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N_2O Decomposition over Fe-Ferrierite: Primary and Secondary Reactions with Reducing Agents

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Abstract The decomposition of N_2O either alone or with several reducing agents (CH_4, CO, NO and D_2) was followed by temperature-programmed desorption of surface species formed during the reactions. TPD products formed in these “primary” reactions were compared with the TPD products after “secondary” reactions of the same set of reducing agents with the surface species formed during the primary reactions. Changes in TPD products after reactions measured under various conditions were analyzed in detail. These experiments provided a background for studies of the nature and reactivity of surface species formed during N_2O reactions over Fe-ferrierite. The relevance of these experimental results to the mechanism of the N_2O elimination is discussed.

Keywords N_2O decomposition · Reactivity of surface species · Fe-ferrierite

1 Introduction

Capture of oxygens from decomposing nitrous oxide at active Fe centers in zeolites and the high reactivity of these oxygen species (Oact.) have been reported in many papers since Panov′s pioneering studies [1]. Later on, formation of NO_x surface species during the decomposition of nitrous oxide was also reported [2–6] and their active role in the process was suggested [6]. A mechanism based on a cooperation of Oact and NO_x species was assumed for the complex behavior of oscillations specific for the N_2O decomposition over Fe-ferrierites [7]. In relation to the simultaneous presence of reducing agents with nitrous oxide, a difference between the simultaneous and sequent introduction of the reductant was found. A “decay effect” depending on the time interval appeared in the latter case (e.g. [8]).

This contribution is aimed to elucidate the nature and reactivity of surface species formed during direct and reductant-assisted decomposition of nitrous oxide (primary reactions). Analysis of the products of thermal desorption of the relevant primary surface species as well as products of secondary reactions of the same reductants with surface species from primary reactions was used for this purpose.

2 Experimental

2.1 Fe-ferrierite

Fe-FER (Si/Al = 8.7, TOSOH Co) in the Na–K form was converted into the NH_4 form and ion-exchanged by treatment in $FeCl_3$ solution in acetyl-acetone [9]. The iron content is 0.98 wt%, i.e., the Fe/Al ratio equals 0.12. Our previous studies have shown that most of the iron at this relatively low iron loading is located in cationic sites, predominantly in β positions [10] and the formation of iron-oxidic species is suppressed [11].

2.2 Catalytic Experiments

All the samples were pretreated in situ in vacuum at 450 °C, followed by treatment in oxygen to remove the carbon impurities, then again in vacuum, constantly at the same temperature. The temperature was then decreased to

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280 °C permanently in a vacuum. Pretreatment at 450 °C in O_2 removed just prior to the N_2O decomposition at 280 °C was also carried out. The “primary” decompositions of N_2O alone or of N_2O-reductant mixture were performed in a batch arrangement. Usually 33 μmol of N_2O (alone or in a mixture with 3–12 μmol of NO, CH_4, ^{13}CO or D_2) in a 175 mL vessel was allowed to react for 7–70 min at 280 °C over 100 mg of the Fe-FER. The reaction vessel was then briefly evacuated, the sample was cooled to 150 °C, and evacuated at this temperature for 10 min to a pressure of ca. 0.01 Pa. Surface species accumulated on Fe-FER during the above primary reactions were removed by temperature-programmed desorption (TPD) in a vacuum, in the temperature region of 150–450 °C with a ramp of 5 °C/min.

In special experiments, the reaction was re-started using a fresh dose of nitrous oxide without elimination of the surface species formed during the preceding N_2O decomposition.

The reactivity of the surface species accumulated on the Fe-FER surface during the primary reactions was checked in “secondary” reactions: the surface species were exposed at 280 °C (after removal of the gas phase) to NO, CH_4, ^{13}CO and D_2 (amounts ranging from 3 to 20 μmol). The subsequent TPD of secondary surface species was then performed in the same way as for the primary surface species.

2.3 Instruments

The reaction progress was checked by introducing a negligible part of the gas phase via a needle valve into a Balzers QMG 400 quadrupole mass spectrometer. The individual components were characterized by their *m*/*z* ratios. The molecular ions were calibrated using pure compounds and, if necessary, fragmentation corrected (e.g., molecular ion of N_2 for the fragment ion of N_2O). During the TPD, the desorbed products were introduced directly into the vacuum system of the mass spectrometer.

3 Results

3.1 Decomposition of N_2O and Captured Surface Species

3.1.1 *Pretreatment Effect*

Figure 1a displays the course of N_2O decomposition over Fe-FER pretreated in vacuum (a) and in oxygen (b). The following TPD curves are depicted in sections (a′) and (b′), respectively. It follows that there is no difference in the outcome of these two pretreatment procedures, either in the course of oxygen release during the decomposition step, or in the composition of the desorbed products released during the following TPD run. This is typical for Fe-FER with low iron loading, in contrast to Fe-ZSM-5 (e.g., [12]). The initial sharp decrease in the N_2O concentration during the first minute of the decomposition was also systematically observed in the absence of a catalyst; this is an artifact caused by the pressure drop after the introduction of the gas into the reaction vessel from the auxiliary volume.

3.1.2 *Reaction Stoichiometry*

The release of oxygen is delayed compared to nitrogen, as is shown in Fig. 1a (sections (a) and (b)); this is typical for the N_2O decomposition at low temperatures. TPD curves (Fig. 1a, sections (a′) and (b′)) show that the desorbed products (i.e., O_2, NO_2 and NO) contain far more oxygen than N atoms. Actually, the N_2/N_2O ratio, i.e., the amount

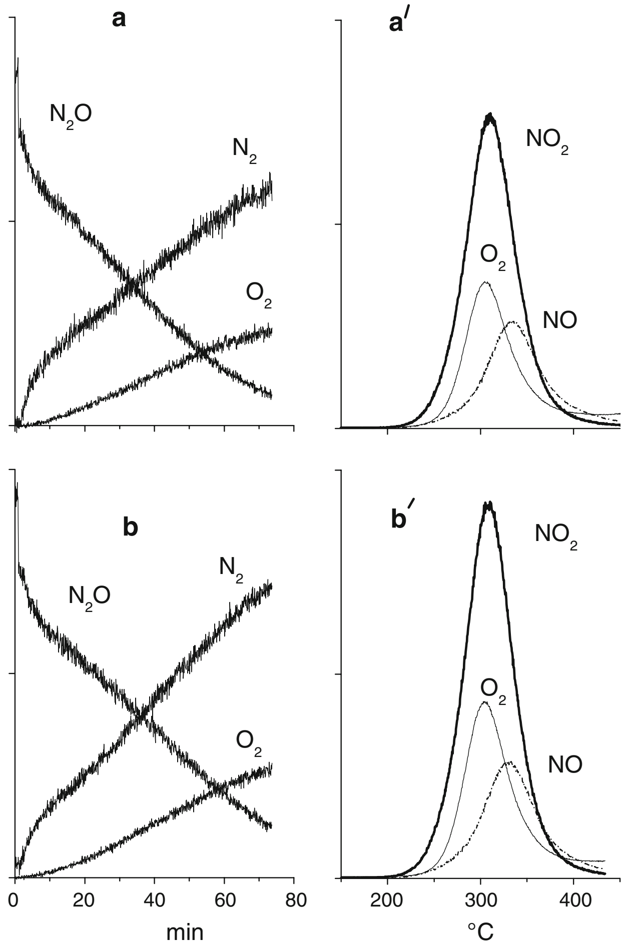

Fig. 1 Decomposition of N_2O at 280 °C over Fe-FER pretreated in vacuum and in oxygen; following TPD. (**a**) and (**b**) Pretreatment in vacuum and in O_2, respectively, (**a′**) and (**b′**) respective TPD products, *solid curve* for NO_2, *thin* for O_2 and *dash-dotted* for NO

of released nitrogen per decomposed N_2O, is slightly below the stoichiometric value of 1. On the other hand, the initial O_2/N_2O ratio is a substantially lower value than the stoichiometric values of 0.5. Accordingly, the N_2/O_2 ratio of 2 ($N_2O \rightarrow N_2 + 1/2O_2$), is attained only for decomposition running for more than 20 min in the batch static arrangement employed (considering the amount of oxygen captured at the beginning of the decomposition).

3.1.3 Role of Captured Surface Species on the Progress of N_2O Decomposition

If the surface species accumulated on Fe-FER are removed by TPD, the progress of the next N_2O decomposition on the same sample (as well as following TPD) is the same as on the fresh sample. However, this does not hold for the repeated N_2O decomposition over Fe-FER, from which the surface species were not removed by TPD. This is illustrated in Fig. 2. The N_2O decomposition repeated on the same sample without removal of surface species proceeds more rapidly, and the delay in the release of dioxygen is shorter (cf. sections (a) and (a′)). This is even more pronounced if the repeated N_2O decomposition is carried out over Fe-FER, over which the first decomposition of N_2O was measured in the presence of NO (ratio 0.1:1 for NO:N_2O, sections (b) and (b′)). It was shown in Fig. 1 that the treatment in oxygen prior to the decomposition of N_2O does not affect the decomposition. In contrast, pretreatment in NO (10 times lower pressure than that of N_2O) has an even greater effect than the surface species left after the NO + N_2O decomposition (sections (c) and (c′)). Short-time decomposition of nitrous oxide leaves sufficient surface species able to accelerate the repeated N_2O decomposition (sections (d) and (d′)).

3.2 Changes in the TPD Products with the Duration of N_2O (and N_2O + Reductants) Decomposition

3.2.1 N_2O Alone

As follows from the latter preceding experiment, the very short time of the N_2O decomposition leaves a sufficient number of surface species able to positively affect the subsequent decomposition of nitrous oxide. Consequently, the time dependence of the N_2O decomposition followed by TPD was examined. Figure 3a shows that the maximum

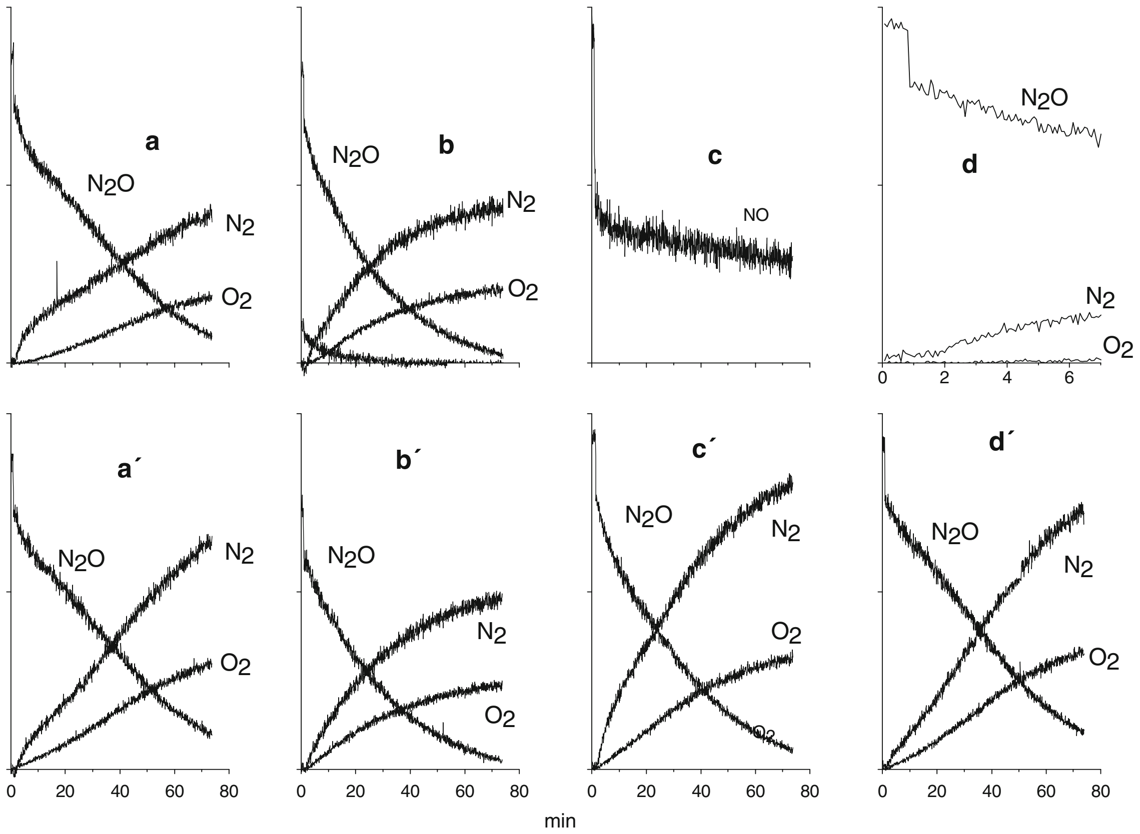

Fig. 2 Effect of surface species left on Fe-FER after N_2O, N_2O + NO and NO reactions on the following decomposition of nitrous oxide. *Top*—from *left to right*—time course of the decomposition of (**a**) N_2O alone, (**b**) N_2O + NO (10:1 ratio), (**c**) NO alone (10 times lower amount than N_2O), (**d**) short decomposition of N_2O, *bottom* (**a′**–**d′**) N_2O decomposition repeated after (**a**–**d**), respectively

fraction of O_2 is released after the shortest reaction time; this fraction decreases with increasing time of the N_2O decomposition, while the amount of NO_2 and NO remains practically unchanged. It should be mentioned that Fe-FER with lower iron loading (i.e., 0.55 wt%) exhibit an increasing amount of NO_x species with increasing reaction time.

3.2.2 N_2O + Reductants

The effect of added NO ($NO:N_2O = 0.1$) is given in Fig. 3b. Contrary to N_2O alone, NO_2 predominates over O_2 and NO during the TPD runs from the shortest time of decomposition, and is released in higher amounts than during the preceding experiment (cf. Fig. 3a). Addition of carbon monoxide adds CO_2 to the TPD products (Fig. 3c), the release of dioxygen is relatively high, although lower than after the decomposition of nitrous oxide alone, and the amount of NO_x is low. Addition of methane (Fig. 3d) results in a very small amount of all the evolved TPD products (cf. axis y), in which CO_2 and O_2 are more abundant than NO_x. Addition of deuterium also leads to a small amount of TPD products with composition more similar to that after the decomposition of N_2O alone.

3.2.3 Effect of the Amount of Added Reductants to N_2O on the TPD Products

This is shown in the upper parts of Figs. 4 and 5 for the addition of methane and carbon monoxide, respectively. The amounts of NO_x are suppressed in the TPD products from the lowest amounts of added reductants, while some O_2 persists for higher reductant fractions, especially with carbon monoxide.

3.2.4 Effect of the Reductant Amount on the TPD Products After Secondary Reactions of Reductants with Surface Species from Decomposed Nitrous Oxide

The bottom parts of Figs. 4 and 5 display these effects: contrary to the above effect of reductants + N_2O, secondary reactions of CH_4 and/or of ^{13}CO eliminate NO_2 and O_2 from the TPD products, while NO persists in higher reductant amounts, especially for methane.

4 Discussion

The stability of Fe(II) ions in ferrierite (for $Fe/Al \leq 0.1$) follows from figure. In contrast to iron ions in ZSM-5 (e.g., [12]) neither pretreatment in a vacuum nor in oxygen affect the decomposition of nitrous oxide.

4.1 N_2O Alone and N_2O + NO

Unlike gaseous oxygen molecules, oxygen atoms (radicals according to Panov et al. [12]) from decomposing nitrous oxide are readily captured on Fe ions in ferrierite. This capture of oxygens occurs as a first step in the N_2O decomposition (Fig. 3a), and then the N_2O decomposition proceeds almost stoichiometrically. The composition of the surface species changes in time with proceeding decomposition of nitrous oxide: NO_x—especially NO_2—appears in higher fractions in the TPD products. This is presumably formed due to the reaction of incoming nitrous oxide with active captured oxygens (Oact.). Gaseous compounds identified in the TPD measurements are, of course, not the real surface species (e.g., nitrates and nitrites); they represent their decomposed products forming NO_2, NO and O_2. The presence of NO_x species can be assumed as the most important intermediate in the decomposition of nitrous oxide. This follows from the appearance of NO_2 in the TPD products from the beginning of the N_2O decomposition (Fig. 3a), further from the accelerating effect of surface species from preceding N_2O decomposition on the next decomposition (Fig. 2), as well as from the enhanced decomposition in the presence of even a small fraction of NO in N_2O (Fig. 2, section (b) and Fig. 3b). An active role of NO_x species in the decomposition of N_2O + NO mixtures has already been assumed in literature (e.g., [8, 13]), but only rarely in the decomposition of N_2O alone [6]. It should be mentioned that the surface NO_x species incorporate zeolite oxygens which can be easily exchanged for ^{18}O (see [14]).

4.2 N_2O + Reductants (except NO)

The amount of surface NO_x after the reaction of N_2O with methane, carbon monoxide and or deuterium is substantially lower than after the reaction of N_2O alone and, notably, of N_2O + NO (Fig. 3c–e vs. a, b). It has been commonly assumed that the recombination of oxygen atoms is the slowest step in the N_2O decomposition. The reducing agents remove these oxygen atoms and thus accelerate the N_2O decomposition. Under our batch experimental conditions, when the catalyst is exposed to all the reaction products formed, part of the by-products—carbon dioxide and water—remains at the zeolite surface and probably retards the N_2O decomposition (these by-products are desorbed above the reaction temperature, see TPD in Fig. 3c and d). Under our experimental conditions, not all the oxygen atoms are removed from the surface species, as follows from the persisting O_2 in the TPD products (Figs. 4, 5, top sections). The reaction pathway in the presence of carbon monoxide, methane and partially deuterium is evidently different from that of nitrous oxide either alone or mixed with nitric oxide. In the latter two

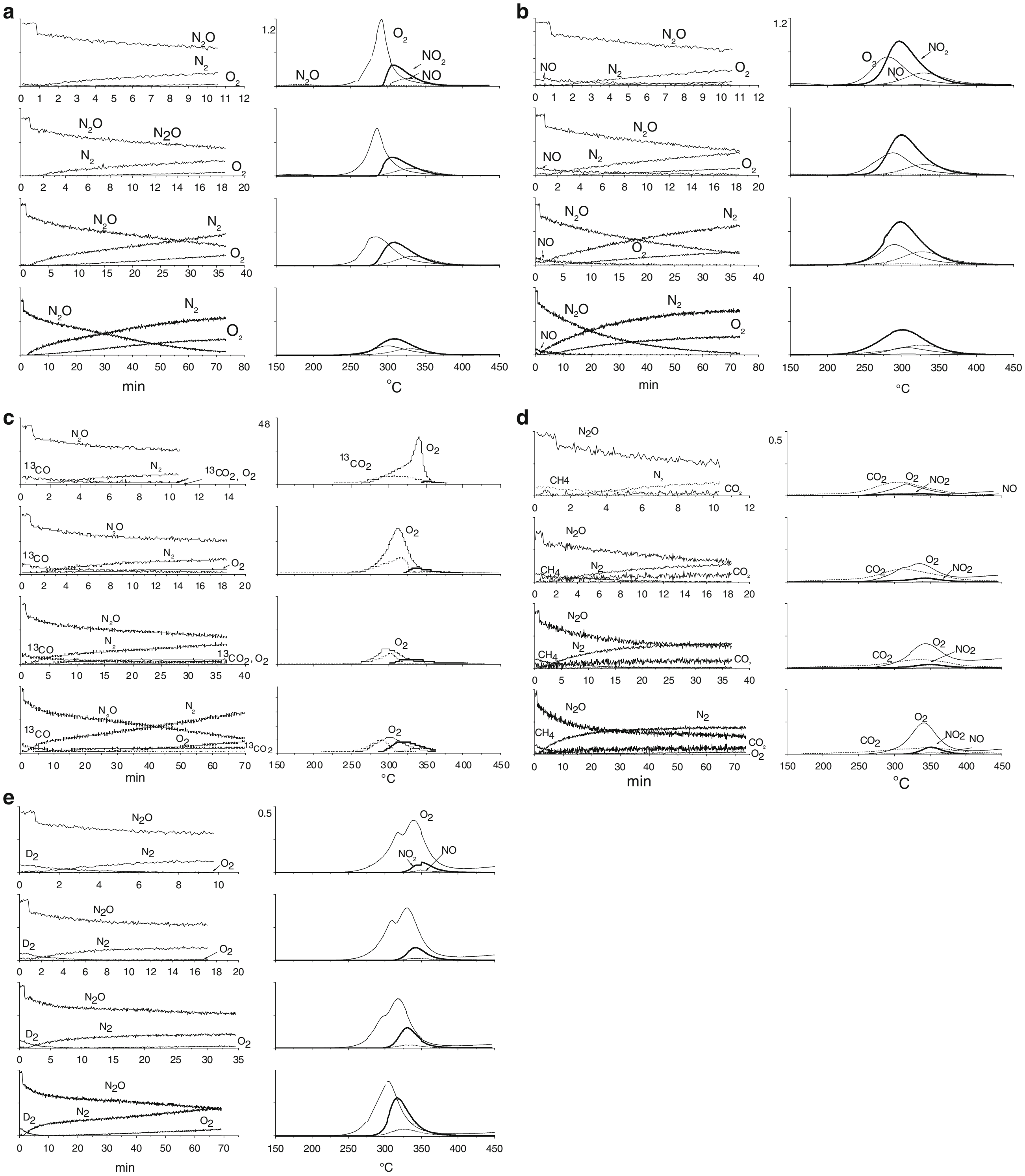

Fig. 3 Decomposition of N_2O and N_2O + reductants during various time intervals; following TPD. *Left-hand side* for reaction course, *right-hand side* for TPD, *bold curves* for NO_2, *thin* for O_2, and *dash-dot* for NO. (**a**) N_2O alone, (**b**): N_2O + NO (10:1), (**c**): N_2O + ^{13}CO (10:1), (**d**): N_2O + CH_4 (10:1) and (**e**): N_2O + D_2 (10:1)

cases, NO_x species either formed due to the Oact–N_2O reaction, or due to NO addition, are active intermediates in the decomposition of nitrous oxide. These compounds are formed in substantially lower amounts in the presence of methane, carbon monoxide and deuterium (Fig. 3c–e) thus pointing to a different reaction route.

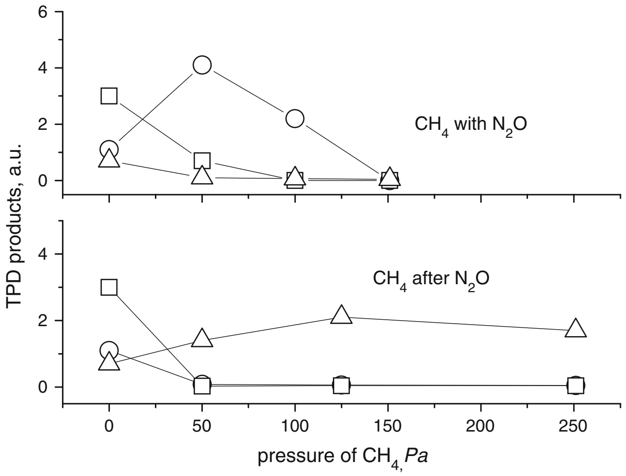

Fig. 4 TPD products after the primary reaction of $N_2O + CH_4$ compared with those after the secondary reaction of CH_4 with surface species left after the N_2O decomposition. *Bottom*: TPD after $N_2O + CH_4$ decomposition, *Top*: TPD after CH4 reaction with surface species left during N_2O decomposition; *circle* for O_2, *square* for NO_2 and *triangle* for NO

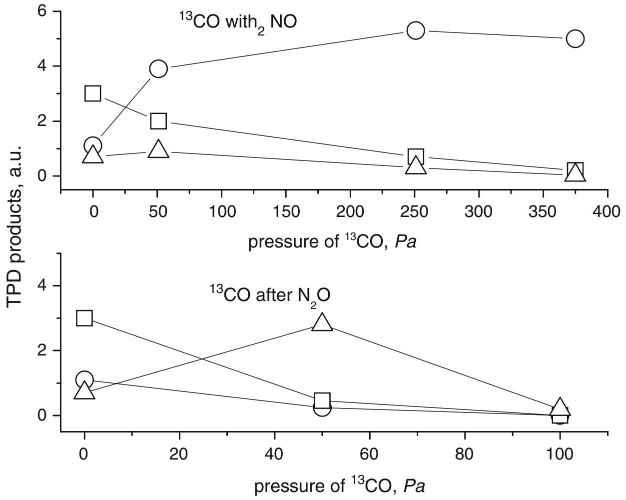

Fig. 5 TPD products after the primary reaction of $N_2O + {}^{13}CO$ compared with those after the secondary reaction of ${}^{13}CO$ with surface species left after the N_2O decomposition. *Bottom*: TPD after $N_2O + {}^{13}CO$ decomposition, *Top*: TPD after ${}^{13}CO$ reaction with surface species left during N_2O decomposition; *circle* for O_2, *square* for NO_2 and *triangle* for NO

4.3 Secondary-Reactions of CO and CH_4 with Surface Species After the N_2O Decomposition

These reductants remove NO_2 and O_2 from the TPD products, and only NO appears, in a higher amount after reaction with carbon monoxide than with methane. The absence of NO_2 and O_2 agrees with scavenging of active oxygens by the reductants. Apparently, NO originates from more firmly held surface species and is more difficult to remove.

5 Conclusions

Active iron cations in ferrierite, when present in Fe/Al ratios below 0.1, are mostly stable towards treatment in dioxygen, but readily interact with oxygen from nitrous oxide. The primary formed active oxygens, captured at Fe ions, are able to react with another N_2O molecule to form surface NO_x species, accelerating the N_2O decomposition and serving as oxygen reservoirs and carriers. Formation of surface NO_x species is hindered by the presence of reducing agents, e.g., CO or methane and, to a lower extent, also by hydrogen. These reductants are active in direct reduction of the active oxygens and thus change the reaction route and eliminate the role of NO_x species. Reaction of methane and CO with surface products accumulated during the decomposition of nitrous oxide exhibits much lower reactivity of the surface species which are desorbed in the form of NO, with preferential reaction with Oact and with the surface species decomposing into NO_2 during the TPD run.

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