JOURNAL OF CATALYSIS **130**, 447–458 (1991)

Selective Chemisorption and Oxidation/Reduction Kinetics of Supported Copper Oxide Catalysts Prepared from Copper(II) Acetylacetonate

JEFFREY C. KENVIN[1] AND MARK G. WHITE[2]

School of Chemical Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332-0100

Received December 18, 1990; revised February 28, 1991

Copper(II) oxide catalysts, prepared by non-aqueous adsorption of Cu(acac)$_2$ on Cab-O-Sil followed by thermal decomposition, were titrated by NO and N_2O to characterize the dispersion of the copper ions. These catalysts showed molar ratios of NO/Cu close to unity when the Cu loadings were less than 2.5 wt%. For samples having loadings greater than 3.8 wt% Cu, the NO/Cu molar ratios were near 0.7. The NO/Cu molar ratio also depended upon the catalyst preparation technique subsequent to the initial impregnation with Cu(acac)$_2$ when the Cu loadings were $\geq$ 3.5 wt%. Samples washed with fresh acetonitrile showed NO/Cu ratios close to unity, whereas, those not so washed showed NO/Cu ratios near 0.7. IR spectra of NO sorbed on partially decomposed samples showed only "bent" Cu–N–O, whereas, NO sorbed to the sample which was totally decomposed showed both linear and bent Cu–N–O. Selected samples (3.8 and 8.6 wt% Cu) were reacted with N_2O to determine the dispersion of the Cu. The sample having 8.6 wt% Cu reacted with the N_2O to give a dispersion of 0.43; whereas the other sample (3.8 wt%) did not react with the N_2O. This dispersion determined by N_2O agreed with that calculated from NO titration (0.47) if the NO/Cu stoichiometry was assumed equal to unity. Subsequently, these catalysts were reduced in H_2 and reoxidized in O_2 to determine the oxidation and reduction kinetics as a function of copper loading. The 3.8 wt% Cu sample lost 1 O/Cu upon reduction in H_2 and gained 1 O/Cu for reoxidation in O_2 for up to five redox cycles; whereas, the 8.6 wt% Cu sample showed a stoichiometry of O/Cu which decreased from 1.00 to 0.57 after five redox cycles. © 1991 Academic Press, Inc.

INTRODUCTION

Supported copper oxide catalysts have been used for selective reductions (*1*) and oxidations (*2*). These catalysts are usually prepared by aqueous impregnation of the support with a copper salt. The unfavorable solubility of the copper(II) ion in aqueous solutions having a pH near 7 results in a low dispersion of the copper (II) ions (*3*). We reported the preparation of monolayer films of polynuclear metal complexes containing two metal ions (Cu^{2+} and M^{3+}; M = Al, Cr, and Fe) on silica which could be thermally decomposed to a fine dispersion of metal oxides (*4*). These samples appeared to sinter into crystallites about 50 nm in diameter when the decomposition temperature was $\geq$ 350°C (*4*). This system was too complicated to allow definitive conclusions regarding the sintering properties; thus we sought a simple metal complex.

Metal acetylacetonates have been supported on oxides (*5*) and activated charcoal (*6*) with some success for dispersing the complex. These metal complexes appeared to be suitable for a study of the support-complex interactions. Initially, we determined the conditions for which the complexes were dispersed on silica. Monolayer films of copper acetylacetonate, Cu(acac)$_2$ (Fig. 1), have been prepared on Cab-O-Sil using acetonitrile as the solvent when the loadings of complex are $\leq$540 μmol com-

---

[1] Present address: Mobil Research and Development, Billingsport Road, Paulsboro, NJ 08066.

[2] To whom correspondence should be addressed.

0021-9517/91 $3.00
Copyright © 1991 by Academic Press, Inc.
All rights of reproduction in any form reserved.

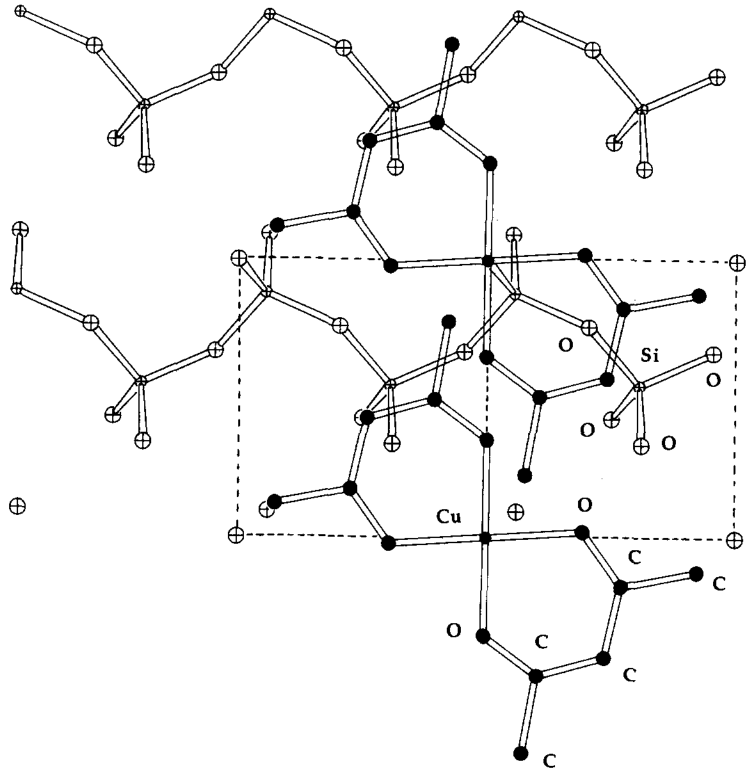


FIG. 1. ORTEP diagram of copper acetylacetonate on α-quartz (100). Dotted lines are projections of the silica unit cell on (100) plane. Solid circles depict atoms of the two $Cu(acac)_2$ molecules. Open circles are atoms of silicon and oxygen. Hydrogens have been omitted for clarity.

plex/g Cab-O-Sil; whereas, the sample showed multiple layers of the complex for loadings >540 μmol complex/g Cab-O-Sil (*7*). Moreover, these supported metal complexes may be thermally decomposed to produce CuO/silica (*7*).

In the present study, these samples are characterized for active surface area by selective chemisorption of NO and N_2O as a function of Cu loading in the sample. The oxidation and reduction kinetics are described to indicate the stability of the copper ions to sintering. These properties are related to the initial arrangement of the metal complexes on the surface of the silica prior to thermal decomposition.

EXPERIMENTAL

Catalysts preparation. The desired amount of $Cu(acac)_2$ was dissolved in 250 cm^3 of acetonitrile. Ten grams of M-5 Cab-O-Sil was added with stirring for 24 h at room temperature. The mixture was vacuum filtered and dried at 60°C for 24 h. Selected samples (1 g) were treated further by washing with five aliquots of acetonitrile (50 cm^3 each), vacuum filtered, and dried at 60°C for 24 h. These samples are referred to as "washed" samples. These samples were characterized for metal content by atomic absorption spectroscopy (*7*). The M-5 Cab-O-Sil shows a surface area of 200 m^2/g (*7*).

Selective chemisorption. The strong chemisorption was determined in a thermal gravimetric apparatus (TGA); the apparatus and procedures were described previously (*8, 9*). In the present case, the adsorption isotherms were developed at 100°C using either NO (3 Torr) or CO (10 Torr; 1 Torr = 133.3 Pa). The adsorption time (3 h) was sufficient to produce no further changes in the uptake. This weight gain was referred to as total adsorption. The samples were then purged with N_2 for 1 h to produce a residual weight gain. This weight gain is defined as strong adsorption.

Oxidation and reduction kinetics. Samples (2–5 mg) were introduced into the thermal gravimetric apparatus to measure the redox kinetics in the presence of H_2 or O_2 (380 Torr). The temperature was programmed between 100 and 300°C at 5°C/min. Between treatments the samples were purged in dry N_2 at 100°C for 1 h. Samples were weighed at the beginning and end of each reduction and oxidation in dry N_2 at 100°C.

N_2O reaction. Nitrous oxide (N_2O) was reacted over the decomposed and reduced samples of Cu/silica to determine the dispersion of the copper atoms. The samples were reduced with H_2 (380 Torr) in the TGA at 300°C for 1 h, purged with N_2 for 1 h at 100°C, and the sample weight was recorded. Samples were exposed to N_2O at 380 Torr for 1 h at 100°C, purged with N_2 at 100°C for 1 h, and the new weights recorded. The number of surface Cu atoms was calculated from the weight increase according to the following stoichiometry (*10*).

$$N_2O(g) + 2Cu(s) \rightarrow Cu_2O(s) + N_2(g)$$

The number of surface Cu atoms was divided by the total number of Cu atoms in the sample to give the fractional dispersion of Cu.

Gases. Gases for gravimetric studies, including 10.35% NH_3 (balance N_2, Matheson), 1.09% NO (balance N_2, Matheson), N_2 and O_2 (Holox, UHP), CO (1.08%, balance N_2, Matheson), and 26% H_2 (balance N_2, Matheson) were dried through beds of activated molecular sieves on delivery. NO for IR studies (99.0%, Matheson) was pretreated in a similar manner. N_2O, obtained from Union Carbide (UHP), was used without pretreatment.

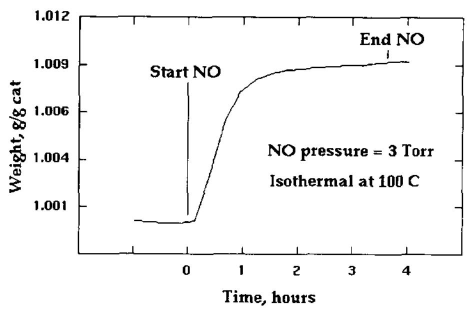


FIG. 2. Isothermal adsorption of NO on supported CuO prepared from the thermal decomposition of Cu $(acac)_2$ on silica (3.8 wt% Cu).

RESULTS

Selective chemisorption of NO and CO. Samples of supported $Cu(acac)_2$ (3.81 wt% Cu) sorbed NO reversibly at 100°C. No strong chemisorption of NO was observed at 100°C.

Our earlier results (*7*) showed that the samples decomposed in a stepwise fashion to remove the acetylacetonate ligands. The sample having 3.81 wt% Cu was decomposed by heating to 400°C in air to show a weight loss of 0.115 g/g cat. The predicted weight loss for this sample was 0.109 g/g cat as modeled (*7*) by the following stoichiometry:

$$Cu(C_5H_7O_2)_2 + O_2 \rightarrow CuO + \text{volatiles}$$

We prepared a sample (3.81 wt% Cu) by heating to 230°C and measuring the total sample weight. When the sample lost a mass equal to one (acac) per Cu ion, the sample was cooled to 100°C and it was exposed to NO at 380 Torr. The partially decomposed sample showed a weight increase equaling 1 mol NO/mol Cu ion. This same sample permitted only physically adsorbed CO at 100°C.

Subsequent studies were performed on samples decomposed in air at 400°C in the TGA prior to the NO adsorption at 100°C. The initial weight increase and the residual weight gain upon switching the gas to N_2 is shown by the initial and final parts of the curve in Fig. 2. Note that no weight decrease is observed after the gas was switched to inert N_2 (data have been corrected for buoyancy effects). These data are summarized in Table 1 as mol NO adsorbed/mol Cu for samples having copper loadings between

TABLE 1

Selective Chemisorption of NO to CuO/silica

Sample	Mol of NO per mol Cu
3.81 wt%, not decomposed	0.0
3.81 wt%, heated to 230°C	1.00
0.90	1.04
0.90[a]	0.98
2.41[b]	0.98
2.50	0.91
3.52	0.70
3.81[c]	0.94
3.81[d]	0.96
4.55	Not tested
5.77	0.76
8.60	0.70
8.60[a]	0.47

Note. Error in the measurements of NO adsorption results in uncertainty of NO/Cu = 0.05.

[a] Sample cycled 5 times through oxidation and reduction cycles.

[b] Prepared by washing 4.55 wt% Cu samples with five aliquots of fresh acetonitrile.

[c] Prepared by washing 5.77 wt% Cu samples with five aliquots of fresh acetonitrile.

[d] 3.8 wt% Cu sample cycled 10 times through oxidation and reduction cycles.

0.90 and 8.6 wt% Cu. The NO could be desorbed by heating the sample to 350°C and the weight decreases upon desorption equaled the weight increase upon chemisorption.

The data in Table 1 for the 0.9, 2.41, and 3.81 wt% Cu samples show NO/Cu molar ratios of 1.04, 0.98, and 0.94, respectively. The samples at 2.50, 3.52, 5.77, and 8.6 wt% Cu show NO/Cu molar ratios of 0.91, 0.70, 0.76, and 0.70. The samples at 3.52 and 3.81 wt% Cu were prepared by the same impregnation procedure; however, one sample was washed with acetonitrile so that the final copper content was reduced from 5.77 wt% to 3.81 wt% Cu. Note this sample shows an NO/Cu ratio of 0.94, whereas, the 3.52 wt% Cu sample (not washed) produced an NO/Cu ratio of 0.70. Apparently, the washing step produced a sample having more Cu ions available for NO sorption than the unwashed sample at nearly the same Cu loading. Two other samples showed similar NO/Cu molar ratios (0.98 and 0.91) for similar copper loadings (2.41 and 2.50 wt% Cu, respectively), but one (2.41 wt% Cu) was prepared by washing with acetonitrile. The effect of washing upon the NO/Cu ratio becomes significant only when the copper loading is greater than 3 wt%.

One sample (3.81 wt% Cu, 599 μmol Cu/g cat) was heated to 350°C to drive off the NO, then exposed to CO/N_2 (not shown). This sample showed a total weight gain of 0.0147 g CO/g catalyst (525 μmol CO/g cat). This total sorption was removed in 4 min by switching to N_2 indicating that no strong chemisorption of CO occurred on this sample at 100°C.

The results of this study and the previous work (*7*) led us to pick two catalysts which represented the characteristics of the samples we studied. The sample containing 3.81 wt% Cu shows a monolayer dispersion of the Cu(acac)$_2$ prior to thermal decomposition (*7*). Thus, we chose the 3.81 wt% Cu sample to represent the well-dispersed samples. The 8.6 wt% Cu sample was chosen to represent those samples generated from the thermal decomposition of multiple layers of the Cu(acac)$_2$ on silica (*7*). This sample is characteristic of the samples having weight loadings ≥5.77 wt% Cu.

IR spectra of chemisorbed NO. The supported Cu samples were analyzed by IR spectroscopy prior to and after adsorption of NO. A description of the apparatus and procedures appears in Ref. (*9*). A sample (3.81 wt% Cu) was partially decomposed by heating to 230°C and then exposed to NO at 100°C (3 Torr) for 4 h and evacuated for 1 h. This sample developed peaks at 1805 and 1705 cm^{-1} (Fig. 3a). At the same conditions the NO pickup was 1 NO/Cu as measured in the TGA. This same sample was heated to 350°C in vacuum and was exposed to NO (3 Torr, 100°C, evacuated 1 h) to develop the spectrum of Fig. 3b. This sample shows peaks at 1910, 1826, and 1672 cm^{-1}. The NO pickup for a similar sample was 0.94 mol NO/mol Cu as measured in the TGA.

Oxidation and reduction kinetics. Two

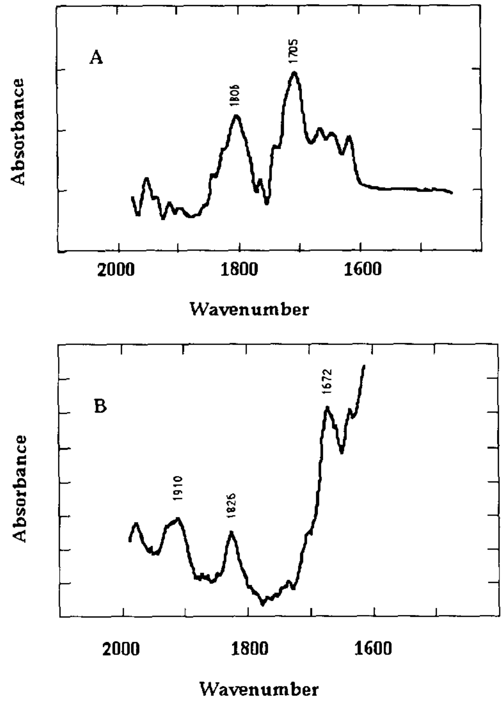


FIG. 3. IR spectra of NO adsorbed on supported CuO prepared from the thermal decomposition of $Cu(acac)_2$ on silica (3.8 wt% Cu). (a) Sample was decomposed by heating to 230°C and exposed to NO (3 Torr) at 100°C for 4 h and evacuated to 1 mTorr for 1 h at 100°C; (b) sample was decomposed by heating to 350°C and exposed NO (3 Torr) at 100°C for 4 h and evacuated to 1 mTorr for 1 h at 100°C.

samples (3.81 and 8.6 wt% Cu) were decomposed in air, then reduced in H_2 by temperature programming at 5°C/min between 100 and 300°C. One sample (3.81 wt% Cu, Fig. 4a) lost weight with increasing temperature between 100 and 230°C. A drastic weight loss occurred between 230 and 280°C. The initial and final weights of this sample in N_2 at 100°C were compared to show the loss of 1 mol O/mol Cu. This sample was exposed to O_2/N_2 with temperature programming between 100 and 300°C at 5°C/min (Fig. 5a). The sample gained weight, lost weight, then gained weight. The overall weight gain upon oxidation is reported by subtracting the initial weight from the final weight in N_2 at 100°C. This oxidation and reduction cycle was repeated 5 times with the following results: the weight loss upon reduction equaled the weight gain upon reoxidation for each cycle. These weight changes corresponded to the addition/removal of one mol O per mol Cu in the sample. The data together with the initial O/Cu stoichiometry were used to calculate the overall O/Cu stoichiometry of the sample after the reoxidation step of each cycle (Table 2).

The 8.6 wt% Cu sample lost weight between 190 and 230°C upon reduction (Fig. 4b). This weight loss was less than one mol O per mol Cu (0.75 mol O lost/mol Cu) and it occurred at a temperature which was lower than that observed for the sample prepared at 3.81 wt% Cu (230–280°C). Subsequent reoxidation showed a weight gain which was less than the weight loss upon reduction such that the overall O/Cu was 0.8 after the first redox cycle (Fig. 5b, Table 2). Reduction and reoxidation of the sample showed a weight loss upon reduction which was slightly greater than the weight gain upon reoxidation. Apparently reoxidation of the samples is slower than reduction such that the O/Cu stoichiometry decreases from 1.0 to 0.57 mol O/mol Cu after five cycles (Table 2).

The 3.81 and 8.6 wt% Cu samples were exposed to NO again after the oxidation and reduction cycles to determine the NO/Cu molar ratio. These samples retained by strong chemisorption 0.96 and 0.47 mol NO/mol Cu, respectively. We compare these NO titrations before and after redox to discover the effects of redox on the NO chemisorption. The oxidation and reduction cycles show little effect on the NO/Cu ratio (0.94 to 0.96) of the 3.81 wt% Cu sample; however, the NO adsorption on the 8.6 wt% Cu suffers a significant decrease (0.7 to 0.47 mol NO/mol Cu) as a result of the oxidation and reduction cycles.

N_2O reaction. The 3.8 and 8.6 wt% samples were reacted with N_2O to determine the Cu atom dispersion. Reduced samples, which had been cycled through five redox cycles were exposed to N_2O. The 3.8 wt% Cu sample did not react with the N_2O, whereas, the 8.6 wt% showed a dispersion of 0.43. This same sample (8.6 wt%) showed

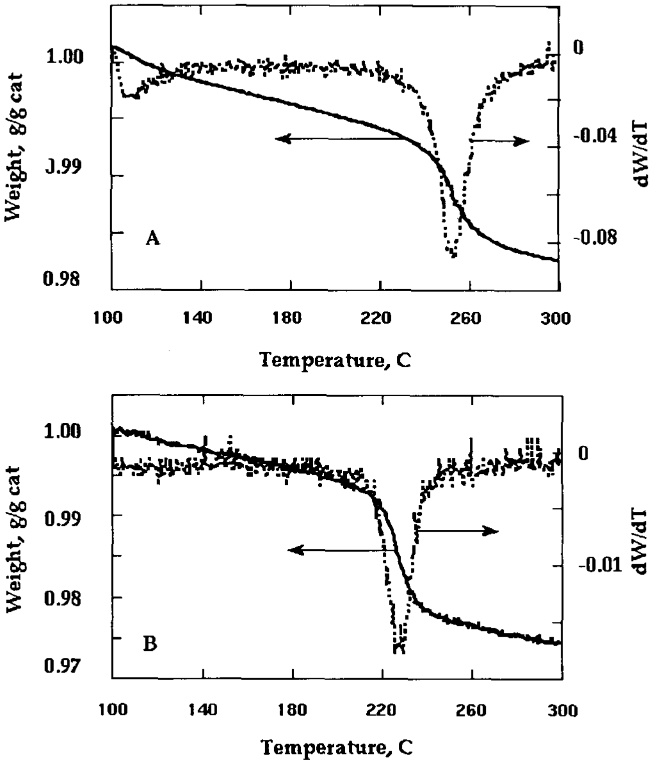


FIG. 4. Temperature-programmed reduction in H_2 of supported CuO: (a) Prepared from $Cu(acac)_2$ on Silica (3.8 wt% Cu); (b) prepared from $Cu(acac)_2$ on Silica (8.6 wt% Cu).

an NO/Cu molar ratio of 0.47 which suggests that the assumption of 1 NO/Cu is correct for calculating the Cu dispersion from the NO adsorption data.

DISCUSSION

We have evidence from DRIFTS (*7*) to show that the $Cu(acac)_2$ forms a monolayer on silica at weight loadings $\leq$ 3.81 wt% Cu (599.6 μmol/g cat). This observed monolayer loading compares favorably with what we calculate assuming that each complex occupies an area equal to the projections of two unit cells on to the (100) plane of α-quartz (Fig. 1). The dimensions of the projections of two unit cells (5.393 Å × 4.903 Å × 2 = 52.88 $Å^2$) suggest that the complex develops a monolayer film on M-5 Cab-O-Sil (200 m^2/g) at a loading of 540 μmol/g cat. We speculated that the complexes sorb to the surface as a consequence of the interaction between the silanol protons and the (acac) ligands (*7*).

The supported $Cu(acac)_2$ complexes do not sorb NO which agrees with the results reported in the literature for NO adsorption on unsupported $Cu(acac)_2$ (*11*). Other complexes of Cu(II) adsorb NO when the ligands are thiooxine, dithiocarbamate, or dithiophosphate (*11*). These results are consistent with a model for which the equatorial ligands influence ability of the Cu(II) ion to accept axial ligands. The NO adsorption properties of supported $Cu(acac)_2$ are in contrast to those we reported earlier for a 4-coordinate copper(II) complex (*9*) which quantitatively adsorbs NO. The equatorial ligands in this complex were two alkoxides, a hydroxide, and a tertiary amine. Apparently, the coordination of the Cu(II) determines its ability to accept axial ligands (*9*).

Heating the supported $Cu(acac)_2$ sample

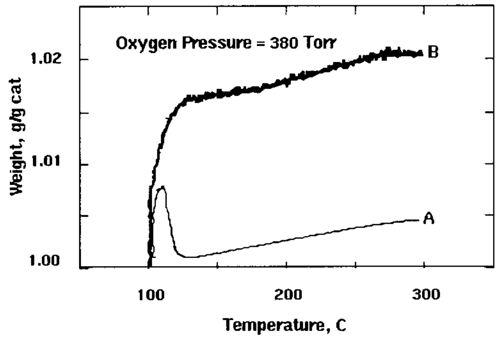
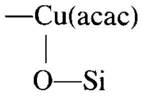


FIG. 5. Temperature-programmed reoxidation in O_2 of supported CuO: (a) Prepared from $Cu(acac)_2$ on Silica (3.8 wt% Cu); (b) prepared from $Cu(acac)_2$ on Silica (8.6 wt% Cu).

removes the (acac) ligands from the Cu ion. One sample (3.81 wt% Cu) when heated to 230°C showed only partial decomposition as indicated by a weight loss corresponding to the loss of one (acac) plus a proton per Cu ion (*7*). We interpreted these data by a model where one (acac) ligand reacts with the proton of a siloxide near the Cu in the complex (*7*). The sample adsorbed 1 mol NO/mol Cu ion when exposed to NO at 100°C. Apparently, this sample shows one adsorption site per Cu on the average, perhaps as a result of the loss of one (acac). The IR spectrum of this partially decomposed sample shows relaxations at 1575, 1552, and 1531 cm^{-1} which confirms the presence of an (acac) group (*7*). IR of NO chemisorbed to the partially decomposed sample (Fig. 3a) shows two vibrations (1806 and 1705 cm^{-1}) at frequencies similar to those we reported (*9*) for NO sorbed to a partially decomposed polynuclear metal complex containing Cu(II) and Fe(III). These frequencies below 1850 cm^{-1} are characteristic of bent *M*–N–O ligands (*12*). The partially decomposed complex only physically adsorbs CO which suggests that the Cu ion is not monovalent. Thus, we speculate the structure of the partially decomposed complex is given by **I** which shows one adsorption site per Cu ion. This divalent ion is bonded to an (acac) ligand and a surface siloxide to balance the charge on the Cu(II) ion.



$$\begin{array}{l}\text{—Cu(acac)}\\ \;\;\;| \\ \;\;\text{O—Si}\end{array}$$

I, Partially Decomposed

TABLE 2

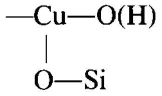
Oxidation and Reduction of Supported CuO

Sample	Mol O^a/mol Cu after reoxidation				
	Cycle number				
	Initial	1	2	3	5
3.81 wt% Cu^b	1.00	0.99	0.99	1.00	1.00
8.6 wt% Cu	1.00	0.80	0.65	0.6	0.57

[a] Average stoichiometry of O/Cu determined from the initial stoichiometry and from the moles removed upon reduction and moles of O added upon reoxidation. The initial stoichiometry of O/Cu was determined from the observed weight loss for temperature-programmed decomposition of the supported $Cu(acac)_2$. The moles of O here does not include that associated with the silicon ions in the Cab-O-Sil.

[b] Prepared by washing 5.77 wt% Cu sample with acetonitrile.

Subsequent heating of the sample removes fragments of (acac), and the weight loss upon decomposition suggests that Cu and one O remain from the original complex. These gravimetric results are confirmed in that no vibrations characteristic of the original complex are observed in the IR spectrum of the decomposed sample (*7*). The amounts of NO strongly adsorbed to these samples were 0.94–0.98 mol NO/mol Cu ion and the IR spectrum of chemisorbed NO showed peaks at 1910, 1826, and 1672 cm^{-1} (Fig. 3b). The peak at 1910 cm^{-1} is characteristic of linear *M*–N–O (*12*). Apparently, the subsequent decomposition caused a significant change in the metal environment such that the bonding of the NO to the Cu was changed from that observed in the partially decomposed sample. This unusual sensitivity of the IR spectrum of NO bound to various metals has been reported (*12*). This totally decomposed sample did not chemisorb CO; thus monovalent Cu is not present in this sample. We speculate that the structure of the decomposed Cu(acac)$_2$ on silica is given by **II** which has one adsorption site per Cu (II) ion. This divalent Cu ion is bonded to a hydroxyl group and a surface siloxide.



$$\begin{array}{l} -\mathrm{Cu}-\mathrm{O(H)} \\ \quad | \\ \ \ \mathrm{O}-\mathrm{Si} \end{array}$$

II, Totally Decomposed

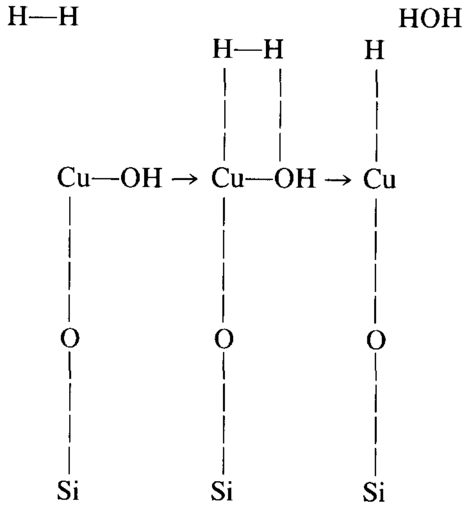
The ligands about the Cu(II) in species **I** and **II** are different; thus, we expect that the chemisorbed states of NO bound to the Cu(II) in species **I** and **II** will be different. Moreover, the large bidentate (acac) ligand is replaced by the smaller unidentate OH ligand which should offer less steric hindrance to the NO adsorbate than the (acac) ligand. The difference in size of the Cu ligands could explain the difference in the Cu–N–O shape between structures **I** and **II**. We have included an H on the oxygen to balance its charge, although, the gravimetric data are not sufficiently sensitive to confirm the existence of this H.

Two samples reduced in H_2 (3.81 and 8.6 wt% Cu, after the redox cycles) were exposed to NO and reacted with N_2O in separate experiments to establish the stoichiometry of NO to surface Cu. The 8.6 wt% Cu sample adsorbed 0.47 mol NO/mol Cu, and this same sample showed a Cu dispersion of 0.43 as determined by N_2O. These results suggest that the percentage dispersion may be calculated from data of NO adsorption by multiplying the NO/Cu stoichiometry by 100. The 3.81 wt% sample shows an NO/Cu ratio of 0.96; however, the same sample did not react with N_2O. We speculate that the 3.81 Wt% Cu sample does not have ensembles of Cu atoms which are sufficiently close to react with N_2O molecules. Furthermore, a stoichiometry of 1 NO/Cu may be used to determine the dispersion of the Cu atoms in the other samples from a measurement of NO adsorption to these samples. The dispersion of the Cu in the 8.6 wt% Cu is probably reflected accurately by the NO adsorption since the N_2O technique obviously does not account for the isolated Cu atoms in the 3.81 wt% Cu sample.

The selective chemisorption of NO was used to determine the dispersion of the complexes (Table 1) using the measured stoichiometry of 1 NO/Cu. Samples washed with acetonitrile (2.41 and 3.81 wt%) show dispersions of 98 and 94%. Other samples (0.9, 2.50, 3.52, 5.77, and 8.6 wt% Cu, not washed in acetonitrile) show dispersions of 100, 91, 70, 76, and 70%, respectively. The washing with acetonitrile removed some of the complexes as evidenced by the decreased Cu loadings (e.g., the 4.55 and 5.77 wt% Cu decreased to 2.41 and 3.81 wt% Cu after washing). From these results we conclude that the dispersion of the Cu in these samples after thermal decomposition depends upon the initial arrangement of the metal complexes on the silica. The DRIFTS of these samples showed that all the complexes were hydrogen-bonded to the silica in the washed samples, whereas, some of the complexes were not hydrogen-bonded in the unwashed samples (*7*). We interpreted these data by a model showing some complexes as an overlayer to the complexes which were hydrogen-bonded to the silica. The complexes in the overlayer are not hydrogen-bonded one to another. Moreover, washing the sample with acetonitrile removes the complexes from the overlayer to produce a sample having all the complexes hydrogen-bonded to the silica. The NO adsorption data confirm this model as evidenced by the nearly 100% dispersion of Cu in the 3.81 wt% Cu samples compared to 70% dispersion in the 3.52 wt% Cu sample.

The initial dispersion of the Cu ions in these samples prepared by non-aqueous impregnation is greater (100–70% at Cu loadings 0.9–8.6 wt%) than what has been reported for Cu/Cab-O-Sil catalysts prepared by aqueous impregnations or by ion exchange (36% dispersion Cu atoms, 0.25 wt% Cu; 20%, 3 wt% Cu; 25%, 8 wt% Cu, Ref. (*10*)). We speculate that the high dispersion of the Cu(acac)$_2$ precursor on the silica is promised by the combined effects of (1) hydrogen-bonding between the silanol hydrogens and the quasi-pi electrons of the (acac) ligands, plus (2) the direct interaction of the siloxide and the copper ion (*7*). Moreover, the (acac) ligands ensure a minimum separation of 4.9–5.3 Å between each Cu in the supported samples of monolayer or less (Fig. 1) so that interactions between the Cu ions are minimized. The combination of strong, support-complex interactions and weak Cu–Cu interactions minimize the driving force of the Cu ions to sinter in the monolayer samples. Supported samples showing multiple layers of the complex produce upon decomposition low dispersions of the Cu atoms after reduction. We speculate that the low dispersion of Cu species arises as a result of interaction of the coppers between the adjacent layers of Cu(acac)$_2$ complexes prior to decomposition. Furthermore, we believe that the complexes in the overlayers are arranged not unlike those in the unsupported complex (*7*). Single crystal data of the unsupported Cu(acac)$_2$ show that Cu ions in adjacent layers are nearly 4Å apart and thus may interact upon thermal decomposition (*14*).

The weight changes upon reduction suggest that 1 mol O is removed per mol of copper ions in the 3.8 wt% Cu sample. We propose the following mechanism for the reduction of the supported CuO produced by the thermal decomposition of a monolayer of Cu(acac)$_2$ on silica. We speculate that structure **II** chemisorbs 1 H_2 to produce structure **III**.



II **III** **IV**

Structure **III** rearranges to give H_2O plus structure **IV**. The difference in mass between structures **II & IV** corresponds to the loss of 1 O per Cu ion which agrees with the data. This model assumes that hydrogen is adsorbed heterolytically to form a proton-hydride pair. This assumption of heterolytic hydrogen adsorption on Cu^{2+} appears reasonable since heterolytic cleavage of hydrogen occurs in Cu^{2+} solutions (*15*). In the present model the proton interacts with the hydroxyl group to form water, whereas the hydride reacts with the Cu^{2+}. For this model, the Cu is not reduced to zero-valent metal, but it remains as a divalent ion bonded to the siloxide and the hydride.

The reoxidation of the 3.81 wt% Cu sample proceeds with the addition of 1 mol O/mol Cu. This sample will add/lose 1 O/Cu for each reoxidation/reduction in the redox cycle. Apparently, all Cu ions in the sample experience redox. The weight changes upon redox and the NO titrations support this conclusion. The Cu in this monolayer sample do not sinter into large crystallites and remain available to the gas phase. This sample will not decompose N_2O so we conclude that the Cu species are separated so that the oxygen atom in N_2O cannot react with two Cu's.

The properties of the 8.6 wt% Cu are similar to those reported for supported Cu (*10*). The dispersion of the Cu atoms in this multilayer sample is less than unity and the atoms sinter into larger crystallites with reduction and oxidation cycles. This multilayer sample activates N_2O; thus some surface Cu atoms must be in close proximity to affect the decomposition.

The reoxidation kinetics of the monolayer sample (3.81 wt% Cu) saturated with hydrogen shows an unusual weight loss after a rapid, initial weight gain (Fig. 5a). This complicated response to the addition of O_2 gas

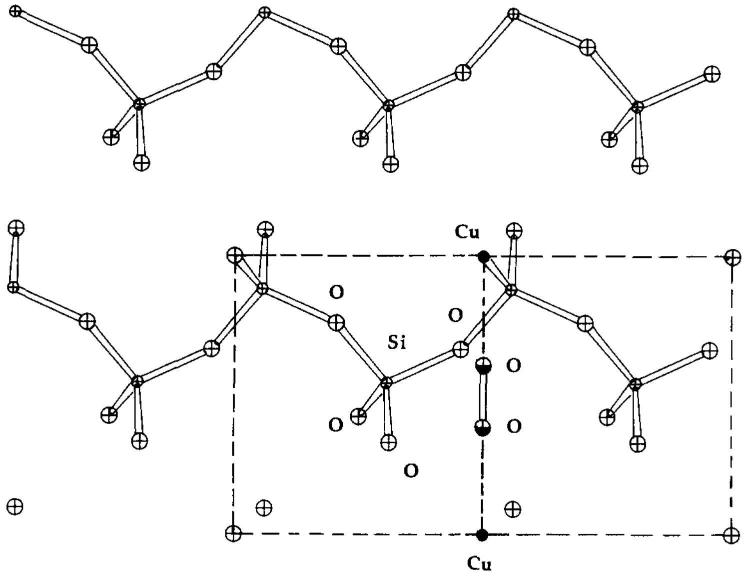


FIG. 6. ORTEP diagram of isolated Cu atoms deposited on α-quartz (100). Dotted lines are the projections of the silica unit cell on the (100) plane. Solid circles are Cu atoms developed from decomposition of Cu(acac)$_2$. Open circles are silicon, oxygen atoms. Half-filled circles are O atoms of molecular O_2.

suggests that several reactions occur simultaneously to form a volatile and a non-volatile. The rapid, initial weight gain is probably the reaction of gaseous oxygen with adsorbed hydrogen to form water. The rapid weight loss is probably the evolution of water from Cu. The final stage of slow weight gain is not explained easily. It is known that the Cu species in this sample are separated too widely to activate N_2O and it is doubtful that an isolated Cu could activate molecular oxygen. Thus, we are left with the task of finding a slow mechanism for activating dioxygen over Cu's separated by at least 4–5 Å. Consider the model (Fig. 6) of isolated Cu's on the (100) surface of silica which have been generated by the thermal decomposition of supported Cu(acac)$_2$ (Fig. 1). The size of the Cu(acac)$_2$ molecule coupled the requirement that it is coordinated to siloxides and it is hydrogen-bonded to another silanol defines the constraints by which the complexes are placed on this surface. In one configuration the internuclear distance between Cu atoms in adjacent Cu(acac)$_2$ is 5.393 Å; for another configuration, this distance is 4.903 Å. The internuclear distance in O_2 is 1.2 Å. If we place molecular oxygen midway along a line connecting two adjacent copper atoms which are separated by 5.393 (or 4.903) Å in the monolayer sample, the copper–oxygen distances are 2.097 (or 1.852) Å. Both of these distances are acceptable for the formation of Cu–O bonds. This process is slow due to the strict geometric requirement for placing the O_2 molecule exactly halfway between the two copper atoms so that the proper Cu–O bond distance is satisfied. The multilayer sample (8.6 wt% Cu) reoxidizes rapidly since the Cu atoms are sufficiently close to decompose N_2O; thus, the atoms should be oxidized easily by O_2. The multilayer sample will show the rapid weight increase which is the reaction of oxygen with adsorbed hydrogen and then a slower weight increase which is the reaction of dioxygen with adjacent surface Cu atoms. This simple geometric model predicts that the rate of Cu atom reoxidation will be faster in the multilayer sample than the reoxidation rate of the monolayer sample which agrees with the observed results.

The present results must be discussed in connection with the pertinent literature (1, 3, 10, and 13). Kohler *et al.* (13) report on the preparation and characterization of CuO/silica prepared by ion exchange from aqueous solutions. These catalysts were reported to show 10–25% of the Cu atoms as ion exchanged onto neighboring silanol groups to form isolated Cu atoms; the remaining Cu atoms are concentrated in small Cu particles having a diameter less than 6 nm. The unfavorable solubility of the Cu ions in aqueous solutions prevents all of the Cu ions from exchanging with surface silanols and the water probably competes with the Cu ions for available surface sites. The authors show data of X-ray photoelectron spectra (XPS) which suggests that the isolated Cu ions cannot be reduced to the zerovalent state, whereas, the Cu ions in the small particles can be reduced to Cu metal (*13*). In the present work we suggest that surface bound Cu(II) ions may be reduced to SiO–Cu^{2+} H- on silica (structure **IV**). Thus, isolated surface Cu(II) ions bonded to siloxides may lose one O per Cu upon reduction in H_2, but the SiO–Cu^{2+} H- surface species may show an electronic spectrum different from bulk Cu atoms. Kohler *et al.* (*13*) report that the isolated Cu species in their samples do not sinter into larger ensembles; these results agree with those we report here for the isolated Cu(II) ions prepared from the monolayer dispersions of $Cu(acac)_2$ on silica. The authors report that the isolated Cu species are harder to reduce than the CuO particles which agrees with our data. They speculate that a high activation energy barrier for breaking Cu–O–Si bonds is responsible for the slow reduction of these isolated ions; we propose a similar mechanism for retarding the reduction of the isolated Cu(II) ions in our samples. Whereas, the cited work (*13*) reports the supported samples contain 10–25% of the copper as isolated ions, we report 100% such isolated copper ions for the samples prepared from monolayers of the $Cu(acac)_2$ on silica.

The temperature-programmed reduction of samples from the cited work (*13*) proceeds with peaks at 232°C for the first reduction; second and subsequent reductions proceeded with maximum reaction rates at 191 and 203°C. These results compare favorably with those presented here except the samples prepared from decomposition of a monolayer of $Cu(acac)_2$ show the reduction of only one type of species occurring between 230 and 280°C, whereas, the reduction of multiple layers of $Cu(acac)_2$ occurs between 190 and 230°C. We are observing the reduction of species similar to that of Kohler *et al.;* however, our samples appear to have fewer phases of Cu.

The reoxidation of the samples from the cited work (*13*) proceed with up to four peaks in the spectrum which the authors attribute to different oxidation states and surface morphologies. Our results show the oxidation of surface hydrogen into volatile water and the slow reoxidation of only one type of surface species with the addition of one O per Cu for the oxidation of a monolayer sample. The reoxidation of a multilayer sample proceeded without the apparent loss of a volatile but the reoxidation spectrum clearly showed a fast, initial reaction rate followed by a slower reaction rate. We speculate that surface hydrogen is reacting with molecular oxygen to produce water but (1) the parallel reaction of molecular oxygen with large ensembles of surface Cu atoms proceeds sufficiently fast to mask the weight change of the desorbing water and/or (2) the product water sorbs to the large ensembles of Cu atoms more readily than it sorbs to isolated Cu atoms.

SUMMARY

Supported $Cu(acac)_2$ form monolayers at weight loadings of Cu less than or equal to 3.8 wt% for the samples prepared by washing with fresh acetonitrile. This washing step removes supermonolayer complexes and redistributes some of the complexes into the monolayer. These samples will not sorb NO or CO. These results are in agreement with the NO adsorption data on unsupported Cu(acac)$_2$. Stepwise thermal decomposition removes one (acac) initially to develop a coordinately unsaturated site and thus accept the NO in a bent Cu–N–O configuration. Subsequent heating removes fragments of the (acac) to leave a hydroxyl group on the surface Cu(II). NO will adsorb to the decomposed sample in both the bent and linear Cu–N–O configurations. The supported Cu catalysts prepared by the thermal decomposition of monolayer Cu(acac)$_2$ show unusual properties. The dispersion of the Cu atoms in these samples is 100% and the redox reactions show quantitative removal and addition of 1 O per Cu in the sample. This 100% dispersion of the Cu atoms in the sample is unchanged with redox cycles. The Cu atoms in the monolayer samples are separated such that a multiple site demanding reaction such as N_2O decomposition will not occur on the sample. The robust nature of the Cu to resist sintering is a result of the separation of the Cu atoms and the strong interaction of the atoms with the silica surface.

ACKNOWLEDGMENTS

The authors acknowledge the helpful discussions with Professor J. Aaron Bertrand of the School of Chemistry, Georgia Institute of Technology and with Professor Mark B. Mitchell, School of Chemistry, Clark-Atlanta University.

REFERENCES

1. Monti, D. M., Wainwright, M. S., and Trimm, D. L., *Ind. Eng. Chem. Prod. Res. Dev.* **24,** 397 (1985); Agarwal, A. K., Cant, N. W. Wainwright, M. S. and Trimm, D. L., *J. Mol. Catal.* **43** 79 (1987).
2. Inui, T., Ueda, T., and Suehiro, M., *J. Catal.* **65,** 166 (1980); Wood, B. J., Wise, H., and Yolles, R. S., *J. Catal.* **15,** 355 (1969).
3. Kohler, M. A., Lee, J. C., Trimm, D. L., Cant, N. W., and Wainwright, M. S., *Appl. Catal.* **32,** 309 (1987).
4. Beckler, R. K., and White, M. G., *J. Catal.* **112,** 157 (1988).
5. van Ommen, J. G., K. Hoving, H. Bosch, A. J. van Hengstrum, and P. J. Gellings, *Z. Phys. Chem.* **N.F. 134,** 99 (1983); van Henstum, A. J., J. G. van Ommen, H. Bosch, and P. J. Gellings, *Appl. Catal.* **5,** 207 (1983).
6. Chiou, C. T. C., and Janes, M., *J. Phys. Chem.* **77** (6), 809 (1973).
7. Kenvin, J. C., and White, M. G., *in* "CATL 55, 198th National Meeting of the ACS, Miami Beach, FL, Sept. 1989; Kenvin, J. C., Ph.D. thesis, School of Chemical Engineering, Georgia Institute of Technology, Atlanta, GA, 1990; Kenvin, J. C. White, M. G., and Mitchell, M. B., *in* "200th National Meeting of the ACS, COLL 173, Washington, D. C., August, 1990;" Kenvin, J. C., White, M. G., and Mitchell, M. B., *Langmuir*, in press.
8. Babb, K. H., and White, M. G., *J. Catal.* **102,** 252 (1986).
9. Beckler, R. K., and White, M. G., *J. Catal.* **109,** 25 (1988).
10. King, T. S., Goretzke, W. J., and Gerstein, B. C., *J. Catal.* **107,** 583 (1987); Evans, J. W., Wainwright, M. S., Bridgewater, A. J., and Young, D. J., *Appl. Catal.* **7,** 75 (1983).
11. Yordanov, N. C., Terzev, V., and Zhelyazkowa, B. G., *Inorg. Acta. Chim* **58,** 213 (1982).
12. Kung, M. C., and Kung, H. H., *Catal. Rev.-Sci. Eng.* **27,** 425 (1985).
13. Kohler, M. A., Curry-Hyde, H. E., Hughes, A. E., Sexton, B. A., and Cant, N. W., *J. Catal.* **108,** 323 (1987).
14. Starikova, Z. A., and Shugam, E. A., *Zh. Strukt. Khim* **10**(2), 290 (1969).
15. Halpern, J., MacGregor, E. R., and Peters, E., *J. Phys. Chem.* **60,** 1455 (1956).