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Stoichiometry of Oxidation Reactions Involving α-Oxygen on FeZSM-5 Zeolite[1]

K. A. Dubkov, E. A. Paukshtis, and G. I. Panov

Boreskov Institute of Catalysis, Siberian Division, Russian Academy of Sciences, Novosibirsk, 630090 Russia

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Abstract—The stoichiometry of the low-temperature reaction between surface α-oxygen formed by decomposing N_2O over Fe-containing ZSM-5 zeolite and methane, hydrogen (deuterium), and carbon monoxide is studied. Methane and hydrogen react with α-oxygen in stoichiometric ratios of 1 : 1.8 and 1 : 1.6, respectively. The observed stoichiometry is due to the mechanisms of the corresponding reactions. According to a mechanism proposed for the interaction of α-oxygen with methane and hydrogen, this reaction is accompanied by the dissociation of CH_4 and H_2 molecules. For hydrogen, such a mechanism is supported by IR spectroscopic studies of resulting surface compounds, namely, of new hydroxyl groups that were formed on the zeolite surface in the course of the reaction. α-Oxygen reacts with CO in the ratio of 1 : 1 to form CO_2 in amounts equal to those of α-oxygen on the surface.

INTRODUCTION

It is known that the decomposition of N_2O over FeZSM-5 zeolites at temperatures below 300°C is accompanied by the formation of a new form of surface oxygen (α-oxygen) [1–3]:

$$N_2O + (\ )_\alpha = N_2 + (O)_\alpha. \qquad \text{(I)}$$

The catalytic properties of zeolites in this reaction are determined by the presence of active sites (α-sites), which, according to the data of Mössbauer spectroscopy, are the non-framework complexes of reduced iron (Fe^{2+}) [4]. α-Oxygen exhibits an extremely high reactivity: it participates in oxygen isotope exchange even at room temperature and oxidizes CO, H_2, and different hydrocarbons including benzene and methane [5–7]. The stoichiometric reaction between α-oxygen and methane results in the selective formation of methanol, which can be extracted from the zeolite surface.

The previous studies showed that the fraction of α-oxygen that participated in the reaction with methane significantly depended on its concentration on the zeolite surface [7]. It was 100% at a concentration of α-oxygen of $\sim 4 \times 10^{18}$ O atom/g and almost halved at a concentration of 2×10^{19} O atom/g. Therefore, the stoichiometry of the reaction or the ratio of the amount of reacting methane to that of O_α present on the surface changed from 1 : 1 to 1 : 2 depending on the concentration of α-oxygen. A similar result was obtained in the oxidation of hydrogen (deuterium) by α-oxygen [7].

The system of ZSM-5 zeolite micropores involves two types of intersecting channels with a cross-section of ~5.5 Å [8] comparable with molecule sizes. Taking into account the fact that α-sites are localized inside the micropore space, we assumed that the observed dependence of the stoichiometry of the reaction on the concentration of α-oxygen may be due to partial site blocking by the reaction product firmly bound to the zeolite surface inside micropores [7]. In this case, part of α-oxygen may be inaccessible to reagents and, therefore, will fail to participate in the reaction. Because the pore space of ZSM-5 zeolite has a three-dimensional structure, the formation of the reaction product in small amounts must not hinder the accessibility of α-sites. However, when their concentration exceeds some critical value, they can be blocked. It is this circumstance that explains the dependence of the fraction of reacting α-oxygen on its concentration on the zeolite surface.

To verify this assumption and to elucidate the actual factors responsible for the observed stoichiometry of reactions involving α-oxygen, in the present work, we also studied the interaction of CO with α-oxygen, along with the oxidation of methane and hydrogen (deuterium). It is obvious that the blocking of a part of the zeolite pore space by the reaction product should decrease the accessible volume of micropores. To reveal this effect, we determined the micropore volume of FeZSM-5 zeolite before and after the interaction between methane and α-oxygen.

EXPERIMENTAL

We prepared FeZSM-5 zeolite (SiO_2/Al_2O_3 = 72) containing 0.53 wt % Fe by hydrothermal synthesis introducing iron as $FeCl_3$ in the initial gel [9]. This sample was analogous to that described previously in [7]. The sample was transformed into the H-form by exchanging with an ammonia buffer solution and then calcined in air at 550°C. The degree of crystallinity of

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the zeolite determined from the XRD analysis was more than 95%, the specific surface area of the sample was ~400 m^2/g. To increase the concentration of active sites, the sample was additionally calcined at 900°C, whereupon the concentration reached 1.8×10^{19} site/g.

The decomposition of N_2O and the oxidation of methane, D_2, and CO were carried out in a static vacuum setup at pressures of at least 10^{-7} torr. A zeolite sample (0.5 g of a 0.5–1-mm fraction) was placed in a quartz microreactor and subjected to standard treatment that included alternate 1-h oxidative and vacuum treatments at 550°C with the exposure of the sample to oxygen at a pressure of 1 torr at the end. The isolated volume of the microreactor (~5 cm^3) comprised an insignificant part of the total reaction volume of the setup (620 cm^3). The use of such a microreactor allowed, in particular, considerable enhancement in the accuracy of adsorption and kinetic measurements. In thermal desorption experiments, the reactor was heated from 25 to 550°C at a linear rate of 6 K/min. The composition of the gas phase was analyzed by mass spectrometry.

The concentration of α-oxygen on the zeolite surface (C_{O_α}) after N_2O decomposition at 250°C (reaction (I)) was calculated either by measuring the amount of liberated N_2 (or that of consumed N_2O) or by the isotope exchange with $^{18}O_2$ [7]. The values of C_{O_α} found by these two methods were in good agreement.

DRIFT spectra were recorded at room temperature at 2100–6000 cm^{-1} using a Shumadzu 8300 spectrometer with a resolution of 2 cm^{-1} and with the accumulation of 100 scans. The reflectance spectra were plotted in Kubelka–Munk coordinates.

RESULTS AND DISCUSSION

Oxidation of Methane and Deuterium

The reactions of methane and deuterium with α-oxygen were carried out in the following steps:

(1) The standard treatment of zeolite at 550°C;

(2) The formation of surface α-oxygen by decomposing N_2O at 250°C;

(3) The interaction of α-oxygen with CH_4 or D_2 at 100°C;

(4) The freezing of condensed products in a trap at –196°C for 30 min; and

(5) Thawing out the trap and analysing the composition of the gas phase.

The idea of the experiments was as follows. Assuming that the blocking of some part of the zeolite micropore space with the oxidation products of methane and deuterium is responsible for a decrease in the stoichiometric ratios in these reactions, we proposed to eliminate this effect by removing the reaction products from the zeolite surface in the course of the reaction. In this case, it might be expected that all of the surface α-oxygen will enter into the reaction, and the amount of methane or deuterium reacted with it will increase. For this purpose, experiments were performed at 100°C, and the condensed products were additionally frozen out of the gas phase.

Figure 1 presents the results for the interaction of methane with α-oxygen on the surface of FeZSM-5. Before the experiment, α-oxygen in a concentration of 1.8×10^{19} O atom/g was generated on the zeolite surface by decomposing N_2O (0.41 torr) at 250°C. The sample was cooled to 100°C, the reactor was closed, and CH_4 was admitted into the reaction volume of the setup until the pressure reached 0.6 torr. It can be seen from Fig. 1 that methane was significantly consumed at the moment *A* when reactor is opened. Because methane is not adsorbed by zeolite at 100°C [7], this consumption resulted from the interaction between CH_4 and α-oxygen. The amount of reacted methane can be determined from the experimental data. It follows from Table 1 that the amount of reacted methane was only almost half the total amount of α-oxygen present on the surface; that is, the ratio between reacted CH_4 and α-oxygen was 1 : 1.8.

At time *B*, the reaction volume was connected to the trap cooled with liquid nitrogen. The reactor was closed after 30 min, the trap was thawed out (at time *C*), and the composition of the gas phase was analyzed. As follows from Fig. 1, once the trap was thawed, the gas phase contained no additional products of desorption from the zeolite surface. Contrary to the expectations, the amount of reacted methane remained unchanged as the gas phase was cooled. The product of interaction between CH_4 and α-oxygen is impossible to remove from the zeolite surface even by raising the reaction temperature to 100°C, because it is apparently bound firmly to the zeolite surface. This conclusion was supported by the results of the control experiment on the programmed heating of a sample after the oxidation of methane by α-oxygen at 100°C (Fig. 2). Before heating the sample, unreacted methane was evacuated from the gas phase. Figure 2 shows that, even at 200°C, the reaction product did not desorb into the gas phase. At temperatures higher than 250°C, the decomposition of the reaction product and the liberation of CO and CO_2 in the gas phase took place. The amount of CO and CO_2 corresponded to that of reacted methane (Table 1).

Figure 3 demonstrates the results of a similar experiment in which the interaction of deuterium with α-oxygen at 100°C was studied. Note that, at this temperature, H–D exchange with the zeolite surface was not observed. Figure 3 shows that, at the instant the reactor was opened (*A*), D_2 rapidly reacted with α-oxygen. The amount of deuterium that entered the reaction was somewhat higher than that of reacted methane (compare Tables 1 and 2) and comprised ~63% of the total amount of α-oxygen present on the zeolite surface. The ratio between the amounts of reacted D_2 and α-oxygen was 1 : 1.6 (Table 2).

Neither the freezing of the trap that began at time *B* nor the subsequent thawing of the trap (at time *C*) changed the composition of the gas phase or the amount of reacted D_2. Thus, as in the case of methane, the product of the reaction between D_2 and α-oxygen did not desorb in the gas phase, because it was firmly bound to the zeolite surface. For this reason, the repeated loading of α-oxygen from N_2O on the sample surface required the additional treatment of zeolite at a high temperature after the oxidation of methane or deuterium. The results obtained generally agree with data reported in [7] and do not contradict the assumption concerning the possible blocking of a part of the zeolite micropore space with the reaction product. It is of interest to examine how the stoichiometry of the reaction change if the reaction product is weakly bound to the zeolite surface. With this goal, we studied the oxidation of CO to CO_2 by α-oxygen.

CO Oxidation

First, we carried out a control experiment on the adsorption of CO_2 on FeZSM-5 zeolite that was preliminarily treated in a standard way and the subsequent thermal desorption of CO_2 during programmed heating from room temperature (Fig. 4). CO_2 adsorbed significantly upon admitting it at room temperature. With an increase in temperature, ~70% CO_2 desorbed at even 100°C, and it regained its initial pressure at 200°C. In a similar experiment on the thermal desorption of CO from the zeolite sample, only ~20% carbon monoxide remained on the surface at 100°C, and it desorbed completely at ~175°C (Fig. 5).

Thus, in contrast to the oxidation of methane and hydrogen, the product of CO oxidation by α-oxygen was weakly bound to the zeolite surface and easily desorbed in the gas phase upon heating. Therefore, in this case, the effect of blocking can be entirely eliminated by the performance of the reaction at a higher temperature and by the additional removal of the product by freezing. The experiments on CO oxidation were carried out in the same way as reactions with methane and deuterium.

Figure 6 presents the results on the interaction between CO and the zeolite surface at 100°C after loading α-oxygen in a concentration of 1.8×10^{19} O atom/g. At instant *A*, admitted CO was quickly consumed and CO_2 was liberated in the gas phase. This pointed to the oxidation of CO with α-oxygen. The freezing of the product in the trap cooled by liquid nitrogen began at instant *B* and resulted in a drop in the CO_2 pressure to zero, while the pressure of CO remained unchanged. After thawing the trap (beginning with instant *C*), CO_2

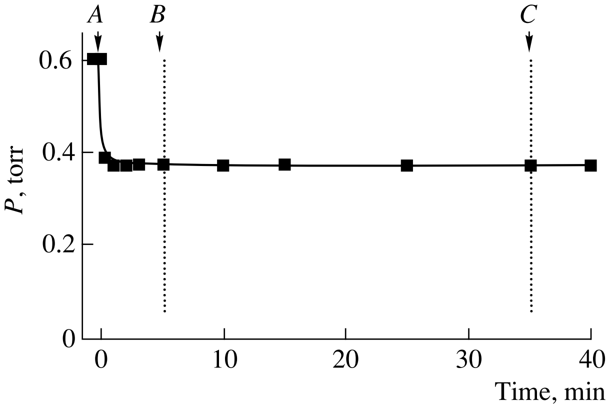

Fig. 1. Oxidation of CH_4 by α-oxygen over the FeZSM-5 zeolite surface at 100°C (*A* is the instant of opening the microreactor; *B* is the beginning of freezing; and *C* is the beginning of thawing the trap).

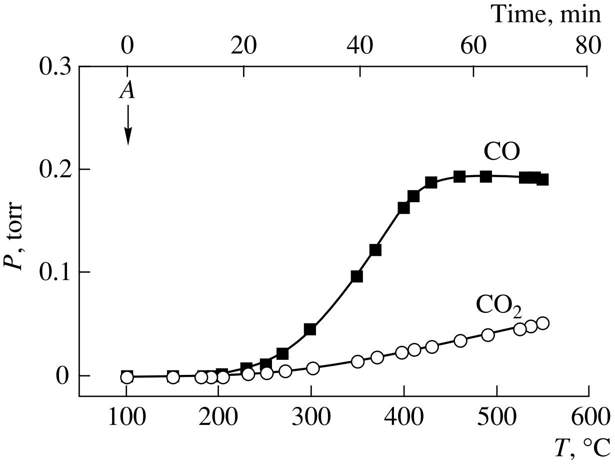

Fig. 2. Temperature-programmed desorption of the product of the oxidation of CH_4 by α-oxygen (*A* is the beginning of thawing).

Table 1. Stoichiometry of the reaction between CH_4 and α-oxygen over FeZSM-5 zeolite at 100°C

No.	Amount of O_α on the surface, O atom/g	Amount of reacting CH_4, molecule/g	Amount of desorbed CO and CO_2*, molecule/g	$CH_4 : O_\alpha$ stoichiometric ratio	
				found from CH_4 amount	found from CO and CO_2 amount
1	1.8×10^{19}	1.01×10^{19}	1.05×10^{19}	1 : 1.8	1 : 1.7
2	1.9×10^{19}	1.05×10^{19}	1.06×10^{19}	1 : 1.8	1 : 1.8

* Found by decomposing the reaction product at temperatures up to 550°C.

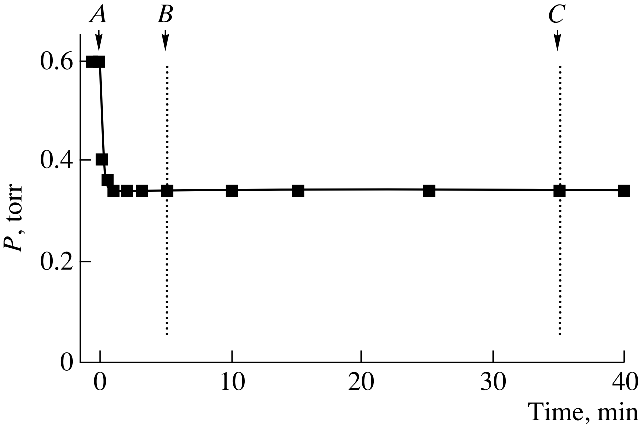

Fig. 3. Oxidation of D_2 by α-oxygen over the FeZSM-5 zeolite surface at 100°C (*A* is the instant of opening the microreactor; *B* is the beginning of freezing; and *C* is the beginning of thawing the trap).

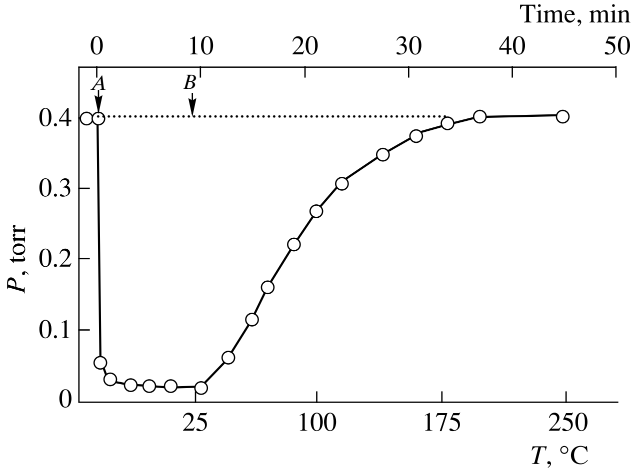

Fig. 4. Temperature-programmed desorption of CO_2 from the FeZSM-5 zeolite surface (*A* is the instant of opening the microreactor and admitting CO_2 and *B* is the beginning of thawing).

desorbed. It turned out in this case that the reaction product can be completely removed from the zeolite surface. The amount of CO_2 formed was equal to that of α-oxygen on the surface (Table 3). Thus, in the oxidation of CO, all α-oxygen participated in the reaction and zeolite micropores were not blocked.

Note that the above procedure allowed the complete removal of α-oxygen with the product of the stoichiometric reaction at a moderate temperature. If, after the oxidation of CO by α-oxygen and the subsequent evacuation of the sample at 100°C, N_2O was repeatedly decomposed at 250°C, α-oxygen was formed again in a concentration close to C_{O_α} after the standard treatment of the sample.

At first glance, the data on the oxidation of CO, CH_4, and D_2 by α-oxygen confirm the assumption of the possible blocking of the zeolite pore space with the reaction product firmly bound to the zeolite surface. However, one should take into account the property of a CO molecule that distinguishes it from CH_4 and H_2 (or D_2) molecules. Carbon monoxide can chemically bind only one oxygen atom, whereas, in the oxidation of methane and hydrogen, the possibility of their interaction with two α-oxygen atoms cannot be excluded. Such an interaction may, for example, involve the abstraction of a H atom from the oxidized molecule with the subsequent formation of surface OH or CH_3 groups. In this case, the stoichiometric ratio between the reagents and α-oxygen must be 1 : 2, which is close to the experimental value. This prevents the obtained results from being considered as the ultimate proof of the above-mentioned assumption. The strongest evidence for blocking could be a decrease in the accessible micropore volume of the zeolite after the stoichiometric reaction involving α-oxygen.

Determination of the FeZSM-5 Zeolite Micropore Volume

The volume of zeolite micropores was determined by argon adsorption at the temperature of liquid nitrogen. Note that the radius of the Ar atom (r = 3.84 Å) is close to the sizes of reacting molecules of CH_4 (r = 4.25 Å) and H_2 (r = 3.24 Å) [10]. Therefore, it might be expected that, in the case of micropore space blocking by the product of the stoichiometric reaction, it will be inaccessible not only to reactants but to argon molecules as well. To elucidate whether or not the microporous volume decreased after the stoichiometric reaction involving α-oxygen, two experiments were carried out at the temperature of liquid nitrogen. In the first experiment, argon was adsorbed by FeZSM-5 zeolite subjected to standard treatment. In the second experiment, before argon adsorption, methane was oxidized by α-oxygen at room temperature. The measurements were carried out at

Table 2. Stoichiometry of the reaction between D_2 and α-oxygen over FeZSM-5 zeolite at 100°C

No.	Amount of O_α on the surface, O atom/g	Amount of reacting D_2, molecule/g	$D_2 : O_\alpha$ stoichiometric ratio
1	1.8×10^{19}	1.14×10^{19}	1 : 1.6
2	1.9×10^{19}	1.20×10^{19}	1 : 1.6

pressures when P/P_0 was 0.3, which, according to the data reported in [11], corresponded to the filling of micropores of ZSM-5 zeolite. The volume of micropores was calculated from the amount of adsorbed argon assuming that the adsorbate density equaled the density of liquid argon ($d_{Ar} = 1.419$ g/cm^3) [11].

It turned out that the micropore volume of ZSM-5 zeolite did not decrease after the interaction of methane with α-oxygen (Table 4). This indicates that the effect of micropore space blocking was absent after the oxidation of methane by α-oxygen. Thus, the difference in the stoichiometry of oxidation by α-oxygen for methane and hydrogen and for carbon monoxide is due to other reasons, most probably, to the mechanisms of the corresponding reactions. The assumption that the interaction of methane and hydrogen with α-oxygen involved the dissociation of reacting molecules seems to be the most probable. To verify this assumption, we studied the products formed in the reaction of hydrogen with α-oxygen on the surface of FeZSM-5 zeolite by IR spectroscopy.

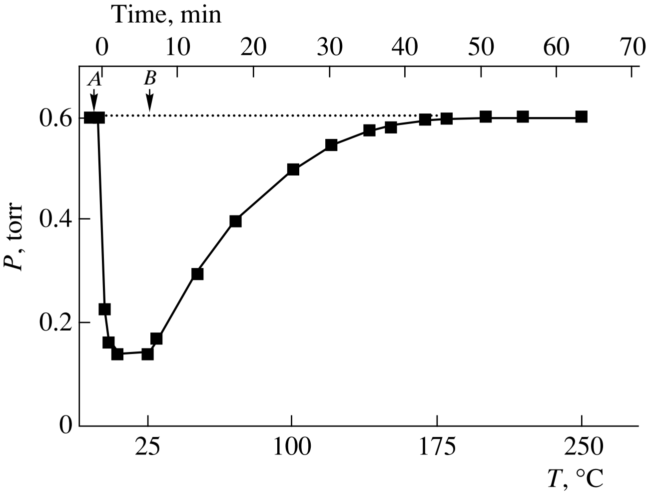

Fig. 5. Temperature-programmed desorption of CO from the FeZSM-5 zeolite surface (*A* is the instant of opening the microreactor and *B* is beginning of thawing).

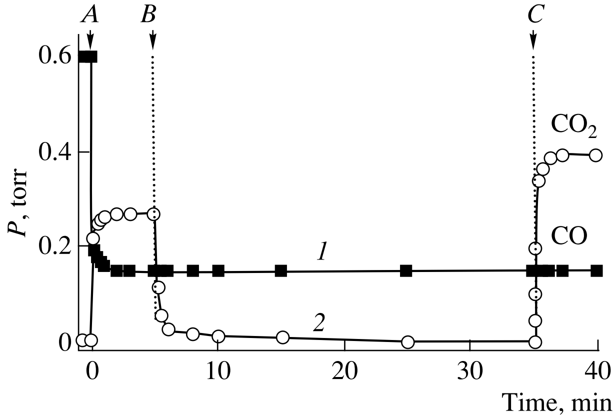

Fig. 6. Oxidation of CO with α-oxygen over FeZSM-5 zeolite surface at 100°C (*A* is the instant of opening the microreactor; *B* is the beginning of freezing; and *C* is the beginning of thawing the trap): (*1*) the amount of CO and (*2*) the amount of CO_2.

Study of the Interaction of H_2 with α-Oxygen by IR Spectroscopy

Figure 7 presents the IR spectra of FeZSM-5 zeolite in the region of the stretching vibrations of OH groups. The initial spectrum of the sample subjected to standard treatment exhibited three main absorption bands, which corresponded to vibrations of zeolite OH groups. According to the published data, absorption bands at 3740 and 3610 cm^{-1} are related to the terminal silanol Si–OH [12–15] and bridge Al–OH–Si [14–16] groups, respectively. A less intense absorption band at 3670 cm^{-1} is usually assigned to OH groups bound to extra-framework forms of Al [16, 17]. Because hydrogen was weakly adsorbed on the zeolite after standard treatment, short evacuation was sufficient to completely remove it, and it gave no new absorption band. The spectrum also remained unchanged after loading α-oxygen in a concentration of 1.8×10^{19} O atom/g on the zeolite surface (Fig. 7, spectrum *2*).

A qualitative change in the spectrum was observed after the interaction of H_2 with the zeolite surface on which α-oxygen was present (Fig. 7, spectrum *3*). In the region of the stretching vibrations of OH groups, an intense new absorption band at 3674 cm^{-1} with a shoulder at 3635 cm^{-1} appeared. These bands may be assigned to the terminal Fe–OH and bridge Fe–OH–Si groups, respectively [18]. They are well seen in the difference spectrum *4* obtained by subtracting the spectrum of the initial sample from spectrum *3*. Obviously, these absorption bands are related to new surface OH groups that were formed during the oxidation of hydro-

Table 3. Stoichiometry of the reaction between CO and α-oxygen over FeZSM-5 zeolite at 100°C

No.	Amount of O_α on the surface, O atom/g	Amount of CO_2, formed, molecule/g	CO : O_α stoichiometric ratio
1	1.8×10^{19}	1.76×10^{19}	1 : 1.02
2	1.8×10^{19}	1.73×10^{19}	1 : 1.04

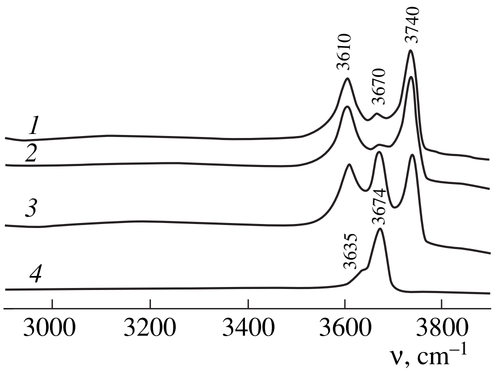

Fig. 7. IR spectra of FeZSM-5 zeolite in the region of OH vibrations recorded (*1*) after the standard treatment of the zeolite, (*2*) after the formation of α-oxygen on the zeolite surface; (*3*) after the reaction between H_2 and α-oxygen; and (*4*) after subtracting spectrum *1* from spectrum *3* (the difference spectrum).

gen. Note that the results obtained here qualitatively agree with data reported in [19].

Thus, the occurrence of the reaction between hydrogen and α-oxygen via the dissociation of H_2 molecules was confirmed. The mechanism of the reaction can be outlined in the following way. The interaction with α-oxygen was accompanied by the rupture of the bond in H_2 molecules and the formation of HO_α groups on the zeolite surface. The second hydrogen atom reacted with the nearest α-oxygen atom. This resulted in the formation of two OH groups per each molecule of the reactant:

$$H_2 + 2O_\alpha \longrightarrow 2HO_\alpha. \qquad \text{(II)}$$

If the residual hydrogen was removed from the gas phase by evacuating after the reaction, the subsequent heating of the sample at temperatures higher than 350°C resulted in the desorption of O_2 [7]. It can be assumed that, with an increase in temperature, the OH groups were removed from the zeolite surface as H_2O and the remaining α-oxygen desorbed as O_2:

$$2HO_\alpha \longrightarrow H_2O + \frac{1}{2}O_2 + 2(\,)_\alpha. \qquad \text{(III)}$$

Because methane reacted with α-oxygen almost in the same stoichiometric ratio, it can be assumed that, in this case, the reaction also proceeded via a similar dissociative mechanism. The reaction with methane should also include the abstraction of H atoms from the CH_4 molecules with the formation of the hydroxy and methoxy groups on the zeolite surface. Note that the kinetic isotope effect in the reaction of methane with α-oxygen demonstrated that the reaction really involved the rupture of the C–H bond the methane molecule as a rate-limiting step [20].

It can be assumed that, for such a dissociative mechanism, α-sites in the zeolite matrix should be arranged in pairs in which two active sites are at a rather close distance from each other. The dependence of the stoichiometry of methane oxidation on the concentration of α-oxygen on the zeolite surface [7] may be due to the behavior of α-oxygen in the filling of such pair sites during the decomposition of N_2O. At a low concentration of α-oxygen on the surface, single O_α atoms are mainly formed; with an increase in the concentration, the fraction of pairs of O_α atoms increased and approached 100% when the coverage of α-sites was maximum. In this case, the interaction of the substrate molecule with two atoms of O_α was made possible, and, as a result, the stoichiometric ratio approached 1 : 2. In the reaction involving methane, this value was close to an experimental value of 1 : 1.8 (Table 1), whereas it was somewhat lower (1 : 1.6) in the reaction with hydrogen (Table 2). The reason for underestimating this ratio remains unclear. We cannot exclude that a small part of hydrogen reacted in such a way that hydrogen atoms formed in the dissociation of H_2 molecule were bound not to the nearest O_α atoms but to other sites of the surface. It is also possible that some of the H_2 molecules were bound to one rather than two O_α atoms. Nevertheless, the obtained results leave no doubts that the major part of hydrogen reacted with α-oxygen via the dissociative mechanism.

In contrast to methane and hydrogen, CO reacted with α-oxygen in a stoichiometric ratio of 1 : 1 to give CO_2, which desorbed into the gas phase and freed the active site:

$$CO + O_\alpha \longrightarrow (\,)_\alpha + CO_2. \qquad \text{(IV)}$$

Thus, the observed difference in the stoichiometry of the oxidation of methane, hydrogen, and carbon monoxide reflected the difference in the mechanisms of the interaction of these molecules with α-oxygen. Our studies gave better insight into the properties of the active oxygen formed during the decomposition of N_2O on Fe complexes in FeZSM-5 zeolites and the mechanisms of oxidation reactions involving active oxygen.

Table 4. Micropore volume of FeZSM-5 zeolite before and after the reaction between CH_4 and α-oxygen at 25°C

No.	Treatment	Initial pressure of Ar, torr	Ar pressure after adsorption, torr	Amount of adsorbed Ar, torr	Micropore volume, cm^3/g
1	Vacuum, O_2, 550°C	43.4	6.8	36.6	0.159
2	Vacuum, O_2, 550°C	43.4	6.5	36.9	0.160
3	$CH_4 + O_\alpha$	43.4	7.1	36.3	0.157

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