

Acidity, Catalytic Activity, and Deactivation of H-Gallosilicate (MFI) in Propane Aromatization: Influence of Hydrothermal Pretreatments

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Effect of various hydrothermal pretreatments [at different temperatures (400–800°C) and concentrations of steam (13–80 mol%) or with liquid water at 150°C under autogenous pressure] to H-gallosilicate (MFI) zeolite (bulk Si/Ga = 33 and Na/Ga = 0.1) on its acidity/acid strength distribution (determined by chemisorption and step-wise thermal desorption of pyridine from 100–400°C), acid function (studied by acid catalyzed model reactions viz. isooctane cracking for external acidity and *o*-xylene isomerization and toluene disproportionation for internal or intracrystalline acidity), and deactivation due to coking in propane aromatization (at 550° and time-on-stream of 8.5 ± 0.5) has been thoroughly investigated. With the increase in the severity of hydrothermal treatment to the zeolite, its crystallinity, framework (FW) Ga (observed by ⁷¹Ga and ²⁹Si MAS NMR and FTIR), acidity (measured in terms of the pyridine chemisorbed at 400°C and activity in the model reactions), and catalytic activity in the propane aromatization are decreased, but its deactivation due to coking and shape selectivity are increased appreciably. These effects are attributed to the extensive degallation of the zeolite due its hydrothermal treatments. Its product selectivity, dehydrogenation/cracking (D/C) activity ratio, and aromatics/(methane + ethane) mass ratio in the propane aromatization are also influenced by its hydrothermal treatments, depending upon the conversion. The product and shape selectivity of the zeolite are also affected by its deactivation due to coking. The influence of hydrothermal treatments on the activity/selectivity and catalyst deactivation are attributed to a combined/complex effect produced by the decreased zeolitic acidity (i.e., FW Ga) and increased non-FW Ga oxide species in the zeolite channels, depending upon the severity of hydrothermal treatment. The hydrothermal stability of H-gallosilicate (MFI) is much lower than that H-ZSM-5.

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INTRODUCTION

H-Gallosilicate having MFI structure (H-GaMFI) shows high aromatization activity/selectivity in the aromatization

of lower alkanes (1–7), which is a process of great commercial importance. An isomorphous substitution of Ga for Al in H-ZSM-5 results in an enhancement of the primary dehydrogenation activity of the zeolite and also an appreciable decrease in the primary cracking/dehydrogenation rate ratio, thus causing a large increase in its alkane aromatization activity (3, 6, 8). Non-FW Ga species, when existing in close proximity with the FW Ga, are found to be the active Ga species (2, 3, 5, 6). The non-FW Ga species in the zeolite may be formed during its hydrothermal synthesis and/or thermal and hydrothermal pretreatments (3, 6, 9–11).

Earlier studies (12) reveal that hydrothermal treatment under different conditions to H-ZSM-5 results in appreciable changes in its acidity and catalytic properties. Since H-GaMFI is expected to be hydrothermally less stable, as compared to H-ZSM-5, it is very interesting to study in detail the influence of various hydrothermal treatments to H-GaMFI zeolite under different conditions on its acidity/acid strength distribution, acid catalysis function, activity/selectivity, shape selectivity, and deactivation due to coking in the propane aromatization process. The present work was undertaken for this purpose.

EXPERIMENTAL

The various hydrothermal pretreatments (at different temperatures and partial pressures of steam and also with liquid water at 150°C under autogenous pressure) given to H-GaMFI (bulk Si/Ga = 33, crystal size = 6–7 μm and Na/Ga = 0.1) are given in Table 1. The hydrothermal treatment with steam was carried out by passing a steam–N₂ mixture with a total gas hourly space velocity of about 5000 h⁻¹ over the zeolite in a quartz reactor for 4 h at different temperatures (400–800°C) and concentrations of steam (13–80 mol%). The H-GaMFI was prepared by synthesizing TPA-GaMFI by its hydrothermal crystallization from a gel (pH 9–10) consisting of Na-trisilicate (Fluka), gallium nitrate (Aldrich), tetrapropyl ammonium bromide (TPABr) (Aldrich), sulfuric acid (AnalaR, BDH),

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TABLE 1

Distribution of Aromatics Formed and Coke Deposition in the Propane Aromatization over H-GaMFI Treated Hydrothermally under Different Conditions

Hydrothermal treatment		Water vapors in feed (mol%)	Distribution of aromatics (wt%)				Coke deposition wt% carbon
Temp. (°C)	Concn. of steam (mol%)		Benzene	Toluene + ethyl benzene	Xylenes	C ₉₊	
400	48.0	0.0	45.8 ± 1.1 ^a	34.5 ± 0.5 ^a	17.3 ± 0.4 ^a	2.5 ± 1.3 ^a	1.57
600	0.00	0.0	47.5 ± 0.8 ^a	33.2 ± 1.0 ^a	15.5 ± 0.6 ^a	2.8 ± 0.8 ^a	1.69
600	13.0	0.0	48.2 ± 1.2 ^a	34.2 ± 0.5 ^a	15.5 ± 0.7 ^a	2.1 ± 0.3 ^a	1.63
600	48.0	0.0	57.7 ^b –72.6 ^c	32.0 ^b –24.1 ^c	10.3 ^b –3.3 ^c	0.0	1.50
600	80.0	0.0	64.1 ^b –89.4 ^c	25.6 ^b –10.6 ^c	10.0 ^b –3.6 ^c	0.0	1.28
800	48.0	0.0	—No formation of aromatics—				0.18
600	0.00	4.0	43.3 ± 0.5 ^a	39.5 ± 0.7 ^a	15.6 ± 0.8 ^a	1.4 ± 0.2 ^a	1.37

^a Distribution not affected significantly due to the deactivation.

^b Initial (i.e., for fresh catalyst).

^c Final (i.e., for deactivated catalyst).

and demineralized water in a stainless steel autoclave at 180°C for 24 h. The zeolite crystals were then washed, dried, and calcined at 550°C for 15 h in static air to remove the occluded organic template. The zeolite was exchanged with 1 M ammonium nitrate solution at 80°C for 1 h four times, dried at 120°C for 4 h, pressed binder-free, and crushed to particles of 0.2–0.3-mm size. Finally it was calcined to convert its NH₄ form to H form at 600°C in static air for 4 h. The MFI framework structure of the gallosilicate was confirmed by the XRD and FTIR analysis and its composition was determined by chemical analysis.

The hydrothermally treated zeolite samples were characterized by XRD (using a Phillips diffractometer-1700 series and a CuK α radian), FTIR (using a Perkin–Elmer FTIR-1600 series), SEM (using a JOEL scanning electron microscope), and ²⁹Si and ⁷¹Ga MAS NMR (using a Bruker MSL300 MHz NMR, 2 μ sec pulse, a flip angle of 45°, and samples spun at 3–3.5 kHz).

The acidity/acid strength distribution on the samples was determined by measuring the chemisorption and stepwise thermal desorption (STD) of pyridine (chemisorbed at 100°C) from 100 to 400°C in a number of temperature steps (viz. 100–175, 175–250, 250–325, and 325–400°C) by using the GC adsorption/desorption techniques (13, 14). The determination of acidity/acid strength distribution of zeolites by the GC methods was described in detail earlier (7, 13, 14). The chemisorption of pyridine has been defined as the amount of pyridine retained by a presaturated zeolite after it is swept with pure nitrogen for a period of 1 h.

The acid function of the zeolite samples was studied by carrying out acid catalyzed model reactions, viz. isooctane cracking (at 400°C) for studying external acidity and *o*-xylene isomerization (at 400°C) and toluene disproportion-

ation (at 500°C) for measuring overall acidity, over them in a pulse microreactor (made up of quartz, 4.5-mm i.d., 6.0-mm o.d., and containing 0.1 g zeolite) connected to a gas chromatograph. The pulse reactions were carried out by injecting a pulse (0.4 μ l) of isooctane (at 400°C), *o*-xylene (at 400°C), and toluene (at 500°C) in the microreactor and analyzing the reaction products by a Varian GC with FID, computing integrator, and Benton-34 (5%) dinonylphthalate (5%) on a Chromosorb-W column (3 mm \times 5 m), using moisture-free N₂ (>99.99%) as a carrier gas. The detailed procedures for carrying out the pulse reactions and product analysis were described earlier (15, 16).

Time-on-stream activity/selectivity of the zeolite in the propane aromatization (at 550°C) was determined using a continuous flow quartz reactor (i.d. = 13 mm), packed with about 1 g particles of the zeolite and provided with a Cr–Al thermocouple located at the center (axially) of the catalyst bed, at atmospheric pressure, using a 33 mol% propane and 67 mol% N₂ gas mixture as a feed at a gas hourly space velocity of 3100 cm³ (at STP) \cdot g⁻¹ \cdot h⁻¹. The reaction products were analyzed by an on-line GC using PoropaK-Q (3 mm \times 3 m) and Benton-34 (5%) dinonylphthalate (5%) on Chromosorb-W (3 mm \times 5 m) columns for separating C₁–C₄ and aromatics, respectively. The carbon deposited on the catalyst was determined by microanalysis. The catalytic activity/selectivity data at different space velocities (440–121,000 cm³ \cdot g⁻¹ \cdot h⁻¹) were obtained in the absence of catalyst deactivation (i.e., initial activity/selectivity) at 550°C by carrying out the propane aromatization under steady state for a short period (2–5 min) and then replacing the reactant by pure N₂ during the period of product analysis by GC.

Before the catalytic reactions, the zeolite samples were

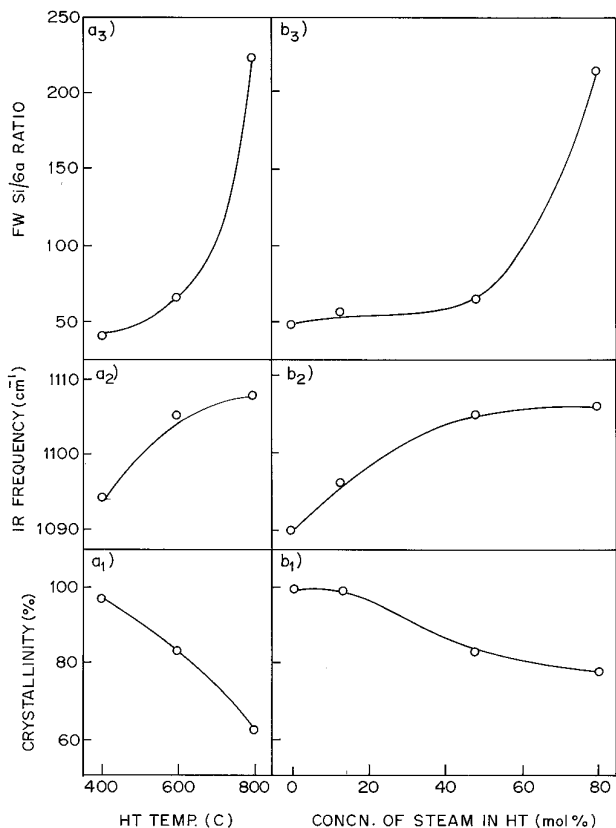


FIG. 1. Influence of (a) hydrothermal treatment (HT) temperature (concn. of steam: 48 mol%) and (b) concentration of steam in HT (at 600°C) on crystallinity, IR asymmetric stretching frequency, and framework Si/Ga ratio of H-GaMFI.

pretreated *in situ* under a flow of moisture-free N₂ 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 conversion and selectivity data are reproducible within 2–4% error.

RESULTS

Catalyst Characterization

The influence of the hydrothermal treatments (HT) at different temperatures and concentrations of steam on the crystallinity, IR asymmetric stretching frequency, and framework Si/Ga ratio (estimated from ²⁹Si MAS NMR) of H-GaMFI zeolite is shown in Fig. 1. The zeolite crystallinity and FW Si/Ga ratio are very strongly affected by the severity of the treatment (i.e., HT at higher temperatures and/or concentrations of steam).

⁷¹Ga MAS NMR spectra of the hydrothermally treated

zeolite under different conditions are shown in Fig. 2. The intensity of the NMR peak for ⁷¹Ga is drastically reduced at the higher temperature and/or steam concentration of the treatment. No peak for ²⁷Al MAS NMR is observed.

The acid strength distribution on the hydrothermally treated zeolite at different conditions, measured by the STD of pyridine (initially chemisorbed at 100°C) from 100–400°C in different temperature steps, is presented in Fig. 3. The columns in this figure show acid strength distribution of the sites involved in the chemisorption at 100°C. Each column of the acid strength distribution represents the number of acid sites measured in terms of the pyridine desorbed in the corresponding temperature step. The acid strength of these sites is expressed in terms of the desorption temperature, T_d , which lies in the range of temperature, $T_1 < T_d \leq T_2$, in which the chemisorbed pyridine is desorbed. T_d^* corresponds to the temperature at which all the chemisorbed pyridine is desorbed (or it is the tempera-

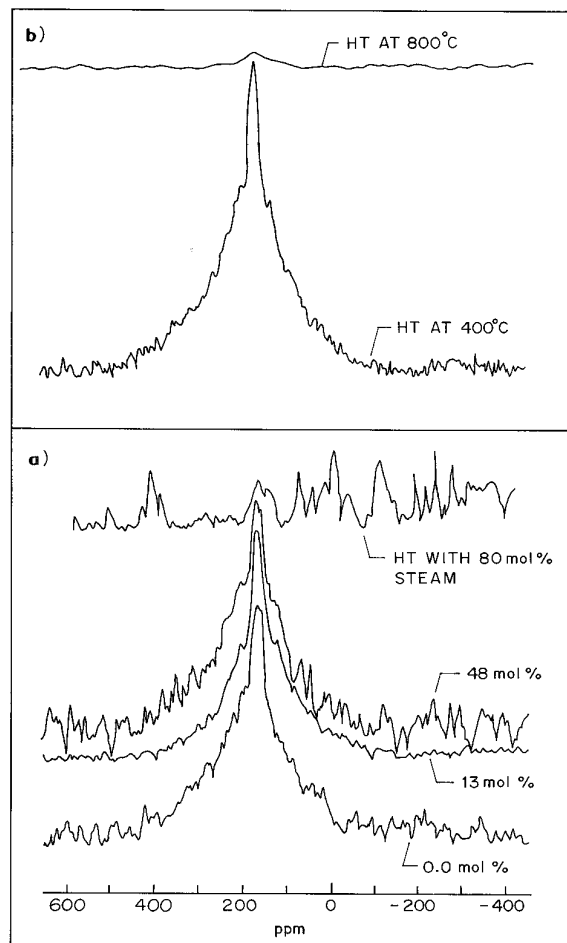


FIG. 2. ⁷¹Ga MAS NMR of H-GaMFI treated hydrothermally at 600°C with different concentrations of steam (a) and at 400 and 800°C with 48 mol% steam in N₂ (b).

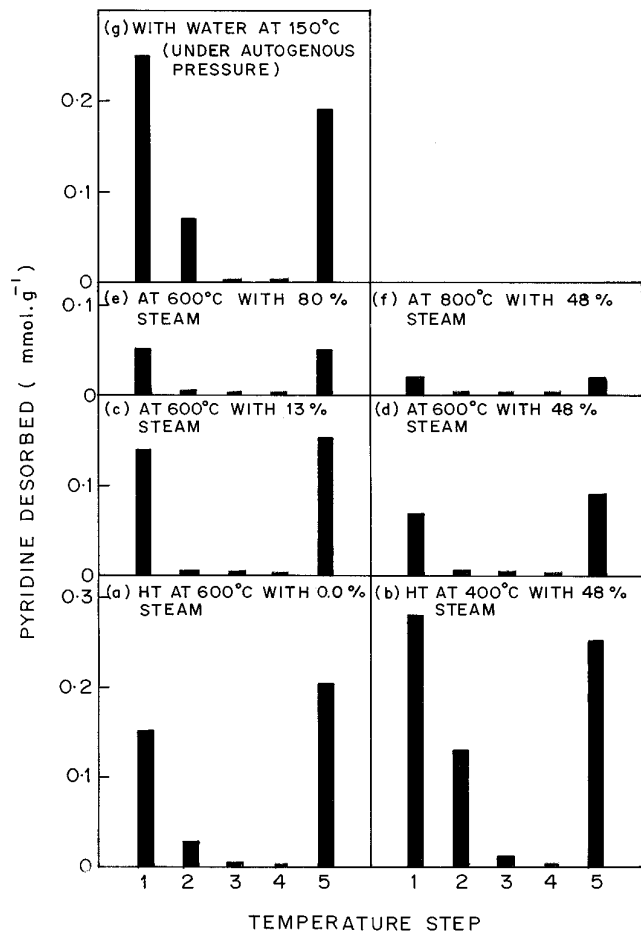


FIG. 3. STD of pyridine (chemisorbed at 100°C) on H-GaMFI treated hydrothermally under different conditions [Temperature steps: (1) $100 < T_d \leq 175^\circ\text{C}$, (2) $175 < T_d \leq 250^\circ\text{C}$, (3) $250 < T_d \leq 325^\circ\text{C}$, (4) $325 < T_d \leq 400^\circ\text{C}$, (5) $400 < T_d \leq T_d^*$].

ture at which pyridine is not chemisorbed). The data for $400 < T_d \leq T_d^*$ were obtained as the chemisorption of pyridine at 400°C, measured by the GC pulse technique (12). A variation of the pyridine chemisorption with temperature is shown in Fig. 4.

Both the STD of pyridine and the chemisorption of pyridine at different temperatures (Figs. 3 and 4) reveal that the acid strength distribution on the zeolites is quite broad and it is strongly influenced by the HT conditions. Figures 5a and 5b show a sharp decrease in the strong acid sites (measured in terms of the pyridine chemisorbed at 400°C) with an increase in HT temperature or concentration of steam in the HT. The treatment of the zeolite with liquid water at 150°C under autogenous pressure also causes a decrease in the strong acidity (Fig. 4). The strong acidity of the zeolite is directly proportional to its FW Ga (Fig. 5c).

H-GaMFI (bulk Si/Ga = 33) and H-AlMFI (or H-ZSM-

5) (bulk Si/Al = 34) zeolites are compared in Table 2 for the influence of HT on their stability against structural break down, degallation, or dealumination and also for a decrease in their strong acidity due to the HT with 48 mol% steam at different temperatures. The comparison clearly shows that the hydrothermal stability of H-GaMFI is much lower than that of H-ZSM-5.

Acid Catalyzed Model Reactions

The influence of the HT conditions on the external (i.e., intercrystalline) acidity of the zeolite has been investigated by the isooctane cracking (at 400°C) reaction and on the overall acidity (i.e., both the external and internal) by the *o*-xylene isomerization (at 400°C) and toluene disproportionation (at 500°C) reactions.

Figure 6a shows a sharp decrease in the isooctane cracking activity and consequently in the external acidity of the zeolite with an increase in the severity of the HT treatment. The results in Fig. 6b show that the xylene conversion is decreased with increased HT temperature or the concentration of steam in HT. The influence on the catalytic activity due to the increase in the HT temperature is, how-

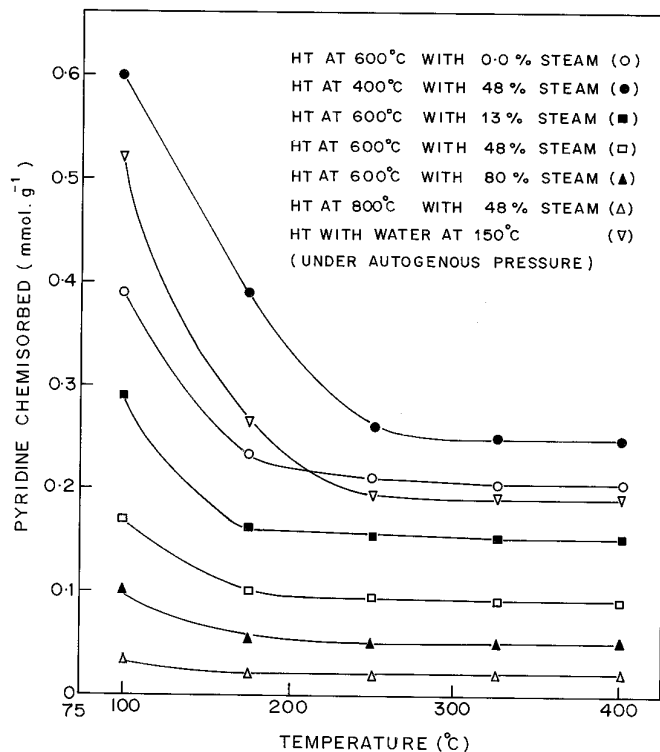


FIG. 4. Temperature dependence of the chemisorption of pyridine on H-GaMFI treated hydrothermally under different conditions. [HT at 600°C with 0.0 mol% steam (○), HT at 400°C with 48 mol% steam (●), HT at 600°C with 13 mol% steam (■), HT at 600°C with 48 mol% steam (□), HT at 600°C with 80 mol% steam (▲), HT at 800°C with 48 mol% steam (△), HT with water at 150°C (under autogenous pressure).]

TABLE 2

Comparison of H-GaMFI and H-AlMFI Zeolites Hydrothermally Treated with 48 mol% Steam at Different Temperatures for Their Crystallinity, FW Composition, and Strong Acidity

Hydrothermal treatment temp. (°C)	Crystallinity (%)		FW Si/(Ga or Al) ratio		Strong acidity (mmol · g ⁻¹)	
	H-GaMFI	H-AlMFI	H-GaMFI	H-AlMFI	H-GaMFI	H-AlMFI
400	97	100	44	37	0.24	0.26
600	83	99	64	51	0.09	0.20
800	62	92	224	66	0.04	0.14

ever, very large. The toluene conversion activity is also decreased with increased severity of the HT. The catalytic activity of the zeolite in all these reactions is also decreased but to a small extent due to its pretreatment with liquid water at 150°C under autogenous pressure.

A variation in the catalytic activity in the *o*-xylene and toluene conversion reactions with the strong acidity (measured in terms of pyridine chemisorbed at 400°C) of the zeolite is shown in Fig. 7. A linear correlation between the catalytic activity and the strong acidity is observed for both the reactions over the zeolite.

Time-on-Stream Activity/Catalyst Deactivation in Propane Aromatization

Influence of HT on deactivation kinetics. Variation of propane conversion (at 550°C), total and to aromatics, over the zeolite pretreated hydrothermally under different conditions with the time-on-stream is presented in Fig. 8. The catalyst deactivation rate is affected by the HT conditions. The dependence of the deactivation rate constant, k_d , on the HT temperature and concentration of steam is shown in Fig. 9. The deactivation rate constant was estimated from linear plots of $\ln\{\ln[1/(1-x)]\}$ vs time-on-stream (where, x is fractional conversion) according to the following rate expression for the case of a first-order catalyst deactivation in a plug flow fixed-bed reactor (17):

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

For both the propane conversion and aromatization, k_d is increased with increased HT temperature and concentration of steam. However, the deactivation rate is reduced very significantly when water vapors (4 mol%) are added to the feed in the propane aromatization (Fig. 8); the value of k_d is found to be 0.04 h⁻¹ for the total propane conversion and 0.07 h⁻¹ for the propane-to-aromatics conversion. In this case the zeolite was not pretreated with steam but the HT occurs continuously during the reaction over the zeolite.

In our earlier study (7), it was shown that the deactivation of H-GaMFI in the propane aromatization process is mainly due to the coke formation on the catalyst. The amount of coke deposited on the zeolite (pretreated hydrothermally at different conditions) during its time-on-stream of 8.5 ± 0.5 h is given in Table 1.

Influence of HT and time-on-stream on product selectivity. The effect of time-on-stream (or extent of catalyst deactivation) on the selectivity for aromatics, propylene, ethylene, ethane, and methane in the aromatization of propane over the zeolite pretreated hydrothermally at different concentrations of steam (at 600°C) and temperatures

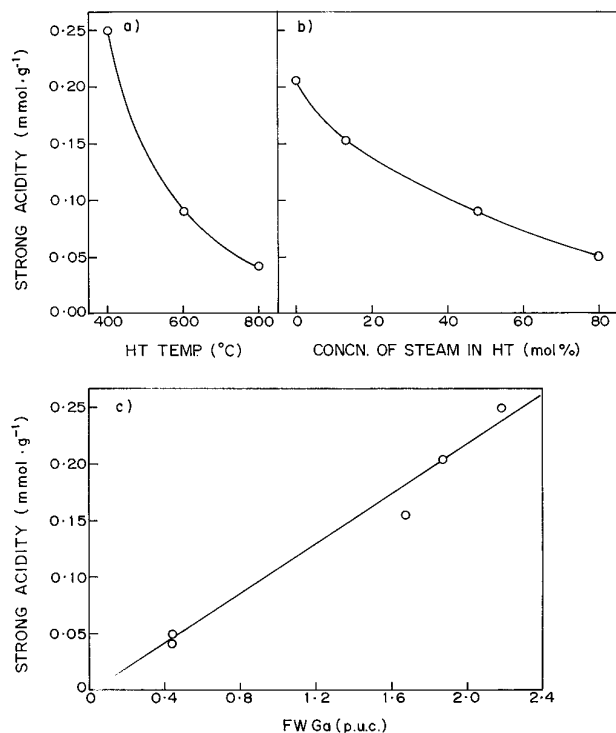


FIG. 5. Influence of (a) HT temperature (concn. of steam: 48 mol%), (b) concentration of steam in HT (at 600°C), and (c) framework (FW) Ga on the strong acidity of H-GaMFI.

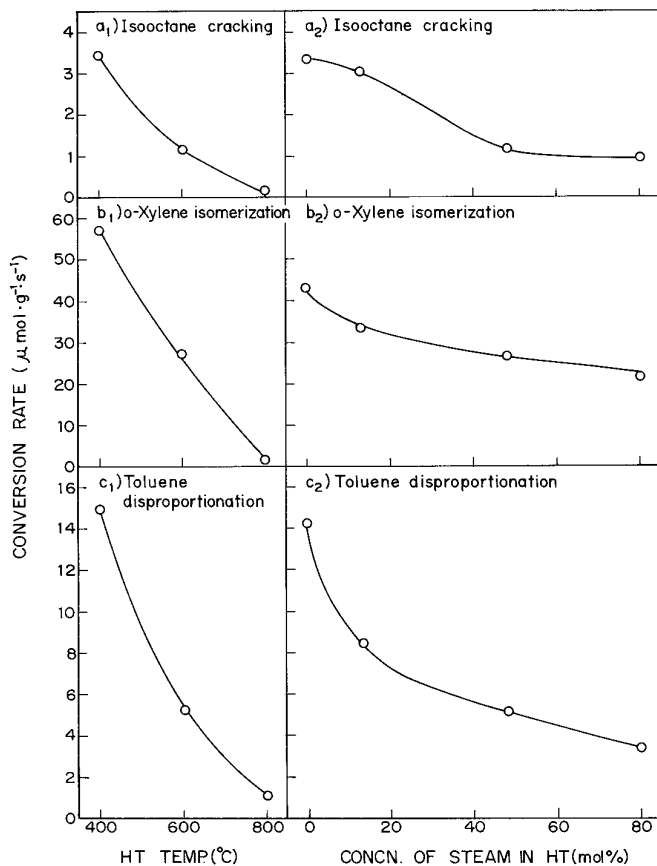


FIG. 6. Influence of HT temperature (concn. of steam: 48 mol%) and concentration of steam in HT (at 600°C) on the conversion rate in (a) isooctane cracking (at 400°C), (b) *o*-xylene isomerization (at 400°C), and (c) toluene disproportionation (at 500°C) reactions.

(with 48 mol% steam) is shown in Figs. 10 and 11, respectively. In general, the propylene selectivity is increased and the aromatics selectivity is decreased appreciably with increased time-on-stream. The effect of time-on-stream on the selectivity for C₁ and C₂ hydrocarbons depends upon the HT condition and it is relatively smaller. However, the aromatic selectivity is very strongly influenced by the HT condition; there is a large increase in the propylene selectivity but a large decrease in the aromatic selectivity with an increase in the HT temperature and/or concentration of steam. No formation of aromatics is observed for the zeolite pretreated with 48 mol% steam at 800°C.

The distribution of aromatics formed in the propane aromatization is presented in Table 1. The aromatic distribution is strongly affected by the HT condition. The distribution, except for the zeolite pretreated at 600°C with 48 and 80 mol% steam, is not affected significantly due to the catalyst deactivation. For the zeolite pretreated with 48 and 80 mol% steam at 600°C, the concentration of benzene in the aromatics is increased while that of toluene and C₈-aromatics is decreased with increased catalyst deactivation.

Since the selectivity in propane aromatization depends on the conversion (6, 7), which is decreased with increased time-on-stream (Fig. 8), the observed influence of the time-on-stream or catalyst deactivation on the selectivity (Figs. 10, 11) is quite apparent. Hence, in order to know the influence of deactivation on the product selectivity, the fresh and deactivated catalysts are to be compared at all the same conversion level. The fresh and deactivated (extent of deactivation ≈ 40%) zeolite, pretreated hydrothermally under the different conditions (or having different non-FW Ga/FW Ga ratios), are compared in Table 3 for their selectivity for aromatics, propylene, and C₁ + C₂ hydrocarbons and also for their dehydrogenation/cracking (D/C) and aromatization/cracking (A/C) activity ratios [D/C activity ratio = (100 = selectivity for C₁ and C₂)/(selectivity for aromatics) and A/C activity ratio = (selectivity for aromatics)/(selectivity for C₁ and C₂)] and *p*-X/*m*-X ratio, at nearly the same propane conversion. The comparison reveals that for the zeolite pretreated hydrothermally under mild conditions (or for those zeolites with non-FW Ga/FW Ga ratio ≤ 0.68), because of the deactivation, the selectivity for aromatics and propylene is decreased but that for C₁ + C₂ hydrocarbons (i.e., propane cracking products) is increased; the D/C and A/C activity ratios are also decreased appreciably. However, when the severity of HT

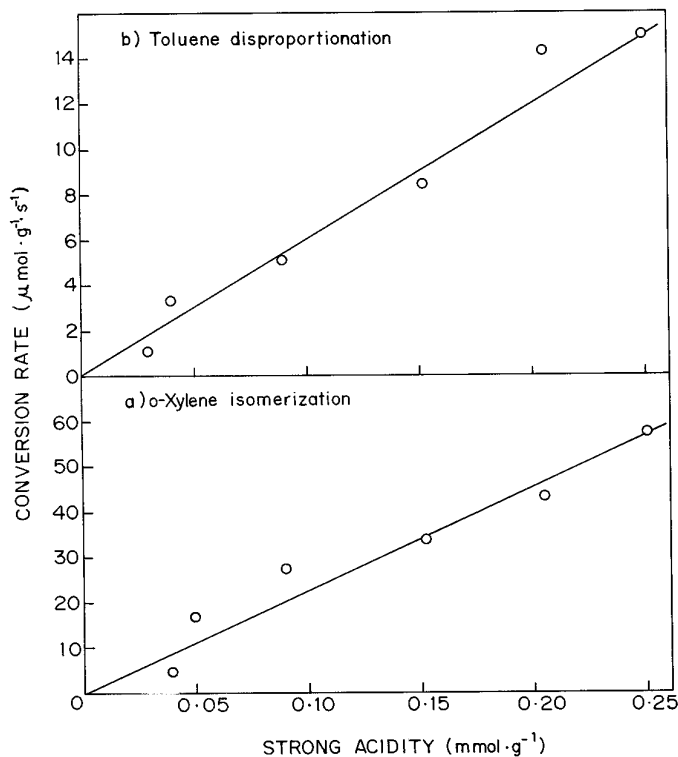


FIG. 7. Relationship between the strong acidity and catalytic activity of the hydrothermally treated H-GaMFI in (a) *o*-xylene isomerization and (b) toluene disproportionation.

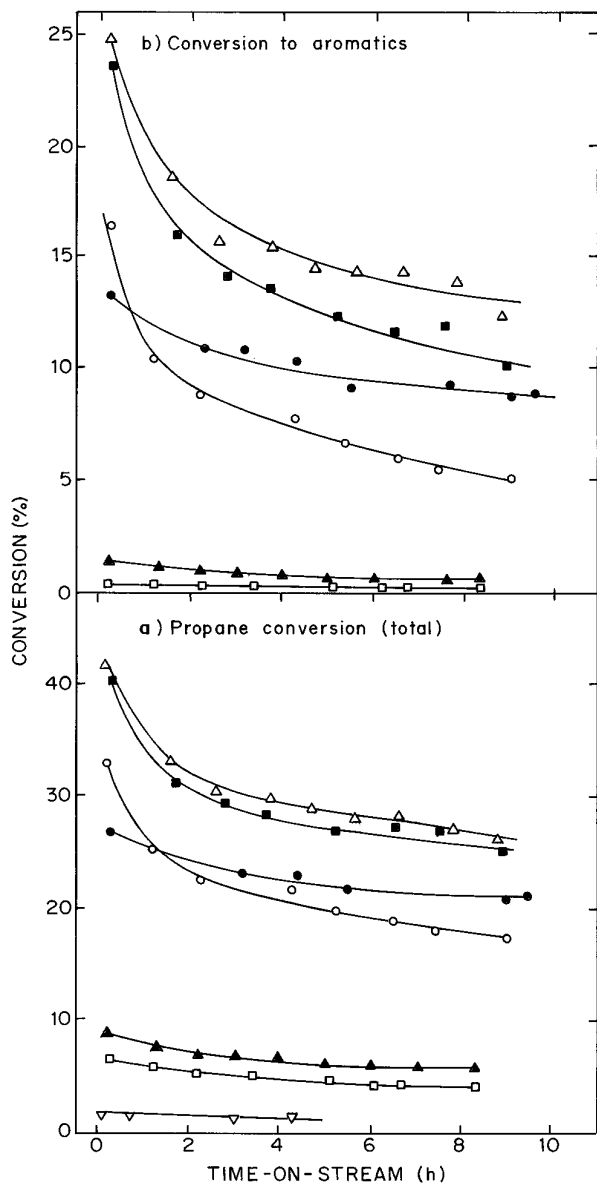


FIG. 8. Variation with time-on-stream of (a) propane conversion and (b) conversion to aromatics in the propane aromatization over H-GaMFI pretreated hydrothermally under different conditions (■, without HT; ●, without HT but with 4.0 mol% vapors in the feed; △, HT at 400°C with 48 mol% steam; ○, HT at 600°C with 13 mol % steam; ▲, HT at 600°C with 48 mol% steam; □, HT at 600°C with 80 mol% steam; and ▽, HT at 800°C with 48 mol% steam).

to the zeolite is increased (i.e., when non-FW Ga/FW Ga ratio ≥ 0.88), the influence of the catalyst deactivation on the product selectivity and activity ratios is reversed. Thus, the influence of catalyst deactivation on the selectivity of the zeolite pretreated hydrothermally is quite complex and depends strongly on the severity of HT.

Influence of HT and time-on-stream on shape selectivity. Results showing the influence of HT and time-on-

stream on the p -X/ m -X and p -X/ o -X ratios in products of the aromatization over the zeolite are presented in Fig. 12. At the equilibrium, the p -X/ m -X and p -X/ o -X ratios (at 550°C) are 0.45 and 0.89, respectively. The results suggest that the para selectivity or shape selectivity of the zeolite is strongly influenced by the HT at different conditions. It is generally increased with increased severity of the treatment (Table 3 and Fig. 12) and also is increased with increased catalyst deactivation, depending upon the HT conditions (Fig. 12). The influence of catalyst deactivation on the shape selectivity is increased with increased severity of the HT. A comparison of the fresh and deactivated zeolite samples for their p -X/ m -X ratio at nearly the same conversion further confirms the increase in the shape selectivity of the zeolite due to the catalyst deactivation.

Initial Activity in Propane Aromatization

Figure 13 shows that the initial catalytic activity for propane conversion (both total and to aromatics) is sharply decreased with increased temperature or concentration of steam in the hydrothermal pretreatment. The initial activity data were obtained by extrapolating the time-on-stream activity data to zero time-on-stream. These results are consistent with that obtained using a pulse microreactor (18).

Variation in the propane conversion activity with the strong acidity (measured in terms of pyridine chemisorbed at 400°C) and FW Ga/(FW Ga + non-FW Ga) ratio of the zeolite treated hydrothermally under the different con-

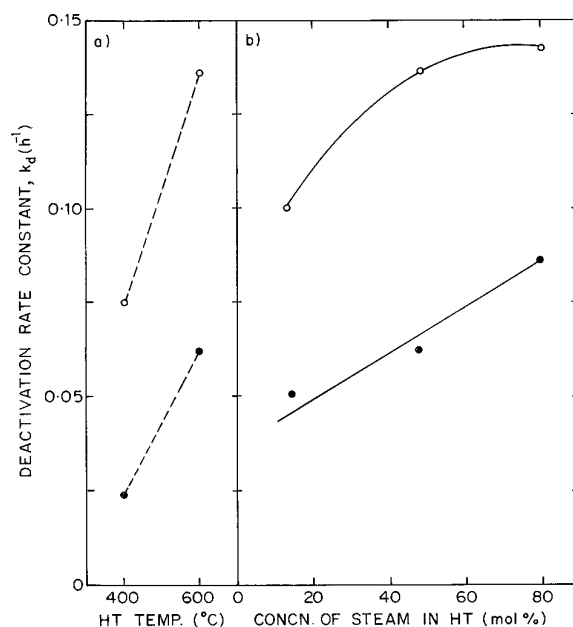


FIG. 9. Influence of (a) HT temperature (concn. of steam: 48 mol%) and (b) concentration of steam in HT (at 600°C) on the deactivation rate constant (k_d) for total conversion (●) and conversion to aromatics (○) in the propane aromatization over H-GaMFI.

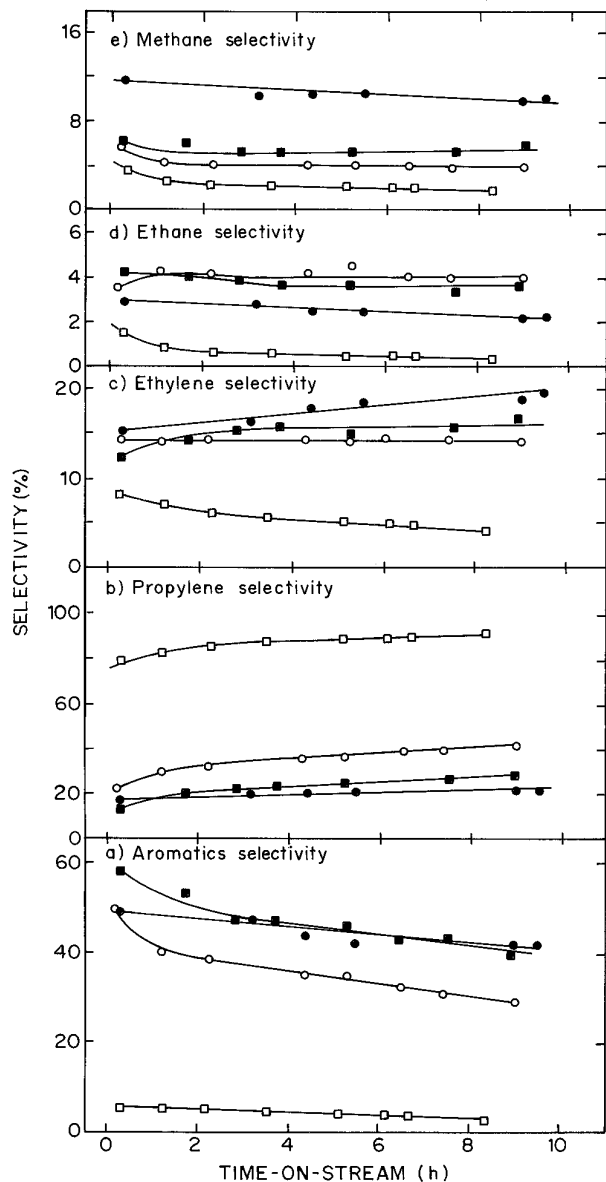


FIG. 10. Variation with time-on-stream of the product selectivity in the propane aromatization over H-GaMFI pretreated at 600°C with steam at different concentrations (■, without HT; ●, without HT but 4.0 mol% water vapors in feed; ○, HT with 13 mol% steam; and □, HT with 80 mol% steam).

ditions is shown in Fig. 14. The activity is increased with increased acidity or the FW Ga of the zeolite; the increase in the activity follows an S-type curve in both the cases. This reveals the importance of the acidity or FW Ga of the zeolite in the propane aromatization.

Initial Selectivity in Propane Aromatization

Because of a strong dependence of the selectivity in propane aromatization on the conversion (6, 7), the

zeolite catalysts are compared for their selectivity for aromatics and propylene, D/C activity ratio, and aromatics/(methane + ethane) mass ratio at the same conversion. Results showing the influence of HT conditions on the selectivity, activity, and product ratios at the propane conversion of 5, 15, and 30% are presented in Figs. 15 and 16. The aromatics/(methane + ethane) ratio at all the conversions is decreased with increased severity of the HT. The D/C activity ratio is also decreased with increased

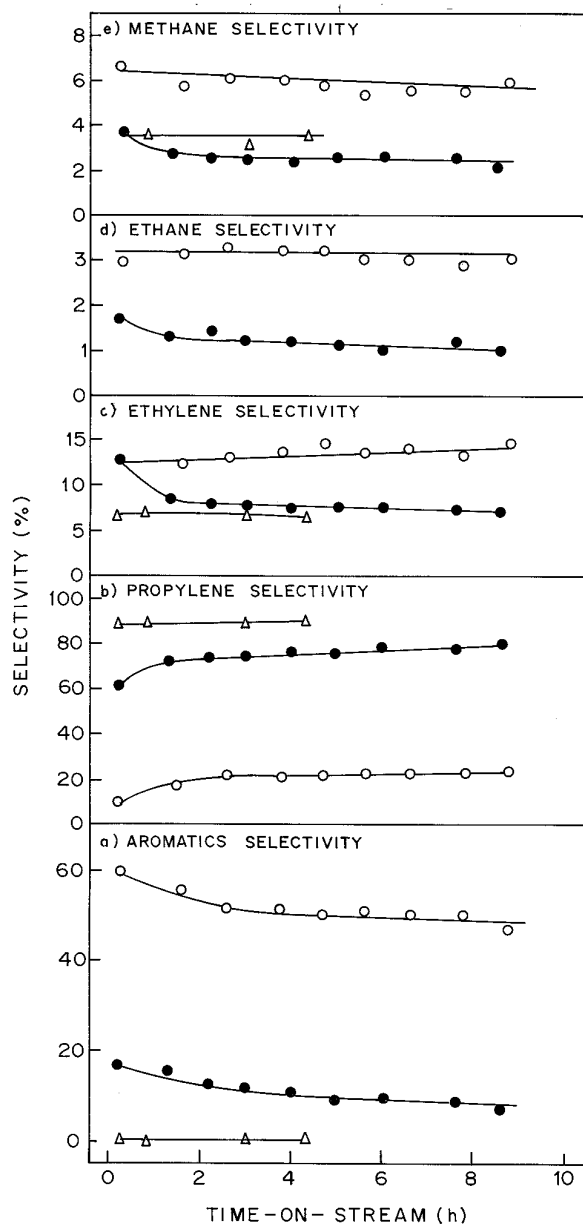


FIG. 11. Variation with time-on-stream of the product selectivity in the propane aromatization over H-GaMFI pretreated with 48 mol% steam at different temperatures (○, HT at 400°C; ●, HT at 600°C; and Δ, HT at 800°C).

TABLE 3

Influence of Catalyst Deactivation on the Selectivity, Dehydrogenation/Cracking (D/C) and Aromatization/Cracking (A/C) Activity Ratios, and Shape Selectivity (p -X/ m -X ratio) in the Propane Aromatization over H-GaMFI Treated Hydrothermally under Different Conditions

Temp. (°C)	Concn. of steam (mol%)	Non-FW Ga/FW Ga	Catalyst (Fresh or deactivated)	Propane conversion (%)	Selectivity (%)			Activity ratio		p -X/ m -X ratio
					Aromatics	Propylene	C ₁ + C ₂	D/C	A/C	
400	48.0	0.29	Deactivated (40.2%) ^a	26.0	47.2	24.3	23.4	3.27	20.1	0.55
			Fresh	25.8	49.3	27.7	19.5	4.10	2.53	0.44
600	00.0	0.50	Deactivated (40.4%) ^a	25.3	39.5	28.1	26.1	2.83	1.51	0.82
			Fresh	25.1	43.5	29.0	20.0	4.05	2.30	0.65
600	13.0	0.68	Deactivated (41.1%) ^a	17.8	28.7	41.8	22.2	3.50	1.30	2.0
			Fresh	17.6	29.2	43.1	18.0	4.65	1.60	1.2
600	48.0	0.88	Deactivated (40.0%) ^a	5.8	7.70	80.8	10.0	9.00	0.77	
			Fresh	6.0	6.20	75.5	15.2	5.60	0.41	
600	80.0	5.26	Deactivated (38.6%) ^a	4.3	2.90	91.0	6.3	14.9	0.46	
			Fresh	4.2	1.55	86.0	10.6	8.4	0.15	

^a Percentage of deactivation given in parentheses.

HT temperature but it is passed through a maximum with increased concentration of steam in HT, particularly for the lower conversions (at $x = 5\%$ and 15%). The observed maximum is decreased with increased conversion; it vanished at higher conversion ($x = 30\%$). The influence of HT on the selectivity for aromatics and propylene is, however, complex and also depends on the conversion.

Figure 17 shows a strong influence of non-FW Ga or FW Ga of the zeolite (non-FW Ga + FW Ga = constant) on the D/C activity and aromatics/(methane + ethane) product ratios. Both the activity and product ratios are passed through a maximum (between non-FW Ga of 30–45%) with increased non-FW Ga due to the HT, depending upon the conversion.

The results (Figs. 15–17) also show a strong influence of the conversion on the selectivity and also on the activity and product ratios. With the increase in the conversion, the aromatics selectivity is increased, the propylene selectivity is decreased, the D/C activity ratio is decreased, and the aromatics/(methane + ethane) ratio is increased. These observations are consistent with those made earlier (7).

Results in Fig. 18 and Table 3 show the strong influence of the non-FW Ga on the p -X/ m -X ratio (i.e., para selectivity) of the zeolite. The shape selectivity of the zeolite is increased pronouncedly with increased concentration of extra-FW Ga in the zeolite.

DISCUSSION

Influence of HT on FW-Si/Ga Ratio and Crystallinity

The sharp increase in the FW-Si/Ga ratio of H-GaMFI (Fig. 1) clearly shows heavy degallation of the zeolite depending upon the severity of the hydrothermal pretreatment. The determination of the FW Si/Ga ratio from ²⁹Si MAS NMR is not very accurate as the T sites in ZSM-5-type zeolites are crystallographically not identical (19). Nevertheless, the change in the FW-Si/Ga ratio is large and hence provides clear evidence for the degallation. The transformation of the FW Ga into non-FW Ga is further confirmed by observing the increase in the IR asymmetric stretching frequency (Fig. 1) as expected (5) and also by observing the decrease in the ⁷¹Ga MAS NMR peak intensity (Fig. 2). The observed large decrease on the zeolite crystallinity (Fig. 1), particularly under the severe HT conditions, reveals that during the degallation at high temperatures and concentration of steam the original crystal structure is distorted, leaving defected structure with lesser crystallinity.

Influence of HT on Acidity/Acid Function

The results (Figs. 3–5) reveal a very strong influence of HT on the acidity/acid strength distribution on the zeolite, depending upon the severity of the treatment. Both the

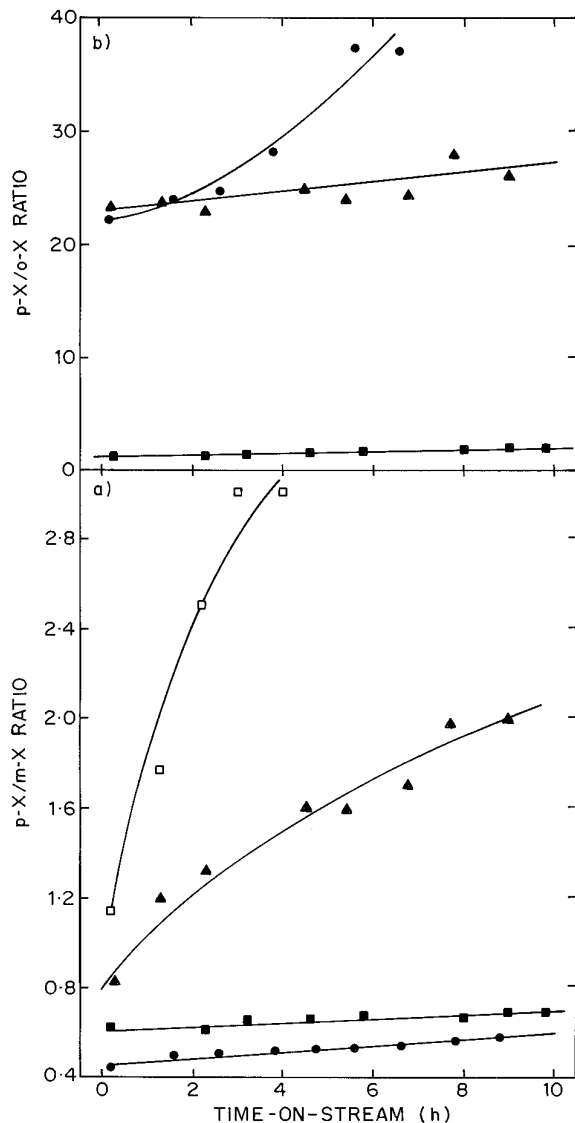


FIG. 12. Variation with time-on-stream of (a) p -X/ m -X and (b) p -X/ o -X product ratios in the propane aromatization over H-GaMFI pre-treated hydrothermally under different conditions (●, HT at 400°C with 48 mol% steam; ▲, HT at 600°C with 13 mol% steam; □, HT at 600°C with 48 mol% steam; and ■, without HT but 4.0 mol% water vapors in feed).

total and strong acid sites (measured in terms of the pyridine chemisorbed at 100 and 400°C, respectively) are decreased, except for the mild HT (at 400°C). The decrease in the acidity is further confirmed by observing the corresponding decrease in the catalytic activity of the zeolite in the model reactions catalyzed by acid sites (Fig. 6). There is a good linear correlation between the catalytic activity in the o -xylene and toluene conversion reactions and the strong acidity of the zeolite (Fig. 7). The observed sharp decrease in the acidity with an increase in the severity of

HT is obviously due to the degallation of the zeolite because, similar to H-ZSM-5 (20, 21), the acidity of H-GaMFI is attributed to the tetrahedral Ga in its frame work (7). Indeed, the acidity (measured by pyridine chemisorption at 400°C) is found to be directly proportional to the FW Ga (Fig. 5c). It may be noted that the decrease in the acidity for the HT at higher temperature (800°C) may also be to some extent due to the dehydroxylation of the zeolite apart from its degallation.

The external acidity is also decreased appreciably with increased severity of HT. It is characterized by the isooctane cracking reaction because isooctane cannot penetrate the ZSM-5-type zeolites even at 400°C (22, 23). Since, the isooctane cracking occurs on strong acid sites (22, 23), the decrease in the isooctane cracking activity provides information on the external strong acid sites. The decrease in the external acidity is expected to be mostly due to the degallation of FW Ga present on the external surface of the zeolite crystallites.

Influence of HT on Initial Activity/Selectivity and Deactivation in Propane Aromatization

The observed pronounced effect of the HT temperature and/or concentration of steam on the propane conversion and aromatization activity (Fig. 13) is a result of the exten-

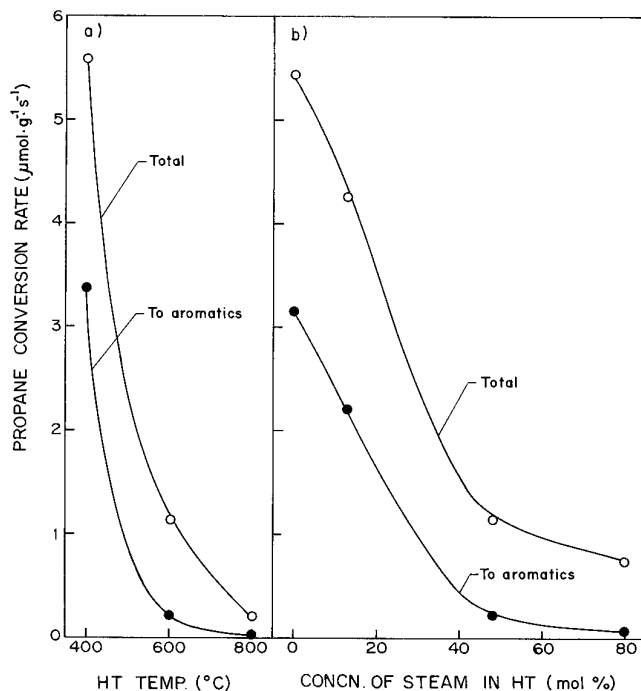


FIG. 13. Influence of (a) HT temperature (concn. of steam: 48 mol%) and (b) concentration of steam in HT (at 600°C) on the propane conversion rates (total and to aromatics) in the propane aromatization over H-GaMFI treated hydrothermally under different conditions.

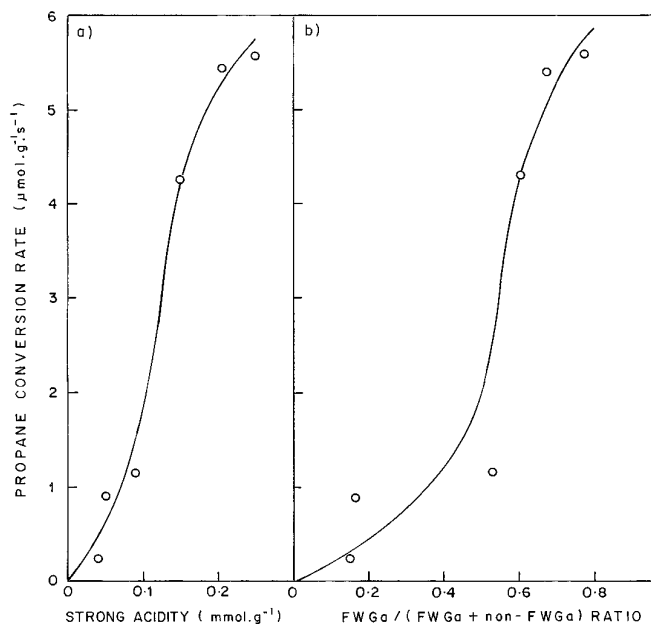


FIG. 14. Influence of strong acidity (a) and FW Ga/(FW Ga + non-FW Ga) ratio (b) on the propane conversion rate in the propane aromatization over H-GaMFI pretreated hydrothermally under different conditions.

sive degallation of the zeolite, causing large changes in its acidity and extra-framework Ga. The decrease in the acidity or FW Ga results in a large decrease in the propane conversion activity (Fig. 14). This indicates the importance of zeolitic acidity or FW Ga in the propane aromatization and supports our earlier conclusion that high concentration of zeolitic acid sites is essential for obtaining high propane-to-aromatics conversion (7).

The influence of HT on the product selectivity (compared at the same conversion) is quite complex (Figs. 15 and 16) and also it depends on the conversion. However, at all the conversions, the aromatics/(methane + ethane) ratio is decreased with increased severity of the HT. The D/C activity and aromatics/(methane + ethane) ratios (methane and ethane are undesirable products) are passed through a maximum with increased non-FW Ga in the zeolite (Fig. 17). The maximum in both the cases occurs at the non-FW Ga concentration of 30–45%. This suggests that to obtain a high aromatics/(methane + ethane) ratio an optimum concentration of non-FW Ga relative to that of FW Ga (i.e., zeolitic acid sites) is essential.

The non-FW Ga species formed in the HT are expected to be well-dispersed Ga_2O_3 and/or $[\text{GaO}]^+$. The results, showing a strong influence of the relative concentration of FW Ga and non-FW Ga in the zeolite on its activity (Fig. 14) and D/C activity and aromatic/(methane + ethane) ratios reveal that although the non-FW Ga species have high dehydrogenating activity (5, 6, 10) these species are

active only in combination/association with the zeolitic acid sites (or FW Ga) at high concentration. This is consistent with the earlier observations (5, 18, 24).

The observed large increase in the para-shape selectivity of the zeolite with an increase in the severity of the HT (or an increase in the non-FW Ga) (Fig. 18 and Table 3) is expected to be mostly due to the increased diffusional resistance resulting from the presence of non-FW Ga species (which causes a significant decrease in the effective channel diameter) in the zeolite.

The deactivation of the zeolite, which is mostly due to coking, is found to be increased with increased severity of HT (Figs. 8 and 9). This is attributed to the increased dehydrogenation activity of the zeolite due to formation of extra-framework Ga oxide species in the HT.

Because of the presence of water vapors in the feed, the propane conversion and aromatization activity of the zeolite decrease appreciably but the rate of catalyst deactivation is reduced. The decrease in the activity is attributed to the degallation and hence, to the reduction in the zeolitic acidity due to the hydrothermal treatment received by the zeolite during the reaction. As commonly observed,

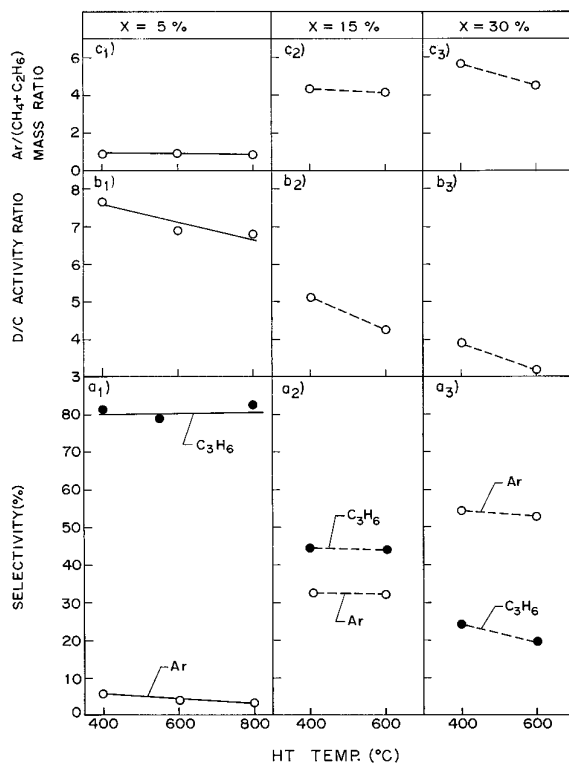


FIG. 15. Influence of HT temperature (concn. of steam: 48 mol%) on the selectivity for aromatics and propylene (a), dehydrogenation/cracking (D/C) activity ratio (b), and aromatics/(methane + ethane) mass ratio (c) at the propane conversion (X) of 5, 15, and 30% in the propane aromatization over hydrothermally treated H-GaMFI.

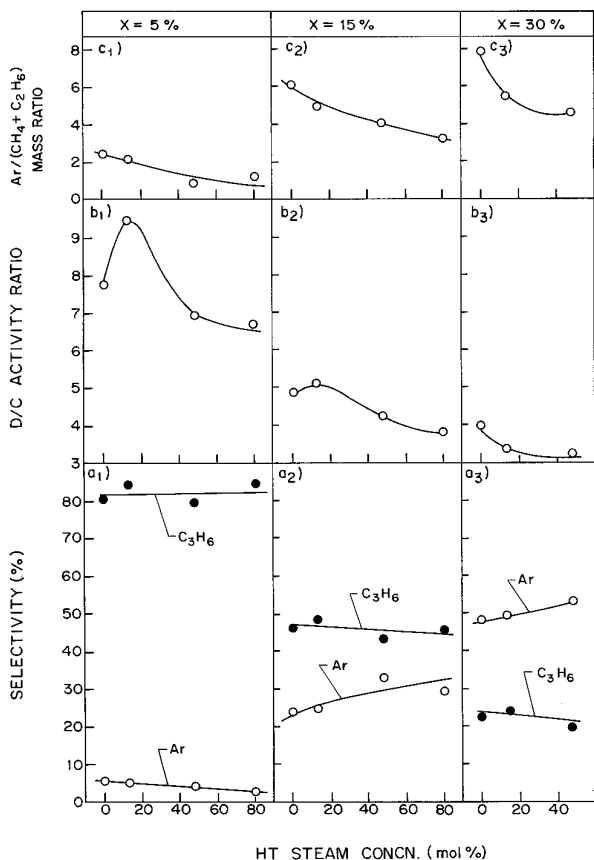


FIG. 16. Influence of steam concentration in HT (at 600°C) on the selectivity for aromatics and propylene (a), dehydrogenation/cracking (D/C) activity ratio (b), and aromatics/(methane + ethane) mass ratio (c) at the propane conversion (X) of 5, 15, and 30% in the propane aromatization over hydrothermally treated H-GaMFI.

the rate of coking (which is a cause of the catalyst deactivation) decreases due to the presence of steam in the reaction.

Influence of Deactivation on Product and Shape Selectivity in Propane Aromatization

Results in Figs. 10 and 11 show a strong influence of time-on-stream on the selectivity. Since the conversion is decreased appreciably with increased time-on-stream, the observed influence of the catalyst deactivation on the selectivity could also be due to the change in the conversion. However, the comparison of fresh and deactivated catalysts at the same conversion (Table 3) clearly shows the influence of catalyst deactivation on the selectivity for aromatics, propylene, and cracking products (i.e., C₁ + C₂ hydrocarbons), the D/C and A/C activity ratios, and the para shape selectivity of the zeolite.

It is interesting to note that the influence of catalyst deactivation is strongly dependent upon the severity of HT or non-FW Ga/FW Ga ratio. For the zeolite with a

lower non-FW Ga/FW Ga ratio (≤ 0.68), the dehydrogenation and aromatization activity relative to the cracking activity are decreased due to the deactivation, whereas an opposite trend is observed for the zeolite with a higher non-FW Ga/FW Ga ratio. It is also interesting to note that the distribution of aromatics formed is not changed significantly due to the catalyst deactivation for the zeolite treated hydrothermally under milder conditions but not for that treated under severe conditions (Table 1). These observations indicate that the activity/selectivity and deactivation of the zeolite pretreated hydrothermally are controlled by a combined effect (which is complex) produced by the decreased FW Ga (or zeolitic acidity) and the increased non-FW Ga species, which in the presence of acid sites are responsible for high dehydrogenation activity in the propane aromatization process (25, 11), due to the degallation of the zeolite.

The para-shape selectivity is increased with increased catalyst deactivation (Fig. 12 and Table 3); the influence of the catalyst deactivation on the shape selectivity is very strong particularly for the zeolite pretreated hydrother-

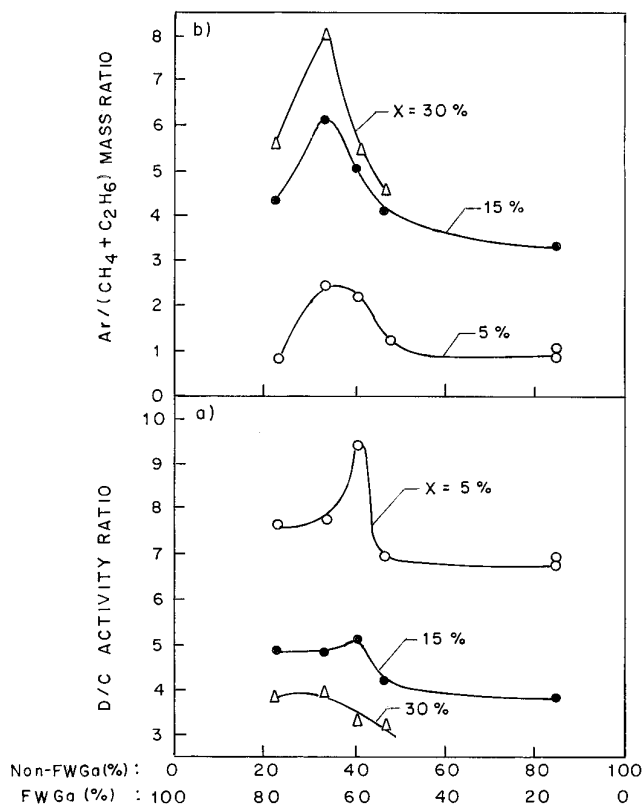


FIG. 17. Influence of FW Ga or non-FW Ga on the dehydrogenation/cracking (D/C) activity (a) and aromatics/(methane + ethane) mass ratios (b) [at the propane conversion (X) of 5% (\circ), 15% (\bullet), and 30% (Δ)] in the propane aromatization over H-GaMFI pretreated hydrothermally under different conditions.

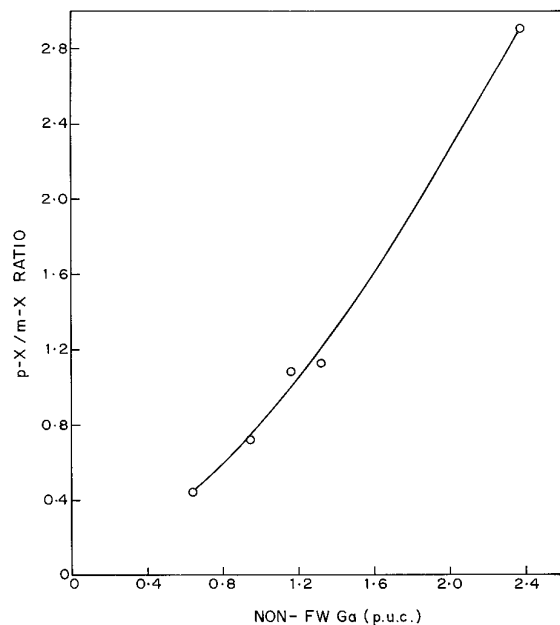


FIG. 18. Influence of non-FW Ga on the p -X/ m -X ratio in the propane aromatization (at 550°C and GHSV = 3100 cm³ · g⁻¹ · h⁻¹) over H-GaMFI pretreated hydrothermally under different conditions.

mally under more severe conditions (i.e., when the non-FW Ga/FW Ga ratio is very high). The increase in the shape selectivity due to the deactivation is expected to be most probably due to a partial or complete blockage of some of the channel openings on the external surface by the coke and also to some extent due to the presence of bulky or high molecular weight hydrocarbon molecules (or coke precursors) at the channel intersections, both causing an increase in the diffusional resistance in the zeolite. The diffusional resistance is expected to be increased further with increased non-FW Ga species in the zeolite due to reduction in its effective channel diameter.

Hydrothermal Stability of H-ZSM-5 and H-GaMFI

A comparison of the H-GaMFI and H-ZSM-5 zeolites (having nearly same Si/Ga or Al ratio) for their hydrothermal stability (Table 2) reveals that the former has much lower stability. Since the ionic radius of Ga³⁺ (0.62 Å) is larger than that of Al³⁺ (0.51 Å), the isomorphous substitution of Al by Ga is expected to result in a less stable MFI structure, more susceptible to degallation due to the thermal and/or hydrothermal treatments.

CONCLUSIONS

The following main conclusions were drawn from this investigation about the influence of various hydrothermal treatments on the acidity, activity/selectivity, and deactivation of H-GaMFI in propane aromatization.

(i) Both the total and the strong acidity (measured in terms of pyridine chemisorbed at 100 and 400°C, respectively) of H-GaMFI and also its external acidity are decreased sharply with increased severity of hydrothermal treatment (i.e., increased temperature and/or concentration of steam in the treatment) due to extensive degallation of the zeolite. The strong acidity is directly proportional to the FW Ga of the zeolite. A good correlation exists between the strong acidity and catalytic activity in the *o*-xylene isomerization and toluene disproportionation reactions.

(ii) The decrease in the acidity is reflected by the corresponding decrease in the propane conversion and aromatization activity of the zeolite. A close relationship exists between the strong acidity and the propane conversion/aromatization activity. The degallation of the zeolite due to its hydrothermal treatments causes not only a decrease in the zeolitic acidity (i.e., FW Ga) but also an increase in the non-FW Ga oxide species (which when in the association with the zeolitic acid sites are responsible for high dehydrogenation activity) dispersed uniformly in the zeolite channels. The activity/selectivity and deactivation of the zeolite in propane aromatization are controlled by a combined/complex effect produced by the decreased zeolitic acidity and increased non-FW Ga oxide species, depending upon the severity of the hydrothermal treatment or extent of degallation of the zeolite. The influence of degallation on the product selectivity and also on the dehydrogenation and aromatization activity relative to cracking activity is quite complex.

(iii) The deactivation rate in propane aromatization is increased with increased severity of the hydrothermal treatment, mostly due to an increase in its dehydrogenation activity. The product selectivity, dehydrogenation and aromatization activity relative to cracking activity, and parashape selectivity of the zeolite in propane aromatization are influenced appreciably by the catalyst deactivation due to coking. The influence of catalyst deactivation, however, depends strongly on the relative concentrations of FW and non-FW Ga in the zeolite.

(iv) The presence of water vapors in the feed causes a large decrease in the catalytic activity of the zeolite due to its degallation during the propane aromatization but also causes a decrease in the rate of catalyst deactivation.

(v) As compared to H-AlMFI (i.e., H-ZSM-5), H-GaMFI zeolite has lower hydrothermal stability for its FW Ga or zeolite acidity and crystal structure.

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