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Role of zeolitic oxygens during the decomposition of $^{15}N_2{}^{18}O$ over Fe-ferrierite

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Isotopic species of dioxygen released during the decomposition of $^{15}N_2{}^{18}O$ over Fe-ferrierite show that the zeolite oxygens participate in the reaction. While Fe-ferrierite alone does not exchange its oxygens with $^{18}O_2$ below 400 °C, this exchange is very rapid in the mixture of $^{18}O_2 + N_2O$. The amount of participating zeolite oxygen (ca. 1–6 per iron atom) is practically the same in the latter case as in the decomposition of $^{15}N_2{}^{18}O$. The time dependence of individual dioxygen isotope species released during the $^{15}N_2{}^{18}O$ decomposition points to the primary release of $^{18}O_2$ which is very rapidly exchanged for the zeolite oxygen by a single-step mechanism.

KEY WORDS: Fe-ferrierite; decomposition of $^{15}N_2{}^{18}O$; participation of zeolite oxygens.

1. Introduction

The involvement of oxygens from Fe-Y, Fe-mordenite and Fe-ZSM-5 during the decomposition of nitrous oxide above 350 °C was reported by Hall and co-workers using either ^{18}O exchanged zeolite or ^{18}O labeled N_2O [1–3]. These authors assume that ca. 10% of all zeolitic oxygens can participate in the reaction which is enabled by their high mobility; the desorption of dioxygen can proceed from sites not identical with those on which the oxygen from nitrous oxide was captured. Similarly, the participation of Fe-ferrierite oxygens was reported using the desorption of dioxygen after the decomposition of N_2O and subsequent exchange of captured oxygen for $^{18}O_2$ at ambient temperature [4,5]. Pirngruber enriched Fe-ZSM-5 by the exchange with $^{18}O_2$ and analyzed the isotopic composition of dioxygen formed during the decomposition of nitrous oxide. He assumes an equilibrated "oxygen pool" of ca. one zeolite oxygen per Fe atom with low reactivity of these oxygens [6]. The present paper concerns the decomposition of ^{18}O labeled nitrous oxide on Fe-ferrierite and is focused on the route of the involvement of zeolitic oxygens into the reaction products.

2. Experimental

Fe-ferrierite further Fe/FER (Si/Al 8.5; 0.55 wt% of Fe; Fe/Al 0.055) was prepared according to patent [7]. Forty to 200 mg of the sample was placed in a quartz reactor (reaction volume 165 mL) and pretreated *in situ* at 450 °C in vacuum, followed by treatment in oxygen (2 kPa), and cooled to reaction temperature in vacuum.

Nitrous oxide $^{15}N_2{}^{18}O$ (supplied by Medical Isotopes Inc., USA, 99 atom%) was allowed to react with Fe/FER at 280 °C (in some cases at 300, 350 and 400 °C) under the pressure of 120–1500 Pa. The simultaneous reaction of unlabeled nitrous oxide mixed with $^{18}O_2$ (Technabsexport, Russia, 87 atom%) was also measured.

Temperature programmed desorption (TPD, 5 °C/min) of surface species formed during the reaction was also checked.

Analysis of the gas phase was carried out using a QMG 420 Balzers quadrupole mass spectrometer. A negligible part of the reaction mixture during the reaction was introduced into the mass spectrometer using a needle valve, while the gases released during TPD were led directly into the vacuum system of the mass spectrometer.

3. Results

The amount of zeolitic oxygens taking part in the decomposition of N_2O depends, besides the reaction temperature, on the ratio of ^{18}O in the gas phase and ^{16}O in the zeolite. This ratio is designated as R. Figure 1a and b depict the time dependence of the individual dioxygen isotope species in the left-hand side and the ^{18}O concentration in the right-hand side of the figure. It can be seen that the differences in isotope dioxygen species increase with increasing R – at the lowest R value the amount of the ion 34 ($^{18}O^{16}O$) predominates over the ion 32 ($^{16}O_2$) and over the ion 36 ($^{18}O_2$). The fraction of the latter ion increases with increasing R, and is the highest for $R \approx 5$. However, in all cases ion 36 is present at the very beginning of the decomposition.

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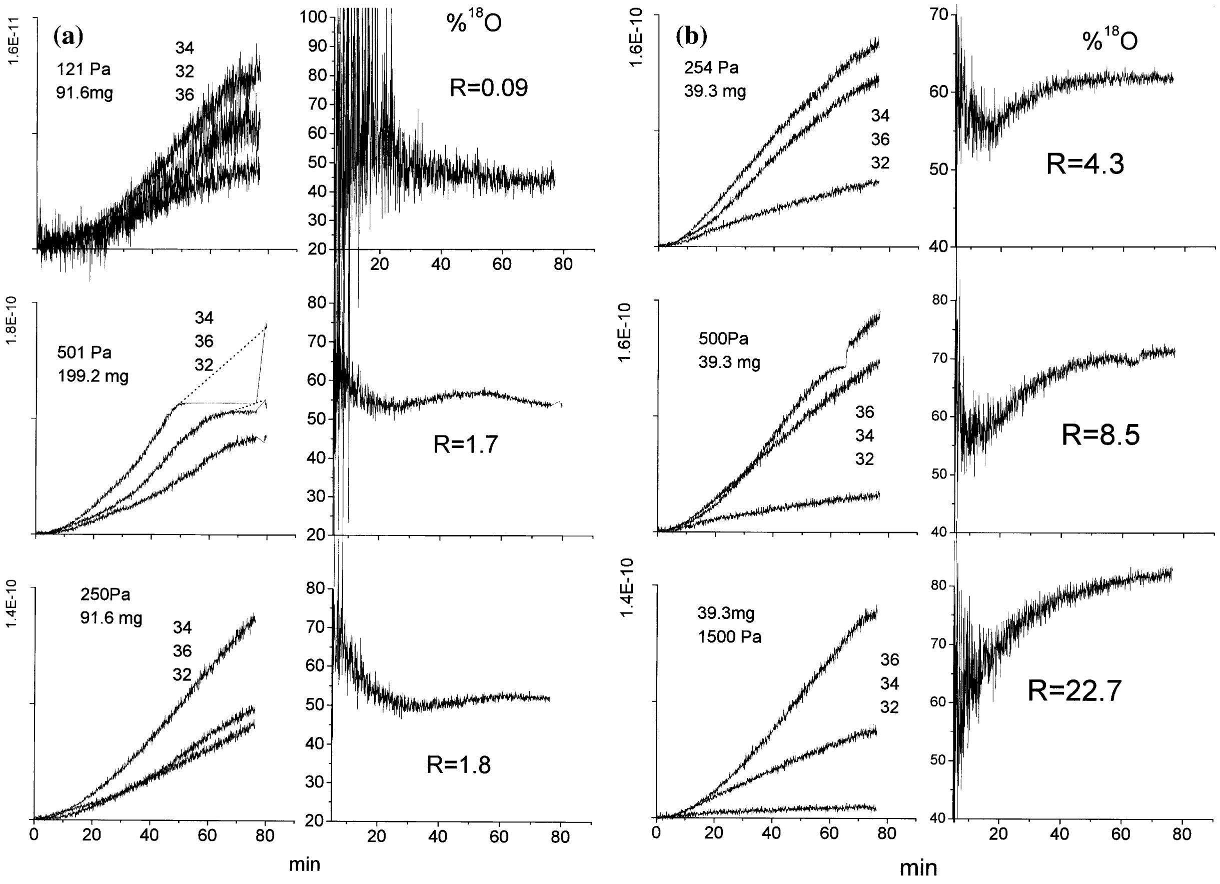


Figure 1. Isotope composition of oxygen during the decomposition of $^{15}N_2{}^{18}O$ at 280 °C over Fe/FER. M/e 32, 34 and 36 stand for molecular ions of $^{16}O_2$, $^{16}O^{18}O$ and $^{18}O_2$, respectively. The ratio of the number of oxygen atoms in nitrous oxide to the number of iron atoms in Fe/FER is denoted as R. The pressure of nitrous oxide and the sample weight are given in the figure. (a) For R 0.09, 1.7 and 1.8. (b) For R 4.3, 8.5 and 22.7.

The ^{18}O concentration reaches a constant value (increasing with increasing R) after a relatively short time. The N_2O decomposition in the same time interval corresponds to ca. 60% of the value achieved in 80 min. The number of oxygens from Fe/FER (m) was calculated using the number of ^{18}O from decomposed N_2O (N, initial concentration of ^{18}O is $c_0 = 100\%$) and ^{18}O concentration in the minimum (c_{00}): $m = (100 - c_{00}) \times N / c_{00}$. The same was done at the end of the reaction, with N equal to all decomposed N_2O and c_{00} to the final ^{18}O concentration. The average value of Ozeol per Fe in the minimum of ^{18}O – time plot was 0.6 ± 0.2 and at the end 2 ± 0.3. When the decomposition of $^{15}N_2{}^{18}O$ was carried out above 300 °C, the number of zeolite oxygen per iron atom increased to the value between 4–6.

The dioxygen isotope species are rapidly equilibrated ($[^{18}O^{16}O]^2/[^{16}O_2]^*[^{18}O_2] = 4$). This is exemplified in figure 2 for the case with $R = 4.3$: section a illustrates the decomposition of nitrous oxide, section b and c are repeated from figure 1b, section d shows the equilibration. The ratio of released dinitrogen to the sum of dioxygen species is close to the value of 12, which means that the remaining oxygen is captured in the zeolite (similar fractions of $^{18}O_2$, $^{16}O^{18}O$ and $^{16}O_2$ appeared above 250 °C when the amount of captured oxygens was almost negligible). The final ^{18}O concentration in the gas phase is close to 61%. The isotopic composition of dioxygen and NO_x species released during TPD from this sample can be seen in figure 3. The amount of ^{18}O in all TPD products is somewhat lower than that during the reaction: in dioxygen and nitrogen dioxide is of about 45–50%, in nitric oxide even lower (of about 30%). However, the latter value is approximate, as the amount of NO is low and the fraction of NO includes several calculation steps.

^{18}O labeled dioxygen does not undergo the isotopic exchange for oxygens of Fe/FER alone at 280 °C (and only in a very low extent above 350 °C). However, in simultaneous reaction with nitrous oxide at 280 °C the exchange proceeds readily, as is displayed in figure 4A: section a shows a very similar decomposition of unlabeled nitrous oxide as that of $^{15}N_2{}^{18}O$ in figure 2 (it is well known that the presence of dioxygen does not affect the rate of the N_2O decomposition), section b the individual dioxygen isotope species (the amount $^{16}O_2$ is higher by dioxygen released during the reaction, i.e., by the fraction which does not remain captured in the zeolite), section c the decrease of atomic ^{18}O concentration, and section d the equilibration Q and the 36/34 ratio (molecular ion 36 for $^{18}O_2$, 34 for $^{18}O^{16}O$). The

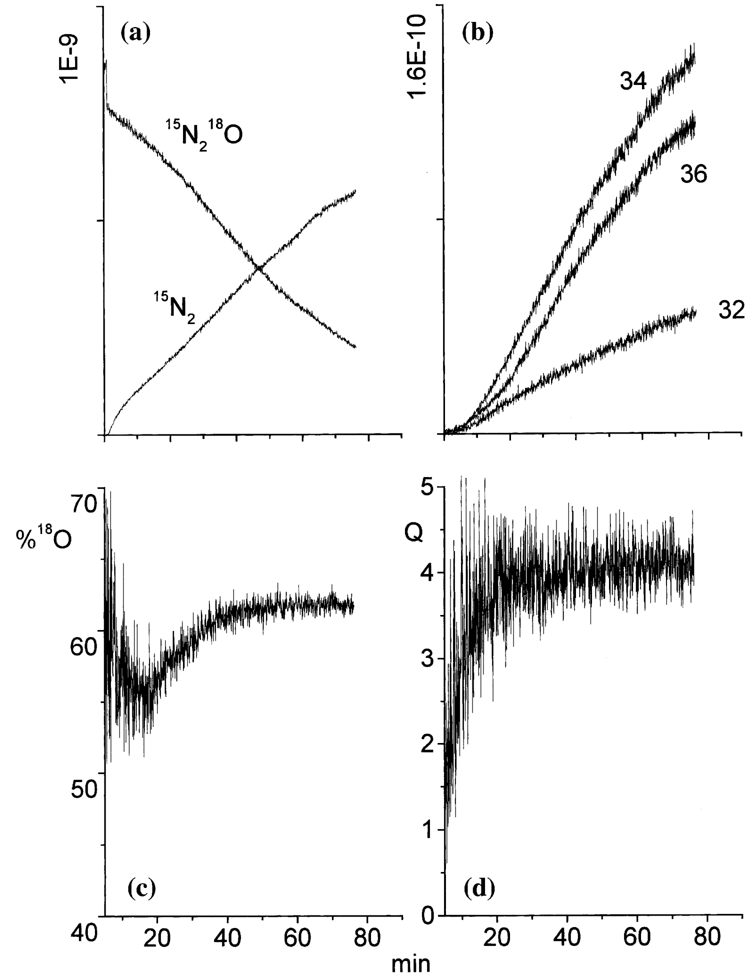


Figure 2. Decomposition of $^{15}N_2{}^{18}O$ at 280 °C over Fe/FER for $R = 4.3$ (a) decrease of $^{15}N_2{}^{18}O$ and increase of $^{15}N_2$ in time, (b) corresponding molecular ions of dioxygen, (c) atomic concentration of ^{18}O, b and c from figure 1b, (d) equilibration Q in dioxygen isotope species, equilibrium value of $[34]^2/[32]^*[36] = 4$.

time dependence of logarithmic ^{18}O concentration is displayed in figure 4B; it follows that all exchanging oxygen atoms behave in the same way opposite to the isotopic exchange of captured oxygen at room temperature which exhibit some heterogeneity [8]. TPD following the reaction of $N_2O + {}^{18}O_2$ can be seen in figure 4C. Again, the ^{18}O concentration in dioxygen and in NO_x is by ca. 10% lower than at the end of the reaction.

4. Discussion

The individual O_2 isotope species during the decomposition of $^{15}N_2$ ^{18}O show that the desorption of dioxygen from Fe/FER does not proceed exclusively via the interaction of two ^{18}O atoms – either between two oxygens at the surface or between one at the surface and one from impinging nitrous oxide: if this happened, the desorbed dioxygen should be constantly only $^{18}O_2$, which is not the case (figure 1a and b), scheme 1. If the labeled nitrous oxide interacted with ^{16}O in the close neighbourhood of iron ion, only $^{18}O^{16}O$ should be created – scheme 2. This also disagrees with the experimental data. Desorption of dioxygen from a model complex containing two labeled and two unlabeled (zeolitic) oxygens should yield $^{18}O_2$, $^{16}O_2$ and $^{18}O^{16}O$ in ratio 1:1:4 which also is not found. A pool of zeolitic oxygens (in 1:1 ratio to iron) suggested by Pirngruber and Roy [6] in a "statistical equilibrium" with oxygens from nitrous oxide or the Hall and co-workers [3] idea of one "porthole" for impinging labeled ^{18}O and another one for desorption of unlabeled oxygen can better describe the experimental data. Nevertheless, because of the readily proceeding isotopic exchange of gaseous $^{18}O_2$ in the presence of N_2O (figure 4A) which includes the number of zeolitic oxygens similar to the decomposition of ^{18}O labeled nitrous oxide, it is tempting to assume the following route: the first step is the deposition of ^{18}O onto the zeolite. This is followed by the $^{18}O_2$ desorption with the aid of a further ^{18}O (either by a Eley–Rideal or by Langmuir–Hinschelwood mechanism). Actually, $^{18}O_2$ always appears from the very beginning of the $^{15}N_2{}^{18}O$ decomposition. Then this $^{18}O_2$ undergoes the isotopic exchange with the oxygen atoms of the zeolite, and, dependent on the amount of

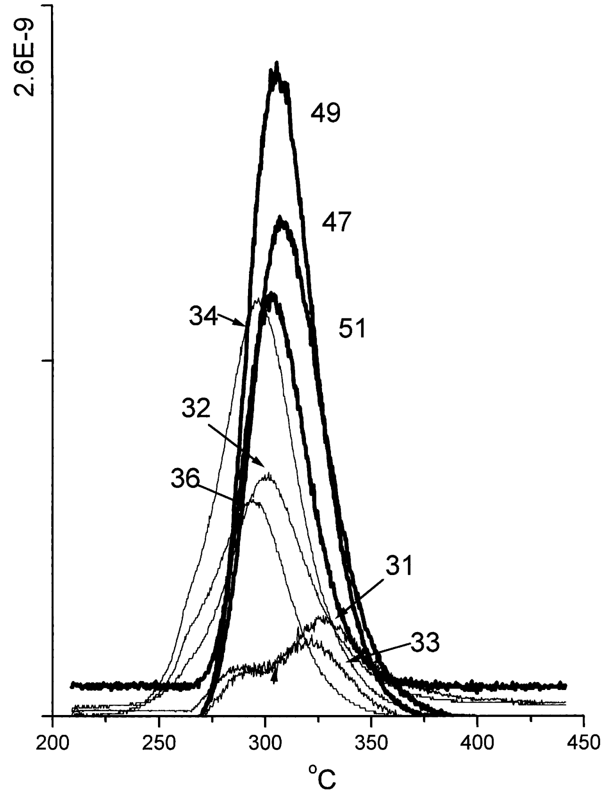


Figure 3. TPD after the decomposition of $^{15}N_2{}^{18}O$ over Fe/FER ($R=4.3$). Molecular ions of dioxygen 32, 34 and 36, of nitrogen dioxide $^{15}N^{18}O_2$ (51), $^{15}N^{16}O^{18}O$ (49) and $^{15}N^{16}O_2$ (47), of nitric oxide $^{15}N^{18}O$ (33) and $^{15}N^{6}O$ (31).

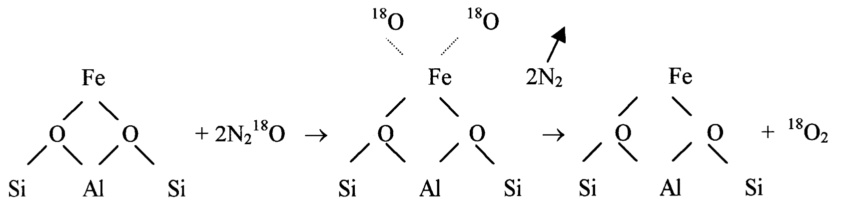
^{18}O in nitrous oxide and the amount of ^{16}O in the zeolite, different dioxygen isotopic species are released (figure 1a). It follows from figure 1a and b that the ^{18}O concentration in the gas phase is practically constant after a not strongly pronounced minimum at the beginning of the reaction. Because the decomposition of $^{15}N_2\,{}^{18}O$ keeps proceeding which adds further ^{18}O, a continuous incorporation of zeolitic oxygens should occur. The isotopic species of dioxygen reach the equilibrium value at the beginning of the constant ^{18}O concentration. This rapid equilibration agrees with a "single-step" mechanism – one oxygen atom from the O_2 is exchanged and the molecule desorbed [9] – which seems to match the equilibration better than the desorption of dioxygen from a statistical distribution of ^{18}O and ^{16}O oxygen atoms in the zeolite, as suggested e.g., in ref. [6]. This evidently does not exclude a rapid mixing of the part of zeolite oxygens with ^{18}O which is also supported by the first-order law kinetics in the exchange of $N_2O + {}^{18}O_2$ (figure 4B).

Schemes 1–3: only one iron atom is employed for simplification; main conclusions are not changed if assuming more iron atoms and a rapid mobility of ^{18}O atoms.

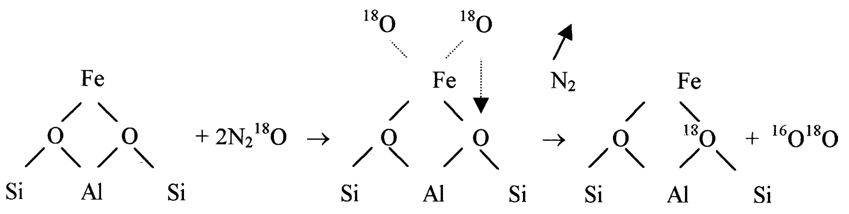
Release of only $^{18}O_2$ – no agreement with experiments.

Release of only $^{16}O^{18}O$, at least at the beginning of the decomposition – no agreement with experiments.

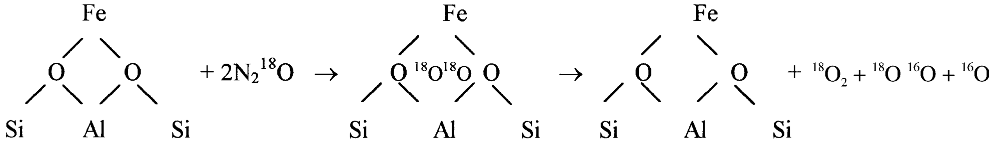
In 1:4:1 ratio, which again does not agree with experimental data.



Scheme 1.



Scheme 2.



Scheme 3.

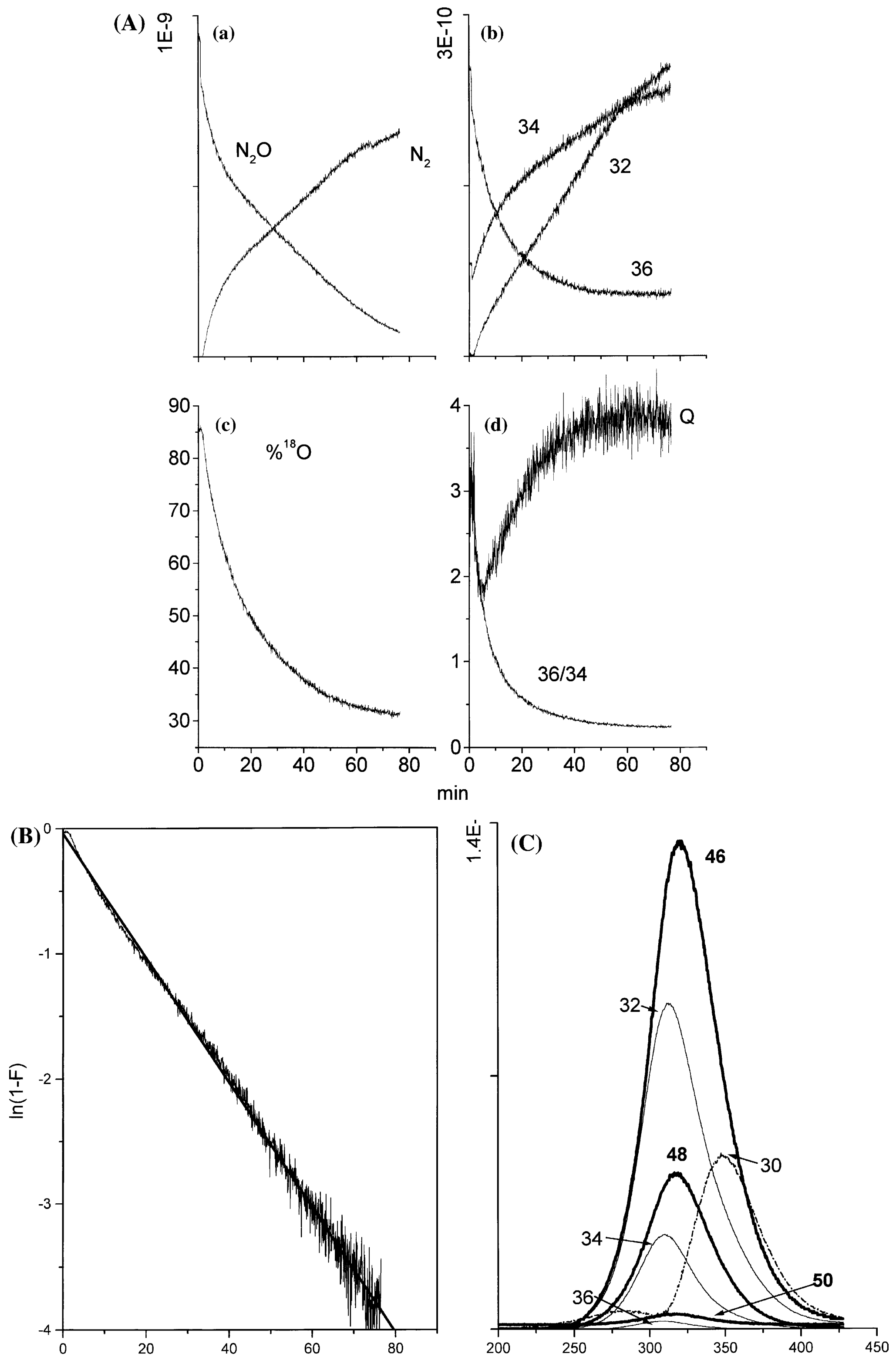


Figure 4. Decomposition of unlabeled N_2O in the presence of $^{18}O_2$ at 280 °C over Fe/FER, 500 Pa $N_2O + 217$ Pa $^{18}O_2$, 199.2 mg FeF/ER. (A) Decrease of N_2O and increase of N_2 (a), dioxygen isotope species (b), concentration of ^{18}O (c), equilibration Q and 36/34 ratio (d), (B) time dependence of In $(1-F)$, $F = (c_0 - c_t)/(c_0 - c_{00})$, where c_0, c_t and c_{00} stand for the ^{18}O concentration in time 0, t and at the end of the exchange, (C) TPD after the reaction, molecular ions 32, 34 and 36 for dioxygen isotope species, 46, 48 and 50 for $N^{16}O_2$, $N^{16}O^{18}O$ and $N^{18}O_2$, respectively, 30 for $N^{16}O$.

It should be mentioned that mechanism of the release of dioxygen during the decomposition of nitrous oxide has to depend on the experimental conditions: e.g., in flow experiments at higher temperatures the recombination of oxygen atoms will be favored. The back-exchange of dioxygen with framework oxygen will decrease, however, higher temperature will increase the labilization of zeolite oxygens as well as their involvement in the released dioxygen.

5. Conclusions

^{18}O labeled nitrous oxide was employed to study the route of dioxygen formation from the decomposing N_2O. The oxygen of Fe-ferrierite participates in the decomposition of nitrous oxide. With increasing decomposition temperature (200–400 °C) 2–6 oxygen atoms per iron ion (ca. 2% of all zeolite oxygens) are involved in the reaction.

Simple mechanisms considering either reaction of oxygen from impinging N_2O with oxygen deposited by another decomposed N_2O or very rapid association of ^{18}O atoms (exclusive desorption of $^{18}O_2$) as well as the reaction of oxygen from N_2 ^{18}O with one zeolite oxygen in the vicinity of iron (exclusive desorption of $^{18}O^{16}O$ were excluded. The rapid isotopic exchange of $^{18}O_2$ created by the N_2 ^{18}O is assumed to explain the distribution of the individual dioxygen isotopic species during the decomposition: a rapid exchange of $^{18}O_2$ mixed with non-labeled nitrous oxide includes very similar number of zeolitic oxygens as the decomposition of $^{15}N_2{}^{18}O$.

The equilibration in isotopic dioxygen species is suggested to proceed by a "single-step" mechanism between evolved dioxygen and zeolitic oxygens.

Acknowledgments

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