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Studies of the Desorption of Oxygen from Cu-Zeolites during NO Decomposition

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The problem of the desorption of oxygen from transition metal ion base-exchanged zeolites during NO decomposition is considered. The TPD patterns of fully oxidized CuZSM-5-14-114 and CuY-2.5-75 were determined. Both contained nearly identical peaks from O_2 that desorbed at $T < 450$ K and at $T > 773$ K, but the former zeolite also had two peaks that appeared in the range 572 K $< T <$ 723 K which have been associated with that formed during the NO decomposition reaction. The TPD data could be related to binding energies obtained from van't Hoff plots of dissociation pressures from preparations preevacuated at several different temperatures. The low-temperature form is probably a molecular chemisorption, while those with substantial binding energies desorbing at higher temperatures are atomically bound extralattice oxygens. The exchange of $^{18}O_2$ with the ^{16}O of the catalyst was studied, as well as the products formed from the decomposition of $^{15}N^{18}O$ into the elements. The results from these experiments defined an important role for the lattice oxygen in the atom recombination and desorption of O_2 from the catalyst.

INTRODUCTION

The decomposition of NO over Cu-exchanged zeolites has been studied intensively during the last decade (*1, 2*). In general, the experimental data suggest that the reaction proceeds via a redox-type mechanism (*2c*). Accordingly (*1e, 2b*), a fraction of the Cu^{2+} becomes reduced to Cu^{+} through spontaneous desorption of oxygen. Reoxidation with NO regenerates the oxidized Cu^{2+} sites and N_2 is formed. These redox steps operate in a catalytic cycle. This chemistry was first described for the FeY system by Delgass *et al.* (*3*), who discovered that when the Na^{+} base-exchange cations of a Y-zeolite were replaced with Fe^{2+}, the latter could be oxidized to Fe^{3+} with the stoichiometric uptake of one O atom for each 2 Fe. They further showed that the oxygen bearing $Fe^{3+}Y$ could be reduced back to the original $Fe^{2+}Y$ (and no further) with H_2, forming a stoichiometric amount of H_2O. These changes were unambiguously confirmed by Mössbauer spectroscopy. Shortly thereafter, we showed (*4a*) that NO could equally well serve as the oxidant and CO as the reductant and that these two steps could be combined to produce $CO_2 + N_2$ in stoichiometric amounts. Thus it was concluded that this chemistry proceeded by a *redox* mechanism in which the altervalent base-exchange cations of the zeolite were reduced by 1 e by the reducing agent and reoxidized by 1 e by the oxidizing agent. When the latter is O_2, the question naturally arises as to how this molecule can be dissociated and the two ions diffuse over long distances (on the atomic scale) to locations where they can be stabilized as extralattice oxygen (ELO). This is a four electron process and must involve the formation of at least two O^{-2} ions and the oxidation of four Fe^{2+} ions. The process by which this can occur has been a puzzle. It is clear, how-

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ever, that these systems are oxygen carriers and that this oxygen is associated with the base-exchange cations, i.e., as extralattice oxygens (ELO).

A very similar mechanism was suggested for decomposition of N_2O over Fe-exchanged zeolites (*4b*). Here, the N_2O was the oxidizing agent and O_2 was desorbed in the reduction step. In contrast, NO oxidized reduced Fe-zeolites producing N_2, but when oxidation of the reduced sites was complete, the reaction ceased. With N_2O both N_2 and O_2 continued to form after the zeolite had become fully oxidized, i.e., the reaction continued. This paradox was resolved by suggesting that N_2O acts as its own reducing agent whereas NO does not, at least with the Fe-zeolites.

Cu-zeolites, especially CuZSM-5, are active catalysts for both N_2O and NO decomposition. If a redox mechanism prevails, the question arises of what is the reduction step. It has been shown (*2b, 5a, 6a*) that reduction of Cu^{2+} to Cu^{+} occurs concomitantly with the spontaneous desorption of O_2 from Cu-zeolites at temperatures above about 573 K. How these processes can occur poses a dilemma similar to the one described above.

The possibility that NO decomposition may occur in a cyclic process involving an ON–Cu–NO_2 intermediate has also been considered (*5b,c*) and shown to be in agreement with the observed kinetics. Here it is supposed that Cu^{+}–NO_2^{-} is formed by reaction of NO with an ELO. (The intermediate is formed by addition of a second molecule of NO.) Moreover, it has been suggested that this extralattice oxygen (ELO) is held bridged between two Fe^{3+} or Cu^{2+} ions. Recent MAS NMR (*5a*) and IR (*6a*) studies have substantiated the existence of such species in CuY and CuZSM-5.

Unlike CuY, the CuZSM-5 can be overexchanged very easily [Cu/Al > 0.5 (*6b*)]. These overexchanged samples were more active than underexchanged preparations. They had higher turnover frequencies (activity per Cu ion) for NO decomposition. Furthermore, the CuZSM-5 catalysts were much more active than CuY. The reason for this is not completely understood, but it has been shown (*5b*) that the properties and identities of possible intermediate species differ for the two catalysts. These preparations have been further investigated in the present work—this time documenting their response to the desorption of O_2.

Are these oxygen carrying sites the active centers in the NO decomposition or do the cations simply act as sites which furnish or accept electrons on demand as oxygen is somehow added to or subtracted from the lattice? Leglise *et al.* (*4c*), seeking an answer to this question, examined the decomposition of N_2O over FeM containing 34% of its initial oxygen content as ^{18}O. It was argued that the ^{18}O concentration should be much higher close to the redox sites (estimated to be 64% in the exchangeable box). Thus, the first O_2 formed, on decomposition of N_2O, was expected to be mainly $^{18}O^{16}O$. In fact, however, the initial product was $^{16}O_2$, creating still another puzzle requiring an explanation.

The decomposition of NO and N_2O has been described by redox mechanisms on various metallic oxides (*7*), although none of these was nearly as active in NO decomposition as CuZSM-5. In these cases the reactant has been considered to be the oxidizing agent and the reduction step of the catalytic cycle has been supposed to occur through the desorption of O_2. Correlations have been found between the reaction parameters of these decomposition reactions and those of ^{18}O exchange between the O_2 gas and the solid surface over a wide range of oxides (*7b*). These results have suggested that the desorption of O_2 plays an important part in all three reactions. In general, this should lead, as observed (*2b*), to an inverse dependence of the decomposition rate on oxygen pressure.

The catalyst oxygen may be characterized by its binding energy. Boreskov and coworkers (*8*) reported that these correlated with the rate of the homomolecular isotopic oxygen exchange, as well as with the rates

of oxidation of hydrogen and methane over various metal oxides. The desorption of O_2 molecules with the simultaneous formation of reduced and coordinatively unsaturated metal ion sites can be easily visualized for most oxides, e.g., CuO. With these, two neighboring vacancies may be formed which can adsorb two NO molecules and serve as a template for NO decomposition (*7b*). The oxygen isotopic work of Winter (*9*) showed that the oxide surface is in dynamic motion (a quasiliquid). Hence, neighboring vacancy pairs and single unsaturated sites are in equilibrium. The single sites may be active centers for the decomposition of N_2O, but not for NO decomposition. With the transition metal cation zeolites it is supposed that the base-exchange cations form the active redox centers and that these are widely separated by electrostatic repulsive and attractive interactions with each other and with the lattice, respectively. Moreover, the cation nearest neighbor distance must increase with the Si/Al ratio; for Si/Al = 25 there are only about four Al T-sites/uc. A single cation can act as a template, holding a dinitrosyl pair of NO molecules (*2c, d, 5b, c, 10a*), which may decompose into an N_2O molecule (thus forming the N–N bond) and leaving an oxygen behind (*10*). However, this would upset the charge balance unless a second reduced ion were in close proximity to furnish the second electron required to form the O^{2-} which must occur as the $(NO)_2$ is reduced. Since cation diffusion is rapid at reaction temperatures, this problem may be resolved by allowing the second cation to find and bond with the eliminated oxygen forming the bridged ELO species often suggested in the literature (*1f, 3, 5, 6, 11, 12*). We are then faced with a still more difficult problem. How do two such $[Cu^{2+}–O–Cu^{2+}]^{2+}$ sites eliminate their oxygens and how do these atoms find each other to release the O_2 which is formed spontaneously as Cu^{2+} ions of the catalyst are reduced? The present work was undertaken to shed light on these problems. The decomposition of the ON–Cu–NO_2 intermediate (*5b, c*) is a possible solution—as are related mechanisms (*13, 14*) suggested in the literature.

The methods and concepts which proved useful for the characterization of metal oxide systems were employed in the present study for Cu-zeolites. The binding energy of catalyst oxygen was determined and the isotopic oxygen exchange between the zeolite ^{16}O and $^{18}O_2$ or $^{15}N^{18}O$ was studied. The data suggest that in the most active CuZSM-5 catalysts, activity cannot be assigned to identifiable ELO-copper ion ensembles, but it is rather a collective property of the copper zeolite system.

EXPERIMENTAL

Catalysts. The Cu-zeolites studied in the present work have been characterized in detail and reported elsewhere (*2b, 5a, b*). They are identified here as CuZ-14-114 and CuY-2.5-74, where the cationic form is defined first; this is followed by the type of the zeolite (Z represents ZSM-5), Si/Al ratio, and percent exchanged. The Cu-forms were prepared from the sodium forms using conventional ion-exchange procedures. The unit cell compositions of the CuZ and the CuY samples were $Na_{0.20}Cu_{3.63}(ALO_2)_{6.36}(SiO_2)_{89.64}$ and $Na_{14}Cu_{20}(ALO_2)_{55}(SiO_2)_{137}$, respectively, and their Cu loadings were 0.62 and 1.56 mmol/g. The zeolite powder was pressed into tablets, crushed and sieved. The 40–80 mesh fraction was used for the experiments.

Temperature-programmed desorption of O_2. Pure He was passed through a quartz microreactor containing the zeolite held between quartz-wool plugs. The flow rate was maintained constant using a Brooks mass flow controller at the outlet of the reactor. The composition of the gas was continuously monitored using a QUAD 250 A type quadruple mass spectrometer (E.A.I., Palo Alto, California). The output was fed into a computer for data processing. The MS and the flow system were interfaced with a jet separator. The time-lag between the reactor and the MS was about 10 s. The system was

calibrated for oxygen using a 0.1% O_2/He mixture. The signal from the calibrating gas was determined under flow and MS conditions identical with those used during the experiments. The amount of O_2 desorbed from the catalysts into the He flow was estimated from the area under the TPD curves. The temperature was measured by a thermocouple positioned at the middle of the catalyst bed. An Omega CN2011 temperature programmer was used to increase the temperature at a rate of 10 K/min. The samples were pretreated in flowing O_2 overnight, cooled in O_2 to 303 K and purged with He for 1 h before initiating the TPD at a flow rate of 30 cm^3/min.

"Equilibrium O_2" pressure measurements. A 2-g catalyst sample was transferred into a 20-mm-diameter quartz tube attached to a UHV flange via a glass to metal seal. The sample tube was thus attached to a stainless steel manifold built from UHV elements. The manifold was equipped with valves for gas inlet and outlet and for evacuation. An MKS Baratron gauge capacitance manometer was connected to the manifold (vol = ~500 cm^3) for pressure measurements. For readout a Type 390HA-0010 pressure sensor with a 270B high-accuracy electronic signal conditioning and pressure display unit was used. The connecting tube between the pressure sensor and the manifold had a glass coldfinger to remove possible traces of H_2O. The finger was immersed in a liquid nitrogen bath during the pressure measurements. An electric furnace was used to heat the sample. The temperature was measured by a thermocouple close to the sample. (The pretreatment and measurement conditions varied as given in the legend of Fig. 2.)

The pressure reached in the evacuation step was $<10^{-4}$ Torr. The system was then isolated and the final "equilibrium" pressure was determined. Usually it took more than 24 h until no further pressure increase could be observed for a given point in an additional 5 h. P vs T plots were determined by changing the temperature from lower to higher values only. When the temperature was lowered the readsorption of O_2 was much slower than the desorption at the higher temperature. Thus it was impossible to reach thermodynamic equilibrium in any reasonable time. The system could be returned to its initial condition, however, by treatment in flowing O_2 at 773 K. Therefore, since we have not proved that equilibrium was reached, we have used quotation marks on "equilibrium." These data are generally consistent with the findings of Boreskov and co-workers (*8*) who reported similar effects and showed that the final "equilibrium" pressures attained were dependent on pretreatment conditions. These workers reported that the binding energy increased with the removal of oxygen from the catalyst. The underlying physical chemical basis for these effects was discussed by Sachtler *et al.* (*15*) many years ago.

Isotopic exchange. Experiments were carried out at an oxygen pressure of 100 Torr in an all-glass recirculation system having a volume of about 320 cm^3. (Catalyst pretreatment and exchange conditions are given in the legends of Figs. 3 and 4.) After pretreatment, the catalysts contained only the ^{16}O isotope. The preparations were exchanged at different temperatures with either $^{18}O_2$ or with an equilibrated equimolar mixture of $^{18}O_2$ and $^{16}O_2$. The mixture was equilibrated to $^{18}O_2 + 2\ ^{18}O^{16}O + {}^{16}O_2$ by contacting an electrically heated hot Pt filament with the circulating gas until the equilibrium composition was reached.

The isotopic distribution in the gas phase was monitored as a function of exchange time for a period of at least 2 h. The circulating gas was sampled and analyzed by a mass spectrometer (LKB 9000A, LKB-Produkter AB, Sweden). With each sample about 1% of the gas was withdrawn from the system for which correction was made. In a typical experiment, 1 g zeolite was exchanged with 40 cm^3 (NTP) of $^{18}O_2$. The amount of ^{18}O in the system was about 10% of the total oxygen content of the solid, but it was about ten times the redox capacity of CuY-2.5-74.

The redox capacities of the zeolites were determined in CO/O_2 reduction–oxidation cycles, by volumetric and/or microbalance methods (*2b*, *5a*). It was about 0.5 O/Cu for both Cu-zeolites at 773 K.

Decomposition of $^{15}N^{18}O$. The nitric oxide (Isotec Inc., Matheson) contained 99.9 atom% ^{15}N and 96.3 atom% ^{18}O. The 1% $^{15}N^{18}O$/He mixture was prepared by pressurizing the lecture bottle containing the NO with ultrahigh purity He (Matheson, USA). The NO content of the mixture was determined by GC. For studying the catalytic NO decomposition reaction the same microcatalytic reactor was used as for the O_2 TPD measurements. The mass spectrometric analysis allowed the gas composition to be recorded about every 30 s. The quantitative evaluation of the data was based on integrated areas of the MS signal vs time plots. The maximum absolute experimental error in the points shown was estimated to be ±10%. The errors stem from concentration-dependent fragmentation–recombination in the mass spectrometer and from mass dependent properties in the jet separator. The MS signals were calibrated using 1% NO/He, 0.1% O_2/He, and 0.1% N_2/He mixtures under conditions identical to those used for the experiments. The catalyst pretreatment and reaction conditions are given in the figure legends.

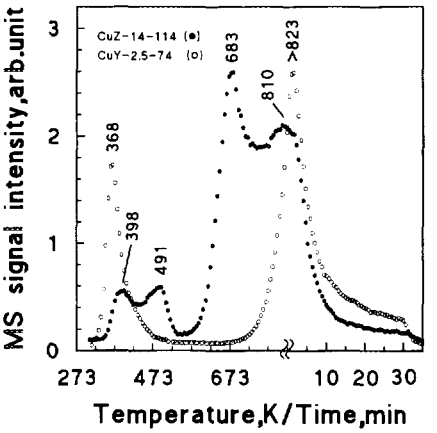

FIG. 1. Temperature-programmed desorption of O_2 from Cu-zeolites. Sample weights were chosen to contain equally 1.5×10^{20} Cu atoms. Samples were pretreated in flowing O_2 at 773 K overnight, cooled in O_2 to 303 K, and purged with a 30 cm^3/min He flow for 1 h. Then the temperature was raised at a rate of 10 K/min to 823 K, where it was maintained for an additional 35 min. The amounts of oxygen desorbed were 0.1 and 0.2 O/Cu for the CuY and the CuZ samples, respectively.

RESULTS

TPD. No desorption of O_2 could be detected from NaZ at temperatures up to 823 K. In contrast, the results obtained with CuZ and CuY are shown in Fig. 1. Two desorption peaks were found for CuY, one at about 368 K and the other above 823 K where the temperature ramp was stopped while the He flow continued for an additional 30 min. Similar results are shown for CuZ. With this preparation, *four* different peaks were obtained: two at lower temperatures (398 and 491 K) and two at higher temperatures (683 and above 810 K), i.e., the same two peaks found for CuY and two others at intermediate temperatures. The total amounts of O_2 desorbed corresponded to 0.12 and 0.16 mmol/g for CuZ and CuY, respectively. Since the CuZ and CuY contained 0.618 and 1.56 mmol Cu, the desorbed O_2 amounted to about 0.2 and 0.10 O/Cu for these two preparations, i.e., the CuZ gave up about twice as much oxygen per Cu as the CuY, but in both cases a substantial fraction of the ELO was released.

Decomposition pressures. The final pressure reached in the evacuation step at various temperatures prior to determining an isostere was $<10^{-4}$ Torr. On isolating the system at this temperature the O_2 pressure slowly increased over a period of several days to a final invariant value (no detectable change in an additional 5 h or more). Here we have assumed that the system is approaching equilibrium for this temperature and catalyst composition. The P vs T plots (Fig. 2) were determined from lower to higher temperatures only. When the temperature was lowered the readsorption of O_2 was much slower at the lower temperature

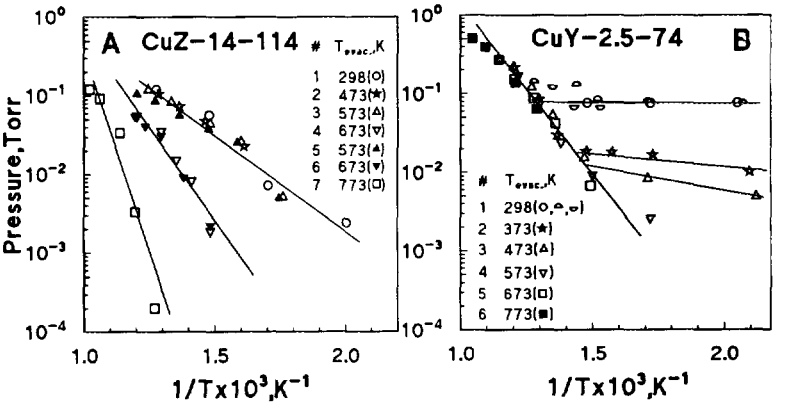

FIG. 2. The temperature dependence of the O_2 pressure above Cu-zeolites. Samples were pretreated in flowing pure O_2 at 773 K overnight, cooled to the evacuation temperature (T_{evac}), and evacuated for 1 h. After the oxygen pressure reached its equilibrium value in the closed system, the temperature was raised to the next higher value and the equilibrium O_2 pressure was redetermined. Once the van't Hoff plot was established, the process was repeated. After the overnight O_2 treatment, the sample was evacuated again at a different temperature and a new plot was determined.

than the desorption at the higher temperature. Thus it was impossible to return to the same "equilibrium" pressure assigned to the lower temperature in any reasonable amount of time. We have assumed that this is a kinetic, not a thermodynamic, limitation. The "equilibrium" pressure values recorded in this way are thought to be approaching equilibrium, but we cannot be sure. These findings are generally consistent with those of Boreskov and co-workers (*8*) and those of Sachtler *et al.* (*15*), who also reported the final "equilibrium" pressures attained were dependent on pretreatment (particularly on the amount of O_2 removed) as well as T; they also noted the lack of reversibility on lowering the temperature. The physical chemical basis for these effects has been discussed by Sachtler *et al.* (*15*), who showed that if a separate immiscible phase of a lower oxide is not formed, one or both ΔH and ΔS for the process will become a function of the extent of reduction. Thus both ΔG and the equilibrium constant K will be affected. Given true equilibrium data, application of the Clausius–Clapeyron equation will yield true enthalpies. As shown in Fig. 2, our experimental data could be fitted reasonably well by straight lines from which we have deduced the *binding energies* listed in Table 1.

A single plot described the data for CuZ (Fig. 2) for pretreatment by evacuation at all temperatures up to 573 K; a second curve

TABLE 1

Apparent Binding Energy of Oxygen in Zeolites after Evacuation at Different Temperatures[a]

$T_{evac.}$ (K)	B. E. (kcal/mol)		
	CuZ-5-14-114	CuY-2.5-74[b]	
		$T \leq 667$ K	$T \geq 667$ K
298	11	0.1	—
373	—	0.6	20
473	11	2.6	20
573	11	—	20
673	24	—	20
773	54	—	20

[a] Data were calculated from the results shown in Fig. 2 using the Clausius–Clapeyron equation and the slopes of the lines.

[b] After evacuation at $T_{evac} \leq 473$ K, the van't Hoff plots had two slopes, one at $T \leq 667$ K and the other at higher temperatures. As indicated, these correspond to a weakly bound species and a much more strongly held species, respectively.

was found after evacuation at 673 K and a third for 773 K. Interestingly, after moving to the second curve in Expt. 4 following pretreatment at 673 K, data falling onto the first curve could be obtained by repeating the pretreatment used in Expt. 3, and from thence back to the second curve by repeating the pretreatment of Expt. 4.

The data recorded for CuY had different characteristics. A single van't Hoff plot fitted all of the data for preparations evacuated at 573 K and above. After lower temperature pretreatments, substantial amounts of weakly held O_2 were evolved in the low temperature regime. These curves changed abruptly to the master curve for higher temperatures when they intersected it. This behavior suggested the presence of two distinct forms of chemisorbed oxygen, e.g., a weak chemisorption (possibly molecular), stable at low temperatures, superimposed on a much more strongly held atomic (ionic) chemisorption.

The various binding energies associated with the ELO obtained in these experiments are listed in Table 1. CuZ in its most oxidized condition holds oxygen with a binding energy of only 11 kcal/mol, but this increased dramatically as more and more oxygen was removed by increasing the evacuation temperature. The lowest value was only about half of the one obtained for CuY, although CuY carries in its most oxidized states also a weakly bound form (<3 kcal/mol) which was not found with the CuZ sample. We do not know what value is applicable in the isotope exchange experiments that follow. These were made with P_{O_2} = 100 Torr and it seems probable that a lower rather than a higher energy is effective. These data demonstrated vividly an essential feature required for NO decomposition, viz., an easily measurable oxygen vapor pressure at the temperatures required for this reaction.

Isotopic experiments. Results of the exchange of gaseous $^{18}O_2$ with catalyst ^{16}O are presented in Figs. 3 and 4. The data shown in Fig. 3 refer to exchange of pure $^{18}O_2$ and

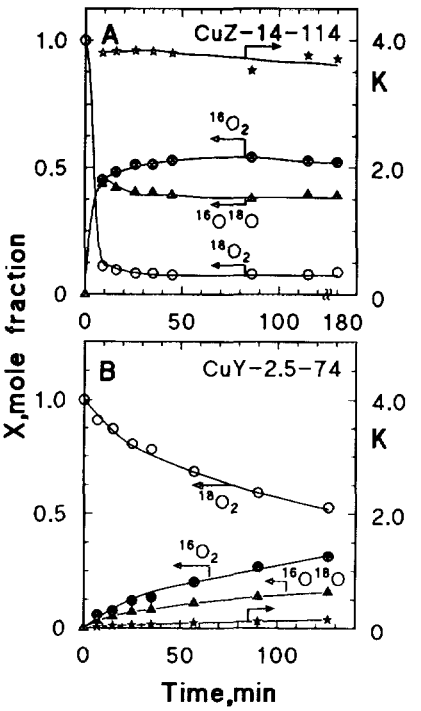

FIG. 3. Isotopic exchange of oxygen at 773 K in the presence of Cu-zeolites: 1 g zeolite was pretreated in flowing $^{16}O_2$ at 773 K overnight, cooled to 473 K, and evacuated for 30 min. The temperature was then raised to 773 K and the catalyst was contacted with 40 cm^3 (NTP) $^{18}O_2$ at a pressure of 100 Torr. Oxygen gas was circulated through the catalyst bed in a closed recirculation system at a rate of about 40 cm^3 (NTP)/min, and the gas phase was periodically sampled for MS analyses. K is the pseudoequilibrium constant calculated from the gas-phase composition.

that in Fig. 4 to exchange with the preequilibrated $^{18}O_2 + 2\ ^{18}O^{16}O + {}^{16}O_2$ mixture. The equilibrium constant for the latter system is close to 4.0. During the exchange a flux of ^{16}O from the pretreated solid moves into the gas phase and is replaced by ^{18}O in an equal amount from the gas. Pseudoequilibrium constants can be calculated from the gas-phase composition at any point in time and the deviation from 4.0 is a measure of the relative rate of homomolecular exchange of the gas phase molecules, i.e., the equilibration

$$^{18}O_2 + {}^{16}O_2 \overset{K}{\rightleftharpoons} 2\ ^{18}O^{16}O, \qquad (1)$$

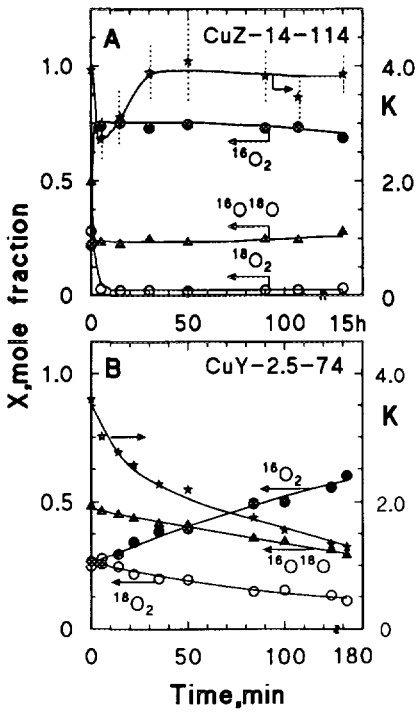

FIG. 4. Isotopic exchange of oxygen at 773 K in the presence of Cu-zeolites. A 50–50 mixture of $^{16}O_2$ and $^{18}O_2$ was preequilibrated over a hot platinum filament; 40 cm^3 (NTP) of the equilibrated mixture was contacted with 1 g zeolite at 773 K and an O_2 pressure of 100 Torr. Catalyst pretreatment and experimental conditions are specified in Fig. 3. Error bars were added where required; they show the maximum possible error where this exceeds the size of the points.

to the rate of the exchange process disturbing the equilibrium. The data presented in Figs. 3 and 4 show that for CuY, Eq. (1) is slow compared with the $^{16}O_2$ flux into the gas phase: the system remains far from equilibrium after 2 h. With the CuZ preparation this is no longer true, but the salient point is the extremely rapid transfer of ^{16}O into the gas phase with the consequent rapid removal of ^{18}O from the gas phase. With this catalyst, K values did not deviate much from 4 over the whole range of the experiment, so it is not possible to decide the relative importance of Eq. (1) vis-à-vis exchange with the solid in bringing the system to equilibrium, but this is irrelevant. The important lesson is that the lattice oxygen may be involved in the transport of O between Cu-ion sites, which evidently act as portholes for the entry of oxygen into the catalyst, and the sites where they are stabilized as ELO. NaZ and MgZ do not act in this way; hence, Cu or another altervalent ion is essential for this process, presumably acting as a redox center.

CuY appears to function in the same way, but much less efficiently. With this material, $K \rightarrow O$ (Fig. 3) or moves further and further from its equilibrium value as the experiment proceeds (Fig. 4). Hence, the exchange data are kinetically significant; they are not disguised by the homomolecular exchange [Eq. (1)]. It is significant that $^{16}O_2$ appears to be a primary product on exchange with $^{18}O_2$. Similar and some additional conclusions may be reached from the data shown in Fig. 4, *vide infra*.

When NO decomposition was studied with a conventional flow system using $^{15}N^{18}O$, the response was immediate and surprising. The data are presented in Fig. 5. At a conversion to N_2 of about 40%, about 60% of the NO fed remained in the reactor effluent, but was mainly $^{15}N^{16}O$, not the entering $^{15}N^{18}O$. Thus the unreacted gas had undergone almost complete exchange with zeolite oxygen during the contact time of about 0.25 s. Moreover, although $^{15}N_2$ was released at a rate which increased slowly with time, no $^{18}O_2$ and very little $^{18}O^{16}O$ was contained in the initial product; this was almost exclusively $^{16}O_2$. The $^{18}O_2$ and $^{18}O^{16}O$ products were produced in increasing amounts, however, while the $^{16}O_2$ decreased as time went on and the ^{18}O content of the solid increased. After the 100-min run was finished, integration of the curves of Fig. 5 yielded the following information: 1.8 ^{16}O/Cu was removed as $^{16}O_2$, 2.2 ^{16}O/Cu as $^{18}O^{16}O$, and 1.6 ^{16}O/Cu as $^{15}N^{16}O$; thus, a total of at least 5.6 ^{16}O/Cu was removed from the catalyst. (More may have gone undetected as NO_2.) Evidently the lattice oxygen is intimately involved in the reaction mechanism.

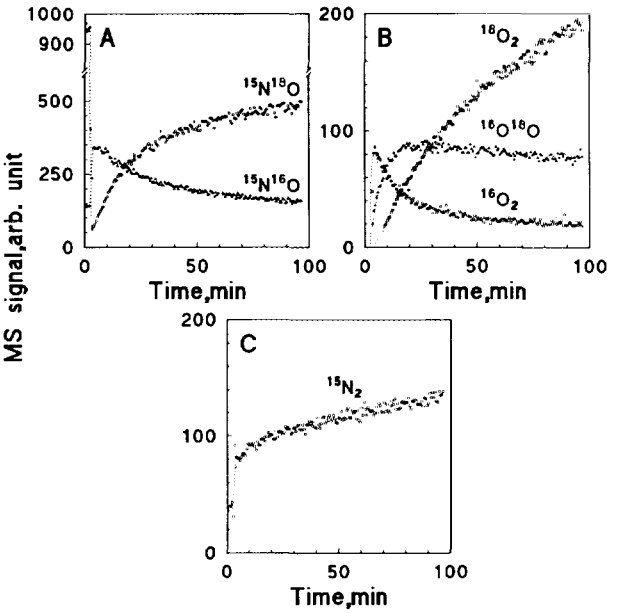

FIG. 5. Decomposition of $^{15}N^{18}O$ over CuZ-14-114 zeolite: 340 mg zeolite was pretreated in flowing $^{32}O_2$ at 773 K overnight, purged at the same temperature with flowing He for 1 h, and contacted with 1% $^{15}N^{18}O$/He mixture. The flow rate was 100 cm^3/min ($W/F = 4.9 \times 10^5$ g s/mol). Gas composition was continuously monitored by MS. Data given for the first 2 min represent the composition of the reactant as it enters the reactor.

In the above experiment, the catalyst had been given the standard pretreatment immediately prior to contact with $^{15}N^{18}O$. Thus, it had been partly reduced by the spontaneous desorption of oxygen. For comparison, an experiment was attempted in which the catalyst was first put in steady-state reaction using $^{14}N^{16}O$ and then suddenly switching to $^{15}N^{18}O$. The results from the transient response which followed qualitatively resembled very closely those shown in Fig. 5, but unfortunately they were not unambiguous. Using our experimental setup, it was not possible to separate cleanly the peaks at mass 30 and mass 32. Thus, $^{15}N_2$ could not be distinguished from $^{14}N^{16}O$ nor $^{14}N^{18}O$ from $^{16}O_2$. If the reasonable assumption was made that the $^{14}N^{16}O$ was washed from the gas phase in the first couple of minutes (required to sweep the gas from the system), then the NO species replicated almost exactly those shown in Fig. 5A and the O_2 species those in Fig. 5B. The chief difference appeared in the curves for the N_2 produced. Now, instead of the single curve for $^{15}N_2$, curves for $^{14}N_2$ and $^{15}N^{14}N$ were also observed. The former was the gas being produced before the switch and its concentration fell to about $1/e$ of its initial value in the first minute, but then the exponential decay continued over the twenty minute duration of the experiment approaching zero asymptotically. Most interesting was the very small amount of $^{15}N^{14}N$ formed; this reached a maximum of about 2.5% of the N_2 during the first minute or so of the experiment. The results suggest that N_2 is released very rapidly from the template of the species in which the N–N bond is formed and that this species is very short lived, i.e., ordinarily it is either a dinitrosyl

containing two $^{15}N^{18}O$ or two $^{14}N^{16}O$ species. Evidently there is very little opportunity to form the mixed dinitrosyl.

DISCUSSION

It is now widely recognized that the Cu-zeolites may undergo self-reduction (Cu^{2+} becomes Cu^{+}) with the elimination of O_2. More recently attention has been focused on how this oxygen is held by the catalyst and how it is introduced in the first place (*5*). The data suggest that extralattice oxygen (ELO) is introduced during preparation of the catalyst in amounts less than the Cu^{2+} loading. Indeed, evidence exists suggesting that an important part of it is held bridged between two Cu^{2+} ions. Thus, two such sites (or four Cu^{2+} ions) would be required to hold a single pair of O atoms necessary to form an O_2 molecule released by spontaneous desorption of oxygen.

The desorption of oxygen from CuZ and CuY is compared in Fig. 1. Both zeolites release a small amount of O_2 at fairly low temperatures and larger amounts at higher temperatures. The CuZ, however, has four TPD peaks while the CuY has only two. Moreover, the CuZ released a substantial portion of its O_2 around 683 K where the NO decomposition reaction takes off, whereas the CuY zeolite showed no desorption in this region. This may be the primary reason why the CuZ is a much better catalyst than the CuY for this reaction. Another may be that the fraction of the ELO released by the former is much greater than the latter (0.21 O/Cu vs 0.10 O/Cu, respectively). These data demonstrate the phenomenon while we are seeking to understand.

Teraoka *et al.* (*11*) studied the TPD of O_2 from CuZSM-5. Our data for samples of comparable Cu-loadings and under similar experimental conditions are in good agreement with theirs. They found two poorly resolved peaks below 473 K, a principal peak around 673 K and an additional peak above 823 K. The integrated concentration of the desorption below 823 K was 0.17 O/Cu. Earlier reports (*17*) of the O_2 TPD from CuY are in reasonable agreement with those shown in Fig. 1 when differences in composition, pretreatment, etc, are taken into account. Two weak peaks were observed below 373 K and additional peaks at 600 K and above. The total oxygen desorbed below 823 K corresponded to about 0.1 to 0.2 O/Cu, in agreement with our results.

Boreskov and co-workers (*8*) studied the apparent decomposition pressure of various oxides as a function of temperature. Different van't Hoff plots were obtained as the solids were degassed at increasing temperatures prior to isolating the systems. In general, the higher the evacuation temperature, the larger was the binding energy of the oxygen. It was supposed that these observations reflected changes in composition (variations in stoichiometry) of the solids prior to the experiments.

The data presented in Fig. 2 may be best understood when considered in conjunction with the TPD data of Fig. 1. The CuY system was the simplest; it showed only two forms of chemisorbed oxygen (or two desorption processes); one desorbed below 473 K and one above 700 K. Thus, the portions of the van't Hoff plots of low slope at the right correspond to the desorption of O_2 from the low-temperature TPD peaks, and the steeper slope on the left to desorption of the high-temperature form. The low heat (or activation energy) of the former suggests that it is molecular, whereas the much higher value (20 kcal/mol) which fits all of the data for samples pre-evacuated at $T \geq 473$ K stems from a strongly bound form and presumably corresponds to the ELO held bridged between two Cu^{2+} cations.

The TPD from CuZ showed two additional peaks at 491 and 683 K. This was reflected on Fig. 2A by formation of three separate plots: one yielding a heat of 11 kcal/mol fitting the points for all evacuation temperatures below 573 K, a second with heat of 24 kcal/mol for samples evacuated at 673 K, and a third with heat of 54 kcal/mol for 773 K. These curves represent, in reverse order, the ELO remaining after evacuation

at 773, the sum of the former and the ELO contained in the 683 K peak, and the third all of the bound oxygen acting cooperatively. So far as the authors are aware, this is the first time data of this kind have been associated with specific forms of surface bound oxygen. It is notable that after formation of the second curve by evacuation at 673 K, the system could be returned to the first curve and then back to the second by repeating the appropriate pretreatment.

The TPD curves reflect different activation energies for desorption. These are the heats of adsorption plus the activation energies for adsorption. For systems at equilibrium, rates of adsorption are equal to the rates of desorption. If the system is perturbed by desorption at higher temperature, it should relax to its original state more rapidly than on desorption because it does not need to overcome the barrier imposed by the heat of adsorption. This was not the case. On lowering the temperature much longer times were required to restore the system to its initial state than the total time required for desorption on ramping the temperature upward. This shows, if nothing more, that the activation energy for adsorption is high; otherwise, readsorption would be fast. As noted above, this is not an unusual circumstance in experiments of this kind (*8, 15*). The observed hysteresis results from the fact that readsorption does not take place on the same surface from which O_2 was desorbed.

In the case of the CuY there was clear evidence for a molecular precursor state, and thus an activation energy for dissociation may be required. In this picture two distinct forms of adsorbed oxygen are defined. With CuZ two additional states or processes are present and one of these (peak at 683 K) may be associated with the oxygen desorption following NO decomposition at room temperature (*16*). The high temperature peak at $T > 823$ K [reportedly at 950 K (11)] may correspond to loss of oxygen from the lattice. Presumably these three principal forms communicate with each other via a catenary chain to effect the spontaneous desorption of O_2; the binding energy derived from van't Hoff plots represents the highest barrier to be overcome in the pathway. Interestingly, the maximum amount of O_2 actually desorbed in these experiments was 0.002 O/Cu, i.e., only a small fraction of the ELO.

The kinetics of isotope exchange between $^{18}O_2$ and the oxygens held by metal oxides have been considered in detail (*9, 17, 18*). In particular two processes have been distinguished for situations where mainly surface oxygens are involved in the gas–solid exchanges. These may be written as

$$^{18}O_2(g) + {}^{16}O(s) \overset{R_1}{\rightleftharpoons} {}^{16}O^{18}O(g) + {}^{18}O(s) \quad (2)$$

and

$$^{18}O_2(g) + 2{}^{16}O(s) \overset{R_2}{\rightleftharpoons} {}^{16}O_2(g) + 2{}^{18}O(s). \quad (3)$$

The former would be expected if a gas-phase O_2 molecule reacted with a single ELO atom; the latter would function when an O_2 molecule adsorbs at one place and another O_2 is released from elsewhere on the surface. These are simple examples but, of course, are not unique. Moreover, the heteromolecular exchange process may be disguised by a fast homomolecular exchange (Eq. (1)). This has been frequently found and in these cases no mechanistic information can be deduced (*18d, e*). This was approximately the situation with the CuZ catalyst, but fortunately not with CuY. As shown in Fig. 3, when $^{18}O_2$ was exchanged with CuZ containing only ^{16}O, the three isotopic gaseous species, $^{18}O_2$, $^{18}O^{16}O$, and $^{16}O_2$ were close to thermodynamic equilibrium ($K \approx 4$) over the entire course of the reaction. The mole fraction of each gas remained nearly constant. Note, however, the drastic change in composition during the first couple of minutes as $^{16}O_2$ flooded into the gas phase. With CuY, on the other hand, the system moved further from equilibrium (K

decreased away from 4) and as time went on more and more ^{16}O was transported into the gas phase and ^{18}O onto the solid. Moreover, $^{16}O_2$ increased faster than $^{18}O^{16}O$, indicative of a process described by Eq. (3).

Experiments of the kind shown in Fig. 4 are more diagnostic. In these a pre-equilibrated equimolar $^{16}O/^{18}O$ mixture ($^{16}O_2$ + $2^{18}O^{16}O$ + $^{18}O_2$) was used as the exchange gas with the ^{16}O of the solid. Here there is less net transport of the isotopes so that the process is effectively slowed down; the homomolecular exchange thus becomes less important. Klier *et al.* (*18b*) showed, theoretically as well as experimentally, that if the exchange process is dominated by Eq. (3), then K decreases while the ratio of $^{18}O^{16}O/^{18}O_2$ remains constant. Reference to Fig. 4B shows clearly that both of these conditions are fulfilled and the two at a time process is operative. Presumably the same is true for the CuZ, but the process is hidden by the rapid homomolecular exchange (Eq. (1)). The dip in K near the start of the experiment (Fig. 4A) may confirm this. Thus, the data suggest that an O_2 molecule is adsorbed as a precursor state at one point in the solid while another is released elsewhere. The process does not appear to involve interaction of a molecule of $^{18}O_2$ with a single ^{16}O ELO held at isolated centers. Similar K vs t plots have been reported (*18e*) for this exchange with MgO. In this case a similar but deeper dip was obtained and the time to recover the near equilibrium value of K varied with t between 100 and 2000 min, compared with <30 min in our experiments at T = 773 K. In these cases the dissociative adsorption of O_2 is faster than the exchange reaction. The time dependence of K for CuY resembles that reported (*18e*) for V_2O_5 and WO_3.

The net transport of ^{16}O from the catalyst into the gas phase per Cu ion has been calculated, and these results are listed in Table 2. Even at temperatures as low as 673 K several times as much ^{16}O was removed from the CuZ by exchange than its redox capacity (0.5 O/Cu). The degree of exchange increased with temperature and with the increasing relative amount of ^{18}O in the solid–gas system. The highest value obtained (16.5 O/Cu) in our experiments amounted to about 33% of the total oxygen content of the zeolite. This is in fair agreement with the exchange level obtained by Leglise *et al.* (*4c*) for Cu-mordenite.

TABLE 2

Amount of ^{16}O Removed from CuZ-5-14-114 and CuY-2.5-74 Zeolites by Exchange with $^{16}O_2$ Data Are Expressed as O/Cu[a]

Temperature (K)	Pure $^{18}O_2$		Equilibrated 1-to-1 mixture of $^{18}O_2$ and $^{16}O_2$	
	CuZ	CuY	CuZ	CuY
673	2.3	0.3	1.7	—
723	3.6	0.7	—	—
773	4.5	1.1	2.2	0.6
	16.5[b]	2.8[b]	—	—
823	—	—	2.6	—

[a] Various exchange temperatures were used. Otherwise, pretreatment and exchange conditions are the same as given for Figs. 3 and 4. The Cu contents of the CuZ and the CuY samples are 0.62 and 1.56 mmol/g, respectively.

[b] Instead of 1 g, 0.1 g of catalyst was used; the other exchange parameters remained unchanged. The solid phase and the gas phase contained about equivalent amounts of oxygen.

The exchange levels obtained with CuY under identical conditions were generally lower. The reason for this is that CuY contains twice as much copper as CuZ and comparison is made on the basis of O/Cu. This basis was chosen because the isotopic oxygen exchange is closely related to the presence of an altervalent base-exchange cation. Otherwise no exchange was obtained under our experimental conditions, e.g., with the Mg-forms of the zeolites. Nevertheless, the comparison of the exchange levels on a mass basis also showed that the exchange into CuZSM-5 is favored over CuY.

The oxygen from $^{15}N^{18}O$ mixed extensively with the catalyst oxygen under the conditions of NO decomposition (Fig. 5). Exchange also occurred with the unreacted $^{15}N^{18}O$. When first exposed to the catalyst more $^{15}N^{16}O$ than $^{15}N^{18}O$ exited the reactor. This, of course, reversed as readily accessible ^{16}O was removed from the system. Similarly, $^{16}O_2$ was the largest initial product, not $^{18}O_2$ which left the reactor initially more slowly than $^{18}O^{16}O$. The total ^{16}O removed from the catalyst over the 100-min experiment as $^{15}N^{16}O$ amounted to 1.6 O/Cu; also 1.8 O/Cu appeared as $^{16}O_2$ and 2.2 O/Cu as $^{18}O^{16}O$. These data demonstrate the important role played by the lattice oxygen and afford an explanation of how widely separated ELO atoms can desorb to form O_2. Oxygen is introduced as atoms during NO decomposition at the cationic centers; it desorbs as O_2 by acting cooperatively with the lattice oxygens. These findings are in accord with the heteromolecular oxygen exchange data discussed above.

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