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# Adsorption Properties of Oxidized Gallium-Modified Zeolite ZSM-5 from Diffuse Reflectance IR and Quantum-Chemical Data: 1. Interaction with Hydrogen and Ethane

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**Abstract**—Diffuse reflectance IR spectroscopy was used to study adsorption and subsequent high-temperature hydrogen and ethane transformations on gallium ions in gallium-modified ZSM-5 zeolite. The results were correlated with the corresponding quantum-chemical calculations. From the experimental and calculated data, it follows that trivalent gallium oxo ions are reduced to the univalent state in a hydrogen or ethane atmosphere even at moderate temperatures. Therefore, gallium oxo ions can function as active sites only at the early stages of light-paraffin aromatization. At the later stages, the dehydrogenation of light paraffins involves univalent gallium ions through the formation of intermediate gallium and alkylgallium hydrides.

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Modification of the hydrogen form of zeolite ZSM-5 with gallium ions greatly enhances its activity in the aromatization of light paraffins [1, 2]. It is commonly believed that the role of gallium is to enhance the dehydrogenation ability of these catalysts. However, the valence state of gallium in the active sites is still under debate. Some authors ascribe the dehydrogenation function to univalent gallium ions [3–5]. Others believe that oxidized species whose active sites are gallium(III) oxo ions are more active in the dehydrogenation of light paraffins [6, 7].

We have recently studied the adsorption and catalytic properties of modifying univalent gallium ions [8, 9]. It was established that light paraffins can add dissociatively to the $Ga^+$ ion to form gallium and alkylgallium hydrides. The subsequent decomposition of the alkyl groups yields gallium dihydrides and olefins:

$$\begin{aligned} &Ga^+ + RH \longrightarrow [H\text{–}Ga\text{–}R]^+, \\ &[H\text{–}Ga\text{–}R]^+ \longrightarrow [H\text{–}Ga\text{–}H]^+ + \text{olefin}. \end{aligned} \qquad (I)$$

At a high temperature, gallium dihydrides liberate molecular hydrogen:

$$[H\text{–}Ga\text{–}H]^+ \longrightarrow Ga^+ + H_2. \qquad (II)$$

Continuing that series of studies, here we report the adsorption properties of gallium-modified zeolite ZSM-5 subjected to oxidizing treatment. Our experiments were conducted using high-sensitivity diffuse reflectance IR spectroscopy and volumetric measurements. The results were correlated with quantum-chemical calculations carried out for the model proposed in [10] and augmented with an extended triple-zeta basis set with diffuse components on all cluster atoms except the hydrogen atoms. The calculations were performed for the temperatures used in our experiments. Calculations were performed for the structures considered in [10], as well as for some other adsorption structures and for the activation barrier to the direct reduction of the $[GaO]^+$ ion by a hydrogen molecule with the formation of a water molecule.

## EXPERIMENTAL

The hydrogen form of ZSM-5 (Alsi-Penta) zeolite with a framework Si : Al ratio of 25 was taken as the starting material for sample preparation. As in our previous investigations [8, 9], it was modified with gallium ions by two methods. In the first, zeolite was impregnated with an aqueous solution of gallium nitrate, whose amount was sufficient to replace all protons with gallium ions. This yielded a zeolite containing 4.5 wt % Ga. Its total aluminum content was $3.7 \times 10^{20}$ at/g. The resulting materials were reduced with hydrogen under static conditions for 5 h at 773 K and were then pumped at the same temperature. After this treatment, the intensity of the absorption band at 3610 cm$^{-1}$ from acidic hydroxyl groups decreased almost tenfold, indicating the nearly complete replacement of protons by reduced, univalent gallium ions.

In the second case, the hydrogen form of the zeolite was modified by reacting it with trimethylgallium vapor at 323 K with intermediate reduction in hydrogen at 723 K. This procedure was repeated three times; as a

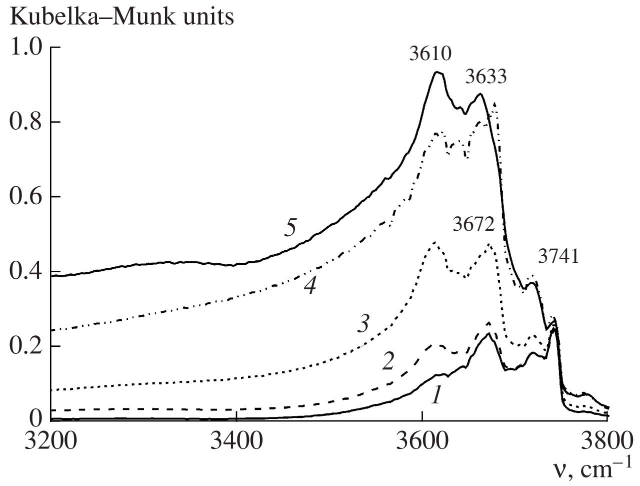

**Fig. 1.** Diffuse reflectance IR spectra of Ga/ZSM-5 (*1*) oxidized at 673 K in $N_2O$, (*2*) recorded after $H_2$ adsorption, and (*3–5*) after heating in $H_2$ at (*3*) 373, (*4*) 473, and (*5*) 573 K.

result, the protons were almost completely replaced by gallium ions. This was indicated by the disappearance of the band at 3610 $cm^{-1}$ in the diffuse reflectance spectrum. The dimethylgallium ions grafted to the zeolite surface were then decomposed in hydrogen at 723 K, and the product was pumped at the same temperature. The samples prepared by these methods will be designated Ga/ZSM-5 and TMG/ZSM-5, respectively.

To obtain oxidized gallium-modified samples, prereduced zeolite was oxidized with nitrous oxide under static conditions at 673 K. It followed from the amount of evolved molecular nitrogen that the extent of oxidation of univalent gallium was 80–90%.

To measure diffuse reflectance IR (DRIFT) spectra, zeolite samples were placed in a quartz cell with a side arm having a $CaF_2$ window. IR spectra were recorded at room temperature on an FTIR spectrophotometer (Nicolet Impact 410) with a diffuse reflectance attachment. The spectra were converted to the Kubelka–Munk units under the assumption that the zeolite reflectance at 5000 $cm^{-1}$ is 0.9. In some cases, the zeolite background was subtracted from the overall spectrum.

The interaction of gallium oxo ions with hydrogen or ethane was studied in the temperature range 300–673 K at a pressure of 0.1 or 150 Torr. At each chosen temperature, the samples were heated in hydrogen or ethane for 0.5 h, whereupon IR measurements were performed at room temperature.

Quantum-chemical calculations were carried out using density functional theory with a B3LYP functional [11–13] in the 6-311+G* basis set and the GAUSSIAN 98 program [14]. Before calculating the total energy, the geometric parameters of all structures were fully optimized. For the stationary points found on the potential energy surface, force-constant matrices were calculated and normal mode analysis was performed. The vibrational frequencies obtained were used to directly (without introducing scale factors) calculate the zero-point energies, enthalpies, and free energies at the given temperatures and pressures. The transition states were found by the QST2 and QST3 methods. Calculations for the saddle-point geometries demonstrated that there is a single imaginary vibrational frequency corresponding to the surmounting of the potential barrier. The fit of the calculated transition states with the starting reactants and final products was confirmed by IRC calculations.

## RESULTS AND DISCUSSION

### *Interaction of Oxidized Samples with Hydrogen*

Hydrogen adsorption on the oxidized samples and their reduction were studied between room temperature and 673 K at a hydrogen pressure of 150 Torr over the samples. One can see from spectra *1* and *2* in Fig. 1 that adsorption at room temperature has only a slight effect on the DRIFT spectrum of the oxidized sample. Subsequent heating of this sample in a hydrogen atmosphere at a temperature gradually increasing from 373 to 573 K gives rise to a broad absorption band almost identical to the band observed upon water adsorption on oxidized gallium-modified zeolite (the spectrum is not shown). Simultaneously, a band at ~5170 $cm^{-1}$ appears in the spectral range characteristic of the combination bands of adsorbed water (~5000 $cm^{-1}$, the combination of stretching and bending modes). These changes are evidence that water results from the interaction of the oxidized sample with hydrogen at the indicated temperatures. At the same time, the intensities of the narrow bands at 3610 and 3672 $cm^{-1}$, which are due to the bridging acidic hydroxyl groups and GaOH groups, respectively, increase upon heating. At 573 K, the band at 3672 $cm^{-1}$ is shifted to 3663 $cm^{-1}$, likely because of the change in the number of gallium-bonded $OH^-$ groups.

Upon further heating, a band at 2059 $cm^{-1}$ from gallium monohydrides appears at 573 K (Fig. 2). Heating in hydrogen at a still higher temperature (673 K) followed by pumping out the hydrogen and water at the same temperature leads to the total disappearance of the broad absorption band.

Similar results were obtained for the reduction of the TMG/ZSM-5 sample in hydrogen.

Our experimental results and quantum-chemical calculations suggest that the interaction between hydrogen and gallium oxo ions at high temperatures results in their reduction and hydride formation by the reactions

$$[Ga{=}O]^+ + H_2 \longrightarrow Ga^+ + H_2O, \qquad (III)$$

$$[Ga{=}O]^+ + H_2 \longrightarrow [GaH(OH)]^+. \qquad (IV)$$

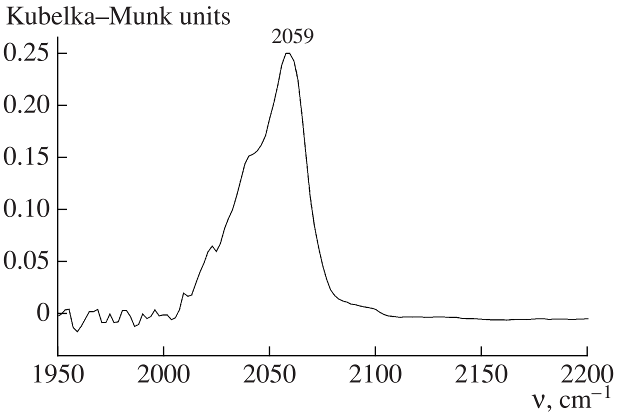

**Fig. 2.** Diffuse reflectance IR spectrum of gallium hydride obtained by reducing GaZSM-5 in $H_2$, oxidizing the product in $N_2O$ at 673 K, and heating the product in hydrogen at 573 K.

According to our quantum-chemical calculations (table), the first reaction is thermodynamically very favorable: $\Delta H^\circ_{673\ K}$ = –37.3 kcal/mol, $\Delta G^\circ_{673\ K}$ = –42.7 kcal/mol, and $E_a$ = 38.3 kcal/mol (the structure of the transition complex is shown in Fig. 3). As the temperature increases to 773 K, the enthalpy slightly decreases to –37.6 kcal/mol and the free energy decreases to –43.5 kcal/mol. The adsorbed water formed in this reaction can then be dissociatively adsorbed on the trivalent gallium oxo ions by the reaction

$$[Ga{=}O]^+ + H_2O \longrightarrow [HO{-}Ga{-}OH]^+. \quad (V)$$

This follows from the fact that the IR spectra of the samples heated in water at 373 K are identical to the spectra of the samples heated in hydrogen at 573 K. Reaction (IV) is also thermodynamically favorable: $\Delta H^\circ_{673\ K}$ = –52.3 kcal/mol, $\Delta G^\circ_{673\ K}$ = –33.2 kcal/mol, and $E_a$ = 18.9 kcal/mol, and these values increase with temperature. Indeed, the formation of gallium monohydrides is indicated by IR spectra even at 573 K. These data agree well with earlier results [10].

The $GaH(OH)^+$ ions produced by reaction (IV) can undergo further transformations. Their decomposition with water elimination and gallium reduction to the univalent state,

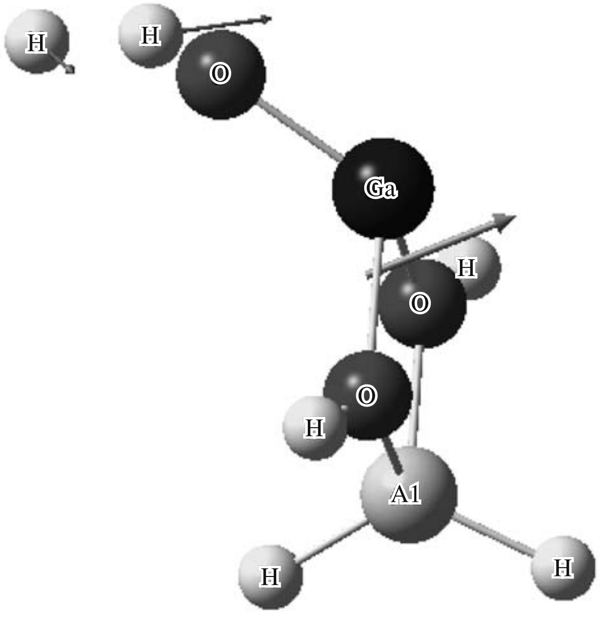

**Fig. 3.** Transition state structure and transition vector for reaction (III).

$$[GaH(OH)]^+ \longrightarrow Ga^+ + H_2O, \quad (VI)$$

does not proceed readily [10]. According to our calculations, the heat of this endothermic reaction is $\Delta H^\circ_{673\ K}$ = +15 kcal/mol, while the change in the free Gibbs energy is negative: $\Delta G^\circ_{673\ K}$ = –9.5 kcal/mol. However, the corresponding activation barrier is rather high; $E_a$ = 52.9 kcal/mol. Because of this, water can be desorbed only at very high temperatures, whereas, at low temperatures, other transformations must occur. Indeed, hydrogen can substitute for adsorbed water in a hydrogen atmosphere:

$$[GaH(OH)]^+ + H_2 \longrightarrow [HGaH]^+ + H_2O. \quad (VII)$$

According to our calculations, this is a moderately endothermic reaction with $\Delta H^\circ_{673\ K}$ = +11.9 kcal/mol and $\Delta G^\circ_{673\ K}$ = +8.8 kcal/mol. The corresponding activation barrier, $E_{a,\,673\ K}$ = 33.0 kcal/mol, is appreciably lower than the barrier for reaction (VI) (the transition

Quantum-chemical enthalpies, free energies, and activation energies (in kcal/mol) for reactions at 673 and 773 K

| Reaction | Δ*H*, 673 K | Δ*H*, 773 K | Δ*G*, 673 K | Δ*G*, 773 K | $E_a$, 673 K | $E_a$, 773 K |
|---|---|---|---|---|---|---|
| $[Ga{=}O]^+ + H_2 \longrightarrow Ga^+ + H_2O$ (III) | –37.3 | –37.6 | –42.7 | –43.5 | 38.3 | 38.3 |
| $[Ga{=}O]^+ + H_2 \longrightarrow [GaH(OH)]^+$ (IV) | –52.3 | –52.2 | –33.2 | –30.4 | 18.9 | 18.9 |
| $[HGaOH]^+ \longrightarrow Ga^+ + H_2O$ (VI) | 15 | 14.6 | –9.5 | –13.1 | 53.0 | 52.9 |
| $[GaH(OH)]^+ + H_2 \longrightarrow [HGaH]^+ + H_2O$ (VII) | 11.9 | 11.6 | 8.8 | 8.3 | 33 | 32.9 |
| $[HGaH]^+ \longrightarrow Ga^+ + H_2$ (VIII) | –3.1 | –3.0 | +18.3 | +21.5 | 70.0 | 70.9 |

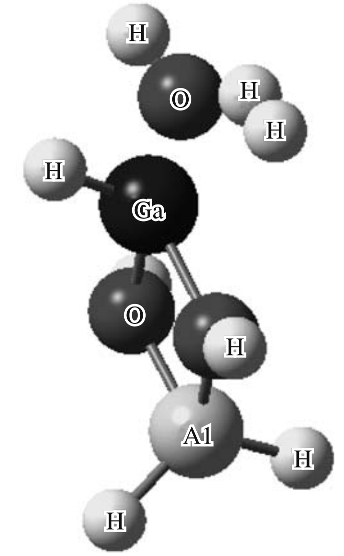

**Fig. 4.** Transition state structure and transition vector for reaction (VII).

state structure is shown in Fig. 4). For this reason, reaction (VI) can proceed to some extent at relatively low temperatures. Ultimately, oxo ions can be reduced to univalent gallium ions as a result of subsequent hydrogen desorption by the reaction

$$[GaH_2]^+ \longrightarrow Ga^+ + H_2. \qquad (VIII)$$

As is mentioned above, univalent gallium can also be produced by reaction (VI). The activation barriers for both reactions are very high: 71 and 52.9 kcal/mol, respectively. For this reason, these reactions can proceed only at rather high temperatures. Indeed, it was demonstrated experimentally in our recent work [9] that gallium dihydride decomposes starting only at 723 K. Unfortunately, the IR spectra of gallium dihydride were not recorded in this work because of the presence of adsorbed water produced by reaction (III).

In spite of the high energy barrier to reaction (VIII), the oxidized form of gallium-substituted zeolite reacts with hydrogen to give univalent gallium ions as the final product. To explain this fact, we suggested a scheme (Fig. 5) of consecutive hydrogen elimination from $[GaH_2]^+$ via an intermediate corresponding to the gallium monohydride $Z^-[H]^+[GaH]$ adsorbed in the vicinity of a Brønsted proton. The activation energy for the first reaction,

$$Z^-[GaH_2]^+ \longrightarrow Z^-H^+[GaH]^0 \qquad (IX)$$

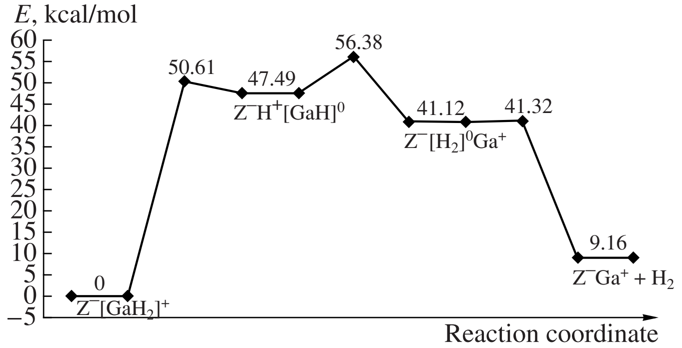

**Fig. 5.** Energy profile for the $[GaH_2]^+$ decomposition into $Ga^+$ and $H_2$.

is 50.6 kcal/mol (Fig. 5). However, the energy of the corresponding intermediate is high (47.5 kcal/mol higher than for $[GaH_2]^+$), so the intermediate is unstable. It was established that subsequent decomposition to $Ga^+$ proceeds via another intermediate, which is a hydrogen molecule tightly clamped between the gallium atom and the zeolite framework, $Z^-[H_2]^0Ga^+$. In spite of the fact that the energy barrier to the reaction

$$Z^-H^+[GaH]^0 \longrightarrow Z^-[H_2]^0Ga^+ \qquad (X)$$

is higher (8.9 kcal/mol) than to reaction (IX) (3.1 kcal/mol), the $Z^-[H_2]^0Ga^+$ intermediate is less stable and decomposes without activation (the calculated activation energy is as low as 0.2 kcal/mol; Fig. 5) to a univalent gallium ion and a free hydrogen molecule:

$$Z^-[H_2]^0Ga^+ \longrightarrow Z^-Ga^+ + H_2. \qquad (XI)$$

Although the transition state is energetically and geometrically similar to the starting reactant, its structure was, nevertheless, obtained and proved by IRC calculations. Normal mode analysis for both structures confirms that they correspond to the local minimum and the transition state, respectively.

Therefore, for reaction (VIII) to proceed via the three-step route (IX)–(XI), the system must overcome a combined barrier of 56.4 cal/mol, which is almost 15 kcal/mol lower than the activation energy for the one-step process.

Therefore, even at moderate temperatures (~573 K), the reaction of gallium oxo ions with hydrogen can yield gallium mono- and dihydrides, whose subsequent decomposition at higher temperatures can also give univalent gallium.

The conclusion about the formation of univalent gallium was also confirmed volumetrically. After reducing an oxidized sample in a hydrogen atmosphere at 673 K and pumping it at 773 K, its interaction with $N_2O$ was studied at 643 K. Heating in $N_2O$ was accompanied by oxygen absorption and the evolution of nitrogen, whose amount was ~45% of the gallium oxo ion content of the initial sample. The IR band from GaOH slightly increased (Fig. 6, curve *3*) because of the oxidation of gallium hydrides with atomic hydrogen. The occurrence of this reaction was proved in our earlier

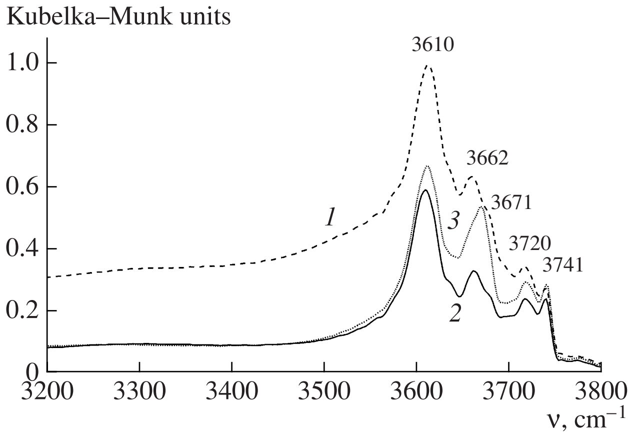

**Fig. 6.** Diffuse reflectance IR spectra of TMG/ZSM-5 oxidized in $N_2O$ at 673 K recorded (*1*) after heating in hydrogen at 673 K, (*2*) after subsequent pumping at 773 K, and (*3*) after another oxidation in $N_2O$ at 643 K.

work [9]. Thus, the reaction of hydrogen with gallium oxo ions yields reduced, univalent gallium ions and gallium hydrides even at 673 K. The water molecules produced in reactions (III), (VI), and (VII) can further react with oxo ions via reactions (V) to give acidic protons, whose absorption bands were also observed in the IR spectrum:

$$[\mathrm{HO{-}Ga{-}OH}]^+ \longrightarrow [\mathrm{O{=}Ga{-}OH}]^0 + \mathrm{Z{-}H}^+$$

or

$$[\mathrm{HO{-}Ga{-}OH}]^+ + \mathrm{H_2O} \longrightarrow [\mathrm{Ga{-}(OH)_3}]^0 + \mathrm{Z{-}H}^+.$$

### *Interaction of Gallium Oxo Ions with Ethane*

The spectra of ethane adsorbed on the gallium-modified oxidized samples and on the initial HZSM-5 zeolite are shown in Fig. 7. They exhibit four absorption bands with nearly the same peak positions and intensity ratios. A decrease in the equilibrium ethane pressure in the gas phase leads to a symbatic decrease in the intensities of all bands, which disappear after pumping at room temperature. Hence, at low temperatures, ethane is adsorbed both on the oxidized gallium-modified sample and on the hydrogen form of zeolite, but only weakly.

To reveal specific adsorption forms on the oxidized Ga/HZSM-5, adsorption was carried out at a very low ethane pressure (0.01 Torr). The band positions in the range 2800–3000 $cm^{-1}$ are similar to those in the high-pressure ethane spectrum, and a new, low-intensity band with a maximum at ~2740 $cm^{-1}$ is observed below 2800 $cm^{-1}$ (Fig. 7c). A similar band was observed for ethane adsorption on gallium oxide at room temperature [15], and its appearance is evidence of the strong polarization of ethane adsorbed by low-coordinated $Ga^{3+}$ cations. Upon further heating of the $Ga_2O_3$ samples containing adsorbed ethane, the latter is dissociated heterolytically at 423 K on the acid–base pairs consisting of $Ga^{3+}$ cations and oxygen atoms. Thus, ethane is polarized upon adsorption on the oxidized

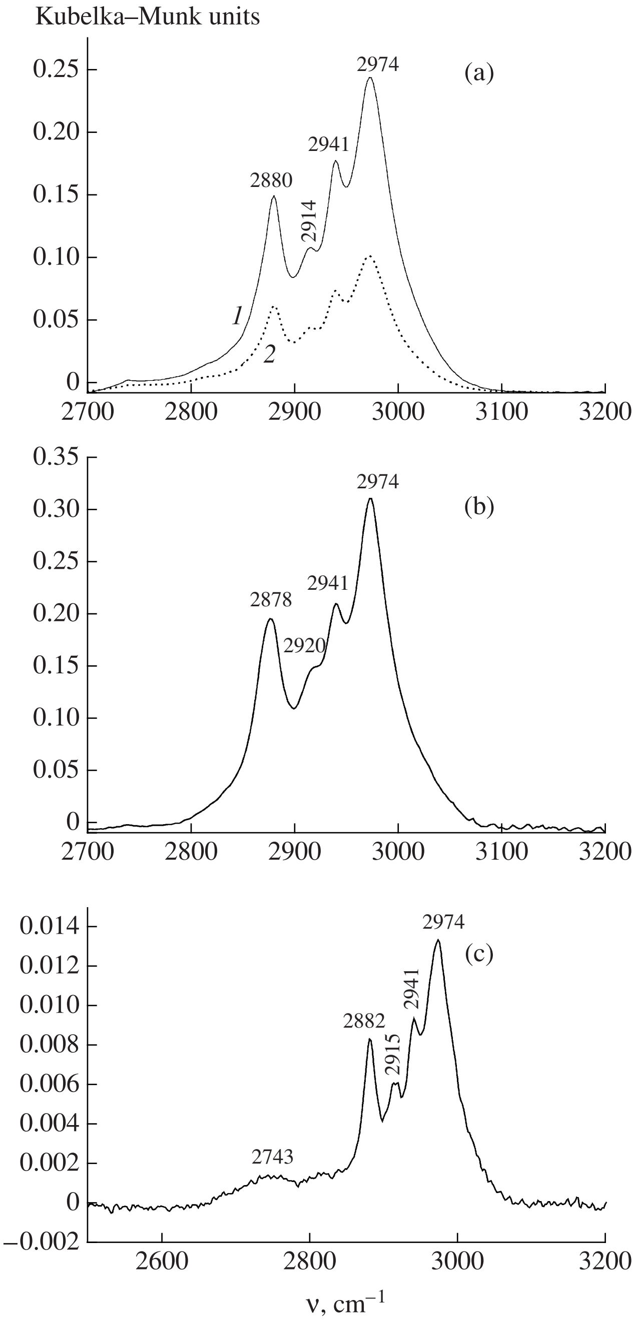

**Fig. 7.** Diffuse reflectance IR spectra recorded for ethane adsorbed at room temperature on different zeolite samples: (a) Ga/HZSM-5 reduced in $H_2$ and then oxidized in $N_2O$ at $T$ = 673 K and equilibrium pressures of (*1*) 1.50 and (*2*) 0.30 Torr; (b) HZSM-5 oxidized at an equilibrium pressure of 0.73 Torr; and (c) Ga/HZSM-5 reduced in $H_2$ and then oxidized in $N_2O$ at 673 K and an equilibrium pressure of 0.01 Torr.

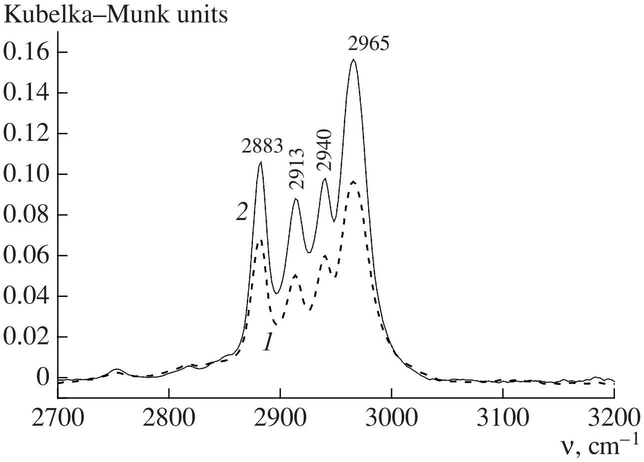

**Fig. 8.** Diffuse reflectance IR spectrum of Ga/HZSM-5 reduced in $H_2$ and then oxidized in $N_2O$ at 673 K, recorded after heating in ethane ($P$ = 14 Torr) at (*1*) 423 and (*2*) 473 K followed by pumping at room temperature.

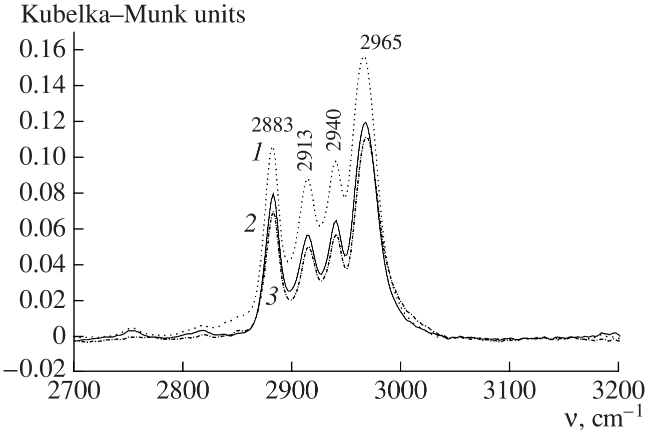

**Fig. 9.** Diffuse reflectance IR spectrum of Ga/HZSM-5 reduced in $H_2$ and then oxidized in $N_2O$ at 673 K, recorded after heating in ethane ($P$ = 14 Torr) at 473 K and pumping at (*1*) room temperature, (*2*) 523, and (*3*) 573 K.

gallium-substituted ZSM-5 samples, as in the case of adsorption on pure gallium oxide, confirming the presence of gallium oxide structures in zeolite pores.

On heating of GaZSM-5 in an ethane atmosphere followed by pumping at room temperature, a series of new bands appear in the spectral range characteristic of CH vibrations. Their peak positions differ from the peak positions of adsorbed ethane (Fig. 8). As the heating temperature is raised to 473 K, these bands grow. They disappear only after pumping above 573 K (Fig. 9). Therefore, they are assignable to grafted alkyl groups. At the same time, a broad band similar to the band observed after water adsorption appears in the IR spectrum after heating gallium-modified samples in ethane (Fig. 10). No new bands characteristic of hydrides were observed in this case.

These results can likely be explained by the occurrence of the following reactions, in which gallium is also reduced with ethane to the univalent state at elevated temperatures:

$$[Ga{=}O]^+ + C_2H_6 \longrightarrow [HO–Ga–C_2H_5]^+, \qquad (XII)$$

$$[HO–Ga–C_2H_5]^+ \longrightarrow Z^-–[HO–Ga–H]^+ + C_2H_4 \qquad (XIII)$$

and, by analogy with reaction (X),

$$[HO–Ga–H]^+ \longrightarrow Ga^+ + H_2O \qquad (XIV)$$

or

$$Z^-–[HO–Ga–C_2H_5]^+ \longrightarrow Z^-–Ga^+ + C_2H_5OH. \qquad (XV)$$

Furthermore, by analogy with reaction (III), one can also expect the reaction

$$[Ga{=}O]^+ + C_2H_6 \longrightarrow Ga^+ + C_2H_5OH.$$

The finding that reaction (XII) proceeds comparatively readily is confirmed by quantum-chemical calculations [16, 17]. Water formation in reaction (XIV) can also explain both the increase in the concentration of bridging hydroxyl groups and the appearance of a broad absorption band (see *Interaction of Oxidized Samples with Hydrogen*).

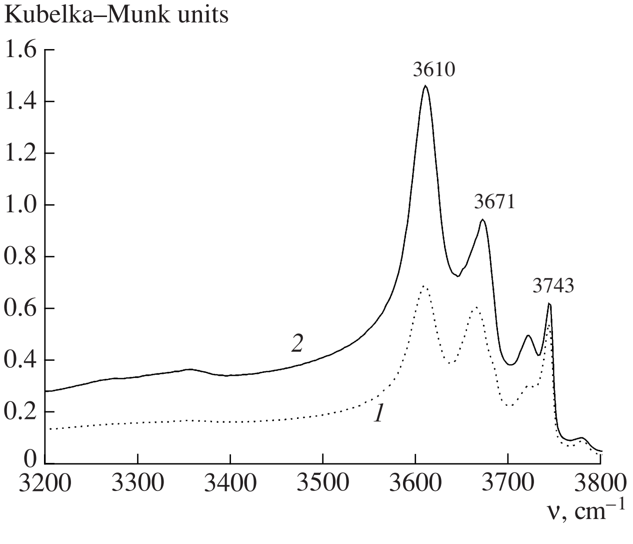

**Fig. 10.** Diffuse reflectance IR spectrum of Ga/HZSM-5 in the OH vibration range: (*1*) sample reduced in hydrogen and then oxidized in $N_2O$ at 673 K and (*2*) the same after heating in ethane ($P$ = 14 Torr) at 523 K and pumping at room temperature.

## CONCLUSIONS

From the experimental results obtained in this work and confirmed by quantum-chemical calculations, it follows that, in a reducing medium, trivalent gallium oxo ions can be reduced to the univalent state at elevated temperatures. For this reason, the conclusion drawn by some authors that the oxo ions are more active than the univalent gallium ions is correct only for the early stages of light-paraffin aromatization. In [7], the conversion and yield of aromatic compounds in the propane aromatization reaction on Ga/ZMS-5 preliminary oxidized in oxygen were carefully compared with the same data for the zeolite reduced in hydrogen. To do this, multiple cyclic redox treatments were conducted and catalytic tests were made after each oxidation and reduction step. For the oxidized samples, the conversion and yield of aromatic compounds were slightly higher. Based on this fact, the conclusion was made that the oxo ions are more active. Nevertheless, we believe that this conclusion is not entirely correct, because the conversions and yields reported in [7] were determined only within two minutes after the beginning of the reaction. For a long-term reaction, values other than those reported in [7] would be obtained and light-paraffin aromatization on the gallium-modified high-silica zeolites would involve the set of reactions considered in our previous work [9] for reduced Ga/ZSM-5.

The results presented in this work are in good agreement with a recent work by other authors [18], where it is shown that the $GaO^+$ oxo ion is more active in propane dehydrogenation than the $Ga^+$ ion. Unfortunately, such catalysts are deactivated within a short time because of the high energy barrier to the oxo ion regeneration reaction.

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