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Kinetics and Mechanism of CO Oxidation over Cu Mordenite

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Cu mordenite (CuM) has proved to be highly active for the oxidation of CO with oxygen. The effect of pretreatment, the kinetics, and the mechanism of the CO + O_2 reaction have been studied using a continuous-stirred tank reactor (CSTR), Bennett-type unit, and standard BET system. Redox cycles performed using CO/O_2 showed that the sample was stable and could be reversibly reduced and oxidized many times at temperatures up to 500°C. The extent of reduction was 0.8 e/Cu. Pretreatment in CO at 750°C did not affect the reversibility of the redox cycles but produced a larger valence change, 1.8 e/Cu, even at reduction temperatures as low as 300°C. XRD patterns show the appearance of finely dispersed CuO on the partially destroyed mordenite lattice. This solid, CuM*, shows different catalytic behavior compared to CuM. The kinetic studies on the latter were performed in the range 200–340°C. Between 200 and 250°C the rate function was zero order in CO and close to first order in O_2. In the upper temperature range this pressure dependency became first order in CO and zero order in O_2. The Arrhenius plot shows a break at 250°C. At temperatures higher than 250°C the oxidation reaction on CuM is severely limited by mass transport. On CuM* the reaction rate was first order in CO and zero order in O_2 over the entire temperature range, 200–325°C. The reduction and catalytic behavior of CuO/SiO_2 and $CuO/\gamma\text{-}Al_2O_3$ were also studied to confirm the important role played by copper oxide produced by the CO pretreatment on CuM*. The results obtained are analyzed in terms of the reaction mechanisms, and the predominance of individual steps, due to either different pretreatments and/or operating conditions, is assessed.

INTRODUCTION

The possible elimination of contaminants from gas effluents using base–metal altervalent cation-exchanged zeolites has been reported in several publications in the last decade or so (*1–4*). In this vein, Petunchi and Hall (*5, 6*) have characterized the catalytic behavior of FeY zeolite (FeY), Fe mordenite (FeM), and CuY zeolite (CuY) for CO oxidation with either O_2 or NO. In those works, through the use of gravimetric and tracer techniques, they concluded that the reaction proceeds through a redox mechanism. The reactivity order was CuY* (pretreated in CO at 750°C) > FeM > FeY > CuY (untreated).

Cu mordenite (CuM) has been little studied for CO oxidation despite the high activity reported in a couple of publications. Paetow and Riekert (*7*) have found that a 5%, cation-exchange capacity (CEC) exchanged CuM is two orders of magnitude more active than a 22% CEC exchanged CuY on a per gram of catalyst basis (at 167°C). Vandamme (*8*), who has studied this reaction on several Cu-exchanged crystalline silicoaluminates, claims that the most active catalysts at 350°C are CuX (81% CEC) and CuM (66% CEC).

We have previously studied the oxidation of CO on CuY in a continuous-stirred tank reactor (CSTR) to obtain information abut the adsorption, diffusion, and intrinsic chemical reaction phenomena (*9*). There is a certain number of articles in which these phenomena were studied through transient methods applied to several reactor types. Bennett (*10*) and Kobayashi and Kobayashi (*11*) have studied the oxidation of CO and

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the decomposition of N_2O on metallic oxides. Both authors have also published excellent reviews on the subject (*12, 13*). Schobert and Ma (*14*), using the pulse technique, have studied the influence of adsorption and diffusion processes on isomerization reactions carried out over Y zeolites.

This work was undertaken with the goal of elucidating the effect of catalyst pretreatment on the catalytic behavior of Cu mordenite, as well as the kinetic and mechanistic aspects of the oxidation reaction.

EXPERIMENTAL

Catalyst and pretreatment. The starting material was a high-crystallinity Linde sodium mordenite, $Na_{11}(AlO_2)_{11}(SiO_2)_{40}$ (LZM5 Lot 8350-5). The exchange was done using a 0.01 *M* solution of $Cu(NO_3)_2$, a mordenite/solution ratio of 2 g/dm^3 at pH 5, at room temperature, for 24 h. The exchanged sieve was washed with distilled water and dried at 80°C for 12 h. In this way, 55% of the original sodium was replaced by copper with no loss in crystallinity according to the XRD patterns. At liquid nitrogen temperature, the N_2 uptake at $p/p^0 \cong 0.5$ was 100 cm^3 STP for both the starting sieve and the CuM.

An aliquot of the CuM was treated as follows: slow heating in flowing oxygen up to 500°C, then in a stream of nitrogen up to 750°C. At this temperature CO was flowed for 1 h; after a switch back to N_2, the sample was cooled to 500°C and then maintained for another hour in flowing oxygen. In this way, the catalyst designated CuM* was obtained. With this treatment the solid became dark gray due to the presence of CuO. The XRD patterns show a significant loss in crystallinity of the sieve matrix and the appearance of two wide low-intensity peaks due to CuO ($2\theta = 35.6°$ and $38.8°$). The N_2 uptake at 77 K, $p/p^0 \cong 0.5$, was 20% lower than in the untreated CuM.

CuO was supported on both silica (celite, 17 m^2/g) and γ-Al_2O_3 (Alcoa F110, 116 m^2/g). These supported catalysts contained 5% by weight Cu and were prepared by the incipient wetness technique, using a solution of $Cu(NO_3)_2$. The solid was impregnated for 24 h, dried at 120°C for 12 h, and then calcined in flowing air at 500°C for 12 h.

Before each kinetic run all the catalysts were heated at 400°C in flowing air. The samples used in the BET system were heated in flowing oxygen and then evacuated overnight at the same temperature. Before the redox experiments the catalyst was treated with dry oxygen at 400°C for 1 h and evacuated until a vacuum better than 10^{-5} Torr was reached.

Gases. All CP-grade gases were dried with 5A molecular sieves before use. The CO tubing included a section surrounded by an oven maintained at 300°C to eliminate carbonyls, followed by a sintered metal filter.

Reaction system and procedure. The redox behavior of the CuM was studied in a conventional BET system connected to a gas recirculation loop to allow the *in situ* reduction of the catalyst. To ascertain its redox stability, the solid was exposed to several cycles of reduction with CO and oxidation with O_2 at 500°C; after each treatment the amounts of CO consumed, CO_2 formed, and oxygen taken up were measured.

The kinetic experiments were performed in a Bennett-type reactor coupled with a gas-feeding manifold which allowed the system to be operated in either the transient or the steady-state regimes. The system has been described elsewhere (*9*). The reactor was loaded with variable amounts of catalyst, between 0.3 and 3.0 g, and operated at 4000 rpm. Satisfactory mixing tests were run at various temperatures and flow rates. The external mass transfer was negligible above 1500 rpm.

In the pulse mode, the system was operated as follows: (a) In catalytic experiments the temperature was adjusted to the desired value while the reactor was fed with a gas mixture of $N_2 + O_2$ (20%), at flow rates between 5 and 10 cm^3/s, and maintained at the reaction temperature for 30 min. At this point a pulse of CO was injected through a 5-cm^3 loop into the reactor, and the response signal was measured at time intervals of 5 to 10 s. (b) To study the reduction of solid the steps in (a) were repeated, but the gas feed did not contain oxygen. (c) To determine the adsorption behavior the solid was prereduced at the desired temperature with pure CO for 1 h. The CO was displaced with flowing N_2 and then a pulse of adsorbate was injected.

In the step function experiments, designed to study either the CO oxidation or the reduction of the catalyst, the temperature was adjusted to the desired value while a gas mixture containing N_2 + O_2 (0–20%) was flowing through the reactor. At the same time a gas stream of N_2, O_2 (0–20%), and CO (5–10%) was flowing through a bypass. At time zero, the reactant mixture was switched into the reactor and either the CO or CO_2 concentration was measured until the steady-state regime was reached.

RESULTS

Redox Behavior

The TPR experiments were performed between room temperature and 500°C (Fig. 1). CuM* (prereduced in CO at 750°C) shows only one peak centered at 150°C, reaching an extent of reduction of 1.8 e/Cu at 300°C.

CuM shows two peaks: one centered at 150°C and the other at 300°C. It should be noted that the TPR experiment produced a negative peak due to the CO desorption between 50 and 150°C (not shown in Fig. 1). It may be that the double peak originates in the relatively slow desorption at temperatures lower than 250°C. This is further substantiated by the results shown in Table 1, which shows the stability of both CuM and CuM* to CO/O_2 redox cycles performed at 500°C. Note that the amount of CO consumed is larger than the CO_2 produced for CuM, due to the strong CO chemisorption. The amount of O_2 consumed in the reoxidation was higher than the stoichiometric amount of CO_2 formed. This could be attributed to self-reduction during evacuation (*15*).

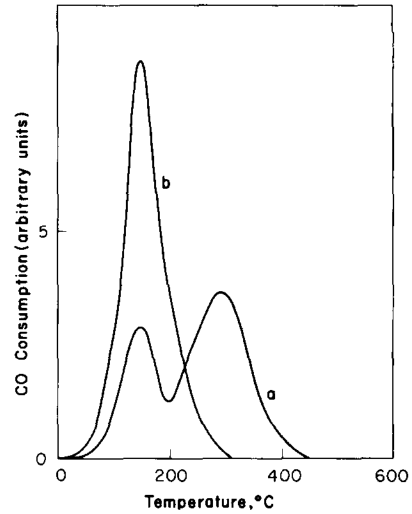

FIG. 1. TPR experiments with Cu mordenite. (a) Fresh sample after standard pretreatment (CuM). (b) After treatment in CO for 1 h at 750°C followed by treatment in O_2 for 1 h at 500°C (CuM*). TPR conditions: 5°C/min, in recirculation system, CO pressure 200 Torr. Catalyst weight: 1 g (powder).

From the average amount of oxygen consumed in reoxidizing the reduced sample, the extent of reduction of CuM at 500°C was 0.8 e/Cu. The CO treatment at 750°C

TABLE 1

Oxidation–Reduction Cycles of CuM by CO/O_2 at 500°C as Determined by the Volumetric Method[a]

Cycle No.	V (cm^3 STP/g)					
	CuM[b]			CuM*[c]		
	CO	CO_2	O_2	CO	CO_2	O_2
1	11.0	5.3	3.0	17.0	16.1	8.4
2	11.6	6.7	4.0	16.1	16.0	8.3
3	11.6	7.0	3.7	16.1	15.4	8.5
4	12.5	7.5	3.8	15.5	15.9	8.4
5	11.1	7.5	4.0	16.9	16.4	8.3

[a] Amount of CO for the complete reduction ($Cu^{2+} \rightarrow Cu^0$) was 19 cm^3 (STP)/g (calculated from percentage of Cu).

[b] Fresh sample after standard pretreatment.

[c] After treatment in CO for 1 h at 750°C followed by O_2 for 1 h at 500°C.

greatly increases the redox capacity of the mordenite system.

The reduction was also studied in the CSTR through the analysis of the response curve to a step function of CO. In Fig. 2 the response functions from CuM in terms of both the CO and CO_2 concentrations are shown for two sample experiments which were conducted at 180 and 300°C. From the area under the curve of CO_2 the extent of reduction was calculated at several temperatures (Table 2).

Steady-State Experiments

The kinetic experiments for both CuM and CuM* were carried out at temperatures between 200 and 340°C. The reaction orders were determined by changing the reactant concentrations. For CuM two regions of different kinetic order for each reactant were detected (Fig. 3). At 225°C the reaction was zero order in CO and unity or fractional close to one in O_2. This was exactly the opposite at 300°C. On the other hand, when CuM* was the catalyst, the order remained zero for O_2 and one for CO over the entire temperature range studied.

Figure 4 shows the Arrhenius plots for CuM, CuM*, and CuY*, the latter obtained from (*9*). In Table 3 the steady-state kinetic data for CuM and CuM* are summarized and compared to those previously reported for CuY and CuY* (*9*). Note the close similarity in behavior of CuM* and CuY*.

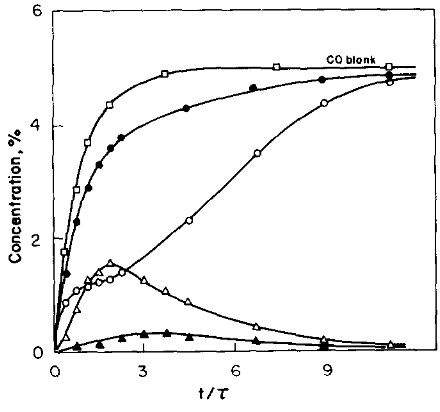

FIG. 2. Cu Mordenite reduction with CO. CSTR response curves to step functions. (●, ▲) CO and CO_2 response curve at 180°C; (○, △) CO and CO_2 response curve at 300°C. τ, residence time. Gas composition: 5% CO in N_2. Flow rate: 10 cm^3/s. Catalyst weight: 2 g (powder).

TABLE 2

Extent of Reduction (α) for Cu Mordenite (CuM) at Different Temperatures[a]

T (°C)	α (e/Cu)
125	0.04
175	0.10
200	0.16
225	0.25
250	0.36
300	0.60

[a] α was calculated from the area under the $CO_2(t)$ CSTR response curve to a step function (see Fig. 2). Reduction time, 10 min.

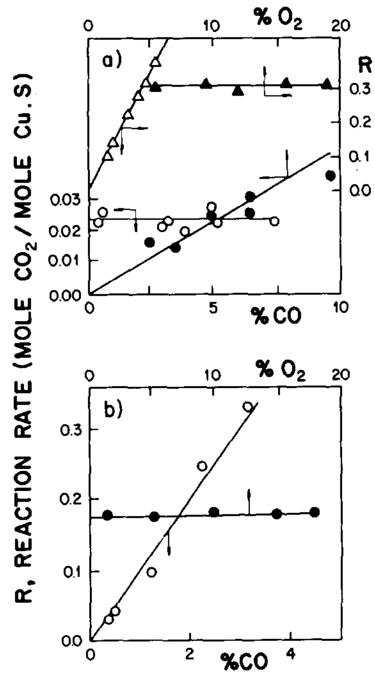

FIG. 3. Reaction order plots for Cu mordenite. (a) CuM (○, ●) 220°C, (△, ▲) 320°C; (b) CuM* (○, ●) 300°C. Gas composition range: 1–20% O_2, 0.5–7.5% CO (in N_2). Flow rate: 5–15 cm^3/s. Catalyst weight: 1 g (powder).

TABLE 3

Summary of Kinetic Information

Catalyst	TMI (g)	Temperature range (°C)	Rate[a] (mol/g · s)	Rate law[b]	Activation energy (kcal/mol)	
					Apparent	Diffusion corrected
CuY	8.5×10^{20}	300–500	2.1×10^{-6}	kP_{O_2}	23.0	23.0
CuY*	8.5×10^{20}	200–300	2.2×10^{-4}	kP_{CO}	8.0	12.0
CuM	5.6×10^{20}	200–250	—	kP_{O_2}	21.8	21.8
CuM	5.6×10^{20}	250–320	2.5×10^{-4}	kP_{CO}	17.6	30.0
CuM*	5.6×10^{20}	200–320	1.7×10^{-4}	kP_{CO}	8.0	11.8

[a] Reaction conditions: %CO = 2, $\%O_2$ = 20 (in N_2). Flow rate = 10 cm^3/s. T = 300°C.
[b] Oxidizing atmosphere, $CO/O_2 < 2$.

Transient Studies and Reaction Mechanism

To study the various steps of the catalytic oxidation, pulse and/or step functions of CO, O_2, and CO_2 were used.

Figure 5 shows the responses to steps of CO into a flowing O_2/N_2 mixture, at 200 and 300°C, when CuM was the catalyst. Note the sharp difference in the dynamic behavior of the system at these two temperatures. The catalytic deactivation process observed at 220°C disappears at 300°C. The square point corresponds to the conversion obtained when a pulse of CO was sent into the reactor under conditions otherwise identical to those of the step experiment.

In Fig. 6 the response curves to pulses of CO in a stream of $N_2 + O_2$ (reaction conditions) are compared to those obtained when pure N_2 was used (reduction mode). They overlap each other.

The reoxidation of Cu^+ to Cu^{2+} consti-

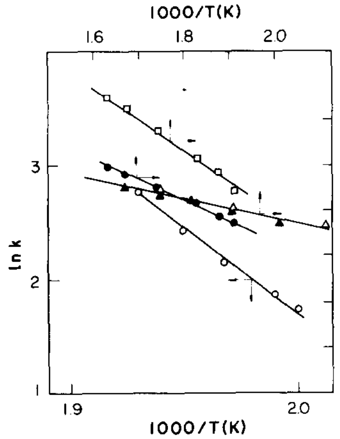

FIG. 4. Arrhenius plot. (○) CuM, temperature range: 220–250°C; (●) CuM, temperature range: 250–340°C; (▲) CuM*; (△) (200–325°C); (□) diffusion-corrected rate constant for CuM in the range 250–320°C (*18*). Gas composition: 1–5% CO, 20% O_2 (in N_2). Flow rate: 5–15 cm^3/s.

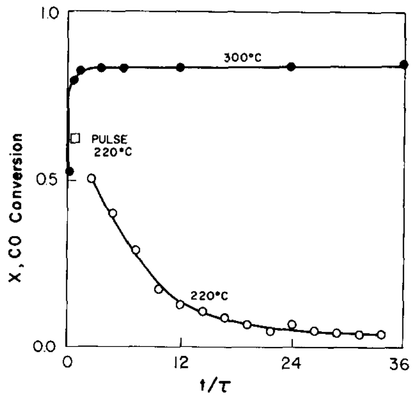

FIG. 5. CO oxidation over CuM. CSTR response curve to step functions. Gas composition: 5% CO, 20% O_2 (in N_2). Flow rate: 5.5 cm^3/s. (The square corresponds to the conversion of a CO pulse under conditions identical to those of the step experiments.)

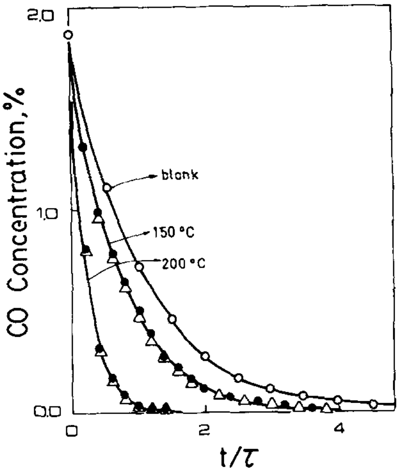

FIG. 6. CSTR response curves to CO pulses (with and without oxygen) over CuM. Gas composition: (△) 20% O_2 (in N_2), (●) 100% N_2. CO pulse: 4.6 cm^3 STP. Flow rate: 6.0 cm^3/s. Catalyst weight: 3 g (powder).

tutes one of the steps of the reaction mechanism. Figure 7 shows the response to pulses of O_2 sent over the CuM prereduced with CO at three temperatures. At 240°C the reoxidation rate is very low; the conversion of the oxygen pulse is almost zero. However, at 260°C a sharp increase in conversion is observed, which indicates a high activation energy for the reoxidation process.

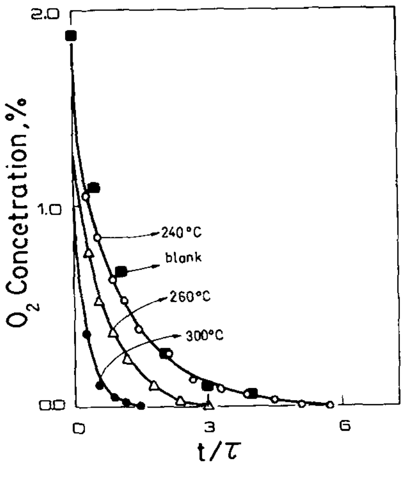

FIG. 7. Oxidation of reduced CuM. Reduction and oxidation temperatures are indicated. Gas composition: 100% N_2. O_2 pulse: 4.6 cm^3 STP. Flow rate: 7.5 cm^3/s. Catalyst weight: 1 g (powder).

The relative adsorption of CO, CO_2, and O_2 was also investigated. For this purpose the catalyst was prereduced at several temperatures and pulses of each of the three adsorbates were sent into the reactor. Much more CO was adsorbed than either CO_2 or O_2. The responses to two pulses of CO at different temperatures are shown in Fig. 8. These experiments confirmed that CO_2 does not reoxidize Cu^+, as no CO could be detected in the exit stream when a CO_2 pulse was fed to the reactor containing prereduced CuM.

To obtain further information about the reduction of the catalyst and the CO adsorption under reaction conditions a careful study of the CO_2 response curve was done. In Fig. 9 the response curves to pulses of CO in reaction conditions are compared to those obtained in the reduction mode and to the response curves to steps of O_2 in a stream of pure N_2 (oxidation curve). It should be noted that at 220°C it is possible, by adding the reduction to the oxidation curve, to reconstruct the reaction response. This is not the case, however, at 300°C.

The dynamic behavior of CuM* is markedly different from that shown by CuM. In fact, CuM* resembles very much CuY*, a

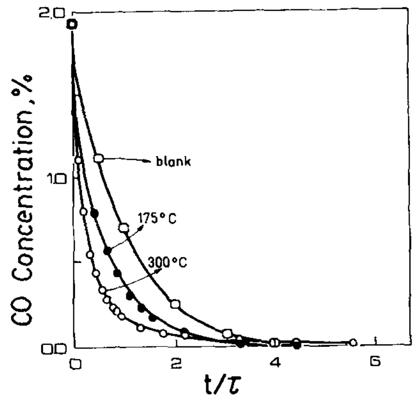

FIG. 8. CO adsorption. CSTR response curves to CO pulses over reduced CuM. Gas composition: 100% N_2. CO pulse: 4.6 cm^3 STP. Flow rate: 6.2 cm^3/s. Catalyst weight: 1 g (powder).

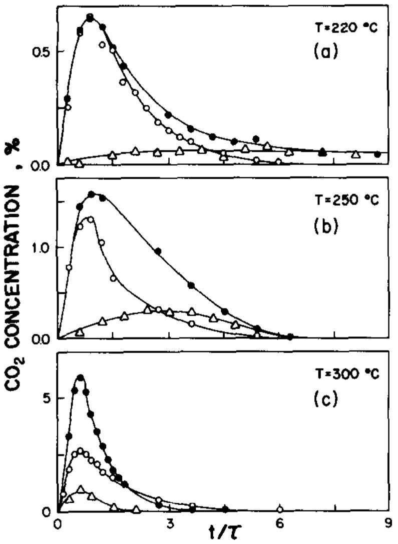

FIG. 9. Reaction steps as compared with overall reaction. CO_2 response curves. (○) CO pulse in reduction mode (△) O_2 step after reduction. (●) CO pulse in reaction mode. Flow rate: 7 cm^3/s. Catalyst weight: 1 g (powder).

catalyst obtained when CuY was similarly reduced in CO at 750°C [see Fig. 4, Table 3, and Ref. (*9*)]. The response to a step function of CO in $N_2 + O_2$ shows a maximum in the CO curve or an induction period in the CO_2 vs time plot (Fig. 10). In the previous work (*9*) this was interpreted as an *in situ* activation of the catalyst (CuY*). To further investigate this behavior and suspecting that the CuO formed during the severe treatment with CO could be responsible for this behavior, the response to step functions on both CuO/SiO_2 and CuO/Al_2O_3 was studied. The response curves obtained are strikingly similar to those observed in both CuM* and CuY* (Fig. 10).

The α plots of both supported oxides at different temperatures, as well as those of CuM and CuM* included for reference purposes, are shown in Fig. 11. The oxide reduction curves show the expected induction period. CuM* also behaves in a similar way, while a differently shaped plot is obtained in the case of CuM.

DISCUSSION

The redox results, the X-ray patterns, and the variation in nitrogen adsorption capacity of CuM and CuM* clearly indicate that the severe treatment with CO at 750°C produces irreversible transformations in the solid which are in turn reflected in a different catalytic behavior.

CuM* is much easier to reduce than CuM. The former is almost completely re-

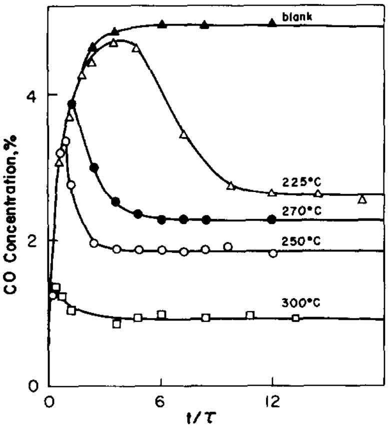

FIG. 10. Catalyst activation. CSTR response curve to a step function. (△) CuM*, (□) CuY*, (○) CuO/γ-Al_2O_3, (●) CuO/SiO_2. Reaction conditions identical to those in Fig. 5. Catalyst weight: 0.3–0.5 g (powder).

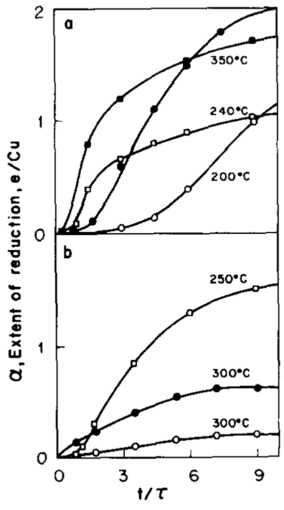

FIG. 11. Catalyst reduction. CSTR response curve to a step function. (a) (○, ●) CuO/SiO_2, (□, ■) CuO/Al_2O_3; (b) (○) CuY, (●) CuM, (□) CuM*. Reduction conditions identical to those in Fig. 2.

duced to Cu^0 when treated with CO at 300°C, while the latter, even at 500°C, is partially transformed to Cu(I) mordenite (see below). This low extent of reduction is close to that reported by Vandamme (*8*) under similar conditions.

CO is strongly adsorbed on the reduced CuM. This is shown in the responses to step functions of CO (Fig. 2). The CO uptake can be calculated from the difference between the blank and the pertinent response curve at each temperature. The amount of CO calculated was always larger than the amount of CO_2 produced. A similar difference is observed in the redox cycles of CuM (Table 1). However, this is not the case when CuM* is subjected to the same cycles (Table 1). Therefore, it is concluded that CO is strongly adsorbed on Cu^+M but not so on Cu^0M. This is consistent with the data obtained by Huang (*16*), who reported a selective adsorption of CO on Cu(I)Y zeolite, much higher than the adsorption of O_2, CO_2, and N_2.

Reaction Mechanism on CuM

The changes in reaction order and activation energy within the temperature range studied may be diagnostic of a change in either the reaction mechanism and/or the rate-limiting step. Between 200 and 250°C the rate function is first order in oxygen and zero order in carbon monoxide pressure (Fig. 3), with an activation energy of 21.8 kcal/mol (Fig. 4). Vandamme (*8*) and Petunchi and Hall (*5*) have reported the same kinetic order for CuY zeolite. The former states that this kinetic law is consistent with a large coverage of the surface of Lewis sites where oxygen dissociates. Petunchi and Hall (*5*), on the other hand, propose a redox mechanism with the oxidation as the rate-limiting step.

In the temperature range 250–340°C the reaction becomes first order in CO and zero order in O_2 (Fig. 3). The apparent activation energy decreases to 17.6 kcal/mol (Fig. 4). It is likely that at these higher temperatures a redox mechanism applies, the overall rate being limited by the reduction step.

The transient experiments now come into play to elucidate the role of the individual steps that constitute the reaction mechanism. At low temperatures CO is strongly held on the Cu^+ sites produced by the reacting mixture, while both O_2 and CO_2 are much weakly adsorbed. The reoxidation of the catalyst surface is very slow. Five pieces of evidence that support these conclusions:

(i) The response to a step function of CO shows a steep decrease in conversion vs time at 220°C. This is not observed at 300°C (Fig. 5).

(ii) The identical response curves are obtained under reduction and reaction conditions (Fig. 6). It is interesting to note in Fig. 5 that the extrapolation of the function $Y(t)$ is coincident with the conversion of a pulse of CO calculated from the area under the curve in Fig. 6.

(iii) The strong adsorption of CO over the reduced catalyst is seen in Fig. 8 and is consistent with the results shown in Table 1 for CuM and in Fig. 2.

(iv) At 240°C the reoxidation rate with O_2 is negligible as shown by the area under the corresponding curve in Fig. 7.

(v) At 220°C the reaction curve (Fig. 9a) can be interpreted as the composite of two processes; the first one is assigned to the catalyst reduction and the second is due to the slow oxidation of the CO adsorbed.

The onset of a much faster reoxidation rate between 240 and 260°C (Fig. 7) should be noted at this point. This may be the reason why a change in reaction order occurs precisely in this temperature range.

It is now useful to write all the reaction steps that may be involved in the catalytic oxidation of CO.

$$CO + OS \rightarrow CO_2 + \square \qquad (I)$$

$$CO + \square \rightleftarrows CO_{(a)} \qquad (II)$$

$$O_2 + \square \rightleftarrows O_{2(a)} \qquad (III)$$

$$O_{2(a)} \rightarrow 2O_{(a)} \quad \text{(IV)}$$

$$O_{(a)} + CO_{(a)} \rightarrow CO_2 + 2\square \quad \text{(V)}$$

$$O_{(a)} + CO \rightarrow CO_2 + \square \quad \text{(VI)}$$

$$O_2 + 2CO_{(a)} \rightarrow 2CO_2 + 2\square \quad \text{(VII)}$$

$$O_2 + \square \rightarrow 2OS \quad \text{(VIII)}$$

The recombination of steps I, II, III, IV, and VI leads to a mechanism similar to that proposed by Vandamme (*8*) for CuY. Reactions I and VIII are characteristic of a redox mechanism. At temperatures below 250°C both mechanisms are consistent with the steady-state results. It is in fact possible that both approaches are applicable in this case since the very low rate of reoxidation and the weak adsorption of O_2 on Cu^+ (*10*) are consistent with the low overall rate of CO oxidation over CuM in this temperature range.

At temperatures between 250 and 340°C step VIII sharply increases in rate (Fig. 7). It is then possible that the reduction becomes rate limiting and the rate function becomes first order in CO. It is likely that at these higher temperatures the redox mechanism dominates.

Additional evidence in the same vein is given by the results shown in Fig. 9c. At 300°C it is not possible to reconstruct the reaction response by adding the reduction and oxidation curves. This may be due to the catalytic reoxidation step (VIII), which becomes increasingly important at higher temperatures (Fig. 7).

Table 3 shows that CuM is two orders of magnitude more active than CuY for CO oxidation, in agreement with previous findings of Paetow and Riekert (*7*) and Vandamme (*8*). Other authors (*6, 17*) have reported that FeM is also more active than FeY for several redox reactions. Petunchi and Hall (*6*) pointed out two factors that may cause this marked difference in activity: (i) better accessibility of the exchanged cations in mordenite compared to Y zeolite and (ii) the effect of the chemical environment that would modify the oxygen-carrying capacity and even the lability of the O that participates in the reaction. This latter factor has been further substantiated in these studies. At 300°C the extent of reduction of CuY is 0.18 e/Cu, while for CuM it reaches 0.6 e/Cu. Even more important is the difference in rate of reduction between both samples at 300°C, 140 times faster for CuM than for CuY (*18*).

*Reaction Mechanism and Active Sites on CuM**

The rate for this system shows a first-order dependence in CO and a zero-order dependence in O_2 throughout the temperature range studied (Fig. 3). The apparent activation energy, $E = 7.8$ kcal/mol, is much lower than in the case of CuM. In fact, the kinetic behavior of CuM* is very similar to that of CuY* (*5, 9*). Petunchi and Hall (*5*) have proposed a redox mechanism for the latter, the reduction step being the one that controls the overall rate of reaction. The data obtained in the transient experiments further substantiate this overall picture.

The CuM and CuM* show completely different transient behavior. The response CO(t) to a step function of CO in $N_2 + O_2$ shows a maximum (Fig. 10) similar to that reported for CuY* (*9*). This is caused by the presence of CuO in both CuM* and CuY*. Support for this statement is found in Fig. 10 where both $CuO/\gamma\text{-}Al_2O_3$ and CuO/SiO_2 show the same type of curve. CuM* and CuY* are more active, however, due to the higher dispersion of CuO in the matrix. Pierron *et al.* (*19*) also reported an activation of $CuO/\gamma\text{-}Al_2O_3$ when the catalyst was pretreated with CO + air at 270°C. They have associated the active sites with either the appearance of interfaces between Cu_2O and Cu° or the formation of nonstoichiometric phases of copper oxides. They restrict the applicability of their model to reaction temperatures between 100 and 160°C, suggesting that at higher temperatures a redox mechanism may be operative.

A study of the $Cu^{2+} \rightarrow Cu^\circ$ reduction process clarifies the picture. Figure 11 shows an induction period in the reduction of CuO/SiO_2 and, to a lesser extent, in CuO/γ-Al_2O_3. The reduction curve for CuM shows a completely different behavior. The induction period in the reduction of Cu^{2+} is likely to be the cause of the transient behavior of the type shown in Fig. 10 when copper oxides become the loci of catalytic activity as in the cases of CuY*, CuM*, CuO/γ-Al_2O_3, and CuO/SiO_2. Voge and Atkins (*20*) and Pease *et al.* (*21*) have studied the oxidation of CuO with H_2 and reported sigmoideal $\alpha(t)$ curves, such as those in Fig. 11. They explain the shape of the curve on the basis of either a nucleation mechanism or an autocatalytic effect. Consequently, it is possible that the activation effect observed on these catalysts originates in the reduction of the CuO particles. The similar activation energy values reported for CuY*, CuM* (Table 3) and CuO (*22*) further substantiate the role of the copper oxide phase.

In summary, the CO pretreatment of CuM at 750°C produces a new solid CuM* which contains small particles of CuO on a partially destroyed mordenite lattice. This solid shows a reduction and catalytic behavior similar to those of CuY* and supported copper oxide. CuM, on the other hand, shows a catalytic activity two orders of magnitude higher than that of CuY. A redox mechanism is most likely in operation but the rate-limiting step switches from the oxidation to the reduction stage within the temperature range studied.

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