

DRIFTS study of the chemical state of modifying gallium ions in reduced Ga/ZSM-5 prepared by impregnation

I. Observation of gallium hydrides and application of CO adsorption as a molecular probe for reduced gallium ions

V.B. Kazansky^a, I.R. Subbotina^a, R.A. van Santen^b, E.J.M. Hensen^{b,*}

^a *Zelinsky Institute of Organic Chemistry, Leninsky Prospect 47, Moscow, Russia*

^b *Schuit Institute of Catalysis, P.O. Box 513, 5600 MB Eindhoven University of Technology, The Netherlands*

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Abstract

Reduction in hydrogen at 773 K of gallium-modified HZSM-5 zeolite prepared by incipient wetness impregnation results in complete substitution of acidic hydroxyl groups. The modification of the zeolite with gallium suppresses dealumination of the hydrogen form due to substitution of protons by gallium species. When the reduction at 773 K is followed by evacuation, coordinatively unsaturated Ga⁺ ions are formed. These species can be reversibly oxidized by nitrous oxide at 673 K. Alternatively, these Ga⁺ ions adsorb molecular hydrogen at lower temperatures resulting in several types of hydride species. The latter species are completely decomposed only in vacuum at relatively high temperatures (773 K). We propose that the oxidation of gallium upon cooling of reduced samples to room temperature in hydrogen can be attributed to an oxidative addition of H₂ resulting in the formation of gallium dihydrides.

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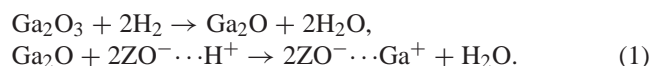
Keywords: High silica zeolite; ZSM-5; Gallium; DRIFT spectroscopy; Oxidation state; Hydrides

1. Introduction

Acid ZSM-5 zeolites modified by gallium ions are known to be active catalysts for the aromatization of light paraffins [1]. The mechanisms associated with alkane dehydrogenation and subsequent oligomerization and aromatization of the resulting olefins have been extensively studied by several research groups [2–10]. However, the state of gallium in these catalysts has not been elucidated yet. Various studies [9,10] show that only a small part of the protons is substituted by gallium ions upon calcination of catalysts prepared by ion exchange or incipient wetness impregnation. Instead, gallium is mostly present as small oxide particles at the external surface of the zeolite micrograins. To increase

the extent of proton substitution by gallium, such zeolites can be reduced in a hydrogen or hydrocarbon atmosphere at elevated temperatures, i.e., around 773 K [2–8]. These treatments facilitate the migration of the reduced gallium species into the micropores of the zeolite particles resulting in more complete substitution of the acid protons.

The high mobility of gallium upon reduction is believed to be connected to the formation of unstable gaseous Ga₂O oxide [5,6]. Subsequently, this oxide can react with acid protons in the zeolite micropores:



It has been put forward that univalent Ga⁺ cations are highly unstable [2,7]. Cooling a reduced sample in a hydrogen atmosphere to room temperature would result in the oxidation of Ga⁺ by traces of residual water or framework

* Corresponding author. Fax: +31-40-2455054.

E-mail address: e.j.m.hensen@tue.nl (E.J.M. Hensen).

oxygen atoms with formation of $(\text{Ga}(\text{OH})_2)^+$, $(\text{GaO})^+$ or even Ga_2O_3 species.

In the present study we investigated the state of gallium in reduced Ga/HZSM-5 zeolite by highly sensitive DRIFT spectroscopy using adsorbed CO as a molecular probe. Modification of HZSM-5 with gallium was achieved by incipient wetness impregnation with an aqueous solution of gallium nitrate. The amount of gallium was chosen such that a Ga/Al atomic ratio of about unity was obtained. This implies that in principle all protons can be replaced by cationic gallium species. Before DRIFT measurements the zeolites were reduced in hydrogen at high temperature or oxidized by nitrous oxide after preliminary reduction in hydrogen. Previously, IR spectroscopy of adsorbed carbon monoxide has been used for the identification of gallium species in isomorphously substituted gallosilicates with the MFI structure mainly by Zecchina's group [11]. However, we do not know any other works where the CO probe was used for testing of the modifying gallium ions introduced in high silica zeolites by incipient wetness impregnation or ion exchange.

2. Experimental

The hydrogen form of ZSM-5 was prepared by decomposition of the ammonium form of SM-55 zeolite (Alsi-Penta, framework $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio equal to 40–48) in an oxygen flow at 773 K for 5 h. Modification of the hydrogen form by gallium was carried out by incipient wetness impregnation with an aqueous solution of $\text{Ga}(\text{NO}_3)_3$. The amount of modifying gallium ions was chosen to be ~ 5 wt% corresponding to a Ga/Al atomic ratio of about unity.

The impregnated zeolite powder was dried in air at 373 K and pressed into thin pellets with dimensions 15×5 mm. The pellets were then placed into a quartz part of the vacuum cell equipped with an CaF_2 window as shown in Fig. 1a

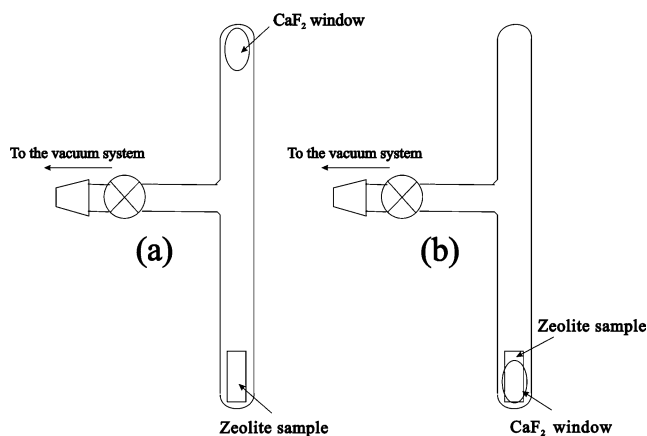


Fig. 1. Layout of DRIFT equipment: (a) position of the zeolite pellet for vacuum or redox pretreatments; (b) position of the zeolite pellet for DRIFTS measurements.

and pretreated in the following manner. At first the zeolite was evacuated at 423 K for 2 h. Then the temperature was increased to 773 K at a heating rate of 3 K/min and the samples were further evacuated for 3 h followed by calcination in 70 Torr oxygen for 1 h. Finally, the zeolite was evacuated at 773 K and cooled in vacuo to room temperature. For reduction, the samples were exposed to 50 Torr hydrogen at 773 K. The exposure time was varied between 1 and 7 h. After such pretreatment the samples were characterized by DRIFT spectra at room temperature as prepared or probed by adsorbed carbon monoxide at room temperature (carbon monoxide pressure was varied from 10 to 200 Torr). Before CO adsorption hydrogen was evacuated at various temperatures. For spectral measurements the zeolite pellet was transferred from the quartz part of the vacuum cell to its opposite part equipped with the CaF_2 window as shown in Fig. 1b. DRIFT spectra of the thin pellets were recorded in the presence of gaseous carbon monoxide with a Nicolet Impact 410 spectrophotometer by means of a home-made diffuse reflectance attachment. All of the spectra were converted into Kubelka–Munk units. The reflection ability of the zeolite at the wavelength of 5000 cm^{-1} was set equal to 0.9 unit and the background spectrum of the zeolite was subtracted.

3. Results

3.1. DRIFT spectra of gallium-modified samples in the region of OH stretching vibrations and UV–vis spectra of reduced samples

After calcination in oxygen and evacuation at high temperature the DRIFT spectra of the gallium-modified samples were similar to those of the initial hydrogen form after a similar pretreatment. This indicates that the modifying gallium ions mainly form small Ga_2O_3 particles on the external surface of the zeolite grains or small neutral particles in the micropores. Substitution of the bridging hydroxyl groups by gallium ions in the zeolite micropores was only of a minor importance.

After reduction in hydrogen at 773 K the intensity of the DRIFT band from acidic OH groups around $\sim 3610 \text{ cm}^{-1}$ gradually decreased. This indicates substitution of the bridging hydroxyl groups by the modifying gallium ions. After prolonged reduction in hydrogen substitution of the acidic protons was practically complete (Fig. 2). Simultaneously, a new weak DRIFT band at 3665 cm^{-1} appeared after the first hour of reduction. A similar band has been earlier observed after reduction of Ga/HZSM-5 in hydrogen and was ascribed to GaOH groups [12]. More prolonged reduction practically did not change the intensity of this band. Unlike gallium-modified samples, a similar high-temperature vacuum pretreatment or reduction in hydrogen of the non-modified HZSM-5 results in a much lower extent of dehydroxylation (Fig. 3). This is obviously connected with the

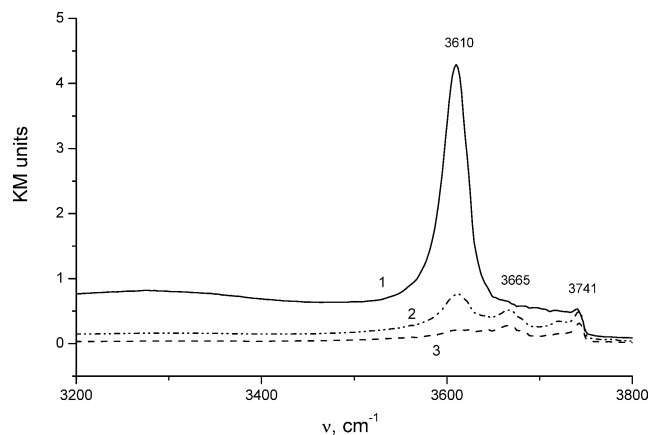


Fig. 2. DRIFT spectra of OH groups in GaZSM-5 before (1) and after reduction in hydrogen at 773 K for 1 (2) and 4 (3) h and subsequent evacuation at 773 K. DRIFT spectra taken at room temperature.

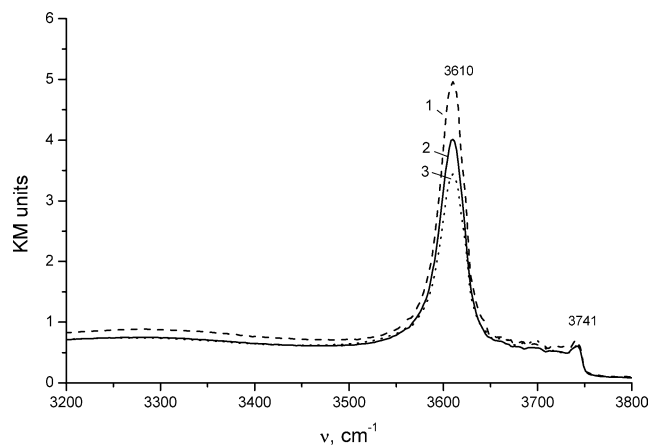


Fig. 3. DRIFT spectra of OH groups of HZSM-5 evacuated after calcination in oxygen at 773 K (1) and after reduction in hydrogen at 773 K for (2) 2 and (3) 7 h. DRIFT spectra taken at room temperature.

more difficult removal of hydroxyl groups in HZSM-5 due to the absence of other cationic species than protons that provide the necessary compensation of the negative lattice charges.

The dispersion of Ga_2O_3 upon reduction in hydrogen is also found upon comparison of UV–vis spectra of oxidized and reduced samples in Fig. 4. The spectrum of Ga/HZSM after calcination in oxygen is similar to that of Ga_2O_3 , whereas the intensity of the charge-transfer band at approximately 245 nm connected to Ga_2O_3 particles has strongly decreased after reduction in hydrogen. This reduction of gallium oxide is in line with the results from DRIFT spectra that show the substitution of acidic hydroxyl groups by reduced gallium ions.

3.2. Formation of gallium hydrides upon high-temperature hydrogen adsorption by reduced gallium ions

Reduction of GaZSM-5 in hydrogen at 773 K and subsequent prolonged evacuation at 873 K did not show any

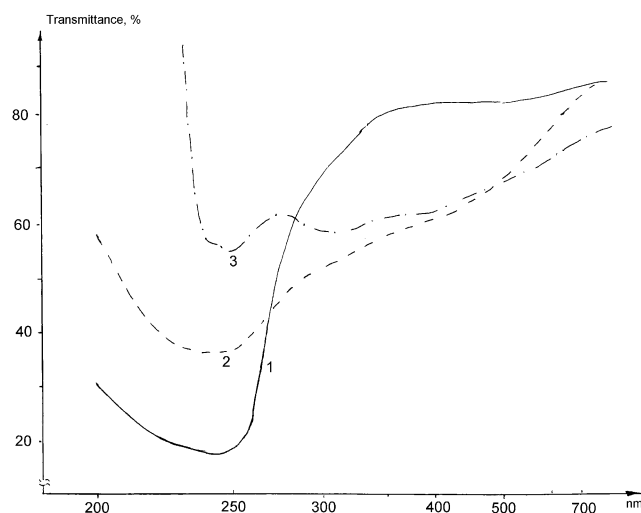


Fig. 4. UV–vis spectra of (1) Ga_2O_3 , (2) Ga/HZSM after calcination in oxygen and evacuation at 773 K, and (3) after reduction in hydrogen at 773 K for 4 h and subsequent evacuation at 773 K.

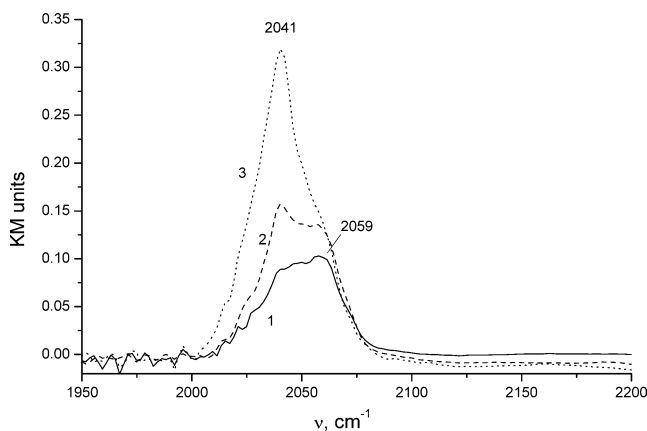


Fig. 5. DRIFT spectra of gallium hydrides resulting from hydrogen adsorption at different temperatures by Ga/HZSM-5 preliminary reduced in hydrogen at 773 K and evacuated at 873 K: (1) hydrogen adsorption at 573 K, (2) hydrogen adsorption at 673 K, and (3) hydrogen adsorption at 773 K (H_2 pressure equal to 50 Torr; DRIFT spectra taken at room temperature).

infrared bands in the spectral range of 1900–2100 cm^{-1} associated with gallium hydrides [17]. These bands were also not observed after admission of hydrogen to the evacuated samples at room temperature. However, heating of such samples in a hydrogen atmosphere to 773 K with subsequent cooling of the zeolite in hydrogen to room temperature resulted in the appearance of two bands with maxima at 2041 and 2059 cm^{-1} (Fig. 5). We surmise that these bands relate to two different kinds of gallium hydrides. The band with the highest Ga–H stretching frequency appears at lower temperatures compared to the other one. This points to the presence of multiple adsorption sites. Above 573 K the formation of hydrides with the lower stretching frequency of 2041 cm^{-1} was predominant.

To obtain further insight into the stability of the hydrides, a hydrogen desorption experiment was carried out

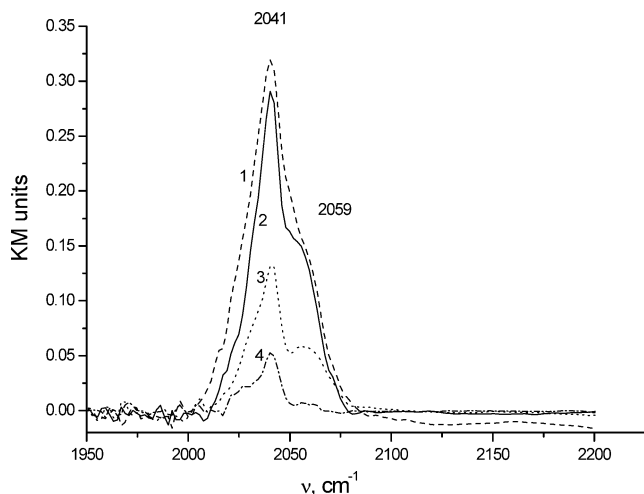


Fig. 6. Decomposition of gallium hydrides upon heating in vacuum at elevated temperatures: (1) DRIFT spectrum of hydrides in the Ga/HZSM-5 sample that was reduced in hydrogen at 773 K and then cooled in hydrogen to room temperature, (2) the same sample after evacuation at 573 K, (3) evacuation at 673 K, and (4) evacuation at 773 K (DRIFT spectra taken at room temperature).

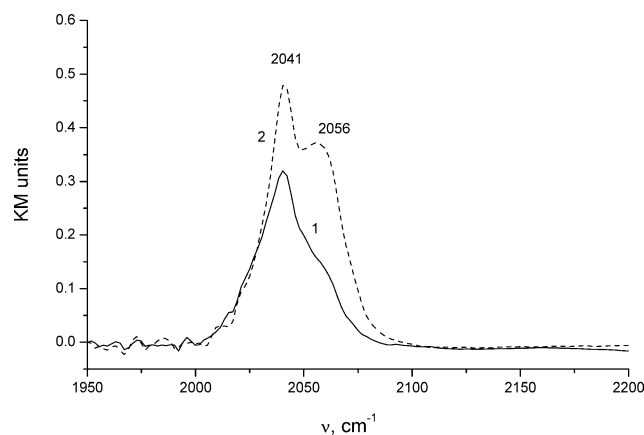


Fig. 7. DRIFT spectra of gallium hydrides resulting from reduction of GaZSM in hydrogen at 773 K after fast cooling in hydrogen atmosphere to room temperature during (1) 5 min or (2) 120 min.

for a Ga/HZSM-5 sample that was previously reduced in hydrogen at elevated temperature and then cooled to room temperature in hydrogen. The corresponding DRIFT spectra that are shown in Fig. 6 indicate that the hydrides are stable upon evacuation below 573 K. The Ga–H bands start to disappear above 573 K and are lost at 773 K. The remaining weak band is additionally split into two components indicating further inhomogeneity of the adsorption sites.

We also studied the formation of gallium hydrides upon fast and slow cooling of reduced samples in a hydrogen atmosphere from 773 K to room temperature. The corresponding DRIFT spectra in the region of the Ga–H stretching vibrations are shown in Fig. 7. These data indicate that rapid cooling in hydrogen atmosphere results in a lower amount of hydride species when compared to slow cooling. Thus, a very slow cooling rate (from 773 K to room temperature

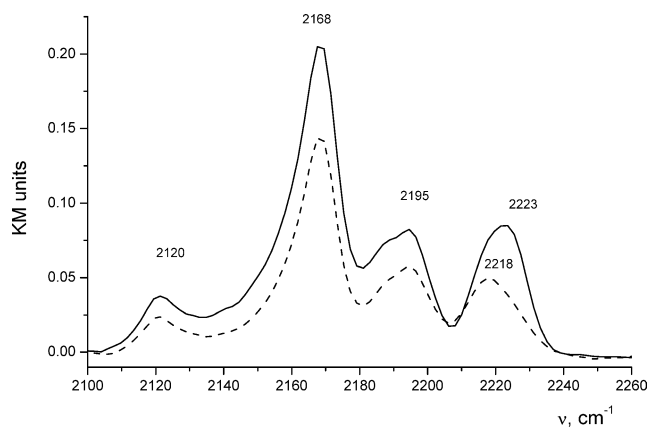


Fig. 8. DRIFT spectra of CO adsorbed at a pressure of 10 Torr at room temperature by HZSM-5 evacuated after calcination in oxygen at 773 K (the dotted line) and after similar pretreatment of Ga/HZSM (the solid line). DRIFT spectra taken at room temperature. The CO pressure was 10 Torr.

in 2 h) resulted in a maximum yield of gallium hydrides. In addition, a lower cooling rate resulted in a stronger increase of the amount of hydrides with the highest Ga–H stretching frequency compared to those with a lower stretching frequency. According to these results adsorption of hydrogen by reduced gallium species occurs only at high temperatures. The resulting gallium hydride species are inhomogeneous and thermally relatively stable.

3.3. DRIFT spectra of carbon monoxide adsorbed by HZSM-5 and GaZSM-5

Fig. 8 shows the DRIFT spectrum of carbon monoxide adsorbed by HZSM-5 at room temperature after calcination in oxygen at 773 K. The bands with maxima at 2168 and 2120 cm^{-1} belong to two different isomeric forms of CO adsorption on acidic hydroxyl groups [13]. Their intensities only moderately decreased upon vacuum pretreatment or calcination in oxygen. This is in agreement with the only moderately lower intensity after a similar pretreatment of the band from hydroxyl groups with a stretching frequency of 3610 cm^{-1} in Fig. 3.

Infrared bands with maxima at 2223 cm^{-1} and at 2188–2195 cm^{-1} have been ascribed earlier to CO molecules interacting with low-coordinated Al^{3+} ions on the surface of small aluminum oxide or aluminum hydroxide particles produced upon partial dealumination of the zeolite framework by high-temperature pretreatment [13,14]. The band at 2223 cm^{-1} has been also assigned to carbon monoxide perturbed by $(\text{Al}=\text{O})^+$ oxo-ions deriving from dealumination [15,16]. These species may compensate the negatively charged aluminum-occupied oxygen tetrahedra instead of the protons that were removed via dehydroxylation. Thus, calcination of HZSM-5 in oxygen at 773 K results only in a minor degree of dehydration and dealumination resulting either in the small particles of aluminum oxide or in substitu-

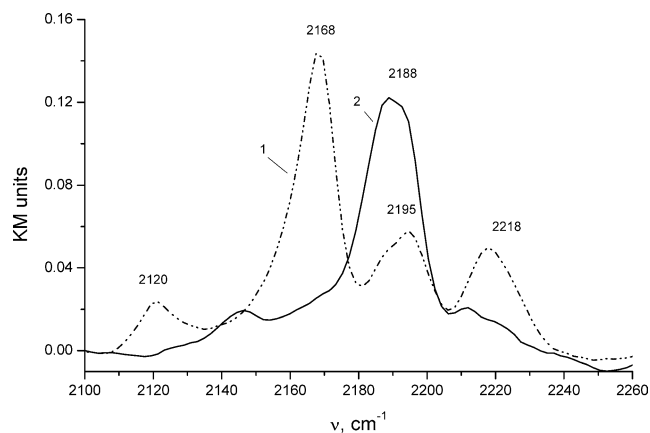


Fig. 9. DRIFT spectra of CO adsorbed at a pressure of 10 Torr by Ga/HZSM-5 at room temperature: (1) after calcination in oxygen and evacuation at 773 K, (2) after subsequent reduction in hydrogen at 773 K for 4 h and evacuation at this temperature.

tion of the removed protons by $(\text{AlO})^+$ oxo-ions. This could be described by the following reactions:



This conclusion is also supported by DRIFT spectra (Fig. 3) that point to the partial removal of protons, even after prolonged calcinations of the sample in oxygen.

The DRIFT spectrum of CO adsorbed on the calcined gallium-modified sample is also shown in Fig. 8. It is very similar to the spectrum of CO adsorbed by the nonmodified HZSM-5. In agreement with DRIFT spectra of OH groups in Fig. 2, somewhat lower intensities of the bands of adsorbed CO with the maxima at 2168 and 2120 cm^{-1} also indicate the minor substitution of acidic protons by modifying gallium ions, whereas the lower intensity of the band at 2195 cm^{-1} is evidence of the suppression of dealumination. This conclusion is also supported by the lower intensity of the high-frequency band at 2223 cm^{-1} , whereas a slight negative shift ($\sim 5 \text{ cm}^{-1}$) of its maximum may indicate substitution of some protons by GaO^+ species instead of AlO^+ oxo-ions.

When the gallium-modified samples were reduced in hydrogen at 773 K, we observed that the bands from carbon monoxide adsorbed by hydroxyl groups at 2120 and 2168 cm^{-1} did not appear after CO exposure at room temperature (Fig. 9). This coheres with the complete substitution of acidic protons by reduced Ga^+ ions as inferred from the absence of the band related to bridging hydroxyl groups at 3610 cm^{-1} in Fig. 2. Concomitantly, reduction results in a much higher intensity of the band around 2188 cm^{-1} and also strongly decreased the intensity of the band with a maximum at 2218 cm^{-1} when compared to the oxidized sample. This is also most likely related to the transformation of the oxidized species into reduced gallium ions. A band around 2218 cm^{-1} has been previously assigned to edge ions in Ga_2O_3 [18], but could be also associated with cationic

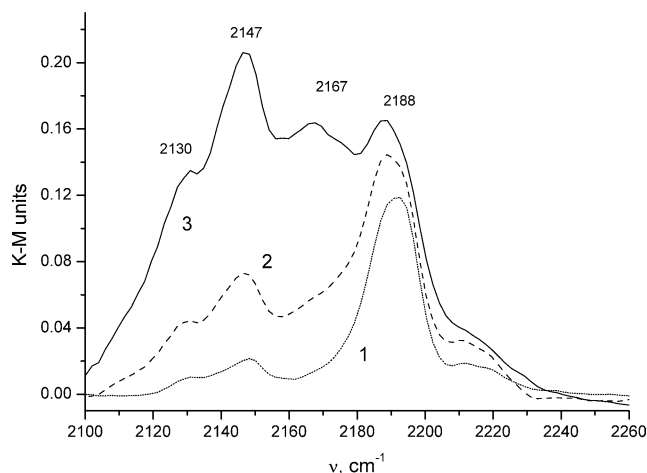
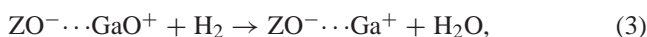


Fig. 10. DRIFT spectra of CO adsorbed at pressures of (1) 10, (2) 50, and (3) 200 Torr by Ga/HZSM-5 after reduction in hydrogen at 773 K for 5 h (DRIFT spectra taken at room temperature).

$(\text{GaO})^+$ oxo-ions. Their reduction by hydrogen may result in formation of the low-coordinated univalent gallium or in different gallium hydrides:



Indeed, as follows from Figs. 5–7, DRIFTS measurements upon reduction indicate the formation of at least two different hydrides while according to Fig. 9, CO adsorption at higher pressures indicated the existence of several different sites connected with reduced gallium species.

Spectrum 1 in Fig. 10 corresponding to room temperature CO adsorption at the lowest pressure of 10 Torr is similar to that presented in Fig. 9. However, upon increasing CO pressures, the intensities of the weak bands at 2130 and 2147 cm^{-1} strongly increased and at the highest pressure of 200 Torr the band around 2147 cm^{-1} predominates. Simultaneously, a new band appears at 2167 cm^{-1} that was invisible at the low CO pressure. In contrast, the intensity of the band with the maximum at 2188 cm^{-1} increased at higher CO pressures to a much smaller extent. Thus, as follows from spectrum 3 in Fig. 3, instead of only one main band of CO adsorption by the reduced sample at the lowest pressure of 10 Torr, the DRIFT spectrum of CO adsorption at the highest pressure exhibits four different bands connected with reduced gallium species. The important argument for their assignment is provided by the DRIFT spectrum of CO adsorbed by the reduced sample that was subsequently oxidized by N_2O at 673 K and evacuated at 673 K (spectrum 2 in Fig. 11). This oxidative treatment destroyed the bands of adsorbed CO with maxima around 2130, 2147, and 2188 cm^{-1} . Therefore, these bands are definitely connected with reduced gallium species, presumably with CO adsorption by the low-coordinated Ga^+ ions. In contrast, upon oxidation the band of adsorbed CO with the maximum

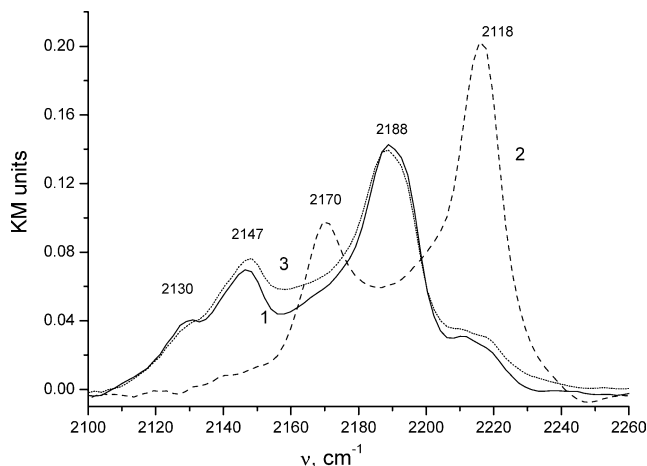


Fig. 11. DRIFT spectra of CO adsorbed by Ga/HZSM-5 at a pressure 50 Torr after (1) reduction in hydrogen at 773 K for 5 h, (2) oxidation in N_2O at 673 K, and (3) subsequent reduction of the oxidized sample in hydrogen (DRIFT spectra taken at room temperature).

at 2167 cm^{-1} that has been ascribed to adsorption of carbon monoxide by hydroxyl groups increased in intensity. Simultaneously, intensities of the DRIFT bands from hydroxyl groups in the OH stretching region also increased. Therefore, this band of adsorbed carbon monoxide most likely belongs to CO adsorption by protons resulting from oxidation of gallium dihydrides:



Thus, for the oxidized samples we have two different kinds of gallium species: the GaO^+ oxo-ions with a stretching frequency of adsorbed CO equal to 2218 cm^{-1} and $(HGaOH)^+$ species with a CO stretching frequency of $2167\text{--}2170\text{ cm}^{-1}$. It also follows from Fig. 11 that the subsequent reduction and oxidation of gallium species is reversible.

Finally, in order to discriminate the low-coordinated Ga^+ ions from the gallium hydrides, we studied CO adsorption on the reduced gallium-modified sample that was evacuated after reduction in hydrogen at 823 K or slowly cooled to room temperature in hydrogen. The corresponding DRIFT spectra are shown in Fig. 12. Clearly, the intensity of the CO stretching bands is lower after cooling in hydrogen due to the screening of univalent gallium cations by the resulting hydrides.

4. Discussion

The present study confirms previous findings that reduction of Ga/ZSM-5 zeolite in hydrogen results in the substitution of acid protons by cationic Ga species. Our results also show that replacement of acidic protons by reaction with Ga_2O is easier and more complete than by the species resulting from dealumination. The modification of HZSM-5 by gallium suppressed dealumination that is thought to result in the positively charged $(AlO)^+$ oxo-ions according to Eq. (2).

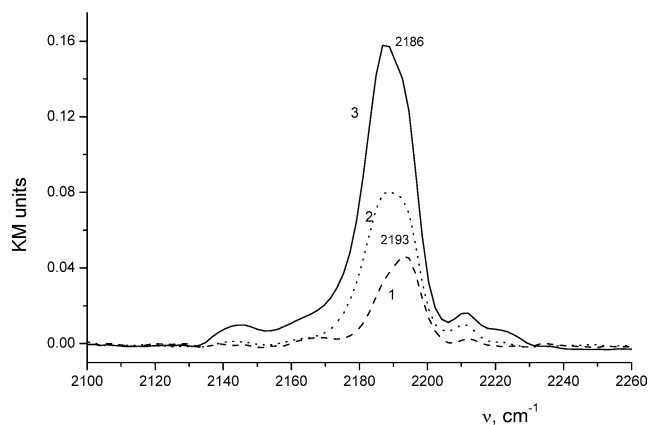
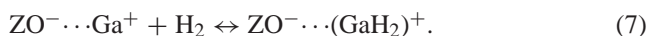


Fig. 12. DRIFT spectrum of CO adsorbed at room temperature at the pressure of 10 Torr by GaZSM-5 that was preliminary reduced in H_2 at 773 K and evacuated at 823 K.

Suppression of dealumination for the gallium-modified samples is then connected with compensation of the negatively charged aluminum-centered oxygen tetrahedra by gallium oxo-ions instead of $(AlO)^+$ species. Another point worthy of note is that for a sample with a Ga/Al atomic ratio of unity all acid protons are replaced by gallium. This means that the distantly separated acidic protons must have been substituted. Therefore, it is very likely that the cationic gallium species possess a single positive electric charge since neutralization of distantly separated negative charges by multivalent cations is difficult to imagine.

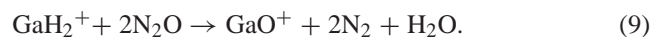
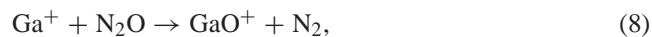
After evacuation at high temperature the univalent cationic gallium species exhibit DRIFT bands of weakly adsorbed CO with stretching frequencies of 2130 and 2147 cm^{-1} . Furthermore, hydrogen adsorption by such reduced Ga^+ species results in the formation of cationic gallium dihydride species [7]:



The presently observed stretching frequencies for these hydrides ($2040\text{--}2060\text{ cm}^{-1}$) are somewhat higher than the value reported for hydrides on reduced silica-supported gallium oxide, i.e., $\sim 2020\text{ cm}^{-1}$ [17]. The latter hydrides were ascribed to $Ga^{\delta+}\text{--}H$ species without indication of the valence state of gallium. This might explain the small difference in the stretching frequencies.

The formation of gallium hydrides by adsorption of hydrogen on univalent gallium cations is reversible by evacuation at 773 K. This observation tallies with the desorption peak of hydrogen from GaZSM-5 at about 770 K reported earlier in Ref. [19]. On the other hand, the formation of gallium hydrides is an activated process because they are observed only at temperatures in excess of 573 K. This explains the higher amount of hydrides after slow cooling to room temperature as compared to a fast cooling procedure (Fig. 7). Fig. 12 shows that the formation of these hydrides prevents subsequent adsorption of carbon monoxide. This results in a much lower intensity of the bands of adsorbed CO around 2188 cm^{-1} .

Oxidative treatment of univalent gallium or gallium dihydrides with N₂O results in their oxidation into singly positively charged oxo-ions:



When reaction (9) applies, GaHOH⁺ species could be also formed in parallel according to Eq. (6). CO adsorption by GaO⁺ oxo-ions is associated with a stretching band at 2218 cm⁻¹ whereas adsorption by GaHOH⁺ ions leads to a band at 2170 cm⁻¹. One more band of adsorbed CO with a stretching frequency of 2188 cm⁻¹ most likely belongs to CO adsorption by low-coordinated gallium ions on the surface of the small gallium oxide particles that are formed upon modification of the parent hydrogen form with gallium concomitant with substitution by gallium of the acidic hydroxyl groups.

As this study provides some new insight into the chemistry of zeolite-occluded gallium, we will compare our interpretation to that proposed in other studies of Ga/ZSM-5. The most extensive in situ study of the state of gallium in the working GaZSM-5 catalyst for propane aromatization has been carried out in Refs. [2–4,7]. The authors interpreted X-ray absorption data in the following way. Reduction of octahedrally coordinated Ga³⁺ ions leads to the formation of reduced univalent Ga⁺ ions or Ga metal. Subsequent cooling in a hydrogen atmosphere to room temperature resulted in the formation of Ga³⁺ ions either by oxidation of the reduced species by traces of water present in the hydrogen flow or due to interaction with the zeolite framework oxygen. Similar redox changes of gallium were observed in the present work. However, we directly observed the formation of gallium hydrides by DRIFT measurements. Moreover, DRIFT spectra of adsorbed CO gave insight into coordinatively unsaturated gallium species. Reduction of gallium at high temperatures leads to the formation of low-coordinated Ga⁺ ions and to dihydride species to some extent. The amount of the latter strongly increased after slow cooling of the gallium-modified samples to room temperature in hydrogen. Therefore, we propose that oxidation of the univalent gallium ions does not proceed via traces of water but by the oxidative addition of hydrogen giving trivalent gallium hydride species.

5. Conclusions

All acid protons can be replaced by univalent Ga species upon reduction at 773 K of Ga/HZSM-5. The replacement of protons by Ga suppresses dealumination to a large extent.

Evacuation of a reduced sample at 773 K leads to coordinatively unsaturated Ga⁺ ions. These ions can be reversibly oxidized by nitrous oxide at 673 K. On the other hand, cooling of a reduced sample in molecular hydrogen leads to the formation of gallium hydride species that compensate the negative framework charge. The latter species are quite stable and can only be completely decomposed at relatively high temperature (773 K). Carbon monoxide probe DRIFT spectroscopy further allows the identification of the various Ga species in the micropore space of ZSM-5 zeolite. These results suggest that the earlier observed oxidation of reduced Ga/HZSM-5 can also be related to the oxidative addition of hydrogen.

Acknowledgments

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