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DRIFTS study of the nature and chemical reactivity of gallium ions in Ga/ZSM-5

II. Oxidation of reduced Ga species in ZSM-5 by nitrous oxide or water

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Abstract

The oxidation of reduced Ga species in ZSM-5 zeolite modified via anchoring of trimethyl gallium or by incipient wetness impregnation with a solution of gallium nitrate was studied. Reduction of such materials in hydrogen and evacuation at high temperature resulted in quantitative replacement of the Brønsted acidic protons by Ga^+ ions. However, the extent of dealumination of the material prepared by incipient wetness impregnation was higher. Oxidation of univalent gallium species by nitrous oxide at 673 K by either preparation method led to the quantitative formation of charge-compensating $[Ga^{3+}(O^{2-})]^+$ fragments. Ga^+ ions can also be oxidized at 573 K by water vapor, whereupon approximately 25% of the Ga^+ ions are transformed into $[GaO]^+$ with concomitant release of molecular hydrogen. Dissociative chemisorption of molecular hydrogen via oxidative addition of hydrogen atoms to Ga^+ cations at 773 K resulted in the formation of gallium dihydride species, which are very stable and are decomposed only in vacuum above 673 K. Oxidation of such $[Ga^{3+}(H^-)_2]^+$ cations by N_2O at 573 K gave positively charged $[Ga^{3+}(H^-)(OH)^-]^+$ species. At higher temperature (673 K), the latter are further oxidized by nitrous oxide, giving neutral GaOOH species and Brønsted acidic protons. The similarity of infrared spectra of ethane adsorbed on Ga/ZSM-5 and HZSM-5 at 298 K indicates weak polarization of ethane molecules by Ga^+ cations. However, oxidative addition of ethane at 523 K led to the formation of $[Ga^{3+}(H^-)(C_2H_5{}^-)]^+$ species. Above 573 K the grafted ethyl fragments decomposed to gallium hydride species and ethylene. Indications were also found for subsequent oligomerization and aromatization of the resulting olefin.

Keywords: High-silica zeolite; ZSM-5; Gallium; DRIFT spectroscopy; Oxidation state; Hydrides; Alkane activation

1. Introduction

The hydrogen form of ZSM-5 zeolite modified with zinc or gallium ions may be used to convert light paraffins to aromatics [1–16]. The reaction mechanism is thought to consist of a complex scheme involving dehydrogenation, oligomerization, and ring-closure steps [3–11]. The modifying cations play a key role in the dehydrogenation of the paraffins [3–6], and Brønsted acid protons catalyze the oligomerization of the produced olefins. It is less clear whether ring closure takes place over Brønsted acid sites or gallium and zinc play a role in further dehydrogenation of the growing hydrocarbon oligomers, creating conjugated unsaturated fragments that are subsequently converted into aromatics [7–11]. The structure of the active intrazeolite Ga species has not been fully understood yet, because of the wide variety of possible structures. These include bulky Ga_2O_3 aggregates on the external zeolite surface, small gallium oxide particles occluded in the zeolite micropore space, reduced Ga species such as Ga_2O, and cationic Ga species in oxidized or reduced form.

Recently we studied Ga/ZSM-5 zeolite by diffuse-reflectance infrared spectroscopy [15]. The catalyst was prepared

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by incipient wetness impregnation with gallium nitrate followed by calcination. This work indicated that all acidic protons can be replaced by monovalent Ga^+ ions upon reduction at 773 K. Cooling of such a reduced sample in hydrogen resulted in dissociative oxidative addition of hydrogen to Ga^+ ions, thus forming charge-compensating GaH_2^+ species. An alternative preparation method involving the reaction of HZSM-5 with trimethyl gallium replaces all acidic protons directly by a dimethyl gallium species [16]. Reduction of this material also leads to Ga^+ cations [16,17], as confirmed by in situ Ga K edge X-ray absorption spectroscopic measurements [17].

In the present study, we applied both preparation methods to study the oxidation of univalent Ga^+ species by hydrogen, nitrous oxide, and water. These experimental results were carefully compared with those obtained by recent quantum-chemical calculations for a zeolite cluster containing Ga^+ ions [18]. The results indicate that under typical reaction conditions involving hydrocarbons at elevated temperatures (∼823 K), reduced Ga^+ ions are most likely predominant. Therefore, we also studied the activation of ethane over reduced Ga^+ ions.

2. Experimental

HZSM-5 was prepared by decomposition of the ammonium form of ZSM-5 (SM-55 zeolite from AlSi-Penta with a SiO_2/Al_2O_3 ratio in the framework equal to 44) in flowing oxygen at 773 K. The resulting hydrogen form was pressed into thin pellets and modified by gallium via reaction of the acidic hydroxyl groups with trimethyl gallium (TMG) vapor (Strem Chemicals) at 323 K in a quartz optical cell that was used for subsequent DRIFT measurements. Before DRIFT characterization, the samples were reduced in hydrogen at 723 K and evacuated at this temperature. These materials are referred to as TMG/HZSM-5. Alternatively, similar to our earlier study [15], we prepared a catalyst by incipient wetness impregnation of HZSM-5 with gallium nitrate, followed by calcination and reduction in hydrogen at 773 K. This catalyst is referred to as Ga/ZSM-5.

DRIFT spectra were recorded at room temperature with a Nicolet Impact 410 spectrophotometer equipped with a home-made diffuse-reflectance attachment that is described in more detail elsewhere [15]. The spectra were converted into Kubelka–Munk units by means of a standard program. The reflection ability of the samples at a wave number of 5000 cm^{-1} was taken to be equal to 0.9. The background created by the zeolites was subtracted.

Volumetric measurements made during oxidation of reduced samples by nitrous oxide or by water vapor were carried out for larger amounts of granulated zeolite. After adsorption of N_2O or H_2O at elevated temperatures, condensable gases were eliminated by freezing in a side finger of the reactor that was cooled by liquid nitrogen. Such volumetric measurements allowed determination of the noncondensable gases, nitrogen or hydrogen, generated during oxidation of reduced gallium species.

3. Results and discussion

Fig. 1 shows that the elimination of acidic protons via reaction of the bridging hydroxyl groups with $Ga(CH_3)_3$ starts slightly above room temperature. This results in a gradual decrease of the DRIFT band at 3610 cm^{-1} and in the ap-

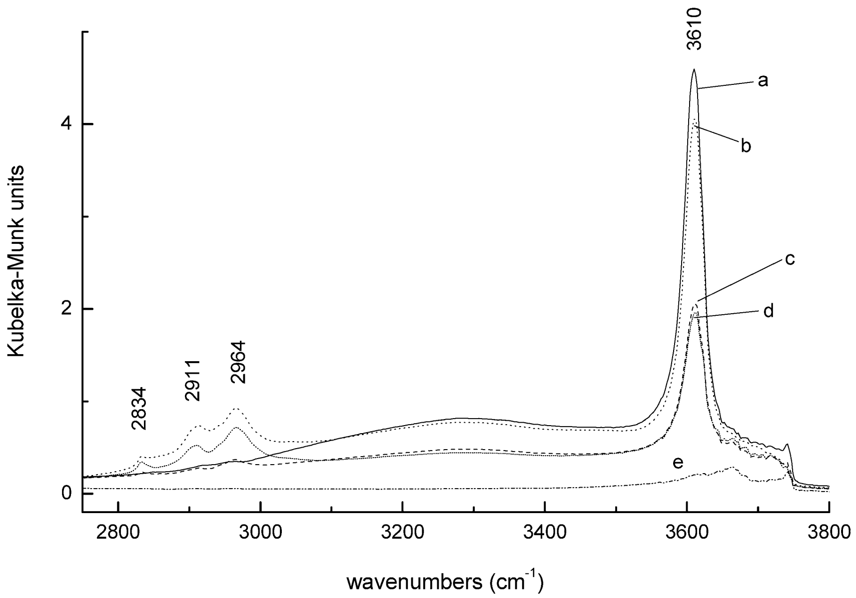

Fig. 1. Room-temperature DRIFT spectra of the hydroxyl region and of anchored dimethyl gallium species: (a) dehydrated parent HZSM-5, (b) HZSM-5 contacted with $Ga(CH_3)_3$ for 1 h at 323 K, (c) subsequent reduction in H_2 for 1.5 h at 823 K, (d) subsequent contacting with $Ga(CH_3)_3$ for 1 h at 323 K, and (e) subsequent reduction in H_2 at 823 K for 3 h.

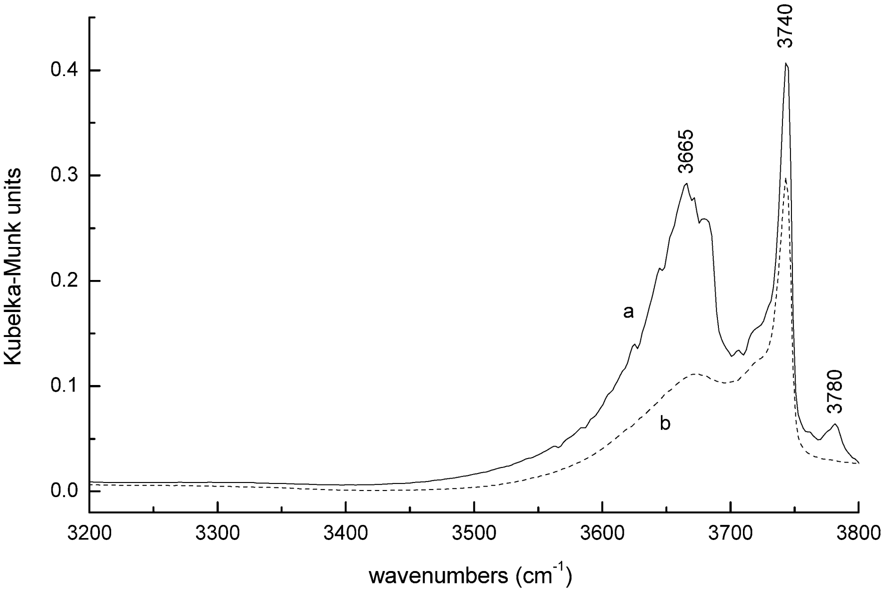

Fig. 2. Comparison of room-temperature DRIFT spectra of the hydroxyl region of Ga/ZSM-5 zeolites prepared by (a) incipient wetness impregnation followed by calcination at 773 K and reduction in hydrogen at 773 K, and (b) TMG/ZSM-5 reduced in hydrogen at 723 K.

pearance of C–H stretching bands below 3000 cm^{-1} from the grafted $Ga(CH_3)_2$ species. The rate of this reaction rather quickly decreased, most likely because of the blocking of the zeolite micropores by the anchored $Ga(CH_3)_2$ fragments. To eliminate the bulky methyl groups and to increase the accessibility of protons for $Ga(CH_3)_3$, the samples were reduced between subsequent treatments with $Ga(CH_3)_3$ vapor in hydrogen at 723 K. Repetition of this procedure several times resulted in complete replacement of protons by the univalent gallium ions according to

$$ZO^{-}\cdots H^{+} + Ga(CH_3)_3 \rightarrow ZO^{-}\cdots[Ga(CH_3)_2]^{+} + CH_4,$$
$$ZO^{-}\cdots[Ga(CH_3)_2]^{+} + H_2 \rightarrow 2CH_4 + ZO^{-}\cdots Ga^{+}. \quad (1)$$

A clear difference was noted between the reaction rate of the present parent zeolite and of a HZSM-5 material studied earlier [16]. The observation that in the latter case almost quantitative substitution can be rather easily obtained in one step is in agreement with the smaller particle size and shorter diffusion lengths in that zeolite.

As reported before [15], reduction in hydrogen of Ga/ZSM-5 prepared by incipient wetness impregnation also resulted in complete substitution of univalent gallium ions for protons. Fig. 2 compares the DRIFT spectra of the two zeolites in the hydroxyl region after reduction. Clearly, the extent of dealumination in Ga/ZSM-5 is substantially higher than in TMG/ZSM-5. This follows from the more intense DRIFT band around 3665 cm^{-1}, which is due to extraframework AlOH groups. The stronger dealumination is most likely due to a combination of a higher reduction temperature and the production of water resulting from the reduction of Ga_2O_3. In contrast, the reduction of the grafted gallium alkyl species occurs under anhydrous conditions. Reduction of the grafted gallium alkyl species is preferred over oxidation, because we have shown that extensive dealumination occurs in the latter case because of formation of water [17].

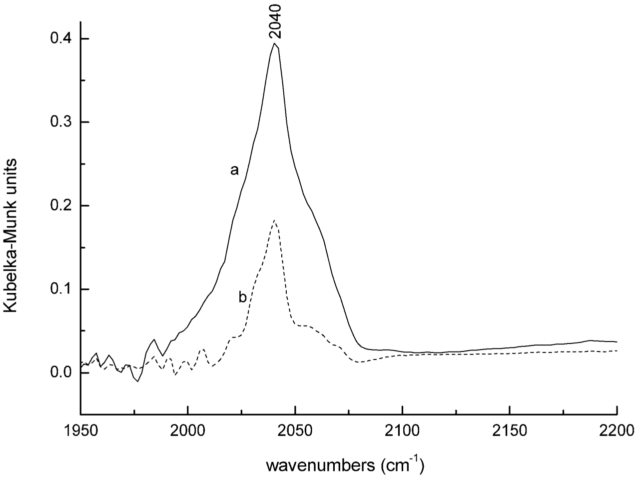

Fig. 3. Room-temperature DRIFT spectra of gallium hydrides resulting from hydrogen adsorption by reduced TMG/ZSM-5 (a) after cooling in hydrogen from 823 K and (b) after evacuation at 673 K followed by cooling in vacuum.

After reduction of TMG/ZSM-5 in hydrogen and subsequent evacuation at 723 K, no signature of gallium hydrides was observed in the spectral range of 1900–2100 cm^{-1}. However, slow cooling of the modified zeolite in a hydrogen atmosphere from 773 K to room temperature led to the appearance of a new DRIFT band at 2040 cm^{-1} (Fig. 3). This band is ascribed to gallium dihydrides [15], resulting from oxidative addition of hydrogen to reduced gallium ions according to

$$ZO^{-}\cdots Ga^{+} + H_2 \rightarrow ZO^{-}\cdots[GaH_2]^{+}. \quad (2)$$

Table 1
Volumetric measurements of nitrous oxide and water adsorption by reduced TMG/ZSM-5 (reduction in hydrogen at 773 K followed by extensive evacuation at 773 K). The zeolite contains 3.95×10^{20} Al atoms g^{-1}

Procedure	Amount of released gases (molecules g^{-1})	
	N_2	H_2
N_2O at 673 K	3.8×10^{20}	–
H_2O at 573 K	–	1×10^{20}

To compare the thermal stability of these hydrides with the stability of those reported in our earlier work for Ga/ZSM-5 prepared by incipient wetness impregnation [15], we reduced TMG/ZSM-5 in hydrogen, subsequently cooled it in a hydrogen atmosphere to room temperature, and finally evacuated the sample at different temperatures in the range of 293–700 K. The intermediate DRIFTS measurements were carried out at room temperature. Fig. 3 shows that the stability of the dihydrides is rather high. After evacuation at 673 K the intensity of the DRIFT band related to the Ga–H species decreased by a factor of approximately 2. This result is similar to the one previously reported for hydrogen desorption from a reduced Ga/HZSM sample prepared by incipient wetness impregnation [15]. Therefore, we conclude that upon cooling of the reduced material in hydrogen, both preparation methods resulted in the formation of similar gallium hydride species. In both cases, the hydrides were completely destroyed in vacuum only above 700 K. These results are in good agreement with results of quantum-chemical calculations reported by Bell and co-workers [18]. The high thermal stability of gallium dihydrides agrees with the calculated high activation barrier (74 kcal/mol) for their decomposition. In contrast, the enthalpy of hydrogen desorption at 800 K is predicted to be relatively small (12 kcal/mol).

Volumetric measurements after adsorption by reduced granulated TMG/ZSM-5 samples of nitrous oxide or water at high temperature were carried out in parallel with DRIFT measurements. The resulting data are collected in Table 1. Before modification with gallium, the initial HZSM-5 sample contained 3.95×10^{20} Al atoms per gram of zeolite. The amount of nitrogen released after exposure of the reduced TMG/ZSM-5 to excess nitrous oxide at 673 K was close to this value. This shows that the amount of nitrogen released at 673 K corresponds to the stoichiometric oxidation of reduced gallium species according to

$$ZO^{-}\cdots Ga^{+} + N_2O \rightarrow ZO^{-}\cdots GaO^{+} + N_2. \qquad (3)$$

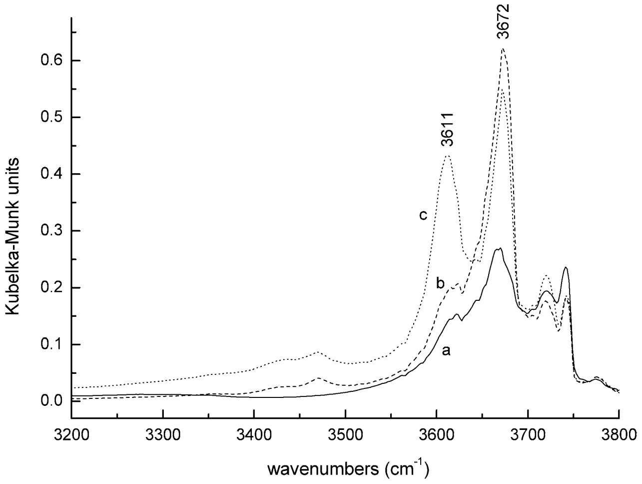

Fig. 4. Room-temperature DRIFT spectra of hydroxyl region of TMG/ZSM after (a) heating in hydrogen at 773 K and subsequent evacuation at 773 K, (b) subsequent oxidation by nitrous oxide at 573 K, and (c) oxidation by nitrous oxide at 673 K.

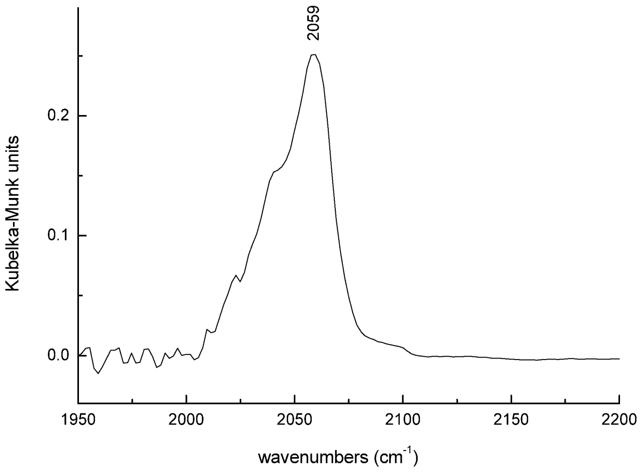

Fig. 5. Room-temperature DRIFT spectrum in the region of gallium hydrides for TMG/ZSM-5 obtained after reduction at 773 K, oxidation by nitrous oxide at 673 K and heating in hydrogen to 573 K, followed by evacuation and cooling.

In a separate experiment with a mass spectrometer we found that no molecular oxygen was evolved during the decomposition of nitrous oxide. Parallel DRIFTS measurements (Fig. 4) showed that the oxidation of reduced gallium species at 573 K by nitrous oxide resulted in an increase of the infrared band at 3672 cm^{-1} that was assigned to hydroxyl groups attached to the extraframework Ga species. Simultaneously, the band assigned to the Ga–H vibrations in the GaH_2^{+} species at 2040 cm^{-1} shifted by about 20 to 2059 cm^{-1} (compare Figs. 3 and 5) after oxidation and exposure to hydrogen. This suggests that a small amount of gallium dihydrides remaining after evacuation was oxidized by nitrous oxide according to

$$ZO^{-}\cdots[GaH_2]^{+} + N_2O \rightarrow ZO^{-}\cdots[Ga^{3+}(OH^{-})(H^{-})]^{+} + N_2. \qquad (4)$$

However, since the intensity of the band from hydroxyl groups connected to extraframework Ga in the sample obtained by oxidation by nitrous oxide (Fig. 4) is almost 10 times lower than that of the band from the initial acidic protons (Fig. 1), the formation of $[Ga^{3+}(OH^{-})(H^{-})]^{+}$ species is considered to be a side reaction of minor importance. This agrees well with the very low intensity of the DRIFT band from dihydrides in the initial sample.

Fig. 4c then shows that oxidation at higher temperature (673 K) resulted in an increasing intensity of the band at

3610 cm^{-1} related to Brønsted acidic protons. Simultaneously, the band from gallium hydride species in the region of 1900–2100 cm^{-1} disappeared. This most likely indicates the subsequent decomposition of $[\mathrm{Ga}^{3+}(\mathrm{OH}^-)(\mathrm{H}^-)]^+$ cations via their transformation into electroneutral extraframework gallium species and acidic protons via

$$\mathrm{ZO}^-\cdots[\mathrm{Ga}^{3+}(\mathrm{OH}^-)(\mathrm{H}^-)]^+ + \mathrm{N_2O} \rightarrow \mathrm{ZO}^-\cdots\mathrm{H}^+ + \mathrm{GaOOH} + \mathrm{N_2}. \quad (5)$$

However, as follows from the approximately one order of magnitude lower intensity of the band from the resulting bridging hydroxyl groups, this transformation also constitutes only a minor side reaction.

Quantum-chemical calculations [18] indicate that formation of $[\mathrm{Ga}^{3+}(\mathrm{OH}^-)(\mathrm{H}^-)]^+$ species is also possible via reduction of $[\mathrm{GaO}]^+$ by molecular hydrogen:

$$\mathrm{ZO}\cdots[\mathrm{GaO}]^+ + \mathrm{H_2} \rightarrow \mathrm{ZO}^-\cdots[\mathrm{Ga}^{3+}(\mathrm{OH}^-)(\mathrm{H}^-)]^+. \quad (6)$$

At 800 K this reaction is strongly exothermic (−54.5 kcal/mol), with a change in the Gibbs free energy of −28.3 kcal/mol. Subsequent desorption of water at high temperature may regenerate the univalent Ga^+ species:

$$\mathrm{ZO}^-\cdots[\mathrm{Ga}^{3+}(\mathrm{OH}^-)(\mathrm{H}^-)]^+ \rightarrow \mathrm{ZO}^-\cdots\mathrm{Ga}^+ + \mathrm{H_2O}. \quad (7)$$

In contrast to reaction (6), this is a moderately endothermic reaction at 800 K ($\Delta H = +29.5$ kcal/mol and $\Delta G = +1$ kcal/mol). This indicates that at high temperature desorption of water and regeneration of Ga^+ species are likely.

At lower temperatures, the probability of detecting $\mathrm{ZO}^-\cdots[\mathrm{Ga}^{3+}(\mathrm{OH}^-)(\mathrm{H}^-)]^+$ intermediates is higher. Indeed, reduction of oxidized TMG/ZSM-5 in molecular hydrogen at 573 K followed by cooling in a hydrogen atmosphere to room temperature shows that such pretreatment results in the appearance of bands at 3672 and 2059 cm^{-1} related to GaOH and Ga hydride species, respectively (Figs. 4 and 5). The position of the latter band is about 20 cm^{-1} higher than that of the band related to dihydride species at 2040 cm^{-1}. Hence, we infer that the vibrational band at 2059 cm^{-1} belongs to gallium monohydride in $[\mathrm{Ga}^{3+}(\mathrm{OH}^-)(\mathrm{H}^-)]^+$ formed according to Eq. (6). As mentioned earlier, a similar band with a lower intensity was also observed after oxidation of preliminarily reduced dihydride species (Eq. (4)).

Oxidation of the preliminarily reduced and subsequently evacuated gallium-modified zeolite by water vapor was studied at 573 K. For this purpose, the sample was kept at 573 K at a total water vapor pressure of 7 Torr for 1 h. Subsequently, the water vapor was frozen in the side finger of the reaction vessel that was cooled by liquid nitrogen. Formation of molecular hydrogen followed from the presence of a certain amount of noncondensable gas in an amount equal to 1×10^{20} molecules/g via

$$\mathrm{ZO}^-\cdots\mathrm{Ga}^+ + \mathrm{H_2O} \rightarrow \mathrm{ZO}^-\cdots[\mathrm{GaO}]^+ + \mathrm{H_2}. \quad (8)$$

This indicates oxidation of approximately 25% of the total amount of Ga^+ ions. The corresponding quantum-chemical calculations [18] indicate that oxidation of Ga^+ ions by water with concomitant formation of molecular hydrogen (reaction (8)) is energetically unfavorable ($\Delta H = +25$ kcal/mol and $\Delta G = +28.3$ kcal/mol at 800 K). In contrast, oxidation of univalent gallium by two water molecules is strongly exothermic, with corresponding values of $\Delta H = -47$ kcal/mol and $\Delta G = -14.4$ kcal/mol at 800 K:

$$\mathrm{ZO}^-\cdots\mathrm{Ga}^+ + 2\mathrm{H_2O} \rightarrow \mathrm{ZO}^-\cdots[\mathrm{Ga}^{3+}(\mathrm{OH}^-)_2]^+ + \mathrm{H_2}. \quad (9)$$

Therefore, oxidation of the univalent gallium species by water most likely proceeds via two consecutive steps:

$$\mathrm{ZO}^-\cdots\mathrm{Ga}^+ + \mathrm{H_2O} \rightarrow \mathrm{ZO}^-\cdots[\mathrm{Ga}^{3+}(\mathrm{OH}^-)(\mathrm{H}^-)]^+, \quad \Delta G_{800\ \mathrm{K}} = -1\ \mathrm{kcal/mol} \quad (10)$$

and

$$\mathrm{ZO}^-\cdots[\mathrm{Ga}^{3+}(\mathrm{OH}^-)(\mathrm{H}^-)]^+ + \mathrm{H_2O} \rightarrow \mathrm{ZO}^-\cdots[\mathrm{Ga}^{3+}(\mathrm{OH}^-)_2]^+ + \mathrm{H_2}, \quad \Delta G_{800\ \mathrm{K}} = -13.4\ \mathrm{kcal/mol}. \quad (11)$$

Moreover, the calculations show that the subsequent decomposition of the resulting $\mathrm{ZO}^-\cdots[\mathrm{Ga}^{3+}(\mathrm{OH}^-)_2]^+$ species via

$$\mathrm{ZO}^-\cdots[\mathrm{Ga}^{3+}(\mathrm{OH}^-)_2]^+ \rightarrow \mathrm{ZO}^-\cdots[\mathrm{GaO}]^+ + \mathrm{H_2O} \quad (12)$$

is highly endothermic, with $\Delta H_{800\ \mathrm{K}} = +72.1$ kcal/mol and $\Delta G_{800\ \mathrm{K}} = +42.8$ kcal/mol.

After evacuation at 573 K and cooling to room temperature, the resulting DRIFT spectrum also indicated a partial regeneration of the bands at 3610 cm^{-1} from the acidic hydroxyl groups (Fig. 6). This should be explained by an easier alternative decomposition of $[\mathrm{Ga}^{3+}(\mathrm{OH}^-)_2]^+$ species according to

$$\mathrm{ZO}^-\cdots[\mathrm{Ga}^{3+}(\mathrm{OH}^-)_2]^+ \rightarrow \mathrm{ZO}^-\cdots\mathrm{H}^+ + \mathrm{GaOOH}. \quad (13)$$

In accordance with the amount of released hydrogen, the extent of such recovery of acidic hydroxyls was also equal to

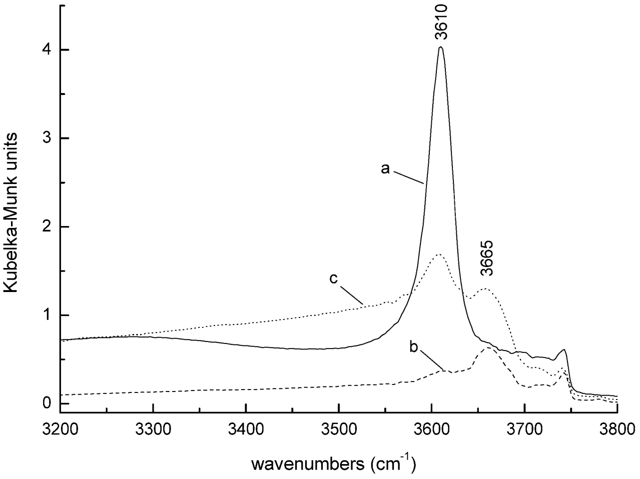

Fig. 6. Room-temperature DRIFT spectra of hydroxyl region of HZSM-5 and TMG/HZSM zeolites, (a) dehydrated parent HZSM-5, (b) TMG/HZSM-5 reduced in $\mathrm{H_2}$ at 773 K and evacuated at 773 K, and (c) subsequent oxidation by $\mathrm{H_2O}$ at 573 followed by evacuation at this temperature and cooling.

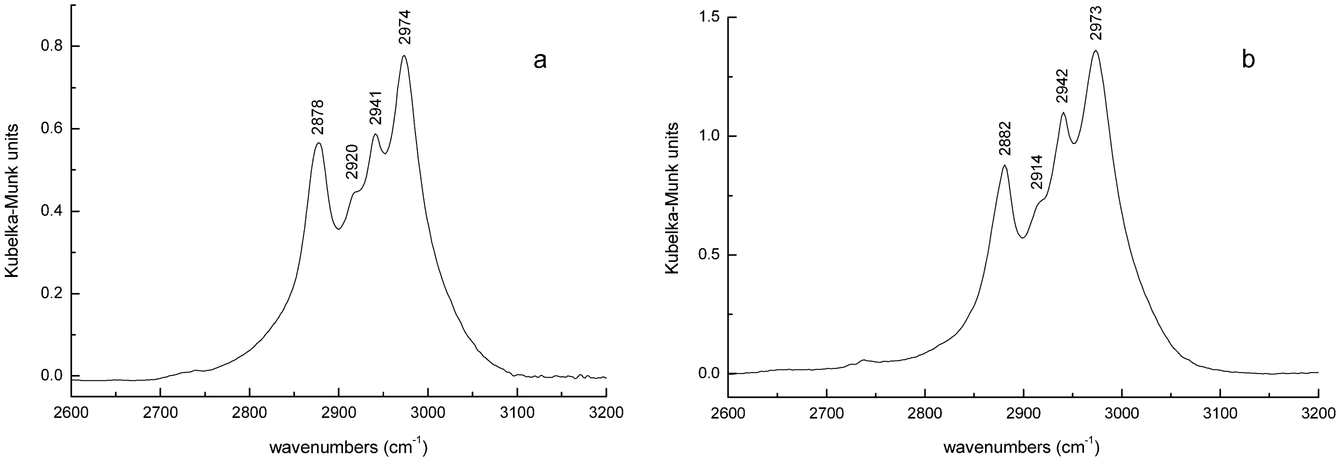

Fig. 7. Room-temperature DRIFT spectra of ethane adsorbed at room temperature at a pressure of 1 Torr by (a) HZSM-5 and (b) reduced TMG/HZSM-5.

about 25%. Thus, it is probable that oxidation of univalent gallium by water at high temperature follows the sequence of reactions (10)–(11)–(13). Unfortunately, the energetics of reaction (13) are not available.

Gallium-promoted ZSM-5 finds application in the conversion of light paraffins to aromatics, for example, in the Cyclar process [1,2]. Our present and earlier results [15–17] indicate the under typical reaction conditions (elevated temperatures, reducing atmosphere) monovalent Ga^+ species are predominant, although it cannot be ruled out that $GaH_2{}^+$ species are also present. Moreover, it is clear that the activation energy for the regeneration of the gallyl ($[GaO]^+$) ion from an intermediate $[Ga^{3+}(OH^-)(H^-)]^+$ species is high [18,19], and the regeneration of Ga^+ species is more likely. In a first step to study the activation of light paraffins over Ga/ZSM-5, we discuss the interaction of univalent Ga^+ species with ethane.

DRIFT spectra of ethane adsorbed by the parent HZSM-5 and by reduced TMG/ZSM-5 samples are shown in Figs. 7a and 7b, respectively. The positions of the C–H stretching bands in the two spectra differ by no more than 5 cm^{-1}. This indicates a weak perturbation of ethane by Ga^+ ions. This conclusion is further supported by the observation that for both zeolites a decrease in the ethane partial pressure leads to a similar decrease in the intensities of the C–H stretching bands. Moreover, in both cases the features of ethane completely disappear after prolonged evacuation at room temperature. Such weak adsorption of ethane over the gallium-modified sample is in contrast with ethane adsorption by Zn/ZSM-5 [20], where strong polarization of adsorbed ethane takes place at room temperature. Apparently, Ga^+ cations do not perturb adsorbed ethane strongly.

On the other hand, after heating of TMG/ZSM-5 in an ethane atmosphere to 523 K and subsequent evacuation at room temperature, four weak C–H stretching bands with maxima at 2882, 2914, 2939, and 2962 cm^{-1} remain visible in the DRIFT spectrum, as follows from Fig. 8. These bands disappear only after evacuation above 573 K and therefore belong to the grafted alkyl species. The important difference with the heterolytic dissociative adsorption of ethane by the zinc–oxygen acid–base pairs of Zn/ZSM-5 zeolite [20] is the appearance of gallium alkyl and gallium hydride species. The latter species is identified by a band at 2057 cm^{-1} with a shoulder at 2040 cm^{-1}, whereas, unlike with ZnZSM-5, no regeneration of acidic protons was observed. Therefore, in contrast to the heterolytic dissociation of ethane over Zn/ZSM-5, the dissociative chemisorption of ethane by Ga/ZSM-5 corresponds to the oxidative addition to reduced Ga^+ species according to

$$ZO^- \cdots Ga^+ + C_2H_6 \to ZO^- \cdots [Ga^{3+}(H^-)(C_2H_5{}^-)]^+. \tag{14}$$

The occurrence of such species is further supported by the stretching frequency of Ga–H species, 2059 cm^{-1}, which is close to the frequency for gallium monohydrides that were formed upon heating of TMG/ZSM-5 in hydrogen at 573 K followed by oxidation with nitrous oxide. Subsequent heating of reduced TMG/ZSM-5 with dissociatively chemisorbed ethane results in an increasing intensity of the DRIFT band from gallium dihydrides around 2040 cm^{-1} at the expense of the feature at 2059 cm^{-1} (Fig. 9). This DRIFT band is similar to the one observed after adsorption by reduced gallium ions of molecular hydrogen (Fig. 3). This most likely indicates decomposition of the grafted $[Ga^{3+}(H^-)(C_2H_5{}^-)]^+$ fragments, resulting in ethylene and gallium dihydrides:

$$\begin{aligned} &ZO^- \cdots [Ga^{3+}(H^-)(C_2H_5{}^-)]^+ \\ &\quad \to ZO^- \cdots [GaH_2]^+ + C_2H_4. \end{aligned} \tag{15}$$

Moreover, heating to 673 K leads to the appearance of additional DRIFT bands characteristic for olefinic hydrocarbons (Fig. 9). This could indicate the formation of oligomeric products and possibly of benzene, which has characteristic vibrational bands above 3000 cm^{-1}.

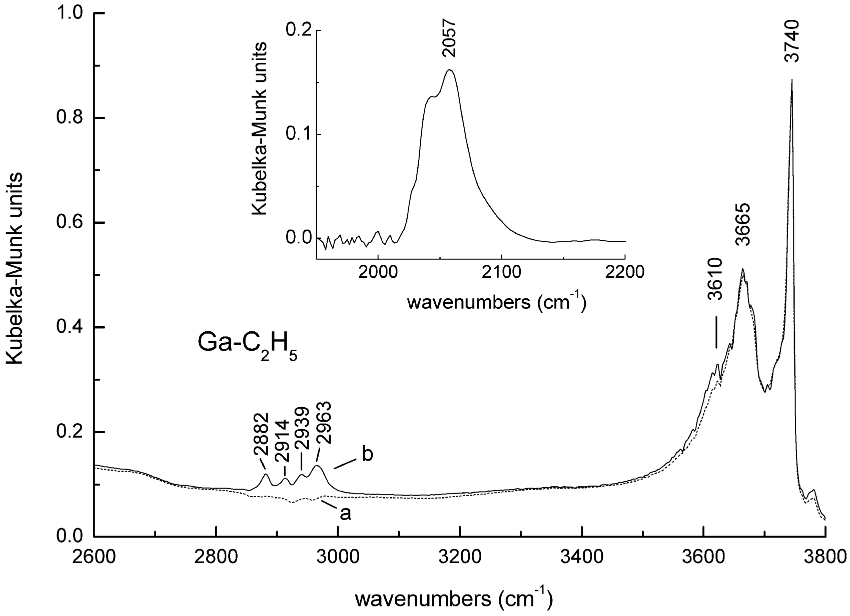

Fig. 8. Room-temperature DRIFT spectra of reduced TMG/ZSM-5, (a) before and (b) after heating in ethane at 523 K and prolonged evacuation at room temperature.

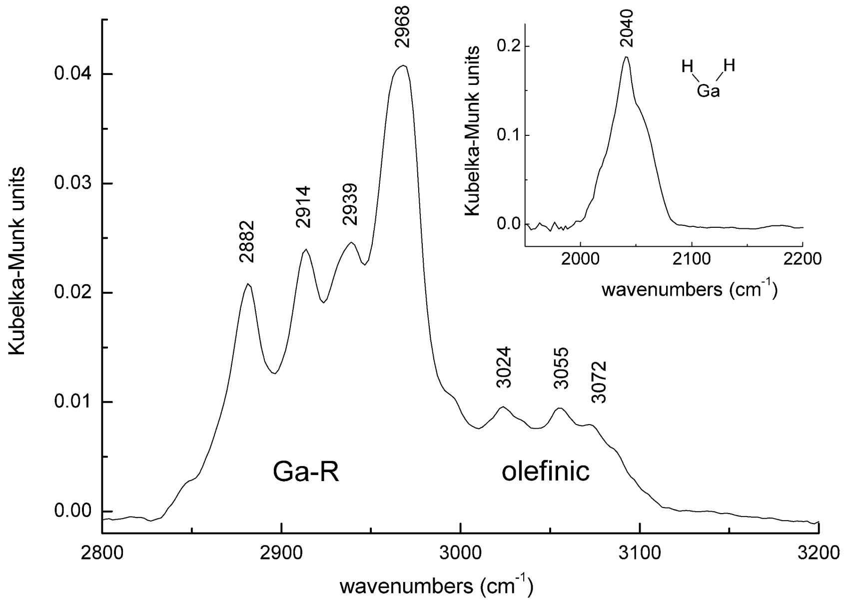

Fig. 9. Room-temperature DRIFT spectra of TMG/ZSM-5 after heating in ethane at 673 K and prolonged evacuation at room temperature.

4. Conclusions

The present study demonstrates that modification of HZSM-5 catalysts with gallium ions via anchoring of trimethyl gallium and by incipient wetness impregnation with gallium nitrate followed by subsequent reduction in hydrogen and evacuation at high temperature results in similar quantitative substitution of all Brønsted acid protons by Ga^+ ions. The difference between the two modification methods consists of the somewhat higher temperature of reduction required and water production in the impregnated samples. This leads to a higher extent of dealumination of such materials.

The monovalent Ga^+ species may be quantitatively oxidized by nitrous oxide to $[GaO]^+$ oxo-species. Interaction of reduced Ga^+ species with water at 573 K also results in oxidation of a substantial amount of Ga^+, as indicated by the evolution of molecular hydrogen. This reaction is also accompanied by the partial hydrolysis of $[GaO]^+$ species, leading to the partial regeneration of Brønsted acidic protons. Oxidative addition of molecular hydrogen to Ga^+ cations via dissociative chemisorption results in the formation of gallium dihydride species. These dihydrides are quite stable and are decomposed in vacuum only above 673 K. Oxidation of $[Ga^{3+}(H^-)_2]^+$ species with N_2O at 573 K results in charge-compensating $[Ga^{3+}(H^-)(OH^-)]^+$ species. Subsequent oxidation by N_2O at higher temperature results in the formation of electroneutral extralattice GaOOH species and regeneration of Brønsted acidic protons.

Although ethane is only weakly adsorbed to reduced Ga^+ species at room temperature, we found that similar to oxidative addition of hydrogen, ethane can chemisorb dissociatively at 523 K, leading to grafted ethyl and monohydride species. Above 573 K the gallium ethyl fragments decomposed, resulting in the formation of dihydrides and the evolution of ethylene. The latter may then be involved in subsequent oligomerization and aromatization.

Acknowledgments

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