Available online at www.sciencedirect.com
SCIENCE DIRECT®

Journal of Catalysis 239 (2006) 478–485

JOURNAL OF CATALYSIS

www.elsevier.com/locate/jcat

Characterization and reactivity of Ga^+ and GaO^+ cations in zeolite ZSM-5

N. Rane [a], A.R. Overweg [b], V.B. Kazansky [c], R.A. van Santen [a], E.J.M. Hensen [a,*]

[a] Schuit Institute of Catalysis, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands
[b] Interfacultair Reactor Institute, Delft University of Technology, Mekelweg 15, 2629 JB, Delft, The Netherlands
[c] Zelinsky Institute of Organic Chemistry, Leninsky Prospect 47, Moscow, Russia

Received 2 September 2005; revised 6 March 2006; accepted 6 March 2006

Abstract

The reduction of $Ga(CH_3)_3$/ZSM-5 was closely followed by Fourier transform infrared spectroscopy and Ga K-edge X-ray absorption near-edge spectroscopy. Chemical vapor deposition of trimethylgallium on HZSM-5 (TMG/ZSM-5) resulted in the replacement of nearly all Brønsted acid protons by dimethylgallium species. Removal of the methyl ligands from the cationic Ga clusters gave charge-compensating Ga^+ and $GaH_2{}^+$ species. At high temperatures and in the absence of hydrogen, the Ga^+ species were the most stable, although decomposition of the $GaH_2{}^+$ species was very slow. Ga^+ ions can be oxidized by nitrous oxide at low temperature (473 K), resulting in the formation of gallyl (GaO^+) cations. A detailed comparison of the reactivity of Brønsted acid protons (HZSM-5) and Ga^+ ions (reduced TMG/ZSM-5) in propane dehydrogenation showed that the former converted propane via protolytic cracking with methane, ethane, and propene as hydrocarbon products, whereas monovalent Ga^+ ions produced propene almost exclusively. The reaction data suggest that propane was converted over Ga^+ cations but not over $GaH_2{}^+$ cations. The initial rate of propane dehydrogenation was highest for GaO^+ ions, although rapid deactivation was observed, due to the higher barrier for regeneration of GaO^+ ions than for formation of less active Ga^+ ions.

Keywords: Trimethylgallium; HZSM-5; Chemical vapor deposition; Brønsted acid sites; Dehydrogenation; Reduction

1. Introduction

Alkanes can be converted to alkenes and aromatics over promoted medium-pore zeolites. The presence of cations such as Ga and Zn in the micropores of ZSM-5 increases the rate of dehydrogenation reactions of alkanes and the subsequent aromatization of unsaturated oligomers into aromatics at the expense of monomolecular and bimolecular cracking reactions [1]. This shift favorably influences the selectivity to alkenes and aromatics over undesired paraffins, such as methane and ethane. Brønsted acid protons also play a role in the formation of conjugated oligomers and possibly in their subsequent aromatization. Gallium has an advantage over zinc of being less volatile under practical reducing conditions at high temperatures [2]. A commercial application of Ga/ZSM-5 is the production of aromatics (Cyclar process) [3,4].

Determining the precise role of Ga in these reaction steps has proven difficult [5–14], mainly because the nature of the active Ga species remains unclear. Gallium may be present as gallium oxide, in aggregated form on the external zeolite surface or as small particles in the zeolite micropore space, or in cationic form as oxidic GaO^+ or reduced Ga^+ or $GaH_2{}^+$ species. Most preparation methods (e.g., ion exchange, impregnation, physical admixture, chemical vapor deposition of $GaCl_3$ [5,7,8,15,16]) often lead to a variety of species. Aqueous ion exchange results mainly in gallium oxide particles on the external surface because of the large size of the hydrated Ga^{3+} cation; washing of gallium-containing zeolites prepared by vapor deposition of $GaCl_3$ also does not lead to a high Ga dispersion. Reduction in molecular hydrogen at high temperature results in highly mobile gallium oxide, presumably Ga_2O, leading to a protolysis reaction with the Brønsted acid protons to give reduced cationic species. Nevertheless, the release of water at elevated temperatures damages the zeolite framework to some extent [17,18]. The difficulties in characterizing the active species are amplified taking into account the high reactivity of reduced Ga

---

[*] Corresponding author. Fax: +31 40 2455054.
E-mail address: e.j.m.hensen@tue.nl (E.J.M. Hensen).

0021-9517/$ – see front matter
doi:10.1016/j.jcat.2006.03.004

species. For instance, a detailed in situ X-ray absorption study by Iglesia et al. [6] revealed the oxidation of reduced Ga species in zeolites (Ga^+) to Ga^{3+} ions on cooling in hydrogen. This oxidation was believed to result from the enhanced interaction of Ga cations with zeolite framework oxygen atoms.

The present study aimed to compare the catalytic activities of various well-defined charge-compensating Ga species (Ga^+, $GaH_2{}^+$, and GaO^+) encaged in the micropore space of HZSM-5 zeolite. We recently addressed a completely anhydrous route for the preparation of Ga/ZSM-5 consisting of chemical vapor deposition of trimethylgallium (TMG) with subsequent removal of the methyl groups by treatment with hydrogen or oxygen [17–20]. The reductive route is preferred, resulting in better gallium dispersion, because oxidation of the methyl groups leads to water formation and hydrolysis of cationic Ga species. Moreover, clear indications of steaming effects due to produced water, leading to partial dealumination of the zeolite lattice, were found [17]. The route of chemisorbed alkylgallium species reduction with methane release causes less damage to the zeolite framework, because no water is formed [18]. The chemical nature of reduced and oxidized species was followed by Fourier transform infrared spectroscopy and X-ray absorption near-edge spectroscopy (XANES) spectroscopy at the Ga K-edge. Infrared spectroscopy of adsorbed carbon monoxide was used in an attempt to probe the various Ga species. The reactivity of these cationic Ga species in propane dehydrogenation was studied. We discuss the critical role of the various cationic Ga species for the reaction mechanism of alkane dehydrogenation.

2. Experimental

2.1. Preparation of materials

NH_4ZSM-5 (Akzo Nobel, $Si/Al = 19.4$) was calcined in a mixture of 20 vol% oxygen in nitrogen at a flow rate of 100 N ml/min while heating to 823 K at a rate of 2 K/min, followed by an isothermal period of 4 h to obtain HZSM-5. TMG/ZSM-5 was prepared by chemical vapor deposition of TMG (Strem Chemicals, purity >99%) on dehydrated HZSM-5. To a glass vessel containing dehydrated HZSM-5, 1 ml of TMG was added in an Ar-flushed glove box. After 24 h, the resulting material was evacuated for 2 h to remove excess TMG. The material was kept in argon atmosphere before XANES characterization and catalytic activity measurements. The resulting Ga/Al ratio was close to 1.2.

2.2. Characterization

Infrared spectra were recorded on a Bruker IFS113v Fourier transform infrared spectrometer with a DTGS detector at a resolution of 2 cm^{-1}. HZSM-5 zeolite was pressed into a self-supporting wafer of about 12 mg and placed in a controlled-environment transmission cell (KRS-5 windows). Before spectra were recorded, the zeolite was dehydrated in a flow of oxygen while heating from room temperature to 823 K at a rate of 5 K/min (isothermal period of 15 min at 373 K). After an isothermal period of 1 h at 823 K, the sample was cooled to room temperature in vacuum.

The dehydrated zeolite was exposed to TMG at a total pressure of 40 mbar for a prolonged period. After extensive evacuation, the material was reduced in a mixture of 20 vol% hydrogen in nitrogen at a flow rate of 5 ml/min, followed by heating to 823 K at a rate of 5 K/min. The resulting material is denoted as TMG/ZSM-5(red). TMG/ZSM-5(red) was further oxidized by exposing the evacuated sample to 50 mbar nitrous oxide at various temperatures. The resulting catalysts are denoted as TMG/ZSM-5 (red, ox, T), where T refers to the oxidation temperature. Infrared spectra of adsorbed CO were recorded after cooling the cell with liquid nitrogen. In this way, a constant temperature of 90 K could be maintained. Infrared spectra were measured as a function of CO pressure in a decreasing manner from 40 to 0.05 mbar.

Ga K-edge X-ray absorption spectroscopy measurements were performed at beamline 17C of the European Synchrotron Radiation facility in Grenoble (ESRF, France). The electron energy and ring current were 2.0 GeV and 200 mA. XANES spectra were recorded with energy steps of 0.5 eV in the XANES region. An amount of catalyst was pressed into a self-supporting wafer calculated to have an absorbance μx of 2.5 and placed in a controlled-environment transmission cell. TMG/ZSM-5(red) was obtained by reduction of TMG/ZSM-5 in a flow of 100 ml/min (20 vol% hydrogen in nitrogen) at a heating rate of 4 K/min to 793 K. TMG/ZSM-5(red) was further cooled in a flow of 100 ml/min (20 vol% hydrogen in nitrogen) at a rate of 4 K/min to 423 K. During these steps, near-edge spectra were recorded at regular intervals. Alternatively, TMG/ZSM-5 (red) was also cooled in inert atmosphere in a flow of 100 ml/min nitrogen at a rate of 4 K/min. Thereafter, TMG/ZSM-5(red, ox) was obtained by exposuring TMG/ZSM-5(red) to a mixture of 30 ml/min of N_2O and 10 ml/min of nitrogen for 30 min at 673 and 473 K.

2.3. Catalytic measurements

Propane conversion was carried out in an atmospheric-pressure single-pass quartz microflow reactor at 823 K. The feed mixture was delivered by thermal mass flow controllers and consisted of 5 vol% C_3H_8 in He at a total flow rate of 100 N ml/min. The weight hourly space velocity was kept at 11.7 h^{-1}. Gas-phase products were collected in a heated 16-loop storage system and analyzed offline by a Shimadzu GC-17A gas chromatograph equipped with a PLOT KCl/Al_2O_3 column and a flame ionization detector.

TMG/ZSM-5 was loaded into a closeable quartz reactor in an Ar-flushed glove box, to avoid contact with air. Before the reaction, TMG/ZSM-5 was reduced in a hydrogen flow of 100 ml/min while heating to 823 K at a rate of 5 K/min, followed by an isothermal period of 2 h [TMG/ZSM-5(red)]. Another sample was pretreated in the same manner as TMG/ZSM-5(red) and also kept in He for 1 h at 823 K. This sample is denoted as TMG/ZSM-5(red, He). Another catalyst was prepared by cooling TMG/ZSM-5(red) to 473 K in He, followed by exposure to a flow of 1 vol% N_2O in He of 100 ml/min for

1 h. Finally, the catalyst was brought to reaction temperature (823 K) in flowing He. This material is denoted as TMG/ZSM-5(red, ox, 473 K). For comparison, the proton form of ZSM-5 was brought to the reaction temperature in a flow of 20 vol% O_2 in He (HZSM-5).

3. Results and discussion

3.1. Preparation of TMG/ZSM-5(red)

The exposure of parent ZSM-5 zeolite to TMG followed by reduction results in the quantitative substitution of the Brønsted acid sites of the zeolite [20]. The following reactions were proposed to occur at the cationic positions of the zeolite [18,20]:

$$ZO^{-}\ldots H^{+} + Ga(CH_3)_3 \rightarrow ZO^{-}\ldots\left[Ga(CH_3)_2\right]^{+} + CH_4, \quad (1)$$

$$ZO^{-}\ldots\left[Ga(CH_3)_2\right]^{+} + H_2 \rightarrow ZO^{-}\ldots Ga^{+} + 2CH_4, \quad (2)$$

and

$$ZO^{-}\ldots\left[Ga(CH_3)_2\right]^{+} + 2H_2 \rightarrow ZO^{-}\ldots[GaH_2]^{+} + 2CH_4. \quad (3)$$

In contrast to the incomplete exchange in acidic mordenite, attributed to blockage of the one-dimensional pores [19], the higher dimensionality of the MFI pore system leads to complete replacement of the Brønsted acid sites [20]. Cationic Ga species compensate the negative framework charge of the ZSM-5 zeolite. Previous density functional theory calculations have shown that the cationic exchange site of zeolites is the preferred position of Ga clusters [19]. Given the high silica content of the parent ZSM-5 zeolite, we assume that most of the Ga species are present as mononuclear Ga species. Gallium may thus compensate the framework charge as monovalent Ga^{+} ions or as trivalent gallium hydride species. Whereas the compensation of the negative framework charge by monovalent gallium has been proposed earlier [8], only recently has evidence of gallium hydrides been found by a detailed diffuse reflectance infrared spectroscopic study [18]. Kazansky et al. [18] found that hydrogen oxidatively adds to monovalent Ga^{+} ions in reduced Ga/HZSM-5 prepared by incipient wetness impregnation. Such gallium dihydride species form at temperatures below 723 K in hydrogen atmosphere. At higher temperatures, monovalent Ga^{+} species are dominant in the absence of hydrogen. Gallium hydride species are relatively stable and decompose only above 723 K. They are completely eliminated only in vacuum at such temperatures [18]. In agreement with this finding, quantum chemical calculations of Bell et al. [21] predicted a high activation barrier for the desorption of hydrogen from ${GaH_2}^{+}$ ($E_{act} = 74$ kcal/mol at 800 K),

$$ZO^{-}\ldots[GaH_2]^{+} \leftrightarrows ZO^{-}\ldots Ga^{+} + H_2. \quad (4)$$

Thus it is likely that $[GaH_2]^{+}$ species formed via Eq. (3) decompose only partially in a reductive hydrogen atmosphere at elevated temperatures.

The complete replacement of Brønsted acid sites by cationic Ga species is confirmed by the infrared spectra of adsorbed CO in Fig. 1. In line with our earlier report [18], two prominent bands are observed at 2139 and 2147 cm^{-1}, which are assigned to physically adsorbed CO in the zeolite micropores [22] and CO coordinating to monovalent Ga^{+} species [18], respectively. Monovalent Ga^{+} species are thought to replace the charge-compensating protons of the original HZSM-5 zeolite, as corroborated by the absence of the band at 3610 cm^{-1}. In accordance with this view, the band due to carbon monoxide coordinating to the bridging hydroxyl groups is also not present at 2173 cm^{-1} [23]. The band at 2167 cm^{-1} most likely relates to CO coordinating to a small fraction of $[Ga^{3+}(H^{-})(OH^{-})]^{+}$ species [18]. These species are formed by hydration of Ga^{+} species via residual water molecules according to

$$ZO^{-}\ldots Ga^{+} + H_2O \rightarrow ZO^{-}\ldots\left[Ga(H^{-})(OH^{-})\right]^{+}. \quad (5)$$

The band around 3680 cm^{-1} in the hydroxyl region relates to Ga–OH species [24]. Its relative weakness suggests that the number of such species is relatively low.

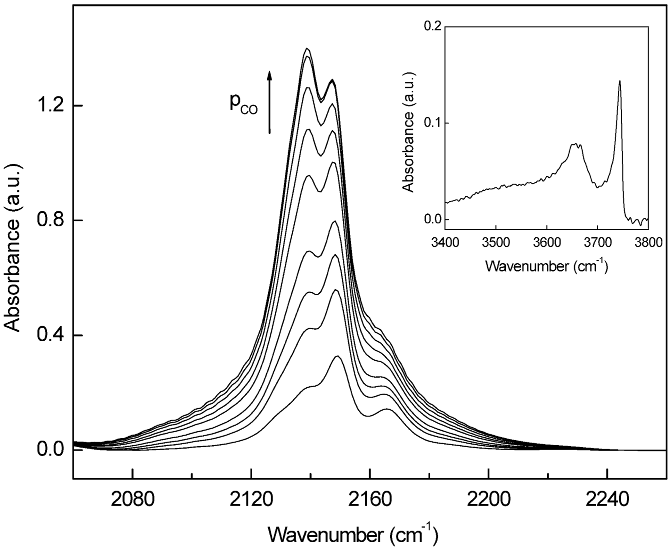

Fig. 1. FTIR spectra of TMG/ZSM-5(red) cooled from 823 K in vacuum at liquid nitrogen temperature after CO absorption at pressures of 40, 20, 10, 5, 2, 1, 0.5, and 0.05 mbar. The spectra were recorded from high to low CO pressure. The inset shows the FTIR spectrum of the hydroxyl region of TMG/ZSM-5(red) at room temperature.

To confirm the oxidation state of Ga species, in situ XANES at the Ga K-edge was performed during the reduction of TMG/ZSM-5. To protect the sample from exposure to moisture or oxygen, TMG/ZSM-5 prepared at the home laboratory was transported in a glass ampoule under protective atmosphere to the synchrotron facility. The sample was transferred to a controlled-environment transmission cell in an Ar-flushed glove box. Fig. 2 displays the evolution of the XANES spectra during reduction of TMG/ZSM-5 from room temperature to 793 K in a mixture of nitrogen and hydrogen. At low temperatures, an edge position of about 10,373 eV is observed, corresponding to dimethylgallium species [17]. Pronounced changes of the XANES region are observed between 573 and 673 K. The main absorption feature shifts to higher energies, whereas a shoulder at lower energy becomes visible at 673 K. A further increase in reduction temperature leads to a strong growth of the feature with a maximum at 10,371.5 eV. This latter edge is attributed to monovalent Ga^{+} species [6,17], which exhibit

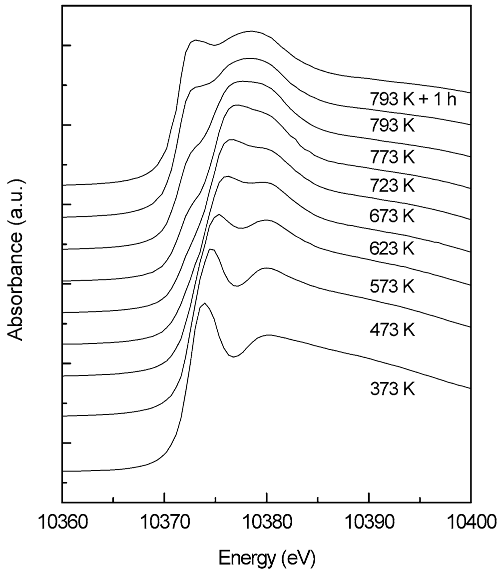

Fig. 2. Ga K-edge XANES spectra of TMG/ZSM-5 during reduction from 373 to 793 K.

a somewhat higher absorption maximum than Ga metal [6]. The data suggest that between 573 and 673 K, the methyl ligands of the dimethylgallium species are removed and $[GaH_2]^+$ species are mainly formed, with a higher absorption maximum.

At higher temperatures, the spectra contain an increasingly larger contribution of Ga^+ species that are most likely formed by partial decomposition of the gallium dihydride species. The removal of hydrogen is indeed a slow process [18] and requires evacuation or purging in He for a prolonged period at high temperature. Hence, we surmise that the XANES spectrum after reduction at 793 K for 1 h points to a mixture of $GaH_2{}^+$ and Ga^+ species. Meitzner et al. [6] argued that the strong interaction of Ga^+ with the framework oxygen atoms stabilize these cationic species against further reduction to Ga^0.

Fig. 3 displays the XANES spectra for TMG/ZSM-5(red) cooled from 793 K in reduction atmosphere. Clearly, the maximum belonging to Ga^+ species slowly vanishes with decreasing temperature, concomitant with an increase of the feature around 10,377 eV. The Ga K edge shifts to 10,374.5 eV. We attribute these changes to the oxidative addition of H_2 to Ga^+ to form $GaH_2{}^+$ (Ga^{3+}) species by the reverse reaction of Eq. (4). This finding is in line with our recent infrared data providing evidence of the addition of oxidative hydrogen to Ga^+ [18]. An alternative explanation for this oxidation was put forward by Meitzner et al. [6], who attributed the higher-energy edge shift to an increased interaction of the Ga species with the zeolite framework oxygen atoms.

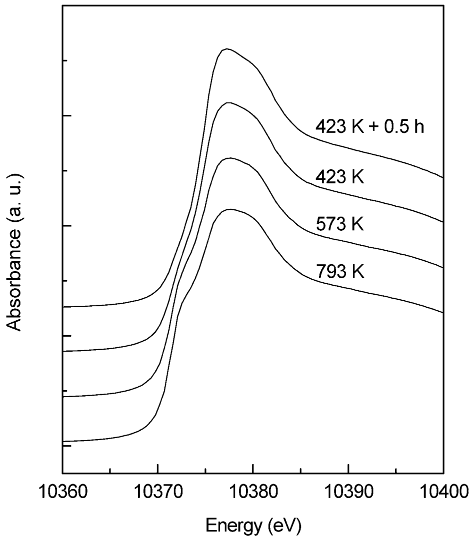

Fig. 3. Ga K-edge XANES spectra of TMG/ZSM-5(red) during reduction and cooling from 793 to 423 K.

3.2. Oxidation of TMG/ZSM-5(red)

Reduced samples were oxidized by nitrous oxide to prevent extensive oxidation, leading to the removal of cationic Ga species from the zeolite exchange sites [20]. The CO absorption spectra for TMG/ZSM-5(red, ox, 473) and TMG/ZSM-5(red, ox, 673) are shown in Fig. 4. The infrared spectrum of TMG/ZSM-5(red, ox, 473) gives no evidence of the regeneration of Brønsted acid protons. Kazansky et al. [20] have shown by volumetric titration that the ratio of converted nitrous ox-

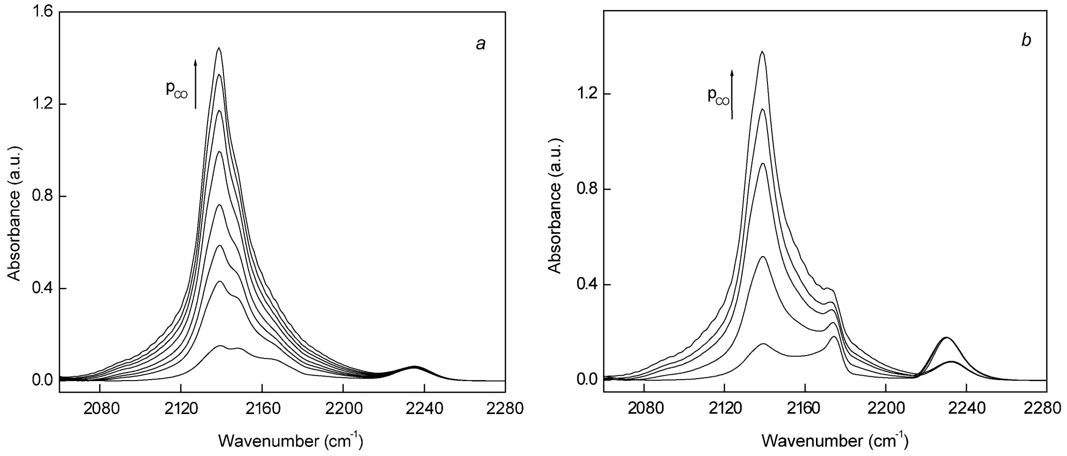

Fig. 4. FTIR spectra taken at liquid nitrogen temperature after CO adsorption of (a) TMG/ZSM-5(red, ox, 473) and (b) TMG/ZSM-5(red, ox, 673).

ide and Ga atoms is close to unity. These observations can be explained by the oxidation of univalent Ga^+ ions via

$$ZO^- \ldots Ga^+ + N_2O \rightarrow ZO^- \ldots [GaO]^+ + N_2. \qquad (6)$$

In the infrared spectrum of adsorbed carbon monoxide on TMG/ZSM-5(red, ox, 473), the band due to CO adsorbed on univalent Ga^+ species around 2147 cm^{-1} is substantially reduced. A small portion of Ga^+ species persists after low-temperature oxidation. The presence of a band at 2167 cm^{-1} is related to CO on extra-framework GaOH species [18]. We surmise that these GaOH species derive from oxidation of some remaining GaH_2^+ species according to

$$ZO^- \ldots GaH_2^+ + N_2O \rightarrow ZO^- \ldots \left[Ga(H^-)(OH^-)\right]^+ + N_2. \qquad (7)$$

The low intensity of this band suggests that the extent of Eq. (7) is small. When the temperature of oxidation is increased to 573 K, regeneration of bridging hydroxyl groups occurs, as demonstrated by the reappearance of the band around 3610 cm^{-1} [20]. In addition, the band of gallium hydroxide species increases somewhat. The regeneration of Brønsted acid protons is more pronounced in TMG/ZSM-5(red, ox, 673). Concomitantly, the band due to Ga–OH species decreases after oxidation at 673 K [20]. Tentatively, we attribute the regeneration of Brønsted acidity to the following reaction:

$$\begin{aligned} &2ZO^- \ldots \left[Ga(H^-)(OH^-)\right]^+ + 2N_2O \\ &\quad \rightarrow 2ZO^- \ldots H^+ + Ga_2O_3 + 2N_2 + H_2O. \end{aligned} \qquad (8)$$

The more heterogeneous Ga speciation after high-temperature oxidation is confirmed by the infrared spectrum of adsorbed CO in Fig. 4b. Although the band of CO adsorbed on monovalent Ga^+ species has completely vanished, the spectrum contains vibrational bands of CO adsorbed to Brønsted acid sites (2173 cm^{-1}) and exposed Ga^{3+} sites in gallium oxide microphases (2235 cm^{-1}) [22]. A small amount of the latter species is also present in TMG/ZSM-5(red, ox, 473).

No evidence was found for carbon monoxide absorption to charge-compensating GaO^+ species; therefore, it appears that these species are not amenable to experimental observation by infrared spectroscopy of adsorbed CO. This finding is in line with recent quantum chemical calculations of interaction of CO with various gallium-oxo clusters showing a very weak interaction between CO and GaO^+ species [25]. Fig. 5 shows the XANES spectra on oxidation of reduced TMG/ZSM-5 by nitrous oxide at 473 and 673 K. Clearly, there is a pronounced shift of the Ga K-edge to higher binding energies, due to oxidation of the Ga^+ to Ga^{3+} cations.

In summary, univalent Ga^+ species in TMG/ZSM-5(red) can be oxidized to charge-compensating GaO^+ species by nitrous oxide at 473 K. Oxidation at higher temperatures leads to the regeneration of a small portion of Brønsted acid protons due to further oxidation of $[Ga(H^-)(OH^-)]^+$ species arising from oxidation of a small amount of GaH_2^+ remaining from the reductive pretreatment.

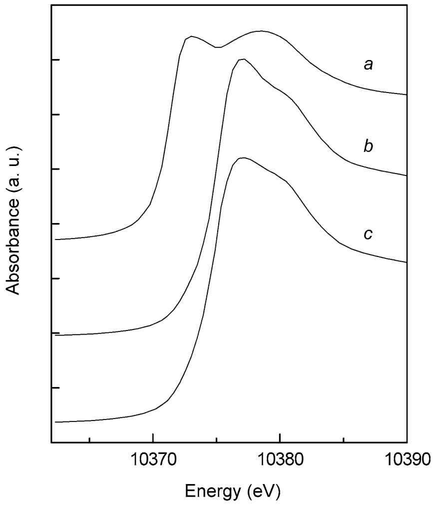

Fig. 5. Ga K-edge XANES spectra of (a) TMG/ZSM-5(red) at 793 K, (b) TMG/ZSM-5(red, ox, 673), and (c) TMG/ZSM-5(red, ox, 473).

3.3. Catalytic measurements

The conversion of propane as a function of the reaction time for HZSM-5, TMG/ZSM-5(red), TMG/ZSM-5(red, He), and TMG/ZSM-5(red, ox) is shown in Fig. 6. The corresponding selectivities are listed in Table 1. The conversion of propane over the Brønsted acid protons of HZSM-5 at 823 K results primarily in the formation of methane and ethene in equal amounts, along with a small amount of propene. No higher-boiling hydrocarbons are observed in the product mixture. The conversion remains nearly constant, indicating that no strong coking deactivation occurs under the given reaction conditions. However, the mass balance is not closed, pointing to the production of some coking products. The composition of the product mixture corresponds to that of protolytic cracking, which has been proposed to proceed via a pentacoordinated carbonium ion transition state [26].

TMG/ZSM-5(red) exhibits a very different catalytic behavior. Whereas the initial conversion is relatively low, it increases with reaction time and remains constant at prolonged reaction times. Propene is the main hydrocarbon product identified in the reactor effluent, with selectivity close to 80%; minor amounts of methane and ethane are also found. Despite the observation that the carbon balance is not totally closed, which points to coke formation, catalyst deactivation is again limited. Deactivation might be partially masked by the increase in conversion with reaction time. The very different product compositions of HZSM-5 and TMG/ZSM-5(red) derive from the difference in charge-compensating species in HZSM-5 (Brønsted acid protons) and TMG/ZSM-5(red) (reduced Ga species).

An important question relates to the nature of the active species for alkane activation. Kazansky et al. [20,27] have shown that dissociation of ethane may occur over Ga^+ species in reduced Ga/HZSM-5, leading to grafted ethyl and hydride species according to

$$ZO^- \ldots Ga^+ + C_2H_6 \rightarrow ZO^- \ldots \left[Ga(H^-)(C_2H_5^-)\right]^+. \qquad (9)$$

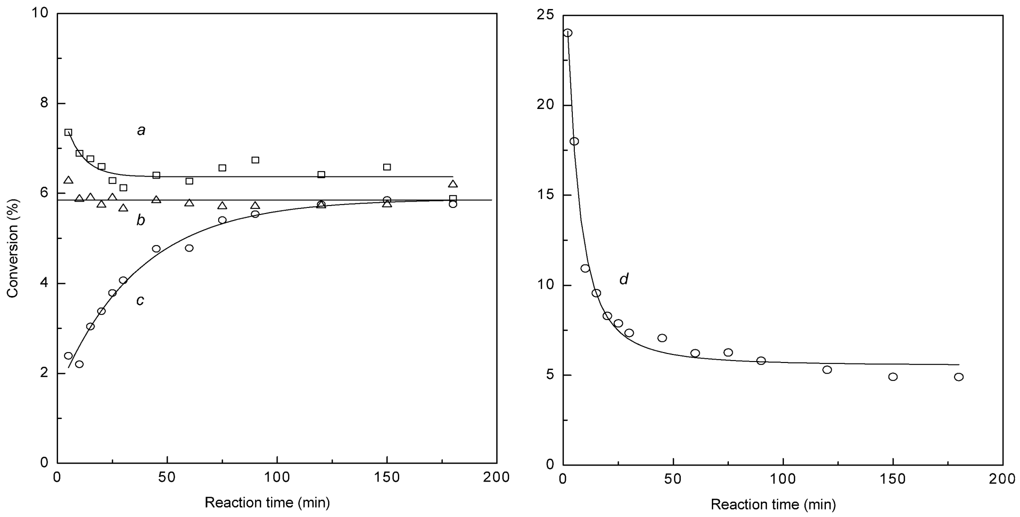

Fig. 6. Conversion of propane as a function of reaction time at 823 K (WHSV = 11.7 h^{-1}) over (left): (squares) HZSM-5, (circles) TMG/ZSM-5(red), (triangles) TMG/ZSM-5(red, He) and over (right) (circles) TMG/ZSM-5(red, ox, 473).

Table 1
Propane dehydrogenation over HZSM-5, TMG/ZSM-5(red), and TMG/ZSM-5(red, He) at 823 K (WHSV = 11.7 h^{-1}, $p = 1$ atm)

TOS (min)	Conversion (%)	Selectivity (%)			
		CH_4	C_2H_4	C_3H_6	Coke[a]
HZSM-5					
5	7.3	37	36	13	14
30	6.1	39	38	15	8
90	6.7	37	37	16	10
150	6.5	39	38	16	7
TMG/ZSM-5(red)					
5	2.3	3	3	83	11
30	4.1	3	3	76	18
90	5.5	3	4	76	17
150	5.8	3	5	76	16
TMG/ZSM-5(red, He)					
5	6.2	5	9	85	1
30	5.6	5	8	86	1
90	5.7	4	7	88	1
150	5.7	4	7	82	7

[a] Selectivity to coke is defined as 100% − $S_{\text{methane}} - S_{\text{ethene}} - S_{\text{propene}}$.

The resulting grafted alkyl species were found to decompose to yield ethene. Earlier quantum-chemical calculations have suggested that alkane activation over GaH_2^+ species is preferred over GaO^+ species [28]. However, Ga^+ species were not considered in that previous study [28] or in other recent theoretical works [29,30].

The experimental observation of increasing propane conversion with reaction time for TMG/ZSM-5(red) is in favor of Ga^+ cations as the active species. Before reaction, TMG/ZSM-5(red) was kept in molecular hydrogen at 823 K. Under these conditions, a significant part of the charge-compensating species will be gallium-dihydrides [18,21]. These species are relatively stable and decompose slowly in the absence of hydrogen, even at high temperature [18]. Replacement of the pretreatment hydrogen flow by the reactant mixture (C_3H_8/He) will result in a slow increase in the number of Ga^+ species at the expense of GaH_2^+ species. The increase in activity with reaction time agrees with the assignment of Ga^+ species as the active sites. We propose that the reaction mechanism for propane conversion over TMG/ZSM-5(red) comprises made up by the following (not necessarily elementary) reaction steps:

$$ZO^-\ldots Ga^+ + C_3H_8 \leftrightarrows ZO^-\ldots\left[Ga(H^-)(C_3H_7{}^-)\right]^+ \quad (10)$$

and

$$ZO^-\ldots\left[Ga(H^-)(C_3H_7{}^-)\right]^+ \rightarrow ZO^-\ldots Ga^+ + H_2 + C_3H_6. \quad (11)$$

We thus propose that the increase in conversion with reaction time is due to an increase of the number of Ga^+ species at the expense of less active GaH_2^+ species. This proposal also implies that the rate of Eqs. (10) and (11) (i.e., the rate of propene formation) is lower than the rate of hydrogen removal from GaH_2^+ species or that GaH_2^+ is not a necessary intermediate, but actually suppresses the reaction. The need for a low H_2 partial pressure agrees with the view of Iglesia et al. [9], who proposed that Ga increases the rate of hydrogen desorption in the complex scheme of hydrocarbon conversion. Further reactions may include further dehydrogenation of olefins to coke products, which explains the nonclosed carbon balance.

Further support for this hypothesis is provided by an experiment in which TMG/ZSM-5(red) was exposed to inert He atmosphere at 823 K for 1 h. In this case, the propane conversion was nearly constant from the start of the reaction, as follows from Fig. 6. Extensive exposure to a He flow led to the decomposition of a significant part of GaH_2^+ species [18]. A small difference was noted in the product composition of TMG/ZSM-5(red) and TMG/ZSM-5(red, He). Although the propene selectivity in both cases was close to 90%, the latter material produced slightly more ethene and methane. This may point to a small contribution of protolytic cracking. The required Brønsted acid protons can derive from trace amounts of water in the He flow via [18,21]

$$ZO^-\ldots Ga^+ + 2H_2O \rightarrow ZO^-\ldots\left[Ga^{+3}(OH^-)_2\right]^+ + H_2 \quad (12)$$

Table 2
Propane dehydrogenation over TMG/ZSM-5(red, ox, 473 K) at 823 K (WHSV = 11.7 h^{-1}, $p = 1$ atm)

TOS (min)	Conversion (%)	Selectivity (%)				
		CH_4	C_2H_4	C_3H_6	Aromatics	Coke[a]
TMG/ZSM-5(red, ox, 473 K)						
2	24.0	7	13	63	7	10
10	10.9	5	8	80	0	7
30	7.3	5	6	84	0	5
90	5.8	4	5	84	0	7
150	4.9	4	5	87	0	4
Regenerated TMG/ZSM-5(red, ox, 473 K)						
2	23.6	7	13	65	5	10
10	12.8	5	9	78	3	5
30	9.9	4	7	82	0	7
90	8.6	4	6	82	0	8
150	6.8	4	5	87	0	4

[a] Selectivity to coke is defined as 100% $- S_{\mathrm{methane}} - S_{\mathrm{ethene}} - S_{\mathrm{propene}} - S_{\mathrm{aromatics}}$.

and

$$ZO^{-}\left[Ga^{+3}(OH^{-})_2\right]^{+} \rightarrow ZO^{-}\ldots H^{+} + GaOOH. \tag{13}$$

The catalytic performance of the oxidized gallium-containing zeolites differs from that of their reduced counterpart. TMG/ZSM-5(red, ox, 473) has a higher initial propane conversion than TMG/ZSM-5(red); however, the activity decreases strongly during the first 20 min. Initially, the product mixture comprises mainly propene with ethene, methane, and aromatics as minor side products (Table 2). At prolonged reaction times, the selectivity to propene increases significantly. The higher conversion of TMG/ZSM-5(red, ox, 473) compared with TMG/ZSM-5(red) indicates that propane reacts at a higher rate over GaO^{+} species than over Ga^{+} species. Tentatively, we propose that propane is activated over GaO^{+} species via

$$ZO^{-}\ldots GaO^{+} + C_3H_8 \leftrightarrows ZO^{-}\ldots\left[Ga(OH^{-})(C_3H_7^{-})\right]^{+}. \tag{14}$$

Decomposition of this complex gives propene via

$$\begin{aligned} &ZO^{-}\ldots\left[Ga(OH^{-})(C_3H_7^{-})\right]^{+} \\ &\quad\leftrightarrows ZO^{-}\ldots\left[Ga(OH^{-})(H^{-})\right]^{+} + C_3H_6. \end{aligned} \tag{15}$$

Further dehydrogenation of propene over GaO^{+} species might then lead to aromatics. On the other hand, the importance of Brønsted acid sites for dehydrocyclization has been stressed [9]. Although infrared spectroscopic characterization has clearly shown negligible Brønsted acid site regeneration in TMG/ZSM-5(red, ox, 473), we cannot rule out the possibility that a small number of such sites is regenerated on heating in inert atmosphere to 823 K. The presence of a small amount of such acidic protons also explains the formation of small amounts of methane and ethene. Thus, preparing a GaO^{+}/ZSM-5 catalyst with only GaO^{+} cations compensating the negative zeolite framework for kinetic studies is very difficult.

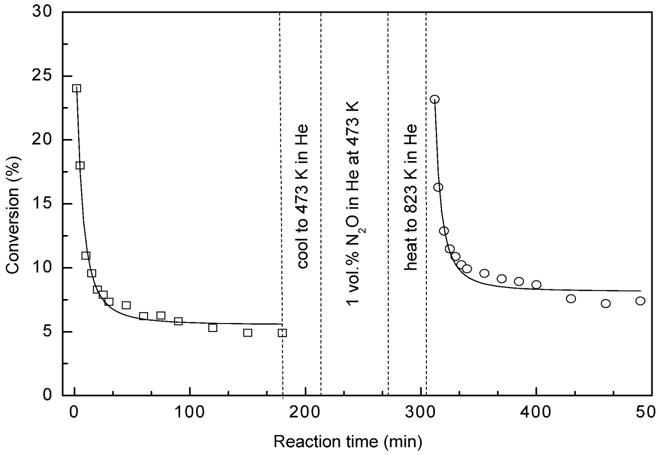

Fig. 7. Conversion of propane as a function of reaction time at 823 K (WHSV = 11.7 h^{-1}) over TMG/ZSM-5(red, ox) with intermittent oxidation by nitrous oxide for 1 h at 473 K.

Although deactivation of zeolite-catalyzed hydrocarbon conversion is often attributed to coke formation, we propose an alternative mechanism for the deactivation of TMG/ZSM-5(red, ox, 473) during propane conversion. Regeneration of the GaO^{+} species requires the reaction of

$$ZO^{-}\ldots\left[Ga(H^{-})(OH^{-})\right]^{+} \leftrightarrows ZO^{-}\ldots[GaO]^{+} + H_2. \tag{16}$$

An alternative reaction pathway is provided by

$$ZO^{-}\ldots\left[Ga(H^{-})(OH^{-})\right]^{+} \leftrightarrows ZO^{-}\ldots Ga^{+} + H_2O. \tag{17}$$

The reactions of GaO^{+} and Ga^{+} with hydrogen and water, respectively, were recently experimentally verified [20]. Moreover, Gonzales et al. [21] showed that the formation of univalent species by desorption of water according to Eq. (17) ($E_{\mathrm{act}} = 62$ kcal/mol; $\Delta G_{800\ \mathrm{K}} = 1.0$ kcal/mol) is more favorable than regeneration of the initial GaO^{+} species according to Eq. (16) ($E_{\mathrm{act}} = 73$ kcal/mol; $\Delta G_{800\ \mathrm{K}} = 28.6$ kcal/mol). This finding is in line with the computed difficult regeneration of gallyl ions [28]. Another pathway proceeds via reduction of GaO^{+} species with hydrogen produced by propane dehydrogenation,

$$ZO^{-}\ldots[GaO]^{+} + H_2 \leftrightarrows ZO^{-}\ldots Ga^{+} + H_2O, \tag{18}$$

for which Bell et al. [21] calculated $\Delta G_{800\ \mathrm{K}} = -28.3$ kcal/mol. It is thus likely that deactivation is due largely to the formation of less active Ga^{+} from the initially predominant GaO^{+} species. We stress that the difference in total turnover number (mol propane per mol gallium) between TMG/ZSM-5(red, ox, 473) and TMG/ZSM-5(red) during the reaction is much larger than unity. We calculate that on average 1000 molecules of propane are converted per GaO^{+} species before being reduced to Ga^{+}. This implies that GaO^{+} regeneration is possible under the reaction conditions, providing a more facile pathway to the olefin than Ga^{+} regeneration

To validate the hypothesis that deactivation is due to GaO^{+} reduction, spent TMG/ZSM-5(red, ox, 473) was cooled from reaction temperature to 473 K in flowing He. Subsequently, the catalyst was exposed to a flow (100 ml/min) of 1 vol% N_2O in He, heated in inert He atmosphere to 823 K, and again exposed to the reaction mixture. Fig. 7 combines the results of these successive catalytic experiments. Clearly, a mild oxidation at low temperature by nitrous oxide results in regeneration of the initial catalytic activity. The relatively low oxidation temperature precludes the oxidation of coke deposits. The clear inference to be drawn is that the deactivation of TMG/ZSM-5(red, ox, 473) in propane dehydrogenation is due to reduction of GaO^+ to Ga^+ species with a lower intrinsic activity.

4. Conclusion

Well-defined cationic Ga species can be prepared by reacting a HZSM-5 precursor with TMG. The methyl ligands of the resulting cationic $Ga(CH_3)_2{}^+$ species can be removed by reduction in hydrogen, resulting in Ga^+ and $GaH_2{}^+$ species that compensate for the negative zeolite framework charge. At elevated temperatures, Ga^+ and $GaH_2{}^+$ species coexist in a hydrogen atmosphere, whereas the latter ones are slowly decomposed to Ga^+ species only at high temperature in the absence of hydrogen. Oxidation by nitrous oxide at 473 K oxidizes Ga^+ to GaO^+ species. The presence of minor amounts of $GaH_2{}^+$ cations not eliminated during pretreatment results in the formation of $[Ga^{3+}(H^-)(OH^-)]^+$. Oxidation of such species at higher temperatures leads to clustered gallium-oxide particles and regeneration of Brønsted acid protons.

A distinct difference in the product distribution during propane dehydrogenation is noted between protons (HZSM-5) and Ga^+ ions (reduced Ga/ZSM-5). Whereas HZSM-5 cracks propane via protolytic cracking, yielding methane, ethane, and propene (paraffinic C–C and C–H bond activation), propane is dehydrogenated with high selectivity to propene (paraffinic C–H bond activation) over monovalent Ga^+ ions. The experimental data indicate that the monovalent Ga^+ species are more active than $GaH_2{}^+$ species. Compared with these cations, GaO^+ cations are most active, with propene being the main product, indicating that paraffinic C–H bond activation is preferred. However, deactivation in this case is pronounced which is due to the high energy barrier associated with regeneration of the gallyl (GaO^+) ion compared to the elimination of water to produce less active Ga^+ species.

Acknowledgments

The authors thank Professor R. Prins (ETH Zürich) for making available his equipment for X-ray absorption measurements. NWO is gratefully acknowledged for funding the X-ray absorption measurements at Dubble (ESRF). E.H. thanks the Technology Foundation STW, the applied science division of NOW, and the technology program of the Ministry of Economic Affairs for financial support.

References

[1] T. Waku, J.A. Biscardi, E. Iglesia, J. Catal. 222 (2004) 481.
[2] V.I. Hart, M.B. Bryant, L.G. Butler, X. Wu, K.M. Dooley, Catal. Lett. 53 (1998) 111.
[3] J.R. Mowry, R.F. Anderson, J.A. Johnson, Oil Gas J. 83 (1985) 1288.
[4] C. Doolan, P.R. Pujado, Hydrocarbon Proc. 68–69 (1989) 72.
[5] El-M. El-Malki, R.A. van Santen, W.M.H. Sachtler, J. Phys. Chem. B 103 (1999) 4611.
[6] G.D. Meitzner, E. Iglesia, J.E. Baumgartner, E.S. Huang, J. Catal. 140 (1993) 209.
[7] K.M. Dooley, C. Chang, G.L. Price, Appl. Catal. A 84 (1992) 17.
[8] G.L. Price, V. Kanazirev, J. Catal. 126 (1990) 267.
[9] J.A. Biscardi, E. Iglesia, Catal. Today. 31 (1996) 207.
[10] H. Kitagawa, Y. Sendoda, Y. Ono, J. Catal. 101 (1986) 12.
[11] N.S. Gnep, J.Y. Doyemet, M. Guisnet, J. Mol. Catal. 45 (1988) 281.
[12] M. Guisnet, N.S. Gnep, F. Alario, Appl. Catal. A 89 (1992) 1.
[13] E. Iglesia, J.E. Baumgartner, G.L. Price, J. Catal. 134 (1992) 549.
[14] J. Yao, R. Le Van Mao, L. Dufresne, Appl. Catal. A 65 (1990) 175.
[15] B.S. Kwak, W.M.H. Sachtler, J. Catal. 145 (1994) 456.
[16] V.R. Choudhary, K. Mantri, C. Sivadinarayana, Microporous Mesoporous Mater. 37 (2000) 1.
[17] E.J.M. Hensen, M. Garcia-Sanchez, N. Rane, P.C.M.M. Magusin, P. Liu, K. Chao, R.A. van Santen, Catal. Lett. 101 (2005) 79.
[18] V.B. Kazansky, I.R. Subbotina, R.A. van Santen, E.J.M. Hensen, J. Catal. 227 (2004) 263.
[19] M. Garcia-Sanchez, P.C.M.M. Magusin, E.J.M. Hensen, P.C. Thüne, X. Rozanska, R.A. van Santen, J. Catal. 219 (2003) 352.
[20] V.B. Kazansky, I.R. Subbotina, R.A. van Santen, E.J.M. Hensen, J. Catal. 233 (2005) 351.
[21] N.O. Gonzales, A.K. Chakraborty, A.T. Bell, Top. Catal. 9 (1999) 207.
[22] C. Otero Arean, G. Turnes Palomino, F. Geobaldo, A. Zecchina, J. Phys. Chem. 100 (1996) 6678.
[23] J. Szanyi, M.T. Pafett, Microporous Mater. 7 (1996) 201.
[24] A.Y. Khodakov, L.M. Kustov, T.N. Bondarenko, A.A. Dergachev, V.B. Kazansky, K.M. Minachev, G. Borbely, H.K. Beyer, Zeolites 10 (1990) 603.
[25] G.M. Zhidomirov, personal communication.
[26] J.A. Lercher, R.A. van Santen, H. Vinek, Catal. Lett. 27 (1994) 91.
[27] V.B. Kazansky, I.R. Subbotina, N. Rane, R.A. van Santen, E.J.M. Hensen, Phys. Chem. Chem. Phys. 7 (2005) 3088.
[28] M. Frash, R.A. van Santen, J. Phys. Chem. A 104 (2000) 2468.
[29] X. Rozanska, M. Garcia-Sanchez, E.J.M. Hensen, R.A. van Santen, Comptes Rendus 8 (2005) 509.
[30] Y.V. Joshi, K.T. Thomson, Catal. Today 105 (2005) 106.