

[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 CH₂CN dendrimer-containing solutions. The electrodes thus coated were rinsed with CH₂CN to remove any adhering solution and dried in air. The surface coverage \( \Gamma \) of the dendrimer on the electrode was determined from the integration of the redox waves, and for the example shown in Figure 1 B was found to be \( 9.7 \times 10^{-10} \text{mol Fccm}^{-2} \) and \( 1.8 \times 10^{-9} \text{ mol Fccm}^{-2} \).

[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 NaClO₄ 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 \( S + \text{enzyme}_{eq} \rightarrow P + \text{enzymeeout} \) and \( \text{enzymeout} + \text{M}_{eq} \rightarrow \text{M}_{out} + \text{M}_{atd} \), where \( M \) = mediator, \( M_{eq} = \text{O} \), or ferrocenium, \( S \) = substrate (glucose), \( P \) = product (glucolactone).

[11] \( E_0 \) of the O2 reduction – 0.83 V versus SCE at a bare carbon glassy electrode, and −0.70 V at the dendrimer modified electrode.

**Structure of Homoleptic CuI(CO)₃ Cations in CuI-Exchanged ZSM-5 Zeolite: An X-ray Absorption Study**

Carlo Lamberti, Gemma Turnes Palomo, 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(II)-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. Copper-exchanged zeolites are usually prepared by standard exchange procedures with aqueous solutions of CuI salts. Depending on the preparation and pretreatment conditions, they contain variable mixtures of copper species in different oxidation and aggregation states.[1, 2] Products containing exclusively isolated CuI ions can be prepared by reaction of H-zeolites with CuI in the gas phase.[3] Structural and spectroscopic studies have shown that the Cu-ZSM-5 thus obtained contains solely isolated CuI ions,[4] located in structurally and energetically well defined positions.[5] Hence, these materials have model character and are suitable for theoretical investigations.[5, 6]

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.[1, 2] Although binary compounds of the type CuI(CO)₃ were observed in strongly acidic media such as \( \text{H}_2\text{SO}_4, \text{CF}_3\text{SO}_3\text{H}, \text{FSO}_3\text{H}, \text{BF}_3, \text{H}_2\text{O}, \text{and HF} \),[7] none of these complexes could be isolated as solids. Only recently did Rack et al.[8] report the formation and the structural and spectroscopic characterization of \([\text{CuI(CO)}_3]^+ \) AsF₆⁻ \( (n=1-3) \).[9]

Infrared spectroscopy (Figure 1) has been very informative on the structure of intrazeolitic \([\text{CuI(CO)}_3]^+ \) species \( (n=1-3) \), and the main results can be summarized as follows:[10-12] 1) at low CO equilibrium pressures \( P_{\text{CO}} \) linear CuI(CO)₂ complexes are formed;[13, 14] 2) on increasing \( P_{\text{CO}} \) the formation of \( C_n \)-symmetric CuI(CO)₂ adducts is observed;[13, 14] 3) on decreasing the temperature, CuI(CO)₂ complexes of \( C_n \)

Figure 1. IR spectra of \([\text{CuI(CO)}_3]^+ \) 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 \([\text{CuI(CO)}_3]^+ \) aduct is shown after additional subtraction of the band of the physisorbed component at 2138 cm⁻¹. [17]
symmetry are obtained at about 80 K (see Figure 1a), characterized by the appearance of a new IR doublet at \( \nu(CO) = 2167, 2192 \text{ cm}^{-1}\).\(^{[17]}\) Note that the homogeneous counterparts form planar adducts of \( D_{\text{sh}} \) symmetry.\(^{[18]}\) 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.\(^{[3]}\), 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 \( \text{AsF}_3^- \) 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 \( \text{Cu}(\text{CO})_3 \) complexes at room temperature causes a consistent elongation of the distance between the \( \text{Cu} \) 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 \( \text{Cu} \) ions hosted in the \( \text{Cu}^2 \)-ZSM-5 matrix and the mobility of the \( \text{Cu} \) ions under the influence of the interaction with CO adsorbates.

To more deeply investigate the analogies between the chemistry of \( \text{Cu} \) in \( \text{Cu}^2 \)-ZSM-5 and that of \( \text{Cu} \) in superacidic media, we performed an EXAFS and X-ray absorption near-edge structure (XANES)\(^{[13]}\) study aimed at determining the three-dimensional structure of the \( \text{Cu}(\text{CO})_3 \) 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 carbonyl copper ions. In fact, powder XRD can not be used in this case because the low \( \text{Cu} \) content in ZSM-5 (due to the high Si/Al ratio) makes the contribution of \( \text{Cu} \) nearly insignificant with respect to that of the framework and the solvation effect induced on \( \text{Cu} \) cations by interaction with CO implies a consistent loss of long-range ordering of the reutilizing \( \text{Cu}(\text{CO})_3 \) complexes.

The results are illustrated in Figure 2 and Table 1. In Figure 2a the calculated and experimental EXAFS signals together with the partial contributions of the different two- and three-body configurations are compared; Figure 2b compares the Fourier transforms (FT) of the experimental and calculated spectra. Table 1 lists the results of the quantitative analysis. The \( \text{Cu}^2 \)-C distance obtained for the \( \text{Cu}(\text{CO})_3 \) complex (1.93 ± 0.02 Å) is very close to that previously measured for the \( \text{Cu}(\text{CO})_3 \) 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.\(^{[10]}\) (1.89 Å), Ramprasad et al.\(^{[88]}\) (1.90 Å), and Sodupe et al.\(^{[10]}\) (1.96 Å). The \( \text{Cu} \)--O distance extrapolated from this determination is 3.03 Å with a related Debye–Waller factor of \( \sigma^2_{\text{Cu}--\text{O}} = 0.013 \text{ Å}^2 \). 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 bond angle is linear within the error bars, in agreement with indirect IR evidence.\(^{[88]}\) The negative correlation parameter \( C_{RR} \) of the \( \text{Cu}^2 \)--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 carbonyl coper adduct on the basis of the orbital approach.\(^{[19]}\)

It is noteworthy that we were able to simulate the experimental signal using a bare \( \text{Cu}(\text{CO})_3 \) cluster, and this implies that the complexation effect, already evident at room temperature in the \( \text{Cu}(\text{CO})_3 \) complex,\(^{[11]}\) is now stronger and that \( \text{Cu}(\text{CO})_3 \) 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 \( \nu_{\text{sym}} \) stretching of a Si-O-Al moiety that is perturbed by the presence of \( \text{Cu} \) (see Figure 1b). In fact, the stepwise formation of intrazeolitic \( \text{Cu}(\text{CO})_3 \) complexes is accompanied by the simultaneous stepwise perturbation of the IR band at 980 cm\(^{-1}\), already attributed to \( \nu_{\text{asym}}(\text{Si-O-Al}) \) stretching that is perturbed by \( \text{Cu} \), which progressively shifts in frequency and nearly disappears upon formation of \( \text{Cu}(\text{CO})_2 \) and \( \text{Cu}(\text{CO})_2 \) complexes.\(^{[11]}\) In other words, the \( \nu_{\text{sym}}(\text{Si-O-Al}) \) frequency (usually in the range 1100–1250 cm\(^{-1}\) for zeolites) moves from a value (980 cm\(^{-1}\)) reflecting the perturbation induced by the

![Figure 2](image-url)  
**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 SS 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 \( \chi \) space.

<table>
<thead>
<tr>
<th>( r_{\text{Cu-C}} ) [Å]</th>
<th>( \sigma^2_{\text{Cu-C}} ) [Å]</th>
<th>( r_{\text{Cu-O}} ) [Å]</th>
<th>( \sigma^2_{\text{Cu-O}} ) [Å]</th>
<th>( \theta_{\text{Cu-C-O}} ) [°]</th>
<th>( \sigma^2_{\text{Cu-C-O}} ) [°]</th>
<th>( C_{RR} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.93 ± 0.02</td>
<td>0.022 ± 0.006</td>
<td>1.12 ± 0.03</td>
<td>0.005 ± 0.02</td>
<td>180 ± 10</td>
<td>100 ± 50</td>
<td>−0.65 ± 0.30</td>
</tr>
</tbody>
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Table 1. Quantitative results of the EXAFS data analysis with the coordination number \( N \) fixed at three; errors were calculated by a \( \chi^2 \) statistical analysis with a confidence level of 95%.
bonded Cu$^+$ 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$^+$ 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(II) 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(II)CO$_3$ cluster from EXAFS data was not possible.

Further information on the geometry of the Cu(II)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(II)CO$_3$ clusters with $C_n$ “umbrella-shaped” structures by starting from the planar configuration ($D_{4h}$: $\alpha = 90^\circ$) and reducing the polar angle $\alpha$ of the CO ligands with respect to the $z$ axis down to $\alpha = 30^\circ$. 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 $\alpha$ 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 $70 < \alpha < 90^\circ$.

At $\alpha = 54^\circ$ 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 $\alpha = 60^\circ$. A value of $\alpha = 90^\circ$ or close to $90^\circ$ must be rejected on the basis of the IR spectroscopic data[10, 11] (only one IR-active band is expected for a Cu(II)CO$_3$ complex with $D_{4h}$ symmetry). In addition, the steric hindrance of the zeolitic walls makes values of $\alpha$ larger than 80° unreasonable. Hence, we concluded that, due to the interaction with the zeolitic walls, the structure of the Cu(II)CO$_3$ complexes deviates from the planar form typical of the homogeneous counterparts, with an $\alpha$ value in the range of 60 – 80°. The interaction must however be sufficiently weak to preclude the determination of the Cu-O distance by EXAFS. From the above XAS data, the high structural definition of the Cu$^+$ complexes in ZSM-5 is emerging.[20] This result allows them to be classified among the best heterogeneous counterparts of the homoleptic Cu(II)CO$_3$ cations ($n = 1 – 3$) synthesized under homogeneous conditions.

**Experimental Section**

Cu$^+$-ZSM-5 (Si/Al = 14/1) was prepared by reaction of the corresponding protic form with gaseous CuCl at 673 K.[21] 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 $N_x$ and Ar-filled ion chambers for measuring the incident ($I_i$) and transmitted ($I_t$) beams, respectively. A reliable energy calibration was achieved by measuring the fluorescence of Cu metal foil placed after $I_i$. XAS and IR spectra were obtained by using the same cell equipped with Mylar and KBr windows, respectively. The Cu(II)CO$_3$ complex was measured at 80 K ($p_{\text{CO}} = 10$ Torr), and the Cu(II)CO$_3$ and Cu(II)CO$_3$ 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.[22] 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.[23] Muffin Tin radii were chosen according to the Norber criterion,[24] and a 10% overlap was allowed between contiguous spheres. A detailed description of both EXAFS and XANES computations is available as supporting information.

Received: January 21, 2000 [Z14582]

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

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Many methods have been described that bring about the controlled polymerization of acrylate monomers 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-piperidinyl)[8] and coordination polymerization systems based on electrophilic metal centers such as samarium,[9] zirconium,[10] and aluminum.[11] There continues to be great

[7] The XANES spectrum of the sample before CO dosage (not reported) shows a prominent pre-edge peak due to the 1s P →4p electronic transition, with an intensity of 0.08 in normalized absorption and an inflection point at 8982.7 eV (−0.25 Ry in the scale of Figure 4). Note that the zero energy point (0.00 Ry) has been located by the program CONTINUUM[22] at 8984.8 eV. Upon formation of Cu(CO)3 complexes (top curve in Figure 3) the peak loses intensity (0.42 in normalized absorption) and shifts towards lower energies (8981.2 eV i.e. −0.26 Ry). For comparison, note that the first inflection point in Cu foil, Cu2O and CuO model compounds are observed at 8979.0, 8980.9 and 8983.9 eV respectively (i.e. −0.43, −0.29 and −0.07 Ry). A real energy calibration was achieved by measuring the absorption of a metal foil located after the sample, for more detail see: G. Turnes Palomino, P. Fissac, G. Iamello, S. Bordiga, C. Lamberti, A. Zecchina, J. Phys. Chem. B 2000, 104, 4064–4073.
[16] The observation of an IR-active doublet ν(CO) = 2151 and 2178 cm−1 indicates that the infraredactive Cu(CO)3 adducts have local Cu−CO−O symmetry, while the homogenous counterpart in [Cu(CO)3]+ (A2V+) is linear (D3h). Recently, Strauss et al. reported the stabilization of the dicarbonylcomplex(λ) ion by larger anions: [Cu6(CO)2(SO4)2]2− and [Cu(CO)3]2−/[(λ-BN-C6H4)2]+ have bent Cu(CO)3 moieties like those observed in ZSM-5: O. G. Poldyakov, S. M. Ivanova, C. M. Gaudiani, S. M. Miller, O. P. Anderson, S. M. Strauss, Organometallics 1999, 18, 3769–3771; S. M. Ivanova, S. V. Ivanov, S. M. Miller, O. P. Anderson, K. A. Solntsev, S. M. Strauss, Inorg. Chem. 1999, 38, 3756–3757. The formation at room temperature of dicarbonyls indicates that there is a strong similarity between the chemistry towards CO of Cu in superacidic media (where they are in contact with extremely weak bases like AsF5−) and in Cu/ZSM-5 (where the role of counterion is assumed by a zeolite anion). This result is in agreement with the fact that the conjugate acid H-ZSM-5 is very strong (like trifluoroacetic acid or phosphoric acid) and Cu2− is a very strong Lewis base (like BF3). This system has been extensively studied by many authors[21] and it is now considered to be a typical example of a metal−ligand coordinate covalent bond.
[17] The IR spectrum of the Cu(CO)3 complex shown in Figure 1a (solid line) was obtained after the subtraction of the band at 2358 cm−1, which is presumably due to liquidlike CO physisorbed in the zeolite channels (S. Bordiga, D. Scarano, G. Spoto, A. Zecchina, C. Lamberti, C. Otero Areán, Vib. Spectrosc. 1993, 5, 69–74). This band was previously wrongly attributed by us to a third component of the tricarbonyl adduct.[10,11]