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Ga speciation in Ga/H-ZSM-5 by in-situ transmission FTIR spectroscopy

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ABSTRACT

H-ZSM-5 supported Ga (Ga/H-ZSM-5) has long been recognized as a promising catalyst for nonoxidative dehydrogenation and dehydroaromatization of alkanes. However, Ga speciation under reaction conditions remains controversial. In this work, in-situ transmission Fourier Transform infrared (FTIR) spectroscopy is employed to systematically investigate Ga speciation in Ga/H-ZSM-5 with three Si/Al ratios (15, 28 and 39) and a wide range of Ga/Al ratios (0–1.7). Quantitative FTIR spectroscopy with pyridine reveals that one Ga atom roughly replaces one Brønsted acid site (BAS) at Ga/BAS ratio up to 0.7, however, only up to ~80% of the BAS on the H-ZSM-5 can be exchanged even with excess amounts of Ga. At a low Si/Al ratio of 15, the intensity of GaH_x bands on reduced Ga/H-ZSM-5 at 550 °C increases almost linearly at low Ga loadings (Ga/Al < 0.13), and then levels off. In contrast, no detectable GaH_x bands are observed on Ga/H-ZSM-5 with a high Si/Al ratio of 39, with Ga/Al ratios up to 1.3. The dependence of GaH_x bands on both the Si/Al ratios and the Ga/Al ratios shows that Ga speciation varies with BAS density in the zeolite. We hypothesize that paired BAS sites are preferentially exchanged with Ga^+, leading to the formation of Ga^+–H^+ pair sites, while the exchange of isolated BAS form isolated Ga^+ species. Using water as a probe molecule, we show that isolated Ga^+ and Ga^+–H^+ pair sites have distinct properties, i.e., the former can be easily oxidized by water at 150 °C to form GaOOH species, while the latter is inactive under the same conditions. These results provide direct experimental evidence for the existence of two types of Ga species on reduced Ga/H-ZSM-5, highlighting the possibility that they have different catalytic activities in alkane dehydrogenation reactions.

1. Introduction

Propylene plays a central role in the chemical industry infrastructure and it is used for the production of a wide range of chemicals, including polypropylene, acrylonitrile, propylene oxide, and cymene [1]. Propylene is currently obtained as a by-product from naphtha steam crackers and fluidized catalytic cracking (FCC) units in refineries [2]. However, there has been a growing gap between the demand and supply of propylene, due to a marked increase in the abundance of natural gas as a feedstock [3]. Propane dehydrogenation (PDH) is potentially an effective alternative to producing propylene, and two PDH processes, i.e., the Catofin process with a CrO_x/Al_2O_3 catalyst and the Oleflex process using a Pt-based catalyst, have been commercialized [4,5]. The high cost of Pt and the health and environmental concerns associated with Cr, have incentivized development of other PDH catalysts [4], such as Ga- [6–12], Zn- [13], Co- [14–16], V-based [17] and ZrO_2 [18–20] catalysts. Among these, Ga/H-ZSM-5 has long been recognized as an efficient catalyst for both dehydrogenation and dehydroaromatization of alkanes (the Cyclar process), however, Ga speciation, the identity of catalytic active sites and the reaction mechanism of the PDH reaction remain topics of active discussion despite decades of research [9–11,21–23].

Various experimental techniques including in-situ Ga K edge X-ray absorption near edge structure (XANES), ex-situ FTIR and NH_3-temperature-programmed desorption (NH_3-TPD) have been employed to probe Ga speciation in Ga/H-ZSM-5 and identify the active site in the PDH reaction [9–11,24]. Typically, Ga is introduced to H-ZSM-5 via impregnation and followed by calcination forming Ga_2O_3 crystallites supported on the external surface of H-ZSM-5. Upon reduction in the presence of H_2 above 500 °C, Ga^{3+} species are believed to be reduced and diffuse into the micropores of the zeolite [25], displacing protons of Brønsted acid sites (BAS) [26–28]. A number of Ga species, such as Ga^+, $[GaO]^+$, $[Ga(OH)]^{2+}$, $[Ga(OH)_2]^+$, $[GaH_2]^+$, $[GaH]^{2+}$, have been proposed to form after the reduction of Ga/H-ZSM-5 based on several experimental and computational techniques [9–11,24,26–28]. Early in-situ

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X-ray absorption study showed that isolated Ga^+ ions are the main species in Ga/H-ZSM-5 independent of the gallium loading and the utilized reducing gas [24,29], which is consistent with a more recent report by Schreiber et al. [10] Alternative interpretations of edge shifts in Ga K-edge XANES spectra acquired under reaction conditions have been proposed, as XANES spectra are not sufficiently resolved to differentiate Ga^+ from low-coordinate Ga-alkyl or hydride species [11,30]. Hensen and coworkers [27,28] first identified Ga monohydride and dihydride species on reduced Ga/H-ZSM-5 with diffuse reflectance infrared Fourier Transform spectroscopy (DRIFTS), suggesting that these species could play an active role in the PDH. However, they collected spectra at room temperature after reducing samples with H_2 at 500 °C, and the state of the catalyst at room temperature after cooling may not be representative of the catalyst state at 500 °C. Recently, Phadke et al. [9] proposed that single $[GaH]^{2+}$ sites are the active centers for the PDH reaction, and the catalyst's reactivity is independent of Ga/Al ratio. This was supported by FTIR spectroscopic and NH_3-TPD results, along with thermodynamic stability analysis [11]. FTIR and NH_3-TPD experiments in these studies were conducted on Ga/H-ZSM-5 in its oxidized state [11], where the Ga speciation could be quite different from that of the reduced sample. Schreiber et al. [10] reported that the Ga^+-H^+ paired sites were more active than single Ga^+ sites and the parent H-ZSM-5 catalyst based on a combination of reactivity, quantitative pulse reactions, and DFT calculations. The hypothesis of Ga^+-H^+ pair sites and isolated Ga^+ species having different reactivities has been put forth in recent investigations by both the Bell and the Lercher groups [9–11,21], however, the existence of these distinct sites is largely indirect; inferred from reactivity data, indirect experimental characterizations and computational investigations.

In this work, we employ in-situ transmission FTIR spectroscopy to systematically investigate Ga speciation in Ga/H-ZSM-5 samples with three Si/Al ratios (15, 28 and 39) and a wide range of Ga/Al ratio (0–1.7). Quantitative correlations between the consumption of the BAS and the Ga loading are obtained by determining the BAS density after reduction using pyridine as a probe molecule. Ga hydride species are characterized at the temperature close to that of typical PDH conditions, revealing the inhomogeneity of Ga species exchanged with BAS after reduction. These observations offer direct experimental evidence for the presence of Ga^+-H^+ pair sites and isolated Ga^+ species. This conclusion is further supported by FTIR investigations using water as a probe molecule; these show that isolated Ga^+ sites on reduced Ga/H-ZSM-5 samples can be quickly oxidized by water at 150 °C while Ga^+-H^+ pair sites cannot.

2. Experimental section

2.1. Catalyst preparation

H-ZSM-5 samples were prepared by calcining commercial NH_4-ZSM-5 samples (Zeolyst, CBV 3024E, CBV 5524G and CBV 8014) at 550 °C for 8 h in flowing air with a ramp rate of 2 °C min^{-1}. The Si/Al ratios of the samples were determined to be 15.4 ± 1.3, 27.5 ± 1.9 and 39.0 ± 2.8 by X-ray fluorescence (XRF). Ga/H-ZSM-5 samples with varying Ga/Al ratios (0.014–1.70) were prepared via the incipient wetness impregnation with an aqueous solution of gallium(III) nitrate hydrate (Sigma-Aldrich), followed by drying at 80 °C for 6 h and calcination at 600 °C for 2 h in flowing air with a ramp rate of 5 °C min^{-1}. Ga/MFI (8 wt% Ga) was prepared by the same method with siliceous MFI prepared according to a previous report [31]. Ga_2O_3 was obtained by calcination of gallium(III) nitrate hydrate at 600 °C in flowing air for 2 h with a ramp rate of 5 °C min^{-1}.

2.2. Transmission Fourier Transformed Infrared studies

In-situ Fourier Transformed Infrared (FTIR) spectra were collected on an Agilent CARY 660 spectrometer equipped with an MCT detector and a custom in-situ transmission cell. In general, the signal was collected at 128 scans per spectrum at a spectral resolution of 2 cm^{-1}. Vacuum levels of <0.01 mTorr were achieved through connection to a vacuum manifold equipped with a mechanical pump and a diffusion pump. The transmission cell was heated by heating tapes controlled by a PID controller. Catalyst were pressed into self-supporting wafers of about 20 mg, which were then loaded into a custom-made sample holder for vertical alignment in the infrared beam. The samples were dehydrated at 550 °C for 30 min under vacuum before all experiments. Chemicals such as H_2, H_2O, D_2O and pyridine were introduced to the transmission cell with their pressures controlled via the vacuum manifold.

Pyridine adsorption was conducted to quantify the amount of BAS and Lewis acid sites (LAS) [10]. The self-supporting wafer was dehydrated at 550 °C, followed by a H_2 (1 atm) treatment at the same temperature. H_2 was introduced to the cell three times for 10 min each to ensure that the catalyst was fully reduced. The sample was then cooled down to 150 °C under vacuum, followed by the introduction of 100 mTorr of pyridine and evacuation. This dosing procedure was repeated until intensity of the bands corresponding to adsorbed pyridinium increased by < 1% between doses before spectrum was collected. Concentrations of BAS were determined by integrating the area of the band corresponding to protonated pyridine (1540 cm^{-1}) and using the extinction coefficient determined in our recent work [32,33]. All infrared spectra with different Ga/Al ratios were normalized to the intensity of Si–O–Si framework overtone bands [11] between 1700 and 2000 cm^{-1}. The relative consumption of BAS in Ga/H-ZSM-5 samples after reduction compared to the support H-ZSM-5 was calculated using the equation (1).

$$\text{Consumption of BAS} = \left(1 - \frac{\text{integrated area of pyridinium band, Ga/H-ZSM-5}}{\text{integrated area of pyridinium band, H-ZSM-5}}\right) \times 100\% \quad (1)$$

Water treatment of the reduced samples was conducted to investigate different properties of two Ga species. In general, the self-supporting sample was reduced at 550 °C and cooled down to 150 °C under dynamic vacuum, followed by the introduction of ~1000 mTorr of water vapor repeatedly until the intensity of the bands at 2030–2070 cm^{-1} increased by < 1% between doses. The peak area of this peak was integrated and normalized to the intensity of Si–O–Si framework overtone bands [11] between 1700 and 2000 cm^{-1}.

3. Results and discussion

3.1. Reduction of Ga/H-ZSM-5

Although there is a general understanding of the reduction process of Ga/H-ZSM-5 in H_2 prior to the introduction of propane in the PDH, much of this information has been inferred from ex-situ characterizations. The Ga^{3+} species in Ga_2O_3 crystallites supported on the external surface of H-ZSM-5 crystals of Ga/H-ZSM-5 are believed to be reduced and mobilized in the presence of H_2 above 500 °C to diffuse into the micropores of the zeolite [25] and displace protons of BAS [26–28]. However, several key aspects of how this "activation" process in the PDH occurs, e.g., the dependence of Ga speciation on the Si/Al ratio of the zeolite and the Ga/Al ratio of the catalyst, remain topics of considerable discussion [9–11,21]. To address these questions, in-situ transmission FTIR spectroscopy is employed to investigate the Ga speciation in Ga/

H-ZSM-5 samples with three Si/Al ratios (15, 28 and 39) and a wide range of Ga/Al ratio (0–1.7). Composition and textural properties of the three H-ZSM-5 samples are summarized in Table S1, showing that these samples are pure and are highly crystalline. The BAS densities of the samples were 636, 460, 281 μmol/g for samples with Si/Al ratios of 15, 28 and 39, respectively, by quantitative transmission FTIR with pyridine as the probe molecule (Table S1). These values are consistent with previous reports of H-ZSM-5 samples with comparable Si/Al ratios [34,35]. The measured BAS densities are lower than those determined from Si/Al ratios of zeolites, which is likely due to the presence of small amounts of extraframework Al. This is consistent with a weak feature at ~0 ppm in ^{27}Al solid-state nuclear magnetic resonance (SS-NMR) spectra (Fig. S1), corresponding to octahedrally coordinated extraframework Al (Al_{EF}). Ga/H-ZSM-5 samples with varying Ga loadings were prepared by impregnation followed by calcination, and the Ga loadings were determined by XRF (Table S2).

In-situ FTIR investigations of the reduction of Ga/H-ZSM-5 confirm the replacement of BAS with Ga species. After dehydration under vacuum at 550 °C, the FTIR spectrum of the dehydrated Ga/H-ZSM-5 (Si/Al = 15 and Ga/Al = 1.0) shows three peaks centered at 3735 cm^{-1}, 3645 cm^{-1}, 3591 cm^{-1} (Fig. 1(i)), which are assigned to the external silanol group (Si-OH), Al_{EF}-OH and bridge-OH group associated with BAS, respectively [11]. The bands for these O-H stretching modes generally blueshift and become more intense as temperature decreases (Fig. S2). At lower temperatures, a band at 3780 cm^{-1}, attributable to Al_{EF}-OH, becomes better defined. The presence of bands at both 3645 cm^{-1} and 3780 cm^{-1} is consistent with the detection of octahedral-Al species by ^{27}Al SS-NMR. Upon reduction with H_2 (1 atm) at 550 °C, the BAS band (3591 cm^{-1}) disappears (Fig. 1(ii)), indicating the replacement of BAS by Ga species [27,28,36]. Interestingly, the band at 3735 cm^{-1} increases in intensity upon reduction (Fig. 1(iii)), which could be interpreted as the result of external silanol groups formed after Ga species initially located at the external surface migrate into the zeolitic micropores in the H_2 atmosphere. These observations at reaction temperature and atmosphere are in line with literature [27,28,36,37]. FTIR spectra were collected on Ga/H-ZSM-5 (Si/Al = 15) in the Ga/Al range of 0–1.7 at 550 °C before and after reduction with H_2 (Fig. 2a). Without Ga (Ga/Al = 0), spectra collected before and after the reduction procedure overlap completely (Fig. 2a(i), black and red traces, respectively), as expected. As the Ga/Al ratio increases to 0.56, the fraction of the BAS band which remains after reduction decreases, indicating a larger fraction of BAS is replaced by Ga species. At Ga/Al ratios at or above 0.7, the BAS band completely disappears after reduction. Similar observations were made on Ga/H-ZSM-5 with Si/Al ratios of 28 and 39 (Fig. 2b and c), except that the Ga/Al ratio above which no visible BAS band exist after reduction was found to be 1.0.

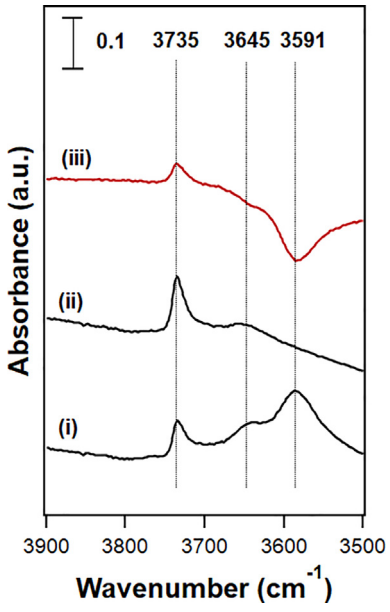


Fig. 1. FTIR spectra collected during the H_2 reduction process of Ga/H-ZSM-5 (Si/Al = 15 and Ga/Al = 1.0) at 550 °C: (i) dehydrated Ga/H-ZSM-5 at 550 °C; (ii) reduced Ga/H-ZSM-5 by H_2 (1 atm) at 550 °C; (iii) spectrum (i) subtracted from spectrum (ii). Background spectrum was collected in the spectral cell without a sample pellet at the room temperature under vacuum.

It is important to contrast the conditions at which spectra in Fig. 2 were collected with those in previous reports to understand the discrepancies. Hensen and coworkers reported the disappearance of the BAS IR band after reduction of Ga/H-ZSM-5 (Si/Al = 20–24, Ga/Al = 1) [28], and also detected the formation of Ga-OH (3665 cm^{-1}). This Ga-OH band is absent in this work after reduction, likely due to different experimental procedures. Hensen and coworkers collected IR spectra at room temperature after reduction; the inevitable exposure of the reduced sample to trace amount of water vapor during the cooling period, even under dynamic evacuation, could lead to the oxidation of the reduced Ga species to form Ga-OH. This possibility is eliminated in this study by collecting spectra at 550 °C directly following the reduction procedure. This hypothesis is supported by a control experiment in which the reduced Ga/H-ZSM-5 (Si/Al = 15 and Ga/Al = 1.0) is intentionally exposed to water vapor at 550 °C leading to the evolution of the Ga-OH band and the reappearance of the BAS band (Fig. S3(i-iv)). Phadke et al. [11] recently reported that the BAS band did not disappear on Ga/H-ZSM-5 with Ga/Al ratios up to 0.7; this is likely due to the fact that spectra were collected in an oxidizing environment (flowing air at 500 °C). To verify this hypothesis, dry air is introduced to the reduced Ga/H-ZSM-5 (Si/Al = 15 and Ga/Al = 1.0) at 550 °C, leading to the appearance of Ga-OH and BAS bands (Fig. S3(v, vi)). These control experiments show that not only reduced Ga species are susceptible to oxidation by both air and water, but also that in-situ characterization is vital to capture the dynamic process of catalyst reduction.

Quantitative FTIR experiments with pyridine show that not all BAS can be exchanged by Ga species even at Ga/Al ratios up to 1.7 during the reduction treatment. Although results in Fig. 2 unequivocally demonstrate the occurrence of the replacement of BAS with Ga species during the reduction treatment, it could be deceiving when used as the basis for quantitative analysis. This is because the BAS OH band of zeolite samples is easily obscured by the background at low densities [38]. To determine the density of the BAS left on Ga/H-ZSM-5 after reduction, pyridine was introduced to reduced samples at 150 °C. Cooling from 550 °C to 150 °C in vacuum takes ~30 min, as compared to ~1.5 h to the room temperature, in the absence of active cooling. The absence of the BAS and the Ga-OH bands on reduced Ga/H-ZSM-5 (Si/Al = 15, Ga/Al > 0.7) after cooling to 150 °C indicates that exposure of the reduced sample to the trace mount of water vapor under vacuum, if occurred at all, was minimal (Fig. S4). Quantitative analysis of FTIR spectra of reduced Ga/H-ZSM-5 with pyridine provides insight into the stoichiometry of the replacement process. Upon dosing pyridine on H-ZSM-5 (Si/Al = 15), three peaks appear at 1540 cm^{-1}, 1455 cm^{-1}, and 1490 cm^{-1} (Fig. 3a), attributable to protonated pyridinium ion (BAS), coordinatively adsorbed pyridine on the LAS, and a combination of pyridine adsorbed on BAS and LAS, respectively [10]. As expected, the BAS band at 3605 cm^{-1} disappears upon pyridine introduction (data not shown).

As the Ga/Al ratio of the sample with a Si/Al ratio of 15 increases from 0 to 1.7, several interesting trends emerge. The integrated

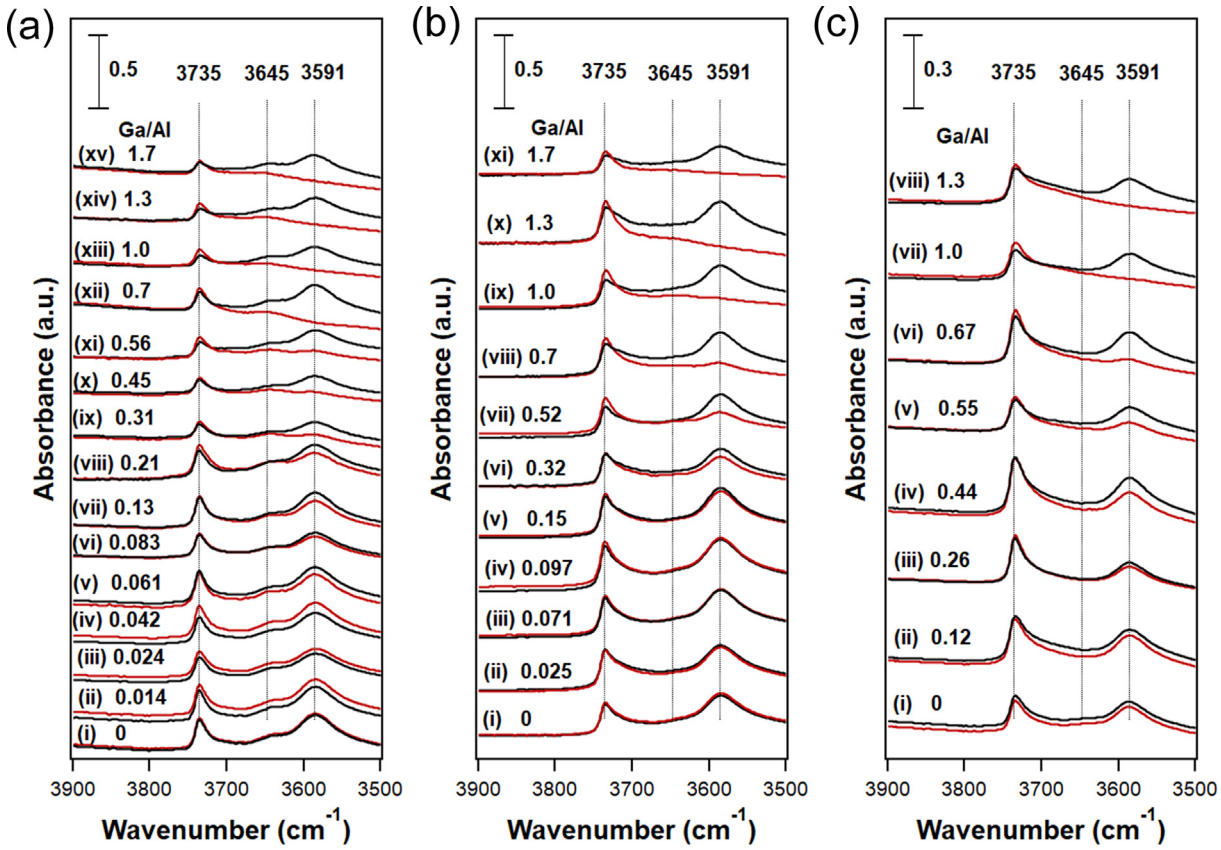


Fig. 2. FTIR spectra of Ga/H-ZSM-5 with Si/Al ratios of (a) 15, (b) 28 and (c) 39 and Ga/Al ratios ranging from 0 to 1.7 (indicated in the figure legends). Black and red traces represent spectra before and after reduction by H_2 (1 atm) at 550 °C, respectively. Background spectrum was collected in the spectral cell without a sample pellet at the room temperature under vacuum.

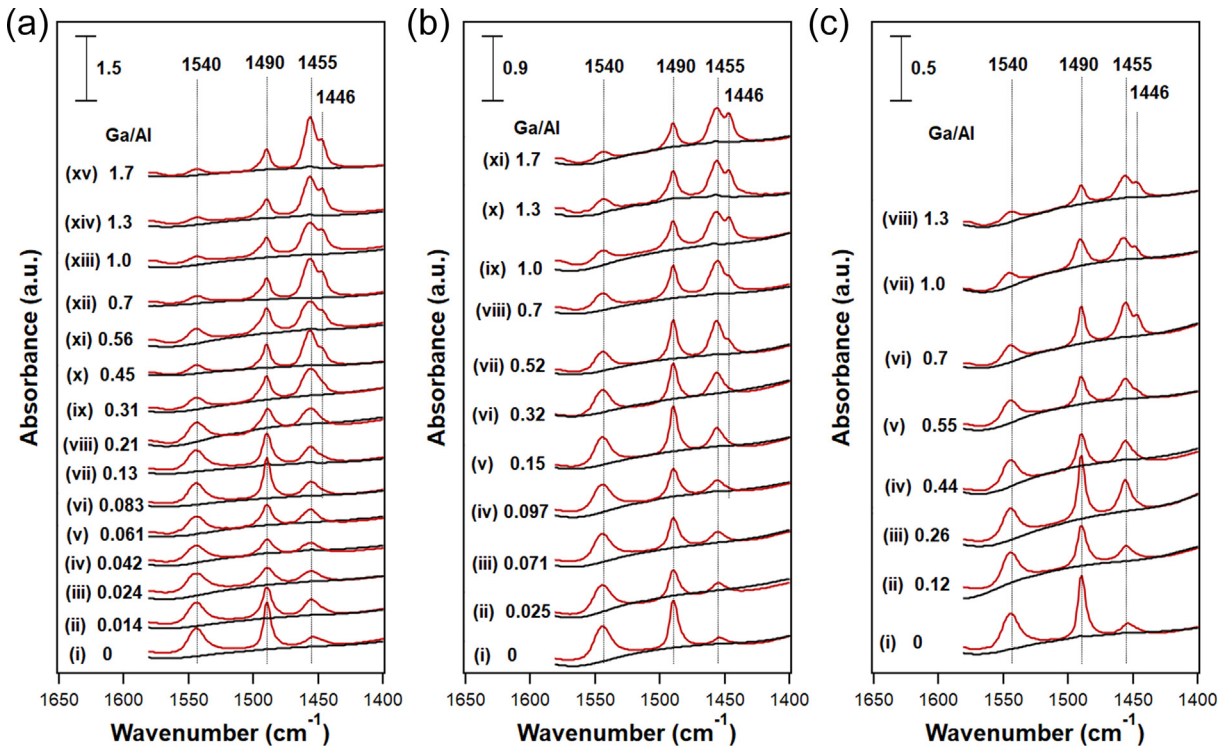


Fig. 3. FTIR spectra of Ga/H-ZSM-5 with Si/Al ratios of (a) 15, (b) 28 and (c) 39 and Ga/Al ratios ranging from 0 to 1.7 (indicated in the figure legends). Black and red traces represent spectra before and after pyridine adsorption at 150 °C on reduced Ga/H-ZSM-5. Background spectrum was collected in the spectral cell without a sample pellet at the room temperature under vacuum.

area of the pyridinium band decreases by ~75% as the Ga/Al ratio increases from 0 to 0.7 (Fig. 3a(i-xii)), and then levels off at ~80% at higher Ga/Al ratios (Fig. 3a(xiii-xv)). It is important to note that the BAS cannot be completely replaced by the Ga species even at a Ga/Al ratio of 1.7, which is different from the conclusions reached in the literature [11]. Conducting the pyridine experiments on reduced Ga/H-ZSM-5 samples without air or water exposure is key to obtaining reliable BAS densities on reduced Ga/H-ZSM-5, as BAS can reappear upon catalyst re-oxidation (Fig. S3(v)). Thus, ex-situ methods such as NH_3-TPD are unlikely to produce results relevant to reduced catalysts [11] unless proper catalyst pretreatment is included. A slope of nearly one is observed between percentage of consumed BAS band and the Ga/BAS ratio up to the Ga/BAS ratio of 0.7 (Fig. 4), corresponding to one Ga atom replacing one BAS. This is likely due to abundance of BAS relative to Ga at lower Ga/BAS ratios, and is consistent with a previous report [10]. In contrast, Phadke et al. reported the same ratio as close to 2 [11]; this discrepancy is likely caused by the different BAS quantification method employed as discussed above. The consumption of BAS increases with Ga/Al ratio and reached about 70% for samples with Ga/Al ratios near unity. This slope increasingly deviates from unity as the Ga/BAS ratio exceeds 0.7, and largely levels off at Ga/BAS ratios above 1.5. This trend could be attributed to the difficulty for Ga species to find the increasingly scarce BAS. Similar trends are observed on Ga/H-ZSM-5 with higher Si/Al ratios (28 and 39). The Ga/BAS ratio beyond which the slope deviates from unity occurs at ~0.5 for Ga/H-ZSM-5 (Si/Al = 28), and the Ga/BAS starts at ~0.4 for samples with a Si/Al ratio of 39. This could be in part because for samples with higher Si/Al ratios (lower Al densities), it is more difficult for Ga to encounter BAS to react with. These observations agree with previous XANES results showing the formation of GaO_x oligomers at Ga/Al > 0.3 [11]. The highest percentage of BAS consumption in Ga/H-ZSM-5 with all three Si/Al ratios is similar (~80%), suggesting a thermodynamic barrier rather than a purely diffusional one to achieve complete BAS replacement. One possible explanation is the formation of Ga oligomers in the zeolite micropores which become more energetically favorable than exchanging with the rest of BAS, as suggested by Bell and coworkers [11].

Ga speciation of reduced Ga/H-ZSM-5 is also found to depend on the Ga/Al ratio. When pyridine was introduced to the reduced Ga/H-ZSM-5 (Si/Al = 15), the band corresponding to pyridine adsorbed on the LAS (1455 cm^{-1}) increases in intensity with increasing Ga/Al ratio. This could be attributed to pyridine adsorbed on the Ga^+ species. A shoulder at 1446 cm^{-1} appears at a Ga/Al ratio of 0.45 and grows as the Ga loading rises. There is no significant increase of this LAS peak as the Ga/Al ratio increases from 0.7 to 1.7 for both bands at 1455 cm^{-1} and 1446 cm^{-1} (Fig. S6). The leveling off the integrated area of the band corresponding to pyridine on Ga^+ (1455 cm^{-1}) is expected as few additional BAS are replaced by Ga^+ when the Ga/Al ratio is above 0.7 (Fig. 3a). The near constant magnitude of the intensity of the 1446 cm^{-1} band with Ga loading at high Ga/Al ratios suggests that it is unlikely to correspond to pyridine adsorbed on unreduced Ga_2O_3, as there is an increasing fraction of Ga not exchanged with BAS as the Ga/Al ratio increases. The lack of the band at 1446 cm^{-1} upon introduction of pyridine on Ga/H-ZSM-5 (Si/Al = 15, Ga/Al = 1.0) without reduction (Fig. S7(ii)), on which the majority of Ga is expected to exist in the form of Ga_2O_3, supports this conclusion. Thus, the 1446 cm^{-1} band could be attributed to a reduced form of gallium oxide. Bell and coworkers proposed the formation of GaO_x oligomers at Ga/Al ratio higher than 0.3 [11]. Control experiment of pyridine adsorbed on Ga_2O_3 reduced by H_2 at 550 °C shows a band centered at 1451 cm^{-1} (Fig. S7), which is likely a convoluted band corresponding to pyridine adsorbed on a mixture of unreduced and partially reduced Ga sites. Similar observations have been made on Ga/H-ZSM-5 at Si/Al ratios of 28 and 39 (Fig. 3b and c).

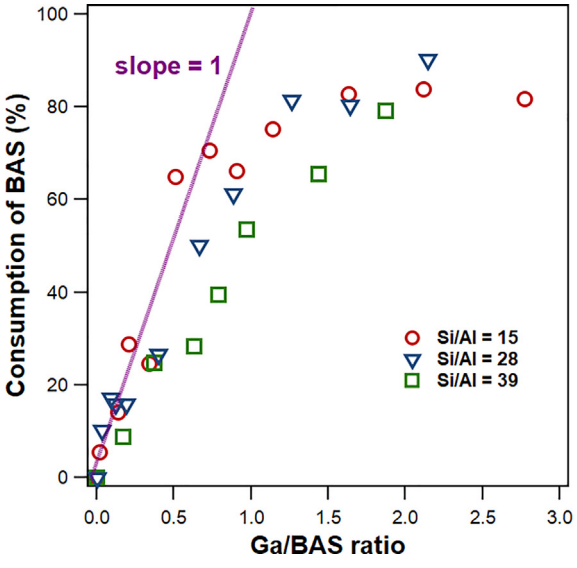


Fig. 4. Consumption of BAS determined by quantitative infrared spectroscopy as a function of Ga/BAS ratios on Ga/H-ZSM-5 samples with varying Si/Al ratios. Consumption of BAS vs. Ga/Al ratios are plotted in Fig. S5.

3.2. Gallium hydride species

The dependence of the formation and relative abundance of the gallium hydride species formed upon reduction on the Ga/Al ratios and Si/Al ratios provides another dimension to differentiate different Ga species on Ga/H-ZSM-5. Hensen and coworkers [27,28] first identified Ga monohydride (GaH, 2059 cm^{-1}) and Ga dihydride (GaH_2, 2041 cm^{-1}) after reduction of Ga/H-ZSM-5 using DRIFTS. The spectra collected by Hensen and coworkers were obtained at room temperature after reducing the sample with H_2 at 500 °C, and the observed spectral features for Ga hydrides could be different from those at reaction temperatures. Regardless, this is an important discovery, as the ability of Ga species to form hydrides could be used to gauge their homogeneity (or the lack thereof).

In-situ FTIR spectroscopy is employed to monitor the formation of Ga hydride species at 550 °C on reduced Ga/H-ZSM-5 samples with multiple Si/Al ratios and Ga/Al ratios. After reducing the Ga/H-ZSM-5 (Si/Al = 15) with different Ga/Al ratios with H_2 (1 atm) at 550 °C, bands corresponding to GaH and GaH_2 (at 2053 cm^{-1} and 2037 cm^{-1}, respectively) appeared after the cell was evacuated at the same temperature (Fig. 5a) [26–28]. The bands for these Ga-H stretching modes generally blueshift as Ga/H-ZSM-5 (Si/Al = 15, Ga/Al = 1) cools down under vacuum (Fig. S8), which explains the slight shifts of the hydride bands reported in this work compared to those by Hensen and coworkers [27,28]. In addition, the hydride bands become more intense when the sample temperature decreases (Fig. S8), with the invisible GaH band at 550 °C appearing as a relatively well-defined peak at 150 °C [28]. Since the sample was cooled relatively quickly under dynamic vacuum (~30 min), the GaH_x density is expected to remain unchanged. The increase in the peak area is likely due to the thermally driven dynamic nature of the GaH_x species at high temperatures, which weakens and broadens the vibrational bands. Following this logic, the GaH structure appears more dynamic than GaH_2, unless there is a temperature dependent interconversion of these two species. As expected, no Ga hydride is observed on H-ZSM-5 (Si/Al = 15) without Ga (Fig. 5a(i)). The GaH_2 band is barely detectable at a Ga/Al ratio of 0.014 (Fig. 5a(ii)), but becomes better defined as the Ga/Al ratio

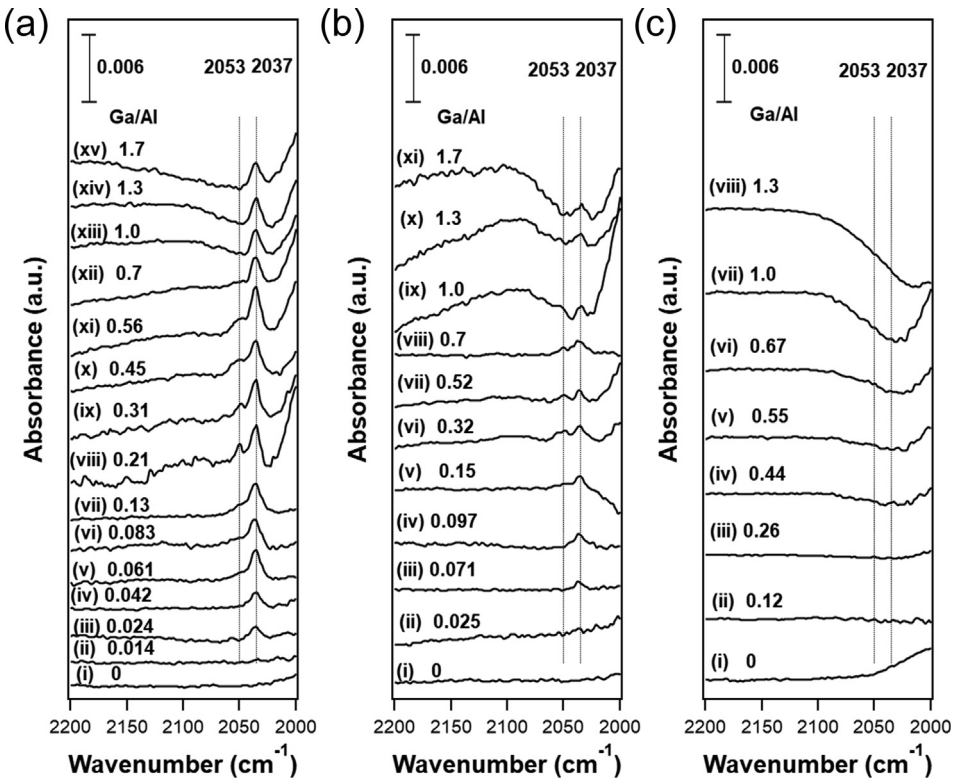


Fig. 5. FTIR spectra of H_2 treatment on Ga/H-ZSM-5 with Si/Al ratios of (a) 15, (b) 28 and (c) 39 and Ga/Al ratios ranging from 0 to 1.7 (indicated in the figure legends). Background spectrum was collected in the spectral cell with a dehydrated sample pellet at 550 °C under vacuum.

rises. The intensity of the GaH_2 increases almost linearly at low Ga loadings, levels off when the Ga/Al ratio exceeds 0.1, and declines slowly with the increase of the Ga/Al ratio above 0.56 (Fig. 5a). A discernable GaH band does not appear until the Ga/Al ratio exceeds 0.08, and disappears at Ga/Al ratios above 0.7. The combined peak area of Ga hydrides as a function of the Ga/Al ratio is plotted in Fig. 6; this combined area is dominated by the GaH_2 band, due to its higher intensity. Pyridine FTIR spectra show that consumption of the BAS by Ga exchange upon reduction does not stop until the Ga/Al ratio exceeds 0.7 (Fig. 3a and 4). These diverging trends

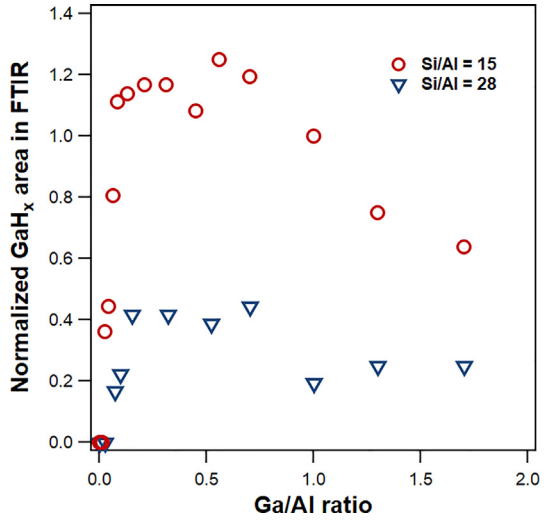


Fig. 6. Integrated GaH_x peak area determined via quantitative infrared spectroscopy (normalized to the GaH_x peak area of Ga/H-ZSM-5 (Si/Al = 15, Ga/Al = 1)) as a function of the Ga/Al ratio.

for the Ga hydride formation and the BAS consumption indicate that not all Ga species exchanged with the BAS are capable of forming Ga hydrides upon reduction. This is clear evidence of the heterogeneity of the exchanged Ga species, in addition to the those remaining on the external surface of zeolite crystals (especially at higher Ga loadings) [11]. We note that GaH_x bands are more intense in H_2 atmospheres than under vacuum (Fig. S9), which is likely due to a dynamic equilibrium between hydrided and non-hydrided Ga species, which favors hydrides at high partial pressure of H_2. The integrated GaH_x band area decreases by 40–60% within 30 min (Fig. S10) upon evacuation. All spectra of reduced sample under vacuum were collected 30 s after evacuation. The intensity of Ga hydride bands decreases with the increase of the Si/Al ratio of H-ZSM-5 at the same Ga/Al ratio (Fig. 5b and c), which could be, in part, attributed to lower the absolute Ga weight loadings. It should be noted that the integrated area of the GaH_x band is a factor of 5.7 lower on Ga/H-ZSM-5 (Si/Al = 28, Ga/Al = 0.15) than that on Ga/H-ZSM-5 (Si/Al = 15, Ga/Al = 0.083) even at similar Ga weight loadings (~0.6 wt%), suggesting the Ga loading is not the sole parameter in determining the band intensity. Further, no detectable spectral feature is observed on Ga/H-ZSM-5 (Si/Al = 39) with the Ga/Al ratio up to 1.3 (Ga wt% up to 3.68%). Considering that at the same Ga/Al ratio, the Ga content in Ga/H-ZSM-5 (Si/Al = 39) is less than Ga/H-ZSM-5 (Si/Al = 15), then it is necessary to compare the amount of GaH_x formed on Ga/H-ZSM-5 with the comparable Ga loading. At a Ga/Al ratio of 0.12, the Ga loading in Ga/H-ZSM-5 (Si/Al = 39) is higher than that of Ga/H-ZSM-5 (Si/Al = 15, Ga/Al = 0.042). The former shows no spectral feature for GaH_x species (Fig. 5c(ii)), while the latter shows a clear GaH_2 band (Fig. 5a(iv)). More strikingly, Ga/H-ZSM-5 (Si/Al = 39, Ga/Al = 1) has a comparable Ga weight loading to Ga/H-ZSM-5 (Si/Al = 15, Ga/Al = 0.45), on which the intensity of GaH_x bands is close to maximum (Fig. 6). Similar arguments could be made regarding the

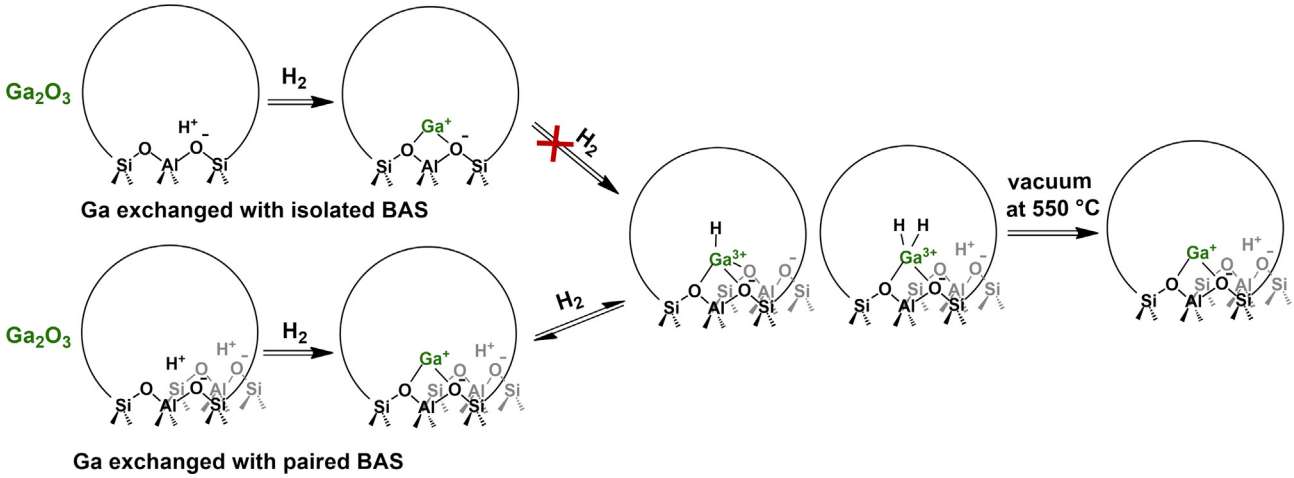
amount of exchanged Ga with the BAS, i.e., comparable amounts of exchanged Ga (Ga/BAS $\geq$ 0.07 in Fig. 4) lead to well-defined GaH_x bands on Ga/H-ZSM-5 (Si/Al = 15) but no detectable spectral signature on Ga/H-ZSM-5 (Si/Al = 39). Thus, the ability to form GaH_x species after H_2 treatment at 550 °C is only present on Al-rich zeolites (with lower Si/Al ratios). This provides the first direct experimental evidence that the speciation of exchanged Ga in reduced Ga/H-ZSM-5 is dependent on the Al density in the zeolite.

The combined results of our spectroscopic investigations could be largely rationalized by the formation of two distinct types of Ga species in zeolitic micropores through ion-exchange with BAS, i.e., Ga exchanged with isolated and paired BAS (Scheme 1). Isolated and paired BAS are loosely defined as BAS without and with a neighboring BAS to interact with, respectively. We acknowledge that this definition is less specific than those proposed by recent investigations [9–11,21], but would argue that such flexibility/ambiguity is justified based on the heterogeneity of the exchanged Ga species in reduced Ga/H-ZSM-5 samples. The dependence of the GaH_x formation on the Si/Al ratio of the zeolite (Fig. 5), i.e., the BAS density, suggests that the environment of BAS has an impact on the properties of the exchanged Ga species, as has also been concluded in recent reports [11,39,40]. Zeolites with lower Si/Al ratios, or higher Al contents, have higher densities of paired BAS assuming Al is distributed uniformly across the zeolite framework. This is generally a valid assumption except for special cases with uneven distributions of Al in the zeolite framework [41,42]. On a sample with a high Si/Al ratio, e.g., 39 in this work, the majority of the BAS are isolated. Thus Ga^+ species that replace the protons via ion-exchange should also be isolated and lack interaction with neighboring BAS. The lack of GaH_x spectral features on Ga/H-ZSM-5 (Si/Al = 39) with Ga/Al ratio as high as 1.3 strongly indicates that these isolated Ga^+ sites cannot form stable GaH_x species at 550 °C (under vacuum or in the H_2 atmosphere). Meanwhile, at lower Si/Al ratios, e.g., Ga/H-ZSM-5 (Si/Al = 15), there is a higher probability of BAS to occur as paired BAS sites. We propose that the Ga^+–H^+ pair sites formed by exchanging Ga^+ with one of the paired BAS is the species capable of forming GaH_x species based on the spectroscopic observation (Fig. 5a and b). This hypothesis agrees with the charge balance requirement that two adjacent BAS are needed for GaH (Scheme 1) assuming a +3 valence for the Ga cation. For samples with both isolated and paired protons, paired protons are preferentially exchanged with Ga^+ to form Ga^+–H^+ pair sites, as GaH_x bands are observed on Ga/H-ZSM-5 (Si/Al = 15) at low Ga loadings.

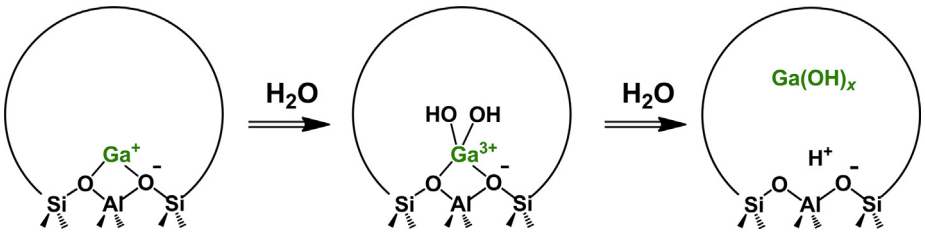
3.3. Water as a probe molecule for Ga hydride species

Water interacts extensively with Ga^+ and GaH_x species leading to distinct spectral features, and thus is an excellent probe molecule of Ga speciation in reduced Ga/H-ZSM-5. Several reports have mentioned that reduced Ga^+ is sensitive to trace amounts of water [26,27], leading to its oxidation. Introducing water vapor to reduced Ga/H-ZSM-5 (Si/Al = 15, Ga/Al = 1.0) at 550 °C leads to the appearance of bands at 3591 and 3662 cm^{-1} (Fig. S11), attributable to recovered BAS and $Ga(OH)_x$, respectively [26]. This suggests that water is able to oxidize Ga^+ at this condition to reform BAS and $Ga(OH)_x$ (Scheme 2). Thus, maintaining a high level of vacuum and reducing the time between H_2 treatment and spectral collection are important in FTIR measurements to minimize the undesired impact of water. Meanwhile, this sensitivity also makes water a suitable probe molecule to characterize Ga species on reduced Ga/H-ZSM-5.

IR spectra collected after introducing water vapor to reduced Ga/H-ZSM-5 provide further evidence of the heterogeneity of exchanged Ga species. Ga/H-ZSM-5 after H_2 treatment at 550 °C is quickly cooled down to 150 °C under vacuum (within ~30 min). A control experiment confirms negligible impact of the trace amount of water in the evacuated cell on the spectra based on the absence of the $Ga(OH)_x$ band at ~3672 cm^{-1} at 150 °C (Fig. S12). Upon water introduction to the reduced Ga/H-ZSM-5 (Si/Al = 15, Ga/Al = 1.0) at 150 °C, an intense band centered at 2052 cm^{-1} appears (red trace of Fig. 7a(ix)), completely masking the GaH_x bands in the same spectral range. Although this band is located in close proximity to the GaH_x bands, they are unlikely to be of a similar origin; as it would be quite unlikely for water to further reduce Ga species on samples that had been already reduced with H_2 at 550 °C (and produce O_2 based on stoichiometry). It has been proposed that reduced Ga^+ can react with water to form GaOOH [26,27], and bands at 2065–2092 cm^{-1} and 1946–2038 cm^{-1} could be attributed to the Ga-OH bending mode of GaOOH [43–47]. Introduction of water to the reduced Ga/H-ZSM-5 (Si/Al = 15, Ga/Al = 1.0) at 150 °C leads to the production of H_2, in agreement with water acting as an oxidant (Fig. S13). Based on literature precedents and the water introduction reaction results, we assign the band at 2052 cm^{-1} to GaOOH. Interestingly, introduction of water to Ga/H-ZSM-5 (Si/Al = 15) with lower Ga/Al ratios ($\leq$0.13) has a much less pronounced impact than those observed on samples with higher Ga/Al ratios (Fig. 7a(i-iv)). In particular, the GaH band on Ga/H-ZSM-5 (Si/Al = 15, Ga/Al = 0.042)



Scheme 1. Proposed mechanisms of exchanged Ga species in Ga/H-ZSM-5 after reduction.



Scheme 2. Schematic of water reacting with reduced Ga/H-ZSM-5.

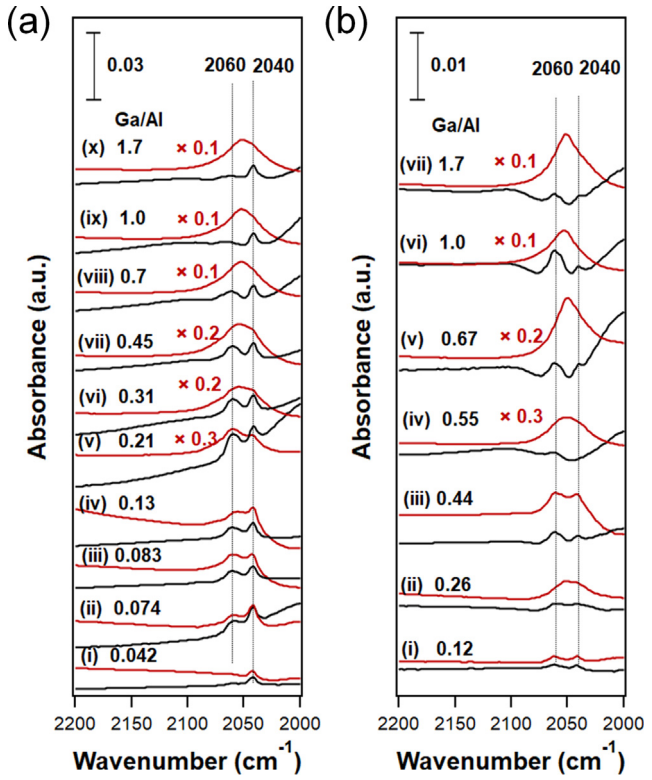


Fig. 7. FTIR spectra of Ga/H-ZSM-5 with Si/Al ratios of (a) 15, (b) 39 and Ga/Al ratios ranging from 0 to 1.7 (indicated in the figure). Black and red traces represent spectra before and after water vapor treatment at 150 °C on the reduced Ga/H-ZSM-5, respectively. Background spectrum was collected in the spectral cell with a sample pellet dehydrated at 550 °C and cooled down to 150 °C under vacuum.

barely changes after water introduction (black and red traces of Fig. 7a(i)). These observations suggest that the Ga species is different at low Ga/Al ratios (≤0.13) and high Ga loadings, supporting our hypothesis of two distinct exchanged Ga species. Importantly, the threshold Ga/Al ratio (0.13) on Ga/H-ZSM-5 (Si/Al = 15) at which this transition occurs coincides with the point at which the combined GaH_x band area levels off as Ga loading increases (Fig. 6), indicating that the same change in Ga speciation is likely responsible for changes in the trends of both GaH_x and GaOOH bands. It follows that GaH_x species formed after treating $Ga^+–H^+$ pair with H_2 at 550 °C (Ga/Al ratio ≤ 0.13) do not react with water to form GaOOH at 150 °C, and only isolated Ga^+ species are oxidized. Although no detectable GaH_x band is observed on Ga/H-ZSM-5 (Si/Al = 39) after reduction at 550 °C (Fig. 5c), GaH_x bands appear after the sample is cooled to 150 °C under vacuum (black traces of Fig. 7b), which is similar to that on Ga/H-ZSM-5 (Si/Al = 15), as shown in black traces of Fig. 7a. In line with this observation, for the lowest Ga/Al ratio investigated (0.12) on Ga/H-ZSM-5 (Si/Al = 39), water introduction hardly has an effect on the spectra (Fig. 7b(i)). The GaOOH band after water introduction grows with the Ga/Al ratio on Ga/H-ZSM-5 (Si/Al = 39), which is consistent with results on samples with a lower Si/Al ratio of 15 (Fig. 7).

Isotopic labeling experiments verify that GaH_x species do not react with water at 150 °C. The hypothesis that the exchanged Ga species exist in two distinct environments (isolated and paired with a neighboring proton), together with the spectral features observed upon water introduction (Figs. 7 and 8), lead to the prediction that water does not react with GaH_x at 150 °C. The intense band corresponding to GaOOH in most cases overwhelms the GaH_x features, preventing the unambiguous identification of GaH_x bands after water introduction. H-D exchange experiments were conducted to probe the reactivity of GaH_x with water. The FTIR spectra of the reduced Ga/H-ZSM-5 (Si/Al = 39, Ga/Al = 1) at 150 °C shows a positive and a negative peaks at 3740 and 3605 cm^{-1}(Fig. 9a(i)), which can be attributed to the partial restoration of external silanol groups and consumed BAS upon reduction and Ga exchange with BAS, respectively, as discussed previously (Fig. 1). Weak but distinct GaH_2 and GaH band centered at 2040 and 2060 cm^{-1}, respectively, are also present (Fig. 9b(i)). Upon introduction of H_2O (1000 mTorr), a board band spanning 2040–2060 cm^{-1} appears, corresponding to the formation of GaOOH (Fig. 9b(ii)). The broad width of this band makes it difficult to discern whether GaH_x bands remain. D_2O is subsequently introduced (1000 mTorr), leading to the appearance of the SiO-D bands at 2600–2800 cm^{-1} via the H-D exchange. The broad band at 2040–2060 cm^{-1} largely disappears (Fig. 9b(iii)) while a similarly broad band at 1476 cm^{-1} appears (Fig. 9c(iii)), attributable to GaOOD due to the H-D exchange. This assignment is supported by the ratio (1.39) between the wavenumbers of the two bands, which is similar to that between SiOH and SiOD (1.36). Importantly, the band at 2060 cm^{-1} (and to a lesser degree the 2040 cm^{-1} band) remains

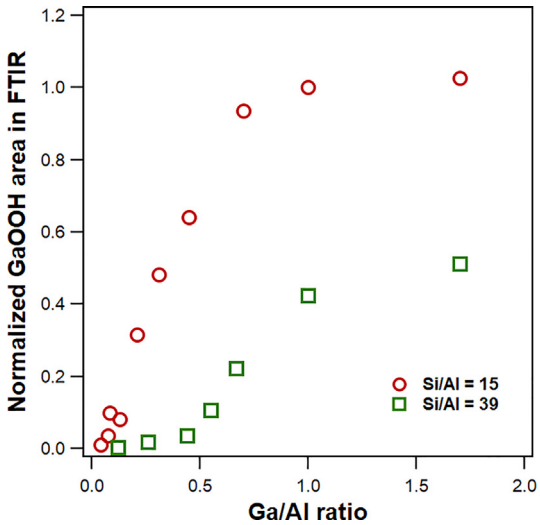


Fig. 8. Integrated GaOOH peak area (subtracted from the integrated peak area before water vapor treatment) determined from infrared spectra (normalized by the GaOOH peak area of Ga/H-ZSM-5 (Si/Al = 15, Ga/Al = 1)) as a function of Ga/Al ratio on Ga/H-ZSM-5 samples with Si/Al ratios of 15 and 39.

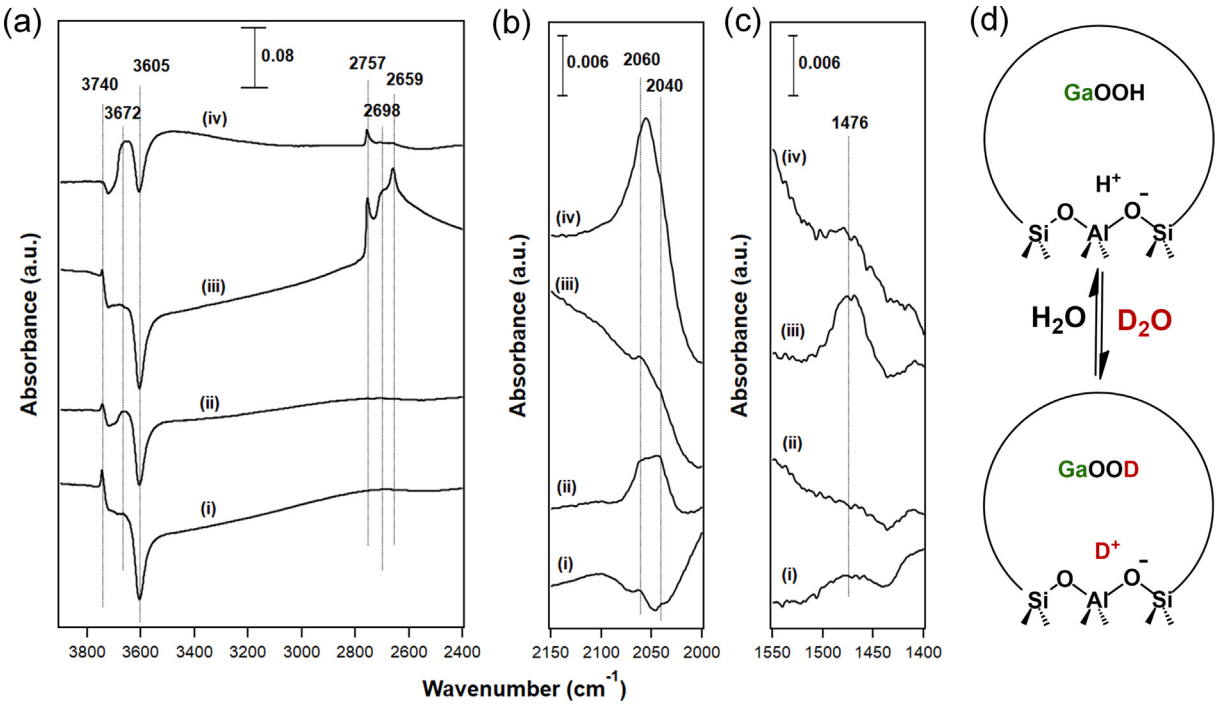


Fig. 9. FTIR spectra of water vapor treatment on Ga/H-ZSM-5 (Si/Al = 39 and Ga/Al = 1.0) at 150 °C in (a) high and (b, c) low wavenumber ranges: (i) reduced at 550 °C and evacuated at 600 °C for 30 min before cooling down to 150 °C under vacuum; (ii) H_2O treatment; (iii) D_2O treatment; (iv) H_2O treatment. Background spectrum was collected in the spectral cell with a sample pellet dehydrated at 550 °C and cooled down to 150 °C under vacuum. (d) Schematic of H-D exchange on water treated reduced Ga/H-ZSM-5 at 150 °C.

after the introduction of excess of D_2O (Fig. 9b(iii)), indicating the presence of GaH_x. This results confirms the prediction that GaH_x does not react with water at 150 °C; proposed based on the lack of change of GaH_x bands upon water introduction for samples with low Ga/Al ratios (Fig. 7a(i) and b(i)). Reintroduction of H_2O in excess is able to largely replace the SiOD and GaOOD bands with SiOH and GaOOH bands, respectively (Fig. 9(iv)).

Additional spectroscopic investigations confirm that Ga^+–H^+ pair sites, unlike isolated Ga^+ sites, cannot react with water at 150 °C, further confirming that these two Ga species possess distinct properties. To avoid the complication of having both Ga^+–H^+ pair sites and isolated Ga^+ sites, Ga/H-ZSM-5 (Si/Al = 15, Ga/Al = 0.042) is used to investigate the ability of Ga^+–H^+ pair to react with water, as we have shown that this sample has a negligible concentration of isolated Ga^+ sites (Fig. 7a(i)). Two independent sets of experiments were conducted in which the Ga/H-ZSM-5 (Si/Al = 15, Ga/Al = 0.042), after H_2 treatment at 550 °C, was either directly cooled to 150 °C under vacuum or cooled to 150 °C after undergoing 30 min of annealing at 600 °C under vacuum. Based on the observed slow decomposition of GaH_x species at 550 °C in vacuum (Fig. S10), annealing at 600 °C is expected to more effectively convert GaH_x species to Ga^+–H^+ pair sites. This is confirmed by the much weaker GaH_x bands on the annealed sample than those of the sample without annealing (Fig. 10a(iii) and a(i), respectively), as shown in schematically in Fig. 10b. Thus, a significant fraction of Ga^+ species in the sample after annealing are pre-

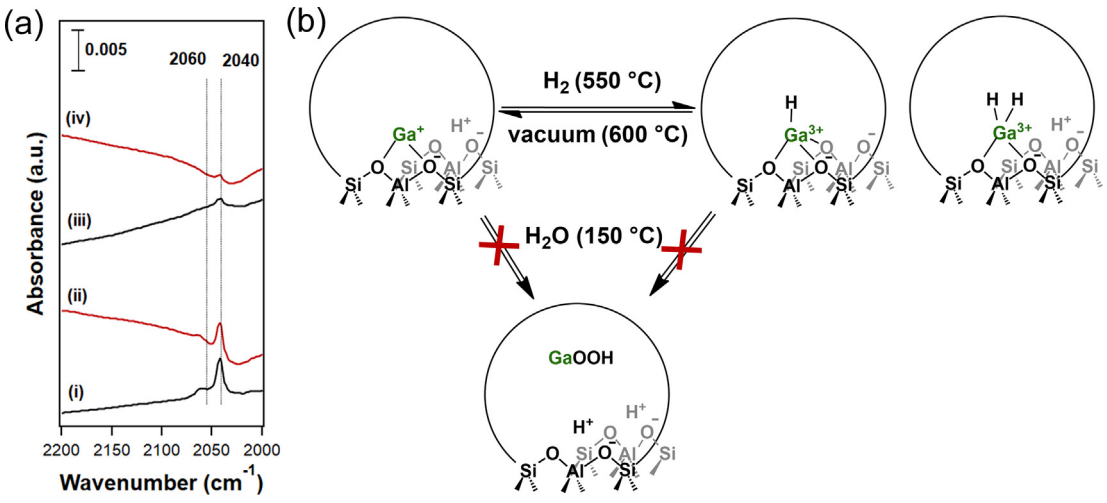


Fig. 10. (a) FTIR spectra of water vapor treatment on Ga/H-ZSM-5 (Si/Al = 15 and Ga/Al = 0.042) at 150 °C: (i) before and (ii) after water vapor treatment for the sample which was reduced at 550 °C and cooled down to 150 °C under vacuum; (iii) before and (iv) after the water treatment for the sample which was reduced at 550 °C and evacuated at 600 °C for 30 min before cooling down to 150 °C under vacuum. Background spectrum was collected in the spectral cell with a sample pellet dehydrated at 550 °C and cooled down to 150 °C under vacuum. (b) Schematic of reaction of H_2 treatment (550 °C) or H_2O treatment (150 °C) on reduced Ga/H-ZSM-5.

sent in the form of Ga^+-H^+ pair sites, rather than GaH_x. No detectable change is observed upon water introduction to both samples at 150 °C, indicating that the Ga^+-H^+ pair is unreactive with water under this condition (Fig. 10a(ii) and a(iv), and Fig. 10b). This is in stark contrast with the isolated Ga^+ species, which readily form GaOOH when exposed to water at 150 °C. This result then verifies that the reactivity of isolated Ga^+ and Ga^+-H^+ pair species are quite different. The drastically different properties of Ga^+-H^+ pair and isolated Ga^+ sites on Ga/H-ZSM-5 upon exposure to H_2 at 550 °C and water at 150 °C strongly suggest the possibility that they could have different catalytic properties in the PDH, which will the subject of study in a future work.

4. Conclusions

Detailed in-situ transmission FTIR spectroscopic investigations of reduced Ga/H-ZSM-5 with three Si/Al ratios (15, 28 and 39) and a wide range of Ga/Al ratio (0–1.7) show that Ga speciation depends on both Si/Al and Ga/Al ratios. Upon reduction with H_2 at 550 °C, Ga species initially located on the external surface migrate into the zeolitic micropores of H-ZSM-5 and exchange with BAS to form Ga^+. Ga^+ preferentially exchanges with single protons in paired BAS sites over protons in isolated BAS, to form Ga^+-H^+ pair sites on samples with low Si/Al ratios. Mainly isolated Ga^+ exchanged with isolated BAS are produced on samples with a high Si/Al ratio. A one-to-one correspondence in the consumption of BAS and Ga loading is found in samples with low Si/Al and Ga/Al ratios by quantitative FTIR spectroscopy with pyridine, however, exchange with BAS becomes increasingly difficult at higher Ga loadings due to the scarcity of BAS. Up to ~80% of BAS are consumed at Ga/Al ratios as high as 1.7, suggesting complete removal of BAS cannot be achieved with excess Ga. Spectral features of GaH_x observed on reduced Ga/H-ZSM-5 samples at 550 °C show that Ga hydrides can only form on Ga^+-H^+ pair sites, rather than isolated Ga^+ sites, which provides the first direct experimental evidence of inhomogeneity of exchanged Ga species. This is supported by spectral observations with water as a probe molecule, in which only isolated Ga^+ can be oxidized by water at 150 °C to form GaOOH, while Ga^+-H^+ pair sites, regardless of the existence of GaH_x species, do not react with water. The drastically different properties of Ga^+-H^+ pair sites and isolated Ga^+ sites on Ga/H-ZSM-5 upon reaction with H_2 at 550 °C and water at 150 °C strongly suggest the possibility that they could have different catalytic properties in the PDH.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcat.2020.11.004.

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