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# Decomposition of nitrous oxide over Fe-ferrierites. Effect of high-temperature pretreatment on the formation of deposited oxygen

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The dehydration of Fe-ferrierites doubled the decomposition of $N_2O$ at 200 °C and corresponding deposition of oxygen. The rehydration resulted in a reversible process. Samples with iron located predominantly in cationic positions (Fe/Al 0.05–0.25) exhibited the $O_{dep}$/Fe ratio of ca. 0.5 and 1 after pretreatment at 450 and 700 °C, respectively.

**KEY WORDS:** Fe-Ferrierite; high-temperature treatment; effect on $N_2O$ decomposition.

## 1. Introduction

There is a general agreement concerning the dominant role of iron in the decomposition of nitrous oxide to nitrogen and dioxygen over zeolites, e.g., [1–5]. The function of Brönsted and/or Lewis acid sites alone in this reaction has been excluded [4]. Since the pioneering work of Panovś group [6], most efforts have been focused on iron in MFI structures. The $N_2O$ decomposition was examined to a substantially lesser extent over other zeolites, e.g., Fe–silicalites, Fe–Bea and Fe-Ferrierite [7–12]. In spite of many sophisticated experimental as well as theoretical methods used, the mechanisms of nitrous oxide decomposition as well as the nature of the active site have not been unambiguously established. Iron active sites were proposed as mono- or bi-nuclear Fe complexes, or as enzyme-like species bonded to one or two Al atoms (see e.g. refs. [13–23]).

The nature of oxygen atoms captured during the decomposition of nitrous oxide, denoted by Panov as $\alpha$-oxygen, has been widely discussed. The fraction of active iron sites participating in oxygen atoms bonding, i.e. the formal $O_{dep}$/Fe ratio, has been found in a surprisingly broad scale, ranging over various zeolites between 0.1 and 1, and even above the value of 1 [16–24]. Different preparation and pretreatment as well as different experimental methods used make the explanation of this broad interval difficult.

The values of $O_{dep}$/Fe ratio can be employed to rationalize the nuclearity of iron complexes:$O_{dep}$/Fe = 0.5 agrees with a binuclear Fe complex bridged by a single deposited oxygen, while $O_{dep}$/Fe = 1 is in line with mononuclear isolated Fe–$O_{dep}$ complex. The $O_{dep}$/Fe ratios can be obtained at low temperatures of the $N_2O$ decomposition, when only $N_2$ is released, and oxygen ($O_{dep}$) remains captured in the zeolite.

Captured oxygens are known to react with many reductants at mild temperature, and thus TPR has become a suitable method for the quantification of $O_{dep}$. The reduction of any iron oxide starts at substantially higher temperature [13, 18, 25, 26]. Determination of captured oxygen also can be realized either by analyzing the amount of nitrogen molecules formed in the $N_2O$ decomposition, or by the desorption of dioxygen at higher temperature. Panov *et al.* [1, 2] evaluated the number of $\alpha$-oxygens using the isotopic exchange (IE) of deposited oxygens for $^{18}O$ of the labeled dioxygen at an ambient temperature; they found a coincidence between the data calculated from IE and the amount of nitrogen generated by the decomposition of nitrous oxide.

It has been found that the activity of Fe–zeolites for the $N_2O$ decomposition is substantially affected by the zeolite pretreatment. Several processes were suggested to explain this effect, including the extraction of iron from its skeletal position, their relocation between various cationic sites, formation of iron oxide clusters and their movement to the external surface (e.g. refs. [4,21]), or a change of the Fe oxidic species to active cationic species by reaction with Brönsted protons [27].

We have previously studied the effect of iron loading in ferrierites on the location of iron ions and on their catalytic activity in NOx related processes[10–12]. We found that iron is located predominantly in cationic positions provided that Fe-ferrierites are prepared by the procedure [28], and the iron loading is less than Fe/Al $\leq 0.2$. These samples exhibited the highest activity in the decomposition of nitrous oxide and oxidation of nitric oxide by dioxygen [10,11]. In the present paper, the study is extended by the effect of high temperature pretreatment of Fe-ferrierites on the $N_2O$ decomposition under mild conditions, i.e. with negligible desorption of dioxygen, and on the amount of deposited oxygens. The amount of deposited oxygens, expressed as $O_{dep}$/Fe ratio, is evaluated using the amount of the

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decomposed nitrous oxide together with a corresponding amount of released dinitrogen, and from TPR of $O_{dep}$. These values are compared with those calculated from the IE of $^{18}O_2$ for the deposited oxygens.

## 2. Experimental

*Fe-ferrierites* (Si/Al = 8.5, further Fe/FER$_n$, index $n$ within 0.026–0.556 stands for the Fe/Al ratio) were prepared by the reaction of $NH_4$–ferrierite with a $FeCl_3$ solution in acetyl acetone [28]. Samples with a Fe/Al ratio below 0.2 contained predominantly cationic iron [10], while some oxidic Fe species were also present above this ratio. Fe/FERs were pretreated *in situ* at 450–700 °C in a vacuum or in a He stream. In some cases, the samples were additionally calcined at the same temperatures in dioxygen, and further evacuated at a temperature below 350 °C. It was found that the amount of iron in cationic positions, as well as its distribution between the individual cationic sites was not substantially changed by the increase of the pretreatment temperature between 450 and 700 °C. This implied from the local zeolite framework perturbation in the IR spectra within the region of 980 and 820 cm$^{-1}$.

The reversibility of the high temperature pretreatment was checked by rehydration of the samples pretreated at 700 °C exposing them to air saturated with water vapors at room temperature (RT) for several days.

*Temperature programmed desorption (TPD)* between RT and 700 °C, with the heating rate of 5 °C/min, was registered by a Balzers QMG 420 quadrupole mass spectrometer using a direct inlet of the gases evolved into the spectrometer (details in [11,12]). Ions with the mass-to-charge ratios 2, 12, 14, 16, 17, 18, 28, 30, 32 (34, 36 after IE), 44, 46 and 48 were detected.

*Decomposition of $N_2O$* was carried out with 50–350 mg of the sample in a quartz reactor (163 cm$^3$) with 500 Pa of nitrous oxide at 200 °C for 2 h. The gas phase was analyzed continuously by introducing a negligible amount into the mass spectrometer via a needle valve.

TPR was measured with a ZETON- ALTAMIRA AMI 200 instrument using a $H_2/Ar$ (9.44% $H_2$) flow of 24 ml/min over 100 mg samples. The temperature increase was 20 °C/min, samples were pretreated either in an Ar or in an $O_2/Ar$ flow for 1–12 h at 450–700 °C, followed by the interaction with $N_2O$ (flow rate of 2 ml/min) at 200 °C for 60 min. TPR was registered after the sample cooling in the $N_2O$ stream to 30 °C and flushing with argon at the same temperature for 25 min. It has been observed that the prolonged time of interaction with $N_2O$ does not modify the TPR results.

*IE* was examined following the decomposition of nitrous oxide, cooling the reactor to RT, and brief evacuation of the sample for 15 min at RT. The labeled dioxygen of 50 Pa (Technabsexport, Russia, 87% of $^{18}O$) was allowed to react with the sample for 1–1.5 h. In some cases, the exchange was extended overnight or the temperature was raised to 150 °C.

## 3. Results

### 3.1. TPD–gases released during the pretreatment of Fe/FERs

Heating of freshly prepared samples with low Fe loading (Fe/Al < 0.15) at temperatures up to 700 °C generates only water vapors, while those with higher iron content release, in addition to water, also a noticeable amount of dioxygen. This is exemplified in figure 1 for Fe/FER$_{0.05}$ (curves 1) and Fe/FER$_{0.56}$ (curves 2). These two samples are also differently colored, the former being white, while the latter is fox-colored. The release of dioxygen and the changing zeolite color started above the Fe/Al ratio of about 0.15–0.2.

### 3.2. Decomposition of $N_2O$ at 200 °C

This reaction over Fe–zeolites proceeds at this temperature with a negligible evolution of dioxygen, which thus remains captured in the sample ($O_{dep}$). A typical reaction course is shown in figure 2 for Fe/FER$_{0.09}$. Section 1 displays the reaction after the sample pretreatment at 450 °C, and Section 2 after the pretreatment at 700 °C. The increase of the decomposition in the latter case is evident. It is obvious that even after the 2-h reaction time the amount of the decomposed $N_2O$ and

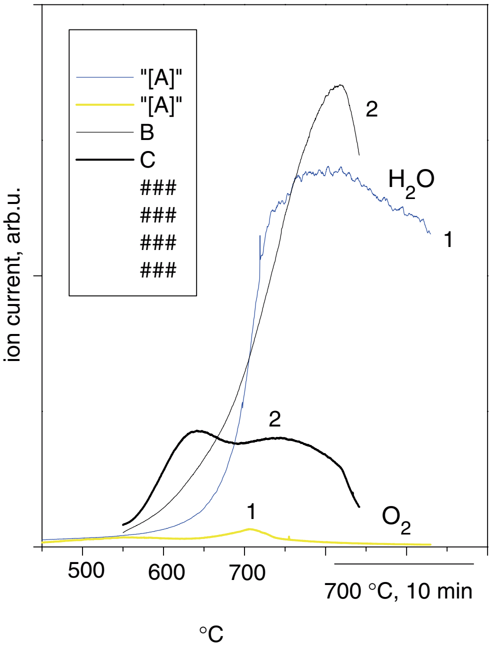

Figure 1. TPD of Fe/FER samples during high-temperature pretreatment. 1, Fe/FER$_{0.055}$; 2, Fe/FER$_{0.556}$.

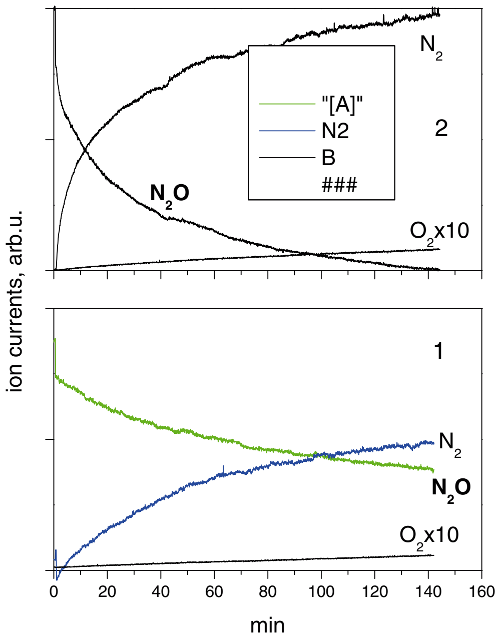

Figure 2. Decomposition of $N_2O$ at 200 °C over Fe/FER$_{0.09}$. 1, after pretreatment at 450 °C; 2, at 700 °C.

evolved $N_2$ did not reached the final values, and accordingly the calculated $O_{dep}$/Fe values could be in both cases slightly higher.

It should be mentioned that the additional calcination in dioxygen after the pretreatment in vacuum has no effect on Fe/FERs with low iron content, and decreases the $N_2O$ decomposition by less than 15% over samples with an Fe/Al ratio above 0.25.

Samples rehydroxylated after the high temperature pretreatment by exposition to the wet air and again treated at 450 °C displayed the activity at about 20% lower than the samples originally treated at 450 °C. This clearly shows that the increase of the $N_2O$ decomposition over Fe–ferrierites due to the high-temperature pretreatment is mostly reversible. The same reversibility was found while analyzing the IR spectra of hydroxyl groups: when the intensity of the structural Brönsted OH groups strongly decreases above 600 °C, Lewis sites are generated instead, and the process is reversible with rehydration [29].

The ratio of nitrous oxide decomposed at 200 °C (equal to the amount of deposited oxygen atoms) to the iron content is shown in figure 3: after the pretreatment at 450 °C in section A as solid squares, after the pretreatment at 700 °C in Section B as open squares. The maximum $O_{dep}$/Fe values were reached over samples with Fe/Al ratio of around 0.05 for both pretreatment temperatures. The $O_{dep}$/Fe value was close to 0.5 after pretreatment at 450 °C and between 0.8 and 1 after the high-temperature treatment. These values appeared for the most active samples (Fe/Al $\leq 0.05$), however, all samples exhibited an increased decomposition activity after the pretreatment at 700 °C.

## 3.3. TPR

The typical TPR spectra are exemplified in figure 4 by Fe/FER$_{0.05}$ pretreated at 450 °C (1) and 700 °C (2), both after the exposure to nitrous oxide at 200 °C. The reduction peak with $T_{max}$ of about 250 °C is typical for the reduction of the labile oxygen captured during the $N_2O$ decomposition and is missing over Fe/FERs with low iron loading pretreated only in oxygen (3). That approximate twofold increase of dihydrogen consumed with the sample pretreated at high temperature is evident. TPD of dioxygen after the $N_2O$ decomposition is in line with the TPR results (see the insert in figure 1, curves 1–3).

The $O_{dep}$/Fe ratios calculated from the amount of consumed hydrogen molecules during the TPR experiments over Fe/FERs after the $N_2O$ decomposition are included in figure 3 for the samples pretreated at 450 and 700 °C. It its obvious that the trends as well as the actual $O_{dep}$/Fe values derived from the TPR experiments are in good agreement with the values obtained from the $N_2O$ decomposition.

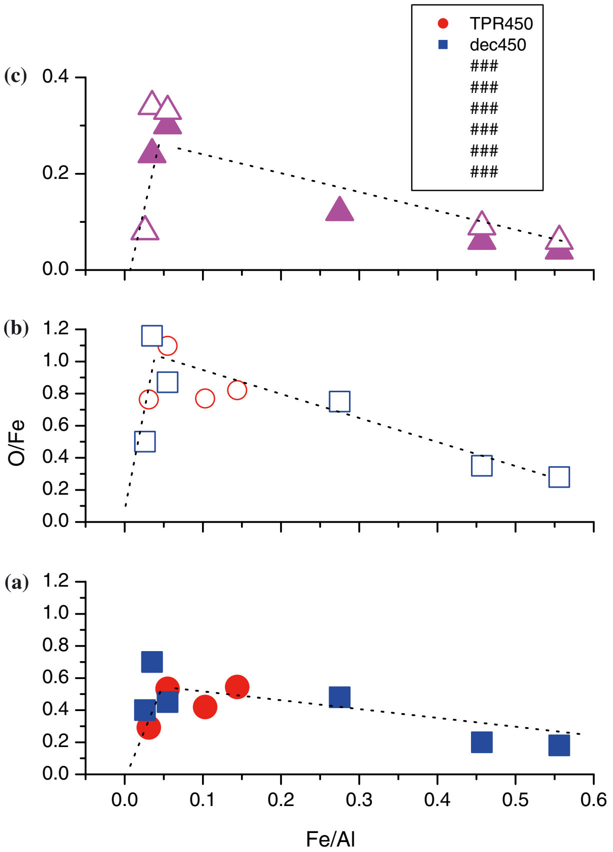

Figure 3. $N_2O$ decomposed at 200 °C over samples with various Fe/Al ratios. Data for captured oxygens are related to iron content. a, pretreatment at 450 °C, solid squares for $N_2O$ decomposition (= $O_{dep}$), solid circles for dihydrogen consumption in reduction of $O_{dep}$; b, pretreatment at 700 °C, open squares for $N_2O$ decomposition, open circles for dihydrogen consumption; c, oxygen exchange at RT with deposited oxygens, solid triangles for samples pretreated at 450 °C, open triangles at 700 °C.

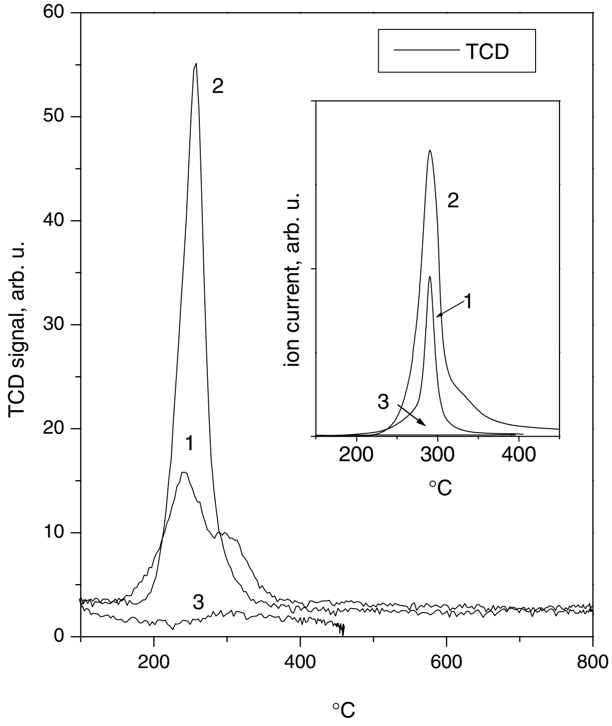

Figure 4. TPR of deposited oxygens and TPD of dioxygen after $N_2O$ decomposition at 200 °C over $Fe/FER_{0.055}$. Pretreatment: at 450 °C (1), at 700 °C (2). TPR of the sample pretreated at 450 °C prior to the treatment in $N_2O$ (3). Insert: TPD of dioxygen, pretreatment: at 450 °C (1), at 700 °C (2). TPD of the sample pretreated at 450 °C prior to the treatment in $N_2O$ (3).

### 3.4. IE at room temperature after the nitrous oxide decomposition

A typical time plot of the decrease of $^{18}O$ concentration is depicted in figure 5a for $Fe/FER_{0.09}$ pretreated at 450 °C (curve 1) and 700 °C (curve 2). The highest IE extent (figure 3c) occurs at the same Fe/Al ratio as those of $N_2O$ decomposition and TPR, but the IE data differ in two basic respects: (i) the $O_{ex}/Fe$ values ($O_{ex}$ stand for the exchanged O atoms) are systematically lower than those of $O_{dep}/Fe$, so that the part of deposited oxygens participating in IE presents only about 30% of captured oxygens, and (ii) the increase of the $O_{ex}/Fe$ values due to high temperature heating is much lower (only about 10–15%) than of $O_{dep}/Fe$.

Moreover, the detailed analysis of the IE data provides evidence for the deviation of the IE process from the first order-law kinetics and points thus to the heterogeneity of the exchangeable oxygen atoms (see figure 5b). The deviation from the first-order law kinetics was not reported in our previous papers [11,12], but it is evident from figure 5b and agrees with Jiaś results [18]. However, the heterogeneity seems to be of a more complex nature and cannot be assigned to only two oxygen pools as suggested for Fe/MFI [18].

## 4. Discussion

The experimental data show that Fe/FERs with low iron content provide a suitable model for the evaluation

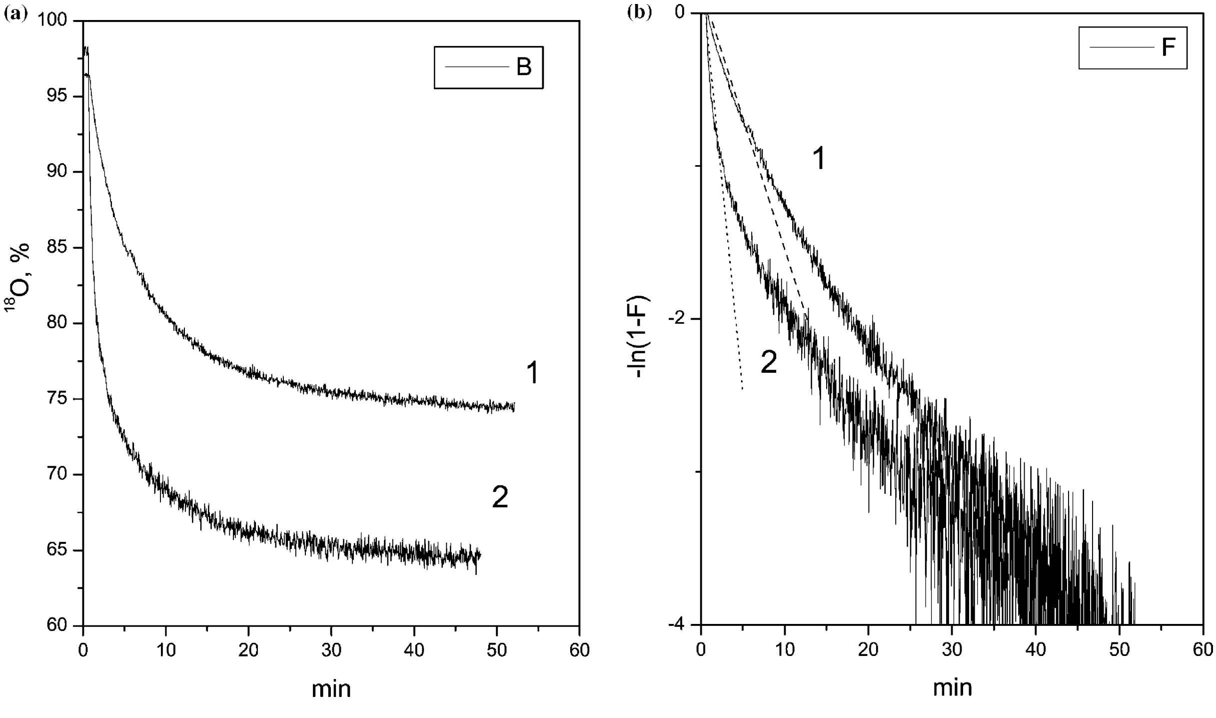

Figure 5. IE of deposited oxygen on $Fe/FER_{0.09}$ at RT. (a). Time plot of the decrease of $^{18}O$ concentration, 1 and 2 after sample pretreatment at 450 and 700 °C, respectively. (b). The ln dependence of IE, $F = (c_0\text{-}c_t)/(c_{00}\text{-}0.002)$, $c_0$, $c_t$, $c_{00}$ and 0.002 are the $^{18}O$ concentrations in time 0, $t$, at equilibrium, and of natural isotope concentration, respectively, with pretreatment at 450 °C (1), at 700 °C (2).

of the stoichiometry of Fe–O species. Fe cations are located predominantly in cationic positions ($\alpha$, $\beta$, and $\gamma$) [10]. This is supported by the Mössbauer spectra and NO adsorption [30], and by the presented results–the $O_2$ release only from colored samples with Fe/Al $\geq 0.2$ and not from white samples below this Fe/Al ratio. Therefore, this discussion will be focused on Fe/FERs with low iron content. The $O_{dep}$/Fe ratio of 0.5 in Fe/FERs after low-temperature pretreatment agrees with the commonly suggested Fe–O–Fe model. The only change in the high-temperature pretreatment consists in an extensive dehydroxylation accompanied by the formation of Lewis sites [29]. No relocation of iron cations, whether surface enrichment or release of dioxygen were found. The amount of oxidic iron species was too low to react noticeably with protons to new cationic species as reported in ref. [27]. The $O_{dep}$/Fe ratio of 1, formally corresponding to mononuclear Fe–O species, can be realized assuming that the dehydroxylation leads to local irregularities of the Si–O–Al framework, where about 20% of the Al atoms participate in bonding iron cations in (Al–O–Si) Fe units, while most of the remaining Al atoms form Lewis acid sites. Thus a high density of cleaved Si–O–Al bonds occurs. It is not yet clear whether the density of the defect sites affects the $O_{dep}$//Fe ratio or whether there is a cooperative effect of the framework defects with cationic iron. The importance of lattice aluminum removal for the generation of active sites in Fe-ZSM-5 was reported e.g., in ref. [30].

The experimental fact that only a part of the deposited oxygens participates in the isotopic exchange with $^{18}O_2$ and that the IE kinetics does not obey the first-order law, while all the oxygen atoms are reduced in a single TPR peak, provides arguments for the heterogeneity and complex nature of the deposited oxygen, and indirectly also of the adsorption sites. Thus the captured oxygen atoms could be described as a highly heterogeneous pool of species of varying activity. The difference in the IE and TPR cannot be assigned to the higher temperature of TPR (250°C versus RT), as carbon monoxide completely reduces the oxygens also at RT (Z. Sobalík *et al.*, in preparation).

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