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Adsorption Properties of Oxidized Gallium-Modified Zeolite ZSM-5 from Diffuse-Reflectance IR-Spectroscopic and Quantum-Chemical Data:
II. Interaction with Carbon Monoxide and Water

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Abstract—Diffuse-reflectance IR spectroscopy was used to study the adsorption and subsequent high-temperature transformations of water and carbon monoxide molecules on the oxidation-treated gallium-modified zeolite Ga/HZSM-5. The results were correlated with the corresponding quantum-chemical calculation data. Usually, it is thought that the oxo ions $[Ga{=}O]^+$ are formed in the oxidation of Ga/HZSM-5. Based on the experimental and calculated data, the possible reactions of the gallium oxo ions with the above molecules are considered. The oxo ions were found highly reactive, and it is likely that polynuclear gallium oxide nanoclusters were formed in the oxidation of the gallium-substituted zeolite Ga/HZSM-5. The Ga^+ ions, which appeared in the course of Ga/HZSM-5 reduction, were partially oxidized by water at 573 K; in turn, this could initiate the formation of polynuclear nanoclusters. It was found that ~25% of the Ga^+ ions were oxidized in the interaction with water to liberate molecular hydrogen. The thermal reduction of a nitrous oxide–preoxidized Ga/HZSM-5 sample with carbon monoxide was studied, and a conclusion on dissimilar states of oxygen bound to gallium was drawn.

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INTRODUCTION

This work is a continuation of our studies [1] on the reactivity of high-silica zeolites ZSM-5 modified with gallium ions. In this case, attention is focused on the states of an active component in oxidized zeolite samples. As noted previously, these systems are of interest because the activity of oxidized trivalent gallium ions in the dehydrogenation of light paraffins is higher than that of univalent gallium in accordance with published data [2, 3]. Previously [1], we used IR spectroscopy and quantum-chemical calculations to study the interaction of gallium zeolites with reducing agent molecules (hydrogen and ethane). We found that an active component can be reduced to univalent gallium even at moderate temperatures in a reducing atmosphere of hydrogen or ethane or intermediate species can be formed, which undergo degradation to generate Ga^+ ions. We also found that water molecules can be released in the course of these reactions. Water can react with both Ga^{3+} structures and Ga^+ produced in the course of reduction reactions. In this context, it was of interest to study the interaction of the resulting water with oxidized and reduced gallium ions. These studies were performed using IR spectroscopy and quantum-chemical calculations. The study of the thermal reduction of preoxidized Ga/HZSM-5 samples with carbon monoxide was also continued.

EXPERIMENTAL AND QUANTUM-CHEMICAL CALCULATIONS

As in the previous study [1], high-silica zeolite HZSM-5 with the modulus Si/Al = 25 was used in this work. This zeolite was modified with gallium ions in accordance with a procedure described previously [1].

The interaction of the oxidized form of the gallium-substituted zeolite with water was studied over the temperature range 300–673 K at a water vapor pressure of 0.1 Torr. The heating time was 0.5 h for each particular temperature; thereafter, the IR spectra were measured at room temperature.

Carbon monoxide was initially adsorbed at 15 Torr and room temperature; then, the sample was heated at 623 K in an atmosphere of CO for 1 h. Carbon dioxide released in the course of reduction was collected in a trap cooled with liquid nitrogen. After the completion of the experiment and the evacuation of residual CO, the trap contents were thawed and the amount of

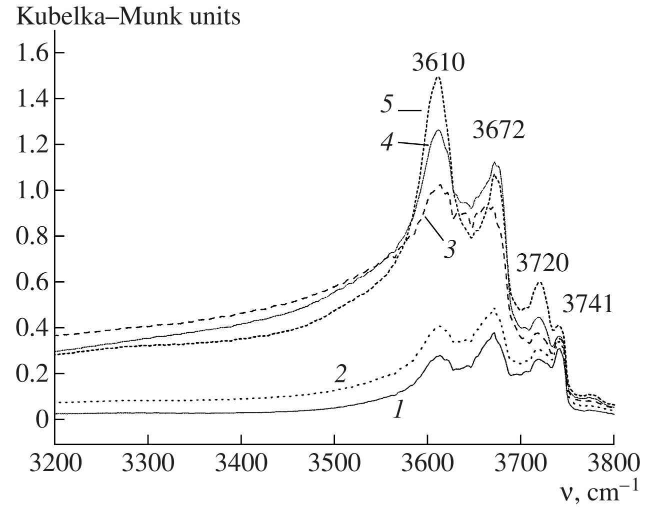


Fig. 1. Diffuse-reflectance IR spectrum of TMG/ZSM-5 (*1*) after oxidation in N_2O at 673 K or (*2*) after water adsorption at room temperature followed by heating at (*3*) 373, (*4*) 473, or (*5*) 673 K.

reacted CO was determined from the amount of released CO_2.

The IR spectra were measured in accordance with a procedure analogous to that described previously [1].

The quantum-chemical calculations were performed using density functional theory (DFT) with the hybrid B3LYP functional [2–4] and the 6-311+G* basis set and using the GAUSSIAN 03 program [5]. As found by Baker et al. [6], this B3LYP functional adequately reproduces the geometries of surface complexes, as well as the heats of reactions, energy barriers, and the vibrational frequencies of adsorbed molecules.

The calculations were performed for various clusters that simulated a zeolite cation position formed by a lattice aluminum ion. The first model was analogous to that accepted by Gonzales et al. [7] and implied the aluminum center $H_2Al(OH)_2^-$. The adsorption and reaction structures constructed for this model were fully optimized. In a number of calculations, the cluster structure was extended to $Al(OH)_4^-$, whose position corresponded to the T12 position of the zeolite [8]. In this case, a tetrahedron was restricted by hydrogen atoms arranged in the direction of O–Si dangling bonds [8] at a distance of 1 Å from oxygen atoms. At the first step of the optimization of these structures, the entire aluminum–oxygen tetrahedron was frozen and the positions of the gallium atom and O–H distances were optimized at fixed directions of O–H bonds along O–Si bonds in the crystal. The found positions of the restricting hydrogen atoms were then saved and used in the subsequent calculations. Next, the framework was defrosted and the Cartesian coordinates of hydrogen atoms were fixed. The subsequent calculations of stationary points were performed with the unchanged positions of the fixing hydrogen atoms.

For the stationary points found on the potential energy surface, force-constant matrices were calculated and normal mode analysis was performed. The resulting vibrational frequencies were subsequently used to calculate directly (without introducing correlation factors) the zero-point energies (ZPEs), enthalpies, and free energies at the given temperatures and pressures.

Reaction paths for the oxidation of the CO molecule with the $[Ga{=}O]^+$ oxo ions were calculated based on the well-known cluster model $Al(OSiH_3)_4^-$ of the T5 cationic position in the zeolite. The adsorption complex $CO–GaO/Al(OSiH_3)_4$ and the transition state (TS) of the reaction were characterized using frequency analysis, and the found TS structure was checked by the standard method of intrinsic reaction coordinate calculations.

RESULTS AND DISCUSSIONS

Interaction of Oxidized and Reduced Ga/ZSM-5 Samples with Water

After the adsorption of water by oxidized gallium-modified samples at room temperature and an equilibrium pressure of 10^{-1} Torr, the diffuse-reflectance IR spectra exhibited a very broad absorption band in the region 3000–3400 cm^{-1} (Fig. 1, spectrum *2*). As the samples with adsorbed water were further heated to 373 K, the intensity of this broad band, as well as the intensities of narrow absorption lines due to bridging hydroxyl groups and GaOH groups with maximums at 3610 and 3665 cm^{-1}, respectively (Fig. 1, spectrum *3*), dramatically increased. This is indicative of the partial hydrolysis of gallium ions. This trend continued as the heating temperature was further increased from 473 to 673 K. In this case, the band maximum from gallium hydroxides shifted to 3672 cm^{-1} as the temperature was increased. This suggests the formation of gallium compounds $Ga(OH)_x$ ($x = 1–3$) bound to different numbers of OH groups in the course of heating in an atmosphere of water. Note that the maximum intensity of an absorption band from acidic bridging groups at the end of the experiments remained lower than that in the initial sample of the hydrogen form of the zeolite by a factor of about 3 (cf. spectra *1* and *3* in Fig. 2).

The interaction of oxidized samples with water to form dihydroxide cationic species in the zeolite can be represented by the following reaction:

$$[Ga{=}O]^+ + H_2O \longrightarrow [HO–Ga–OH]^+. \qquad (I)$$

According to the results of quantum-chemical calculations (Table 1), which are consistent with published data [7], this reaction is strongly exothermic with a heat effect of –60.6 kcal/mol. In this case, the thermody-

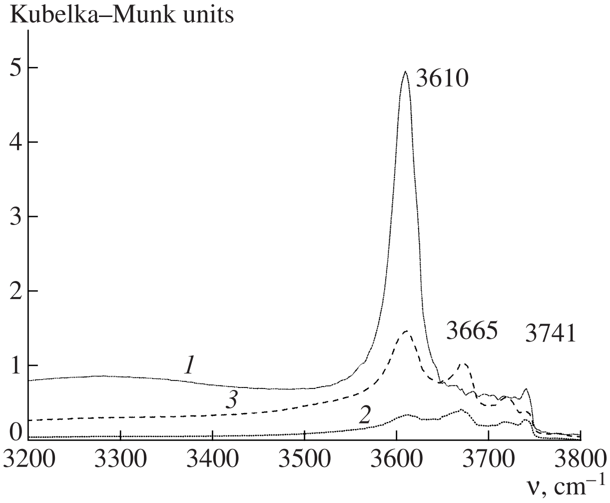


Fig. 2. Diffuse-reflectance IR spectrum (in the region of OH groups) of (*1*) HZSM-5 or (*2*) TMG/ZSM-5 after reduction in hydrogen at 773 K and oxidation in N_2O at 673 K. Spectrum *3* was measured after heating sample *2* in H_2O at 673 K.

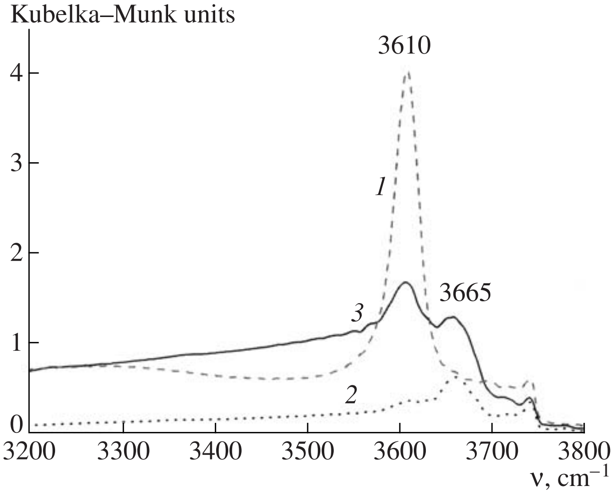


Fig. 3. Diffuse-reflectance IR spectrum (in the region of OH groups) of (*1*) HZSM-5 or (*2*) TMG/ZSM-5 after reduction in hydrogen at 773 K and vacuumized at this temperature. Spectrum *3* was measured after heating sample *2* in H_2O at 573 K and vacuumizing it at 573 K.

namic potential at 800 K changed by –34.4 kcal/mol. Thus, it is believed that the reaction equilibrium is completely shifted to the right even at moderately high temperatures. However, the appearance of a broad absorption line in the diffuse-reflectance spectrum suggests the formation of hydrogen bonds between the resulting hydroxyl groups in the gallium dihydroxide cation and the basic oxygen of the zeolite lattice.

The oxidation of univalent gallium with water at 573 K was studied using samples that were prereduced in hydrogen at 723 K and vacuumized at the specified temperature. The resulting samples were exposed to water vapor at 7 Torr and 573 K for 1 h. Thereafter, water was frozen in a trap cooled with liquid nitrogen and the gas amount in the unfrozen fraction was measured. The formation of molecular hydrogen, which was identified by mass spectrometry, as a result of the oxidation of univalent gallium ions with water was detected. The hydrogen amount was about 25% of the total initial amount of Ga^+ ions. The IR spectra were measured after evacuating the sample, which was heated in water, at 573 K and cooling it to room temperature (Fig. 3). From Fig. 3, it follows that the oxidation resulted in the partial regeneration of a band at 3610 cm^{-1} due to bridging hydroxyl groups and in the formation of gallium hydroxyl groups.

As found previously [9], the interaction of water with reduced samples occurred with the release of hydrogen in accordance with the following reaction scheme:

$$Z^-[Ga]^+ + H_2O \longrightarrow Z^-[H\text{–}Ga\text{–}OH]^+; \qquad \text{(II)}$$

$$Z^-[H\text{–}Ga\text{–}OH]^+ + H_2O \longrightarrow Z^-[HO\text{–}Ga\text{–}OH]^+ + H_2. \qquad \text{(III)}$$

According to published data [7], the occurrence of these reactions is favorable. Thus, reaction (II) occurs with a free energy change of –1 kcal/mol, which implies the almost equilibrium course of this reaction, whereas reaction (III) is characterized by ΔG = –13.4 kcal/mol and an activation energy of 13.5 kcal/mol, which are responsible for an equilibrium shift to the formation of the gallium dihydroxide cations $[Ga(OH)_2]^+$ at the cationic positions of the zeolite.

Table 1. Calculated reaction enthalpies (ΔH) and free energies (ΔG) at 1 atm and 800 K

Reaction	ΔH, kcal/mol	ΔG, kcal/mol
$[Ga{=}O]^+ + H_2O \longrightarrow [HO\text{–}Ga\text{–}OH]^+$ (I)	–60.6	–34.4
$[HO\text{–}Ga\text{–}OH]^+ \longrightarrow [O{=}Ga\text{–}OH]^0 + Z\text{–}H^+$ (V)	84.5	59.6
$[HO\text{–}Ga\text{–}OH]^+ + H_2O \longrightarrow [Ga\text{–}(OH)_3]^0 + Z\text{–}H^+$ (VI)	27.8	27.5
$[HO\text{–}Ga\text{–}OH]^+ \longrightarrow [O{=}Ga\text{–}OH]_{ads}\text{–}Z\text{–}H^+$ (VII)	49.8	50.5
$[HO\text{–}Ga\text{–}OH]^+ + H_2O \longrightarrow [Ga\text{–}(OH)_3]_{ads}\text{–}Z\text{–}H^+$ (VIII)	–11.8	15.4

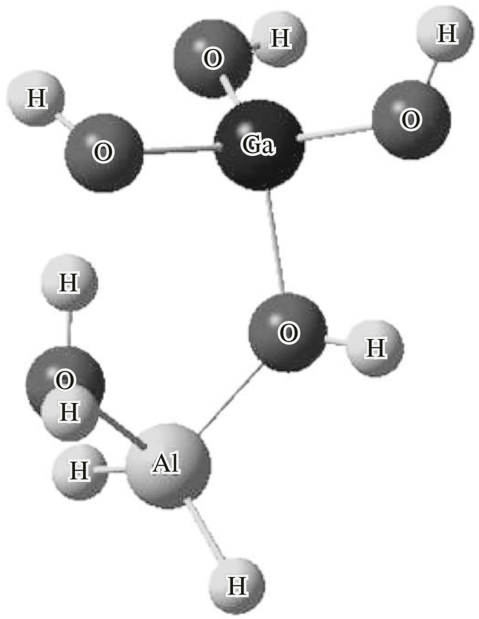


Fig. 4. Structure of $[Ga(OH)_3]$ adsorbed near the Brønsted proton.

The oxidation of univalent gallium with water in accordance with the following reaction could also be taken into consideration:

$$Z^-[Ga]^+ + H_2O \longrightarrow Z^-[GaO]^+ + H_2. \quad (IV)$$

However, it occurs with a high activation barrier.

Thus, we arrived at the conclusion that the interaction of gallium-substituted zeolites with water affords gallium dihydroxide cations. However, none of these reactions implied the formation of protons, whose signals were detected in the IR spectrum. It was reasonable to assume the thermal degradation of $[Ga(OH)_2]^+$ cations, as proposed previously [9], with the formation of neutral GaOOH species in the reaction

$$Z^-[HO–Ga–OH]^+ \longrightarrow O{=}Ga–OH + Z^-–H^+ \quad (V)$$

or the subsequent hydrolysis

$$Z^-[HO–Ga–OH]^+ + H_2O \longrightarrow Ga–(OH)_3 + Z–H^+. \quad (VI)$$

As can be seen in Table 1, reactions (V) and (VI) are strongly endothermic and occur with a large increase in the thermodynamic potential: 59.6 or 27.5 kcal/mol for reaction (V) or (VI), respectively. However, the formation of neutral O=Ga–OH and $Ga(OH)_3$ species does not have to be accompanied by the removal of these species. As a result, adsorbed complexes can be formed (e.g., see Fig. 4):

$$Z^-[HO–Ga–OH]^+ \longrightarrow [O{=}Ga–OH]_{ads}–Z–H^+, \quad (VII)$$

$$Z^-[HO–Ga–OH]^+ + H_2O \longrightarrow [Ga–(OH)_3]_{ads}–Z–H^+. \quad (VIII)$$

We found that even these reactions are characterized by $\Delta G > 0$ (Table 1). Thus, we can conclude that a high positive change in free energy prevents the formation of protons in the zeolite by the thermal decomposition or the subsequent hydrolysis of dihydroxide cations.

We can also propose another reaction path for proton formation by the condensation of gallium dihydroxide cations

$$2Z^-[HO–Ga–OH]^+ \longrightarrow Z^-[HO–Ga–O–Ga(OH)_2]^+ + Z^-–H^+. \quad (IX)$$

In the general case, these transformations can also be described by the following reactions of the dihydroxide gallium cation with Ga^+ and $[GaO]^+$ cations (the occurrence of the latter cation in an oxidized form can be assumed):

$$Z^-Ga^+ + Z^-[HO–Ga–OH]^+ \longrightarrow Z^-[Ga_2O_2H]^+ + Z^-–H^+; \quad (X)$$

$$Z^-[Ga{=}O]^+ + Z^-[HO–Ga–OH]^+ \longrightarrow Z^-[Ga_2O_3H]^+ + Z^-–H^+; \quad (XI)$$

$$Z^-[Ga(OH)_2]^+ + Z^-[HO–Ga–OH]^+ \longrightarrow Z^-[Ga_2O_4H]^+ + Z^-–H^+. \quad (XII)$$

The resulting cationic species $[Ga_2O_2H]^+$, $[Ga_2O_3H]^+$, and $[Ga_2O_4H]^+$ are various binuclear gallium oxide nanoclusters (Fig. 5) localized at the cationic positions of the zeolite lattice.

We calculated the heats and free energies of reactions (X)–(XII) for these binuclear clusters at atmospheric pressure and 298 K using the DFT method (Table 2). As can be seen, in each of these three cases, there is at least one reaction that is characterized by negative changes in both enthalpy and free energy. For example, it is evident that the cationic species $[Ga_2O_2H]^+$ (**Ia**), which is shown in Fig. 5, is the predominant product of reaction (X), whereas species **IIb**, which is most likely formed by the cyclization of structure **IId**, is the predominant product of reaction (XI). Finally, species **IId**, which corresponds to reaction (IX), is the most favorable product of reaction (XII). We can substantiate the high energetic stability of structures **Ia**, **IId**, and **IIId**, which allows reactions (X)–(XII) to occur with the generation of protons, by the formation of an additional stabilizing Ga–O bond between the cluster gallium atom and the third oxygen atom of an aluminum tetrahedron, which produces a cationic position, in the zeolite (correspondingly, the first two oxygen atoms of the tetrahedron are bound to the other gallium atom of the cluster).

Table 2. Calculated reaction enthalpies (ΔH) and free energies (ΔG) for the formation of gallium–oxygen nanoclusters* at 1 atm and 298 K

Reaction	ΔH, kcal/mol	ΔG, kcal/mol
$Ga^+ + [Ga(OH)_2]^+ \longrightarrow$ cluster **Ia**	–0.5	–12.5
$Ga^+ + [Ga(OH)_2]^+ \longrightarrow$ cluster **Ib**	7.1	–6.2
$Ga^+ + [Ga(OH)_2]^+ \longrightarrow$ cluster **Ic**	57.0	41.4
$[Ga{=}O]^+ + [Ga(OH)_2]^+ \longrightarrow$ cluster **IIa**	–0.1	–13.8
$[Ga{=}O]^+ + [Ga(OH)_2]^+ \longrightarrow$ cluster **IIb**	–30.3	–42.5
$[Ga{=}O]^+ + [Ga(OH)_2]^+ \longrightarrow$ cluster **IIc**	38.9	27.3
$[Ga{=}O]^+ + [Ga(OH)_2]^+ \longrightarrow$ cluster **IId**	–10.9	–22.4
$[Ga(OH)_2]^+ + [Ga(OH)_2]^+ \longrightarrow$ cluster **IIIa**	37.5	26.3
$[Ga(OH)_2]^+ + [Ga(OH)_2]^+ \longrightarrow$ cluster **IIIb**	6.8	–4.3
$[Ga(OH)_2]^+ + [Ga(OH)_2]^+ \longrightarrow$ cluster **IIIc**	5.9	–6.0
$[Ga(OH)_2]^+ + [Ga(OH)_2]^+ \longrightarrow$ cluster **IIId**	–6.8	–18.1

* See Fig. 5 for cluster numbering.

Table 3. Volumetric data for the oxidation of Ga^+ in N_2O and the reduction of the oxidized form of the gallium-modified zeolite with carbon monoxide in TMG/ZSM-5 and Ga/ZSM-5 samples

Treatment sequence	Amount of oxidized or reduced* Ga, %			
	TMG/ZSM-5		Ga/ZSM-5	
	on the basis of the total gallium content of the sample**	on the basis of the amount of oxo ions*** $(Ga{=}O)^+$	on the basis of the total gallium content of the sample**	on the basis of the amount of oxo ions*** $(Ga{=}O)^+$
Oxidation in N_2O at 673 K	78	100	90	100
Reduction of an oxidized sample in CO at 623 K	25	32	18	20
Reduction of an oxidized sample in CO at 723 K	–	–	30	33
Reduction of an oxidized sample in CO at 823 K	–	–	51	57
Heating in N_2O at 623 K after reductive treatments	35	45	–	–

*The amount of oxidized or reduced gallium was determined from the amount of released N_2 or CO_2, respectively.

**The amount of initial gallium in the sample after the introduction was taken as 100%.

***The amount of hypothetical oxo ions $(Ga{=}O)^+$ obtained after the oxidation of a sample prereduced in hydrogen was taken as 100%.

Thus, the condensation of two gallium dihydroxide cations with the formation of a binuclear nanocluster hydroxide cation and a proton is exothermic with $\Delta H = -6.8$ kcal/mol and $\Delta G = -18.1$ kcal/mol, which explains the appearance of signals from protons in the IR spectrum (Fig. 2).

According to IR-spectroscopic data, the degradation of gallium hydroxides formed by the interaction of the gallium-substituted zeolite with water occurs only at temperatures higher than 773 K. In this case, the intensity of a broad absorption band also gradually decreased.

Interaction of Oxidized Samples with Carbon Monoxide

The heating of the oxidized gallium-modified ZSM-5 zeolite samples in an atmosphere of CO was accompanied by the formation of CO_2 even at 623 K, as supported by the results of the mass-spectrometric analysis of the released gas. The gas amount was determined volumetrically by freezing the CO_2 obtained in the course of the reaction in a trap cooled to 196 K (Table 3). As follows from Table 3, in the TMG/ZSM-5 sample, only 25% of the initial amount of gallium atoms introduced into the zeolite reacted with carbon

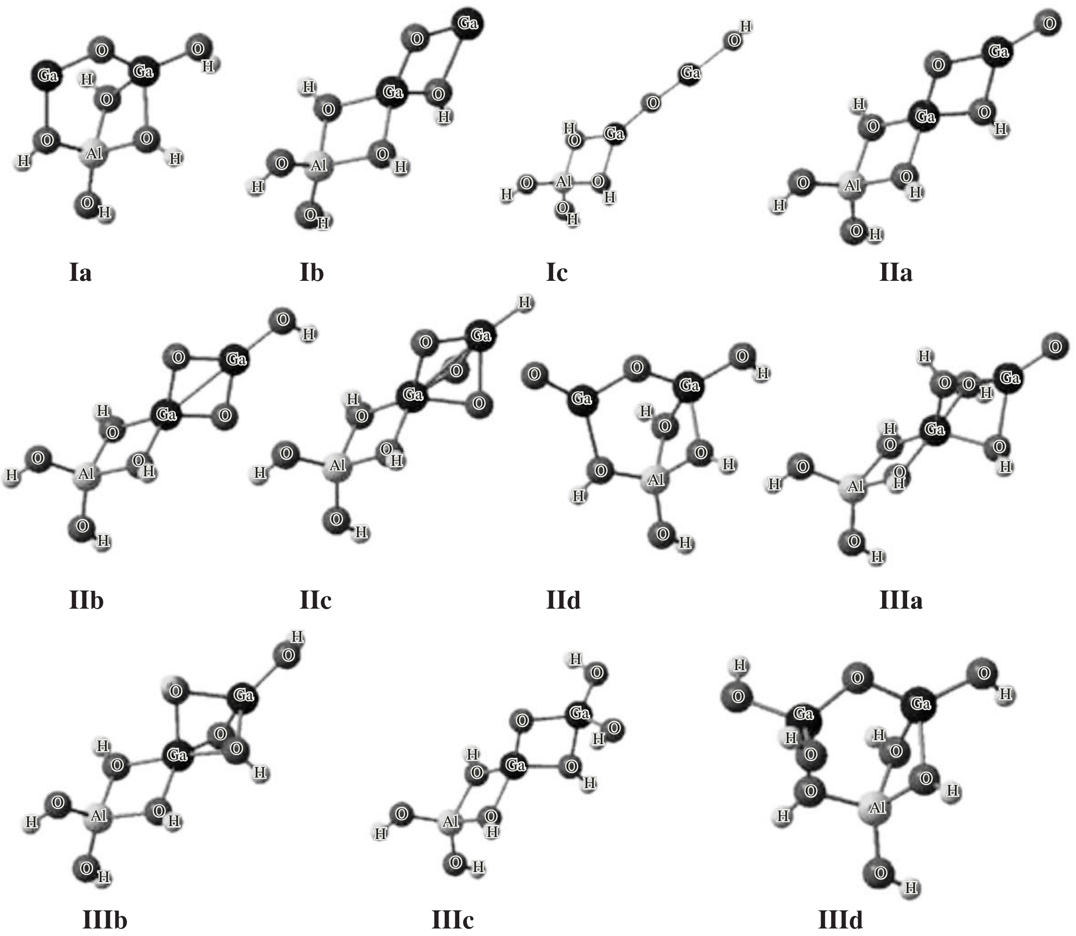
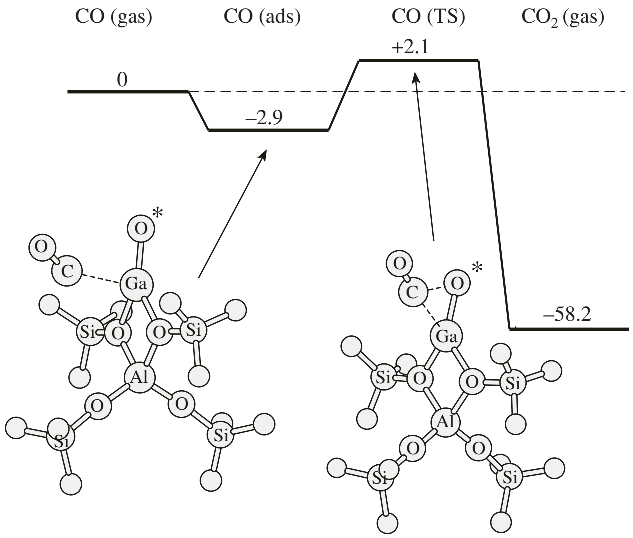


Fig. 5. Binuclear gallium oxide structures resulting from the trapping of O=Ga–OH by (**I**) the univalent gallium ion, (**II**) the oxo ion, and (**III**) the $[Ga(OH)_2]^+$ ion.

monoxide at 623 K. The subsequent heating of this reduced sample in N_2O at 673 K led to its reoxidation (Table 3).

An increase in the temperature of heating oxidized gallium-modified samples in an atmosphere of CO led to further reduction of the samples. Thus, an additional amount of CO_2 was generated from the Ga/ZSM-5 sample at 823 K; this amount was greater than that obtained at 623 K, by a factor of 1.5. Thus, we can state a considerable heterogeneity of the states of oxygen in oxidized gallium-modified samples; in this case, the ratio between the amounts of introduced oxygen atoms and gallium atoms was approximately equal to 1 : 1. Thus, we can assume that various polynuclear gallium oxide nanoclusters occurred in the oxidized form. These clusters resulted from the oligomerization of $[Ga=O]^+$ species, which exhibit different resistance to reduction in CO. In this respect, the calculation of the reduction reaction of the $[Ga=O]^+$ ion and the CO molecule is significant. Although the interaction in the adsorption complex CO–$[Ga=O]^+$ is very weak (a few kcal/mol), this does not mean that the above components are inert with respect to reactions with one another. We calculated the reaction of the oxidation of the CO molecule by the $[Ga=O]^+$ center stabilized in various zeolite structures. In all cases, comparatively low activation barriers, which were no higher than 10 kcal/mol, were found. For example, Fig. 6 shows the energy diagram of the reaction, which was found for the $Al(OSiH_3)_4^-$ cluster model of the T5 cationic position in the zeolite. Based on the above analysis, we can draw the main conclusion that the $[Ga=O]^+$ oxo ions are comparatively unstable in an atmosphere of CO even as the temperature is increased only slightly; this is clearly inconsistent with the experimental results. This raises questions as to whether these centers can really be stabilized in gallium zeolites and whether they can undergo rearrangements to more stable structures. The latter allowed us to explain the necessity of high temperatures for performing the reaction of CO oxidation in gallium zeolites. It is likely that the formation of polynuclear gallium oxide nanoclusters is one of the most probable reaction paths of this stabilization.



$\Delta\nu_{CO} = 0$ cm^{-1}
$A_{CO} = 142$ km/mol
$d_{C–O} = 1.126$ Å
$d_{Ga–C} = 2.53$ Å
$d_{Ga–O*} = 1.69$ Å
$d_{C–O*} = 2.95$ Å
$q_{Ga} = 1.242$

$d_{C–O} = 1.148$ Å
$d_{Ga–C} = 2.06$ Å
$d_{Ga–O*} = 1.75$ Å
$d_{C–O*} = 1.96$ Å
$q_{Ga} = 1.374$

Fig. 6. Energy diagram of the oxidation of the CO molecule by the $[Ga=O]^+$ oxo ion.

The occurrence of these clusters was demonstrated by Kuzmin et al. [10], who considered the rapid evolution of the active structure $[Ga=O]^+$ to more stable species.

CONCLUSIONS

The experimental study of the interaction of water with Ga/HZSM-5 after oxidative and reductive treatments exhibited the release of hydrogen in the latter case and the formation of acidic protons in both cases. With the use of theoretical simulation, we explained the release of hydrogen by the formation of $[Ga(OH)_2]^+$ cations and the appearance of signals due to acidic protons by the condensation of these cations to binuclear gallium oxide–hydroxide nanoclusters. The reduction of oxidized Ga/HZSM-5 by treatment with CO occurred only at comparatively high temperatures. In this case, the amount of the resulting CO_2 continued to increase with temperature. The simulation of the reduction of $[Ga=O]^+$ oxo ions by carbon monoxide demonstrated that this reaction occurred with a low activation barrier and a considerable decrease in the energy of the system; this is inconsistent with experimental data. Thus, the findings suggest that active gallium in oxidized Ga/HZSM-5 species mainly occurred as polynuclear gallium oxide or gallium oxide–hydroxide nanoclusters.

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