

Supported Catalysts Prepared from Mononuclear Copper Complexes: Catalytic Properties

JEFFREY C. KENVIN¹ AND MARK G. WHITE²

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

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Model surfaces of copper on silica (Cab-O-Sil) were prepared and characterized by four probe reactions: methyl acetate hydrogenolysis, ethanol and methanol decomposition, and acetaldehyde hydrogenation. The model catalysts were prepared by thermal decomposition of copper acetylacetonate {Cu(acac)₂} deposited on silica either as a monolayer or as multiple layers. The prior characterizations suggested that thermal decomposition of monolayer films of Cu(acac)₂ produced isolated copper species which could be oxidized and reduced up to 10 times without changing the dispersion of the copper. Thermolysis of the multiple layers of Cu(acac)₂ produced a copper surface of lower dispersions (ca. 70%) which decreased to 30% after only five oxidation/reduction cycles. These two surfaces were appropriate models to study the catalysis of oxygenates over Cu ensembles. © 1992 Academic Press, Inc.

INTRODUCTION

We demonstrated the usefulness of supporting some polynuclear metal complexes on silica to serve as models for supported oxide catalysts (1-6). Polynuclear metal complexes prepared from perchlorate salts could be supported intact on Cab-O-Sil as a monolayer film and the properties of these complexes were related to the structure. The strong affinity of these large, cationic complexes for the silica was attributed to ion exchange of the complexes with surface protons with the subsequent elimination of the perchlorate anion to the complex as perchloric acid. These first studies demonstrated the technique for creating well-defined catalytic surfaces by decorating silica with discrete metal complexes. The complexes of these studies showed activity for the probe reaction without resorting to thermolytic activation. However, these catalysts showed limited application and we turned to a more general technique of cata-

lyst preparation which involves thermal activation.

Subsequently, we examined a neutral metal complex, Cu(acac)₂, attached to the Cab-O-Sil (7). Monolayer films of Cu(acac)₂ were developed for loadings of complex (3.8 wt% Cu, 598 μmol/g catalyst) near that predicted from a simple model assuming a close-packed arrangement on the silica surface (553 μmol/g catalyst). From these studies, we concluded that hydrogen bonding between the (acac) ligands and surface silanols was responsible for the strong affinity between the surface and the metal complex (7). The Cu(acac)₂ complex does not require a high density of ion exchange sites on the SiO₂ surface to form a monolayer because this neutral complex requires only hydrogen bonding sites for the initial attachment on the surface. Thus, Cu(acac)₂ does not face some of the same problems reported for other Cu systems which require ion exchange sites to form a monolayer (8).

Multiple layers of Cu(acac)₂ could be developed on the silica by contacting the required amount of complex with the support and eliminating the final wash-step with

¹ Present address: Mobil R. & D. Corp., Room 2554, Billingsport Road, Paulsboro, NJ 08066.

² To whom correspondence should be addressed.

fresh acetonitrile (7). These films were decomposed thermally to develop copper oxide on silica. Decomposition of monolayer films of $\text{Cu}(\text{acac})_2$ produced a catalyst having a high dispersion of copper (>90%, determined by NO titration) at metal loadings up to 3.8 wt% (9). Moreover, the properties of the catalysts developed from monolayer films were different from that observed for supported copper prepared from aqueous solutions of the nitrates. The temperature ($T > 250^\circ\text{C}$) required to reduce the novel copper catalysts in hydrogen was greater than that required for unsupported copper oxide (ca., 190°C) (9). The copper species in these new samples did not react with N_2O at the conditions normally used to determine copper metal surface area (10). We concluded that "isolated" copper species were developed from decomposition of a monolayer film of $\text{Cu}(\text{acac})_2$. These surface coppers may be separated by as much as 5 Å. Moreover, the fine dispersion of copper species in these samples did not change with subsequent oxidation and reduction cycles (9). Samples prepared by thermolysis of multiple layers of $\text{Cu}(\text{acac})_2$ showed physical properties similar to those reported for supported copper samples prepared from aqueous impregnation of copper salts. These properties include an initially low metal dispersion which decreases with oxidation and reduction cycles, and a reactivity to N_2O (10). Thus, we report in this work the catalytic properties of the copper oxides prepared by thermolysis of supported $\text{Cu}(\text{acac})_2$.

Two types of catalysts were prepared from $\text{Cu}(\text{acac})_2$ to explore the reactivity of copper surfaces (isolated Cu species and crystallites of Cu) toward several probe reactions. Two samples containing isolated Cu species were prepared from thermolysis of a submonolayer and monolayer of $\text{Cu}(\text{acac})_2$, whereas the sample having crystallites of Cu was developed from the thermal decomposition of a multilayer sample of $\text{Cu}(\text{acac})_2$. We chose methyl acetate hydrogenolysis as one reaction suspected to

demand more than one copper site (11). If the copper species are truly separated in these monolayer catalysts, then no activity should be observed for the methyl acetate reaction. The ethanol dehydrogenation reaction to acetaldehyde is reported to occur on isolated Cu sites (12). Thus, the ethanol dehydrogenation should occur on the monolayer catalyst. Since, the dehydrogenation of ethanol to acetaldehyde is equilibrium-limited at typical reaction conditions, we include the reverse reaction in this study. The multilayer catalyst should be active for all reactions. The site demanding nature of the methanol decomposition reaction is not clear although single crystal studies on ZnO suggest that it is a demanding reaction (13). The results of our work should shed light on this question.

EXPERIMENTAL

Microreactor. A Varian 920 gas chromatograph was modified to accommodate a microcatalytic reactor constructed from $\frac{1}{4}$ " stainless steel tubing having a length of 3" ($1" = 2.54$ cm). The tubing was wrapped with heating tape connected to a temperature control device inside the Varian GC. The inlet to the reactor was connected to the outlet of a heated liquid injection port of the GC maintained at 125°C . The reactor outlet was connected to a $\frac{1}{8} \times 20'$ (6.1 m) stainless steel GC column packed with Porapak Q (60/80 mesh, 177–250 μm). The separated peaks were detected by a thermal conductivity detector with the output connected to a Spectra Physics Minigrator for peak analysis. A standard mixture (25 mol% H_2 , balance He) purchased from Matheson was the carrier gas. The carrier gas flow rate was constant at 15.5 STP cm^3/min for all tests in which the bed of catalyst was varied between 100 and 350 mg. One to two μL of liquid reactant were introduced to the reactor by a Hamilton syringe. The reactor temperature was 275°C , whereas the column temperature was controlled separately at 150°C . The pressure at the in-

jection port was 65 psig (14.7 psi = 101.3 kPa).

The reaction conditions for the probe reactor were as follows: temperature = 275°C; pressure = 65 psig at injection port of GC; flow rate is 15.5 STP cm³/min; total weight of supported catalysts was 320 mg of 2.4 wt% Cu (7.68 mg Cu), 145 mg of 3.8 wt% Cu (5.51 mg Cu), or 110 mg of 8.6 wt% Cu (9.46 mg Cu).

Catalyst preparation. Three catalyst samples were prepared having copper metal loadings of 2.4, 3.8, and 8.6 wt%, respectively. Two of these catalysts (2.4 and 3.8 wt% Cu) showed dispersions near 100% which did not change with repeated redox cycling, whereas the 8.6 wt% Cu sample showed a dispersion which decreased to 30% after the same redox treatments. The precursors were deposited on the silica (Cab-O-Sil, M-5 grade, surface area = 200 m²/g) from solutions of Cu(acac)₂ in dry acetonitrile. The details of the catalysts preparation were reported earlier (7, 9). Samples of supported Cu(acac)₂ were dried in dry N₂ at 100°C for 1 h. The complexes were decomposed in a nitrogen/oxygen mixture ($P_{\text{OXYGEN}} = 380$ Torr) by heating

from 100 to 400°C at 10°C/min. Small aliquots (ca. 1 g) were treated in this manner to prevent overheating of the sample during thermal decomposition. The samples were subsequently introduced to the microreactor, heated in the carrier gas to 300°C for 12 h, and cooled to the reaction temperature. This reduction pretreatment is necessary to develop catalysts having high activity and selectivity. Catalysts prepared without the benefit of the reduction at 300°C show little or no activity.

RESULTS

The results of the probe reactions over the three catalysts (2.4, 3.8 and 8.6 wt% Cu) are shown in Fig. 1 and Tables 1 and 2. Consider first the activity of the methanol and methyl acetate reactions over the model catalysts. The 2.4 and 3.8 wt% Cu catalysts show no activity for the methanol decomposition and the methyl acetate hydrogenolysis, whereas the 8.6 wt% Cu sample shows conversions of 56 and 15% for these two reactions (Fig. 1). These data are also reported as specific activities by dividing the percent conversion of reactant by the mass of Cu in the sample (Table 1). The

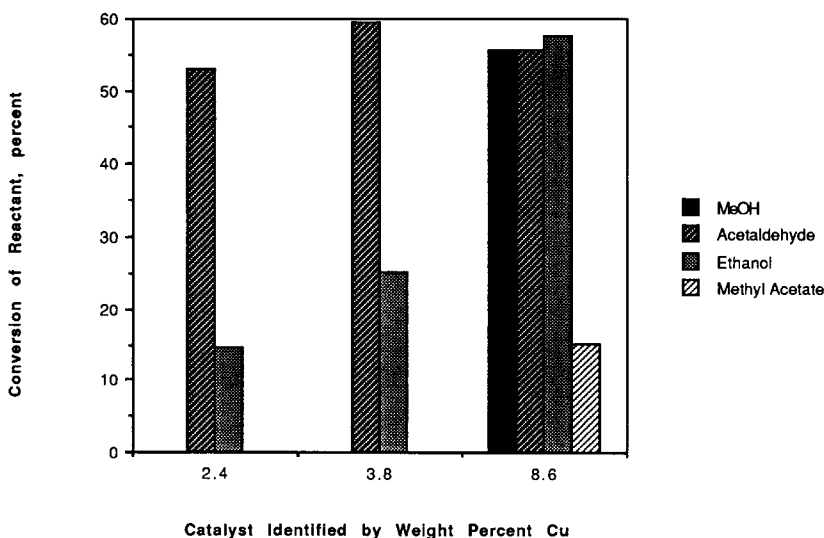


Fig. 1. Activity of supported CuO catalysts. The results of the probe reactions over the three catalysts (2.4, 3.8, and 8.6 wt% Cu) are reported as percent conversion of reactant at 275°C. No conversion of methanol or methyl acetate was observed for the catalysts having 2.4 and 3.8 wt% Cu.

TABLE 1
Activities of Supported Copper Catalysts

Model reaction	Activity (% conversion/mg Cu)		
	2.4 wt% Cu (96%) ^a	3.8 wt% Cu (91%) ^a	8.6 wt% Cu (31%) ^a
Methanol decomposition	0	0	5.9[19.1]
Ethanol decomposition	1.9[2.0]	4.9[5.4]	6.1[19.8]
Acetaldehyde hydrogenation	6.9[7.2]	10.8[11.9]	5.9[19.1]
Methyl acetate hydrogenolysis	0	0	1.6[5.1]

Note. Activity is reported in % conversion/mg Cu. Entries in brackets reflect the fractional dispersion of Cu thus have the units % conversion/mg surface Cu.

^a Percent dispersion of Cu in sample determined by NO titration (9).

specific activities for the methanol and methyl acetate reactions over the 8.6 wt% Cu are 5.9 and 1.6 %/mg Cu (Table 1). Shown in the same table is the dispersion of Cu in the sample as determined by NO titrations (9). The specific activities may be divided by the fractional dispersion of Cu to give the activities specific to the mass of surface Cu. The data for activity per unit surface copper appear in brackets (Table 1).

The model catalysts show activity for the ethanol decomposition and the acetaldehyde hydrogenation reactions (Fig. 1). The activities of the three model catalysts for the acetaldehyde reaction are 53, 59.5, and 56%, respectively, for the 2.4, 3.8, and 8.6 wt% catalysts. As these conversions are very near that expected for equilibrium at these reaction conditions, these results cannot be interpreted as characteristic of the kinetics of the reaction over these samples. Indeed, if we compare the specific activities of these samples for the acetaldehyde reaction, it appears that the 3.8 wt% catalyst is more active than the 2.4 and 8.6 wt% samples (10.8 versus 6.9 and 5.9% per mg Cu, respectively). The activity for the ethanol reaction increase with increasing Cu loading: 2.4 wt% (15% conversion) < 3.8 wt% (25% conversion) < 8.6 wt% Cu (58% conversion). The ethanol reaction at these re-

action conditions may be limited by equilibrium only for the 8.6 wt% catalyst. Thus, the results for the 2.4 and 3.8 wt% catalyst may represent the effect of catalyst structure upon kinetics. These same data may be examined for specific activity as shown in Table 1. The order of reactivity according to these results is as follows: 2.4 < 3.8 < 8.6 wt% Cu. The same ordering of catalyst activity is observed for ethanol activity specific to surface Cu.

The selectivity data are reported in Table 2 for ethanol and acetaldehyde reactions over the three model catalysts. The selectivity to species *i* is defined as 100 times the moles of reactant converted to the product *i* divided by the moles of reactant converted. Examine first the selectivity of ethanol decomposition over the 2.4 and 3.8 wt% Cu samples. Acetaldehyde was the major product over these two catalysts with light gases as the only other products. The ethanol decomposition over the 8.6 wt% Cu sample showed aldehyde (27% selectivity) and ethyl acetate (73% selectivity). Apparently, the ethanol reaction stops at the simple dehydrogenation over the 2.4 and 3.8 wt% samples to produce acetaldehyde, but the same reaction continues over the 8.6 wt% sample to produce ethyl acetate.

TABLE 2
Selectivity of Supported Copper Catalysts

Probe reaction/ products	Selectivities over model catalysts		
	2.4 wt% Cu (96%)	3.8 wt% Cu (91%)	8.6 wt% Cu (31%)
Ethanol decomposition			
Acetaldehyde	92.6	100	27
Ethyl Acetate	0	0	73
Light Gases	7.4	0	0
Acetaldehyde hydrogenation			
Ethanol	95.7	98	45
Ethyl Acetate	0	0	45
Light Gases	4.3	2	0

Note. The selectivities over the 8.6 wt% Cu samples are as follows: 56% for the combined yields of methanol and acetaldehyde, 14% for ethanol, 29% for ethyl acetate, and 1% to light gases.

The reverse reaction to ethanol dehydrogenation is the acetaldehyde hydrogenation to ethanol. This reaction shows almost quantitative conversion of the aldehyde to the alcohol over the 2.4 and 3.8 wt% Cu samples; however, the same reaction over the 8.6 wt% Cu samples shows a 45% selectivity to the alcohol with significant yields of ethyl acetate (55% selectivity). The large size of the copper ensembles in this sample apparently catalyzes reactions other than simple hydrogenation of the acetaldehyde.

The multi-site demanding hydrogenolysis of methyl acetate to methanol and ethanol is not catalyzed by the 2.4 and 3.8 wt% Cu samples but does react over the 8.6 wt% Cu catalyst. The selectivities over the 8.6 wt% Cu sample are as follows: 56% for the combined yields of methanol and acetaldehyde, 14% for ethanol, 29% for ethyl acetate, and 1% to light gases.

DISCUSSION

These results suggest that the catalytic activity and selectivity of the probe reactions differ over the model catalysts. Our interpretation of these activity/selectivity data depends upon the characterizations of the same samples we reported earlier (7, 9). The characterization of supported copper metal catalysts remains an active topic of research (10) with some groups favoring unsteady state chemisorption (10b), others reporting dispersion based on reaction of the surface with N₂O (10a), and our efforts to characterize Cu ion site densities using NO titration (1, 3, 4, 9). The NO adsorption to a monolayer film of polynuclear metal complexes supported on Cab-O-Sil suggested that the number of exposed Cu(II) ions was related to the NO adsorption amount by a stoichiometry of 1 NO per surface Cu(II) ion (3, 4). These results over pristine metal complexes encouraged us to use NO as a titre for samples of polycrystalline Cu/Cab-O-Sil as an alternative to the N₂O decomposition technique. We reported a close agreement of the Cu dispersion in one sample using the NO titration and N₂O decomposition techniques (9).

The success of the NO titration technique to measure the number of exposed Cu ions in supported metal complexes of known structures and the agreement of the Cu dispersion determined by NO and N₂O decomposition gives us reason to use the NO technique as a means to measure Cu dispersion. The previous characterizations show that the 2.4 and 3.8 wt% Cu samples contain highly dispersed Cu species for which reduction and reoxidation at temperatures up to 300°C does not change the state of the Cu dispersion (9). Moreover, the 3.8 wt% Cu samples when reduced in hydrogen did not react with nitrous oxide but did react with molecular oxygen. These results suggest that the Cu species are separated by at least 4–5 Å (9). From these previous results we may formulate a model of the catalyst surface.

The genesis of this sample was modeled by a mechanism where a Cu(acac)₂ mounts the surface of the silica (α -SiO₂ [100]) as shown in Fig. 2. In this configuration, the nearest approach of the coppers in adjacent complexes is 4–5 Å (7). Upon thermal decomposition, the (acac) ligands leave Cu species on surface siloxide oxygens in a model α -quartz lattice shown in Fig. 3. In this model the distance between crystallographical similar features is 4.903 and 5.398 Å. This model explains the NO chemisorption results (100% dispersion) and the inactivity toward the N₂O reaction while still showing activity to the O₂ reaction (9). Notice that molecular O₂ may be placed between the Cu species so that Cu–O bonds develop at the optimum distance of 1.9–2.0 Å; however, the N₂O molecule cannot be placed between the Cu species to develop a Cu–O–Cu bridge with acceptable Cu–O bond distances. This model for the arrangement of Cu species on silica is used to explain the reactivity and selectivity results.

Ethanol Decomposition and Acetaldehyde Hydrogenation

Consider C₂ oxygenate fragments placed on two adjacent Cu species. These fragments may represent the dissociative chem-

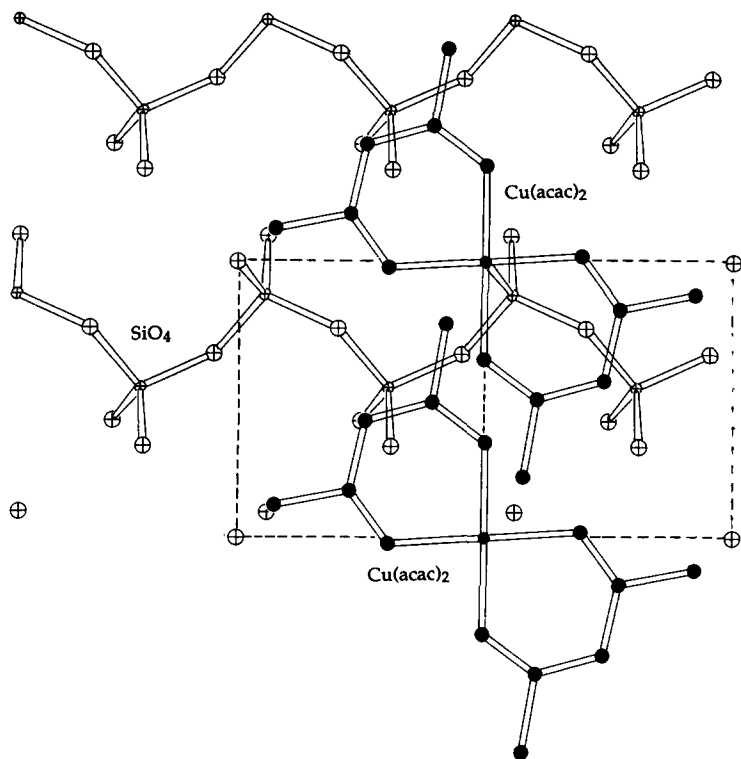


Fig. 2. Model of $\text{Cu}(\text{acac})_2$ monolayer film on α -quartz (100). Dotted lines are projections of the silica unit cell on (100) plane. Solid circles depict atoms of the two $\text{Cu}(\text{acac})_2$ molecules. Open circles are atoms of silicon and oxygen. Hydrogens have been omitted for clarity.

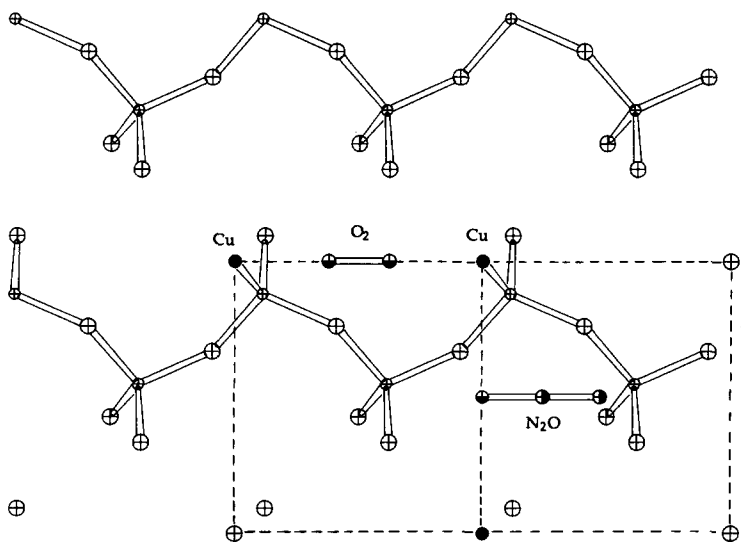


Fig. 3. Model of Cu on α -quartz (100). The chemisorption of molecular oxygen is depicted on this figure along with the attempt to chemisorb nitrous oxide.

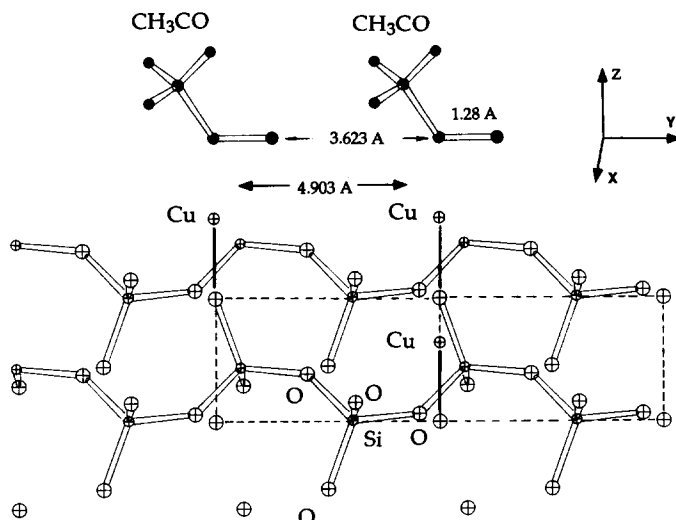


Fig. 4. Model of CH_3CO fragments chemisorbed on supported Cu. The model of Cu on α -quartz (100) shown in Fig. 3 is rotated about the y-axis to show the arrangement of the chemisorbed CH_3CO fragments. The dotted lines are projections of the silica unit cell on the (100) plane.

isorption of ethanol or acetaldehyde. Many different arrangements are possible for placing these fragments on the Cu species. For example, the fragment could be sorbed to the Cu through the O with the alkyl group pointing away from the surface or it may bond to the copper through the carbonyl carbon. Recent infrared (IR) results of ethyl acetate on Cu/silica reported by Trimm and co-workers (11) suggest that an acetyl intermediate was formed on a Cu with one bond between the Cu and the carbonyl C and another, weaker interaction between another Cu and the π system of the CO (11). These results suggest that the methyl acetate surface intermediate is bonded to a Cu through the carbonyl C in a similar fashion. In the present work we model the adsorption of C_2 oxygenates on a surface of isolated copper species as shown in Fig. 4. For all configurations, the distance between the carbonyl carbons corresponds to the distance between the Cu species: 4.903 or 5.398 Å. This distance is too large to allow direct interactions between the carbonyl C's. However, the distances between other atoms in the fragments de-

pend upon the orientations of the fragments on the Cu species. We investigate these other possibilities by examining the oxygenates placed on a Cu-Cu distance of 4.903 Å.

Several configurations are possible which involve rotations about the Cu-C axis, or the z-axis in Fig. 4. Some of these arrangements of chemisorbed intermediates are unlikely to result in products either as a consequence of the distance apart and/or the relative position. For example, one configuration may have the methyl groups "pointing" toward each other along a common axis and separated by 1.843 Å; however, this arrangement is unlikely to result in a product. One arrangement likely to result in reaction to form ethyl acetate shows the oxygen of one fragment pointing to the carbonyl carbon of an adjacent fragment (Fig. 4). However, the separation of the carbon and oxygen is too large (3.623 Å) to result in a covalent bond. For another configuration (not shown) for which the two oxygens define an axis collinear with the carbonyl carbon atoms, the closest approach distance of these oxygen atoms is 3.503 Å. No peroxy

intermediate is possible at this long distance. This geometric study shows that coupling of the C_2 fragments is unlikely over the 2.4 and 3.8 wt% Cu samples. Thus, for a feed of acetaldehyde and hydrogen the only possible product is ethanol. The hydrogenation of the aldehyde occurs probably as a result of the addition of hydrogen which has been chemisorbed to the same Cu as the chemisorbed oxygenate. This mechanism was postulated by Trimm to explain the hydrogenation of the acetyl fragment of the ethyl acetate (11). The distance between Cu species makes it unlikely that hydrogen is added to the chemisorbed oxygenate from adjacent Cu species.

Kazanskii describes the dehydrogenation of ethanol to acetaldehyde and hydrogen over a Cu/Y-zeolite (12). Electron paramagnetic resonance (EPR) analysis of the sample confirmed that the Cu(II) species are magnetically isolated; thus, he presumed that the Cu(II) ions were physically separated. He explains the dehydrogenation to occur with the interaction of one ethanol molecule with the unfilled d -orbital of one Cu(II) ion. This same mechanism could describe the dehydrogenation of ethanol over the isolated Cu(II) ions in the 2.4 and 3.8 wt% Cu samples. The intermediates to acetaldehyde would be C_2 oxygenates adsorbed on the isolated Cu (II) ions as in Fig. 4. These oxygenates are separated too far to recombine into higher molecular weight species and the Cu species are too far removed to activate a C-C bond to form lower molecular weight species.

The model of isolated Cu species also explains the apparent inactivity of the 2.4 and 3.8 wt% Cu samples to catalyze the methanol decomposition and the methyl acetate hydrogenolysis. Methanol is decomposed to methyl formate and hydrogen over Cu-based catalysts (14) and Cu/ZnO catalyzes the reaction of CO and H_2 to methanol (15). These Cu catalysts show low dispersions of the metal (30%) and hence large Cu crystallites. In the light of the present results over the 2.4 and 3.8 wt%

Cu sample, it appears that the methanol decomposition reaction appears to demand a Cu ensemble size greater than one. The large distances between Cu species in the model (Fig. 3) suggest that methanol chemisorbed through the oxygen to the Cu cannot eliminate more than one hydrogen molecule, as no adjacent Cu species are sufficiently close to accept more hydrogen atoms, which is necessary to form CO from methanol. The methanol reaction did not show any measurable conversion on the 2.4 and 3.8 wt% sample; thus, we conclude that formaldehyde could not be formed on these isolated Cu species in the reducing environment. These results stand in contrast to the apparent ease with which the 8.6 wt% sample catalyzes the total decomposition of methanol to light gases at the same conditions. The methanol decomposition reaction must demand Cu ensembles larger than one.

The mechanism (11) for ethyl acetate hydrogenolysis suggests that the C-O bond must be activated to produce an acetyl fragment (CH_3-CO) and an ethoxy fragment (CH_3CH_2O). These acetyl and ethoxy fragments are stabilized on the surface until hydrogen atoms are added. This mechanism is employed to understand the results of reacting methyl acetate and hydrogen over the catalysts. The isolated Cu^{2+} species in the present model are bonded to one siloxide and a hydride (9). Thus, an isolated Cu cannot activate the C-O bond directly as no vacant orbitals are present to accept the electron pair from the methoxy fragment and to interact with the p orbitals of the carbonyl. The hydride may be accepted by the slightly electropositive acetyl carbon; however, this single Cu^{2+} cannot supply the two more hydrogen atoms necessary to produce the products: methanol and ethanol. Thus, the isolated Cu species cannot satisfy the needs of the methyl acetate reaction. The site requirements of this reaction must be satisfied by more than one Cu species.

Consider adjacent Cu species in the iso-

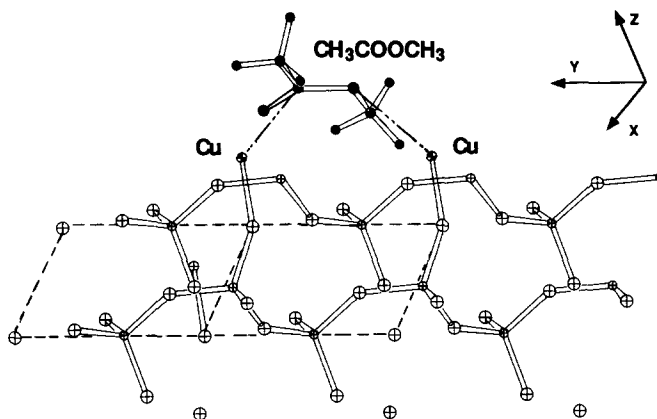


Fig. 5. Model of methyl acetate chemisorbed on supported Cu. The model of Cu on α -quartz (100) shown in Fig. 3 is rotated about the y-axis and z-axis to reveal the details of the chemisorption. The methyl acetate is positioned 2 Å above the plane of the Cu atoms. Interactions between the Cu-C and Cu-O are depicted by broken lines.

lated Cu catalysts (Fig. 5). Each Cu will accommodate one hydride, thus a pair of coppers can supply the minimum reactant requirements to produce acetaldehyde and methanol from methyl acetate. However, the pair of Cu-H⁻ species are separated by 4.903 Å so that the configuration which places the C-O bond of methyl acetate along the line connecting the two Cu-H⁻ results in a minimum C-H distance and O-H distance of 1.737 Å. This distance is too large to result in bond formation. Other configurations of the methyl acetate on the surface are possible which place the acetyl carbon directly atop one Cu species. In this configuration, no bond is possible between the methoxy oxygen and an adjacent Cu species as this bond distance is 3.473 Å. These two configurations suggest that no possible orientation of the methyl acetate on this model surface will allow two Cu species to interact in a productive manner as required by the published mechanism (11).

The 8.6 wt% Cu sample catalyzes the methyl acetate reaction probably as a result of a specific arrangement of copper species on the surface. The yields over the 8.6 wt% Cu catalyst are similar to those reported by Trimm and co-workers (16) for a Cu/silica

catalyst. No detailed picture of our catalyst is possible as the material was developed from multiple layers of Cu(acac)₂ which were thermally decomposed to form CuO/silica. The dispersion of this material changed from 71 to 31% as a result of the reaction in reducing conditions for 2 weeks (9). These samples were not analyzed by transmission electron microscopy as our earlier efforts failed to detect small crystallites of supported copper catalysts (less than 10 nm) prepared by thermal decomposition polynuclear metal complexes (6). Thus, we estimate the average crystallite size by NO adsorption assuming the cube model for the Cu crystallite. These cubes may be as large as 8.5 nm using the dispersion of 31% measured by NO adsorption and assuming the crystallites are face-centered cubic with a specific gravity of 8.96 (17). The Cu atoms in FCC crystallites show an interatomic distance of 2.59 Å (17). This arrangement of Cu atoms could accommodate the requirements of the methyl acetate reaction.

The same geometric models may be used to explain the selectivity results over the model catalysts. Ethyl acetate is formed over the 8.6 wt% catalysts for both the methyl acetate and the acetaldehyde reac-

tions, whereas this product is not observed over the 2.4 and 3.8 wt% Cu catalysts for the acetaldehyde hydrogenation. Ethyl acetate is the product of the coupling of an acetyl fragment (CH_3CO) and an ethoxy fragment ($\text{CH}_3\text{CH}_2\text{O}$). These fragments may be present during the dissociative chemisorption of acetaldehyde (CH_3CO) and subsequent partial hydrogenation ($\text{CH}_3\text{CH}_2\text{O}$). Thus, the fragments may combine to form ethyl acetate if the distance and orientation of the fragments allow. In the case of the isolated Cu species model, the distance between adjacent fragments will not allow the coupling reaction to occur (Fig. 4). However, the distance between Cu atoms in a Cu crystallite (2.59 Å) may permit the coupling of acetyl fragment (CH_3CO) and an ethoxy fragment ($\text{CH}_3\text{CH}_2\text{O}$) over the 8.6 wt% Cu catalysts. These simple geometric models explain the observed yields of ethyl acetate over the 8.6 wt% Cu and the absence of ethyl acetate over the 3.8 wt% Cu catalyst.

The geometric model described here may be used to explain the qualitative differences between the performance of the catalysts developed from thermolysis of monolayers and multiple layers of $\text{Cu}(\text{acac})_2$ films. However, this model does not exclude the satisfactory explanation of the same data by a ligand effect model (i.e., electronic effects). Indeed, isolated copper atoms residing on siloxides are not expected to show the same electronic configuration as supported crystallites of copper containing hundreds of atoms. The model giving the proper quantitative description of supported copper catalysts may show elements of both the geometric and electronic effects models.

The results presented here add to the fundamental understanding of catalysis by supported copper and may be used to understand the performance of commercial catalysts. For example, the present results suggest that the activity and selectivity of copper catalysts for the methyl acetate re-

action may depend upon copper ensemble size, and these data suggest that an optimum ensemble size may exist which shows high activity for the methyl acetate hydrogenolysis but low activity for the decomposition of methanol to light gases and low activity for the further reaction of acetaldehyde and ethanol to form ethyl acetate. These results for the methyl acetate reaction may be pertinent in developing catalysts for the hydrogenolysis of methyl laurate to lauryl alcohol.

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