Comparison of ^{18}O isotopic exchange after and during the interaction of N_2O, NO, and NO_2 with Fe ions in ferrierites

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Nitrous oxide deposits its oxygens on Fe-ferrierites at 200–250 °C in contrast with nitric oxide and nitrogen dioxide. This oxygen is readily exchangeable for $^{18}O_2$ at room temperature and the reaction proceeds via a single-step exchange mechanism. All three nitrogen oxides in a mixture with ^{18}O labeled dioxygen undergo isotopic exchange (IE) at 200–250 °C, N_2O via the same single-step mechanism, while NO and NO_2 react via a multiple-step mechanism. Zeolitic oxygens participate in IE above 250 °C during temperature-programmed desorption of surface species formed in the reaction of nitrogen oxides with $^{18}O_2$.

KEY WORDS: Fe-ferrierite; N oxides; $^{18}O_2$ exchange; mechanism of.

1. Introduction

It is well known that the decomposition of N_2O over iron containing zeolites produces very active oxygen species [1–9]. These oxygens are able to oxidize, e.g., hydrocarbons at low temperatures [1–3,5,6,8,9] and convert benzene to phenol [5,8,10,11]. Isotopic exchange of $^{18}O_2$ (further only IE) following the decomposition of nitrous oxide helps to quantify the number of active oxygens captured by the iron species in the catalyst. The nature of these oxygens has not been completely recognized although numerous experimental methods have been employed. Our preceding paper [7] dealt with the isotopic exchange of $^{18}O_2$ for oxygens left by the decomposition of nitrous oxide over Fe-ferrierites in which iron was present predominantly in cationic form. It appeared that the number of active oxygens exhibits a maximum value at an Fe/Al ratio of about 0.1. Maximum activity in the vicinity of this ratio was also found on Fe-ferrierites during the reduction of nitrogen oxides by hydrocarbons [12]. The ratio of active oxygens to the iron content ($O/Fe \cong 0.5$) in IE at room temperature after the N_2O decomposition over ferrierites with low Fe content increased above 200 °C ca. 4 times, thus indicating the involvement of zeolitic oxygens in IE.

Panov (e.g., in reference [3]) reported that the interaction of NO does not leave any active oxygen in the Fe/MFI structures, in contrast with N_2O. Hall's group [13,14] did not find any decomposition of NO over Fe/Y and Fe/M up to 700 °C but NO oxidized Fe(II). These authors reported IE between N_2O and zeolitic oxygens and, in reference [15], also between NO and zeolitic oxygens over Fe/M at a relatively high temperature of 500 °C.

This study compares reactions of N_2O, NO, and NO_2 at 200–250 °C over Fe-ferrierites using IE at room temperature after the above reactions as well as IE in a mixture of $^{18}O_2$ + nitrogen oxides at 200–250 °C. The mechanisms of IE are discussed. Temperature-programmed desorption in the region 200–450 °C is used to obtain information on the possible role of zeolitic oxygens at an elevated temperature.

2. Experimental

The preparation of Fe-ferrierites (Fe/FER) with 0.026, 0.035, and 0.07 Fe/Al ratio was described in reference [7]. The nitrogen oxides employed were N_2O (99.9%), NO (MG 2.5), and NO_2 (prepared by reaction of NO in excess of O_2 at RT); the gases were purified by freeze–thaw cycles. Prior to the following reactions, Fe/FERs were pretreated in vacuum at 420 °C for 2 h. Two sets of experiments were then performed: (i) 500 Pa of the respective nitrogen oxide was left to react at 200 °C (NO_2 also at 250 °C) for 1 h with 100–300 mg of the sample. The gas phase was then evacuated at room temperature (RT) for 15 min. $^{18}O_2$ (50 Pa) was added and possible IE checked by leaking a negligible amount of the gas phase into a QM 400 Balzers mass spectrometer, (ii) the mixture of 50 Pa of $^{18}O_2$ with 500 Pa of N_2O and/or NO or NO_2 was allowed to react with the catalysts for 1 h at 200 °C (NO_2 also at 250 °C). The gas phase was quickly evacuated (for 1 min) at the same temperature and for 15 min at RT. For comparison, the mixtures of nitrogen oxides with unlabeled dioxygen were also examined under the same conditions. The temperature-programmed desorption (TPD, 5 °C/min)

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was performed after each set of experiments between RT and 420 °C. The desorbed products were fed directly (without any leak) into the quadrupole.

The reactants and reaction products were determined using the characteristic m/z ratios for the individual compounds: m/z 28 for N_2 (corrected for fragment values from N oxides), 30 for NO (also corrected for fragment values from N_2O and NO_2), 44 for N_2O and 46 for NO_2. Pure nitrogen oxides were used for calibration. Dioxygen was characterized by the ions 32 ($^{16}O_2$), 34 ($^{16}O^{18}O$), and 36 ($^{18}O_2$), labeled NO_2 by the ion 48 ($N^{16}O^{18}O$). $N^{18}O_2$ (ion 50) was not found. Possible ^{18}O exchange in N_2O ($N_2^{18}O$, ion 46) and $N^{18}O$ (ion 32) was estimated by comparing the reactions of $^{18}O_2$ with those of $^{16}O_2$. The gas-phase composition followed in time at constant temperature is given in arbitrary units (= 1 for the initial mixture, which corresponds to 1E-9 for 500 Pa and 1E-10 for 50 Pa). The amounts of gases released during the TPD directly into the mass spectrometer are given in total ion currents.

3. Results and discussion

IE at RT over Fe/FER (Fe/Al 0.07) after N_2O decomposition at 200 °C is exemplified in figure 1, where the changes in time of the individual isotopic dioxygen species are shown in figure 1(a), the decrease of ^{18}O concentration in figure 1(b), the Q value (ratio of ions $(34)^2/(32 \times 36)$) in figure 1(c), and the 36/34 ratio in figure 1(d). The equilibrium Q value of 4 and the decreasing value of the 36/34 ratio point to the "single-step" isotope mechanism (R′ [16,17]), which means that only one oxygen atom of O_2 is exchanged in one reaction step. The dotted curve in figure 1(c) represents the theoretical Q course for this case. The "multiple-step" mechanism R″ (the exchange of both O atoms of dioxygen during one interaction step) accompanied by IE proceeding without incorporation of the oxygen atoms from the solid—in our case from oxygen left by N_2O decomposition (R, see reference [16])—could also explain the experimental course of Q and of the 36/34 ratio. However, a small decrease in the Q value at the very beginning of IE does not exclude partial participation of the R″ mechanism at this stage. The calculated course of the operation of only the multiple R″ mechanism (dashed curve in figure 1(c)) deviates considerably from the experimental curve, so that IE most probably proceeds exclusively by the "single-step" R′ mechanism. The same behavior was found for the two Fe/Fers with lower Fe/Al ratios.

No decrease in ^{18}O concentration in labeled dioxygen was found after the interaction with NO at 200 °C or with NO_2 at 200–250 °C in contrast to IE after the N_2O decomposition. This agrees with the findings reported by Panov *et al.* [3], so that the creation of very active

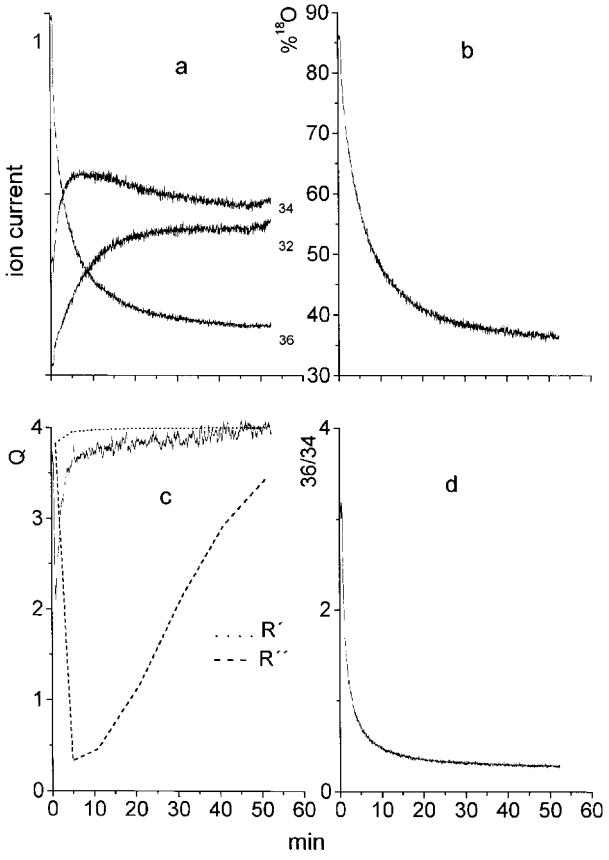

Figure 1. $^{18}O_2$ IE at room temperature after the interaction of N_2O with Fe/FER (Fe/Al 0.07) at 200 °C. (a) The time dependence of individual isotopic dioxygens. (b) Corresponding decrease in the ^{18}O concentration. (c) The equilibration Q of isotopic dioxygens during IE ($[^{16}O^{18}O]^2/[^{16}O_2] \times [^{18}O_2]$, dotted curve—calculated for the R′ mechanism alone, dashed curve—for the R″ mechanism alone. (d) Ratio of labeled dioxygens $[^{18}O_2]/[^{16}O^{18}O_2]$ (36/34).

oxygens on the iron-containing ferrierites is characteristic only for the reactions of nitrous oxide.

The reactions of N_2O/O_2 at 200 °C over Fe/FER (Fe/Al = 0.026) and following TPD are depicted in figure 2—above 200 °C for N_2O alone (a), for $N_2O + ^{16}O_2$ (b) and for $N_2O + ^{18}O_2$ (c). The left column gives the reaction in time and the right column lists the TPD products. It follows that the presence of dioxygen practically does not affect the conversion of nitrous oxide—only dinitrogen appears as the product, while oxygen from N_2O remains on the catalyst. The amount of added oxygen in the gas phase is not changed (figure 2(b)), but IE proceeds (figure 2(c)—see the decreasing amount of $^{18}O_2$ and increasing amounts of $^{18}O^{16}O$ and of $^{16}O_2$). Unlabeled dioxygen is the main TPD product, the low fraction of labeled dioxygens (figure 2(c), right column) confirms the conclusion of our preceding paper [7] on the participation of zeolitic oxygens in IE (14% of ^{18}O should be present in the captured oxygen under the conditions used, but the desorbed oxygen contains ca. 4 times lesser value).

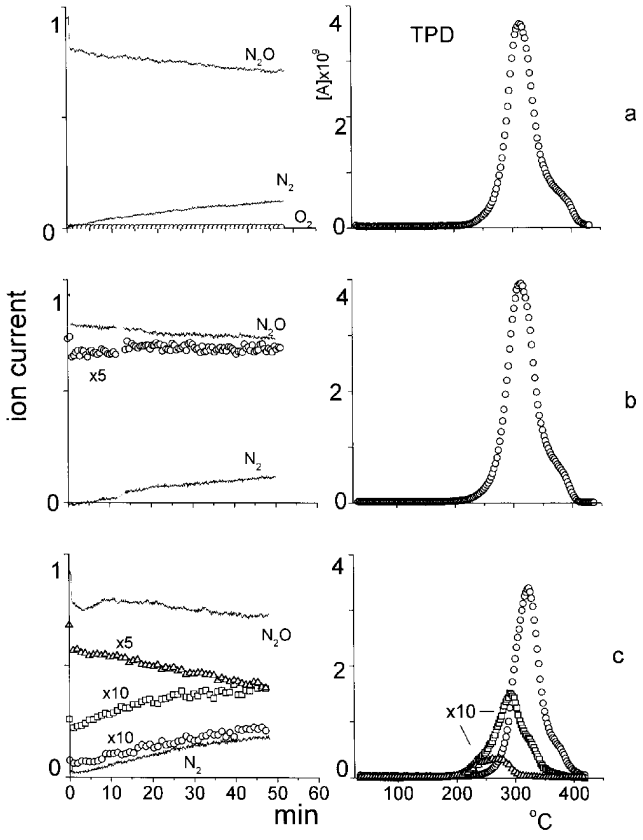

Figure 2. Interaction of N_2O alone and with dioxygen over Fe/FER (Fe/Al 0.026) at 200 °C. Left column: the time dependence of the amounts of reactants and products and right column: following TPD. (a) N_2O alone, (b) $N_2O + {}^{16}O_2$, 1/10 ratio, (c) $N_2O + {}^{18}O_2$, 1/10 ratio, circles for $^{16}O_2$ (multiplied by factor 10), squares for $^{18}O^{16}O$ (multiplied by factor 10), triangles for $^{18}O_2$ (multiplied by factor 5); points skipped (frequency 20).

Figure 3 depicts in the left column the time course of NO alone (a), NO + unlabeled (b) and NO + labeled oxygen (c); the respective TPD curves are shown in the right column. Obviously, there is a substantial difference compared to the reactions of nitrous oxide: (i) the presence of oxygen in the gas phase approximately doubles the consumption of NO (figure 3(b) and (c) *versus* 3(a)), (ii) the TPD products after the $NO + O_2$ interaction consist predominantly of NO_2 and are more abundant than those of NO alone. The consumption of dioxygen roughly corresponds to one half of the consumed NO; the amounts of NO and NO_2 are also close during TPD. The concentration of ^{18}O decreases greatly (figure 3(c)). If all the oxygens in NO were mixed with $^{18}O_2$, the ^{18}O concentration would have decreased to 14% (experimental value ca. 13%); the desorbed products contain substantially lower ^{18}O concentrations: $NO_2 \sim 6\%$ (not shown) and $O_2 \sim 0.1\%$ (if a part of ion 32 corresponds to $N^{18}O$, the $^{18}O\%$ content in dioxygen is lower than 1%). This means that, at least during TPD, zeolitic oxygens are incorporated into the products. This agrees with Valyon's experiments [15] performed at 500 °C.

The mechanism of IE in NO atmosphere also differs from that of N_2O: the "multiple-step" (R″) exchange clearly operates—the Q value strongly decreases, but the 36/34 ratio remains constant (figure 4(a)). The dashed curve calculated for the operation of R″ mechanism is close to the experimental curve and strongly deviates from the theoretical "single-step" mechanism (dotted). Dioxygen obviously stays at the catalyst for time that is sufficiently long to exchange both atoms prior to the desorption. For comparison, the Q and 36/34 ratio time dependencies for the $N_2O + {}^{18}O_2$ reaction at 200 °C are depicted in figure 4(b): the single R′ mechanism operates in this case similarly, as was found for the IE at RT after N_2O decomposition (cf. figure 1—Q value increases and the 36/34 ratio decreases).

IE during the reaction of the $NO_2 + {}^{18}O_2$ mixture at 250 °C proceeds obviously via the R″ mechanism, as follows from figure 4(c). Interaction of NO_2 alone and of its mixture with $^{18}O_2$ over Fe/FER (Fe/Al = 0.026) at 250 °C is displayed in figure 5 (a) and (b), respectively. The TPD curves are given in the right column of the figure. The reaction of NO_2 alone leads to a partial

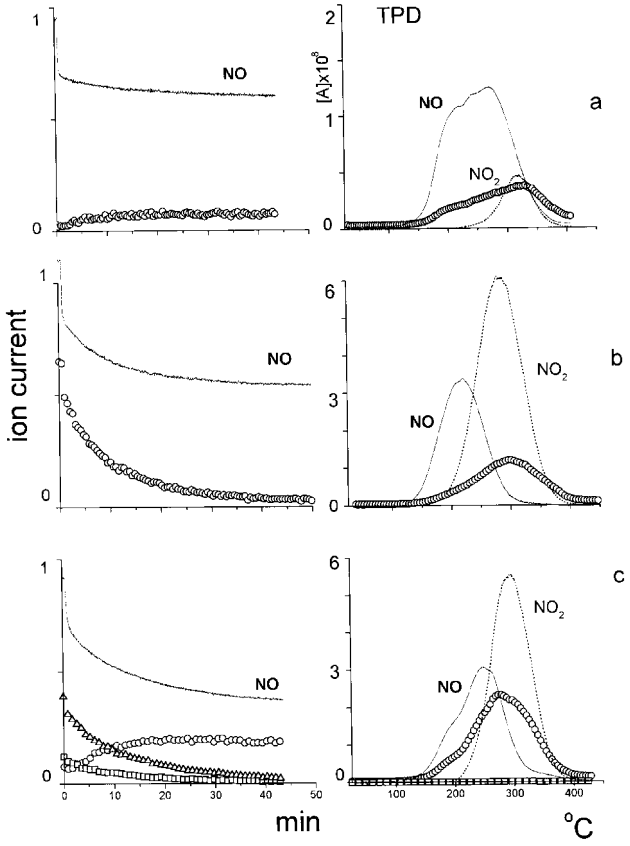

Figure 3. Interaction of NO alone and with dioxygen over Fe/FER (Fe/Al 0.026) at 200 °C. Left column: the time dependence of the amounts of reactants and right column: following TPD. (a) NO alone, (b) $NO + {}^{16}O_2$, 1/10 ratio and (c) $NO + {}^{18}O_2$, 1/10 ratio, all dioxygens are multiplied by a factor of 10; circles for $^{16}O_2$, squares for $^{18}O^{16}O$, triangles for $^{18}O_2$, points skipped (frequency 20).

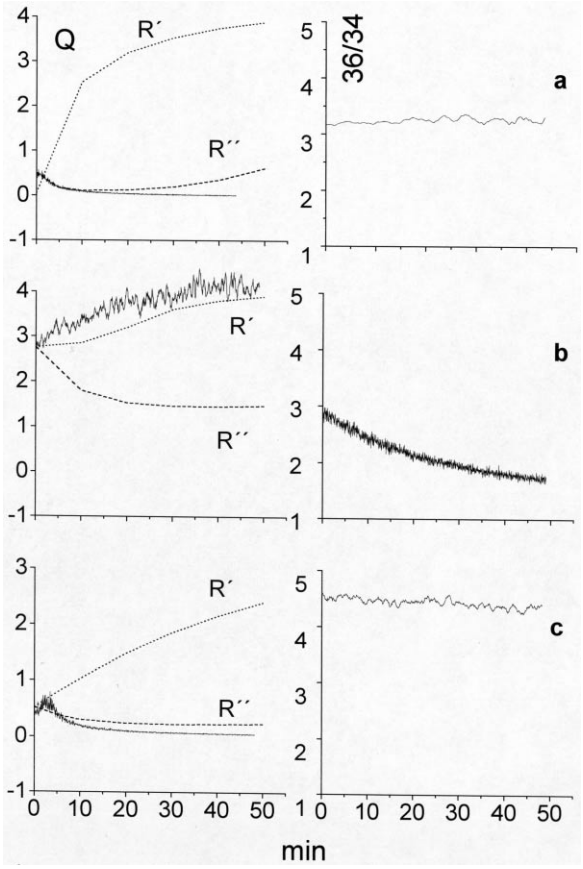

Figure 4. Q and $[^{18}O_2]/[^{16}O^{18}O_2]$ values during the reactions of nitrogen oxides at 200–250 °C. Left-hand side: experimental Q values (solid), Q values calculated for the operation of the R′ mechanism alone (dotted curve) or the R″ mechanism alone (dashed curve). Right-hand side: the ratios of ions 36/34 ($^{18}O_2/^{16}O^{18}O$), (a) NO, (b) N_2O, and (c) NO_2.

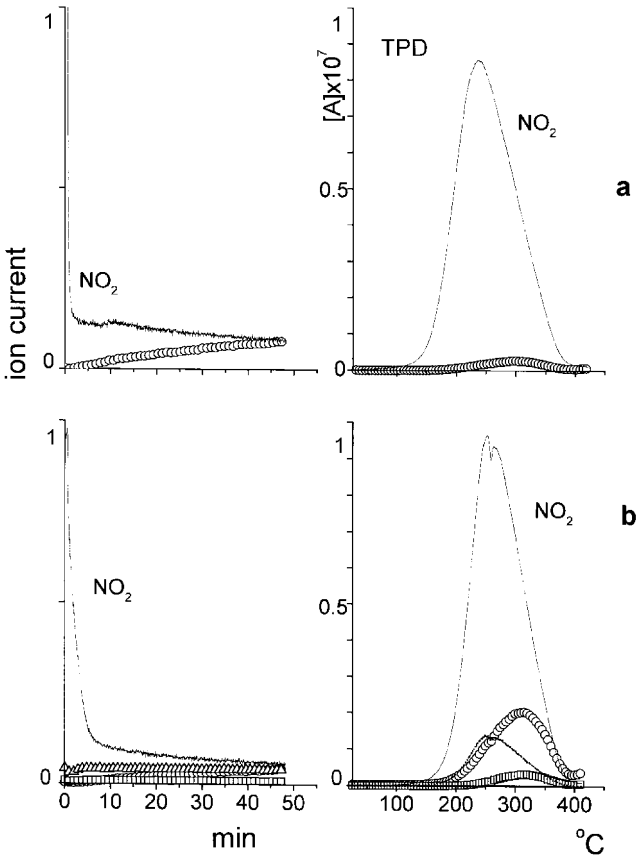

Figure 5. Interaction of NO_2 alone and with labeled dioxygen over Fe/FER (Fe/Al 0.026) at 250 °C. Left column: the time dependence of the amounts of reactants and right column: following TPD. (a) NO alone and (b) NO + $^{18}O_2$, 1/10 ratio, dioxygen displayed in both columns is multiplied by a factor of 10; circles for $^{16}O_2$, squares for $^{18}O^{16}O$, triangles for $^{18}O_2$, points skipped (frequency 20), TPD column: dotted curve for $N^{18}O^{16}O$ is multiplied by a factor of 10.

decomposition: dioxygen appears in the gas phase (figure 5(a), left); this is evidently due to the equilibrium between nitric and dioxygen molecules. The presence of $^{18}O_2$ (figure 5(b), left) does not affect the consumption of NO_2. However, the ^{18}O concentration during the reaction decreases, mainly because of the release of unlabeled dioxygen from NO_2. Complete mixing of all oxygens from NO_2 with labeled oxygens should give only 8.5% of ^{18}O, while the experimental value is ca. 47%. TPD products contain 15% of ^{18}O in NO_2 and 8% in dioxygen which means that some zeolitic oxygens are again included in the desorption products. The amount of surface species released during the TPD is not affected by the presence of dioxygen and is lower than from NO. When the interactions of NO_2 were examined at 200 °C, no release of dioxygen nor any IE was found.

It should be noted that all the reactions under study behave basically in the same way regardless of the Fe/Al ratio (0.026–0.07). All these samples contain very low amounts of iron, predominantly in cationic form (cf. papers cited in reference [7]).

4. Conclusions

Only nitrous oxide leaves active oxygen species on Fe-ferrierites (Fe/Al < 0.1) at 200–250 °C. This oxygen is exchangeable for $^{18}O_2$ at room temperature and the isotopic exchange proceeds via the "single-step" mechanism. This mechanism also operates during the reaction of an $N_2O/^{18}O_2$ mixture at 200 °C.

The oxygens of NO are readily exchanged with labeled dioxygen at 200 °C; IE proceeds via the "multiple-step" route. Desorbed surface species following NO + O_2 reaction consist predominantly of nitrogen dioxide.

Nitrogen dioxide alone does not release dioxygen when interacting with Fe-ferrierites and does not undergo IE in $NO_2/^{18}O_2$ mixture at 200 °C. However, both processes occur at 250 °C. The IE mechanism corresponds to the "multiple-step" exchange mechanism similarly to that of NO.

The isotopic composition of dioxygen released during the TPD of all the nitrogen oxides used shows that zeolitic oxygens participate in IE above 250 °C. Higher temperature is, therefore, needed for labialization of the

zeolitic oxygens during the interaction with nitrogen oxides.

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