The desorption of O_2 during NO and N_2O decomposition on Cu- and Fe-zeolites

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The decomposition of NO and of N_2O over a CuZSM-5 zeolite and a Fe-mordenite, respectively, has been studied using tracer techniques. The results demonstrate the high mobility of the lattice oxygen ions in self-diffusion. They afford a possible explanation for the problem of how two extralattice oxygens located at positions remote from each other may combine to form the O_2 molecules which are spontaneously desorbed in these redox reactions. They show that a portion of the lattice oxygen mixes into the O_2 released on decomposition. The data also show that $N^{18}O$ and $N_2{}^{18}O$ undergo exchange with the catalyst oxygen under reaction conditions.

Keywords: Self-diffusion of O in zeolites; oxygen atom recombination; O_2 desorption; oxygen transport; NO decomposition mechanism

1. Introduction

Until recently, a suitable catalyst for *decomposition* of NO had not been found and the prospects of finding one were not considered good [1]. However, reduction of NO by CO was facile and is used in automative applications. Many catalysts exist which will decompose NO on their surfaces with desorption of N_2, but which require a reducing agent to remove the oxygen.

Boudart and co-workers [2,3] discovered that when the Na^+ base-exchange cations of a Y-zeolite were replaced with Fe^{2+}, the latter could be readily oxidized to Fe^{3+} with the uptake of one atom of oxygen for each two Fe^{3+} formed. Their Mössbauer, IR and stoichiometric data led them to conclude that these O^{2-} ions were held as bridges between two Fe^{3+} ions sited on adjacent six-rings within the sodalite cages, i.e., were held as extralattice oxygen (ELO) within the zeolite. They further observed that the oxidized zeolite could be reduced with H_2 to its initial

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Fe^{2+} state forming a stoichiometric amount of H_2O. The Fe^{2+} ions could not be further reduced to Fe^0 at temperatures as high as 1100 K. In extensions of this work we found that CO could be effectively substituted for H_2 as a reducing agent and NO for O_2 as the oxidizing agent [4]. Reactions which can be carried out in two separate steps (an oxidation and a reduction step) can be combined into one, in the present case utilizing the Fe^{2+}/Fe^{3+} couple as a catalyst. Thus, these preparations were active catalysts for the reaction: $NO + CO \rightarrow \frac{1}{2}N_2 + CO_2$. This redox chemistry was confirmed by kinetic studies [5]. Among such reactions N_2O decomposition was found to fit [6] even though NO decomposition was undetectable over Fe^{2+}-zeolites at temperatures up to 1100 K. NO decomposition did proceed, however, by a redox mechanism over CuZSM-5 catalysts [7,8]. In these cases, NO oxidized Cu^+ to Cu^{2+} [7] even at room temperature with release of N_2, although it was necessary to heat the catalyst above 573 K to effect the spontaneous desorption of O_2 [9].

Current thought holds that the ELO is bound to the Cu^{2+} or Fe^{3+} sites and is independent of the lattice oxygen. Indeed, there is independent Mössbauer and IR evidence [3] to support this view. Therein lies the problem to which this Letter is addressed. How can two ELO atoms, held by base-exchange cations which are remote from each other in silica-rich zeolites, be transported to "portholes" where they can recombine and form O_2?

2. Experimental

Catalysts

The CuZMS-5 samples were prepared from the sodium forms using conventional ion-exchange procedures. The unit cell compositions of these materials were $Na_{0.20}Cu_{3.63}(AlO_2)_{6.36}(SiO_2)_{89.64}$ and $Na_{1.35}Cu_{2.95}(AlO_2)_{3.55}(SiO_2)_{92.45}$. They are identified here as CuZ-14-114 and CuZ-26-166, respectively. The Fe-mordenite sample was made from the Norton preparation. Its unit cell composition was $Na_{3.8}Fe_{1.4}(AlO_2)_{6.8}(SiO_2)_{41.2}$ and it is identified herein as FeM-6-14. In all instances the redox cationic form is designated first; this is followed by the type of the zeolite (Z represents ZSM-5 and M, mordenite), the Si/Al ratio and the per cent exchanged. Both CuZ samples contained copper in excess of the stoichiometric amount. The Cu loadings corresponded to 0.62 mmol/g (CuZ-14-114) and 0.49 mmol/g (CuZ-26-166). The Fe loading of the mordenite was 0.47 mmol/g. The zeolite powders were pressed into tablets, crushed and sieved. The 40–80 mesh fractions were used for the experiments. Samples studied in the present work have been characterized in detail and are reported elsewhere [7].

Materials

The 1% $^{14}N^{16}O$/1% Ar/He mixture was obtained from Matheson Gas Products. The 1% $^{15}N^{18}O$ mixture was prepared by pressurizing the lecture bottle containing the NO (99.9 at% ^{15}N and 96.3 at% ^{18}O, Isotec Inc., Matheson, USA) with ultrahigh purity He (Matheson, USA). The NO content of the mixture obtained was determined by GC. The $N_2{}^{18}O$ was obtained from U.S. Isotopes, Chicago. Its purity was >96% as ^{18}O.

Equipment and procedures

The microreactors were made from capillary tubing and the catalyst was contained between quartzwool plugs. The reactors were connected to stainless-steel flow systems and the flow rates of the gases were maintained using Brooks electronic mass flow controllers at the outlet of the reactors. At the University of Pittsburgh the composition of the gas was continuously monitored by a QUAD 250A type quadrupole mass spectrometer (E.A.I., Palo Alto, CA) attached to a computer for processing the data. The MS and the flow system were interfaced by a jet separator using a two-stage pressure letdown. The experiments using $N_2{}^{18}O$ over FeM were made at UW-Milwaukee using a similar apparatus interfaced with an UTI 100c-02 quadrupole spectrometer equipped with an UTI spectralink process control computer. Masses 28, 30, 32, 34, 36, 44, 46 and 48 were recorded every 2 s and averaged every 20 s. The conversion level was maintained at about 18% for the duration of the experiment.

Experiments using $^{15}N^{18}O$ over the CuZSM-5 preparations were carried out at the University of Pittsburgh. In the first application, a stream containing $^{15}N^{18}O$ was switched over the freshly pretreated CuZ-14-114 (containing only ^{16}O). In a second kind of experiment, a steady state reaction over CuZ-26-166 was established with unlabeled gases and then a sudden switch was made to the labeled compound under identical conditions (T, P and F). At UW-Milwaukee a 214 mg aliquot of FeM-6-14 was used at 570 K and at a total flow rate of 110 ml/min of He containing 2% $N_2{}^{18}O$. Similarly, 340 mg of CuZ-14-116 or 250 mg of CuZ-26-166 was used at a total flow rate of 100 ml/min of He containing 1% $^{15}N^{18}O$. The time-lag from the flow selector valve to the detector was about 2 to 3 s. The quantitative evaluation of the data is based on the integrated areas of the MS signal versus time plots using the trapezoid rule. The MS signals obtained from 1% NO/He, 0.1% O_2/He and 0.1% N_2/He mixtures were used as reference standards. A completely quantitative analysis of the data was not possible. Even when using the lowest feasible ionization voltages, some NO was fragmented and about 20% of these N atoms recombined to N_2 and appeared in the spectrum. The fragmentation and recombination was probably concentration dependent. A further source of error was that the jet separator led to mass specific and concentration dependent enrichment of the components. Because of the reasonably high masses involved, however, this effect was limited. The maximum error in the calculated data is estimated to be about ±10%.

The standard pretreatment for the copper-containing catalysts involved flowing pure O_2 overnight followed by a 1 h flushing with helium at 773 K, i.e., these catalysts were initially partially reduced (~ 10%) due to spontaneous desorption of

O_2. The FeM catalyst was pretreated in a 10% O_2/He mixture at 573 K for 2 h before raising the temperature to 773 K overnight. The flow was maintained as the temperature was lowered to that required for the reaction.

3. Results and discussion

3.1. NO DECOMPOSITION

NO decomposition over CuZ-14-114 catalyst was studied and the results obtained on switching $^{15}N^{18}O$ onto the freshly pretreated catalyst are shown in fig. 1. Over the 60 min period the conversion level was fairly constant at about 60% decomposition of the NO at 773 K. At 723 K the NO conversion was significantly smaller, but the concentration of the components in the effluent showed a similar time dependence at both temperatures.

The initial concentrations of the $^{15}N^{18}O$ in the flowing stream were determined with the reactor bypassed. When the streams were turned over the catalyst at $t = 0$, the $^{15}N^{18}O$ concentration dropped abruptly to near zero and then recovered slowly (fig. 1A). Interestingly, over the first 10 to 20 min, more $^{15}N^{16}O$ emerged from the catalyst bed than $^{15}N^{18}O$. After reaching the point of equal concentration, the latter species finally dominated. Thus, initially, the unreacted gas underwent almost complete exchange with the zeolite oxygen during a calculated contact time of about 0.5 s. At the lower temperature no NO species was detected in the effluent for the first few seconds. At 673 K (not shown) it took about 90 s until NO became detectable, first as $^{15}N^{16}O$ and later also as $^{15}N^{18}O$. These results suggested that exchange between the NO and the catalyst oxygen was preceded by the rapid adsorption of the $^{15}N^{18}O$ which served to reoxidize the catalyst and to possibly form adsorbed NO_2 intermediates [10] before adsorption as $^{15}N^{16}O$ began. This was confirmed (fig. 1C) by the immediate release of N_2 on adsorption of NO as reported previously [9]. As the ^{18}O content of the catalyst increased, the $^{15}N^{18}O$ concentration in the effluent gas also increased at the expense of the $^{15}N^{16}O$. The high initial peak concentration of $^{15}N_2$ may be partially attributable to this reoxidation. The system then relaxed into its steady-state decomposition activity (fig. 1C). At 773 K the steady state rate of NO decomposition was reached much faster than at 723 K. The sharp N_2 peak was now less pronounced than at 723 K where the reoxidation of the catalyst was slower and the initial N_2 peak was quite sharp (fig. 1C, 723 K).

No $^{18}O_2$ and relatively little $^{16}O^{18}O$ were formed in the first few seconds of these experiments. The initial product was exclusively $^{16}O_2$ (fig. 1B). The former two products were produced in increasing amounts while $^{16}O_2$ decreased as time went on and as the ^{18}O content of the solid increased. At 773 K the $^{18}O^{16}O$ concentration passed through a maximum at about 20 min time on stream.

Interpretation of these data is not straightforward, nor can it be complete. Cer-

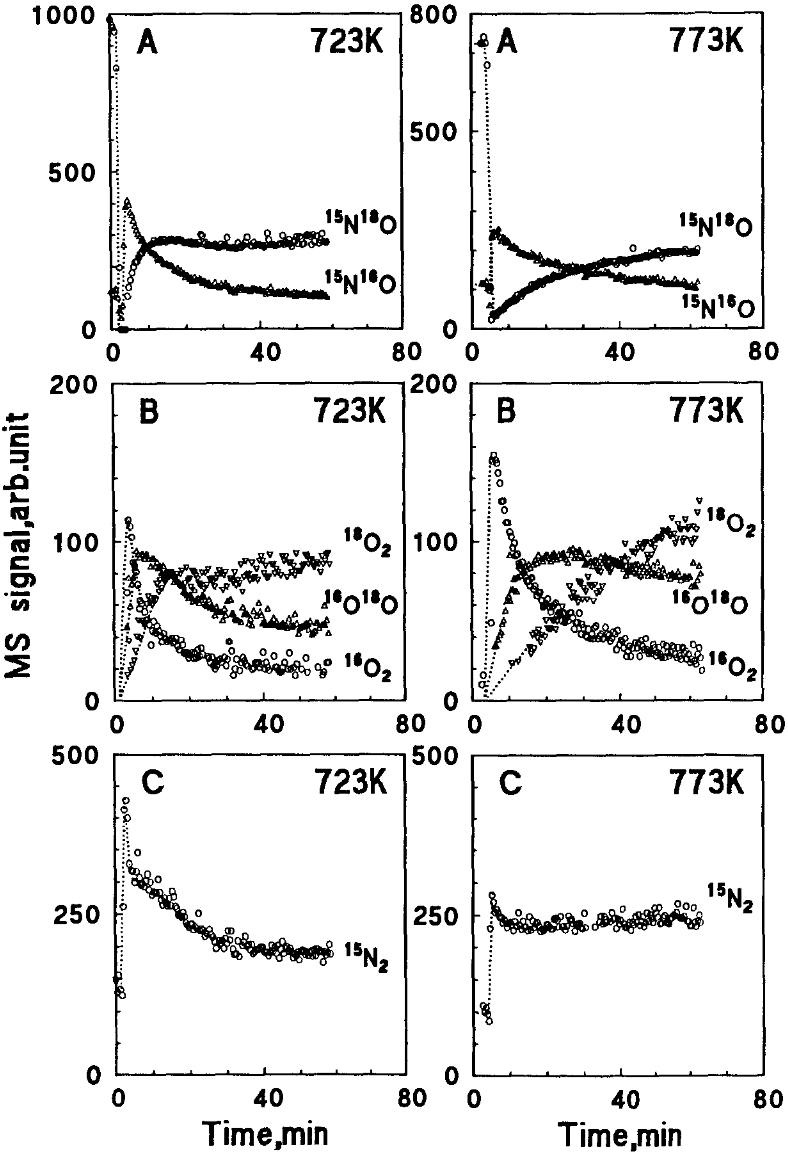

Fig. 1. Isotopic composition of the products obtained from the steady-state decomposition of $^{15}N^{18}O$ over 340 mg of an unlabeled sample of catalyst CuZ-14-114 at 723 and at 773 K. The flow rate was 100 cm^3/min ($W/F = 4.9 \times 10^5$ g s/mol) of He containing 1% $^{15}N^{18}O$. The NO products are plotted in (A), the O_2 products in (B) and the N_2 in (C). The MS data for the first 5 min were obtained with the reactor bypassed; then the stream was suddenly switched over the pretreated catalyst.

tain facts are unquestionable, e.g., that the lattice oxygen is involved in the NO decomposition, that the $^{16}O_2$ product is desorbed first and that nearly complete exchange of the entering $^{15}N^{18}O$ to $^{15}N^{16}O$ is achieved initially. The catalysts were in the *same* partially reduced state at the start of the reaction at both temperatures. Evidently they initially contained substantial amounts of excess ^{16}O which acted as reactant with the entering $^{15}N^{18}O$. Moreover, the likelihood of formation of a variety of N-containing surface species including adsorbed NO_2 exists [10]. Possibly the point where the $^{15}N_2$ curves reach a steady state (become invariant with time) may be taken as the point where the surface has been reoxidized into its steady state value. This reoxidation is fairly facile, N_2 evolution occurring at room temperature [9]; the attainment of steady state populations of the variety of N-containing surface species is much slower, but increases with temperature [10]. Recall also that the overall rate of decomposition to N_2 is substantial at the higher temperature, but much lower at the lower one. This makes the interpretation of the shapes of the isotopic O_2 and NO curves ambiguous.

After completion of the run (60 min), integration of the O_2 curves gave the amounts of ^{16}O removed from the catalyst. At 773 K 2.2 $^{16}O/Cu$ were released, 1.0 $^{16}O/Cu$ as $^{15}N^{16}O$ and 1.2 $^{16}O/Cu$ as $^{16}O_2 + {}^{18}O^{16}O$. At 723 K the corresponding data were 1.2, 0.6 and 0.6 $^{16}O/Cu$. These amounts may be lower limits if some oxygen was reacted to N_2 and went undetected. The results suggest that oxygen is deposited on the catalyst at one location by the decomposition of NO, and that O_2 is released from the catalyst elsewhere, or sometimes at the same centers. Conceivably these are at Cu^+ and $Cu^{2+}O$-sites which act as portholes for the entry and exit of oxygen to and from the zeolite, respectively. Clearly lattice oxygen is involved in the transport from the port of entry to locations where the ELO can be stabilized and in its transport to the same, or more generally to other, portholes for recombination and escape from the catalyst. Thus, the oxygen atoms that are added to the catalyst are usually not the same ones which are released.

In the above experiments no ^{14}N atoms were involved and the mass spectral analyses were straightforward. Complications developed when tracer transient response experiments were attempted because $^{16}O_2$ and $^{14}N^{18}O$ have the same parent masses, as do $^{15}N_2$ and $^{14}N^{16}O$. The mass spectrometer used was not sufficiently sophisticated to resolve these overlaps. Nevertheless the data obtained were sufficient to show general agreement between the two sets of data.

The data recorded in fig. 2 were obtained as follows: the system was first brought into the steady state NO decomposition without the use of tracers, i.e., using $^{14}N^{16}O$ over a fresh sample of CuZ-26-166. After the initial 10 min period (shown starting at time zero), an abrupt switch was made to $^{15}N^{18}O$. Before the switch only three gases were present, viz., $^{14}N^{16}O$, $^{16}O_2$ and $^{14}N_2$. The latter disappeared abruptly on making the switch; $^{14}N_2$ was replaced by $^{15}N_2$ with the formation of only a trace amount of $^{15}N^{14}N$. The $m/e = 30$ peak, however, contains any $^{14}N^{16}O$ retained by the catalyst from before the switch so that the yield of $^{15}N_2$ must be considered as an upper limit. Clearly, however, the change from $^{14}N_2$ to $^{15}N_2$ was quite sharp; it is only the magnitude of the conversion that is in doubt. When, after 40 min the feed was switched back to $^{14}N^{16}O$, *both* ^{15}N labeled NO species disappeared within 3 to 4 min (fig. 2A). It may therefore be concluded that the $m/e = 30$ peak (fig. 2C) is almost exclusively from $^{15}N_2$. Argon was used with

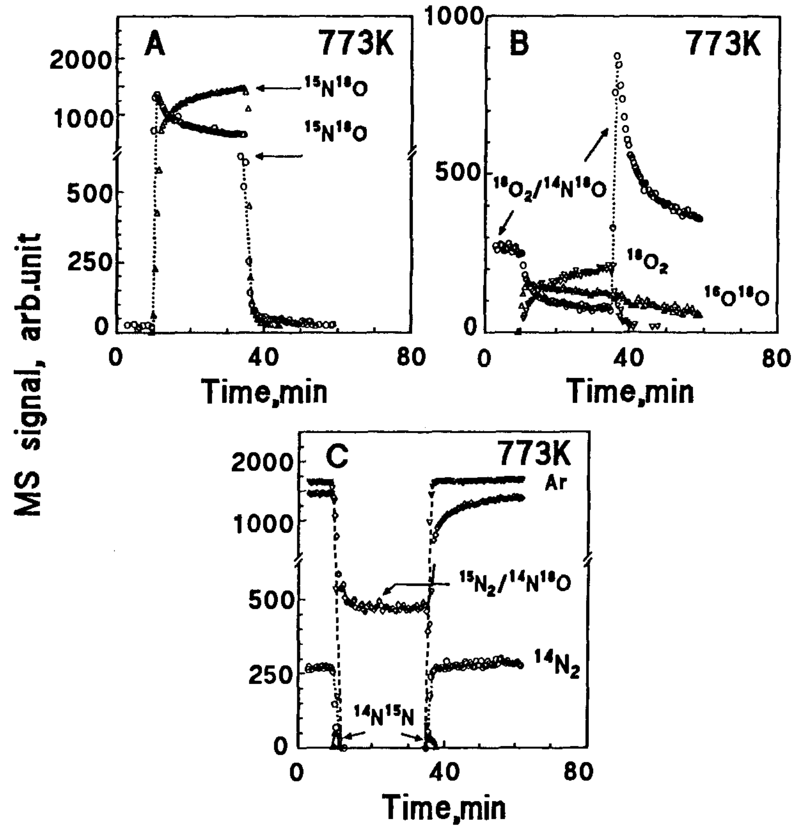

Fig. 2. The transient isotopic response obtained during NO decomposition over 250 mg of CuZ-26-166 at 773 K. A steady state conversion with unlabeled NO (1% in He containing 1% Ar) was first established and the results recorded over the initial 10 min period. The Ar ($m/e = 40$) response shows the minimal time lag involved in sweeping the ambient gas from the system on switching to a stream containing 1.6% $^{15}N^{18}O$ in He. The flow rate in both cases was 100 cm^3/min ($W/F = 3.6 \times 10^5$ g s/mol). The transients were followed for 25 min before the reactant was switched back to the original NO/Ar/He stream. The mass interferences at $m/e = 30$ and 32 are noted. See the text for interpretation.

$^{14}N^{16}O$ as an internal indicator to measure the response time required to empty the reactor from components not interacting with the catalyst (fig. 2C).

A similar analysis may be carried out for the O_2 formed in the reaction. In the initial 10 min only $^{16}O_2$ was formed; $^{14}N^{18}O$ was not present since no ^{18}O had yet entered the system. When the feed was switched to $^{15}N^{18}O$, the three oxygen profiles (fig. 2B) resembled closely those of fig. 1 and similar conclusions can be drawn. On switching back to $^{14}N^{16}O$, the $^{18}O_2$ decayed sharply and the $^{18}O^{16}O$ more slowly. The rather high concentration at $m/e = 32$ is most probably largely $^{14}N^{18}O$ formed by the exchange of $^{14}N^{16}O$ with ^{18}O remaining on the catalyst. The actual $^{16}O_2$ yield would be expected to be about equivalent to that formed in the initial 10 min.

3.2. N_2O DECOMPOSITION

N_2O decomposition was studied in a similar way, but over FeM-6-14. With this reaction the problem of mass overlap does not exist since N_2, N_2O and O_2 are the only products. Thus the transient response could be obtained clearly. The results are reported in fig. 3. The reaction was initiated by passing unlabeled N_2O over the fully oxidized Fe^{3+} form of the zeolite which carried about 1 ELO for each 2 Fe. After 200 s, an abrupt switch was made to $N_2{}^{18}O$ under otherwise identical conditions. The capillary reactor had a volume of about 1 ml and the flow rate was about 2 ml/s. As confirmed by use of an argon tracer (not shown) the lag time to wash the reactor volume was estimated to be 2 to 3 s. Thus virtually all the ^{16}O appearing in the gas phase after the switch, either in N_2O or in O_2, originated from the catalyst.

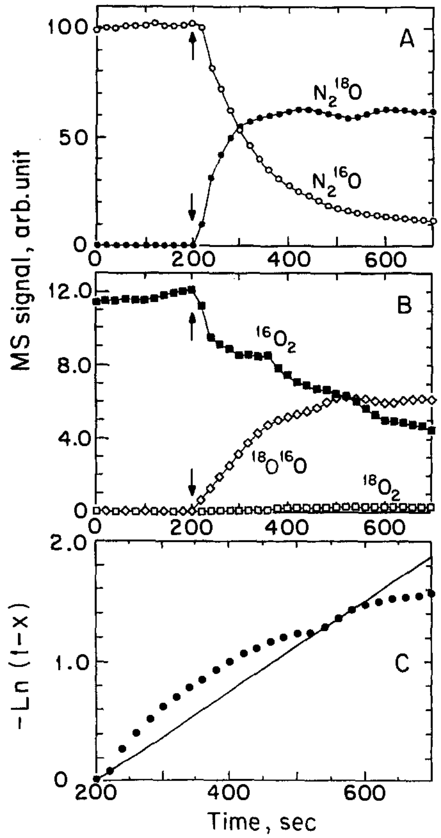

Fig. 3. The transient response observed in the decomposition of N_2O over FeM-6-14. Unlabeled N_2O in He was passed over the catalyst and a steady state was established. Data were recorded during the first 200 s before an abrupt switch was made to a nearly identical stream of $N_2{}^{18}O$. The changing isotopic distributions were recorded during the next 400 s. The N_2O products are shown in (A) and the O_2 products in (B). No mass replications occur with this reaction. These data were used to calculate the points shown in (C); see text for interpretation.

As with the NO experiment shown in fig. 1, $N_2{}^{18}O$ underwent exchange with ^{16}O from the catalyst. As shown in fig. 3A, over the first 85 s following the switch more $N_2{}^{16}O$ appeared in the gas phase than $N_2{}^{18}O$. After the curves crossed the exponential decay in $N_2{}^{16}O$ continued as the $N_2{}^{18}O$ curve leveled off. Comparison of the ordinates of figs. 3A and 3B suggests that ^{16}O is being removed from the catalyst considerably faster by this exchange than by reaction to form O_2 (1.4×10^{-4} mmol O_2/s).

As shown in fig. 3B, most of the O_2 produced following the switch consisted of ^{16}O. Only trace amounts of $^{18}O_2$ were produced over the entire course of the experiment and more $^{16}O_2$ than $^{18}O^{16}O$ was formed for the first 320 s following the switch in which the total O_2 formed was about 0.045 mmol (0.09 mmol of O). During the same period 0.40 mmol N_2O emerged unreacted. These figures may be compared with the ELO content present (0.05 mmol) and the total zeolite oxygen (6.8 mmol of O). Thus it may be concluded that the ^{16}O transported from the solid is several times greater than the ELO, but a small fraction of the total.

These results may be contrasted with those expected if only the ELO were replaced with ^{18}O during decomposition reaction. In this case the $^{16}O_2$ should approximate a step function in an abrupt drop to zero. The initial product should be mainly $^{18}O^{16}O$ whose concentration should pass through a maximum and be replaced by $^{18}O_2$ as the final product during the time scale of this experiment.

Practically no $^{18}O_2$ was formed as would be expected if $N_2{}^{18}O$ reacted with ^{18}O held by Fe^{3+} ions to release O_2 from the catalyst as postulated to satisfy the kinetics [6]. Possibly this means that these sites are mainly populated by ^{16}O relocated from the lattice concomitant with the deposit of ^{18}O elsewhere in the zeolite. These results are generally consistent with the findings of Leglise et al. [11]. These workers did not have available a source of $N_2{}^{18}O$ so they attempted the reverse experiment. The FeM was exhaustively exchanged with $^{18}O_2$ whose redox capacity was 1.5×10^{20}, and whose total oxygen content was 193×10^{20} atoms/g. At the end of six consecutive exchanges, the overall ^{18}O content was 34% of the total, but it was estimated, using Winter's model [12], that the readily exchangeable box surrounding the redox centers ($\sim 45 \times 10^{20}$ atoms/g) should contain $\sim$ 65% ^{18}O. Thus it was reasoned that the initial oxygen formed from decomposition of 1.2×10^{19} N_2O/g should contain $\sim$ 64% $^{18}O^{16}O$ and $\sim$ 36% $^{16}O_2$. This result was not obtained; the data clearly indicated that the initial product was nearly 70% $^{16}O_2$. Yet the kinetic data strongly supported a redox mechanism. This apparent paradox can now be understood in terms of the present porthole model. Oxygen enters the catalyst through oxygen ion vacancy sites and then enters the zeolite lattice while *other* oxygens pop out at sites where the ELO may be destabilized. Note that after 300 s following the switch more $N_2{}^{18}O$ was present in the gas phase than $N_2{}^{16}O$, yet 3 out of 4 atoms in the O_2 forming were ^{16}O. This result cannot be readily explained by exchange processes unrelated to the mechanism of decomposition.

The data of figs. 3A and 3B are amenable to the treatment used by Keulks et al.

[13] to estimate the fraction of the catalyst oxygen which is participating in the reaction. The problem is treated as a tank full of ^{16}O atoms into which ^{18}O atoms are flowing at rate F (mmol/s). Assuming complete mixing of the ^{18}O with the participating ^{16}O of the solid, the atom fraction x of the ^{18}O in the effluent procedure will be given by

$$-\ln(1-x) = (F/V)t\,, \tag{1}$$

where V (mmol) is the capacity of the tank and t (s) is the time. The boundary conditions are $x = 0$ when $t = 0$ (defined from the point where the switch was made). Thus a straight line passing through the origin is predicted. Since F is a known constant, V may be calculated from the slope of a plot of $-\ln(1-x)$ versus t. As shown in fig. 3C, the data do not fit the model very well, but nonetheless provide some perspective. The slope of the line drawn to approximate the data is 4×10^{-3} s^{-1}. Since the flow rate was 1.53×10^{-3} mmol ^{18}O s^{-1}, V may be estimated as 0.4 mmol O or about 6% of the total oxygen, but about 8 times the ELO. These figures for FeM are in reasonable agreement with those deduced for CuZ from the data of figs. 1 and 2. Clearly lattice oxygen is involved in the release of O_2 from the catalyst in amounts which increase with temperature. These amounts, however, do not appear to involve a large fraction of the total lattice oxygen.

4. Conclusions

(1) Over both the CuZSM-5 and FeM catalysts, lattice oxygen appears to be involved in the decomposition mechanism and in the desorption of O_2.

(2) As decomposition occurs, the identity of the oxygen atoms introduced into the solid is not conserved; oxygen atoms may be introduced at one place and O_2 may be formed and released from elsewhere on the solid.

(3) A limited amount ($\leqslant 10\%$) of the lattice oxygen participated in this experiment. It should be noted, however, that this value may vary with the zeolite composition and the external variables. We regret that circumstances did not permit us to extend these experiments with N_2O to the CuZSM-5 catalysts. A model which fits the observations envisages ^{18}O atoms formed by decomposition entering the solid through portholes (at reduced sites), mixing with nearby lattice oxygens and an *equivalent* number of the latter diffusing to positions where they can be stabilized as ELO. The reverse process may occur; O atoms may diffuse and recombine at oxidized sites and exit as $^{16}O_2$ via these (or other) portholes.

(4) Presumptive evidence of reoxidation of reduced sites followed by formation of adsorbed NO_2 was obtained from the rapid initial exchange of $^{15}N^{18}O$ to form $^{15}N^{16}O$ with $^{15}N_2$ being rapidly released on initial contact with the pretreated (partly reduced) zeolite. This follows the chemistry documented elsewhere [7,9,10,14].

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