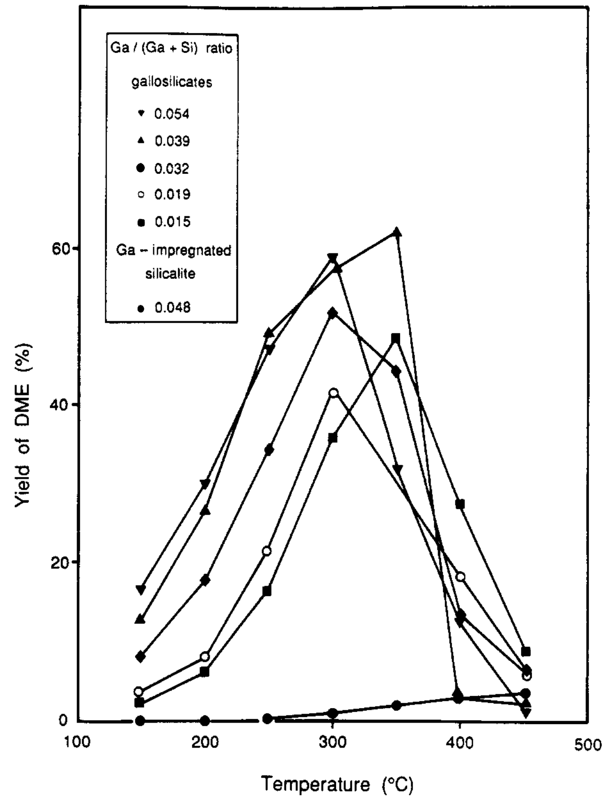


Figure 4. Yield of DME from methanol over series of ZSM-5 gallosilicates and over Ga-impregnated silicalite.

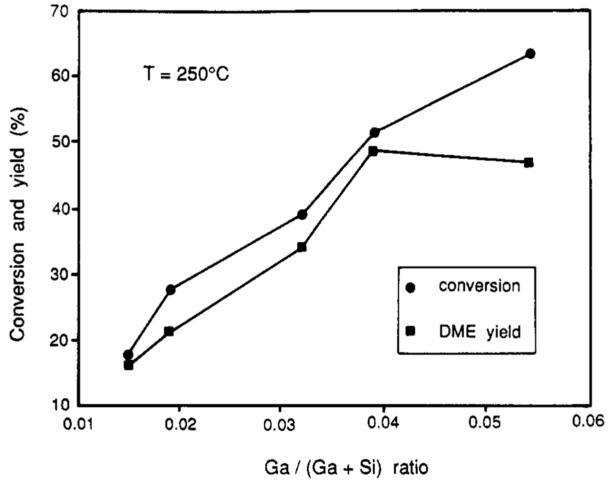


Figure 5. Conversion of MeOH and yield of DME at 250 °C versus the Ga/(Ga + Si) ratio.

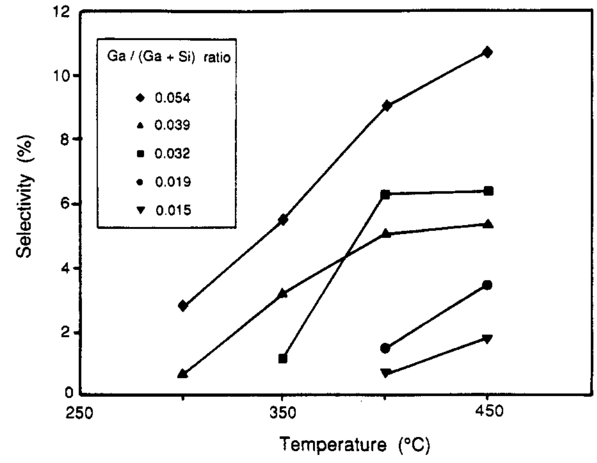


Figure 6. Selectivity for aromatic hydrocarbons over [Si,Ga]-ZSM-5.

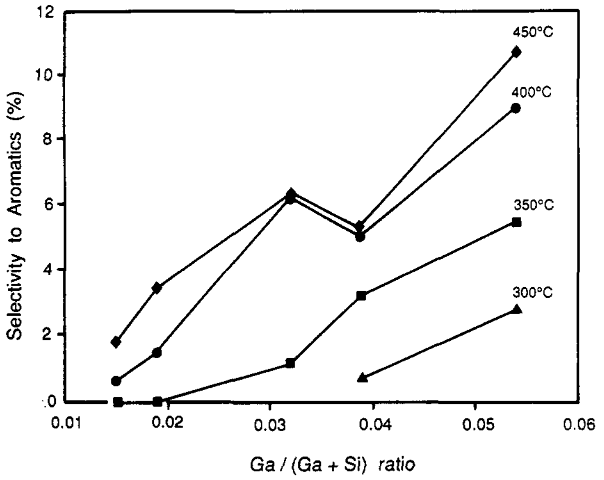


Figure 7. Selectivity for aromatics as a function of the Ga/(Ga + Si) ratio at different temperatures.

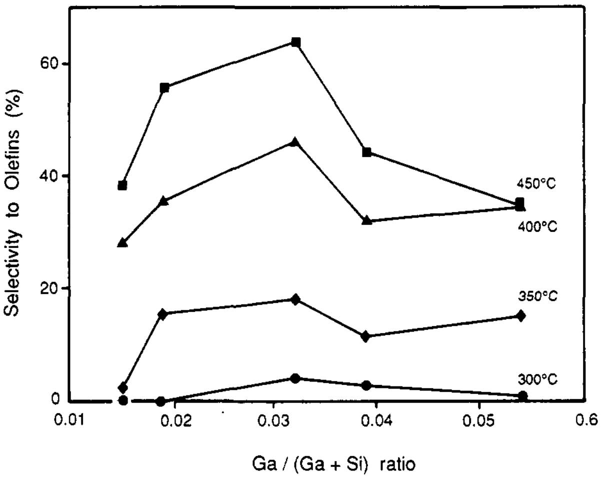


Figure 8. Selectivity for olefins as a function of the Ga/(Ga + Si) ratio at different temperatures.

by NMR spectroscopy in materials of high Ga contents[34] and in samples which had been subjected to treatment with acetylacetone.[28] The ^{71}Ga MAS NMR spectrum of calcined [Si,Ga]-ZSM-5 with Si/Ga = 13 quoted in ref 34 shows the presence of 6-coordinated gallium, but the signal at 0 ppm corresponding to 6-coordination is very weak. Since our most highly gallous sample (Ga-0.054) has Si/Ga = 17.5, the amount of gallium expelled from the framework may be so small as to be undetectable by solid-state NMR spectroscopy. The sensitivity of a catalytic reaction to chemical environments is higher, so that the aromatization reaction may still "see" the 6-coordinated gallium. Finally, it is possible that gallium is present as a 4-coordinated extraframework species, such as β-Ga_2O_3.[38] Therefore, MAS NMR spectroscopy does not confirm the involvement of nonframework gallium in the reaction.

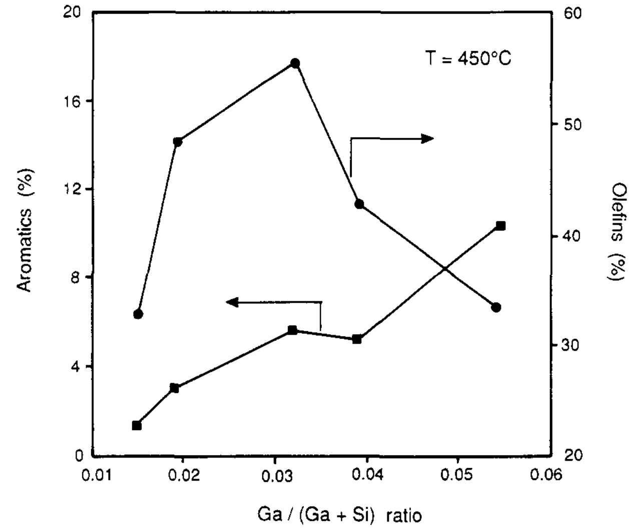


Figure 9. Yield of olefins and aromatics at 450 °C versus the Ga/(Ga + Si) ratio.

We conclude that gallium, and not aluminum impurities, generates Brønsted acidity in the ZSM-5 structure, making zeolite [Si,Ga]-ZSM-5 a suitable diagnostic system for the study of the structural origins of catalytic activity. Four-coordinated gallium is responsible for the aromatization of olefins, and the efficiency of this process strongly depends on the concentration of Ga. The conversion of methanol over [Si,Ga]-ZSM-5 proceeds via the same sequence of steps as that over [Si,Al]-ZSM-5:

$$\text{MeOH} \rightarrow \text{DME} \rightarrow \text{olefins (mainly propylene)} \rightarrow \text{aromatics and paraffins}$$

Finally, the conversion of MeOH may also be a useful diagnostic reaction in the investigation of catalytic cracking of hydrocarbons to gasoline and the Cyclar process over [Si,Ga]-zeolites.

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Registry No. DME, 115-10-6; Ga, 7440-55-3; MeOH, 67-56-1.

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