Influence of O_2 and H_2 pretreatments on acidity/acid strength distribution and acid functions of Ga/H-ZSM-5, H-GaMFI and H-GaAl MFI zeolites

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Abstract. H-gallosilicate (H-GaMFI), H-galloaluminosilicate (H-GaAlMFI) and Ga, impregnated H-ZSM-5 (Ga/H-ZSM-5) zeolites pretreated with O_2 and H_2 (at 600°C for 10 h) have been characterized for their acidity/acid strength distribution (by chemisorption and stepwise thermal desorption of pyridine from 100°–400°C) and also for their acid functions by acid catalysed reactions [viz. isooctane cracking (at 400°C) (for characterizing external acid sites) and toluene disproportionation (at 500°C) and methanol-to-aromatics conversion (400°C)] using a pulse microreactor. The catalysts were also characterized by XPS, ^{29}Si, ^{27}Al and ^{71}Ga MAS NMR. The acidity/acid strength distribution, activity in the acid catalyzed reactions, framework Si/Ga ratio and surface Ga/Si ratio of the zeolites are significantly affected by their pretreatment by O_2 or H_2.

Keywords. Acid catalysed reactions; H-gallosilicate MFI; H-galloaluminosilicate MFI; Ga-impregnated H-ZSM-5, acidity of zeolites; acid catalysed reactions; O_2 and H_2 pretreatments.

1. Introduction

Gallium modified ZSM-5 type zeolites viz. Ga^{+3} exchanged or Ga-impregnated H-ZSM-5, physically mixed Ga_2O_3 and H-ZSM-5, H-gallosilicates (H-GaMFI) and H-galloaluminosilicates (H-GaAlMFI) show high activity/selectivity in the lower alkane aromatization (Changyu *et al* 1988; Guisnet *et al* 1992; Ono 1992). This is a process of great practical importance. In a number of earlier studies (Kanazirev *et al* 1990; Price and Kanazirev 1990; Joly *et al* 1992; Dooley *et al* 1992; Jia *et al* 1993; Choudhary *et al* 1996b), a beneficial effect of the high temperature H_2 pretreatment to the physically mixed Ga_2O_3 and H-ZSM-5 and Ga/H-ZSM-5 catalysts on their propane aromatization activity/selectivity was observed. Recently we have observed a strong influence of O_2 and H_2 pretreatments (at 600°C) to the H-GaMFI and H-GaAlMFI zeolites on their aromatization activity/selectivity and catalyst deactivation during a short initial reaction period in propane aromatization process (Choudhary *et al* 1996b).

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The H_2 pretreatment to Ga_2O_3 (or Ga)/H-ZSM-5 is found to cause a surface migration of gallium species in the zeolite channels increasing gallium dispersion (Joly *et al* 1991; Kanazirev *et al* 1991a, b; Dooley *et al* 1992; Jia *et al* 1993; Choudhary *et al* 1996b). Formation of Ga^{+3} (Kanazirev *et al* 1991a, c) or $(GaO)^+$ (Dooley *et al* 1992) located at cation exchange sites of the zeolite and also a decrease in protonic acidity (Meriaudeau and Naccache *et al* 1991) due to the H_2 pretreatment have been suggested. A significant increase in the dehydrogenating and hydrogenolysis activity of Ga_2O_3/H-ZSM-5 due to its H_2 pretreatment has also been observed (Barre *et al* 1993). It is, therefore, interesting to study in detail the influence of O_2 and H_2 pretreatments on the acidity/acid strength distribution and acid function (by acid-catalysed model reactions) of the important Ga-modified ZSM-5 type zeolites, such as H-GaMFI, H-GaAlMFI and Ga/H-ZSM-5. The present investigation was undertaken for this purpose.

2. Experimental

The H-GaMFI (Si/Ga = 33) and H-GaAlMFI (Si/Ga = 82 and Si/Al = 68) were obtained from their NH_4-form. The NH_4-GaMFI and NH_4-GaAlMFI zeolites were prepared by exchanging their Na-form with 1M ammonium nitrate solution at 80°C four times. The Na-GaMFI and Na-GaAlMFI zeolites were synthesized by their hydrothermal crystallization from a gel (*pH* ≅ 9–10) consisting of Na-trisilicate (Fluka), gallium nitrate (Aldrich) with or without aluminum chloride (BDH), tetrapropyl ammonium bromide (TPABr) (Aldrich), sulphuric acid and deionized water in a stainless steel autoclave at 180°C for 24 h, followed by washing and drying the resulting zeolite crystals at 120°C for 4 h and then calcining at 550°C in static air for 15 h to remove the occluded organic template.

The Ga impregnated NH_4-ZSM-5 (Si/Al = 48 and Ga-content 1 wt%) was prepared by impregnating NH_4-ZSM-5 with gallium nitrate solution by the incipient wetness technique. The NH_4-ZSM-5 was obtained by exchanging ZSM-5, synthesized according to the patent literature (Argauer and Landolt 1972), with 1 M ammonium nitrate solution at 80°C four times and drying at 120°C for 4 h.

All the zeolites in their NH_4-form (NH_4^+ exchange ≅ 95%) were pressed binder free, crushed to particles of 0·2–0·3 mm size and calcined at 600°C at 4 h in static air to get them in their H-form. The MFI framework structure of the zeolites was confirmed by XRD and FTIR analysis.

The O_2 and H_2 pretreatments to the zeolite catalysts were given in a flow of pure moisture-free O_2 or H_2 at 600°C for 10 h.

The O_2 and H_2 pretreated zeolite catalysts were characterized by XRD (using Philips diffractometer-1700 series) and ^{29}Si, ^{27}Al and ^{71}Ga MAS NMR (using Burker MSL 300 MHz FT-NMR spectrometer).

The acidity/acid strength distribution on the pretreated zeolite catalysts was measured by determining the chemisorption of pyridine and stepwise thermal desorption (STD) of pyridine by using the GC adsorption/desorption methods (Choudhary and Nayak 1982; Choudhary 1983). The STD of pyridine was carried as follows. The catalyst was saturated with the base at 100°C by injecting a pyridine pulse and the reversibly adsorbed pyridine at this temperature was desorbed in the flow of nitrogen. Pyridine chemisorbed irreversibly at 100°C was desorbed thermally in the flow of nitrogen (10 cm^3·min^{-1}) by heating the catalyst from 100°C to 400°C in four steps (each representing a jump of 75°C). The temperature in each step was raised at a linear heating rate of 10°C·min^{-1}. After the maximum temperature of the respective step was attained, it was maintained for

a period of 1 h to desorb the base reversibly adsorbed on the catalyst at that temperature. The pyridine desorbed in each step was measured quantitatively by GC (with FID). The chemisorption of pyridine in this study is defined as the amount of pyridine retained by a presaturated zeolite after it is swept with pure N_2 for a period of 1 h. The determination of acidity/acid strength by the GC methods is described in detail earlier (Choudhary and Nayak 1982; Choudhary 1983; Choudhary *et al* 1996a).

The acid-catalysed model reactions, viz. isooctane cracking (at 400°C) for studying external acidity, toluene disproportionation (at 500°C) and methanol-to-aromatics conversion (at 400°C) over the pretreated zeolite catalysts have been carried out in a pulse microreactor (made up of a quartz tube with i.d.: 4·5 mm and o.d.: 0·6 mm) connected to a gas chromatograph using high purity N_2 (passed over molecular sieves and oxysorb) as a carrier gas (20 $cm^3 \cdot min^{-1}$). The catalyst pretreatment by H_2 or O_2 was given *in situ* before carrying out the pulse reactions. The pulse microreactor with arrangement for the *in situ* pretreatment has been described earlier (Choudhary *et al* 1991, 1996b). After the pretreatment, the catalyst was flushed with pure N_2 (free from traces of moisture and O_2) and then the pulse reactions were carried out by injecting a pulse of (0·4 μl) of isooctane, toluene and methanol in the microreactor (containing of 0·1 g catalyst) at the above mentioned temperatures and analysing the reactions products by the on-line gas chromatographs with FID and computing integrator and using a gc column (3 mm × 5 m) containing Benton − 34 (5%) and dinonylphthalate (5%) on Chromosorb-W. The detailed procedures for carrying out the pulse reactions and products analysis are described earlier (Nayak and Choudhary 1982, 1983a).

3. Results

The data on composition and crystal size of the gallium modified ZSM-5 type zeolites are presented in table 1.

3.1 ^{27}Al, ^{29}Si and ^{71}Ga MAS NMR

Figure 1 shows the ^{27}Al, ^{29}Si and ^{71}Ga MAS NMR spectra of the H_2 and O_2 pretreated zeolites. The ^{27}Al spectra (figure 1a) show that there is absence of Al in the H-GaMFI. The H-GaAlMFI zeolite contains framework Al (i.e. tetrahedral Al) but no non-framework (i.e. octahedral) Al. However, the Ga/H-ZSM-5 zeolite contains a small amount of octahedral Al along with the tetrahedral one. As expected the ^{71}Ga spectra indicate incorporation of gallium in the framework (FW) of the H-GaMFI

Table 1. Composition and crystal size of the zeolites.

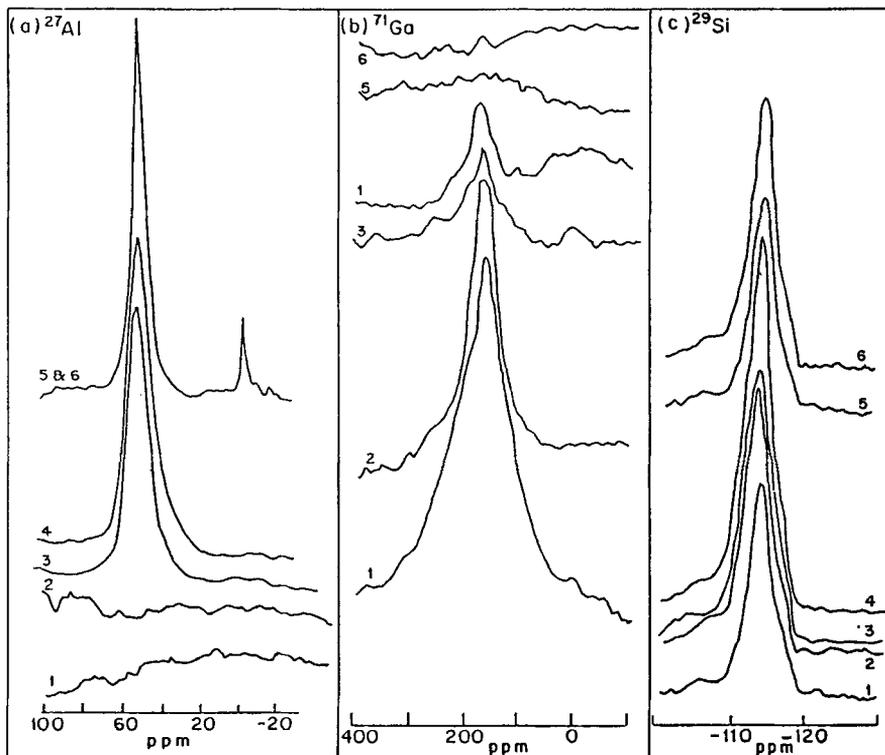| Zeolite	Si/Ga ratio		Si/Al ratio		Crystal size (μm)
	Bulk	FW	Bulk	FW	
H-GaMFI	32·9	42(O_2) 47(H_2)	> 10000	> 10000 O_2 > 10000 H_2	4–6
H-GaAlMFI	82·0	118(O_2) 236(O_2)	68	68(O_2) 68(H_2)	5–8
Ga/H-ZSM-5	97·0	> 10000(O_2) > 10000(H_2)	48	53(O_2) 53(H_2)	5–7

Figure 1. ^{27}Al (a), ^{71}Ga (b) and ^{29}Si (c) MAS NMR of H_2 and O_2 pretreated zeolite catalysts [(1) H-GaMFI (H_2), (2) H-GaMFI (O_2), (3) H-GaAlMFI (H_2), (4) H-GaAlMFI (O_2), (5) Ga/H-ZSM-5 (H_2), (6) Ga/H-ZSM-5 (O_2)].

and H-GaAlMFI zeolites and absence of tetrahedral Ga in the Ga/H-ZSM-5. The FW-Si/Ga or Si/Al ratios, estimated from the ^{29}Si spectra, for the H-GaMFI and Ga/H-ZSM-5 zeolites are included in table 1. The FW-Si/Ga ratio of the H-GaMFI and H-GaAlMFI zeolites pretreated with H_2 is higher than that for the zeolite pretreated with O_2. However, no significant effect is found on the FW-Si/Al ratio of the Ga/H-ZSM-5 and H-GaAlMFI zeolites due to the pretreatment. The octahedral Al observed in the Ga/H-ZSM-5 was already present in the synthesised sample. A composition of the bulk and FW-Si/Ga ratios of H-GaMFI and H-GaAlMFI zeolites shows the presence of significant non-FW Ga (i.e. gallium oxide) in the zeolites formed due to degalliation of the zeolites during their pretreatment.

3.2 XPS

Results on XPS of the O_2 and H_2 pretreated zeolites are given in table 2. For the H_2 pretreated H-GaMFI and H-GaAlMFI zeolites, the concentration of gallium (i.e. Ga/Si ratio) at the external crystal surface is found to be higher than that for the corresponding O_2 pretreated zeolites. But the reverse trend is observed in the case of Ga/H-ZSM-5. This indicates migration of gallium species from the zeolite channels to the external crystal surface for the H-GaMFI and H-GaAlMFI zeolites and the migration in reverse for the Ga/H-ZSM-5 during the H_2 pretreatment.

Table 2. XPS data on the O_2 and H_2 pretreated zeolites.

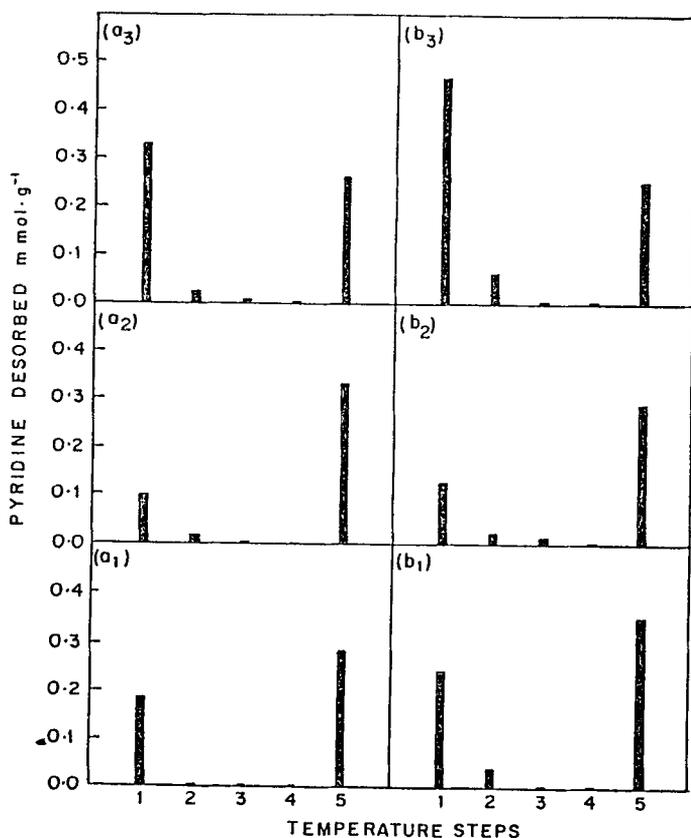| Zeolite	Pretreatment	Binding energy (eV)			Surface Ga/Si ratio
		$O(1s)$	$Si(2p)$	$Ga(2p\,3/2)$	
H-GaMFI	O_2	532·3	104·1	1119·0	0·008
	H_2	532·0	103·4	1119·0	0·011
H-GaAlMFI	O_2	532·0	103·6	1119·4	0·005
	H_2	531·6	103·0	1118·2	0·008
Ga/H-ZSM-5	O_2	533·1	103·0	1120·0	0·018
	H_2	533·4	104·1	1120·2	0·016

Figure 2. Stepwise thermal desorption of pyridine (chemisorbed at 100°C) on H-GaMFI, H-GaAlMFI and Ga_2O_3/H-ZSM-5 pretreated in (a) H_2 and (b) O_2 (temperature steps: (1) $100° \leqslant T_d < 175°C$, (2) $175° \leqslant T_d < 250°C$, (3) $250° \leqslant T_d < 325°C$, (4) $325° \leqslant T_d < 400°C$, (5) $400°C \leqslant T_d < T_d^*$).

3.3 *Acidity/acid strength distribution*

Results showing the influence of Ga-modification of ZSM-5 type zeolite and gas pretreatment on the acid strength distribution, obtained by the STD of pyridine
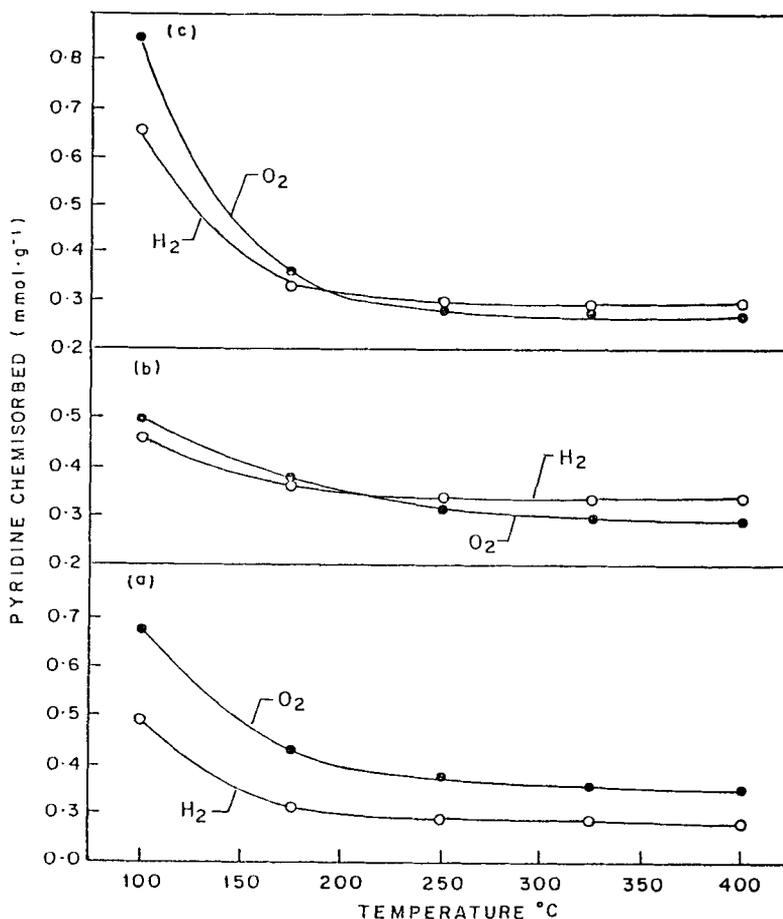
Figure 3. Temperature dependence of pyridine chemisorption on O_2 and H_2 pretreated H-GaMFI (a), H-GaAlMFI (b) and Ga_2O_3/H-ZSM-5 (c) zeolites.

(chemisorbed initially at 100°C) from 100° to 400°C in five successive temperature steps and also by the chemisorption of pyridine at different temperatures are presented in figures 2 and 3 respectively.

The columns in figure 2 show energy distribution of the acid sites involved in the chemisorption of pyridine at 100°C. Each column of the site energy distribution represents the number of acid sites measured in terms of pyridine molecules desorbed in the corresponding temperature step. The acid strength of these sites is expressed in terms of the desorption temperature (T_d) of pyridine, which lies in the range of temperature $(T_1 < T_d \leqslant T_2)$ in which the chemisorbed pyridine is desorbed. T_d^* corresponds to the temperature at which all the chemisorbed pyridine is desorbed from the zeolite.

The temperature-dependence of pyridine chemisorption on the zeolites (figure 3) also shows acid strength distribution on them. In this case, the acid strength is expressed in terms of the chemisorption temperature. Both the STD data and the decrease in the pyridine chemisorption with increase in temperature reveal that the acid sites on the zeolites are of different strengths and their distribution is quite broad.

The zeolite catalysts can be arranged in the order of their total and strong acidity (measured in terms of the pyridine chemisorbed at 100° and 400°C respectively), as follows.

For total acidity

H$_2$ pretreated catalysts	: H-GaAlMFI < H-GaMFI < Ga/H-ZSM-5.
O$_2$ pretreated catalysts	: H-GaAlMFI < H-GaMFI < Ga/H-ZSM-5.

For strong acidity

H$_2$ pretreated catalysts	: H-GaMFI < H-GaAlMFI < Ga/H-ZSM-5.
O$_2$ pretreated catalysts	: H-GaAlMFI < H-GaMFI < Ga/H-ZSM-5.

The influence of pretreatment on the total and strong acidity of the catalysts is as follows.

• The total acidity of all the three H$_2$ pretreated catalysts is lower than that of the corresponding O$_2$ pretreated catalysts (i.e. total acidity is decreased due to the H$_2$ pretreatment).
• The strong acidity of the Ga/H-ZSM-5 and H-GaAlMFI is increased but that of the H-GaMFI is decreased due to the H$_2$ pretreatment. However, the change in the strong acidity is small for the Ga/H-ZSM-5 but more significant for the other two catalysts.

3.4 *Acid catalysed reactions*

Results showing the influence of the O$_2$ or H$_2$ pretreatment to the zeolite catalysts on their activity and selectivity (or product distribution) in the isooctane cracking (at 400°C), toluene disproportionation (at 500°C) and methanol-to-aromatics conversion (at 400°C) reactions, catalysed by strong acid sites (Nayak and Choudhary 1982, 1983) are presented in tables 3 and 4.

3.4a *Isooctane cracking*: The pretreatment has little or no influence on the isooctane cracking activity and consequently on the strong acid sites present on the external surface of the H-GaMFI and H-GaAlMFI zeolites (table 3). However, the influence on
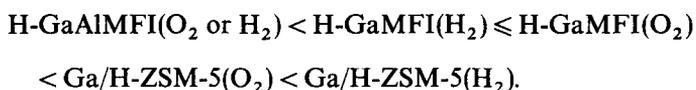
Table 3. Activity of the O$_2$ and H$_2$ pretreated zeolite catalysts in isooctane cracking (at 400°C) and toluene disproportionation (at 500°C).

Zeolite	Pretreatment	Catalytic activity conversion (%)	
		Isooctane cracking	Toluene disproportionation
H-GaMFI	O$_2$	1·7	11·5
	H$_2$	1·6	8·1
H-GaAlMFI	O$_2$	0·8	13·0
	H$_2$	0·8	15·8
Ga/H-ZSM-5	O$_2$	3·8	18·0
	H$_2$	5·1	22·8

Table 4. Activity/selectivity of the O_2 and H_2 pretreated catalysts in methanol-to-aromatics conversion (at 400°C) (conversion of methanol to hydrocarbons = 100%).

Conversion/ product distribution	H-GaMFI		H-GaAlMFI		Ga/H-ZSM-5	
	O_2	H_2	O_2	H_2	O_2	H_2
Conversion to aromatics (%)	34·2	26·7	35·1	38·5	36·1	39·2
Distribution of aromatics (wt %)						
B	11·2	0·2	11·1	12·4	13·6	9·3
T	43·7	44·4	44·4	46·1	46·4	26·2
X + EB	43·9	55·4	44·5	41·5	39·8	45·8
C_{9+}	1·2	0·0	0·0	0·0	0·2	18·7
Distribution of non-aromatics (wt %)						
CH_4	3·6	1·1	2·9	2·9	3·6	2·5
C_2	9·3	8·5	6·5	8·6	10·0	8·4
C_3	24·0	20·2	26·0	31·4	26·3	19·4
C_4	48·5	48·2	48·1	40·7	52·6	53·0
C_{5+}	14·6	22·0	16·3	16·4	7·5	16·7

the activity of Ga/H-ZSM-5 is quite significant; the isooctane cracking activity is higher for the H_2 pretreated catalyst. Based on the results, the concentration of strong external acid sites on the catalysts is in the following order.

$$H\text{-}GaAlMFI(O_2 \text{ or } H_2) < H\text{-}GaMFI(H_2) \leqslant H\text{-}GaMFI(O_2)$$

$$< Ga/H\text{-}ZSM\text{-}5(O_2) < Ga/H\text{-}ZSM\text{-}5(H_2).$$

3.4b *Toluene disproportionation*: In case of the toluene disproportionation over the catalysts, the gas pretreatment has a very significant influence on the toluene conversion (table 3). The toluene conversion activity is higher when the H-GaAlMFI and Ga/H-ZSM-5 catalysts are pretreated with H_2 but is higher when the H-GaMFI catalyst is pretreated with O_2.

3.4c *Methanol-to-aromatics conversion*: The formation of aromatics over all the O_2 pretreated catalysts is more or less the same (34–36% of the hydrocarbons formed); the conversion of methanol to hydrocarbons over all the H_2 or O_2 pretreated catalysts is found to be almost 100% (table 4). However, the pretreatment has a very significant influence on the aromatization. The aromatization is increased due to the H_2 pretreatment to the H-GaAlMFI and Ga/H-ZSM-5 but is decreased due to the H_2 pretreatment to the H-GaMFI.

The distribution of aromatics and non-aromatics, formed in the methanol conversion process, is affected to a small extent for the H-GaAlMFI by its pretreatment by H_2 or O_2 but the influence of the pretreatment on the distribution is relatively larger for the other two catalysts.

Figure 4 shows that there is a good correlation between the activity in the toluene and methanol-to-aromatics conversion reactions and the strong acidity (measured by the pyridine chemisorption at 400°C) of the zeolite catalysts.
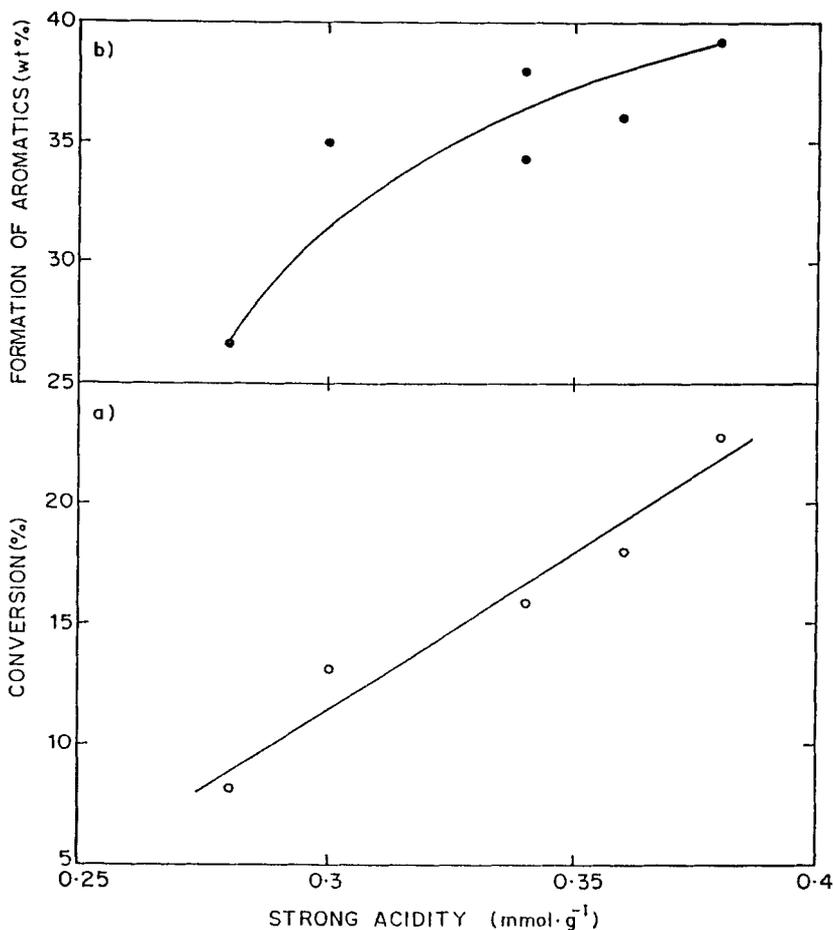
Figure 4. Relationship between the catalytic activity of the zeolite catalysts in (a) toluene disproportionation and (b) methanol-to-aromatics conversion and their strong acidity.

4. Discussion

In this section, the influence of H_2 pretreatment is discussed by comparing the results with those obtained on the respective zeolite catalyst pretreated with O_2.

4.1 *Influence of H_2 pretreatment on degalliation*

The observed increase in the FW-Si/Ga ratio of the H-GaMFI and H-GaAlMFI zeolites due to the H_2 pretreatment relative to that observed for the O_2 pretreatment (table 1) clearly shows that the degalliation of the zeolites is enhanced due to the H_2 pretreatment. As expected, both the total and strong acidities of the H-GaMFI zeolite are decreased as a result of its degalliation (i.e. conversion of tetrahedral Ga into its octahedral form by the removal of the former from the zeolite framework). The strong acidity of the zeolite is attributed to the presence of FW tetrahedral Ga, similar to H-ZSM-5 zeolite (Choudhary *et al* 1996a). However, the observed small increase in the

strong acidity of H-GaAlMFI may be because of the formation of $[GaO]^+$ species in the vicinity of tetrahedral Al of the zeolite due to its degalliation during H_2 treatment.

In case of Ga/H-ZSM-5, no significant dealumination is observed due to the H_2 or O_2 pretreatment.

4.2 *Influence of H_2 pretreatment on migration of Ga-species*

The XPS results on surface Ga/Si ratio of the catalysts (table 2) suggest that there is a migration of Ga-species from zeolite channels to external surface of zeolite crystallites for the H-GaMFI and H-GaAlMFI due to their H_2 pretreatment. The migration is attributed to the formation of more volatile Ga-oxide species from the Ga_2O_3 occluded in the zeolite channels during synthesis and/or to the volatile degalliation species formed during the H_2 pretreatment. The latter seems to be the most likely reason.

The migration of Ga for the Ga/H-ZSM-5 due to the H_2 pretreatment is in the reverse direction. This is because of the formation of more volatile Ga-oxide species from the Ga_2O_3 already present on the external surface of the zeolite. This is consistent with that observed earlier (Joly *et al* 1991; Kanazirev *et al* 1991a; Meriaudeau and Naccache 1991). However, the change in surface Ga/Si ratio due to the H_2 pretreatment is smaller for the Ga/H-ZSM-5 as compared to that for the H-GaMFI and H-GaAlMFI. This suggests that the migration of Ga-species is faster in these two zeolites. It seems that the migration is enhanced due to the degalliation, forming more mobile Ga-species during the H_2 pretreatment. Because of this, H-GaAlMFI zeolite with its controlled degalliation is expected to result in a better alkane aromatization catalyst because of the possibility of obtaining Ga/H-ZSM-5 or Ga/H-GaAlMFI with very high Ga dispersion.

4.3 *Influence of H_2 pretreatment on acidity/acid functions*

The acidity and acid functions of the zeolite catalysts are affected significantly by the pretreatment (figures 1 and 3 and tables 3 and 4).

Both the total and strong acidity of H-GaMFI are decreased due to the H_2 pretreatment mostly due to the degalliation of the zeolite causing a decrease in the FW Ga responsible for the acidity and also the migration of some of the gallium species to cation positions, replacing some of the protons. The decrease in the strong acidity is very much consistent with the decrease in the catalytic activity of the zeolite due to the H_2 pretreatment.

The total acidity of H-GaAlMFI is also decreased but only to a small extent, most probably due to some degalliation. However, the strong acidity is increased and the increase in the acidity is consistent with the increase in the catalytic activity in both the toluene disproportionation and methanol-to-aromatics conversion reactions. The increase in the strong acidity may be due to formation of reduced Ga-oxide species $[GaO]^+$ and its migration to the FW Al, similar to the formation of $[AlO]^+$ species present in the H-ZSM-5 due to a mild hydrothermal treatment.

The total acidity of Ga/H-ZSM-5 is decreased but its strong acidity is increased to a small extent. Since the acidity of the zeolite is due to the presence of FW Al and also because of the non-FW metal oxides, the change in the total acidity is mostly due to the reduction of Ga_2O_3. The increase in the strong acidity is very small, probably because the reduction of Ga^{3+} in Ga_2O_3/H-ZSM-5 to $[GaO]^+$ by the H_2 pretreatment is difficult (Jia *et al* 1993). The small increase in the strong acidity is reflected in a small but

significant increase in the catalytic activity in both the toluene conversion and formation of aromatics from methanol.

The product distribution in the methanol-to-aromatics conversion is changed significantly due to the change in the acidity and the nature and/or migration of the Ga-oxide species of the catalysts by the H_2 pretreatment.

The external acidity of the H-GaMFI and H-GaAlMFI zeolites is not affected significantly due to the H_2 pretreatment. However, the external acidity of the Ga/H-ZSM-5 is increased significantly, probably due to an increase in the dispersion of Ga-oxide species becuase of the formation of reduced Ga-oxide species on the external surface due to the H_2 pretreatment. The isooctane cracking activity can be taken as a measure of strong acidity at the external surface of the ZSM-5 type zeolite crystallites because isooctane cannot penetrate through the zeolite channels at the reaction temperature (Choudhary *et al* 1996a).

4.4 *Comparison of zeolite catalysts*

The surface concentration of Ga is highest for the Ga/H-ZSM-5 and lowest for H-GaAlMFI. The order of the isooctane cracking activity of the catalyst is the same as that of the surface Ga concentration.

The order of the catalysts (both H_2 and O_2 pretreated) for their activity in the toluene disproportionation and formation of aromatics from methanol is more or less similar to their order for the strong acidity, as indicated by a good correlation between their catalytic activity and strong acidity (figure 4).

It may be noted that the pretreatment causes not only a change in the acidity but also a change in the non-acid function (e.g. dehydrogenation activity) of the Ga-modified zeolites. The observed descrepancy in the variation of formation of aromatics from methanol with strong acidity (figure 4b) is mostly due to a change in the activity for some of the aromatization steps (e.g. dehydrogenation), resulting from a change in the nature of the Ga-oxide species, due to the pretreatment, along with the change in the acidity.

5. Conclusions

This investigation leads to the following conclusions on the influence of H_2 pretreatment (at 600°C) on the degalliation and migration of Ga-oxide species, the acidity and acid function of H-GaMFI, H-GaAlMFI and Ga/H-ZSM-5 zeolite catalysts.

1. H_2 pretreatment causes degalliation on the H-GaMFI and H-GaAlMFI zeolites and migration of Ga-oxide species to the external surface of zeolite crystallites.
2. It causes a decrease in both the total and strong acidity of H-GaMFI but a decrease in the total acidity and an increase in the strong acidity of H-GaAlMFI and Ga/H-ZSM-5.
3. The changes in strong acidity are directly reflected by the corresponding changes in the catalytic activity of the zeolite catalysts for toluene disproportionation and methanol-to-aromatics conversion reactions, which are catalysed by the zeolitic (i.e. strong) acid sites. There exists good correlation between the activity and strong acidity of the catalysts.
4. The external acidity (measured in terms of the isooctane cracking activity) of the zeolite catalysts depends mostly on the nature and concentration of Ga-oxide species on the external surface.

Acknowledgement

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