SYNTHESIS AND CHARACTERIZATION OF GALLOSILICATE (MFI) AND GALLOALUMINOSILICATE (MFI) ZEOLITES FOR PROPANE AROMATIZATION

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BY

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DEDICATED TO

MY FATHER *Shri. Kisan Hari Kinage*

AND

MY MOTHER *Sou. Shudhamati Kisan Kinage*

CERTIFICATE AS PER FORM 'A'

Certified that the work incorporated in the thesis "**SYNTHESIS AND CHARACTERIZATION OF GALLOSILICATE (MFI) AND GALLOALUMINO-SILICATE (MFI) ZEOLITES FOR PROPANE AROMATIZATION**" submitted by Mr. Anil Kisan Kinage was carried out by the candidate under my guidance. Such material as has been obtained from other sources has been duly acknowledged in the thesis.

(Dr. V.R.Choudhary)

Research Guide

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(Anil K. Kinage)

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OBJECTIVES/SCOPE, SUMMARY AND CONCLUSIONS

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OBJECTIVES AND SCOPE

Aromatization of lower alkanes (viz. C_2 - C_4 parafins) over Ga-modified ZSM-5 type catalysts (Ga/H-ZSM-5, H-gallosilicate and H-galloaluminosilicate with MFI structure) is a process of great practical importance. The Ga-modified ZSM-5 type zeolite catalysts - Ga-impregnated H-ZSM-5 (Ga/H-ZSM-5), physically mixed Ga_2O_3 and H-ZSM-5, and ZSM-5 type H-gallosilicate (H-GaMFI) and H-galloaluminosilicate (H-GaAlMFI) zeolites show high activity in the aromatization of lower alkanes. These zeolite catalysts are bifunctional; they have strong acid functions (which is attributed to the tetrahedral Al or Ga) and high dehydrogenation activity (which is attributed to the presence of extraframework Ga-oxides species in combination with the zeolitic acid sites). It is found that H-GaMFI and H-GaAlMFI zeolites are more effective than Ga/H-ZSM-5 and physically mixed Ga_2O_3 and H-ZSM-5 in aromatization of lower alkanes. Because of the importance of the H-GaMFI and H-GaAlMFI, it is of practical interest to investigate in details their hydrothermal synthesis under different conditions and their characterization, and also their performance in the aromatization of propane.

The present work for the Ph.D thesis was under taken as a part of the comprehensive research program in our group on the aromatization of lower alkanes over various Ga-modified ZSM-5 type zeolites. The objectives and scope of the Ph.D work are as follows :

- Study the various effects of hydrothermal synthesis parameters on the crystallinity and crystal size and morphology of gallosilicate (MFI) (i.e. H-GaMFI) and galloaluminosilicate (MFI) (i.e. H-GaAlMFI) zeolites
- Characterization of the Ga/H-ZSM-5, H-GaMFI and H-GaAlMFI zeolites (pretreated with H_2 or O_2) and evaluation of their initial activity/selectivity in propane aromatization using a pulse microreactor
- Characterization of H-GaMFI with different Si/Ga ratios, H^+ exchange and the zeolite pretreated thermally and hydrothermally at different conditions and evaluation of its initial activity/selectivity in propane and methanol aromatization reactions using a pulse microreactor

- Study of the influence of Si/Ga ratio of H-GaMFI zeolite on its acidity/acid strength distribution, activity/selectivity and deactivation due to coking in propane aromatization
- Study of the influence of presence of higher alkane or olefin in feed on propane aromatization over H-GaAlMFI zeolite.

SUMMARY AND CONCLUSIONS

The thesis has been divided into the following three parts.

i) Hydrothermal synthesis of gallosilicate (MFI) and galloaluminosilicate (MFI) zeolites

ii) Characterization of Ga-modified ZSM-5 type zeolites and aromatization of propane and methanol over the zeolites using pulse micro-reactor

iii) Characterization of H-GaMFI and H-GaAlMFI zeolites and their performance in propane aromatization.

PART-I : HYDROTHERMAL SYNTHESIS OF GALLOSILICATE (MFI) AND GALLOALUMINOSILICATE (MFI) ZEOLITES

Chapter 1.1 : Hydrothermal synthesis of gallosilicate (MFI) zeolite : factors influencing crystallization kinetics and crystal size/growth

Kinetics of hydrothermal synthesis of gallosilicate (MFI) zeolite (under autogeneous pressure at 180^{o}C) from a gel containing a source of silica (Na-trisilicate or fumed silica), gallium nitrate, templating agent (TPA-Br or TPA-OH), deionised water and sulfuric acid have been thoroughly investigated for knowing the influence of various synthesis parameters (viz. gel composition, source of silica, template, method of gel preparation and pH of gel) on the crystallization kinetics and crystal size/growth of the zeolite. The zeolite samples were characterized for their crystallinity by XRD and crystal size and morphology by SEM. The crystallization rate and crystal size of the zeolite are found to be strongly influenced by the above synthesis parameters.

Chapter 1.2 : Hydrothermal synthesis of galloaluminosilicate (MFI) zeolite crystals having uniform size, morphology and Ga/Al ratio

The hydrothermal synthesis of galloaluminosilicate (MFI) zeolite from a gel containing source of silica (Na-trisilicate), source of gallium (Ga-nitrate or Na-gallate), source of aluminium (Al-nitrate or Na-aluminate), templating agent (TPA-Br), deionized water and sulfuric acid has been thoroughly investigated to know the influence of various synthesis parameters (viz. source of Al and Ga, gel composition, pH of gel and crystallization temperature) on the size and morphology of the zeolite crystals formed and also on the Al and Ga content (or Ga/Al ratio) of individual crystals. The zeolite samples were characterized for bulk concentration by chemical analysis, crystalline nature by XRD, crystal size and morphology by SEM and Ga/Al ratio of the individual crystals by EDS analysis. The morphology and Ga/Al ratio of zeolite crystals are strongly influenced by the source of Al and Ga in the synthesis gel. The use of Na-aluminate and Na-gallate as source of Al and Ga, respectively, results in the zeolite crystals with uniform shape/morphology (spherical-hexagonal) and Ga/Al ratio. Whereas, use of the other source for Al and Ga, particularly for the pH of gel ≥ 9.0, results in the zeolite crystals with two different shapes, spherical crystals with high Ga/Al ratio and hexagonal crystals with low Ga/Al ratio.

PART-II : CHARACTERIZATION OF Ga-MODIFIED ZSM-5 TYPE ZEOLITES AND AROMATIZATION OF PROPANE AND METHANOL OVER THE ZEOLITES USING PULSE MICRO-REACTOR

Chapter 2.1 : Characterization of O_2 and H_2 pretreated Ga-modified ZSM-5 type zeolites.

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 10h), have been characterized for their acidity/acid strength distribution (by chemisorption and step wise thermal desorption of pyridine from 100° - 400°C) and also for their acid functions by acid catalyzed model 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 micro-reactor. 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.

Chapter 2.2 : Pulse reaction studies on variation of initial activity/selectivity of O_2 and H_2 pretreated Ga-modified ZSM-5 type zeolite catalysts in propane aromatization

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Chapter 2.3 : Initial activity/selectivity of H-gallosilicate (MFI) zeolites in propane aromatization.

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 $400^{o}C$) 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.

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PART-III : CHARACTERIZATION OF H-GaMFI AND H-GaAlMFI ZEOLITES AND THEIR PERFORMANCE IN PROPANE AROMATIZATION.

Chapter 3.1: Influence of Si/Ga ratio on acidity, activity/selectivity and deactivation due to coking of H-gallosilicate (MFI) zeolite in propane aromatization.

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^{o}- $400^{o}C$ 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^{o}C) has been investigated. Framework Si/Ga ratio was measured by ^{29}Si MAS NMR. An information on the external acid sites is obtained by iso-octane 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) of 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.

Chapter 3.2 : Simultaneous aromatization of propane and higher alkane or olefin over H-GaAlMFI zeolite

Influence of the addition of higher alkane (viz. n-hexane) or olefin (viz. ethylene, n-butene or isobutene) in feed on the aromatization of propane over H-GaAlMFI zeolite [bulk Si/(Al + Ga) = 14.7, Ga/Al = 1.5, framework (FW) Si/Ga = 49.9, FW Si/Al of 40.3 (with no non-FW Al), Na/(Ga + Al) = 0.03, non-FW Ga = 0.32 mmol.g^{-1}, crystal size = 5.5 ± 1.5 μm, crystal shape = spherical-hexagonal and strong acidity = 0.46 mmol.g^{-1}

(measured in terms of the pyridine chemisorpted at 400°C)] at 450°C and GHSV of 6200 $cm^3.g^{-1}.h^{-1}$ has been investigated. The zeolite is thoroughly characterized for its crystallinity (by XRD), crystal size and morphology (by SEM), framework Si/(Al + Ga) ratio (by ^{29}Si and ^{27}Al MAS NMR) and acidity by the chemisortion of pyridine at 400°C. Results reveal that the conversion of propane in its aromatization over H-GaAlMFI zeolite can be enhanced by a factor of about two by carrying out the aromatization of propane simultaneously with that of higher alkanes or olefins, mostly due to hydrogen transfer reactions between propane and higher olefins. This has high practical importance.

PART - I

HYDROTHERMAL SYNTHESIS OF GALLOSILICATE (MFI) AND GALLOALUMINOSILICATE (MFI) ZEOLITES

CHAPTER 1.1 : HYDROTHERMAL SYNTHESIS OF GALLOSILICATE (MFI) ZEOLITE : FACTORS INFLUENCING CRYSTALLIZATION KINETICS AND CRYSTAL SIZE/GROWTH

CHAPTER 1.2 : HYDROTHERMAL SYNTHESIS OF GALLOALUMINOSILICATE (MFI) ZEOLITE CRYSTALS HAVING UNIFORM SIZE, MORPHOLOGY AND Ga/Al RATIO

CHAPTER 1.1

HYDROTHERMAL SYNTHESIS OF GALLOSILICATE (MFI) ZEOLITE : FACTORS INFLUENCING CRYSTALLIZATION KINETICS AND CRYSTAL SIZE/GROWTH

1.1.1 INTRODUCTION

H-gallosilicate (MFI) is a highly active/selective catalyst for the aromatization of lower alkanes (1-7), which is a process of great practical importance. It is also found to be more effective than Ga/H-ZSM-5 in aromatization of n-hexane (8) and light alkanes (5,9) and more active/selective than H-ZSM-5 in methanol-to-aromatics conversion and aromatization of propylene (10). Because of the importance of gallosilicate (MFI), it is of practical interest to investigate in details its hydrothermal synthesis under different conditions, using different sources of SiO_2, templates, gel compositions and methods of preparation and also at different pH of gel and periods of crystallization.

A few studies have been reported earlier (11-13) on the influence of SiO_2/Ga_2O_3, $(TPA)_2O/SiO_2$ and Na_2O/SiO_2 molar ratios in the gel on the crystallization kinetics of gallosilicate (MFI) zeolite. However, a little or no information is available on the influence of the other hydrothermal synthesis parameters such as source of SiO_2, method of gel preparation and pH of gel. The present work was, therefore, undertaken with an objective of studying the influence of these hydrothermal synthesis parameters on the crystallization kinetics and also on the crystal size/growth and morphology of the zeolite.

1.1.2 EXPERIMENTAL

The hydrothermal crystallization of gallosilicate (MFI) zeolite from a gel consisting of a silica source [viz. Na-trisilicate (60% SiO_2 and 18% Na_2O) (Fluka) or fumed silica], gallium nitrate (Aldrich), template [viz. tetrapropylammonium bromide (Aldrich) or tetrapropylammonium hydroxide (20% in water) (FLuka)], deionised water and sulfuric acid (which is used for adjusting the pH) has been carried out in a stainless steel autoclave at 180^oC under autogeneuos pressure for different crystallization periods (0-24 h). After the crystallization, the autoclave was cooled under running tap water and depressurised, and the resulting solid was washed thoroughly with deionised water and dried in air oven at 100^oC for 12 h. The gel was prepared by following two different methods.

Method A : In this method, the gel components silica source, deionised water, sulfuric acid (SiO_2/H_2SO_4 mole ratio = 9.8), aqueous gallium nitrate solution and template are mixed in the sequence. The resulting gel was stirred for 30 min and then its pH measured.

Method B : In this method the sequence of the addition of sulfuric acid is different, it is the last component to be added. Whereas, the sequence of addition of the other components is not changed.

The crystallization kinetics of the zeolite was studied for different silica sources and templates used, for different gel compositions and methods of gel preparation and also for two different pH values of gel (Table 1.1.1).

The hydrothermal synthesis solid products was characterized for their crystallinity by powder XRD (using Phillips diffractometer 1730 series and CuKα as a source of radiations), for crystal size and morphology by SEM, (using Leico Cambridge Stereoscan 440 scanning electron microscope) and for the incorporation of Ga in the framework of the zeolites by ^{71}Ga MAS NMR (using a Bruker MSL 300 MHz NMR).

1.1.3 RESULTS AND DISCUSSION

Results showing the influence of the Si/Ga, SiO_2/T and SiO_2/H_2O molar ratios and pH of the gel, source of silica (Na-trislicate or fumed silica), template (TPA-Br or TPA-OH) and method of gel preparation (Method-A or Method-B) on crystallization kinetics of gallosilicate (MFI) zeolite (at 180^oC under autogeneous pressure) are presented in Figs. 1.1.1-1.1.3. SEM photographs of the zeolite showing influence of the above hydrothermal synthesis parameters and the crystallization period on the size and morphology of the zeolite crystals are shown in Figs. 1.1.4-1.1.6. It may be noted that

Table 1.1.1 : Crystallinity and crystal size of gallosilicate (MFI) zeolite synthesized hydrothermally under different conditions (source of Ga = Ga-nitrate and crystallization temperature = 180°C)

Preparation of gel for hydrothermal crystallization								Period of crystallization (h)	Properties of crystals	
Source of SiO_2	Template (T)	Gel composition (molar)				Method of gel preparation	pH of gel		Crystallinity (%)	Crystal size (µm)
		SiO_2	$GaO_{1.5}$	H_2O	T					
Na-trisilicate	TPA-Br	25	1.0	833	3.1	A	9.0	5	12	-
Na-trisilicate	TPA-Br	25	1.0	833	3.1	A	9.0	10	100	2.5
Na-trisilicate	TPA-Br	25	1.0	833	3.1	A	9.0	24	100	9.3
Na-trisilicate	TPA-Br	25	1.0	833	3.1	A	7.3	5	83	3.0
Na-trisilicate	TPA-Br	25	1.0	833	3.1	A	7.3	10	100	6.5
Na-trisilicate	TPA-Br	25	1.0	833	3.1	B	9.0	5	42	6.4
Na-trisilicate	TPA-Br	25	1.0	833	3.1	B	9.0	10	100	9.7
Na-trisilicate	TPA-Br	25	1.0	833	12.5	A	9.0	5	83	3.5
Na-trisilicate	TPA-Br	25	1.0	833	12.5	A	9.0	10	100	8.4
Na-trisilicate	TPA-Br	25	1.0	1666	3.1	A	9.0	5	80	3.6
Na-trisilicate	TPA-Br	25	1.0	1666	3.1	A	9.0	10	100	8.0
Na-trisilicate	TPA-Br	75	1.0	833	3.1	A	9.0	5	100	5.5
Na-trisilicate	TPA-Br	75	1.0	833	3.1	A	9.0	10	100	7.8
Na-trisilicate	TPA-OH	25	1.0	833	3.1	A	9.0	5	41	3.4
Na-trisilicate	TPA-OH	25	1.0	833	3.1	A	9.0	10	100	7.5
Fumed silica	TPA-Br	25	1.0	833	3.1	A	9.0	5	21	2.1
Fumed silica	TPA-Br	25	1.0	833	3.1	A	9.0	10	100	13.7

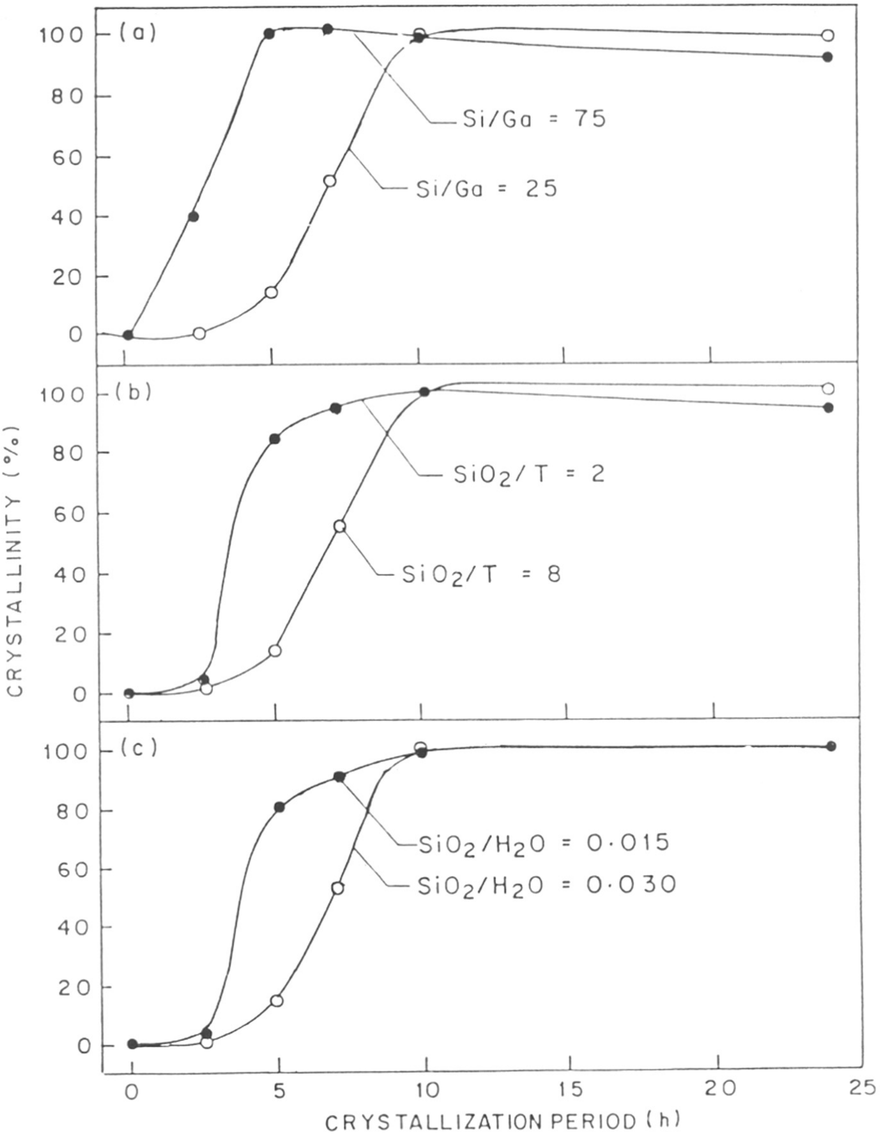


Fig. 1.1.1.: Effect of Si/Ga ratio (a), SiO_2/T ratio (b) and SiO_2/H_2O ratio (c) of gel on the kinetics of crystallization of gallosilicate (MFI) zeolite.

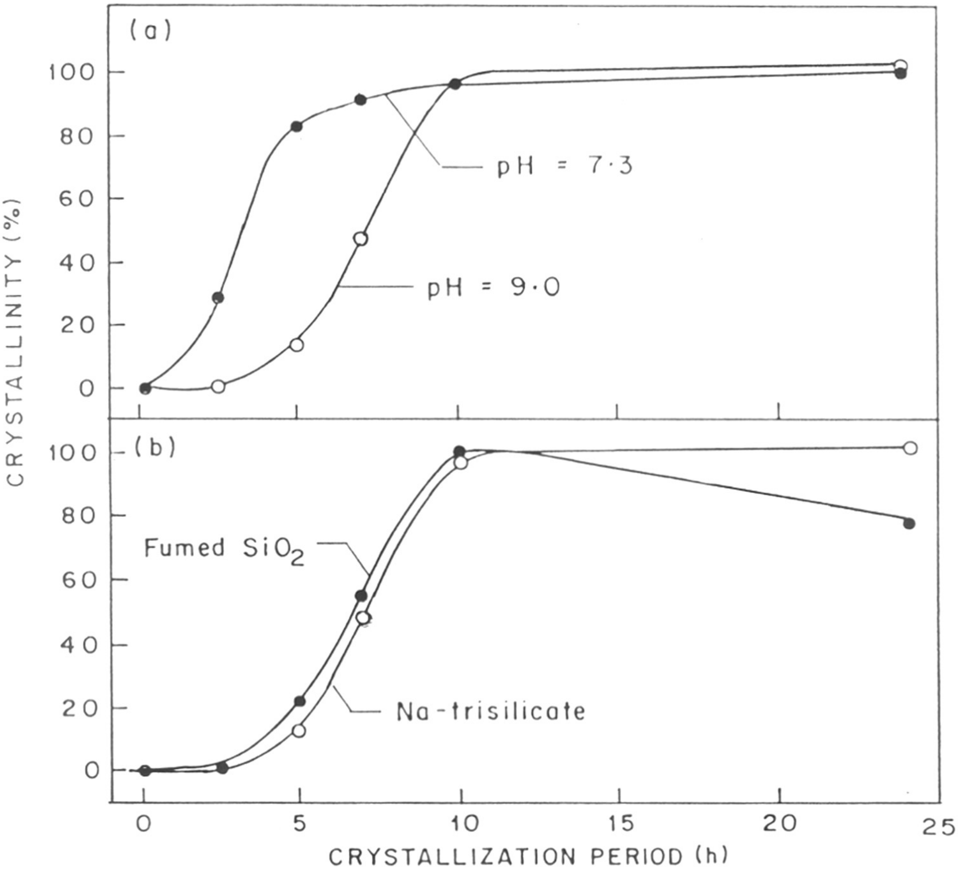


Fig. 1.1.2. : Effect of pH of gel (a) and source of silica (b) on the kinetics of crystallization of gallosilicate (MFI) zeolite

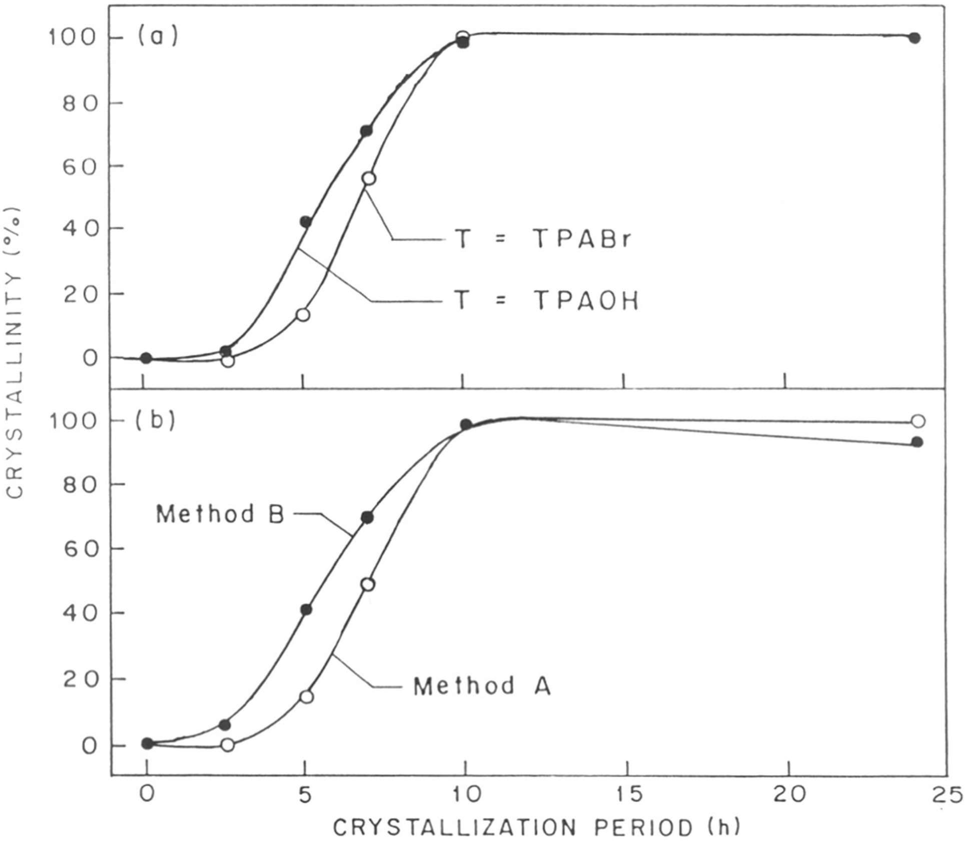
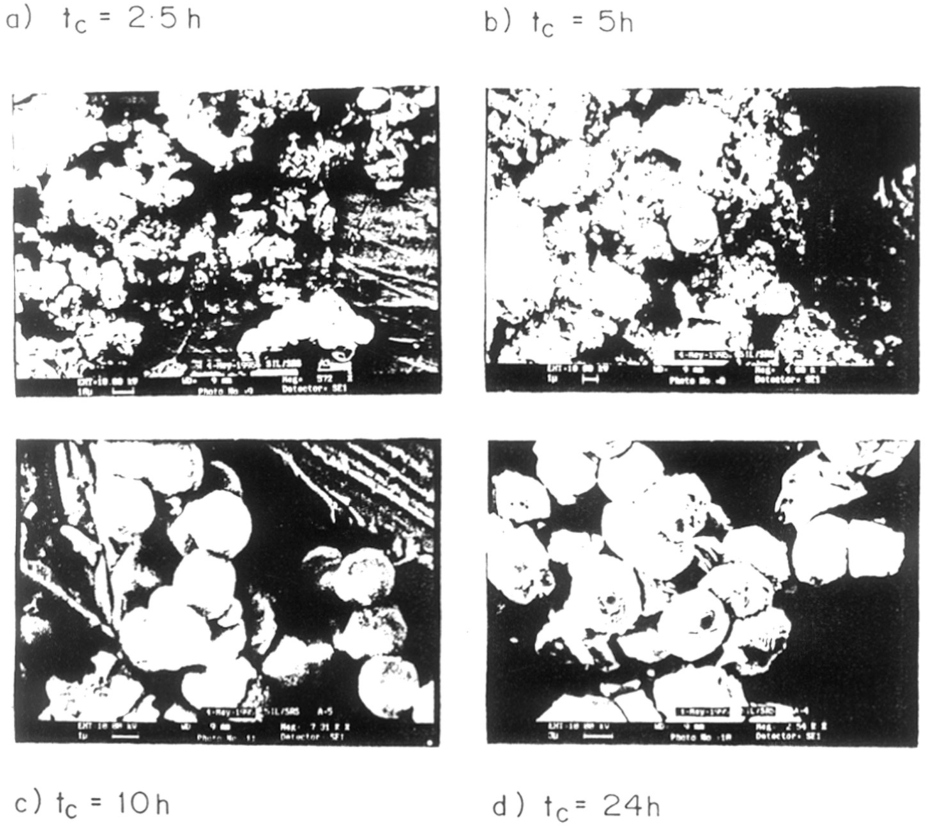


Fig. 1.1.3. : **Effect of templating agent (a) and method of gel preparation (b) on the kinetics of crystallization of gallosilicate (MFI) zeolite**



a) t_c = 2·5 h

b) t_c = 5h

c) t_c = 10h

d) t_c = 24h

Fig. 1.1.4. : SEM photographs of the gallosilicate (MFI) zeolite obtained at the crystallization period of 5h and 10h (silica source = Na-trisilicate, T = TPA-Br, SiO_2/T = 8.0, SiO_2/H_2O = 0.03, method of gel preparation = method-A, and pH of gel = 9.0)

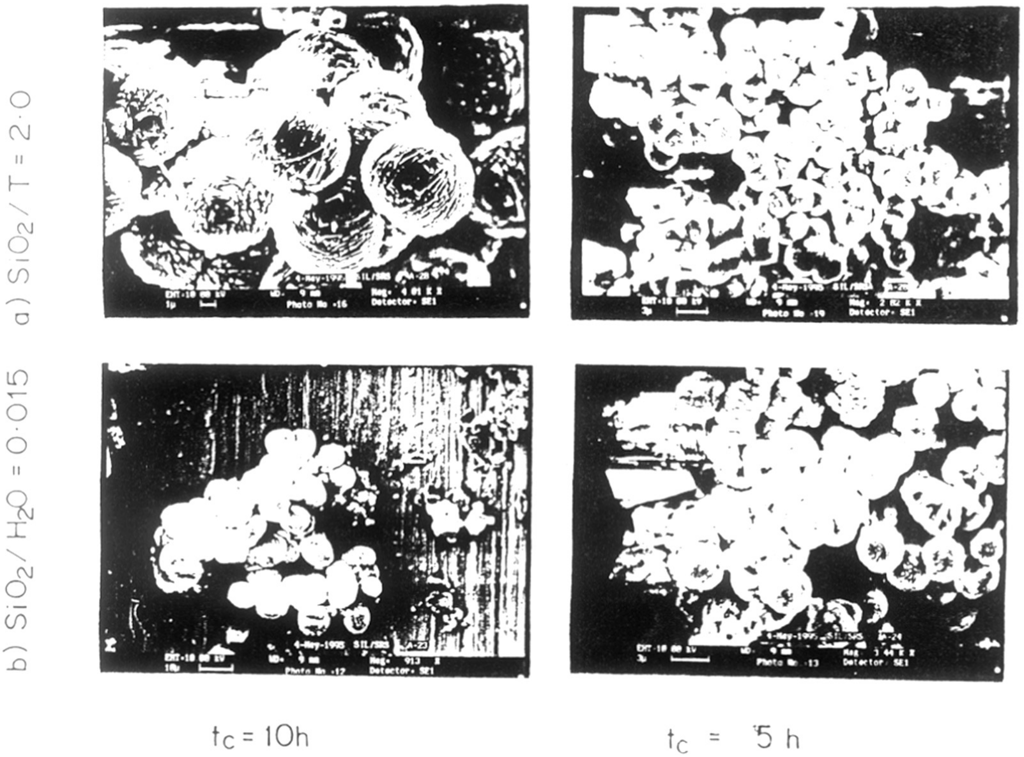


Fig. 1.1.5. : SEM photographs of the gallosilicate (MFI) zeolite synthesized using gel with $SiO_2/T = 2.0$ (a), and $SiO_2/H_2O = 0.015$ (b), for the crystallization period of 5h and 10h.

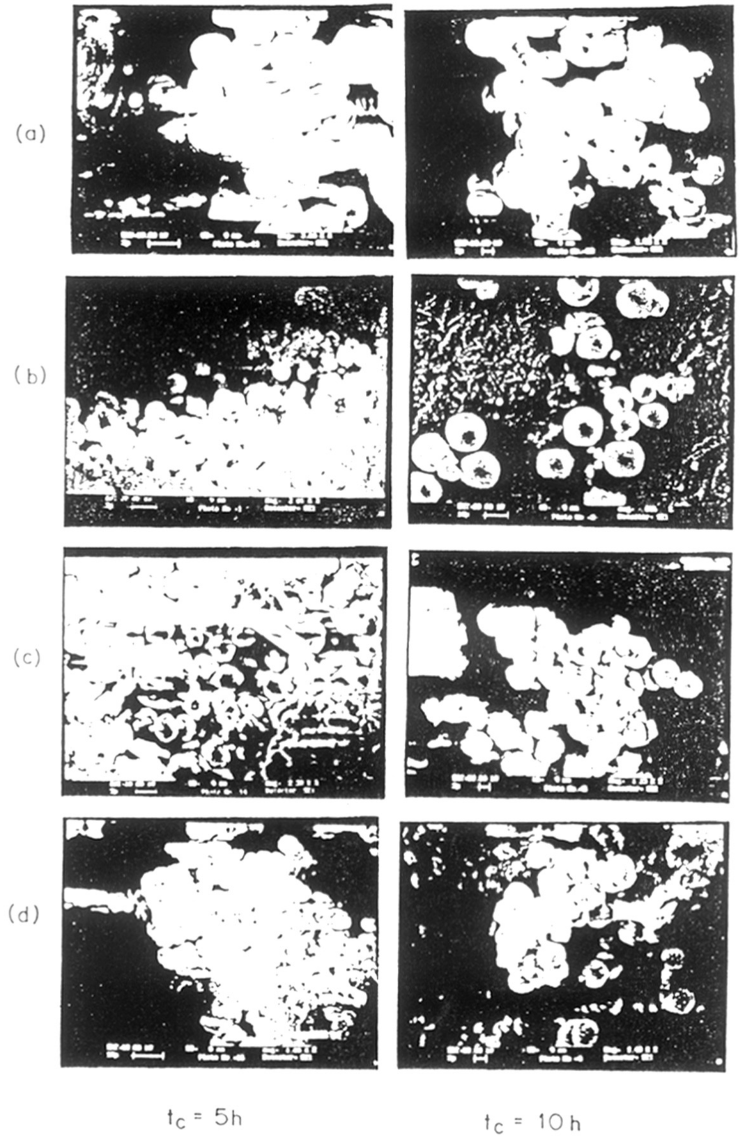


Fig. 1.1.6. : SEM Photographs of the gallosilicate (MFI) zeolite synthesized using gel having pH = 7.3 (a), source of silica = fumed silica (b), template = TPA-OH (c) and gel prepared by method B (d), for the crystallization period of 5h and 10h.

only one hydrothermal synthesis parameter is varied while keeping the other synthesis conditions the same. The common hydrothermal synthesis conditions are as follows : Source of gallium = Ga-nitrate, source of silica = Na-trisilicate, Template (T) = TPA-Br, Si/Ga ratio = 25, SiO_2/T ratio = 8, SiO_2/H_2O ratio = 0.03, Method of gel preparation = Method-A and pH = 9.0. The data on the crystallinity and crystal size of the zeolite under the different hydrothermal synthesis conditions are given in Table 1.1.1. The crystallinity was obtained from the XRD (Figs 1.1.7-1.1.11) data by comparing the intensity of the XRD peaks at 2θ = 22-25. The incorporation of Ga in the zeolite framework was confirmed by observing sharp ^{71}Ga MAS NMR peak at +156 ppm. Representative ^{71}Ga MAS NMR spectra of the zeolites are given elsewhere (Chapter 3.1, Fig. 3.1.2).

1.1.3.1 Influence of Crystallization Period on Crystal Growth/Crystal Size

In general, at all the hydrothermal synthesis conditions, the maximum crystallinity is obtained upto a crystallization period of 10 h (Figs. 1.1.1-1.1.3). However, for a prolonged period of the crystallization (24 h), the crystallinity of the zeolite is decreased significantly for the cases when the gel has Si/Ga ratio = 75, SiO_2/T ratio = 2, silica source = fumed silica and gel preparation method = method-B. A loss of crystallinity due to prolongation of the crystallization period of the zeolite has also been observed earlier (14). In our earlier study (15) a decrease in the crystallinity of GaMFI zeolite due to its hydrothermal treatment has been observed. When the crystallization period (after the zeolite has attented its 100% crystallinity) is prolonged, the zeolite is subjected to hydrothermal treatment under alkaline condition (i.e at high pH). This may be responsible for the observed decrease in the crystallinity at the higher crystallization periods.

In all the cases, the crystal size of the zeolite is found to be increased markedly with increasing the crystallization period (Table 1.1.1, Figs. 1.1.4-1.1.6). This is in accordance with the Oswalt's redissolution/aging, resulting in a growth of lager crystals at the expense of small crystals (16). The increase in the crystal size of the zeolite with increasing its crystallization period is also observed earlier (12).

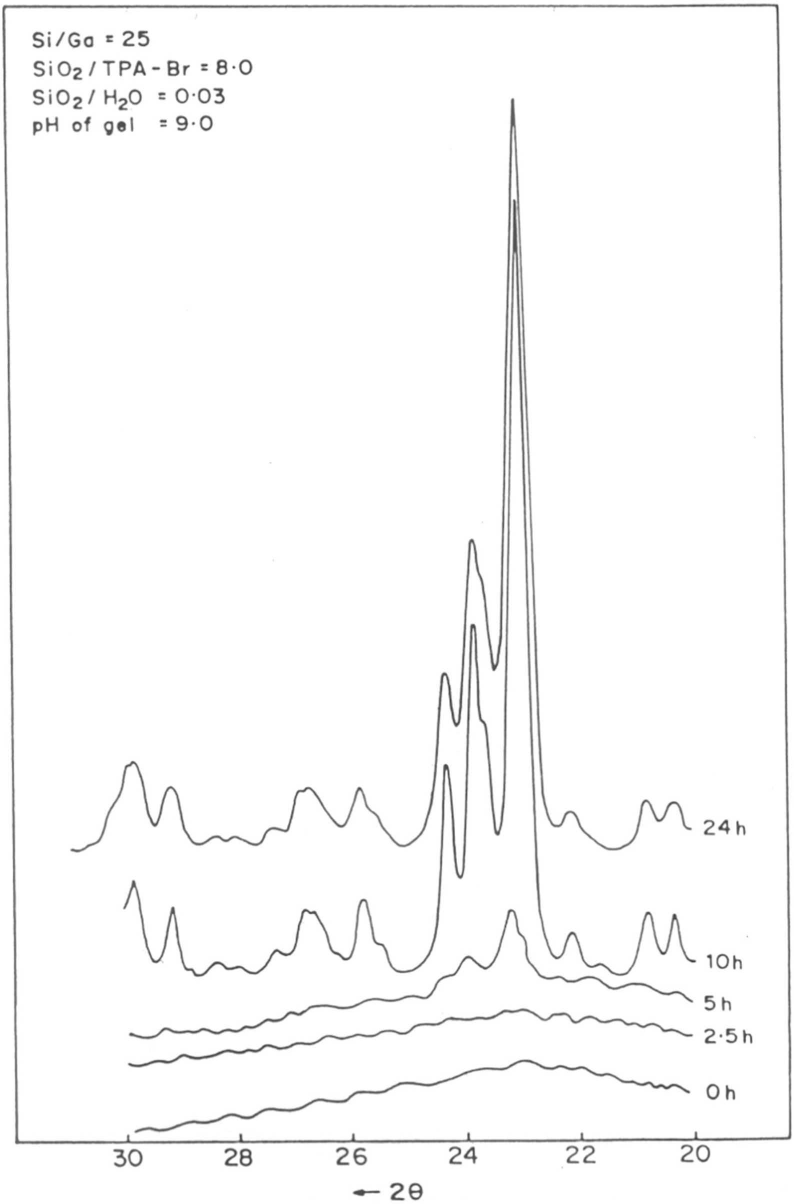


Fig. 1.1.7 : **XRD spectra of gallosilicate zeolite at different crystallization periods.**

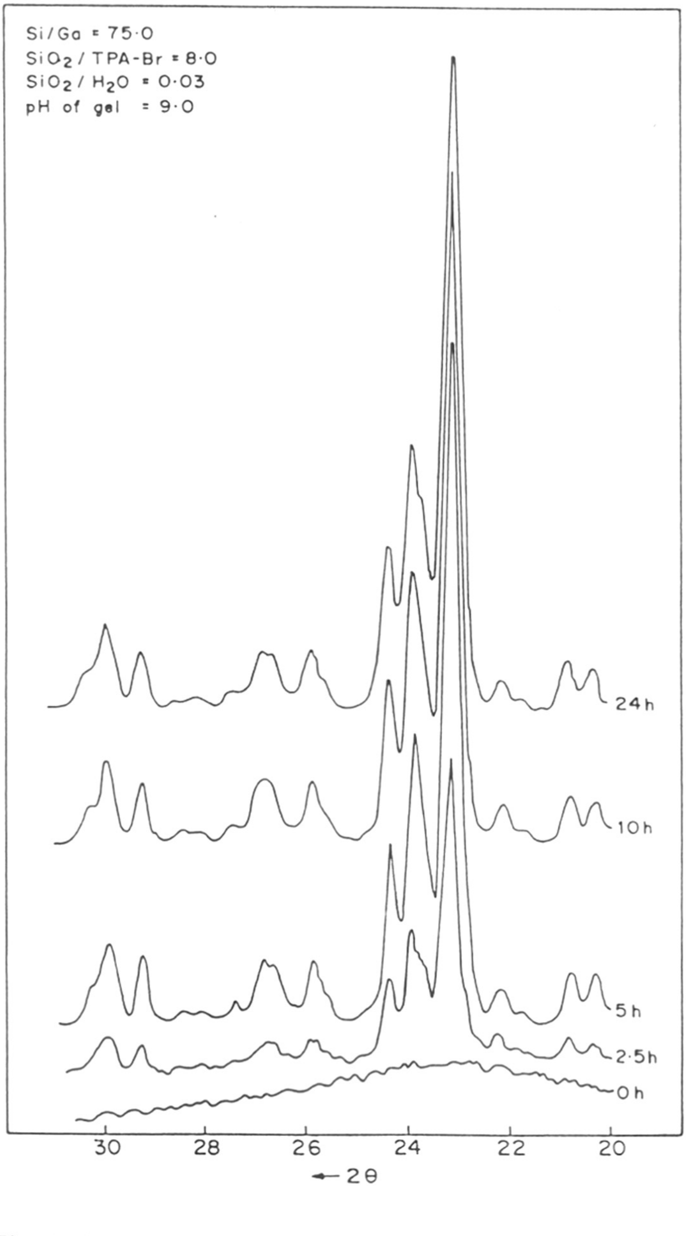


Fig. 1.1.8 : **XRD spectra of gallosilicate zeolite at different crystallization periods showing effect of Si/Ga ratio of gel.**

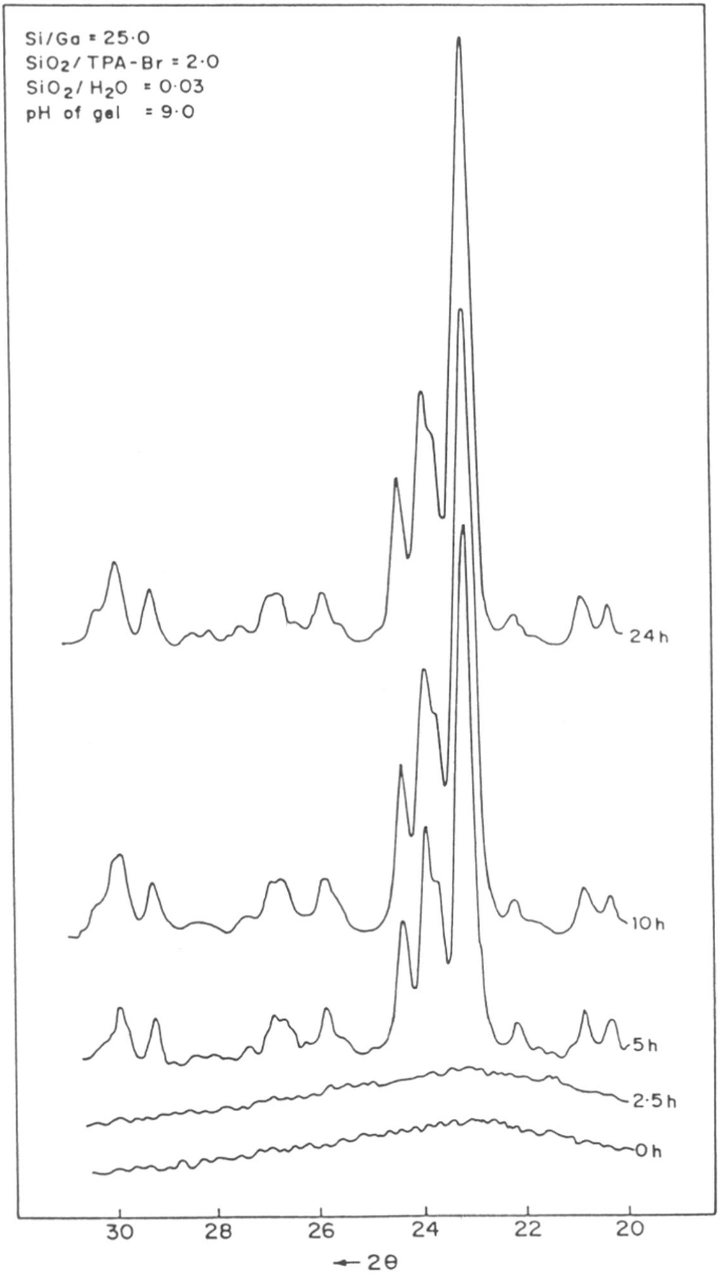


Fig. 1.1.9 : **XRD spectra of gallosilicate zeolite at different crystallization periods showing effect of SiO_2/T ratio of gel.**

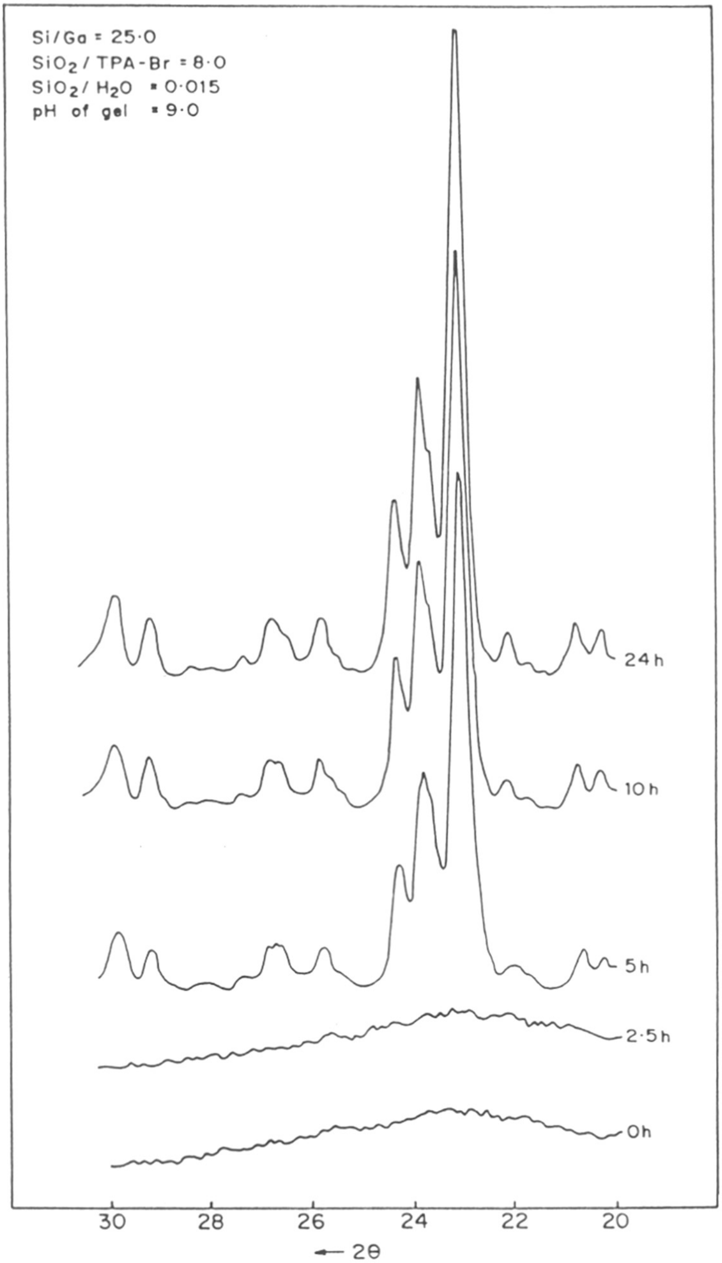


Fig. 1.1.10 : **XRD spectra of gallosilicate zeolite at different crystallization periods showing effect of SiO_2/H_2O ratio of gel.**

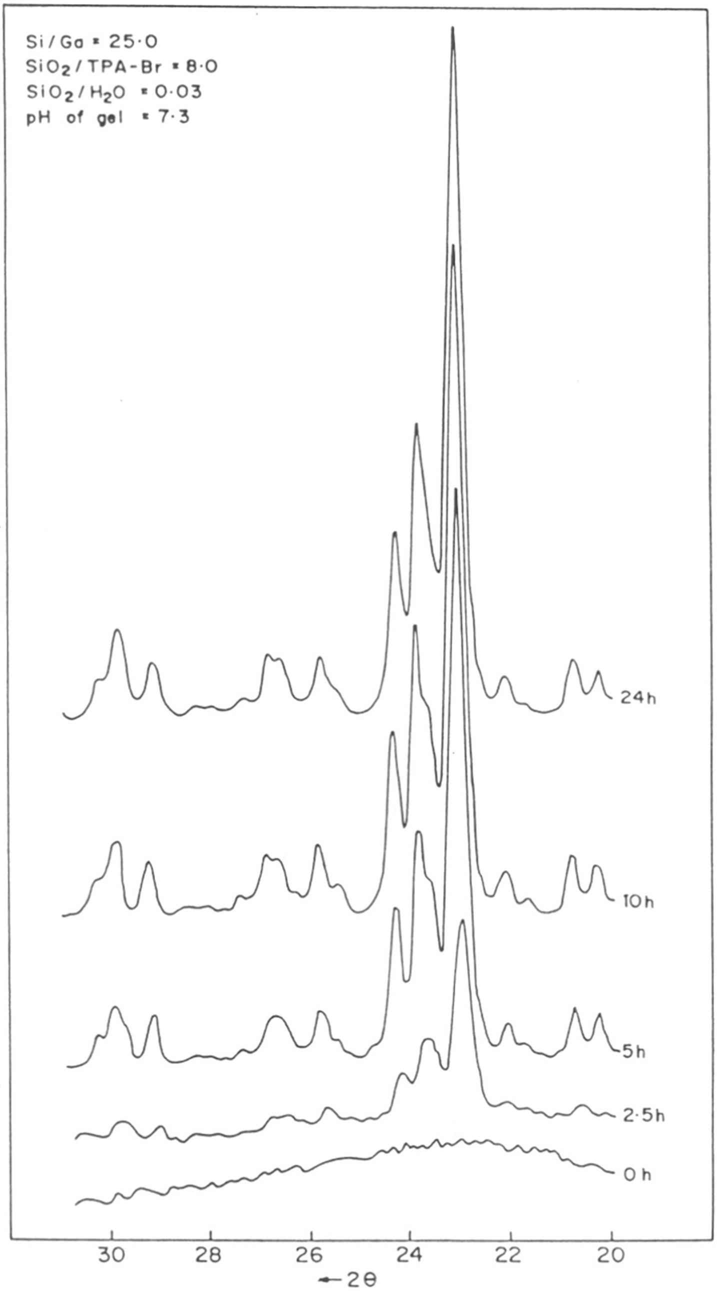


Fig. 1.1.11 : XRD spectra of gallosilicate zeolite at different crystallization periods showing effect of pH of gel.

A comparison of the zeolite obtained under different hydrothermal synthesis conditions for its crystallinity and crystal size (Table 1.1.1) reveals that the hydrothermal synthesis parameters have strong influence on the crystallization of the zeolite.

1.1.3.2 Influence of Silica Source, Template and Gel Preparation Method

The results for the zeolite obtained using the silica source as Na-trisilicate (Figs. 1.1.2b and 1.1.4) and fumed silica (Figs. 1.1.2b and 1.1.6b) indicate that when fumed silica is used, the crystallization rate (or crystallinity) is higher and also the crystals are much larger in size. However, when the crystallization is prolonged (24 h), the crystallinity is reduced markedly in the case of the use of fumed silica, but not Na-tirsilicate, as a source of silica.

The rate of crystallization in both the cases is much higher than that observed earlier (13) when Na-silicate is used as the source of silica. The observed higher crystallization rates in the present case are consistent with that observed earlier (17) when Na-trisilcate is used as the silica source. This shows that the crystallization rates are strongly influenced by the silica source used in the zeolite synthesis. This is consistent with that observed in the crystallization of aluminosilicate (MFI) (18-19).

A comparison of the results (Figs. 1.1.3a, 1.1.4 and 1.1.6c and Table 1.1.1) indicates that the rate of crystallization and also the crystal size are higher when TPA-OH is used instead of TPA-Br as a template. The results (Figs. 1.1.3b, 1.1.4 and 1.1.6d and Table 1.1.1) also show a strong influence of the gel preparation method (i.e. the way by which the different gel components are mixed or sequence of their addition) on the crystallization kinetics and crystal growth. When method-B is used for the gel preparation, both the crystallinity and crystal size for the same crystallization period are increased pronouncely. This suggests that the nucleation and growth of zeolite crystals depends on the gel preparation method.

1.1.3.3 Influence of Gel Composition and pH

Figure 1.1.1a shows a strong influence of the Si/Ga ratio of gel on the crystallization rate. For the higher Si/Ga ratio, the crystallization is much faster. This is consistent with that observed by Kosslick et.al. (12). However, Giannetto et.al. (13) observed no effect of the initial Si/Ga ratio on the crystallization. This may probably be due to the use of different silica source (Na-silicate) by them in their zeolite synthesis.

The crystal size of the zeolite is also found to be larger when the Si/Ga ratio in the gel was higher (Table 1.1.1). This is consistent with our earlier observations for the zeolite with different Si/Ga ratios (7).

The crystallization rate is also found to be strongly influenced by the SiO_2/T (Fig. 1.1.1b) and SiO_2/H_2O (Fig. 1.1.1c) ratios of the gel. The crystallization rate (Figs. 1.1.1b and 1.1.1c) and also the crystal size (Figs. 1.1.4 and 1.1.5, Table 1.1.1) are higher when the concentration of template or water in the gel is larger. In this case also our results are contradictory to that of Giannetto et.al. (13). They observed that the crystallization is quasi-independent of the gel chemical composition. It seems that silica source plays important role in deciding the influence of gel composition on the crystallization kinetics.

The initial pH of the gel also has a strong influence on both the crystallization kinetics (Fig. 1.1.2a) and crystal growth (Figs. 1.1.4 and 1.1.6a, Table 1.1.1). The crystallization is faster and also the crystal size is larger when the pH of the gel is 7.3 (i.e. close to neutral pH) instead of 9.0.

1.1.4 CONCLUSIONS

The crystallization of gallosilicate (MFI) zeolite is strongly influenced by a number of hydrothermal synthesis parameters, such as source of silica, template, chemical composition of gel (viz. concentration of Ga_2O_3, template and H_2O relative to SiO_2), method of gel preparation and pH of gel. The crystal size of the zeolite is increased with increasing the crystallization period because of the Oswalt's redissolution/recrystallization. It is also strongly influenced by the hydrothermal synthesis parameters. An influence of a particular synthesis parameter on the crystallization kinetic is seems to be dependent upon the other synthesis parameter(s).

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CHAPTER 1.2

HYDROTHERMAL SYNTHESIS OF GALLOALUMINOSILICATE (MFI) ZEOLITE CRYSTALS HAVING UNIFORM SIZE, MORPHOLOGY AND Ga/Al RATIO

1.2.1 INTRODUCTION

H-galloaluminosilicate (MFI) zeolites show high activity in conversion of n-hexane (1,2) to aromatics. They are more active/selective in the propane aromatization, compared to the other Ga-modified ZSM-5 type zeolites viz. physically mixed Ga_2O_3 and H-AlMFI (3), Ga-impregnated H-AlMFI and H-GaMFI (4). The high activity/ selectivity of H-galloaluminosilicate (MFI) is attributed to the presence of highly dispersed gallium oxides species in a close vicinity of the zeolitic acid sites (4). The high dispersion of the Ga-oxides species is expected due to the degalliation of the zeolite during its thermal treatments.

In our preliminary work on the hydrothermal synthesis of galloaluminosilicate (MFI) zeolite, crystals of two distinctly different morphologies, spherical and hexagonal, similar to those commonly observed for GaMFI (5-8) and AlMFI zeolites, respectively, were obtained. It is interesting to characterize these two different crystals for their composition to know whether they differ widely in their Ga/Al ratio. It is necessary to develop synthesis of the zeolite with crystals of uniform morphology and composition. This investigation was undertaken with this objective. We show here that, among the different hydrothermal synthesis parameters (viz. source of Al and Ga, gel composition and pH, and crystallization temperature), the source of Al and Ga, and also the pH of gel plays a vital role in deciding the crystal morphology and relative concentration of Al and Ga in the individual crystals of the zeolite.

1.2.2. EXPERIMENTAL

Hydrothermal synthesis of galloaluminosilicate (MFI) from a gel, consisting of Na-trisilicate (Fluka) as source of Si, Ga-nitrate (Aldrich) or Na-gallate as a source of

Ga, Al-nitrate (BDH) or Na-aluminate as a source of Al, tetrapropylammonium bromide (TPA-Br) (Aldrich) as a template, deionised water and sulfuric acid (which is used for adjusting pH), at different pH values and Ga/Al ratios of the gel and crystallization temperatures has been carried out in a closed stainless steel autoclave kept in a constant temperature air oven. The Si/(Al + Ga), TPA-Br/SiO_2 and H_2O/SiO_2 ratio in the synthesis gel were 25, 0.13 and 33.3, respectively, and the period of crystallization was 24h. The reaction mixture was shacked occasionally. The clear solutions of Na-gallate and Na-aluminate were obtained by the procedure described elsewhere (9). After the zeolite crystallization, the resulting crystalline material was washed thoroughly with deionised water and dried in air oven at 100°C for 12h. The conditions for synthesis of different samples of the zeolite are given in Table 1.2.1.

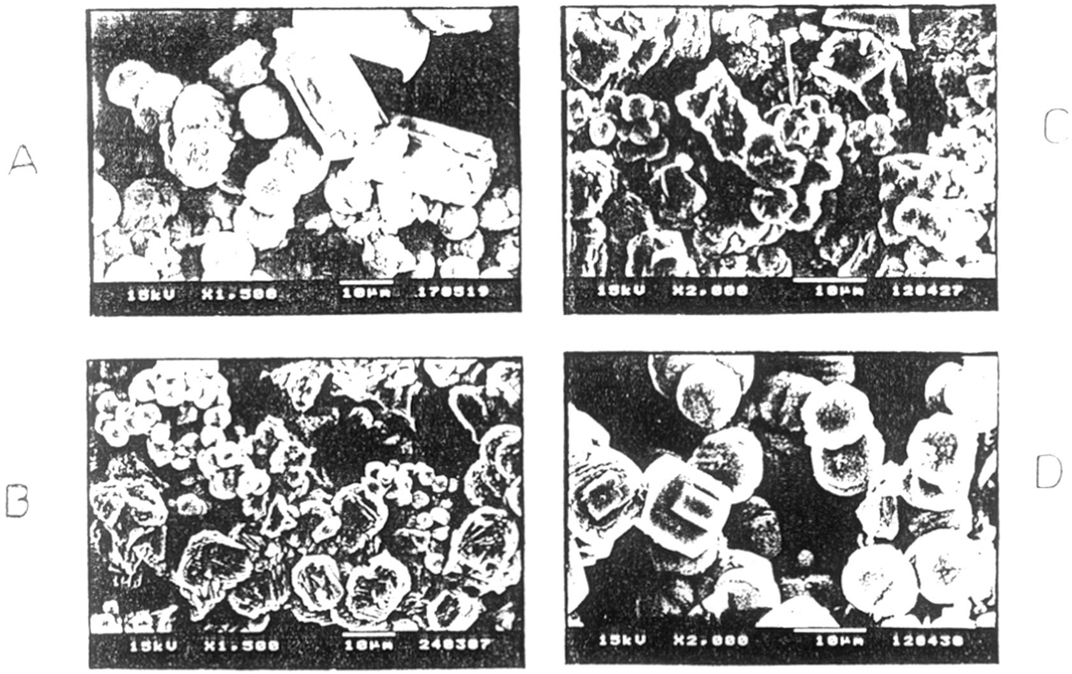
The zeolite samples (as synthesized) were characterized for their crystalline nature by powder XRD (using Philips diffractometer 1730 series and CuKα as a source of radiation), crystal size and morphology by SEM (using JOEL scanning electron microscope), concentration of gallium and aluminum in the different crystals by EDS analysis (using KEVEX Energy dispersive spectrometer for X-ray microanalysis), bulk concentration of gallium and aluminum by chemical analysis and also for the tetrahedral (framework) Ga and Al by ^{71}Ga and ^{27}Al MAS NMR, respectively (using a Bruker MSL 300 MHz NMR).

1.2.3 RESULTS AND DISCUSSION

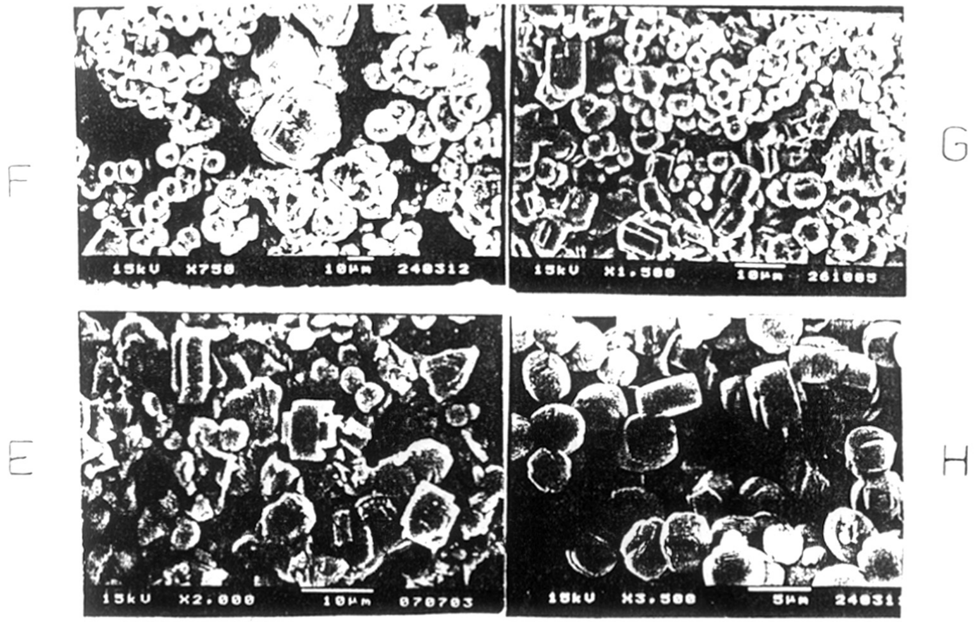
Results showing influence of the hydrothermal synthesis parameters (viz. source of Al and Ga, gel composition and pH, and crystallization temperature) on the composition of the zeolite and particularly, on its crystal size and shape (or morphology) are presented in Table 1.2.1. The SEM microphotographs of the zeolite samples synthesized using the different sources for Ga and Al and/or synthesized under different conditions are presented in Figs. 1.2.1-1.2.3. The XRD patterns of all the zeolite samples were quite similar and indicated that all the samples are highly crystalline and have ZSM-5 type (MFI) structure. Representative XRD spectra of the zeolite with uniform and non-

Table 1.2.1 : Hydrothermal synthesis conditions and crystal size and morphology of galloaluminosilicate (MFI) zeolite samples. [source of Si = Na-trisilicate, TPA-Br/SiO_2 = 0.13, H_2O/SiO_2 = 33.3 and crystallization period = 24h.]

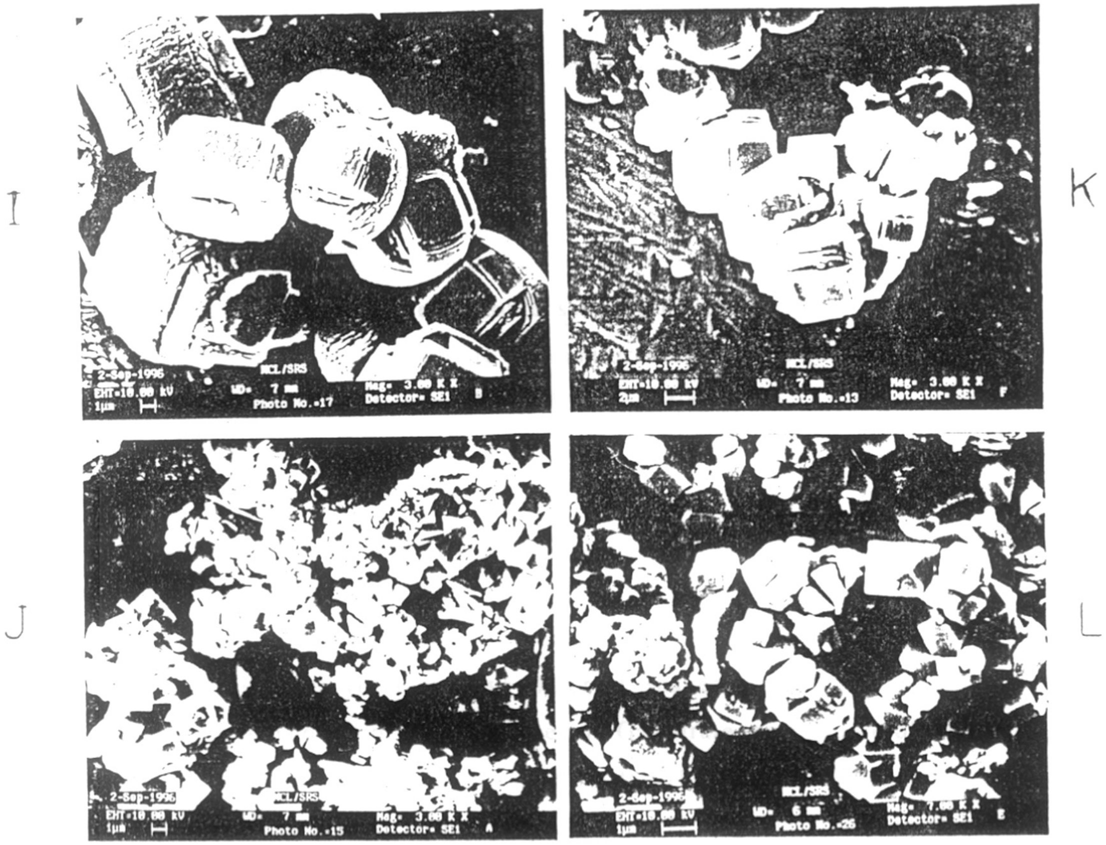
Zeolite sample	Source of Ga and Al		pH of gel	Crystallization temp. (^oC)	Si/(Al + Ga) ratio		Ga/Al ratio		Crystal size (av.) (μm) (morphology)
	Ga	Al			gel	zeolite	gel	zeolite	
A	Ga-nitrate	Al-nitrate	9.0	160	25	30.8	1.0	1.04	11.0 (spherical) and 15x25 (hexagonal)
B	Ga-nitrate	Al-nitrate	9.0	200	25	37.5	1.0	1.18	4.5 (spherical) and 6x11 (hexagonal)
C	Ga-nitrate	Al-nitrate	11.2	180	25	31.6	1.0	1.26	3.5 (spherical) and 5x8 (hexagonal)
D	Ga-nitrate	Al-nitrate	7.0	180	25	27.8	1.0	0.98	9.5 (spherical), 10 (spherical-hexagonal) and 10x12 (hexagonal)
E	Ga-nitrate	Al-nitrate	9.0	180	25	30.8	0.33	0.30	3.5 (spherical) and 5.5x9 (hexagonal)
F	Ga-nitrate	Al-nitrate	9.0	180	25	38.0	3.0	2.49	9.5 (spherical) and 18x27 (hexagonal)
G	Ga-nitrate	Al-nitrate	9.0	180	25	37.0	1.0	0.83	3.0(spherical) and 6x11 (hexagonal)
H	Na-gallate	Na-aluminate	9.0	180	25	28.1	1.0	1.28	4.7 (spherical-hexagonal)
I	Na-gallate	Na-aluminate	7.5	180	25	28.7	1.0	1.17	7.5 (spherical-hexagonal)
J	Na-gallate	Na-aluminate	11.0	180	25	29.9	1.0	1.06	non-uniform crystals
K	Na-gallate	Al-nitrate	9.0	180	25	28.5	1.0	1.20	7.2 (spherical-hexagonal)
L	Ga-nitrate	Na-aluminate	9.0	180	25	31.3	1.0	0.97	non-uniform crystals



1.2.1. SEM microphotographs of the zeolite samples A,B,C and D.



1.2.2. SEM microphotographs of the zeolite samples E,F,G and H.



1.2.3. SEM microphotographs of the zeolite samples I,J,K and L.

uniform crystals are presented in Fig.1.2.4. The incorporation of Ga and Al in the zeolite framework was confirmed by observing a sharp peak at +156ppm for the ^{71}Ga MAS NMR and at about +54ppm for the ^{27}Al MAS NMR, respectively. No peak for ^{27}Al MAS NMR at zero ppm was observed for all the zeolite samples, indicating the absence of octahedral Al. However, it was not possible to know from the ^{71}Ga MAS NMR about the presence or absence of nonframework Ga-species in the zeolite samples. This is because of the fact that, in the zeolite, the extraframework Ga exists in such a distorted environment that its resonance is too broad to be detected (10).

A comparison of the different zeolite samples (A-L) for their crystal size and morphology clearly shows that the zeolite with uniform crystal size and shape (spherical-hexagonal) can be synthesized using Na-gallate and Na-aluminate (or Al-nitrate) as source of Ga and Al, respectively (Figs. 1.2.2H and 1.2.3I,K). When Ga- and Al-nitrates were used as source of Ga and Al, the zeolite crystals with two different shapes (spherical and hexagonal) and sizes are formed (Figs. 1.2.1 A-D and 1.2.2E-G); the size of spherical crystals being smaller than that of the hexagonal one. Only for the zeolite sample 'D', synthesized from the gel of lower pH (pH = 7.0); the crystals are uniform (Fig. 1.2.1D) in size but yet they have different shapes (spherical, hexagonal and spherical-hexagonal). The use of Na-aluminate and Ga-nitrate, as a source of Al and Ga, respectively, also results in non-uniform zeolite crystals (Fig. 1.2.3L). Thus, results show a strong influence of the source of Ga, and also the pH of gel on the crystal size and morphology of the zeolite. At high pH (11.0), even the use of Na-gallate (as a source of Ga) results in the non-uniform zeolite crystals (Fig. 1.2.3J).

The number of hexagonal crystals (which are commonly observed for Al-MFI or ZSM-5 zeolite) relative to that of spherical crystals [which are commonly observed for Ga-MFI zeolite (Chapter 1.1 and ref. 5-8)] are found to increase with decreasing the Ga/Al ratio of the synthesis gel (Fig. 1.2.2). This indicates a possibility of forming separate crystals of Ga-MFI with small concentration of Al (spherical crystals) and of Al-MFI with small concentration of Ga (hexagonal crystals). This is confirmed by the EDS analysis of the spherical and hexagonal crystals of zeolite sample 'G' (Table 1.2.2). The

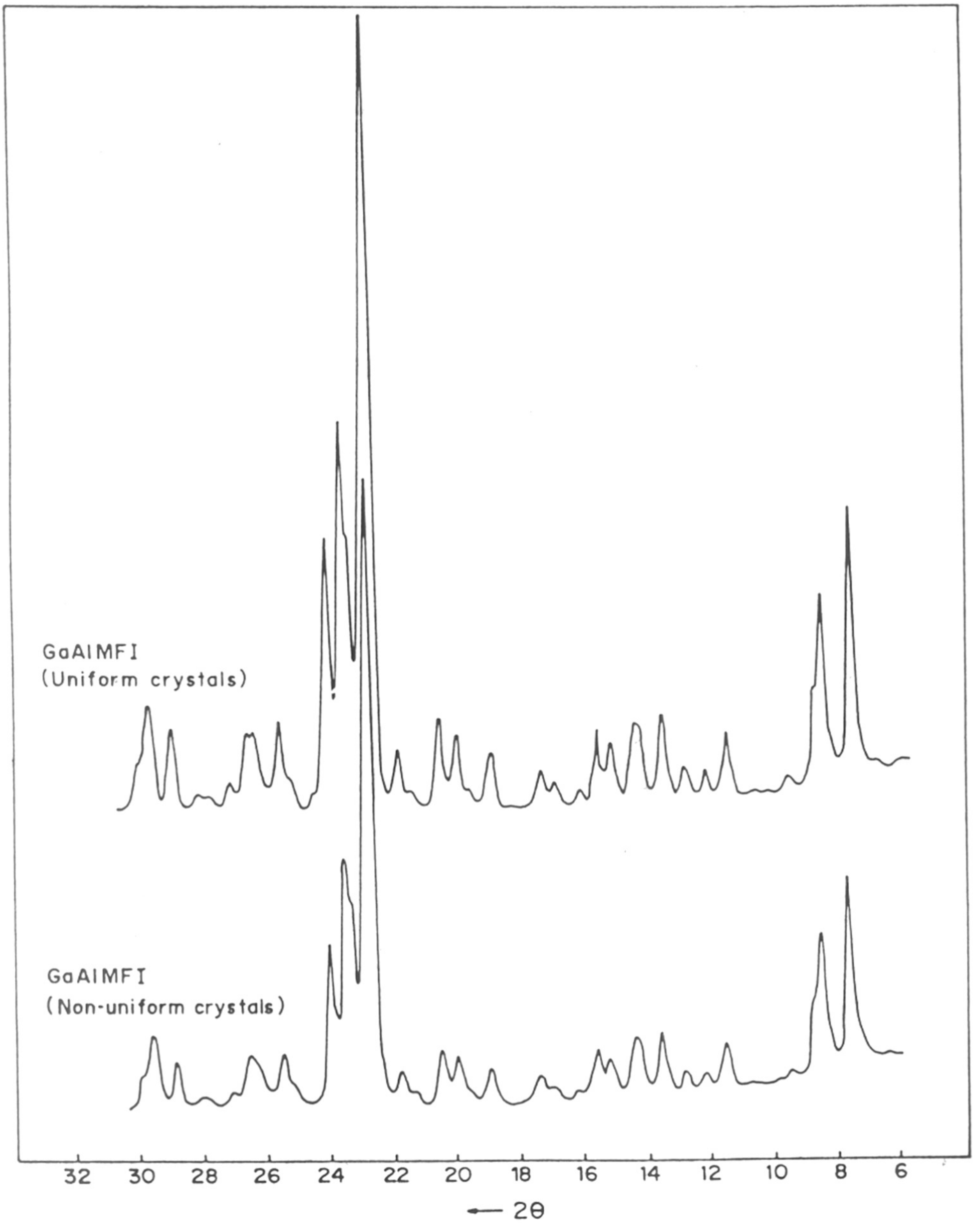


Fig. 1.2.4 : XRD spectra of galloaluminosilicate zeolite.

Table 1.2.2 : Ga/Al atomic ratios of individual crystals of the zeolite samples G and H by EDS analysis.

Zeolite sample	Individual crystals	Ga/Al ratio by EDS analysis
G	Spherical crystals	2.2 ± 0.70
	Hexagonal crystals	0.5 ± 0.17
H	Spherical-hexagonal crystals	1.2 ± 0.20

spherical crystals have much higher Ga/Al ratio and richer in Ga; where as, the hexagonal ones are richer in Al and have lower Ga/Al ratio. However, the EDS analysis of 30 crystals of zeolite sample 'H', having only one kind of crystals (spherical-hexagonal) of nearly same size and morphology shows that the zeolite crystals are also similar in their composition (Ga/Al ratio). These observations indicate that the simultaneous incorporation of Al and Ga in the zeolite framework, resulting zeolite crystals with uniform size and shape, is strongly dependent upon the source of Ga used in the synthesis gel and also on the pH of the gel. The simultaneous incorporation of Al and Ga seems to be favored by the presence of gallate in the gel. The source of Al, however, has no significant effect.

1.2.4 CONCLUSIONS

In the hydrothermal synthesis of galloaluminosilicate (MFI), when Al-nitrate (or Na-aluminate) and Ga-nitrate are used as a source of Al and Ga, respectively, the zeolite crystals of two different shapes (spherical crystals with high Ga/Al ratio and hexagonal ones with low Ga/Al ratio) are formed. However, the use of Na-gallate as source of Ga and low pH (≤ 9.0) of the synthesis gel results in the zeolite crystals with uniform size, shape (spherical-hexagonal) and composition (Ga/Al ratio). The size of the non-uniform crystals (spherical and hexagonal crystals) is also strongly influenced by the pH and composition of synthesis gel and also by the crystallization temperature.

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PART - II

CHARACTERIZATION OF Ga-MODIFIED ZSM-5 TYPE ZEOLITES AND AROMATIZATION OF PROPANE AND METHANOL OVER THE ZEOLITES USING PULSE MICROREACTOR

CHAPTER 2.1 : 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-GaAlMFI ZEOLITES

CHAPTER 2.2 : PULSE REACTION STUDIES ON VARIATION OF INITIAL ACTIVITY/SELECTIVITY OF O_2 AND H_2 PRETREATED Ga-MODIFIED ZSM-5 TYPE ZEOLITE CATALYSTS IN PROPANE AROMATIZATION

CHAPTER 2.3 : INITIAL ACTIVITY/SELECTIVITY OF H-GALLOSILICATE (MFI) IN PROPANE AROMATIZATION : INFLUENCE OF H^+ EXCHANGE AND THERMAL/ HYDROTHERMAL PRETREATMENTS

CHAPTER 2.4 : METHANOL-TO-AROMATICS CONVERSION OVER H-GALLOSILICATE (MFI) : INFLUENCE OF Si/Ga RATIO, DEGREE OF H^+ EXCHANGE, PRETREATMENT CONDITIONS AND POISONING OF STRONG ACID SITES

CHAPTER 2.1

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-GaAlMFI ZEOLITES

2.1.1 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 (1-3). This is a process of great practical importance. In a number of earlier studies (4-9), 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 has been observed. Recently we have observed a strong influence of O_2 and H_2 pretreatments (at 600^oC) 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 (9).

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 (7,8,10-13). Formation of Ga^{+3} (12,13) or $(GaO)^+$ (7) located at cation exchange sites of the zeolite and also a decrease in protonic acidity (10) 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 (14). It is, therefore, interesting to study in details the influence of O_2 and H_2 pretreatments on the acidity/acid strength distribution and acid function (by acid catalyzed 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.

2.1.2 EXPERIMENTAL

2.1.2.1 Catalyst preparation

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 for 4 times. The Na-GaMFI and Na-GaAlMFI zeolites were synthesized by their hydrothermal crystallization from a gel ($p^H \cong 9$-10) consisting of Na-trisilicate (Fluka), gallium nitrate (Aldrich) with or without aluminum chloride (BDH), tertrapropylammonium bromide (TPA-Br) (Aldrich), sulfuric 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 15h to remove the occluded organic template. The detailed procedures for the hydrothermal synthesis of GaMFI and GaAlMFI are described in Chapter 1.1 and 1.2, respectively.

The Ga impregnated NH_4-ZSM-5 (Si/Al = 40 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 (15), with 1M ammonium nitrate solution at 80°C for 4 times and drying at 120°C for 4h.

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

2.1.2.2 Catalyst Characterization

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 from 100^{o} to $400^{o}C$ in a number of temperature steps (viz. 100^{o}-175^{o} C, 175^{o}-$250^{o}C$, 250^{o}-$325^{o}C$ and 325^{o}-$400^{o}C$) by using the GC adsorption/desorption methods (16,17). 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 1h. The determination of acidity/acid strength by the GC methods is described in details earlier (16-18).

2.1.2.3 Catalytic Pulse Reactions

The acid catalyzed model reactions, viz. isooctane cracking (at $400^{o}C$) for studying external acidity, toluene disproportionation (at $500^{o}C$) and methanol-to-aromatics conversion (at $400^{o}C$), over the pretreated zeolite catalysts have been carried out in a pulse micro-reactor (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 $cm^3.min^{-1}$). The catalyst pretreatment by H_2 or O_2 was given insitu before carrying out the pulse reactions. The pulse microreactor with arrangement for the insitu pretreatment (9,19) has been described in details later (in the next Chapter 2.2). 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 0.1g catalyst) at the above mentioned temperatures and analyzing the reactions products by the on line gas chromatograph with FID and computing integrator and using a GC column (3mm x 5m) 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 (20-22) and also in the next Chapter (Section 2.2.2.3).

2.1.3 RESULTS

The data on composition and crystal size of the gallium modified ZSM-5 type zeolites is presented in Table 2.1.1.

TABLE 2.1.1: Composition and crystal size of the zeolites.

Zeolite	Si/Ga ratio		Si/Al ratio		Crystal size (μm)
	Bulk	FW[a]	Bulk	FW	
H-GaMFI	32.9	42.2 (O_2)	>10,000	>10,000 (O_2)	4-6
		47.1 (H_2)		>10,000 (H_2)	
H-GaAlMFI	82	118 (O_2)	68	68 (O_2)	5-8
		236 (H_2)		68 (H_2)	
Ga/H-ZSM-5	97	>10,000 (O_2)	48	53 (O_2)	5-7
		>10,000 (H_2)		53 (H_2)	

[a] Obtained from ^{29}Si MAS NMR

2.1.3.1 ^{27}Al, ^{29}Si and ^{71}Ga MAS NMR

Figure 2.1.1 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 (Fig. 2.1.1a) 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 small amount of octahedral Al along with the tetrahedral one. The ^{71}Ga spectra indicates incorporation of gallium in the framework (FW) of the H-GaMFI and H-GaAlMFI zeolites and absence of tetrahedral Ga in the Ga/H-ZSM-5, as expected. 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 2.1.1. The FW-Si/Ga ratio of the H-GaMFI and H-GaAlMFI zeolites pretreated with H_2 is higher than that for the zeolites 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 as synthesized 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 pretreatments.

2.1.3.2 XPS

Results on XPS of the O_2 and H_2 pretreated zeolites are given in Table 2.1.2. 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 for 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 way for the Ga/H-ZSM-5 during the H_2 pretreatment.

2.1.3.3 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

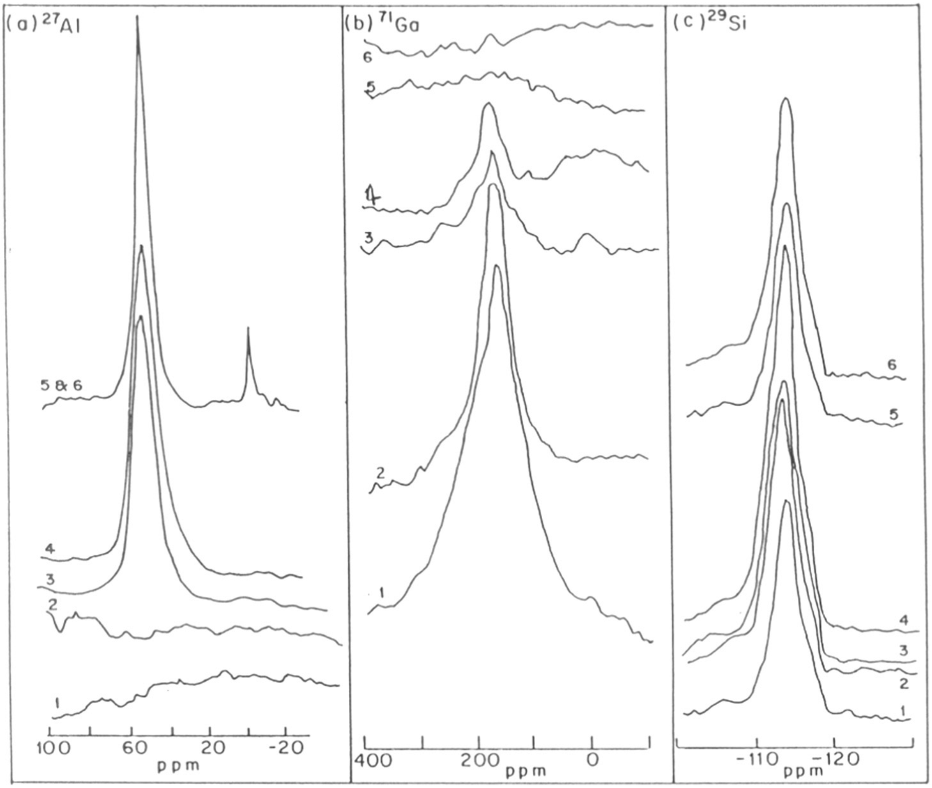

Fig. 2.1.1 : ^{27}Al (a), ^{71}Ga (b) and ^{29}Si (c) MAS NMR of H_2 and O_2 pretreated zeolite catalysts [1). H-GaMFI (H_2) 2). H-GaMFI (O_2), 3). H-GaAlMFI (H_2) 4).H-GaAlMFI(O_2), 5). Ga/H-ZSM-5 (H_2) 6). Ga/H-ZSM-5 (O_2)].

TABLE 2.1.2 : 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

(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 Figs. 2.1.2 and 2.1.3, respectively.

The columns in Fig. 2.1.2 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 ($T_1 < T_d \leq T_2$) 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 (Fig. 2.1.3) 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 increasing the 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:

<u>For total acidity</u>

H_2 pretreated catalysts : H-GaAlMFI < H-GaMFI < Ga/H-ZSM-5.

O_2 pretreated catalysts : H-GaAlMFI < H-GaMFI < Ga/H-ZSM-5.

<u>For strong acidity</u>

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).

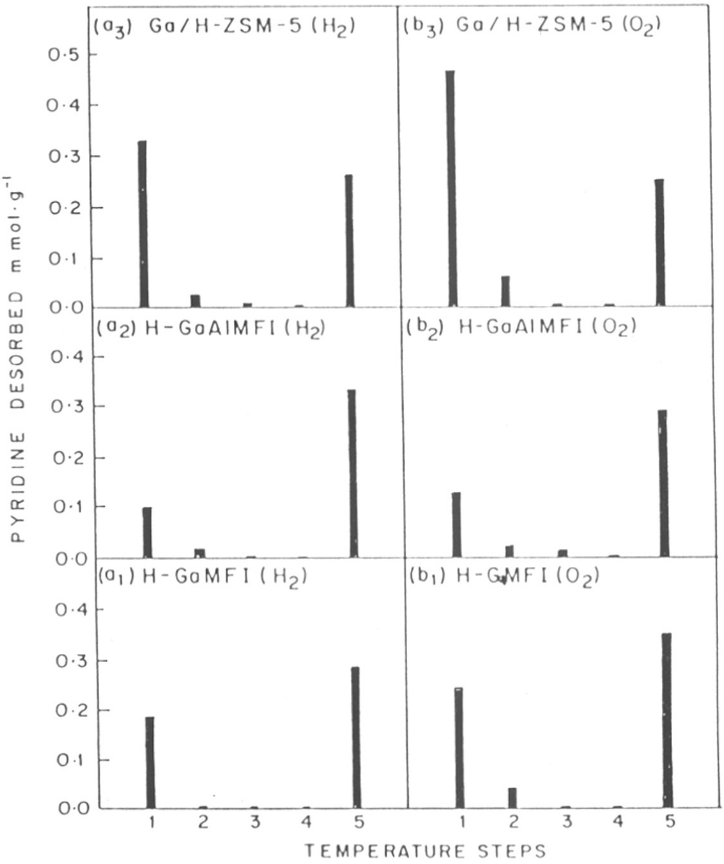

Fig. 2.1.2 : Stepwise thermal desorption of pyridine (chemisorbed at 100°C) on H-GaMFI, H-GaAlMFI and Ga_2O_3/H-ZSM-5 pretreated in a) H_2 and b) O_2 -(temperature steps : 1) $100^0 \leq T_d < 175^0C$ 2) $175^0 \leq T_d < 250^0C$ 3) $250^0 \leq T_d < 325^0C$ 4) $325^0 \leq T_d < 400^0C$ 5) $400^0C \leq T_d < T_d^*$

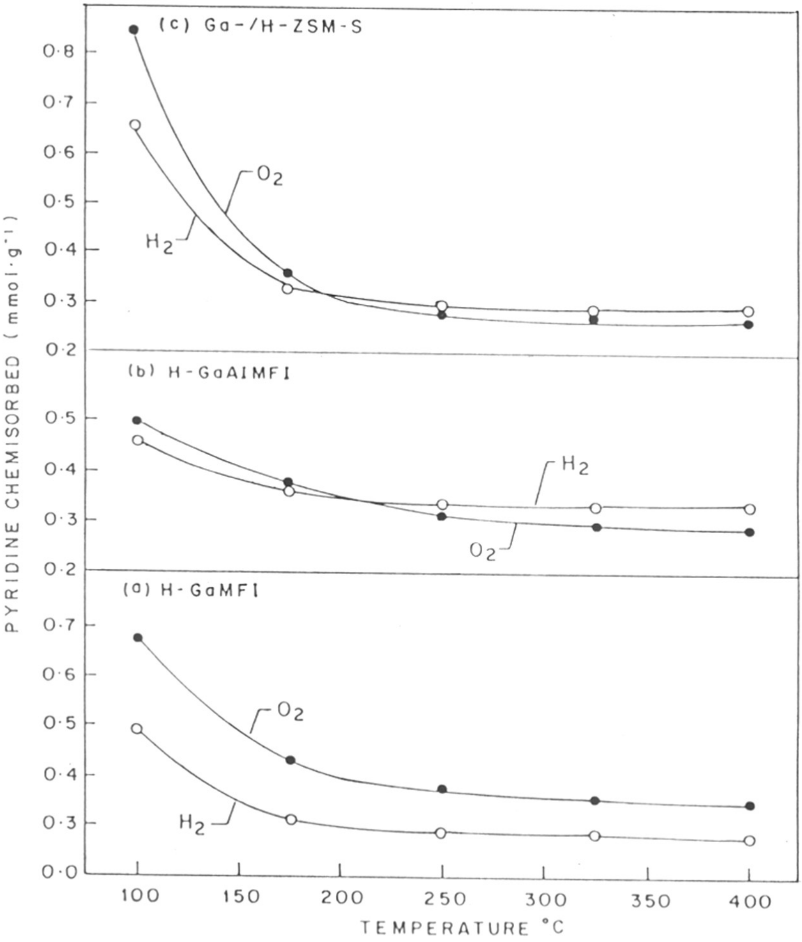

Fig. 2.1.3 : Temperature dependence of pyridine chemisorption on the O_2 and H_2 pretreated H-GaMFI, H-GaAlMFI and Ga_2O_3/H-ZSM-5 zeolites.

- 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.

2.1.3.4 Acid Catalyzed 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, catalyzed by strong acid sites (21,23-25) are presented in Tables 2.1.3 and 2.1.4.

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 2.1.3). However, the influence on 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-GaAlMFI (O_2 or H_2)< H-GaMFI (H_2) $\leq$ H-GaMFI (O_2) < Ga/H-ZSM-5 (O_2) < Ga/H-ZSM-5 (H_2).

Toluene disproportionation

In case of the toluene disproportionation over the catalysts, the gas pretreatment has a very significant influence on the toluene conversion (Table 2.1.3). The toluene conversion activity is higher when the H-GaAlMFI and Ga/H-ZSM-5 catalysts are pretreated with H_2 but it is higher when the H-GaMFI catalyst is pretreated with O_2.

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 2.1.4). However, the pretreatment has a very significant influence on the

TABLE 2.1.3 : 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
	H2	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 2.1.4 : 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 %)						
Benzene	11.2	0.2	11.1	12.4	13.6	9.3
Toluene	43.7	44.4	44.4	46.1	46.4	26.2
Ethylbenzene + Xylenes	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

aromatization. The aromatization is increased due to the H_2 pretreatment to the H-GaAlMFI and Ga/H-ZSM-5 but it 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 2.1.4 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.

2.1.4 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.

2.1.4.1 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 2.1.1) clearly shows that the degalliation of the zeolites is enhanced due to the H_2 pretreatment. As expected, both the total and strong acidity of the H-GaMFI zeolite are decreased as a result of its degalliation (i.e. conversion of tetrahedral Ga into octahedral by the removal of former from the zeolite FW). The strong acidity of the zeolite is attributed to the presence of FW tetrahedral Ga, similar to H-ZSM-5 zeolite (26,27). 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.

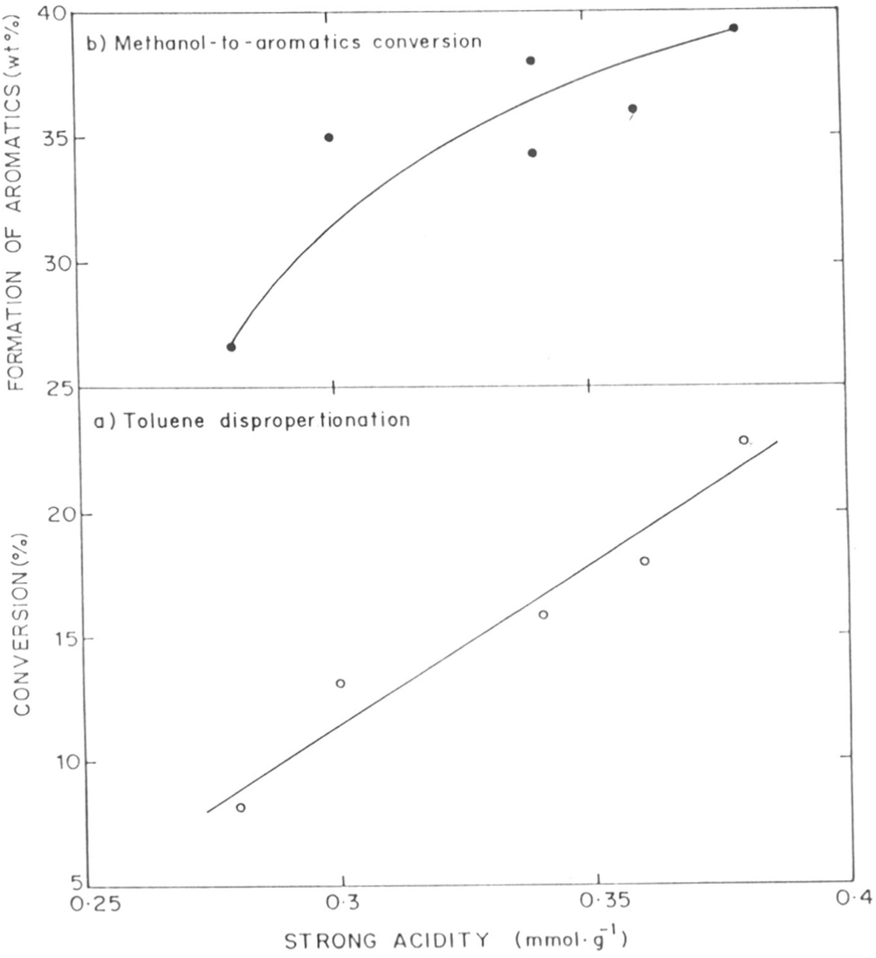

Fig. 2.1.4 : **Relationship between the catalytic activity of the zeolite catalysts in a) toluene disproportionation and b) methanol-to-aromatics conversion and their strong acidity.**

2.1.4.2 Influence of H_2 Pretreatment on Migration of Ga-species

The XPS results on surface Ga/Si ratio of the catalysts (Table 2.1.2) 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 later 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 (10-12). 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.

2.1.4.3 Influence of H_2 Pretreatment on Acidity/Acid Functions

The acidity and acid functions of the zeolite catalysts are affected significantly by the pretreatment (Figs. 2.1.1 and 2.1.3 and Tables 2.1.3 and 2.1.4).

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 (28).

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 (8). 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 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 because 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 (25).

2.1.4.4 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 (Fig. 2.1.4). The acidity of Ga/H-ZSM-5 is higher even if its Si/Al ratio is higher. A comparison of the zeolites for their acidity and Si/Ga and Si/Al ratios reveals that the isomorphous substitution of Al by Ga results in a decrease in the acidity or acid strength of ZSM-5 type zeolite.

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 some discrepancy in the variation of aromatics formation from methanol with the strong acidity (Fig. 2.1.4b) 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 Ga-oxide species, due to the pretreatment, along with the change in the acidity.

2.1.5 CONCLUSIONS

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

1. The H_2 pretreatment causes degalliation of 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 the H-GaAlMFI and Ga/H-ZSM-5.

3. The changes in the strong acidity are directly reflected by the corresponding changes in the catalytic activity of the zeolite catalysts for the toluene disproportionation and methanol-to-aromatics conversion reactions, which are catalyzed by the zeolitic (i.e. strong) acid sites. There exists a 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.

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CHAPTER 2.2

PULSE REACTION STUDIES ON VARIATION OF INITIAL ACTIVITY/SELECTIVITY OF O_2 AND H_2 PRETREATED Ga-MODIFIED ZSM-5 TYPE ZEOLITE CATALYSTS IN PROPANE AROMATIZATION

2.2.1 INTRODUCTION

Gallium-modified ZSM-5 type zeolite catalysts, Ga-impregnated H-ZSM-5 (Ga/H-ZSM-5), physically mixed Ga_2O_3 and H-ZSM-5, and ZSM-5 type H-gallosilicates(H-GaMFI) and H-galloaluminosilicates(H-GaAlMFI) zeolites show high activity in the aromatization of lower alkanes (1-3), which is a process of great commercial importance. A beneficial effect of high temperature hydrogen pretreatment to physically mixed Ga_2O_3 and H-ZSM-5 and Ga/H-ZSM-5 zeolites on their alkane aromatization activity/selectivity has been observed earlier in a number of studies (1,4-6). However, the influence of H_2 pretreatment on the alkane aromatization activity/selectivity for the H-GaMFI and H-GaAlMFI zeolites has not been investigated so far. It is also interesting to know the effect of H_2 pretreatment for the zeolites having gallium in their framework.

For the gallium exchanged/impregnated H-ZSM-5 and physically mixed Ga_2O_3 and H-ZSM-5 zeolites, the H_2 treatment is believed to cause a surface migration of gallium species in the zeolite channels, resulting in a highly dispersed gallium phase located close to the acid sites (7-12). A significant increase in the dehydrogenation and hydrogenolysis activity but a small decrease in protonic acidity of physically mixed Ga_2O_3 and H-ZSM-5 catalyst due to its H_2 treatment have been observed (13). Hydrogen in an appreciable quantity, is produced in the alkane aromatization process over these Ga-modified zeolites (1). Hence, the state of gallium and its dispersion are also expected to be changed during the alkane aromatization process particularly in the initial short period. It is, therefore, interesting to know the initial activity (at zero reaction time) and its variation with the time-on-stream in the alkane aromatization process over the H-ZSM-5 with externally added gallium and also over the H-GaMFI and

H-GaAlMFI zeolites, pretreated with both H_2 and O_2. An information on the initial state (or initial activity/selectivity) of catalyst can very well be obtained using a pulse micro-reactor combined with GC (14).

This investigation was undertaken with the above objective. The H-GaMFI, H-GaAlMFI and Ga/H-ZSM-5 zeolites pretreated with H_2 and O_2 have been compared for the influence of gas pretreatment under oxidizing and reducing atmospheres (i.e. under O_2 or H_2) on their initial activity/selectivity and its variation with the time-on-stream in the propane aromatization process, using a micro-reactor operated in both pulse reaction and continuous reaction modes.

2.2.2 EXPERIMENTAL

2.2.2.1 Catalyst Preparation

The Ga-impregnated H-ZSM-5 (Ga/H-ZSM-5, with 1.0 wt. % Ga and Si/Al ratio of 48) was prepared by impregnating NH_4-ZSM-5 with gallium nitrate solution by the incipient impregnation technique. The NH_4-ZSM-5 (NH_4^+ exchange = 96% and crystal size = 5-7 μm) was obtained by exchanging ZSM-5, [prepared by the hydrothermal synthesis according to the patent of Argauer and Landolt (15)] repeatedly (4 times) with 1M ammonium nitrate solution at 80°C. The H-gallosilicate (H-GaMFI, with Si/Ga ratio of 33) and H-galloaluminosilicate (H-GaAlMFI, with Si/Al=68 and Si/Ga=82) were obtained from their NH_4-form. The NH_4-GaMFI and NH_4-GaAlMFI zeolites (NH_4^+ exchange = 95% and crystal size = 5-8 μm) were prepared by exchanging GaMFI and GaAlMFI zeolites [obtained by hydrothermal synthesis from a gel (pH = 9-10), consisting of Na-trisilicate (Fluka), gallium nitrate (Aldrich) with or without aluminum nitrate (BDH), TPA-Br (Aldrich), sulfuric acid and deionized water, in a stainless steel autoclave at 180°C for 24h, followed by washing and drying the resulting zeolite crystals at 120°C for 4h and calcining at 550°C in static air for 15h to remove the occluded organic template] with 1M ammonium nitrate solution at 80°C for 1h; the ion exchange was repeated for 4 times. All the zeolites (after the impregnation or the ion exchange) were pressed binder-free, crushed to particles of 0.2-0.3mm size and calcined in static air at 600°C for 4h to get the zeolite catalysts in their H-form. The H_2 or O_2 pretreatment to the zeolites was given insitu in a flow of pure H_2 or O_2 at 600°C for 10h.

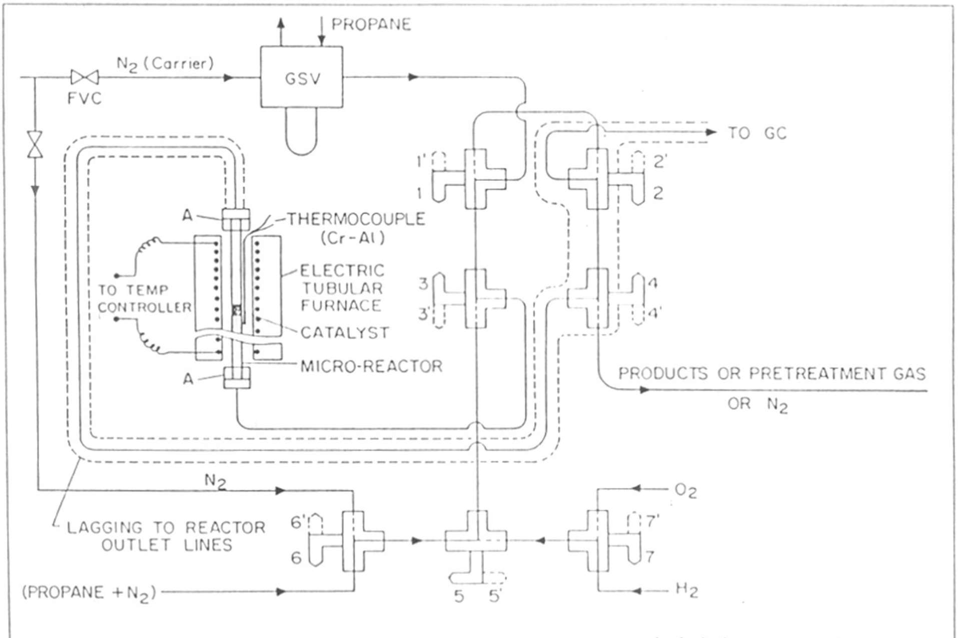
2.2.2.2 Catalyst Characterization

The MFI frame work structure of the zeolites has been confirmed by their XRD analysis. The XRD pattern for GaMFI and GaAlMFI zeolites are shown in Chapter 1.1 and Chapter 1.2, respectively. The bulk composition of the zeolites was determined by the chemical analysis of Si by the complete dissolution method (16), Ga by the gravimetric method using 5,7 dibromo-8-hydroxyquinoline as a complexing agent (17,18), Al by gravimetric method using 8-hydroxyquinoline as a complexing agent (19) and Na by the flame photometric method. The incorporation of Ga in the framework of the GaMFI and GaAlMFI zeolites was confirmed by observing ^{71}Ga MAS NMR peak at +156 ppm, which corresponds to tetrahedral gallium in the zeolite framework. The framework Si/Al, Si/Ga and Si/(Al + Ga) ratios of the zeolites were obtained from ^{29}Si MAS NMR peaks for Si(0Ga or Al) at about -112 ppm and Si(1Ga and/or Al) at about -104 ppm (20). The ^{71}Ga and ^{29}Si MAS NMR spectra were obtained using Bruker MSL 300 MHz NMR instrument. The surface Si/Ga ratio of the catalysts was determined by XPS of Si(2p) and Ga (2p), using a VG-Scintific ESCA-3 MKII electron spectrometer. The number of strong acid sites on the zeolites were determined by the chemisorption of pyridine at 400°C using the GC pulse method (21).

2.2.2.3 Propane Aromatization Reaction

The initial (zero reaction time) activity/selectivity of the pretreated zeolites and the variation of the activity/selectivity with time-on-stream in a continuous propane aromatization (at 600°C) have been determined by a pulse reaction of pure propane (>99.99%) at 600°C, using a quartz micro-reactor (i.d. :4.5mm, o.d. :6mm and length

:30cm, packed with 0.1gm catalyst between quartz wool plugs) connected to a gas chromatograph, with an arrangement to operate the reactor in a pulse reaction mode or in a continuous reaction or catalyst pretreatment mode (by bypassing the reactor from the GC unit), as shown in Fig. 2.2.1A.The micro-reactor and procedure for insitu catalyst pretreatment are described in details earlier (22,23). High purity nitrogen (>99.99), passed over molecular sieves and Oxysorb for removing traces of moisture and oxygen, respectively, is used as a carrier gas (flow rate : 20 $cm^3.min^{-1}$) in the pulse reaction. The procedure for the propane pulse reaction studies is as follows. The microreactor is bypassed from the GC unit and the catalyst is pretreated in the flow of H_2 or O_2 (flow rate : 30$cm^3.min^{-1}$) at 600°C for 10h. After the pretreatment, the catalyst is flushed with the pure (moisture- and O_2-free) N_2 (50 $cm^3.min^{-1}$) for 10min, the reactor is connected to the GC unit and a pulse of pure propane (0.2 cm^3) is passed over the pretreated catalyst to obtain its initial activity/selectivity. After the determination of the initial activity/selectivity, the reactor is bypassed from the GC to operate in a continuous reaction mode by passing continuously over the catalyst a mixture of propane and nitrogen (50 mol% propane) at 600°C and gas hourly space velocity (GHSV) of 3100 $cm^3.g^{-1}.h^{-1}$ (measured at STP). After the continuous propane aromatization reaction for a time-on-stream of 5 min, the reactant gas mixture is replaced by pure N_2 (50$cm^3.min^{-1}$) for 10 min to flush the catalyst to remove adsorbed reaction species. Then immediately the reactor was reconnected to the GC and the propane pulse reaction was carried out. This procedure was repeated to obtain the propane pulse reaction data at the different times-on-stream (5, 65, and 185 min) for the continuous propane aromatization to find the change in the catalytic activity/selectivity due to the change in the catalyst state resulting from the continuous propane aromatization in the initial short reaction period. The three-way valve positions during the above operations is given in Fig. 2.2.1A. The products of the propane pulse reaction were analyzed by the on-line gas chromatograph (with FID and computing integrator), using Poropak-Q (3mm x 3m) and



THREE-WAY VALVE ON-POSSITIONS : FOR PRETREATMENT - 1', 2', 3', 4' AND 7 OR 7';
FOR PULSE REACTION - 1 2 3 AND 4 ;
FOR CONTINUOUS REACTION - 1', 2', 3', 4', 5 AND 6 ;
FOR FLUSHING CATALYST WITH N_2 - 1', 2', 3', 4', 5 AND 6'

Fig. 2.2.1A. : Micro-reactor assembly operating in pulse reaction, continuous reaction and insitu catalyst pretreatment modes(GSV = gas sampling valve, A = Ultratorr 1/4" to 1/8" swagelok connector, all valves with 1/8" swagelok end connections and lines with 1/8" ss tubings).

Benton-34 (5%) and dinonylphthalate (5%) on chromosorb-W (3mm x 5m) columns for separating C_1-C_4 and aromatics, respectively (Fig. 2.2.1B), as follows.

Before injecting the reactant pulse in the microreactor, the two columns (column A and column B) are connected in series (i.e. with the three way valves position 5a and 6a) and the GC oven was programmed ($50^{o}C \xrightarrow{8\ min} 50^{o}C \xrightarrow{4^{o}C/min} 150^{o}C \xrightarrow{50\ min} 150^{o}C \longrightarrow 50^{o}C$). After the elution of methane, ethylene and ethane from column B (i.e. after 20 min, from the reactant pulse injection), the three way valve 6 is turned to position 6b and C_{5+} hydrocarbons eluted from column A are analyzed. During this analysis, the C_3 - C_4 hydrocarbons are retained on column B. After the analysis of C_{5+} hydrocarbons, the GC oven is cooled to $50^{o}C$, the position of three way valve 5 and 6 are changed to 5b and 6a, the GC oven is programmed as above and the C_3 - C_4 hydrocarbons eluted from column B are analyzed.

2.2.3 RESULTS AND DISCUSSION

2.2.3.1 Characterization of Zeolites

The bulk composition of the Ga/H-ZSM-5, H-GaMFI and H-GaAlMFI zeolites and the influence of pretreatment (in H_2 or O_2) on their framework (FW) composition, non-FW Ga/FW (Ga + Al) (i.e. non-FWGa/H^+) ratio, surface Si/Ga ratio and strong acidity (measured in terms of pyridine chemisorbed at $400^{o}C$) are presented in Table 2.2.1. The bulk Si/(Al + Ga) ratio of all the zeolite catalysts is more or less the same (34 ± 2.5).

In case of the Ga/H-ZSM-5, the as synthesized form of ZSM-5 (TPA-ZSM-5) showed presence of a small amount of octahedral Al (indicated by ^{27}Al MAS NMR peak at about 0 ppm) and its FW Si/Al ratio (53.0) was not changed significantly due to its calcination and/or pretreatment in H_2 or O_2. However, for the GaMFI and GaAlMFI zeolites in their TPA-form, no significant difference is observed in their bulk and framework Si/Ga or Si/(Al + Ga) ratios. But in their H-forms, the FW Si/Ga ratio is significantly higher than the bulk Si/Ga ratio and also the FW Si/Ga is influenced by the gas (H_2 or O_2) treatment

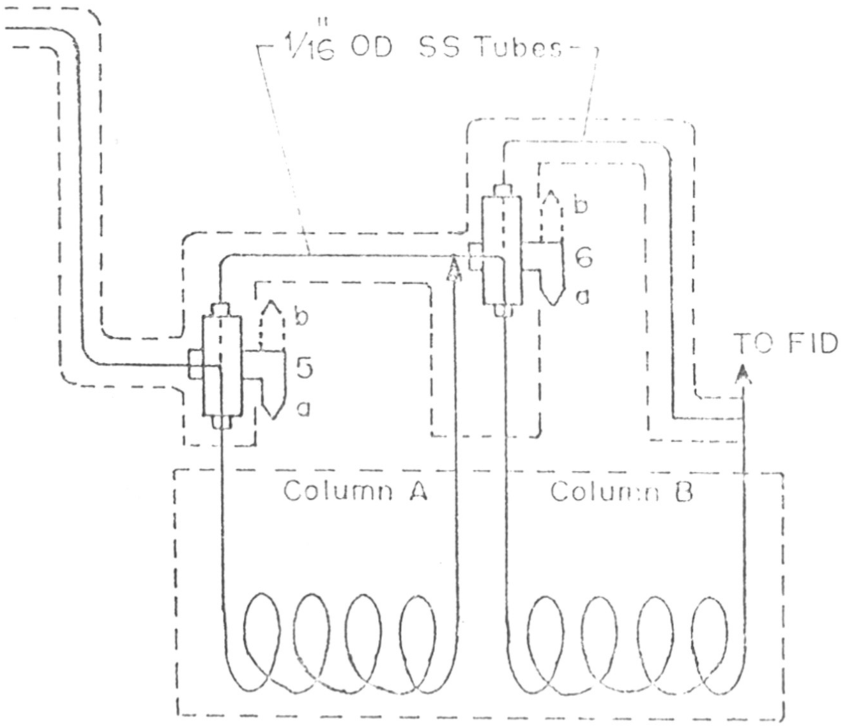


Fig.2.2.1B. : **Arrangement of GC columns [Column A : Benton-34 (5 %) and dinonylphthalate (5 %) on chromosorb-w (3mm x 5m), Column B : Poropak-Q (3mm x 3m)] for products analysis.**

able 2.2.1 : Data on characterization of Ga-modified ZSM-5 type zeolites pretreated in H_2 or O_2

eolite	Bulk composition[a]			Pretreatment (H_2 or O_2)	Framework composition[b]			Non-FW Ga / FW (Al + Ga) ratio	Surface Si/Ga ratio[c]	Acidity[d] (mmol.g^{-1})
	Si/Al	Si/Ga	Si/(Al + Ga)		Si/Al	Si/Ga	Si/(Al + Ga)			
a/H-ZSM-5	48	97	33	O_2	53	> 10,000	53	0.49	56	0.26
				H_2	53	> 10,000	53	0.49	67	0.28
-GaMFI	> 10,000	33	33	O_2	> 10,000	42	42	0.27	125	0.36
				H_2	> 10,000	47	47	0.42	91	0.29
-GaAlMFI	68	82	37	O_2	68	118	43	0.16	200	0.30
				H_2	68	236	53	0.43	125	0.34

btained by chemical analysis. [b]obtained from ^{29}Si MAS NMR. [c]obtained by XPS. [d]Measured in terms of pyridine chemisorption at
)0 °C.

and consequently, the non-FW/FW Ga ratio is strongly influenced by the pretreatment; the ratio is much higher for the H_2 treated catalysts. These observations suggest that the GaMFI and GaAlMFI zeolites are degalliated to an appreciable extent during the conversion of their TPA-form to H-form; the degalliation of the zeolites due to H_2 pretreatment is larger than that due to the O_2 pretreatment.

It may be noted that, for estimating the FW Si/Ga ratio of H-GaAlMFI, it is assumed that the FW Si/Al ratio is not changed in the conversion of TPA-GaAlMFI to H-GaAlMFI, which is consistent with that observed for the Ga/H-ZSM-5. It may also be noted that since the T-sites in MFI structure are not crystallographically identical, the estimation of framework Si/Ga , Si/Al or Si/(Al + Ga) ratios from ^{29}Si MAS NMR is not very accurate (24). Nevertheless, the changes in the FW Si/Ga or Si/(Al + Ga) are large enough to give some idea about the degalliation and the presence of extraframework gallium species.

The observed changes in the surface Si/Ga ratio (obtained from the XPS) for the catalysts due to the pretreatment indicate that for the H_2 pretreated H-GaMFI and H-GaAlMFI zeolites, the surface concentration of Ga is higher than that for the corresponding O_2 pretreated zeolite. But exactly opposite trend is observed in case of the Ga/H-ZSM-5. These results suggest that there is migration of Ga-oxide species (formed by the degalliation) from zeolite channels to external surface of crystallites for the H-GaMFI and H-GaAlMFI zeolites, due to their H_2 pretreatment. The migration of Ga for the Ga/H-ZSM-5 due to H_2 pretreatment is in the reverse direction because of the formation of more volatile Ga-oxide species from the Ga_2O_3 already present on the external surface of the H-ZSM-5 zeolite. This is consistent with that observed earlier (9-11).

The strong acidity of the zeolite catalysts (Table 2.2.1) is also influenced by the pretreatment. However, the influence is quite small for the Ga/H-ZSM-5 and H-GaAlMFI catalysts. The observed changes in the acidity due to the pretreatment are the result of degalliation to different extends and/or formation of different extraframework Ga-oxide species having different acidity. The oxidation state of extraframework Ga and its role in the alkane-to-aromatics conversion reaction sequence are not yet clearly understood (25).

2.2.3.2 Influence of Pretreatment on Initial Activity/Selectivity

Results on the initial (zero time) activity/selectivity of the O_2 and H_2 pretreated Ga-modified zeolite catalysts in propane aromatization (at 600°C), measured under transient conditions by pulse reaction of propane, are presented in Table 2.2.2. The initial aromatization activity/product selectivity in propane aromatization is strongly influenced by the pretreatment. When compared with the results obtained due to the O_2 pretreatment, the H_2 pretreatment has following influence on the initial activity and product selectivity :

- Both the total propane conversion activity and aromatization activity (or aromatics yield) for the H-GaMFI are decreased appreciably, without affecting its aromatics selectivity. However, the aromatization activity and aromatics selectivity are increased markedly for the H-GaAlMFI and Ga/H-ZSM-5 catalysts. The changes in the catalytic activity are consistent with the changes in the acidity of the catalysts due to the O_2 or H_2 pretreatment.
- The propylene selectivity is increased very markedly for the H-GaMFI and also are increased for the H-GaAlMFI but to a small extent; whereas the Ga/H-ZSM-5 shows almost no selectivity for propylene.
- The ethylene and methane selectivity are decreased for all the catalysts.
- The ethane selectivity is increased for the H-GaMFI and Ga/H-ZSM-5 catalysts but decreased for the H-GaAlMFI.
- The aromatics/(methane + ethane) mass ratio is increased for all the catalysts; however, the increase is much more for the H-GaAlMFI.
- The methane/(ethane + ethylene) mole ratio for all the catalyst is decreased; the decrease is however, appreciable for the H-GaMFI and H-GaAlMFI catalysts.

The distribution of aromatics is almost not affected for the H-GaMFI, affected to a very small extent for the Ga/H-ZSM-5, but it is influenced significantly for the Hble 2.2.2 : Initial activity/product selectivity of the O_2 and H_2 pretreated Ga-modified ZSM-5 type zeolites in propane aromatization (at 600°C).

tivity/selectivity/product ratio/product distribution	H-GaMFI		H-GaAlMFI		Ga/H-ZSM-5	
	O_2 treated	H_2 treated	O_2 treated	H_2 treated	O_2 treated	H_2 treated
Initial Catalytic Activity						
pane Conversion						
tal (%)	99.9	89.7	99.9	98.4	100	100
aromatics (%)	68.6	61.5	70.5	82.0	69.0	81.9
Product Selectivity Ratio						
matics selectivity (%)	68.7	68.5	71.0	82.9	69.0	81.9
pylene selectivity (%)	1.8	9.6	1.6	1.9	0.2	0.0
ylene selectivity (%)	12.1	10.9	9.1	6.5	4.7	3.1
ane selectivity (%)	3.2	4.7	3.3	1.5	3.4	3.9
thane selectivity (%)	14.1	6.4	15.2	7.4	13.3	11.1
$_4/(C_2H_4 + C_2H_6)$ mole ratio	1.63	0.73	2.16	1.64	2.96	2.88
matics/$(CH_4 + C_2H_6)$ mass ratio	4.0	6.2	3.9	9.5	4.1	5.5
Distribution of Aromatics (wt. %)						
zene	68.6	68.0	73.0	74.1	76.7	78.5
uene	31.4	31.2	27.0	23.7	23.3	21.5
aromatics	00.0	00.0	00.0	2.20	00.0	00.0

GaAlMFI (Table 2.2.2). In the later case, the concentration of toluene is decreased and that of Xylenes is increased.

The increase in the aromatics/(methane + ethane) ratio clearly indicates the beneficial effect of the H_2 pretreatment for all the catalysts because the formation of gases (CH_4 and ethane) having only fuel value is greatly reduced. The aromatics/(methane + ethane) ratio for the different catalysts (pretreated with H_2) is in the following order:

H-GaAlMFI > H-GaMFI > Ga/H-ZSM-5.

The observed superior performance of the H-GaAlMFI over the Ga/H-ZSM-5 in the propane aromatization is attributed mostly to a formation of highly dispersed Ga-species throughout the zeolite channels in close proximity of the protonic acid sites, due to partial degalliation (or removal) of framework gallium during the H_2 pretreatment. The increase in the aromatization activity/selectivity of the Ga/H-ZSM-5 due to the H_2 pretreatment is also expected to be mostly due to migration of reduced gallium oxide species from the external crystal surface towards the protonic acid sites in the zeolite channels (7-12).

The decrease in the propane conversion and aromatization activity of the H-GaMFI due to the H_2 pretreatment is attributed mostly to removal of some of the framework gallium under the reducing conditions, thus decreasing the protonic acid sites responsible for the oligomerization and cyclization and also for the propane conversion in the propane aromatization process.

The product selectivity in propane aromatization is found to be dependent upon the propane conversion (1,27,28). However, in the present case, the propane conversion over all the catalysts (pretreated in H_2 or O_2) is 95 ± 5% (Table 2.2.2). Hence, the catalyst can be compared for their product selectivity.

2.2.3.3 Influence of Pretreatment on the Variation of Activity/Selectivity

Influence of time-on-stream (for a short initial period, 0-180 min) and catalyst pretreatment on the propane conversion (both total conversion and to aromatics), product selectivity and distribution of aromatics in the propane aromatization (at 600°C) over the H-GaMFI, H-GaAlMFI and Ga/H-ZSM-5 catalysts is shown in Figs. 2.2.2, 2.2.3 and 2.2.4, respectively. Figure 2.2.5 shows the effect of time-on-stream and catalyst pretreatment on the aromatics/(methane + ethane) mass ratio obtained in the propane aromatization over the catalysts. The variation of the propane conversion and aromatization activity relative to the corresponding initial activity in the catalytic process over the catalysts is presented in Figs. 2.2.6 and 2.2.7, respectively.

The results (Figs. 2.2.2-2.2.7) reveal that the catalyst pretreatment has a strong and also complex effect, which also depends on the catalyst, on the variation of catalytic activity/selectivity with the time-on-stream in the propane aromatization process.

2.2.3.4 Variation of Catalytic Activity with Time-On-Stream

The propane conversion and aromatization activity of the H_2 and O_2 pretreated catalysts (Figs 2.2.2a, 2.2.3a and 2.2.4a) or that relative to the initial ones (i.e. At/Ao, where At and Ao are catalytic activity determined at time-on-stream of t and zero, respectively) (Figs. 2.2.6 and 2.2.7) are found to be changed with increasing the time-on-stream, as follows.

Propane conversion activity :

- For the H_2 pretreated H-GaMFI, the propane conversion activity is increased initially, passed thorough a maximum and then decreased. Whereas for the O_2 pretreated H-GaMFI, it is decreased continuously.
- For the O_2 pretreated Ga/H-ZSM-5, it is decreased markedly.
- The effect of time-on-stream and pretreatment on the propane conversion activity of H-GaAlMFI is quite small.
- The effect of time-on-stream on the propane conversion activity of H_2 pretreated Ga/H-ZSM-5 is also very small.

Aromatization activity :

- For the H_2 or O_2 pretreated GaMFI, the aromatization activity is increased initially to a small extent and then decreased; the decrease being very sharp for the H_2 pretreated catalyst.

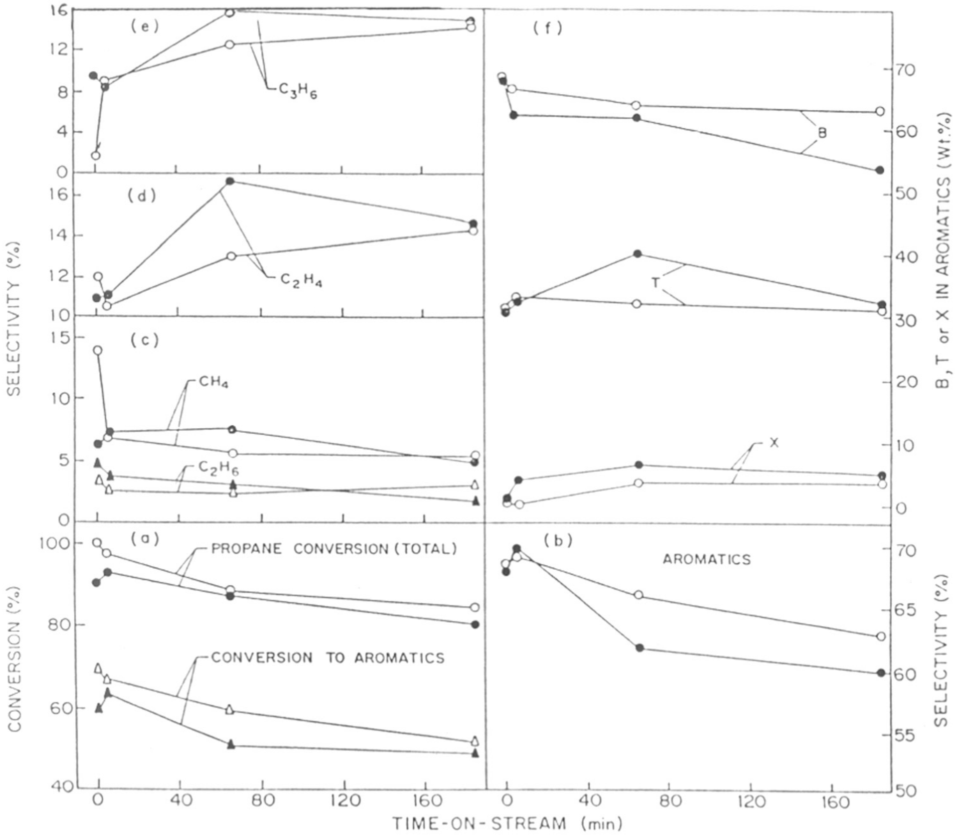


Fig. 2.2.2 : Influence of time-on-stream on the conversion, selectivity and distribution of aromatics in propane aromatization over the O_2 and H_2 pretreated H-GaMFI. (open symbols for O_2 pretreated Catalyst and solid symbols for H_2 pretreated catalyst).

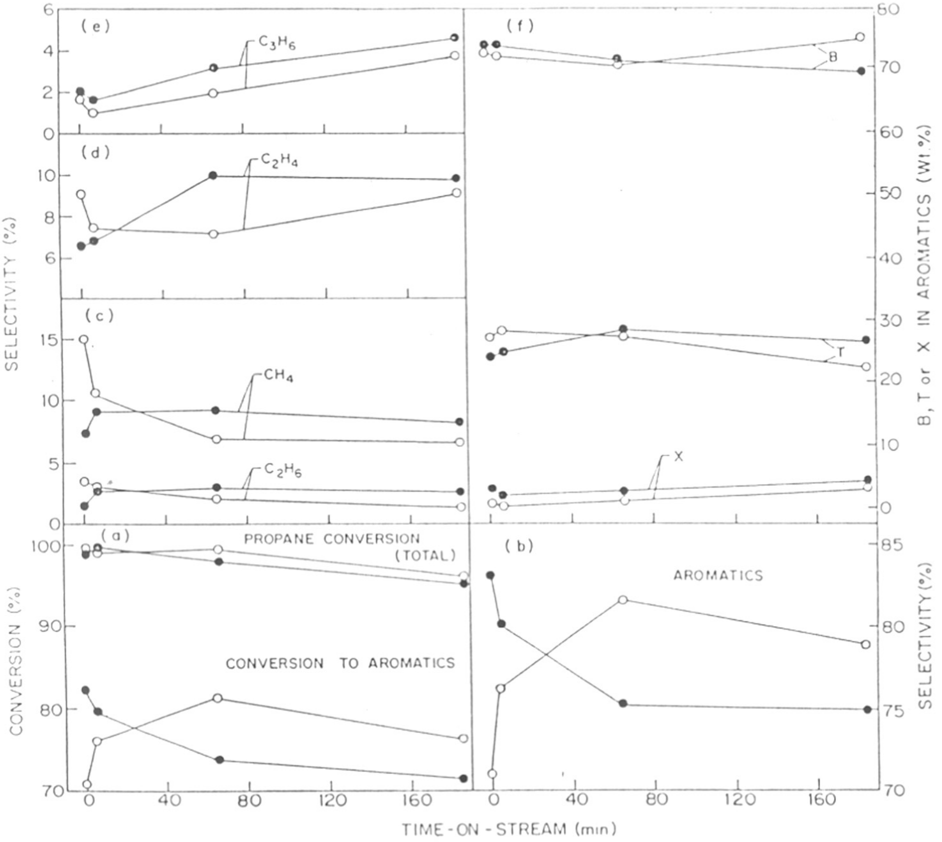


Fig. 2.2.3. : **Influence of time-on-stream on the conversion, selectivity and distribution of aromatics in propane aromatization over the O_2 and H_2 pretreated H-GaAlMFI. (open symbols for O_2 pretreated zeolite and solid symbols for H_2 pretreated catalyst).**

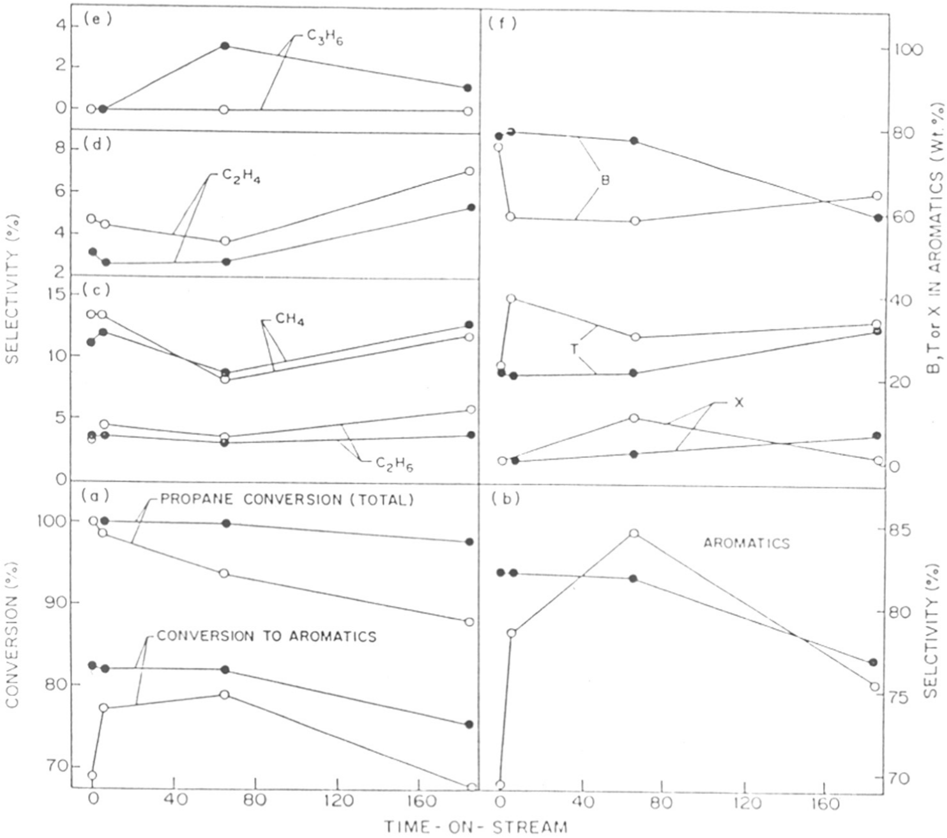


Fig. 2.2.4. : Influence of time-on-stream on the conversion, selectivity and distribution of aromatics in propane aromatization over the O_2 and H_2 pretreated Ga/H-ZSM-5. (open symbols for O_2 pretreated catalyst and solid symbols for H_2 pretreated catalyst).

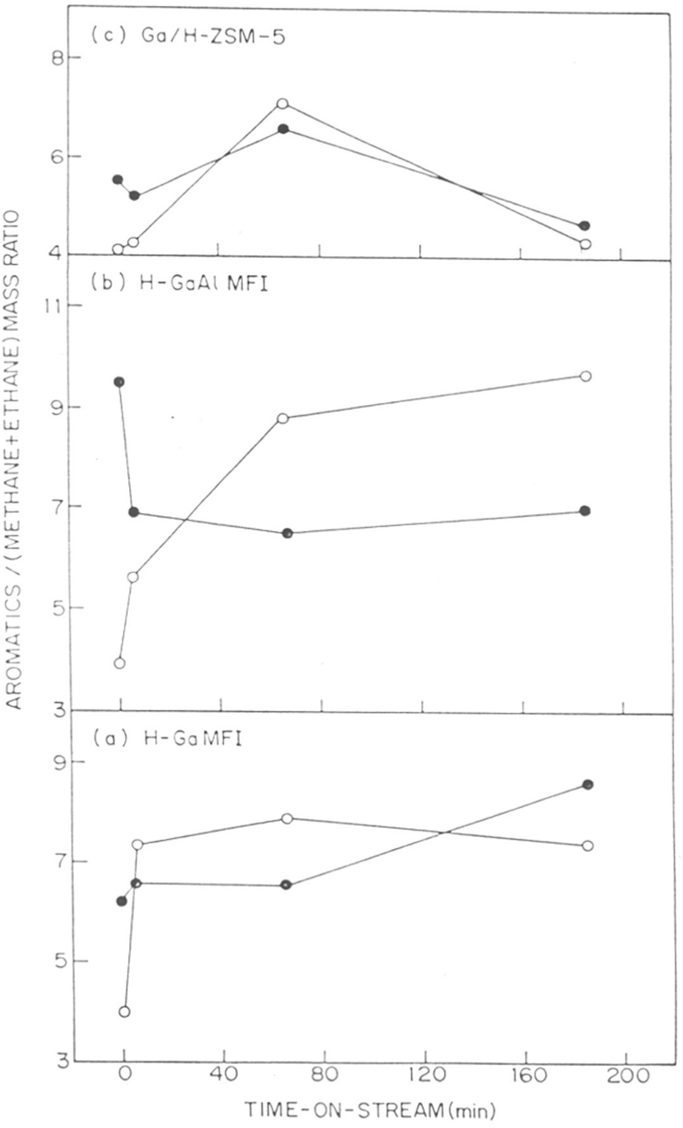


Fig. 2.2.5. : **Influence of time-on-stream on aromatics/(methane + ethane) mass ratio in the aromatization of propane over O_2 pretreated (open symbol) and H_2 pretreated (solid symbol) Ga-modified zeolite catalysts.**

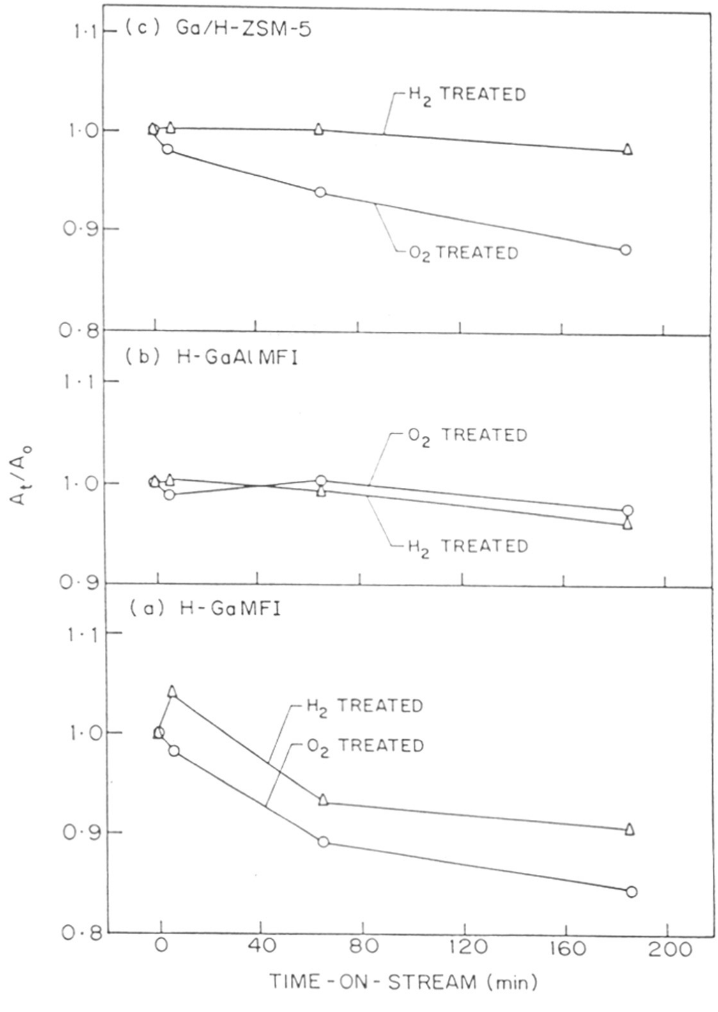


Fig. 2.2.6. : **Variation with time-on-stream the total conversion of propane, relative to that at t=0, over the O_2 and H_2 pretreated Ga-modified zeolite catalysts.**

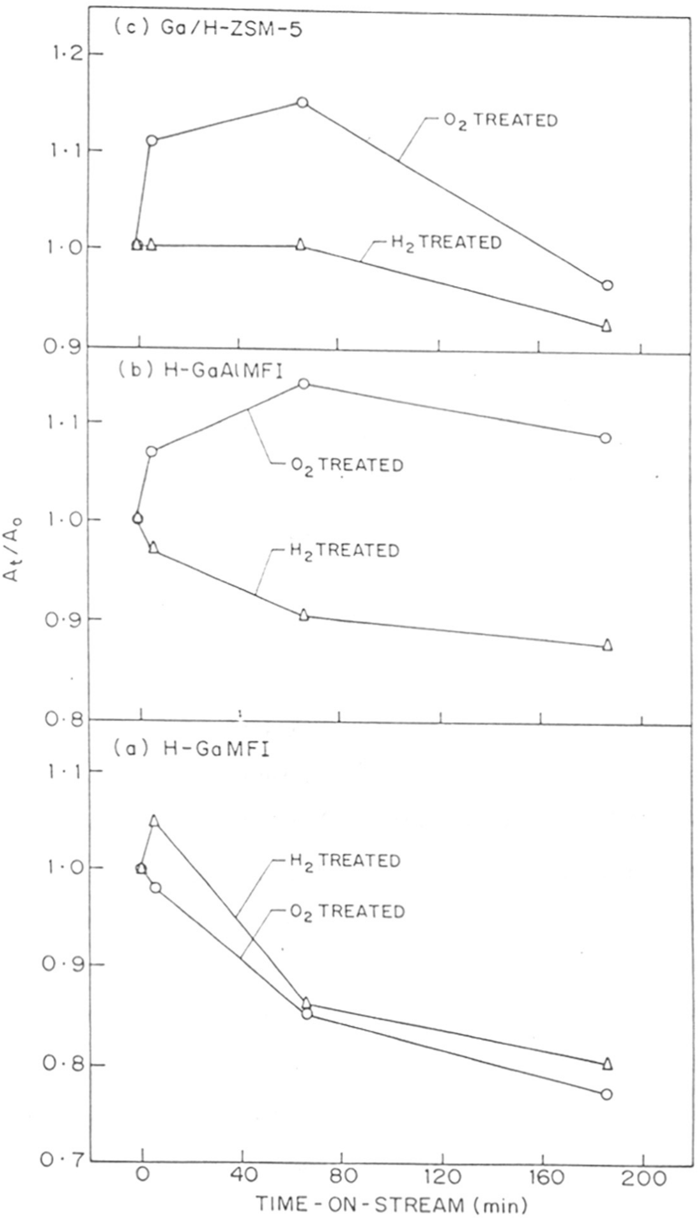


Fig. 2.2.7. : Variation with time-on-stream the conversion of propane, to aromatics, relative to that at t=0, over the O_2 and H_2 pretreated Ga-modified zeolite catalysts.

- For the O_2 pretreated H-GaAlMFI and Ga/H-ZSM-5, it is increased sharply and then passed through a maximum.
- For the H_2 pretreated H-GaAlMFI and Ga/H-ZSM-5, it is decreased. However, the trends for the decrease are different.
- Its variation with the time-on-stream is very strongly affected by the pretreatment for the H-GaAlMFI and Ga/H-ZSM-5 catalysts but the pretreatment effect on its variation is relatively much smaller for the H-GaMFI catalyst. The effect of pretreatment in these two cases is opposite. (Fig. 2.2.7)

The observed decrease in the aromatization activity with increasing the time-on-stream for all the H_2 pretreated catalysts is mostly due to the catalyst deactivation caused by coke deposition during the propane aromatization process. After the removal of coke by oxidative treatment to the catalysts (at 550°C with 5% in N_2 for 1h), the catalyst activity is recovered almost completely. The initial small increase in the activity of H_2.pretreated H-GaMFI (Figs. 2.2.2a, 2.2.6 and 2.2.7) may be due to a change in the state of the catalyst in the initial reaction period. However, the exact reason for this change is not known. The observed initial sharp increase followed by continuous increase in the aromatization activity for an appreciably long period (more than 1h) for the O_2 pretreated H-GaAlMFI and Ga/H-ZSM-5 catalysts (Figs. 2.2.3a, 2.2.4a and 2.2.7) is expected to be mostly due to the change in the catalyst state resulting in increased intrinsic catalytic activity due to their insitu (during the catalytic process) pretreatment by the hydrogen produced in the aromatization process. The effect produced by the H_2 formed during the process is expected to be similar to that observed due to the H_2 pretreatment of these catalysts discussed earlier. Thus, the results reveal that the O_2 pretreated H-GaAlMFI and Ga/H-ZSM-5 catalysts are activated during the initial period of the propane aromatization process. After the reaction period (or time-on-stream) of about 1h, the catalytic activity is decreased, mostly due to the catalyst deactivation by coking. It may be noted that the variation (with the time-on-stream) in the total propane conversion activity of all the H_2 and O_2 pretreated catalysts is relatively much smaller than that in the aromatization activity (Figs 2.2.6 and 2.2.7).

2.2.3.5 Variation of Product Selectivity with Time-On-Stream

The results (Figs. 2.2.2b-e, 2.2.3b-e and 2.2.4b-e) reveal that the product selectivity in the propane aromatization is very strongly influenced by both the catalyst pretreatment and the catalyst activation/deactivation (or the time-on-stream), and its variation also depends upon the catalyst used and the catalyst pretreatment. The important observations on this are summarized below.

With the increase in the time-on-stream,

- the aromatic selectivity is passed through a maximum (with an initial sharp increase) for the O_2 pretreated H-GaAlMFI and Ga/H-ZSM-5 and also for both the H_2 and O_2 pretreated H-GaMFI but decreased continuously for the H_2 pretreated H-GaAlMFI and Ga/H-ZSM-5;
- the propylene selectivity is passed through first minimum and then maximum for the H_2 pretreated H-GaMFI but increased continuously (with initial sharp increase) for the O_2 pretreated H-GaMFI; passed through a minimum for both the H_2 and O_2 pretreated H-GaAlMFI; but passed through a maximum for the H_2 pretreated Ga/H-ZSM-5;
- the ethylene selectivity is passed through a minimum for the O_2 pretreated H-GaMFI and H-GaAlMFI and also for the H_2 and O_2 pretreated Ga/H-ZSM-5 but passed through a maximum for the H_2 pretreated H-GaMFI and H-GaAlMFI catalysts;
- the methane selectivity is decreased continuously (with initial sharp decrease) for the O_2 pretreated H-GaMFI and H-GaAlMFI but passed through a maximum for the H_2 pretreated H-GaMFI and H-GaAlMFI, a minimum for O_2 pretreated Ga/H-ZSM-5 and both maximum and minimum for the H_2 pretreated Ga/H-ZSM-5.

The ethane selectivity is however, affected relatively to smaller extent due to the pretreatment or catalyst activation/deactivation during the propane aromatization.

The results in Fig. 2.2.5 show a strong influence of the catalyst pretreatment and the catalyst activation deactivation during propane aromatization on the aromatics/(methane + ethane) mass ratio. It is very essential to get high value for this ratio in order to decrease the formation of undesirable methane and ethane, which have only fuel value, so that the process economics can be improved. The increase in the time-on-stream causes the ratio to pass through a maximum for the H_2 and O_2 pretreated Ga/H-ZSM-5, and the O_2 pretreated H-GaMFI (with a sharp initial increase) to increase continuously for the O_2 pretreated H-GaAlMFI and the H_2 pretreated H-GaMFI and to pass through a maximum (with a sharp initial increase) for the O_2 pretreated H-GaMFI. The influence of pretreatment on the variation of the ratio for the Ga/H-ZSM-5 is quite small, but for the other two catalysts is very large and almost opposite.

Figures 2.2.2f, 2.2.3f and 2.2.4f reveal that the distribution of aromatics (BTX) produced in the process is influenced by both the catalyst pretreatment and the catalyst activation/ deactivation during the process. The influence is however, very pronounced for the Ga/H-ZSM-5 but relatively much smaller for the H-GaAlMFI.

2.2.3.6 Comparison of Catalysts for Their Initial Activity/Selectivity and Deactivation

Initial activity/selectivity

Based on the results (Table 2.2.2 and Figs. 2.2.2-2.2.7), the catalysts pretreated with H_2 or O_2 are compared for their initial activity/selectivity as follows.

A) H_2 pretreated catalysts

Propane conversion activity : H-GaAlMFI $\cong$ Ga/H-ZSM-5 > H-GaMFI
Propane aromatization activity : H-GaAlMFI $\cong$ Ga/H-ZSM-5 >> H-GaMFI
Aromatics selectivity : H-GaAlMFI > Ga/H-ZSM-5 >> H-GaMFI
Aromatics/(CH_4 + C_2H_6) mass ratio : H-GaAlMFI > H-GaMFI > Ga/H-ZSM-5

b) O_2 pretreated catalysts

Propane conversion activity	: H-GaAlMFI ≅ Ga/H-ZSM-5 ≅ H-GaMFI
Propane aromatization activity	: H-GaAlMFI > Ga/H-ZSM-5 ≥ H-GaMFI
Aromatics selectivity	: H-GaAlMFI > Ga/H-ZSM-5 ≅ H-GaMFI
Aromatics/(CH_4 + C_2H_6) mass ratio	: H-GaAlMFI ≅ Ga/H-ZSM-5 ≅ H-GaMFI

It may be noted that the O_2 pretreated catalysts have different non-FW Ga/FW(Ga + Al) ratios but the H_2 pretreated ones have more or less similar non-FW Ga/FW(Ga + Al) ratios. The comparison of the catalysts, particularly the H_2 pretreated ones, as their non-FW Ga/FW(Ga + Al) is more or less the same, leads to the conclusion that the catalysts containing extraframework Ga-species in association with the FW Al (i.e. stronger zeolitic acid sites) are more active as well as more selective in the propane-to-aromatics conversion.

For catalyst deactivation due to coking

The catalyst order for the deactivation of aromatization activity for the H_2 and O_2 pretreated catalysts (Fig. 2.2.7) is as follows.

H_2 pretreated catalysts : H-GaMFI > H-GaAlMFI > Ga/H-ZSM-5.

O_2 pretreated catalysts : H-GaMFI ≅ Ga/H-ZSM-5 > H-GaAlMFI.

For the deactivation of propane conversion activity, the catalysts can be ordered as follows.

H_2 pretreated catalysts : H-GaMFI >> Ga/H-ZSM-5 ≅ H-GaAlMFI.

O_2 pretreated catalysts : H-GaMFI > Ga/H-ZSM-5 > H-GaAlMFI.

The deactivation of propane conversion activity of the H-GaAlMFI is not influenced significantly by the pretreatment. The comparison of O_2 pretreated catalysts for their deactivation is however not very reliable because of the activation and deactivation process occurring simultaneously during the initial reaction period.

The above comparison reveals that H-GaAlMFI, which shows superior performance, has a very high potential for developing a highly active and selective catalyst for lower alkane aromatization. In order to obtain desirable conversion and aromatics selectivity in lower alkane aromatization, the catalyst must contain strong acid sites with high density and also highly dispersed active gallium species in close proximity of the zeolitic acid sites, thus the maintaining a balance between the acid and dehydrogenating function (1, 26-28). This could very well be achieved in the case of H-GaAlMFI, the density of strong acid sites can be controlled by the framework Si/Al ratio and the highly dispersed active gallium species can be obtained by degalliation of the zeolite under controlled conditions.

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

2.2.4 CONCLUSIONS

This investigation leads to the following important conclusions.

1. The initial aromatization activity/selectivity and product distribution in the propane aromatization over H-GaMFI, H-GaAlMFI and Ga/H-ZSM-5 catalysts are strongly influenced by their high temperature pretreatment with O_2 or H_2.

2. The variation of activity (both propane conversion and aromatization) and product selectivity with time-on-stream are strongly affected by the catalyst pretreatment and the catalyst activation (caused by the interaction of hydrogen, produced in the aromatization, with the catalysts pretreated with O_2) or deactivation (due to coking), depending upon the catalyst.

3. The initial aromatization activity and selectivity are appreciably increased due to the H_2 pretreatment given to the H-GaAlMFI and Ga/H-ZSM-5 catalysts and also due to the activation (by the H_2 produced in the reaction) of these catalysts (when pretreated with O_2), in the aromatization process during a short initial reaction period. However, the H_2 pretreatment results in a decrease in both the propane conversion and aromatization activity of the H-GaMFI.

4. The aromatics/(methane + ethane) mass ratio for all the catalysts is increased by their H_2 pretreatment and also by the catalyst activation by the H_2 produced during the aromatization process (for a short initial period) over the O_2 pretreated catalysts.

5. Comparison of the catalysts for their initial activity/selectivity, and aromatics/(methane + ethane) ratio and variation of these parameters with time-on-stream in the propane aromatization process leads to the following order for the catalysts for their choice : H-GaAlMFI > Ga/H-ZSM-5 > H-GaMFI. Zeolite (MFI) catalysts containing extraframework Ga-species in association with framework Al (i.e. stronger protonic acid site) rather than with framework Ga are more active as well as more selective in the propane aromatization. Galloaluminosilicates (MFI) have high potential for developing commercial propane (or lower alkanes) aromatization catalyst having desirable activity/selectivity and life.

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CHAPTER 2.3

INITIAL ACTIVITY/SELECTIVITY OF H-GALLOSILICATE (MFI) IN PROPANE AROMATIZATION : INFLUENCE OF H^+ EXCHANGE AND THERMAL/HYDROTHERMAL PRETREATMENTS

2.3.1. 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/H-ZSM-5 in aromatization of n-hexane (2) and light alkanes (6,7). The isomorphous 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 favorable combination of Lewis and Bronsted 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, 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 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 Bronsted 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 correlation between the acidity and the initial catalytic activity of the zeolite.

2.3.2 EXPERIMENTAL

2.3.2.1 Catalysts Preparation

Gallosilicate (MFI) with Si/Ga ratio of 33 was synthesized 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 deionized water in SS autoclave at 180°C for 24h, washing drying and calcining the zeolite crystals at 600°C in static air for 15h to remove the occluded organic template, exchanging with 1M ammonium acetate at 80°C, drying, pressing binder-free and crushing to particles of 0.2-0.3mm size and again calcining in static air at 600°C for 4h. The thermal and hydrothermal treatments given to H-GaMFI (H^+exchange = 90 %) are listed in Table 2.3.1.

2.3.2.2 Catalysts Characterization

The MFI framework structure of the GaMFI zeolites was confirmed by the XRD. The X-ray powder diffraction patterns (Chapter 1.1) were collected on a Philips PW 1730 instrument with Cukα as a source of X-ray radiations. Crystallinity of the zeolite samples was estimated by comparing the XRD peak intensities at $2\theta = 22\text{-}24^\circ$. The incorporation of Ga in the zeolite framework was confirmed by ^{29}Si and ^{71}Ga MAS NMR obtained 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 -104ppm and -113ppm, respectively

(15). The strong acidity of the zeolite samples (Table 2.3.1) was determined by the chemisorption of pyridine at 400°C using the GC pulse method (16).

2.3.2.3 Catalytic Pulse Reaction

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 gm) packed in a quartz microreactor (i.d. : 4.5mm and o.d. :6.0mm) connected to a GC (17,18) and analyzing the reaction products by the on-line GC with FID and computing integrator, using Poropak-Q column (3mm x 5m) and Benton-34 (5%)- dinonylphthalate (5%) on Chromosorb-W column (3mm x 5m). Pure N_2 [flow rate : 20 cm^3 (at STP). min^{-1}] was used as a carrier gas. Before the reaction, the catalyst was pretreated insitu in a flow of pure N_2 at 500°C for 1h. The detailed procedures for carrying out the pulse reactions and product analysis are described earlier in Chapter 2.2.

2 3.3. 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 2.3.1. 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. 2.3.1, 2.3.2 and 2.3.3, respectively. Figures 2.3.4 and 2.3.5 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 above parameters on the distribution of aromatics formed in the propane aromatization are included in Table 2.3.1. Dependence of the propane conversion, both total and to

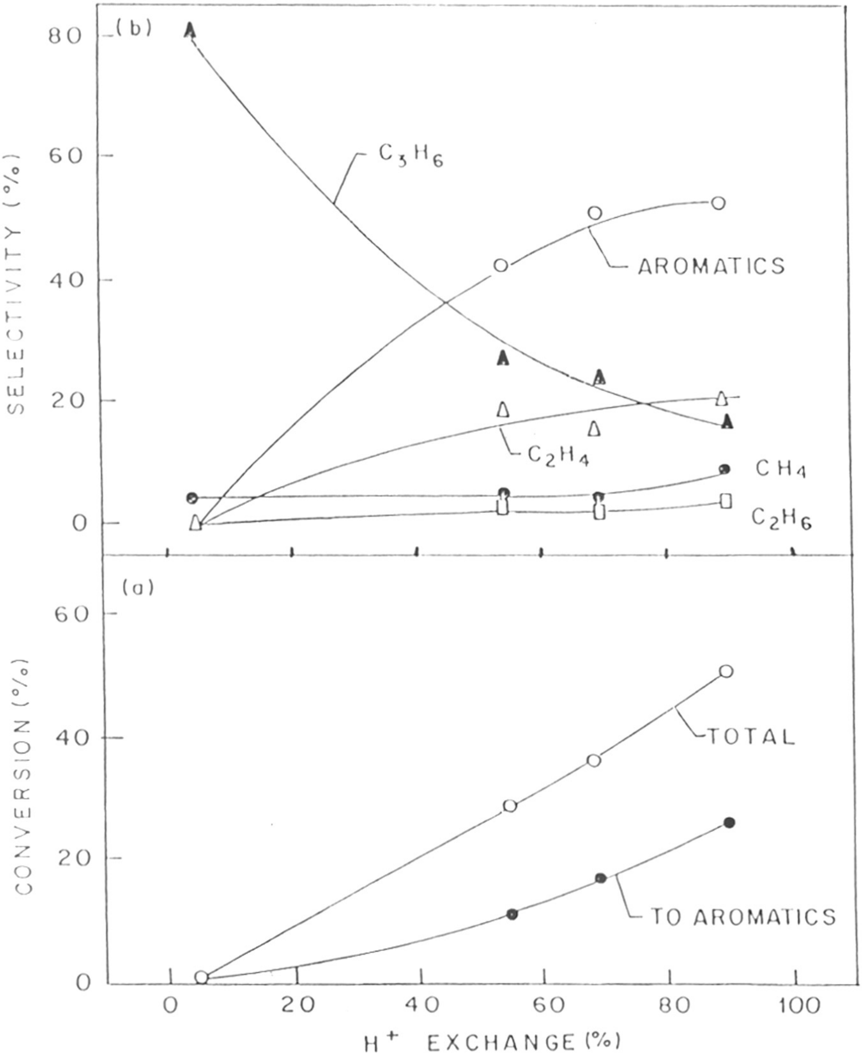

Fig. 2.3.1 : Influence of H^+exchange on a) propane conversion, total and to aromatics and b) selectivity in aromatization of propane over H-GaMFI (calcined at 600°C).

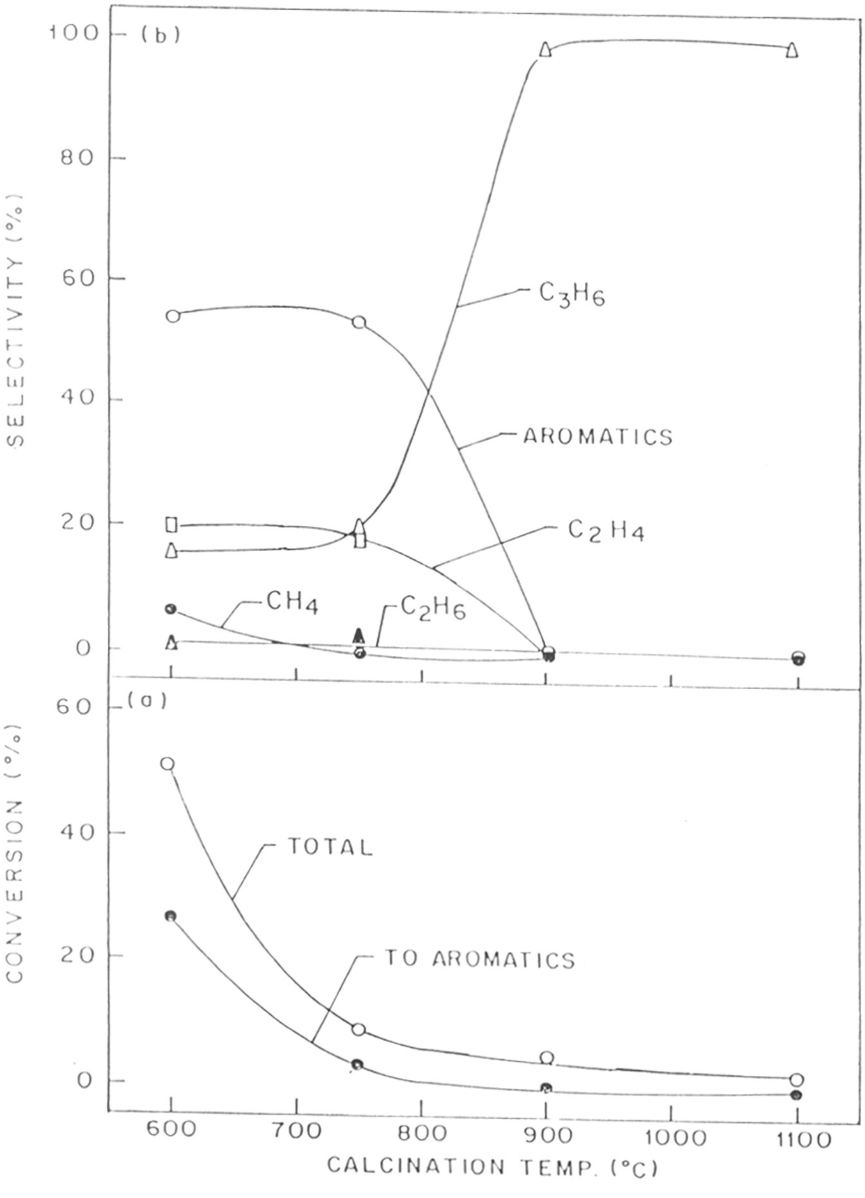

Fig. 2.3.2 : **Influence of catalyst calcination temperature on a) propane conversion and b) selectivity in aromatization of propane over H-GaMFI (H^+exchange = 90%).**

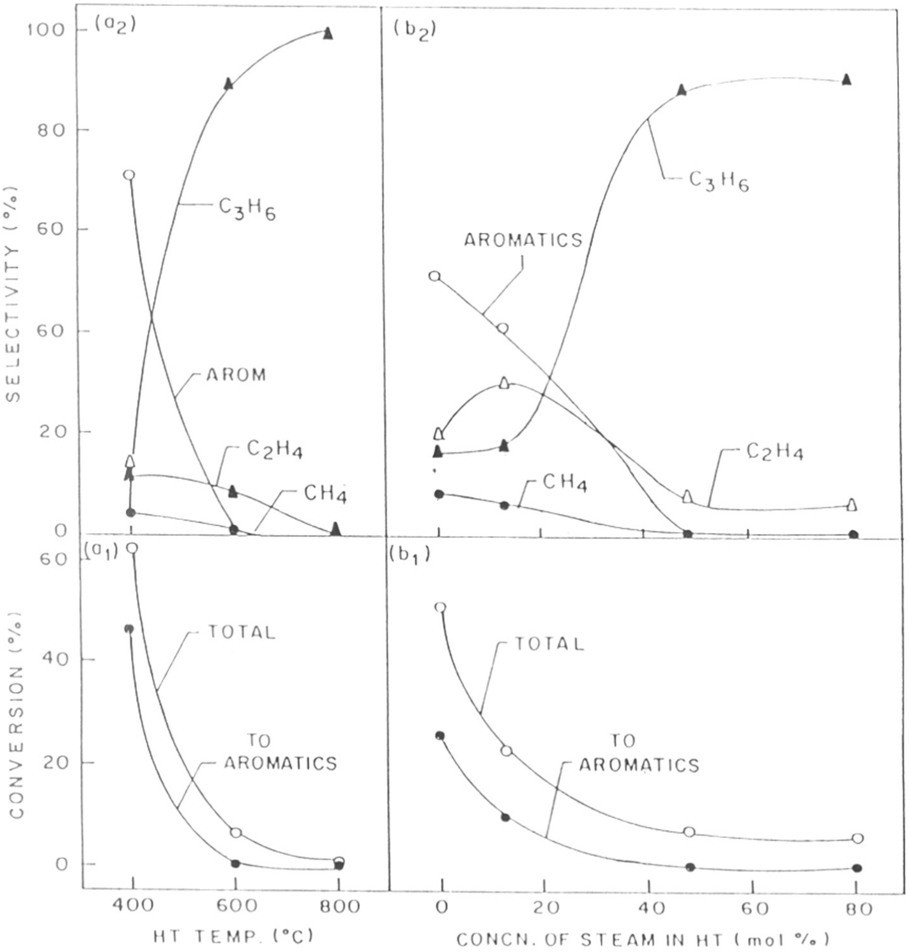

Fig. 2.3.3 : **Influence of hydrothermal treatment a) temperature (concentration of steam : 48 mol %) and b) concentration of steam (at 600°C) on propane conversion and selectivity in aromatization of propane over H-GaMFI (H^+exchange :90%), calcined at 600°C before the hydrothermal treatment.**

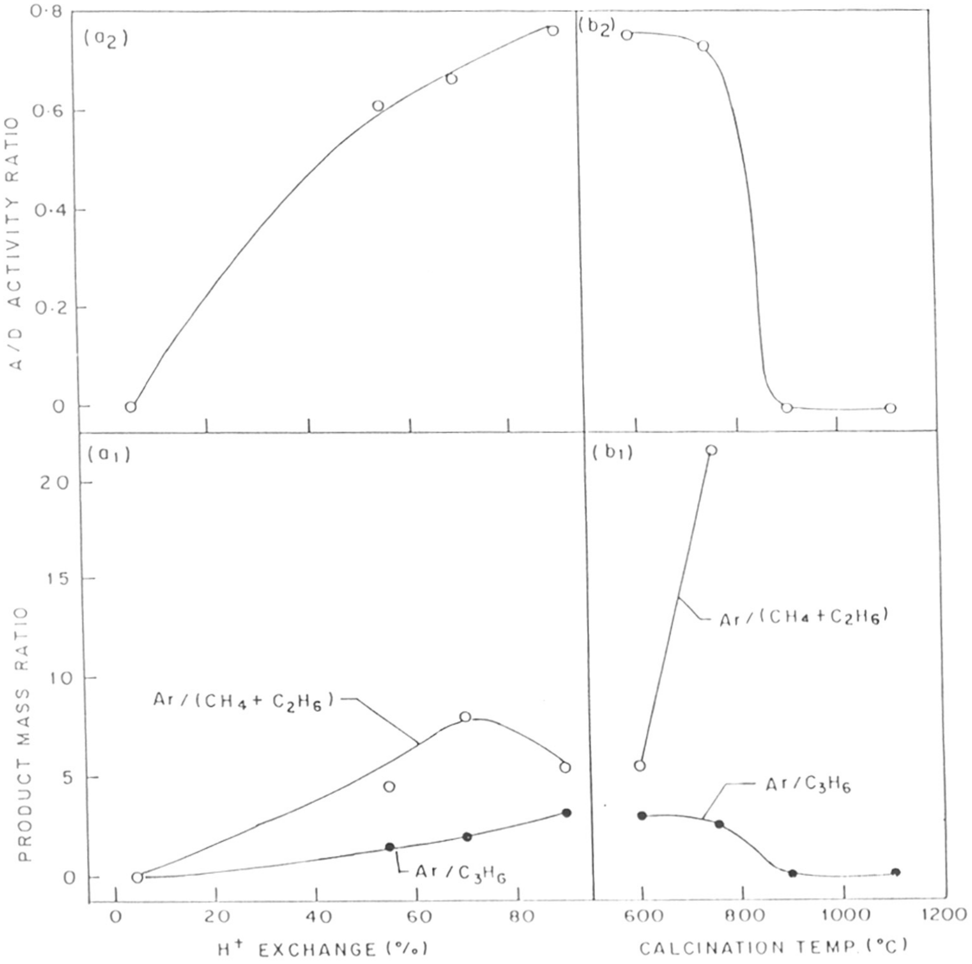

Fig. 2.3.4 : **Influence of a) H^+exchange (calcination temperature = 600^{0}C) and b) calcination temperature (H^+exchange = 90%) on aromatics/(CH_4 + C_2H_6) and aromatics/C_3H_6 product mass ratios and aromatization/dehydrogenation (A/D) activity ratio in the propane aromatization over H-GaMFI.**

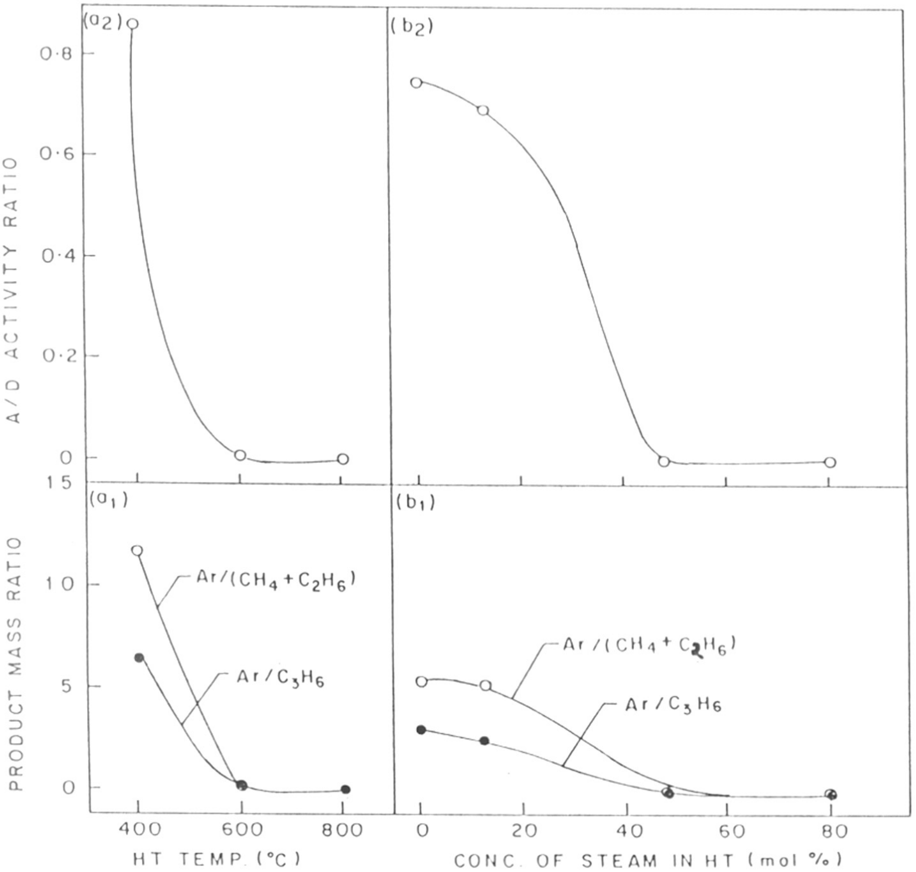

Fig. 2.3.5 : **Influence of hydrothemal treatment a) temperature (concentration of steam = 48 mol%) and b) concentration of steam (at 600°) on aromatics/(CH_4 + C_3H_6) and aromatics/C_3H_6 product mass ratio and aromatization / dehydrogenation (A/D) activity ratio in propane aromatization over H-GaMFI.**

Table 2.3.1: 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 (%)	Calcination[a] temperature (°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				Benzene	Toluene	Ethylbenzene + xylene
5	600	Without HT		100	0.56	0.04	No aromatic 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 aromatic formed		
90	1100	Without HT		67	very high	0.01	No aromatic 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 aromatic formed		
90	600	600	80	78	5.53	0.05	No aromatic formed		
90	600	800	48	62	5.78	0.02	No aromatic formed		

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

aromatics (i.e. yield of aromatics), on the strong acidity of the GaMFI zeolite is shown in Fig. 2.3.6.

2.3.3.1 Influence of H^+ Exchange

The results in Fig. 2.3.1 reveal that, with increasing the degree 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 2.3.1). It is also interesting to note from Fig. 2.3.4a that the aromatics/propylene ratio and the aromatization/dehydrogenation (A/D) activity ratio are increased whereas, the aromatics/(methane+ethane) ratio is passed through a maximum with increasing the 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 the H^+ exchange and consequently with increasing the acidity (Table 2.3.1).

2.3.3.2 Influence of Calcination Temperature

The results (Fig. 2.3.2 and 2.3.4b) 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°C to 1100°C, the propane conversion is decreased exponentially with almost no formation of aromatics for $T_c \geq 900^\circ C$, 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, favoring the formation of benzene over the higher aromatics (Table 2.3.1). 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

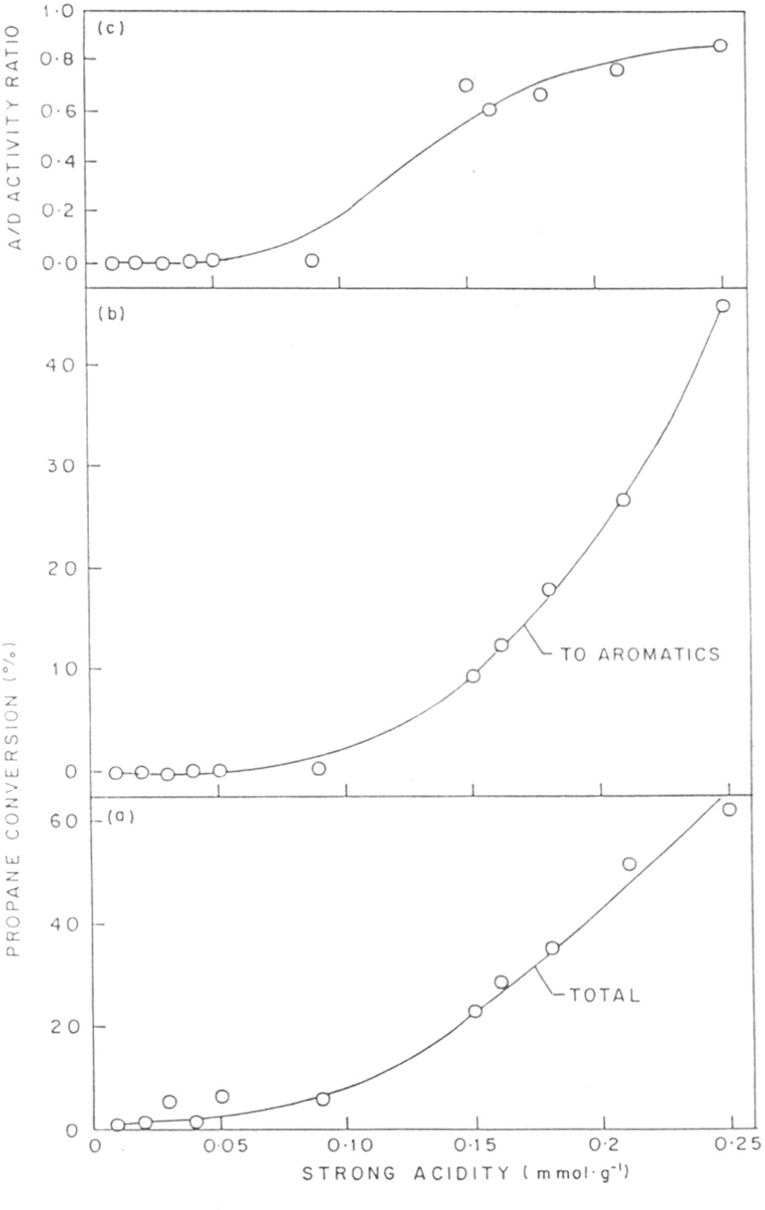

Fig. 2.3.6 : **Variation of a) total propane conversion, b) propane-to-aromatics conversion and c) aromatization /dehydrogenation (A/D) activity ratio in propane aromatization over H-GaMFI with its strong acidity.**

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 degalliation (i.e. conversion of framework Ga into non-framework Ga_2O_3) during the calcination at higher temperatures (Table 2.3.1). Almost a complete degalliation 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.

2.3.3.3 Influence of Hydrothermal Treatments

Figures 2.3.3 and 2.3.5 show a very strong influence of the hydrothermal treatment at different 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 (600°C and 48 mol % steam). However, the influence of hydrothermal treatment on the distribution of aromatics formed is small (Table 2.3.1). 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 degalliation to different extents, depending upon the severity of hydrothermal treatment (Table 2.3.1). The degalliation is increased and the crystallinity is decreased with increasing the temperature and/or concentration of steam in the hydrothermal treatment given to the zeolite.

2.3.3.4 Correlation between Acidity and Propane Conversion/Aromatization Activity.

The results in Fig. 2.3.6 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 the acidity reveals the importance of strong acid sites in the propane aromatization. The aromatization/dehydrogenation activity ratio is also increased markedly with increasing the acidity. The results reveal that a high concentration of the acid sites are necessary for the zeolite to be active in the propane aromatization.

2.3.4 DISCUSSION

The results (Figs. 2.3.1-2.3.3) 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. 2.3.1-2.3.6) 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.

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 2.3.1 and Figs. 2.3.1-2.3.6) 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 the earlier observation (5,12).

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

.3.5. CONCLUSIONS

The initial propane conversion/aromatization activity of H-GaMFI is strongly nfluenced by the degree of H^+exchange, calcination temperature and hydrothermal reatment (at different conditions) of the zeolite. The propane conversion activity is lecreased to a large extent with increasing the severity of thermal and hydrothermal reatments or decreasing the H^+ exchange of the zeolite. There exists a close relationship etween the propane conversion and aromatization activity and the acidity (measured in erms of pyridine chemisorbed at 400^{o}C) of the zeolite. The acid sites at high oncentrations are essential for the zeolite to be active in the propane aromatization. The on-framework Ga-oxide species are active only in the presence of the acid sites (which re attributed to FW-Ga) at high concentration.

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CHAPTER 2.4

METHANOL-TO-AROMATICS CONVERSION OVER H-GALLOSILICATE (MFI) : INFLUENCE OF Si/Ga RATIO, DEGREE OF H^+ EXCHANGE, PRETREATMENT CONDITIONS AND POISONING OF STRONG ACID SITES

2.4.1 INTRODUCTION

Isomorphous substitution of Ga for Al in H-ZSM-5 results in an increase in the aromatization activity/selectivity of the zeolites in propane aromatization (1-3). The increase in the activity/selectivity is due to the increase in the dehydrogenation activity of the zeolites for both the propane-to-propene and naphthenes-to-aromatics conversion (1,3). It is therefore, interesting to compare the methanol-to-aromatics conversion over H-gallosilicate (H-GaMFI) and H-ZSM-5 zeolites having same Si/(Ga or Al) ratio and also to study the influence of factors affecting the acidity of H-GaMFI (viz. Si/Ga ratio, degree of H^+ exchange and thermal and hydrothermal pretreatments and poisoning of strong acid sites) on its activity/selectivity (or product distribution) in methanol-to-aromatics conversion process. The present investigation was undertaken for this purpose. The H-GaMFI zeolite, because of its higher dehydrogenation activity, is deactivated quite fast due to coking (2,4,5) and also its initial activity is expected to be changed due to the hydrothermal treatment received by it, due to the water formed in the dehydration of methanol during the methanol-to-aromatics conversion process [its acidity is found to be strongly influence by hydrothermal pretreatment (6)]. For avoiding these problems, the initial catalytic activity/selectivity of the H-GaMFI zeolites in methanol-to-aromatics conversion was determined, using a pulse microreactor.

2.4.2 EXPERIMENTAL

2.4.2.1 Catalyst Preparation

The composition of H-GaMFI zeolites with different Si/Ga ratios, degrees of H^+ exchange and pretreated at different thermal and hydrothermal conditions is given in

Table 2.4.1. The H-GaMFI with different Si/Ga ratios was prepared by synthesizing TPA-GaMFI by hydrothermal crystallization from a gel (pH=9-10) consisting of Na-trisilicate (Fluka), gallium nitrate (Aldrich), TPA-Br (Aldrich), sulfuric acid (AnalaR, BDH) and deionized water in a stainless steel autoclave at 180°C for 24h, washing, drying and calcining the resulting zeolite crystals at 600°C in static air for 15h to remove the occluded organic template, exchanging with 1M ammonium nitrate at 80°C and drying, pressing binder free, crushing to 0.2-0.3mm size particles and again calcining the zeolite under static air at 600°C for 4h to convert its NH_4-form to H-form. The H-ZSM-5 (Si/Al = 33) was prepared by the procedure described earlier (7). The thermal and hydrothermal treatments (Table 2.4.1) were given to the H-GaMFI (with Si/Ga=33 and H^+ exchange = 95 %) in a quartz reactor by passing a steam-N_2 mixture at total space velocity at 5050 cm^3 (at STP) $g^{-1}.h^{-1}$ over the zeolite at different temperatures and concentrations of steam (Table 2.4.1).

2.4.2.2 Catalyst Characterization

The MFI framework structure of the synthesized zeolite sample was confirmed by their XRD. The incorporation of Ga in the zeolite framework was confirmed by ^{29}Si and ^{71}Ga MAS NMR (5) and also by measuring its strong acidity attributed to the presence of tetrahedral (i.e. framework) gallium in the zeolite, as described earlier (Chapter 2.1 and 2.3).

The number of strong acid sites on the zeolite samples were determined by the chemisorption of pyridine at 400°C using the GC pulse method (8). The acidity data are included in Table 2.4.1.

2.4.2.3 Methanol-to-Aromatics Conversion Reaction

The initial activity/selectivity of the H-GaMFI zeolite samples (Table 2.4.1) in methanol-to-aromatics conversion was determined in a pulse microreactor (i.d. : 4.5mm, o.d. : 6.0mm and length : 30cm) made up of quartz, similar to that described earlier

Table 2.4.1: Composition of zeolites and their thermal/hydrothermal treatment conditions and acidity data

Zeolite	Si/(Ga or Al) ratio	H^+ exchange (%)	Calcination temperature (°C)	Hydrothermal treatment		Acid sites ($mmol.g^{-1}$)
				Temp. (°C)	Conc. of steam (mol %)	
NH_4 -ZSM-5	33.2	96	600	Without HT		0.31
NH_4 -GaMFI	33.0	90	600	Without HT		0.21
NH_4 -GaMFI	33.0	90	750	Without HT		0.09
NH_4 -GaMFI	33.0	90	900	Without HT		0.03
NH_4 -GaMFI	33.0	90	1100	Without HT		0.01
NH_4 -GaMFI	33.0	90	600	400	48	0.25
NH_4 -GaMFI	33.0	90	600	600	48	0.09
NH_4 -GaMFI	33.0	90	600	800	48	0.02
NH_4 -GaMFI	33.0	90	600	600	13	0.15
NH_4 -GaMFI	33.0	90	600	600	80	0.05
NH_4 -GaMFI	33.0	5	600	Without HT		0.04
NH_4 -GaMFI	33.0	55	600	Without HT		0.16
NH_4 -GaMFI	33.0	70	600	Without HT		0.18
NH_4 -GaMFI	33.0	96	600	Without HT		0.30
NH_4 -GaMFI	50	96	600	Without HT		0.25
NH_4 -GaMFI	68	96	600	Without HT		0.21
NH_4 -GaMFI	129	96	600	Without HT		0.16

(9-11). The pulse reaction was carried out by injecting a pulse of methanol (0.4 μl) in the microreactor (containing 0.1 g catalyst) at 400°C and analyzing the reaction products by an on-line GC with FID and computing integrator, using a GC column (3mm x5m) of Benton-34 (5%)-dinonylphalate (5%) on Chromosorb-W. Pure N_2 (passed over molecular sieves to remove the traces of moisture) was used as a carrier gas (flow rate : 20 cm^3 min^{-1}). Before the pulse reaction, the catalyst was pretreated insitu in a flow of pure N_2 (20 cm^3. min^{-1}) at 500°C for 1h. Detailed procedure for carrying out the pulse reaction and product analysis are given earlier (12) and also in Chapter 2.2. The poisoning of strong acid sites with pyridine chemisorbed at 400°C was done by the procedure described earlier (7,13). For this purpose the microreactor was disconnected from the gas chromatograph and the catalyst was saturated with pyridine at 400°C by injecting a number of pyridine pulses (pulse size 3 μl). The reversibly adsorbed pyridine was desorbed at 400°C in the flow of nitrogen (20 cm^3 min^{-1}) for 1h. The microreactor was then connected to the gas chromatograph and the activity of the poisoned catalyst in the methanol-to-aromatics conversion (at 400°C) was determined by the procedure described above.

2.4.3 RESULTS AND DISCUSSION

Results showing the influence of Si/Ga ratio and degree of H^+ exchange of H-GaMFI on its methanol-to-aromatics conversion (at 400°C) activity and product distribution are presented in Figs. 2.4.1 and 2.4.2, respectively. Figures 2.4.3 and 2.4.4 shows the effect of calcination temperature and hydrothermal treatment (at differed temperatures and concentrations of stream), respectively, on the activity and product distribution in the methanol conversion process over zeolite (with Si/Ga = 33 and H^+ exchange = 90%). The influence of the above parameters on the distribution of C_1-C_4 hydrocarbons formed in the methanol conversion is presented in Figs. 2.4.5 and 2.4.6. The data on the strong acidity (measured in terms of pyridine chemisorption at 400°C) of the zeolites are included in Table 2.4.1. A relationship between the methanol-to-aromatics conversion

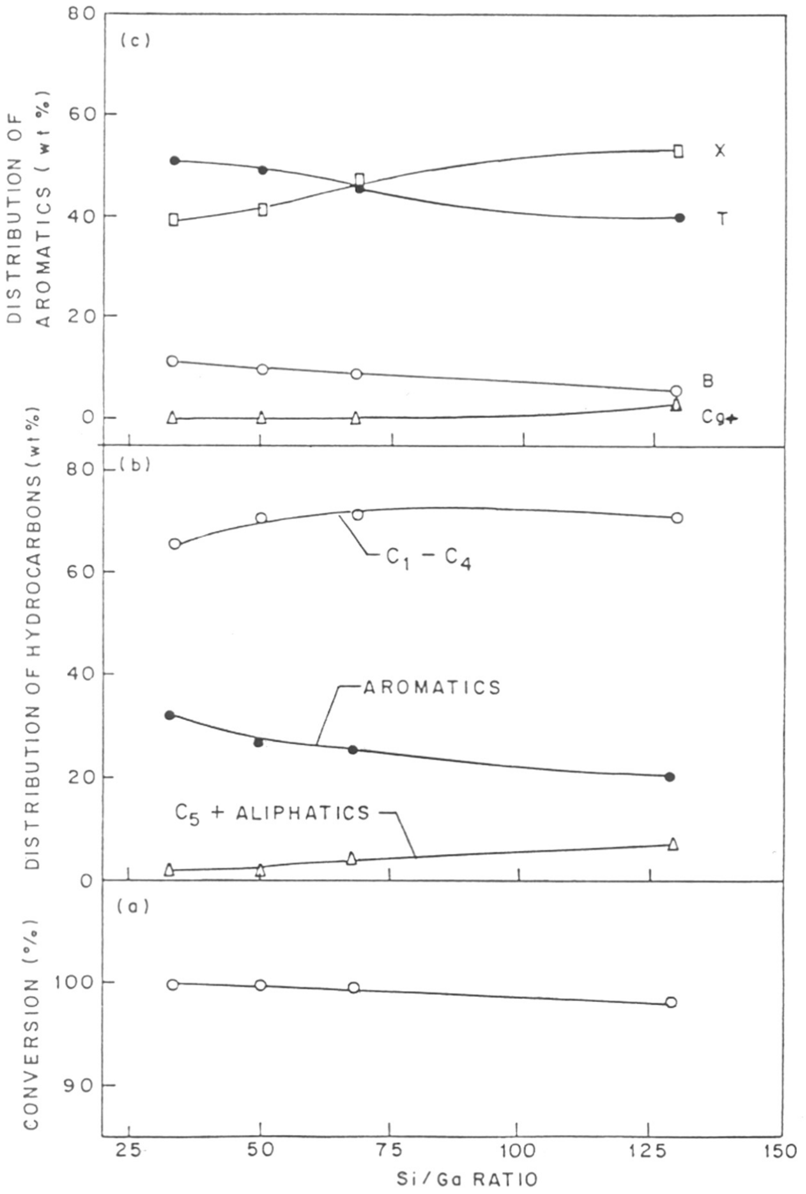

Fig. 2.4.1 : **Influence of Si\Ga ratio on a) methanol conversion and distribution of b) hydrocarbons and c) aromatics in the methanol-to-aromatics conversion over H-GaMFI (H^+ exchange = 95 % and T_c = 600°C).**

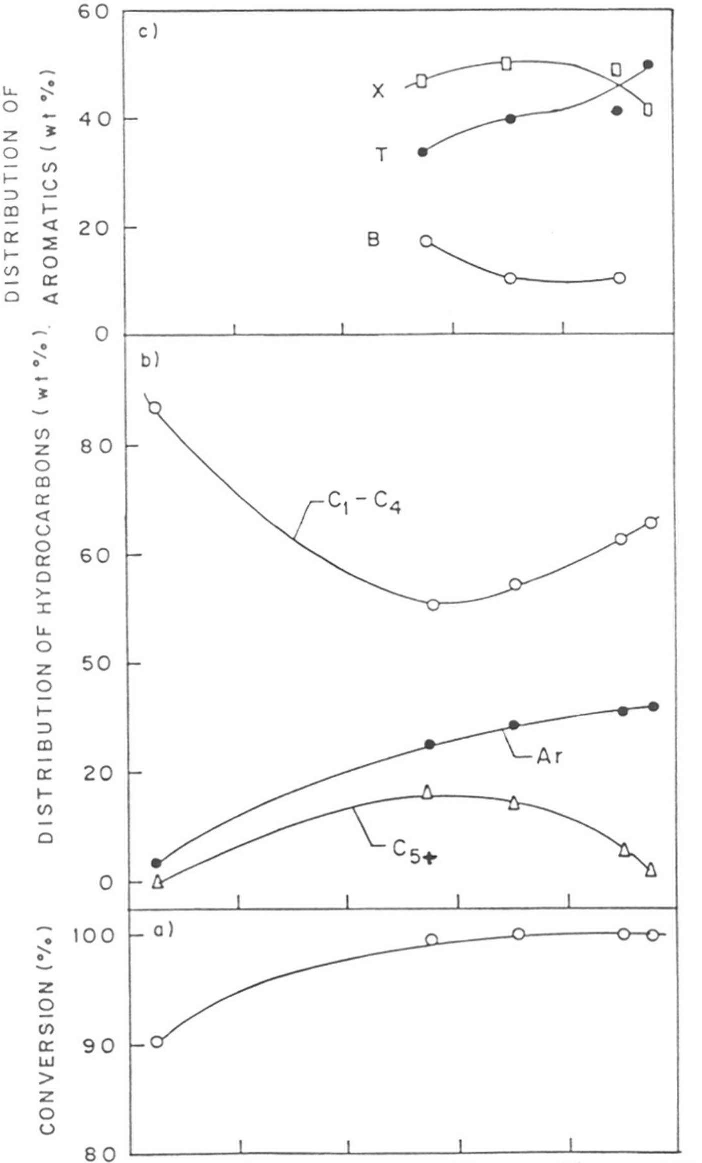

Fig. 2.4.2 : **Influence of H^+exchange on a) methanol conversion and distribution of b) hydrocarbons and c) aromatics in the methanol-to-aromatics conversion over H-GaMFI (Si\Ga = 33 and T_c = 600°C).**

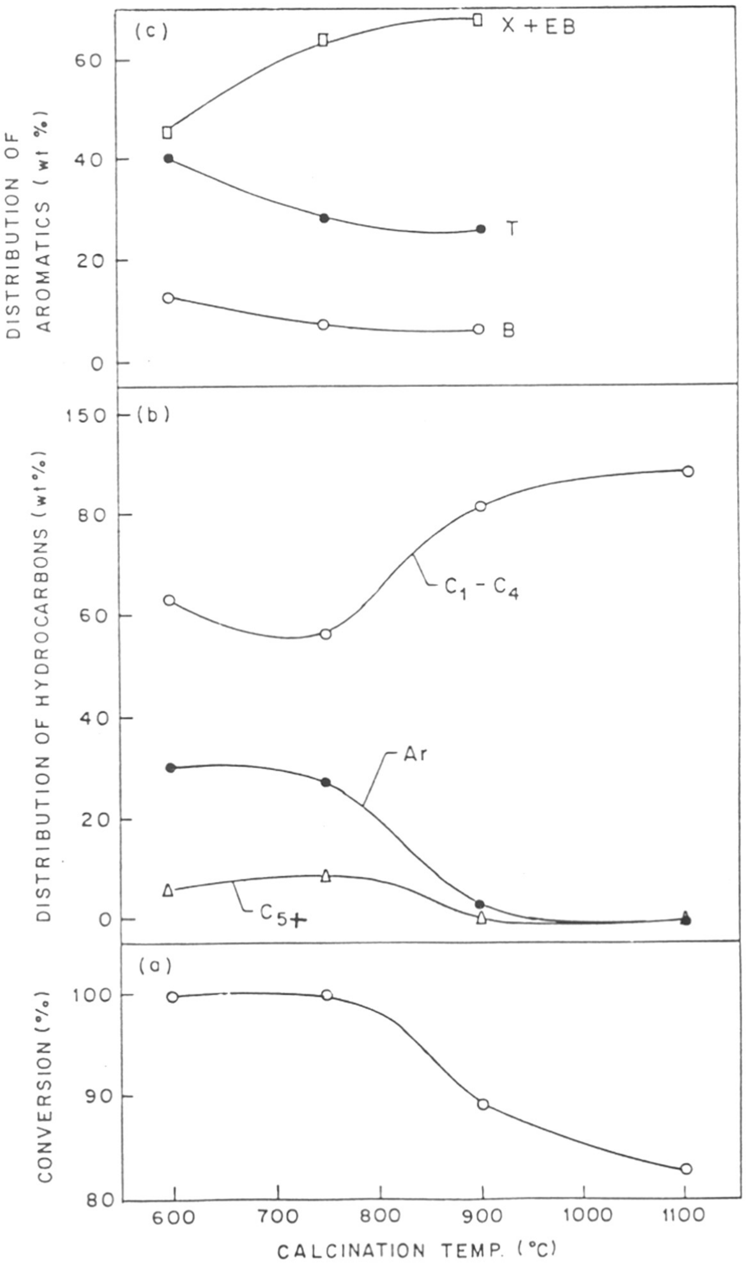

Fig. 2.4.3 : **Influence of catalyst calcination temperature on a) methanol conversion and distribution of b) hydrocarbons and c) aromatics in the methanol-to-aromatics conversion over H-GaMFI (Si\Ga = 33 and H^+exchange = 90 %).**

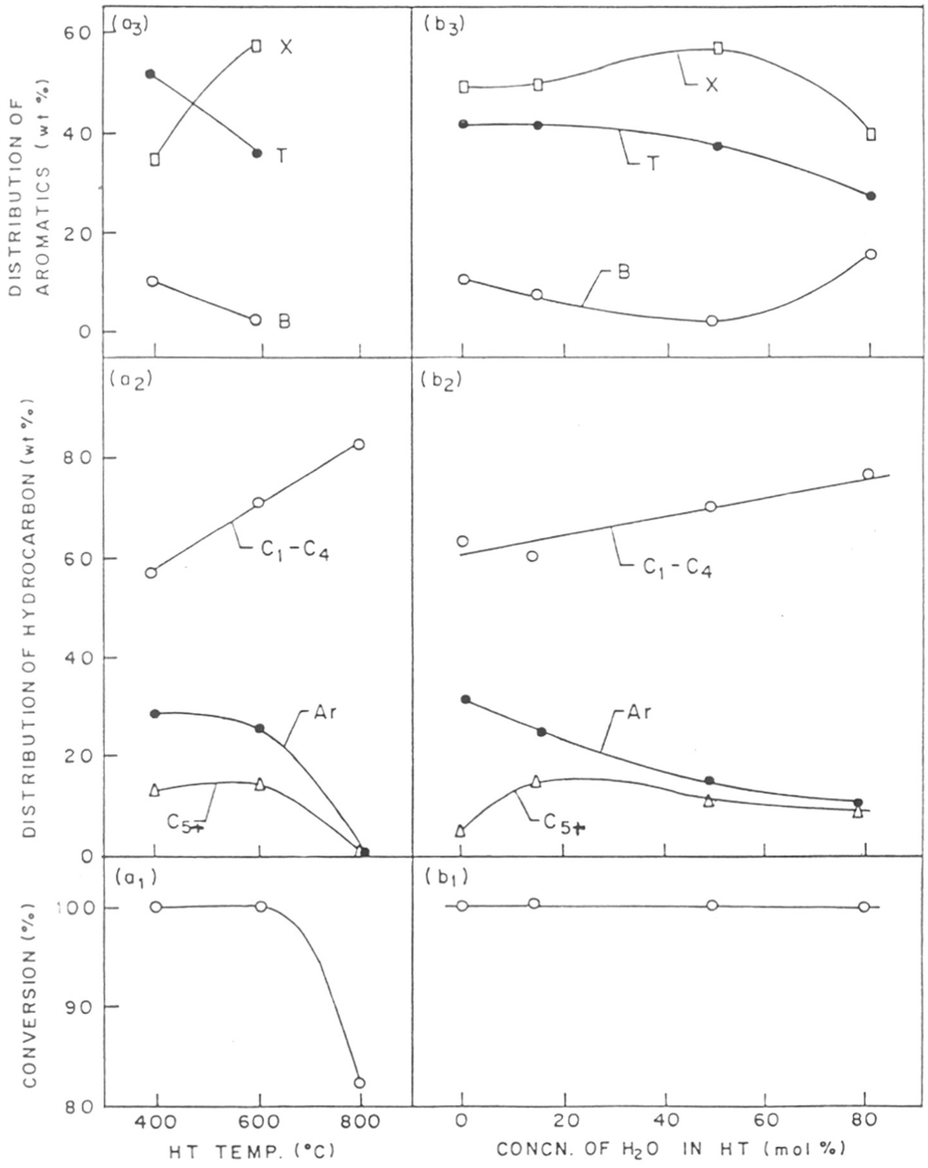

Fig. 2.4.4 : **Influence of catalyst hydrothermal treatment a) temperature (concentration of steam : 48 mol %) and b) concentration of steam (at 600°C) on methanol conversion distribution of hydrocarbons and aromatics in the methanol-to-aromatics conversion over H-GaMFI (Si\Ga = 33, H^+exchange = 90%) calcined at 600°C before the hydrothermal treatment.**

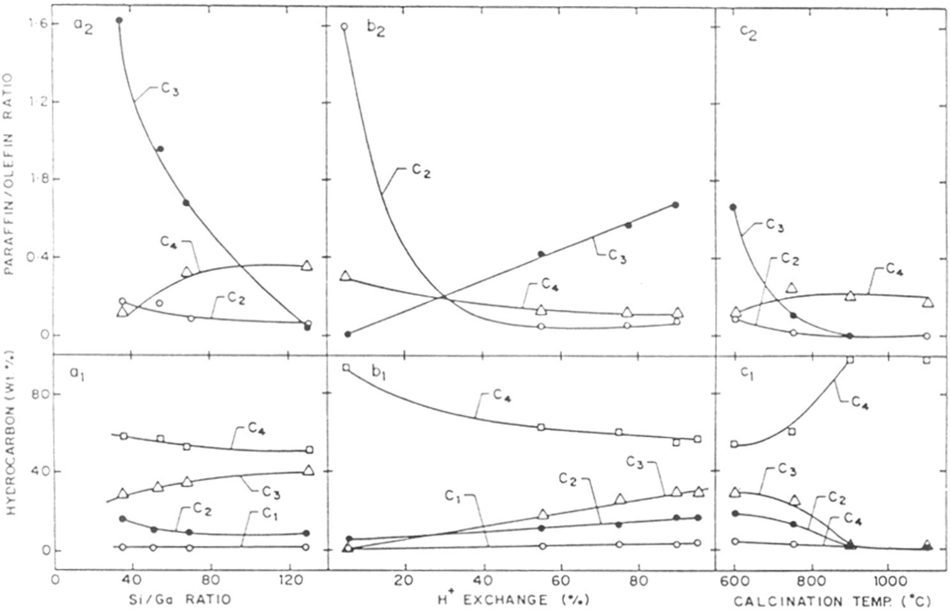

Fig. 2.4.5 : **Influence of a) Si/Ga ratio, b) degree of H^+exchange and c) calcination temperature of H-GaMFI on distribution of hydrocarbons formed in the methanol conversion.**

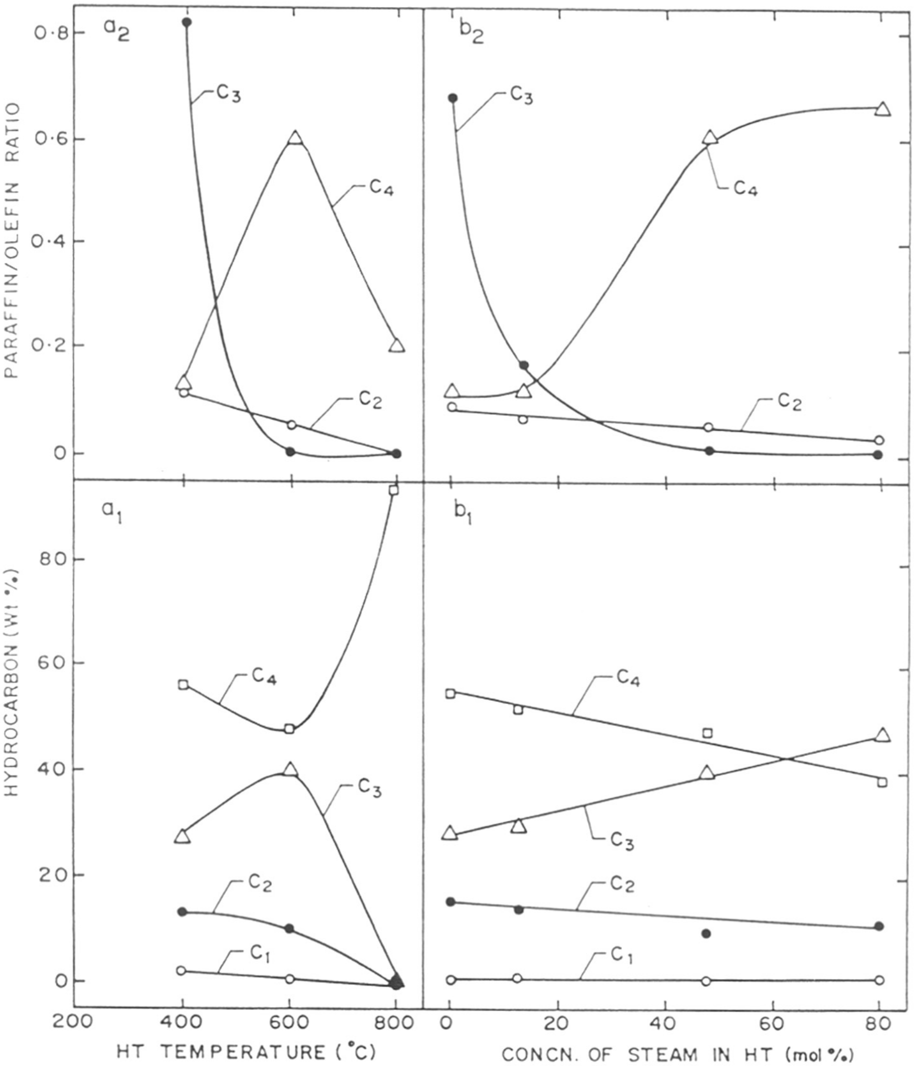

Fig. 2.4.6 : **Influence of hydrothermal treatment a) temperature (concentration of steam : 48 mol %) and b) concentration of steam (at 600°C) on distribution of C_1-C_4 hydrocarbons formed in the methanol conversion.**

activity and the acidity of H-GaMFI zeolite is shown in Fig 2.4.7. Results on the propene aromatization over H-GaMFI are given in Table 2.4.2. The H-GaMFI and H-ZSM-5 zeolites, having almost the same Si/(Ga or Al) ratio (33.0), H^+ exchange (95%) and pretreated under identical conditions (calcined at 600°C for 4h in static air), with or without poisoning of their acid sites by pyridine chemisorption at 400°C are compared for their activity/selectivity in the methanol-to-aromatics conversion in Table 2.4.3. The important observations are summarized below.

2.4.3.1 Influence of Si/Ga ratio

Figure 1 shows a mild influence of Si/Ga ratio on the methanol conversion but effect on the formation of aromatics in the process and their distribution is strong. With increasing Si/Ga ratio formation of aromatics is decreased appreciably and accordingly the formation of C_1-C_4 and C_{5+} aliphatics is increased. Among aromatics, the formation of benzene and toluene is decreased but that of higher alkyl benzene is increased. This is expected to be mostly due to a decrease in number of acid sites of the zeolite with increasing the Si/Ga ratio, thus resulting in a lower aromatization activity and also a lower dealkylation activity of the zeolite. The distribution of C_1-C_4 hydrocarbons (Fig. 5a) is strongly influenced by the Si/Ga ratio.

A comparison of these results with that for H-ZSM-5 (14) reveals that the aromatization activity of H-GaMFI is very significantly higher. The effect of Si/Ga ratio on the methanol-to-aromatics conversion and distribution of aromatics is more or less similar to that observed for H-ZSM-5 expect that the formation of C_{9+} aromatics over H-GaMFI is negligibly small.

2.4.3.2 Influence of H^+ Exchange

Results in Fig. 2.4.2 shows that both methanol conversion and aromatization activity of H-GaMFI are increased by increasing its H^+ exchange, similar to that observed for H-ZSM-5 (Si/Al = 17.2) (14). However, the concentration of C_1-C_4 and C_{5+} aliphatic hydrocarbons is passed through a minimum and a maximum, respectively, with increasing

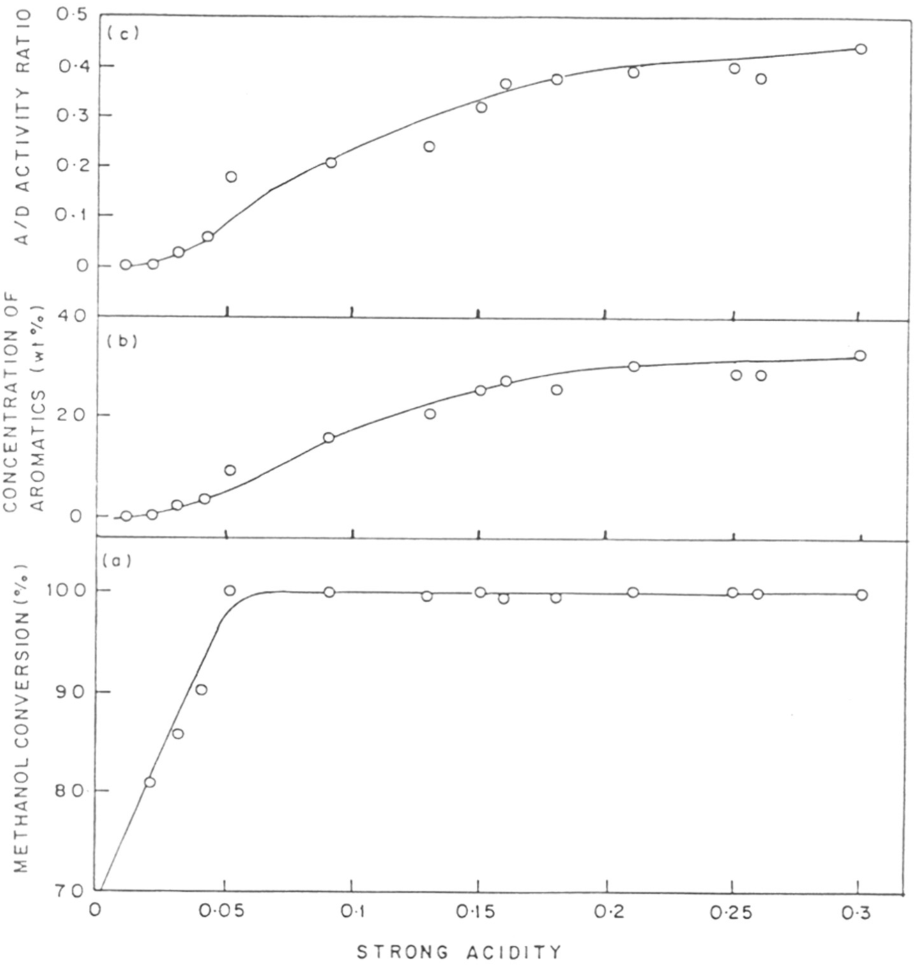

Fig. 2.4.7 : **Dependence of a) methanol conversion b) concentration of aromatics (in hydrocarbons) and c) aromatics\dehydration (A\D) activity ratio in the aromatization of methanol over H-GaMFI on its strong acidity.**

Table 2.4.2 : Results on propylene aromatization over H-GaMFI (Si/Ga ratio 33.0 and H^+ exchange = 96 %) at 400°C. (Pulse size : 0.2 ml)

Conversion (%)	90.7
Conc. of aromatics in hydrocarbons (wt %)	41.8
Distribution of hydrocarbons (wt %)	
C_1-C_4	56.7
C_{5+} aliphatics	1.5
Distribution of aromatics (wt %)	41.8
Benzene	25.4
Toluene	51.7
Ethylbenzne + xylenes	22.6
C_{9+}	0.3
Distribution of C_1-C_4 (wt %)	
CH_4	4.3
C_2H_4	10.7
C_2H_6	2.2
C_3H_6	16.0
C_3H_8	28.5
C_4H_8	30.2
C_4H_{10}	8.1

Table 2.4.3 : Influence of isomorphous substitution of Al by Ga in H-ZSM-5 and poisoning of strong acid sites (by pyridine chemisorption at 400°C) of H-ZSM-5 and H-GaMFI zeolites on the activity/selectivity and distribution of aromatics formed in the methanol-to-aromatics conversion

	Without Poisoning		With poisoning of strong acid sites[a]	
	H-ZSM-5	H-GaMFI	H-ZSM-5	H-GaMFI
Methanol conversion (%)	99.8	99.9	87.1	91.4
Conc. of aromatics in hydrocarbons (wt %)	19.1	32.7	0.0	16.3
Distribution of hydrocarbons (wt %)				
C_1-C_4	79.5	56.7	85.7	65.8
C_{5+} aliphatics	1.1	10.5	1.4	9.3
Aromatics	19.1	32.7	0.0	16.3
Distribution of aromatics (wt %)				
Benzene	8.1	3.5	-	2.2
Toluene	39.4	45.8	-	18.7
Ethylbenzene + xylenes	51.1	50.5	-	79.0
C_{9+}	1.5	0.2	-	0.1
Distribution of C_1-C_4 (wt %)				
CH_4	1.0	1.6	0.6	0.8
C_2H_4	8.1	9.5	5.8	10.
C_2H_6	0.5	1.6	0.4	0.0
C_3H_6	13.8	10.9	32.1	43.8
C_3H_8	22.0	17.8	0.8	0.0
C_4H_8	44.9	52.4	37.7	31.6
C_4H_{10}	9.7	6.2	22.6	13.6

[a] number of strong acid sites poisoned are 0.30 and 0.31 mmol.g $^{-1}$ for H-GaMFI and H-ZSM-5 , respectively.

the H^+ exchange. The distribution of C_1-C_4 hydrocarbons is strongly affected by the degree of H^+ exchange (Fig. 2.4.5b). The distribution of aromatics (Fig. 2.4.2c) is also changed appreciably due to a change in the H^+ exchange. The concentrations of benzene and xylenes are decreased at lower and higher H^+exchange, respectively, and that of toluene is increased continuously with increasing the H^+ exchange. The distribution of aromatics and its variation with the H^+ exchange are some what different from that observed for the H-ZSM-5 (14). Also, there is almost no formation of C_{9+} aromatics over H-GaMFI. The influence on the activity/selectivity of H-GaMFI is attributed to an increase in its acidity with increasing the H^+ exchange.

2.4.3.3 Influence of Calcination Temperature

Figure 2.4.3 shows a strong influence of calcination temperature particularly above 750°C, on the conversion of methanol and distribution of hydrocarbons and formation of aromatics in the methanol conversion process over H-GaMFI. When the calcination temperature of the zeolite is increased, the methanol conversion and concentration of aromatics in the hydrocarbons formed are decreased very markedly, particularly at higher calcination temperatures. The distribution of aromatics formed is also changed very significantly. The concentration of xylenes and ethyl benzene are increased whereas, those of benzene and toluene are decreased with increasing calcination temperature. The observed variation of the concentration of aromatics in the hydrocarbons formed and that of benzene, toluene and xylenes in the aromatics (i.e. distribution of aromatics) with the calcination temperature is quite similar to that observed earlier in the methanol-to-aromatics conversion over H-ZSM-5 (Si/Al =17.2) (12). The distribution of C_1-C_4 hydrocarbons is strongly influenced by the calcination temperature (Fig. 2.4.5c).

The observed effects of calcination temperature are attributed mostly to a decrease in the acidity of H-GaMFI, caused by its dehydroxylation and partial or complete degalliation (i.e. transformation of framework gallium into non-framework one in the form of octahedral gallium oxide species in the zeolite channels) to different extent, depending upon the calcination temperature. A nearly complete degalliation of the zeolite without significant change in its bulk Si/Ga ratio but with a small change in the zeolite crystallinity (from 100 % to 95 %) is observed at the calcination temperature of 900°C (15).

2.4.3.4 Influence of Hydrothermal Treatment

Results (Fig. 2.4.4) reveal a strong influence of hydrothermal treatment at different temperatures and concentrations of steam on the formation of aromatics and also their distribution in the methanol conversion over H-GaMFI. When the temperature or concentration of steam in the hydrothermal treatment is increased, the concentration of aromatics in the hydrocarbons formed is decreased, that of C_1-C_4 hydrocarbons is increased and that of C_{5+} aliphatics is passed through a maximum. The concentration of xylenes and ethyl benzene in aromatics is increased and that of benzene and toluene is decreased with increasing the hydrothermal treatment temperature. The influence of concentration of steam in the hydrothermal treatment on the distribution of aromatics is, however, quite complex. Figure 2.4.6 shows a strong influence of the hydrothermal treatments on the distribution of C_1-C_4 hydrocarbons. The observed influence of hydrothermal treatments to H-GaMFI on its aromatization activity and on the distribution of aromatics (except for HT at 80 mol% steam) is quite consistent with that observed for H-ZSM-5 (16).

The decrease in the aromatization activity of H-GaMFI with increasing the severity of hydrothermal treatment to the zeolite is mostly due to its degalliation to different extents, ultimately resulting in a decrease in the acidity. The degalliation is increased markedly with a small but continuous decrease in the crystallinity of H-GaMFI (from 100 % to 60 %) with increasing the temperature and/or concentration of steam in the hydrothermal treatment given to the zeolite (15).

2.4.3.5 Relation between Acidity and Aromatization Activity

Figure 2.4.7 shows a strong dependence of the formation of aromatics in the methanol conversion over H-GaMFI (with different Si/Ga ratios, degree of H^+ exchange. and pretreated under different thermal and hydrothermal conditions) on its strong acid sites (measured in terms of pyridine chemisorbed at 400°C, similar to that observed for H-ZSM-5 (12,14,16). For the complete conversion of methanol a few strong acid sites are enough (Fig. 2.4.7a) but, for the formation of aromatics to an appreciable extent, a larger number of acid sites are essential; the concentration of aromatics in the hydrocarbons formed and the aromatization/dehydration activity ratio [i.e. aromatics/(aromatics + olefins) mass ratio] are increased with increasing the acid sites and the increase for both follows a similar trend (S type curve). These results show the close relationship between the acidity and the formation of aromatics in the methanol conversion process.

2.4.3.6 Comparison of Conversion of Methanol and Propylene over H-GaMFI

A comparison of results of the propylene aromatization (Table 2.4.2) with that of the methanol-to-aromatics conversion (Table 2.4.3) over the H-GaMFI (Si/Ga = 33) reveals the followings. The distribution of hydrocarbons in both the cases is some what similar. However, in case of the propylene aromatization, the formation of aromatics is higher, and the C_{5+} aliphatics formation is lower. The distribution of aromatics in the two cases is also quite different.

2.4.3.7 Comparison of H-GaMFI with H-ZSM-5 for Methanol-to-Aromatics Conversion

The H-GaMFI and H-AlMFI (H-ZSM-5) zeolites, having similar Si/(Ga or Al) ratio (33), acidity (0.30 and 0.31 mmol g^{-1}, respectively, measured by chemisorption of pyridine at 400°C) and crystal/particle size (6-7μm), with or without poisoning of their strong acid sites by the chemisorption of pyridine at 400°C, are compared for their activity and product distribution in the methanol-to-aromatics conversion at 400°C in

Table 2.4.3. The results show a strong influence of the isomorphous substitution of Al by Ga in ZSM-5 type zeolite on the activity and selectivity of the zeolite. The isomorphous substitution enhances very appreciably the aromatization activity in the methanol conversion, most probably due to an increase in the dehydrogenation activity (1,3). Further, in the absence of strong acid sites, the H-ZSM-5 shows no aromatization activity but the H-GaMFI shows appreciable aromatization activity. Thus the reaction controlling aromatization over H-ZSM-5 occurs essentially on the strong acid sites. Although the aromatization activity of H-GaMFI is decreased very significantly in the absence of strong acid sites, the aromatization can occur to an appreciable extent even in presence of weak acid sites. It may be noted that both the zeolites, after poisoning, show high methanol dehydration activity, indicating presence of appreciable weak acid sites on them. The observed higher aromatization activity of the poisoned H-GaMFI is attributed mostly to its higher dehydrogenating activity in combination with its weak acidity.

2.4.4 CONCLUSIONS

The aromatization activity and distribution of hydrocarbons formed in methanol-to-aromatics conversion over H-GaMFI are strongly influenced by the Si/Ga ratio, degree of H^+ exchange, calcination temperature and hydrothermal treatments of the zeolite. The changes in the acidity of the zeolite due to variation of these parameters are directly reflected on its catalytic activity and product selectivity, indicating a close relationship between the acidity (measured in terms of pyridine chemisorbed at 400°C) and the aromatization activity; the aromatization/dehydration activity ratio is increased with increasing the acidity. Unlike H-ZSM-5, the aromatization over H-GaMFI can occur to an appreciable extent even in the presence of weak acid sites because of its higher dehydrogenating activity.

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PART - III

CHARACTERIZATION OF H-GaMFI AND H-GaAlMFI ZEOLITES AND THEIR PERFORMANCE IN PROPANE AROMATIZATION.

CHAPTER 3.1 : H-GALLOSILICATE (MFI) PROPANE AROMATIZATION CATALYST : INFLUENCE OF Si/Ga RATIO ON ACIDITY, ACTIVITY AND DEACTIVATION DUE TO COKING

CHAPTER 3.2 : SIMULTANEOUS AROMATIZATION OF PROPANE AND HIGHER ALKANE OR OLEFINS OVER H-GaAlMFI ZEOLITE

CHAPTER 3.1

H-GALLOSILICATE (MFI) PROPANE AROMATIZATION CATALYST : INFLUENCE OF Si/Ga RATIO ON ACIDITY, ACTIVITY AND DEACTIVATION DUE TO COKING

3.1.1 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 selectivity (3,4). However, because of the higher dehydrogenating activity due to the presence of extraframework 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, 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.

3.1.2 EXPERIMENTAL

3.1.2.1 Catalyst Preparation

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 24h. The TPA-gallosilicate crystals were washed, dried at 120°C for 4h and calcined at 550°C for 15h in static air to remove the occluded organic template. The calcined gallosilicates were ion exchanged with 1M NH_4NO_3 solution at 80°C for 1h ; 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 4h 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.

3.1.2.2 Catalyst Characterization

The MFI structure of the gallosilicates was confirmed by the XRD (using Phillips diffractometer 1730 series and a CuKα source of radiation) 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 2μsec, 1μsec and 2μsec pulse, 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 stepwise 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 analyzer. The gallosilicate (0.15g) in the column (s.s. tube with i.d. 2mm and length 12cm) 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 ($20cm^3. min^{-1}$). 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 $10^oC/min^{-1}$. After the maximum temperature of the respective step was attained, it was maintained for a period of lh 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 1h.

The gallosilicates were also characterized for their acidity by carrying out on them the acid catalyzed model reactions (viz. cracking of iso-octane and toluene disproportionation), using a pulse microreactor (quartz tube with o.d. 6mm, i.d. 4.5mm and length 300mm) connected to a gas chromatograph. The gallosilicate (0.1g) in the microreactor was pretreated insitu at 500°C in a flow of moisture-free N_2 ($15 cm^3.min^{-1}$) for 1h. The catalytic activity/selectivity was determined using moisture-free N_2 as carrier gas (flow rate : $15cm^3.min^{-1}$) by injecting a pulse of iso-octane, cumene, o-xylene and toluene (0.5μl) at 400°, 300°, 400° and 500°C, respectively, and analyzing the reaction products, using an on-line GC with FID and computing integrator [column : Benton-34 (5%) and dinonylphthalate (5%) on Chromosorb-W (3mm x 5m)]. The pulse quartz micro-reactor unit was similar to that described earlier (10). The microreactor and experimental procedure are described in Chapter 2.2.

Selective poisoning of stronger acid sites by pyridine for these 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) and also in Chapter 2.2.

3.1.2.3 Propane Aromatization

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 (1g) 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 $cm^3.g^{-1}.h^{-1}$. 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 analyzed by an on-line gas chromatograph using Poropak-Q (3mm x 3m) and Benton-34 (5%) and dinonylphthalate (5%) on chromosorb-W (3mm x 5m) columns for separating C_1-C_4 hydrocarbons and aromatics, respectively. Before the reaction, the catalysts were pretreated insitu in a flow of moisture-free N_2 at 550°C for 1h. 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)] x 100. The results are reproducible within 2-6% error.

The reaction set-up used for the propane aromatization is shown schematically in Fig. 3A. It consists of a quartz continuous flow tubular reactor (i.d. 12 mm.) connected to a Nucon (5765) gas chromatograph with FID and two GC columns through three gas sampling valves (GSV1, GSV2 and GSV3). The reactor details are given in Fig. 3B.

The reactor packed with the zeolite catalyst (1 g) was kept in a tubular electric furnace (25 mm dia.) such that the catalyst lies in the constant temperature zone of the furnace. The furnace temperature was measured by a Cr-Al thermocouple located in a gap between the reactor and the furnace wall as shown in Fig. 3A. The temperature of the catalyst was measured by the other thermocouple located axially in the catalyst bed. The GSV1 and the SS gas connecting tubes (3 mm o.d.) between the gas sampling valve and the reactor outlet or GC were heated by heating tapes to avoid condensation of higher hydrocarbons in the product stream. The product stream leaving GSV1 was cooled by passing it through a coiled condenser immersed in a ice-water slurry to condense C_{5+} hydrocarbons. The gaseous hydrocarbons (C_1 - C_4 hydrocarbons) were sampled using GSV 2. Thus, it was possible to sample the products with or without containing C_{5+} hydrocarbons simultaneously using GSV1 and GSV2, respectively. Before entering the GC column B (Poropak Q), the gaseous sample from GSV2 was passed for a short period (which is just enough to elute the C_1 - C_4 hydrocarbon fraction from the column) through a pre-column [Benton - 34 (5%) and dinonylphthalate (5%) on Chromosorb W 3mm X 5m] for removing the traces of higher (C_{5+}) hydrocarbons present in the gaseous sample. After its use, the pre-column was continuously back flushed by N_2 to elute the higher hydrocarbons absorbed at the entrance of the column.

GC column A [Benton - 34 (5%) and dinonylphthalate (5%) on Chromosorb W 3mm X 5m] was used for separating the individual C_{5+} aliphatics, and aromatics from

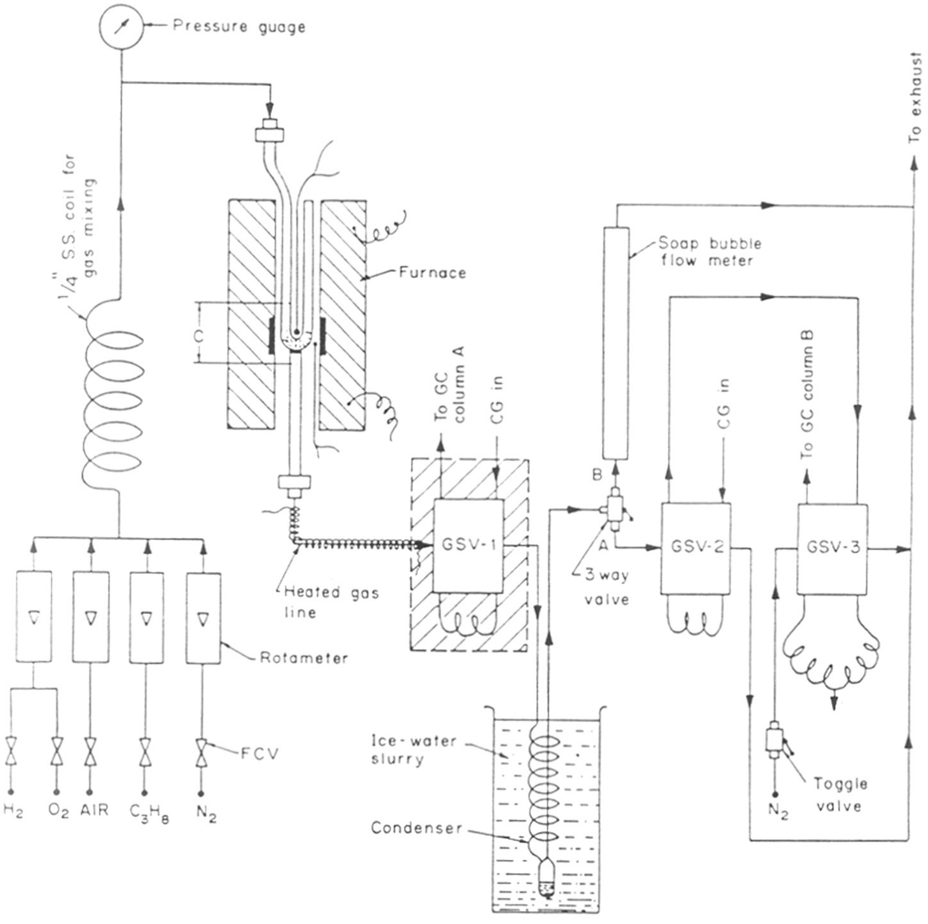


Fig. 3A : Experimental set up for propane aromatization [GSV1 = heated gas sampling valve, GSV2 and GSV3 = gas sampling valves, Column A = Benton-34 (5%) and dinonylphthalate (5%) on Chromosorb-W, Column B = Poropak-Q, CG = carrier gas, FCV = flow control valve].

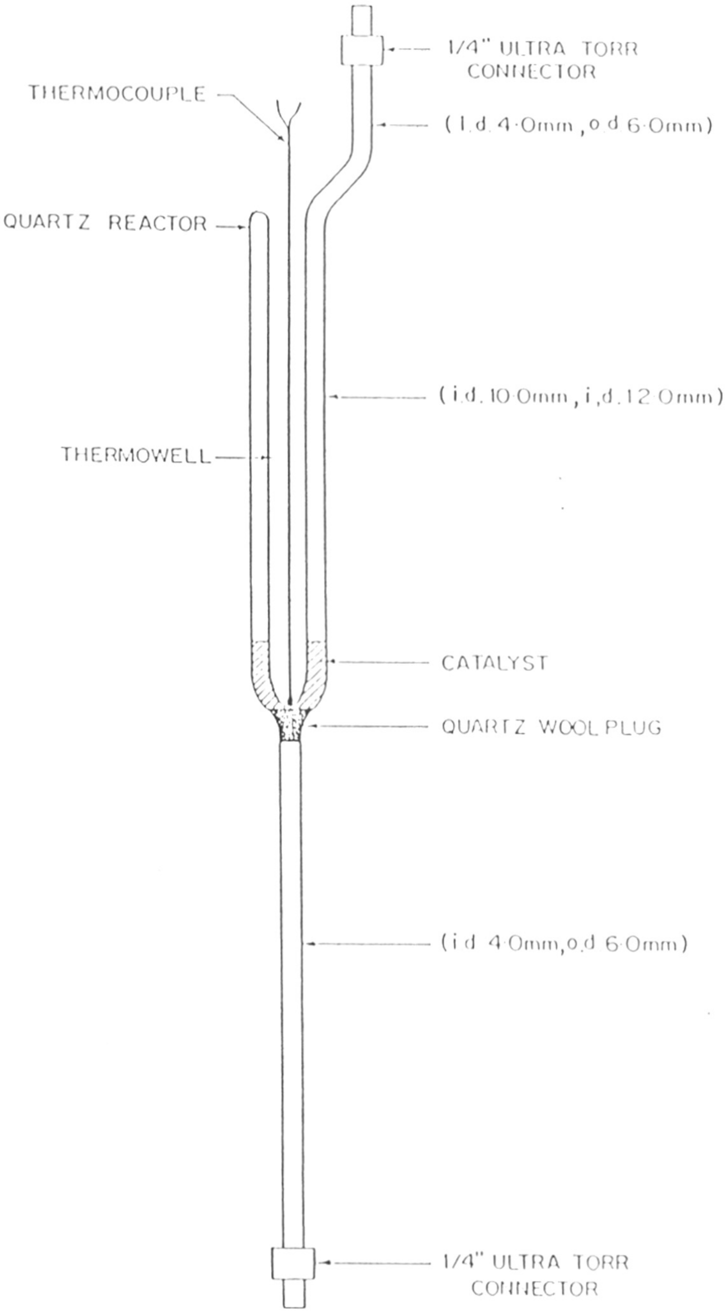


Fig. 3B : Continuous micro-reactor for propane aromatization.

the reaction products (C_1-C_4 hydrocarbons are not separated on this column; these are eluted as a single peak).

As mentioned above the reaction products with and without containing C_{5+} hydrocarbons are sampled by GSV1 and GSV2, respectively, at the same time. However, the sample (total products) from GSV1 is analyzed first and then the analysis of sample from GSV2 (i.e. gaseous sample containing C_1-C_4 hydrocarbon) is performed . The flow rates of feed gases were controlled by fine needle valves and measured by rotameters. For thorough mixing, the feed gases were passed through a long SS tube (6 mm o.d. 5 mm i.d. and 4 m long) in form of a coil. The feed entered the reactor at the top and the reaction products left the reactor at the bottom.

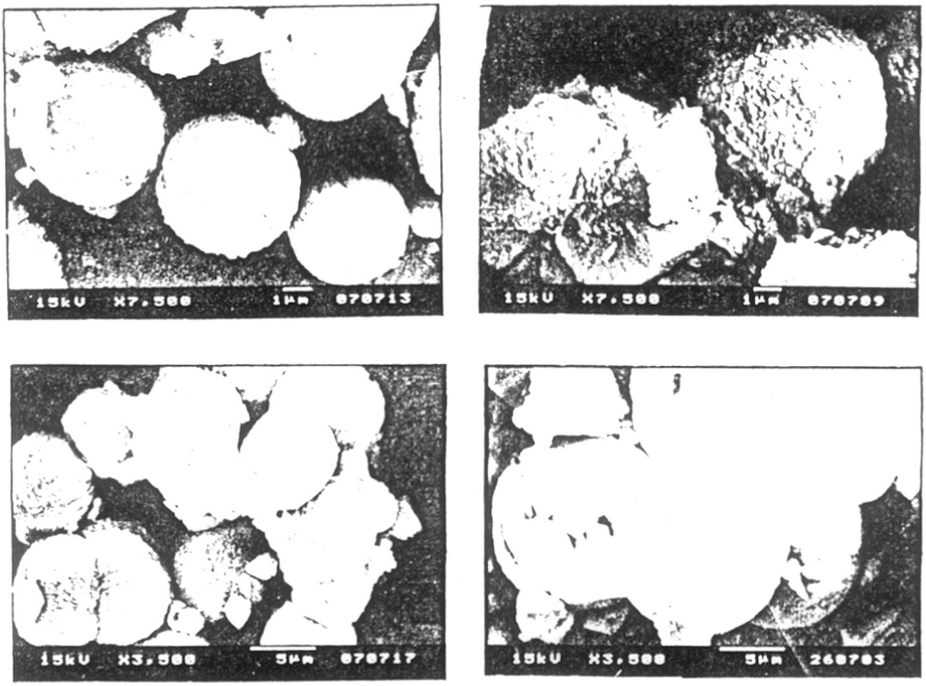
3.1.3 RESULTS

3.1.3.1 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 $2\theta = 24.5^o$ and $2\theta = 29.3^o$, indicating high crystallinity and MFI structure for the gallosilicates.

SEM microphotographs of particles of the TPA-gallosilicates are presented in Fig. 3.1.1. 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 3.1.1.

^{29}Si and ^{71}Ga MAS NMR spectra of the H-gallosilicates are shown in Fig. 3.1.2. No peak for ^{27}Al MAS NMR is observed. The ^{29}Si MAS NMR shows a sharp large peak for Si (0Ga) at about -111 ppm and a small shoulder peak for Si (1Ga) at about -104 ppm for all the gallosilicates. As expected the peak area of Si (1Ga) peak relative to that of Si (0Ga) 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



(a) Si/Ga = 32·9

(b) Si/Ga = 50·5

(c) Si/Ga = 68·4

(d) Si/Ga = 129·6

Fig. 3.1.1 : SEM photographs of H-gallosilicate(MFI) zeolites.

Table 3.1.1 : Framework and non-framework 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.

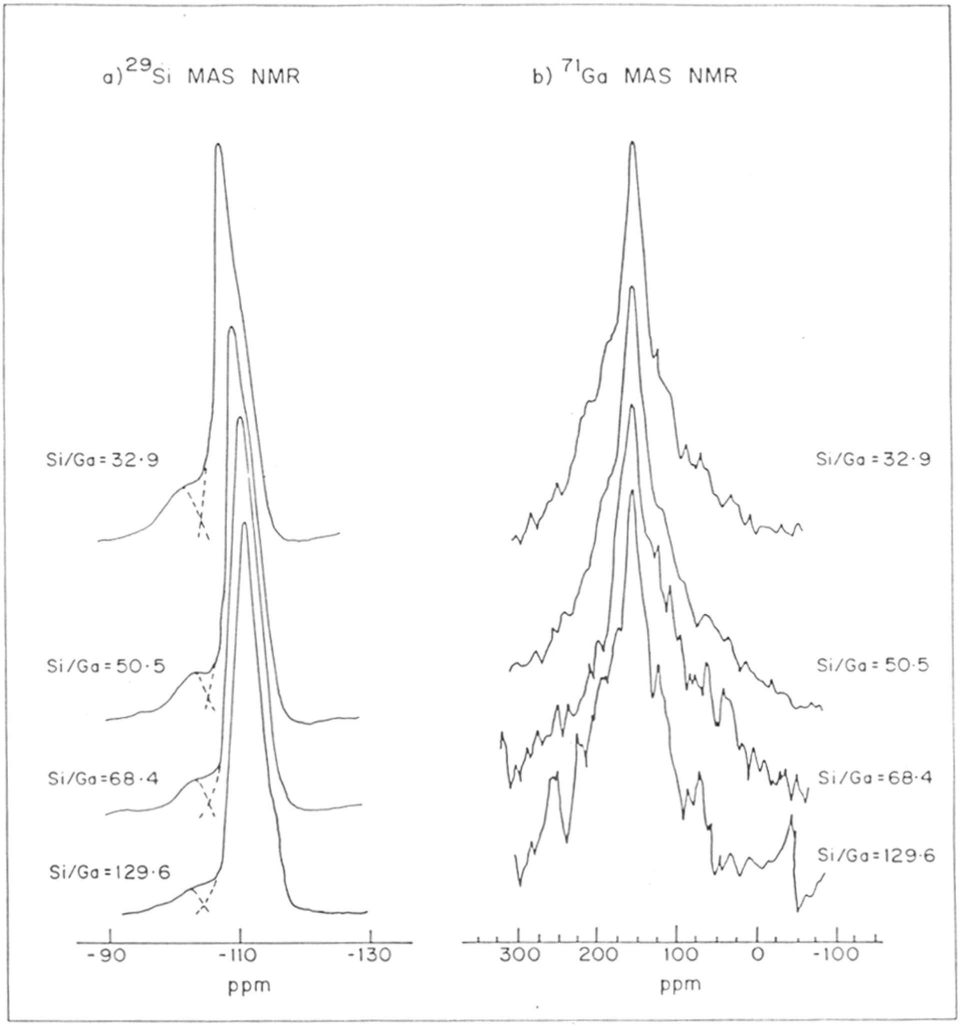


Fig. 3.1.2 : ^{29}Si and ^{71}Ga MAS NMR spectra of H-gallosilicate(MFI) zeolites.

increased after the removal of TPA from the TPA-gallosilicates and also increased further when the zeolites are converted to their H-form (Table 3.1.1).

3.1.3.2 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. 3.1.3. 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 number 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. 3.1.4. 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. 3.1.5. A linear dependence of the strong acidity on the FW-Ga is shown in Fig. 3.1.6. The strong acid site/FW-Ga ratio is found to be very close to 1.0 for all the gallosilicates.

3.1.3.3 Acid Catalyzed Model Reactions

The acidic function of the gallosilicate has also been studied by carrying out following model reactions (catalyzed by strong acid sites) over them : iso-octane

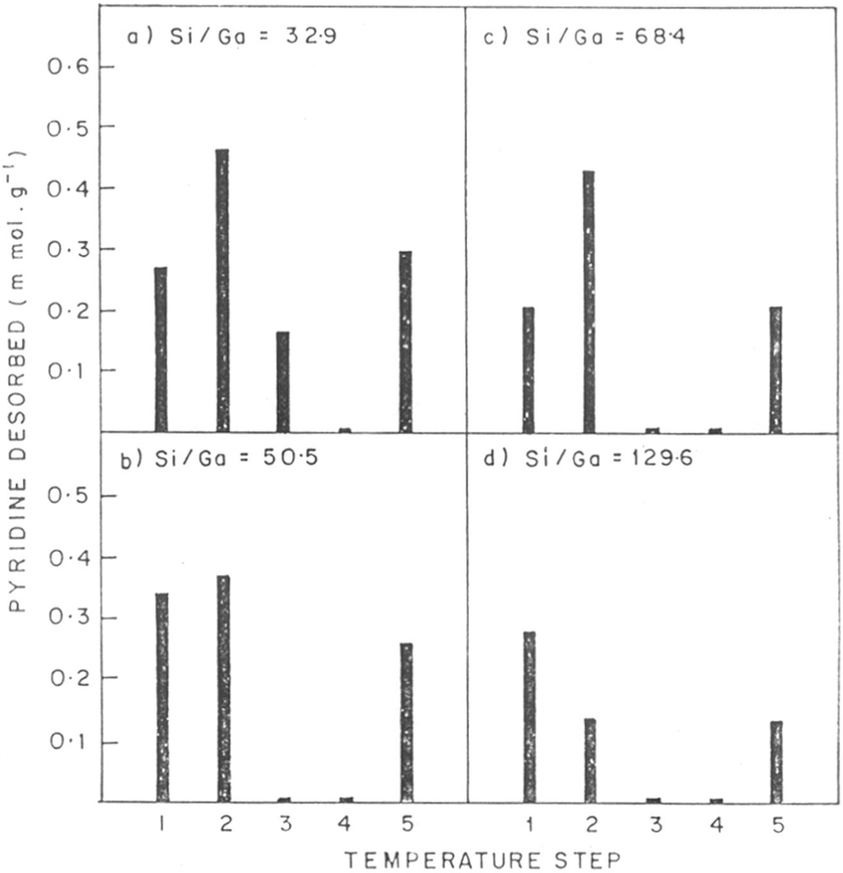


Fig. 3.1.3 : Stepwise thermal desorption of pyridine (chemisorbed at $50^{o}C$) from H-gallosilicate(MFI) zeolites temperature steps : (1) $50^{o}C < T_d \leq 100^{o}C$ (2) $100^{o}C < T_d \leq 200^{o}C$ (3) $200^{o}C < T_d \leq 300^{o}C$ (4) $300^{o}C < T_d \leq 400^{o}C$ (5) $400^{o}C < T_d \leq T_d^*$.

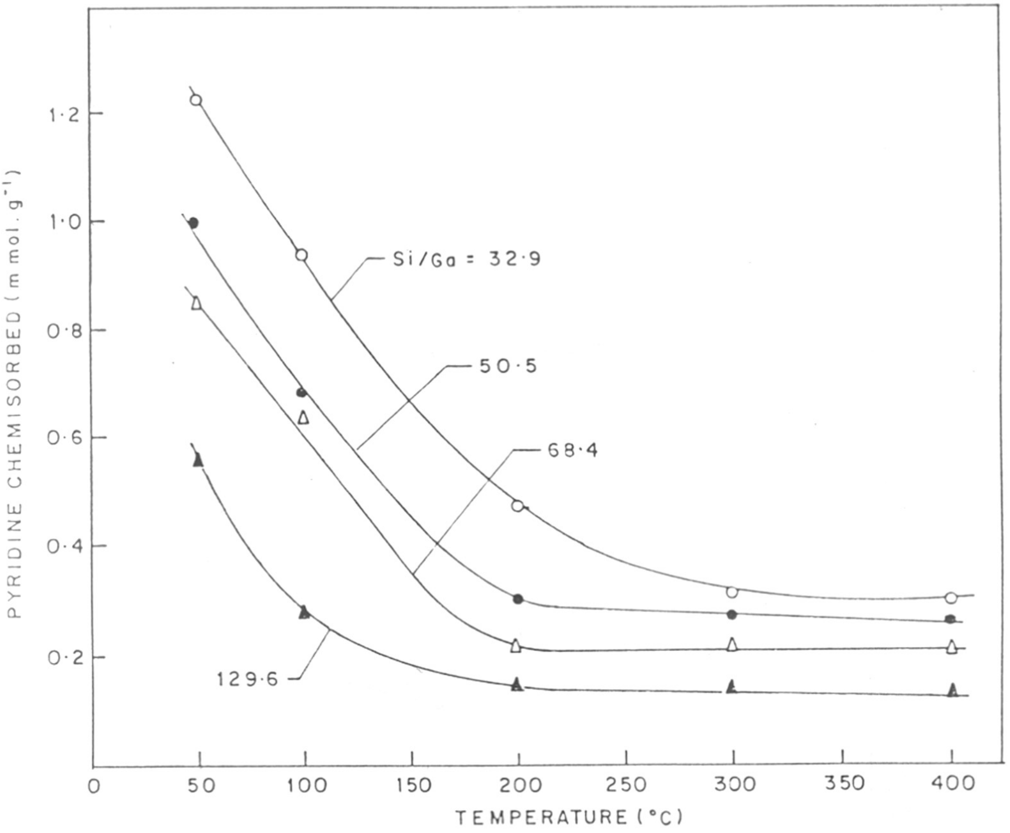


Fig. 3.1.4 : Temperature dependence of chemisorption of pyridine in H-gallosilicate (MFI) zeolites.

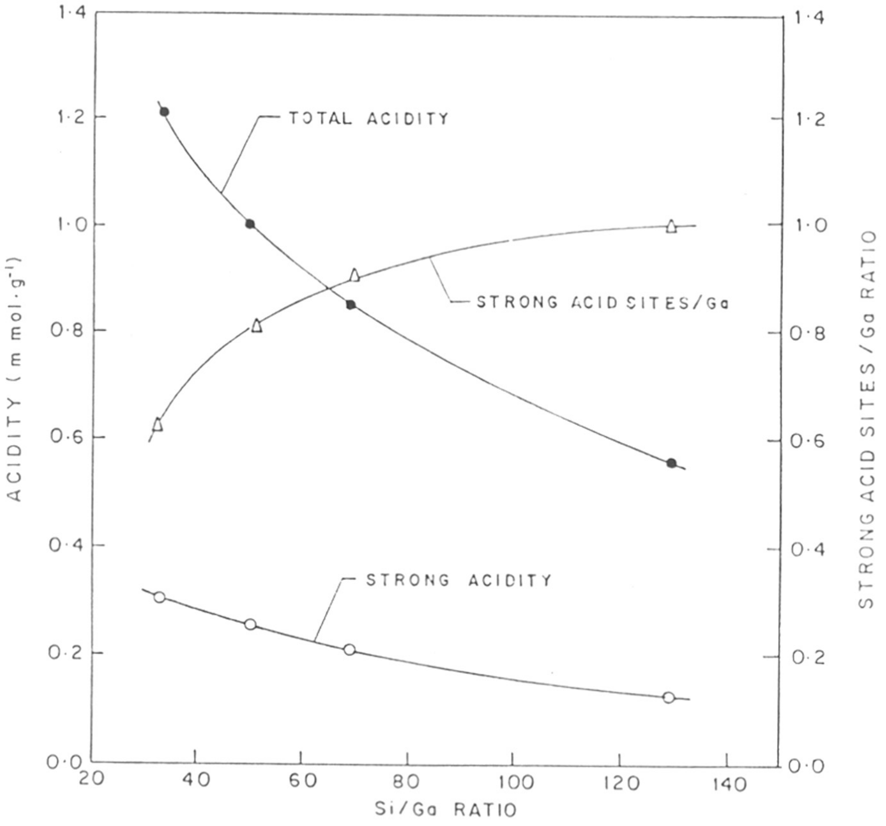


Fig. 3.1.5 : **Influence of bulk Si/Ga ratio on the total acidity and strong acidity of H-gallosilicate(MFI) zeolite.**

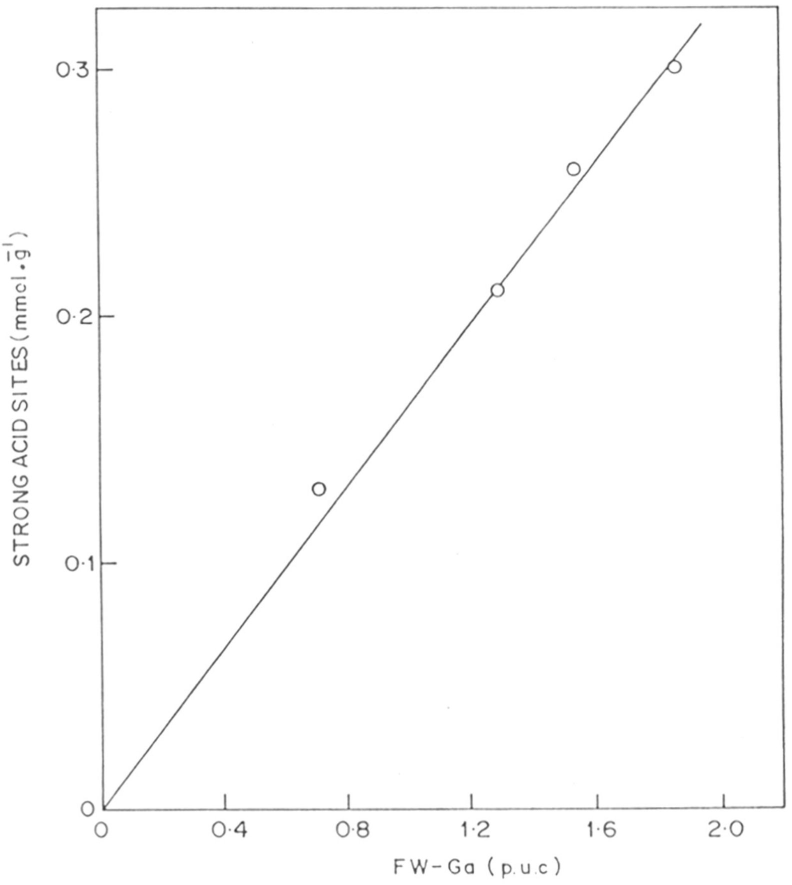


Fig. 3.1.6 : Variation of strong acid sites of H-gallosilicate (MFI) with its framework gallium.

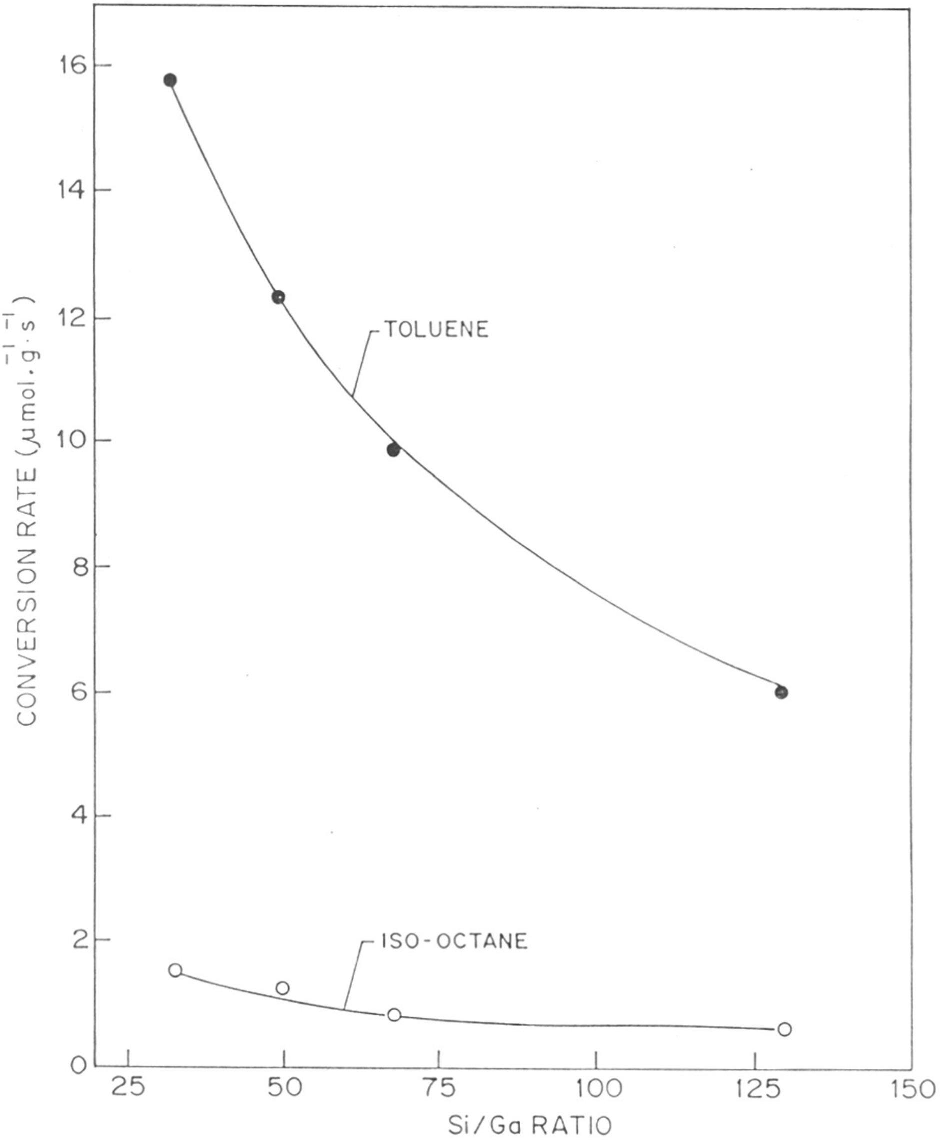


Fig. 3.1.7 : **Influence of bulk Si/Ga ratio on conversion rate in (a) iso-octane cracking (at 400°C) and (b) toluene disproportionation (at 500°C) over H-gallosilicate(MFI) zeolite.**

cracking (at 400^{o}C) for studying external (or intercrystalline) acid sites and toluene disproportionation (at 500^{o}C) for characterizing the internal (or intracrystalline) acid sites.

Results on the iso-octane cracking and toluene disproportionation reactions over the gallosilicates are given in Fig. 3.1.7. 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. 3.1.4 and 3.1.5). 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 iso-octane cracking and toluene disproportionation reactions on the strong acidity (measured in terms of pyridine chemisorbed at 400^{o}C) of the gallosilicate, as shown in Fig. 3.1.8, 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 iso-octane cracking rate) is proportional to the acidity (measured by pyridine chemisorption at 400^{o}C).

3.1.3.4 Selective Poisoning of Stronger Acid Sites

Influence of the poisoning of stronger acid sites by the chemisorption of pyridine at 400^{o}C [for the iso-octane cracking (at 400^{o}C) and cumene cracking (at 300^{o}C) and o-xylene isomerization (at 400^{o}C) reactions] and at 500^{o}C [for the toluene disproportionation (at 500^{o}C) and propane aromatization (at 500^{o}C) reactions] on the activity of the gallosilicate (Si/Ga = 32.9) is shown in Table 3.1.2.

The catalytic activity in the iso-octane 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

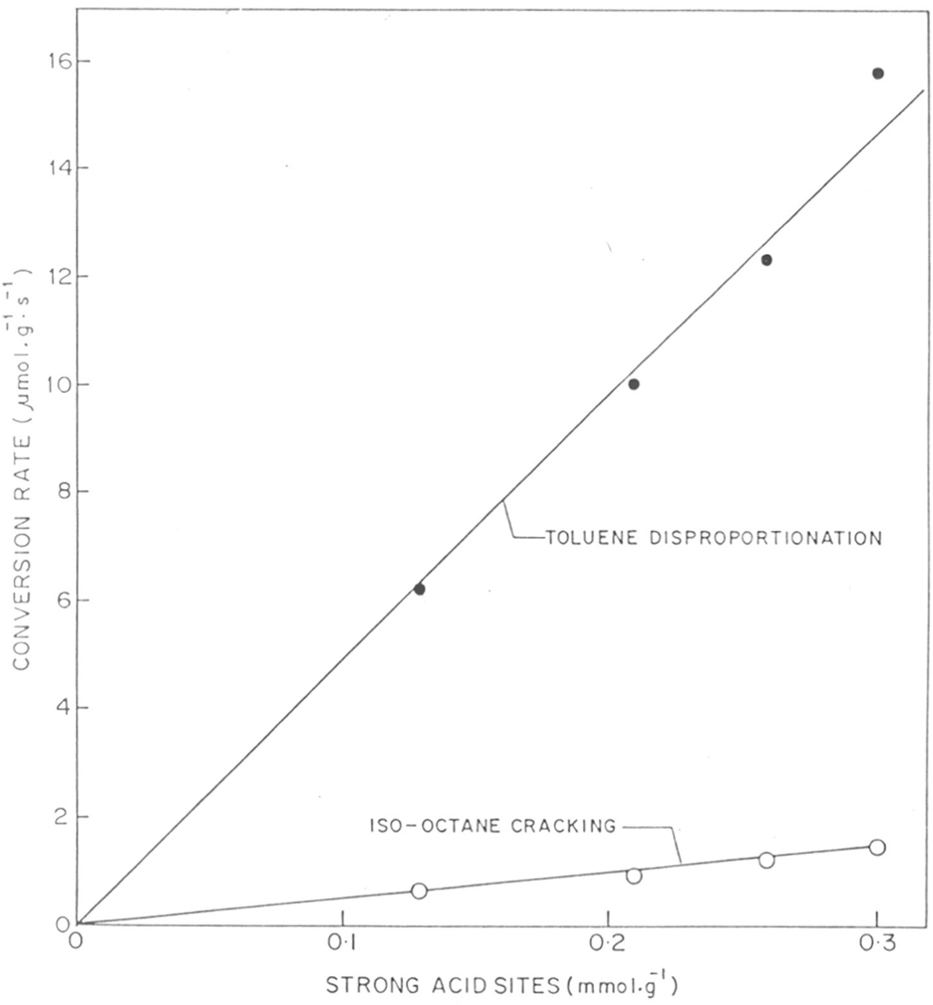


Fig. 3.1.8 : Dependence of conversion rate on strong acidity of H-gallosilicate (MFI) zeolite in the iso-octane cracking and toluene disproportionation reactions.

Table 3.1.2 : Results on poisoning of stronger acid sites by pyridine in the model reactions over H-gallosilicate (MFI) with Si/Ga=32.9.

Reaction	Conversion (%)		No. of strong acid sites poisoned (mmol.g^{-1})
	Without poisoning	With poisoning	
Isooctane 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).

extent. This shows a strong influence of the acidity on the propane conversion (both total and to aromatics) activity of the zeolite.

3.1.3.5 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. 3.1.9 and 3.1.10, 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. 3.1.11 and 3.1.12, respectively. The results reveal a strong influence of Si/Ga ratio on the deactivation kinetics in the propane aromatization over the gallosilicate.

Figure 3.1.13 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 the following rate expression developed for the case of a first order catalyst deactivation in a plug flow fixed bed reactor (15) :

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

The decrease in the deactivation rate constant with increasing the Si/Ga ratio is consistent with the observed decrease in the catalyst deactivation (Figs. 3.1.11 and 3.1.12). The data on coke deposition on the catalysts during the deactivation runs are given in Table 3.1.3.

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. 3.1.10 and 3.1.14, respectively. The

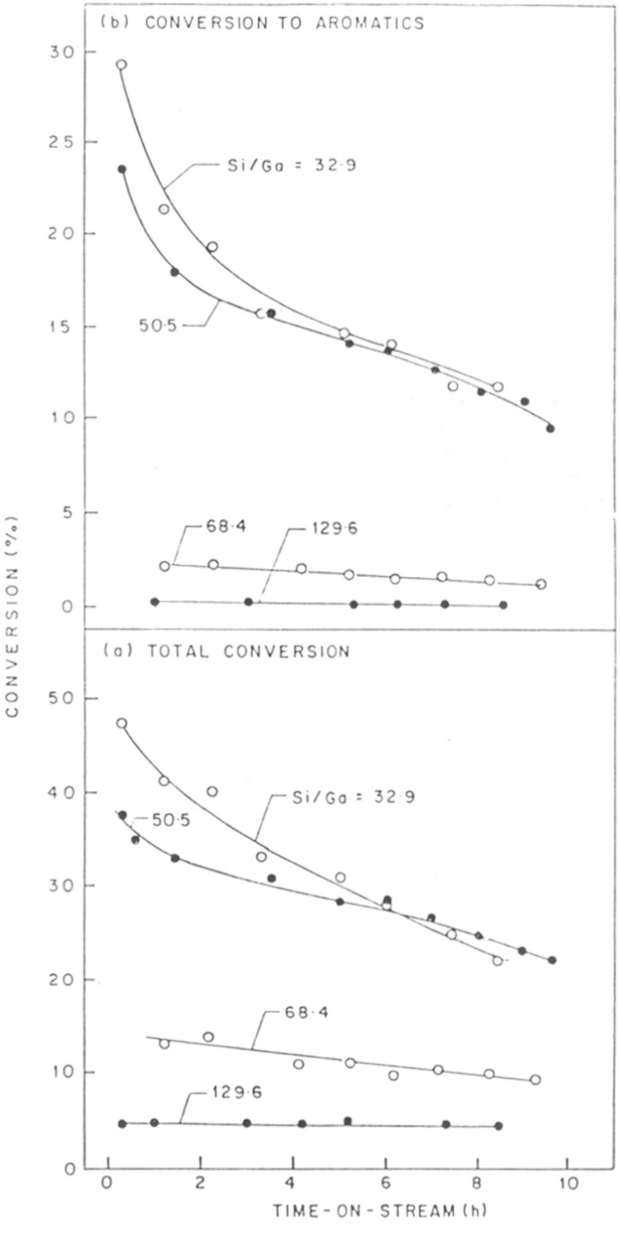


Fig. 3.1.9 : Variation with time-on-stream of the propane conversion, a) total and b) to aromatics, in the propane aromatization (at 550°C) over H-gallosilicate(MFI) with different Si/Ga ratios.

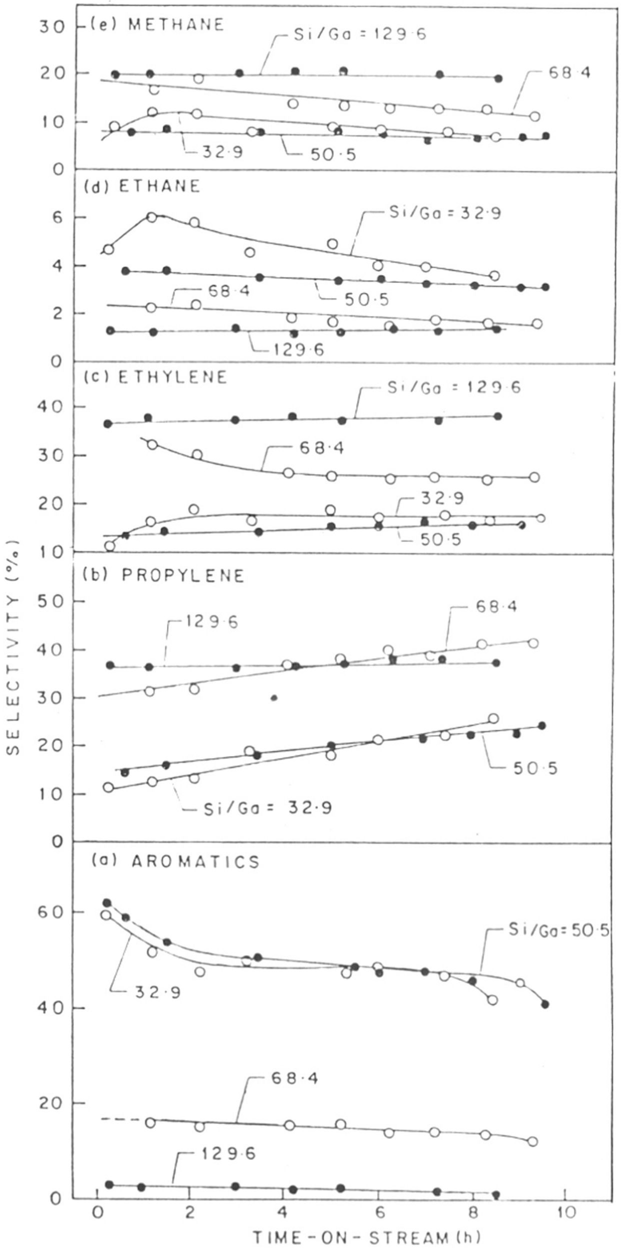


Fig. 3.1.10 : Variation with time-on-stream of the product selectivity of H-gallosilicate (MFI) with different Si/Ga ratios in the propane aromatization (at 550°C).

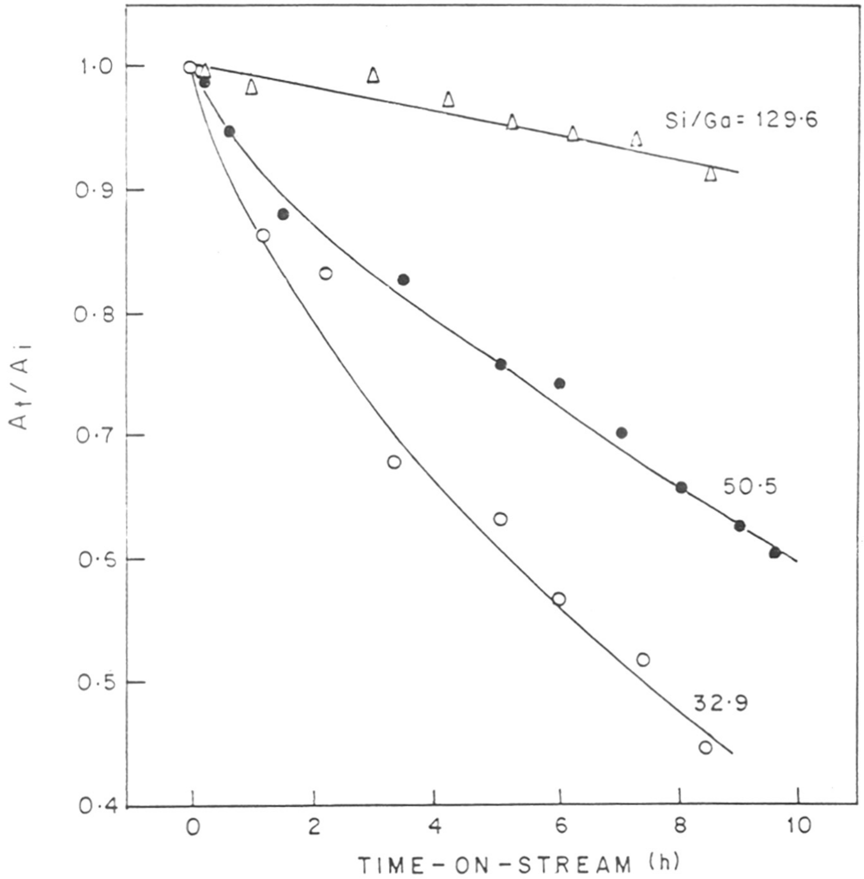


Fig. 3.1.11 : Variation of the propane conversion activity, relative to that at zero time-on-stream of H-gallosilicate (MFI) with time-on-stream in the propane aromatization (at 550°C).

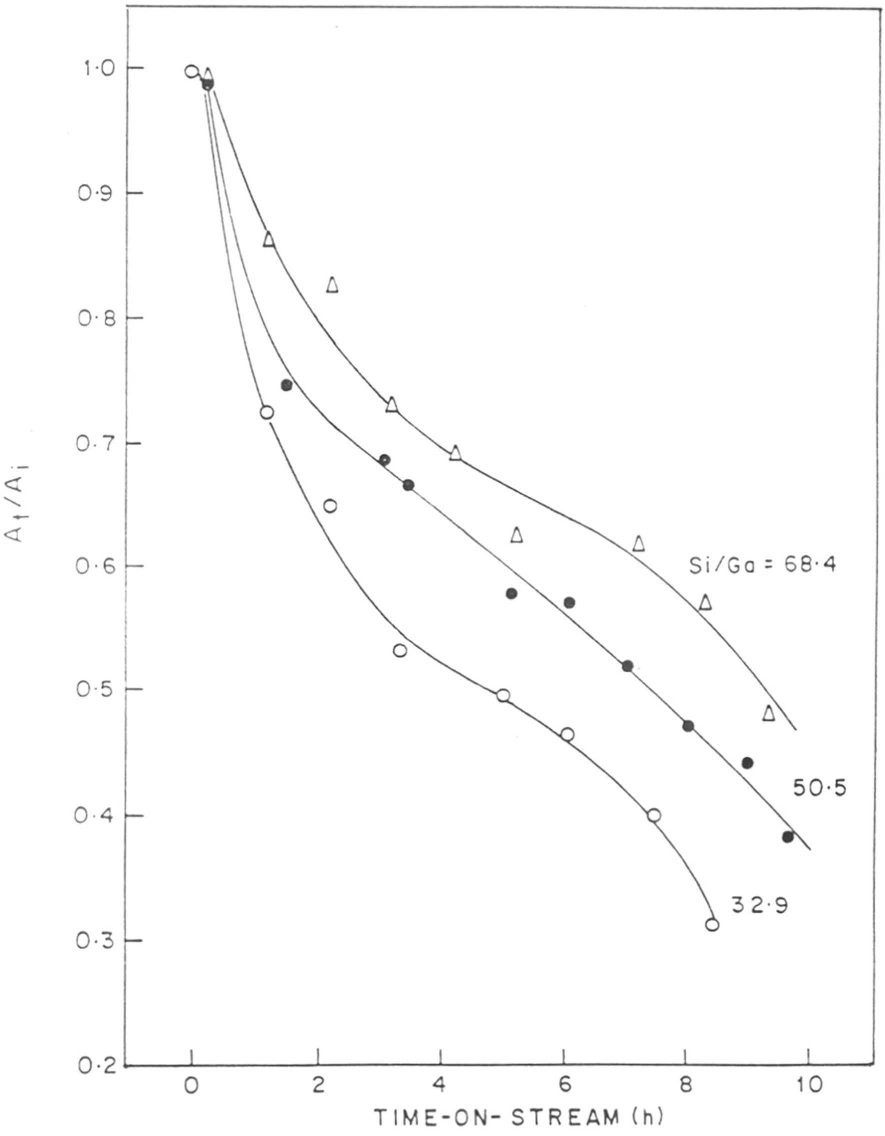


Fig. 3.1.12 : **Variation of the propane-to-aromatics conversion of activity, relative to that at zero time-on-stream, of H-gallosilicate (MFI) with time-on-stream in the propane aromatization (at 550^{o}C).**

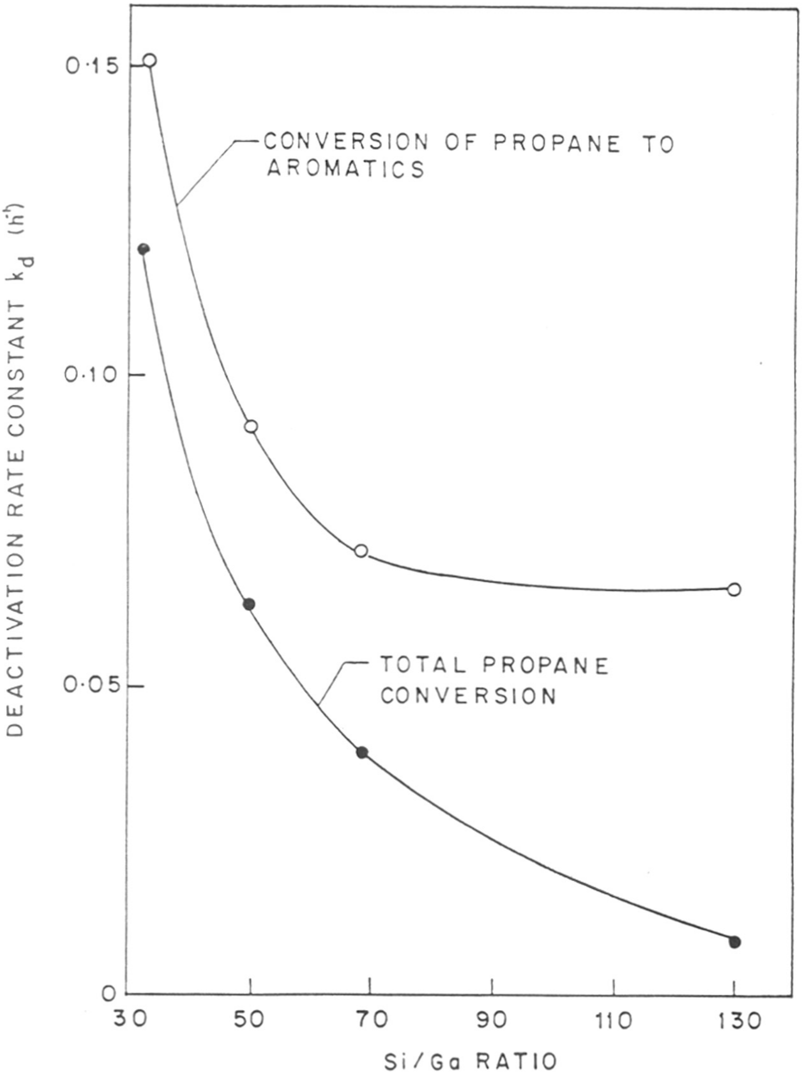


Fig. 3.1.13 : Influence of bulk Si/Ga ratio on the deactivation rate constant for total conversion and conversion to aromatics in the propane aromatization over H-gallosilicate (MFI) zeolite.

Table 3.1.3 : Distribution of aromatics formed and amount of coke deposition in propane aromatization over H-gallosilicates (MFI) (time-on-stream:9±0.5h)

Si/Ga	Distribution of aromatics (wt. %)				Coke deposition (Wt.% Carbon)
	Benzene	Toluene	Xylenes+Ethyl benzene	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

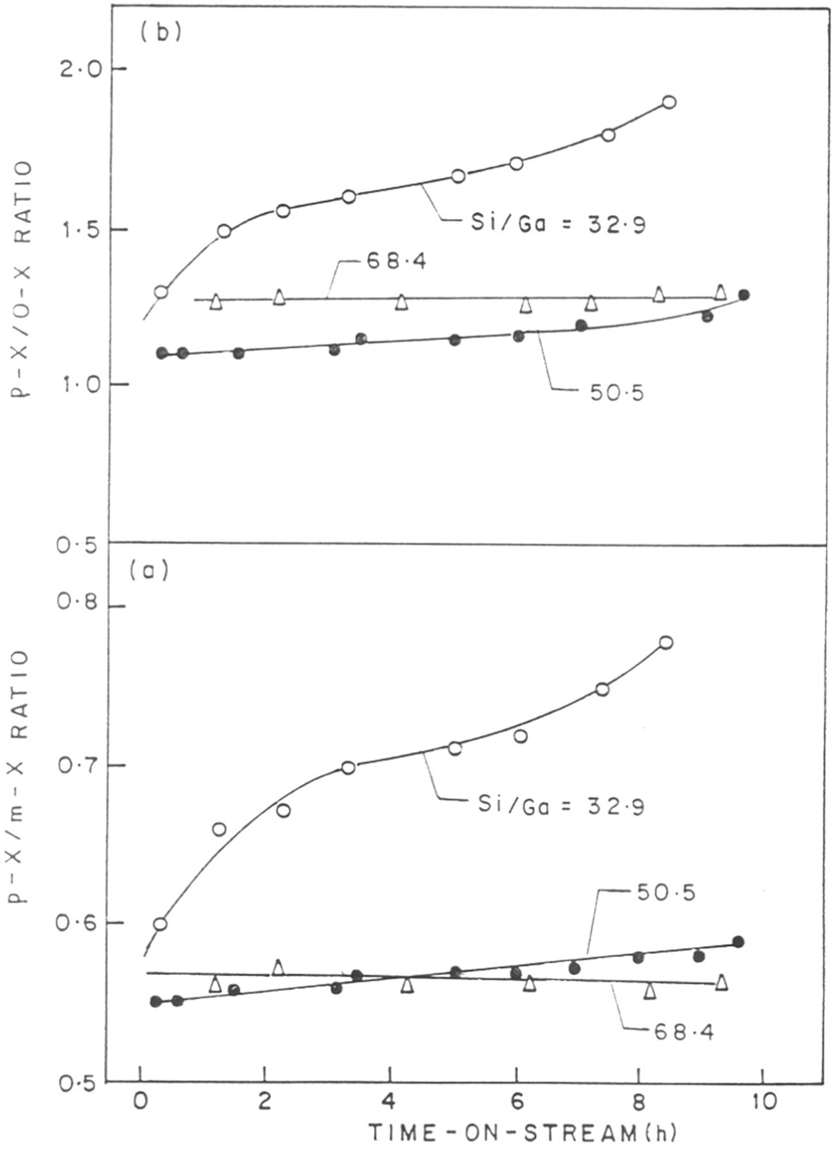


Fig. 3.1.14 : Variation with time-on-stream of the xylene ratios in the propane aromatization (at 550^{0}C) over H-gallosilicate (MFI) zeolites.

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 3.1.3. 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 8.4h 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 14h), 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 0.25h) on the gallosilicate (Si/Ga=32.9), when pretreated with H_2 at 600°C for 10h 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 8.4h 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 8.4h is much more than that could have been resulted due to the H_2 pretreatment to the catalyst for 10h (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 burning the coke on the deactivated catalyst at 500°C in a flow of O_2-N_2 mixture (5% O_2) for 2h and observing the regeneration of its original activity due to the removal of coke.

3.1.3.6 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 $cm^3.g^{-1}.h^{-1}$) for studying the influence of conversion on product selectivity and also for comparing the catalysts for their selectivity/product distribution at same conversion levels.

Effect of GHSV on initial activity in propane aromatization

Effect of GHSV on the propane conversion, aromatics and propylene selectivity and also on dehydrogenation/cracking (D/C) ratio and aromatics/cracking (A/C) activity ratio in propane aromatization at 550°C over H-GaMFI with different Si/Ga ratios is shown in Fig. 3.1.15A. When the GHSV is increased,

- as expected, the propane conversion is decreased markedly,
- the aromatics selectivity is decreased, whereas, propylene selectivity is increased and
- the A/C activity ratio is decreased but the D/C activity ratio is increased.

These results suggest a strong influence of GHSV on the formation of aromatics and propylene and also on the A/C and D/C activity ratios in the propane aromatization. The effect is, ingeneral, large for the zeolite with lower Si/Ga ratios.

Effect of propane conversion on product selectivity

Figure 3.1.15B shows a strong influence of propane conversion on the product selectivity over the H-gallosilicate (Si/Ga = 32.9). The aromatics selectivity,

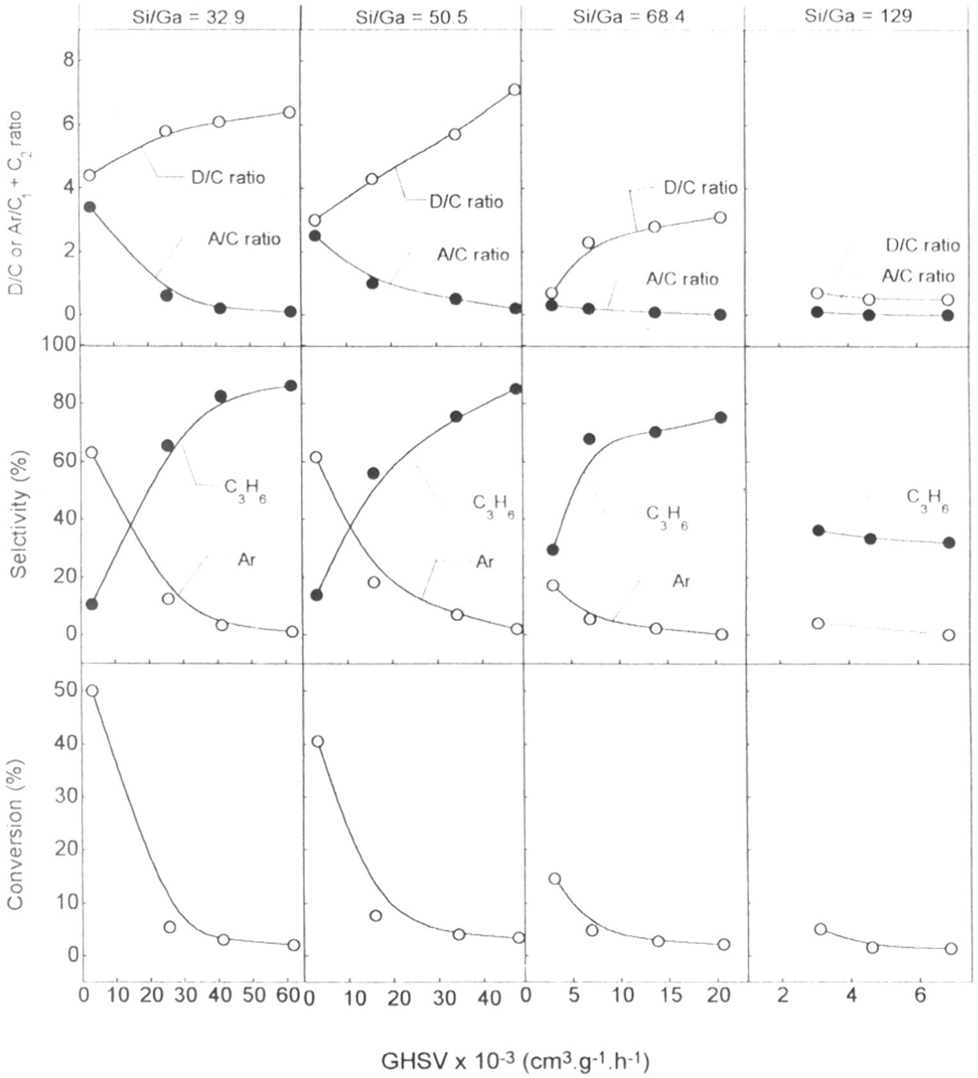


Fig. 15A : Influence of GHSV on the propane conversion, selectivity of aromatics and propylene and dehydrogenation/cracking (D/C) ratio and aromatics/ cracking (A/C) activity ratio in the propane aromatization at 550°C over H-GaMFI zeolites with different Si/Ga ratios

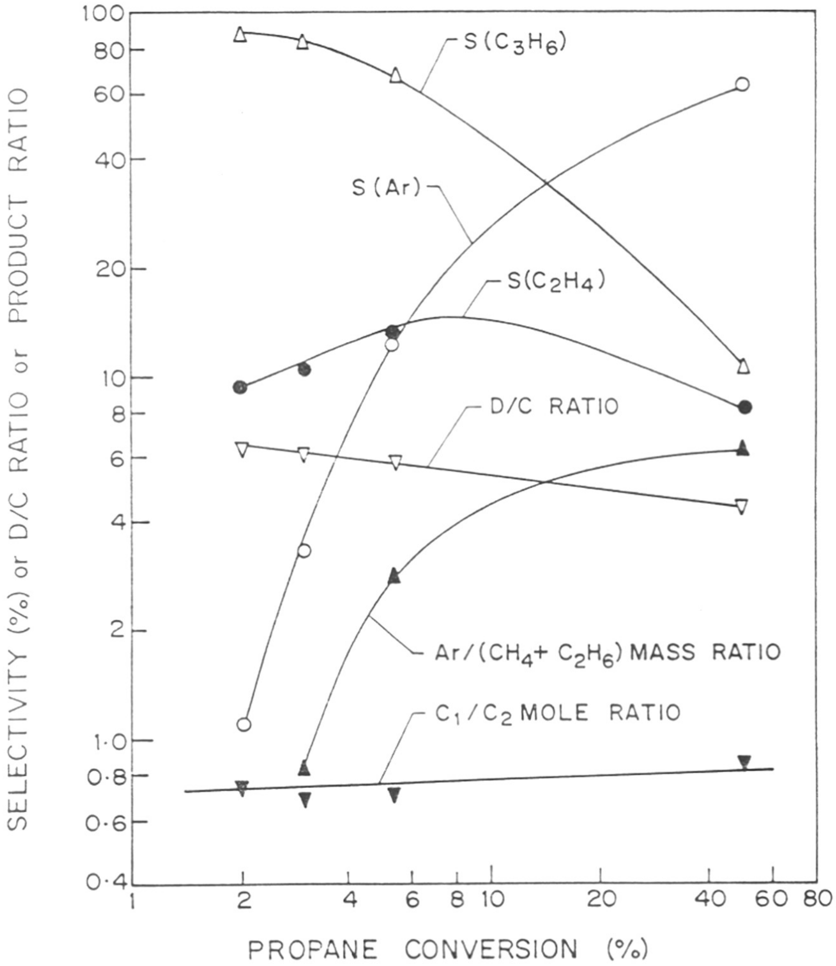


Fig. 3.1.15B : Variation with propane conversion of the selectivity for aromatics and propylene, D/C activity ratio and product ratios in the propane aromatization over the H-gallosilicate (Si/Ga=32.9).

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. 3.1.16 and 3.1.17. 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 3.1.18 and 3.1.19 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.

3.1.4 DISCUSSION

3.1.4.1 Incorporation of Ga in MFI Framework

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

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

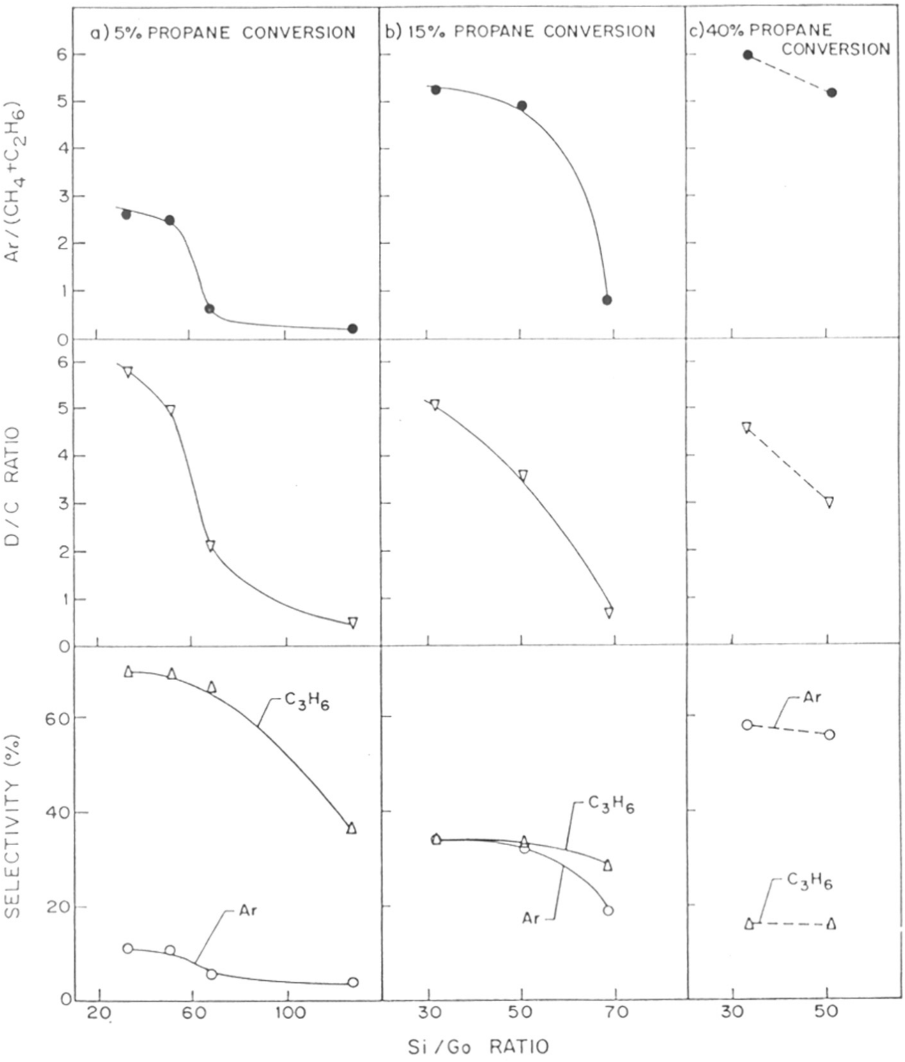


Fig. 3.1.16 : Influence of Si/Ga ratio on the selectivity for aromatics and propylene, dehydrogenation/cracking (D/C) activity ratio and aromatics/(methane + ethane) ratio in the propane aromatization at a) 5% , b) 15% and c) 40% conversion of propane.

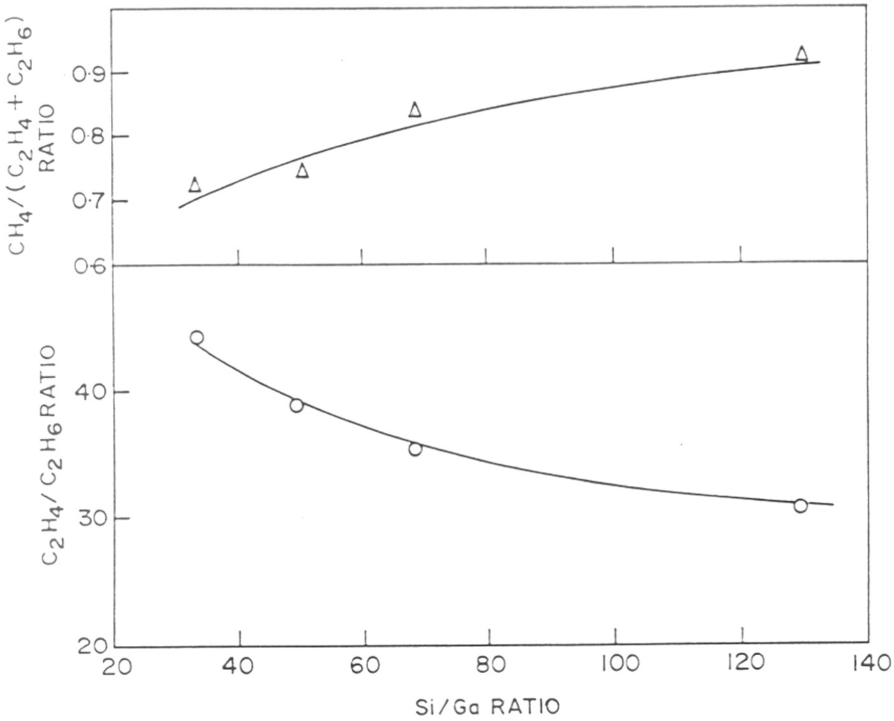


Fig. 3.1.17 : **Dependence on bulk Si/Ga ratio of the product mole ratios of methane, ethane and ethylene formed in the propane aromatization (at 5% propane conversion) over the H-gallosilicate.**

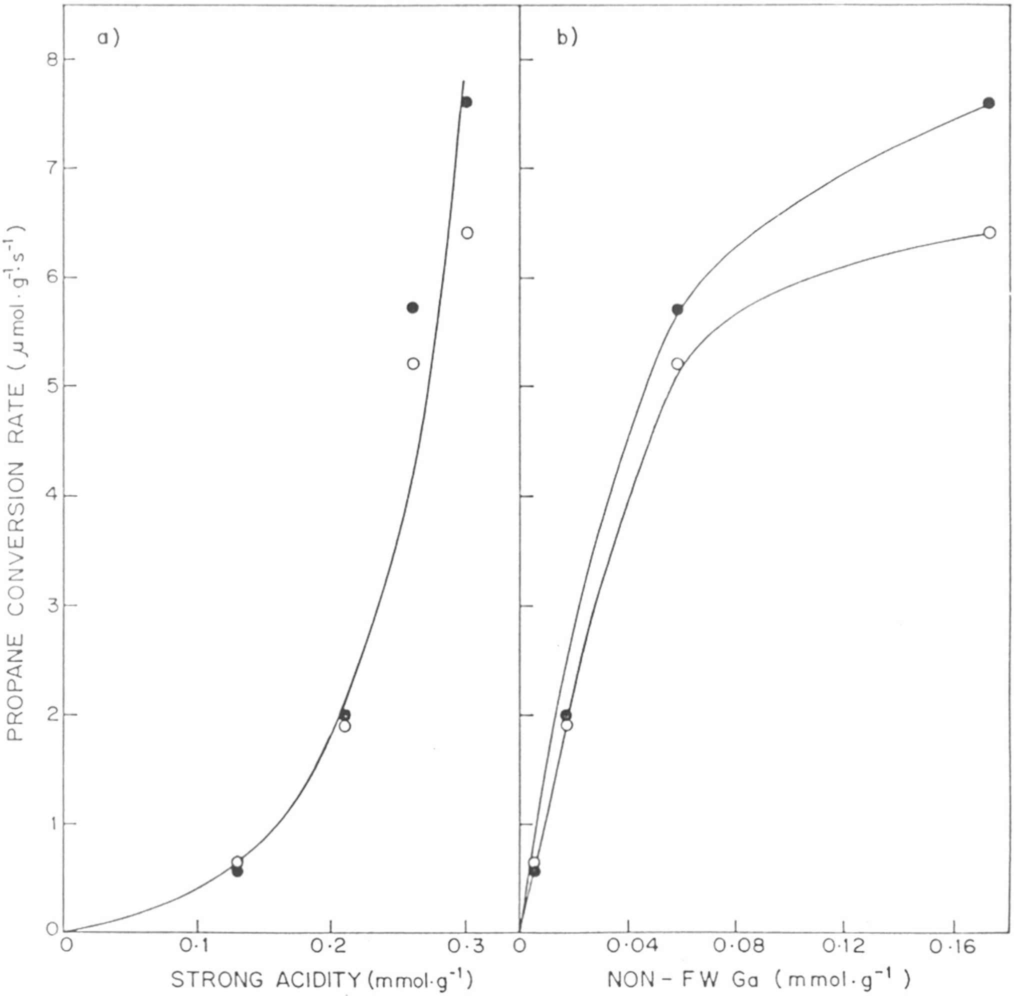


Fig. 3.1.18 : Dependence of propane conversion rate on a) strong acidity and b) non-FW Ga of the gallosilicate (GHSV = 3075 (o) and 7000 (•) $cm^3.g^{-1}h^{-1}$).

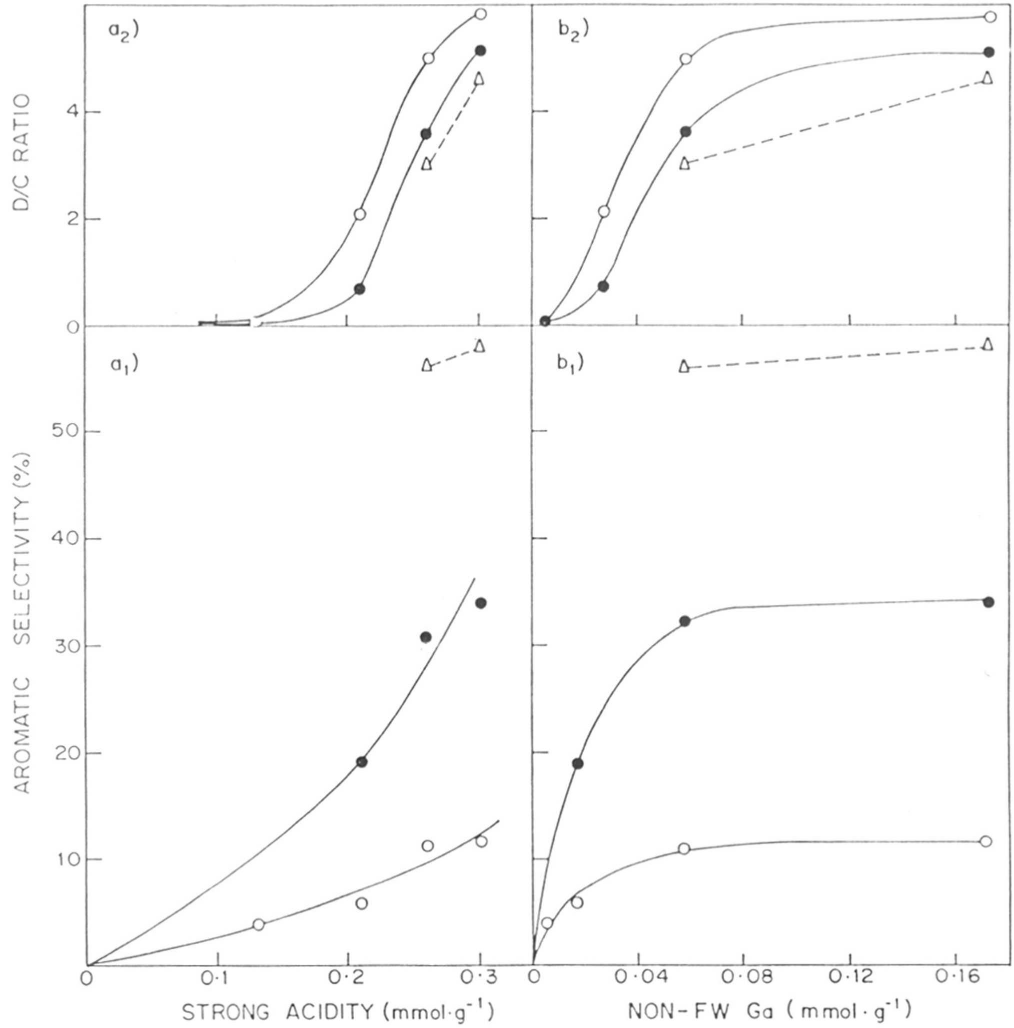


Fig. 3.1.19 : Dependence of the aromatics selectivity and D/C activity ratio on a) strong acidity and b) non-FW Ga in the gallosilicate, at the propane conversion of 5% (o), 15% (•) and 40% (Δ).

- ^{71}Ga MAS NMR peak at +156 ppm (which corresponds to tetrahedral Ga) (Fig. 3.1.2b).
- ^{29}Si MAS NMR peak at -104 ppm for Si (1Ga) decrease in its intensity or area with increasing Si/Ga ratio (Fig. 3.1.2a).
- Framework Si/Ga ratio (obtained from ^{29}Si MAS NMR) close to the bulk Si/Ga ratio in all the gallosilicates (Table 3.1.1).
- The decrease in the acidity, particularly strong acid sites, with increasing the Si/Ga ratio (Fig. 3.1.5).

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.

3.1.4.2 Degalliation of Gallosilicate (MFI)

The results in Table 3.1.1 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.

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 (19). 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. 3.1.6) is very much consistent with that observed for H-ZSM-5 (17).

3.1.4.3 Influence of Si/Ga Ratio on Acidity

The results on the acid strength distribution (Figs. 3.1.3 and 3.1.4) reveal a strong influence of the bulk Si/Ga ratio on the distribution of acid sites of different strengths in the gallosilicate. Both the total acid sites (measured in terms 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. 3.1.5). The decrease in the acidity is consistent with the decrease in the catalytic activity of the gallosilicate in the iso-octane cracking and toluene disproportionation reactions (Figs. 3.'1.7) (which are model reactions catalyzed by acid sites) with increasing the Si/Ga ratio. A very good relationship exists between the catalytic activity for the iso-octane 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. 3.1.8.

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 3.1.1). 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. 3.1.5). 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.

3.1.6) 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 iso-octane cracking reaction. Since iso-octane does not penetrate the ZSM-5 type zeolites even at 400°C (20,21), its reaction is expected to provide an information on the external acid sites of the gallosilicates. Iso-octane cracking occurs essentially on strong acid sites (20,21) and, therefore, the decrease in the isooctane cracking activity of the gallosilicate with increasing its Si/Ga ratio (Fig. 3.1.7) 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 iso-octane cracking by the chemisorption of pyridine at 400°C (Table 3.1.2).

3.1.4.4. Poisoning of Acid Sites

The results in Table 3.1.2 indicate that although the catalytic activity in the acid catalyzed reactions is reduced very appreciably due to the poisoning of the strong (for the iso-octane 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°C 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.

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

The results in Fig. 3.1.15B 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, inorder 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 3.1.16 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. 3.1.17) ; 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. 3.1.9) is also strongly influenced by the Si/Ga ratio; it is decreased very sharply with increasing the Si/Ga ratio. The propane conversion activity (Fig. 3.1.18) and the aromatics selectivity and D/C activity ratio (Fig. 3.1.19) are found to increase sharply with increasing the density of the acid sites and non-framework 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. 3.1.5 and Table 3.1.1). These observations suggest that both the acidity and the non-framework 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 non-framework 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 non-framework Ga of the zeolite, resulting from the change in its Si/Ga ratio. Very likely, the zeolite acidity and non-framework 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. 3.1.15) 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.

$C_3H_8 \rightarrow CH_4 + C_2H_4$ - - - - - - - - - - - - - - -(1)

$C_3H_8 \rightarrow C_3H_6 + H_2$ - - - - - - - - - - - - - - - - -(2)

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

$C_3H_8 + H_2 \rightarrow CH_4 + C_2H_6$ - - - - - - - - - - -(3)

occurring parallel to the above primary reactions. The ethylene and propylene formed in reactions 1 and 2, respectively, are expected to undergo oligomarization, cyclalization 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. 3.1.15). 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. 3.1.17). 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 hydrocraking activity is decreased with increasing the Si/Ga ratio.

If the primary cracking (reaction 1) and dehydrogenation (reaction 2) reactions are catalyzed only by the acid sites of the zeolite, the dehydrogenation/cracking activity ratio is expected to be unaffected by the strength of acid sites (22). 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. 3.1.16). The observed large decrease in the D/C activity ratio is expected mostly because of the decrease in the non-framework 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 non-framework Ga (Fig. 3.1.18 and 3.1.19). However, it may be noted that when the Si/Ga ratio is increased both the acidity and the non-framework 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 cyclalization) and the non-framework Ga (which is essential for dehydrogenation of propane and naphthenes) at high concentrations are necessary for obtaining high conversion and selectivity in the propane aromatization over the gallosilicate zeolite.

3.1.4.6 Influence of Si/Ga Ratio on Deactivation

The observed catalyst deactivation in the propane aromatization (Figs. 3.1.9, 3.1.11 and 3.1.12) 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^oC 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 2h.

The results (Figs. 3.1.9, 3.1.11 and 3.1.12) 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. 3.1.13), 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.

3.1.4.7 Influence of Deactivation on Product Distribution/Selectivity

The results (Figs. 3.1.10 and 3.1.14) 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 3.1.3) 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. 3.1.15). 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. 3.1.14) 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. 3.1.14), the coke is expected to be deposited gradually in the zeolite channels and/or on the external crystal surface.

3.1.5 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 iso-octane cracking (at 400°C).
    - a large increase in the non-framework 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 iso-octane 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 $400^{o}C$) and also of the non-framework 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 non-framework Ga. The high dehydrogenation activity of the zeolite is attributed to the non-framework 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 non-framework Ga and also at the outer crystal surface blocking some of the channel openings.

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CHAPTER 3.2

SIMULTANEOUS AROMATIZATION OF PROPANE AND HIGHER ALKANE OR OLEFIN OVER H-GaAlMFI ZEOLITE

3.2.1 INTRODUCTION

Aromatization of propane or lower alkanes over Ga-modified ZSM-5 type zeolites is a process of great practical importance (1-3). The high aromatization activity of these zeolites is attributed to their bifunctional activity, high dehydrogenation function due to the presence of extraframework Ga-oxide species (in combination with zeolitic protons) and high acid function due to the framework Al and/or Ga. Among the zeolites (Ga/H-ZSM-5, H-GaMFI and H-GaAlMFI), H-GaAlMFI zeolite shows highest activity/ selectivity in the aromatization of alkanes (4,5). This is because of the uniform distribution and/or high dispersion of the extraframework Ga-oxide species in the channels, resulting from the degalliation of framework Ga during the calcination and/or pretreatment of the zeolite. We show here that the conversion of propane in its aromatization over H-GaAlMFI zeolite is enhanced to a large extent when the aromatization of propane is carried out simultaneously with that of olefins or higher alkane. Because of this, propane can be converted into aromatics with high conversion, even at lower temperatures

3.2.2 EXPERIMENTAL

H-GaAlMFI (H-galloaluminosilicate of ZSM-5 type) zeolite, having framework (FW) Si/Ga of 49.9, FW Si/Al of 40.3 (with no non-FW Al), Na/(Ga + Al) of 0.03, non-FW Ga of 0.32 mmol.g^{-1}, spherical-hexagonal crystals of 5.5 ± 1.5 μm size and strong acid sites of 0.46 mmol.g^{-1} (measured in terms of the pyridine chemisorpted at 400^{o}C), was prepared and characterized as follows :

The TPA-GaAlMFI zeolite was synthesised by its hydrothermal crystallization from a gel (pH = 10.5) consisting of Na-trisilicate (Fluka), gallium nitrate (Aldrich), aluminium nitrate (BDH), TPA-Br (Aldrich), Sulfuric acid and deionized water in a stainless steel autoclave at 180^oC for 96 h. The TPA-GaAlMFI zeolite crystals were washed, dried at 120^oC for 4 h and calcined at 550^oC for 15 h in static air to remove the occluded organic template. The calcined galloaluminosilicate zeolite crystals were ion exchanged with 1M NH_4NO_3 solution at 80^oC for 1 h; the ion exchange was repeated 4 times. After exchange, the zeolite crystals were washed with deionized water and dried at 120^oC for 10 h. The resulting NH_4-galloaluminosilicate zeolite crystals were pressed binder-free and crushed to 52-72 mesh size particles and then calcined under static air at 600^oC for 1 h to convert the zeolite to H-form.

The MFI structure of the zeolite was confirmed by XRD (using Philips X-ray diffractometer 1730 series and CuKα radiation). The bulk composition of galloaluminosilicate zeolite was determined by the chemical analysis (after removal of the organic template). The crystal size and morphology of the zeolite was obtained by SEM (using JOEL scanning electron microscope). The incorporation of Ga in the framework of GaAlMFI zeolite was confirmed by the ^{71}Ga MASS NMR peak at +156 ppm. The framework (FW) Si/(Al + Ga) ratio of the zeolite was obtained from ^{29}Si MAS NMR peak, Si(0Ga and Al) at about -112 pmm and Si(1Ga and Al) at about -104 ppm) by the method described earlier (6). The ^{27}Al MAS NMR showed peak at +54 ppm which corresponds to tetrahedral Al but no peak at 0 ppm indicating absence of octahedral (non-framework) Al in the zeolite. Stronge acid sites on the zeolite were measured in terms of the pyridine chemisorption at 400^oC, using GC adsorption/desorption method (7).

The propane aromatization reaction was carried out in a continues flow tubular quartz reactor (i.d. 13 mm) by passing a mixture of propane (>99.95%), with or without olefin or higher alkane, over the zeolite catalyst (0.5 g) in the absence of catalyst deactivation due to coking, using a square pulse technique (described earlier in Chapter 3.1). The feed and product streams were analyzed by an on-line GC. The carbon balance across the reactor was within 2-5% error. Detailed experimental procedures are described earlier (Chapter 3.1).

The conversion and selectivity data were obtained from the feed and product composition, as follows :

Conversion (%) = [(wt % of reactant in the feed hydrocarbons - wt % of reactant in the product hydrocarbons)/(wt % of reatant in the feed hydrocarbons)] x 100.

Aromatics selectivity (%) = [(wt % of aromatics in the hydrocarbon products)/(100 - Wt % of reactant(s) in the hydrocarbon products)] x 100.

3.2.3 RESULTS AND DISCUSSION

Results showing enhancement in the conversion of propane in its aromatization over the zeolite due to presence of various olefins or higher alkane are presented in Table 3.2.1. The enhancement is quite large; it is about two fold. The aromatics selectivity in the simultaneous aromatization of propane and higher alkane (or olefin) is higher than that in the aromatization of propane alone. The product distribution in the individual experiments (Table 3.2.1) is presented in Table 3.2.2.

The observed enhancement in the propane conversion (Table 3.2.1) can be explained by a hydrogen transfer reaction between propane and higher olefine,

$$C_3H_8 + C_nH_{2n} \rightarrow C_3H_6 + C_nH_{2n+2} \quad \text{(Where } n > 3\text{)} \qquad (1)$$

forming propylene and higher alkane. Since the higher alkane has higher reactivity, it undergoes faster dehydrogenation than propane,

$$C_nH_{2n+2} \xrightarrow{\text{H+ and Ga-oxide}} C_nH_{2n} + H_2 \qquad (2)$$

The propylene and higher olefins then undergo olegomerization and dehydrocyclization or aromatization reactions.

$$C_nH_{2n} \xrightarrow{H^+} C_6 - C_{10} \text{ olefins} \xrightarrow{H^+ + \text{Ga-oxide}} \text{aromatics} \qquad (3)$$

The enhancement due to higher alkane also involves the above reactions but their sequence is as follows : reaction 2, reaction 1, reaction 2 and then reaction 3. However,

Table 3.2.1 : **Results of the simultaneous aromatization of propane and olefins or higher alkanes over H-GaAlMFI zeolite at 450°C**

Expt. No.	Reactant other than propane (A)	A/C_3H_8 mole ratio	Space velocity ($cm^3.g^{-1}.h^{-1}$)	Conversion (%)		Aromatics selectivity (%)
				Propane	A	
1	-	0.0	6,200	14.3	-	65.5
2	Ethylene	1.0	6,200	27.5	97.8	91.4
3	n-Butylene	0.6	6,200	25.0	90.4	87.6
4	Iso-butylene	0.5	6,200	31.1	100	89.5
5	n-Hexane	0.5	6,200	23.1	94.5	76.7
6	-	0.0	12,400	7.0	-	54.3
7	n-Hexane	0.5	12,400	12.1	65.7	60.5

Table 3.2.2 : Product Distribution in the individual experiments (Table 3.2.1)

Product distribution (wt %)	Experiment number						
	1	2	3	4	5	6	7
CH_4	1.1	1.1	0.5	0.8	1.8	0.5	1.0
C_2H_4	0.8	0.9	1.2	0.7	1.5	0.7	2.0
C_2H_6	0.7	1.3	0.8	0.6	1.6	0.3	1.1
C_3H_6	1.1	0.0	1.8	0.8	2.0	1.1	3.1
C_3H_8	85.7	43.4	42.4	43.0	39.6	93.0	44.1
C_4H_8	0.0	0.0	4.2	0.0	0.0	0.0	0.0
C_4H_{10}	1.2	2.4	2.5	3.1	6.5	0.6	8.1
C_{5+} aliphatics	0.0	0.0	0.0	0.0	2.7	0.0	17.1
Benzene	3.2	6.9	3.8	4.7	4.4	1.4	2.8
Toluene	3.4	22.6	17.7	23.2	15.6	1.4	8.8
Ethylbenzene + Xylenes	2.3	17.8	21.0	20.0	20.3	0.9	9.8
C_{9+} aromatics	0.5	3.6	4.1	3.1	4.0	0.1	2.1

the enhancement due to ethylene is expected by the hydrogen transfer reaction between propane and the butylene formed by dimerization of ethylene.

In case of the higher alkane addition, the enhancement also results from the hydrogen transfer reaction of propane with the olefin formed from the alkanes by their dehydrogenation (reaction-2) over the zeolite, which is a bifunctional catalyst having both the dehydrogenation and acid functions.

Following reaction path and elementary reaction steps for the propane aromatization over the zeolite, which contains both Lewis (extraframework Ga-species) and Bronsted (zeolitic protons) acid sites, are proposed for explaining the beneficial effect of the additive. In the absence of additive, the dehydrogenation of propane is expected to occur by its interaction with the Lewis acid site (G) located close to the zeolitic proton, similar to that proposed for the propane dehydrogenation (8-11), as follows : C-H bond cleavage (which is facilitated in the presence of proton) and abstraction of H^- by the Lewis site,

$$C_3H_8 + G \Leftrightarrow C_3H_7^+ + GH^- \qquad (4)$$

regeneration of the Lewis site by its interaction with the nearby proton and H_2 desorption,

$$GH^- + H^+ \Leftrightarrow G + H_2 \qquad (5)$$

and finally desorption of propylene by the release of proton from the carbanium ion,

$$C_3H_7^+ \Leftrightarrow C_3H_6 + H^+ \qquad (6)$$

The enhancement in propane conversion by the presence of higher (C_{3+}) olefin, however, results from the change in the propane activation mechanism, as follows. First, the olefin is activated by its interaction with zeolitic proton, forming carbonium ion by the equilibrium reaction,

$$C_nH_{2n} + H^+ \Leftrightarrow (C_nH_{2n+1})^+ \qquad (7)$$

The carbonium ion undergoes hydrogen transfer reaction with propane, as follows.

$$C_3H_8 + (C_nH_{2n+1})^+ \Leftrightarrow C_3H_7^+ + C_nH_{2n+2} \qquad (8)$$

The pentasil (ZSM-5 type) zeolites show high activity for the hydrogen transfer reaction between alkane and olefin, even at 400°C (12,13). The propyl carbonium ion undergoes reaction-6, forming propylene with the release of proton. The activation of propane by reaction-8 is much faster than reaction-4. Because of its high reactivity, the higher alkane formed in reaction-8 is converted back to the olefin, involving the reactions similar to that involved in the propane-to-propylene conversion in the absence of olefin additive (reactions 4-6).

The propylene and higher olefin are converted to aromatics on the Bronsted acid sites, involving their oligomerization reactions,

C_3H_6 or (C_nH_{2n}) $+ C_3H_7^+$ [or $(C_nH_{2n+1})^+$] $\Leftrightarrow (C_NH_{2N+1})^+$ (9)

(where N = 6-10)

followed by a successive dehydrogenation of the C_6-C_{10} carbonium ions (14) by the overall reaction,

$(C_NH_{2N+1})^+ \Leftrightarrow C_NH_{2N-6}$ (aromatics) $+ H^+ + 6H_{[ad]}$ (10)

forming aromatics, releasing proton and leaving adsorbed H-atoms. The desorption of H-adatoms from the zeolite surface as molecular hydrogen, which controls the formation of aromatics and hence the aromatics selectivity (15), is facilitated by their spillover to the gallium sites followed by recombinative desorption (14,15).

$H_{[ad]} + G \Leftrightarrow H\text{-}G$ (11)

$2H\text{-}G \Leftrightarrow H_2 + 2G$ (12)

The observed very high aromatics selectivity is, therefore, attributed to the presence of well dispersed non-framework Ga-species in the zeolite channels in a close vicinity of the zeolitic protons.

Thus, the enhancement involves internal recycle of the higher olefins or higher alkanes (which have higher reactivity than propane) in the catalytic process, resulting in faster conversion of propane to propylene (by the hydrogen transfer reactions) than the dehydrogenation of propane [which is a limiting step in the propane aromatization (1)]. Further detailed studies are necessary for understanding the hydrogen transfer reactions over the bifunctional zeolite catalyst.

3.2.4 CONCLUSIONS

By carrying out propane aromatization simultaneously with olefin or higher alkane aromatization over H-GaAlMFI, the propane conversion can be enhanced to large extent and/or propane can be converted into aromatics with high conversion even at lower temperatures. This has high practical implications.

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