Effects of Molecular Structure Upon Complex-Support Interactions

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Two cationic, copper metal complexes with different ligands were synthesized: ethylenediamine (en) $[Cu(C_2N_8N_2)(ClO_4)_2]$ *and diethanolamine (Deta)* $\{[CuC_8H_{21}N_2O_4]ClO_4\}$*. These complexes were mounted on Cab-O-Sil using nonaqueous impregnation techniques, and the loadings were determined at which multilayers formed. These samples were analyzed for copper, carbon, nitrogen and hydrogen content to determine if ligand dissociation occurred during the impregnation. Samples were decomposed in a thermal gravimetric apparatus to determine the kinetics of the thermolysis reaction in air, and the evolved gases were analyzed by gas chromatograph-mass spectrometry to determine the products of the thermolysis reaction. The results of these and earlier studies are summarized in a model that describes the effects of molecular structure upon complex-support interactions. Complexes with the ability to form hydrogen bond interactions between the ligand and the support form strong interactions with the surface of silica, whereas complexes without such hydrogen bond interactions are only weakly attracted to the silica surface. Strong interactions with the surface may also arise as a result of ligand dissociation and direct interaction of the metal ion with the surface oxygens. The charge on the complex and its shape play less important roles in determining the affinity of the metal complex with the silica.*

Introduction

Catalyst preparation is an important set of unit operations for which engineers and scientists are beginning to elucidate the fundamental principles. Adsorbents and catalysts are ubiquitous in the petrochemical industry and these materials will find many future uses in the technologies of pollution abatement. Chemical engineers use the adsorbents and catalysts in such operations as separations by pressure-swing adsorption, gas cleaning, and drying, as well as the more familiar uses such as chemical conversions. Although catalyst manufacturers have prepared catalyst and adsorbents for many years, the goal of *designing* and synthesizing highly efficient materials having uniform and controlled surface morphologies remains an elusive target. Equally important to this goal is the cost-effective synthesis of commercial catalysts with a minimum of empiricism using the accepted design techniques common to modern chemical engineering practice. Progress toward these goals will be realized after the fundamentals have been established which relate to the mechanism by which metal ion(s) attach to the surface of a fluid-solid interface. These fundamentals may be discovered using the model approach in which the structures of the metal complexes and the ceramic surface are varied in a systematic manner to be related to the observed affinity of the metal complex to the surface.

The preparation of some supported metal oxides proceeds by a process in which an aqueous solution of a metal salt is contacted with a ceramic support having the appropriate surface area and porous properties. The amount of solution may be in excess of that required to fill the pores so that a filtration step is necessary to separate the solid from the supernatant liquid or only that amount of solution is employed to just fill

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the pores of the ceramic support, thus eliminating the filtration. In either case, the mechanism by which the metal ions attach to the ceramic surface is not completely known, and the resulting surface morphology is not controlled well in all systems. Some metal ions form facile equilibria among many different, discrete molecular complexes in different phases according to the solubility of the species in the aqueous solution. The solubility of the phases is keenly influenced by the pH of the impregnating solution. We avoid many of these complicating factors inherent to transition metal ions in aqueous solutions by using nonaqueous solvents in the model systems. The objective of this work is to study in a systematic manner those factors that govern the attachment of the metal ions to the ceramic support. We hope to assemble these results into a model which will describe in a general manner the interactions between catalyst precursors and the surface of the model, ceramic oxide. This work is relevant to the preparation of supported metal and metal oxide catalysts.

Recently, researchers have prepared model catalysts using metal complexes to exercise more control over catalyst preparation and to prepare materials having well-defined surface morphologies (Yermakov, 1981; Psaro et al., 1986; Basset et al., 1988). Models of supported metal catalysts have been prepared from metal carbonyl clusters applied to silica (Brenner et al., 1979), alumina (Commereuc et al., 1980), magnesia (Lamb and Gates, 1986), and titania (Deeba et al., 1981). The results of several studies suggest that an anionic complex formed in solution interacts with surface cations of the support oxide, such as Mg^{2+} (Lamb and Gates, 1986). Thus, the mechanisms of ionic bonding are important to attach these metal clusters to the support. Other studies attempted to model supported metal oxide catalysts by using polynuclear metal complexes as the precursor. Polynuclear metal complexes show oxide and hydroxide bridges between adjacent metal ions. The results of these studies suggest that cation complexes may be formed in solution and become attached to surface anions such as the siloxides found on silica (Babb, 1986; Beckler, 1986, 1987a,b, 1988). Prior work showed that polynuclear cationic complexes, such as the hexameric copper complex $\{M^{3+}[(\mu\text{-}OH)Cu(\mu\text{-}OCH_2CH_2N(CH_2CH_3)_2]_6(ClO_4)_3\ M^{+3} =$ Al, Cr, or Fe$\}$, ion-exchanged with the protons of the surface silanols to form a monolayer at weight loadings to 28.4 wt. % (Beckler, 1986). We predicted the weight loading at completion of a monolayer to be 28–29 wt. % using a simple model which assumes a closed-packed arrangement of the complexes on the support surface. The model required only the size of the complex and the specific surface area of the silica (Beckler, 1986). This agreement between observed and predicted saturation weight loading suggested that all available surface was employed in the ion exchange process. Moreover, the ion exchange process could be frustrated by steric hindrance of the *n*-butyl ligands of a related, hexameric, copper complex: $M^{3+}[(\mu\text{-}OH)Cu(\mu\text{-}OCH_2CH_2N(C_4H_9)_2]_6(ClO_4)_3$. Apparently the ion exchange required the complex to approach the surface to within a few angstroms.

Neutral metal acetylacetonates have been attached as a monolayer film to silica surfaces without the benefit of ion exchange or ligand exchange reactions (Kenvin, 1989, 1990, 1991). These materials showed the unusual tendency to maintain monolayer dispersions even at high loadings of the complexes. The $Cu(acac)_2$ complex completed a monolayer at 579-μmol/g SiO_2 which is close to the predicted value of 553-μmol/g SiO_2 (Kenvin, 1991). Others have documented the formation of monolayers by these materials on ceramic supports such as alumina and titania (van Hengstum et al., 1983). The mechanism for binding some of these metal acetylacetonates $[M^{n+}(acac)_n$: $M = Cu^{2+}$, $acac = C_5H_7O_2]$ to the surface was hydrogen bonding between the surface silanols and the π-electrons of the acac ligands. It appeared prudent to study the relationship between molecular structure of the precursor and its interaction with the surface. For these studies we continued to use silica as the support owing to the wealth of knowledge regarding its surface chemistry.

We reasoned from the early studies that the ionic interaction between the complex metal ions and the support was the primary mechanism for anchoring the complex to the support (Beckler, 1986). However, the results of the studies involving neutral complexes (Kenvin, 1989, 1990, 1991) lead us to consider the effects of hydrogen bonding upon the complex-surface interaction. In the present study, we examine the affinity of the complex for the support as we change the possibility of hydrogen bonding between cationic complexes and silica. The degree of hydrogen bonding between the cation complex and the support is varied by choice of functional groups present in the complex. Our choice for a complex with little hydrogen bonding is *bis*-ethylenediamine copper(II) perchlorate $\{Cu(en)_2(ClO_4)_2\}$. This complex (Figure 1a) shows no nucleophilic groups which can hydrogen-bond to the protons of surface silanols. We compare the affinity for the silica of this complex to that of copper (II) *bis*-(2,2′-dihydroxydiethylamine) perchlorate $\{Cu(H_2Deta)(HDeta)ClO_4\ [Deta = HN(C_2H_4O)_2]\}$, which is similar in size and shape to the $[Cu(en)_2]^{2+}$ (Figure 1b) but contains nucleophilic, alkoxide, functional groups.

In the ion exchange mechanism, the silanol must lose a proton and then hydrogen bond to a proton on the ligand or bond directly to the metal. The activation of the surface silanols is a necessary step in the ion exchange mechanism which anchors the cationic complex to the surface siloxides. For cationic complexes to hydrogen bond, they either need an electron-pair (hydrogen bond acceptor) or a proton (hydrogen bond donor). The results of this study will determine the relative importance of hydrogen bonding functional groups upon the overall affinity of cationic complexes to the silica surface.

Experimental Studies

Preparation of catalyst precursors

$[Cu(en)_2](ClO_4)_2$. To a solution of hydrated copper(II) perchlorate (18.52×10^{-3} kg, 50 mmol, Alfa Inorganics) in distilled water (30×10^{-6} m^3) was added to the bidentate, chelating-agent ethylenediamine (6.68×10^{-6} m^3, 899.5 kg/m^3, 100 mmol, Alfa Inorganics). Due to the highly exothermic nature of the reaction, the ethylenediamine was added dropwise to avoid temperature excursions. Absolute ethanol (50×10^{-6} m^3) was added as a cosolvent to reduce the solubility of the complex and the solution was filtered. The solution was cooled in an ice bath for 1 h. The precipitate that developed was needle-shaped crystals having a violet color. The solution was filtered and the crystals dried under vacuum at room temperature. Single-crystal, X-ray diffraction of this sample confirms the structure, as shown in Figure 1a (Pajunen, 1967).

$[Cu(H_2Deta)(HDeta)]ClO_4$. The complex was prepared

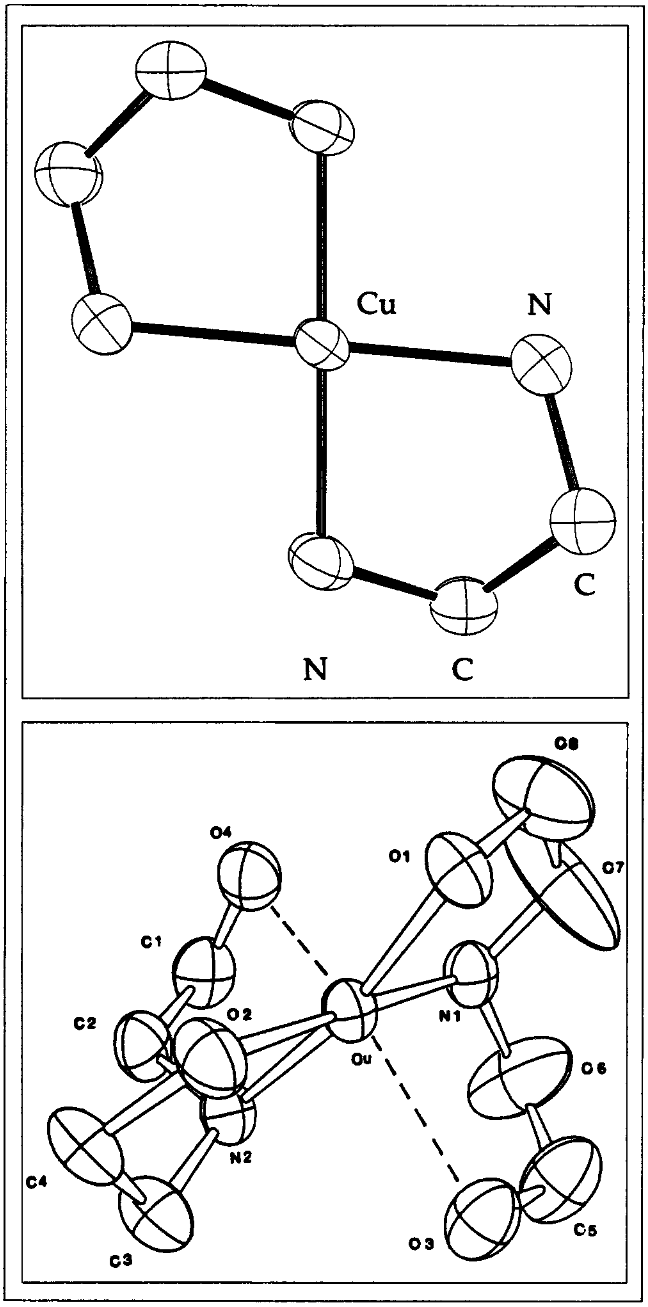

Figure 1. ORTEP for (a) copper ethylenediamine and (b) copper *bis*-(2,2′-dihydroxydiethylamine).
Hydrogen atoms have been omitted for clarity.

according to Bertrand (1986). Diethanolamine (2.1×10^{-3} kg, 20 mmol, Fisher Scientific Co.) was added to a solution of hydrated copper(II) perchlorate (1.9×10^{-3} kg, 5 mmol) in reagent-grade methanol (30×10^{-6} m^3, Fisher Scientific Co.). The deep blue solution was stirred for 0.5 h and filtered. The flask was left unstoppered in a fume hood for 18 h to allow the complex to precipitate from solution. Blue, rod-shaped crystals were separated by filtration, and these crystals were dried under vacuum at room temperature. The melting point of the crystals (413–415 K) compares well to the value obtained earlier for this complex (Bertrand, 1986). A representative sample of the crystals was selected for single crystal XRD. The unit cell dimensions of this sample were compared to previous X-ray data to confirm the crystal structure (Venable, 1990).

Preparation of supported catalysts

The catalysts were prepared by the batch adsorption method using Cab-O-Sil, M-5 grade (200 m^2/g, Kodak) as the support. Two procedures were used in preparing the supported metal complexes. The difference between the two procedures relates to the final washing of the materials with fresh solvent. In procedure I, the samples are not washed, whereas, the samples are washed in procedure II with fresh acetonitrile as many as three times before the solid is dried. Catalysts prepared by procedure I will be designated as such with a roman numeral I as the suffix; catalysts prepared by procedure II will show a designation ending with roman numeral II.

Varying amounts of the desired complex ($0.10\text{–}3.00\times10^{-3}$ kg) were dissolved in 150×10^{-6} m^3 of reagent-grade acetonitrile (Fisher Scientific Co.), and 3.00×10^{-3} kg of Cab-O-Sil was added to the solution with stirring at room temperature for 6 h. Samples prepared to have high loadings of the metal complexes were refluxed in the solvent for 2 h with constant stirring. The samples were vacuum-filtered and -dried under vacuum at room temperature.

Elemental analyses

Elemental analyses were performed for carbon, nitrogen, and hydrogen by Atlantic Microlabs, Inc. in Norcross, GA. Analysis for copper was performed by Applied Technical Services, Inc. in Marietta, GA using atomic absorption spectrophotometry.

Quantitative perchlorate analysis

Quantitative analysis for ClO_4^- ion on supported metal complex samples was performed according to the procedure of Geilmann and Voight (1965) as modified by Beckler (1986).

Gravimetric analysis of thermal decomposition

The thermal decomposition of the supported metal complexes was studied using the apparatus described earlier (Beckler, 1988; Kenvin, 1991a). Fresh samples were equilibrated for 0.5 h under dry nitrogen flowing at 25×10^{-6} m^3/min at 373 K. The temperature was programmed to 723 K at a constant rate of 5 K/min. The final sample weight was recorded at 373 K in flowing dry nitrogen. The weight loss derivative spectra were developed from the weight vs. temperature spectra using a fourth-order, backward-difference routine with corrective curve smoothing.

Mass spectrometry

The thermal decomposition of the supported metal complexes was carried out in a VG model 70 SE mass spectrometer system. The samples were dried for 10 min under vacuum at 373 K and equilibrated for 10 min under helium (UHP grade) flowing at 373 K. The sample temperature was heated to 723 K at a rate of 60 K/min. The sample off-gases were ionized by electron impact at 70 eV.

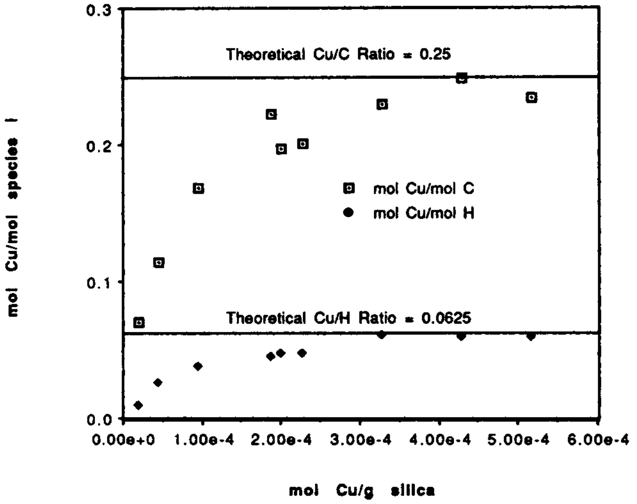

Figure 2. Elemental analysis of copper ethylenediamine perchlorate supported on silica.

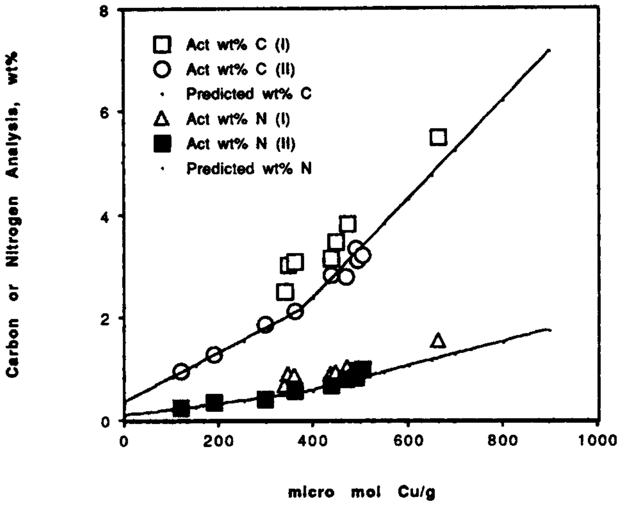

Figure 3. Elemental analysis of copper *bis*-(2,2′-dihydroxydiethylamine) perchlorate supported on silica.

Data on carbon analyses prepared by method I (□) and method II (○) are compared to the model (——). The nitrogen analyses prepared by method I (△) and method II (■) are compared to the predictions (——).

Quantitative UV-Vis analysis of filtrate

The wash filtrate solutions from the preparation of the metal complexes were collected for UV-Vis absorption analysis at 660 nm on a Milton Roy Spectronic 601. These UV-Vis absorbances were related to concentrations of the complex using a calibration developed from standard solutions of the complex at known concentrations. Quantitative values for metal uptake by the support were obtained by difference between the initial and final concentrations of the metal complex in the impregnating solution. These data were compared to the AA analysis of the supported catalysts.

Results

Elemental analyses: copper, carbon and hydrogen

The elemental analyses for the $Cu(en)_2(ClO_4)_2$ and $Cu(H_2Deta)(HDeta)ClO_4$ supported on silica are shown in Figures 2 and 3. The average ratios of copper to carbon and copper to hydrogen are 0.24 mol Cu/mol C and 0.06 mol Cu/mol H (Figure 2) for the higher loadings of $Cu(en)_2(ClO_4)_2$ complex on silica. These data agree well with the atomic ratios of Cu/C and Cu/H in the crystalline form of the unsupported complex: Cu/C = 0.25 and Cu/H = 0.0625. The supported $Cu(H_2Deta)(HDeta)ClO_4$ samples prepared by method I showed atomic ratios of Cu/C equaling 0.16 for loadings of complex >375 μmol complex/g silica (Figure 3). The ratios of Cu/C and Cu/N in the $Cu(H_2Deta)(HDeta)ClO_4$ supported samples which were prepared by method II were 0.239 and 1.09 mol Cu/mol, respectively, for loadings <375 μmol/g silica (Figure 3), whereas these ratios were 0.168 and 0.645, respectively, for loadings >375 μmol/g silica. The carbon to nitrogen ratios in these samples prepared by methods I and II were 4.10 and 3.94 mol C/mol N, respectively, which are close to the ratio of C/N in the Deta ligand (C/N = 4). Shown in the same figure is the model prediction of the elemental analysis. This model is described in the Discussion section.

Because of questions about the AA analysis for Cu, an alternate analysis method, based on visible absorption, was used. We examined the filtrate solutions from the samples containing the $[Cu(H_2\ Deta)(HDeta)]ClO_4$ complex as a means to confirm the Cu analyses in the sample. The UV-Vis absorption at 660 nm, as discussed by Harvey (1949), is appropriate for the quantitative analyses of solutions containing $[Cu(H_2Deta)(HDeta)]ClO_4$ complex. A calibration of this absorbance was constructed from standard solutions of the complex in acetonitrile (Figure 4). This plot shows the system obeys Beer's law for concentrations up to 73 milli-molar with an extinction coefficient of 58.9 ± 0.4.

The uptake of complex by the support is given by the difference between the amount of metal complex in the filtrate

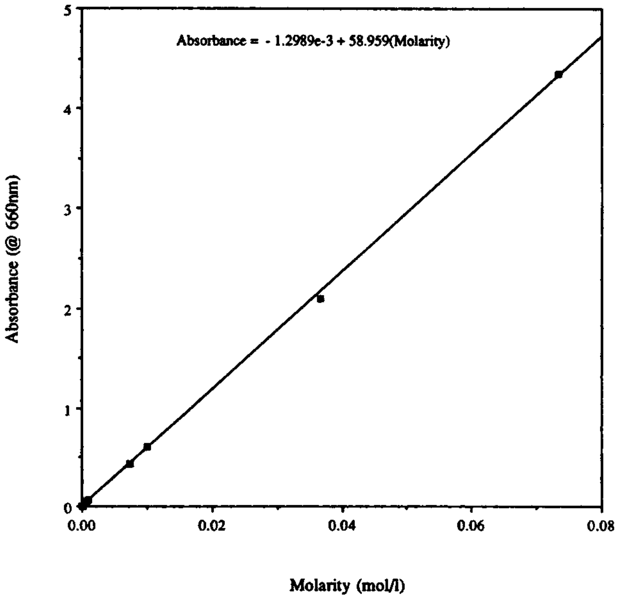

Figure 4. Calibration for UV-Vis absorbance of copper *bis*-(2,2′-dihydroxydiethylamine) perchlorate.

Table 1. Copper Metal Loadings for $Cu(H_2Deta)(HDeta)ClO_4$ Supported on Silica

Loading Obs. in AA	Loading Calc. from UV	% Error
0.77	0.69	10.4
1.23	1.28	3.8
1.99	2.00	0.5
2.43	2.46	1.1
2.74	2.98	8.1
3.40	3.30	2.8
2.95	3.40	13.2
3.13	3.18	1.4
3.50	3.45	1.4
Average % Difference = 4.7		

and the initial amount of metal complex in the impregnating solution. The observed copper loadings by AA and the calculated loadings by UV-Vis absorbance are shown in Table 1. The average percent difference in these samples is 4.7%. The close agreement between the elemental analyses of copper in the Cu(Deta) determined by AA and by UV-Vis of the supernatant liquid leads us to conclude that the analyses for copper ion is accurate.

Quantitative perchlorate analysis

These samples were analyzed for perchlorate content (Figure 5) using the technique reported previously (Beckler, 1986, 1987a; Geilmann, 1965). The samples prepared from $Cu(en)_2(ClO_4)_2$ showed no measurable perchlorate for copper analyses up to the equivalent of 76.1-μmol/g SiO_2. Statistical analysis of the data showed that the perchlorate content increased linearly with copper content for loadings greater than 76.1-μmol Cu/g SiO_2 with a slope of 2.16-mol perchlorate per mole of complex. The data are presented in Figure 5 together with data from an earlier study of three cationic complexes: $\{M^{3+}[(\mu\text{-}OH)Cu(\mu\text{-}OCH_2CH_2N(CH_2CH_3)_2]_6(ClO_4)_3M^{+3} = Al, Cr, \text{ or } Fr\}$ (Beckler, 1986). The perchlorate analyses of these complexes described a single curve of molarity perchlorate vs. molality of complex having a slope of 3.01-mol ClO_4/mol complex and an X intercept of 252-μmol complex/g SiO_2.

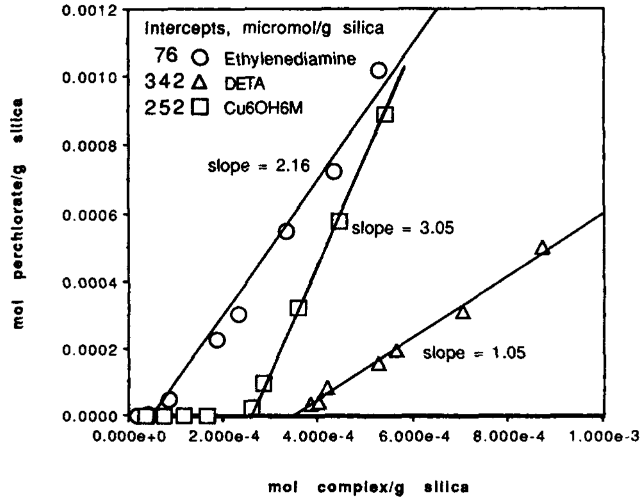

Figure 5. Perchlorate analyses of supported catalysts.

Shown here are the perchlorate analyses of the copper ethylene diamine perchlorate complex on silica (○); copper *bis*-2,2′-dihydroxydiethylamine) perchlorate on silica (△); and copper aminoalkoxide hexamer on silica (□).

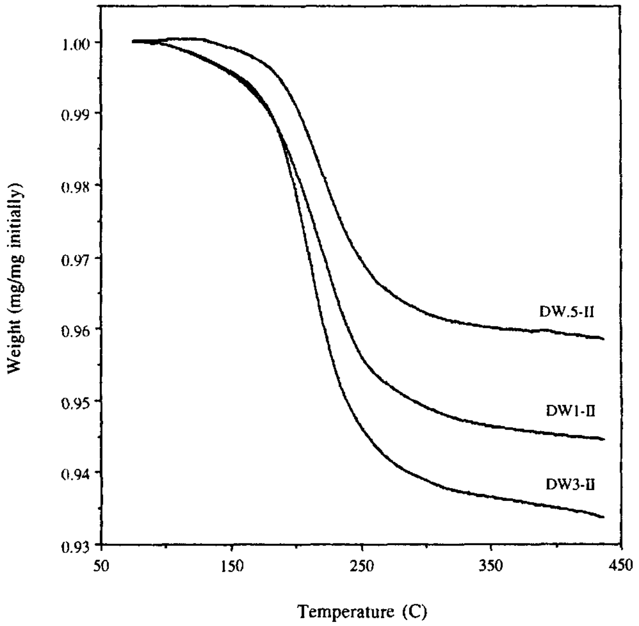

Figure 6. Thermal analysis of supported catalyts: weight vs. temperature.

Weight loss spectra of copper *bis*-2,2′-dihydroxydiethylamine) perchlorate on silica for samples washed in fresh acetonitrile having a copper loading of 1.23 wt. % (DW 0.50-II); 2.43 wt. % (DW 1.00-II), and 3.13 wt. % (DW 3.00-II).

The perchlorate analyses of the samples of supported $[Cu(H_2Deta)(HDeta)]ClO_4$ prepared by method I shows no measurable perchlorate for copper analyses up to the equivalent of 375-μmol Cu/g SiO_2; however, samples contained perchlorate for loadings >390-μmol Cu/g SiO_2. These data were fit to a simple correlation to yield the slope (1.05-mol ClO_4/mol Cu) and X-intercept (342-μmol complex/g SiO_2). Other samples containing $[Cu(H_2Deta)(HDeta)]ClO_4$ were prepared by method II and analyzed for perchlorate. These samples did not contain any perchlorate for copper loadings up to 489-μmol/g SiO_2.

Thermal decomposition of supported Cu(Deta) complexes

The supported Cu(Deta) complexes were decomposed by heating from 373 to 773 K at a constant rate of 10 K/min. The weight loss vs. temperature for three samples washed with acetonitrile (Figure 6) show only one region of weight loss beginning at 463 K and ending at 623 K; whereas, the weight loss spectra for two samples not washed with solvent (Figure 7) show two regions of rapid weight loss separated by a very small region of low weight loss between 423–623 K. The weight losses for these and additional samples are summarized in Table 2. Included in the same table are the weight losses predicted for these same samples assuming either one or two Deta ligands are lost from every Cu ion present in the sample (see Discussion). The samples designated as DW-x.x-I were not washed

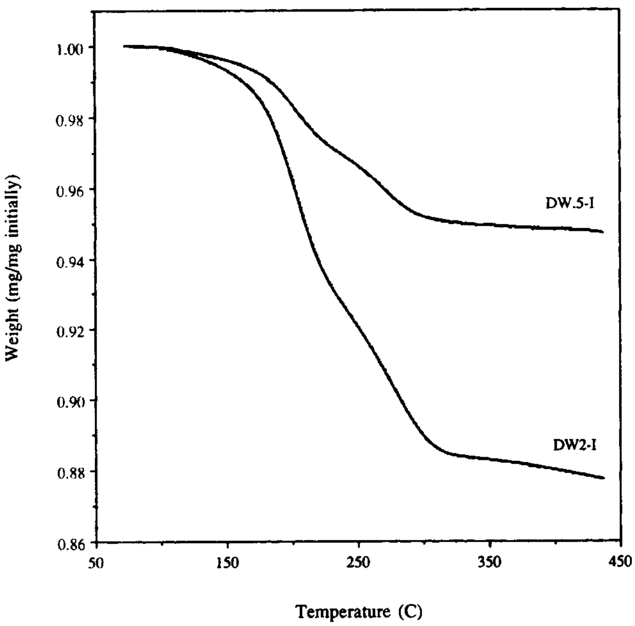

Figure 7. Thermal analysis of supported catalysts: weight vs. temperature.

Weight loss spectra of copper *bis*-2,2′-dihydroxydiethylamine) perchlorate on silica for samples not washed in fresh acetonitrile. The copper loadings are as follows: 2.28 wt. % (DW.5-I) and 3.89 wt. % (DW2-I).

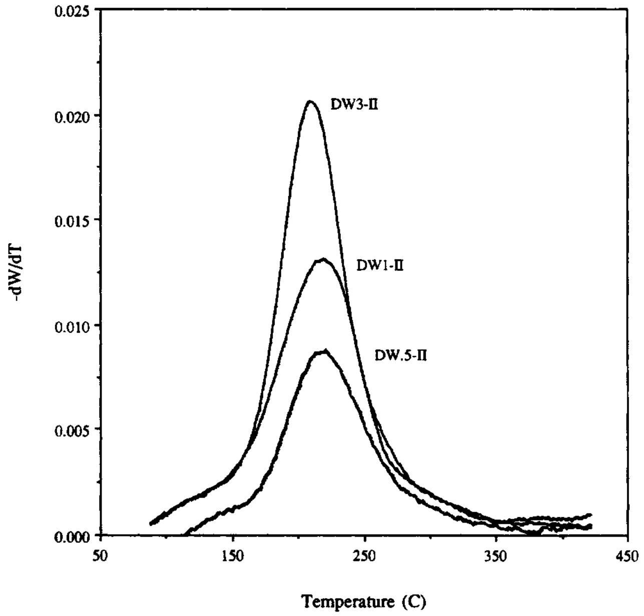

Figure 8. Thermal analysis of supported catalysts: derivative of weight vs. temperature.

Derivative of weight loss spectra of copper *bis*-2,2′-dihydroxydiethylamine) perchlorate on silica for samples washed in fresh acetonitrile. The copper weight loadings are 1.23 wt. % (DW0.50-II); 2.43 wt. % (DW1.00-II), and 3.13 wt. % (DW3.00-II).

with solvent (method I); whereas, the samples designated as DW-x.x-II were washed with acetonitrile (method II).

The thermal decomposition phenomena may be inferred by examining the derivative of these spectra (dW/dT) shown in Figures 8 and 9. The samples not washed in acetonitrile show two regions of weight loss centered at 513 and 593 K; whereas, the samples washed in acetonitrile show only one region of weight loss around 533 K. The volatiles leaving the unwashed at the lower temperature peak may be similar to those leaving the samples washed in acetonitrile. We appeal to analysis of the evolved gases by mass spectrometry to determine the chemical nature of the evolved gases.

Analysis of evolved gases by GC-MS

The mass spectra of the gases evolved during thermal decomposition of $[Cu(H_2Deta)(HDeta)]ClO_4$ supported on silica at near monolayer loadings were recorded for one sample of catalyst (DW-3.0-II) which shows only one peak at 533 K in the derivative spectrum of the weight loss. The sample was heated from 373–673 K and the evolved gases were sampled

Table 2. Weight Losses upon Thermal Decomposition

Sample*	Washed in Solvent	Obs. Wt. Loss, mg/mg Sample	Pred. Wt. Loss/Cu Loss of	
			1 Ligand	2 Ligands
DW-0.5-I	No	0.0526	0.0384	0.0768
DW-1.0-I	No	0.0662	0.0542	0.1084
DW-2.0-I	No	0.1220	0.0655	0.1310
DW-2.0-I	No	0.1279	0.0655	0.1310
DW-3.0-I	No	0.1406	0.0778	0.1556
DW-0.5-II	Yes	0.0239	0.0207	0.0414
DW-0.5-II	Yes	0.0256	0.0207	0.0414
DW-1.0-II	Yes	0.0398	0.0414	0.0828
DW-3.0-II	Yes	0.0553	0.0527	0.1057

*The samples designated as DW-x.x-I were not washed with solvent (method I), whereas the samples designated as DW-x.x-II were washed with acetonitrile (method II).

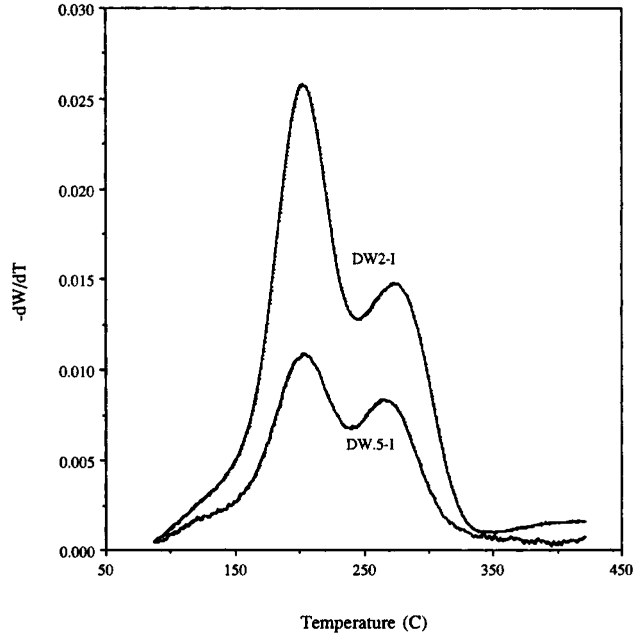

Figure 9. Thermal analysis of supported catalysts: derivative of weight vs. temperature.

Derivative of weight loss spectra of copper *bis*-2,2′-dihydroxydiethylamine) perchlorate on silica for samples not washed in fresh acetonitrile. The copper loadings are as follows: 2.28 wt. % (DW0.5-I) and 3.89 wt. % (DW2-I).

continuously. The mass spectrum of the gases evolved at 523-543 K shows major peaks at m/e = 42(100), 56(67), 74(23), and 86(42); the numbers in parenthesis are the relative size of the peaks. No peaks are present near that value of m/e expected for the molecular ion (105.1). The mass spectrum of gaseous diethanolamine shows major peaks at m/e = 42(56), 56(84), 74(100), and 86(10), where the numbers in the parenthesis are the relative abundance of each peak.

Discussion

The elemental analyses of the *bis*-copper ethylenediamine supported on silica suggested the stoichiometry of the supported complex is that of the precursor complex. Figure 2 shows the molar ratios of Cu/C and Cu/H in the supported samples. The ratios of Cu/C and Cu/H approach constant values of 0.24 and 0.06, respectively, at high copper loadings (>300-μmol Cu/g silica). The stoichiometry of *bis*-copper ethylenediamine $[Cu(C_2H_8N_2)_2]^{2+}$ suggests the elemental ratios Cu/C and Cu/H should be 0.25 and 0.0625. The observed data agree with the theoretical so we conclude that the stoichiometry of the supported *bis*-copper ethylenediamine is the same as that of the precursor complex.

The carbon and nitrogen analyses for the supported Cu(Deta) complexes prepared by methods I and II are shown in Figure 3. The slopes of the curves are used to estimate the molar ratios Cu/C and Cu/N. The data suggest a change in the Cu/C and Cu/N stoichiometry near a copper loading of 375 μmol/g silica. For copper loadings less than 375-μmol/g silica, the slopes correspond to Cu/C = 0.239 and Cu/N = 1.09 mol Cu/mol which reflects the stoichiometry of the samples prepared by method II. For copper loadings greater than 375-μmol/g silica, the data from samples prepared by methods I and II are averaged to give slopes of Cu/C = 0.167 and Cu/N = 0.645. Thus, the apparent stoichiometry in the samples changes from C/N/Cu = 4.2/0.92/1 at near loadings near 375-μmol/g silica to C/N/Cu = 12.2/3.1/2 for higher loadings. The C/N ratio of one diethanolamine ligand is 4/1 and the parent complex shows a C/N/Cu = 8/2/1.

One model to interpret the elemental analyses has the complex surrendering one Deta ligand as the stable diethanolamine molecule $[HN(C_2H_5OH)_2]$ upon contacting the surface of the silica during the ion exchange event. Thus, two surface protons would be necessary to accomplish both the ion exchange and the ligand exchange reactions. The supported metal complex without one Deta ligand would have a C/N/Cu = 4/1/1 which agrees with the observed ratios at loadings less than 375-μmol/g silica (Figure 3). This ratio of C/N/Cu would continue up to that loading for which the loss of the ligand occurred. Beyond that loading, the complex would mount the surface without the loss of a ligand. We show a comparison of actual carbon and nitrogen analyses and the predicted analyses using the model described above (Figure 3) for which the complex loses one ligand for loadings $\leq$375-μmol/g silica. The model also assumes that the solvent contributes to the observed carbon and nitrogen analyses by adding an intercept term to account for the amount of solvent retained by the support. These predictions agree well with the analyses of the samples prepared by method II; however, the samples prepared by method I show more carbon and nitrogen than that predicted by the model at each loading of copper. Thus, we conclude that crystallization of the complexes may occur in the second layer before all of the silica has been covered in the samples prepared by method I. This premature crystallization would result in the elemental analyses showing higher values than what is predicted by the model.

The two methods of preparing the Cu(Deta) catalysts differ in the use of fresh acetonitrile as a final wash in method II. We speculate that this wash is necessary to redisperse crystalline Cu(Deta) complex onto the bare silica when it is desired to prepare samples having high loadings of the complex on the support. Beckler (1987a) observed the necessity of this final wash in the preparation of the supported copper hexamers at loadings near the monolayer saturations.

The GC-MS data of the gases evolved during the thermolysis of the Cu(Deta) samples may be interpreted upon a comparison with the mass spectrum of the neutral molecule diethanolamine. If the diethanolamine ligand of the Cu(Deta) complex reacts with a surface proton, we expect that diethanolamine would be present in the gases evolved from the solid upon heating. The GC-MS of the gases evolved from the Cu(Deta) sample shows peaks at m/e = 42, 56, 74, and 86 in the proportions of 1/0.67/0.23/0.42; whereas, the spectrum of diethanolamine shows peaks at 42, 56, 74, and 86 in the proportions of 0.56/0.84/1.0/0.10. The agreement between the m/e peaks appearing in the standard and the catalyst confirms that diethanolamine is released during thermolysis of the catalysts; however, the apparent disagreement between the mass spectra peak ratios/intensities between the catalyst sample and the standard is a result of the difference between the method of sample introduction to the GC/MS. The pure diethanolamine standard was introduced into the ionization source using a batch inlet which permitted a slow leak of sample in the device. The Cu(Deta) sample was volatilized in a reaction tube and the evolved gases separated by GC before introduction into the ionization source of the MS. Thus, the Deta ligand was decomposed by both thermolysis and ionization from the solid sample; whereas, the diethanolamine standard was subjected to ionization, only. We reported other systems for which the evolved gas analyses data confirmed the loss of ligands during thermolysis {$Cu(acac)_2$ (Kenvin, 1991a) and $M^{3+}[(\mu\text{-}OH)Cu(\mu\text{-}OCH_2CH_2N(CH_2CH_3)_2]_6(ClO_4)_3$ (Beckler, 1988c)}.

We believe the evolved gas analyses confirm that the diethanolamine ligand is removed during the thermolysis at temperatures >523 K. This fact is necessary to interpret the data of the thermal decomposition of the supported Cu(Deta) samples prepared by methods I and II. The observed weight losses from the samples prepared by method II are predicted well by assuming that only one ligand was volatilized per Cu ion in the sample; whereas, the unwashed samples show weight losses intermediate to that predicted by the loss of one to two ligands per Cu ion. The weight loadings of Cu in these samples prepared by method I are 200-500-μmol/g silica; whereas, the samples prepared by method II show molalities of less than 400-μmol/g silica. These loadings suggest that the samples prepared by method I will have complexes containing one and two ligands per complex; whereas, the samples prepared by method II show 1 ligand per complex. These results support the assumptions of the model used to predict the C and N analyses of the Cu(Deta) samples.

The perchlorate analysis is a sensitive indicator of multiple layer formation in catalysts prepared from perchlorate salts of metal complexes (Beckler, 1986). Samples having all the metal complexes ion exchanged for surface protons show no perchlorate. The metal loading at the onset of the appearance of perchlorate characterizes the formation of multilayers of the complex. In the present case, we fit the data of perchlorate analyses to the copper metal analyses to develop Figure 5. The data should show a linear relationship between perchlorate content and moles of complex in excess of the monolayer loading; the slope of this curve should be equal to the perchlorate/complex stoichiometry in the unsupported metal complex. The X intercept corresponds to the complex loading for the onset of multilayer formation. The fitted data show intercepts of 76-μmol complex/g SiO_2 for the copper ethylenediamine complex. These data may be compared to a predicted loading at monolayer completion from a simple model. The model assumes a close-packed arrangement of the complex, and uses the dimensions of the complex and the specific surface area of the support to predict the loading in a monolayer. The copper ethylenediamine shows a projected area of 52.9 Å^2 calculated from the dimensions of the complex in the single crystal. The model predicts a monolayer loading of 628 μmol of complex/g SiO_2. This comparison of predicted to observed loading at multilayer formation is used to evaluate the affinity of the complex for the support. If the onset of multilayer formation occurs at a value much lower than that predicted from the model, then we conclude that the affinity of the complex for the surface is low. However, if the observed onset of multilayer formation agrees with the predictions, we conclude that the complex shows a high affinity for the surface. Thus, we conclude that the copper ethylenediamine shows a very low affinity for the silica.

One model for the arrangement of a "complete" Cu(Deta) complex (a complex which has not surrendered any of its ligands) on the surface demands six-unit cells of α quartz (100) per complex. We have used the α quartz (100) plane to model the surface of SiO_2 in earlier work (Kenvin, 1991b). This plane shows silanol surface population densities (OH/nm^2) not much different from the silanol densities on the other low index planes of α quartz such as (001), (110), and (111) (Kenvin, 1991a). This SiO_2 is synthesized by the thermolysis of a silicon metal complex at high temperatures in a flame. It appears appropriate to model the structure of this X-ray amorphous material with a high-temperature phase of SiO_2 such as α quartz. The projected area of these (100) unit cells is 90 Å^2 (12×7.5 Å^2) so that the predicted number of complexes in this monolayer is 366-μmol/g SiO_2. The observed loading for multilayer formation in samples prepared by method I is 342 μmol complex/g SiO_2; almost 92% of the predicted saturation loading. Recall from the earlier discussions that these samples appear to have a C/N/Cu stoichiometry which suggests that the complexes lost ligands upon contacting the surface. Thus, a simple model assuming all the complexes cover the same amount of surface area may not be appropriate.

The elemental analyses data of samples prepared by method II were predicted well by a model. (Figure 3) which requires the loss of one ligand of Cu(Deta) per complex up to a loading of 375-μmol/g SiO_2. These results taken together with the data of the perchlorate analyses of the Cu(Deta) sample prepared by method II suggests that the observed completion of the monolayer may be as high as 489 μmol/g SiO_2. Accordingly, the actual arrangement of the Cu(Deta) complexes on the surface of these samples cannot be predicted from the model of Cu(Deta) which requires six-unit cells of α quartz (100) per complex. Thus, we suggest that the monolayer of these complexes shows a fraction of the surface covered by complexes having only one ligand (375/489 = 0.77) and the remainder of the surface (0.23) covered by the cationic complex having both ligands.

The projected surface area of the complex with only one ligand may be estimated by assuming a configuration of the complex as mounted on the silica. Molecular modeling of this complex with one ligand suggests that many configurations are possible with the assumption that the Cu^{2+} ion is bonded to either one or two siloxide groups so as to balance the charge of the complex. Two arrangements of the complex describe the extremums in projected surface area. One arrangement of this complex shows the plane formed by the O-Cu-O bonds perpendicular to the surface. In this arrangement, one part of the Deta ligand shows a plane containing H-N-CH_2-CH_2-OH in a position directly over the Cu^{2+} ion and perpendicular to the surface; whereas the other part of the ligand has the plane containing H-N-CH_2-CH_2-OH nearly parallel to the surface of the silica. This configuration, designated as I, shows a projected area on 56.26 Å^2. The second configuration, II, shows the two parts of the Deta ligand oriented so that the parts of the ligand are equidistant from the surface of the silica. In this configuration, the plane describing the O-Cu-O bonds is tilted at an angle to the surface of the silica. The projected surface area for configuration II is 66.30 Å^2. Thus, we may predict the μmol of complexes in a monolayer per g of SiO_2 by dividing the support surface area (200 m^2/g) by the weighted-average, projected area per complex. This weighted-average projected surface area is estimated from product of the fraction of complexes having one ligand (0.77) and the projected area (either 56.26 or 66.30 Å^2/complex for configurations I or II, respectively) added to the product of the fraction of complexes having two ligands (0.23) and the area of the complex (90 Å^2/complex). These estimates show completion of a monolayer at a loading of 463–518-μmol/g SiO_2, for configurations II and I, respectively. The observed completion of a monolayer by method II is 489 μmol/g SiO_2, which suggests that the actual arrangement of the complexes on the support may be explained by a configuration which is intermediate to the two we discussed here.

With each of these models, the affinity of the Cu(Deta) complex is stronger than the *bis*-ethylenediamine copper salt. The essential structural differences between the (en) and Deta complexes are 1) the Deta complex shows hydrogen-bonding ligands; whereas, the (en) complex does not, and 2) the Deta ligands are sufficiently labile to participate in ligand exchange; whereas, the (en) ligands are inactive towards these exchange reactions.

These results may be compared to those reported earlier (Beckler, 1986) for another perchlorate salt: $M^{3+}[(\mu\text{-OH})Cu(\mu\text{-OCH}_2CH_2N(CH_2CH_3)_2]_6(ClO_4)_3$. The fitted equation shows a slope of 3.04-mol ClO_4/mol complex and an X intercept of 252-μmol complex/g silica. These observations are compared to a model prediction for the completion of a monolayer using the projected area of the complex equaling 132.8 Å^2. This projected area is derived from the dimensions of the complex obtained from single crystal data (Bertrand, 1986). This area results in a monolayer film having 250-μmol complex/g SiO_2.

The agreement between predicted and observed saturation loading suggests that these perchlorate salts show a strong affinity for the support.

The results of an earlier study using neutral metal acetylacetonates [$M^{n+}(acac)_n$] suggested that monolayer coverages of copper $(acac)_2$ could be achieved as a result of hydrogen bonding interactions between the (acac) ligands of the complex and the support (Kenvin, 1991a,b). The acetylacetonate ligands showed an affinity for the surface protons which allowed an easy confirmation of monolayer coverage (Kenvin, 1991b). This system showed the completion of a monolayer at the value calculated from a simple geometric model (553-μmol/g SiO_2) which compares well to the observed completion of a monolayer at 579-μmol/g SiO_2. These data are reported in Table 3 for loading at completion of a monolayer.

The results of this work and those reported earlier (Kenvin, 1991a,b) may be taken together to construct a model which relates the structure and chemistry of the metal complex and its affinity for a surface such as silica. The factors affecting the interaction between the complex and the surface are as follows: shape, charge, stability, and functional groups on the complex. Each factor will be discussed separately in the following paragraphs.

The shape of the complex influences the orientation of the complex with respect to the surface of a nonporous support. Consider the work of Kenvin (1991b) who prepared samples of supported, neutral, metal acetylacetonates on silica. The stable, trivalent $Cr(acac)_3$ shows a spherical shape described by the three acetylacetonate ligands; whereas, the equally stable, $Cu(II)(acac)_2$ shows a planar shape described by the two acetylacetonate ligands. The $Cr(III)(acac)_3$ complex did not show any affinity for the surface; whereas $Cu(II)(acac)_2$ was attracted to the surface. This study emphasized the importance of the orientation of the (acac) ligands with respect to the surface silanol groups. The $Cr(III)(acac)_3$ having the octahedral arrangement of the ligands would not permit the silanols to hydrogen bond to the (acac) ligands; whereas, the planar $Cu(acac)_2$ permitted easy access of silanols into the (acac) groups. However, the shape of the complex is not a sufficient condition to ensure a strong interaction with the surface as Kenvin demonstrated for two other divalent metal acetylacetonates (Pd^{+2} and Pt^{+2}) which would not adhere to the silica (Kenvin, 1991b). These results were explained by a model in which the specific interaction between the metal ion and the surface dominated the process (Kenvin, 1991b). In a separate study, Beckler (1986) reports the steric hindrance effects of bulky substituent groups on a cationic complex. The *n*-butyl groups of the complex prevent a close association of the complex with the surface such that ion exchange does not occur; whereas, the ion exchange readily occurs with a complex having smaller ethyl groups (Beckler, 1986).

The charge on the complex apparently has a secondary effect on the affinity of the complex with the surface compared to the effects of stability of the complex relative to ligand exchange reactions and compared to the functional groups present in the complex. Both cationic and neutral metal complexes form monolayers on the surface of silica when the complexes show functional groups such as OH which interact with SiO^- (Beckler, 1986) or O which hydrogen bond to SiOH (Kenvin, 1991b). In the present work, the charge on the complex was not sufficient to ensure a strong interaction with the surface as the cationic $Cu(en)_2^{2+}$ would not ion exchange with the surface. The hexameric cationic complex reported in (Beckler, 1986) readily ion exchanges with the surface as a result of the hydrogen-bonding groups present in the complex. Thus, the charge of the complex plays a secondary role to that of the functional groups in anchoring the complexes to the surface of silica.

Table 3. Summary of Monolayer Loadings

Metal Complex	Hydrogen Bonding Ligands?	Monolayer Loading (μmol/g silica)	
		Predicted	Observed
$Cu(en)_2ClO_4$	No	628	76
$Cu(acac)_2$	Yes	553	579
$Cu(H(Deta)_2)ClO_4$	Yes	366	342 Method I
		463–518	489 Method II
$M^{3+}\{\mu\text{-OH-Cu}^{2+}\text{-Ae})\}_6ClO_4$	Yes	250	252

The ability of the complex to surrender ligands also shows an effect on the affinity of the complex to the surface. Kenvin (1991b) reports on the affinity of $Fe(III)(acac)_3$ and $Mn(III)(acac)_3$ for the silica surface as a result of the ligand loss. These complexes are known to have low stabilities relative to the copper and chromium complexes which do not surrender the ligands upon contacting the surface (Rollison, 1963; Kemmet, 1973). In the present case, the very stable $Cu(en)_2^{2+}$ ion will not permit the ligands to leave; whereas, the Deta ligand readily leaves the Cu(Deta) complex to facilitate bonding to the surface and the complex also participates in ion exchange. The loss of the ligand affords the possibility of forming a direct bond between the metal of the complex and the surface siloxide. The anionic ligand present in the complexes (HDeta and acac) all require a proton to become the stable molecule (diethanolamine and pentanedione). Thus, protons from the surface silanols are activated during the impregnation to form the stable molecules from the ligands which are surrendered from the parent complex when the stability of the complex permits this ligand exchange.

Conclusions

Metal complexes have been used to discover factors important to the process of supporting metal ions on ceramic surfaces. The use of metal complexes permit a systematic study in which the structure of the complex may be changed to evaluate its importance to the affinity to the ceramic surface. Nonaqueous solvents allow the solvation of the complexes in a medium which does not compete with the complex for surface sites and does not affect rearrangement of the structure by solvolysis. This model approach allows us to draw conclusions regarding the factors important to the interaction between metal complexes and the support. By analogy, we hope this understanding may be exploited to design new catalysts having greater control on the surface morphology.

The results of this and prior studies lead us to conclude that the stability of the complex to ligand exchange reactions and the presence of nucleophilic groups in the complex have the greatest effect on the affinity of the complex for the surface. The ligand exchange reaction permits the access of a surface oxygen directly into the coordination sphere of the metal ion to form a strong metal oxide bond. The nucleophilic groups assist the complex in acquiring the surface perhaps as a result of hydrogen-bonding between the complex and the surface. The effects of shape and charge of the complex play a secondary role in determining the affinity of the complex for the surface. Overall, the affinity of the metal complex to the surface is important to the morphology of the metal ion on the surface and the resulting stability of the species on the surface. Metal ions which can form strong interactions to the surface result in high dispersions of the metal ions which resist sintering under high temperature operation. High dispersion of the metal ion is desired when the catalyst designer wishes to expose every metal ion to the reaction atmospheres. Stability of this high dispersion against prolonged heating leads to long catalyst life.

In a more general sense, the fundamentals which lead to formation of monolayer films of the precursor allow the engineer to design catalytic ensembles in the form of a discrete molecule which may be applied to the surface of a ceramic oxide having the desirable physical properties. These ensembles may be catalytically active in the pristine state and if so, the task of creating a uniform surface of these replicates becomes possible. If the ensembles are not active in the pristine state, then the ligands may be removed by controlled heating to produce a dispersion of the metal ion ensembles which resist sintering under normal reaction conditions. We speculate that the separation of the ensembles on the surface in the pristine state inhibits the migration of the metal ions during heating. As such, the procedure we have discussed here may be a viable means of producing a robust and uniform dispersion of supported metal ions.

Acknowledgment

The authors acknowledge the Georgia Institute of Technology for partial support of this research under the auspices of the Focused Research Program in Surface Science and Catalysis.

Literature Cited

Atlas of Spectral Data and Physical Constants for Organic Compounds, CRC Press, J. G. Grasselli, ed., B-139.

Babb, K. B., and M. G. White, "Polynuclear Metal Complexes as Model Mixed Oxide Catalysts," *J. Catal.*, **98**, 343 (1986).

Basset, J. M., B. C. Gates, J. P. Candy, A. Choplin, M. Leconte, F. Quignard, and C. Santini, "Surface Organometallic Chemistry, Molecular Approaches to Surface Catalysis," Kluwer Academic Publishers, Dordrecht, The Netherlands (1988).

Beckler, R. K., and M. G. White, "Polynuclear Metal Complexes as Model Mixed Oxide Catalysts: Characterization," *J. Catal.*, **102**, 252 (1986).

Beckler, R. K., "Polynuclear Metal Complexes as Model Mixed Oxide Catalysts," PhD Thesis, Georgia Institute of Technology, Atlanta (1987a).

Beckler, R. K., and M. G. White, "Effects of Adsorbate Coverage on the Infrared Spectrum of Chemisorbed NH_3," *Langmuir*, **3**, 1074 (1987b).

Beckler, R. K., and M. G. White, "Polynuclear Metal Complexes as Model Mixed Oxide Catalysts: Selective Chemisorption of NH_3 and NO," *J. Catal.*, **109**, 25 (1988a).

Beckler, R. K., and M. G. White, "Polynuclear Metal Complexes as Model Mixed Oxide Catalysts: Isomerization Activity," *J. Catal.*, **110**, 364 (1988b).

Beckler, R. K., and M. G. White, "Preparation and Characterization of Supported Mixed Metal Oxides: Thermal Decomposition of Heteropoly Metal Complexes Immobilized on Silica," *J. Catal.*, **112**, 157 (1988c).

Bertrand, J. A., private communication (1986).

Brenner, A., D. A. Hucul, and S. Hardwick, "The Remarkable Decarbonylation of Chromium, Molybdenum, and Tungsten Hexacarbonyls Supported on Silica and the Nature of these Materials as Heterogeneous Catalysts," *Inorg. Chem.*, **18**, 1478 (1979).

Commereuc, D., Y. Chauvin, F. Hugues, J. M. Basset, and D. Olivier, "Catalytic Synthesis of Low Molecular Weight Olefins from CO and H_2 with $Fe(CO)_5$, $Fe_3(CO)_{12}$, and $HFe_3(CO)_{11}$-Supported on Inorganic Oxides," *J. Chem. Soc. Chem. Commun.*, 154 (1980).

Deeba, M., J. P. Scott, R. Barth, and B. C. Gates, "CO Hydrogenation Catalyzed by Magnesia-Supported Osmium Derived from $Os_3(CO)_{12}$," *J. Catal.*, **71**, 373 (1981).

Geilmann, W., and A. Voight, *Z. Anorg. Chem.*, **193**, 311 (1930); L. Erdey, "Gravimetric Analysis," Part III, Vol. 7, p. 15, Pergamon Press, London (1965).

Harvey, J. L., C. I. Tewksbury, and H. M. Haendler, "Copper(II) and Nickel(II) Complex Ions of Hydroxyethylethylenediamine," *J. Amer. Chem. Soc.*, **71**, 3641 (1949).

Kemmet, R. D. W., "Manganese," in *Comprehensive Coordination Chemistry*, Pergamon Press, Austria, p. 872 (1973).

Kenvin, J. C., and M. G. White, "Preparation and Characterization of Supported Mononuclear Metal Complexes as Model Complexes," ACS Meeting, Miami Beach (Sept. 10-15, 1989).

Kenvin, J. C., M. G. White, and M. B. Mitchell, "Hydrogen Bonding of Mononuclear Metal Complexes to Cab-O-Sil," ACS Meeting, Washington, DC (Aug. 26-31, 1990a).

Kenvin, J. C., and M. G. White, "Mononuclear Metal Complexes Supported on Cab-O-Sil: A Study by Infrared Spectroscopy and Thermogravimetry," ACS Meeting, Washington, DC (Aug. 26-31, 1990b).

Kenvin, J. C., M. G. White, and M. B. Mitchell, "Preparation and Characterization of Mononuclear Metal Complexes as Model Catalysts," *Lang.*, **7**, 1198 (1991a).

Kenvin, J. C., and M. G. White, "Selective Chemisorption and Oxidation Reduction Kinetics of Supported CuO Prepared from Copper Acetylacetonates on Cab-O-Sil," *J. Catal.*, **130**, 447 (1991b).

Lamb, H. H., and B. C. Gates, "Molecular Organosmium Chemistry and Catalysis on the Basic Magnesium Oxide Surface," *J. Amer. Chem. Soc.*, **108**, 81 (1986).

Psaro, R., and R. Ugo, *Metal Clusters in Catalysis*, Elsevier, Amsterdam, p. 427 (1986).

Rollison, C. L., "Chromium, Molybdenum, & Tungsten," *Comprehensive Coordination Chemistry*, Pergamon Press, New York, p. 390 (1987).

van Hengstum, A. J., J. G. van Ommen, H. Bosch, and P. J. Gellings, "Preparation of Supported Vanadium & Molybdenum Oxide Catalysts Using Metal Acetylacetonate Complexes," *Appl. Catal.*, **5**, 207 (1983).

Venable, M. H., "Synthesis, Structures, and Support Interactions of Potential Metal Oxide Catalyst Precursors," M.S. Thesis, Georgia Institute of Technology (1990).

Yermakov, Yu. I., B. N. Kuznetsov, and V. A. Zakharov, *Catalysis by Supported Complexes*, Elsevier, Amsterdam (1981).

Manuscript received Oct. 14, 1992, and revision received Apr. 13, 1993.