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[8] The heterometallic dendrimers were electrodeposited onto Pt or carbon glassy electrodes by continuous scanning between 0 and -1.10 V versus SCE in degassed CH_3CN dendrimer-containing solutions. The electrodes thus coated were rinsed with CH_3CN to remove any adhering solution and dried in air. The surface coverage Γ of the dendrimer on the electrode was determined from the integration of the redox waves, and for the example shown in Figure 1B was found to be 9.7×10^{-10} mol Fc cm^{-2} and 1.8×10^{-9} mol Cb cm^{-2}.

[9] The dendrimer-modified electrodes were immersed in an electrochemical cell containing an enzyme solution (0.1% of GOx in acetate buffer, pH = 6.3, and $NaClO_4$ 0.1 M). A potential of +0.6 V versus SCE was applied to the dendrimer-coated electrodes for 30 min with stirring, and the electrodes were subsequently rinsed in deionized water and air-dried before use.

[10] The electrode enzymatic reactions are $S + \text{enzyme}_{ox} \rightarrow P + \text{enzyme}_{red}$ and $\text{enzyme}_{red} + M_{ox} \rightarrow \text{enzyme}_{ox} + M_{red}$, where M = mediator, M_{ox} = O_2 or ferrocenium, S = substrate (glucose), P = product (gluconolactone).

[11] E_p of the O_2 reduction -0.83 V versus SCE at a bare carbon glassy electrode, and -0.70 V at the dendrimer modified electrode.

Structure of Homoleptic $Cu^I(CO)_3$ Cations in Cu^I-Exchanged ZSM-5 Zeolite: An X-ray Absorption Study**

Carlo Lamberti,* Gemma Turnes Palomino,
Silvia Bordiga, Gloria Berlier, Francesco D'Acapito,
and Adriano Zecchina

Copper is a transition metal that plays a remarkable role in redox catalysis by several selective, three-dimensionally organized, inorganic, organic, and biological systems.[1–3] In all these catalysts the structure of the active sites is rather complex, and often the interplay between two adjacent copper centers is required for their operation.

Copper(I)-exchanged zeolites can be considered the best known type of inorganic three-dimensionally organized catalysts, because of their crystalline structure and the controlled dispersion of the metal centers, which impart a good structural definition to the adsorbing sites.[4] Copper-exchanged zeolites are usually prepared by standard exchange procedures with aqueous solutions of Cu^{II} salts. Depending on the preparation and pretreatment conditions, they contain variable mixtures of copper species in different oxidation and aggregation states.[1, 5] Products containing exclusively isolated Cu^I ions can be prepared by reaction of H-zeolites with CuCl in the gas phase.[6] Structural and spectroscopic studies have shown that the Cu-ZSM-5 thus obtained contains solely isolated Cu^I ions,[7] located in structurally and energetically well defined positions.[8] Hence, these materials have model character and are suitable for theoretical investigations.[9, 10]

In addition, Cu complexes of well-defined structure can be synthesized in zeolitic materials, and the zeolitic framework can often stabilize complexes that would otherwise be unstable.[11, 12] Although binary compounds of the type $Cu^I(CO)_n$ were observed in strongly acidic media such as H_2SO_4, CF_3SO_3H, FSO_3H, $BF_3\cdot H_2O$, and HF,[3] none of these complexes could be isolated as solids. Only recently did Rack et al.[13] report the formation and the structural and spectroscopic characterization of $[Cu^I(CO)_n]^+AsF_6^-$ ($n = 1-3$).[14]

Infrared spectroscopy (Figure 1) has been very informative on the structure of intrazeolitic $[Cu^I(CO)_n]^+$ species ($n = 1-3$), and the main results can be summarized as follows:[6b, 8] 1) at low CO equilibrium pressures p_{CO} linear $Cu^I(CO)$ complexes are formed;[15] 2) on increasing p_{CO} the formation of C_{2v}-symmetric $Cu^I(CO)_2$ adducts is observed;[16] 3) on decreasing the temperature, $Cu^I(CO)_3$ complexes of C_{3v}

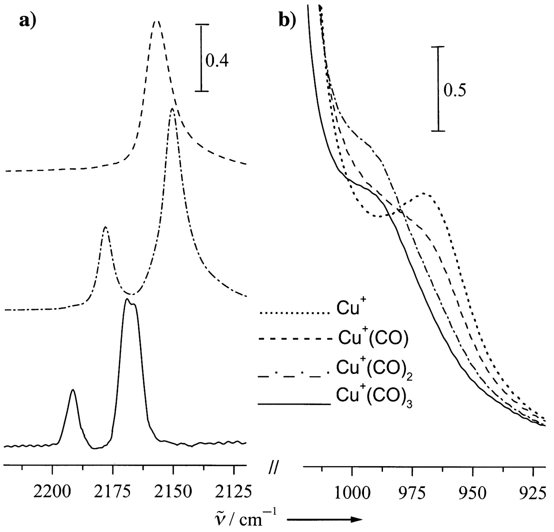

Figure 1. IR spectra of $[Cu^I(CO)_n]^+$ species ($n = 1-3$) in ZSM-5 zeolite in the C≡O (a) and framework stretching (b) regions. The spectrum obtained before CO addition was used as background and was subtracted from the spectra in (a). The spectrum of the $[Cu^I(CO)_3]^+$ adduct is shown after additional subtraction of the band of the physisorbed component at 2138 cm^{-1}.[17]

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[*] Dr. C. Lamberti,[+] Dr. G. Turnes Palomino, Dr. S. Bordiga, G. Berlier, Prof. A. Zecchina
Dipartimento di Chimica IFM
Via P. Giuria 7, 10125 Torino (Italy)
Fax: (+39) 11-6707-855
E-mail: Lamberti@ch.unito.it

Dr. F. D'Acapito
INFM-OGG, c/o ESRF, GILDA CRG
BP220,38043 Grenoble (France)

[+] INFM UdR di Torino Università, Torino (Italy)

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symmetry are obtained at about 80 K (see Figure 1 a), characterized by the appearance of a new IR doublet at $\tilde{\nu}(CO) = 2167, 2192\ cm^{-1}$.[17] Note that the homogeneous counterparts form planar adducts of D_{3h} symmetry.[13] The distortion from ideal linear and planar symmetry observed for the di- and tricarbonyl species is associated with interactions with the zeolite walls, which act as polydentate ligands. According to ref.[3e], this distortion can be considered as an external parameter that reflects the interaction with the negatively charged framework, which is the heterogeneous counterpart of the AsF_6^- ion in the homogeneous complexes synthesized by Rack et al.[13]).

Further and more direct information about the internal and external parameters can be obtained by X-ray absorption spectroscopy (XAS). In particular, previous extended X-ray absorption fine structure (EXAFS) studies[8, 11] showed that the formation of $Cu^I(CO)_2$ complexes at room temperature causes a consistent elongation of the distance between the Cu^I ions and the framework oxygen atoms (from 2.00 to 2.16 Å). This experimental evidence clearly indicates both the high complexation capability of CO molecules with respect to Cu^I ions hosted in the Cu^I-ZSM-5 matrix and the mobility of the Cu^I ions under the influence of the interaction with CO adsorbates.

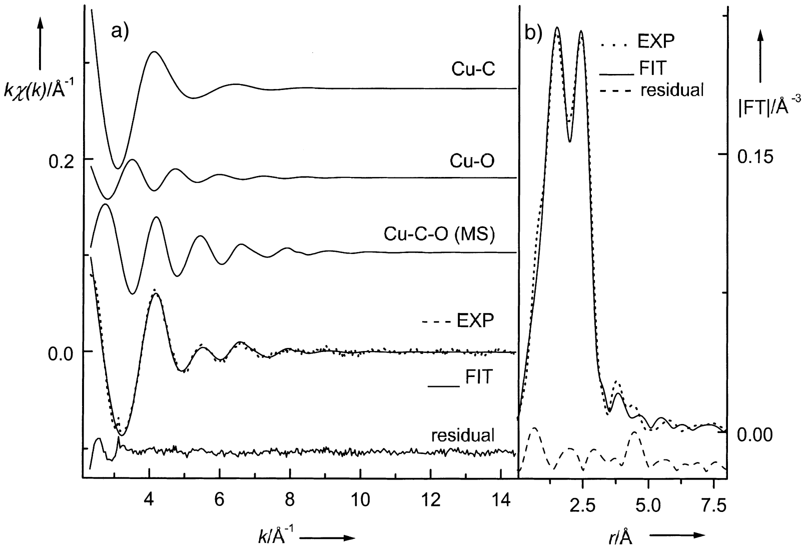

Figure 2. a) k-weighted k functions of (from top to bottom): Cu-C single-scattering (SS) contribution, Cu-O SS contribution, Cu-C-O MS contribution, the sum of the three previous theoretical contributions (FIT), the experimental curve (EXP), superimposed for comparison, and the corresponding residual function. b) Phase-uncorrected FTs of the last three functions, giving a view in r space.

Table 1. Quantitative results of the EXAFS data analysis with the coordination number N fixed at three; errors were calculated by a χ^2 statistical analysis with a confidence level of 95 %.

$r_{Cu\text{-}C}$ [Å]	$\sigma^2_{Cu\text{-}C}$ [Å^2]	$r_{C\text{-}O}$ [Å]	$\sigma^2_{C\text{-}O}$ [Å^2]	$\Theta_{Cu\text{-}C\text{-}O}$ [°]	$\sigma^2_{Cu\text{-}C\text{-}O}$ [°^{2}]	C_{RR}
1.93 ± 0.02	0.022 ± 0.006	1.12 ± 0.03	0.005 ± 0.02	180 ± 10	100 ± 50	− 0.65 ± 0.30

To more deeply investigate the analogies between the chemistry of Cu^I in Cu^I-ZSM-5 and that of Cu^I in superacidic media, we performed an EXAFS and X-ray absorption near-edge structure (XANES)[18] study aimed at determining the three-dimensional structure of the $Cu^I(CO)_3$ complexes formed in the channels of ZSM-5 at 80 K. The combined use of EXAFS and XANES techniques (the results interpreted by using a multiple-scattering approach) is the only method that can determine the local structure of such carbonylcopper ions. In fact, powder XRD can not be used in this case because the low Cu content in ZSM-5 (due to the high Si/Al ratio) makes the contribution of Cu nearly insignificant with respect to that of the framework and the solvation effect induced on Cu^I cations by interaction with CO implies a consistent loss of long-range ordering of the reulting $Cu^I(CO)_3$ complexes.

The results are illustrated in Figure 2 and Table 1. In Figure 2 a the calculated and experimental EXAFS signals together with the partial contributions of the different two- and three-body configurations are compared; Figure 2 b compares the Fourier transforms (FT) of the experimental and calculated spectra. Table 1 lists the results of the quantitative analysis. The Cu–C distance obtained for the $Cu^I(CO)_3$ complex ((1.93 ± 0.02) Å) is very close to that previously measured for the $Cu^I(CO)_2$ complex at room temperature (1.95 Å)[11] and is in good agreement with the values recently obtained by advanced quantum mechanical calculations: Lupinetti et al.[10a] (1.891 Å), Ramprasad et al.[10b] (1.900 Å), and Sodupe et al.[10c] (1.969 Å). The $Cu–O_{CO}$ distance extrapolated from this determination is 3.03 Å with a related Debye–Waller factor of $\sigma^2_{Cu\text{-}O} = 0.013$ Å^2. Note that the C–O distance ((1.12 ± 0.03) Å) is in good agreement with the gas-phase value (1.128 Å) and that the Cu-C-O bond angle is linear within the error bars, in agreement with indirect IR evidence.[6b, 8] The negative correlation parameter C_{RR} of the Cu–C and C–O vibrations indicates that while the former stretches the latter compresses, and vice versa. This behavior is exactly what is expected for the vibrational motion of the carbonylcopper adduct on the basis of the orbital approach.[19]

It is noteworthy that we were able to simulate the experimental signal using a bare $Cu^I(CO)_3$ cluster, and this implies that the complexation effect, already evident at room temperature in the $Cu^I(CO)_2$ complex,[11] is now stronger and that $Cu^I(CO)_3$ moieties have only a very weak interaction with the framework oxygen atoms and exhibit mobility. This result confirms the conclusion based on the observation of the influence of CO polyadsorption on the ν_{asym} stretching of a Si-O-Al moiety that is perturbed by the presence of Cu^I (see Figure 1 b). In fact, the stepwise formation of intrazeolitic $Cu^I(CO)_n$ complexes is accompanied by the simultaneous stepwise perturbation of the IR band at 980 cm^{-1}, already attributed to ν_{asym}(Si-O-Al) stretching that is perturbed by Cu^I, which progressively shifts in frequency and nearly disappears upon formation of $Cu^I(CO)_2$ and $Cu^I(CO)_3$ complexes.[11] In other words, the ν_{asym}(Si-O-Al) frequency (usually in the range 1100–1250 cm^{-1} for zeolites) moves from a value (980 cm^{-1}) reflecting the perturbation induced by the bonded Cu^{I} ion at $r_{\text{Cu-O}} = 2.00$ Å to a higher value (more similar to that of an unperturbed Si-O-Al moiety) which reflects the lower perturbation induced by a Cu^{I} ion at a larger $r_{\text{Cu-O}}$.[11] The IR skeletal mode and the $r_{\text{Cu-O}}$ values measured by EXAFS are very sensitive to "external parameters" and thus give information on the bonding between Cu^{I}(CO)$_n$ and the zeolite. Unfortunately, due to the weakness of the C-Cu-C three-body signal, determination of the global geometry (planar or pyramidal) of the Cu^{I}(CO)$_3$ cluster from EXAFS data was not possible.

Further information on the geometry of the Cu^{I}(CO)$_3$ cluster was obtained by analyzing the absorption coefficient in the vicinity of the edge (XANES). In this region the photoelectron has a wavelength longer than the interatomic distances and a long mean free path, and this results in a marked sensitivity of the shape and position of the edge structures to the local geometry of the complex. On the basis of the IR evidence (Figure 1), we considered a series of Cu^{I}(CO)$_3$ clusters with C_{3v} "umbrella-shaped" structures by starting from the planar configuration (D_{3h}: $\alpha = 90°$) and reducing the polar angle α of the CO ligands with respect to the z axis down to $\alpha = 30°$. From these trial geometries, the XANES spectra were calculated in the region between 0 and 4 Ry (54.4 eV) above the interstitial potential level and compared with the experimental results. The results of the simulations for α values between 30 and 90° (planar cluster) are shown in Figure 3. The position and relative intensities of peaks A and B are reasonably reproduced for $70 < \alpha < 90°$. At $\alpha = 54°$ the two peaks are too close, and for smaller angles peak B becomes more intense than peak A. The XANES results are thus compatible with a planar or slightly bent molecule with a minimum acceptable bending angle of $\alpha = 60°$. A value of $\alpha = 90°$ or close to 90° must be rejected on the basis of the IR spectroscopic data[6b, 8] (only one IR-active band is expected for a Cu^{I}(CO)$_3$ complex with D_{3h} symmetry). In addition, the steric hindrance of the zeolitic walls makes values of α larger than 80° unreasonable. Hence, we concluded that, due to the interaction with the zeolitic walls, the structure of the Cu^{I}(CO)$_3$ complexes deviates from the planar form typical of the homogeneous counterparts, with an α value in the range of 60–80°. The interaction must however be sufficiently weak to preclude the determination of the Cu^{I}–O distance by EXAFS. From the above XAS data, the high structural definition of the Cu^{I} complexes in ZSM-5 is emerging.[20] This result allows them to be classified among the best heterogeneous counterparts of the homoleptic Cu^{I}(CO)$_n$ cations ($n = 1-3$) synthesized under homogeneous conditions.

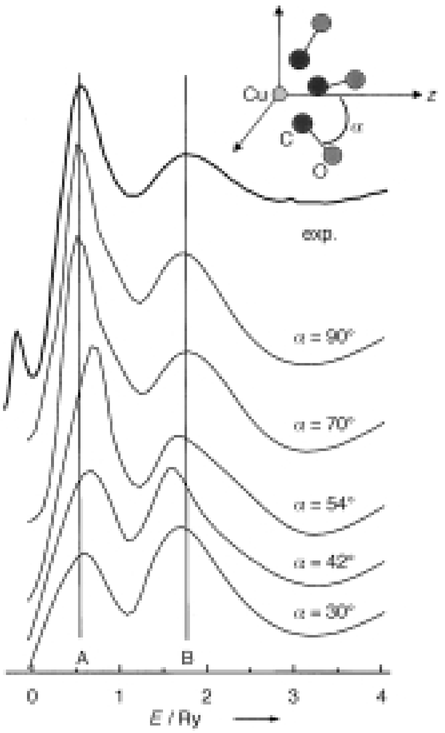

Figure 3. Comparison between experimental (top curve) and simulated XANES curves as a function of the angle α of the Cu(CO)$_3$ adduct in C_{3v} symmetry (1 Ry ≈ 13.6 eV). Simulated spectra are calculated above the interstitial potential level only ($E > 0$). Vertical lines indicate the position of bands A and B of the experimental spectrum. The schematic diagram represents the Cu^{I}(CO)$_3$ adduct in C_{3v} symmetry and defines the angle α.

Experimental Section

Cu^{I}-ZSM-5 (Si/Al = 14/1) was prepared by reaction of the corresponding protic form with gaseous CuCl at 673 K.[6] For IR measurements, we have used an IR cell designed to allow in situ high-temperature treatment, gas dosage, and low-temperature measurements. The IR spectra were recorded with a resolution of 2 cm^{-1} on a BRUKER FTIR-66 spectrometer equipped with a MCT detector. X-ray absorption measurements were performed at the Cu K edge at GILDA, the general purpose Italian beamline at the ESRF. The monochromator was equipped with a pair of Si(311) flat crystals; efficient harmonic rejection was achieved by using a pair of Pd-coated mirrors with an energy cutoff of 21 keV. Measurements were performed at 80 K in transmission mode with N$_2$- and Ar-filled ion chambers for measuring the incident (I_0) and transmitted (I_1) beams, respectively. A reliable energy calibration was achieved by measuring the fluorescence of Cu metal foil placed after I_1. XAS and IR spectra were obtained by using the same cell equipped with Mylar and KBr windows, respectively. The Cu^{I}(CO)$_3$ complex was measured at 80 K ($p_{\text{CO}} = 10$ Torr), and the Cu^{I}(CO)$_2$ and Cu^{I}(CO) complexes at room temperature ($p_{\text{CO}} = 1$ and 10 Torr, respectively).

EXAFS data were analyzed in the framework of the multiple-scattering theory by using GNXAS.[21] Theoretical calculations of XANES spectra were made on the basis of the multiple-scattering formalism and the Muffin Tin approximation by using the CONTINUUM package developed at the Laboratori Nazionali di Frascati of INFN.[22] Muffin Tin radii were chosen according to the Norman criterion,[23] and a 10% overlap was allowed between contiguous spheres. A detailed description of both EXAFS and XANES computations is available as supporting information.

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Nickel-Catalyzed Generation of Schiff Base Aluminum Enolate Initiators for Controlled Methacrylate Polymerization**

Paul A. Cameron, Vernon C. Gibson,* and
Derek J. Irvine

Many methods have been described that bring about the controlled polymerization of acrylate monomers[1] including, for example, classical anionic techniques,[2] screened anionic polymerization (SAP),[3] group-transfer polymerization (GTP),[4] catalytic chain transfer (CCT),[5] reversible addition – fragmentation chain transfer (RAFT),[6] atom transfer radical polymerization (ATRP),[7] TEMPO-mediated free radical polymerization (TEMPO = 2,2,6,6-tetramethyl-1-piperidinoxyl),[8] and coordination polymerization systems based on electrophilic metal centers such as samarium,[9] zirconium,[10] and aluminum.[11] There continues to be great

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[*] Dr. P. A. Cameron,[+] Prof. V. C. Gibson
Department of Chemistry
Imperial College
South Kensington, London, SW7 2AY (UK)
Fax: (+44) 171-594-5810
E-mail: v.gibson@ic.ac.uk

Dr. D. J. Irvine
ICI Uniqema
P.O. Box 90, Wilton, Middlesbrough
Cleveland, TS90 8JE (UK)

[+] Present Address: Ineos Acrylics
P.O. Box 90, Wilton, Middlesbrough
Cleveland, TS90 8JE (UK)

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