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Isotopic Study of NO_x Decomposition over Cu- or Co-Exchanged ZSM-5 Zeolite Catalysts

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The decomposition of NO_x over Cu^{2+}- and Co^{2+}-exchanged ZSM-5 zeolites was investigated using isotope labeled $^{15}N^{18}O$ and temperature-programmed desorption (TPD) technique. We found that formation of NO_2 intermediates is responsible for enhancing the rate of NO_x decomposition when the catalysts were treated in both $^{15}N^{18}O$ and O_2. Co-adsorption of $^{15}N^{18}O$ and O_2 led to a dramatic increase in the amount of NO_x and O_2 adsorbed. The surface NO_x species decomposed or desorbed to form NO, O_2, N_2, and NO_2 during the TPD. This results in formation of equal amounts of $^{15}N^{16}O$ and $^{15}N^{18}O$ in NO products and 50% $^{15}N^{16}O^{18}O$, 25% $^{15}N^{16}O_2$, and 25% $^{15}N^{18}O_2$ in NO_2 products. In the absence of O_2, formation of N_2O was observed at <300°C but not NO_2. For Cu−NaZSM-5, its N_2O products are exclusively $^{15}N_2{}^{18}O$, suggesting that lattice oxygen is not involved in the formation of N_2O (it is derived solely from $^{15}N^{18}O$) and the isotope exchange between $^{15}N_2{}^{18}O$ with the zeolite lattice oxygen (^{16}O) is not significant. However, for Co−ZSM-5, formation of either N_2O or NO_2 is negligible with $^{15}N^{18}O$ treatment. Treatment in both $^{15}N^{18}O$ and O_2 resulted in some formation of N_2O, consisting of equal amounts of $^{15}N_2{}^{16}O$ and $^{15}N_2{}^{18}O$, suggesting either isotopic exchange occurred between N_2O and lattice oxygen, or between NO and lattice oxygen, or formation of N_2O involved lattice oxygen. Except that the low-temperature activity for N_2 formation for Cu−NaZSM-5 treated in $^{15}N^{18}O$ alone is due to formation of N_2O, the majority of activity for N_2 formation is due to formation of NO_2 intermediates. The main difference between Cu−NaZSM-5 and Co−NaZSM-5 is that for Cu−NaZSM-5, in addition to the low-temperature activity shared by Co−NaZSM-5, it showed significant activity for nitric oxide decomposition at high temperatures (>360°C) while Co−NaZSM-5 showed little. A TOF of $2.88 \times 10^{-4}\ s^{-1} \cdot Cu^{-1}$ for Cu−NaZSM-5 at 122°C and at 0.1 vol.% $^{15}N^{18}O$ and 0.4 vol.% O_2 is even higher than $\sim 2 \times 10^{-4}\ s^{-1} \cdot Cu^{-1}$ reported in the literature at >350°C, but at a much lower temperature. In terms of N_2 formation, Co−NaZSM-5 is about 2–3 times more active than Cu−NaZSM-5 at low temperatures (<200°C). For Cu−NaZSM-5, its activity for NO_2 decomposition is approximately 4 times higher than that for NO at 320–370°C. Co−NaZSM-5 does not show any significant activity for NO decomposition but its activity for NO_2 decomposition is comparable to Cu−NaZSM-5.

INTRODUCTION

Among the NO_x abatement strategies, direct decomposition of NO_x is preferred because no reductants are required, thus eliminating possible pollutants derived from reactions involving reducing reagents and thus simplifying the operation. Normally, direct decomposition of NO requires higher temperature than reduction by using reducing reagents. However, decomposition of NO was achieved at 400°C over Cu−ZSM-5 zeolite (1). Since then tremendous research efforts have been devoted to understanding the mechanism of NO_x activation aiming at finding more active catalysts because Cu−ZSM-5 is not sufficiently active for practical use and has stability problems.

The temperature-programmed desorption (TPD) of adsorbed NO on Co–ferrierite showed (2) in addition to the desorption of NO, a major peak of N_2 at 40–100°C and a peak of N_2O at 200–300°C, but no desorption of O_2. However, a TPD carried out in the flow of 10% O_2 in He showed a similar peak for N_2 but disappearance of the N_2O peak. It was believed that formation of N_2O indicates disproportionation of NO to N_2O and NO_2 though NO_2 was not observed as a major desorption product, and the lack of N_2O as a desorption product when O_2 is present in the carrier gas stream suggests that the O_2 suppresses the disproportionation reaction. In another TPD study (3), the formation of N_2O_3-like intermediates by co-adsorbing NO and NO_2 on Na−ZSM-5, Na−Y, and Cu−ZSM-5 zeolites was proposed. These results strongly indicate that O_2 plays an important role in the adsorption and decomposition of NO on zeolite catalysts. To address the involvement of O_2 in the decomposition of NO, its interaction with zeolite lattice oxygen, and its role in the formation of NO_x intermediates, isotope exchange and temperature-programmed experiments were conducted. The two most frequently investigated zeolite catalysts, Cu−ZSM-5 and Co−NaZSM-5, were chosen

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to compare their NO_x adsorption and decomposition behaviors.

EXPERIMENTAL

Catalysts

Cu–NaZSM-5 and Co–NaZSM-5 were prepared by refluxing a mixture containing Na–ZSM-5 (molar ratio of SiO_2 to Al_2O_3: 60) zeolite powder and 1.0 *M* $Co(NO_3)_2$ (Aldrich, AR reagent) or $Cu(NO_3)_2$ (Aldrich, AR reagent) aqueous solution at a ratio of 1 g zeolite to 20 cm^3 solution, respectively. The parent ZSM-5 zeolite contains 560 $\mu mol \cdot g^{-1}$ exchangeable protons determined by exhaustive ion exchange using 1.0 *M* $NaNO_3$ solution at room temperature. After the exchange, the solid was washed and dried, then calcined at 550°C for 6 h. Elemental analysis showed that Co–NaZSM-5 catalyst contained 1.6 wt% Co, which is equivalent to replacing 97% of the Na^+; and Cu–NaZSM-5 contained 1.9 wt% Cu, which represents 107% of the total ion exchange capacity of the parent material.

Materials

Isotope double-labeled $^{15}N^{18}O$ (1 vol.% $^{15}N^{18}O$, 1 vol.% Ar, and 98 vol.% He) was obtained from ISOTECH, and O_2 (4 vol.% O_2, 1 vol.% Ar, and 95 vol.% He) and high-purity helium (99.999 vol.% He) were obtained from Liquid Carbonic.

Temperature-Programmed Experiments

The TPD experiments were conducted in a quartz reactor. The catalyst sample (200 mg) was pretreated in 2 vol.% O_2 flowing at 100 $cm^3 \cdot min^{-1}$ before adsorption of $^{15}N^{18}O$ or $^{15}N^{18}O$ and $^{16}O_2$ was carried out. It was heated to 600°C and then held at this temperature for 60 min before being cooled to 40°C. The adsorption of $^{15}N^{18}O$ or the co-adsorption of $^{15}N^{18}O$ and O_2 was conducted for 30 min at 40°C in a 100 $cm^3 \cdot min^{-1}$ flowing stream of 0.2 vol.% $^{15}N^{18}O$ or 0.1 vol.% $^{15}N^{18}O$ and 0.4 vol.% O_2, respectively. The treated catalyst was purged in a stream of He at 100 $cm^3 \cdot min^{-1}$ for 30 min before TPD was begun. The He flow used during TPD was 40 $cm^3 \cdot min^{-1}$. The effluent was monitored by an on-line mass spectrometer (Electronic Associates, Inc.) for the following species: m^+/e: 30 for $^{15}N_2$, 31 for $^{15}N^{16}O$, 32 for $^{16}O_2$, 33 for $^{15}N^{18}O$, 34 for $^{16}O^{18}O$, 36 for $^{18}O_2$, 40 for Ar, 46 for $^{15}N_2{}^{16}O$, 47 for $^{15}N^{16}O_2$, 48 for $^{15}N_2{}^{18}O$, 49 for $^{15}N^{16}O^{18}O$, and 51 for $^{15}N^{18}O_2$. The mass spectrometer was calibrated with N_2, N_2O, NO, O_2, Ar, and NO_2. Also, under our mass spectrometer conditions, NO_2 generates a very low amount of molecular ion NO_2^+. As a result of this, when we presented NO_2 results, a large multiplying factor was used to convert the NO_2 signal to actual levels of NO_2. This made the actual levels of NO_2 have poor signal-to-noise ratio.

We were aware of previous work on gas phase reaction of NO with O_2 to form NO_2. Generally speaking, most of NO_2 formation is due to contact of the mixture of NO and O_2 with stainless-steel metal surfaces. In our experiments, we took precautions to reduce possible NO_2 formation by mixing NO and O_2 just upstream of the quartz reactor to minimize gas phase reaction. We also conducted blank experiments by passing the reaction gas stream through the empty quartz reactor. We found that the amount of NO_2 or N_2O_4 is the result of contact with catalyst surface.

RESULTS

During TPD, all possible isotope products involved using $^{15}N^{18}O$ and O_2 were monitored. However, only the critical data are presented here to elucidate the formation of different NO_x isotope species, and O_2 isotope species.

Figures 1 and 2 show the desorption of nitric oxide from Cu–NaZSM-5 and Co–NaZSM-5, after being treated either in $^{15}N^{18}O$ or in both $^{15}N^{18}O$ and O_2, respectively. There appear to be two distinct desorption regions, <280°C and >280°C. It should be pointed out that caution must be taken in interpreting the TPD data obtained using mass spectrometry operated under high ionization energy when it deals with NO and NO_2 at the same time. In our experiments, we found that NO_2 contributes substantially to NO due to its fragmentation. Therefore, the "NO" signals recorded by mass spectrometer is the sum of that from nitric oxides ($^{15}N^{16}O$ and $^{15}N^{18}O$) and that from nitrogen dioxides ($^{15}N^{16}O_2$, $^{15}N^{16}O^{18}O$, and $^{15}N^{18}O_2$). To get the actual nitric oxide signal, contributions from NO_2 are subtracted from the total "NO" signal. In this regard, $^{15}N^{16}O_2$ contributes twice as much as $^{15}N^{16}O^{18}O$ for the signal of $^{15}N^{16}O$. Likewise, $^{15}N^{18}O_2$ contributes twice as much as $^{15}N^{16}O^{18}O$

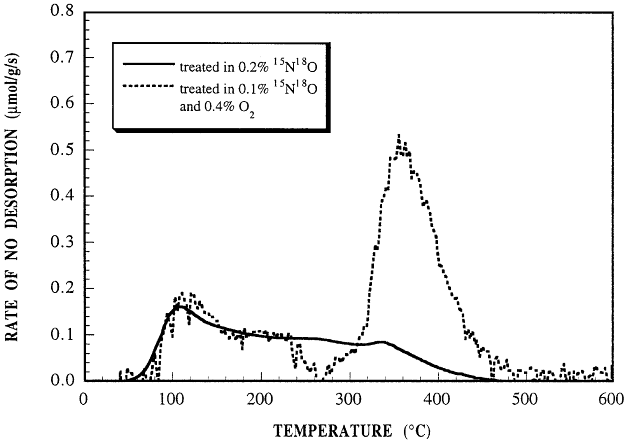


FIG. 1. Desorption of NO from Cu–NaZSM-5 zeolite during TPD after being treated in either 0.2 vol.% $^{15}N^{18}O$ or 0.1 vol.% $^{15}N^{18}O$ and 0.4 vol.% O_2 (100 $cm^3 \cdot min^{-1}$) at 40°C for 30 min; catalyst mass: 0.2 g; flow of He: 40 $cm^3 \cdot min^{-1}$; ramp rate: 30°C $\cdot$ min^{-1}.

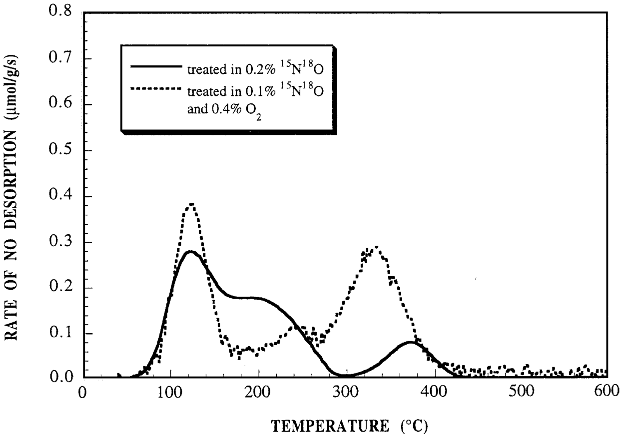


FIG. 2. Desorption of NO from Co–NaZSM-5 zeolite during TPD after being treated in either 0.2 vol.% $^{15}N^{18}O$ or 0.1 vol.% $^{15}N^{18}O$ and 0.4 vol.% O_2 (100 cm$^3 \cdot$ min^{-1}) at 40°C for 30 min; catalyst mass: 0.2 g; flow of He: 40 cm$^3 \cdot$ min^{-1}; ramp rate: 30°C $\cdot$ min^{-1}.

for $^{15}N^{18}O$. $^{15}N^{16}O^{18}O$ contributes to both $^{15}N^{16}O$ and $^{15}N^{18}O$.

The desorption of $^{15}N^{18}O$-treated Cu–NaZSM-5 occurred at 80–400°C, giving a broad desorption band at 100–350°C. Treating the same catalyst in both $^{15}N^{18}O$ and O_2 led to great enhancement in the amount of NO adsorbed at high temperatures (>300°C) but seemed to have little effect on the broad peak in the low-temperature region. The NO peak at 370°C was increased by a factor of 6.

For Co–NaZSM-5 (Fig. 2), the TPD of $^{15}N^{18}O$ treatment shows at least three NO desorption peaks, at 130, 210, and 370°C. Treating in both $^{15}N^{18}O$ and O_2 led to a significant increase in the amount of NO adsorbed at 280–400°C and disappearance of the peak at ~210°C. In addition, it also results in shifting the high-temperature peak to a lower temperature by 40–50°C.

The isotope compositional change of desorbed NOs during the TPD is given in Figs. 3a and 3b for Cu–NaZSM-5 treated in 0.2 vol.% $^{15}N^{18}O$ or in both 0.1 vol.% $^{15}N^{18}O$ and 0.4 vol.% O_2, respectively. When treated in $^{15}N^{18}O$ alone, $^{15}N^{18}O$ is the predominant desorption product at <350°C. Desorption of $^{15}N^{16}O$ was insignificant until reaching 300°C. When treated in both $^{15}N^{18}O$ and O_2, the desorption of $^{15}N^{18}O$ and $^{15}N^{16}O$ has virtually the exact same characteristics and equal amounts with respect to the two corresponding peaks at 140 and 350°C.

The product distribution during TPD of Co–NaZSM-5 treated in either $^{15}N^{18}O$ or $^{15}N^{18}O$ and O_2 are given in Figs. 4a and 4b, respectively. Unlike Cu–NaZSM-5, treating in $^{15}N^{18}O$ resulted in formation of a significant amount of $^{15}N^{16}O$ at temperatures 100–300°C. Despite this, $^{15}N^{18}O$ is the major desorption product until the temperature reached 300°C. Above this temperature, there is more $^{15}N^{16}O$ desorbed than $^{15}N^{18}O$. Similar to Cu–NaZSM-5, the TPD of $^{15}N^{18}O$ and O_2 treatment led to desorption of equal amounts of $^{15}N^{16}O$ and $^{15}N^{18}O$. The desorption characteristics of the two products are identical, suggesting that they may come from the same intermediate.

The formation of N_2 during the TPD of Cu–ZSM-5 treated either in $^{15}N^{18}O$ or in both $^{15}N^{18}O$ and O_2 is given in Fig. 5. This clearly shows that formation of N_2 occurs at temperature above 70°C. However, the amount of N_2 formed in the $^{15}N^{18}O$-treated catalyst is much less than that treated in both $^{15}N^{18}O$ and O_2. Most of N_2 is formed at below 300°C in the former, while there are two peaks, at 130 and 335°C, in the latter.

Figure 6 gives the formation of N_2 during TPD of Co–NaZSM-5 treated in 0.2 vol.% $^{15}N^{18}O$ or in 0.1 vol.% $^{15}N^{18}O$ and 0.4 vol.% O_2. Formation of N_2 is negligible when reacted in $^{15}N^{18}O$ alone. However, when treated in both $^{15}N^{18}O$ and O_2, formation of N_2 has drastically increased, especially at temperatures below 400°C.

Figures 7a and 7b give the formation of N_2O and NO_2 from Cu–NaZSM-5 during the TPD. For the $^{15}N^{18}O$-treated

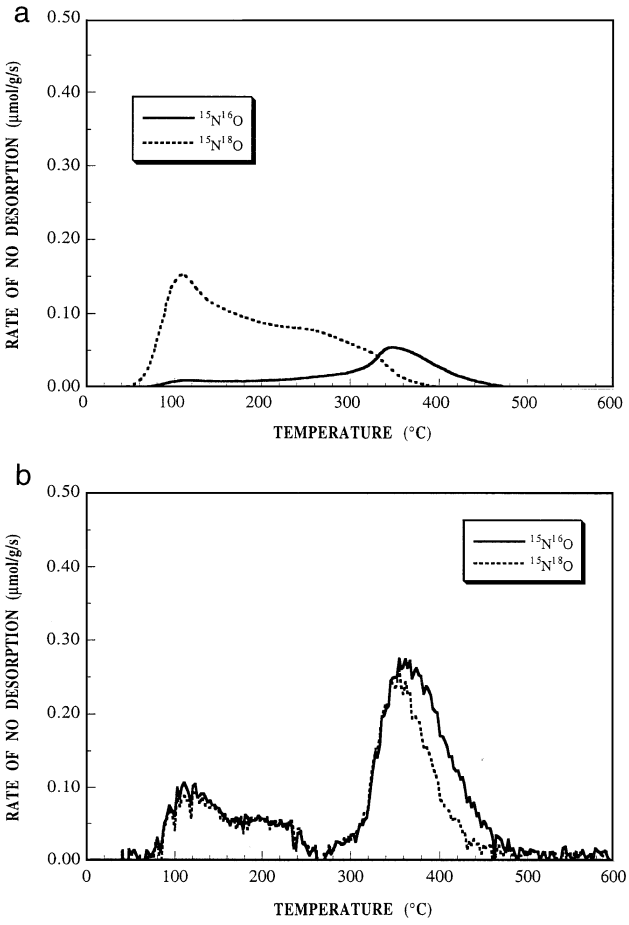


FIG. 3. Desorption of different NO isotope products from Cu–ZSM-5 zeolite catalyst during TPD after being treated in (a) 0.2 vol.% $^{15}N^{18}O$ (100 cm$^3 \cdot$ min^{-1}) and (b) 0.1 vol.% $^{15}N^{18}O$ and 0.4 vol.% O_2 (100 cm$^3 \cdot$ min^{-1}) at 40°C for 30 min; catalyst mass: 0.2 g; flow of He: 40 cm$^3 \cdot$ min^{-1}; ramp rate: 30°C $\cdot$ min^{-1}.

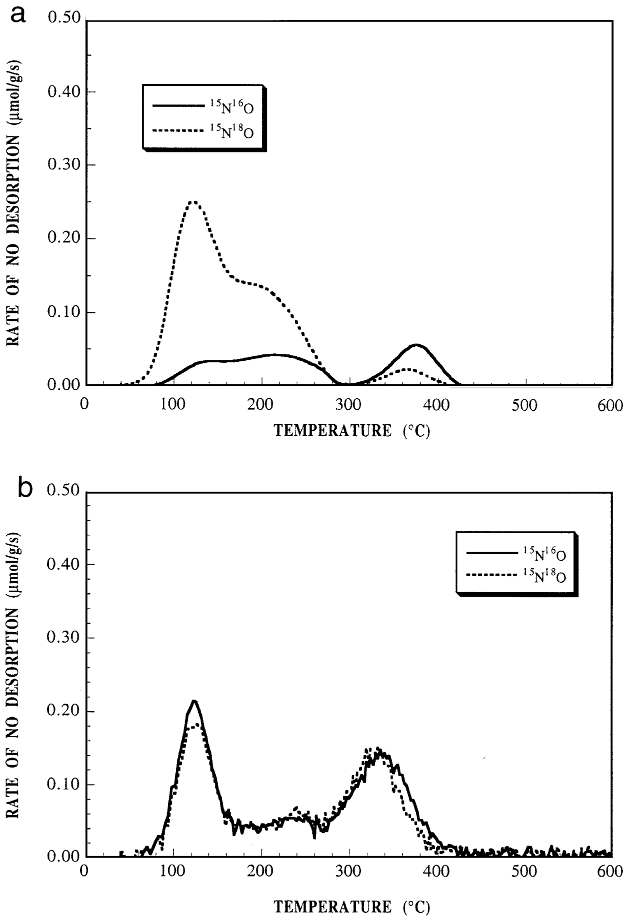


FIG. 4. Desorption of different NO isotope products from Co–ZSM-5 zeolite catalyst during TPD after being treated in (a) 0.2 vol.% $^{15}N^{18}O$ (100 $cm^3 \cdot min^{-1}$) and (b) 0.1 vol.% $^{15}N^{18}O$ and 0.4 vol.% O_2 (100 $cm^3 \cdot min^{-1}$) at 40°C for 30 min; catalyst mass: 0.2 g; flow of He: 40 $cm^3 \cdot min^{-1}$; ramp rate: 30°C $\cdot$ min^{-1}.

catalyst, no desorption of NO_2 was observed; $^{15}N_2{}^{18}O$ was the exclusive N_2O product. It was formed at temperature $\leq$250°C. When treated in both $^{15}N^{18}O$ and O_2, large amounts of NO_2 were formed but no N_2O was detected. There are two NO_2 peaks, at 260 and 330°C.

The formation of N_2O and NO_2 during the TPD of Co–NaZSM-5 treated in both $^{15}N^{18}O$ and O_2 are given in Figs. 8a and 8b, respectively. Desorption of N_2O mostly occurred at temperatures below 300°C. The desorptions of $^{15}N_2{}^{18}O$ and $^{15}N_2{}^{16}O$ follow the same pattern and their amounts are virtually the same. There is also a single broad NO_2 peak at temperatures <300°C. Three NO_2 products are formed, $^{15}N^{18}O^{16}O$, $^{15}N^{18}O_2$, and $^{15}N^{16}O_2$. Their desorption characteristics are identical. The amount of $^{15}N^{18}O_2$ is equal to that of $^{15}N^{16}O_2$, and each represents 25% of the total; the remaining 50% is a mixed isotope product, $^{15}N^{18}O^{16}O$. When treated in $^{15}N^{18}O$ alone, neither N_2O nor NO_2 are formed.

Formation of O_2 during the TPD of Cu–NaZSM-5 treated in $^{15}N^{18}O$ is shown in Fig. 9a. Significant desorption of O_2 occurred at temperatures above 300°C when treated in $^{15}N^{18}O$ alone (Fig. 9a). All three isotope O_2 products are formed, but $^{16}O_2$ is predominant, followed by $^{16}O^{18}O$. The amount of $^{18}O_2$ formed is very small. Formation of O_2 during the TPD of Cu–NaZSM-5 treated in $^{15}N^{18}O$ and O_2 is given in Fig. 9b. It shows two desorption peaks, at 125 and 350°C. The low-temperature peak consists exclusively of $^{16}O_2$, while the high-temperature peak contains all three isotope products, their quantities decreasing in the order $^{16}O_2$, $^{16}O^{18}O$, and $^{18}O_2$. The amount of O_2 desorbed from the $^{15}N^{18}O$-and-O_2-treated catalyst is more than one order of magnitude greater than that treated in $^{15}N^{18}O$ alone. To highlight the importance of treatment gas stream on the composition of adsorbed NO_x intermediates, the desorption results are presented in Table 1 as NO, N_2O, NO_2, and O_2 at <280°C and >280°C.

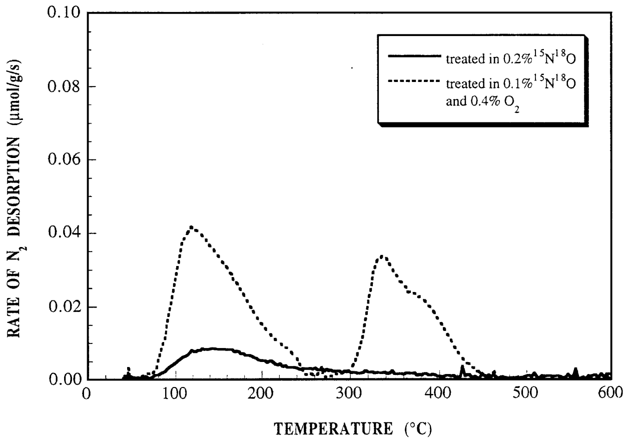


FIG. 5. Formation of $^{15}N_2$ from Cu–ZSM-5 zeolite catalyst during TPD after being treated in either 0.2 vol.% $^{15}N^{18}O$ or 0.1 vol.% $^{15}N^{18}O$ and 0.4 vol.% O_2 (100 $cm^3 \cdot min^{-1}$) at 40°C for 30 min; catalyst mass: 0.2 g; flow of He: 40 $cm^3 \cdot min^{-1}$; ramp rate: 30°C $\cdot$ min^{-1}.

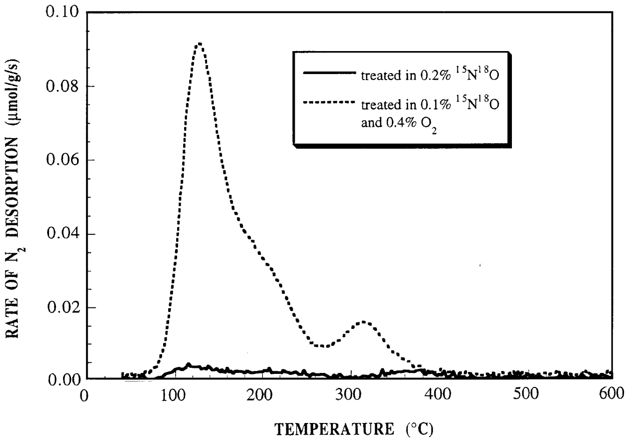


FIG. 6. Formation of $^{15}N_2$ from Co–ZSM-5 zeolite catalyst during TPD after being treated in either 0.2 vol.% $^{15}N^{18}O$ or 0.1 vol.% $^{15}N^{18}O$ and 0.4 vol.% O_2 (100 $cm^3 \cdot min^{-1}$) at 40°C for 30 min; catalyst mass: 0.2 g; flow of He: 40 $cm^3 \cdot min^{-1}$; ramp rate: 30°C $\cdot$ min^{-1}.

Figure 9c compares the O_2 desorption profiles of Cu–NaZSM-5 treated in different gas streams, in 1 vol.% O_2, in 0.2 vol.% $^{15}N^{18}O$, and 0.1 vol.% $^{15}N^{18}O$, and 0.5 vol.% O_2. It clearly shows that the treatment in O_2 only leads to adsorption of a small amount of O_2.

Formation of O_2 during the TPD of Co–NaZSM-5 treated in 0.2 vol.% $^{15}N^{18}O$ or in both 0.1 vol.% $^{15}N^{18}O$ and 0.4 vol.% O_2 is given in Figs. 10a and 10b, respectively. When treated in $^{15}N^{18}O$ alone, major desorption occurred at >300°C, and a small broad peak occurred at 80–260°C. In the low-temperature region, it is exclusively $^{16}O_2$. For the high-temperature peak, both $^{16}O_2$ and $^{16}O^{18}O$ are major products, while $^{18}O_2$ is minor. When treated in both 0.1 vol.% $^{15}N^{18}O$ and 0.4 vol.% O_2, it shows two desorption peaks, at 130 and 330°C. The low-temperature peak is exclusively $^{16}O_2$, while the high-temperature peak contains all three isotope products. Figure 10c shows the effect of the composition of treatment gas stream on the desorption of O_2 from Co–NaZSM-5.

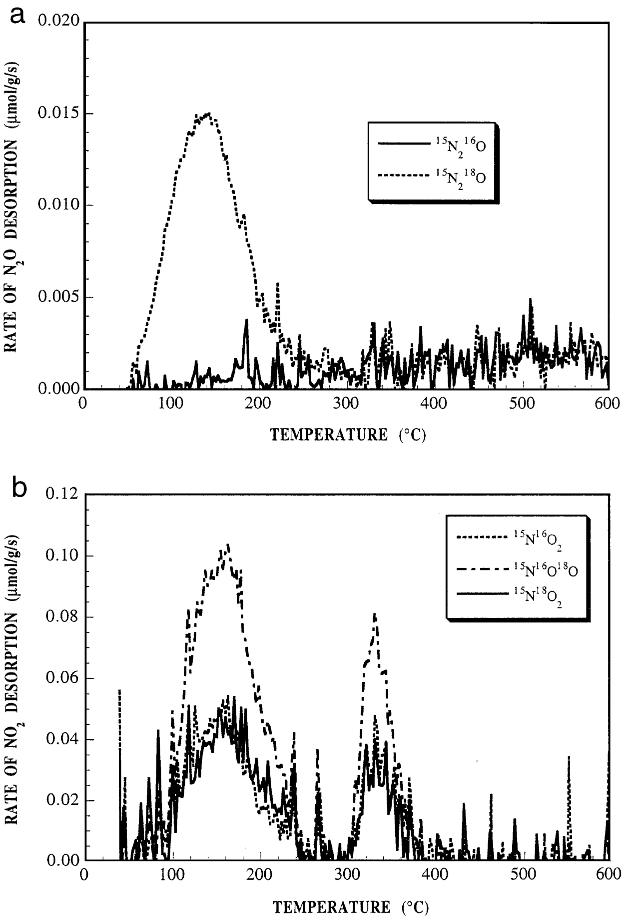


FIG. 7. Desorption of different (a) N_2O isotope products from Cu–ZSM-5 zeolite catalyst during TPD after being treated in 0.2 vol.% $^{15}N^{18}O$ (100 $cm^3 \cdot min^{-1}$) and (b) NO_2 isotope products after being treated in 0.1 vol.% $^{15}N^{18}O$ and 0.4 vol.% O_2 (100 $cm^3 \cdot min^{-1}$) at 40°C for 30 min; catalyst mass: 0.2 g; flow of He: 40 $cm^3 \cdot min^{-1}$; ramp rate: 30°C $\cdot$ min^{-1}.

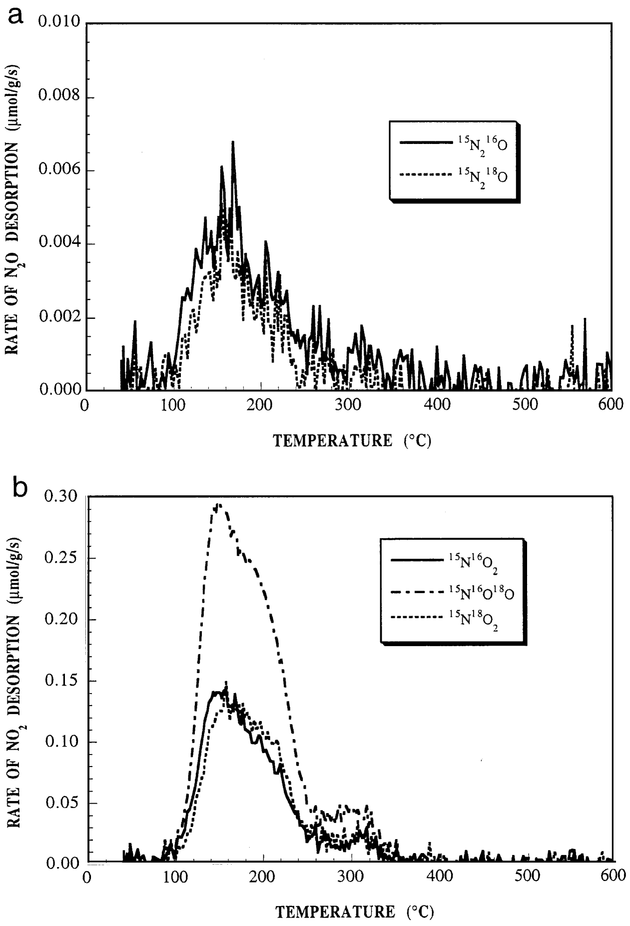


FIG. 8. Desorption of different (a) N_2O isotope products and (b) NO_2 isotope products from Co–ZSM-5 zeolite catalyst during TPD after being treated in 0.1 vol.% $^{15}N^{18}O$ and 0.4 vol.% O_2 (100 $cm^3 \cdot min^{-1}$) at 40°C for 30 min; catalyst mass: 0.2 g; flow of He: 40 $cm^3 \cdot min^{-1}$; ramp rate: 30°C $\cdot$ min^{-1}.

DISCUSSION

Upon exposure of zeolite catalysts to either $^{15}N^{18}O$ or a mixture $^{15}N^{18}O$ and O_2, a significant amount of $^{15}N^{16}O$ was observed in the reactor effluent. This indicates that isotope exchange between $^{15}N^{18}O$ and the zeolite framework oxygen, or oxygen adsorbed on the catalyst, occurred at this low temperature. The amount of such isotope exchange varied with the catalyst. The exchange ceased when saturation adsorption was achieved, suggesting that the process occurred by adsorption of $^{15}N^{18}O$ on the zeolites. No other products were found in the effluent, suggesting that neither disproportionation to form N_2O and NO_2 nor decomposition to N_2 and O_2 were significant at this temperature. No attempts were made to quantify the degree of exchange. A detailed analysis of isotope exchange between $^{15}N^{18}O$ and the framework oxygen (^{16}O) of Cu–ZSM-5 and Fe–MOR zeolites at high temperatures (∼500°C) was reported previously (4).

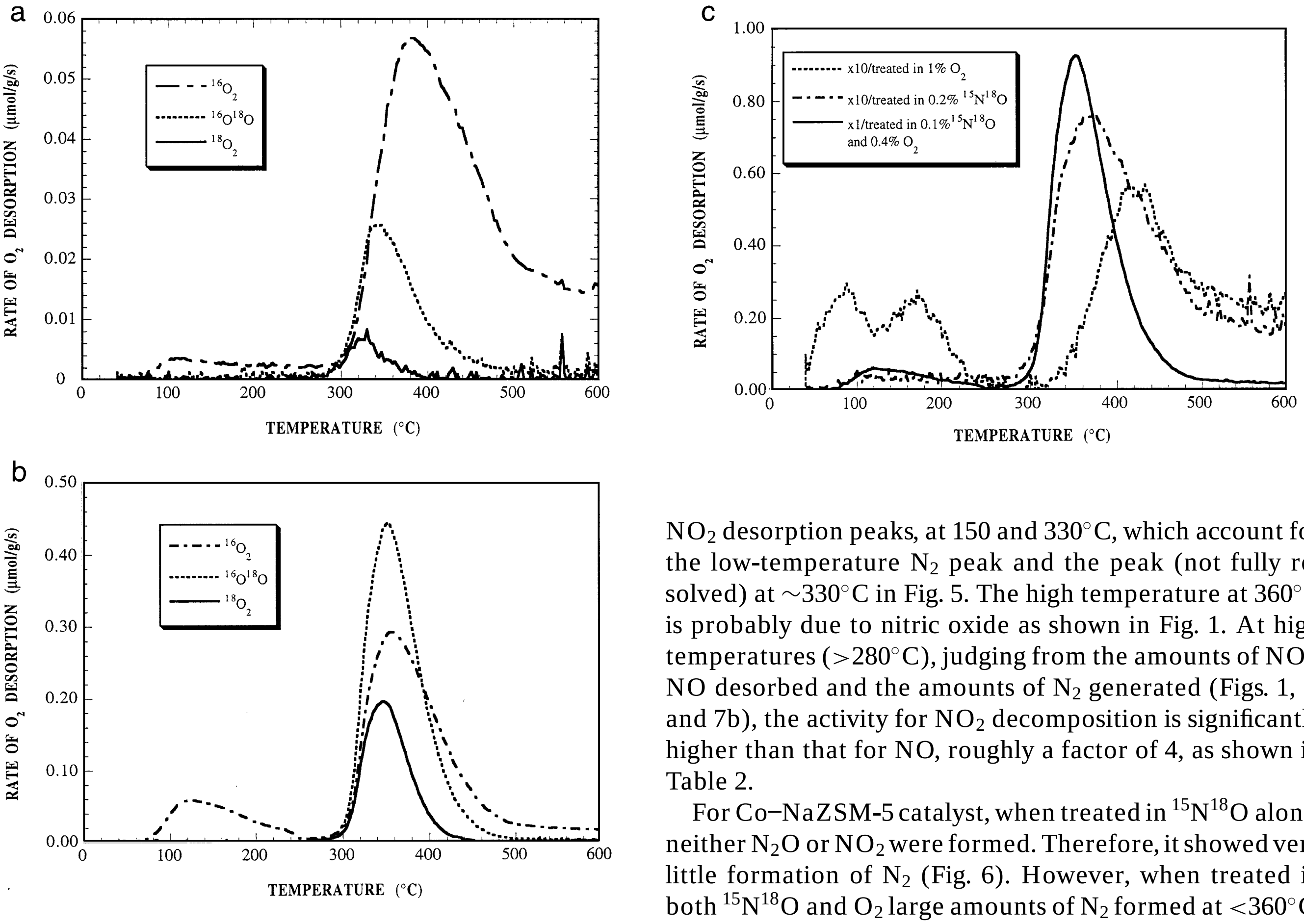


FIG. 9. Desorption of different O_2 isotope products from Cu–ZSM-5 zeolite catalyst during TPD after being treated in (a) 0.2 vol.% $^{15}N^{18}O$, (b) 0.1 vol.% $^{15}N^{18}O$ and 0.4 vol.% O_2, and (c) different treatment gas streams (100 $cm^3 \cdot min^{-1}$) at 40°C for 30 min; catalyst mass: 0.2 g; flow of He: 40 $cm^3 \cdot min^{-1}$; ramp rate: 30°C $\cdot$ min^{-1}.

Figures 5 and 6 show that the decomposition of NO_x measured as the formation of $^{15}N_2$ over Cu–NaZSM-5 and Co–NaZSM-5 is strongly affected by the composition of treatment gas streams. When treated in $^{15}N^{18}O$ alone, formation of $^{15}N_2$ is small. However, treating in a mixture of $^{15}N^{18}O$ and $^{16}O_2$ results in great enhancement in the rate of $^{15}N_2$ formation. This enhancement cannot be explained by the adsorbed nitric oxide species because the amount and adsorption characteristics of adsorbed NO did not change much (Figs. 1 and 2), particularly, relative to the great enhancement in low-temperature activity. For Cu–NaZSM-5, the enhancement in N_2 formation rate at 130°C is increased by a factor of >4; for Co–NaZSM-5, the rate of N_2 formation at 130°C is increased by a factor of >20.

The similarity between the N_2 formation (Fig. 5) and the desorption of NO_2 (Fig. 7b) leads us to suggest that the formation of N_2 is the result of formation of NO_2. In Fig. 5, it appears that there are two peaks at temperatures above 300°C, around 330 and 360°C. Figure 7b shows two NO_2 desorption peaks, at 150 and 330°C, which account for the low-temperature N_2 peak and the peak (not fully resolved) at ~330°C in Fig. 5. The high temperature at 360°C is probably due to nitric oxide as shown in Fig. 1. At high temperatures (>280°C), judging from the amounts of NO_2, NO desorbed and the amounts of N_2 generated (Figs. 1, 5, and 7b), the activity for NO_2 decomposition is significantly higher than that for NO, roughly a factor of 4, as shown in Table 2.

For Co–NaZSM-5 catalyst, when treated in $^{15}N^{18}O$ alone, neither N_2O or NO_2 were formed. Therefore, it showed very little formation of N_2 (Fig. 6). However, when treated in both $^{15}N^{18}O$ and O_2 large amounts of N_2 formed at <360°C. This corresponds to formation of predominantly NO_2 at <340°C shown in Fig. 8b.

Figures 5 and 7a show that the formation of N_2 on Cu–NaZSM-5 treated in NO alone is cocurrent with the desorption of N_2O, suggesting that the NO_x decomposition activity may be due to N_2O rather than NO. The formation of N_2 is also accompanied by the formation of O_2 and the ratio of N_2 to O_2 is roughly close to 2 to 1, as expected from N_2O decomposition.

We found that in the low-temperature region, $^{16}O_2$ is the only isotope product. This seems to contradict to the results presented in Figs. 3a and 7a, where ^{18}O is shown to be the predominant oxygen source in both NO and N_2O species. There could be two explanations for this, one being that the isotope exchange between $^{18}O_2$ formed from decomposition of $^{15}N_2{}^{18}O$ undergoes fast exchange with lattice oxygen of Cu–NaZSM-5, which is predominantly ^{16}O, the other being that the ^{18}O formed from decomposition of $^{15}N_2{}^{18}O$ exchanges with lattice ^{16}O at a much faster rate then the rate of combination of two ^{18}O moieties. Previous work on temperature-programmed isotope exchange between gas phase $^{18}O_2$ and zeolite lattice oxygen or chemisorbed O_2 on Cu–NaZSM-5 zeolite catalyst by Chang *et al.* (5) showed that isotope exchange at temperatures below 250°C is negligible. It was found that significant amounts of lattice oxygen

TABLE 1

Composition of Adsorbed NO$_x$ Species on Cu–NaZSM-5 and Co–NaZSM-5 Catalysts

	Amount of products desorbed (μmol $\cdot$ g^{-1})							
	NO		N_2O		NO_2		O_2	
Catalyst	$^{15}N^{18}O$	$^{15}N^{18}O + O_2$	$^{15}N^{18}O$	$^{15}N^{18}O + O_2$	$^{15}N^{18}O$	$^{15}N^{18}O + O_2$	$^{15}N^{18}O$	$^{15}N^{18}O + O_2$
Co–NaZSM-5	69.6[a]	74.6	0	1.8	0	115.8	2.2	19.4
	10.4[b]	42.3	0	0.2	0	8.5	9.3	30.4
Cu–NaZSM-5	49.2[a]	43.6	4.1	0	0	38.7	1.2	12.2
	14.4[b]	98.4	0	0	0	8.4	23.5	153.3

Note. Catalyst mass: 0.2 g; NO-treated: 0.2 vol.% $^{15}N^{18}O$ at 100 cm^3/min; NO + O_2 treated: 0.1 vol.% $^{15}N^{18}O$ and 0.4 vol.% O_2 at 100 cm^3/min; TPD: heating rate: 30°C/min in He at 40 cm^3/min.

[a] Desorbed at ≤280°C.

[b] Desorbed at >280°C.

could be exchanged with gas phase $^{18}O_2$ but at higher temperature (>250°C). Both doubly exchanged $^{16}O_2$ and singly exchanged $^{16}O^{18}O$ were formed. It has been suggested (6) that for transition metal oxides isotope exchanges between gas phase oxygen and lattice oxygen involving two oxygen atoms from surface oxide predominate. Such an exchange occurs by virtue of dissociative adsorption of dioxygen followed by desorption of molecules with modified isotope composition and requires high temperatures (>250°C). In any case, it is unlikely that at low temperatures (<250°C), the lack of $^{18}O_2$ or $^{16}O^{18}O$ as products is caused by isotope exchange between $^{18}O_2$ formed and lattice oxygen (^{16}O).

In ZSM-5 zeolite, all its lattice oxygens (either bridging an aluminum atom and a silicon or two silicon atoms) may be treated as surface oxygens because they all are accessible to incoming molecules. Thus, if the surface ^{16}O and ^{18}O mix rapidly enough, the isotope composition of desorbed molecules corresponds to the ratio of the surface concentration of isotopes. To estimate surface population of ^{16}O and ^{18}O on the catalyst surface amounts of ^{18}O and ^{16}O adsorbed on Cu–NaZSM-5 and Cu–NaZSM-5, catalysts measured as No, N_2O, NO_2, and O_2 are given in Table 3. The surface of Cu–NaZSM-5 after being treated in $^{15}N^{18}O$ alone in populated with roughly the same amount of ^{16}O (54.5 μmol $\cdot$ g^{-1}) and ^{18}O (58.4 μmol $\cdot$ g^{-1}); however, a predominant amount (40 μmol $\cdot$ g^{-1}) of the ^{16}O is in the form of $^{16}O_2$ which is unable to participate in the isotope exchange at low temperature. In effect, it is much more heavily populated by exchangeable ^{18}O than by ^{16}O. Thus, we should expect to see more ^{18}O-rich O_2 products. This is in contradiction with exclusive formation of $^{16}O_2$ which we observed (Fig. 9a). This is because the amount of oxygen adsorbed on the surface only accounts for a very small fraction of the total oxygen available for isotope exchange which is the sum of adsorbed and zeolite lattice oxygen. The latter is estimated as 3.317×10^4 μmol $\cdot$ g^{-1}. Although we do not have an exact measurement of how much lattice ^{16}O is exchanged by ^{18}O, based on the pretreatment condition (40°C) used in our experiments, it is estimated significantly below 1%, implying that the surface actually is predominantly ^{16}O (>99%). Also, given the low concentration of $^{15}N_2{}^{18}O$ on the surface, the concentration of ^{18}O formed from $^{15}N_2{}^{18}O$

TABLE 2

Summary of NO Decomposition Results Obtained from TPD Measurements[a]

	TPD results			
Catalyst	Max. N_2 formation (μmol $\cdot$ g^{-1} $\cdot$ s^{-1})	TOF × 10^3 (molec $\cdot$ M^{-1} $\cdot$ s^{-1})[b]	Max. conversion (%)	Temperature (°C)
Cu–NaZSM-5-107	0.042	0.288	29.6 (NO_2)	122
	0.033	0.227	30.6 (NO_2)	335
	0.025	0.172	8.3 (NO)	365
Co–NaZSM-5-97	0.092	0.686	23.5 (NO_2)	130
	0.015	0.112	23.1 (NO_2)	320

[a] TPD: 0.2 g catalyst, He: 40 cm^3 $\cdot$ min^{-1}, ramp rate: 30°C $\cdot$ min^{-1}; catalyst pretreated in 0.1 vol.% $^{15}N^{18}O$ and 0.4 vol.% O_2 at 40°C for 30 min (flow rate: 100 cm^3 $\cdot$ min^{-1}).

[b] TOF: turnover frequency number of NO$_x$ molecules converted per metal site per second.

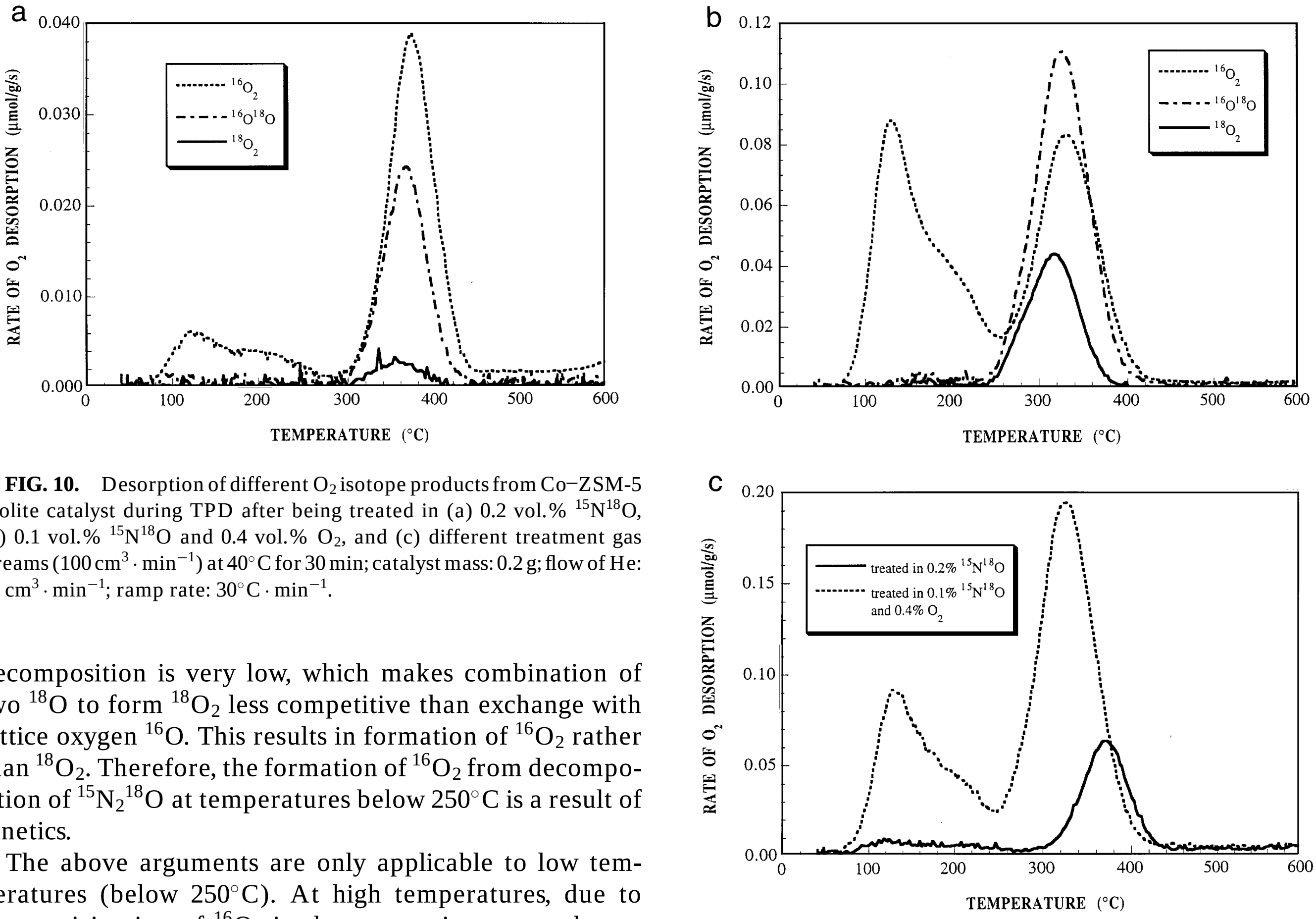


FIG. 10. Desorption of different O_2 isotope products from Co–ZSM-5 zeolite catalyst during TPD after being treated in (a) 0.2 vol.% $^{15}N^{18}O$, (b) 0.1 vol.% $^{15}N^{18}O$ and 0.4 vol.% O_2, and (c) different treatment gas streams (100 $cm^3 \cdot min^{-1}$) at 40°C for 30 min; catalyst mass: 0.2 g; flow of He: 40 $cm^3 \cdot min^{-1}$; ramp rate: 30°C · min^{-1}.

decomposition is very low, which makes combination of two ^{18}O to form $^{18}O_2$ less competitive than exchange with lattice oxygen ^{16}O. This results in formation of $^{16}O_2$ rather than $^{18}O_2$. Therefore, the formation of $^{16}O_2$ from decomposition of $^{15}N_2{}^{18}O$ at temperatures below 250°C is a result of kinetics.

The above arguments are only applicable to low temperatures (below 250°C). At high temperatures, due to the participation of $^{16}O_2$ in the oxygen isotope exchange processes isotope product distribution becomes complex. Table 3 shows that amounts of adsorbed surface ^{16}O and ^{18}O are drastically increased when catalysts are treated in both $^{15}N^{18}O$ and O_2. Due to substantial increases in surface concentration of ^{16}O and ^{18}O (e.g., 360 $\mu mol \cdot g^{-1}$ ^{16}O and 246 $\mu mol \cdot g^{-1}$ ^{18}O for Cu–NaZSM-5 treated in 0.1 vol.% $^{15}N^{18}O$ and 0.4 vol.% O_2), rates of recombination of two adsorbed surface oxygens to form O_2 become significant relative to rates of exchange with lattice oxygen, which results in a distribution of different isotope O_2 products reflecting the surface population of ^{16}O and ^{18}O.

Results from both Cu–NaZSM-5 and Co–NaZSM-5 show unambiguously that the NO_x decomposition activity observed at low temperatures (<340°C) is solely due to decomposition of N_2O when treated in $^{15}N^{18}O$ alone or

TABLE 3

Summary of TPD Results of Different Zeolite Catalysts Treated Either in $^{15}N^{18}O$ Alone or in Both $^{15}N^{18}O$ with $^{16}O_2$ at 40°C

		Amount of oxygen desorbed ($\mu mol \cdot g^{-1}$)							
		as NO		as N_2O		as NO_2		as O_2	
Catalyst	Treated in	^{16}O	^{18}O	^{16}O	^{18}O	^{16}O	^{18}O	^{16}O	^{18}O
Cu–NaZSM-5	$^{15}N^{18}O$	3.9[a] : 8.1[b]	40 : 7.6	0 : 0	4.1 : 0	0 : 0	0 : 0	2.5 : 40.0	0.3 : 6.4
	$^{15}N^{18}O + O_2$	38 : 56.5	38 : 42.5	0 : 0	0 : 0	39 : 11.5	39 : 11	24 : 191	0 : 116
Co–NaZSM-5	$^{15}N^{18}O$	12 : 7	51 : 3	0 : 0	0 : 0	0 : 0	0 : 0	3 : 14.2	0.2 : 4
	$^{15}N^{18}O + O_2$	83 : 27	83 : 25	0.9 : 0	0.9 : 0	116.5 : 8	116 : 8	36.5 : 41	4.5 : 26.5

Note. Catalyst mass: 0.2 g; NO-treated: 0.2 vol.% $^{15}N^{18}O$ at 100 cm^3/min; NO + O_2 treated: 0.1 vol.% $^{15}N^{18}O$ and 0.4 vol.% O_2 at 100 cm^3/min; TPD: heating rate: 30°C/min in He at 40 cm^3/min.

[a] Desorbed at ≤280°C.

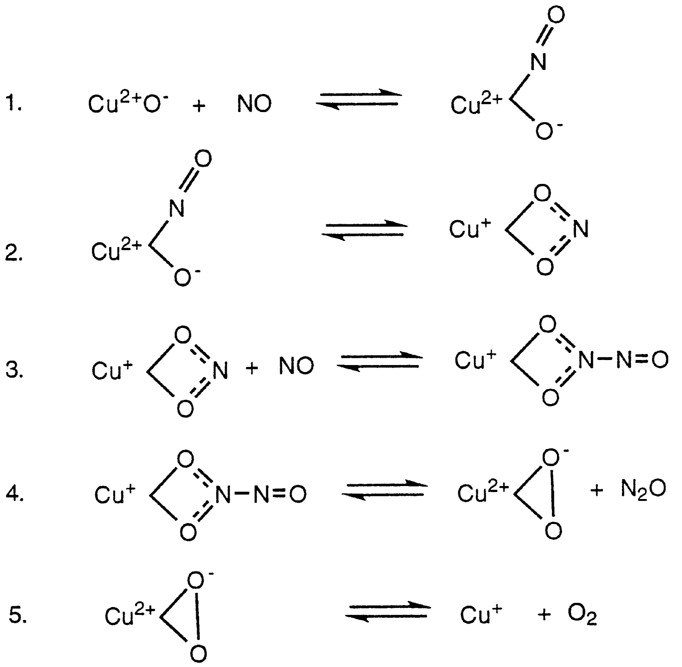
[b] Desorbed at >280°C.

NO_2 when treated in both $^{15}N^{18}O$ and O_2 but not much from direct decomposition of NO. This is in agreement with previous results that Cu–ZSM-5 is only active for NO decomposition at high temperatures (>350°C) and Co–ZSM-5 is not capable of decomposing NO. The combination of NO_2 formation at low temperature during adsorption treatment and subsequent decomposition at temperatures (130–330°C) much lower than that required for NO on Cu–NaZSM-5 (>350°C) demonstrates that significant conversion of NO_x can be achieved. This approach may be an effective way to reduce NO emission from automotive exhaust using transition metal containing ZSM-5 catalysts.

The formation of NO_2 under NO decomposition conditions over Cu–ZSM-5 zeolites was also studied by Ciambelli *et al.* (7). They found that homogeneous oxidation of NO by O_2 to form NO_2 is negligible in a wide temperature range 150–550°C. Above 300°C the catalytic activity was high enough to give the equilibrium conversion of NO to NO_2, whereas at lower temperatures (<300°C) the rate of catalytic reaction was very low, limiting conversion of NO to NO_2. They also reported formation of NO_2 in the absence of added O_2 at high temperatures (>300°C). Our results show that in the absence of O_2 no formation of NO_2 occurs.

Previously, it was concluded by Shelef *et al.* (8) that H–ZSM-5, Cu–ZSM-5, and Cu/Al_2O_3 were capable of oxidizing NO to NO_2 and, more importantly, that the catalyst which has the highest activity for NO oxidation to NO_2 also has the highest activity for NO decomposition. Here, our detailed isotope labeling results provide unambiguous evidence that the NO_x decomposition activity of Cu–NaZSM-5 zeolites is largely due to decomposition of NO_2 or N_2O, not direct decomposition of NO. Decomposition of NO over Cu–NaZSM-5 only becomes significant at high temperatures (>350°C). More importantly, Co–NaZSM-5, an inactive catalyst for direct NO decomposition, is highly active for NO_x reduction via NO_2 intermediates at very low temperatures (<200°C).

Results presented in Figs. 5 and 9 show that desorption of N_2 is accompanied by desorption of O_2 on Cu–NaZSM-5 treated in $^{15}N^{18}O$ alone, and the ratio of N_2 to O_2 is close to 2. This, together with the N_2O peak at 150°C (Fig. 7a), suggests that stoichiometric decomposition of N_2O to N_2 and O_2 is responsible for the NO_x decomposition activity. It ought to be pointed out that no NO_2 formation was observed. Previously, others (9) suggested that lack of NO_2 during TPD is a result of its decomposition at high temperature (>300°C). However, in our experiments, we observed desorption of large amounts of NO_2 at both low temperature (160°C) and high temperature (335°C) (see Fig. 7b) over Cu–NaZSM-5, and multipeak at 140–200°C over Co–NaZSM-5 (Fig. 8b) when they are treated in a mixture of $^{15}N^{18}O$ and O_2. It is obvious that formation of N_2 is via N_2O. It is unlikely that N_2O was formed by disproportionation reaction suggested by others (7, 9) since we did not observe any significant formation of NO_2.



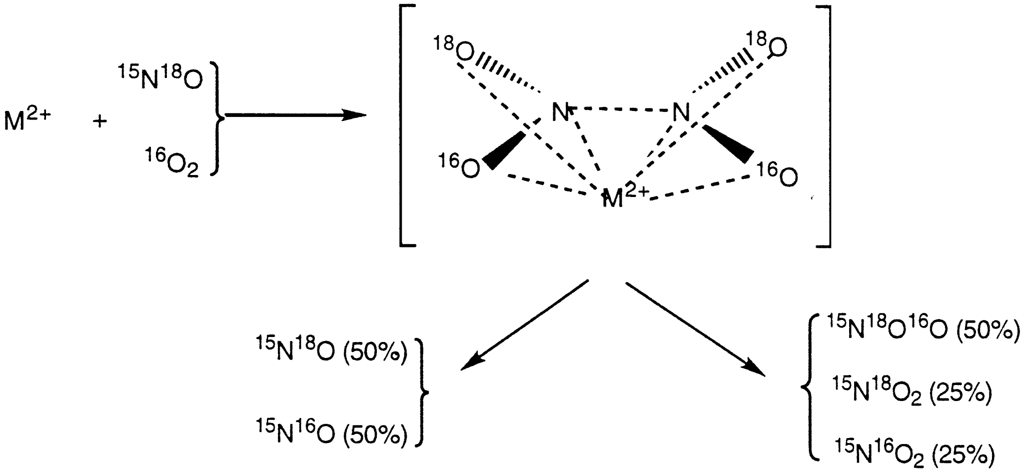
SCHEME I

Based on infrared spectroscopy results, Aylor *et al.* (10) postulate a pathway involving a dinitrosyl $Cu^+(NO)_2$ intermediate, which decomposes to give N_2O, leaving an oxygen on Cu to form $Cu^{2+}O^-$. The mechanism proposed by these authors can also be used to explain why there is only one N_2O isotope product observed (Fig. 7a). The mechanism is given in Scheme I.

Clearly, formation of N_2O requires the active metal site capable of undergoing a redox cycle. This may also explain why no formation of N_2O occurs on Co–NaZSM-5 because Co^{2+} in ZSM-5 cannot undergo Co^{2+}/Co^+ cycling under conditions typical to ours.

For both Co–NaZSM-5 and Cu–NaZSM-5 catalysts, the formation of N_2O and NO_2 was very small when treated in $^{15}N^{18}O$ alone. However, treatment in the gas stream containing both $^{15}N^{18}O$ and O_2 resulted in formation of large amount of NO_2s ($^{15}N^{18}O_2$, $^{15}N^{16}O_2$, $^{15}N^{16}O^{18}O$). This is in agreement with other studies finding that oxidation of NO by O_2 to form NO_2 is effectively catalyzed by H–ZSM-5 (11), H–MOR, Fe–MOR, Cu–MOR (12), and Cu–ZSM-5 (13) at relatively low temperature, e.g., room temperature. Cu–NaZSM-5 showed two major NO_2 desorption peaks at <300°C and >300°C (Fig. 7b) whereas Co–NaZSM-5 (Fig. 8b) showed basically a predominant peak at <300°C and a small shoulder at >300°C.

Similarity in TPD characteristics and equal distribution of two NO isotope products (Figs. 3b and 4b) and



SCHEME II

identical TPD characteristics of different NO_2 isotope products (Figs. 7b and 8b) and an isotope distribution of $[^{15}N^{16}O^{18}O] = 2\,[^{15}N^{16}O_2] = 2\,[^{15}N^{18}O_2]$ leads us to suggest that co-adsorption of $^{15}N^{18}O$ and O_2 over Cu–NaZSM-5 and Co–NaZSM-5 results in formation of a reaction intermediate which has the characteristic of adsorbed "N_2O_4" on transition metal cations (see Scheme II, where M^{2+} represents Cu^{2+} or Co^{2+}). The four oxygen atoms in the adsorbed "N_2O_4" have two ^{18}O which come from two $^{15}N^{18}O$ and two ^{16}O which come from $^{16}O_2$ and they all are chemically indistinguishable. Consequently, breaking the N–N bond will generate either two $^{15}N^{16}O^{18}O$ or one $^{15}N^{16}O_2$ and one $^{15}N^{18}O_2$. Because all N–O bondings are identical the probabilities for both decomposition modes are equal, resulting in $[^{15}N^{16}O^{18}O] = 2\,[^{15}N^{16}O_2] = 2\,[^{15}N^{18}O_2]$. Likewise, further decomposition to form NO and oxygen always generates equal amounts of $^{15}N^{18}O$ and $^{15}N^{16}O$. In the gas phase, N_2O_4 is stable up to 140°C (14). It has a planar structure (symmetry D_{2h}). Another point that supports the formation of "N_2O_4" intermediate is the dramatic increase in amounts of NO and O_2 adsorbed when treated in NO and O_2 is the result of formation of NO_x complex not due to individual NO or O_2 because neither Cu–NaZSM-5 nor Co–NaZSM-5 adsorbs significant O_2 when treated in O_2 alone.

The enhancement of NO_x adsorption by zeolites in the presence of O_2 was also observed by others. For instance, it was reported that the uptake of NO_x by Na–ZSM-5, Na–Y, and Cu–ZSM-5 zeolite catalysts was enhanced by co-adsorbing NO and NO_2 or NO and O_2 (3). The same authors also concluded that the formation of NO_x is facilitated by the zeolite structure, not by the presence of Cu^{2+} though the adsorbed quantities are enhanced by Cu. Further, they postulated the NO_x intermediates are N_2O_3.

TPD results summarized in Table 1 show that the composition of NO_x species formed on both catalysts is complex. When treated in $^{15}N^{18}O$ alone, NO and a very small amount of N_2O are the only NO_x species observed, suggesting a composition close to NO. However, when treated in a mixture of NO and O_2, large amounts of NO_2, NO, and O_2 are adsorbed, resulting in a composition close to N_2O_3 on Co–ZSM-5 and NO_2 on Cu–ZSM-5.

The TPD of oxidized Cu–NaZSM-5 (Fig. 9c) shows two small low-temperature peaks at 80 and 170°C and a major peak at 430°C. The two low-temperature peaks at <200°C are also observed by Teraoka *et al.* (15) and Valyon and Hall (16). Roughly, an amount of 0.2 O/Cu oxygen is released from our Cu–NaZSM-5 catalyst, which is in agreement with others (16). Similar experiments revealed that desorption of O_2 from Co–NaZSM-5 is negligible.

Our TPD (Fig. 2) showed a major amount of desorption at temperatures below 400°C and a lack of any significant desorption at temperatures above 400°C. This feature is similar to that reported by Li and Armor (17) but the detailed desorption features are quite different. On a weight basis, our catalyst adsorbs less than half what was adsorbed on their catalyst, and more importantly, they observed more low-temperature adsorption states (at 85, 160, 225, 300, and 385°C) than ours.

CONCLUSIONS

Co-adsorption of NO and O_2 leads to substantial enhancement in the amount of NO_x adsorbed on the catalysts for both Cu– and Co–NaZSM-5 catalysts. The presence of O_2 is essential during the formation of NO_x intermediates for higher NO_x decomposition activity. We have demonstrated that the low-temperature (<330°C) NO_x decomposition activity observed for both Cu–NaZSM-5 and Co–NaZSM-5 catalysts is mostly due to formation of NO_2 on the catalyst surface. Direct decomposition of NO does not occur on Co–NaZSM-5. It requires high temperatures (>350°C) on Cu−NaZSM-5. Adsorption of NO on Cu−NaZSM-5 also leads to some formation of N_2. This is the result of N_2O formation. In terms of N_2 formation, Co−NaZSM-5 is about 2–3 times more active than Cu−NaZSM-5 at low temperatures (<200°C). For Cu−NaZSM-5, its activity for NO_2 decomposition is approximately 4 times higher than that for NO at 320–370°C. Despite its inability of direct NO decomposition, Co−NaZSM-5 shows good activity for NO_2 decomposition, comparable to that of Cu−NaZSM-5.

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