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H-Gallosilicate (MFI) Propane Aromatization Catalyst: Influence of Si/Ga Ratio on Acidity, Activity and Deactivation Due to Coking

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Influence of bulk Si/Ga ratio of H-gallosilicate (MFI) on its degalliation (during calcination for removal of template and deammoniation of NH_4 form), acidity/acid strength distribution (measured by stepwise thermal desorption and chemisorption of pyridine at 50–400°C using GC techniques and also by acid catalyzed model reactions viz. iso-octane cracking and toluene disproportionation) and initial activity/product selectivity and catalyst deactivation in propane aromatization (at 550°C) has been investigated. Framework Si/Ga ratio was measured by ^{29}Si MAS NMR. Information on the external acid sites is obtained by isooctane cracking. The influence of poisoning of strong acid sites (by pyridine) on acid catalyzed model reactions and the effect of deactivation on the product distribution in the propane aromatization have also been studied. The acidity and degalliation (i.e., non-FW Ga/FW Ga ratio) of the zeolite and its dehydrogenation/cracking activity ratio, aromatics/(methane + ethane) mass ratio, aromatics selectivity and deactivation rate constant in the propane aromatization are decreased to a large extent with increasing the Si/Ga ratio. The catalyst deactivation is found to be mostly due to coking. Because of the deactivation, the conversion to aromatics is decreased substantially with the time-on-stream but with little or no change in the distribution of aromatics. The product selectivity is, however, affected significantly due to the deactivation, depending upon the Si/Ga ratio. In general, the aromatics selectivity is decreased but the propylene selectivity is increased with the time-on-stream, mostly due to the decrease in the propane conversion. The shape selectivity (or *para* selectivity) of the zeolite is increased with increasing the time-on-stream (or deactivation). High concentration (or high density) or zeolitic acid sites is essential for obtaining high propane-to-aromatics conversion. Apart from the acidity, the non-FW gallium species formed due to the degalliation also seem to play an important role by increasing the dehydrogenation activity and consequently the aromatization activity of the zeolite. © 1996 Academic Press, Inc.

INTRODUCTION

Conversion of lower alkanes (viz. C_2–C_4 paraffins) to aromatics is of great practical importance. A number of gallium modified ZSM-5 type zeolite catalysts, such as physically mixed Ga_2O_3 and H-ZSM-5, gallium ion exchanged or impregnated H-ZSM-5, H-gallosilicate (MFI), and H-galloaluminosilicate (MFI), have been used for the aromatization of light paraffins (1). An addition to H-ZSM-5 or incorporation in zeolite framework of gallium results in a bifunctional catalyst having enhanced dehydrogenating activity and consequently the catalyst having much increased selectivity for the formation of aromatics from lower alkanes. Since, the enhanced dehydrogenating activity is attributed to the presence of gallium in the zeolite catalyst, efforts are being made to increase the dispersion of gallium species in the catalyst. One way to achieve this is to substitute isomorphously Ga for Al in ZSM-5. The substitution of Ga for Al in ZSM-5 causes a large enhancement in the primary dehydrogenating activity (2, 3) thus resulting in lower conversion of propane but much higher aromatics selectivities (3, 4). However, because of the higher dehydrogenating activity due to the presence of extra framework gallium species formed by its degalliation during calcination or pretreatment (3), H-gallosilicate (MFI) deactivates due to coking at a much faster rate (4, 5).

In the earlier studies (6), H-gallosilicate (MFI) has been found to be more effective than Ga-ion exchanged H-ZSM-5 in aromatization of light alkanes. In the aromatization of *n*-hexane, H-gallosilicate (MFI) showed much higher activity than Ga-ion exchanged H-ZSM-5 or Ga_2O_3/H-ZSM-5 zeolite (7). The product distribution in propane aromatization over H-gallosilicate (MFI) is found to be dependent on the Si/Ga ratio of the zeolite (3). The product selectivity differences are expected due to the differences in the acidity/acid strength distribution (i.e., acid function) and in the dehydrogenating activity of the gallosilicate. These differences also lead to changes in the deactivation (due to coking) of the gallosilicate. It is, therefore,

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interesting to investigate thoroughly the influence of Si/Ga ratio on the acidity/acid strength distribution and deactivation due to coking and the influence of deactivation on the product selectivity in propane aromatization over H-gallosilicate (MFI). The present work was undertaken for this purpose.

EXPERIMENTAL

The gallosilicates (bulk Si/Ga = 32.9, 50.5, 68.4, and 129.6) were synthesized by their hydrothermal crystallization from a gel (pH = 9–10) consisting of Na-trisilicate (Fluka), gallium nitrate (Aldrich), TPA-Br (Aldrich), sulfuric acid and demineralized water in a stainless steel autoclave at 180°C for 24 h. The TPA-gallosilicate crystals were washed, dried at 120°C for 4 h, and calcined at 550°C for 15 h in static air to remove the occluded organic template. The calcined gallosilicates were ion exchanged with 1 *M* NH_4NO_3 solution at 80°C for 1 h; the ion exchange was repeated five times. The resulting NH_4-gallosilicates were pressed binder free, crushed to particles of 52–72 mesh size and further calcined in static air at 600°C for 4 h to get the gallosilicates in their H-form with the degree of H^+ exchange of 93 ± 2%. Unless otherwise mentioned specifically, the values of Si/Ga ratios reported throughout the paper are based on the chemical analysis.

The MFI structure of the gallosilicates was confirmed by the XRD (using Phillips diffractometer 1730 series and a Cu$K\alpha$ source of radiation) and FTIR (using Perkin Elmer FTIR 1600 Series instrument and Nujol medium) analysis. The composition of the gallosilicates was determined by the chemical analysis (after removal of the organic template) and also by the ^{29}Si, ^{71}Ga, and ^{27}Al MAS NMR. The zeolites were further characterized for their crystal morphology by SEM, using JOEL scanning electron microscope. The ^{29}Si, ^{27}Al, and ^{71}Ga MAS NMR spectra were obtained using Bruker MSL 300 MHz NMR instrument for 2 μsec, 1 μsec, and 2 μsec pulses, respectively, and at a flip angle of 45°; the samples were spun at 3–3.5 KHz.

The acid strength distribution on the H-gallosilicates was measured by the step-wise thermal desorption (STD) of pyridine and also by determining the chemisorption of pyridine at 50–400°C, by the GC adsorption/desorption techniques (8, 9) using a Sigma 3B Perkin–Elmer gas chromatographic analyser. The gallosilicate (0.15 g) in the column (s.s. tube with i.d. 2 mm and length 12 cm) was saturated with pyridine at 50°C and the reversibly adsorbed pyridine at this temperature was desorbed in a flow of moisture-free N_2 (20 $cm^3 \cdot min^{-1}$). The pyridine chemisorbed at 50°C was then desorbed thermally in the flow of N_2 by heating the gallosilicate from 50 to 400°C in six steps (viz. 50–100°C, 100–175°C, 175–250°C, 250–325°C, and 325–400°C). The temperature in each step was raised at a linear heating rate of 10°C $\cdot$ min^{-1}. After the maximum temperature of the respective step was attained, it was maintained for a period of 1 h to desorb the pyridine reversibly adsorbed on the gallosilicate at that temperature. The pyridine desorbed at each temperature step was measured quantitatively by the FID detector. The amount of pyridine chemisorbed at 400°C was measured by the GC pulse method based on the TPD under chromatographic conditions (8). Estimation of the chemisorption data from the STD data is given elsewhere (9). In the present study, the chemisorption of pyridine is defined as the amount of pyridine retained by the presaturated gallosilicate after it has been swept with pure N_2 for a period of 1 h.

The gallosilicates were also characterised for their acidity by carrying out on them the acid catalysed model reactions (viz. cracking of iso-octane and toluene disproportionation), using a pulse microreactor (quartz tube with o.d. 6 mm, i.d. 4.5 mm, and length 300 mm) connected to a gas chromatograph. The gallosilicate (0.1 g) in the microreactor was pretreated *in situ* at 500°C in a flow of moisture-free N_2 (15 $cm^3 \cdot min^{-1}$) for 1 h. The catalytic activity/selectivity was determined using moisture-free N_2 as carrier gas (flow rate : 15 $cm^3 \cdot min^{-1}$) by injecting a pulse of iso-octane, cumene, o-xylene and toluene (0.5 μl) at 400, 300, 400, and 500°C, respectively, and analysing the reaction products, using an on-line GC with FID and computing integrator [column : Benton-34 (5%) and dinonylphthalate (5%) on Chromosorb-W (3 mm × 5 m)]. The pulse quartz microreactor unit was similar to that described earlier (10). Selective poisoning of stronger acid sites by pyridine for those model reactions and also for propane aromatization (at 500°C) over the gallosilicate (Si/Ga = 32.9) has also been studied using the pulse microreactor (pulse size of propane : 0.2 ml). For this purpose, the gallosilicate was first saturated with pyridine (by its chemisorption at 100°C) blocking all the acid sites and then acid sites of increasing strength were made available for the pulse reactions by desorbing the chemisorbed pyridine at 400°C (for the iso-octane and cumene cracking and *o*-xylene isomerization reactions) or at 500°C (for the toluene disproportionation and propane aromatization reactions). The procedures for carrying out the pulse reactions over the catalyst (with or without its stronger acid sites poisoned selectively by pyridine) and product analysis are given earlier (11–13).

Propane aromatization reaction was carried out in a continuous flow quartz reactor (i.d. 13 mm) provided with a thermowell at the center (axially) and packed with particles (52–72 mesh size) of the gallosilicate (1 g) at 550°C and atmospheric pressure, using a propane–N_2 mixture (33.3 mol% propane) as a feed. The reaction temperature was measured by a Cr–Al thermocouple located in the catalyst bed. For the catalyst deactivation studies, the catalytic activity and product distribution in the propane aromatization were determined as a function of time-on-stream at

550°C and gas hourly space velocity (GHSV, measured at 0°C and 1 atm) of 3075 $cm^3 \cdot g^{-1} \cdot h^{-1}$. The activity and selectivity data on the zeolites (in the absence of catalyst deactivation) at different space velocities (at 550°C) were obtained by carrying out the reaction under steady state for a short period (5 min) and then replacing the reactant by pure N_2 during the period of product analysis by GC. The products were analysed by an on-line gas chromatograph using Poropak-Q (3 mm × 3 m) and Benton-34 (5%) and dinonylphthalate (5%) on chromosorb-W (3 mm × 5 m) columns for separating C_1–C_4 hydrocarbons and aromatics, respectively. Before the reaction, the catalysts were pretreated *in situ* in a flow of moisture-free N_2 at 550°C for 1 h. The conversion and selectivity in the catalytic reactions were obtained from the product distribution, as follows. Conversion (%) = 100 − wt% of reactant in products. Selectivity (%) = [(wt% of particular product in products)]/(100 − wt% of reactant in products)] × 100. The results are reproducible within 2–6% error.

RESULTS

Characterization of Gallosilicates

XRD spectra of all the TPA-gallosilicates have sharp intensity peaks, are very much similar to that observed for ZSM-5 and also show single reflection at $2\theta = 24.5°$ and $2\theta = 29.3°$, indicating high crystallinity and MFI structure for the gallosilicates. The ZSM-5 type framework structure has been further confirmed by FTIR spectra of the gallosilicates by observing the structure sensitive stretching vibration near 1100 cm^{-1} and 800 cm^{-1} and double ring vibrations at about 550 cm^{-1}.

SEM microphotographs of particles of the TPA-gallosilicates are presented in Fig. 1. The particles are spherical in shape and it seems that these are agglomerates composed of tiny unit crystallites. However, the agglomerate size is larger for the gallosilicate with higher Si/Ga ratio. Similar spherical agglomerates of gallosilicate were also observed earlier (14). The data on weight loss of the H-gallosilicates due to their dehydration are given in Table 1.

^{29}Si and ^{71}Ga MAS NMR spectra of the H-gallosilicates are shown in Fig. 2. No peak for ^{27}Al MAS NMR is observed. The ^{29}Si MAS NMR shows a sharp large peak for Si (0 Ga) at about −111 ppm and a small shoulder peak for Si (1 Ga) at about −104 ppm for all the gallosilicates. As expected the peak area of Si (1 Ga) peak relative to that of Si (0 Ga) is decreased with increasing the Si/Ga ratio. ^{71}Ga MAS NMR shows a peak at +156 ppm for tetrahedral gallium in the zeolite framework for all the gallosilicates. The Si/Ga ratio for the TPA-gallosilicates calculated from the NMR data is in close agreement with that determined by the chemical analysis. However, the ratio is increased after the removal of TPA from the TPA-gallosilicates and also increased further when the zeolites are converted to their H-form (Table 1).

Acidity/Acid Strength Distribution

The acid strength distribution on the H-gallosilicates was measured by the STD of pyridine (chemisorbed at 50°C) from 50 to 400°C in a number of temperature steps and also by determining the chemisorption of pyridine at different temperatures.

Results on the STD of pyridine, showing the influence of Si/Ga ratio on the pyridine chemisorption site energy distribution on the zeolite are presented in Fig. 3. The columns in this figure show energy distribution of the sites involved in the chemisorption of pyridine at 50°C. Each column of the site energy distribution represents the num-

TABLE 1

Framework and Nonframework Gallium in H-Gallosilicates (MFI) and Their Weight Loss Due to Dehydration

Bulk Si/Ga ratio[a]	FW Si/Ga ratio[b]			Ga (p.u.c.) in H-gallosilicate		Wt loss[c] due to dehydration of H-gallosilicate (%)
	TPA form	Calcined form	H form	FW	Non-FW	
32.9	31.3	45.2	50.6	1.86	1.01	10.5
50.5	48.9	56.4	61.9	1.53	0.34	10.0
68.4	65.1	71.3	73.2	1.29	0.10	8.5
129.6	123.3	132.0	133.5	0.71	0.02	8.1

[a] Obtained by chemical analysis.

[b] Obtained from ^{29}Si MAS NMR data.

[c] Obtained by the thermal gravimetric analysis from 30° to 1000°C (the wt. loss above 550°C was negligibly small).

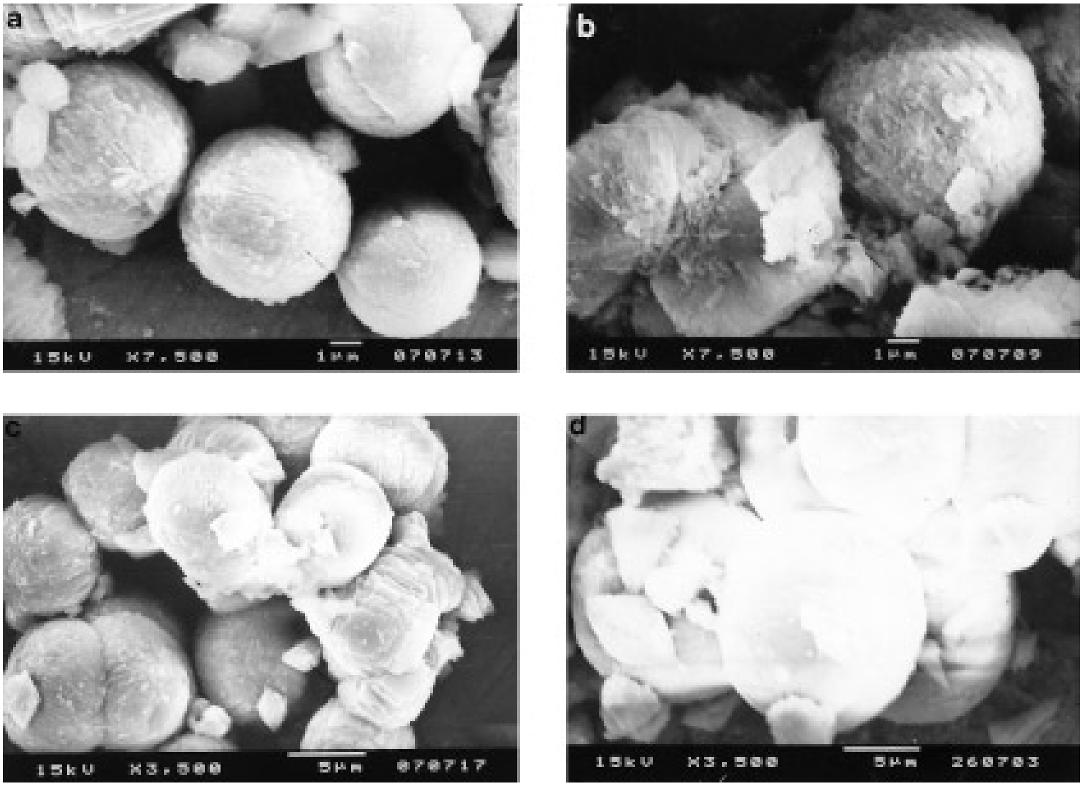

FIG. 1. SEM photographs of H-gallosilicate (MFI) zeolites. Si/Ga = 32.9 (a), 50.5 (b), 68.4 (c), and 129.6 (d).

ber of sites measured in terms of pyridine desorbed in the corresponding temperature step. The strength of these sites is expressed in terms of the desorption temperature of pyridine, T_d, which lies in the range of temperature ($T_1 < T_d \leq T_2$) in which chemisorbed pyridine is desorbed. T_d^* corresponds to the temperature at which all the chemisorbed pyridine is desorbed (i.e., the temperature at which pyridine is not chemisorbed) from the zeolite.

Temperature dependence of the chemisorption of pyridine on the zeolites is shown in Fig. 4. The decrease in the pyridine chemisorption with increasing the temperature reveals that the pyridine chemisorption sites on all the gallosilicates are not of equal strength, thus indicating the presence of a site energy distribution on the zeolites.

The pyridine chemisorption sites are expected to be the acid sites associated with both the FW and non-FW gallium species and also the defect sites (e.g., terminal Si–OH groups having weak acidity). The variation of total acidity (measured in terms of pyridine chemisorbed at 50°C) and strong acidity (measured in terms of pyridine chemisorbed at 400°C) with the bulk Si/Ga ratio of the gallosilicate is shown in Fig. 5. A linear dependence of the strong acidity on the FW-Ga is shown in Fig. 6. The strong acid site/FW-Ga ratio is found to be very close to 1.0 for all the gallosilicates.

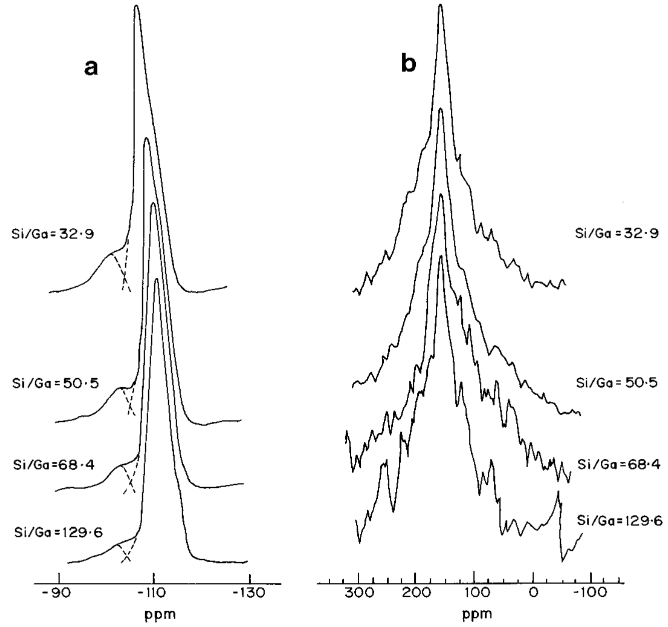

FIG. 2. (a) ^{29}Si MAS NMR and (b) ^{71}Ga MAS NMR spectra of H-gallosilicate (MFI) zeolites.

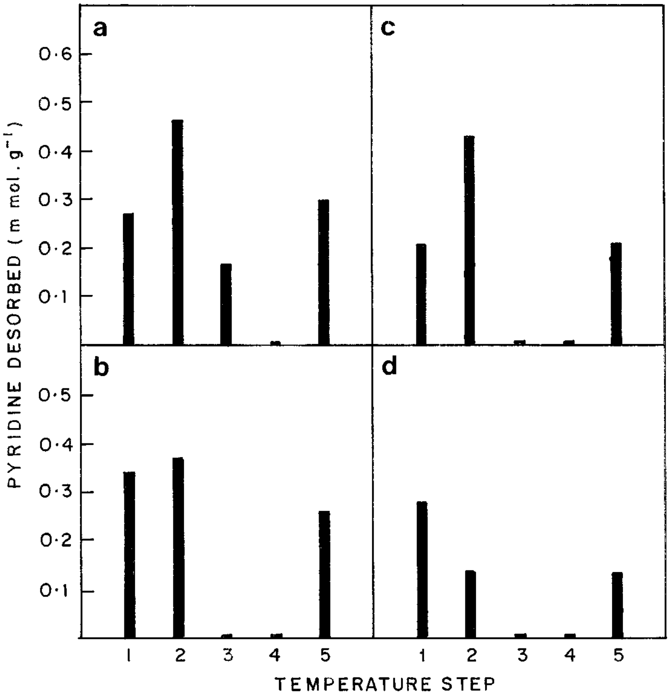

FIG. 3. Stepwise thermal desorption of pyridine (chemisorbed at 50°C) from H-gallosilicate (MFI) zeolites temperature steps: (1) 50°C < $T_{\mathrm{d}} \leq$ 100°C (2) 100°C < $T_{\mathrm{d}} \leq$ 200°C (3) 200°C < $T_{\mathrm{d}} \leq$ 300°C (4) 300°C < $T_{\mathrm{d}} \leq$ 400°C (5) 400°C < $T_{\mathrm{d}} \leq T_{\mathrm{d}}^{*}$. Si/Ga = 32.9 (a), 50.5 (b), 68.4 (c), and (d) 129.6.

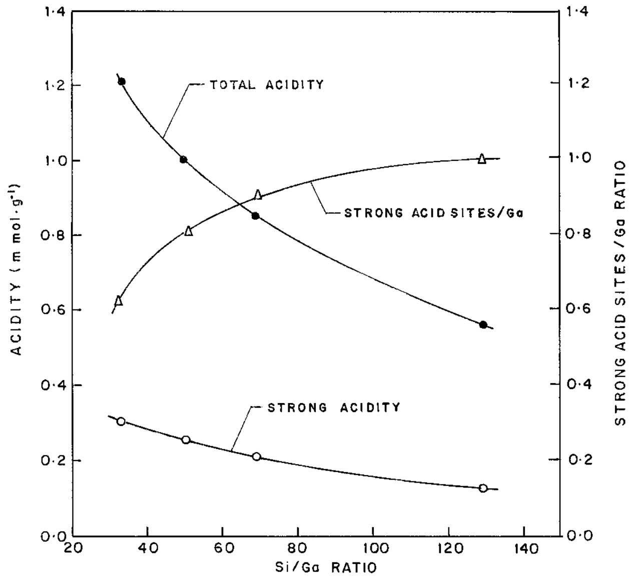

FIG. 5. Influence of bulk Si/Ga ratio on the total acidity and strong acidity of H-gallosilicate (MFI) zeolite.

Acid-Catalysed Model Reactions

The acidic function of the gallosilicate has also been studied by carrying out following model reactions (catalysed by strong acid sites) over them: isooctane cracking (at 400°C) for studying external (or intercrystalline) acid sites and toluene disproportionation (at 500°C) for characterising the internal (or intracrystalline) acid sites.

Results on the isooctane cracking and toluene disproportionation reactions over the gallosilicates are given in Fig.

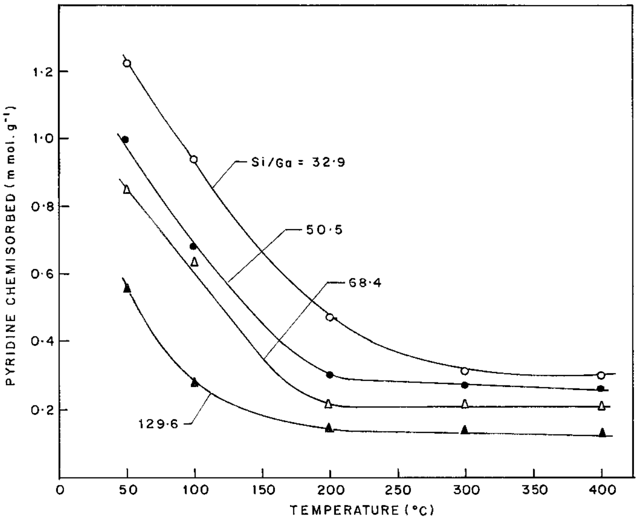

FIG. 4. Temperature dependence of chemisorption of pyridine in H-gallosilicate (MFI) zeolites.

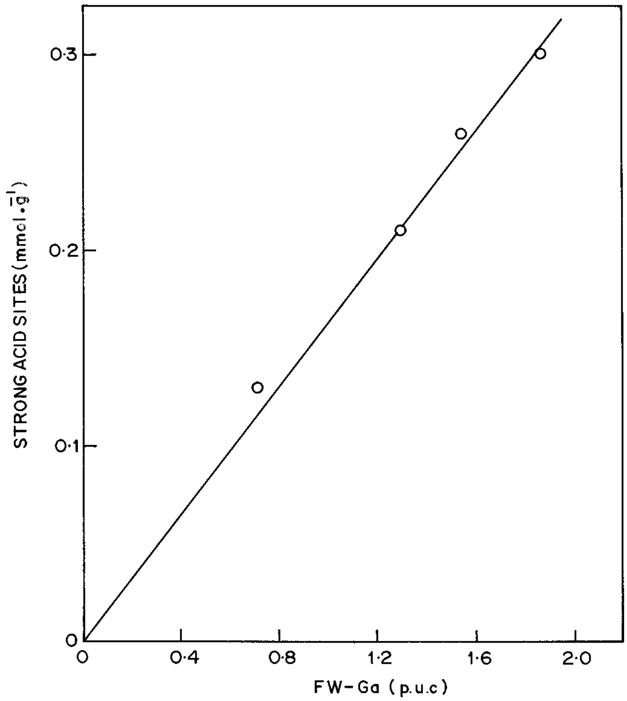

FIG. 6. Variation of strong acid sites of H-gallosilicate (MFI) with its framework gallium.

7. The large decrease of the conversion rate in both the reactions suggests that the zeolite acidity (both the internal and external) is decreased markedly with increasing the Si/Ga ratio. This is consistent with the results obtained by the pyridine chemisorption (Figs. 4 and 5). The large decrease of the conversion in both the reactions with increasing the bulk Si/Ga ratio indicates a substantial decrease in the strong acidity of the gallosilicate.

A linear dependence of the conversion rate in the isooctane cracking and toluene disproportionation reactions on the strong acidity (measured in terms of pyridine chemisorbed at 400°C) of the gallosilicate, as shown in Fig. 8, is observed. This shows a very good correlation between the catalytic activity in these model reactions and the acidity and also indicates that the external acidity (measured in terms of isooctane cracking rate) is proportional to the acidity (measured by pyridine chemisorption at 400°C).

Selective Poisoning of Stronger Acid Sites

Influence of the poisoning of stronger acid sites by the chemisorption of pyridine at 400°C [for the isooctane cracking (at 400°C) and cumene cracking (at 300°C) and o-xylene isomerization (at 400°C) reactions] and at 500°C [for the toluene disproportionation (at 500°C) and propane aromatization (at 500°C) reactions] on the activity of the gallosilicate (Si/Ga = 32.9) is shown in Table 2.

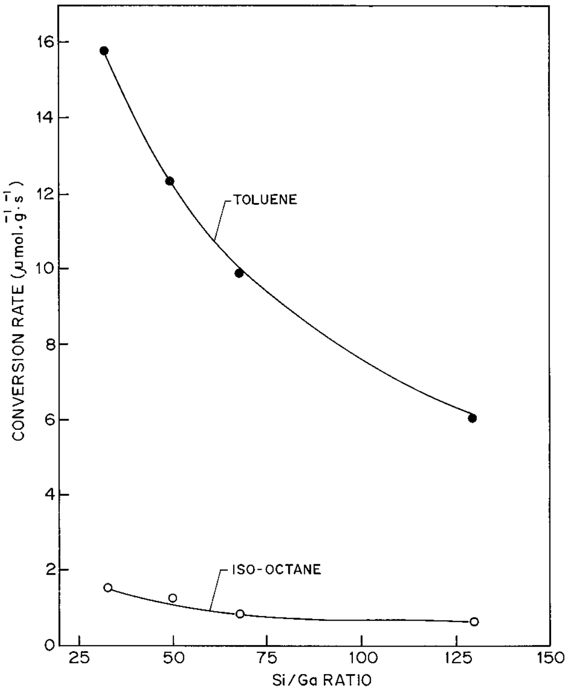

FIG. 7. Influence of bulk Si/Ga ratio on conversion rate in (a) isooctane cracking (at 400°C) and (b) toluene disproportionation (at 500°C) over H-gallosilicate (MFI) zeolite.

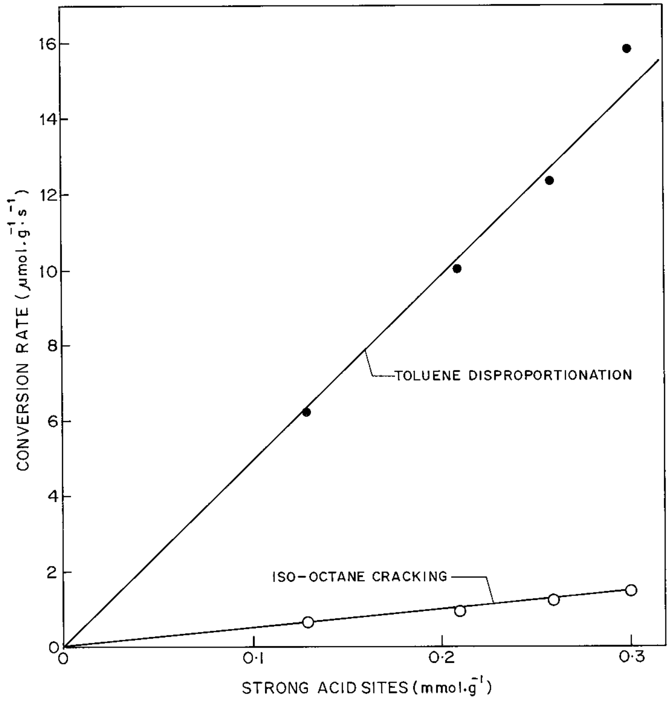

FIG. 8. Dependence of conversion rate on strong acidity of H-gallosilicate (MFI) zeolite in the isooctane cracking and toluene disproportionation reactions.

The catalytic activity in the isooctane cracking, cumene cracking, and *o*-xylene isomerization reactions is decreased substantially due to the poisoning of the strong acid sites (0.3 mmol · g^{-1}). However, when the very strong acid sites (0.21 mmol · g^{-1}) are poisoned, the toluene disproportionation activity is decreased to a small extent but both the propane conversion and propane aromatization activities are decreased to a larger extent. This shows a strong influence of the acidity on the propane conversion (both total and to aromatics) activity of the zeolite.

Deactivation in Propane Aromatization

Effect of Si/Ga ratio on deactivation kinetics. The time-on-stream activity (i.e., propane conversion-total and to aromatics) and product selectivity in propane aromatization over the gallosilicates at 550°C [feed: a mixture of propane (33.3 mol%) and N_2; GHSV: 3075 cm^3 (at STP) · g^{-1} · h^{-1}] and atmospheric pressure are presented in Figs. 9 and 10, respectively. A change in the activity relative to the initial activity (i.e., A_t/A_i, where A_t is the conversion at time t and A_i is the conversion at zero time) with the time-on-stream for the total conversion of propane and the conversion of propane to aromatics over the gallosilicates is shown in Figs. 11 and 12, respectively. The results reveal a strong influence of Si/Ga ratio on the deactivation kinetics in the propane aromatization over the gallosilicate.

TABLE 2

Results on Poisoning of Stronger Acid Sites by Pyridine in the Model Reactions over H-Gallosilicate (MFI) with Si/Ga = 32.9

Reaction	Conversion (%) Without poisoning	Conversion (%) With poisoning	No. of strong acid sites poisoned ($\mathrm{mmol \cdot g^{-1}}$)
Iso-Octane Cracking (at 400°C)	1.7	0.3	0.3
Cumene Cracking (at 300°C)	98.8	18.1	0.3
o-Xylene Isomerization (at 400°C)	52.2	11.5	0.3
Toluene Disproportionation (at 500°C)	10.4	6.7	0.21
Propane Aromatization (at 500°C)			
Total conversion (%)	27.1	6.2	0.21
Conversion-to-aromatics (%)	14.2	3.6	0.21

Note. Stronger acid sites are blocked by the chemisorption of pyridine at 500°C (for toluene disproportionation and propane aromatization) and at 400°C (for the other reactions).

Figure 13 shows a variation of deactivation rate constant, k_d, for total propane conversion and conversion of propane to aromatics over the gallosilicate with its Si/Ga ratio. The deactivation rate constant (k_d) was determined from linear plots of $\ln\{\ln[1/(1-x)]\}$ vs time-on-stream (where, x is fractional conversion) according to the following rate expression developed for the case of a first order catalyst deactivation in a plug flow fixed bed reactor (15):

$$\ln\{\ln[1/(1-x)]\} = \ln(k/k_d) - k_d t$$

The decrease in the deactivation rate constant with increasing the Si/Ga ratio is consistent with the observed decrease in the catalyst deactivation (Figs. 11 and 12). The data on coke deposition on the catalysts during the deactivation runs are given in Table 3.

Effect of time-on-stream on product selectivity/distribution. Effects of the time-on-stream (or the extent of catalyst deactivation) on the product selectivity in the propane aromatization and also on the shape selectivity (or para selectivity) of the gallosilicates are shown in Figs. 10 and 14, respectively. The influence of time-on-stream or catalyst deactivation varies with the Si/Ga ratio. However, in general, the aromatics selectivity is decreased, the propylene selectivity is increased and the para-shape selectivity is also increased with increasing the time-on-stream.

The distribution of aromatics formed in the propane aromatization is included in Table 3. The distribution of BTX for the gallosilicates with Si/Ga = 32.9, 50.5, and 68.4 is found to be more or less the same. However, for the gallosilicate with higher Si/Ga ratio, there is in a large reduction in the formation of C_{9+}-aromatics. The aromatics distribution for all the gallosilicates is, however, not changed significantly due to the catalyst deactivation.

Effect of break in the time-on-stream activity run. When the gallosilicate (Si/Ga = 32.9) deactivated during the time-on-stream for 8.4 h was cooled in oxygen-free N_2, blanketed under N_2 over night and then the propane aromatization on the deactivated catalyst was restarted on the next day (i.e., after 14 h), the results obtained are as follows:

	For first day run		For next day run	
Time-on-stream (h):	0.25	8.4	0.25	5.7
Total conversion (%)	47.3	21.8	27.6	25.0
Conversion to aromatics (%)	29.2	9.2	12.1	8.9

These results clearly indicates a partial regeneration of the deactivated catalyst due the N_2 treatment during the cooling, storage under N_2 at room temperature and reaction restart procedure.

Effect of H_2 pretreatment. The results of propane aromatization (for a time-on-stream of 0.25 h) on the gallosilicate (Si/Ga = 32.9), when pretreated with H_2 at 600°C for 10 h before the reaction, were as follows: total conversion, 43.5% and conversion to aromatics, 24.0%. A comparison of these results with that (total conversion: 21.8% and conversion to aromatics: 9.2%) obtained at the time-on-stream of 8.4 h for the gallosilicate without the H_2 pretreatment show that the observed decrease in the catalytic activity due to the deactivation for a time-on-stream of 8.4 h is much more than that could have been resulted due to the H_2 pretreatment to the catalyst for 10 h (at 600°C). This clearly indicates that the observed catalyst deactivation is certainly not due to the changes in catalyst properties resulting from the interactions of hydrogen produced in the propane aromatization with the catalyst; it is mostly due to the catalyst coking. This was confirmed by buring the coke on the deactivated catalyst at 500°C in a flow of O_2–N_2 mixture (5% O_2) for 2 h and observing the regeneration of its original activity due to the removal of coke.

Initial Activity/Selectivity in Propane Aromatization

The initial activity/selectivity (i.e., the activity/selectivity in the absence of catalyst deactivation) of the catalysts at 550°C was measured at different space velocities (3075–60,000 $cm^3 \cdot g^{-1} \cdot h^{-1}$) for studying the influence of conversion on product selectivity and also for comparing the catalysts for their selectivity/product distribution at same conversion levels.

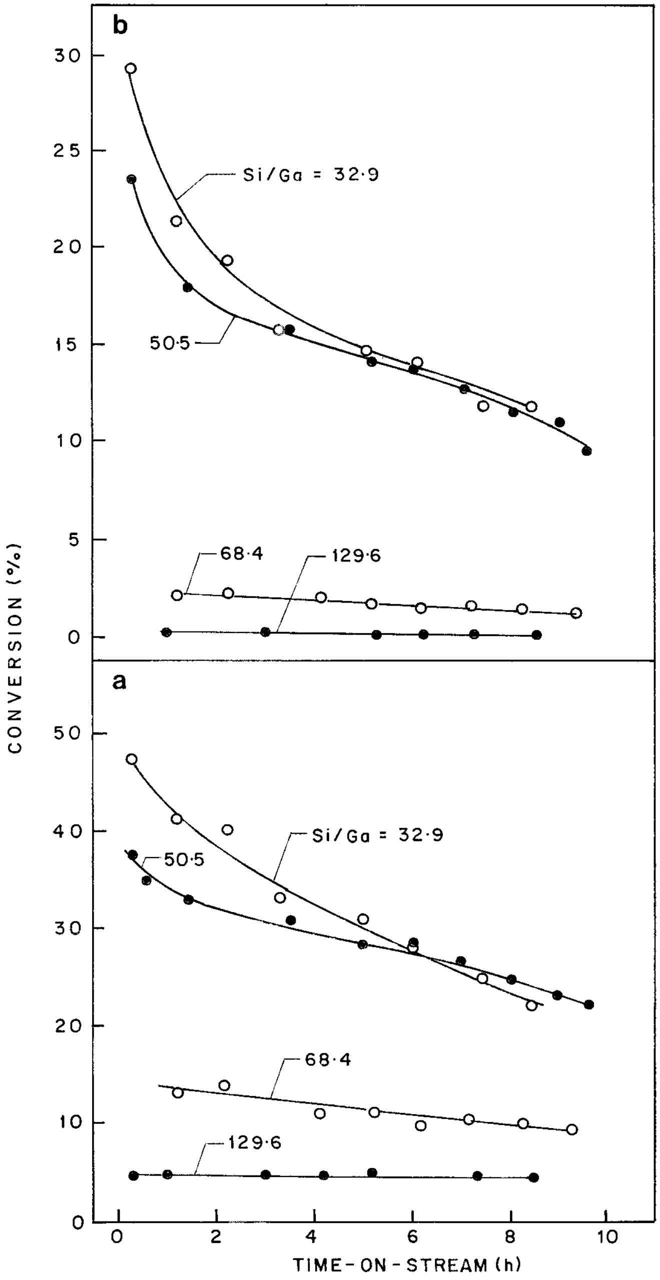

FIG. 9. Variation with time-on-stream of the propane conversion, (a) total conversion and (b) conversion to aromatics, in the propane aromatization (at 550°C) over H-gallosilicate (MFI) with different Si/Ga ratios.

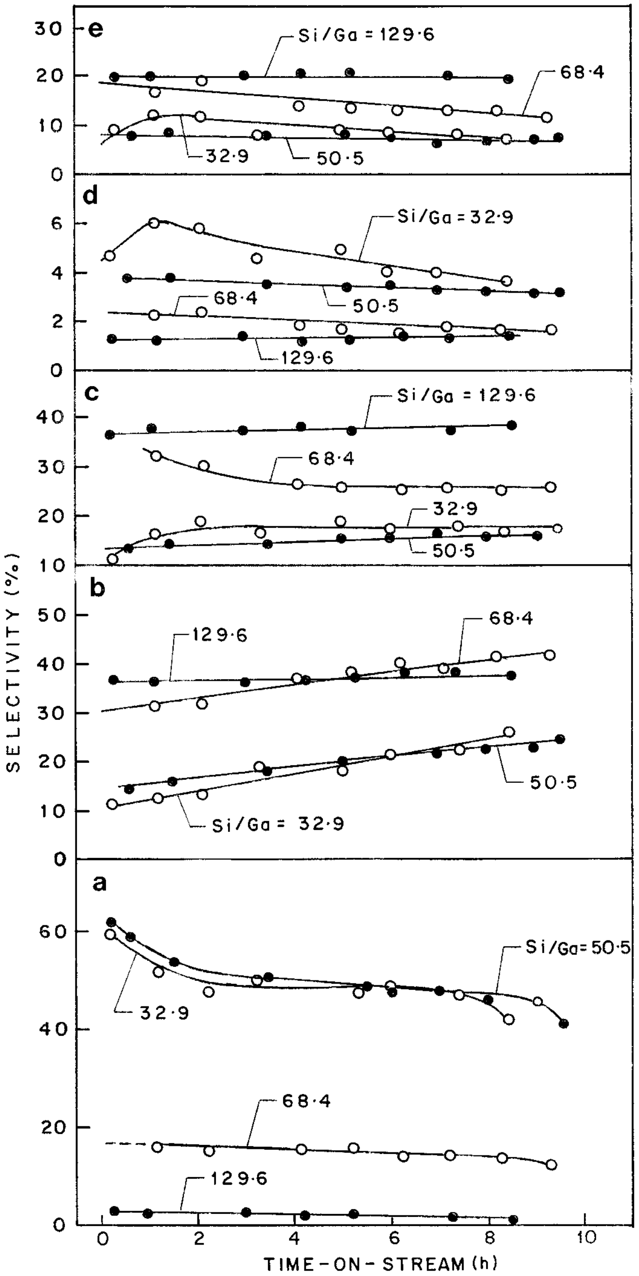

FIG. 10. Variation with time-on-stream of the product selectivity of H-gallosilicate (MFI) with different Si/Ga ratios in the propane aromatization (at 550°C). (a) aromatics, (b) propylene, (c) ethylene, (d) ethane, and (e) methane.

Effect of propane conversion on product selectivity. Figure 15 shows a strong influence of propane conversion on the product selectivity over the H-gallosilicate

(Si/Ga = 32.9). The aromatics selectivity, aromatics/(methane + ethane) mass ratio and C_1/C_2 mole ratio are increased and the propylene selectivity, and dehydrogenation/cracking (D/C) activity ratio [determined as (100 − selectivity for C_1 and C_2)/(selectivity for C_1 and C_2)] are decreased with increasing the conversion. The effect on the selectivity for aromatics and propylene and the ethylene/ethane and aromatics/(methane + ethane) ratios is, however, very large.

Effect of Si/Ga ratio on product selectivity. Influence of Si/Ga ratio on the product selectivity at the same conversion of propane over the catalysts is shown in Figs. 16 and 17. It is interesting to note that the selectivity for aromatics and propylene, D/C activity ratio and aromatics/(methane + ethane) mass ratio are decreased markedly with increasing the Si/Ga ratio at all the conversion levels. Also, the C_2H_4/C_2H_6, and $CH_4/(C_2H_4 + C_2H_6)$ mole ratios (at 5% conversion) are strongly influence by the Si/Ga ratio. These results suggest a strong influence of Si/Ga ratio on the formation of aromatics and the dehydrogenation/cracking activity ratio in the propane aromatization.

Dependence of activity/selectivity on acidity and non-FW gallium. Figures 18 and 19 show a strong dependence of the propane conversion activity and the aromatics selectivity and D/C activity ratio (at the same conversion level), respectively, on both the strong acidity (measured in terms of pyridine chemisorbed at 400°C) and the non-FW gallium of the zeolites. These results indicate that, apart from the acidity, the non-FW gallium species also play an important role, particularly in the dehydrogenation and consequently in the aromatization of propane.

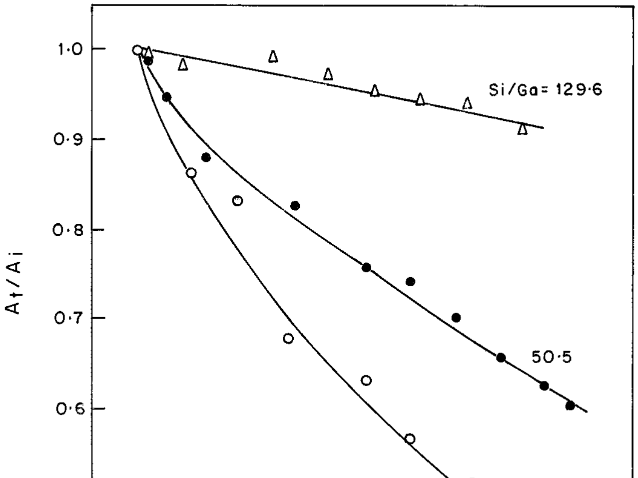

FIG. 11. Variation of the propane conversion activity, relative to that at zero time-on-stream of H-gallosilicate (MFI) with time-on-stream in the propane aromatization (at 550°C).

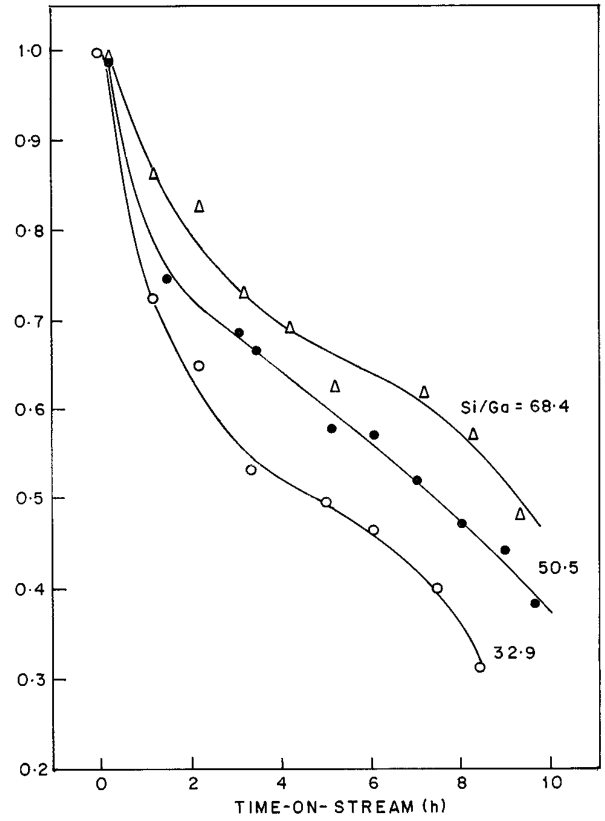

FIG. 12. Variation of the propane-to-aromatics conversion of activity, relative to that at zero time-on-stream, of H-gallosilicate (MFI) with time-on-stream in the propane aromatization (at 550°C).

DISCUSSION

Incorporation of Ga in MFI Frame Work

The isomorphous substitution of Ga for Al in ZSM-5 framework has been confirmed by the following confirmatory tests/observations:

— Single reflection at $2\theta = 24.5°$ and 29.3° in the absence of Al (which is confirmed by the absence of ^{27}Al MAS NMR peak at +56 ppm).

— ^{71}Ga MAS NMR peak at +156 ppm (which corresponds to tetrahedral Ga) (Fig. 2b).

— ^{29}Si MAS NMR peak at −104 ppm for Si (1 Ga) decrease in its intensity or area with increasing Si/Ga ratio (Fig. 2a).

— Framework Si/Ga ratio (obtained from ^{29}Si MAS NMR) close to the bulk Si/Ga ratio in all the gallosilicates (Table 1).

— The decrease in the acidity, particularly strong acid sites, with increasing the Si/Ga ratio (Fig. 5).

The high or strong acidity of ZSM-5 zeolites is attributed to the presence of tetrahedral Al in their framework (17, 18). Similarly, for the gallosilicates having MFI structure, their strong acidity is also expected to be attributed to the presence of tetrahedral Ga in their framework.

Degalliation of Gallosilicate (*MFI*)

The results in Table 1 clearly show that a degalliation to an appreciable extent, depending upon the Si/Ga ratio, occurs during the calcination of the TPA-gallosilicates and also during the conversion of the calcined-form to the H-form of the zeolites. It is, however, interesting to note that the extent of degalliation is decreased with increasing the FW-Si/Ga ratio of TPA-gallosilicate, as follows.

Si/Ga ratio (TPA-form)	31.3	48.9	65.1	123.3
Degalliation (%)	35.2	18.2	7.2	2.7
Non-FW Ga/FW Ga ratio (H-form)	0.54	0.22	0.08	0.03

Thus, both the framework and non-framework gallium species are present in the H-gallosilicates and the concentration of non-FW Ga and non-FW Ga/FW Ga ratio are decreased sharply with increasing the bulk Si/Ga ratio.

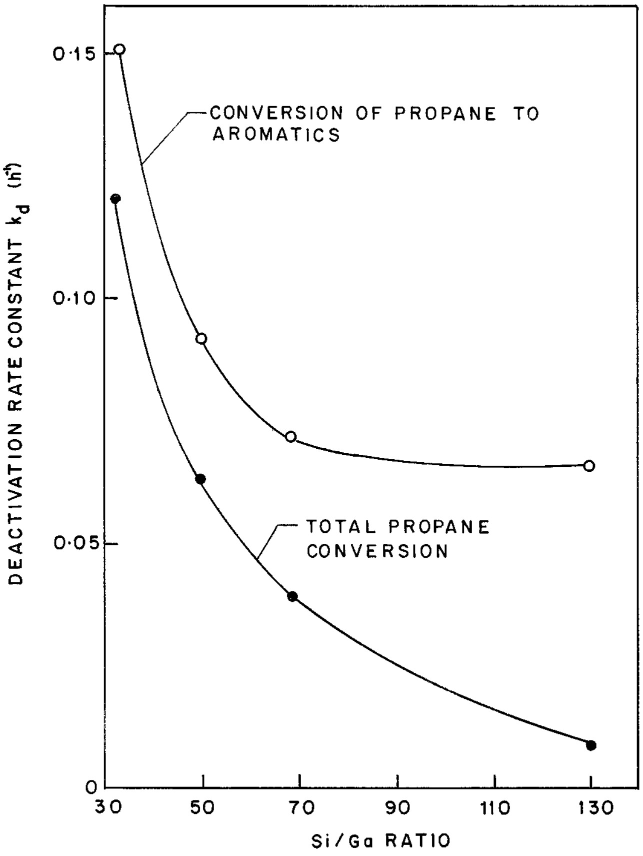

FIG. 13. Influence of bulk Si/Ga ratio on the deactivation rate constant for total conversion and conversion to aromatics in the propane aromatization over H-gallosilicate (MFI) zeolites.

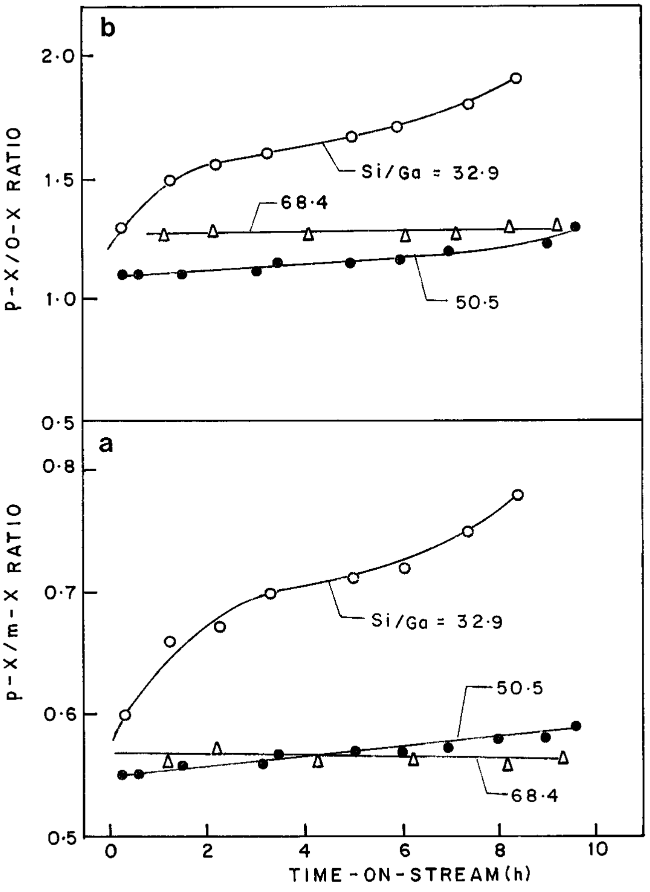

FIG. 14. Variation with time-on-stream of the xylene ratios in the propane aromatization (at 550°C) over H-gallosilicate (MFI) zeolites.

These results also indicate that the stability of gallosilicate (MFI) zeolite against degalliation is increased with increasing its framework Si/Ga ratio.

It may be noted that since the T-sites in MFI structure are not crystallographically identical, the determination of FW Si/Ga ratio from ^{29}Si MAS NMR is not very accurate (16). Nevertheless, the changes in the FW Si/Ga ratio are large enough to draw conclusion about the degalliation. Further, the observed linear dependence of the strong acid sites on the FW Ga (Fig. 6) is very much consistent with that observed for H-ZSM-5 (17).

Influence of Si/Ga Ratio on Acidity

The results on the acid strength distribution (Figs. 3 and 4) reveal a strong influence of the bulk Si/Ga ratio on the distribution of acid sites of different strengths in the gallosiliate. Both the total acid sites (measured in terms

TABLE 3

Distribution of Aromatics Formed and Amount of Coke Deposition in Propane Aromatization over H-Gallosilicates (MFI)

Si/Ga	Distribution of aromatics (wt%)				Coke deposition (wt% Carbon)
	Benzene	Toluene	Xylenes + EB	C_{9+}	
32.9	45.7 ± 0.4	36.5 ± 1.0	16.0 ± 0.5	1.80 ± 0.2	2.61
50.5	45.0 ± 0.5	37.0 ± 1.0	15.7 ± 1.0	2.30 ± 0.3	1.92
68.4	45.5 ± 1.5	37.2 ± 1.0	17.0 ± 0.5	—	0.20
129.6	51.0 ± 2.0	42.0 ± 1.0	7.0 ± 0.5	—	0.12

Note. Time-on-stream: 9 ± 0.5 h.

of pyridine chemisorbed at 50°C) and the strong acid sites (measured in terms of pyridine chemisorbed at 400°C) are decreased with increasing the Si/Ga ratio (Fig. 5). The decrease in the acidity is consistent with the decrease in the catalytic activity of the gallosilicate in the isooctane cracking and toluene disproportionation reactions (Fig. 7) (which are model reactions catalysed by acid sites) with increasing the Si/Ga ratio. A very good relationship exists between the catalytic activity for the isooctane cracking and toluene disproportionation reactions and the strong acid sites measured by the pyridine chemisorption at 400°C, as shown by the linear plots of conversion vs strong acid sites in Fig. 8.

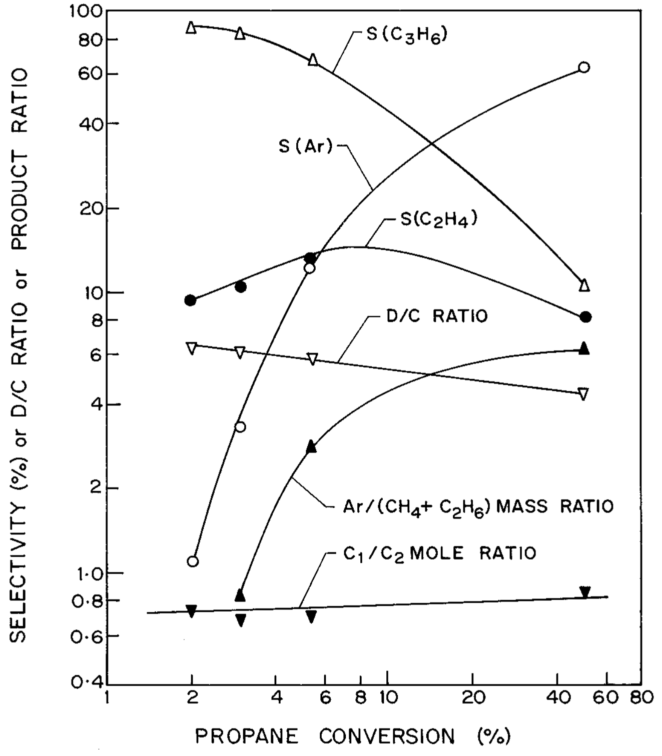

FIG. 15. Variation with propane conversion of the selectivity for aromatics and propylene, D/C activity ratio and product ratios in the propane aromatization over the H-gallosilicate (Si/Ga = 32.9).

Since the acidity of the gallosilicate is attributed to the tetrahedral Ga in its framework, the zeolitic acid sites present in the zeolites are expected to be equivalent to their framework Ga. However, for all the zeolites, their total acid sites are found to be larger than their framework Ga. This may be due to weaker interaction of pyridine (at low temperature) with the defect sites (or terminal Si–OH) and/or with the lewis acid sites on the extra framework gallium oxide species formed due to partial degalliation of the gallosilicates during their calcination and deammoniation (Table 1). It is also interesting to note that the n_{SA}/n_{Ga} ratio (where n_{SA} and n_{Ga} are the number of strong acid sites and Ga, respectively, in the zeolite) is increased with increasing the bulk Si/Ga ratio, almost approaching to 1 for Si/Ga = 130 (Fig. 5). However, the strong acid sites/FW Ga ratio for all the zeolites is very close to 1.0. As expected, an excellent linear relationship between the strong acidity and framework Ga of the H-gallosilicate (Fig. 6) is observed. The observed value of n_{SA}/n_{Ga} smaller than 1 is because of the fact that a significant part of Ga is extra framework.

The external (or intercrystalline) acid sites are characterized by the isooctane cracking reaction. Since isooctane does not penetrate the ZSM-5 type zeolites even at 400°C (19, 20), its reaction is expected to provide an information on the external acid sites of the gallosilicates. Isooctane cracking occurs essentially on strong acid sites (19, 20) and, therefore, the decrease in the isooctane cracking activity of the gallosilicate with increasing its Si/Ga ratio (Fig. 7) indicates a pronounced effect of Si/Ga ratio on the external strong acid sites. This also suggests that the concentration of FW Ga (which is responsible for the strong acidity) on the external surface of the zeolite crystals is decreased with increasing the Si/Ga ratio. These external acid sites could be poisoned for the isooctane cracking by the chemisorption of pyridine at 400°C (Table 2).

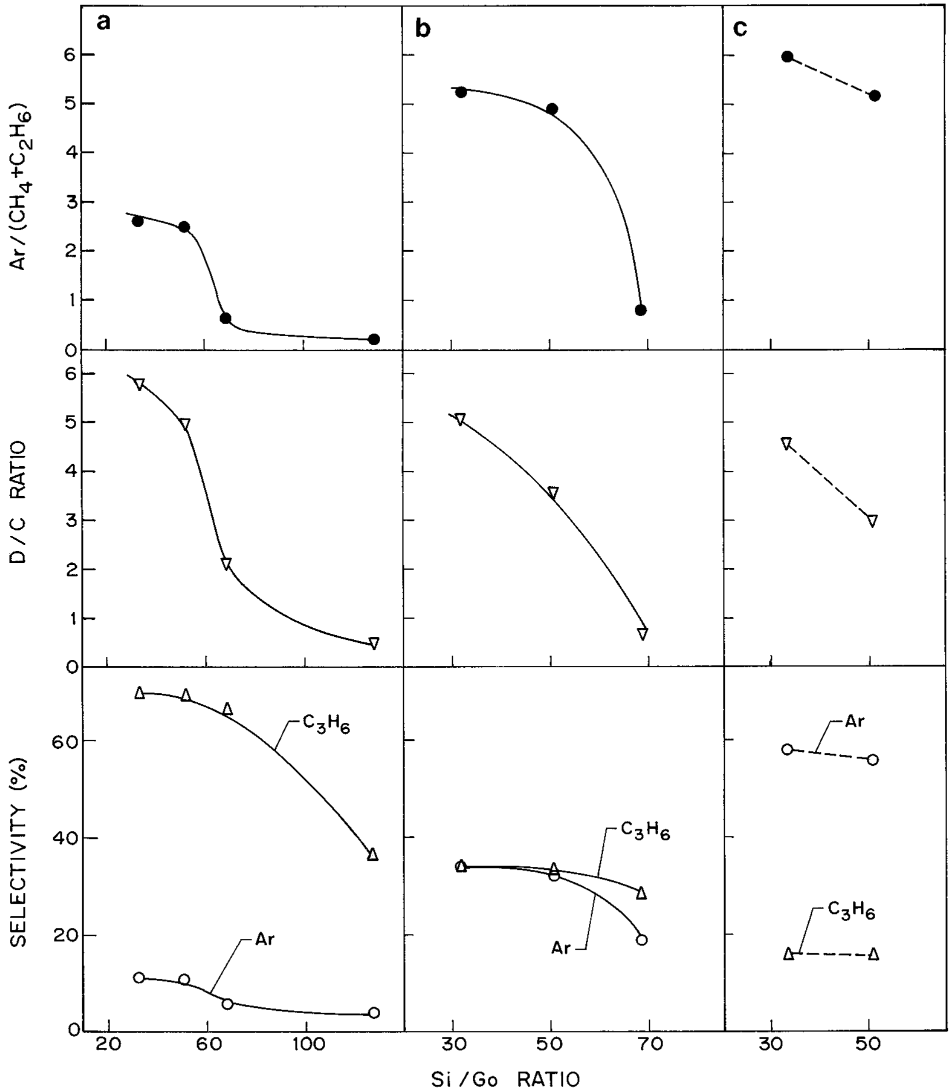

FIG. 16. Influence of Si/Ga ratio on the selectivity for aromatics and propylene, dehydrogenation/cracking (D/C) activity ratio and aromatics/(methane + ethane) ratio in the propane aromatization at (a) 5%, (b) 15%, and (c) 40% conversion of propane.

Poisoning of Acid Sites

The results in Table 2 indicate that although the catalytic activity in the acid catalysed reactions is reduced very appreciably due to the poisoning of the strong (for the isooctane cracking, cumene cracking, and *o*-xylene isomerization reactions) and very strong (for the toluene disproportionation and propane aromatization reactions) acid sites by the chemisorption of pyridine at 400 and 500°C, respectively, the weaker acid sites (i.e. unpoisoned acid sites) show appreciable activity in these reactions. It seems that the Lewis acid sites present on the extra framework gallium oxide species, which are weaker than the protonic acid sites associated with the framework Ga, also play important role in these reactions. Nevertheless, the observed large decrease in the propane conversion and aromatization activity of the zeolite due to the poisoning clearly shows the importance of strong acid sites in the propane aromatization.

Influence of Si/Ga Ratio on Initial Activity/Selectivity in Propane Aromatization

The results in Fig. 15 show a very strong influence of propane conversion on the product selectivity; the propylene selectivity and dehydrogenation/cracking activity ratio are decreased, whereas the aromatics selectivity and aromatics/(methane + ethane) ratio are increased markedly with increasing the propane conversion. However, the effect on C$_1$/C$_2$ mole ratio is quite small. Hence, in order

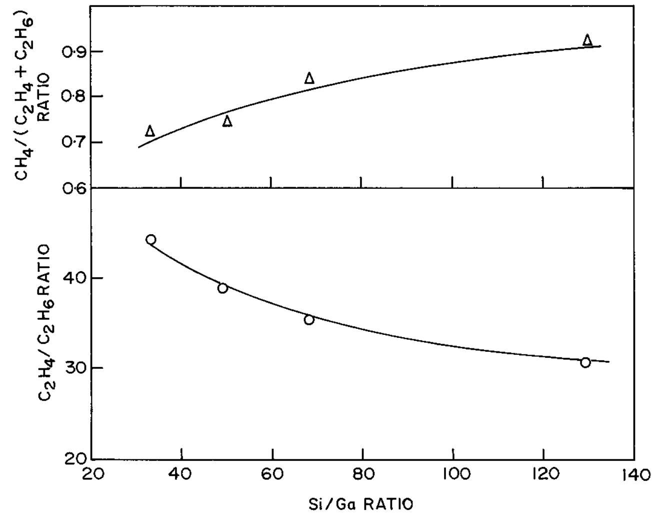

FIG. 17. Dependence on bulk Si/Ga ratio of the product mole ratios of methane, ethane and ethylene formed in the propane aromatization (at 5% propane conversion) over the H-gallosilicate.

to compare the gallosilicates (with different Si/Ga ratio) for their selectivity in the propane aromatization, it is necessary to obtain the product selectivity data at the same conversion level. This is done in the present case; the zeolites are compared for their selectivity at 5%, 15%, and 40% propane conversion levels.

Figure 16 shows that at all the conversion levels, the selectivity for aromatics and also for propylene, the D/C activity ratio and the aromatics/(methane + ethane) ratio are decreased pronouncely with increasing the Si/Ga ratio; the decrease is, however, much larger for the higher Si/Ga ratio. The distribution of C_1 and C_2 hydrocarbons (at 5% propane conversion) is also strongly influenced by the Si/Ga ratio (Fig. 17); the ethylene/ethane ratio is decreased and the methane/(ethylene + ethane) ratio is increased with increasing the Si/Ga ratio. All these results show a strong influence of Si/Ga ratio on the product selectivity.

The initial (i.e., at zero time-on-stream) propane conversion and aromatization activity (Fig. 9) is also strongly influenced by the Si/Ga ratio; it is decreased very sharply with increasing the Si/Ga ratio. The propane conversion

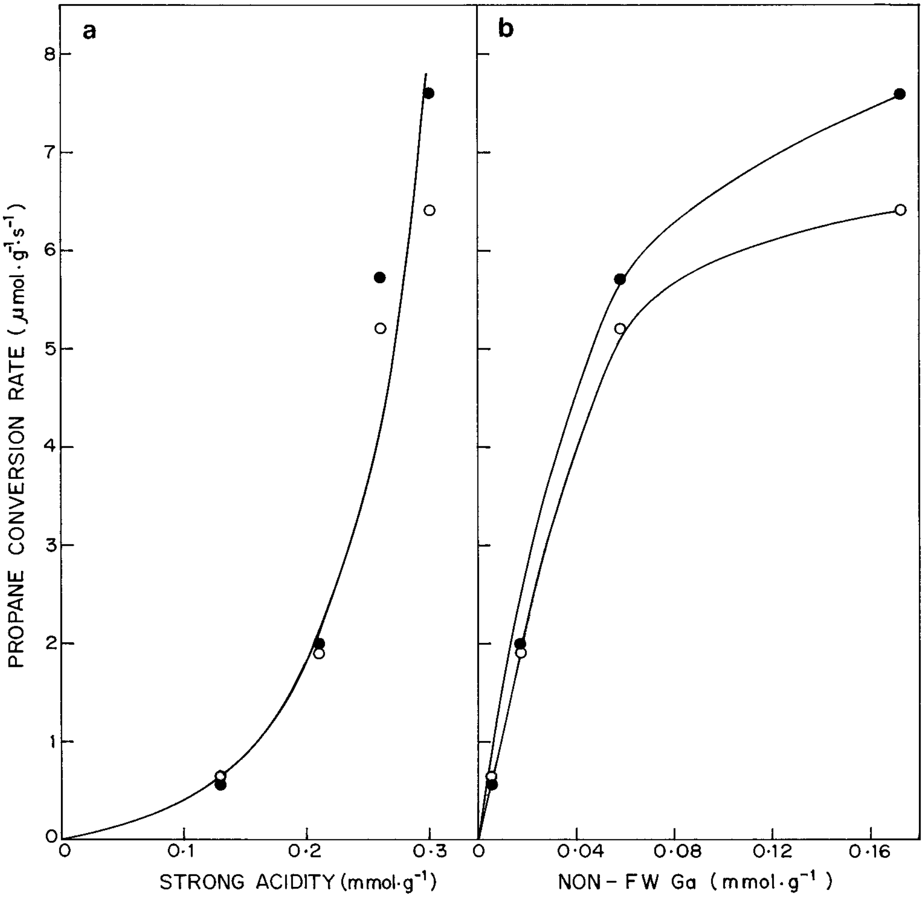

FIG. 18. Dependence of propane conversion rate on (a) strong acidity and (b) non-FW Ga of the gallosilicate (GHSV = 3075 (○) and 7000 (●) $cm^3 \cdot g^{-1}h^{-1}$).

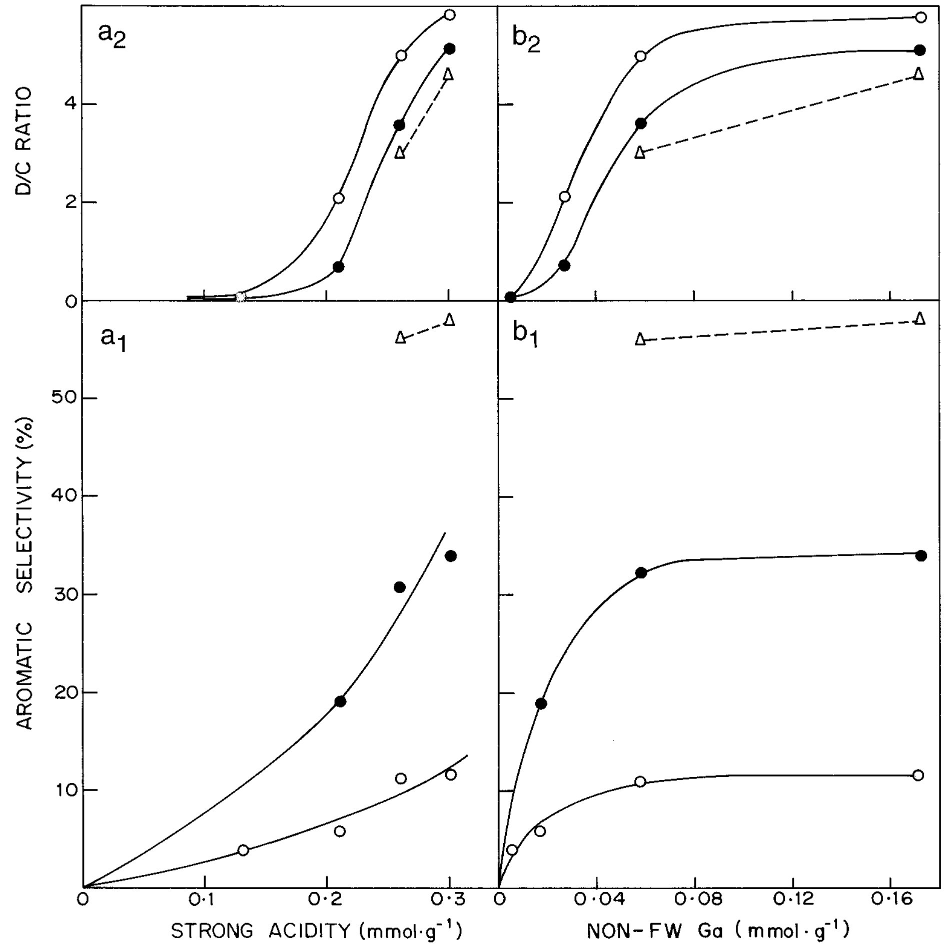

FIG. 19. Dependence of the aromatics selectivity and D/C activity ratio on (a) strong acidity and (b) non-FW Ga in the gallosilicate, at the propane conversion of 5% (○), 15% (●), and 40% (△).

activity (Fig. 18) and the aromatics selectivity and D/C activity ratio (Fig. 19) are found to increase sharply with increasing the density of the acid sites and nonframework Ga (which is well dispersed in the zeolite channels) of the gallosilicate. It may also be noted that the later two are decreased with increasing the Si/Ga ratio (Fig. 5 and Table 1). These observations suggest that both the acidity and the nonframework Ga play an important role in controlling the activity and selectivity of the zeolite in propane aromatization. Giannetto *et al.* (3) have also observed an increase in the activity and selectivity in the propane aromatization due to formation of nonframework Ga by a thermal treatment to H-gallosilicate. The observed strong influence of the Si/Ga ratio on the activity and product selectivity can be, therefore, attributed to the changes in both the acidity and the nonframework Ga of the zeolite, resulting from the change in its Si/Ga ratio. Very likely, the zeolite acidity and nonframework Ga may have a combined (or synergetic) effect in the propane aromatization, particularly for enhancing the dehydrogenating (propane to propene and naphthenes to aromatics) activity in the propane aromatization.

The observed large decrease in the propylene selectivity and consequently the increase in the aromatics selectivity (Fig. 15) is due to an increase in the conversion of propylene (a primary product of propane conversion) to aromatics in the secondary reaction, with increasing the propane conversion (i.e. with increasing the contact time). The decrease in the D/C activity ratio is expected due to an increase in the formation of C_1 and C_2 hydrocarbons by the secondary cracking of higher hydrocarbons and/or dealkylation of aromatics, with increasing the propane conversion.

The primary reactions involved in the propane conversions are the following cracking and dehydrogenation reactions.

$$C_3H_8 \rightarrow CH_4 + C_2H_4. \quad [1]$$

$$C_3H_8 \rightarrow C_3H_6 + H_2. \quad [2]$$

Ethane is formed mostly by the hydrocracking reaction (a secondary reaction),

$$C_3H_8 + H_2 \rightarrow CH_4 + C_2H_6 \qquad [3]$$

occurring parallel to the above primary reactions. The ethylene and propylene formed in reactions 1 and 2, respectively, are expected to undergo oligomarization, cyclization to naphthenes and dehydrogenation of naphthenes to aromatics, following the reaction scheme similar to that proposed for the aromatization of propane over Ga/H-ZSM-5 (1a, 3).

The ethylene selectivity is passed through a maximum with increasing the propane conversion (Fig. 15). The increase in the ethylene selectivity at the lower conversions indicates that ethylene is formed not only by the primary cracking reaction (reaction 1) but also by the cracking of higher hydrocarbons. Whereas, at the higher conversion, because of higher contact time ethylene is expected to be converted to aromatics. The methane/(ethylene + ethane) mole ratio (which is expected to be 1 according to reactions 1 and 3) at a low conversion (5%) for all the zeolites is found to be less than 1 (Fig. 17). This also supports the above view that ethylene is also formed by the cracking of higher hydrocarbons in secondary reactions.

The ethylene/ethane ratio (at 5% propane conversion) is much higher than 1, and also it is decreased appreciably with increasing the Si/Ga ratio. This indicates that the cracking activity of the zeolite is much higher than its hydrocracking activity and also the cracking activity relative to the hydrocracking activity is decreased with increasing the Si/Ga ratio.

If the primary cracking (reaction 1) and dehydrogenation (reaction 2) reactions are catalysed only by the acid sites of the zeolite, the dehydrogenation/cracking activity ratio is expected to be unaffected by the strength of acid sites (21). However, in the present case the D/C activity ratio for the zeolite is found to be very strongly influenced by the Si/Ga ratio (Fig. 16). The observed large decrease in the D/C activity ratio is expected mostly because of the decrease in the nonframework Ga with increasing the Si/Ga ratio. Indeed, the propane conversion activity, D/C activity ratio and aromatics selectivity are also found to be increased with increasing the concentration of nonframework Ga (Fig. 18 and 19). However, it may be noted that when the Si/Ga ratio is increased both the acidity and the nonframework Ga are decreased and hence it is difficult to bringout clearly the influence of either of the two on the activity and selectivity in the propane aromatization. Nevertheless, both the acidity (which is essential for the olegomerization and cylization) and the nonframework Ga (which is essential for dehydrogenation of propane and naphthenes) at high concentrations are neccessary for obtaining high conversion and selectivity in the propane aromatization over the gallosilicate zeolite.

Influence of Si/Ga Ratio on Deactivation

The observed catalyst deactivation in the propane aromatization (Figs. 9, 11, and 12) is mainly due to the coke deposition and not because the interaction of the H_2 (produced in the overall propane aromatization process) with the catalyst. This fact is confirmed by comparing the results obtained for the hydrogen pretreated (at 600°C for 10 h) gallosilicate (Si/Ga = 32.9). Under the identical reaction conditions, the decrease in the initial propane aromatization activity and selectivity due to the H_2 pretreatment (which was given even at a higher temperature and for a longer period) is very small as compared to that observed due to the catalyst deactivation during the reaction. The partial gain in the activity/selectivity of the catalyst due to a break in the time-on-stream activity run also indicates that the deactivation is mostly due to catalyst coking and the break in the run might have resulted in a redistribution and/or removal of part of the volatile coke molecules from the catalyst. The deactivated catalyst could be regenerated by removing its coke by giving an oxidative treatment to it in a flow of O_2–N_2 mixture (5% O_2) at 500°C for 2 h.

The results (Figs. 9, 11, and 12) show a very pronounced effect of Si/Ga ratio on the catalyst deactivation due to coking. Rates of catalyst deactivation for both the total propane conversion and formation of aromatics in the propane aromatization are sharply increased with decreasing the Si/Ga ratio (Fig. 13), mostly due to the increase in the propane conversion resulting in an increase in the coke formation with increasing the acid and dehydrogenation functions of the zeolite.

Influence of Deactivation on Product Distribution/Selectivity

The results (Figs. 10 and 14) reveal that the deactivation causes following changes in the product distribution or selectivity in the propane aromatization, depending upon the Si/Ga ratio.

— The aromatics selectivity is decreased.
— The propylene selectivity is increased markedly.
— The ethylene selectivity (except for Si/Ga = 68.4) is increased.
— The $p - X/m - X$ and $p - X/o - X$ ratios are increased.

The change in the product selectivity due to the deactivation for the gallosilicate with higher Si/Ga ratio is generally found to be smaller because of its lower rate of deactivation. However, for all the gallosilicates, the distribution of aromatics formed in the reaction (Table 3) is not affected significantly due to the deactivation (or the time-on-stream).

The decrease in the aromatics selectivity and the increase in the propylene selectivity with increasing the deactivation are expected to be mostly due to the observed decrease in the propane conversion. The product selectivity may also be affected due to a change in the dehydrogenation and acid function of the catalyst because the coke deposition. However, the influence of propane conversion on the selectivity is very strong (Fig. 15). Hence, it is extremely difficult to bring out a direct effect of coke deposition, if any, on the product selectivity.

The increase in the $p - X/m - X$ and $p - X/o - X$ ratios due to the deactivation (Fig. 14) reveals that the deactivation results in an increase in the shape selectivity of the gallosilicate. This is mostly due to an increase in the resistance for intracrystalline diffusion, resulting from a partial and/or complete blockage of some of the channels of the gallosilicate due the presence of bulky coke molecules at the channel intersections and also from a blockage of some of the channel openings due to coke deposition on the external crystal surface. Since, the increase in the shape selectivity is gradual (Fig. 14), the coke is expected to be deposited gradually in the zeolite channels and/or on the external crystal surface.

Conclusions

This investigation leads to the following important conclusions on the influence of Si/Ga ratio on the acidity, activity/selectivity and deactivation due to coking of H-gallosilicate in the aromatization of propane.

1. The acidity/acid strength distribution and the catalytic activity/selectivity and deactivation due to coking in propane aromatization of H-gallosilicate (MFI) are strongly influenced by its Si/Ga ratio. The decrease in the Si/Ga ratio causes

— a substantial increase in the number (or density) of both total (measured by chemisorption of pyridine at 50°C) and strong (measured by chemisorption of pyridine at 400°C) acid sites, with an appreciable increase also in the external (or intercrystalline) acidity measured by the isooctane cracking (at 400°C).

— a large increase in the nonframework Ga resulted from the degalliation of the zeolite during its calcination for removing the organic template occluded in the zeolite channels and also its deammoniation (the stability of the zeolite against its degalliation is increased with increasing its framework Si/Ga ratio).

— a large increase in the propane conversion (both total and to aromatics), propylene and aromatics selectivity and aromatics/(methane + ethane) ratio.

— a large increase in the dehydrogenation/cracking activity of the zeolite.

— a substantial increase of ethylene/ethane ratio but a decrease in C_1/C_2 mole ratio.

— a large increase in the rate of catalyst deactivation.

2. A good linear correlation exists between the catalytic activity of the zeolite in the toluene disproportionation and isooctane cracking reactions and its strong acidity. The acidity also shows an excellent linear relationship with the framework (i.e., tetrahedral) Ga in the zeolite; the strong acid sites/FW-Ga for all the gallosilicates is nearly 1.

3. The propane conversion activity, dehydrogenation/cracking activity ratio and aromatics selectivity are increased pronouncely with increasing the density of the acid sites (measured in terms of the pyridine chemisorbed at 400°C) and also of the nonframework Ga of the zeolite. The poisoning of the acid sites has also revealed the importance of the zeolitic acid sites in the propane aromatization. Hence, for obtaining high propane conversion with high aromatics yield/selectivity, the zeolite should contain high density zeolitic acid sites along with a substantial amounts of well dispersed nonframework Ga. The high dehydrogenation activity of the zeolite is attributed to the nonframework Ga, probably in combination with the zeolitic acidity.

4. The catalyst deactivation in the propane aromatization is mostly due to the coke deposition on the gallosilicate. Apart from causing a decrease in the catalytic activity, the catalyst deactivation due to coking results in a substantial decrease in the aromatics selectivity but an appreciable increase in the propylene selectivity. The changes in the selectivity are, however, attributed mainly to the decrease in the propane conversion due to the deactivation.

5. The shape selectivity of the gallosilicate is increased due to the deactivation. This is expected mostly due to an increase in the intracrystalline diffusional resistance by the presence of bulky coke molecules at the channel intersections causing blockage of the acid sites and the nonframework Ga and also at the outer crystal surface blocking some of the channel openings.

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