A copper/silica catalyst prepared from a monolayer film of copper 2,2'-bipyridine dimer on Cab-O-Sil [1]

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Abstract

A dinuclear copper complex was supported as a monolayer film on Cab-O-Sil (2.27 wt% Cu) as a model for Cu/silica. The supported and unsupported metal complexes were characterized by elemental analyses, EPR, SQUID, DRIFTS, and mass spectrometry (EI and FAB) techniques. The magnetic properties and infrared vibrational spectra were altered when the complex interacted strongly with the support by an ion exchange mechanism. The samples were subsequently decomposed by heating in oxygen to produce a highly dispersed supported CuO/silica. This sample was reduced in H_2 and the catalyst was exposed to NO and N_2O under controlled conditions in separate experiments. The results of these characterizations are discussed in the framework of the theories of catalytic ensembles.

Keywords: Copper; NO decomposition; Polynuclear copper complex; Silica; SQUID; Supported catalysts

1. Introduction

Our previous work illustrated how metal complexes may be attached as thin films to oxide supports such as silica and alumina [1]. This technology has been used by others to create well-dispersed metal oxides on supports starting with precursors such as the metal acetylacetonates of Fe^{3+}, MoO_2^{2+} and VO^{2+} [2–4]. We have developed well-dispersed metal catalysts on silica and alumina from thin films of the acetylacetonates of Fe^{3+}, Mg^{2+}, Cu^{2+}, Co^{2+}, and Mn^{3+} [5–12]. The

copper-containing catalysts prepared on silica deserve special attention in that the selectivities of several probe reactions were very sensitive to the dispersion of the copper [5,8–10]. Well-dispersed catalysts (>90%) which were prepared from thermolysis of a monolayer film of $Cu(acac)_2$/silica showed high selectivity for the simple hydrogenation of acetaldehyde to ethanol (>95%); whereas, poorly-dispersed catalysts (<30%) created from the thermolysis of multiple layers of $Cu(acac)_2$ showed a selectivity of 45% to the simple hydrogenation product (ethanol) and 45% to the product ethyl acetate [5].

This technique of catalyst synthesis may be applied to develop supported metal catalysts hav-

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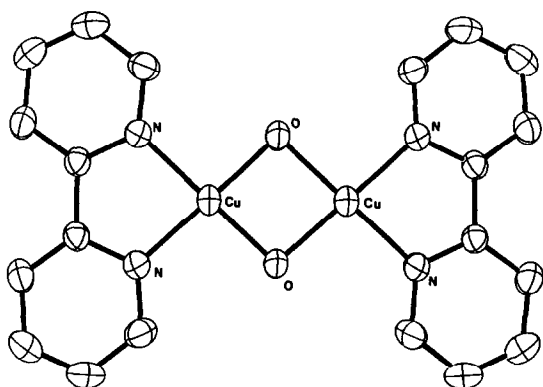[1] Focused Research Program in Surface Science and Catalysis

ORTEP Drawing of [Cu(bipy)(OH)]$_2$ $^{2+}$

Fig. 1. ORTEP diagram of copper 2,2-bipyridine dimer. Hydrogen atoms have been omitted for clarity.

ing controlled ensemble sizes. In the present work, we synthesized and characterized a supported copper catalyst which was developed by decomposing a monolayer film of $[Cu(OH)bipy]_2^{2+}$ cation on silica (Figure 1). The properties of this catalyst were compared to those of other supported copper catalysts reported in the literature.

2. Experimental apparatus and procedures

Preparation of $[Cu(OH)bipy]_2(ClO_4)_2$. The method used to prepare this compound was similar to that reported by McWhinnie [13,14]. A 3.12 g (0.0200 mol) portion of 2,2'-bipyridine (Aldrich) dissolved in 50 mL methanol was warmed and added to a boiling methanol solution containing 7.65 g (0.0200 mol) $Cu(ClO_4)_2 \cdot nH_2O$ (16.6% Cu, Alfa). Potassium hydroxide hydrate (ca. 12.5% H_2O) (1.29 g, 0.020 mol) in boiling methanol was filtered and added to the turquoise copper–bipyridine solution. A bluish-purple solid, mixed with a white solid, was formed, and the white solid, $KClO_4$, was removed by washing first with water during filtration. The blue solid was then washed with ethanol, then ether, and finally dried under vacuum. The structure (Fig. 1) was determined from data of single crystal X-ray diffraction [15].

2.1. Chemicals

Cab-O-Sil (M-5 grade; surface area = 200 m^2/ g silica) was purchased from Cabot Corporation. Acetonitrile, obtained from Fisher, was used without further purification. The gases were (1) extra-dry nitrogen (Holox), (2) oxygen (Holox), (3) 25 vol.% hydrogen (balance helium), (4) mixtures of NO/N$_2$ (1.09 and 0.94 vol.% nitric oxide, Matheson), and (5) nitrous oxide (UHP, Matheson). Each gas was passed through a molecular sieve, replaceable, gas purifier cartridge (Type 452), held in a Type 450 gas purifier (Matheson).

Elemental analyses. The catalyst samples were analyzed for carbon, nitrogen, and hydrogen content by Atlantic Microlab, Inc. (Norcross, GA) and for metal content by Applied Technical Services, Inc (Marietta, GA).

Catalysts preparation. The catalyst was prepared by adding the copper complex, either as a solid or in acetonitrile solution, to a slurry of 3.00 g silica in 150 ml acetonitrile. Triethylamine (Et$_3$N) was added to the slurry to facilitate the ion exchange of cationic complexes onto the surface. Normally, a ratio of 1–2 mol Et$_3$N/mol Cu was used. The slurry was stirred for several hours, filtered and the solid was washed with acetonitrile until the wash solution was colorless. The acetonitrile washing suppresses formation of polycrystalline copper complex. The washed filter cake was dried at ca. 20 Torr and 54°C to avoid decomposition of the complex.

XRD. The powder XRD was collected on a Siemens D5000 instrument using Cu–K$_\alpha$ radiation having a wavelength of 1.5406 Å. Powdered samples of the Cab-O-Sil and the copper catalyst (2.27 wt% Cu) were prepared for analysis.

FT-IR. Characterization of samples without thermal decomposition or gas adsorption was done using a Nicolet 520 FTIR spectrometer with a TGS detector. Samples mixed with KBr (Spectra-Tech) were placed in a stainless steel sample holder with a cavity 3 mm in diameter and 2 mm in depth. The sample holder was mounted on a Spectra-Tech diffuse reflectance attachment

equipped with a blocker device to minimize specular reflectance. Thermal decomposition of the supported metal complex and NO adsorption experiments were completed on a Nicolet 5DXB FTIR spectrometer with a liquid nitrogen-cooled, mercury–cadmium-telluride (MCT) detector. The reflectance accessory accommodated a water-cooled, controlled-atmosphere cell (Harrick Scientific), having a sample cavity about 6 mm in diameter and 4 mm deep. Pinholes in the side of the cavity allow gas to flow through the sample bed, which consists of KBr powder (65 microns mesh size) topped with a thin layer of the sample. A stainless steel dome with KBr windows seals the cell and allows the infrared beam to strike the sample. Careful manipulation of the mirrors on the reflectance accessory allows maximum signal throughput to obtain good spectra. The background signal was taken with KBr. All spectra were taken at 4 cm^{-1} resolution and corrected for water and carbon dioxide in the instrument chamber, using OMNIC, a PC-based, software package from Nicolet, running under Microsoft® Windows. The NO adsorption spectra were developed by subtracting the room-temperature spectrum of the decomposed and subsequently reduced supported sample (prior to exposure) from the spectra of samples exposed to NO.

SQUID. The magnetic properties of the supported copper complex were determined with a Quantum Design Model MPMS SQUID magnetometer. SQUID is an acronym for *S*uperconducting *Qu*antum *I*nterference *D*evice. The procedure was as follows: (1) determine the magnetic moment while warming the sample from 5 to 280 K in a field of 1 T (tesla), (2) cool back to 5 K in a field of 4 T, and (3) reduce the field from 4 T to zero at 5 K. The time was about 30 s for each individual moment determination. A correction was made for the diamagnetic plastic sample container.

Electron paramagnetic resonance. All EPR spectra were measured with a Varian E-Line Century Series Model E-109ES spectrometer equipped with a 9 in. magnet and a Model E-100A microwave bridge. The cavity was tuned for the

resonance condition at a frequency in the X band (8.950 GHz for the unsupported sample and 9.033 GHz for the supported sample). Two samples were examined having nearly the same amount of copper; one was supported complex (2.27 wt% Cu) and the other was unsupported complex. The samples were weighed to give a copper content of 1.323 mg in the unsupported sample and 1.316 mg in the supported sample. The samples were placed in a quartz EPR tube along with a few crystals of DPPH (2,2-diphenyl-1-picrylhydrazyl hydrate, free radical, 95%, Aldrich) in a sealed capillary tube, placed inside the EPR tube. The pen was centered on the recorder and the field set adjusted to center the DPPH signal on the oscilloscope. The 2 h scans were performed at room temperature. The instrumental parameters were as follows: scan range = ± 1000 gauss (G), modulation amplitude = 10 G, receiver gain = 800, modulation frequency = 100 kHz. The field set at the midpoint of the chart was 3009.2 G for the unsupported sample, and 3051.0 G for the supported sample. To compare intensities, the receiver gain was kept constant for both samples.

Thermogravimetric analysis. Thermogravimetric analysis of the supported catalyst (2.27 wt% Cu) was performed on a Perkin Elmer TGS-2
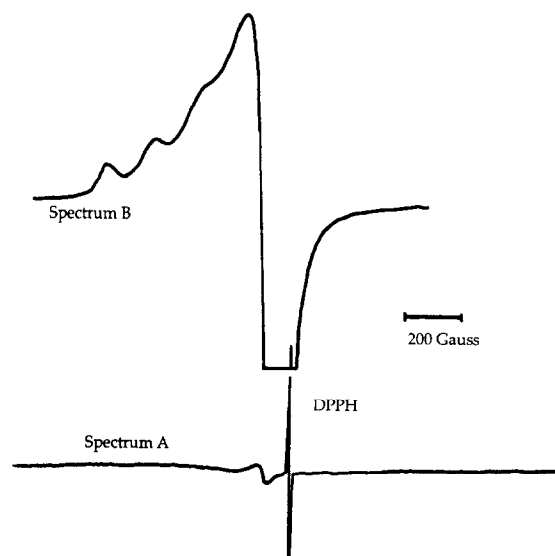

Fig. 2. Electron paramagnetic resonance spectra of copper 2,2′-bipyridine dimer. (a) Spectrum of unsupported metal complex. (b) Spectrum of metal complex supported on Cab-O-Sil.

thermogravimetric system. Flow rates of all gases were controlled with a Matheson multiple flow controller Model 8249, using Model 8141 transducers at a pressure of 18 psig. We monitored the time, temperature, weight and weight change with respect to time (dw/dt); these data were acquired on a computer with an 80286 processor and 640 KB memory.

Before the experiment was started, the catalyst sample was dried in the sample holder under a nitrogen flow at 125–135°C. It was found that samples weighing 4–8 mg gave the most reproducible results.

Gravimetric analysis–thermal decomposition. Samples were decomposed in a controlled atmosphere by heating from ca. 35° to 450°C. The heating rate for all TGA experiments was 5°C/min.
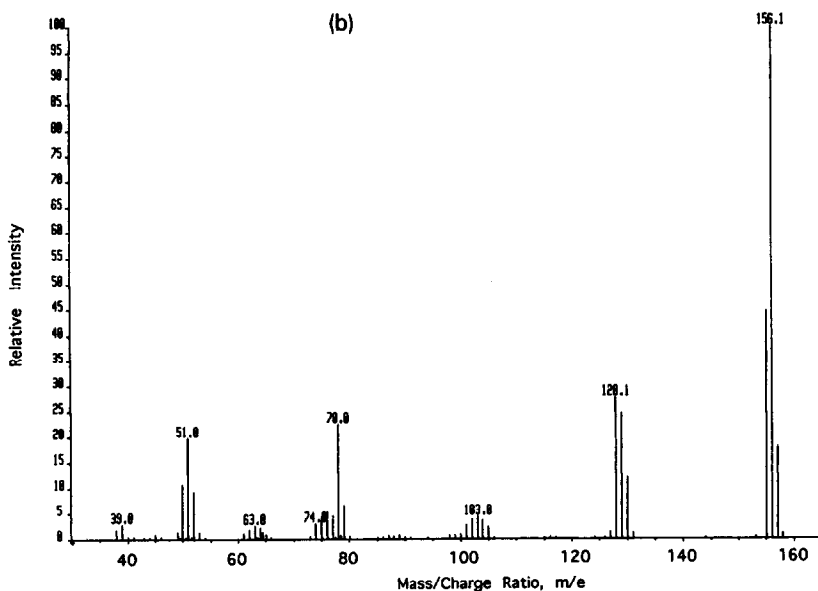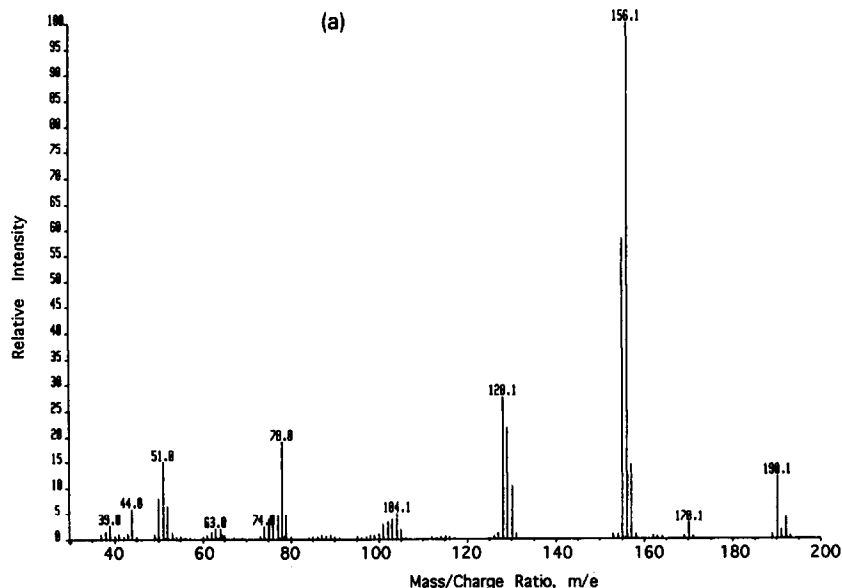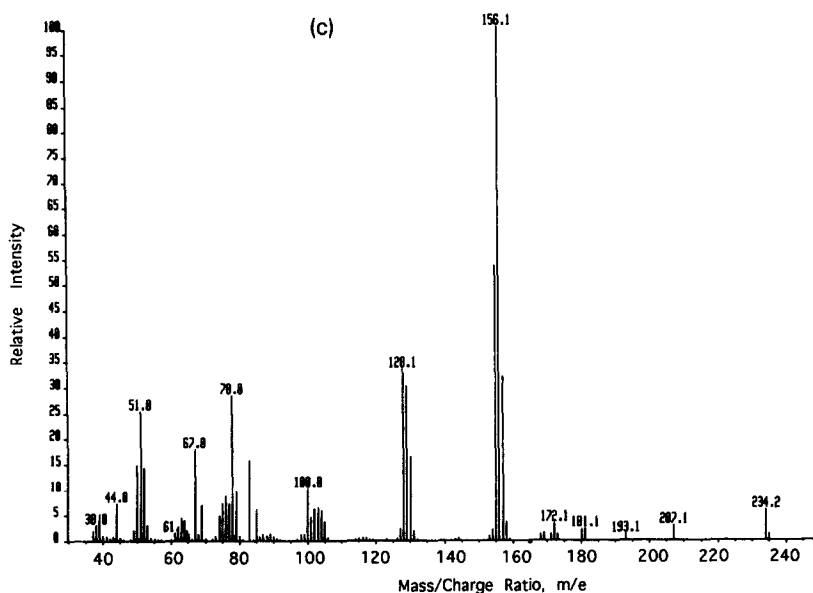
Fig. 3. Electron impact mass spectra of copper 2,2'-bipyridine dimer. (a) Metal complex supported on Cab-O-Sil. (b) 2,2'-Bipyridine. (c) Unsupported metal complex.

NO titration. The sample was decomposed in O_2 and reduced in H_2 before NO exposure. Prior to starting the nitric oxide flow and after adsorption was complete, the sample was flushed with N_2 for 30 min before weighing. NO adsorption was carried out at 100°C, and in one instance at room temperature, with NO partial pressures ranging from 3.3 to 6.8 Torr and the exposure time was 180 to 400 min.

N_2O reaction. The sample was decomposed and reduced before N_2O exposure. Prior to starting the nitrous oxide flow and after adsorption was complete, the sample was flushed with N_2 for 30 min before it was weighed. Nitrous oxide adsorption was completed in an atmosphere showing N_2O partial pressure of 380 Torr (balance nitrogen) at 100°C.

Mass spectrometry–thermal decomposition. Mass spectra were collected on a VG 70-SE mass spectrometer equipped with a two-sector, forward-geometry analyzer and a VG 11-25J data system. Theoretical abundance calculations were completed with the utility ISO, which is a part of the data system. Two types of analyses were completed on the samples: electron ionization (EI) and fast atom bombardment (FAB). For the EI experiment, the powder sample of the supported

metal complex was heated in a vacuum with the temperature programmed at 2°C/s. Volatiles from the sample were introduced to the spectrometer inlet system for mass spectral analyses.

Fast atom bombardment (FAB) experiments were developed using xenon ionized by a saddle field gun to produce the bombarding atoms. Samples of the powder were contacted with acetonitrile and sonicated to ensure dissolution of the copper containing species. The resulting solutions were mixed with *meta*-nitrobenzyl alcohol, *m*-NBA, obtained from Aldrich. The *m*-NBA served as a matrix to hold the solution containing the copper species.

3. Results

Elemental analyses. The unsupported metal complex showed elemental analyses as follows: 35.79 (35.73) wt% C, 2.74 (2.68) wt% H, 8.27 (8.33) wt% N, 10.49 (10.55) wt% Cl, and 20.0 (18.9) wt% Cu. The theoretical analyses are shown in parentheses for each element.

One sample of the supported complex showed elemental analyses as follows: 2.27 wt% Cu; 3.87 wt% C (4.29%), and 0.95 wt% N (1.00%), along

with the theoretical analyses (in parentheses) calculated using the metal content. Only the carbon analysis appeared to be in serious error; whereas, the error was small for the N analyses. The sample was found to have no perchlorate using a modified version of Geilmann's technique [16].

EPR of Cu(bipy) dimer. We recorded the EPR spectra of two samples so as to characterize the
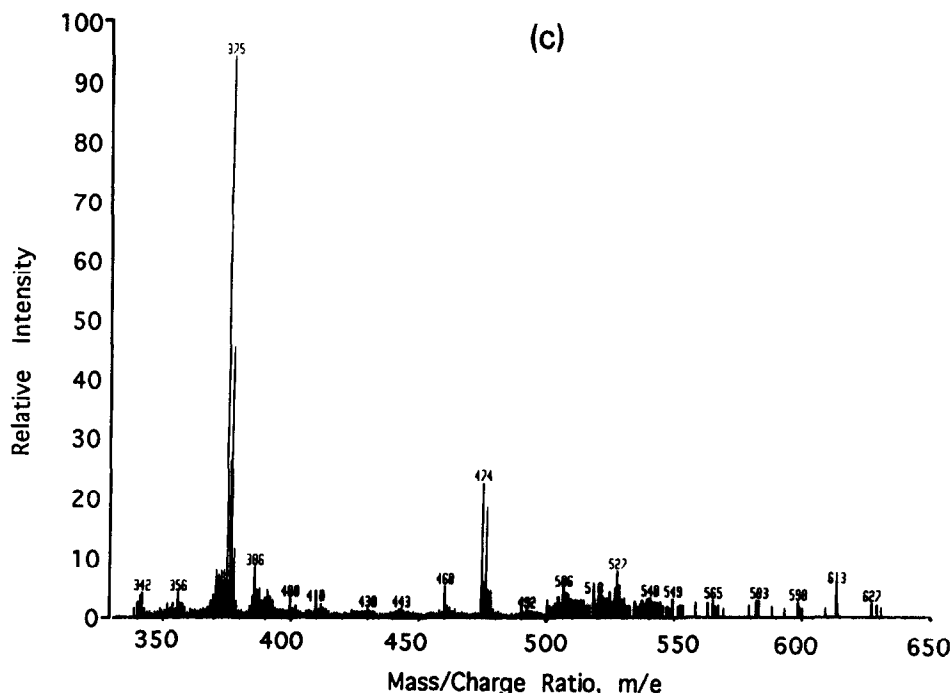

(a)

(b)
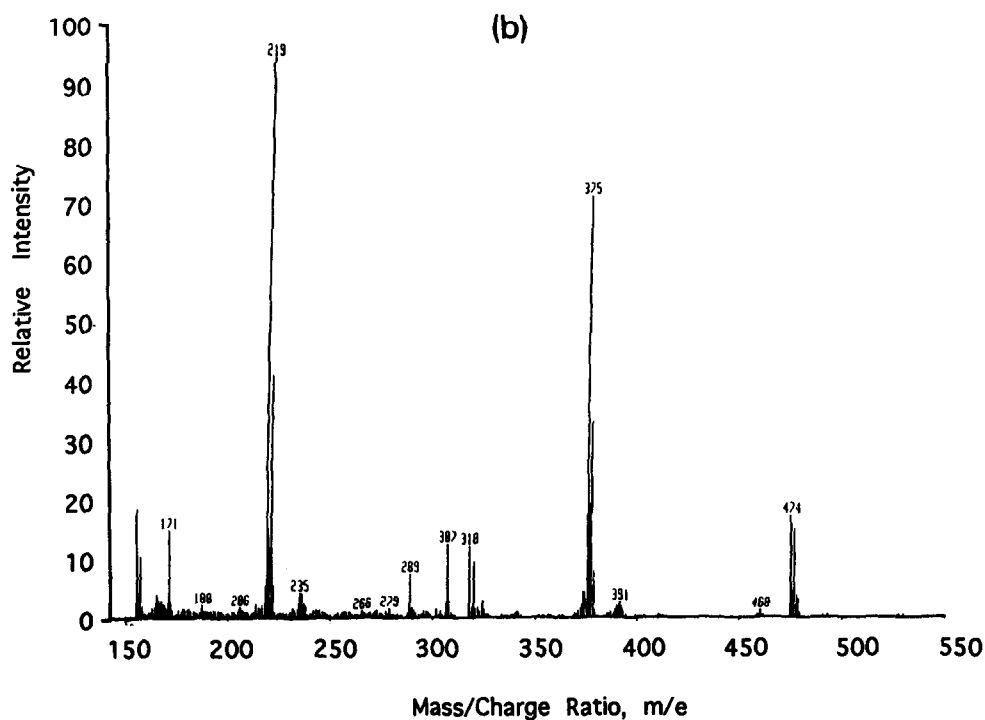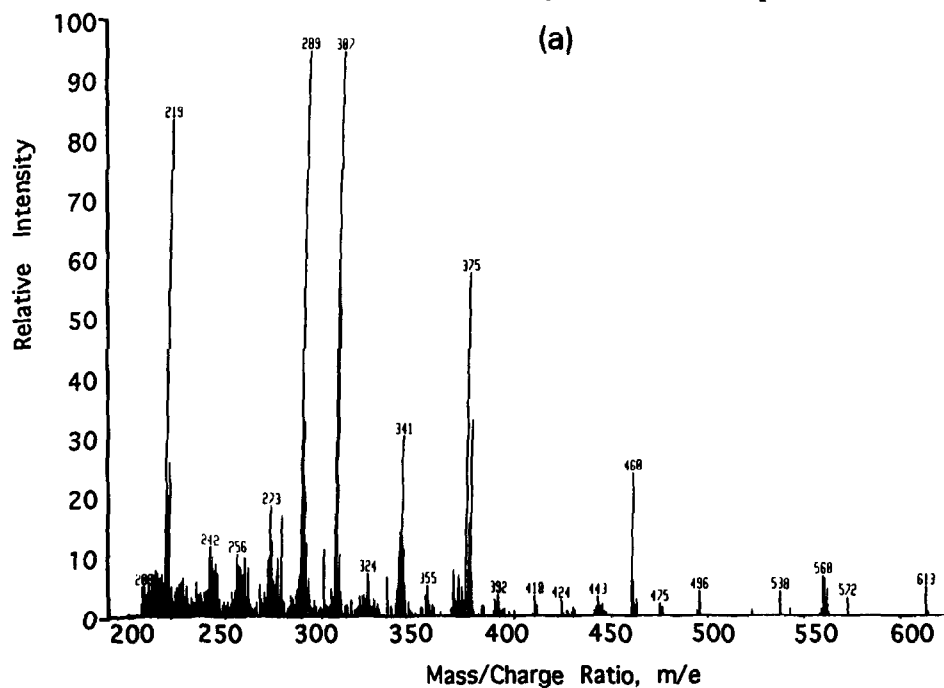
Fig. 4. Fast atom bombardment mass spectra of 2,2'-bipyridine metal complex. (a) Metal complex supported on Cab-O-Sil. (b) Copper bipyridine monomer. (c) Unsupported metal complex.

magnetic properties of the supported metal complex before thermolysis. Two samples were prepared in which equal molar amounts of Cu were present in the unsupported metal complex and the 2.27 wt% Cu/silica (Fig. 2) The sharp peak in each spectrum is the DPPH label. The spectrum of the unsupported metal complex (Fig. 2(a)) shows a small signal near 3000 G; whereas, the supported sample (Fig. 2(b)) shows a very large peak near 3000 G containing the distinct, four-line spectrum normally associated with a Cu^{2+} in an axial field [17]. The spectrum of the supported sample could be modeled by axial field equations using the following parameters for the spin-Hamiltonian: $g_{\parallel} = 2.34$; $g_{\perp} = 2.09$; $A_{\parallel} = 0.0184$ cm^{-1}; $A_{\perp}$ = unresolved.

Gravimetric analysis–thermal decomposition. One sample (2.27 wt% Cu) was analyzed in the thermal gravimetric apparatus for weight loss during thermolysis. This sample showed small weight losses at 190, 280°C and a large weight loss near 335°C; whereas, the unsupported metal complex decomposes rapidly at 296°C. Eighteen aliquots of the supported sample were decomposed in the

TGA to give an average weight loss of 0.0564 mg/mg total sample weight. The predicted weight loss is 0.0562 mg/mg total sample weight assuming the residue is CuO/silica.

Mass spectral analysis of supported Cu–bipy dimer. The 2.27 wt% Cu/silica sample was examined by mass spectrometry using electron impact (EI) and fast atom bombardment (FAB) to develop the spectra. The EI spectrum of the supported sample (2.27 wt% Cu) appears in Fig. 3(a) for the sample heated to 402°C. This spectrum shows large peaks at $m/e = 51$, 78, 128, and 156, plus the small peaks at 170 and 190. The fragmentation pattern of the peaks with m/e < 156 in the supported sample is identical to that of the unsupported sample. The electron impact (EI) mass spectra are identical for the neutral molecule of the ligand: 2,2'-bipyridine, Fig 3(c) [18] and the gases evolved from the unsupported metal complex when heated to 383°C (Fig. 3(c)). The small peak which appears in the spectrum of the supported sample at 190 may be a product of the reaction between the Cu species and a fragment of the 2,2'-bipyridine ligand which is
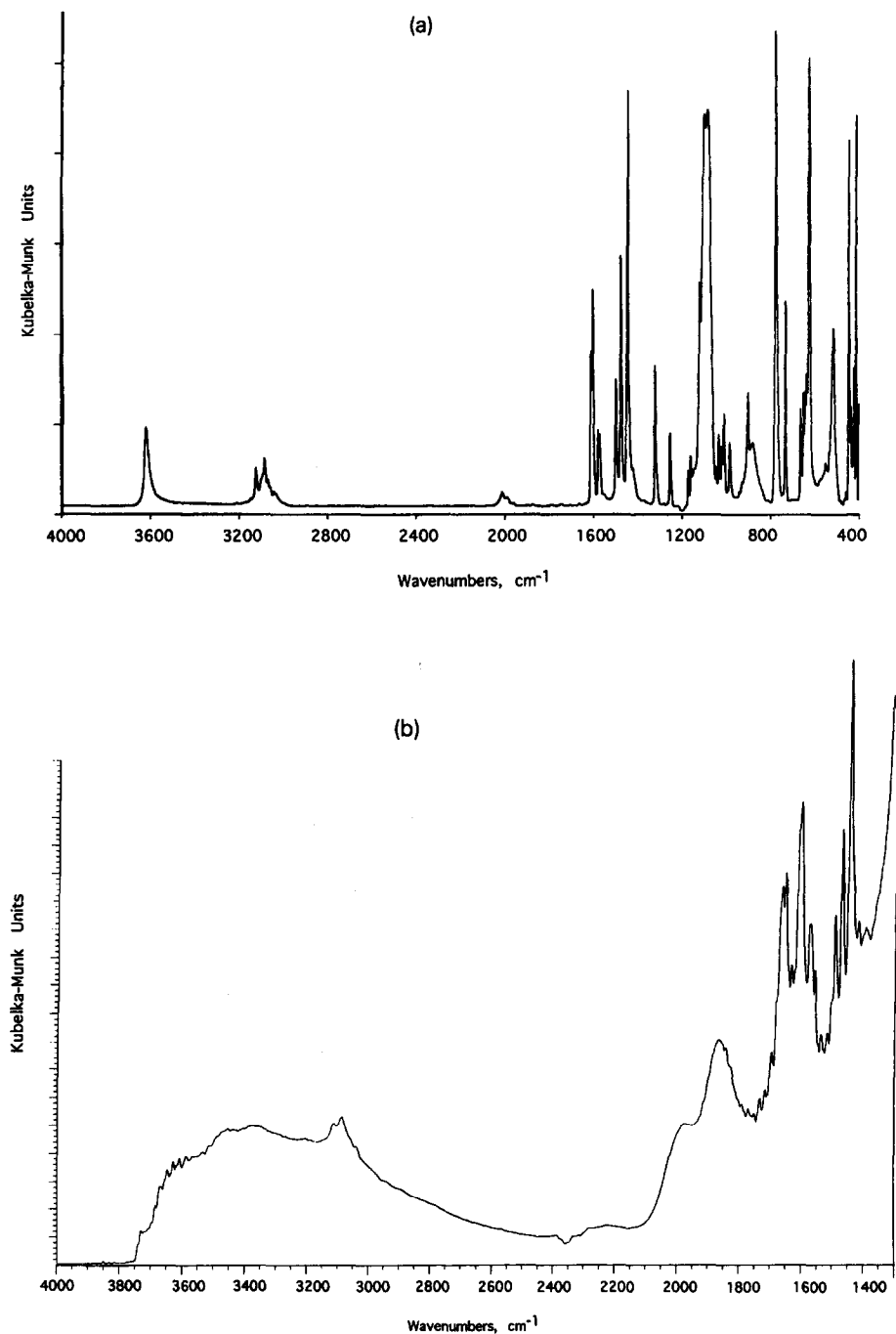
Fig. 5. Fourier transform infrared spectroscopy of supported and unsupported copper 2,2'-bipyridine dimer. (a) Unsupported metal complex. (c) Metal complex supported on Cab-O-Sil.

observed in the fragmentation pattern of the ligand [19–22]. This value of the m/e may be explained by the formation of $Cu + quinoline - 2$ H atoms which show masses of $(Cu + C_9H_7N - 2H$; $63 + 129 - 2 = 190)$. The quinoline formation is

supported by the *normalized* relative intensity ratio of the 190:192 peaks appearing in the ratio of 100:41.2 which is close to the theoretical isotope envelope for these species (100:45.1).

Table 1
Infrared absorption peaks for supported complex

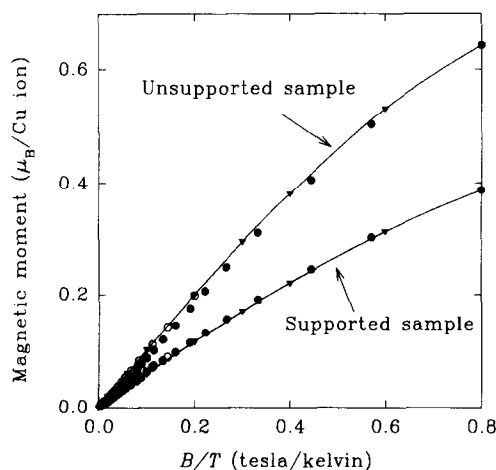| Frequency of absorption, cm^{-1}			Notes and assignments
Supported sample	Unsupported sample	2,2″-bipyridine	
3750			O–H stretch of Cab-O-Sil
3650–3200			O–H
	3616		ν O–H of bipy dimer
3125–3050	3112–3000	3086–3054	ν C–H
2000–1850			Si–O of Cab-O-Sil
1670–1620			?
1605–1450	1605–1443	1577–1415	C–C & C–N ring bending
	1323	1253	C–H, in-plane bending
	1084		perchlorate
	1100–1000	992	ring breathing
	896		perchlorate
	774	759	C–H, out-of-plane bending
	635	616	in-plane deformation
	626		perchlorate
	513		ν Cu–O
	440		perchlorate

Fig. 6. Magnetic moment data of copper 2,2′-bipyridine dimer. Moments are expressed in units of Bohr magnetons per copper ion, as a function of the ratio of magnetic field to temperature. Solid circles represent data collected at 4 T, open circles, 1 T, triangles at 5 K for various magnetic fields. The curves are spline fits through the triangles.

The same samples were examined using fast atom bombardment of the metal complexes in the matrix. The spectrum of the 2.27 wt% Cu/silica (Fig. 4(a)) shows large peaks at 219, 289, 307, 341, 375, and 460. The spectrum of the unsupported Cu–bipy dimer sample (Fig. 4(c)) shows large peaks at 375 [Cu + 2 bipy ligands $(C_{10}H_8N_2) = 63 + 312 = 375$] and 474 [Cu + 2

bipy ligands $(C_{10}H_8N_2)$ + ClO_4^- = $63 + 312 + 99 = 474$] which also appear in the spectrum of the Cu bipy monomer, $[Cu(bipy)_2]ClO_4)_2$ (Fig. 4(b)). A peak at 219 is evident in the spectrum of the monomer, also. The peaks at 219 and 375 have been explained in the spectrum of the unsupported metal complex as characteristic of the monomer; however, the large peaks at 289, 307 and 460 which appear in
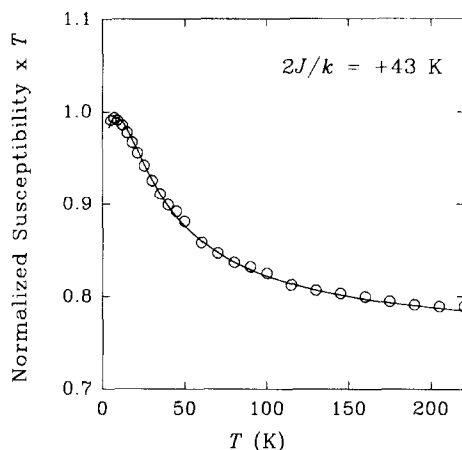

Fig. 7. Product of magnetic susceptibility and temperature for unsupported copper 2,2′-bipyridine dimer. The susceptibility times temperature has been normalized to the value extrapolated to 0 K, 0 T. The parameter $2J/k$ is determined by a curve fit. Measurements were made at 1 T.

Table 2
Infrared absorption peaks and assignments for NO assignments

Frequency of absorption, cm^{-1}				Adsorbed species	Notes and assignments
Cu/ZSM-5	Cu(acac)$_2$	Cubipy	Cu/Y		
2230–2240				N$_2$O	on Cu^{1+} [31]
2238				N$_2$O	[32]
		2200		N$_2$O	
2160|				NO$_2$	on Cu^{2+} [31]
2125|				NO$_2$	[32]
		1952		NO	on Cu^{2+}
			1948|	NO	on Cu^{2+}
			1914|	NO	
	1910			NO	[11]
1906				NO$^+$	[32]
1905				NO	on Cu^{2+} [31]
			1902–1891	NO	on isolated Cu^{2+} moved to accessible position [31]
1895			1912–1907		on Cu^{2+} carrying extra-lattice O [31]
1825|				(NO)$_2$	on Cu$^+$
1730						
	1826			NO	on Cu$^+$ [11]
		1817		NO	
1807–1815				NO	[31]
		1768		?	?
	1672	1654		?	?
1619–1630				NO$_2$	[31]
		1602		NO$_2$	
1575		1579		O(NO$_2$)	Cu
		1375		NO$_3^-$	Cu(?)
1305				NO$_3^-$	[31]

the supported sample are not present as large peaks in the monomer, but they appear as large peaks in the spectrum of the matrix material: *m*-NBA. Thus, the supported sample appears to show the same FAB spectrum as the unsupported monomer and dimer; however, the supported sample does not show a peak at 474 which is the *m/e* for the monomer complex cation plus a perchlorate. Elemental analysis likewise failed to show any perchlorate in the supported metal complex (vide supra).

XRD. No sharp peaks were observed in the X-ray diffraction data of the Cu–bipy dimer on Cab-O-Sil which suggests that the catalyst is amorphous, i.e. no large crystals of metal complex were formed on the surface of the support. In fact, when these data were compared to that for Cab-O-Sil, the resulting spectra were identical. Our prior work with other metal complexes on silica [16,23] showed that XRD was a sensitive tool to

define completion of a monolayer. Samples having loadings of the hexanuclear Cu complex just 2% in excess of a monolayer showed the presence of peaks characteristic of the polycrystalline metal complex [16]. Bruce confirmed the use of XRD to define monolayer completion for the system Cu(en)$_2^{2+}$ on silica [24].

FT-IR. The FT-IR spectra of the supported and unsupported samples (Fig. 5) are summarized in Table 1 along with peak assignments. The spectrum of the unsupported sample shows a sharp peak at 3616 cm^{-1}, which is the stretching frequency of the bridging O–H groups in the complex (Fig. 5(a)). The spectrum of the supported sample (Fig. 5(b)) shows a broad peak between 3650–3200 cm^{-1}, which we interpret as the overlap of the relaxations of O–H from the sample and the support. Note the SiOH from the support is just visible at 3747 cm^{-1}. Our earlier work with other supported metal complexes show IR spectra
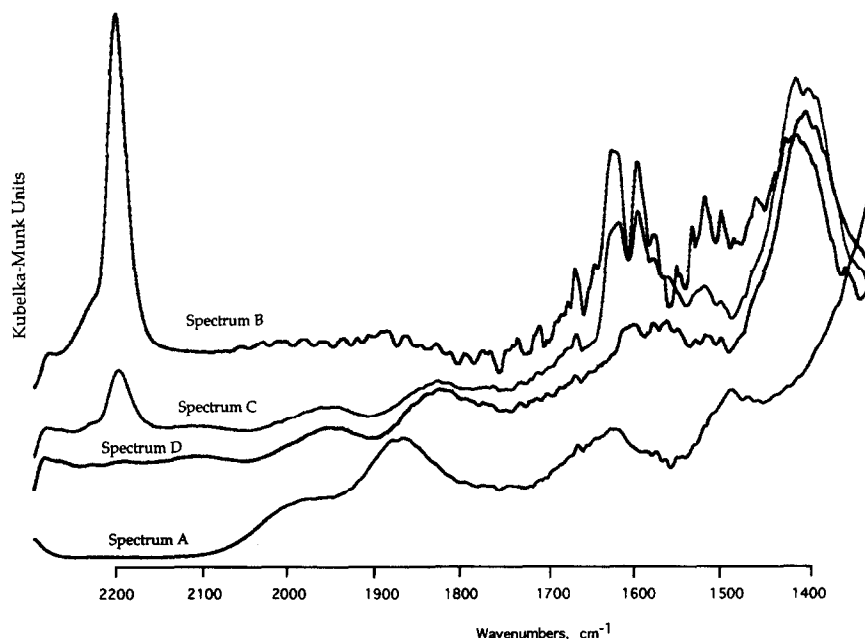
Fig. 8. Diffuse reflectance infrared Fourier transform spectroscopy of NO chemisorbed to Cu/silica. Spectrum A: Sample prepared by thermolysis monolayer of a film of metal complex (2.27 wt% Cu) in O_2 followed by reduction in H_2. Sample was cooled to 32°C and the spectrum was recorded. Spectrum B: Sample of Spectrum A was exposed to NO at 32°C and evacuated at same temperature. Spectrum A was subtracted from these data to produce the difference spectrum shown here. Spectrum C: Sample of Spectrum B was heated to 100°C, exposed to NO at same temperature and then evacuated. Difference spectrum is reported here relative to the sample of Spectrum A. Spectrum D: Sample of Spectrum C was heated to 160°C, exposed to NO at same temperature and then evacuated. Difference spectrum is reported here relative to the sample of Spectrum A.

similar to that we report here [23]. These results suggest that the symmetry of both the surface SiOH and complex OH have been lowered by some interaction. The supported sample also shows a spectrum which contains a broad C–H band at 3200–3100 cm^{-1} which corresponds to two, well-defined peaks in the unsupported sample between 3112–3000 cm^{-1} (ν C–H) [10,25–28]. Both spectra contain six sharp peaks between 1600–1400 cm^{-1} which are characteristic of the C–C and C–N ring deformation vibrations of 2,2′-bipyridine. These data suggest that the bipyridine rings have not been destroyed when the complex mounted the support.

Magnetic properties – SQUID. The magnetic moment data are shown in Fig. 6 for the supported and unsupported metal complex. The data for the unsupported metal complex were used to obtain (vide infra) a g-value of 2.13 and a value for 2J/k = 43 K (i.e., 2J = 30 cm^{-1}). The positive value of the exchange interaction constant, 2J, is con-

sistent with a model for the complex where the Cu ions are ferromagnetically coupled so that the ground state of the electrons is the triplet state (vide infra). The supported metal complex is somewhat less magnetic, which is evidence for anti-ferromagnetic coupling.

Fig. 7 shows the product of the magnetic susceptibility and the temperature for the unsupported sample. This plot removes the dominant T^{-1} Curie law dependence. The low-field, low-temperature data have been used to normalize this plot, which gives a g-value = 2.13. A one-parameter fit of the data to the following equation for the magnetic moment per copper ion M as a function of the field and temperature [29]:

$$M/\mu_B = \frac{g \, \sinh(g\mu_B B/kT)}{[1 + 2 \cosh(g\mu_B B/kT) + \exp(-2J/kT)]} \quad (1)$$

yields the ferromagnetic interaction parameter 2J = 30 ± 3 cm^{-1}. The range of the magnitude variation in Fig. 7 is fit well without an adjustable

parameter, which is evidence for the accuracy of our description. At low temperatures there is paramagnetic behavior with spin = 1 dimers which goes over smoothly to paramagnetic behavior with twice as many spins, each equal to 1/2, at higher temperatures.

Prior magnetic measurements on the unsupported compound are in general agreement with the present measurements. Barnes, et al., reported positive ferromagnetic interactions modeled by the van Vleck equation with $50 < 2J < 100$ cm^{-1} when $g = 2.22$[30]. Crawford et al. [31] discussed a correlation between the Cu–O–Cu bridge angle and the value of $2J$ in the hydroxo-bridged copper dimers. This angle, determined to be 96.94° by Toofan et al. [32], leads to an estimate for $2J = 45$ cm^{-1} which is close to the value reported here. The work of Crawford et al. [31] also shows that a change in $2J$ on the order of 30 cm^{-1} can be caused by changes in the Cu–Cu distance as small as 0.2%, or a corresponding change in the Cu–O–Cu bridge angle of only 0.4°.

NO adsorption – FTIR. The pretreatment of the sample and the conditions of the NO adsorption experiment described earlier were repeated in a controlled atmosphere cell installed in a diffuse reflectance, Fourier transform infrared spectrometer (Table 2). The spectra developed in Fig. 8 show the sample after calcination and reduction in H$_2$ (Fig. 8, Spectrum A). This spectrum was subtracted from the data of the same sample after exposure to NO to develop the difference spectra (Fig. 8, Spectra B, C, and D). Peaks were observed at 2200, 1620, 1580, 1375 cm^{-1} for a sample exposed to 0.03 mol NO at 32°C (Fig. 8, Spectrum B). The sample was heated to 100°C in vacuum and exposed to NO (0.02 mol NO exposure). In Fig. 8, the IR Spectrum C was developed after this treatment to show a decrease in the 2200 cm^{-1} peak with increases in the peaks at 1620, 1580, 1375 cm^{-1} and the appearance of new peaks at 1952, 1817, 1768 cm^{-1}. Heating of the sample to 160°C in vacuum followed by NO exposure at that temperature (0.01 mol NO exposure) gave the Spectrum D in Fig. 8. Heating of the sample causes the peaks at 2200, 1620, and 1580 cm^{-1}

to decrease significantly; whereas, the peaks at 1952, 1817, 1768, and 1375 cm^{-1} remain large. Peak assignments by Valyon and Hall [33] and others [11,34] were used to identify the surface species which give rise to these observed vibrations. These results suggest that N$_2$O, NO$_2$ and NO$_3^-$ are present on the surface with very little molecular NO on the dinuclear Cu catalysts. The N$_2$O and NO$_2$ species disappeared upon heating the sample to 160°C; however, the NO$_3^-$ species appears to grow.

NO adsorption – gravimetric analysis. The conditions of the NO adsorption experiment in the gravimetric experiment were the same as we used in the DRIFTS experiment. The weight gain was 0.281 mg/mg Cu, 0.246 and 0.260 mg/mg Cu for the adsorption of NO in three separate experiments when the exposure time was varied from 240–400 min at 100°C and 6.8 Torr NO. The results of the infrared experiments suggested that very little molecular NO was present on the surface; thus, we conclude that NO decomposed over the Cu/silica developed from the dimer complex. If we assume that oxygen remains on the surface, then the weight increase corresponds to an average O/Cu stoichiometry of 1.04. These data suggest that the Cu ions are completely dispersed in these samples.

N$_2$O Reaction. The samples synthesized from the dinuclear metal complex were examined further by reaction of N$_2$O which has been used previously to measure exposed copper surface area [35]. The reaction stoichiometry [35] for the reaction of N$_2$O on metallic copper crystals is given by the following equation:

$$2Cu(s) + N_2O(g) \rightarrow Cu-O-Cu(s) + N_2(g)$$
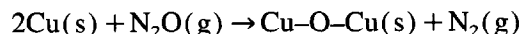
We showed how this reaction did not adequately represent the state of copper dispersion when the surface was created by the decomposition of a monolayer of Cu(acac)$_2$/silica as no reaction occurred between the reduced surface and the gaseous N$_2$O [11]. We explained these results as a consequence of the N$_2$O reaction demanding an ensemble of two Cu atoms no more than 4 Å apart

and that the Cu atoms in the model catalyst were separated by as much as 5 Å [11].

The 2.27 wt% Cu sample was pretreated by reduction in H_2 at 300°C before it was exposed to N_2O gas. After exposure to N_2O, the sample was purged with dry N_2, and the weight increase was found to be 0.252 mg/mg Cu in the sample. This weight increase corresponds to 0.999 mol O/mol Cu in the sample. Therefore, every Cu atom in the sample has acquired another O atom which suggest a stoichiometry of the reaction as follows:

$$2Cu(s) + 2N_2O(g) \rightarrow 2Cu\text{–}O(s) + 2N_2(g)$$
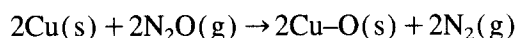
This reaction stoichiometry is quite different from that observed over copper metal crystals [35].

4. Discussion

Copper bipy dimer complex. The elemental analyses and FTIR spectra of the unsupported metal complex suggest that we were successful in synthesizing the metal complex. The magnetic properties data of the unsupported metal complex appear to be consistent with those reported in the literature [29–32].

Supported copper bipy dimer complex. The data of elemental analyses, gravimetric and mass spectral data attending the thermolysis of the supported metal complex are consistent with a picture that the copper bipy complex resides on the support with organic ligands intact but without the perchlorate anions. The EPR data suggest that some of the dimer mounts the surface showing evidence

of unpaired electrons not unlike that we have seen for supported mononuclear metal complexes in which the Cu^{2+} were 'magnetically' isolated [9]. Others report spin-Hamiltonian parameters for 'isolated' Cu^{2+} which are very close to those we report here (Table 3) [17,37,38]. The magnetic properties data collected in the SQUID help to explain these results. It is believed that the copper ions are not present on the silica surface as ferromagnetically-coupled dimers, and the magnetic data are consistent with this belief, but the magnetic data cannot be used to confirm this idea conclusively. The simplest explanation for the reduced moment in the supported sample relative to the unsupported sample, as is evident in Fig. 6, is that the copper dimers have a weak anti-ferromagnetic coupling, which only becomes evident at rather low temperatures. If Eq. 1 is used to fit the data for the supported sample (leaving the g-value fixed at 2.13), then one obtains $2J/k = -6$ K ($2J = -4$ cm^{-1}). As remarked earlier, even small changes in the copper ion positions could be responsible for changing the exchange coupling constant from $+30$ to -4 cm^{-1}. A strong interaction between the complex and the silica surface may be responsible for these small changes in the copper ion positions. Thus, the magnetic properties data imply that the copper ions are very weakly coupled. Moreover, we suggest that ion exchange has occurred to produce a film of copper bipy cations which interact strongly with the Cab-O-Sil surface in a manner similar to that we have reported previously [1,16,23,36].

The results for the reactivity of NO and N_2O over Cu/silica prepared by decomposing a monolayer of a dinuclear Cu complex on silica are in stark contrast to the results we reported for Cu/silica prepared from the thermolysis of a monolayer film of Cu(acac)$_2$/silica [10,11]. We shall designate the sample prepared from the dinuclear Cu complex as 'dinuclear' and the sample prepared from the mononuclear Cu complex as 'mononuclear'. The two samples of Cu/silica showed the same dispersions of Cu (100%) for similar weight loadings (2.27 wt% Cu for the 'dinuclear' sample and 2.4 wt% Cu for the 'mononuclear'

Table 3
EPR spin-Hamiltonian parameters for Cu^{2+}

Sample/reference	$g_\parallel$	$g_\perp$	$A_\parallel$, cm^{-1}	$A_\perp$, cm^{-1}
This work	2.34	2.09	0.0184	–
Cu(acac)$_2$/SiO$_2$ 6	2.26	2.06	0.0200	–
Cu(acac)$_2$/SiO$_2$–Al$_2$O$_3$ 35	2.28	2.06	0.0182	0.0029
Cu^{2+}/charcoal 36	2.32	2.086	0.0152	–
Cu^{2+}/Y–zeolite 27 [a]	2.39	2.06	0.0134	0.0019

[a] Partially reduced sample

sample). However, NO and N_2O could be dissociated on the 'dinuclear' sample; whereas, NO was reversibly adsorbed without dissociation on the 'mononuclear' sample. Nitrous oxide did not react on the 'mononuclear' sample at conditions often used to 'count' surface Cu sites in supported Cu samples: 100°C and 380 Torr of N_2O.

The stoichiometry of 1 O/Cu resulting from the N_2O reaction on the 'dinuclear' catalyst is different from the stoichiometry of 1 O/2 Cu normally used to count surface Cu atoms on supported polycrystalline Cu [35]. We speculate that the coordination number of surface Cu species governs the adsorbate stoichiometry. Consider a model for the surface of polycrystalline Cu which for which the surface Cu atoms show a coordination number of five. Two surface Cu atoms of polycrystalline Cu can share an oxidic oxygen, since each surface Cu atom can accept one more bond. Now consider a model for a small Cu ensemble as might be generated from the thermolysis of a dinuclear Cu complex on silica (Species I).
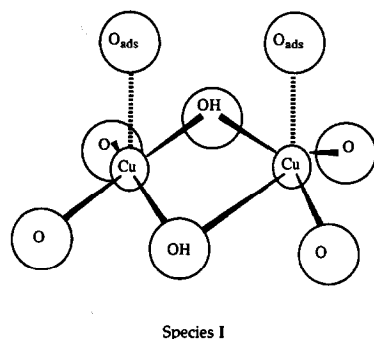
Species I

The Cu atoms in this ensemble may show coordination numbers as small as 3–4. This smaller Cu coordination number may permit the Cu species to form double bonds with each oxidic oxygen so that the oxygen/Cu stoichiometry is 1 O/Cu. We suggest by this discussion that the Cu ion ensemble size will govern the types of interactions between NO and the copper ions.

The 'dinuclear' sample was observed to develop surface N_2O, nitrito and nitrato species after exposure to NO at room conditions in the FTIR. The 'mononuclear' catalyst showed chem-

isorbed NO on Cu^{2+} giving rise to a peak at 1910 cm^{-1}, chemisorbed NO on Cu^+ giving rise to a peak at 1826 cm^{-1}, and an unassigned peak at 1672 cm^{-1}. It would appear that the reaction of NO to products on Cu is a demanding reaction which requires an ensemble size of at least 2. The results for the N_2O reaction confirm the demanding nature of this reaction.

5. Conclusions

Model Cu/silica catalysts were prepared from the thermolysis of a monolayer film of Cu–bipy dimer/Cab-O-Sil. The cationic complex attached to the surface of the silica with its ligands intact apparently by an ion exchange mechanism for which two surface protons left the surface combined with two perchlorate anions. The surface bound Cu–bipy metal complex showed significant interactions with the surface (perhaps, between the surface SiO^{1-} and the OH groups of the complex) as evidenced by a decrease in the magnetic moment of the Cu ions. Thermolysis of the surface film apparently produced a residue showing a Cu/O stoichiometry equal to 1. This residue could be reduced in hydrogen to produce a reactive surface which dissociates NO and N_2O at mild conditions. The stoichiometry of the reaction of the residue with N_2O is quite different from that reported in the literature for supported polycrystalline Cu. The present results call into question the use of N_2O as a proper titrant for copper surface area as well as our use of NO as a titrant for well-dispersed Cu as reported in earlier papers. The reactions of NO and N_2O over small ensembles of Cu are demanding.

Acknowledgements

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