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Studies of a CuY Zeolite as a Redox Catalyst

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The stability and behavior of CuY in the redox cycles with CO/O_2, H_2/O_2, and CO/NO have been studied using a microbalance operating in the flow mode and with a standard (BET) volumetric system. When CO was used as a reducing agent CO_2 was produced, thus removing oxygen from the zeolite lattice, but when H_2 was used only some of the H_2 consumed was evolved as H_2O. The rest was retained as lattice OH groups, but this was minimal when H_2 was used after treating the sample with CO. Oxidation with NO produced only N_2. At 500°C the sample was stable and could be reversibly oxidized and reduced through many cycles using either CO/O_2 or NO/CO. In all cases the ratio O/Cu was close to 0.5, i.e., 1*e*/Cu. Treatment in CO at higher temperatures did not affect the reversible nature of the oxidation, but now the valence change was substantially larger; it approached 2*e*/Cu. The crystallinity of the exchanged zeolite was studied using X-ray diffraction and by measurement of the pore filling with liquid N_2. No significant changes could be detected after the different treatments, even those performed at 750°C. Temperature-programmed reduction, temperature-programmed oxidation, and X-ray diffraction studies were made and the different maxima are reported. CuO and Cu^0 appeared in the oxidized and reduced samples, respectively, after treatment at 750°C in CO but not at lower temperatures. Subsequent redox cycles at 500°C did not appear to affect the size or amount of Cu^0 crystallites. CuY was active in the oxidation of CO with O_2 or NO. Its activity was lower than that of FeY zeolite when it exhibited an oxygen-carrying capacity of 0.5 O/Cu. Treatment with CO at 750°C, however, reversed the situation. Kinetic results showed that the fresh CuY catalyst was close to zero order in CO and fractional order in O_2 with an activation energy of 15 kcal/mole. After treatment at 750°C in CO, the rate law became dependent upon the CO/O_2 ratio. It was close to first order in CO and zero order in O_2 under oxidizing conditions ($CO/O_2 \leq 2$), but the orders were reversed under reducing conditions ($CO/O_2 > 2$). The activation energies were 12 and 15 kcal/mole, respectively. The data suggested that the Cu^{2+} with bound oxygen are the species active in the oxidation reaction.

INTRODUCTION

Transition metal ion-exchanged zeolites are of interest as possible oxidation catalysts. In particular, copper-exchanged Y and X types have been shown to exhibit catalytic activity in the oxidation of CO with O_2 (*1–6*) or NO (*7*). It has been reported that the catalytic activity is a function of the conditions of base exchange (*2*), of the contents of Cu (*1*), and of the pretreatment of the catalyst (*5*), among other variables.

The redox characteristics using H_2/O_2 of CuY have been studied by several researchers using different methods (*8–12*) and mechanisms have been proposed based upon kinetic measurements and spectroscopic evidence. Naccache and Ben Taarit (*12*) reported that the oxidation of CuY with O_2 at 400°C after treatment with H_2 resulted in irreversible CuO formation, but Herman *et al.* (*8*) showed that after a CuY zeolite was reduced in hydrogen, the copper metal could be reoxidized under certain reaction conditions back to Cu^{2+} ions located at their original sites in the small cages of the lattice.

Other gases have also been used as reducing agents. With butadiene and ammo-

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nia Maxwell *et al.* (*13, 14*) reported that the Cu^{2+} was reduced to Cu^{+}. Reduction with CO has yielded Cu^{+} too (*6, 12, 15–17*), except when the treatment at 400°C was for a long time (overnight); then it was possible to obtain Cu^{0} (*18*). When CO was used, as opposed to when H_2 was used, the formation of a kind of Lewis site was proposed to satisfy the charge balance on the lattice (*12, 13, 15*). But while Naccache and Ben Taarit (*12*) and Maxwell and Drent (*13*) represented these sites (formed by removal of an oxide ion from the lattice) by the formalism originally proposed by Uytterhoeven *et al.* (*19*) for a dehydroxylated decationated zeolite, Jacobs and Beyer (*15a*) presented evidence that the true Lewis sites are formed because the lattice is partially dealuminated according to the ideas of Kuhl (*15b*). The charge-balancing cation was $(AlO)^{+}$, its formation being accompanied by a minor lattice rearrangement. On the other hand, Maxwell *et al.* (*14*) have reported that when the Cu^{+}-exchanged Y zeolite was heated in air at above 350°C, CuO was formed as a separate crystalline phase. Its concentration did not increase above 400°C, but remained constant until the zeolite structure collapsed at 750°C. CuO formation did not occur on heating $Cu^{2+}Y$, even after structural breakdown at 800°C. Thus, the surface chemistry of the CuY zeolite has not been completely clarified and not all mechanisms proposed can be correct.

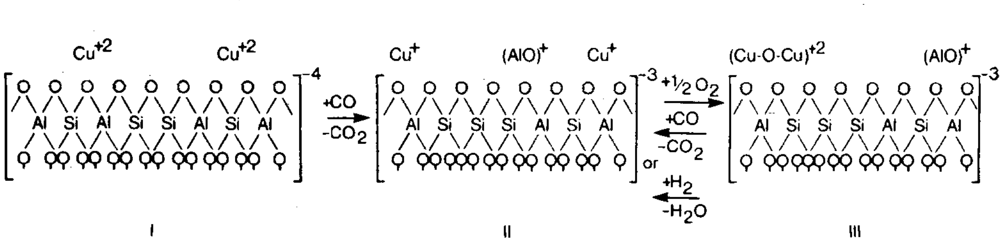
In view of the above and thinking of the possibility of using CuY as a catalyst for automotive exhaust gas cleanup we have made use of gravimetric and volumetric techniques to study the chemistry and stability of these samples in redox cycles. We have used CO as a reducing agent and O_2 or NO as an oxidizing agent. X-Ray diffraction (XRD), temperature-programmed reduction (TPR), and temperature-programmed oxidation (TPO) techniques were used in an attempt to characterize the state of Cu after those treatments. Our studies have yielded favorable evidence of the mechanism proposed by Jacobs and Beyer (*15*) and shown in Scheme 1.

EXPERIMENTAL

Materials

The starting material for the CuY preparation was pure crystalline Linde Y zeolite SK-40, Lot No. 1280-133 $[Na_{59}(AlO_2)_{59}(SiO_2)_{134}]$. It was first washed with excess NaAc–HAc buffer solution (pH = 5).

The CuY was made by the conventional ion-exchanged method using $Cu(NO_3)_2$ (analytical reagent grade). The zeolite was ion-exchanged in a 0.005 *M* solution of $Cu(NO_3)_2$. The zeolite/solution ratio was equal to 0.5 g/liter. The exchange was conducted overnight at pH = 5 and at room temperature. The sample was washed and dried overnight at 80°C. The unit cell composition of the starting material and of the sample was calculated from analytical data for the amount of Na, Cu, Al, and Si provided by Galbraith Laboratories; the result was $Cu_{22}Na_{15}(AlO_2)_{59}(SiO_2)_{133}$ assuming that Si + Al = 192. The excellent agreement between the amount of Na^{+} and Cu^{2+} indicates that the ion exchange was stoichiometric and that no excess of Cu^{2+} or



Scheme 1

H^+ was introduced into the zeolite during the exchange procedure.

The gases used were all CP or research grade. The procedures used to further purify them are described elsewhere (*20*).

Equipment and Procedures

Thermal stability and redox chemistry were studied using a Cahn electrobalance (model RG-2000) in a flow mode. The details of the experimental setup and procedures have been described elsewhere (*20*). The sample was dehydrated in flowing dry O_2 as the temperature was slowly increased to 500°C. The temperature was kept at 500°C until the weight became constant (overnight). This we will call "standard pretreatment." When other temperatures were required (e.g., study of stability at different temperatures) the temperature was always first increased under flowing O_2. Weights in ambient gas were plotted automatically on a recorder chart; lined-out weights were taken after a brief flush with He.

A conventional BET system was used for the volumetric measurements. To this a circulation loop was added containing a liquid N_2 trap and an all-glass pump (*20*). About 1 g of CuY was placed in a quartz reactor. The sample was dehydrated as before. The experiment consisted of a redox cycle (*20*). In the first step following the treatment with O_2 the catalyst was reduced with CO at 500°C. The CO_2 was collected quantitatively in the trap. The uptake of CO was determined from the pressure drop in the calibrated system and the CO_2 was measured volumetrically after removal of the noncondensable gases from the system. The reoxidation step was carried out in a similar manner using O_2 or NO in place of CO. In these cases the liquid nitrogen was replaced by isopentane slush (~ -140°C). After treatment with each gas the sample was evacuated for only a short time to avoid the autoreduction of the preparation. After 1 hr under vacuum at 500°C it was possible to determine an autoreduction equivalent to about 10% of the total Cu^{2+} (to Cu^+).

Catalytic activity and kinetic measurements were made in a continuous-flow single-pass reactor (*21*) operating at near atmospheric pressure. A 0.5- to 1-g sample of CuY (20–40 mesh) was used in all the experiments. It was given the standard pretreatment. Following this it was purged and cooled in a flow of He to a suitable temperature and then contacted with the reactant stream. The gas stream contained different percentages of CO, CO_2, O_2, or NO with the balance to 1 atm being helium. The reactant mixture was calibrated chromatographically before contacting the catalyst. In all cases the activity measurements were begun after the catalyst had been allowed to line-out for 1 hr. The composition of the gas stream leaving the reactor was also determined chromatographically. The rates of CO oxidation were determined under differential reaction conditions as the initial slope of the percentage conversion [α] versus W/F plot, where W was the catalyst weight and F the flow rate of CO. To determine the reaction order, a power rate law was assumed. When the sample was studied under reducing conditions the pressure of CO was varied from 23 Torr (3.1 kPa) to 92 Torr (12.26 kPa), keeping the O_2 pressure at 7.5 Torr (1.0 kPa). The O_2 pressure was then varied from 5 Torr (0.67 kPa) to 40 Torr (5.3 kPa) while the CO pressure was kept constant at 92 Torr (12.26 kPa). Under oxidizing conditions the same pressure-change ranges were used, but in all cases the CO/O_2 ratio was kept below 2. The experiments were conducted at two different temperatures: 350 and 450°C. Given the rate laws, rate constants could be calculated from the rate data and used to make Arrhenius plots.

When the steady-state reaction of CO + O_2 was studied in the Cahn microbalance, the conditions used in the flow system were reproduced. The sample was purged with He both after being oxidized or reduced, and then it was put in contact with the reactant mixture. The studies were conducted keeping the percentage of CO constant and changing the amount of O_2 from overall oxidizing conditions to overall reducing conditions, and vice versa.

X-Ray Characterization

Diffraction patterns were taken with a General Electric reflection diffractometer (model XRD-5) using Cu*Kα* radiation. The data were recorded from $2\theta = 5°$ up to $2\theta = 50°$ at 2°/min at room temperature. The samples examined were first treated in the flow system or the TPR system. Precautions were taken when recording the samples in the reduced state (Fig. 7B); in these cases N_2 atmosphere was used to avoid reoxidation.

Temperature-Programmed Reduction or Oxidation

The system used for TPR and TPO was conventional (*22*). A small aliquot [0.5 to 1.0 g of CuY (20–40 mesh)] was used. A −195°C trap was located downstream from the sample in the TPR experiments and a dry-ice–acetone trap was substituted for TPO. The reducing gas was a mixture of 10% vol CO in He and the total flow rate was 60 cm^3 (STP)/g min. After the standard pretreatment the sample was cooled in O_2 and purged with He. Then the reducing gas was admitted and the catalyst was heated at a linear rate of 5°C/min. Once the preselected maximum temperature was reached, in all cases the baseline was reached. After each TPR the sample was purged with He at 500°C and cooled in the same gas. Then 10% O_2 in He was used as the oxidizing gas in the TPO experiment which was conducted in the same way as described above for TPR.

EPR Experiments

EPR spectra were recorded with a Varian E-115 spectrometer at liquid N_2 temperature at X-band frequencies. The CuY zeolite was treated in a quartz reactor having a 4-mm-o.d. quartz ESR sidearm that could be inserted into the EPR microwave cavity. Treatments with O_2 were made in a flow mode whereas treatments with CO were made in a circulation system.

RESULTS

Stability Tests and Redox Behavior

The criterion of stability was taken as the reproducibility of the data in oxidation–reduction cycles, i.e., the oxygen-carrying capacity should remain constant and stoichiometric with the transition metal ion (TMI) concentration as long as the zeolite structure does not break down. Different oxidation–reduction couples were used, viz., CO/O_2, H_2/O_2, CO/N_2O, and CO/NO, and the experiments were made at different temperatures in the range 500–750°C. In all cases the starting material was the oxidized form of the CuY after the standard pretreatment. Higher temperatures of longer exposure to flowing O_2 did not change significantly the final weight of the sample.

The results for the CO/O_2 and H_2/O_2 couples at 500°C are shown in Fig. 1. The

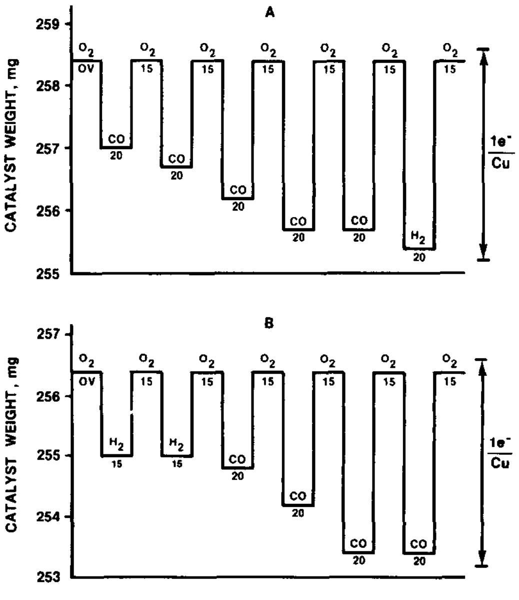


FIG. 1. Flow microbalance studies of CuY in oxidation–reduction cycles at 500°C. The gas flowing over the catalyst is identified above the "lined-out" weights (in He). Values for treatment times (in minutes) are given below (ov = overnight). Two different samples were used in the experiments in Charts A and B.

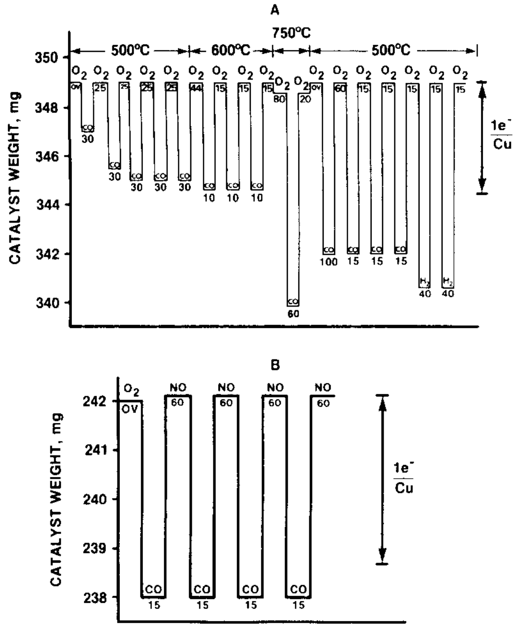


FIG. 2. Flow microbalance studies of CuY zeolites in oxidation–reduction cycles. The gas flowing over the catalyst is identified above the "lined-out" weights; values for treatment time (in minutes) are given below (ov = overnight). Chart A: studies of the oxidation–reduction cycles at different temperatures for O_2/CO and O_2/H_2 couples. Chart B: studies of the oxidation–reduction cycles for the NO/CO couple at 500°C. Data taken after several CO/O_2 redox cycles.

gases in contact with the zeolite are indicated above the lines corresponding to the steady-state weight and the times required to reach the "lined-out" values are given below. The weight of the oxidized state remained invariant, whereas the weight of the reduced state decreased gradually from cycle to cycle until the loss in weight approached 1*e*/Cu. After the initial induction (activation), the redox process became reversible in successive cycles when CO/O_2 or H_2/O_2 were used. When the H_2/O_2 couple was used, we did not observe the step-by-step decrease in weight under these experimental conditions (compare Fig. 1A with B). The induction reappeared, however, if after the H_2/O_2 couple was used, CO was substituted as the reducing gas. Note that when H_2 is used, the weight change may not be a reliable measure of the extent of reduction because lattice oxygen may be converted into OH rather than be evolved as H_2O.

The results obtained at higher temperatures are presented in Fig. 2A. Redox between Cu^{2+} and Cu^{+1} appeared to be stable at temperatures up to 600°C, but Cu^0 evidently formed during a deliberate excursion to 750°C. Thereafter, reversible oxidation–reduction was maintained, but now the valence change was substantially larger: it approached 2*e*/Cu.

The redox data are summarized in Table 1. Up to 600°C there appeared to be a reversible 1*e*/Cu change and the colors of the reduced and oxidized catalysts were generally consistent with this appraisal. After the catalyst had been reduced at temperatures above 600°C, however, the valence change approached 2*e*/Cu and the colors suggested the presence of CuO and Cu in the oxidized and reduced states, respectively. The gray and pink colors of Lines 2 and 3 will be discussed later. At 500°C CuY was stable and could be reversibly oxidized and reduced through many cycles (Fig. 2B); either the NO/CO or O_2/CO couple could be used.

The EPR spectra shown in Fig. 3 are consistent in a qualitative way with the micro-

TABLE 1

Microbalance Studies of CuY in Oxidation–Reduction Cycles

Temperature (°C)	Redox couple	Redox capacity e^-/Cu	Color of the sample	
			Oxidized state	Reduced state
500	O_2/CO	0.88	Green[a]	White
500	O_2/H_2[b]	0.98	Gray	Pink
500	O_2/CO[c]	0.90	Light gray	White
500	NO/CO	1.27	Green	White
600	O_2/CO	0.92	Green	White
750	O_2/CO	1.66	Black	Reddish
500	O_2/CO[d]	1.66	Black	Reddish
500	O_2/H_2[e]	1.80	Black	Reddish

[a] Dehydrated sample. Hydrated sample was light turquoise.
[b] Made after O_2/CO treatment.
[c] Made after O_2/H_2 treatment.
[d] Made after O_2/CO treatment at 750°C and O_2 overnight.
[e] Made after O_2/CO treatment at 750°C; O_2 overnight and O_2/CO at 500°C.

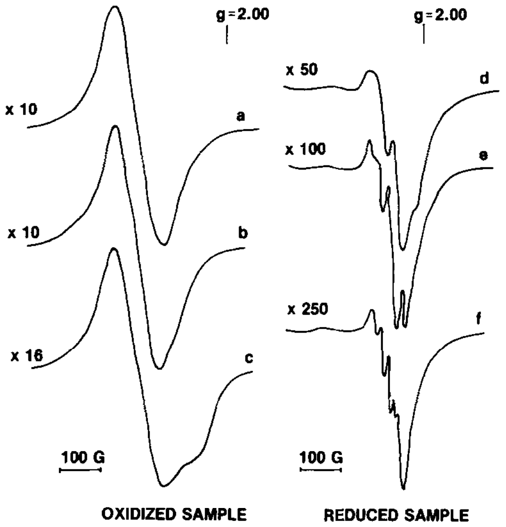


FIG. 3. EPR spectra of the CuY zeolite after the following successive treatments: (a) overnight in flowing O_2 at 500°C; (b) several cycles in CO/O_2 at 500°C; (c) 1 hr in CO at 750°C, several CO/O_2 cycles at 500°C, and overnight in flowing O_2 at 500°C; (d) 1 hr in CO at 500°C; (e) several CO/O_2 cycles at 500°C; (f) treatment in CO for 1 hr at 750°C and several CO/O_2 cycles at 500°C.

balance results. These spectra are similar to those previously reported by other researchers (*8, 23*). The fresh CuY after standard pretreatment (Fig. 3a) yielded the characteristic spectrum of the CuY zeolite with a high spin density (concentration) of Cu^{2+}; Cu^{+} is nonparamagnetic. The spectrum of the reoxidized sample after several cycles in CO/O_2 at 500°C was almost the same (Fig. 3b). Spectrum 3c was obtained from CuY reoxidized after reduction at 750°C and following several CO/O_2 cycles at 500°C. A decrease in the total area and a decided asymmetry are differences which could be easily observed. Spectra 3d, e, and f were from reduced samples. These have low spin densities and are similar to those of the CuY zeolite with a low percentage of base exchange (*23*). After several CO/O_2 cycles at 500°C (Fig. 3e) about 5% of Cu^{2+} remained unreduced, and after reduction under severe conditions (Fig. 3f), about 3% remained unreduced.

The same type of redox cycles were made in the volumetric circulation system. The results of a series of such experiments are outlined in Table 2. In all cases the amount of CO consumed in the reduction step was stoichiometrically related to the O_2 or NO required for complete reoxidation. In every case 1 CO_2 was formed per CO consumed indicating that no carbon was left on the surface. When NO was used as the oxidizing agent, N_2 was released in the oxidation step in stoichiometric amounts; no N_2O was detected.

Catalytic Behavior

It is clear from the above results that CuY could function as a catalyst for reactions of the redox type. Preparations were therefore studied as catalysts for CO/O_2 and CO/NO reactions. Experiments were made with overall oxidizing conditions and the rate of oxidation of CO was determined. Data are presented in Fig. 4 for preparations which either had (Curves A and B) or

TABLE 2

Oxidation–Reduction Cycles of CuY by CO/O_2 and CO/NO as Determined by Volumetric Method

Footnote	Reactant gas	Temp. (°C)	Gas consumed or produced			
			Redn step (cm³(STP)/g)		Oxidn step (cm³(STP)/g)	
			[CO]	[CO_2]	[$2O_2$]	[CO_2]
[a]	CO	500	6.50	6.38		
	O_2	500			6.80	—
[b]	CO	500	12.70	12.50		
	O_2	500			12.50	—
[c]	CO	600	13.91	13.40		
	O_2	600			13.50	—
[d]	CO	500	28.20	27.99		
	O_2	500			28.00	
			[CO]	[CO_2]	[NO]	[N_2]
[e]	CO	500	12.00	11.70		
	NO	500			12.50	6.25

Note. Amount of CO for the complete reduction ($Cu^{2+} \rightarrow Cu^{+}$) was 18.22 cm³(STP)/g (calculated from percentage Cu).

[a] First CO/O_2 cycle after overnight in flowing O_2 at 500°C.

[b,c] After several CO/O_2 cycles at 500°C.

[d] After 1 hr in CO at 750°C, 1 hr in O_2 at 750°C, and overnight in flowing O_2 at 500°C.

[e] New sample after overnight in flowing O_2 and several CO/O_2 cycles.

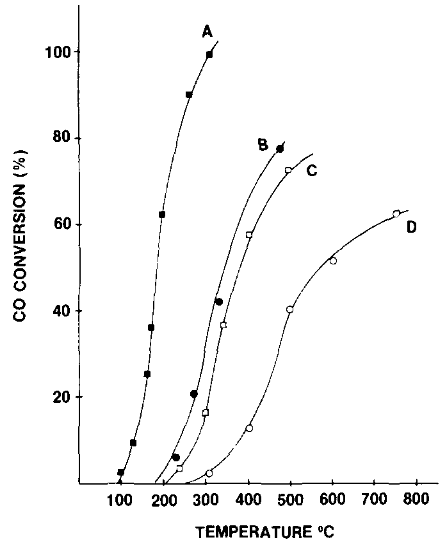


FIG. 4. Comparison of oxidizing agents for CO over CuY zeolites; Curves A and C (■, □) are for 2.0% O_2 after and before reduction by CO at 750°C, respectively. Curves B and D (●, ○) are for 5% NO after and before this treatment, respectively. For all experiments 2% of CO was used with the balance to 1 atm He. Total flow rate: Curves A and B, 1100 cm^3(STP)/g min; Curves C and D, 200 cm^3(STP)/g min.

TABLE 3

Comparison of Catalytic Activities in the Redox Reaction[a] at 300°C

Catalyst	TMI/g	CO + O_2 (mole g^{-1} sec^{-1})	NO + CO (mole g^{-1} sec^{-1})
CuY[b]	9.98×10^{20}	8.0×10^{-7}	4.0×10^{-7}
CuY[c]	9.98×10^{20}	1.60×10^{-5}	3.64×10^{-6}
FeY[b]	6.13×10^{20}	0.40×10^{-5}	2.70×10^{-6}

[a] Reaction conditions: gas composition 2% CO, 2% O_2, or 5% NO with the balance He; total flow rate was 200 cm^3(STP)/g min.

[b] Fresh sample after treating overnight in flowing O_2 at 500°C.

[c] Overnight in flowing O_2 at 500°C after 1 hr in CO at 750°C.

had not (Curves C and D) been reduced by treatment in CO at 750°C. Significantly, the high-temperature preparations were the most active for both reactions. The activity of CuY for the CO/O_2 reaction was greater than that for CO/NO. The activities of these two preparations are compared with those for FeY at 300°C in Table 3.

Experiments were made with much higher partial pressures of NO and CO (in about the same 2 : 1 ratio). These experiments permitted detection of small fractional yields of N_2O, which are shown in Fig. 5. At all temperatures, the chief products were N_2 and CO, but in the lower temperature region N_2O became detectable, suggesting that it may be an intermediate species in the formation of N_2.

The effect of water on the activity of the CuY was investigated. The presence of 7% of H_2O in the feed stream caused approximately a 50% decrease in the conversion of CO, when either O_2 or NO was used as an oxidizing agent. The water, however, did not permanently poison the catalyst; when removed from the stream, the initial conversions were recovered within approximately 45 min.

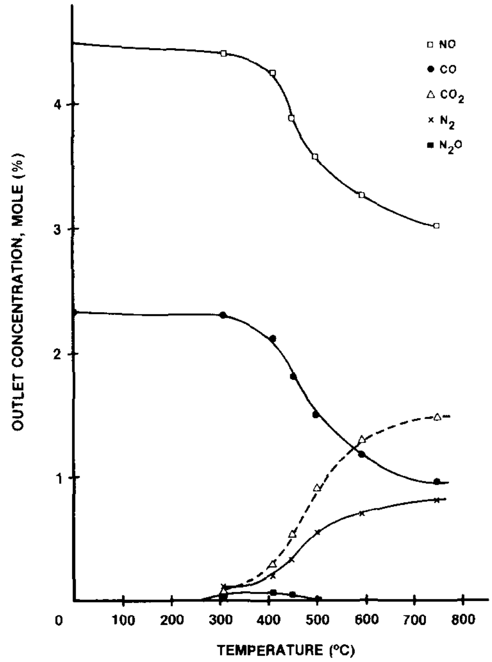


FIG. 5. Change in selectivity with temperature for CO/NO reaction over CuY. The gas composition was 2.3% CO and 4.6% NO with the balance to 1 atm He. The total flow rate was 200 cm^3(STP)/g min.

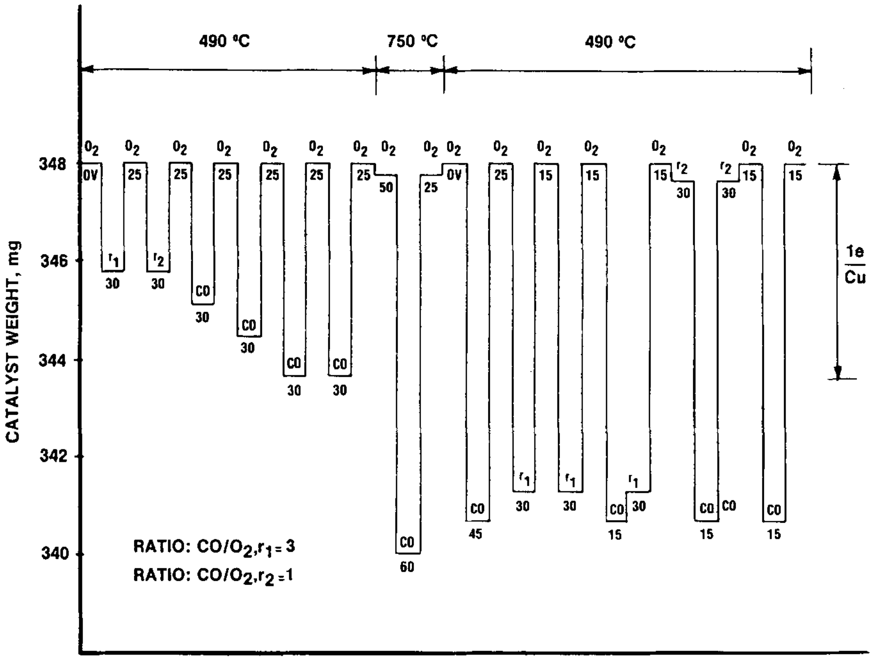


FIG. 6. Flow microbalance studies of the CuY system in the CO/O_2 reaction under reducing conditions (r_1) and oxidizing conditions (r_2). The gases flowing over the catalysts are identified above the line; values for the duration of the experiments (in minutes) below. The feed contained 6 or 2% of CO; 2% of O_2 was used in all experiments with the balance to 1 atm He. The CO or O_2, when used alone, was at 1 atm.

In another set of experiments, after the catalyst reached stable reaction conditions in a flowing gas mixture ($CO + NO + H_2O$ or $CO + \frac{1}{2} O_2 + H_2O$ in 1 hr at 350°C and 200 cm^3(STP)/g min), the temperature was increased until the sample recovered its initial conversion level in the absence of H_2O; an increase of only about 80°C was required.

When the kinetics of the $CO + O_2$ reaction were studied over CuY reduced in CO at 500°C, it was found that the rate law was close to zero order in CO, but of fractional order in O_2: the activation energy was about 15 kcal/mole. This would suggest that under reaction conditions the catalyst works near its reduced state, i.e., the reaction is limited by the rate of oxidation of the catalytic surface. To check this the steady-state reaction was investigated in the flow microbalance and the results obtained in experiments made at 490°C are shown in Fig. 6. Regardless of the CO/O_2 ratio (r_1 or r_2) the catalyst operated near the state of reduction achieved in the early cycles. This happened when the catalyst had not been treated at 750°C with CO. After such treatment, the catalyst weight (valence state of the Cu) was sensitive to the CO/O_2 ratio. The catalyst operated close to the reduced state when the reaction was conducted under overall reducing conditions and close to the oxidized state when it was conducted under overall oxidizing conditions. The pressure dependences of the $CO + O_2$ reaction on CuY treated at high temperature with CO were in agreement with these results; i.e., the rate law was close to first order in CO and zero order in O_2 under overall oxidizing conditions with an activation energy of 12 kcal/mole. Under overall reducing conditions the rate law changed to first order in O_2 and zero order in CO, with an activation energy of 15 kcal/mole.

Although the effects of diffusion might be expected to become important at high turnover frequencies in zeolitic systems, no measurements were made to check for mass transfer limitations. Because of the fixed structure of the zeolite, to do so would be a major task which we have postponed for a separate study. Nevertheless, we can cite indirect evidence that these effects, if present, are not sufficiently important to affect the major conclusions drawn from the present work, which after all was not primarily a kinetic study. The turnover frequencies were rather low (<0.02/Cu pair/sec) and the Arrhenius plots showed no curvature at the high-temperature end suggestive of diffusion. Moreover, in related work yet to be published, higher rates were sometimes observed with mordenites than with faujasites containing the same cations; diffusion limitations would be expected to be more important with the former.

Characterization of the Copper Species in the Zeolite

In view of the above results, X-ray diffraction (XRD), temperature-programmed reduction (TPR), and temperature-programmed oxidation (TPO) measurements were made.

The diffractograms of the NaY (parent zeolite) and the CuY after different treatments are shown in Figs. 7A and B. No significant difference was found between diffractograms 7a and 7b (corresponding to NaY and CuY after the standard pretreatment at 500°C) suggesting that the lattice was little perturbed by exchange of Cu^{2+} for Na^+. Figure 7f shows the diffractogram obtained in the oxidized state after the sample was treated at 750°C for 1 hr in CO, followed by several cycles of CO/O_2 at 500°C. The chief difference from diffractogram 7b is the appearance of two new peaks at $2\theta = 35.6°$ and 38.8°. These are characteristic of CuO. No significant change appeared in the peaks corresponding to the zeolitic structure, suggesting that the long range order of the lattice remained after treatment at 750°C in CO. This supplemented the microbalance data of Fig. 2A, which demonstrated stability but indicated (short range) chemical change. Moreover, no significant change could be detected in the crystal pore volume by measurement of the capillary condensation of N_2, before and after treatment at high temperature. The X-ray diffraction pattern obtained (Fig. 7e), also showed the presence of CuO. These lines did not appear, however, when CuY was treated with H_2/O_2 at 500°C for a short time followed by several cycles of CO/O_2 at the same temperature (Fig. 7c), nor did they appear when the sample was treated only with CO/O_2 at 500°C (Fig. 7d).

XRD studies of preparations in the reduced state after different treatments are shown in Fig. 7B. These experiments were made looking for Cu^0 metal, which appeared only after the sample was treated with CO for about 1 hr at 750°C (Figs. 7h and 7i). Further treatment with CO/O_2 at 500°C did not increase the amount of Cu^0 metal or modify the average particle size. The Cu^0 peaks appeared identical before and after this treatment.

The broadening of the Cu^0 (111) reflection was used to determine the average size of the Cu^0 particles. A value of 142 Å was calculated when the Scherrer relation (*24*)

$$d = K\lambda/\beta \cdot \cos\theta$$

was applied (taking $K = 0.9$ and β as the half-maximum line breadth). Cu^0 metal was not detectable (Fig. 7g) when the sample was treated with the CO/O_2 couple at temperatures below 700°C. These results are in agreement with the ones previously shown in the first five lines of Table 1. All these data demonstrate that a critical change occurred in the zeolite during the treatment at 750°C with CO. Particles of Cu^0 metal or CuO appeared after this severe reduction and this was accompanied by an increase in the reversible oxygen-carrying capacity and color change, as well as catalytic activity. With this technique it is not possible to

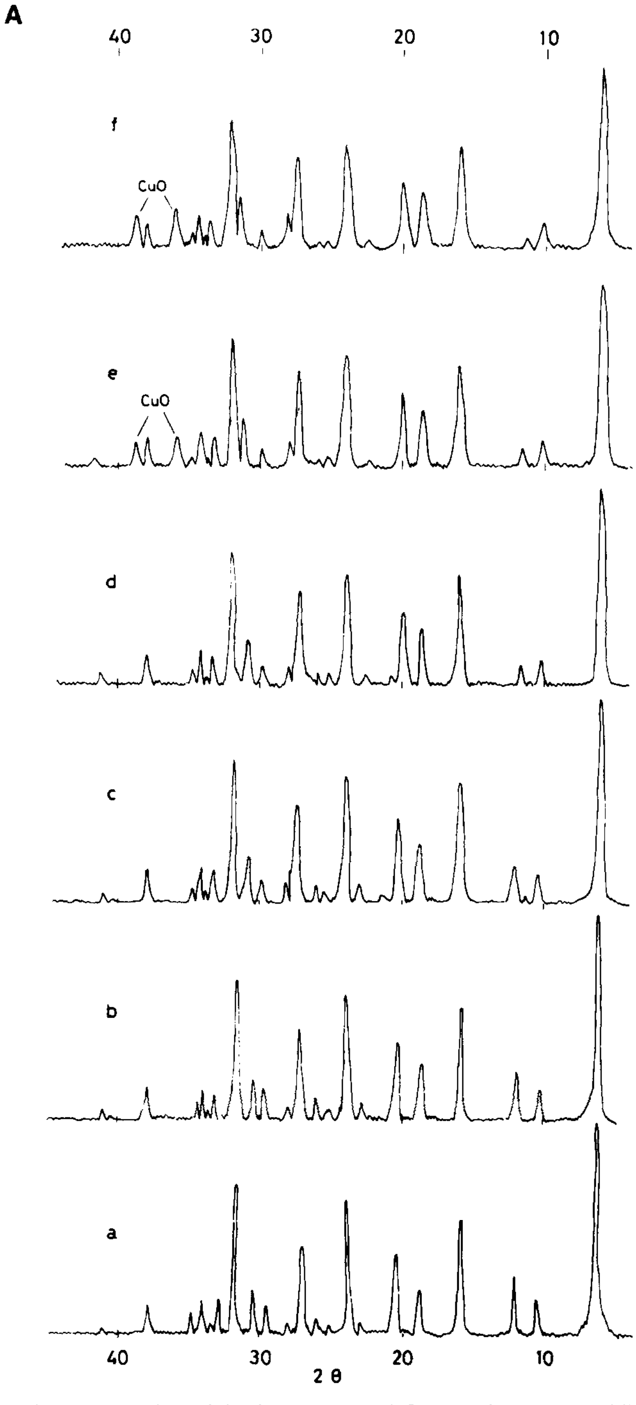


FIG. 7. XRD powder patterns (*I* vs 2*θ*) of the NaY and CuY zeolites. (A) Oxidized samples; the spectra were recorded after the following treatments: (a) parent NaY after standard pretreatment; (b) fresh CuY; (c) H_2/O_2 redox cycles followed by CO/O_2 redox cycles at 500°C; (d) several CO/O_2 redox cycles at 500°C; (e) pattern at the end of experiments of Fig. 2A; (f) 1 hr in CO at 750°C and several CO/O_2 redox cycles at 500°C. (B) Reduced samples; the patterns were recorded after the following treatments: (g) several CO/O_2 cycles at 500°C; (h) 1 hr in CO at 750°C and several CO/O_2 cycles at 500°C; (i) 1 hr in CO at 750°C.

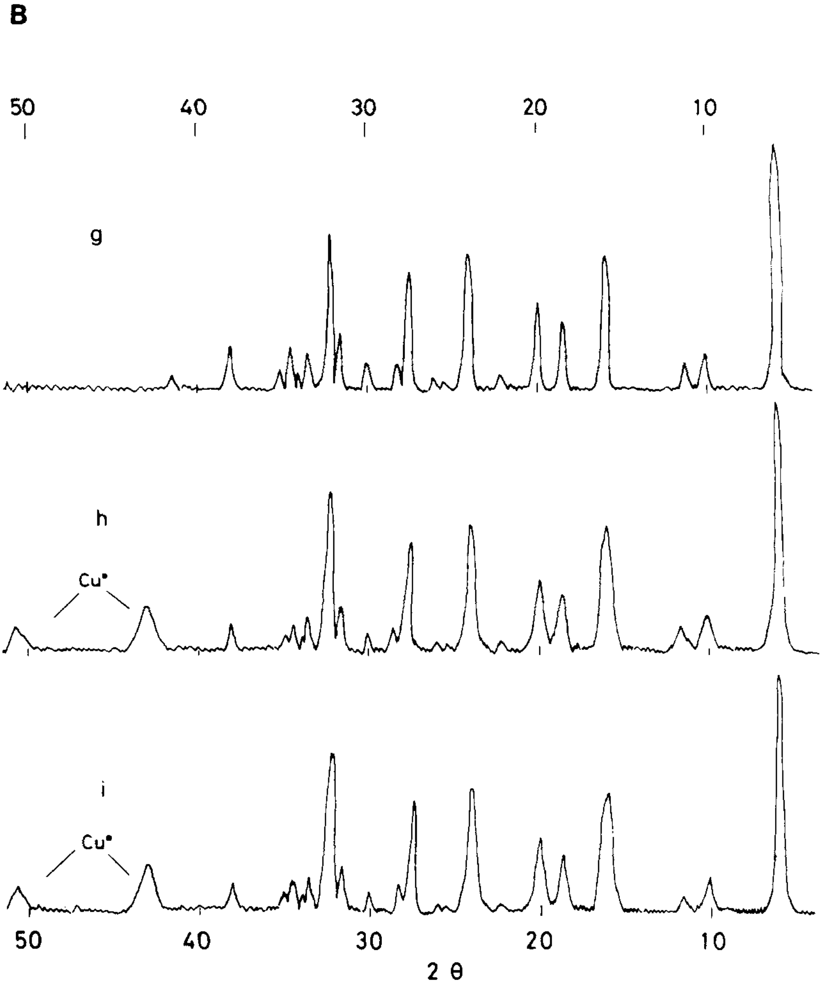


FIG. 7—*Continued.*

determine particles smaller than about 40 Å. Such small particles could go undetected and remain inside the zeolite cages when the reduction is conducted at temperatures below 700°C.

TPR and TPO (*11, 26*) experiments were made and some of the spectra obtained are shown in Fig. 8. Extents of reduction in the several temperature ranges (obtained by integration of the area under these peaks) are shown in Table 4.

Two distinct maxima were observed the first time the sample was reduced (at about 275 and 470°C). The total amount of CO consumed was equivalent to an extent of reduction of 0.35*e*/Cu (Table 4, first and second rows), in good agreement with the data obtained in the microbalance (first step, Fig. 1A) and in the volumetric measurement (Table 2, first row). Only one maximum (at 220°C) appeared in the following TPO experiment (Fig. 8a). Starting with the second TPR, a new maximum appeared at lower temperature (~157°C); the maxima at 275 and 470°C remained. On repeating, the 157°C peak grew while the 275°C peak decreased proportionally; the 470°C peak area hardly changed at all. The total amount of CO consumed increased in each step. These results suggested that a transformation occurred which made some of the Cu^{2+} more easily reducible. After sev-

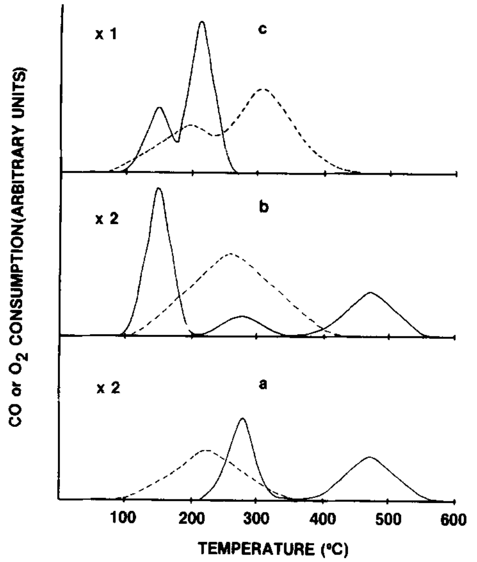


FIG. 8. TPR (solid lines) and TPO (broken lines) experiments with CuY zeolite. (a) Fresh sample after standard pretreatment; (b) after several CO/O$_2$ cycles at 500°C followed by overnight in O$_2$ at 500°C; (c) after treatment in CO for 1 hr at 750°C followed by several CO/O$_2$ cycles at 500°C and treatment in O$_2$ overnight at 500°C. All experiments were terminated at 600°C.

eral cycles the CuY became stable and reproducible. A typical TPR spectrum now became that shown in Fig. 8b. The largest amount of CO consumed, after the stabilization, corresponded now to the first peak; the second peak contributed little, whereas the amount corresponding to the 470°C peak barely changed. The extent of the reduction calculated from the total amount of CO was 0.7*e*/Cu. At this point the corresponding TPO spectrum again showed only one maximum at about 258°C. The area of the TPO peak increased proportionally to the increase in the TPR peaks (Fig. 8b).

After treatment of the catalyst at 750°C in CO for 1 hr the TPR showed two maxima at 150 and 210°C, respectively, which were reproducible after several cycles in CO/O$_2$ at 500°C (Fig. 8c). The amount of CO consumed in the high-temperature peak was almost twice that in the 150°C peak. The extent of reduction (Table 4, last two rows) was 1.48*e*/Cu. On oxidation of this sample two maxima were observed in the TPO, at 302 and 192°C, with an area ratio of 1.96. They also remained constant and stable after several cycles.

DISCUSSION

Redox Cycles up to 600°C

When CuY is reduced with CO, CO$_2$ is produced (Table 2), thus removing oxygen from the lattice. The processes occurring have been described (*15, 16*) as a partial dealumination of the lattice, the base-ex-

TABLE 4

Consumption of CO during TPR Experiments

Treatment of the sample	Maximum temperature peak (°C)	CO consumption (cm^3(STP)/g)	Overall extent of reduction *e*/Cu	
			Each peak	Total
Standard	275	3.28	0.18	0.35
	470	3.15	0.17	
Several CO/O$_2$ redox cycles at 500°C	157	9.00	0.50	
	275	0.69	0.05	0.70
	470	2.85	0.15	
1 hr in CO at 750°C and several CO/O$_2$ redox cycles at 500°C	150	9.4	0.51	1.48
	210	18.0	0.97	

change cations now becoming Cu^+ and AlO^+ species (Scheme 1). On reoxidation, the Cu^+ ions are converted to Cu^{2+} and the zeolite becomes an oxygen carrier analogous to the Fe–Y zeolite (*25*).

When H_2 is used as a reducing agent under mild conditions, Cu^{2+} is again reduced to Cu^+ but H_2O need not be produced, i.e., stable OH groups may be formed as in the HY zeolite. This preparation may become increasingly dehydroxylated as the temperature is raised *in vacuo* or in a flowing dry gas, eventually yielding the same end result as with the CO reduction. Thus, a partial breakdown (or rearrangement) of the zeolite lattice must occur by a hydrothermal process. Once formed, the concentration of AlO^+ presumably remains unchanged, while Cu^+ ions are transformed into Cu^{2+} species as oxygen is added to the system. This redox process became reversible in successive cycles when CO/O_2 or H_2/O_2 were used as indicated by Scheme 1. The results shown in Fig. 1 are consistent with this picture. Two different behaviors were observed. When after the standard pretreatment, the sample was reduced with CO an initial induction (or activation) was required (Fig. 1A) which could be explained by the slow formation of AlO^+ (an activated process). When H_2 was used the results shown in Fig. 1B suggest the formation of some HY sites. The reappearance of the induction period when CO was used after H_2 reduction suggested that these sites can be reversibly oxidized, regenerating the original CuY. Interestingly, these slow changes convert the zeolite from one which carries H to one that carries O as the requirement to neutralize the charge on the lattice is shifted from Cu^{2+} to AlO^+. To compensate for changing all the Cu^{2+} to Cu^+ (Fig. 1A), about one-fifth of the AlO_2^- must be transformed into AlO^+ (*15b*). As is shown in Fig. 2B, the couple CO/NO can also be used. In this case oxygen must be removed from the lattice and the gradual dealumination limits the extent of reduction.

TPR and TPO were used by Jacobs *et al.* (*11*) to characterize the cation distribution in zeolites. Similarly, Gentry *et al.* (*26*) employed TPR in a study of the reduction of the CuY zeolite with H_2. In the former work, the heating rate was 5°C/min in 600 Torr of H_2 in a recirculation system. Two maxima at 147 and 417°C were reported for the TPR experiments. These were assigned to Cu^+ formation (147°C) and Cu^0 formation (417°C). In the following reoxidation two maxima were also found: one at 177°C (assigned to the reversible oxidation of Cu^+ and Cu^0 inside the zeolite to Cu^{2+} ions in their final lattice positions) and one at 400°C (attributed to the oxidation of the larger Cu^0 crystallites outside the zeolite to a detectable CuO phase). These assignments were supported by X-ray measurements. Gentry *et al.* (*26*), working with a lower pressure of H_2 (20 Torr) and a faster heating rate (13.5°C min), reported two maxima at 247 and 377°C, but had no evidence of Cu^0 after the reduction. Consequently, they assigned both maxima to the Cu^+ formation: the two peaks were attributed to two different locations of Cu^{2+} on the lattice.

Our data, using CO as a reducing agent, differed in some respects from those above. Figures 8a and b suggest that three different processes occurred during the TPR experiments. When a fresh sample was used after the standard pretreatment the overall extent of reduction (Fig. 8a) was lower than after several CO/O_2 redox cycles (Fig. 8b), i.e., after the stabilization of the CuY (Fig. 1A and Table 2) by maximum AlO^+ formation. The total area of Fig. 8a is less than that of Fig. 8b in agreement with the data of Tables 1 and 2. Thus, both processes (275 and 470°C peaks) may be assigned to the reduction of Cu^{2+} to Cu^+ at different lattice sites where the lower-temperature peak could be assigned to the reduction at readily accessible positions with the concomitant formation of $(AlO)^+$ as charge-balancing cations. The high-temperature peak would then correspond to the reduction of "hidden" Cu^{2+} to Cu^+ with a higher activation energy. This is necessary because this latter peak remains invariant as the dealumination of the lattice proceeds over several cycles. As a result, no (or little) Cu^0 is produced below 600°C.

Analysis of the results obtained after many CO/O_2 redox cycles at 500°C, after the system had become reproducible, showed that the overall extent of reduction was close to 1*e*/Cu (Tables 1, 2, 4) while 95% of the EPR Cu^{2+} signal had vanished (Fig. 3). These combined results could only have been obtained if most of the Cu^{2+} was transformed into Cu^+. Moreover, no evidence of Cu^0 or CuO appeared in the corresponding XRD patterns (Fig. 7c) and the color of the sample was green in the oxidized state and white in the reduced state. The TPR spectrum now showed three maxima (Fig. 8b). The consumption of CO in each peak (Table 4) indicated that 72% of the total consumption of CO corresponded to the low-temperature peak, the amount in the 275°C peak approached zero, and that involved in the high-temperature process remained constant. This shift in the reduction profile suggested that after dealumination, the oxygen carried as depicted by Species **III** (Scheme 1) is labile to reduction and reoxidation, i.e., the 175°C peak corresponds to the new form of oxygen being carried. Further, the constant value of the 470°C maximum suggests that up to 600°C not all the Cu^{2+} can participate in this process.

In the reoxidation process only one broad maximum could be observed, although this may be an envelope covering several processes. The only differences between the first TPO and those following were a slight shift of the maximum to higher temperature and a slight sharpening of the band accompanying the stabilization of the lattice. Possibly this broad peak results from the slow recapture of Cu^+ by oxygen (assuming they were freed by reduction to diffuse about the lattice). The retention of the high-temperature peak demonstrated that in the oxidized sample not all of the Cu can be represented by Species **III** (Scheme 1). Indeed the representation of the oxygen-carrying cations in this way, although convenient, is open to serious doubt, as discussed elsewhere (*28, 29*).

Redox Cycle after Reduction with CO at 750°C

The CuY could be reversibly oxidized and reduced with CO/O_2 at 500°C after the treatment at 750°C (Fig. 2A), but now the valence change was substantially larger, approaching 2*e*/Cu (Table 1). Cu^0 metal was formed during the high-temperature excursion (Table 1, Row 6, and Fig. 8c). The following redox cycles with CO/O_2 at 500°C did not appear to affect the number or size of particles (Figs. 7h, i). Thus, apparently after treatment at high temperature two different types of Cu^{2+} can exist in the catalyst: Cu^{2+} inside the dealuminated zeolite, which can be reduced to Cu^+ and/or small clusters of Cu^0, and a CuO phase exterior to the zeolite crystallites which can be reduced to 100-Å crystals. The TPR and TPO results obtained after the treatment with CO at 750°C (Fig. 8c) were in good agreement with this picture. Features of the behavior of the CuY before the 750°C treatment were retained. The lower-temperature peak remained unchanged. This would suggest that it corresponds to the removal of carried O as Cu^{2+} is reduced to Cu^+ inside the zeolite, whereas the 210°C peak may be assigned to the reduction of the CuO phase exterior to the zeolite to Cu^0. Calculations from the peak area (Table 4) are in fair agreement with this idea and suggest that about 50% of the total initial Cu^{2+} would appear as CuO. If this were the case the overall extent of the reduction should be 1.5*e*/Cu. The values obtained were 1.66*e*/Cu in the microbalance experiment (Table 1), 1.51*e*/Cu in the circulation system (Table 2), and 1.48 in the TPR experiments (Table 4).

In agreement with the results reported by Jacobs *et al.* (*11*), the reoxidation of the sample now yielded two maxima. The one at lower temperature (192°C) corresponded to the oxidation of Cu^+ and/or small clusters of Cu^0. This was proved by interrupting the oxidation between maxima for an XRD experiment. The diffractogram obtained was the same one that is shown in Fig. 7b, suggesting that no oxidation of Cu^0 occurred at temperatures below 250°C. The higher-temperature maximum must then correspond to the reoxidation of the crystallites of Cu^0 to CuO; this maximum was lower than that reported previously (*11*), possibly because with our treatment smaller particles were obtained. The ratio of peak areas in both reduction and reoxidation was close to 1 : 2 as expected if the former corresponded to a one-electron process and the latter to two. In a general way our results are in accord with the ideas presented by Herman *et al.* (*8*), who worked with the H_2/O_2 couple at a maximum temperature of 450°C for various reduction times. However, our treatment in CO at 750°C yielded a material with the distribution of Cu^0 which did not appear to sinter in the following cycles with CO/O_2 at 500°C.

Catalytic Behavior

It is well known that CuO is a good catalyst for CO oxidation and that its activity is higher than that of Fe_2O_3 (*27*). However, as shown in Table 3, the CuY after the standard pretreatment had a lower activity than the FeY zeolite, but after treatment with CO at 750°C, CuY became more active than FeY.

The kinetic data would suggest a redox mechanism where the rate is limited by the rate of reduction or reoxidation. The *in situ* microbalance results are consistent with this picture (Fig. 6). The fact that the weight of the sample before treatment at 750°C did not exactly coincide with its weight in the reduced state was expected. It indicates that under reaction conditions a steady state exists in which both Cu^{2+} and Cu^+ are present, but with a preponderance of the latter.

After the treatment at 750°C in CO, Cu^+ and Cu^0 coexist in the reduced state. The redox cycles of Fig. 2 suggest that both may play a role in the catalysis. Beyer *et al.* (*5*) suggested that Cu^0 in small clusters was active, whereas Cu in large crystals did not contribute much to the catalysis. The zeolite became a facile oxygen carrier as it was dealuminated. This was described in Scheme 1 as a bridge structure, similar to that deduced for FeY (*25*). We now think (*28*) that another kind of surface species is likely for FeY, viz., a lattice oxygen held specifically on an Fe^{3+} at Site III′. If so, a similar situation may exist for the CuY. In this context the cation assumes the role of a depot to furnish or store electrons as the catalyst is oxidized and reduced, respectively, rather than a specific oxygen trap as previously visualized (*25*). The trap structure, Fe^{2+}–O–Fe^{2+}, which was pictured as an oxygen bridge inside the sodalite cage, has been reported missing in an X-ray study (*29*). The new interpretation permits the redox reaction to occur within the supercage. This would seem essential for such a rapid, facile process. Moreover, since the electrons are now delocalized, it matters not whether a particular Cu atom or ion furnished one or two electrons to the system.

The present results lead to the following deductions:

1. Additional evidence was obtained for the existence of AlO^+ species in the CuY after treatment with CO. This stabilization of the zeolite lattice by self-produced AlO^+ cations constitutes useful advancement in the understanding of the dehydroxylation process of HY over that first described by Uytterhoeven *et al.* (*19*).

2. Treatment in CO at 750°C for 1 hr followed by treatment overnight in O_2 at 500°C yielded a sample of high stability which could be oxidized and reduced reversibly for many cycles without diminishing its redox capacity; Cu^0 was now present.

3. The fresh CuY zeolite was not a very good catalyst for the oxidation of CO. It was less active than CuO or some other ze-

olites with transition metal base-exchange cations. After treatment with CO, however, it became an interesting catalyst for that reaction (100% conversion of CO at 350°C and F/W = 1000 cm^3(STP)/g min).

4. The catalytic activity increased as the CuY became a reversible oxygen carrier.

5. The CuY had, under all conditions studied, a higher activity for the oxidation of CO with O_2 than with NO.

6. H_2O present in the feed stream did not cause permanent damage but acted as a reversible poison; the loss in activity could be recovered by an increase in temperature of about 80°C.

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