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N_2O Decomposition over Iron-Exchanged Mordenite

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The decomposition of N_2O was studied over Fe–M and comparison was made with similar studies for Fe–Y. Neither Na–M nor Na–Y was a catalyst. The Fe^{2+} cations of the reduced form of Fe–Y and Fe–M were oxidized rapidly to Fe^{3+} above 250°C, producing N_2 as the sole product. Following this oxidation, N_2O decomposition proceeded at a lower steady-state rate producing N_2 and O_2 in the expected stoichiometric ratio. Interestingly, this reaction was more rapid over Fe–M than over Fe–Y in spite of the fact that the latter has a more accessible three-dimensional pore system and a redox capacity more than three times higher. The same rate law was obtained, however, for both catalysts, viz., rate = kP_{N_2O}. Neither catalyst effected the decomposition of NO at temperatures up to 700°C nor was the N_2O decomposition inhibited by O_2. The kinetic data conformed to a redox mechanism limited by the rate of reduction by removal of carried oxygen by reaction with N_2O to produce the product molecules. Experiments were made using ^{18}O-labeled catalysts in hopes of better defining the nature of the oxygen-carrying sites. These results did not conform to expectation. They suggested that only a small portion of the redox capacity of the zeolite is used so that $^{32}O_2$ appeared as the primary product from the decomposition of N_2O over an exhaustively ^{18}O-oxygenated catalyst rather than $^{34}O_2$ as anticipated from the kinetic results. Possibly diffusion plays an important role in disguising the reaction mechanism.

INTRODUCTION

The decomposition of N_2O has been studied by a number of investigators. It is a particularly simple reaction in which the same reactant can act as both the oxidizing and reducing agent to produce only N_2 and O_2 in the expected stoichiometric ratio. The more important references include studies made on oxides and mixed-oxides (*1–3, 14*), perovskites (*4*), supported-metal catalysts (*5*), and various zeolites (*6–9*). Invariably the reaction occurs on oxygen saturated surfaces.

In a recent paper (*8*) the kinetics of this reaction were discussed. It was shown that the following reaction scheme accounted for the kinetic data:

(a) catalyst reduction

$$N_2O + O\text{-(s)} \rightarrow N_2 + O_2 + \Box \qquad (1)$$

$$2O\text{-(s)} \rightarrow O_2 + 2\Box \qquad (2)$$

and

(b) catalyst reoxidation

$$N_2O + \Box \rightarrow N_2 + O\text{-(s)} \qquad (3)$$

$$O_2 + 2\Box \rightarrow 2O\text{-(s)} \qquad (4)$$

where □ and O-(s) are empty sites or sites holding oxygen atoms, respectively; thus

$$\Box + O\text{-(s)} = C \qquad (5)$$

where C is a constant. Winter (*1*) has showed previously that when the recombination of oxygen on the surface to produce O_2 [Eq. (2)] was an important reaction step, the rate equation becomes

$$\text{Rate} = kP_{N_2O}/(P_{O_2})^{1/2} \qquad (6)$$

and the reaction is inhibited by gaseous O_2. Thus, when inhibition by O_2 is not ob-

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served, it may be concluded that Eqs. (2) and (4) represent unimportant reaction steps relative to Eqs. (1) and (3). Moreover, if O_2 could be produced by the atom recombination described by Eq. (2), the catalyst should effect decomposition of NO as well as N_2O, both of which readily oxidize the reduced form of the catalyst in the temperature range of interest here (*7*). These and other supporting arguments were used (*8*) to show that over Fe–Y

$$-d(N_2O)/dt = 2Ck_rP_{N_2O}/[1 + (k_r/k_0)] \quad (7)$$

where C is the redox capacity of the catalyst. Under these conditions the rate is first-order in N_2O and the reaction is not inhibited by oxygen.

Both Fe–Y and Fe–M have been reported to act as oxygen carriers (*7–11*). The original authors (*10, 11*) reported that an amount of oxygen equivalent to about 0.5 O/Fe was consumed by or removed from each on oxidation with O_2 or reduction with H_2. These data, together with Mössbauer studies, led them to suggest that the carried oxygen was held as a bridge between two iron ions. This assignment now seems unlikely in view of more recent studies (*12, 13*), but whatever the nature of the oxygen-carrying site, it is clear that the redox process which occurred in two steps when the zeolite was oxidized or reduced separately can also take place simultaneously when both reagents are present. Since CO also can be used as a reducing agent and NO or N_2O as oxidizing agents (*7*), this affords a catalytic pathway for the oxidation of CO with O_2, the reduction of NO with CO and for the catalytic decomposition N_2O.

The present work was undertaken to further define the nature of the redox process. It is a matter of considerable academic and practical interest to know whether the catalyst acts as an oxygen carrier at extra-lattice sites as described by Eqs. (1) and (3). Is one oxygen atom added to or removed from an identifiable cationic site in a continuously reversible cycle as in Eqs. (1) and (3)? Or do cations simply act as sites which furnish or accept electrons on demand as oxygen is somehow added to or subtracted from the lattice? Another motivation was the recently reported fact that the amount of oxygen that could be removed from mordenite on reduction with CO was considerably higher (O/Fe = 0.8) than when H_2 was used as a reducing agent (*9*). It was of interest to learn what effect this apparently greater lability of the carried oxygen might have on the kinetics. Tracer experiments were made in hopes of defining the nature of the oxygen-carrying sites. Fe–Y (*7*) and Fe–M (*9*) both catalyzed the oxidation of CO by N_2O. Over Fe–M, N_2O was found to be more reactive than O_2 (*9*). A similar comparison is made herein for the N_2O decomposition reaction.

EXPERIMENTAL

Materials. The iron-exchanged mordenite, Fe–M, was prepared from a Norton Zeolon (sodium mordenite). The resulting catalyst had the following anhydrous unit-cell composition: $Na_8Fe(II)(AlO_2)_{10}(SiO_2)_{38}$. The preparation method has been described elsewhere (*7*); it was carried out in a glove bag under anaerobic conditions. The specific area as determined by N_2 adsorption at −195°C was 430 m^2g^{-1}. Another preparation having essentially identical properties was made from a high purity (research grade) mordenite furnished by Linde.

The N_2 and He were C.P. grade from Matheson. The methods of purification were the same as used earlier (*7*). The tracer oxygen gas of 99.1% isotopic ^{18}O purity was purchased from Prochem and used without further purification.

All catalysts were pretreated according to the following standard procedure. A 1.0-g aliquot of zeolite was evacuated as the temperature was raised in steps to 500°C where it was treated in flowing dry O_2 for 15 h before cooling to the experimental reaction temperature in the same gas. Thus, the possibility of hydrothermal sintering was avoided.

Kinetic measurements. The kinetic studies were made in a continuous-flow single-pass reactor as described earlier (*7–9*). The rates of N_2O decomposition were expressed as the number of N_2 molecules formed per second per gram of dry catalyst. They were determined under differential reaction conditions as the initial slope of the percentage conversion, α, versus W/F plot, where W was the catalyst weight and F the flow rate of N_2O. Values of F/W from 3.3 up to 33.3 cm^3[NTP] g^{-1}s^{-1} were used.

The formation of the products N_2 and O_2 agreed with the stoichiometry of the decomposition reaction:

$$N_2O \rightarrow N_2 + \tfrac{1}{2} O_2. \quad (8)$$

Hence, the fractional conversions were calculated from:

$$\alpha = (N_2)/[(N_2) + (N_2O)], \quad (9)$$

where the concentrations $[N_2]$ and $[N_2O]$ in molecules per cubic centimeter were obtained by integration of the area of the chromatographic peaks from samples of the eluted gas, using a Perkin–Elmer M-J computing integrator. Thus, the initial slope at low conversion, $\alpha(F/W)$, measures the specific rate of product formation (*9*) in molecules of N_2 formed per gram per second.

The feed gas composition was varied from 1% up to 10% N_2O in He at 1 atm. The same concentration range was used for N_2 and O_2 with 2.7% of N_2O to test for possible inhibition by products.

Isotopic tracer studies. $N_2{}^{16}O$ decomposition experiments were made over ^{18}O-treated catalysts in an all-glass recirculation system having a total volume (including the reactor) of about 210 cm^3. The reaction temperatures ranged from 290 to 500°C and reaction times up to 1 h were employed. The O_2 formed by N_2O decomposition was analyzed by mass spectrometry using small samples of the gas taken at intervals during the reaction. The total gas withdrawn in a typical experiment amounted to $\leq 3\%$ of that present. The data yielded the isotopic distribution in the oxygen, i.e., the mole fractions of $^{32}O_2$, $^{34}O_2$, and $^{36}O_2$.

The tracer-loaded catalysts were prepared as follows. The catalyst was exchanged with $^{36}O_2$ six times at 500°C, each time using a fresh aliquot of $^{36}O_2$. This procedure was designed to saturate the postulated sites with $^{18}O_2$, and then replace most of the surrounding oxygen ions of the lattice (which conceivably could feed back into the oxygen produced by N_2O decomposition). In each step about 3.6 mmol of $^{36}O_2$ were used to treat 1 g of catalyst. Thus, the available ^{18}O in each exchange was over ten times the redox capacity, but only 10% of the total zeolite oxygen.

RESULTS AND DISCUSSION

Kinetics. The NO decomposition was tested over oxidized Fe–M. No reaction was detected up to 720°C. NO reacted with the reduced catalyst producing N_2 as the only product, but when the oxidation was completed the consumption of NO ceased. The same result was reported for Fe–Y (*8*). Similarly, N_2O reoxidized reduced Fe–M and Fe–Y and N_2 was the only reaction product. When the zeolites became fully oxidized, however, in contrast with the results from NO, both N_2 and O_2 continued to appear in the gas phase in the expected stoichiometric ratio = 2.

The Fe–M contained about three times less iron than the Fe–Y, but it was more active for N_2O decomposition than Fe–Y. The Na-zeolites were inactive. A comparison of the rate constants, k, and the turnover number, TON, at several temperatures for these two catalysts is given in Table 1. Here the k values are expressed in terms of molecules per second per Torr per Fe, where the total number of Fe ions per gram of dry catalyst are 6.1×10^{20} and 1.9×10^{20} Fe/g for the Fe–Y and Fe–M, respectively. Interestingly, the overall result would not be changed if comparison were

TABLE 1

Comparison of Catalytic Activities in Terms of the Rate Constant, *k*, and TON for N_2O Decomposition[a]

Temp. (°C)	Fe–Y[b]		Fe–M	
	k (10^5 molec · Fe^{-1} · s^{-1} · $Torr^{-1}$)	TON (10^5 molec · Fe^{-1} · s^{-1})	*k* (10^5 molec · Fe^{-1} · s^{-1} · $Torr^{-1}$)	TON (10^5 molec · Fe^{-1} · s^{-1})
350	<0.01	<0.01	0.05	1.19
498	0.20	5.30	30.0	790.0
530	0.52	13.8	120.0	3194.0
621	6.7	176.8	828.0	22025.0

[a] Gas composition was 3.5% N_2O with the balance to 1 atm He. The *k* calculated from the kinetic rate law: $k = r/P_{N_2O}$. The Fe–Y and Fe–M contained 6.1×10^{20} and 1.9×10^{20} Fe/g, respectively.

[b] From Fu *et al.* (*8*).

made on a unit-weight basis; Fe–M is still more active than Fe–Y. Similar results have been reported for the oxidation of CO with N_2O (*9*).

As found previously for the CO oxidation (*9*), these catalysts had remarkably stable activities. Experiments made to determine activation energies were reproducible on raising and lowering the temperature. The Arrhenius plot of the rate constant was linear over the whole temperature range studied (320 to 625°C). The slope yielded an activation energy of 32 kcal mol^{-1}. This value is slightly lower than the one reported by Fu *et al.* (*8*), viz., 37 kcal mol^{-1} for the same reaction on Fe–Y.

The effect of N_2O and O_2 pressure on the rate of decomposition was studied at two temperatures (350 and 440°C). In Fig. 1, typical plots of ln *r* vs ln P_{N_2O} and vs ln P_{O_2} are shown. A first-order dependence in N_2O and a near-zero-order in O_2 is clearly indicated by the slopes of the graphs. An identical finding was obtained at both temperatures. From these results the rate law can be expressed as

$$\text{rate } (N_2 \text{ formation}) = kP_{N_2O}. \quad (10)$$

Isotopic tracer data. Experiments were made seeking corroboration for the redox mechanism described by Eq. (7) above. If oxygen were produced only by Reaction (1), then the sole initial product from $N_2{}^{16}O$ decomposition over fully oxidized FeM containing only ^{18}O should be $^{34}O_2$, i.e., $^{16}O^{18}O$. As the ^{18}O thus removed is replaced by ^{16}O by Reaction (3), however, $^{32}O_2$ should be formed in increasing amounts as the reaction proceeds. The amount of $^{34}O_2$ produced should be limited by the number

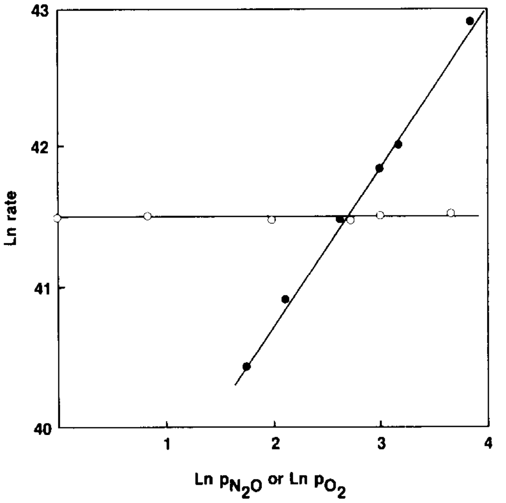

FIG. 1. Power rate law plots for N_2O decomposition over Fe-M. The gas composition was in the 1–10% range for N_2O (solid points) and in the 0–10% range for O_2 with a constant 1.83% of N_2O (open points). In all cases the balance to 1 atm was He.

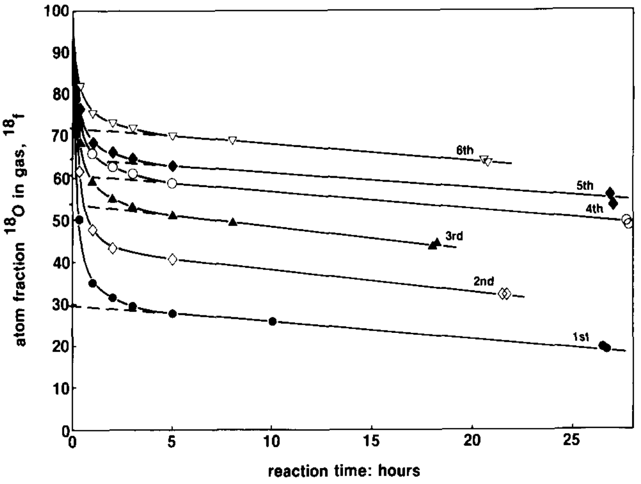

FIG. 2. Exchange with $^{36}O_2$. Note the initial fast process followed by a slow secondary process; see text for details. Curves show variation of ^{18}f, the atom fraction ^{18}O in the gas phase with time.

of sites participating in the reaction as well as the number of N_2O molecules which have undergone reaction. No $^{36}O_2$ would be expected if Reaction (2) is negligible, and any produced may be taken as a measure of the extent of the secondary isotopic exchange reaction,

$$2\,^{34}O_2 \rightleftarrows {}^{32}O_2 + {}^{36}O_2. \qquad (11)$$

A second problem can be the exchange of the gaseous oxygen formed with that of the catalyst. If the latter were initially all ^{18}O and in large excess, then the problem would be one of minimizing the loss of ^{16}O to the zeolite lattice by this exchange process. In fact, it was not found practical to replace all of this latter oxygen with ^{18}O, but the level was raised sufficiently so that meaningful results could be obtained.

When this research was initiated, it was hoped that the $Fe^{2+}M$ could be oxidized to $Fe^{3+}M$ with $^{36}O_2$ at sufficiently low temperatures so that the carried oxygen ^{18}O-(s), could be added in one step and removed in the next without significant isotopic exchange with the lattice. This did not prove possible, however, so we did the next best thing. The redox capacity and the neighboring oxygens were replaced with ^{18}O at temperatures higher than that to be used for N_2O decomposition. Thus, $N_2{}^{16}O$ should have no alternative but to react with ^{18}O-(s). The experimental situation is outlined below.

Six repeated exchanges were carried out with $^{36}O_2$ of 99.1% ^{18}O. The results are presented in Fig. 2. In the first exchange reaction (Curve 1) $N_g = 20 \times 10^{20}$ atoms of ^{18}O (contained in gaseous $^{36}O_2$) was reacted at 500°C with FeM whose redox capacity was 1.5×10^{20} atoms/g, but whose total oxygen content was 193×10^{20} atoms/g.[4] The reaction appeared to take place in two steps, viz., a very fast process followed by a very slow zero-order decrease in the atom fraction ^{18}O in the gas phase (^{18}f). Earlier workers have reported similar results (*1, 14*). If we suppose that the initial fast reaction occurs at the redox sites and that the second slow process can be identified as a slow exchange of this oxygen with that of the lattice by a self-diffusion process, then the *effective redox capacity*, N_{ex} can be calculated, as was suggested by Winter (*1*), from the isotope dilution taking place in the

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[4] For convenience, the data are given as per gram of dry catalyst.

first step. N_{ex} (atoms/g) is the amount of zeolite oxygen which is readily exchangeable with the gas phase (the amount in the exchangeable box); N_{ex} might reasonably be expected to be at least as large as the redox capacity and perhaps larger if neighboring lattice oxygen atoms participate in the exchange process. The isotope dilution equation (*1*, *14–16*) applied to this situation is

$$N_{ex} = N_g \frac{{}^{18}f_0(g) - {}^{18}f_\infty}{{}^{18}f_\infty - {}^{18}f_0(s)} \qquad (12)$$

where ${}^{18}f_0(g) = 0.991$, ${}^{18}f_\infty$ is estimated by extrapolation of the linear portion of the curves to zero time [dashed lines of Fig. (2)], and (for the first exchange) ${}^{18}f_0(s)$ is the natural abundance of ${}^{18}O$ (0.002) in the solid. The assumption is implicit that ${}^{18}f_\infty$ is the same in the gas and in the exchangeable box. After the first exchange, ${}^{18}f_0(s)$ may be taken as the value of ${}^{18}f(g)$ at the time the previous experiment was terminated by quenching to room temperature (the points shown on Fig. 2 at the longest times). This will also be the *composition* of the oxygen in N_{ex}. Thus, ${}^{18}f_\infty$ is estimated as the value which would have resulted, if the secondary self-diffusion process did not exist. Values calculated for N_{ex} at 500°C for the six experiments averaged 43.6×10^{20} atoms/g as compared with 45.7×10^{20} atoms/g calculated for the first exchange, i.e., about 30 times larger than the redox capacity. Moreover, at the end of the sixth exchange the exchangeable box should contain 64 atom% ${}^{18}O$, whereas the corresponding overall value for the zeolite was 34%. Hence, the first oxygen produced from the decomposition of N_2O according to Reaction (1) would be expected to contain 64% ${}^{34}O_2$ and 36% ${}^{32}O_2$. Any contribution from Reaction (2) would increase the percentages of ${}^{32}O_2$ and ${}^{36}O_2$.

Similar experiments carried out at 370 and 290°C yielded much smaller values of N_{ex}, viz., 1.4×10^{20} and 1.4×10^{19} atoms/g, respectively. The former is close to the redox capacity and the latter is much smaller, suggesting that it was not possible to reach equilibrium with all of this carried-oxygen at this low temperature. This should have minimized complications when N_2O decomposition experiments were carried out at this temperature (see below).

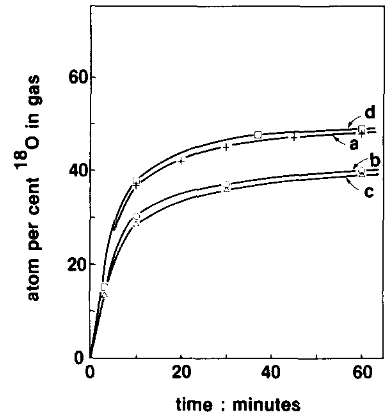

FIG. 3. The ${}^{18}O$ isotopic composition of the product oxygens vs the reaction time during the $N_2{}^{16}O$ decomposition over an ${}^{18}O$-loaded Fe–M in a static reactor. Reaction temperature: (a) 370°C; (b,c,d) 290°C. Before the first Experiment (a), the catalyst was exchanged with ${}^{18}O_2$ six times at 500°C; before Experiment (b) the catalyst was exchanged at 370°C, and before Experiment (d) the catalyst was exchanged at 290°C. The reexchange was omitted before Experiment (c).

Following the experiments shown in Fig. 2, $N_2{}^{16}O$ decomposition (1.2×10^{19} N_2O/g) was carried out at 290 and 370°C with the objective of determining the isotopic composition of the first oxygen molecules produced. The results are shown in Figs. 3 and 4. Interestingly, the data suggest that the initial product was ${}^{32}O_2$ rather than the expected ${}^{34}O_2$. The experiments at 290°C (Curves b, c, and d) and at 370°C (Curve a of Fig. 3) were made using 1.3, 0.9, 1.7, and 1.2×10^{19} N_2O molecules/g, respectively. Between experiments zeolite was reexchanged with ${}^{18}O_2$ (13.2×10^{20} ${}^{18}O$/g) except that this treatment was omitted between experiments b and c. Between c and d this treatment was made at 290°C rather than at 370°C. The data are self-consistent. At the end of an hour, when transport of ${}^{18}O$ into

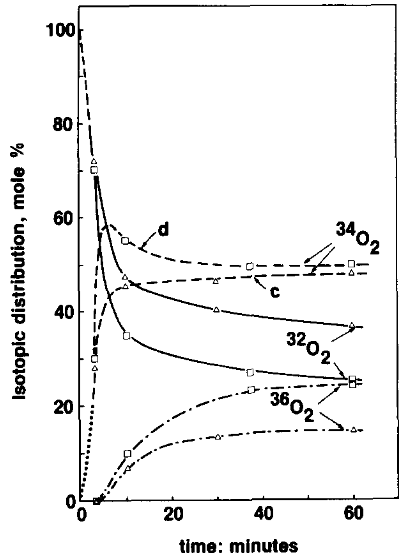

FIG. 4. Isotopic distribution of the oxygen species in mole percentage vs the reaction time. Same symbols as in Fig. 3: the solid lines are for $^{32}O_2$, the dashed lines for $^{34}O_2$ and the dotted dashes for $^{36}O_2$. To avoid confusion only the results of Experiments (c) and (d) are shown, but the others, (a) and (b), were consistent.

the gas phase had become very slow (Fig. 3), the oxygen species were close to statistical equilibrium, i.e. $[(^{16}O^{18}O)^2/(^{32}O_2)(^{36}O_2)] = 4$. Thus, the changes between the initial and final composition was caused partly by equilibration of the O_2 formed [Eq. (11)]. No exchange between $N_2{}^{16}O$ and the catalyst ^{18}O was detected.

CONCLUDING REMARKS

The kinetic data strongly support the redox mechanism for the decomposition of N_2O. Accordingly it has been supposed that extra-lattice oxygen is held by the altervalent cations and may be depicted generically as O-(s). When this oxygen is removed by a reductive process the empty site, □, should become available for reoxidation. The two steps of this redox cycle may be carried out separately (*9*) or simultaneously when the oxidizing agent and the reducing agent are both present. An objective of the present work was to better define the nature of O-(s) and □.

Boudart and co-workers (*9, 10*) pictured O-(s) as an oxygen atom bridged between two Fe cations. This bridge was originally thought to be located within the sodalite unit of Fe–Y. The X-ray studies of Pearce and co-workers (*12*) did not support this assignment and in fact suggested that such bridges do not exist. Moreover, recent spectroscopic studies (*13*) have provided an alternative picture. The altervalent base-exchange cations were found to undergo self-diffusion in the zeolite lattice, even at room temperature. As they appeared in the supercages (or other accessible positions) they became trapped by chemisorption of NO molecules; dinitrosyl species were observed in increasing amounts with time. Such cation substrate complexes could act as templates producing N_2O as an intermediate in the oxidation process. Presumably the cation can be trapped by an extra-lattice oxygen atom in much the same way as the dinitrosyl species, e.g., as O=Fe at site III′ in the supercage with one electron furnished by another Fe cation at a remote, inaccessible position in the zeolite lattice. Perhaps a better way to look at this phenomenon is to assume that both Fe^{2+} donate one electron to the zeolite lattice and thus becoming Fe^{3+}; the lattice can then oxidize an additional oxygen atom which we assume is held in the supercage of FeY at site III. That the ability to furnish electrons is an essential feature of this redox catalysis is established by the fact that the parent Na-forms of the zeolites are inactive.

The N_2O decomposition occurs on the completely oxidized form of the catalyst. Consequently its rate is limited by the rate of reduction, viz., by Eq. (1). Accordingly O_2 is freed on collision of N_2O molecules with the extra-lattice oxygen. The site which is freed is then rapidly reoxidized by another N_2O molecule. Thus, if these sites are preloaded with ^{18}O, the initial product should be $^{34}O_2$. The reoxidation of a site will reload it with ^{16}O and in the second and subsequent steps $^{32}O_2$ will be produced. The experiments were designed so that the total N_2O reacted (~1.2 × 10^{19} molecules/g) would be less than 10% of the total redox capacity (1.5×10^{20}/g). Thus, provided that all sites were equally accessible and reactive, and provided that exchange of the oxygen product with oxygen from the total lattice was slow, the product oxygen should have reflected exactly the overall composition of the redox sites. Moreover, as time went on and more and more ^{16}O was introduced into the oxygens by further N_2O decomposition, the tracer atom fraction, ^{18}f, should have decreased. Figures 3 and 4 show that neither of these expectations was obtained. The data suggest that the initial product is $^{32}O_2$ and that ^{18}O is slowly pumped into the product by secondary reactions, rather than the other way around. Thus, the tracer data did not conform to expectation.

Seemingly a paradox exists. The kinetic information suggests that the redox centers function catalytically; the tracer data, taken at face value, indicate that the product O_2 comes entirely from the N_2O. Seemingly the only way both conditions can be met is if the decomposition reaction utilizes repeatedly only a very small fraction of the total redox centers. Were this the case a value of 5×10^{17} sites/g may be estimated from the data obtained at 290°C after 3 min of reaction. The decreasing size of N_{ex} calculated for decreasing reaction temperatures is indicative of kinetic limitations. Experiments made at 290°C yielded values about 10-fold less than the true redox capacity of the altervalent cations. Perhaps severe diffusion limitations are present. Alternatively, it would seem necessary to conclude that the decomposition reaction is unrelated to the redox chemistry.

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