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NO – oxygen scavenger or reaction intermediate in the decomposition of N_2O?

Jana Nováková and Zdeněk Sobalík*

J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejškova 3, 182 23 Prague 8, Czech Republic

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Nitric oxide and nitrogen dioxide were found during the thermal desorption of surface species left on Fe-ferrierites after the decomposition of nitrous oxide. This demonstrates the formation of surface NOx species during N_2O decomposition. Repeated decomposition and subsequent desorption of surface species confirm the active role of surface NOx species. Addition of NO up to a fraction of 0.1 times the amount of N_2O increased the decomposition of nitrous oxide as well as the amount of surface NOx species. The use of nitrous oxide labeled with ^{18}O demonstrated that the zeolite oxygens participate in the reaction and that the presence of NO enhances this participation.

KEY WORDS: $^{15}N_2{}^{18}O$ and $^{15}N_2{}^{18}O$ + $^{14}N^{16}O$ decomposition; role of NOx intermediates; Fe-zeolites.

1. Introduction

There is widespread agreement on the beneficial role of nitric oxide in the decomposition of nitrous oxide over zeolites containing iron (e.g. [1–3]). The effect of NO has been reported to depend on the NO/N_2O ratio, the temperature and the zeolite matrix, as well as on the type, location and amount of iron. The simplest explanation of the role of NO consists in the oxidation by oxygen atoms from decomposing nitrous oxide to form nitrogen dioxide and liberation of active sites for the decomposition of new incoming N_2O. This, however, was thrown into doubt by the finding of a substantial acceleration of nitrous oxide decomposition by a very low fraction of NO in N_2O and no, or very low effect of increasing the NO/N_2O ratio. Consequently, a catalytic effect of nitrate or nitrite species formed from NO was suggested [4–6].

While the reactions of NO + N_2O in various ratios and also in different sequences of introduction clearly demonstrated the formation of surface NOx intermediates, these species have not been directly identified during the decomposition of nitrous oxide alone. However, the TPD of surface species left after the N_2O decomposition was found to yield NO_2 in addition to NO [7–12]. It thus follows that NOx surface species must be formed. The tailing of dinitrogen formation reported by Bulushev *et al.* [12] during the decomposition of nitrous oxide over Fe-MFI also points to a role of mechanism (2) in addition to the simple reaction (1) (2) formation of surface NO (3) decomposition of surface NO

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\begin{array}{lll}
N_2O + (\ )_{Fe} \rightarrow N_2 + (O)_{Fe} & (1) & \\
N_2O_{ads.} + (O)_{Fe} \rightarrow 2(NO) + (\ )_{Fe} & (2) & \text{formation of surface NO} \\
\qquad\qquad\qquad\qquad\quad \downarrow & & \\
\qquad\qquad\qquad\qquad\ 2\,NO & (3) & \text{decomposition of surface NO}
\end{array}
$$

Active sites $(\ )_{Fe}$ for further N_2O decomposition are thus liberated and more dinitrogen is formed.

Similarly, oscillation features found during the decomposition of nitrous oxide [13] over Fe-ferrierites can also be explained by the formation and decomposition of surface NOx species.

The present contribution is focused on the crucial role of surface NOx species in the decomposition of nitrous oxide alone and in mixture with nitric oxide over Fe-ferrierite and Fe-BEA.

2. Experimental

Fe-ferrierites were prepared according to patent [14] by the reaction of H-ferrierite (TOSOH, Si/Al = 8.5) with an $FeCl_3$ solution in acetyl acetone. A detailed description is given in ref. [15]. Iron in samples containing less than 0.6 wt% of Fe ($Fe/Al \leq 0.06$) is located predominantly in cationic positions (e.g. [16]). The samples (50 mg) were pretreated in vacuum at 450 °C, calcined at the same temperature in dioxygen (10^4 Pa) and evacuated during a decrease in temperature to 280 °C. Fe-BEA (Si/Al = 13.1, 0.76 wt% of Fe, 110 mg) was also used in some experiments.

The decomposition of $^{15}N_2{}^{18}O$ (Medical Isotopes Inc., USA, 99 at. %, 500 Pa in 165 ml) or of unlabeled

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*To whom correspondence should be addressed.

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nitrous oxide, both without or with the addition of unlabeled NO ($N_2O/NO = 10$), was checked at 280 °C. A very small amount of the gas phase was continuously introduced into a 400 QM Balzers quadrupole mass spectrometer using a needle valve, and the mass/charge ratios (m/z) 28, 30–34, 36, 44, 46–51 were registered. Then the gas phase was rapidly removed, the temperature was decreased to 150 °C, and temperature-programmed desorption (TPD, 5 °C/min, 150–450 °C) was commenced. The gas products were fed directly (without any leak) into the mass spectrometer. In some experiments, the gas phase after N_2O decomposition was rapidly removed at the experimental temperature, and a new decomposition was measured over the sample with preserved surface species (without preceding TPD).

The m/z ratios were assigned to the individual compounds by calibration with pure compounds, and in mixtures for the fragment ions.

3. Results

3.1. Unlabeled compounds–effect of surface species

The decompositions of unlabeled nitrous oxide (or of N_2O + NO) at 280 °C are displayed in the upper part of figure 1. TPD after these reactions are shown in the bottom part of the figure. Section a denotes the decomposition of N_2O alone, b denotes the subsequent TPD, c corresponds to the decomposition of N_2O + NO (10:1 ratio), d is the subsequent TPD, e is the decomposition of N_2O alone following c (only after rapid removal of the gas phase, no TPD), and f shows TPD following e. It can be seen that NO accelerates the decomposition (c versus a) and increases the amount of desorbed surface species (d versus b), also changing their composition to more NO_2 and NO and less O_2, which is released at higher temperatures than in the case b. If the surface species left after the N_2O + NO decomposition are not removed, the subsequent decomposition of N_2O alone is very similar to the decomposition of N_2O + NO (cf. e and c). TPD f after decomposition e exhibits the same features as TPD d, but the amount of desorbed species is greater.

It can be seen that the decomposition of nitrous oxide either after initial pretreatment or after removal of surface species during TPD exhibits a special character: after the first approx. 20 min, the decomposition of N_2O is accelerated. The release of dinitrogen is delayed at the beginning of the reaction and that of dioxygen starts even later. This can be seen in figure 1, section a, and is repeated in section a of figure 2. If the decomposition of N_2O is carried out over the sample

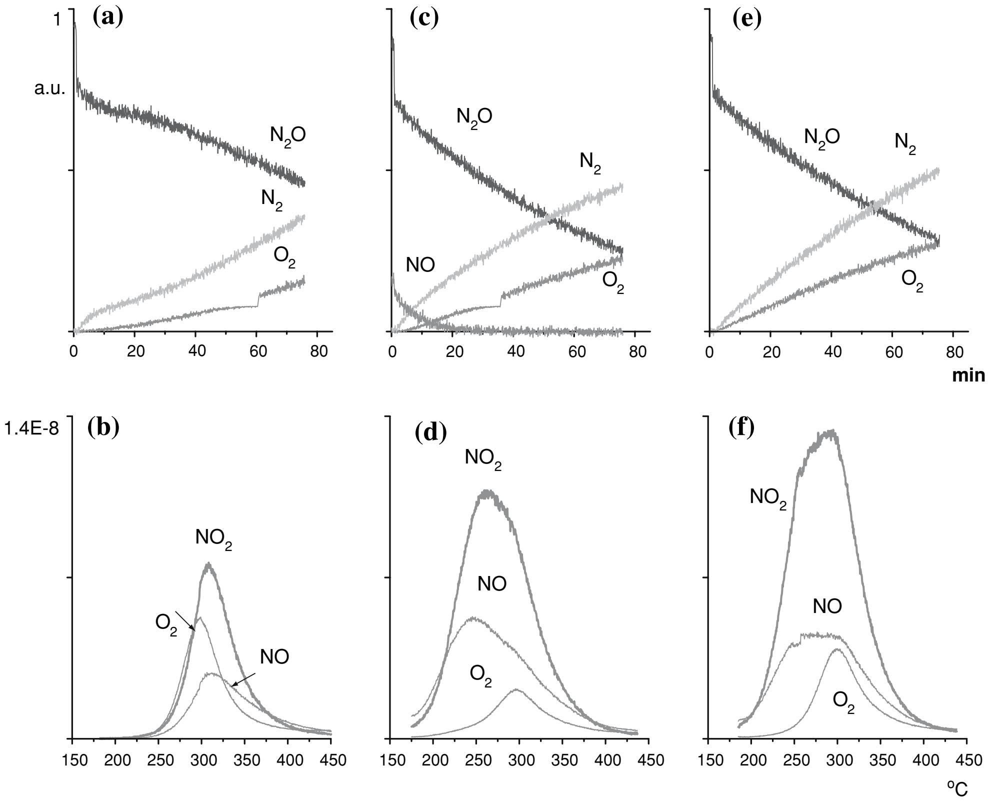

Figure 1. Decomposition of N_2O and N_2O + NO at 280 °C over Fe-ferierite and following TPD (a) N_2O decomposition, (b) following TPD, (c) N_2O + NO (10:1 ratio) decomposition, (d): following TPD, (e) N_2O decomposition after c without TPD, (f) TPD after e; in TPD curves bold: NO_2, dotted: NO, fine: O_2 .

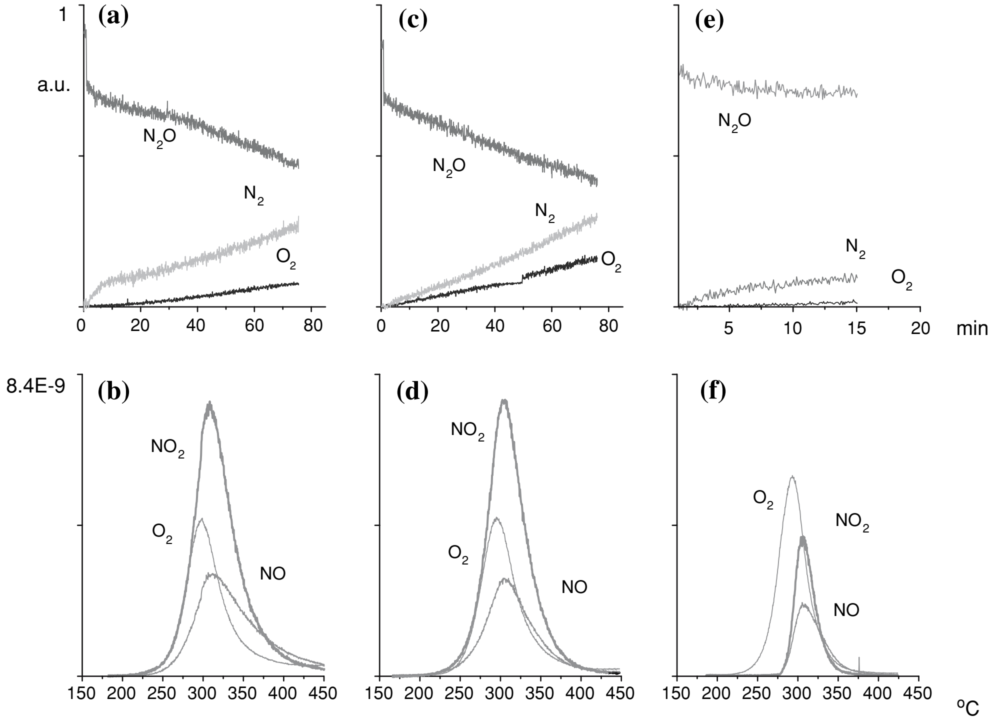

Figure 2. Decomposition of N_2O at 280 °C over Fe-ferrierite, effect of NOx surface species (a) N_2O decomposition, (b) following TPD, (c) N_2O decomposition after a without desorption of surface species, (d) following TPD, (e) N_2O decomposition in the time interval of lower decomposition rate, (f) following TPD.

without removal of surface species by TPD, no change in the decomposition rate nor the delays in N_2 and O_2 appear, as can be seen in section c of figure 2. The composition of desorbed products during TPD either after a or after c is practically the same (cf. TPD b and d). The release of dioxygen in TPD corresponds to oxygens captured during the N_2O decomposition (the N_2: O_2 ratio is higher than 2, contrary to the reaction stoichiometry $N_2O \rightarrow N_2 + 1/2O_2$). The maximum dioxygen release lies at a lower temperature than that for the release of NO_2 and NO, in contrast to that depicted in sections d and f of figure 1.

In order to check whether the surface species are already created at the beginning of the N_2O decomposition in the range of lower rates, the decomposition was interrupted after 15 min (section e of figure 2) and TPD was registered (section f). It follows that surface NOx species are formed, although in lower amounts and with dioxygen partially derived from decomposed NOx and partially from active oxygens left by decomposing nitrous oxide.

The effect of added NO and/or of surface species left after N_2O + NO decomposition is not unique for Fe-ferrierite, as the same process occurs over Fe-BEA, as is shown in figure 3. The sequence of experiments is the same as in figure 1: decompositions a for N_2O alone, c for N_2O + NO, e for N_2O alone after the sample without removal of surface species after c; TPD b, d and f follow the decompositions. The ratios of dioxygen, nitrous and nitric oxides and the peak temperatures in TPD differ from those over Fe-ferrierite, probably because of the different location of Fe active sites [17], which does not affect similar behavior of N_2O decomposition over Fe-ferrierite and Fe-BEA shown in figuers 1 and 3, respectively.

3.2. Decomposition of $^{15}N_2{}^{18}O$ and of $^{15}N_2{}^{18}O$ with $^{14}N^{16}O$

The amount of decomposed $^{15}N_2{}^{18}O$ at 280 °C after 70 min is given in Table 1 for Fe-ferrierite without and with the presence of NO (columns 2 and 4, respectively). The amounts of zeolitic oxygens calculated from the decomposed nitrous oxide and decreased ^{18}O concentration in dioxygen isotopomers are given in columns 3 and 5. The values in brackets are related to the amount of iron. It follows that the amount of participating zeolite oxygens increases much more in the presence of NO than the amount of decomposed nitrous oxide. It should be mentioned that the dilution of the ^{18}O concentration by ^{16}O from nitric oxide is low and does not explain the increased number of participating zeolite oxygens, which, however, is only approx. 2% of all zeolitic oxygens.

The time dependence of released dioxygen isotopomers and concentration of ^{18}O in dioxygen are depicted in figuer 4A, where sections 1 and 2 correspond to the decomposition of $^{15}N_2{}^{18}O$ alone, and sections 3 and 4

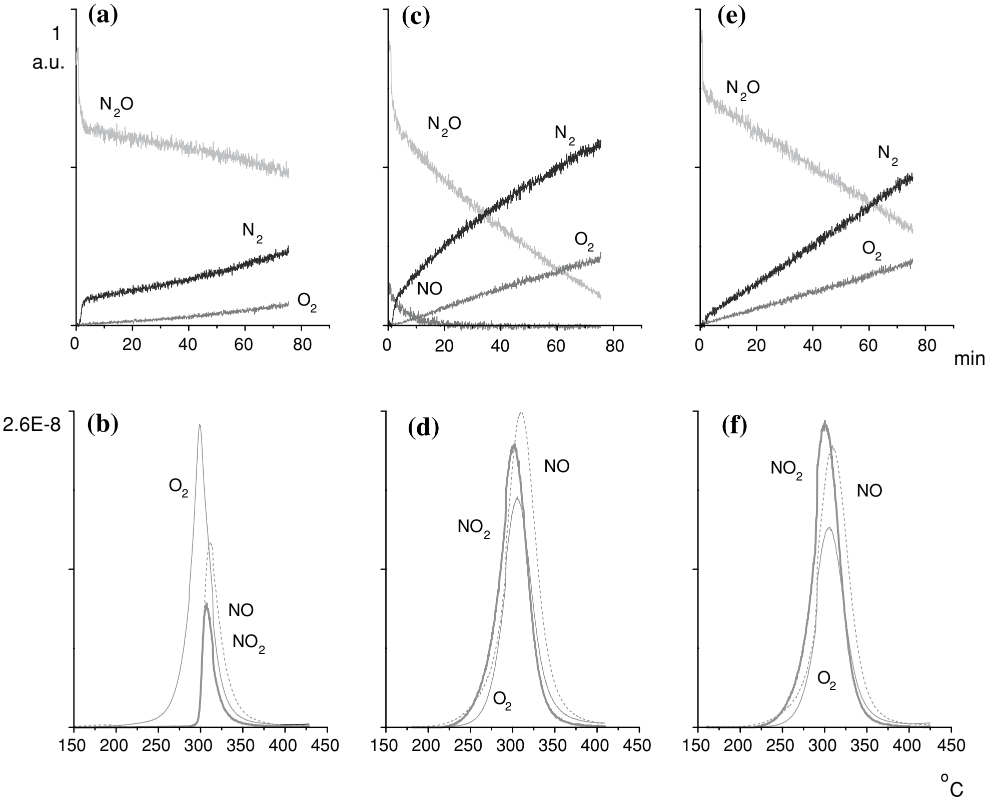

Figure 3. Decomposition of N_2O at 280 °C over Fe-BEA and following TPD (a–f) the same as in figure 1.

Table 1
Amounts of decomposed $^{15}N_2{}^{18}O$ without and with $^{14}N^{16}O$, and of participating zeolite oxygens over Fe-ferrierite

N_2O dec., μmol/g	Ozeol μmol/g	N_2O + NO dec., μmol/g	Ozeol μmol/g
239 (2.3)	162 (1.6)	503 (5.1)	620 (6.3)

Values in brackets are related to the amount of iron.

correspond to $^{15}N_2{}^{18}O$ + $^{14}N^{16}O$. The concentration of ^{18}O decreases in the presence of NO, thus corresponding to increasing fractions of $^{16}O^{18}O$ and $^{16}O_2$ and a decreasing fraction of $^{18}O_2$.

3.3. TPD after decomposition of $^{15}N_2{}^{18}O$ and of $^{15}N_2{}^{18}O$ with $^{14}N^{16}O$

The TPD areas are given in Table 2: the sum of ^{18}O labeled dioxygen, $^{15}NO_2$ and ^{15}NO after the decomposition of $^{15}N_2{}^{18}O$ alone, and, for $^{15}N_2{}^{18}O$ + $^{14}N^{16}O$, the sum of dioxygens, $^{14}NO_2$ and ^{14}NO (the amounts of desorbed ^{15}NOx species are more than one order of magnitude lower than the amounts of the ^{14}NOx species and are not listed in the table). The ^{18}O concentrations in the desorbed products are also shown. These values are of only rough, informative character; nonetheless, it can be seen that the ^{18}O concentration in the desorbed products is lower than at the end of the decomposition after the reaction of nitrous oxide alone by approx. 20–30%, but that this is close to the final concentration after the $^{15}N_2{}^{18}O$ + $^{14}N^{16}O$ reaction.

Figure 4B shows the TPD curves after the decomposition of $^{15}N_2{}^{18}O$ and $^{15}N_2{}^{18}O$ + $^{14}N^{16}O$ in the upper and bottom part, respectively. It follows that the desorption of the ^{14}NOx species begins at a lower temperature than that of the ^{15}NOx species and that the amounts of the ^{15}NOx species are negligible after the $^{15}N_2{}^{18}O$ + $^{14}N^{16}O$ reaction.

Figure 5A shows the decomposition of $^{15}N_2{}^{18}O$ after 80 and 15 min (a and d, respectively), the corresponding release of dioxygen isotopomers (b and e) and the subsequent TPD (c and f). These dependences are similar to those of the unlabeled compounds depicted in figure 2. Dioxygen, NO_2 and NO shown in the TPD spectra after the 15 min reaction are enriched less in ^{18}O than after the 70 min reaction (approx. 10–15% in the former case and about 30% in the latter case). The amount of desorbed dioxygen after the shorter reaction exceeds the amounts of NOx species, in contrast to the TPD products after 80 min. The integrated values of TPD products are depicted in figure 5B.

4. Discussion

Figures 1–3 support the assumption of the catalytic function of surface NOx species. The enhancing effect

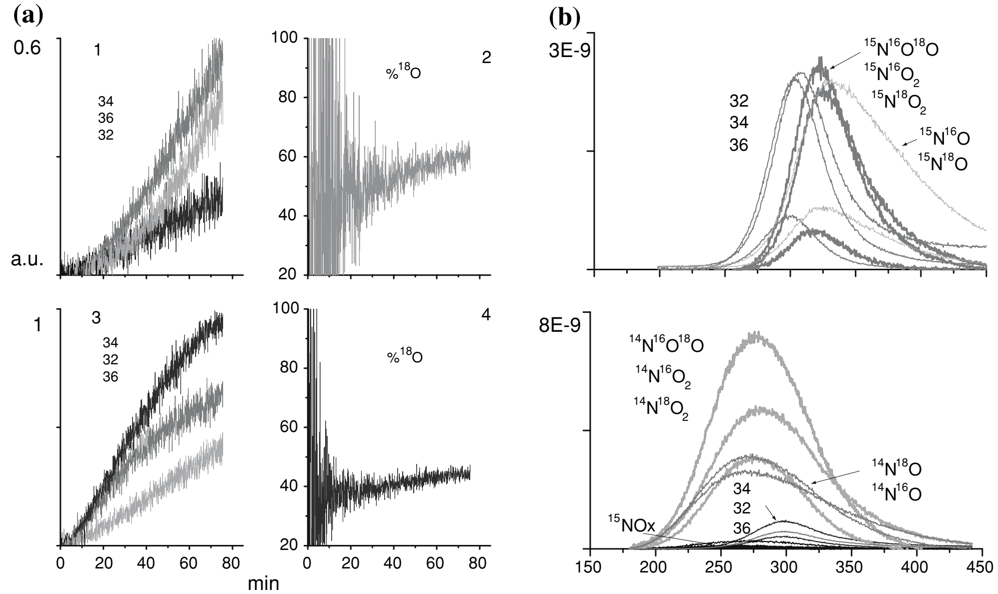

Figure 4. Decomposition of $^{15}N_2{}^{18}O$ and of $^{15}N_2{}^{18}O$ + $^{14}N^{16}O$ over Fe-ferrierite at 280 °C A (1) time plot of dioxygen isotopomers during the decomposition of $^{15}N_2{}^{18}O$ alone, (2) concentration of ^{18}O in dioxygen isotopomers, (3) time plot of dioxygen isotopomers during the decomposition of $^{15}N_2{}^{18}O$ + $^{14}N^{16}O$, (4) concentration of ^{18}O in dioxygen isotopomers B: upper part: TPD products following the decomposition of $^{15}N_2{}^{18}O$ alone, bottom part: TPD products following the decomposition of $^{15}N_2{}^{18}O$ + $^{14}N^{16}O$. 32, 34 and 36 represent isotopomers $^{16}O_2$, $^{16}O^{18}O$ and $^{18}O_2$, respectively.

Table 2

TPD areas of dioxygen, nitrogen dioxide and nitric oxide after decomposition of $^{15}N_2{}^{18}O$ without and with $^{14}N^{16}O$ over Fe-ferrierite

after $^{15}N_2{}^{18}O$ alone			after $^{15}N_2{}^{18}O$ + $^{14}N^{16}O$		
ΣO_2	$\Sigma^{15}NO_2$	$\Sigma^{15}NO$	ΣO_2	$\Sigma^{14}NO_2$	$\Sigma^{14}NO$
3.8 29 %^{18}O	3.3 30 %^{18}O	3.3 22 %^{18}O	1.5 44 %^{18}O	14.2 41 %^{18}O	6.7 50 %^{18}O

of the presence of NO consisting in simple removal of oxygens left from N_2O decomposition seems not to be active under the experimental conditions employed, as no NO_2 is released into the gas phase. Transient oxygen storage by NOx can explain the function of NO; dioxygen may be more readily released directly from these species, irrespective of their location on the same active sites as those for nitrous oxide decomposition, as well as on adjacent centres. The storage function of NOx species must be regularly renewed by desorption of dioxygen, as otherwise the small amount of added NO cannot store all the oxygens from the decomposing nitrous oxide; the decomposition should then be retarded; however, this does not occur. A catalytic effect of surface NOx species of, e.g., electronic or sterical character [18] cannot be excluded, nor can enhanced migration (and the resulting easier recombination) of oxygen atoms be excluded [4, 12]. The latter assumption seems to be valid: it is supported by the increased fraction of participating zeolite oxygens during the $^{15}N_2{}^{18}O$ + $^{14}N^{16}O$ decomposition. This is substantially higher than the increase due to the participation of ^{14}O from NO and exceeds the number of participating zeolite oxygens approx. 4-fold compared to the decomposition of N_2O alone, while the degree of N_2O decomposition is only doubled (Table 1). The role of NOx species operating as an oxygen carrier throughout the lattice follows from the almost constant value of the ^{18}O concentration in the released dioxygen during the $^{15}N_2{}^{18}O$ decomposition (figure 4A, for details, see ref. [10]).

During the decomposition of N_2O alone, surface NOx species are formed and accelerate the reaction after some time delay. The delay in dioxygen release (figures 1 and 2, sections a, and figure 5A, a) could be interpreted as oxidation of reduced Fe species, but this cannot explain the induction period for dinitrogen evolution. Moreover, we have confirmed that the decomposition of nitrous oxide over Fe-ferrierite with small iron loading does not depend on the oxidative or reductive atmosphere of the pretreatment; Fe (II) is present in a stable form. The amount of surface NOx species is relatively high after 20 min decomposition, so that their formation most probably leads to the acceleration of the N_2O decomposition (figures 1–3 and 5A f). However, the amount of NOx species created during the decomposition of nitrous oxide alone is lower than that from the N_2O + NO reaction, as can be seen in Table 2 and in figures 1 and 5B. Not all the captured oxygen species from N_2O alone are consumed in the NOx species, as some dioxygen is released during TPD (figure 1b, figure 2 b, d, f and figure 5A, B). The simultaneous

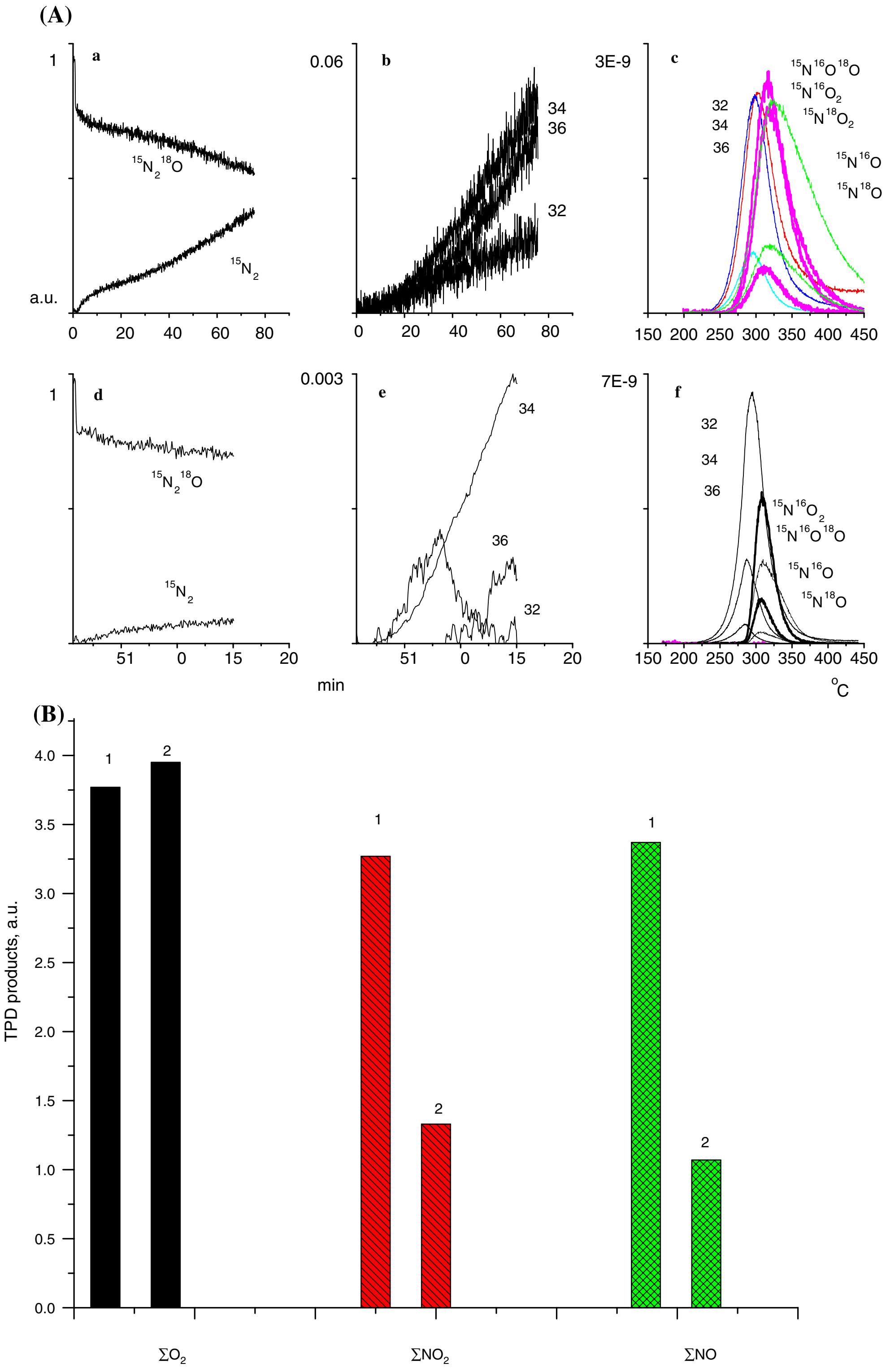

Figure 5. Decomposition of $^{15}N_2{}^{18}O$ over Fe-ferrierite at 280 °C after 80 and 15 min, and following TPD A: (a) $^{15}N_2{}^{18}O$ decomposition after 80 min, (b) release of oxygen isotopomers during the decomposition, (c) following TPD, (d–f) the same during and after 15 min reaction, B: TPD areas of the sums of the isotopic species of dioxygen, nitrogen dioxide and nitric oxide after 80 (1) and 15 (2) min, respectively.

reaction of N_2O + NO (10:1 ratio) removes all the captured oxygens, and dioxygen evolved during TPD apparently originates from the decomposition of NO_2 to NO and ½O_2. The ratios of NO and O_2 in the reaction products do not always correspond to simple decomposition $NO_2 = NO + 1/2O_2$, the release of oxygen not participating in the formation of NOx species and desorption of unreacted NO (probably from FeBEA, figure 3) do not indicate the stoichiometry of the surface NOx species (nitrite, nitrate, N_2O_3 etc.); it seems to be certain that N_2O can react with "active" oxygen from decomposing nitrous oxide to NO ($N_2O + O \rightarrow 2NO$, $NO + O \rightarrow NO_2$) and therefore a mixture of dioxygen, NO and NO_2 appears in the desorption products. It is worth mentioning that dinitrogen released during the $^{15}N_2{}^{18}O + {}^{14}N^{16}O$ decomposition contains only ^{15}N, i.e. nitrogen from NO does not participate in the formation of N_2. No formation of $^{14}N^{15}N$ from the equimolecular mixture of $^{14}N_2O$ and $^{15}N_2O$ was reported in ref. [19].

The ^{18}O concentration in the TPD products after the decomposition of $^{15}N_2{}^{18}O$ alone is approx. one half of that in dioxygen at the end of nitrous oxide decomposition. The remaining captured oxygen is thus presumably able to prolong the isotopic exchange with zeolite oxygens at elevated TPD temperatures. In contrast, the TPD products following the decomposition of $^{15}N_2{}^{18}O + {}^{14}N^{16}O$ contain similar concentrations of ^{18}O as found at the end of the decomposition. Dioxygen released after the N_2O + NO decomposition must be related to the decomposition of NOx species and not to the desorption of captured oxygens (Table 2 and figures 4B, 5B). The presence of NO almost completely prevents the formation of NOx surface species from $^{15}N_2{}^{18}O$: their amount is more than one order of magnitude lower than after the reaction of nitrous oxide alone. The amount of desorbed ^{14}NOx species after the decomposition of $^{15}N_2{}^{18}O + {}^{14}N^{16}O$ is approx. 3× higher than that of the ^{15}NOx species after the decomposition of $^{15}N_2{}^{18}O$ alone. Nitric oxide (1/10 of the amount of N_2O, 3.6 μmol) is consumed at the beginning of the nitrous oxide decomposition (figure 1c): thus, under the reaction conditions employed, the amount of NOx species related to the amount of iron in the sample is 0.7 (0.55 wt%, i.e. 4.9 μmol Fe per the zeolite weight), which is sufficient to increase the decomposition rate and eliminate the induction period during the decomposition of N_2O alone. The amount of surface NOx species created during this induction period is therefore approx. 2–3 × lower. As the increased fraction of NO above 10% does not lead to a higher decomposition of nitrous oxide, the optimum concentration of NOx species is NOx/Fe ÷ 1.

4.1. NOx species in Fe-ferrierite and in Fe-BEA

The accelerating effect of NOx species is very similar over both the zeolite types, although the fractions of NO, NO_2 and O_2 in the TPD products appear in different ratios.

5. Conclusions

- NOx species formed during the decomposition of N_2O alone are catalytically active in the on-going decomposition, however, not all sites able to capture oxygens from N_2O participate in the formation of surface NOx species,
- in contrast, a fraction of 0.1 of NO removes all these oxygens, forming approx. 2–3 × higher number of surface NOx species compared to NOx species from nitrous oxide alone, and inhibits the formation of NOx species from nitrous oxide alone. Optimum ratio of NOx species to Fe ions is close to 1.
- NOx species increase the degree of participation of zeolitic oxygens in the decomposition of nitrous oxide; their function most probably consists in temporary storage of oxygens and enhanced desorption of dioxygen; they also serve as oxygen carriers throughout the zeolite structure. Consequently, surface NOx species play the role of both oxygen scavengers and also reaction intermediates continuously transporting oxygens from nitrous oxide throughout the zeolite lattice,
- This double – or rather triple – function of NOx species is not characteristic only for Fe-ferrierite but is also operative in Fe-BEA and most probably in other suitable zeolite types with Fe cationic species.

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