Introduction of gallium in HZSM5 and HY zeolites by post-synthesis treatment with trimethylgallium

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Framework gallium was introduced in dealuminated HZSM5 and HY zeolites by treatment with trimethylgallium (TMG). The experiments were successful for both zeolites, particularly when performed in a hydrogen atmosphere. Side reactions of TMG with isolated silanol groups or Brønsted acid sites resulted in the formation of extra-framework gallium. The Ga/HZSM5 zeolite showed an enhanced selectivity to aromatics in the propane conversion.

Keywords: ^{71}Ga MAS NMR; HZSM5; HY; dealumination; trimethylgallium; TMG; isomorphous substitution

1. Introduction

Zeolites are crystalline aluminosilicates, which can be prepared by hydrothermal treatment of solutions containing SiO_4 and AlO_4 tetrahedra. Addition of other trivalent ions, like Ga^{3+}, Fe^{3+} or B^{3+}, results in isomorphous substitution of aluminum, altering the acidic properties of the zeolite [1,2]. Isomorphous

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substitution has also been achieved by post-synthesis treatments of zeolites. A well known example in this field is the dealumination of aluminosilicates with $SiCl_4$ or $(NH_4)_2SiF_6$, replacing Si for Al in the zeolite framework [3–5]. Another example is the preparation of titanium silicalite (TS-1) via an indirect method using $TiCl_4$ vapour, as described by Kraushaar and Van Hooff [6].

The conversion of propane over HZSM5 zeolites containing gallium gives high yields of aromatics, which appeared to be independent of the preparation method [7,8]. Catalysts prepared by isomorphous substitution of aluminum by gallium in the HZSM5 zeolite, by impregnation of the HZSM5 zeolite with a gallium salt solution and subsequent calcination, or prepared by physically mixing Ga_2O_3 powder with the HZSM5 zeolite, yielded comparable aromatics selectivities. However, large differences were measured in the deactivation behaviour of differently prepared catalysts. Important factors regarding this aspect are the location of the gallium species (inside or outside the zeolite crystallites) and its dispersion. The introduction of highly dispersed gallium in the zeolite pores yields catalysts with a relatively high resistance against deactivation, as rapid coke formation in the zeolite is prevented by shape selective restrictions.

An interesting question is, whether such highly dispersed gallium species can be achieved in the zeolite pores by the gas phase decomposition of trimethylgallium (TMG), and whether such TMG treatment will lead to framework gallium in dealuminated zeolites.

The present work describes the results of TMG decomposition reactions over dealuminated HZSM5 and HY zeolites in a hydrogen or a nitrogen atmosphere. Attention is given to the location of the gallium species after different dealumination and TMG treatments. Also, the catalytic properties of the so prepared Ga/HZSM5 systems for propane aromatization have been investigated.

2. Chemical and physical properties of trimethylgallium (TMG)

The decomposition of TMG has been studied to a large extent, because of its interesting properties for the preparation of semiconductor materials, like GaAs, etc. [9,10]. TMG is an organometallic substance with a relatively high vapour pressure and a boiling point of 56°C [11]. It is a trigonal monomeric molecule [12] with an effective radius of about 3.89 Å and a C–Ga–C angle of 118.6°. Various studies have been done regarding the decomposition mechanism of TMG. A combination of infrared and mass spectrometric experiments showed that in a nitrogen atmosphere, the decomposition starts at about 500°C, yielding mainly gallium metal and small alkanes [13]. The product distribution indicated that the reaction occurs via a pyrolysis mechanism, in which initially formed methyl radicals react in pairs forming ethane, or react with other paraffins or TMG molecules, forming larger products.

In a hydrogen atmosphere, decomposition of gallium occurs at lower temperatures (approximately 400°C) [13,14], with methane as the main decomposition product and negligible amounts of ethane, indicating a hydrogenolysis mechanism [15]. Further details of the decomposition mechanisms of TMG can be found in refs. [15–17].

On surfaces of solids containing silanol groups, gallosilane structures may be formed [18,19],

$$\text{Si–OH} + \text{Ga(CH}_3\text{)}_3 \longrightarrow \text{Si–O–Ga(CH}_3\text{)}_2 + \text{CH}_4. \qquad (1)$$

An equivalent reaction may occur between TMG and Brønsted acid sites,

$$\text{Si–(OH)–Al} + \text{Ga(CH}_3\text{)}_3 \longrightarrow \text{Si–(O–Ga(CH}_3\text{)}_2\text{)–Al} + \text{CH}_4. \qquad (2)$$

Similar reactions have been observed for the formation of trimethylsiloxysilane from silanol groups and trimethylchlorosilane, as descibed by Kraushaar [20].

3. Experimental

Preparation of the HZSM5 zeolites (Si/Al = 20) was carried out according to the patent of Chen et al. [21], using $Al_2(SO_4)_3 \cdot 18H_2O$ as the aluminum source. After hydrothermal synthesis (72 h, 170°C), the raw products were calcined (3 h, 550°C), ion-exchanged with 2 M NH_4NO_3 (3 times, 1 h, 90°C) and finally calcined for a second time (3 h, 550°C). Zeolite Y (Si/Al = 2.15) was obtained from Akzo Chemie (Ketjen Catalysts), Amsterdam.

For dealumination of the zeolites prior to the TMG treatment, two methods have been applied: *Procedure 1* was a one step method, consisting of three-fold washing of the HZSM5 zeolite with a 1 M HCl solution, or three-fold washing the HY zeolite with a 0.3 M HCl solution. *Procedure 2* was a two-step method, in which the zeolites were treated with $SiCl_4$ vapour for 2 h at 450°C, prior to the acid treatments described above. It is known that in this way, so called silanol-nests can be introduced in the framework [20,22,23].

TMG treatments of the dealuminated zeolites were carried out by saturating a helium stream (20 ml/min) with TMG at 0°C, and passing this stream over the zeolite bed (0.5 g) in a microreactor. The gallium loadings of the samples were controlled by varying the time of the TMG treatment.

Characterization of the samples was carried out by atomic absorption spectroscopy (AAS), X-ray diffraction (XRD), ^{71}Ga (magic angle spinning) nuclear magnetic resonance spectroscopy (^{71}Ga MAS NMR), Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). Some TMG treated HZSM5 samples were also tested regarding the aromatization of propane. The ^{71}Ga MAS NMR measurements were carried out on a Bruker AM 600 NMR spectrometer (^{71}Ga NMR frequency 183.0 MHz), using a home-built probe head, equipped with a Doty double bearing MAS assembly. Spinning rates of approximately 8 kHz were employed and chemical shifts were measured relative to the $Ga(H_2O)_6^{3+}$ ion in a galliumnitrate solution.

Earlier experiments had shown that the NMR detectability of the framework gallium can be improved by equilibration of the samples with H_2O, prior to the ^{71}Ga MAS NMR measurements [24]. However, quantitative measurements have shown that part of the framework gallium may remain undetectable for NMR, even after water equilibration [25]. In some of the water equilibrated samples, also a signal for octahedrally coordinated (non-framework) gallium was detected. The detectability of this signal was in some cases improved by equilibration of the dried samples with acetyl-acetone (acac), but the effect of the latter treatment was not reproducible. Based on these observations, in this study, only samples, equilibrated with water have been measured with NMR, and the NMR signals obtained for the different gallium species (framework and non-framework) will be discussed only qualitatively.

Information about the gallium distribution in the TMG treated zeolites was obtained by comparing the gallium contents of the bulk material with these of the surface, as determined by AAS and XPS measurements, respectively. For the infrared measurements, the KBr method was used: dried, powdered samples (0.5 wt%) were physically mixed with dry KBr powder, and under vacuum pressed to thin tablets using a pressure of 0.2 kPa. Subsequently, transmission infrared measurements were performed on a Hitachi 270-50 spectrometer. FTIR measurements were done on a Bruker IFS113V FTIR spectrometer in the transmission mode, using self-supporting wafers of about 10 mg zeolite.

Activity measurements for propane conversion were carried out in a microreactor, containing 0.5 g catalyst. As catalyst, a gallium loaded HZSM5 zeolite (approximately 3.5 wt% Ga) was used. Measurements were carried out at a temperature of 600°C, with a propane WHSV of 2 h^{-1} at atmospheric pressure. In addition, a duration test was performed to investigate the deactivation behaviour of this catalyst.

Propane aromatization experiments were not performed over gallium loaded HY zeolites, as earlier work showed that over gallium containing catalysts based on HY zeolites, low propane conversions are measured, due to the lower acid strength of the zeolite and probably a high rate of deactivation (less shape selective restrictions for coke formation).

4. Results and discussion

4.1. XRD

The parent HZSM5 and Na(H)Y zeolites were highly crystalline materials with Si/Al ratios of 20 and 2.15, respectively. The Si/Al ratios of the materials after dealumination were higher than 200 and about 6.2, respectively. The latter value was calculated from the IR spectrum of the dealuminated zeolite [26]. No significant changes in the crystallinity of the zeolites were observed by XRD after subsequent dealumination and TMG treatments.

4.2. INFRARED MEASUREMENTS

The IR spectra of the HZSM5 zeolite before and after dealumination by procedure 1 are shown in figs. 1a and 1b, respectively. Comparison of both spectra shows no significant differences. When a $SiCl_4$ treatment is applied prior to the HCl washing (procedure 2), a broadening of the peak around 1100 cm^{-1} appears in the spectrum of HZSM5 (see arrow, fig. 1c). This peak is assigned to Si–O–Si asymmetric stretch vibrations in the framework [26], and the broadening of this peak indicates that dealumination of the HZSM5 zeolite according to procedure 2 induces structural changes, that cannot be observed in the XRD spectra (see above).

Treatment of the zeolite dealuminated by procedure 2 with TMG gives a gradual narrowing of the 1100 cm^{-1} band in the spectrum (fig. 1d), indicating

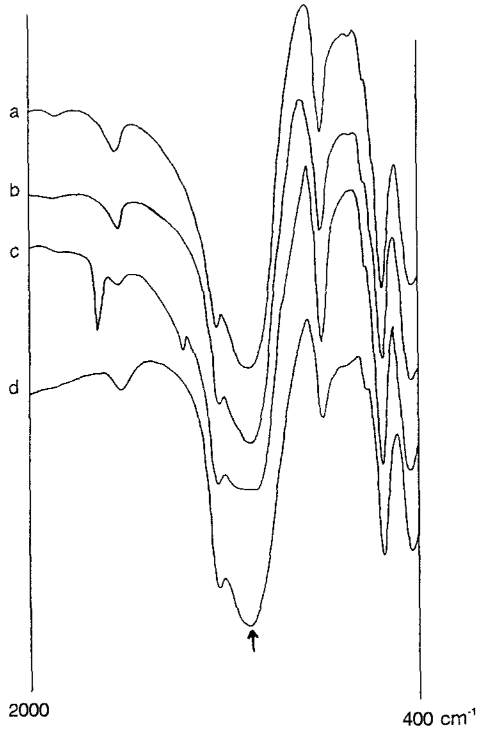


Fig. 1. Infrared spectra of HZSM5 zeolites; (a) untreated, (b) dealuminated according to procedure 1, (c) dealuminated according to procedure 2, (d) dealuminated according to procedure 2 and TMG treated in hydrogen.

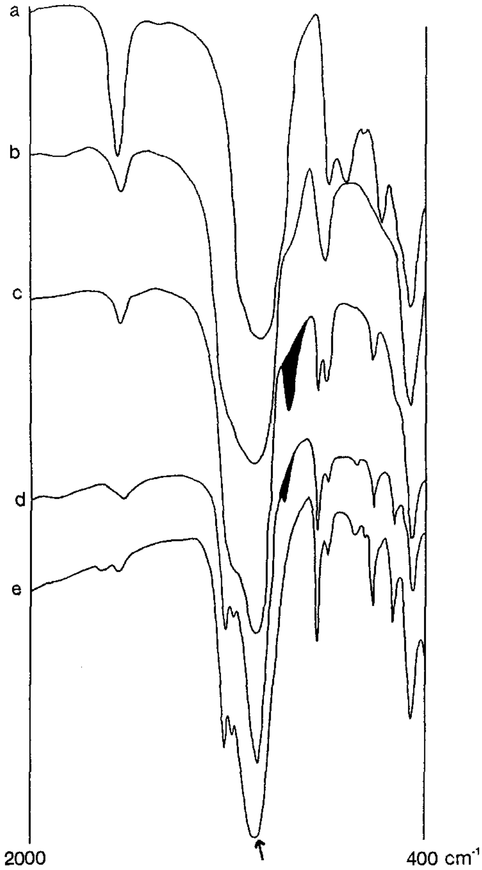


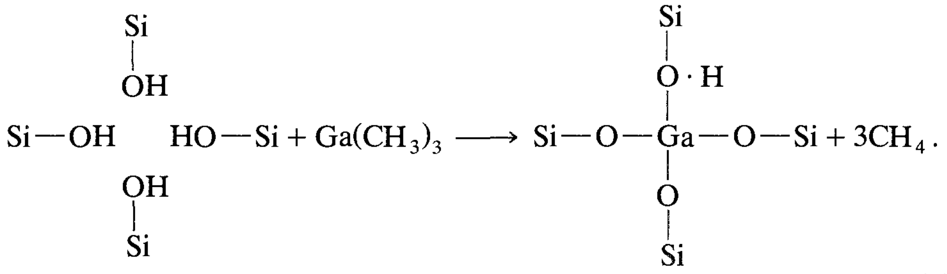
Fig. 2. Infrared spectra of HY zeolites; (a) untreated, (b) dealuminated according to procedure 1, (c) dealuminated according to procedure 2, (d) dealuminated according to procedure 2 and 10 min TMG treatment, (e) dealuminated according to procedure 2 and 20 min TMG treatment.

that the changes introduced by the dealumination procedure are eliminated, probably by reaction with TMG.

The IR spectrum of the parent Na(H)Y zeolite is shown in fig. 2a. Dealumination of this zeolite according to procedure 1 gives a broadening of the peak around 1100 cm^{-1} (see arrow, fig. 2b), while upon dealumination by procedure 2, a separate peak is observed in the IR spectrum at 930 cm^{-1} (see black coloured peak, fig. 2c). Also for this zeolite, no changes in crystallinity were observed in the XRD spectra after the subsequent treatments. A peak at about 930 cm^{-1} was observed earlier in $SiCl_4$/HCl dealuminated HY samples and has been attributed to asymmetric bending vibrations of the bridged Si–OH groups, originating from silanol nests [3,4,20,22,23].

Upon TMG treatment of this zeolite, the 930 cm^{-1} peak reduces in intensity with exposure time (fig. 2d) untill complete disappearance (fig. 2e). This result indicates that silanol nests are consumed by reaction with TMG.

The fact that in the IR spectrum of HZSM5 the peak at about 930 cm^{-1} is not so well resolved, can be due to the fact that, in this zeolite, the initial framework aluminum concentration, and thus the amount of silanol nests introduced by dealumination, is much lower as compared to the HY zeolites. Moreover, these results indicate that dealumination by subsequent $SiCl_4$ and HCl treatments has to be preferred rather than HCl washing only, for obtaining silanol nests in the zeolite structure. The presence of silanol nests is essential for the incorporation of gallium in the framework, according to the following equation:



$$\mathrm{Si{-}OH}\quad \begin{array}{c}\mathrm{Si}\\|\\\mathrm{OH}\\ \\ \mathrm{OH}\\|\\\mathrm{Si}\end{array}\quad \mathrm{HO{-}Si} + \mathrm{Ga(CH_3)_3} \longrightarrow \mathrm{Si{-}O{-}}\begin{array}{c}\mathrm{Si}\\|\\\mathrm{O\cdot H}\\|\\\mathrm{Ga}\\|\\\mathrm{O}\\|\\\mathrm{Si}\end{array}\mathrm{{-}O{-}Si} + 3\mathrm{CH_4}. \qquad (3)$$

In this mechanism, three H atoms are abstracted from Si–OH groups, and react with the methyl groups of the TMG via a hydrogenolysis mechanism, with formation of methane.

4.3. ^{71}Ga MAS NMR MEASUREMENTS

The ^{71}Ga MAS NMR spectrum of the HZSM5 zeolite, after dealumination via procedure 1 and TMG treatment in hydrogen is shown in fig. 3a. It appears that the entire Ga NMR signal is measured in a broad range around 0 ppm, indicating that all NMR detectable gallium is present in an octahedral coordination. Based on earlier work [25], it is reasonable to assume that another part of the (extra-framework) gallium in this sample is undetectable by NMR. The fact that no ^{71}Ga NMR resonance is observed at +159 ppm indicates that no gallium is introduced on framework positions (tetrahedrally coordinated) [26,27], or that the corresponding signal is broadened beyond detection.

The spectrum of the zeolite dealuminated by procedure 2 and subsequent TMG treatment in hydrogen is shown in fig. 3b. In this case, two peaks are observed in the NMR spectrum at chemical shifts of 0 ppm and +159 ppm, corresponding to octahedrally and tetrahedrally coordinated gallium, respectively. The latter peak indicates that part of the gallium is introduced in the zeolite on T site positions [27]. It should be remarked that no quantitative information can be derived from the spectra, as earlier work showed that gallium on certain framework positions of the zeolite, with a specific surrounding, will remain undetectable by NMR, even after water equilibration [25].

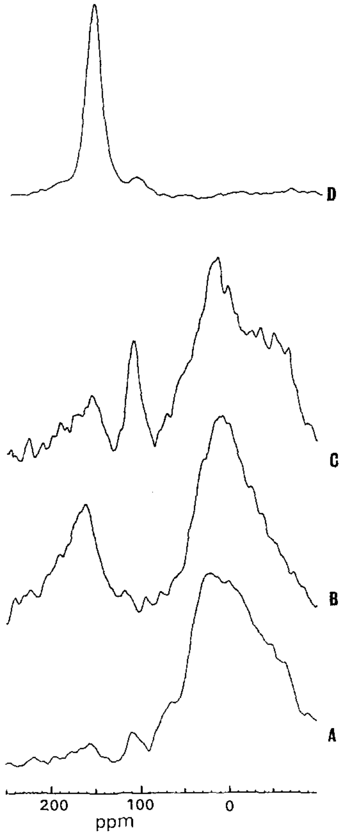


Fig. 3. ^{71}Ga MAS NMR spectra of HZSM5 zeolites; (a) dealuminated according to procedure 1 and TMG treatment in hydrogen, (b) dealuminated according to procedure 2 and TMG treatment in hydrogen, (c) dealuminated according to procedure 2 and TMG treatment in nitrogen, (d) spectrum of isomorphously substituted H(Ga)ZSM5 zeolite.

The spectrum recorded after dealumination according to procedure 2 and TMG treatment in nitrogen is shown in fig. 3c. Obviously, under these circumstances, again most of the Ga NMR signal appears as a broad band in the spectrum at a chemical shift of 0 ppm, which means that a large part of the gallium is introduced as extra-framework gallium. It is assumed that this is due to the different reaction mechanism in nitrogen (pyrolysis), according to which only small amounts of methane are formed. In the spectrum, also little Ga NMR response is measured at the typical chemical shift of tetrahedrally coordinated gallium, indicating that a small amount of gallium is introduced on framework positions.

Furthermore, this spectrum shows a third peak at about 110 ppm, which has not been observed in the ^{71}Ga MAS NMR spectrum of a HZSM5 zeolite until now, to the best of our knowledge. Based on the chemical shift and analogies in chemical properties with aluminum, this peak is tentatively assigned to pentaco-

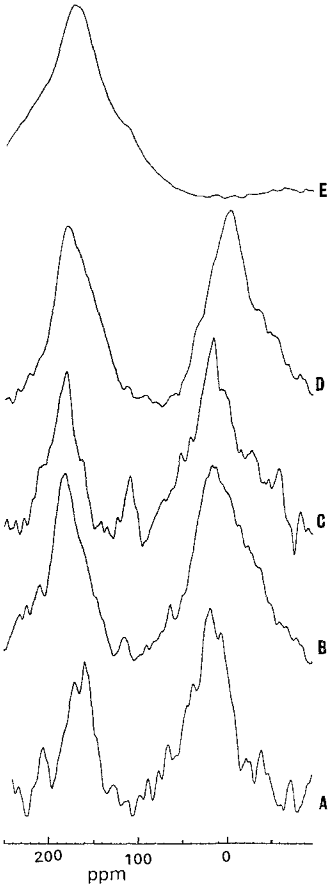


Fig. 4. ^{71}Ga MAS NMR spectra of HY zeolites; (a) dealuminated according to procedure 1 and TMG treatment in hydrogen, (b) dealuminated according to procedure 2 and 10 min TMG treatment in hydrogen, (c) dealuminated according to procedure 2 and 20 min TMG treatment in hydrogen, (d) dealuminated according to procedure 2 and TMG treatment in nitrogen, (e) spectrum of isomorphously substituted H(Ga)Y zeolite.

ordinated gallium, in line with earlier suggestions for the occurrence of pentacoordinated aluminum in dealuminated HZSM5 zeolites [28]. This peak might also originate from gallium bound to only one or two framework oxygen atoms, thus not introduced completely as framework gallium.

Dealumination of the HY zeolite via procedure 1, and TMG treatment in a hydrogen atmosphere, gives two peaks in the NMR spectrum at chemical shifts of about 0 ppm and +170 ppm (fig. 4a) indicating the introduction of both octahedrally and tetrahedrally coordinated gallium. This means that part of the gallium is introduced at framework positions, even after dealumination according to procedure 1, in contrast with the results obtained over zeolite HZSM5.

A similar result is observed after TMG treatment of the HY zeolite, dealuminated via procedure 2 (fig. 4b). For these samples, it seems that the NMR signal intensities of the framework and non-framework gallium increase with TMG exposure time (fig. 4c).

Fig. 4d shows that also after dealumination according to procedure 2 and TMG decomposition in nitrogen, a substantial amount of gallium is introduced on framework positions (tetrahedral coordination), in addition to an amount of octahedrally coordinated gallium (extra framework). In some of the spectra of fig. 4, the Ga NMR signal at a chemical shift of about 110 ppm is also observed (see above).

The fact that the reaction of TMG proceeds much better in hydrogen than in nitrogen was also visible in the colour of the zeolites after the reaction: in the former case, the zeolites were slightly grey after the reaction with TMG, while in the latter case dark-grey to black catalysts were obtained, due to the deposition of carbonaceous residues on the zeolite particles. This will be caused by the different reaction mechanism in hydrogen and nitrogen, as described above, leading to more or less formation of carbonaceous residues on the zeolite.

For comparison, the ^{71}Ga MAS NMR spectra of a HZSM5 gallosilicate and a HY gallosilicate are included in these figures, as figs. 3d and 4e, respectively. Obviously, the Ga NMR lines of the tetrahedrally coordinated gallium in both pure gallosilicates are much narrower than these of the dealuminated/TMG treated zeolites. This will be due to a relatively large chemical shift dispersion of the gallium in the dealuminated/TMG treated zeolites, where the gallium atoms are distributed over different framework positions [26], yielding relatively broad lines. In addition, a substantial part of the gallium will exist in less symmetrical coordinations, with various electric field gradients and are therefore subject to larger quadrupolar interactions. These, in turn, cause a broadening of the Ga NMR signal or even make the gallium NMR undectectable.

4.4. XPS MEASUREMENTS

The Ga/Si ratios of the bulk and the external surface of two $SiCl_4$/HCl/TMG treated HZSM5 zeolites (TMG treatment in hydrogen) with different gallium loadings are presented in table 1. A HY zeolite, after similar treatments, is also included in this table. The surface Ga/Si ratios were determined by XPS measurements, while the bulk Ga/Si ratios were calculated from the AAS results.

Table 1
Comparison of the Ga content of the outer surface of the zeolite particles (XPS) and the bulk gallium content (AAS)

Sample	Pretreatment	Ga/Si (AAS)	Ga/Si (XPS)
HZSM5	$SiCl_4$/HCl	0.09	0.06
HZSM5	$SiCl_4$/HCl	0.06	0.21
HY	$SiCl_4$/HCl	0.26	0.21

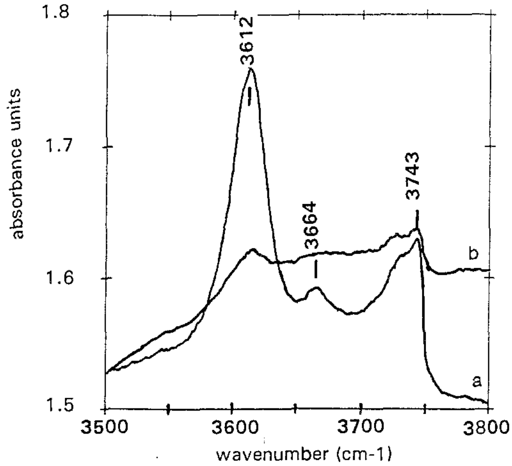


Fig. 5. FTIR spectra of a HZSM5 zeolite (Si/Al = 20); before (a), and after (b) dealumination (procedure 2) and TMG treatment (in hydrogen).

It is clear that the bulk Ga/Si ratio is always higher than the Ga/Si ratio of the surface, which indicates that a large portion of the trimethylgallium is deposited inside the zeolite crystallites.

The occurrence of reactions with isolated silanol groups (e.g. from the outer surface of the crystallites) and with Brønsted acid sites is confirmed by the FTIR spectra of the dealuminated HZSM5 zeolite (procedure 2), before and after TMG treatment in hydrogen, as shown in figs. 5a and 5b, respectively. Obviously, the reaction gives a consumption of both types of OH sites, which become visible in the spectra as reduced intensities of the absorption peaks at about 3612 cm^{-1} (Brønsted sites) and 3743 cm^{-1} (silanol groups). In addition, in fig. 5a, a line is observed at 3664 cm^{-1}, which is ascribed to the presence of extra-framework aluminum. This line is no longer observed after treating the sample with TMG, indicating also a reaction between the extra-framework aluminum species and TMG.

4.5. CATALYTIC PROPERTIES

The effect of 3.5 wt% gallium introduced by TMG treatment on the catalytic properties for the conversion of propane at 600°C over the HZSM5 zeolites is shown in fig. 6. The conversion and product selectivity of the original HZSM5 zeolite and of the TMG treated HZSM5 zeolite, are shown in fig. 6a and 6b, respectively. In the latter case, slightly lower conversions are measured (fig. 6b), while the selectivity to aromatics increases sharply from 36 C% without gallium to 55 C% in the presence of gallium, which is similar to earlier observations on gallium impregnated HZSM5 zeolites and isomorphously substituted gallosilicates [7,8]. The high aromatics selectivities indicate that the gallium introduced

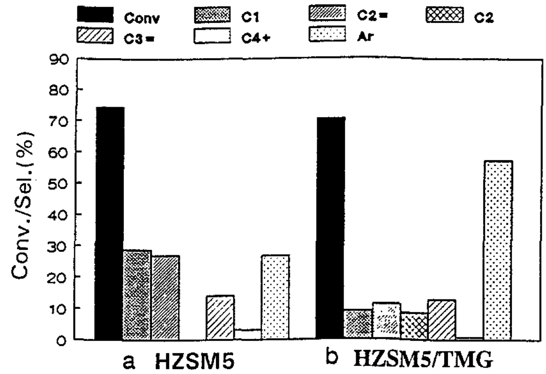


Fig. 6. Influence of dealumination via procedure 2, and subsequent TMG treatment in hydrogen on the catalytic properties of HZSM5 for propane aromatization; (a) standard HZSM5 zeolite, (b) dealuminated/TMG treated HZSM5 zeolite.

in this way is active for molecular hydrogen formation. It cannot be concluded, however, which gallium (framework or extra-framework) is most important for this improvement, as both types of gallium are known to improve the aromatics selectivity to some extent. The slightly reduced activity, as compared to the impregnated catalysts, may be due to a (partial) blockage of the zeolite pores by decomposition products of TMG. The deactivation experiment that was performed with a TMG treated HZSM5 zeolite (gallium content 3.5 wt%), showed a relatively high deactivation rate of this sample, comparable with the deactivation rate of a physical mixture. This behaviour is ascribed to the presence of extra-framework gallium on the outer surface of the zeolite, causing a relatively rapid rate of coke formation, thus blocking part of the active sites.

5. Conclusions

Introduction of framework gallium in dealuminated HY and HZSM5 zeolites by TMG decomposition in hydrogen is possible after a two-step dealumination treatment ($SiCl_4$, HCl) of the zeolite, forming silanol groups. In both zeolites, however, part of the gallium is introduced as extra-framework gallium, probably by reaction on isolated silanol groups. Decomposition of TMG on a dealuminated HY zeolite in a nitrogen atmosphere also yields framework gallium but this was not observed for HZSM5 zeolites.

A problem for the selective introduction in framework positions is the reaction of TMG with the silanol groups on the outer surface of the zeolite particles. Also the reaction between TMG and the Brønsted acid site has been observed. Both reactions lead to the formation of extra-framework gallium. The gallium introduced in this way in HZSM5 zeolites is catalytically active for propane aromatization, and a typical Ga/HZSM5 product pattern is obtained.

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