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O_2 isotopic exchange in the presence of O^- anion radicals on the FeZSM-5 surface

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ABSTRACT

Oxygen anion radicals O^- play an important role in various physico-chemical processes, including those taking place on solid surfaces, where their behavior is especially difficult to follow. This work presents a detailed study on the behavior of O^- radicals adsorbed on FeZSM-5 surface in the reaction of O_2 isotopic exchange carried out over a wide range of temperatures (198–513 K). High concentration of O^- in this unique system (called alpha-oxygen) made it possible to identify two exchange mechanisms, R_0 and R_1, operating in the presence of O_α. The R_1 mechanism ($E = 15$ kJ/mol) dominates in the high-temperature region and can be represented by the following equation:

$$^{18}O_2 + {}^{16}O_\alpha^- \rightleftarrows [O_3^-]_\alpha \rightleftarrows {}^{16}O^{18}O + {}^{18}O_\alpha^-.$$

This mechanism is convincingly supported by several arguments: the first order reaction with respect to O_2; the linear dependence of reaction rate on O_α concentration; the ESR observation of O_3^- species (in other systems); and, according to isotopic exchange theory, by a twofold excess of the rate of homoexchange over the rate of heteroexchange.

The R_0 exchange ($E = 0.8$ kJ/mol) is a new reaction pathway that appears at cryogenic temperatures and leads to isotope redistribution only between O_2 molecules, not affecting the isotopic composition of O_α. This exchange mechanism is not quite clear. The necessity of the presence of O_α without its direct involvement in the exchange process seems to be quite surprising. The reaction may proceed via a hypothetical complex $[O_5^-]_\alpha$, which allows cleavage and redistribution of chemical bonds between two O_2 molecules adsorbed on the α-oxygen. The cleavage and redistribution of such strong bonds at cryogenic temperatures with nearly zero activation energy are an intriguing phenomenon worthy of further study.

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1. Introduction

A long lasting interest in oxygen anion radicals O^- is stimulated by an important role (known or assumed) of these species in various physico-chemical processes taking place in the Earth's ionosphere, in flames, plasmas, photochemistry, radiolysis processes, etc. [1,2]. Due to high reactivity, the radicals interact with most stable molecules and can be used for synthesis of active organic intermediates [2]. The O^- species are considered as one of the possible forms of active oxygen in biological oxidation with monooxygenases [3]. The anion radicals may have particular importance for oxidation processes on solid surfaces. Their catalytic role over metals [4,5] and especially over metal oxides [6–14] has long been discussed in the literature. However, due to low concentrations, the role of O^- in these systems remains poorly understood.

In distinction to gas and liquid media, where O^- are generated by an external energy source, the surface O^- can be prepared in a purely chemical way. This can be done by room temperature adsorption of O_2 or N_2O on the surface of some prereduced oxides. As the temperature increases, O^- disappear due to reoxidation of the surface and transformation into conventional lattice anions O^{2-}.

In this connection, of particular interest are Fe-containing zeolites FeZSM-5. A unique feature of the zeolites is that they do not need a special preliminary reduction and allow generating O^- radicals in the concentration which by 2–3 orders of magnitude exceeds that for oxide systems. This is provided by the so-called α-sites, which are special complexes of bivalent iron stabilized in the micropore space of the zeolite matrix [15–19]. Strong stabilization of the bivalent state prevents the oxidation of α-sites by dioxygen, but they are readily oxidized at 470–520 K by endothermic molecules of nitrous oxide ($\Delta H^0_{f,298} = 81.5$ kJ/mol) leading to the stoichiometric deposition of O^- radicals called the alpha-oxygen for this system, O_α [14,17–21]:

$$(Fe^{2+})_\alpha + N_2O \rightarrow (Fe^{3+}\text{–}O^-)_\alpha + N_2. \quad (1)$$

Above 573 K α-oxygen desorbs into the gas phase, resulting in liberation of α-sites:

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$$2(Fe^{3+}\text{–}O^{-})_{\alpha} \rightarrow 2(Fe^{2+})_{\alpha} + O_2. \quad (2)$$

The properties of α-oxygen were studied in many experimental [14,17,20–32] and quantum-chemical [33–38] works. In particular, at room temperature O_{α} oxidizes methane, benzene and other hydrocarbons to form the surface intermediates that after extraction yield corresponding hydroxylated products [39–42]. This reveals a similarity of α-oxygen with the active oxygen of methane monooxygenases discussed in several papers [12,15,17,43,44]. The reaction of O_{α} with water is quite noteworthy, resulting in the evolution of dioxygen from H_2O [29].

The present work is devoted to the role of O_{α} in the O_2 isotopic exchange. Starting from Haughton and Winter [45], this simplest catalytic reaction has been widely used to study activation of oxygen on the catalyst surface. The early works in the field were extensively reviewed by Winter [46,47], Boreskov et al. [48–51], Novákova [52] and Ozaki [53], the more recent works — by Hargreaves and Mellor [54], and Duprez [55].

In the case of FeZSM-5, several authors showed a dramatic effect of α-oxygen on the rate of O_2 exchange [22,56,57]. In distinction to oxide catalysts, where the reaction is usually observed at 600–800 K, Jia et al. [22] observed the exchange with O_{α} at 523 K, Panov et al. [56] and Novákova et al. [57] — at room temperature. However, these first isotopic works on α-oxygen were mainly of descriptive nature. They did not obtain the kinetic parameters of exchange, while redistribution of isotopes between O_2 molecules of the gas phase was not studied at all. As one can see further, the latter reaction reveals a new remarkable feature of α-oxygen, which is especially pronounced at cryogenic temperatures and may assist to understand fine details in the activation mechanism of dioxygen taking place in catalytic systems.

2. Introductory remarks to O_2 isotopic exchange

In a heterophase system comprising dioxygen in the gas phase and oxygen on the surface of a solid, two isotopic exchange reactions may take place:

1. The heterophase exchange, or heteroexchange (HEE), $^{18}O_2/^{16}O_S$, which is a reversible transfer of oxygen isotopes between the gas phase and the surface. This reaction is usually monitored by a fraction of ^{18}O isotope in the gas phase oxygen ($^{18}f_g$).
2. The homophase exchange, or homoexchange (HOE), $^{18}O_2/^{16}O_2$, which is a reversible transfer of oxygen isotopes between O_2 molecules of the gas phase. This reaction is usually monitored by a parameter $Y = F_{34,\mathrm{eq}} - F_{34}$, which characterizes a deviation of the current fraction of $^{16}O^{18}O$ molecules (F_{34}) from its equilibrium value, $F_{34,\mathrm{eq}} = 2\,^{18}f_g(1 - {}^{18}f_g)$.

Three types (sometimes called also the mechanisms) of exchange are distinguished depending on the number of atoms the O_2 molecule exchanges for the surface oxygen during its one interaction with the solid: zero, one and two. R_0, R_1 and R_2 are the corresponding exchange rates. The exchange reactions of each type can be written as follows:

R_0 type:

$$^{18}O_2 + {}^{16}O_2 \rightleftarrows 2\,^{18}O^{16}O; \quad (3)$$

R_1 type:

$$^{18}O_2 + {}^{16}O_S \rightleftarrows {}^{18}O^{16}O + {}^{18}O_S; \quad (4)$$

R_2 type:

$$^{18}O_2 + 2\,^{16}O_S \rightleftarrows {}^{16}O_2 + 2\,^{18}O_S. \quad (5)$$

The rates of HEE (W) and HOE (R) are connected with exchange rates of various types by the following equations:

$$W = (1/2)R_1 + R_2, \quad (6)$$

$$R = R_0 + R_1 + R_2. \quad (7)$$

The rate of HEE is determined only by R_1 and R_2, while the rate of HOE includes also R_0.

Mainly, we will differentiate between the terms "type of exchange" and "mechanism of exchange", with the mechanism denoting a set of steps providing the exchange of a certain type. Theoretically, several mechanistic versions can be suggested for each type of exchange. Identification of the actual steps is an important target of experimental studies.

A theory considering the exchange types was formulated by Klier et al. [58] and by Muzykantov et al. [59]. The algorithms for analysis of experimental data developed in these works are somewhat different, but give identical results [60]. In our work we will use mainly the algorithm by Muzykantov and co-authors as well as corresponding equations given in their papers [59,61,62] and in the book by Ozaki [53].

Each type of exchange manifests itself in specific kinetic features, which can be identified by analyzing $^{18}f_g$ and Y with time. In more detail the theory of isotopic exchange and the equations are given in the supplementary material to this paper.

3. Experimental

3.1. Sample

A FeZSM-5 sample was prepared by impregnation of the initial HZSM-5 zeolite (Si/Al = 22, Angarsk) with a $FeCl_3$ solution similar to [20]. To increase the α-site concentration, the sample was activated by calcination in vacuum at 1173 K. Iron content in the sample was 0.56 wt%, and concentration of α-sites, C_{α}, was 1.5×10^{19} site/g. The value of C_{α} was determined from the maximum amount of α-oxygen, which can be deposited on the sample surface from N_2O (see Section 3.3) assuming that one α-oxygen atom occupies one α-site. In the FeZSM-5 under study, 25% of the iron are in the active state in form of α-sites.

3.2. Vacuum setup

Experiments were conducted in a vacuum static setup (1.3×10^{-5} Pa) made of stainless steel and described elsewhere [29]. The setup was equipped with two Baratron absolute pressure gauges (MKS Instruments) covering the range of $0.1–1.3 \times 10^5$ Pa. The gas phase composition was analyzed mass-spectrometrically using a PPT quadrupole residual gas analyzer (MKS Instruments). An important feature of the setup is a small reactor (6.5 cm^3), which can be easily isolated from the rest of the reaction volume (715 cm^3). This allows substituting the gas in the setup at a closed reactor, not disturbing the adsorption equilibrium established by a preceding treatment. That significantly enhances the accuracy of kinetic and adsorption measurements. A minor amount of the gas remaining in the reactor usually does not impede the next experiment.

The setup provides a temperature-programmed heating of the sample from 348 to 1173 K, as well as experiments at cryogenic temperatures. For that, a home-made cryostat was used, which allowed one to set a desired temperature in the range from 173 to 273 K.

3.3. α-Oxygen deposition

A FeZSM-5 sample (0.25 g, 0.25–0.5 mm fraction) was loaded into reactor and subjected to a standard pretreatment that included heating at 833 K under the following conditions: 1 h in vacuum; 1.5 h in oxygen at $P(O_2) = 266$ Pa; 20 min in vacuum; and 20 min in oxygen at $P(O_2) = 80$ Pa followed by cooling to the

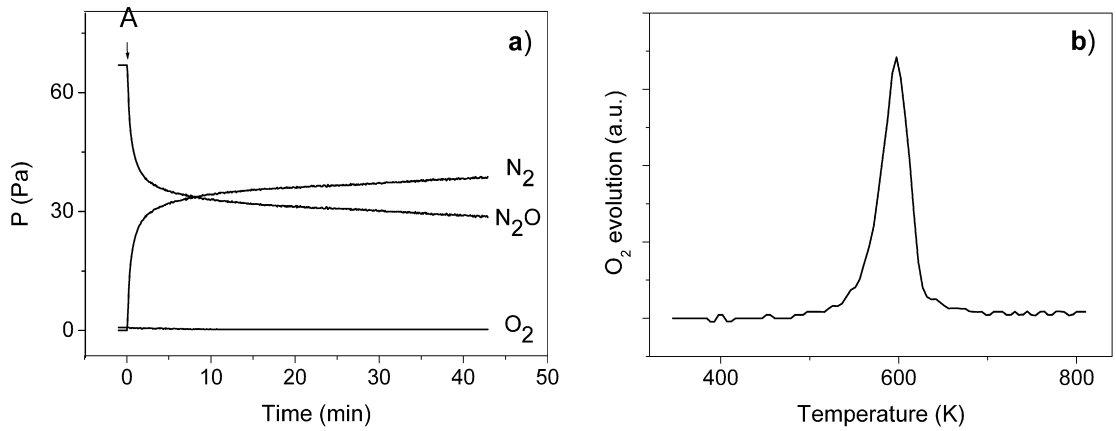


Fig. 1. Deposition of α-oxygen by N_2O decomposition at 513 K (a) and its desorption from FeZSM-5 at TPD experiment (b). A: time of opening the reactor.

required temperature. Such pretreatment provided careful removal of organic impurities and water from the surface as well as full oxidation of the iron that can be oxidized by dioxygen and hence is not the α-sites.

The O_α deposition was provided by N_2O decomposition at 513 K with initial pressure 66 Pa. As Fig. 1a shows, the decomposition at this temperature followed exactly Eq. (1). The entire oxygen generated from N_2O remains adsorbed on the α-sites while equivalent amount of N_2 evolves into the gas phase. At temperature programmed desorption (TPD, 5 K/min), α-oxygen desorbs into the gas phase, providing an O_2 peak at 593 K (Fig. 1b).

The measurements of α-oxygen amount were described elsewhere [63]. In this work we used mainly two methods based on the amount of nitrous oxide decomposed (Eq. (1)), and the equilibrium composition of dioxygen at isotopic exchange $^{18}O_2/^{16}O_\alpha$, which was usually performed at 373 K. Both methods gave close results.

3.4. Isotopic exchange

The HEE and HOE reactions were conducted with the O_α/FeZSM-5 sample having a certain amount of preliminarily deposited α-oxygen. In the HEE experiments, "heavy" oxygen $^{18}O_2$ (97.0%) was used. The rate of HEE was calculated by Eq. (8):

$$-\frac{d^{18}f_g}{dt} = W\frac{m}{N_g}(^{18}f_g - {}^{18}f_S), \tag{8}$$

where m is the catalyst mass, N_g is the number of O_2 molecules in the gas phase, and $^{18}f_S$ is the fraction of ^{18}O isotope on the surface. For that, using computer simulation we selected an exponential function that would fit well the initial part of $^{18}f_g$ dependence on time. The analytic expression of this function was used to find the $(d^{18}f_g/dt)^0$ derivative, which is necessary for calculating W. Hereinafter, superscript "0" refers to the values to zero time.

For HOE, we used a 1:1 mixture of $^{18}O_2$ and $^{16}O_2$ ($^{18}f_g^0 = 48\%$, $Y^0 = 49\%$). To avoid the effect of HEE on the kinetics of homoexchange, the α-oxygen was preliminarily exchanged with $^{18}O_2$ at 373 K to make its isotopic composition identical to the composition of the gas phase mixture ($^{18}f_S = {}^{18}f_g$). In this case, the HOE rate can be found in the most simple way according to Eq. (9):

$$R = -\frac{N_g}{m}\cdot\frac{d\ln(Y/Y^0)}{dt}. \tag{9}$$

Below, the values W and R will be given in O_2 molecules/g s. The HEE rate can be also expressed as TOF by dividing the W value by the number of O_α atoms.

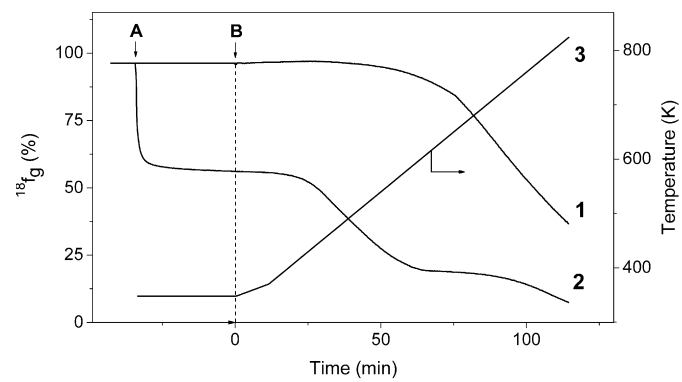


Fig. 2. Temperature-programmed heteroexchange of O_2 with FeZSM-5 surface before (1) and after (2) deposition of α-oxygen. A: time of opening the reactor; B: time of starting TP-heating; line 3: temperature profile.

4. Results

4.1. Preliminary experiments

To determine the upper limit of a temperature region suitable for the O_α study, first we carried out two temperature programmed HEE experiments, which results are shown in Fig. 2. The first experiment was performed before α-oxygen deposition, and the second — after α-oxygen deposition to the surface of FeZSM-5. In the first case, after the standard pretreatment, the sample was cooled to 348 K, and $^{16}O_2$ in the reaction volume was replaced with $^{18}O_2$ (with the closed reactor). At time A the reactor was opened, and at time B the TP-heating was turned on (5 K/min). One can see (Fig. 2, curve 1) that the zeolite oxygen is quite inert toward the exchange, which agrees with the results of other authors [57,64,65]. The $^{18}f_g$ value starts to decrease only at above 600 K.

The picture changes dramatically after deposition of α-oxygen (curve 2). In this case, fast exchange of $^{18}O_2$ with $^{16}O_\alpha$ occurs immediately upon opening the reactor, terminating in 30 min. At heating to 423 K, the isotopic composition of the gas phase remains constant, while at higher temperature, $^{18}f_g$ slowly decreases again. In this region α-oxygen initiates its exchange with the oxygen of zeolite. This process runs rather slowly and virtually terminates at about 600 K due to O_α desorption from the surface. The role of O_α as an intermediate species accelerating the exchange between O_2 and the zeolite oxygen was noted earlier [22,57,66]. Such intermediate role of the adsorbed oxygen species was extensively studied by Valyon and Hall [67] for the case of O_2 isotopic exchange over CuZSM-5. The same phenomenon was recently re-

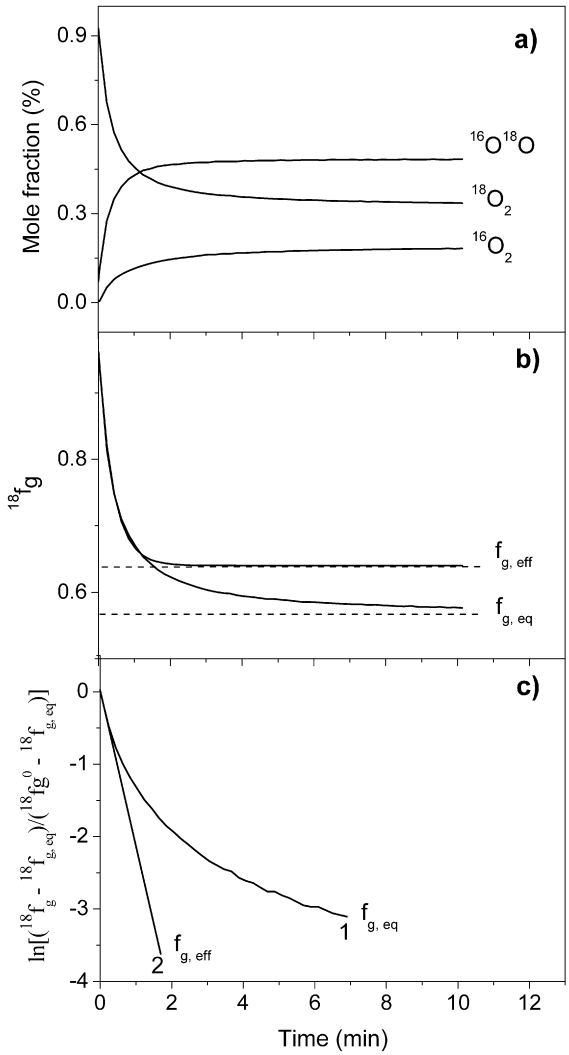


Fig. 3. Heteroexchange of $^{18}O_2$ with $^{16}O_\alpha$/FeZSM-5 (1.5×10^{19} O_α/g, 323 K, 13.3 Pa O_2).

viewed by Duprez [55] for a variety of supported metals and metal oxides.

The obtained review picture shows that the isotopic exchange O_2/O_α may be safely studied up to 450–470 K. The low rate of O_α exchange with lattice oxygen in this region cannot complicate the measurement of much higher rate of its exchange with dioxygen from the gas phase.

4.2. On a uniformity of O_α

Isotopic exchange is a sensitive method for identifying a uniformity or nonuniformity of exchangeable surface oxygen. Fig. 3a shows mole fractions of dioxygen isotopic species versus time of exchange at 323 K. The reaction terminates in 10 min as O_α comes to isotopic equilibrium with O_2. Fig. 3b presents results of this experiment as a function of $^{18}f_g$ on time that, in the limit, tends to the equilibrium value of $^{18}f_{g,\mathrm{eq}} = 56\%$ (marked with the lower dashed line) corresponding to the exchange of the entire α-oxygen amount of 1.5×10^{19} atoms O_α/g. In the case of uniformity of O_α, this dependence would be exponential and could be described by a straight line in the coordinates

$$\ln \frac{^{18}f_g - {}^{18}f_{g,\mathrm{eq}}}{^{18}f_g^0 - {}^{18}f_{g,\mathrm{eq}}} - t. \tag{10}$$

Table 1
Rates of heteroexchange and homoexchange at different temperatures (13.3 Pa O_2, 1.5×10^{19} O_α/g).

Temperature (K)	Exchange rate (10^{16} molec. O_2/g s)		R/W ratio
	Heteroexchange, W	Homoexchange, R	
448	39	75	1.9
423	32	61	2.0
398	27	50	1.8
373	20	41	2.1
348	15	34	2.3
323	10	25	2.5
298	5.5	20	3.6
273	3.4	16	4.6
248	1.5	11	7.3
223	0.6	10.5	17.5
198	0.3 (extrapol.)	10	33

However, one can see that the dependence deviates from the straight line (Fig. 3c, line 1), which points to some smooth nonuniformity of O_α.

For qualitative characterization of a nonuniformity, the value of $^{18}f_{g,\mathrm{eq}}$ in Eq. (10) is replaced with such effective parameter $^{18}f_{g,\mathrm{eff}}$ that allows describing an initial part of the experiment by a linear dependence [68]. Such analysis is illustrated in Fig. 3c (line 2). It is seen that the use of $^{18}f_{g,\mathrm{eff}} = 64\%$ instead of $^{18}f_{g,\mathrm{eq}} = 56\%$ allows describing the results by a straight line to a deep degree of exchange. The selected value of $^{18}f_{g,\mathrm{eff}}$ is a parameter of the effective exponent that best fits the experimental dependence $^{18}f_g - t$ (Fig. 3b).

The effective amount of exchangeable oxygen corresponding to $^{18}f_{g,\mathrm{eff}} = 64\%$ is 1.2×10^{19} atoms O_α/g. A rather small difference between this value and the actual amount of α-oxygen (1.5×10^{19} atoms O_α/g) testifies that heterogeneity of O_α is not pronounced, and it can be considered as nearly uniform, which correlates with the O_2 peak obtained at the TPD experiment (Fig. 1b).

4.3. Temperature dependence

To study temperature dependence of HEE and HOE rates, a series of experiments was conducted in a temperature range from 198 to 448 K, which results are presented in Table 1 and Fig. 4. As seen from Fig. 4, the rate of HEE, W, is satisfactorily described by Arrhenius dependence (line 1) with the activation energy $E_W = 15 \pm 2$ kJ/mol. Unlike that, the rate of HOE, R, does not obey Arrhenius law. In the high-temperature region (373–448 K), this dependence is described by a straight line parallel to the HEE dependence (line 2), and also corresponds to the activation energy $E_R = 15 \pm 2$ kJ/mol. As the temperature drops, the rate deviates more and more from this line following a smooth curve of a gradually decreasing slope. Below 250 K the curve turns into a straight line almost parallel to the abscissa (line 3), which corresponds to $E_R = 0.8 \pm 0.4$ kJ/mol. Such a behavior evidences a complicated reaction mechanism changing with temperature.

Consider data in the high- and low-temperature regions in more detail. In the general case HEE rate, according to Eq. (6), is the sum of exchange rates for monatomic and diatomic mechanisms, $W = (1/2)R_1 + R_2$. However, since α-oxygen is a single O^- atoms bonded to isolated iron sites $(Fe^{III}\text{–}O^-)_\alpha$ [14,20,21], one may expect that HEE will proceed only by the monatomic mechanism R_1.

$$^{18}O_2 + (^{16}O)_\alpha \rightleftarrows {}^{16}O^{18}O + (^{18}O)_\alpha. \tag{11}$$

Indeed, experimental results presented in Table 1 and Fig. 4 confirm this expectation. The exchange at the high-temperature region, 373–448 K, has the following kinetic features:

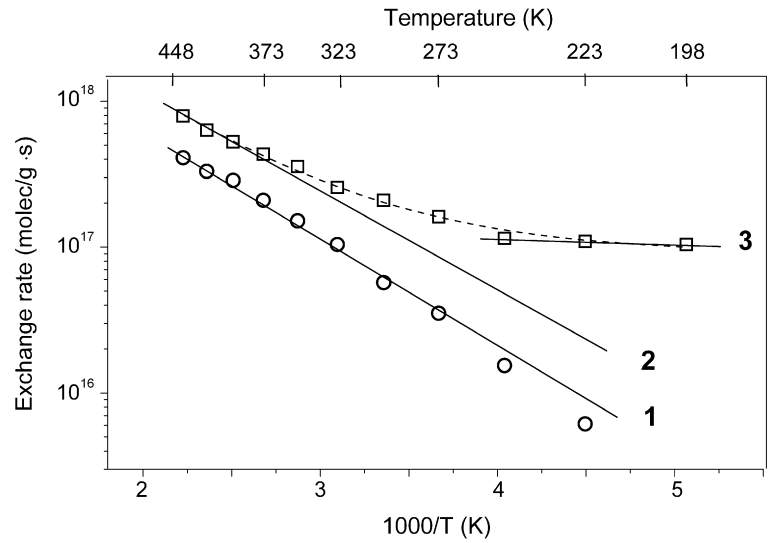


Fig. 4. Arrhenius plot of O_2 isotopic exchange (13.3 Pa O_2, 1.5×10^{19} O_α/g): (1) R_1 heteroexchange ($E_W = 15 \pm 2$ kJ/mol); (2) R_1 homoexchange ($E_R = 15 \pm 2$ kJ/mol); (3) R_0 homoexchange ($E_R = 0.8 \pm 0.4$ kJ/mol). Dotted line is a calculated additive rate of homoexchange, $R = R_1 + R_0$.

1. $R/W = 2$, i.e., the rate of HOE is two times greater than the rate of HEE;
2. $E_W = E_R$, i.e., HEE and HOE have equal activation energies;
3. $Y = 0$, i.e., during heteroexchange the equilibrium distribution of isotopes between dioxygen in the gas phase is retained, and no $^{16}O_2$ molecules appear at the initial time of the reaction.
4. HEE and HOE have equal reaction orders with respect to O_2 (see further).

According to the theory of isotopic exchange [58,59] these features are safe indication that the reaction proceeds by R_1 type without detectable contributions from other exchange types.

As the temperature decreases, the excess of R over W is progressively increasing, becoming at 198 K more than 30-fold. This evidences that in the low-temperature region the exchange predominantly proceeds via R_0 type, i.e. without involvement of α-oxygen. Noteworthy is a remarkable fact, which we will try to explain later: although O_α is not involved in the reaction, its presence on the surface is necessary. In the absence of O_α, exchange R_0 does not occur.

Thus, two types of exchange, R_1 and R_0, take place in the O_2–O_α/FeZSM-5 system. Therefore, the measured homoexchange rate R should have an additive value. With known kinetic parameters of each exchange type, one can describe the HOE temperature dependence presented in Fig. 4. Taking the R and E_R values from the high-temperature region, where R_1 dominates, and from the low-temperature region, where R_0 dominates, one can write the following equations:

$$R_1 = 3.3 \times 10^{19} \cdot e^{-\frac{3500}{RT}} \text{ molec. } O_2/\text{g s}, \quad (12)$$

$$R_0 = 1.5 \times 10^{17} \cdot e^{-\frac{200}{RT}} \text{ molec. } O_2/\text{g s}. \quad (13)$$

These equations make it possible to calculate the total homoexchange rate, $R = R_1 + R_0$, at any temperature. As seen in Fig. 4, the calculated curve (dotted line) satisfactorily describes experimental results.

4.4. Dependences on the O_α concentration and O_2 pressure

As the O_2 isotopic exchange takes place only in the presence of α-oxygen, it is interesting to study dependences of homo- and heteroexchange rates on the O_α concentration. Such dependences on surface species are a very rare case in heterogeneous catalysis because of great experimental difficulties. For that, one should identify the catalytically active species and quantify their concentration, with the possibility of varying the latter within a sufficiently broad range. FeZSM-5 with the α-sites suggests nice opportunity for such a study. The dependences on O_α concentration were measured in both the high-temperature (373 K) and low-temperature (223 K) regions at variation of $C(O_\alpha)$ in the range of $(2.3–12) \times 10^{18}$ atoms/g. Fig. 5 shows the results obtained at 373 K, where the exchange predominantly runs by R_1 mechanism. One can see that the rates of both hetero- and homoexchange increase linearly as the $C(O_\alpha)$ increases. For heteroexchange, a similar linear dependence was observed also in the low-temperature region at 223 K (not shown).

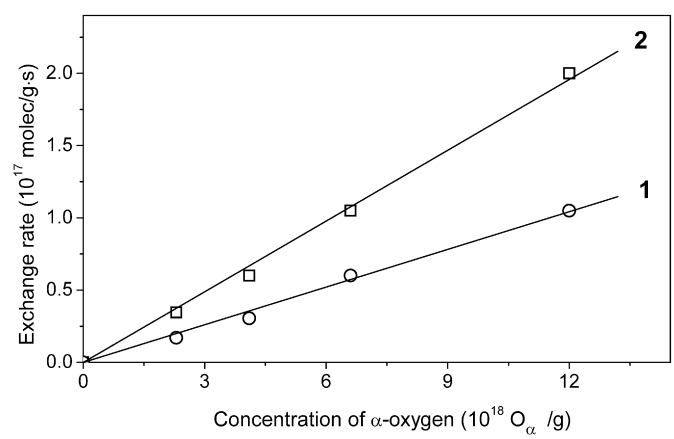


Fig. 5. Effect of α-oxygen concentration on the rate of R_1 exchange (373 K, 5.2 Pa O_2): (1) Heteroexchange; (2) homoexchange.

For the homoexchange, we failed to obtain a reliable dependence at 223 K. In distinction to HEE, reproducibility of HOE experiments in the low-temperature region was unsatisfactory. While experiments with the same portion of O_α were reproduced satisfactorily, the loading of a new portion could considerably change the HOE rate. This may be caused by some minor details of experimental conditions, which are not significant for exchange R_1, but significant for exchange R_0. Qualitatively, the obtained results allow concluding that the dependence of R_0 on $C(O_\alpha)$ is approx-

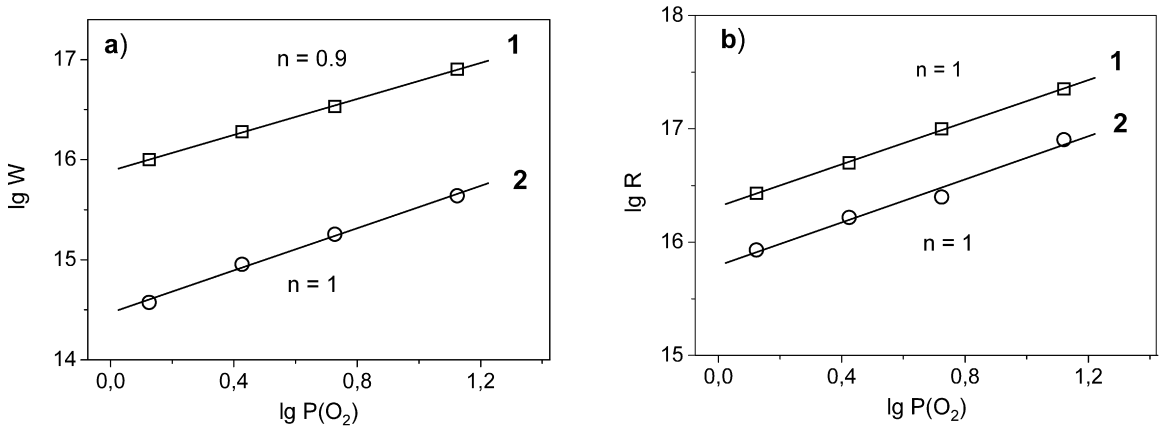


Fig. 6. Effect of O_2 pressure (Pa) on the rate of O_2 isotopic exchange (molec. O_2/g s) at α-oxygen concentration 3×10^{18} atoms O_α/g: (a) Heteroexchange at 373 K (1) and 223 K (2); (b) homoexchange at 323 K (1) and 223 K (2).

imately as strong as the dependence of R_1. However, to make a safe conclusion, an additional study is necessary.

The dependences of HEE and HOE rates on dioxygen pressure (Fig. 6) in both the high- and low-temperature regions are described by linear functions in logarithmic coordinates and in all cases correspond to kinetic orders, n, close to 1.

5. Discussion

5.1. Mechanism of R_1 exchange

According to the literature, R_1 exchange is often observed on transition metal oxides preheated in O_2. It usually proceeds at 600–800 K with activation energy 85–200 kJ/mol. Concerning the types of exchange, one should note a significant disagreement in the literature. According to Boreskov et al. [48,50] main contribution of R_1 is observed only on ZnO and CdO, whereas R_2 is typical of other oxides of transition metals. Unlike this, according to Winter [47], the exchange over oxides, except those of Cu, V, Mo and W, primarily runs by the R_1 type, while Doornkamp et al. [69] simultaneously observed all three types of exchange, their contributions varying with temperature. These disagreements may relate to different origin of the samples, different experimental conditions as well as to insufficient accuracy at identification of exchange types, especially if the results are not corrected by separate measurement of the hetero- and homoexchange rates, which is quite a frequent case.

There are several hypotheses about the mechanism of monatomic exchange [47–52]:

(1) R_1 exchange can be observed when O_2 adsorption proceeds via dissociation into atoms or ions, and desorption occurs by their recombination with the lattice oxygen atoms producing anionic defects:

$$^{18}O_2 \rightleftarrows 2\,^{18}O_{ad}, \tag{14}$$

$$^{18}O_{ad} + {}^{16}O_{latt} \rightleftarrows {}^{18}O^{16}O + \square_{latt}, \tag{15}$$

$$^{18}O_{ad} + \square_{latt}\ {}^{18}O_{latt}. \tag{16}$$

(2) R_1 will be observed also when a dissociative O_2 adsorption takes place on anionic defects of the surface. In this case, one atom of dioxygen fills the defect, while the other migrates over the surface and desorbs via recombination with the lattice oxygen:

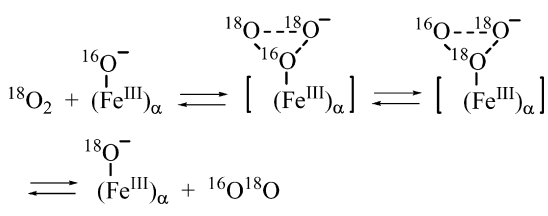
$$^{18}O_2 + \square_{latt} \rightleftarrows {}^{18}O_{latt} + {}^{18}O_{ad}, \tag{17}$$

$$^{18}O_{ad} + {}^{16}O_{latt} \rightleftarrows {}^{16}O^{18}O + \square_{latt}. \tag{18}$$

(3) R_1 may occur via molecular adsorption of O_2 with the reversible formation of intermediate triatomic complex including the lattice oxygen atom:

$$^{18}O_2 + {}^{16}O_{latt} \rightleftarrows [{}^{18}O^{18}O^{16}O] \rightleftarrows {}^{16}O^{18}O + {}^{18}O_{latt}. \tag{19}$$

One should admit that none of these mechanisms can explain our results. We have seen that the presence of α-oxygen is necessary for the R_1 exchange to occur rather than that of anionic defects or the lattice oxygen. In our case, the reaction most probably proceeds via a triatomic complex O_3^-, which comprises an O_2 molecule adsorbed on the O_α anion radical:



(20)

Complexes O_3^- were shown to form upon O_2 adsorption on O^- radicals, and with some oxides can be registered by ESR at low temperatures [70,71]. Equation (20) shows that as the O_3^- forms, an exchange of oxygen atoms within this complex may take place, e.g., via its rotation on the α-site. A subsequent O_2 desorption completes the reaction resulting in isotopically changed compositions of both the α-oxygen and O_2 molecule evolved into the gas phase. In particular, this mechanism explains how α-oxygen may travel into the gas phase without its recombinative desorption from the surface, which is possible only at a much higher temperature (Fig. 1).

At present, it is difficult to identify which of the two steps, i.e. the equilibrium adsorption-desorption or the exchange itself is the rate determining step of the overall exchange reaction. Our experiments showed that O_2 adsorption on O_α is as weak as the physical adsorption of dioxygen on the rest of the surface of the zeolite. Therefore, the adsorption–desorption process should be fast, and we are inclined to conclude that the exchange itself is the rate determining step, its activation energy being 15 kJ/mol.

Earlier, a similar mechanism of O_2 isotopic exchange involving O^- species was suggested by Nikisha et al. [70] for a V_2O_5/SiO_2 sample prereduced in hydrogen. However, having no possibility for quantitative study of HEE, the authors [70] made their conclusions from indirect evidences. In our case, Eq. (20) follows directly from the experimental results presented earlier, including a linear dependence of the exchange rate on the O_α concentration (Fig. 5).

As noted above, R_1 exchange on metal oxides preheated in O_2 proceeds at rather high temperatures, usually over 600 K. However,

one may think that in this case O_3^- species can also participate in the reaction. For that, the reaction should additionally include a step of O^- generation, e.g. by a thermal charge transfer [72]:

$$\begin{array}{ccc} O^{2-} & & O^- \\ \| & & | \\ M^{n+} & \leftrightarrows & M^{(n-1)+} \end{array} \tag{21}$$

This particular step may be responsible for both the high temperature and the high activation energy necessary for R_1 to occur on oxides.

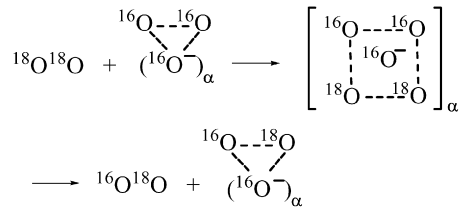
5.2. Mechanism of R_0 exchange

First the exchange of R_0 type was observed by Winter [73] and Stone [74] on some metal oxides after their high-temperature pretreatment in vacuum. Such oxides acquire a remarkable ability to catalyze a homoexchange at room and lower temperatures without evident participation of the catalyst oxygen, i.e. in the absence of heteroexchange. The effect of vacuum pretreatment was especially pronounced with zinc oxide, where the exchange proceeds with activation energy 0.8 kJ/mol and was noticeable even at the temperature of liquid nitrogen [74]. Later, a low-temperature exchange after vacuum pretreatment or partial reduction in H_2 was observed for the majority of simple and complex oxides [49]. This activity is unstable, and heating in O_2 leads to its disappearance.

The R_0 exchange supposedly runs via formation of tetratomic complex consisting of two O_2 molecules adsorbed on an oxygen vacancy. With La_2O_3, Sokolovski et al. [75] have measured the reaction order in dioxygen exceeding 1 (i.e., 1.4), which confirms the idea of molecular oxygen participation. Quantum-chemical calculations [76] also showed that the exchange can proceed via a tetratomic complex. According to the calculations, such complex may form by addition of dioxygen molecule to anion radical O_2^-. The O_2^- species can form (along with O^-) upon O_2 adsorption on the prereduced oxides, but their role in isotopic exchange is contradictory. This issue was reviewed by Che and Tench [77] with a general conclusion that O_2^- anions are inert at cryogenic temperatures and seem to participate only in a place exchange with O_2 molecules of the gas phase.

Sometimes the idea is suggested that R_0 exchange is just an apparent phenomenon. Indeed, if the reaction involves a very small amount of surface oxygen, the exchange will look like R_0 type irrespective of its actual mechanism. In particular, such interpretation was given in the above mentioned work [70] with V_2O_5/SiO_2. On the prereduced sample, HOE was observed at 140–300 K and, according to the authors, proceeded with the involvement of O^- radicals by the mechanism similar to that on O_α/FeZSM-5 (Eq. (20)). The absence of HEE, which should be observed with this mechanism (virtually R_1), was explained by a low concentration of O^- comprising only ca. 4×10^{16} atoms O^-/g as estimated by the ESR. Indeed, such a small amount of oxygen is difficult to detect with the isotopic exchange, therefore there is no possibility to differentiate between R_1 and R_0 mechanism. R_0 exchange was observed also on some metals containing adsorbed oxygen [78].

Prior to this study, the idea of apparent nature of R_0 exchange could be hardly excluded in any case. However, in the case of FeZSM-5 the concentration of O_α is so high (1.5×10^{19} atoms O_α/g) that there is no problem to tell the difference between R_0 and R_1. This is clearly seen from the results presented in Fig. 4. Along with the hetero- and homoexchange by R_1 mechanism with $E = 15$ kJ/mol (lines 1 and 2, respectively), a decrease in the temperature leads to ever-growing contribution of R_0 exchange with $E = 0.8$ kJ/mol. This exchange certainly proceeds without involvement of α-oxygen. The role of O_α in this case remains unclear and needs additional study. As a tentative hypothesis, we may assume that the exchange proceeds via an intermediate complex O_5^- formed by the interaction of O_2 molecule with the O_3^- anion:



(22)

Functionally, such complex can be considered as a tetratomic structure comprising two O_2 molecules adsorbed on the O_α anion radical. Formation and decomposition of such structures with the bond redistribution between the oxygen atoms in O_2 molecules lead to R_0 exchange.

6. Conclusion

This study showed that in addition to many earlier known substrates, α-oxygen exhibits also high reactivity toward dioxygen. The isotopic exchange $^{18}O_2/^{16}O_\alpha$ proceeds with a minor activation energy of 15 kJ/mol and can be observed even at temperatures as low as 223 K. The exchange runs by the monatomic mechanism R_1, which most probably involves an intermediate complex $(O_3^-)_\alpha$ comprising the α-oxygen and adsorbed O_2 molecule.

At cryogenic temperatures, the presence of α-oxygen on the surface opens a new reaction pathway in the form of R_0 exchange, which proceeds without direct involvement of O_α and has an activation energy of only 0.8 kJ/mol. It is speculated that the R_0 exchange operates via an intermediate complex $(O_5^-)_\alpha$ comprising two O_2 molecules adsorbed on the O_α atom, which serves as a catalytic site.

The O_2 molecule has one of the strongest chemical bonds (493 kJ/mol). The R_0 exchange involving the cleavage and redistribution of these strong bonds at cryogenic temperatures with a negligible activation energy is a remarkable phenomenon still scantily investigated. This phenomenon seems especially amazing if one takes into consideration a virtually zero value of the reaction enthalpy.

The results of this study leave some unanswered questions. In particular, what is the exact dependence of the R_0 rate on the surface concentration of α-oxygen, which we failed to measure in this work; is the activation provided by O^- anion radicals sufficient to involve O_2 not only in the isotopic exchange, but also in other chemical reactions; whether this remarkable activation is typical only of dioxygen or may be relevant also to other molecules? These questions require further studies.

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Supplementary material

The online version of this article contains additional supplementary material. The material includes more detailed procedures for analysis of experimental results on O_2 isotopic exchange.

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