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Reactive Oxygen in NaCuX Zeolites

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The amount of oxygen in NaCuX zeolites which is readily available for oxidation of CO has been determined as a function of temperature, copper concentration and catalyst pretreatment. Under fairly mild conditions this reactive oxygen is associated with reduction of part of the Cu(II) to Cu(I). Experiments with N_2O and esr measurements indicate that the reactive oxygen is an O^{2-} species. Prolonged reduction of the catalysts with CO can lead to reduction of zeolite Cu(I) to Cu(0) and an associated increase in reactive oxygen. Reduction of the catalysts with hydrocarbon similarly involves reduction of Cu(I) to Cu(0). However, in this case there is evidence (X-ray, esr) of agglomeration of Cu(0) leading to formation of a CuO phase on oxidation.

INTRODUCTION

Transition metal ion exchanged zeolites are currently of interest as possible oxidation catalysts. The oxidation of CO is widely used as a test reaction. Boreskov (*1*) examined a series of Cu(II) zeolites containing cupric ions, and found that catalytic activity for CO oxidation increased linearly with Cu(II) concentration up to 36% exchange and exponentially between 36% and 90%. Later Ione *et al.* (*2*) suggested that catalytic activity was dependent on conditions of preparation. Following a more detailed study of NaCuY zeolites, Maksimov *et al.* (*3*) suggested that nonlattice oxygen was involved in oxidation of CO and he concluded that its concentration was higher in zeolites containing metal ion clusters (these catalysts exhibiting higher activities). The active oxygen was reported to be in the form of M–O–M bridges, presumably produced during dehydration. Kubo *et al.* (*4*) examined the oxidation of CO over zeolites containing chromium, iron, cobalt, copper or thallium ions. Catalysts which adsorbed oxygen at 400°C, particularly Cu(I) and Fe(II) zeolites, were very active in oxidation of CO.

The redox properties of catalysts are relevant to catalysis and several studies have been made on transition metal zeolites. Rickert (*5*) considered the reduction with hydrogen of zeolites containing Ni^{2+}, Cu^{2+} or Ag^{+} ions. Reduction was observed to be reversible but reduction of Ni^{2+} to Ni^0 at 400°C for 48 hr was followed by a slow recrystallization of Ni^0 outside the zeolite. Leith and Leach (*6*) used esr techniques to demonstrate the reversibility of reduction of Cu^{2+} ions with CO, H_2 and hydrocarbons in CuX zeolites. Herman *et al.* (*7*) observed the reduction with H_2 of Cu^{2+} to Cu^0 in CuY zeolite followed by agglomeration to form a metallic phase which on oxidation produced CuO. The rate of reduction of Cu^{2+} ions in X and Y zeolites by butadiene and ammonia was reported by Maxwell and Drent (*8*). Rates were

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found to be second order in Cu^{2+} in agreement with previous work by Naccache and Ben Taarit (*9*) on the reduction of cupric zeolites by CO, and the proposed mechanism involving zeolitic oxygen was also in agreement with that suggested by those authors. Recently Jacobs *et al.* (*10*) have demonstrated that prolonged evacuation of Cu(II) zeolites leads to reduction to Cu(I) and loss of oxygen which they propose is removed from the zeolite lattice.

Few detailed studies have appeared concerning the reaction of transition metal zeolites with reductants in the absence of oxygen. The activity and selectivity of the available oxygen is clearly of importance in catalytic oxidative reactions. Roginskii *et al.* (*11*) considered the oxidation of ammonia, carbon monoxide and ethylene by a range of transition metal zeolites (in the absence of gaseous oxygen). In most cases a single level of ion exchange was examined. They concluded that the oxidation of CO by oxygen over Cu(II) zeolites involved active oxygen adsorbed on the catalyst.

The present work, which is part of a more general investigation of zeolites as oxidation catalysts, was undertaken to examine further the reactivity of oxygen associated with transition metal zeolites.

EXPERIMENTAL METHODS

MATERIALS

The catalysts were Cu13X zeolites prepared by cation exchange between pure commercial Na13X, and copper acetate solution (pH 5.2). The Na(I) and Cu(II) content were determined separately and the results are shown in Table 1. Measurements indicated some decrease in surface area with increasing ion exchange; in the case of Cu13X(5) this corresponded to a 20% loss in crystallinity. Before the experiments the catalysts were washed with distilled water, dried, pelleted, crushed and then sieved into fractions with known particle size ranges.

TABLE 1

Sample	% Na remaining	% Cu exchanged
Cu13X(1)	87.0	7.15
Cu13X(2)	77.0	14.57
Cu13X(3)	60.25	33.10
Cu13X(4)	48.20	53.85
Cu13X(5)	40.90	62.35

APPARATUS

Experiments were carried out using both a pulse and a static reactor.

The pulse microcatalytic reactor was connected to a gas-liquid chromatograph for analysis. The reactor tube was set in an Al block furnace, accurate to within ±1°C, preceded by a preheater. Normally 0.1–0.2 g of the hydrated catalyst, particle diameter 252–500 μm was used. Commercial grade purity helium was generally used as a carrier gas and the catalyst was dehydrated at 400°C in a stream of helium for 16 hr as a standard pretreatment. Reactants were introduced into the carrier gas via a gas sampling valve (Pye series 104) or by means of a hypodermic syringe through a rubber septum. Oxygen (B. O. C. Ltd.) and carbon monoxide (Air Products Ltd.) were of commercial grad epurity. The tetramethyl ethylene (TME) was commercial material which was further purified by fractional distillation.

The static system consisted of a Pyrex reaction vessel (165 cm^3) incorporating a "metrosil" leak leading directly to a VG Micromass 6 mass spectrometer via a short, heated connection. The whole was enclosed in an Al block furnace, accurate to within ±1°C with a temperature gradient along its length of less than 2°C. The reactor was connected to a mercury diffusion pump and a gas handling system. Greaseless taps (Youngs Ltd.) were used throughout to remove the risk of catalyst contamination. The hydrated catalyst (0.05 g), normally consisting of particles 170–252 μm in diam-

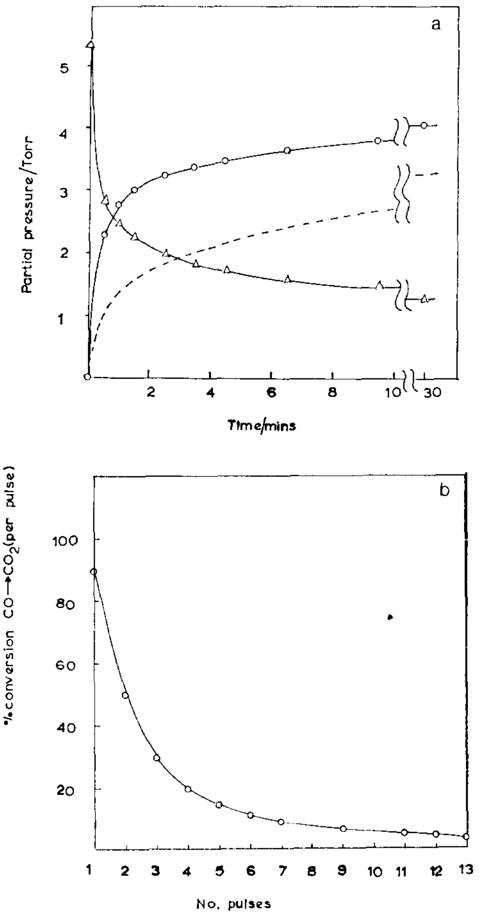


FIG. 1a. Typical results for static reactor. Reaction of CO with oxygenated Cu13X(4) at 390°C. (△) CO; (○) CO_2; (– –) reaction of CO at 390°C with dehydrated catalyst prior to oxygenation. (b) Typical results for pulse reactor. Reaction of CO with oxygenated Cu13X(5) at 400°C.

eter, was dehydrated at 390°C for 16 hr under a vacuum of 2×10^{-5} Torr as a standard pretreatment. The mass spectrometer was calibrated for the gases used after each experiment. Oxygen (99.5% pure), carbon monoxide (99.95%), carbon dioxide (99.995%) were supplied by Air Products and were research grade purity. The nitrous oxide (Air Products) was further purified by freezing in an acetone–cardice trap and pumping away any N_2 or O_2.

The esr measurements were made using a Varian E9 (X-band) spectrometer.

1. Reactive Oxygen Introduction into Cu13X Zeolites by Treatment with Oxygen

Preliminary experiments confirmed that copper zeolites contain a small amount of reactive oxygen removable by CO as CO_2. Further experiments were performed to study the effect of copper content and temperature of reaction on this active oxygen.

In the static reactor the catalyst was

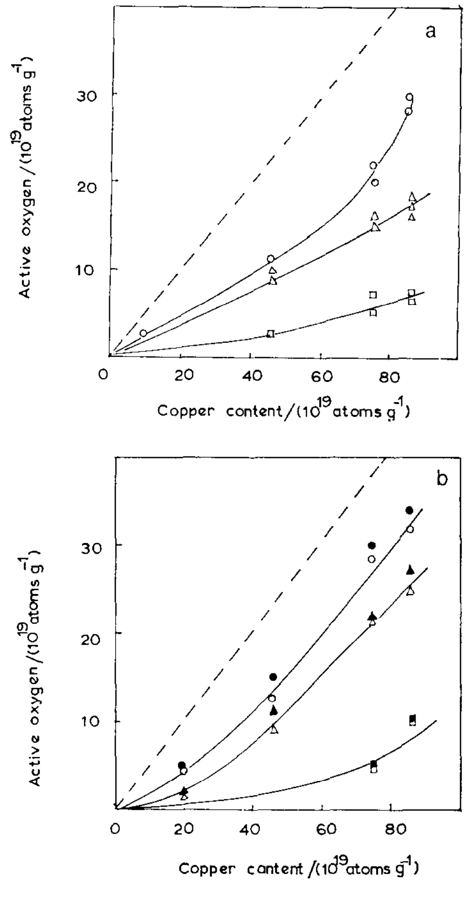


FIG. 2a. Variation in active oxygen with Cu content and temperature of reaction. Static reactor, (°C): (○) 390; (△) 297; (□) 200; (– –) curve expected if every two Cu atoms are associated with one oxygen atom. (b) Variation in active oxygen with Cu content and temperature of reaction. Pulse reactor: oxygen removed by CO → CO_2 (°C): (●) 400; (▲) 300; (■) 200; oxygen adsorbed by reduced catalyst (°C): (○) 400; (△) 300; (□) 200; (– –) curve expected if every two Cu atoms are associated with one oxygen atom.

activated by heating for 30 min in 12 Torr of O_2, followed by evacuation for 3 min. Then CO was admitted (4–12 Torr) and the mass range 28–44 was scanned at 30 sec intervals until no further change was observed. Typical results (Fig. 1a) show that CO_2 evolution occurs instantaneously with no induction period. The reaction shows a slow "tail" at all temperatures and is stoichiometric ($1\ CO_{(g)} \rightarrow 1\ CO_{2(g)}$) and perfectly reproducible even after several [e.g., Ref. *16*)] redox cycles. At lower temperatures (<200°C) there is evidence of CO retention on the surface and on heating the closed reactor after evacuation CO_2 and CO are desorbed.

The final pressure of CO_2 (Fig. 1a) is used to calculate the amount of reactive oxygen. Typical values are shown in Fig. 2a. The amount of reactive oxygen increases with temperature of reaction and copper content (it is virtually zero in Na13X below 400°C). From Fig. 1a it is evident that the dehydrated catalyst already contains reactive oxygen (ca. 80% of the amount measured after oxygen pretreatment) so that the reactive oxygen is generated at some stage during preparation and subsequent dehydration of the zeolite.

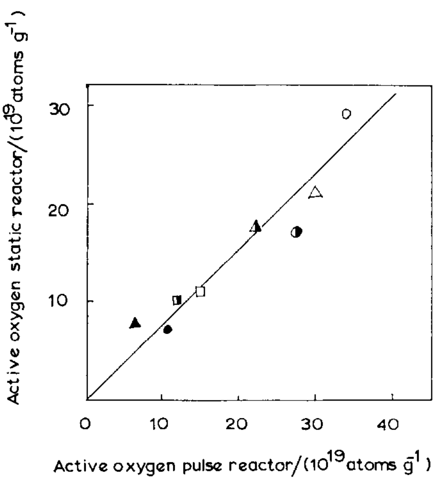


FIG. 3. Comparison of results from pulse and static reactors. Cu13X(5) (○) 400°C, (◑) 300°C, (●) 200°C; Cu13X(4) (△) 400°C, (◭) 300°C, (▲) 200°C; Cu13X(3) (□) 400°C, (◧) 300°C.

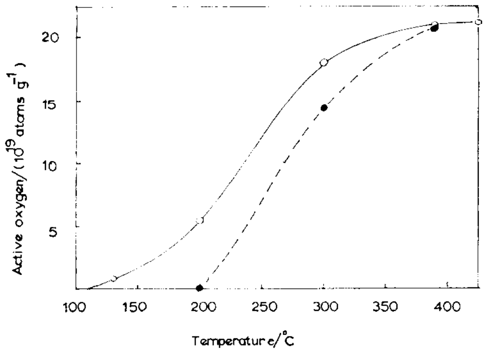


FIG. 4. Comparison of active oxygen deposited by O_2 and N_2O on Cu13X(4) at different temperatures. (○) Oxidized using O_2; (●) oxidized using N_2O.

In the pulse reactor the catalyst was activated at 400°C by streaming 152 Torr O_2 in He for 1 hr. After cooling in He to reaction temperature the reactive oxygen was measured by introducing 0.5 cm^3 pulses of CO at atmospheric pressure. Typical results are shown in Fig. 1b and summation of CO converted to CO_2 gives a measure of reactive oxygen in the catalyst. After reaction with CO the amount of O_2 readsorbed was measured and corresponded well with the amount removed (Fig. 2b).

To ascertain whether the decrease in measurable reactive oxygen with decreasing temperature is an absolute difference, a prolonged reaction with CO at 200°C was followed using the static reactor. Cu13X(4) was oxygenated at 390°C, cooled to 200°C and reacted with CO. After 30 min, 3.5×10^{18} molecules of CO_2 were produced corresponding to 33% of the active oxygen removable at 390°C. The catalyst was reoxygenated once more but this time it was reacted with CO for 16 hr. The amount of CO_2 produced corresponded to 9.5×10^{18} molecules or 85% of the active oxygen removable at 390°C. Thus the decrease in reactive oxygen with temperature is a kinetic effect and even at 200°C the amount is similar although it reacts more slowly. However, the amount of *rapidly* removable

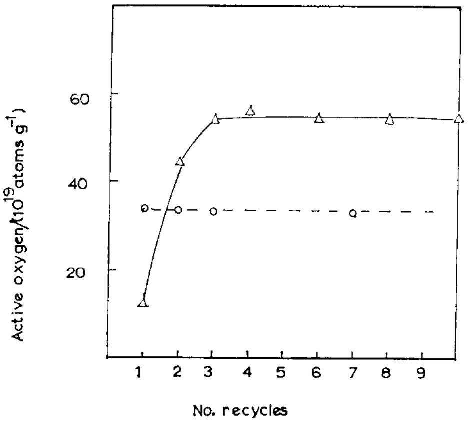


FIG. 5. Effect of redox cycles on active oxygen content of Cu13X(5). (○) With CO at 400°C; (△) with TME at 400°C.

oxygen does increase with temperature. A comparison of the results obtained in the static and pulse reactors is shown in Fig. 3. The results compare reasonably well, results from the pulse reactor being slightly higher than those from the static system. This may be due to the larger CO pressure used in the former case (760 Torr compared with 4–12 Torr) or it may be associated with the evacuation of the oxygenated catalyst in the static reactor before reaction with CO. Experiments showed that reactive oxygen can be removed on evacuation (e.g., 30% by pumping Cu13X(5) at 400°C for 24 hr). This value is comparable with those obtained by Jacobs *et al.* (*10*) on CuNaY.

2. Reactive Oxygen Introduced into Cu13X Zeolites by Treatment with N_2O.

Nitrous oxide has been used in surface chemistry to deposit atomic oxygen on metal catalysts (*12*) and it was felt that it would be of interest to compare the reactivity of oxygen introduced in this manner into the zeolite with that introduced by O_2, which may be either molecular or atomic.

The dehydrated catalyst [Cu13X(4)] was reduced with CO at 390°C in the static reactor, cooled to the temperature of reaction and exposed to N_2O (10.5 Torr) for 30 min. After pumping down CO was introduced and the desorption of CO_2 followed. The amount of oxygen adsorbed, calculated from N_2O consumed or N_2 produced, was found to agree with the amount removable as CO_2 within $\pm 5\%$. Figure 4 shows the variation in active oxygen with temperature of pretreatment for N_2O and O_2. At 200°C the N_2O is unable to oxidize the reduced Cu13X(4) although by 390°C it introduces as much active oxygen as O_2. The shape of the CO_2 desorption curves for N_2O pretreated catalysts are very simi-

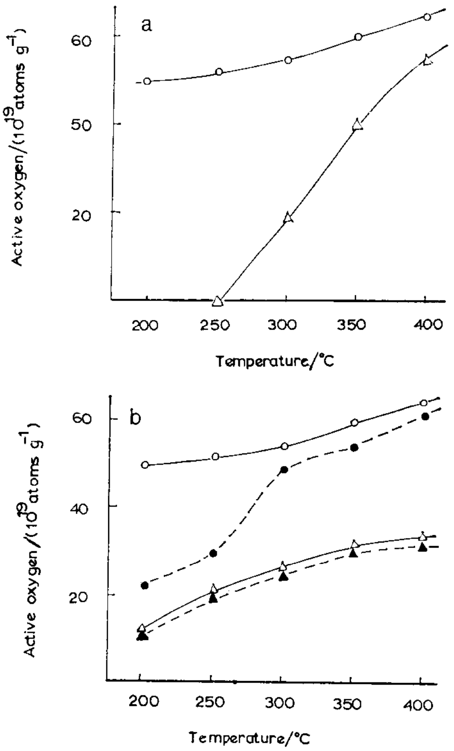


FIG. 6a. Effect of pretreatment with TME on active oxygen in Cu13X(5). (○) Active oxygen removed by CO → CO_2; (△) active oxygen removed by TME → $CO_2 + H_2O$. (b) Comparison of active oxygen in TME-pretreated Cu13X(5) and fresh catalyst. After TME pretreatment: (○) Active oxygen removed by CO → CO_2; (●) active oxygen adsorbed after reduction. Fresh catalyst before TME exposure: (△) Active oxygen removed by CO → CO_2; (▲) active oxygen adsorbed after reduction.

lar to those shown in Fig. 1a at all temperatures. The desorption curve at 390°C, where the amounts of reactive oxygen introduced by the two gases are identical, are superimposable.

As Fig. 4 shows, the N_2O is unable to oxidize the reduced Cu13X(4) at 200°C. In order to test whether there is any oxidation of a CO/N_2O mixture the reduced catalyst was exposed to a 2:1 mixture of N_2O:CO at a total pressure of 13.6 Torr. Since there is no mass change in the major peaks, the $NO^+(30)$ subsidiary peak from N_2O was followed. No oxidation to CO_2 was observed. The experiment was repeated using a CO/O_2 mixture and within 10 min a quantity of O_2 equivalent to 30% of the N_2O used in the experiment above, had reacted. In this case, of course, the oxygen gas is able to oxidize the reduced Cu13X(4). Thus it seems that reactive oxygen is directly involved in the oxidation of CO in CO/O_2 or CO/N_2O gas mixtures and if the catalyst cannot adsorb reactive oxygen oxygen it will not be able to oxidize carbon monoxide.

Since the CO_2 desorption curves at 390°C are identical for the N_2O and O_2 pretreated catalysts, it seems that the adsorbed oxygen is also identical (presumably atomic in form) in both cases.

Rates of reaction of N_2O with the reduced catalyst Cu13X(4) (54% exchanged) are more rapid than values reported for cracking N_2O on a Cu13X catalyst (20% exchanged) (*13*). In the present work the initial rate of reaction,

$$N_2O_{(g)} + [\text{site}] \rightarrow N_{2(g)} + [\text{O-site}], \quad (1)$$

at 298°C and N_2O pressure of 10 Torr is 5×10^{17} molecules s^{-1} g^{-1}, whereas Rudham and Sanders (*13*) quote a cracking rate, at much higher temperatures (437°C) and N_2O pressure of 100 Torr, of 5×10^{16} molecules s^{-1} g^{-1}. Once our reduced catalyst has been oxidized by N_2O at 298°C the cracking reaction,

$$N_2O_{(g)} \rightarrow N_{2(g)} + \tfrac{1}{2}O_{2(g)},$$

is observed and this proceeds at a rate slower (<0.1) than reaction (1).

3. Reaction of Adsorbed Oxygen with Tetramethyl Ethylene (TME)

In addition to varying the oxidizing agent, the reducing agent was varied to examine the effect on the amount of oxygen removable. Experiments were performed in the pulse reactor using TME to examine its reaction with Cu13X(5) pretreated with O_2. The only oxidation product identified was CO_2, but a mixture of isomers of TME, including isomers due to migration of CH_3, was also observed (glc). In this case results were not reproducible (unlike those obtained with CO). It was found that the amount of reactive oxygen increased on recycling the catalyst. A typical set of results is shown in Fig. 5 with results for CO shown for comparison. In the first reaction with TME the amount of reactive oxygen removed is less than that obtained by reaction with CO. However, in the second cycle the amount removed is found to have increased greatly and the reactivity continues to increase until a steady value is finally achieved after ca. 5 cycles.

The reactivity of the catalyst recycled with TME is shown in Fig. 6a. It was activated in O_2 at 400°C and then the oxygen removed by CO and TME in the temperature range 200–400°C was measured. It can be seen that less oxygen is removed by TME than by CO at all temperatures. An interesting property of the TME-treated catalyst is shown in Fig. 6b. The solid lines represent the amount of oxygen removable by CO before and after TME treatment. The TME pretreatment has increased the reactive oxygen content by a factor of 2. The broken lines represent the amount of oxygen readily readsorbed after reaction with CO. As previously noted, on the "fresh" catalyst the oxygen removed by CO is replaced readily by reaction with O_2 at the same temperature. However, on

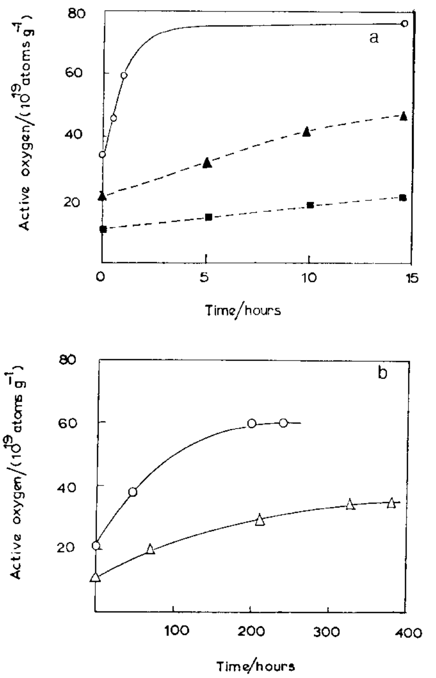


FIG. 7a. Increase in reactive oxygen on prolonged exposure to CO. (○) Cu13X(5), flow system (150 Torr CO); (▲) Cu13X(4); (■) Cu13X(3); static system (corrected to 150 Torr, assuming first order pressure dependence). (b) Increase in reactive oxygen on exposure to CO. (○) Cu13X(4), CO 24 Torr static reactor; (△) Cu13X(3), CO 24 Torr static reactor.

the TME-treated catalyst the oxygen removed by CO cannot be rapidly replaced except above 350°C.

After TME pretreatment the pattern of percentage conversion ($CO \rightarrow CO_2$) per pulse of CO changes from the gradual decline shown in Fig. 1b to a more complicated pattern in which percentage conversion rises for the first few pulses before proceeding to fall smoothly. This suggests that CO and O_2 are competing for adsorption sites and the rate of production of CO_2 depends on both their surface concentrations.

X-Ray examination of the TME-pretreated catalysts showed lines characteristic of a CuO phase. This was confirmed by comparing the diffraction pattern with that for a mixture of CuO and NaX zeolite with a concentration of copper (as oxide) similar to the concentration of copper in the catalyst.

This CuO phase presumably arises from the reduction of Cu^{2+} to Cu^0 followed by migration and coalescence of copper atoms which are subsequently oxidized to form a separate CuO phase. Carbon or organic matter also appears to be deposited on the catalyst after TME treatment with part, at least, of this being removed as CO_2 on heating in oxygen.

4. Effect of Prolonged Pretreatment with CO

Although the reaction of adsorbed oxygen with carbon monoxide was reproducible, it was decided to investigate the effect of prolonged exposure to relatively high pressures of CO. Experiments were performed in both reactors.

a. Pulse reactor. Commercial grade CO (150 Torr in helium) was passed over Cu13X(5) at 400°C, for varying periods; at intervals the catalyst was reoxidized at 400°C with O_2 and the amount of reactive oxygen was measured by reaction with CO. The results are plotted in Fig. 7a which shows a relatively rapid increase in the amount of available active oxygen produced using this treatment. The final amount of active oxygen produced is identical with the amount produced after TME pretreatment. X-Ray examination of these catalysts once more showed CuO lines in the diffraction pattern.

The reaction was repeated using CP grade CO streaming over a fresh catalyst and once more the formation of a CuO phase was observed. However, in both grades impurities are present and we cannot rule out the possibility that trace impurities (e.g., hydrocarbons) are responsible for the reduction to Cu^0 with the subsequent formation of a metallic phase which on oxidation gives CuO.

b. Static reactor. To minimize the possibility of interference by hydrocarbon impurities the effect of prolonged exposure to research grade purity CO (hydrocarbon content 30 vpm) at lower pressures in a static system was also studied.

In these experiments Cu13X(4) and Cu13X(3) at 390°C were exposed to research grade purity CO (99.9% pure) at a pressure of 24 Torr for varying periods up to 400 hr. At intervals throughout the treatment the catalysts were evacuated, treated with O_2 and then the amount of reactive oxygen removable by CO was measured. The results can be seen in Fig. 7b. The amount of reactive oxygen is found to increase with CO treatment, though much more slowly than on exposure to hydrocarbons or to CO in the flow system (see Fig. 7a). The amount of reactive oxygen finally attained is very similar to the amount present after TME pretreatment or prolonged CO treatment in the flow reactor. However, X-ray examination of the catalysts used in these experiments showed no evidence for the presence of either a CuO or a Cu_2O phase. This may mean that no such phase is present or it may be that any oxide phase formed is too dispersed to give a recognizable diffraction pattern.

5. *Electron Spin Resonance Measurements*

For esr studies the pulse microreactor was fitted with a quartz side arm. The esr spectra of Cu13X(3) were recorded at room temperatures and −150°C as oxygen was removed from the catalyst by reaction with pulses of CO. Approximate double integration gave the esr signal intensities which are plotted against oxygen removed in Fig. 8. From the least squares line, the removal of 2.31×10^{20} atoms of oxygen is associated with the reduction of 4.63×10^{20} atoms of copper, consistent with the stoichiometry (copper:active oxygen) of 2:1,

$$[\mathrm{Cu(II)}]_2\mathrm{O} \underset{+\frac{1}{2}\mathrm{O}_2}{\overset{+\mathrm{CO},\ -\mathrm{CO}_2}{\rightleftharpoons}} 2\mathrm{Cu(I)}.$$

The catalyst was then treated with TME to increase its reactive oxygen and after oxidation the Cu^{2+} signal intensity was found to be 60% of that observed originally. Presumably 40% of the Cu was in the form of CuO which is not detectable by esr in zeolites (*7*, *9*).

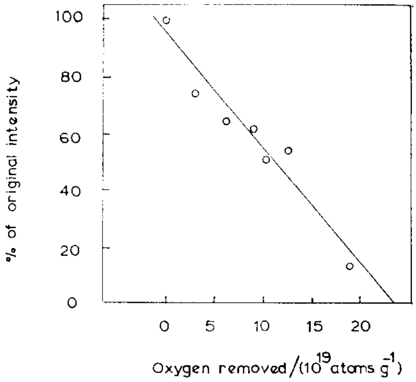


FIG. 8. Decrease in esr Cu^{2+} signal on removal of oxygen by CO → CO_2.

A static reactor fitted with a quartz side arm was used to follow the effect of prolonged CO exposure on the esr signal of Cu13X(4). The catalyst was treated with CO (99.95% pure) at 390°C and 24 Torr for 200 hr and the color of the reduced catalyst changed from pale green to vivid violet and finally to purple grey. The oxidized catalyst was green/black in color but the esr signal intensity did not decrease and on rehydration a signal identical with that of the fresh catalyst was observed, providing supporting evidence for the absence of a CuO phase.

DISCUSSION

Reactive oxygen removable as CO_2 between 200 and 400°C is associated with the copper cations in the zeolite since Na13X shows no activity in this temperature range. Copper ions are closely associated with the active centers for oxygen adsorption since they participate in electronic rearrangements during adsorption/desorption. Electron spin resonance measurements show that Cu^{2+} signal intensities decrease linearly with removal of active oxygen (as

TABLE 2

% Cu exchange	Atomic ratio (active oxygen:copper)[a]							
	Temp (°C)						390°C after prolonged CO pretreatment (s)	400°C after TME pretreatment (p)
	390 (s)	400 (p)	297 (s)	300 (p)	199 (s)	200 (p)		
62	0.33	0.40	0.20	0.32	0.08	0.12	—	0.76
54	0.28	0.40	0.25	0.29	0.10	0.07	0.75	—
33	0.24	0.33	0.22	0.25	0.07	—	0.79	—

[a] (s) static reactor; (p) pulse reactor.

CO_2) and exposure to oxygen restores the Cu^{2+} signal. This redox cycle involving the Cu(II) ions can be performed repeatedly without measurable changes in the amounts of available active oxygen. Only after prolonged treatment with CO at relatively high pressures or exposure to hydrocarbons is the amount of reactive oxygen at any temperature increased.

The amount of adsorbed oxygen removable as CO_2 depends on temperature of reaction with CO, copper content and previous history of the catalyst (Table 2).

Reaction of CO with the oxygenated catalyst is stoichiometric between 300 and 400°C with no evidence of disproportionation. At 200°C a small amount of CO is adsorbed on the surface without production of CO_2, and this effect becomes more pronounced at lower temperatures (consequently quantitative estimates of amounts of available oxygen are unreliable at $T <$ 200°C). The CO adsorbed below 200°C (e.g., 140°C) can be removed as CO_2 and CO by heating the catalyst. Table 2 shows that the dependence of the amount of reactive oxygen on copper content is not strictly linear at fixed temperature, since the atomic ratio (active oxygen:copper) decreases with decreasing copper content. This may be associated with an increasing proportion of copper in inaccessible sites at lower percentage exchange. Traces of water may play a part since nonlinearity is more evident in the pulse reactor, where water is not completely removed, and at lower temperatures, where water has a poisoning effect (*14*).

Table 2 shows that the number of active oxygen atoms per Cu ion increases with increasing temperature of reaction, tending towards a value where each oxygen is associated with two copper ions (0.5). Electron spin resonance results at 400°C correspond to reduction of two Cu^{2+} ions for the removal of each active oxygen (approximately 20% of the Cu^{2+} ions remaining unaffected).

These results are consistent with redox stoichiometries

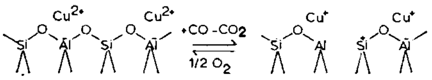
$$2Cu^{2+} + O^{2-} \underset{+\frac{1}{2}O_2}{\overset{+CO,\ -CO_2}{\rightleftharpoons}} 2Cu^{+}. \qquad \text{(i)}$$

The involvement of a single oxygen atom rather than an O_2 species is supported by results using N_2O.

Clearly the temperature effect on reactive oxygen content is a rate effect rather than an absolute difference, since even at 200°C the amount of oxygen removable on prolonged reaction with CO (16 hr) tends towards the same value as the amount removed at 400°C.

A stoichiometry involving one reactive oxygen atom associated with two metal ions agrees with previous work on reduction of copper zeolites with butadiene (*8*) and with the values obtained by Kubo *et al.* (*4*) for chemisorption of oxygen on NaCu(I)X and NaCu(I)Y zeolites (atomic ratio (oxygen:copper) = 0.5). Kubo *et al.* observed no oxygen chemisorption on NaCu(II)Y. In the present work reactive oxygen was already present in NaCu(II)X zeolites after dehydration (which would explain the observed lack of chemisorption of O_2 by Kubo *et al.*). Prolonged evacuation can, however, remove some reactive oxygen (up to 30% depending on temperature and duration of evacuation), which is consistent with recent reports on autoreduction of Cu^{2+} during oxygen desorption (*10*).

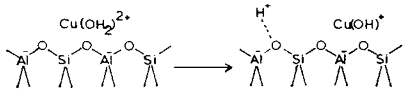
Reactive oxygen may be either zeolitic or extraframework oxygen. If it is the former then reactions of type (ii) will produce Lewis acid sites on removal of oxygen (*8*).



(ii)

Formation of Lewis acid sites is reported during autoreduction of copper zeolites (*10*). Recent isotope exchange experiments on NaY and NaCaY (72% exchanged) using $C^{18}O_2$ show that in the NaCaY zeolite in 1 hr exchange can involve oxygen amounting to about 3.5% of the zeolitic oxygen at 400°C, and 15% at 500°C (*15*). Corresponding values for NaY are much lower, implying that rate of exchange of zeolitic oxygen depends on the countervalent cation. Moreover, at 500°C the amount of lattice oxygen partaking in exchange is considerably greater than the Ca^{2+} content and so it cannot be associated only with hydrolytic fragments. Exchange reactions using $^{18}O_2$ suggest that introduction of Cu^{2+} ions into NaY increases the rate and alters the mechanism of exchange at 670°C (*16*). In the present experiments the rate of removal of oxygen by CO (maximum removed 2.8%) is very rapid and occurs at relatively low temperatures (200°C) so that if the active oxygen is largely lattice oxygen then its removal is greatly facilitated by Cu^{2+} ions.

An alternative source of reactive oxygen may be the extraframework oxygen atoms reported by Gallezot *et al.* (*17*) in their X-ray diffraction study of NaCuY (54% exchanged). These were explained as residual fragments of water molecules removed during dehydration. Because of the strong electrostatic fields in zeolite cavities hydrolytic reactions are said to occur during dehydration (*18*).



(iii)

Further dehydration forms bridged Cu^{2+} pairs

$$2Cu(OH)^+ \rightarrow Cu^{2+}O^{2-}Cu^{2+} + H_2O\uparrow. \quad \text{(iv)}$$

If all the active oxygen removable as CO_2 is from bridged ion pairs then the present results suggest that after dehydration most of the Cu^{2+} ions exist in bridged pairs (50–80%) regardless of the degree of exchange. A similar conclusion is drawn, from esr studies on NaCuY, by Chao and Lunsford (*19*) who report that, even in moderately exchanged NaCuY, isolated Cu^{2+} ions represent only a small fraction of the total copper content. Most Cu^{2+} ions are thought to be present as nonlinear pairs with both Cu^{2+} ions in sites SI′. Kubo *et al.* (*4*) prepared Cu(I) zeolites (X and Y) and found they adsorbed O_2 and were very reactive in oxidation of CO. Cu(I)Y zeolite was about 40 times as active as Cu(II)Y at 200°C. Unless the NH_3 treatment produces lattice defects it seems that in Cu(I) zeolites reactive oxygen must be extraframework. Very high activity may therefore be associated with extraframework oxygen.

Most workers ascribe Cu^{2+} ions in dehydrated zeolites to positions in the sodalite cages rather than supercages. In fully hydrated zeolites the Cu^{2+} ions are in the supercages as hexaquo complexes, rotating freely, but on dehydration they become fairly strongly bound to the lattice. Gallezot *et al.* (*17*) using powder X-ray diffraction methods on dehydrated, 54% exchanged CuNaY found that 75% of the Cu^{2+} ions were in site SI′ and the remaining 25% in the inaccessible site SI. Maxwell and De Boer (*20*) have recently carried out single crystal X-ray analysis on completely copper-exchanged natural faujasite. In these experiments dehydration was at 150°C, (cf. 500°C used by Gallezot *et al.*) and may be incomplete. Maxwell and De Boer found 51% of the Cu^{2+} in site SI′ but only 5% in site SI, 19% in site SII and 12% in the supercage site SIII. From the present work it would appear that at higher temperatures 70–80% of the Cu^{2+} ions are in sites accessible to CO and associated in pairs with a reactive oxygen atom.

The positions of the various sites mentioned and the relevant pore diameters are known (*21*). The CO and O_2 molecules are small enough to enter sodalite cages. Experiments by Huang (*22*) using Cu(I)Y zeolites indicate that CO can be trapped in the sodalite cages by cooling the zeolite in CO from 400 to −196°C and therefore at elevated temperatures the CO molecule has access to the smaller cages. This is further supported by work on copper(I) carbonyls in Y zeolites (*23*) in which all the Cu^+ ions are found to be accessible to CO in the temperature range 0–100°C although they are said to be positioned in the sodalite cages.

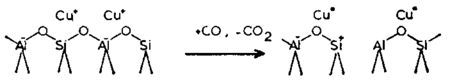
If the active sites in the present work are in the sodalite cages then the effect of temperature on the amount of reactive oxygen may simply be a measure of the ease of diffusion of CO into, or of CO_2 out of, the β cages which increases with increasing temperature. In fact Huang (*22*) found that oxygen uptake on Cu(I)Y is very small at 20°C presumably because the Cu^+ ions are inaccessible, but at 400°C Kubo *et al.* (*4*) found it had risen to an oxygen atom to metal ion ratio of 0.44.

However, it is known that ligands (H_2O, pyridine and NH_3) can move Cu^{2+} ions into the supercages (*24*), suggesting that copper ions migrate to the most favorable positions as conditions are altered. Hence correlation between positions of cations as determined by X-ray analysis and reactivity under quite different conditions may be misleading. Copper ions can migrate in Y zeolite (*14*) and it may be that the effect of temperature in the present work on the amount of reactive oxygen is a measure of the ability of the Cu^{2+} ions to diffuse to more reactive sites in the supercages. Reaction of TME with the reactive oxygen must involve migration of Cu^{2+} ions into the supercage since TME is too bulky to enter sodalite cages.

Table 2 shows that although the redox cycle described above is reproducible, prolonged pretreatment with CO doubles the reactive oxygen content. The original oxidized catalyst reacts rapidly with CO and most of the copper ions are reduced to Cu^+ within 30 min at 400°C. Further exposure to CO at three times the pressure for 400 hr increases the atomic ratio (active oxygen:copper) to 0.8, compatible with the reactions

$$Cu^{2+}O^{2-} \underset{+\frac{1}{2}O_2}{\overset{+CO,\ -CO_2}{\rightleftharpoons}} Cu^0, \qquad \text{(v)}$$

where each reactive oxygen atom is associated with one copper ion. The reduction of Cu^+ to Cu^0 is a slow process which would be consistent with a reaction involving lattice oxygen as shown below.



(vi)

The metallic copper atoms formed can move away from the Lewis acid site produced. On exposure to O_2 the zeolite oxygen may not be replaced but the Cu^0 is oxidized to Cu^{2+} and reactive O^{2-} is associated with it as in Eq. (v). Reaction (vi) is much slower than the reduction of Cu(II) to Cu(I). If this follows reaction (ii) then it appears that Cu^{2+} activates zeolitic oxygen much more than Cu^{+}, presumably by facilitating electron transfer from O^{n-} (zeolite) to Cu^{2+}.

Prolonged pretreatment with TME or with CO containing small amounts of impurities (e.g., H_2, H_2O, hydrocarbons) gives more rapid reduction of Cu^{+} to Cu^{0} with the formation of a distinct CuO phase on reoxidation. In these cases the Cu^{0} migrates to form large clusters of metal atoms some of which do not return to the zeolitic sites on oxidation to Cu^{2+} but form CuO. From the decrease in intensity of the esr signal it appears that about 60% of the copper ions remain in the sodalite cages [Cu13X(3)]. Careful treatment with pure CO reduces Cu^{2+} to Cu^{0} without formation of a separate phase as indicated by the absence of CuO X-ray lines and the fact that the shape and size of the Cu^{2+} esr signal is not greatly affected. (As previously noted this might be a question of the dispersion of CuO.) The formation of Cu^{0} has usually been thought to prevent reversible oxidation to zeolitic Cu^{2+} (*9*, *22*) but recent work (*7*) suggests that reduction of Cu^{2+} ions in CuNaY to Cu^{0} with H_2 produces metallic crystallites which can be reoxidized into Cu^{2+} zeolite lattice ions as well as to CuO. It is suggested that at high temperatures (400°C) Cu^{2+} is at a lower free energy in the zeolite lattice than in the CuO lattice. Thus, depending on the reaction conditions reversible reduction of Cu^{2+} to Cu^{0} is feasible. Similarly the reduction of platinum to the zerovalent state in zeolites has been reported to result in monoatomic dispersions, clusters or sizable crystallites depending upon the conditions of reduction (*26–28*).

In the present experiments, once a CuO phase is formed a different pattern of reaction of the oxygenated catalyst with CO is observed (Fig. 6b). Although the adsorbed oxygen can be removed rapidly at all temperatures it can only be replaced completely and easily above 350°C. Below 350°C only a fraction of the removed oxygen is easily replaceable, the remainder being adsorbed only very slowly (16 hr). Also there is evidence for an induction period with the percentage conversion per pulse of CO to CO_2 rising for the first few pulses before proceeding to fall smoothly as before, suggesting that the reaction rate depends on surface CO concentration.

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