# Epoxidation of ethylene by anion radicals of α-oxygen on the surface of FeZSM-5 zeolite

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## ARTICLE INFO

## ABSTRACT

The stoichiometric oxidation of ethylene by anion radicals of α-oxygen, $(Fe^{III}-O^{\cdot-})_\alpha$, created on the surface of non-modified and Na-modified FeZSM-5 zeolite was studied in the temperature range from 25 down to −60 °C. Upon extraction, the products were identified using the gas chromatography, gas chromatography–mass spectrometry, and nuclear magnetic resonance. Unlike the oxidation of methane, the reaction $C_2H_4 + O_\alpha$ was shown to proceed without hydrogen abstraction from the ethylene (infrared spectroscopy data). It leads to $O_\alpha$ addition over the double C=C bond yielding the ethylene oxide (EO) primary product. Sodium modification of the zeolite strongly increases the selectivity for EO, which attains 80–84% at the reaction temperature of −60 °C. A much lower selectivity at room temperature relates mainly to a secondary reaction of EO with ethylene leading to butyraldehyde.

High epoxidizing selectivity of α-oxygen is discussed in relation to the mechanism of ethylene epoxidation on silver catalyst.

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## 1. Introduction

The epoxidation of ethylene to ethylene oxide (EO) is one of the largest processes in industrial organic chemistry. The world production of EO exceeds 15 million tons per year [1]. Therefore, it is no wonder that numerous works are devoted to the mechanism of this important reaction, including a significant number of reviews [1–6]. The process is carried out on supported silver catalysts that are promoted with alkali metal additives, providing the selectivity of 90%. All attempts to devise alternative catalytic systems with the selectivity approaching that of silver were totally unsuccessful.

The unique performance of silver is a kind of catalytic mystery. Most authors relate it to some specific form of surface oxygen. Several hypotheses were suggested on the nature of this oxygen, including that of molecular species, which was widely accepted for many years [2,7]. According to this idea, one atom of the adsorbed $O_2$ molecule adds to the C=C bond yielding EO, while the other one is consumed for the process of complete oxidation of ethylene. Such mechanism should provide the upper limit of selectivity equal to 6/7 or 85.7%. However, later this limit was exceeded. This disproved the molecular oxygen idea and gave up the place to

efforts aimed to identify the epoxidizing oxygen among the atomic species.

As a result of extensive studies, two types of atomic oxygen species denoted as electrophilic, $O_{elect}$, and nucleophilic, $O_{nucl}$, were identified on the surface of silver catalysts. Their electronic states are different [4,8–12]. The nucleophilic species is characterized by an O1s binding energy of 528.3 eV, whereas the electrophilic one has the binding energy of 530.4 eV. The species are reported to play different catalytic roles. The oxide-like nucleophilic oxygen is active in attacking the ethylene C—H bond, thus initiating its complete oxidation. Unlike that, electrophilic oxygen shows a disposition to interact with double C=C bonds leading to the formation of EO. This disposition is enhanced by the presence of subsurface (dissolved) oxygen, which draws off electrons from the surface oxygen, thus increasing both its electrophilicity and its selectivity.

At present, a key role of electrophilic oxygen in the ethylene epoxidation is accepted by many authors. However, the lack of direct experimental evidence gives also a room for alternative ideas. Some researchers think that both the epoxidation and complete oxidation of ethylene involve the same type of oxygen. This mechanism assumes that ethylene adsorption leads to the formation of a common oxametallacycle intermediate, in which one C atom of the adsorbed molecule binds to surface oxygen atom, while the other binds to silver atom [13–15]. Depending on the way of decomposition, the intermediate may provide both the selective and unselective routes of the reaction. The state of oxygen in the oxametallacycle is usually not considered.

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Besides $O_{elect}$ and $O_{nucl}$, possible involvement of other oxygen species like anion radicals $O^{\cdot-}$ and $Ag-O-O^{\cdot-}$ is discussed [16–19]. Thus, the nature of epoxidizing oxygen remains a subject of debates and needs further studies.

In this connection, the so-called α-oxygen, $O_\alpha$, which represents anion radicals $O^{\cdot-}$ bound to iron, $(Fe^{III}-O^{\cdot-})_\alpha$, is of significant interest. α-Oxygen is generated by special iron complexes $(Fe^{II})_\alpha$ strongly stabilized in the micropore space of FeZSM-5 zeolite (α-sites). The bivalent iron constituting α-sites is not oxidized by $O_2$, but is readily oxidized by endothermic molecules of $N_2O$ ($\Delta H^0_{f,298}$ = 19.5 kcal/mol) to produce $O_\alpha$ [20–24]. Due to a paired arrangement, α-sites may be considered as binuclear complexes, every iron site of which functions independently [20,22]:

$$\left(Fe^{II}\right)_\alpha + N_2O \rightarrow \left(Fe^{III} - O^{\cdot-}\right)_\alpha + N_2 \qquad (1)$$
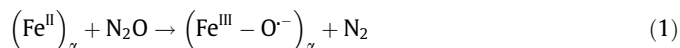
α-Oxygen is thermally stable up to 300 °C, at higher temperature it recombines and desorbs into the gas phase as $O_2$. The properties of α-oxygen were studied in many experimental and theoretical works [25–32] and discussed in some reviews [22,33]. Similar to $O^{\cdot-}$ radicals on metal oxides [34,35], α-oxygen has a very high reactivity, which allows it to react with methane at a high rate at −50 °C [36].

Large number of α-sites and, accordingly, high concentration of α-oxygen, $C_{(O\alpha)}$, are a remarkable feature of FeZSM-5 zeolites. The value of $C_{(O\alpha)}$ may reach up to 100 μmol/g [37], which is by three orders of magnitude higher as compared to $O^{\cdot-}$ concentration on the known systems like $MoO_3/SiO_2$, $V_2O_5/SiO_2$, and MgO [34]. This makes it possible to study in detail the chemistry of α-oxygen in relation to various substrates, using in particular extraction of the surface products for their further analysis [37–39]. Thus, room temperature oxidation of methane, ethane, benzene and other hydrocarbons by α-oxygen was shown to yield respective hydroxylated products. Other forms of oxygen on the FeZSM-5 surface are inert at this low temperature and exert no effect on the results.

The present work is the first attempt to use α-oxygen for the oxidation of ethylene. Since anion radicals $O^{\cdot-}$ have a pronounced electron affinity [32,40], α-oxygen can be considered as a convenient model of electrophilic oxygen. Ability or inability of α-oxygen to form EO may give new arguments for a long-term discussion on the nature of oxygen that epoxidizes ethylene on silver catalyst.

## 2. Experimental

### 2.1. Materials

A part of experiments was carried out with a FeZSM-5 zeolite containing 2.0 wt.% Fe, which is similar to the zeolite employed in recent studies of the reaction $CH_4 + O_\alpha$ [37,41]. A sample was synthesized by introducing iron into initial HZSM-5 zeolite (Si/Al = 11.5, $C_{Na}$ < 0.04 wt.%) by incipient wetness impregnation with a $FeCl_3$ solution. To provide an increased concentration of α-sites, after heating at 550 °C in air, the sample was activated by calcination in vacuum at 900 °C.

The major part of experiments was performed with the modified Na-FeZSM-5 sample. To introduce sodium (0.2 wt.% Na), the activated FeZSM-5 zeolite was subjected to the ion exchange using a $NaNO_3$ solution followed by drying and heating in vacuum at 550 °C.

Texture parameters of the activated FeZSM-5 sample tested by the low-temperature $N_2$ adsorption are typical of the ZSM-5 structure: The micropore and total pore volumes are 0.150 and 0.210 $cm^3$/g, respectively, and the total surface area is 350 $m^2$/g. The introduction of Na caused only minor changes in the parameters. High crystallinity of the samples and the absence of foreign phases are evidenced by the X-ray diffraction.

High purity nitrous oxide (medical quality) and ethylene (polymerization quality) were used in the work. In some experiments, EO, acetaldehyde (AA), and butyraldehyde (BA) purchased from Aldrich were employed.

### 2.2. Experiments in a vacuum setup

The deposition of α-oxygen, its reaction with ethylene, and the temperature-programmed desorption (TPD) of $O_\alpha$ were carried out in a static vacuum setup ($10^{-7}$ Torr) described in detail elsewhere [42]. The setup was equipped with absolute pressure gauges (0.002–100 Torr) and a mass spectrometer PPT Residual Gas Analyzer (MKS Instruments). A zeolite sample (0.1 g) was loaded into a quartz microreactor (6.5 $cm^3$), which can easily be isolated from the rest reaction volume of 720 $cm^3$ capacity. The sample was subjected to a standard pretreatment that included alternate heating at 550 °C in vacuum and in oxygen at 2 Torr pressure. Such pretreatment provides careful removal of water and organic impurities from the surface as well as ensures complete $O_2$ oxidation of the iron not constituting α-sites. The latter point is essential for reliable measurement of the α-site concentration, which was determined from the maximum amount of α-oxygen deposited on the sample by reaction (1).

The $O_\alpha$ deposition was performed by $N_2O$ decomposition at 230 °C (15 min) with initial pressure 0.6 Torr. Procedures for the measurement of $C_{(O\alpha)}$ are described in [27,42]. In the present work, we used mainly two methods based on (i) the amount of $N_2$ evolved (Eq. (1)) and (ii) the equilibrium isotopic composition of dioxygen at the exchange $^{18}O_2/^{16}O_\alpha$. Both methods give close results and are not destructive, so that α-oxygen can be used in further experiments with ethylene.

The concentration of α-sites on the FeZSM-5 sample was $6.0 \times 10^{19}$ sites/g (100 μmol/g) and that on the Na-FeZSM-5 sample was $3.5 \times 10^{19}$ sites/g (58 μmol/g). In TPD experiments, $O_\alpha$ evolves into the gas phase as a single $O_2$ peak (see Fig. S1). For both samples, the amount of dioxygen evolved corresponds to the number of α-sites.

The reaction $C_2H_4 + O_\alpha$ was studied over the temperature range of −60 to +25 °C at different pressures of ethylene ($P_{C2H4}$). Experiments were conducted in the following way. A specified amount of ethylene was admitted into reaction volume at the closed reactor. The time of reactor opening served as the onset of reaction. The reaction time of 3 min was chosen as a standard condition because extension of the time decreases the amount of extracted products due to their secondary transformations. After 3 min, the ethylene was evacuated for 2 min at 25 °C or for 5 min at −20 °C.

### 2.3. Infrared spectra

For recording the infrared (IR) spectra, the zeolite sample was placed in a specially designed IR reactor cell. The cell was made of quartz, which provides a convenient possibility for performing high-temperature treatments of the sample. The cell has a flange for connecting it with the vacuum setup to reproduce conditions of experiments conducted in the microreactor. After experiments, the reactor cell was closed and transferred to the IR spectrometer.

IR spectra were recorded at room temperature on a Shimadzu 8300 Fourier spectrometer in the region of 2200–6000 $cm^{-1}$ at a resolution of 4 $cm^{-1}$. The region of lower frequencies was not informative because of a strong proper IR absorption of quartz. The spectra accumulated from 100 scans were converted from reflection scale to the Kubelka–Munk-F(R) scale, $F(R) = (1 - R)^2/2R$, and normalized to the intensity of absorption band 2260 $cm^{-1}$ (vibrations of the zeolite $Si-O-Si$ fragment).

## 2.4. Product extraction and analysis

In this work, we used an extraction procedure similar to that described for the case of methane oxidation by α-oxygen [41]. To minimize secondary reactions, a brief version of the procedure was used. After termination of the reaction and evacuation of ethylene as described above, the sample was rapidly poured from the reactor to a vial with the extractant. The vial was closed and shaken for 1.5 min and then placed in a centrifuge for 30 s to separate the catalyst. In the absence of catalyst, the composition of extracted products did not change.

For extraction, we used acetonitrile containing 10 vol.% water, which was shown to be an optimal extractant. To identify the extracted products, several techniques were used. The gas chromatographic (GC) analysis was performed with a Kristall 2000 M instrument equipped with an automatic liquid sampler and a capillary column HP Plot U designed for low-boiling oxygen-containing organic substances. The gas chromatography–mass spectrometric (GC–MS) analysis was performed with Agilent Technologies 7000 GC/MS Triple Quad, GC System 7890A equipped with Column HP-5MS. The $^1$H spectra of nuclear magnetic resonance (NMR) were recorded at 400.13 MHz on a Bruker Avance-400 NMR spectrometer. For the calculation of $^1$H chemical shift, the resonance of $CHD_2$ group provided by a $CHD_2CN$ impurity in acetonitrile-$d_3$ was taken equal to 1.94 ppm.

Results of the analysis were used to calculate the composition (selectivity) of extracted products and their total yield with respect to α-oxygen:

$$\text{Yield} = \frac{\text{Amount of products extracted}(\mu mol/g)}{\text{Amount of }\alpha\text{-oxygen deposited}(\mu mol/g)}$$

## 3. Results and discussion

### 3.1. Preliminary experiments

We started the work with the FeZSM-5 sample that was used earlier in the oxidation of methane by α-oxygen [37,41]. The reaction $C_2H_4 + O_\alpha$ was carried out at room temperature and initial ethylene pressure of 1.0 Torr. After opening the microreactor, the adsorption and reaction of ethylene with α-oxygen took place virtually instantaneously with no further change in the pressure. As shown in Table 1, some EO is among the extracted products. However, its fraction is quite low, comprising only 8.0%. The main product is AA comprising 85% of the total product amount. The extract contains also some other unidentified compounds, their sum being equal to ca. 7%. The formation of these compounds also involves α-oxygen. As shown by a blank run (no. 2, Table 1), these compounds do not form in the absence of $O_\alpha$. Note that the yield of oxidation products on the FeZSM-5 sample comprises only 3.5% of the deposited amount of α-oxygen.

The availability of even small amount of EO is quite a meaningful result. It indicates that α-oxygen is capable of adding to the double C=C bond of ethylene. The minor amount of EO and low total yield of products in experiment no. 1 may be explained by

secondary transformations taking place on acid sites available on the FeZSM-5 surface [38]. Besides the well known isomerization of EO to AA [43], the transformation may include also the formation of polymeric compounds that are not extracted from the surface. To suppress the secondary transformations, we modified the FeZSM-5 zeolite by sodium. Indeed, the resulting Na-FeZSM-5 sample shows a much better performance (exp. no. 3): selectivity for EO increased to 19%, while selectivity for AA decreased to 4.5%. The formation of a new compound, i.e. BA, with the selectivity of 71% was observed. Strong increase in the total yield of products (from 3.5% to 72%) also took place.

Taking into account these favorable alterations, all further experiments were carried out with the Na-FeZSM-5 sample.

### 3.2. The formation of BA

So, the data listed in Table 1 allow assuming that EO is the only primary product that resulted from the interaction of ethylene with α-oxygen:

$$C_2H_4 + (O)_\alpha \rightarrow (C_2H_4O)_\alpha \tag{2}$$

Unlike the isomerization to AA, a secondary transformation of EO to BA is a rather unusual reaction, which needs special consideration. Supposedly, this reaction may proceed according to one of the following equations:

$$C_2H_4O_{ads.} + C_2H_4 \rightarrow C_3H_7CHO_{ads.} \tag{3}$$

$$CH_3CHO_{ads.} + C_2H_4 \rightarrow C_3H_7CHO_{ads.} \tag{4}$$
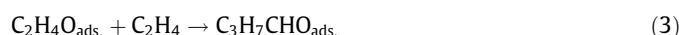
If this assumption is true, a rise in the ethylene pressure should increase the selectivity for BA and decrease that for EO or AA.

To verify this point, we carried out a series of experiments with broad variation in the initial pressure of ethylene (0.25–10 Torr). The results are presented in Table 2 and Fig. 1. One can see that a rise in $P_{C2H4}$ is actually accompanied by a significant increase in the selectivity for BA, from 38% to 90%. However, the results do not allow one to conclude which substrate, i.e. EO or AA, reacts with the ethylene. Indeed, as the ethylene pressure increases, selectivity for both EO and AA decreases: in the first case from 42% to 1.5% and in the second case from 17% to 3.0%.

To resolve this alternative, we conducted additional experiments using commercial EO and AA. The following procedure was employed. After the standard pretreatment, the EO or AA (0.6 Torr) was fed to the Na-FeZSM-5 to be promptly and completely adsorbed by the sample. Then, 1.0 Torr of ethylene was added. After 3 min, the ethylene was evacuated. The results are listed in Table 3. One can see that BA forms only in the case of EO + $C_2H_4$ (exp. no. 1). In the case of either AA + $C_2H_4$ (exp. no. 2) or EO without $C_2H_4$ (exp. no. 3), BA is absent. So, we may conclude that BA forms only by reaction (3), which, to our knowledge, was not reported previously in the literature.

It is noteworthy that in all experiments of Table 3, the total yield of extracted products based on the amount of substrate preadsorbed is less than 100%. This indicates the occurrence of side transformations providing compounds that are strongly bound to

**Table 1**
Reaction $C_2H_4 + O_\alpha$ on the surface of FeZSM-5 and Na-FeZSM-5 (0.1 g; 25 °C).

| Exp. no. | Sample | $C_{(O\alpha)}$, μmol/g | $P_{C2H4}$, Torr | Distribution of products extracted, mol.% | | | | Total yield of products based on $O_\alpha$, % |
|---|---|---|---|---|---|---|---|---|
| | | | | EO | AA | BA | Others | |
| 1 | FeZSM-5 | 100 | 1.0 | 8.0 | 85 | 0.0 | 7.0 | 3.5 |
| 2 | FeZSM-5 | None (blank run) | 1.0 | 0.0 | 0.0 | 0.0 | Traces | None |
| 3 | Na-FeZSM-5 | 58 | 1.0 | 19 | 4.5 | 71 | 5.5 | 72 |
| 4 | Na-FeZSM-5 | None (blank run) | 1.0 | 0.0 | 0.0 | 0.0 | Traces | None |

**Table 2**
Effect of ethylene pressure on the selectivity of $C_2H_4 + O_\alpha$ reaction on Na-FeZSM-5 (0.1 g; 58 μmol $O_\alpha$/g; 25 °C).

| Exp. no. | $P_{C2H4}$, Torr | Distribution of products extracted, mol.% | | | | Total yield of products based on $O_\alpha$,% |
|---|---|---|---|---|---|---|
| | | EO | AA | BA | Others | |
| 1 | 0.25 | 42 | 17 | 38 | 3.0 | 24 |
| 2 | 0.5 | 24 | 6.5 | 66 | 3.5 | 45 |
| 3 | 0.5 | 22 | 6.0 | 68 | 4.0 | 48 |
| 4 | 1.0 | 19 | 4.5 | 71 | 5.5 | 74 |
| 5 | 3.0 | 4.0 | 3.5 | 85 | 7.5 | 73 |
| 6 | 10 | 1.5 | 3.0 | 90 | 5.5 | 73 |
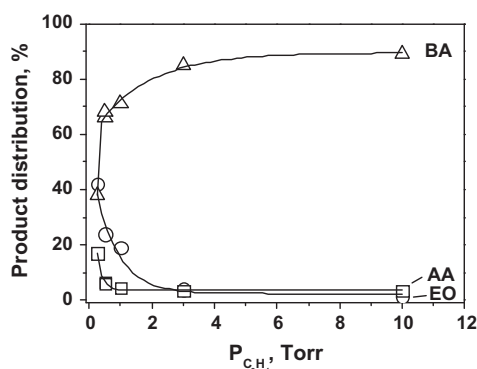


**Fig. 1.** Effect of ethylene pressure on the distribution of products extracted from the surface of Na-FeZSM-5.

the surface. EO enters such transformations most readily. In this case (exp. no. 3), only 11% of the preadsorbed EO is recovered. In the case of AA, the yield is much higher, comprising 78% (exp. no. 2).

These results shed light on the reason for substantial increase in the total yield of products (from 24% to 73%) observed in experiments nos. 1–6 of Table 2. It relates to the growing transformation of EO into a more stable BA.

### 3.3. Low-temperature experiments

In order to increase the reaction selectivity on the surface of Na-FeZSM-5, we tried to find the experimental conditions that would minimize secondary transformations of EO. It is assumed that in the case of silver, the activation energy of epoxidation reaction is lower than that of consecutive side reactions. Taking into account a very high reactivity of α-oxygen, one may think that this assumption holds true for the case of ethylene epoxidation on the zeolite surface. Having this idea in mind, we conducted a number of experiments in which the temperature at all steps (i.e. that of the reaction $C_2H_4 + O_\alpha$; of $C_2H_4$ evacuation; of the sample before its pouring into extractant; and of the extractant itself) was decreased consecutively.

The results are listed in Table 4. In experiment no. 1, all steps were conducted at room temperature, providing only 4.0% of EO in the extraction products. In experiment no. 2, the reaction temperature, evacuation temperature, and temperature of the sample before extraction were decreased to −20 °C. This led to a sharp increase in the EO selectivity, to 35%. In experiment no. 3, the extractant temperature was decreased from 25 to 0 °C, causing further growth of the selectivity to 42%. In experiment no. 4, the reaction temperature was set at −60 °C providing the selectivity of 75%. Finally, before pouring into the extractant, the sample was also cooled to −60 °C, resulting in some additional positive effect on the selectivity, which became 80–84% (exp. nos. 5 and 6).

Note that the increase in selectivity for EO in experiments nos. 1–6 occurs mainly due to suppression of its secondary reaction with ethylene (Eq. (3)). This is evidenced by a decrease in the selectivity for BA from 85% to 12–15%. In all cases, the AA fraction remains insignificant, less than 5%.

Lowering the temperature decreases also the amount of unidentified products from 7.5% to 1.5%, which points out that they also originate from secondary reactions of EO.

**Table 3**
Reactions of preadsorbed EO and AA with ethylene on Na-FeZSM-5 (0.1 g; 25 °C).

| Exp. no. | Reaction condition | | Amount of products extracted, μmol/g | | | | Total yield of products based on the substrate preadsorbed, % |
|---|---|---|---|---|---|---|---|
| | Amount of substrate preadsorbed | Amount of ethylene added | EO | AA | BA | Dioxane | |
| 1 | 0.6 Torr EO (230 μmol/g) | 1.0 Torr (400 μmol/g) | 10 | 10 | 13 | 5 | 17 |
| 2 | 0.6 Torr AA (230 μmol/g) | 1.0 Torr (400 μmol/g) | 0.0 | 180 | 0.0 | 0.0 | 78 |
| 3 | 0.6 Torr EO (230 μmol/g) | none | 11 | 10 | 0.0 | 5 | 11 |

**Table 4**
Effect of temperature on the selectivity of $C_2H_4 + O_\alpha$ reaction on Na-FeZSM-5 (0.1 g; 58 μmol $O_\alpha$/g; 25 °C; 3 Torr ethylene).

| Exp. no. | Reaction temperature, °C | Sample temperature at $C_2H_4$ evacuation, °C | Sample temperature before extraction, °C | Temperature of extractant, °C | Distribution of products extracted, mol.% | | | | Total yield of products based on $O_\alpha$, % |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | EO | AA | BA | Others | |
| 1 | 25 | 25 | 25 | 25 | 4.0 | 3.5 | 85 | 7.5 | 73 |
| 2 | −20 | −20 | −20 | 25 | 35 | 4.5 | 53 | 7.0 | 39 |
| 3 | −20 | −20 | −20 | 0.0 | 42 | 4.0 | 48 | 6.0 | 42 |
| 4 | −60 | −20 | −20 | 0.0 | 75 | 3.0 | 19 | 3.0 | 35 |
| 5 | −60 | −20 | −60 | 0.0 | 80 | 3.0 | 15 | 2.0 | 38 |
| 6 | −60 | −20 | −60 | 0.0 | 84 | 2.5 | 12 | 1.5 | 41 |

### 3.4. Identification of products by GC–MS and $^1$H NMR

A special attention in the work was paid to identification of the reaction products, in particular EO and BA. To this end, in addition to GC analysis, we also used the GC–MS and $^1$H NMR.

In order to identify EO by the GC–MS, we reproduced twice the experiment no. 6 of Table 4. The high concentration of EO provided under these conditions is quite sufficient for its reliable identification. The first experiment was carried out with a natural isotopic form of α-oxygen. The resulted product was found to be EO, because its MS signals were similar to the corresponding signals from the database (Fig. S2a). The second experiment was conducted with the isotopically labeled α-oxygen. In this case, prior to the reaction with C$_2$H$_4$, α-oxygen $^{16}$O$_α$ was replaced by $^{18}$O$_α$ (98%) via the isotopic exchange at 100 °C [27]:

$$\left(^{16}O\right)_α + \,^{18}O_2 \rightarrow \left(^{18}O\right)_α + \,^{16}O^{18}O \qquad (5)$$
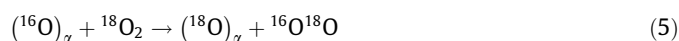
The replacement shifted the corresponding MS signals of the product by two m/e units. Such shift evidences that the EO molecules comprise exactly the α-oxygen.

The GC–MS identification of BA was conducted with the extract obtained by experiment no. 6 of Table 2, which provided a 90% selectivity of the product. The signals of the BA obtained were identical to the corresponding signals from the database (Fig. S2b).

To prepare reaction products for the NMR analysis, we reproduced the experiments no. 6 of Table 4 and no. 6 of Table 2. The first experiment provides high selectivity for EO (84%), and the second one – high selectivity for BA (90%). In both experiments, the extractant was represented by a mixture of deuterated acetonitrile and water (CD$_3$CN + D$_2$O). The $^1$H NMR spectra (Figs. S3a-S3c) testify safely that the resulting products are identical with EO and BA.

### 3.5. The reaction mechanism

The reaction of ethylene with anion radicals O$^{·-}$ has been studied in several works. These radicals can reside both within clusters of the gas-phase metal oxides that are investigated by the ion beam mass spectrometry [44,45] and on the surface of bulk metal oxides investigated by the electron paramagnetic resonance (EPR) [34,46]. In all cases, O$^{·-}$ radicals were shown to be highly reactive toward ethylene. Quite a detailed description of the reaction mechanism was made in Ref. [47] reporting results of the EPR study with MoO$_3$/SiO$_2$ sample. The adsorption of ethylene on MoO$_3$/SiO$_2$ at the liquid nitrogen temperature does not lead to its interaction with O$^{·-}$. The reaction starts at rising temperature to −163 °C, which is indicated by disappearance of the EPR signal from O$^{·-}$. Instead, there appear some signals attributed to new π- or σ-complexes (C$_2$H$_4$O)$^{·-}$, having also the radical nature. Further elevation of the

temperature results in decomposition of these complexes via the hydrogen abstraction step to produce OH groups and adsorbed vinyl radicals:

$$(C_2H_4O)^{·-} \rightarrow \,^·CH = CH_2 + OH^- \qquad (6)$$

Close results were obtained with magnesium oxide [48]. In this case, the contact with O$^{·-}$ immediately causes the hydrogen abstraction from ethylene, without intermediate formation of (C$_2$H$_4$O)$^{·-}$ complexes:

$$H_2C = CH_2O^{·-} \rightarrow \,^·CH = CH_2 + OH^- \qquad (7)$$

Valuable data on the mechanism of surface reactions can be obtained by IR spectroscopy. The application of this very informative method is frequently limited by its not very high sensitivity. In our case, the high concentration of α-oxygen and hence that of the oxidized surface compounds make the application quite convenient.

The IR spectrum of Na-FeZSM-5 after the C$_2$H$_4$ + O$_α$ reaction is displayed in Fig. 2 (spectrum 1). The reaction was conducted at −60 °C with subsequent evacuation of ethylene at −20 °C (like in exp. no. 4 of Table 4). One can see that in the region of CH vibrations (2700–3200 cm$^{-1}$), the reaction produces a complicated spectrum, which testifies to the presence of various surface groups. For interpreting the spectrum, we conducted additional experiments on the adsorption of EO, BA, and ethylene. (The adsorption conditions are given in Fig. S4). The collected spectra are also depicted in Fig. 2 (spectra 2–4). Avoiding a detailed assignment, it can be noted that spectrum 1 after the reaction C$_2$H$_4$ + O$_α$ is described satisfactorily by a combination of bands recorded upon adsorption of the indicated substrates.

Fig. 2 shows also the spectra of Na-FeZSM-5 in the region of OH vibrations (3200–4000 cm$^{-1}$), which are of special interest in terms of the reaction mechanism. The spectrum of initial sample (no. 5) has an intense band 3740 cm$^{-1}$ typical of Si—OH silanol groups of the zeolite. In this region, there are usually two additional bands that are assigned to the bridge zeolite groups of Si—OH—Al (3610 cm$^{-1}$) and to the groups residing on extra-lattice aluminum atoms, Al—OH (3675 cm$^{-1}$) [41,43]. However, in our case, due to high-temperature calcination of the FeZSM-5 sample and its modification with sodium, these groups are not distinct. The main result seen from Fig. 2 is that the initial spectrum in the OH region remains virtually unchanged upon various treatments, including the reaction C$_2$H$_4$ + O$_α$. The latter fact is particularly significant. It means that this reaction does not produce hydroxy groups and therefore proceeds without abstraction of hydrogen from the ethylene. This result distinguishes fundamentally the reaction of ethylene with α-oxygen from that of methane. The stoichiometric methane reaction CH$_4$ + O$_α$ on FeZSM-5 runs
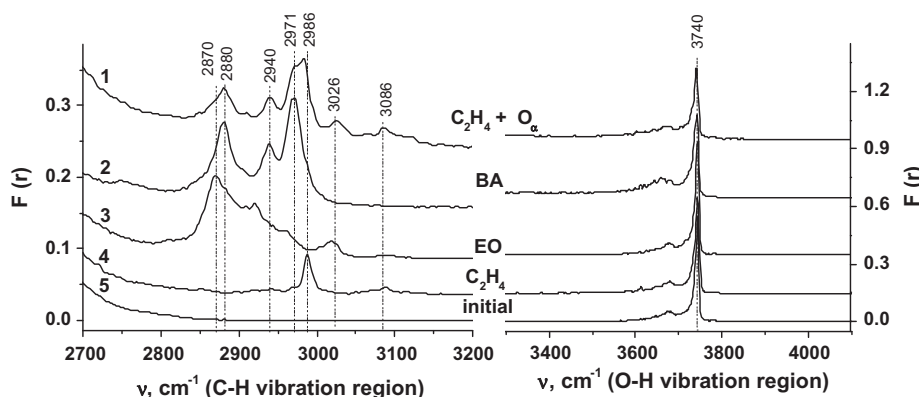


**Fig. 2.** IR spectra of Na-FeZSM-5 after reaction C$_2$H$_4$ + O$_α$ (no. 1) and after adsorption of BA, EO, and ethylene (nos. 2–4). no. 5 is a spectrum of the initial sample.

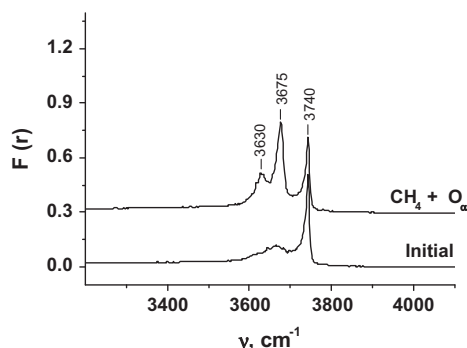**Fig. 3.** IR spectra of Na-FeZSM-5 sample in O—H vibration region before and after $CH_4 + O_\alpha$ reaction.

exactly by the hydrogen abstraction mechanism to produce hydroxy groups that are registered by IR spectroscopy [37,41]. To make sure that this mechanism holds true also for the case of modified zeolite, we carried out a similar experiment with methane on the Na-FeZSM-5 sample. From Fig. 3, one can see that in the region of stretching OH vibrations the reaction $CH_4 + O_\alpha$ leads to an intense band at $3675\ cm^{-1}$ and a less intense one at $3630\ cm^{-1}$. The two types of $(Fe^{III}–OH)_\alpha$ groups may relate with the two types of $\alpha$-sites differing in iron coordination, as shown by Mössbauer data [20]. The assignment of these bands to the $(Fe^{III}–OH)_\alpha$ groups was supported by the isotope shift resulting from the replacement of $^{16}O_\alpha$ by $^{18}O_\alpha$ [33]. Thus, the spectrum in Fig. 3 indicates that the presence of Na does not change the mechanism of $CH_4$ oxidation and does not prevent the observation of $(OH)_\alpha$ groups. Therefore, the absence of such groups in Fig. 2 is safe evidence that the ethylene reaction proceeds without hydrogen abstraction.

The latter result revealed a distinctive feature of $\alpha$-oxygen in comparison with $O^{\cdot-}$ radicals on the oxide systems, i.e. its weaker ability to hydrogen abstraction. Indeed, $O^{\cdot-}$ on metal oxides can abstract hydrogen from both methane and ethylene [34,46,47]. Unlike that, $\alpha$-oxygen can abstract hydrogen from methane but not from ethylene, adding instead to the ethylene C=C bond. It is worth noticing that a C—H binding energy of ethylene is higher than that of methane (111.3 against 104.9 kcal/mol) [49]. The reaction of $\alpha$-oxygen with benzene, which has even a greater binding energy (113.2 kcal/mol), also proceeds without hydrogen abstraction [29,32,38].

Interestingly, the gas-phase anion radicals $O^{\cdot-}$ exhibit an intermediate type of chemistry toward ethylene [50]. The latter radicals can both add to the ethylene double bonds and abstract the hydrogen leading accordingly to EO (58%) and vinyl radicals $H_2C=C^{\cdot-}$ (29%).

## 4. Conclusion

The stoichiometric reaction of ethylene with $\alpha$-oxygen represented by electrophilic species of anion radicals $O^{\cdot-}$ on the surface of FeZSM-5 was studied in the work. The high concentration of $\alpha$-oxygen makes it possible to register the surface products by IR spectroscopy and to extract them from the catalyst for subsequent identification by the GC, GC–MS and $^1H$ NMR techniques. The reaction $C_2H_4 + O_\alpha$ was shown to proceed readily both at room and lower temperatures yielding EO as a primary product. Experiments at $-60\ °C$ with the modified Na-FeZSM-5 sample provided the EO selectivity up to 80–84%.

Among secondary transformations of EO (in addition to isomerization in AA and formation of polymeric non-extractable products), its earlier unknown reaction with ethylene leading to BA was observed. This reaction dominates at room temperature and becomes less important at lower temperatures.

In distinction to $O^{\cdot-}$ radicals on oxide systems, $\alpha$-oxygen has a smaller ability toward hydrogen abstraction. It abstracts the hydrogen from methane ($E_{C–H}$ = 104.9 kcal/mol) but does not abstract from ethylene ($E_{C–H}$ = 111.3 kcal/mol). This feature seems to be the key prerequisite for the addition of $\alpha$-oxygen to the double C=C bond of ethylene.

The results obtained with $\alpha$-oxygen may be useful for getting a better insight into some mechanistic aspects discussed in relation to the ethylene epoxidation on silver catalyst. In particular, the high selectivity of $\alpha$-oxygen can be interpreted as evidence of electrophilic nature of the epoxidizing oxygen on silver.

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