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Mechanism of the Low-Temperature Interaction of Hydrogen with α-Oxygen on FeZSM-5 Zeolite

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Abstract—The mechanism of a low-temperature reaction of hydrogen with the radical anion surface oxygen species (α-oxygen, O_α) formed by decomposing N_2O over FeZSM-5 zeolite was studied using kinetic and isotope techniques. It was found that the reaction is of first order with respect to hydrogen and the rate of the reaction is proportional to the concentration of O_α. The activation energy of the reaction, which was measured for H_2 or D_2 over a temperature range from +20 to –100°C, is equal to 3.2 or 5.3 kcal/mol, respectively. The reaction occurs with a considerable kinetic isotope effect (k_H/k_D), which varies over the range of 3.4–41 depending on the temperature. This fact indicates that the rate-limiting step of the reaction includes the dissociation of the hydrogen molecule. The temperature dependence of the isotope effect gave a value of 2.1 kcal/mol, which is close to the difference between the zero bond energies in the molecules of H_2 and D_2; this fact suggests that a tunnel effect does not significantly contribute to the reaction. The dissociative mechanism is consistent with data obtained by *in situ* IR spectroscopy. The interaction of hydrogen with α-oxygen is accompanied by the formation of new hydroxyl groups $O_\alpha H$ (absorption bands at 3635 and 3674 cm^{-1}) at the surface of the zeolite. The identification of these groups was supported by an isotope shift either on the replacement of H_2 by D_2 or on the replacement of $^{16}O_\alpha$ by $^{18}O_\alpha$. The stoichiometric ratio $H_2 : O_\alpha$ is consistent with the previously drawn conclusion on the paired arrangement of α-sites.

INTRODUCTION

The identification and characterization of surface oxygen species that participate in the oxidation of organic molecules are of considerable interest for understanding the mechanism of oxidation catalysis. In recent years, studies of the reactivity and chemical properties of a so-called α-form of oxygen, which participates in selective oxidation reactions on FeZSM-5 zeolites, have attracted the particular attention of researchers [1–7]. This species is formed by the decomposition of N_2O at α-sites, which are the reduced mononuclear iron complexes Fe_α^{2+} with a paired arrangement in the zeolite matrix [8]. As found by Mössbauer spectroscopy and thermal-desorption measurements, α-oxygen exhibits the nature of radical anions, and its formation is accompanied by the oxidation of Fe^{2+} to Fe^{3+} in the active site [8, 9]

$$Fe_\alpha^{2+} + N_2O \longrightarrow Fe_\alpha^{3+}O_\alpha^{\bullet} + N_2. \qquad (I)$$

α-Oxygen can be formed in a high concentration, and it is stable on the surface of FeZSM-5 zeolites at temperatures lower than 300°C; this provides a good opportunity to study its properties. α-Oxygen acts much like the active oxygen of methane monooxygenase enzymes, oxidizes alkanes, cycloalkanes, and aromatic hydrocarbons at room temperature with the selective formation of hydroxyl-containing products in all cases [10–13].

The kinetics and mechanism of the surface reactions of α-oxygen are difficult to study because of its rate of reaction is too high, it is immeasurably high even in the case of methane [11]. Moreover, the situation is complicated by the strong adsorption of organic molecules on the zeolite surface, which hinders reliable kinetic measurements, particularly at low temperatures.

In preliminary experiments, we found that hydrogen reacts with α-oxygen at room temperature ~20 times slower than methane. It is likely that this unusual ratio between the reactivity of hydrogen and methane can be explained by the special chemical properties of O_α. It is of interest that an analogous ratio was observed by Lipatkina *et al.* [14] in the interaction of hydrogen and methane with O^- radical anions on the surface of reduced metal oxides. In addition to the lower reactivity of hydrogen toward α-oxygen, hydrogen is weakly adsorbed on the surface of zeolites. This fact makes it possible to perform a reliable study of the kinetics and mechanism of the low-temperature interaction of O_α with hydrogen, and this work is devoted to this study.

EXPERIMENTAL

Samples. The FeZSM-5 zeolite (Si/Al = 23; C_{Fe} = 0.3 wt % Fe) prepared by the impregnation of commercial ZSM-5-A zeolite in the H form (AngarskNefteOrgSintez) with a solution of $FeCl_3$ was used for kinetic studies. After the impregnation, the sample was calcined in a vacuum with a gradually increasing temperature up to 500°C and then in oxygen at 500°C. To increase the concentration of α-sites, the resulting catalyst was additionally activated by calcination in a vacuum at 900°C (1 h) and finally exposed to O_2 (5 Torr) at 550°C. The concentration of α-sites in the activated sample was $C_\alpha = 1.36 \times 10^{19}$ site/g.

A sample of FeZSM-5-B zeolite (Si/Al = 72; C_{Fe} = 0.53 wt % Fe) in the H form, which was prepared by hydrothermal synthesis by the introduction of iron as $FeCl_3$ into a parent gel, was used in IR-spectroscopic studies [15]. The concentration of α-sites in the activated sample was $C_\alpha = 1.9 \times 10^{19}$ site/g.

Vacuum unit. Experiments on the decomposition of N_2O and on the interaction of H_2 (D_2) with α-oxygen were performed in a stainless steel static vacuum unit (pressures up to 10^{-7} Torr). The vacuum unit was equipped with a cryostat, which allowed us to control the reactor temperature over a range from 0 to –150°C with a high accuracy. Partial gas pressures in the reaction volume were measured using a PPT Residual Gas Analyzer mass spectrometer (MKS Instruments) and a Baratron absolute pressure gage (MKS Instruments) with a linearity range from 2×10^{-3} to 2 Torr. Before the beginning of experiments, a sample (0.14 g) was placed in a quartz microreactor, whose volume (5 cm^3) is negligible compared to the reaction volume of the unit (730 cm^3). An important property of the reactor is that it can be easily isolated from the reaction volume using a valve. This allows the gas phase to be replaced within the closed reactor without disturbing the adsorption state of the sample surface. This significantly improved the accuracy of the kinetic and adsorption measurements.

Sequence of experiments. The experiments were performed in accordance with the following procedure:

(1) The standard treatment of a sample in a vacuum at 530°C for 1 h and then in O_2 (1 Torr) at 530°C for 1 h.

(2) The formation of α-oxygen by the decomposition of N_2O at an initial pressure of 0.2 Torr at 250°C for 25 min.

(3) The reaction of α-oxygen with H_2 (D_2) at temperatures from +20 to –100°C.

The treatment allowed us to standardize the state of the catalyst and to purify it from possible organic impurities. To form O_α on the surface of FeZSM-5, after the standard treatment, the sample was cooled in O_2 (1 Torr) to 250°C; the reactor was closed, and O_2 in the reaction volume was replaced by nitrous oxide at a pressure of 0.2 Torr. After opening the reactor, the decomposition of N_2O was performed for 25 min until the completion of reaction (I).

To perform the reaction of α-oxygen with hydrogen, the reactor was closed after the decomposition of N_2O and cooled to the reaction temperature; the gas phase in the reaction volume was replaced by H_2 (D_2). The reaction of hydrogen with α-oxygen occurred after opening the reactor.

α-Oxygen concentration measurements. The concentration of α-oxygen $[O_\alpha]$ on the surface of the FeZSM-5 samples was calculated from the amount of N_2 liberated (N_2O consumed) in reaction (I). To refine the value of $[O_\alpha]$, an isotope-exchange reaction between $^{16}O_\alpha$ and $^{18}O_2$ was performed at room temperature. Both of the techniques gave similar results. The average value obtained with the use of these techniques was taken as the true value. The measurement procedure for $[O_\alpha]$ was described in detail elsewhere [11].

Kinetic measurements. The rate of the reaction of hydrogen with α-oxygen was determined by the graphical differentiation of the initial portion of the time dependence of hydrogen pressure in the course of the reaction. The pressure change at this segment did not exceed 5% of the starting value. The concentration of α-oxygen on the surface also decreased insignificantly during this time. The rate of reaction per gram of sample (w_m) was calculated using the following expression:

$$w_m = (dP/dt)A(1/m), \text{ molecule s}^{-1}\text{ g}^{-1}, \quad (1)$$

where dP/dt is the slope of the line tangent to a curve of $P(t)$ at a given pressure; $A = 2.5 \times 10^{19}$ molecule/Torr is a conversion factor; and m is the sample weight, g.

IR spectroscopy. A specially made quartz cell with a high-vacuum stopcock was used for *in situ* studies by diffuse-reflectance IR spectroscopy. A sample (0.5 g) was placed in the cell and subjected to successive treatments in the vacuum unit according to the above procedure. After each of the treatments, the stopcock was closed, the sample was cooled to 20°C, and the cell was detached from the unit. The spectra were measured at room temperature with the use of a Shimadzu 8300 Fourier spectrometer in the region 2100–6000 cm^{-1} with a resolution of 2 cm^{-1}. To accumulate the spectra, 100 scans were used. The spectra were converted from a reflection scale to the Kubelka–Munk scale $F(R) = (1 - R)^2/2R$.

RESULTS AND DISCUSSION

1. Reaction of Hydrogen with α-Oxygen

To determine a temperature region appropriate for kinetic measurements, we initially studied the adsorption of H_2 on a sample of FeZSM-5-A over a temperature range from +20 to –150°C. These experiments demonstrated that the adsorption of hydrogen was negligibly small at temperatures above –100°C.

Figure 1 illustrates the results of two comparative experiments on the interaction of H_2 with the surface of the FeZSM-5-A sample at –100°C. In the first experiment, hydrogen reacted with the zeolite after a standard treatment (Fig. 1a), whereas it in the second experiment reacted with the zeolite surface after the formation of α-oxygen from N_2O on the surface by reaction (I) (Fig. 1b). It can be seen that only weak physical adsorption of H_2 was observed in the absence of α-oxygen.

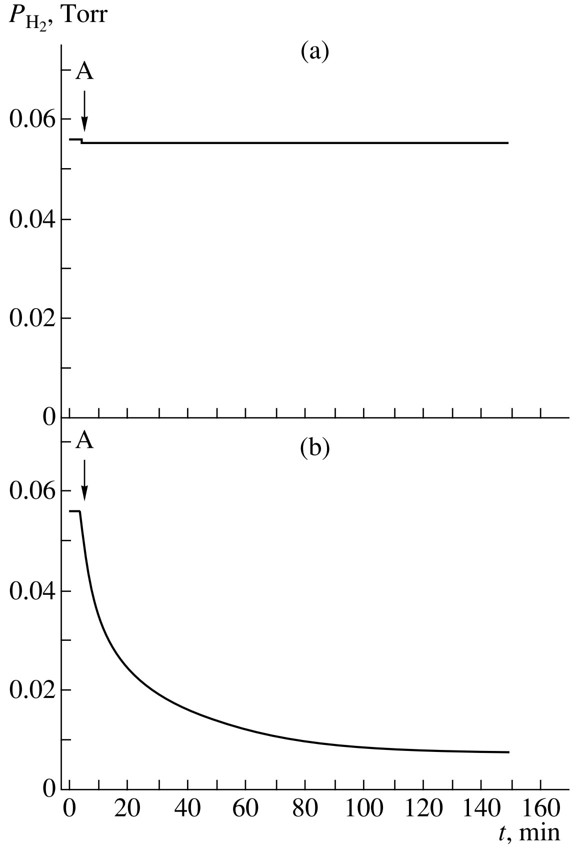

Fig. 1. Interaction of H_2 with FeZSM-5-A zeolite at –100°C: (a) without α-oxygen; (b) in the presence of 1.36×10^{19} (atom O) (g α-oxygen)$^{-1}$. A indicates the moment in time at which the reactor was opened.

Another behavior was observed in the presence of 1.36×10^{19} atom O (g α-oxygen)$^{-1}$ on the surface (Fig. 1b). In this case, after opening the reactor, considerable irreversible absorption of H_2 due to its consumption in the reaction with α-oxygen was observed.

Table 1 summarizes the rates of H_2 and D_2 reactions with α-oxygen at temperatures from +20 to –100°C.

Table 1. The temperature dependence of the rates of H_2 and D_2 oxidation with α-oxygen on FeZSM-5-A

T, °C	w_{m, H_2}, molecule s^{-1} g^{-1}	w_{m, D_2}, molecule s^{-1} g^{-1}	k_H/k_D
+20	3.25×10^{17}	9.6×10^{16}	3.4
0	1.93×10^{17}	4.1×10^{16}	4.7
–20	8.50×10^{16}	1.08×10^{16}	7.9
–50	3.05×10^{16}	2.23×10^{15}	13.7
–70	1.76×10^{16}	7.5×10^{14}	23.4
–100	7.4×10^{15}	1.8×10^{14}	41.1

Note: $P_{0, H_2} = P_{0, D_2} = 0.056$ Torr; $[O_\alpha] = 1.36 \times 10^{19}$ (atom O)/g.

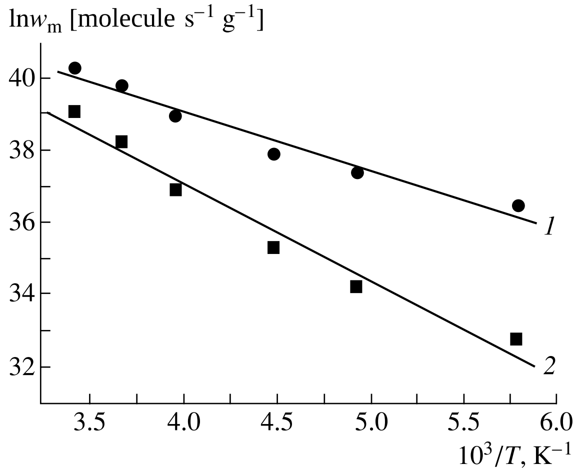

Fig. 2. Arrhenius plots for the interactions of α-oxygen with (*1*) H_2 and (*2*) D_2.

Based on these data, the temperature dependence of the rate of H_2 oxidation was plotted on the Arrhenius coordinates in Fig. 2 (curve *1*). It can be seen that the experimental results are adequately described by a linear function with an activation energy of 3.2 ± 0.3 kcal/mol.

In the case of D_2, the activation energy calculated from the Arrhenius function (Fig. 2, curve *2*) is higher and equals 5.3 ± 0.5 kcal/mol. Note that lower values of activation energies were found for the reactions of H_2 and D_2 with the O^- radical anion oxygen species on the surface of reduced V/SiO_2, Mo/SiO_2, and W/SiO_2 catalysts; these activation energies were approximately equal and comprised 1.0 and 1.3 kcal/mol, respectively [14].

2. Reaction Order with Respect to Hydrogen and α-Oxygen

To find the form of the rate equation that describes the rate of the interaction of hydrogen with α-oxygen, we initially determined the order of reaction with respect to hydrogen. In this case, it was methodologically easier to use the reaction with deuterium because the rate of its oxidation is lower than that of H_2 oxidation (Table 1). For this purpose, we performed experiments on the stoichiometric oxidation of D_2 at 0°C with α-oxygen ($[O_\alpha] = 1.36 \times 10^{19}$ (atom O)/g) by varying the initial pressure of hydrogen over the range of 0.018–0.143 Torr. Figure 3 demonstrates the effect of the D_2 pressure on the reaction rate. It can be seen that the experimental points are adequately described by a linear function, which suggests that the reaction is of first order with respect to deuterium (hydrogen).

For the complete kinetic description, it was also of interest to find the dependence of the reaction rate on the concentration of α-oxygen on the zeolite surface. For this purpose, we oxidized deuterium at 0°C varying the initial amount of O_α on the surface within the limits of one order of magnitude. To form O_α, an appropriate

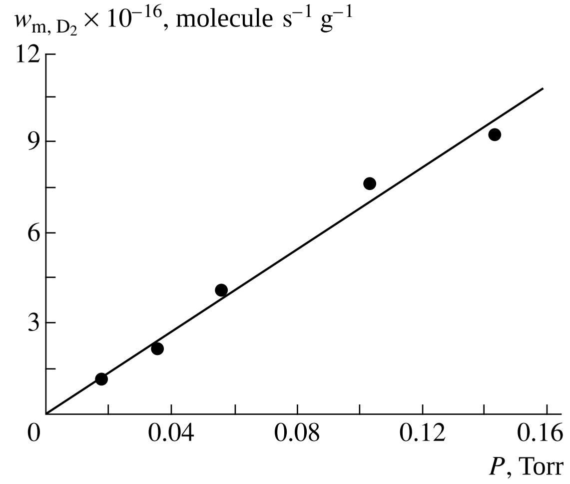

Fig. 3. Effect of the D_2 pressure on the rate of its interaction with α-oxygen at 0°C.

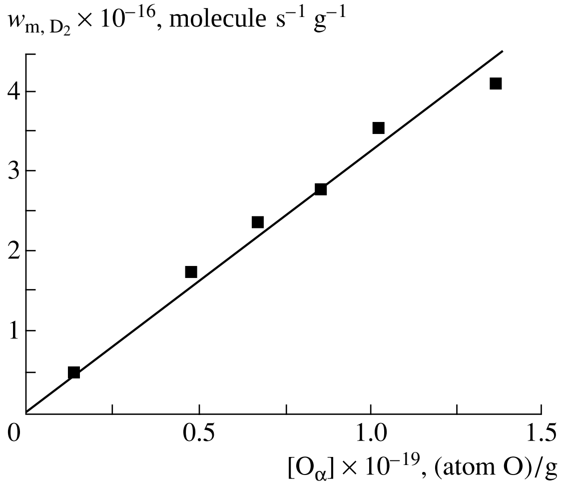

Fig. 4. Effect of the α-oxygen concentration on the rate of its interaction with D_2 at 0°C.

amount of N_2O was decomposed at 250°C before the reaction with D_2. As can be seen in Table 2, the reaction rate w_m changed by approximately one order of magnitude and increased from 5×10^{15} to 4.1×10^{16} molecule s^{-1} g^{-1} as $[O_\alpha]$ increased from 1.4×10^{18} to 1.36×10^{19} (atom O)/g. Data shown in Fig. 4 indicate that the rate is proportional to the concentration of O_α on the sample surface.

Thus, the apparent rate of the reaction of hydrogen with α-oxygen over the test temperature region can be described by the following rate equation:

$$w_{m, H_2} = Ak_{0, H_2}e^{-E_a/RT}P_{H_2}[O_\alpha] \text{ molecule s}^{-1} \text{ g}^{-1}, \tag{2}$$

where $A = 2.5 \times 10^{19}$ molecule/Torr is a proportionality factor, $k_{0, H_2} = 3.2 \times 10^{-18}$ (atom O)$^{-1}$ s^{-1} is a preexponential factor; $E_{a, H_2} = 3.2 \pm 0.3$ kcal/mol is the activation energy; and P_{H_2} is the pressure of hydrogen, Torr; $[O_\alpha]$ is the concentration of α-oxygen, (atom O)/g. In the case of deuterium, $k_{0, D_2} = 3.2 \times 10^{-17}$ (atom O)$^{-1}$ s^{-1} and $E_{a, D_2} = 5.3 \pm 0.5$ kcal/mol. Differences between the preexponential factors for H_2 and D_2 are within the accuracy of the determination from the corresponding Arrhenius functions.

The ratio of the reaction rate (w_m) to the value of $[O_\alpha]$ gives the activity of a single O_α atom in the oxidation of deuterium (w_α). As can be seen in Table 2, this value is approximately constant and does not depend on the surface concentration of O_α. This indicates that α-oxygen is equivalent in its reactivity. At the same time, we can note a small deviation of experimental points from a straight line for the rates of H_2 and D_2 oxidation in Fig. 2. This may be a consequence of a nonuniformity of O_α, which becomes noticeable at low temperatures.

3. Kinetic Isotope Effect

Data given in Table 1 allowed us to calculate the kinetic H_2–D_2 isotope effect in the reaction with α-oxygen, which provides important information on the reaction mechanism. It can be seen in Table 1 that the rates of H_2 and D_2 oxidation under identical conditions are very different; that is, the reaction occurs with a high isotope effect (k_H/k_D), which changed from 3.4 to 41 as the temperature was decreased from +20 to –100°C. This demonstrates that bond cleavage in the hydrogen molecule occurs at the rate-limiting step of the reaction.

A considerably lower isotope effect equal to 4.3 at –100°C was found in the reaction of hydrogen with O^- on the surface of V/SiO_2 [14]. Taking into account the high values of the kinetic isotope effect in our case, we believe that the reaction of H_2 with α-oxygen can occur with a considerable tunnel effect contribution, especially at low temperatures. To test this hypothesis, we plotted the temperature dependence of the kinetic isotope effect in the Arrhenius coordinates based on the

Table 2. Effect of the concentration of α-oxygen on the rate of D_2 oxidation on a FeZSM-5-A sample at 0°C

$[O_\alpha] \times 10^{-19}$, (atom O)/g	$w_{m, D_2} \times 10^{-16}$, molecule s^{-1} g^{-1}	$w_{\alpha, D_2} \times 10^{-3}$, molecule (atom O)$^{-1}$ s^{-1}
0.14	0.50	3.6
0.48	1.74	3.6
0.67	2.36	3.5
0.85	2.78	3.3
1.02	3.55	3.6
1.36	4.10	3.0

Note: $P_{0, D_2} = 0.056$ Torr.

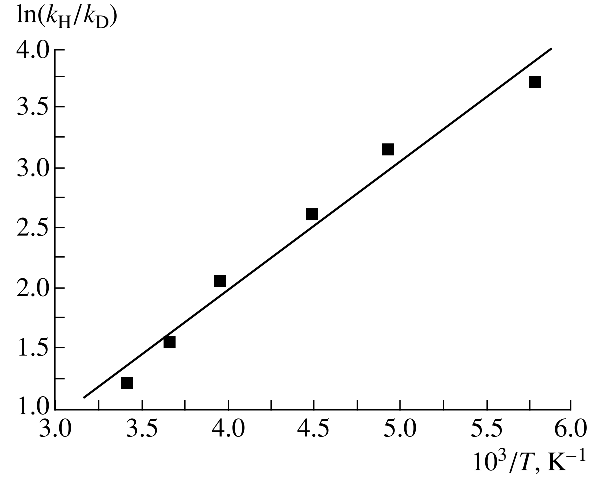

Fig. 5. Arrhenius plot for the isotope effect in the reaction of hydrogen with α-oxygen.

data given in Table 1 (Fig. 5). The difference between the activation energies of D_2 and H_2 oxidation $\Delta E_a = E_{a,D_2} - E_{a,H_2}$, which was found from the slope of this function, was 2.1 ± 0.3 kcal/mol, which is close to the difference between the zero bond energies in D_2 and H_2 molecules, which is equal to 1.7–1.8 kcal/mol [17]. This indicates that the reaction of α-oxygen with hydrogen, as well as with methane [16], occurs without a considerable contribution from the tunnel effect. Note that high values of the kinetic isotope effect are also typical of oxidation reactions with the participation of the active oxygen of methane monooxygenases [18].

4. *Mechanism of the Reaction of H_2 with α-Oxygen*

We used IR spectroscopy in order to reveal a more detailed mechanism for the reaction and to identify the compounds formed on a zeolite surface as a result of this reaction. Figure 6 demonstrates the IR spectra of FeZSM-5-B zeolite in the region of OH-group stretching vibrations. The spectrum of an initial sample after standard treatment (Fig. 6, spectrum *1*) exhibited three main absorption bands. They belong to the vibrations of intrinsic OH groups of the zeolite: terminal Si–OH groups (3470 cm^{-1}), bridging Al–OH–Si groups (3610 cm^{-1}) and OH groups bound to extralattice Al species (3670 cm^{-1}) [19–22]. After the formation of α-oxygen ($[O_\alpha] = 1.9 \times 10^{19}$ (atom O)/g) by the decomposition of N_2O at 250°C, the spectrum remained unchanged.

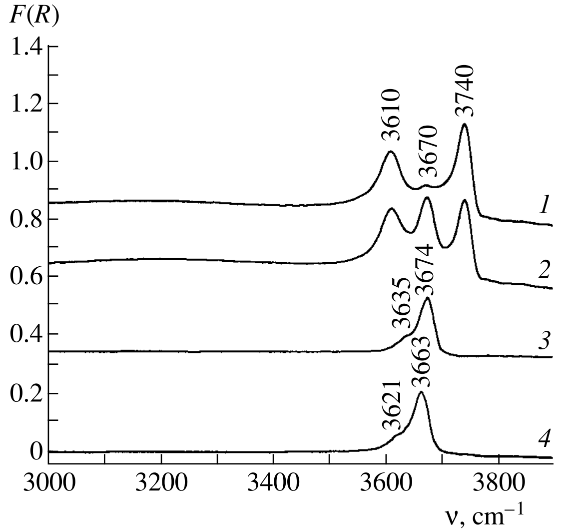

Fig. 6. IR spectra of FeZSM-5-B zeolite in the region of OH vibrations: (*1*) after standard treatment, (*2*) after the reaction of H_2 with α-oxygen ($^{16}O_\alpha$) at 20°C, (*3*) difference spectrum, and (*4*) difference spectrum after the reaction of H_2 with α-oxygen ($^{18}O_\alpha$) at 20°C.

The spectrum qualitatively changed after the interaction of H_2 with the zeolite surface on which α-oxygen was present (Fig. 6, spectrum *2*). As can clearly be seen in the difference spectrum (Fig. 6, spectrum *3*), obtained by subtracting the spectrum of an initial sample, a new intense absorption band at 3674 cm^{-1} with a shoulder at 3635 cm^{-1} appeared in the region of OH vibrations. This demonstrates that the reaction of H_2 with α-oxygen results in the formation of two types of new OH groups on the zeolite surface. Note that these results are qualitatively consistent with the published data [23].

We performed an additional experiment to clarify whether α-oxygen atoms are the constituents of the resulting OH groups. In this experiment, before the reaction with hydrogen, α-oxygen was enriched in the ^{18}O isotope (90% degree of enrichment) by the exchange with $^{18}O_2$ heavy oxygen at room temperature [11]

$$(^{16}O)_\alpha + {}^{18}O_2 = (^{18}O)_\alpha + {}^{16}O^{18}O. \qquad \text{(II)}$$

After the isotopic exchange of $^{16}O_\alpha$ with $^{18}O_\alpha$ followed by the reaction with H_2, the absorption bands of the OH groups shifted to the low-frequency region to give a new intense absorption band at 3663 cm^{-1} with a shoulder at 3621 cm^{-1} (Fig. 6, spectrum *4*). The occurrence of this isotope shift demonstrates that O_α atoms are the constituents of the resulting OH groups.

Figure 7 demonstrates analogous spectra obtained after the reaction of D_2 with α-oxygen. It can be seen that on the replacement of H_2 by D_2 the absorption bands of the resulting hydroxyl groups shifted to the low-frequency region to give new absorption bands at 2712 and 2681 cm^{-1} (Fig. 7, spectra *2*, *3*). Evidently, these absorption bands belong to surface $O_\alpha D$ groups, which were formed in the reaction of D_2 with α-oxygen. This indicates that the reacting hydrogen is the source of hydroxyl groups on the zeolite surface.

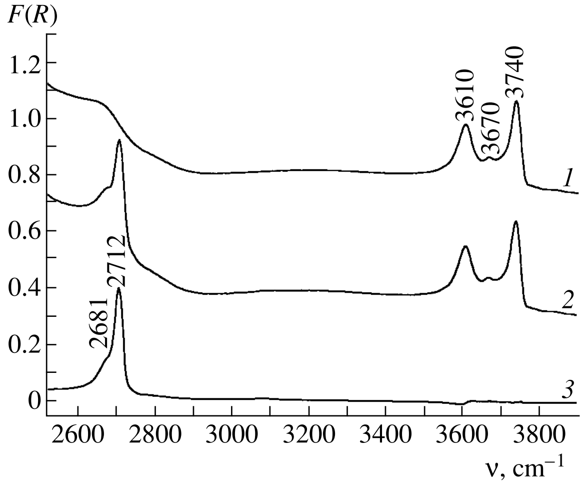

Fig. 7. IR spectra of FeZSM-5-B zeolite in the regions of OH and OD vibrations: (*1*) after standard treatment and α-oxygen formation, (*2*) after the reaction of D_2 with α-oxygen ($^{16}O_\alpha$) at 20°C, and (*3*) difference spectrum.

It is believed that the formation of $O_\alpha H$ groups of two types is associated with the presence of two types of α-sites on the surface of FeZSM-5 zeolite. These sites differ in the coordination of constituent Fe^{2+} ions, and they can be detected by Mössbauer spectroscopy [8].

Thus, according to IR-spectroscopic data, the interaction of hydrogen with α-oxygen occurs by a dissociative mechanism, which is analogous to the mechanism of methane reaction with O_α [16]. The reaction equation can be represented as follows:

$$H_2 + 2(O^\bullet)_\alpha \longrightarrow 2(OH)_\alpha. \qquad \text{(III)}$$

Table 3. Stoichiometry of the reactions of H_2 and D_2 with α-oxygen on FeZSM-5-A

T, °C	Amount of reacting H_2 or $D_2 \times 10^{-18}$, molecule/g	Amount of O_α on the surface $\times 10^{-19}$, (atom O)/g	Stoichiometric ratio $O_\alpha : H_2$ ($O_\alpha : D_2$)
$H_2 + (O_\alpha)$ reaction			
–100	8.56	1.36	1.6
–70	7.74	1.25	1.6
0	7.85	1.23	1.6
20	8.60	1.36	1.6
$D_2 + (O_\alpha)$ reaction			
–70	7.77	1.25	1.6
0	7.52	1.24	1.7
0	7.65	1.27	1.7
20	7.70	1.33	1.7

Based on the kinetic measurements, we believe that reaction (III) actually includes the following two elementary steps:

$$H_2 + (O^\bullet)_\alpha \xrightarrow{k_1} (OH)_\alpha + H^\bullet, \qquad \text{(IV)}$$

$$H^\bullet + (O^\bullet)_\alpha \xrightarrow{k_2} (OH)_\alpha. \qquad \text{(V)}$$

At the former step, the H_2 molecule reacts with the O_α atom; this reaction is accompanied by H-atom abstraction and the formation of the $(OH)_\alpha$ group. At the latter step, the H atom rapidly reacts with the nearest O_α atom. The high isotope effect indicates that the former step is slower, and it limits the rate of reaction. As a result, the reaction is of first order with respect to both reactants.

According to the above mechanism, α-oxygen should react with hydrogen in a stoichiometric ratio of 2 : 1. Table 3 summarizes data on the stoichiometry of H_2 and D_2 reactions with O_α-oxygen at various temperatures. It can be seen that the experimental stoichiometric ratio is lower than 2; on the average, it is 1.6 : 1. An analogous result was obtained previously [13]. It is likely that the underestimated stoichiometric ratio results from the fact that a portion of the hydrogen atoms formed at step (IV) were bound to surface zeolite sites other than O_α It is believed that α-sites should be located in sufficiently close proximity to each other in order for reaction (III) to proceed. This is consistent with the previously drawn conclusion on the paired arrangement of α-sites [8].

Despite its radical–anion nature, the α-form of oxygen differs essentially from other reported radical–anion O^- species on reduced metal oxides [9, 24]. The α-form is generated only from N_2O on active Fe^{2+} complexes in zeolites (α-sites), and it can selectively oxidize various hydrocarbons. The observed differences in the kinetics of hydrogen oxidation with the participation of these oxygen species (higher values of the activation energies and kinetic isotope effects in the case of O_α) also suggest considerable differences in their properties.

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