

## Electron Paramagnetic Resonance of Supported Copper Oxide Catalyst in the Reduction of Nitric Oxide

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Electron paramagnetic resonance (EPR) yields information on two aspects of the structure of supported copper oxide catalyst: the degree of oxidation of the copper and the mode of dispersion of the oxide. These structural features may have a bearing on the catalytic properties. *In situ* EPR measurements of copper oxide on alumina were carried out. Mixtures of gases containing oxygen or nitric oxide as the oxidizing component and hydrogen or carbon monoxide as the reducing component were passed through a microreactor mounted in the EPR cavity, and changes in the relative amounts of isolated and clustered Cu(II) ions were determined. The relations between the structural features of the copper oxide that could be discerned by EPR and the catalytic properties were studied. It appears that crystallites of CuO favor the oxidation of carbon monoxide (CO) by oxygen (O<sub>2</sub>), and that isolated copper ions play a role in the reduction of nitric oxide (NO) by hydrogen (H<sub>2</sub>) or by carbon monoxide (CO).

### INTRODUCTION

Transition metal oxide catalysts for the total oxidation of hydrocarbons, of carbon monoxide and for the reduction of NO with some suitable agent like CO or NH<sub>3</sub> are becoming increasingly important in combating air pollution.

The dependence of the reaction rates of, especially, NO with H<sub>2</sub>, CO, or NH<sub>3</sub> on what may loosely be termed the oxidation state of the catalytic surface, has been recognized for a considerable time. However, there have been few attempts to correlate, simultaneously, the reaction rate under various conditions with the concomitant oxidation state of the surface of a *working* catalyst. This "oxidation state of the surface" of a transition metal oxide catalyst may be looked upon as a static structural feature, e.g., as the distribution of the transition metal ions in different oxidation states and over various sites. But in a gaseous atmosphere, a working catalyst

promoted with a transition metal oxide will be subject to changes that are determined by the rate of reduction of the oxide and by the rate of oxidation of the reduced oxide. In turn, these parameters will depend on the intrinsic rates of reaction of the oxide (reducibility and reoxidizibility), on the nature and concentration of both the reducing and the oxidizing component of the gas, and on the temperature.

There is a variety of techniques that reveal peculiarities of the structure of a catalyst, but their results usually cannot be easily correlated with the dynamic behavior of the catalyst. In principle the technique of *in situ* EPR would seem particularly suited to study both these aspects simultaneously. A flow tube filled with a suitable catalyst placed in the cavity of an EPR spectrometer can be used as a microreactor. By observing EPR spectra of the transition metal oxide one can estimate the oxidation state of the catalyst.

Meanwhile one can separately determine the degree of conversion of the reactant gases. In this way one should obtain insight into the interrelationship between structural features and catalytic performance, and this insight might conceivably be used to optimize catalysts. To test this procedure experimentally, we chose supported copper oxide catalyst. Such catalysts lend themselves almost ideally to the EPR technique, and are important components of many practical catalysts.

EPR spectra of both reduced and oxidized supported copper oxide catalysts (1,2) and of copper ions in zeolites (3,4) have already been resolved. In these materials at least two types of Cu(II) are detectable by EPR: "isolated" and "clustered" ions. The intensity of the EPR spectrum ideally decreases to zero on progressive reduction to Cu(I) and Cu<sup>0</sup>, neither of which shows an EPR signal, the latter because it forms the metallic phase (1). The intensity of the EPR signals from the Cu(II) may thus be regarded as a measure of the degree of oxidation of the catalysts. However, a fraction of the Cu(II) appears to escape detection by EPR, presumably on account of spin-pairing. With supported copper oxide catalysts this fraction may constitute a sizable portion. From the EPR work of Berger and Roth (1) and from the magnetic susceptibility measurements by Selwood *et al.* (5), it can be concluded that the percentage of the measured EPR intensity of the theoretical total intensity due to Cu(II) is correlated with the dispersion of the copper oxide on the surface. The lower the degree of dispersion, the larger the fraction of the copper oxide that escapes detection by EPR. It may be assumed that the greater part of these spin-paired Cu(II) ions are buried in multi-layered crystallites whose spatial structure approaches that of a normal CuO lattice.

The three types of Cu(II) that appear to be present differ in the spatial structure of their environment. Although *in situ* EPR

directly distinguishes changes between only two types of Cu(II), it appeared worthwhile to put the proposed procedure to a test. The observable Cu(II) ions might reflect the state of oxidation of the total active surface. Furthermore, the different types of Cu(II) might show different reactivities toward reducing agents and in the catalytic process proper.

### EXPERIMENTAL

EPR measurements were carried out at X-band employing a JEOL ME-1X spectrometer equipped with a cylindrical cavity. The *in situ* EPR was carried out in a micro-flow reactor mounted in the cylindrical cavity (Fig. 1). An external heating unit

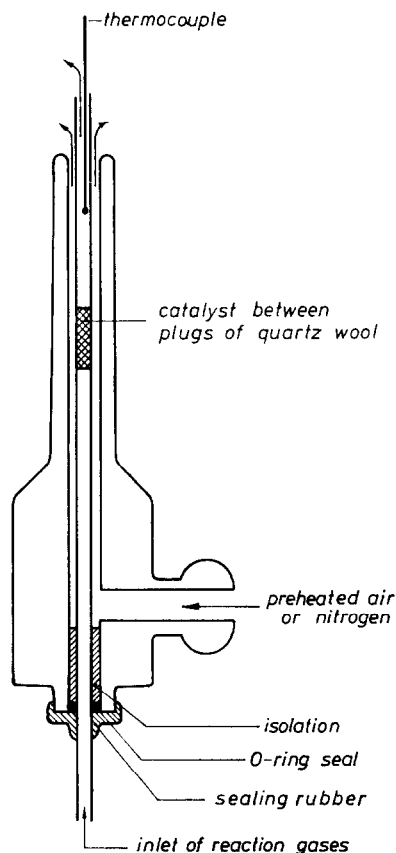


FIG. 1. Assembly of the microreactor and the double-walled quartz tube mounted in the EPR cavity.

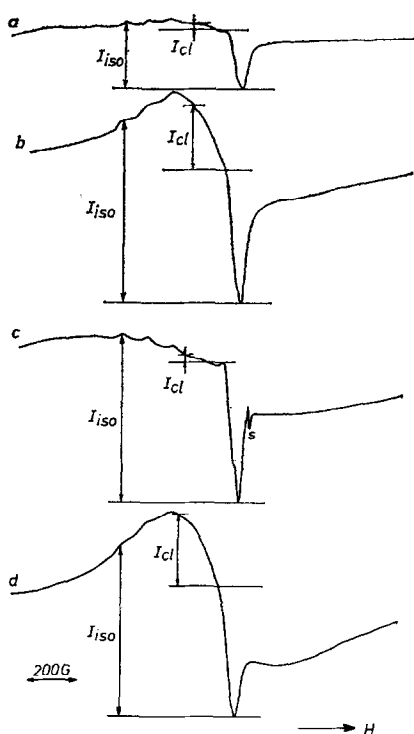


Fig. 2. EPR spectra of reduced and reoxidized copper oxide on  $\gamma$ - $\text{Al}_2\text{O}_3$  at  $300^\circ\text{C}$ . (a) 5% CuO reduced, (b) 5% CuO oxidized, (c) 12% CuO reduced, (d) 5% CuO oxidized.  $I_{iso}$  = intensity of isolated Cu(II) ions,  $I_{cl}$  = intensity of clustered Cu(II) ions. At s (spectrum c) signal of the support at  $g = 2.0038$ . Spectrometer settings: power 10 mW, crystal current 0.2 mA, modulation 1 G, and gain 100 for (a), (b), (c), and 50 for (d).

allowed measurements to be performed at constant temperatures up to  $300^\circ\text{C}$ . The reacting gases ( $\text{H}_2$ , CO,  $\text{O}_2$ , and NO) were passed over the sample of the catalyst in concentrations of 0.5–3% by volume of a carrier gas ( $\text{N}_2$  or He) at a constant space velocity between 5.000 and 25.000  $\text{hr}^{-1}$ . The dosage of the gases was achieved by mixing at constant flow. The gases were used without further purification, except for those experiments which were aimed at reaching a fully reduced state of the catalyst. The hydrogen or the carbon monoxide was then purified with the aid of a column of prerduced BTS catalyst followed by one containing Linde 13X molecular sieves.

The catalysts (5 and 12% CuO on  $\gamma$ - $\text{Al}_2\text{O}_3$ ) were prepared by impregnation (PV saturation method) (6). They were dried at  $105^\circ\text{C}$  and as the last stage in the preparation calcined at  $600^\circ\text{C}$  in a current of air. The percentage conversion of the gases and the material balance of the gas reactions were determined by gas chromatography.

The samples of catalyst were placed in the microflow reactor in the EPR cavity. Each sample was subjected to a series of oxidation and reduction experiments. At a given temperature ( $300^\circ\text{C}$ ) the degree of oxidation of the catalysts was followed by estimating the relative amount of Cu(II) that showed up in the EPR in terms of relative intensities. For each of the two types of Cu(II) that appeared to be present, a pair of reference points at particular values of the magnetic field was chosen (cf. Fig. 2). Between each pair of these reference points the intensity was measured, the spectrometer gain and modulation being taken into account. Finally, the maximum intensity of each type of Cu(II) obtained with one sample was set at 100%.

The relative intensities recorded in this manner are not linearly proportional to the number of Cu(II) ions of the respective types present in the sample. This is due to a number of factors that are not accounted for. The choice of reference points was made such as to minimize the mutual interference of the recorded intensity of one type by the partial spectrum of the other. However, an independent estimate of the amounts of the two types of Cu(II) distinguishable by EPR is not available. Furthermore, two-component analysis requires that the partial spectra of the separate components do not show variations in shape during reduction and subsequent oxidation, and this prerequisite is not fulfilled either. On the contrary, the  $g$ -values and coupling constants of the isolated Cu(II) ions were found to vary (vide infra).

Finally, what are probably the largest deviations from a linear relationship between the relative intensities and the number of Cu(II) ions of a special type arise from a signal already present in the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support. The error due to neglect of this broad signal will be small in the oxidized state of the catalysts, but may be quoted at some 10 or 15% relative intensity in the reduced state.

Altogether, some inaccuracies and some uncertainty are inherent to the values of relative intensities that are obtained. But in view of the gradual variations of the EPR parameters involved and by restricting oneself to measurements at one temperature only, the figures obtained may serve as a tentative estimate of the degree of oxidation which is useful as a basis for comparison.

Changes in conductivity of the samples, as may occur during *in situ* reduction and reoxidation of the supported CuO, were followed by their influence on the quality of the cavity ( $Q$ -value). The cavity  $Q$  was monitored by measuring the level of the frequency-doubled component arising in the AFC (automatic frequency control) when the spectrometer is properly tuned. The variations in the sensitivity of the EPR due to the variations in  $Q$  were calibrated in terms of the signal level in the AFC. The EPR intensity of a DPPH marker and the resulting signal level in the AFC were both recorded while the cavity was loaded with different amounts of material subject to dielectric loss.

During experiments carried out at 300°C only minor variations in cavity  $Q$  were found. This result would seem to contradict that obtained by Lumbeck and Voitländer (2b). They reported large variations in  $Q$  during oxidation which they regard as being indicative of changes in conductivity. However, their result was obtained on powdered mixtures of CuO and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

## RESULTS

During cyclic reduction and oxidation the spectra varied in shape (cf. Fig. 2). In accordance with the view that two types of Cu(II) can be discerned by EPR, the variation in shape could be accounted for as a superposition of two partial spectra.

One partial spectrum exhibited an asymmetric shape with a hyperfine structure. Its characteristic line shape could be regarded as unequivocal proof of the presence of randomly oriented isolated Cu(II) ions in an axially symmetric environment. The residual spectrum consisted of a single line also having a more or less asymmetric shape. It was assigned to the two or more magnetically interacting Cu(II) ions. Dipole broadening might have given rise to the observed shape. However, the mutual interaction of the Cu(II) ions may be much stronger, and spin-spin coupling may lead to triplet or even higher multiplet states (4).

Each of these two partial spectra of Cu(II) represents a different type of Cu(II) ions. Within each type there might exist a number of species exhibiting close similarity of structural features. In the case of the isolated ions this supposition is based upon clear evidence. The EPR parameters of this type showed minor variations:  $g_{||} = 2.33$ – $2.35$ ,  $g_{\perp} = 2.06$ – $2.08$ ,  $A_{||} = 135$ – $145$  G and  $A_{\perp} = 20$  G [cf. Refs. (1,2)]:  $g_{||} = 2.33$ ,  $g_{\perp} = 2.05$ ,  $A_{||} = 140$ – $160$  G and  $A_{\perp} = 20$  G]. Also the partial splitting in the perpendicular band became apparent only when the sample had previously been heated to a higher temperature (450°C) than that at which the EPR was measured. The appearance is seemingly related to dehydration of Cu(II) ions at the surface.

In the case of the clusters one may suppose on general grounds that the size (i.e., number of ions per cluster) is not uniform. However, the spectrum of these clusters consisted of a single line at  $g$  about 2.2, and a further differentiation was not attempted.

Apart from these two signals attributed to copper, three further signals of much lower intensity were observed. Two of these were already present in the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> used as the support:

(a) a slightly asymmetric signal at  $g \sim 4.5$  and with a linewidth 25 to 40 G due to the presence of a trace amount of iron in the form of Fe(III) (?);

(b) a broad symmetrical signal at  $g \sim 2.0$  and with a linewidth of about 1000 G, also most likely originating from some impurity (8).

The third signal consisted of a single symmetric line at  $g = 2.0038 \pm 0.0004$  and a linewidth of 7 G. It appeared only in some samples when these were reduced for the first time. The response of this signal did not vary systematically with subsequent oxidation and reduction procedures. Apparently the signal did not originate from the copper. Samples of different batches of the catalysts behaved differently when brought to reaction for the first time. Freshly calcined samples could be reduced easily at the temperatures that were employed (200 and 300°C). Samples that had been exposed to the atmosphere for some time reacted only sluggishly at 200°C.

The intensity of the EPR signals of Cu(II) in the original samples, whether freshly calcined or stored for some time, was always considerably lower than was found after the first and subsequent cyclic treatment by reduction and reoxidation. This effect might be attributed to the formation of a new surface structure during the first reduction and oxidation cycle. Afterward, the supported copper oxide samples reacted more or less reversibly. In the reduced state after prolonged treatment at 300°C with 3% H<sub>2</sub> or CO the clustered Cu (II) ions of both the 5 and the 12% CuO sample were almost fully reduced, whereas of the isolated ions about one-half to one-third was not reduced in the 5 and 12% CuO samples, respectively. Even when the reducing gas was purified

by means of the BTS column, about the same fractions of isolated Cu(II) ions proved irreducible in our hands. These figures were obtained by taking into account the broad background signal due to the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

The estimates of Cu(II) by relative intensities yielded higher figures for the clustered ions and low figures for the isolated ones. This is because the relative intensities were not corrected for this background signal.

The reduction by hydrogen (H<sub>2</sub>) and by carbon monoxide (CO) differed slightly. Although accurate rate measurements were not carried out, it appeared that in particular the clusters of Cu(II) reacted faster with H<sub>2</sub> than with CO (cf. Fig. 3).

Upon reoxidation of the catalysts by oxygen (O<sub>2</sub>) or nitric oxide (NO) a more distinct difference was observed. Nitric oxide gave the striking result that the largest amounts of the respective types of Cu(II) were measured *during* the reaction. The first maximum to appear was due to the isolated ions. The second maximum, of the clusters, was less pronounced. With O<sub>2</sub> the rate of oxidation, leading initially to isolated Cu(II), appeared to be slower. Altogether, the maxima for the respective types of Cu(II) were not as distinct as those obtained with NO. However, upon prolonged oxidation of the catalysts with O<sub>2</sub> the signal intensity of both types was observed to decrease to some extent. Again the amounts of the two types of Cu(II) detected by EPR would seem to level off to an almost constant value (cf. also Fig. 3). During the oxidation by NO the cavity *Q* showed a maximum that coincided with the maximum in the apparent amount of the clusters. However, the decrease in sensitivity of the EPR corresponding to the decrease in cavity *Q* during the leveling-off was a mere 3%, which is too little to account for the observed decrease of 15–25% in the amount of Cu(II) present as isolated and clustered ions.

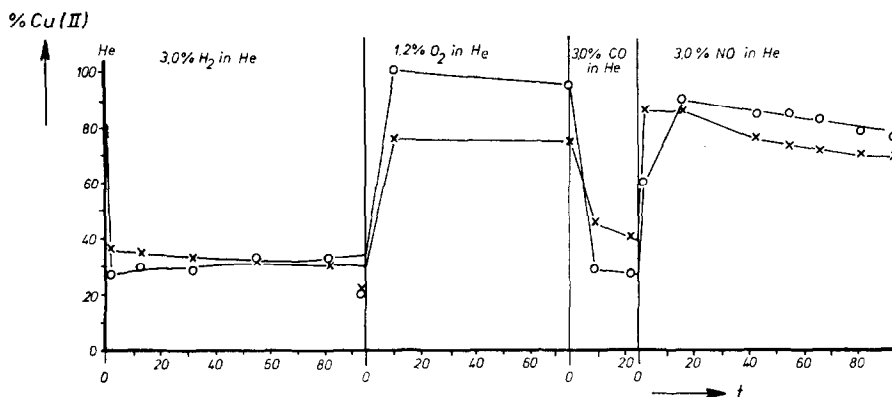


FIG. 3. Reduction and reoxidation of 12% CuO on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> vs time ( $t$ , in minutes). X = isolated Cu(II) ions; O = clustered Cu(II) ions; temperature, 300°C; height of bed, 6 mm.

In the study of the catalytic reaction proper, i.e., in mixtures with an oxidizing and a reducing component, the differences in the reactivity of molecular oxygen and nitric oxide toward the supported copper oxide were even more pronounced. It appeared that in mixtures with molecular oxygen as the oxidizing component, an intermediate degree of oxidation of the catalyst could be attained and maintained. When the ratio of the reducing component to the oxygen was varied it appeared that with the molar ratio CO:O<sub>2</sub> at 2.2 and with H<sub>2</sub>:O<sub>2</sub> at 2.15 an intermediate degree of oxidation could be main-

tained. (Measurements on a 12% CuO catalyst at 300°C, CO or H<sub>2</sub> of about 3% by volume, and O<sub>2</sub> of about 1.2% by volume, resulting catalytic conversion about 90%.)

The mixture with CO and O<sub>2</sub> gave an anomalous response (cf. Fig. 4). When the ratio CO/O<sub>2</sub> was increased from 2.2 to 2.4 or 2.5, the apparent degree of oxidation of the catalyst at first increased. Only after prolonged reaction with the higher CO/O<sub>2</sub> ratio was the expected decrease found (Fig. 4). A corresponding change in  $Q$  could be observed. A maximum in  $Q$ , indicative of a minimum in conductivity of

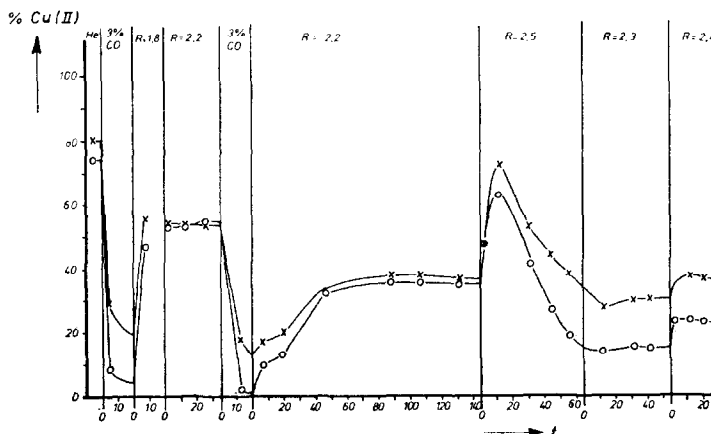


FIG. 4. Anomalous response of Cu(II) by EPR upon variation of molar ratio CO:O<sub>2</sub> ( $R$ ) vs time ( $t$ , in minutes). X = isolated Cu(II) ions; O = clustered Cu(II) ions; CO, constant (3% by volume); temperature, 300°C; 12% CuO on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>; height of bed, 10 mm.

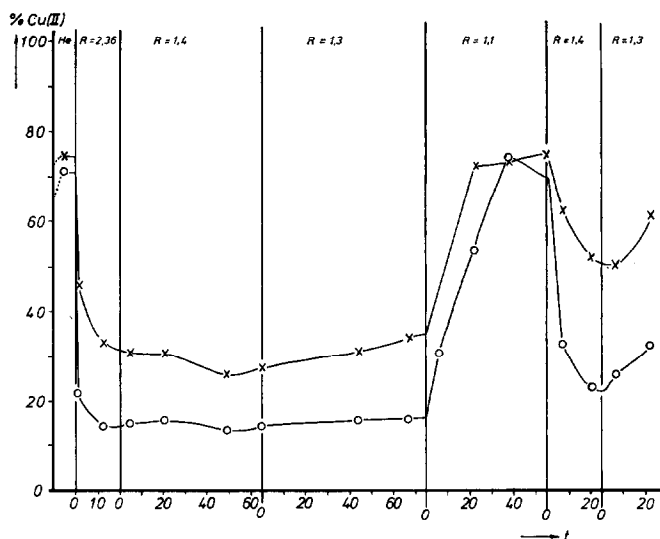


FIG. 5. Changes in the relative amount of Cu(II) by EPR upon variation of molar ratio CO:NO. ( $R$ ) vs time ( $t$ , in minutes).  $\times$  = isolated Cu(II) ions;  $\circ$  = clustered Cu(II) ions; CO, constant (3.3% by volume); temperature, 300°C; 12% CuO on  $\gamma$ - $\text{Al}_2\text{O}_3$ ; height of bed, 30 mm.

the sample, coincided with the apparent maximum of Cu(II) found by EPR. However, the estimated variation in  $Q$  again amounted to a few percent and was therefore too small to account fully for the observed increase in Cu(II).

In the mixtures with NO as the oxidizing component, an intermediate degree of oxidation could not be maintained. In the mixtures with CO and NO an almost

stable degree of low-level oxidation could be observed only in a prerduced sample (cf. Fig. 5).

In the mixtures with  $\text{H}_2$  and NO an intermediate degree of oxidation was not attained at all (cf. Fig. 6). Instead, a range of ratios of  $\text{H}_2/\text{NO}$  between 0.67 and 2 reduced clusters, whereas the isolated copper ions remained largely oxidized. The fraction of the isolated Cu(II) ions

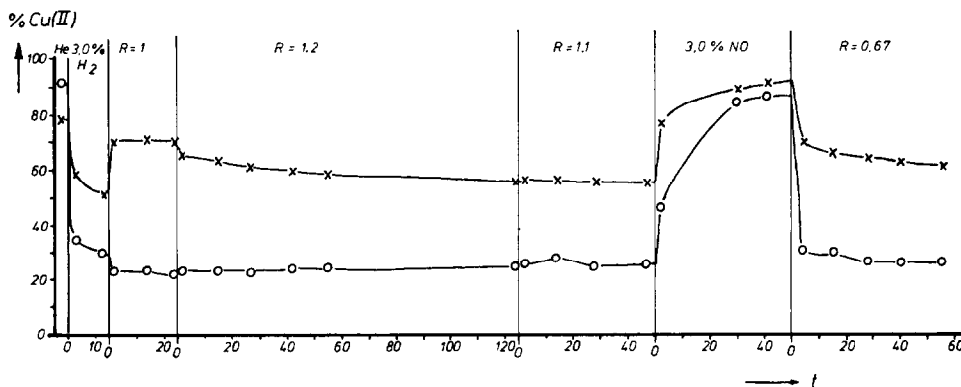


FIG. 6. Changes in the relative amount of Cu(II) by EPR upon variation of molar ratio  $\text{H}_2$ :NO. ( $R$ ) vs time ( $t$ , in minutes).  $\times$  = isolated Cu(II) ions;  $\circ$  = clustered Cu(II) ions;  $\text{H}_2$ , constant 13% by volume except for  $R = 0.67$  ( $\text{H}_2$ , 2%, NO, 3% by volume); 12% CuO on  $\gamma$ - $\text{Al}_2\text{O}_3$ ; height of bed, 6 mm.

was lower than the maximum intensity (100%) observed during the oxidation by NO alone. It was about 60%, and it decreased only little when the H<sub>2</sub>/NO ratio was increased.

#### DISCUSSION

The reason why the reduction at 200°C of catalyst samples that had been exposed to atmosphere for some time proceeds so sluggishly may be that they contain some carbonate. After initial absorption of water, a surface species of copper hydroxide might have formed that in turn could have reacted with carbon dioxide. Hertl and Farranto (9) observed that carbonate on copper chromite does not decompose at temperatures below 200°C.

The first redox cycle applied to a sample always led to an increase in the spin intensity. For this increase in the apparent amount of Cu(II) at a given temperature there are two possible explanations: thermal reduction, leading to a decrease in total amount of Cu(II); and thermal migration, giving rise to transformation of one type of Cu(II) into another, e.g., the spin-paired type into clustered or isolated ions. Which explanation is the right one forms a point of controversy in the literature. However, it appears that both processes may occur. Upon being heated *in vacuo* above 500°C, CuO liberates some oxygen, a reaction that reportedly is facilitated by water (5b). On the other hand, in air or pure oxygen no disproportionation of CuO as bulk material occurs below a temperature of 1000°C (10). This agrees with the finding that supported copper oxide readily reoxidizes at 500°C in the presence of molecular oxygen (5b). Since our samples were calcined and cooled in air, it seems unlikely that thermal reduction would have caused the observed lower degree of oxidation as measured on the fresh samples. It can therefore be assumed that the calcination did result in a large fraction of nonparamagnetic crystallites being formed and frozen in upon cooling.

The observed increase in the amount of copper after the first reduction-oxidation cycle must then be ascribed to the formation of a more irregular structure of the copper oxide, resulting in an increased dispersion, with more of the isolated Cu(II) ions and of the clusters.

From the changeover of one type of Cu(II) to another, as appears in the oxidation by NO, it may also be concluded that thermal migration is facilitated by consecutive reduction and oxidation. However, in the oxidation by O<sub>2</sub>, about the same final relative intensities are usually obtained without any maximum being observed. An alternative explanation based on a specific reaction of Cu(II) with NO has been proposed by Naccache, Che, and Ben Taarit (11). These authors observed a partial disappearance of the EPR signal of Cu(II) in copper-exchanged zeolites. They assumed that NO forms a complex with Cu(II) ions. The proposed structure of the complex Cu(I)-NO<sup>+</sup> emphasizes its diamagnetic nature.

The experimental results in the mixed gases afford evidence about the mechanistic consequences of the differences in affinity of molecular oxygen and nitric oxide toward copper oxide. When O<sub>2</sub> was employed, an intermediate and stable degree of oxidation of the catalyst was attained at a specific ratio of the reducing component to the oxygen. This is in agreement with the view that the copper oxide acts according to a regenerative redox mechanism.

The anomalous response in the CO-oxidation offers further support to this. When after attainment of the intermediate degree of oxidation the CO/O<sub>2</sub> ratio in the gaseous feed was increased, an increase in the amount of isolated and clustered Cu(II) ions was observed (cf. Fig. 4). Strictly speaking, this result implies either that the O<sub>2</sub> oxidizes Cu(I) to isolated and clustered ions, or that the CO reduces nonparamagnetic crystallites of CuO. However, these two reactions may also occur



simultaneously. When the two reactions take place at different sites of the catalyst a gradual rearrangement of the surface structure will be brought about. This actually appears to be the case. In the course of time the initial disturbance of the degree of oxidation of the surface is annulled. The subsequent CO oxidation seems to take place at specific sites, viz freshly reoxidized CuO.

When nitric oxide was employed as the oxidizing component in the mixed gases an intermediate degree of oxidation of the catalyst could not be attained. This may be regarded as unequivocal evidence that the NO-reduction does not follow a regenerative redox mechanism. Already from the course of reaction in the reoxidation of prereduced supported copper oxide by NO, one might have concluded that toward NO the isolated copper ions show enhanced reactivity. The findings in the mixtures, in particular those with H<sub>2</sub> and NO, afford additional evidence. It appears that in the catalytic reduction of NO the isolated copper ions are the preferred reaction sites.

The formation of a paramagnetic Cu<sup>+</sup>-NO complex on reaction of NO with prereduced copper exchanged Y-type zeolite at room temperature has been demonstrated by Chao and Lunsford (12) and by Naccache, Che, and Ben Taarit (11).

The catalytic reaction we studied yielded no evidence for formation of this Cu<sup>+</sup>-NO complex, with its characteristic fourfold splitting in the EPR of the perpendicular orientation (11,12). However, the Cu<sup>+</sup>-NO complex might also form in this case. Its subsequent reaction as postulated by Naccache *et al.* (11) might occur readily. This reaction might be the clue to the ease with which isolated copper ions appear to become oxidized. As the initial step in the

catalytic mechanisms, it would then identify isolated copper ions as the sites at which NO becomes activated.

The same batches of copper-oxide-alumina catalysts have concurrently been subjected to thermogravimetric analysis (TGA). This work and its connection with the EPR will be dealt with in a forthcoming paper.

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