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Initial activity/selectivity of H-gallosilicate (MFI) in propane aromatization: influence of H^+ exchange and thermal/hydrothermal pretreatments

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Initial activity/selectivity of H-gallosilicate (MFI) zeolite with different degrees of H^+ exchange and pretreated under different thermal and hydrothermal conditions in propane aromatization (at 500°C) has been determined using a pulse microreactor connected to GC. It is found to be strongly influenced by the degree of H^+exchange, calcination temperature and hydrothermal treatment at different temperatures and concentrations of steam. There exists a close relationship between the acidity (measured in terms of pyridine chemisorbed at 400°C) of the gallosilicate and its initial propane conversion and aromatization activity. Presence of strong acidic sites (attributed to FW Ga) at high concentration is essential for the well dispersed non-FW Ga oxide species to be active for dehydrogenation in the propane aromatization over the zeolite.

Keywords: H-gallosilicate (MFI) zeolite; propane aromatization; acidity of zeolite; H^+ exchange of GaMFI; thermal pretreatments to H-GaMFI; hydrothermal treatments to H-GaMFI

1. Introduction

H-gallosilicate of ZSM-5 type (H-GaMFI) is known for its high activity/selectivity in the conversion of lower alkanes to aromatics [1–6], which is a process of great practical importance. This zeolite is found to be more effective than Ga/HZSM-5 in aromatization of *n*-hexane [2] and light alkanes [6,7]. The isomorphous

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substitution of Ga for Al in ZSM-5 results in a large increase in the primary propane dehydrogenation activity [8]. H-GaMFI zeolite contains also non-framework Ga-oxide species formed by its degalliation during its calcination [9] and/or hydrothermal treatment [3,10]. The non-framework Ga-oxide species provide strong Lewis acid sites (acid–base pair) responsible for the enhanced dehydrogenation activity [11]. However, these non-framework species are active only in cooperation with the framework gallium [5]. A favourable combination of Lewis and Brønsted acidity, is a necessary condition for an active selective catalyst in the aromatization of lower alkanes [12].

Although H-GaMFI shows high activity/selectivity, this catalyst is deactivated fast due to coke deposition in the alkane aromatization process [4,9]. Also, its catalytic activity in both the total conversion of propane and conversion of propane to aromatics is decreased due to high temperature H_2 pretreatment [9,13]. Since an appreciable amount of hydrogen is produced during the aromatization process over H-GaMFI zeolite [1,6], its activity in the alkane-to-aromatics conversion is expected to be changed not only because of the catalyst deactivation due to coking but also because of the changes in its intrinsic catalytic activity due to the H_2–catalyst interactions during the reaction. Hence, in order to know the influence of other factors affecting the catalytic activity of H-GaMFI, such as its degree of H^+ exchange and pretreatment conditions (viz. calcination temperature and hydrothermal treatments at different temperatures and partial pressures of steam), it is necessary to determine its initial activity. This can best be done using a pulse microreactor combined with GC [14]. The present investigation was undertaken to study the influence of degree of H^+ exchange and various pretreatment parameters which are expected to affect both the Brønsted acidity and the non-framework Ga on the initial activity/selectivity of H-GaMFI in the aromatization of propane in a pulse microreactor and also to find a corelation between the acidity and the initial catalytic activity of the zeolite.

2. Experimental

Gallosilicate (MFI) with Si/Ga ratio of 33 was synthesised by hydrothermal crystallization from a gel (at pH = 9–10) consisting of Na-trisilicate (Fluka), gallium nitrate (Aldrich), TPA-Br (Aldrich), sulfuric acid (AnalaR BDH) and demineralised water in SS bomb at 180°C for 24 h, washing, drying and calcining the zeolite crystals at 600°C in static air for 15 h to remove the occluded organic template, exchanging with 1 M ammonium acetate at 80°C, drying, pressing binder-free and crushing to particles of 0.2–0.3 mm size and again calcining in static air at 600°C for 4 h. The thermal and hydrothermal treatments given to H-GaMFI (H^+exchange = 90%) are listed in table 1. The MFI frame work structure of the GaMFI zeolites was confirmed by the XRD and FTIR analysis. The X-ray powder diffraction patterns were collected on a Philips PW 1730 instrument with Cu Kα

Table 1
Surface acidity of H-GaMFI (with different degrees of H^+ exchange and thermally and hydrothermally pretreated at different conditions) and distribution of aromatics formed in the propane aromatization

H^+ exchange (%)	Calc.[a] temp. (°C)	Hydrothermal treatment[b]		Crystallinity (%)	Non-FW Ga / FW Ga ratio	Strong acidity (mmol g^{-1})	Distribution of aromatics (wt%)		
		temp. (°C)	conc. of steam				B	T	X + EB
5	600	without HT		100	0.56	0.04	no aromatics formed		
55	600	without HT		100	0.56	0.16	39.5	59.3	1.2
70	600	without HT		100	0.56	0.18	66.8	32.5	0.7
90	600	without HT		100	0.56	0.21	58.9	36.3	4.8
90	750	without HT		100	1.25	0.09	80.6	19.4	0.0
90	900	without HT		95	very high	0.03	no aromatics formed		
90	1100	without HT		67	very high	0.01	no aromatics formed		
90	600	400	48	90	0.31	0.25	58.0	35.6	6.4
90	600	600	13	89	0.70	0.15	65.9	34.1	0.0
90	600	600	48	82	0.94	0.09	no aromatics formed		
90	600	600	80	78	5.53	0.05	no aromatics formed		
90	600	800	48	62	5.78	0.02	no aromatics formed		

[a] Calcination carried out in presence of dry air passing over the zeolite in a muffle furnace for 4 h.

[b] Hydrothermal treatment carried out by passing steam–N_2 mixture with a total space velocity of 5050 cm^3 (STP) g^{-1} h^{-1} over the zeolite in a quartz reactor for 4 h.

as a source of X-ray radiations. Crystallinity of the zeolite samples was estimated by comparing the XRD peak intensities at $2\theta = 22-24°$. The incorporation of Ga in the zeolite framework was confirmed by ^{29}Si and ^{71}Ga MAS NMR done on a Bruker MSL FT-300 NMR. The framework Si/Ga ratio was determined from ^{29}Si MAS NMR using Si (1Ga) and Si (0Ga) peaks at −104 ppm and −113 ppm, respectively [15]. The strong acidity of the zeolite samples (table 1) was determined by the chemisorption of pyridine at 400°C using the GC pulse method [16]. The initial activity/selectivity of the zeolite catalysts in propane aromatization was measured at 500°C by passing a pulse (0.2 cm^3) of pure propane over the catalyst (0.1 g) packed in a quartz microreactor (i.d.: 4.5 mm and o.d.: 6.0 mm) connected to a GC [17,18] and analysing the reaction products by the on-line GC with FID and computing integrator, using Poropak-Q column (3 mm × 5 m) and Benton-34 (5%)-dinonylphthalate (5%) on a Chromosorb-W column (3 mm × 5 m). Pure N_2 (flow rate: 20 cm^3 (STP) min^{-1}] was used as a carrier gas. Before the reaction, the catalyst was pretreated in situ in a flow of pure N_2 at 500°C for 1 h.

3. Results

Data on the degree of H^+ exchange and various thermal and hydrothermal pretreatments of H-GaMFI and its crystallinity, non-FW Ga/FW Ga ratio and strong acidity (measured in terms of pyridine chemisorbed at 400°C) are presented in table 1. Results showing influence of the degree of H^+ exchange, calcination temperature and hydrothermal treatment (at different temperatures and concentrations of steam) on the initial catalytic activity and selectivity of H-GaMFI in the propane aromatization pulse reaction (at 500°C) are presented in figs. 1, 2 and 3, respectively. Figs. 4 and 5 show the effect of H^+ exchange and thermal and hydrothermal treatments on the aromatics/(methane + ethane) and aromatics/propylene mass ratios and aromatization/dehydrogenation activity ratio (i.e. aromatics/(aromatics + propylene) mass ratio) observed in the propane aromatization. Data showing the influence of the above parameters on the distribution of aromatics formed in the propane aromatization are included in table 1. Dependence of the propane conversion, both total and to aromatics (i.e. yield of aromatics), on the strong acidity of the GaMFI zeolite is shown in fig. 6.

3.1. INFLUENCE OF H^+ EXCHANGE

The results in fig. 1 reveal that, with increasing the degree of H^+ exchange, the propane conversion (both total and to aromatics) is increased, the selectivity for aromatics, ethylene, ethane and methane is also increased but the selectivity for propylene is decreased. The increase in the selectivity to aromatics and the decrease in the selectivity of propylene are very large. The distribution of aromatics formed is also affected (table 1). It is also interesting to note from fig. 4a that the aromatics/propylene ratio and the aromatization/dehydrogenation (A/D) activity

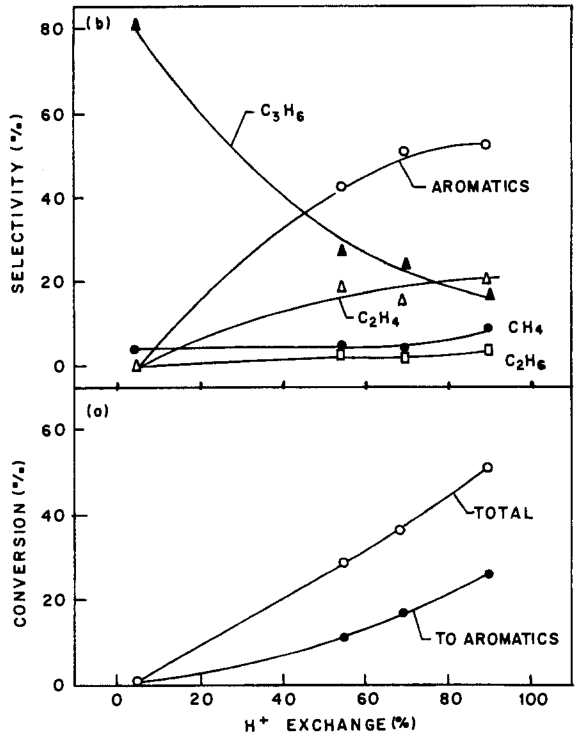

Fig. 1. Influence of H^+ exchange on (a) propane conversion, total and to aromatics, and (b) selectivity in aromatization of propane over H-GaMFI (calcined at 600°C).

ratio are increased whereas, the aromatics/(methane + ethane) ratio passes through a maximum with increasing H^+ exchange; the increase in the A/D activity ratio is very large, approaching to its maximum value of 1.0. The observed changes in the product selectivity are attributed mostly to the increase in the propane conversion with increasing H^+ exchange and consequently with increasing acidity (table 1).

3.2. INFLUENCE OF CALCINATION TEMPERATURE

The results (figs. 2 and 4b) indicate a very strong influence of calcination temperature on the initial activity and selectivity of H-GaMFI. When the calcination temperature is increased from 600 to 1100°C, the propane conversion is decreased exponentially with almost no formation of aromatics for $T_c \geqslant 900°C$, the selectivity for aromatics and propylene is decreased and increased, respectively, sharply particularly above the calcination temperature of 750°C. The selectivity for ethylene and methane is also decreased appreciably but that for ethane is affected only to a small extent. The distribution of aromatics formed is changed markedly, favouring

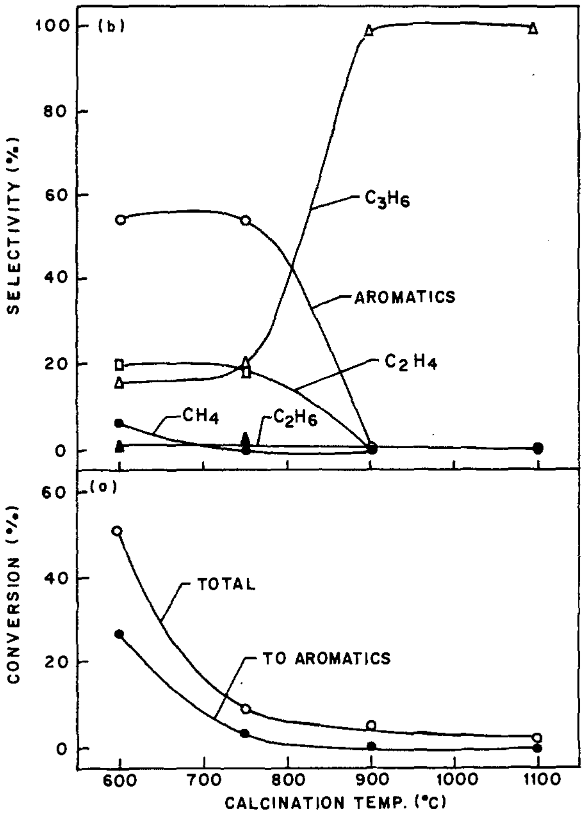

Fig. 2. Influence of catalyst calcination temperature on (a) propane conversion and (b) selectivity in aromatization of propane over H-GaMFI (H^+ exchange = 90%).

the formation of benzene over the higher aromatics (table 1). Also, above the calcination temperature of 750°C, there is a sharp decrease in the aromatics/propylene ratio and the aromatization/dehydrogenation activity ratio. The effects on product selectivity are attributed mostly to the decrease in the propane conversion due to the decrease in the acidity of the zeolite caused by its dehydroxylation and partial or complete degallination (i.e. conversion of framework Ga into non-framework Ga_2O_3) during the calcination at higher temperatures (table 1). Almost a complete degallination of the H-GaMFI without significant change in its bulk Si/Ga ratio, but with small decrease in the zeolite crystallinity is observed at the calcination temperature of 900°C.

3.3. INFLUENCE OF HYDROTHERMAL TREATMENTS

Figs. 3 and 5 show a very strong influence of the hydrothermal treatment at dif-

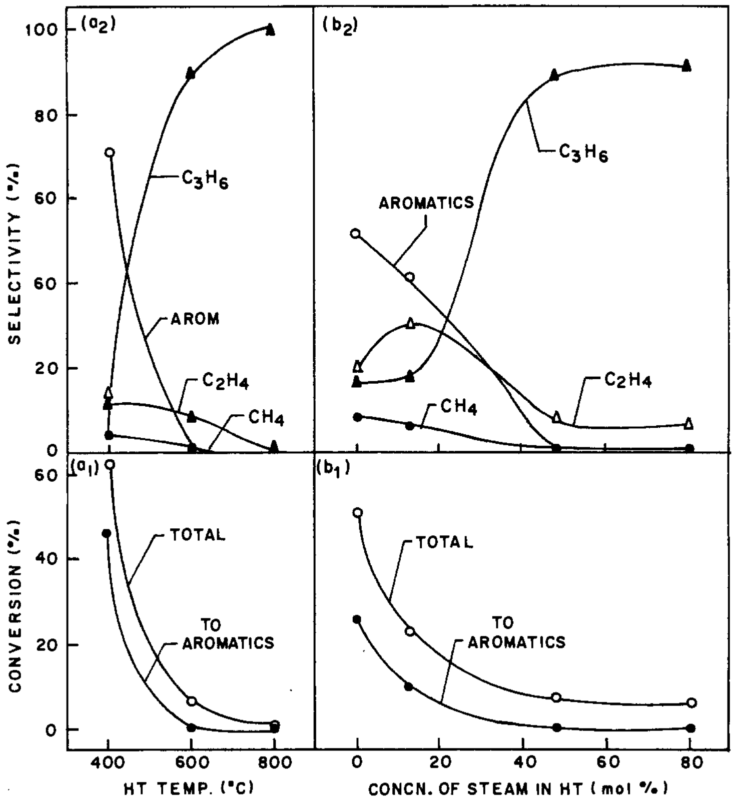

Fig. 3. Influence of hydrothermal treatment (a) temperature (concentration of steam: 48 mol%) and (b) concentration of steam (at 600°C) on propane conversion and selectivity in aromatization of propane over H-GaMFI (H^+ exchange: 90%), calcined at 600°C before the hydrothermal treatment.

ferent temperatures and concentrations of steam on the initial activity and selectivity of the zeolite. When the severity of hydrothermal treatment (i.e. temperature and concentration of steam used in the treatment) is increased, there is a sharp decrease in the conversion of propane (both total and to aromatics) and therefore the selectivity for aromatics, aromatization/dehydrogenation activity ratio, and aromatics/(methane + ethane) and aromatics/propylene ratios are also decreased markedly but there is a large increase in the propylene selectivity. There is little or no formation of aromatics when the zeolite is hydrothermally treated at higher temperatures and concentrations of steam ($\geqslant$600°C and $\geqslant$48 mol% steam). However, the influence of hydrothermal treatment on the distribution of aromatics formed is small (table 1). The influence of hydrothermal treatment on the propane conversion and consequently also on the product selectivity is attributed to a decrease in the strong acidity of the zeolite due to its degallination to different extents, depending upon the severity of hydrothermal treatment (table 1). The degallination is

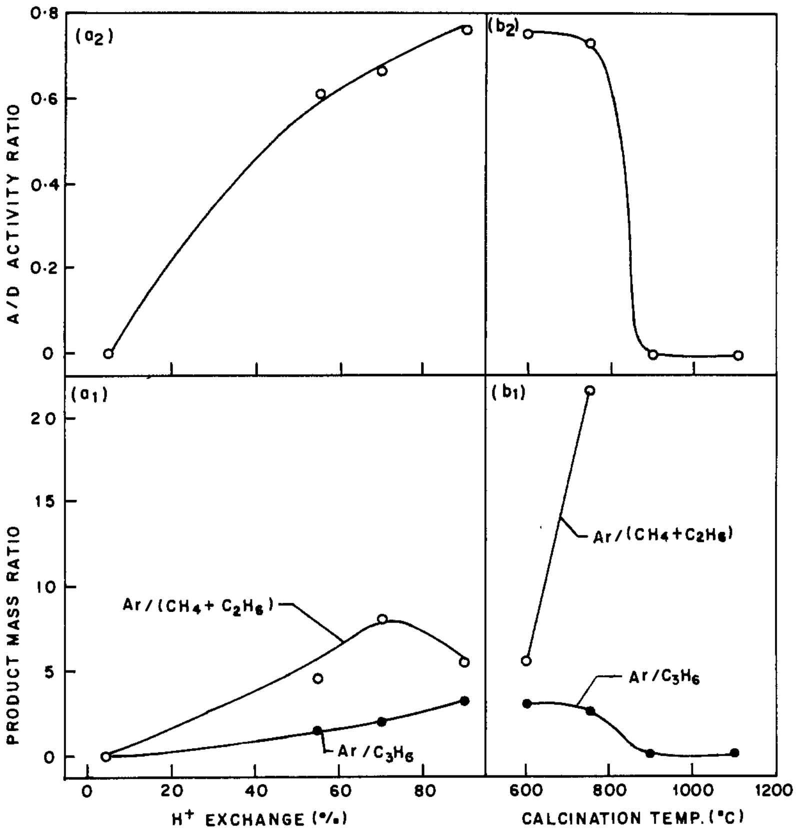

Fig. 4. Influence of (a) H^+ exchange (calcination temperature = 600°C) and (b) calcination temperature (H^+ exchange = 90%) on aromatics / ($CH_4 + C_2H_6$) and aromatics / C_3H_6 product mass ratios and aromatization / dehydrogenation (A/D) activity ratio in the propane aromatization over H-GaMFI.

increased and the crystallinity is decreased with increasing the temperature and/ or concentration of steam in the hydrothermal treatment given to the zeolite.

3.4. CORRELATION BETWEEN ACIDITY AND PROPANE CONVERSION/ AROMATIZATION ACTIVITY

The results in fig. 6 clearly show a strong dependence of the propane conversion (both total and to aromatics) activity and aromatization/dehydrogenation activity ratio (at the corresponding propane conversion) on the acidity (measured in terms of the pyridine chemisorbed at 400°C) of the zeolite. The observed exponential increase in the propane conversion and aromatization activity with increasing acidity reveals the importance of strong acid sites in the propane aromatization. The aromatization/dehydrogenation activity ratio is also increased markedly with

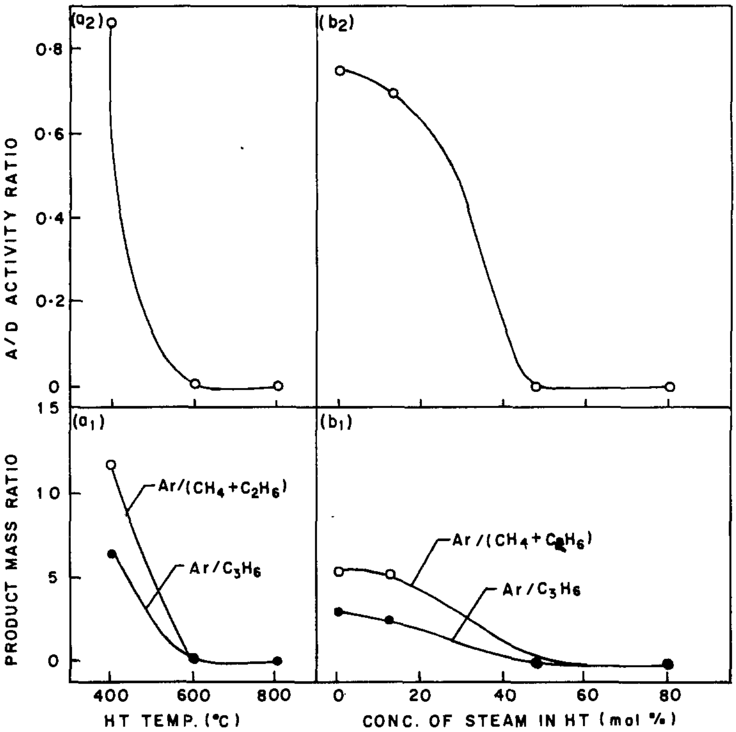

Fig. 5. Influence of hydrothermal treatment (a) temperature (concentration of steam = 48 mol%) and (b) concentration of steam (at 600°) on aromatics/($CH_4 + C_2H_6$) and aromatics/C_3H_6 product mass ratio and aromatization/dehydrogenation (A/D) activity ratio in propane aromatization over H-GaMFI.

increasing acidity. The results reveal that a high concentration of the acid sites is necessary for the zeolite to be active in the propane aromatization.

4. Discussion

The results (figs. 1–3) reveal a strong influence of the degree of H^+ exchange and thermal and hydrothermal treatments on the initial propane conversion activity of the gallosilicate zeolite. Since, the product selectivity depends on the propane conversion [1,6,9], the changes in the propane conversion due to changes in the acidity are likely to be reflected on the product selectivity. It may be noted that the observed product selectivity, product ratios and A/D activity ratios (figs. 1–6) do not correspond to isoconversion of propane. Hence, the observed influence on these selectivity parameters of the degree of H^+ exchange and thermal and hydrothermal treatment parameters of the zeolite is apparent (i.e. not real). The observed variation of the selectivity parameters may also be due to a change in the propane conversion, resulting from a change in the zeolite parameter.

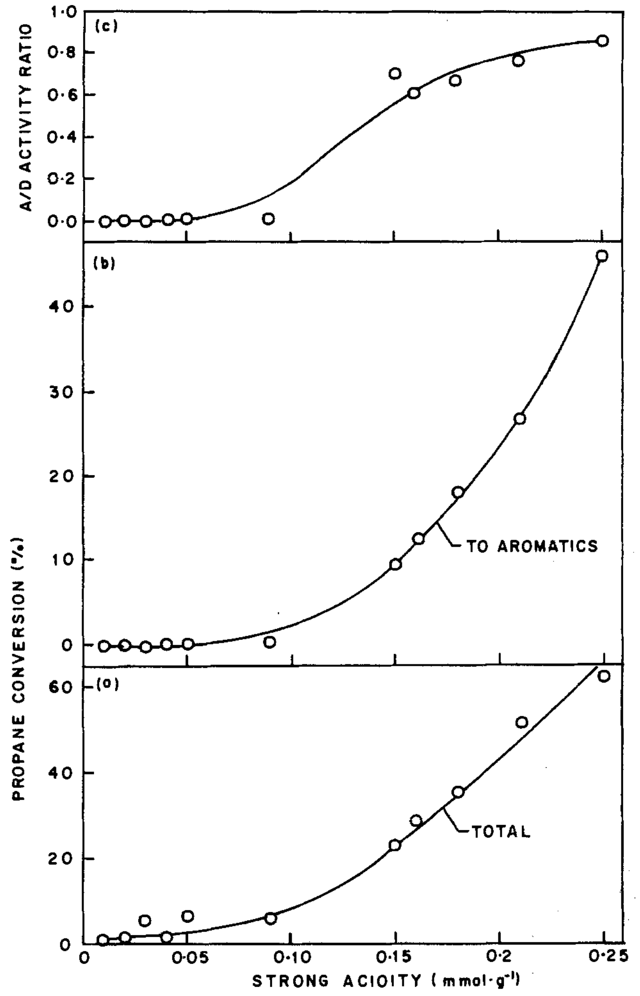

Fig. 6. Variation of (a) total propane conversion, (b) propane-to-aromatics conversion and (c) aromatization/dehydrogenation (A/D) activity ratio in propane aromatization over H-GaMFI with its strong acidity.

The non-framework Ga-species formed in the thermal and hydrothermal treatments are expected to be well dispersed Ga_2O_3 and/or $[GaO]^+$. In the present case, formation of Ga^+ at cation exchange site is not possible because of the fact that zeolite is not prereduced and also only its initial activity is measured. A comparison of the propane conversion/aromatization activity of the zeolite with its non-framework Ga and the acidity or non-FW Ga/FW Ga ratio (table 1 and figs. 1–6) reveals that, although the non-FW oxide species have high dehydrogenating activity [5,6,11], these species are active only in combination with the acid sites (or FW-Ga) at high concentration. This is very much consistent with earlier observations [5,12].

It should be noted that the pulse microreactor results may not reflect the activity/selectivity of the zeolite under steady state conversion. Nevertheless, for the purpose of comparing the initial activity, such studies are very useful.

5. Conclusions

The initial propane conversion/aromatization activity of H-GaMFI is strongly influenced by the degree of H^+ exchange, calcination temperature and hydrothermal treatment (under different conditions) of the zeolite. The propane conversion activity is decreased to a large extent with increasing the severity of thermal and hydrothermal treatments or decreasing the H^+ exchange of the zeolite. There exists a close relationship between the propane conversion and aromatization activity and the acidity (measured in terms of pyridine chemisorbed at 400°C) of the zeolite. The acid sites at high concentrations are essential for the zeolite to be active in the propane aromatization. The non-framework Ga-oxide species are active only in the presence of the acid sites (which are attributed to FW-Ga) at high concentration.

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