

Well defined carbonyl complexes in Ag⁺- and Cu⁺-exchanged ZSM-5 zeolite: a comparison with homogeneous counterparts

S. Bordiga^{a,*}, G. Turnes Palomino^a, D. Arduino^a, C. Lamberti^a, A. Zecchina^a,
C. Otero Areán^b

^a *Dipartimento di Chimica IFM, Via P. Giuria 7, I-10125 Turin, Italy*

^b *Departamento de Química, Universidad de las Islas Baleares, 07071 Palma de Mallorca, Spain*

Abstract

Ag⁺-ZSM-5 and Cu⁺-ZSM-5 samples were prepared starting from (NH₄)⁺-ZSM-5 and achieving, in both cases, a nearly total cation exchange. EXAFS studies have shown that the local environments of Ag⁺ and Cu⁺ ions are very similar, being Cu⁺ surrounded by 2.5 ± 0.3 oxygen atoms at 2.00 ± 0.02 Å and Ag⁺ surrounded by 2.5 ± 0.4 oxygen atoms at 2.30 ± 0.03 Å. Low temperature IR spectroscopy has shown formation of M⁺(CO)_n species where n = 1,2 for Ag⁺ and n = 1,2,3 for Cu⁺. However, the corresponding ν(C–O) values are quite different: Cu⁺(CO) species absorb at 2157 cm⁻¹, while Ag⁺(CO) is associated with a band at 2192 cm⁻¹. Furthermore, Cu⁺(CO)₂ species were observed at 2178 and 2151 cm⁻¹ (symmetric and asymmetric stretching, respectively) while Ag⁺(CO)₂ gave corresponding bands at 2190 and 2184 cm⁻¹. Comparison with literature data for Cu⁺ and Ag⁺ carbonyls formed as homogeneous compounds showed that notable analogies, but also significant differences, exist between homogeneous and heterogeneous systems. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: ZSM-5 zeolite; Ag⁺-ZSM-5; Cu⁺-ZSM-5

1. Introduction

Zeolites and related microporous materials are widely employed to obtain stable entrapped species such as small metal clusters and coordination complexes. The protective effect of the framework [1–5] on the intrazeolite complexes allows to study structures which are not easily obtainable in homogeneous conditions [6–10]. In some cases, metal-exchanged zeolites are active catalysts in economically important processes. For instance, Cu⁺-ZSM-5 has attracted

much interest for the direct conversion of NO into N₂ and O₂ [11–13]. The high activity of Cu⁺-ZSM-5, as compared to other supported copper catalysts, is probably related to the high coordinative unsaturation of extra-framework Cu⁺ ions hosted in the MFI structure-type framework [14,15]. These ions are known to have a high reactivity, as demonstrated by: (i) the formation of end-on Cu⁺(N₂) dinitrogen stable complexes at RT [14,16]; (ii) the formation, upon interaction with NO at 77 K, of Cu⁺(NO) and Cu⁺(NO)₂ stable complexes, which evolve spontaneously with formation of nitrous oxides and oxidized copper species when temperature is increased [14,17,18]; (iii) the for-

* Corresponding author. Tel.: +39-011-670-7858; Fax: +39-011-670-7855; E-mail: bordiga@ch.unito.it

mation, upon contact with CO at 77 K, of well defined and stable $\text{Cu}^+(\text{CO})$, $\text{Cu}^+(\text{CO})_2$ and $\text{Cu}^+(\text{CO})_3$ complexes [14,15,18].

As far as Ag^+ -exchanged zeolites are concerned [19], several catalytic and photocatalytic processes have been performed by exploiting the presence of both isolated Ag^+ ions and aggregated Ag_n clusters. Among them we can mention the photochemical dissociation of H_2O into H_2^+ and O_2 [20,21], the disproportionation of ethylbenzene [22], the oxidation of ethanol to acetaldehyde [23], the aromatization of alkanes, alkenes and methanol [24,25], the selective reduction of NO by ethylene [26] and the photocatalytic decomposition of NO [27–32].

However, the complexity of the interaction between transition-metal-exchanged zeolites and adsorbed molecules is not well understood, and this hinders understanding of many of the above-mentioned processes. It is the aim of this paper to analyse the interaction of CO with Cu^+ and Ag^+ ions in ZSM-5 zeolites and to compare the carbonyl species thus formed with known counterparts in homogeneous systems. Characterization of the heterogeneous (zeolite) systems has been performed by using mainly XANES, EXAFS and FTIR spectroscopies. Similarities with homogeneous complexes have been found but relevant differences also exist.

2. Experimental

Both Ag^+ -ZSM-5 and Cu^+ -ZSM-5 were prepared starting from the same NH_4 -ZSM-5 sample (Si/Al = 14, prepared in EniChem SpA, centro Ricerche di Novara). Ag^+ -ZSM-5 was obtained following a conventional procedure of ion exchange with an aqueous solution of AgNO_3 . For preparing Cu^+ -ZSM-5, gas phase CuCl was used for ion exchange (see Ref. [18] for more details). In both cases, a nearly total exchange has been obtained (corresponding to one Cu^+ or Ag^+ ion for every framework aluminium atom). This was inferred from the fact that corresponding IR spectra obtained after

thermal activation of the sample wafers did not show any appreciable sign of the O–H stretching band of bridged Si–(OH)–Al groups, as shown in Fig. 1. Note that this hydroxy groups would be formed from non-exchanged NH_4^+ ions upon thermal activation. Care was taken to prevent, as much as possible, exposure of Ag^+ -ZSM-5 samples to light, since long exposures could lead to photoreduction of Ag^+ ions and formation of metal clusters.

XANES, EXAFS and IR measurements have been performed on self-supporting wafers carefully activated under a dynamic vacuum at 673 K for 2 h for Cu^+ -ZSM-5, and at 400 K for 1 h for Ag^+ -ZSM-5. These activation temperatures were chosen because of the need to: (i) ensure total evacuation of excess CuCl from Cu^+ -ZSM-5, and (ii) avoid the risk of reduction of Ag^+ ions in the case of Ag^+ -ZSM-5.

Cu and Ag K-edge X-ray absorption measurements were performed using, for Cu^+ -ZSM-5 samples the synchrotron radiation of the EXAFS1 station at LURE (Orsay), and for Ag^+ -ZSM-5 samples the BM29 beamline at the ESRF (Grenoble). In both cases, angle/energy calibration has been achieved by measuring the edge position of the corresponding metal foil. Each EXAFS spectrum, measured in transmission mode, was recorded three times under the same experimental conditions, and extracted $\chi(k)$ functions have been averaged before data analy-

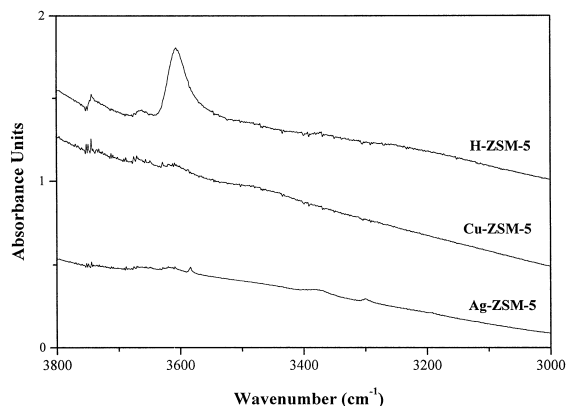


Fig. 1. IR spectra in the OH stretching region of H-ZSM-5 and of the Cu^+ - and Ag^+ -exchanged samples.

sis. Standard deviations calculated from averaged spectra were used to estimate the weight of statistical noise in the evaluation of the error associated with each structural parameter. The EXAFS data analysis has been performed following standard procedures [33] using programs developed by Michalowicz [34].

For IR measurements, we have used an IR cell designed to allow in situ high-temperature treatments, gas dosage and low-temperature measurements. The IR spectra were recorded, at 2 cm^{-1} resolution, on a BRUKER FTIR-66 spectrometer equipped with a MCT detector.

3. Results and discussion

3.1. Cation environment: EXAFS study

Fig. 2 summarizes the results obtained from the EXAFS data analysis on both systems. The

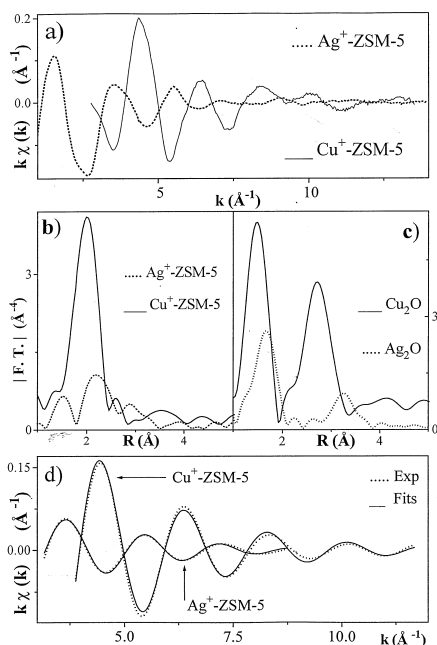


Fig. 2. EXAFS results obtained on Cu^+ -ZSM-5 and Ag^+ -ZSM-5 samples. (a) Experimental $k\chi(k)$ functions; (b) k^3 -weighted and phase-corrected FT functions; (c) same for the Ag_2O and Cu_2O model compounds but without phase correction; (d) back-FIT of the first shell filtered data for Ag^+ -ZSM-5 and Cu^+ -ZSM-5, and corresponding fits.

experimental $k\chi(k)$ functions are reported in part (a). The slightly higher period observed in the oscillation of the $\chi(k)$ for the Cu^+ -ZSM-5 is due to a lower cation-oxygen distance, as compared with Ag^+ -ZSM-5. In both spectra, the absence of any beats in the oscillations of the EXAFS functions suggests that the main contribution to the overall signal is due to only one coordination shell.

Fig. 2b reports the k^3 -weighted and phase corrected FT functions for Cu^+ -ZSM-5 (full line) and Ag^+ -ZSM-5 (dotted). For comparison, corresponding functions for Cu_2O and Ag_2O are reported in Fig. 2c. Fig. 2d shows fits obtained on first-shell-filtered data for Cu^+ -ZSM-5 and Ag^+ -ZSM-5. Cu–O and Ag–O signals were modelled using experimental phase and amplitude functions extracted from Cu_2O and Ag_2O , respectively. EXAFS data analysis gave a metal–oxygen distance of $2.00(\pm 0.02)\text{ \AA}$ for Cu^+ -ZSM-5, and $2.30(\pm 0.03)\text{ \AA}$ for Ag^+ -ZSM-5; corresponding coordination numbers were found to be $2.5(\pm 0.3)$ and $2.5(\pm 0.4)$, respectively. The observed differences in the metal–oxygen distance are readily assign to the larger ionic radius of Ag^+ , as compared to Cu^+ . Coordination numbers can be taken as been equal (within experimental error) in both cases. The (average) value of 2.5 for this parameter can be taken to mean that both zeolites contain two-coordinated and three-coordinated extra framework cation sites in a nearly equal proportion. Note that the much lower intensity of the Ag–O first shell peak (Fig. 2b), as compared to that for Cu–O, is due to a shorter life-time of the $1s$ core hole of excited Ag^+ ions. This effect is also shown by the reference compounds Cu_2O and Ag_2O (Fig. 2c).

For Cu^+ -ZSM-5, the presence of a single significant maximum in the k^3 -weighted FT function (Fig. 2b, full line curve) proves that no aggregates of copper-containing species were formed. For Ag^+ -ZSM-5 (Fig. 2b, dotted line) three maxima are observed: at 1.5, 2.3 and 2.9 \AA , respectively. The peak at 1.5 \AA has no real

meaning, it arises from unsubtracted low frequencies in the extraction of the $\chi(k)$ function. However, besides the 2.3 Å peak corresponding to the Ag–O contribution, there is the smaller peak at 2.9 Å which most likely corresponds to Ag–Ag contributions of small metal clusters. Note however, that the back-scattering amplitude from silver atoms is much greater than that from oxygen atoms. This implies that the fraction of total silver which is present in aggregates is in any case smaller than 3%.

3.2. Formation of carbonyl species upon adsorption of CO: IR spectroscopy

Fig. 3 shows the IR spectra in the C–O stretching region of carbon monoxide adsorbed, at liquid nitrogen temperature on the Cu^+ -ZSM-5 sample previously outgassed at 673 K. At the lowest CO equilibrium pressure (Fig. 3a) the spectrum shows a single absorption band at 2157 cm^{-1} , which according to data reported in the literature [14,18,35–38] is assigned to $\text{Cu}^+ \cdots \text{CO}$ adducts. A similar band was found for CO adsorbed at low pressure on Cu^+ -exchanged mordenite at 2160 cm^{-1} by Kuroda et al. [39] and at 2159 cm^{-1} by us [40], on a Cu^+ -Y zeolite at 2160 cm^{-1} by Huang [41] and on

Cu^+ species supported in dealuminated Y zeolite at 2159 cm^{-1} by Miessner et al. [42]. These values are to be compared with the frequency of 2143 cm^{-1} of the free molecule and to the 2127 cm^{-1} frequency observed for CO adsorbed on the unpolar (111) face of Cu_2O [43]. Fig. 3b shows that upon increasing the CO equilibrium pressure the band at 2157 cm^{-1} is substituted by two new bands at 2178 and 2151 cm^{-1} , respectively. Spectra taken at intermediate pressures (not shown) demonstrated the gradual build up of these new bands and progressive erosion of that at 2157 cm^{-1} ; two isosbestic points were also observed. These facts provide clear proof that the $\text{Cu}^+ \cdots \text{CO}$ adduct adds a second CO ligand to yield a $\text{Cu}^+(\text{CO})_2$ dicarbonyl complex. In agreement with previous reports [14,18,40,42] the bands at 2178 and 2151 cm^{-1} are assigned to the symmetric and asymmetric stretching modes, respectively, of the $\text{Cu}^+(\text{CO})_2$ complex. From the intensity ratio of the two bands in Fig. 3b, and by using the formula [44,45],

$$I_{\text{asym}}/I_{\text{sym}} = \tan^2(\theta/2)$$

(where θ is the angle between CO ligands) an angle of about 125° was inferred for the

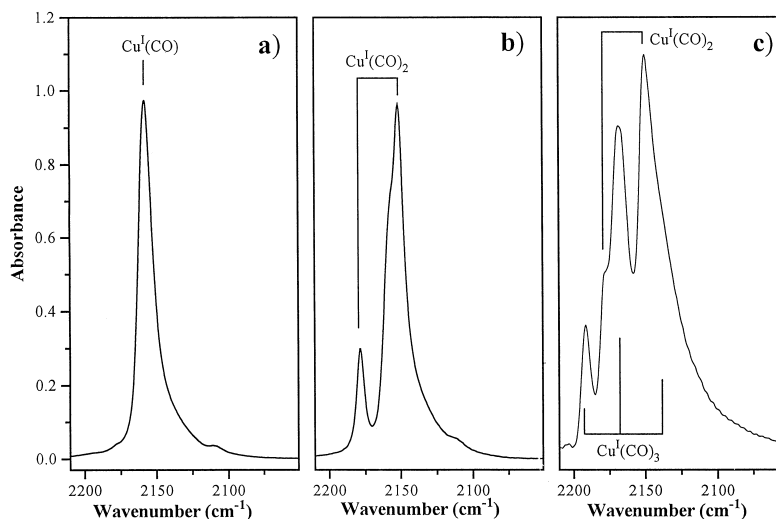


Fig. 3. IR spectra in the C–O stretching region of carbon monoxide adsorbed at liquid nitrogen temperature on Cu^+ -ZSM-5. Equilibrium pressure as follows: (a) 0.1, (b) 1 and (c) 10 Torr.

$\text{Cu}^+(\text{CO})_2$ species formed inside ZSM-5 channels. This result is in qualitative agreement with the $\theta = 113^\circ$ value recently reported by Miessner et al. [42] for a similar $\text{Cu}^+(\text{CO})_2$ complex in dealuminated Y zeolite. In this regard, it is worth noting that, even if the geometrical constraints in the supercage cavity of the faujasitic structure are less important than in the MFI channels, the θ angle shows no tendencies to increase in order to approach the linear configuration (note that due to the consistent uncertainty in the indirect determination of the θ angle, the two values of 125° and 113° should be considered as fully comparable). This means that in the determination of the structure of the intrazeolitic $\text{Cu}^+(\text{CO})_2$ complexes the electronic factors play a non-negligible role.

When the CO equilibrium pressure was further increased (Fig. 3c), new bands developed at 2192 and 2167 cm^{-1} , together with a shoulder at about 2140 cm^{-1} (shadowed by the strong band at 2151 cm^{-1}). According to arguments fully discussed elsewhere [14,15,18], we assign these new bands to $\text{Cu}^+(\text{CO})_3$ tricarbonyl species. The fact that these species give rise to three IR bands implies that the symmetry of the corresponding structure is less than C_{3v} , otherwise only two bands should be observed.

It is relevant to add that at room temperature (spectra not shown) only formation of $\text{Cu}^+(\text{CO})$ and $\text{Cu}^+(\text{CO})_2$ species was observed [14,18]. The IR bands corresponding to the latter disappeared upon outgassing, while the band at 2157 cm^{-1} (corresponding to $\text{Cu}^+ \cdots \text{CO}$ adducts) was found to be very persistent. This implies a high stability of the monocarbonyl.

Fig. 4 shows the IR spectra of CO adsorbed, at liquid nitrogen temperature and increasing equilibrium pressure, on Ag^+ -ZSM-5. At the lowest equilibrium pressures a single band is observed, at 2192 cm^{-1} . We assign this band to the fundamental C–O stretching mode of $\text{Ag}^+ \cdots \text{CO}$ adducts. A similar band, at 2195 cm^{-1} , was observed and equally assigned by Huang [46] for CO adsorbed on the faujasite-type zeolites Ag^+ -X and Ag^+ -Y. For CO adsorbed on

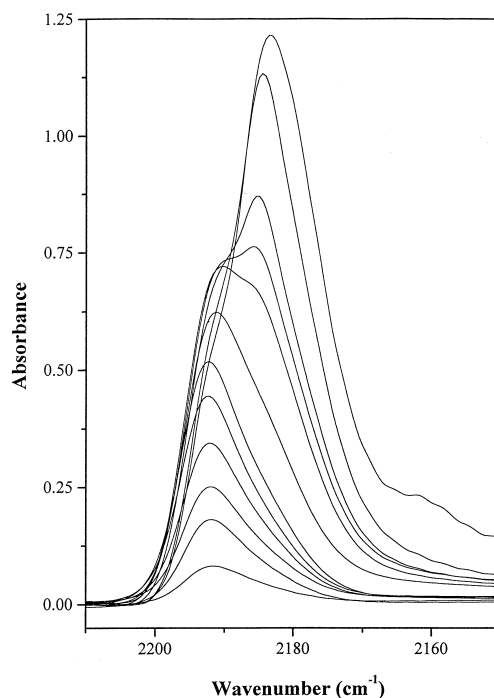


Fig. 4. IR spectra of CO adsorbed at liquid nitrogen temperature on Ag^+ -ZSM-5. Increasing equilibrium pressure from ca. 0.1 to ca. 5 Torr.

Ag^+ -exchanged zeolite A, Baumann et al. [47] reported the corresponding band at 2188 cm^{-1} . The high frequency of this band, as compared to 2157 cm^{-1} for the $\text{Cu}^+ \cdots \text{CO}$ adduct, needs some comments. Two main effects can lead to a hypsochromic shift of the C–O stretching mode (which for the free molecule appears at 2143 cm^{-1}) of CO coordinated to cationic centres: electrostatic interaction, and σ -donation from the weakly antibonding 5σ orbital of CO to the metal cation. The electrostatic effect is expected to be smaller for Ag^+ than for Cu^+ , on account of the larger ionic radius of Ag^+ . In fact, the Ag^+ ion has a size intermediate between Na^+ and K^+ , and reported C–O stretching wavenumbers for CO adsorbed on ZSM-5 exchanged with these cations are 2178 and 2166 cm^{-1} , respectively [48–50]. It should thus be clear that electrostatic effects alone cannot justify the high frequency found for $\text{Ag}^+ \cdots \text{CO}$

adducts. We must invoke a substantial amount of σ -donation. This can be understood from the fact that d^{10} ions (Ag^+ and Cu^+ have this electronic configuration) have an enhanced polarizing power [51], which increases with atomic number. We suggest that strong polarization of the CO 5σ orbital by Ag^+ ions contributes to σ -donation, and therefore to the observed high frequency of the C–O stretching in $\text{Ag}^+ \cdots \text{CO}$ adducts. Note that π -back-bonding should not operate. Absence of π -back-bonding in silver carbonyls has been tentatively justified by Hurlburt et al. [52] on account of a large Ag–C bond length. Note that π -bonding is a more sensitive function of distance than σ -bonding. Regardless the fact that the above explanation must remain tentative, it is true that all known silver carbonyls (see below) show a much higher C–O stretching frequency than other metal carbonyls [52].

When the CO equilibrium pressure is increased (Fig. 4) the band at 2192 cm^{-1} develops a shoulder at ca. 2184 cm^{-1} , which gradually becomes the main band of the spectrum. For the highest CO doses, this band shows a distinctive shoulder at 2190 cm^{-1} . We tentatively assign the band at 2184 and the shoulder at 2190 cm^{-1} to the asymmetric and symmetric stretching modes, respectively, of CO in $\text{Ag}^+(\text{CO})_2$ adducts. Coordination of a second CO molecule by $\text{Ag}^+ \cdots \text{CO}$ species would parallel the phenomenon observed for CO adsorbed on Cu^+ -ZSM-5. However, no more bands (apart from that corresponding to physisorbed CO) were observed when the CO equilibrium pressure was further increased (up to 20 Torr) for the CO/ Ag^+ -ZSM-5 system (spectra not shown). It thus seems that for Ag^+ ions polycordination to CO molecules stops at the dicarbonyl species. Note that $\text{Ag}^+(\text{CO})_2$ formed inside the channels of ZSM-5 must not be linear (otherwise no symmetric mode would be observed in the IR). The low resolution of the spectra in Fig. 4 (for high CO equilibrium pressure) would render very inaccurate any calculation of the angle between CO ligands, however,

the band profile seems to suggest a value not too far from 180° .

Also for Ag^+ -ZSM-5, it is relevant to add that in the same experiment performed at RT only the band at 2192 cm^{-1} is observed and that an increase of the CO equilibrium pressure does not yield to the formation of dicarbonyl species but only to small bathochromic shift at 2189 cm^{-1} . This band has been observed to be resistant to evacuation at RT.

After the submission of this work, an interesting paper by Hadjiivanov has appeared [53], reporting a similar IR study of CO dosed at RT and a low temperature on Ag^+ -ZSM-5. He prepared the Ag^+ -ZSM-5 sample starting from a sodium form, using the same silver salt used by us and achieving an exchange degree of 65%. The results of the experiment performed at RT are in full qualitative and quantitative agreement, and the same holds for the low CO dosages at low temperature since also Ref. [53] reports a single band at 2192 cm^{-1} . At higher CO equilibrium pressures Hadjiivanov has observed two distinct components at 2195 and 2189 cm^{-1} attributed to the symmetric and asymmetric stretching frequency of the $\text{Ag}^+(\text{CO})_2$ adducts respectively. The interpretation is again in agreement with our assignment: however the frequencies of the $\text{Ag}^+(\text{CO})_2$ complexes observed by Hadjiivanov are 5 cm^{-1} higher than those reported by us. This differences can be tentatively ascribed to the different exchange degree of the two sample. Ref. [53] also reports that no nitrosyl complexes are formed by dosing NO at RT on the Ag^+ -ZSM-5. This is in fact correct: in fact we have observed that, in order to obtain the formation of nitrosyl complexes a low temperature experiment must be performed [54].

3.3. Carbonyl species: XAS studies

Fig. 5a reports XANES spectra of Cu^+ -ZSM-5 in vacuo (dotted line) and after admission of CO (50 Torr) at room temperature (continuous line). From the previous IR spectroscopic stud-

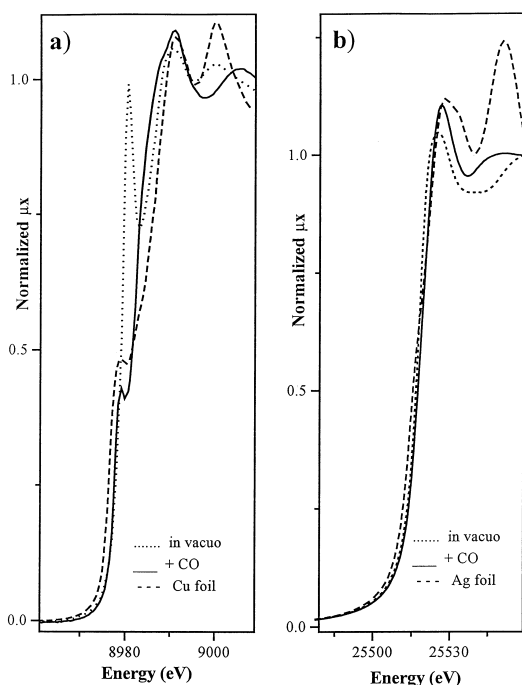


Fig. 5. Normalised XANES spectra (pre- and near-edge region) for (a) the CO/Cu⁺-ZSM-5 system, and (b) the CO/Ag⁺-ZSM-5 system.

ies, Cu⁺(CO)₂ species are known to form under these conditions. For comparison, the XANES spectrum of copper foil is also reported. The pre-edge region of the Cu⁺-ZSM-5 spectrum in vacuo shows a sharp peak at 8393 eV, which corresponds to the dipole-allowed 1s → 4p transition of Cu⁺ [9,14,30,39,55,56], thus proving the 1⁺ oxidation state of the copper ion in the zeolite. For Cu²⁺ this transition appears at 8995–8998 eV [9,39,57,58]. Upon adsorption of CO, a clear reduction of the 1s → 4p peak is observed, together with a red-shift of ca. 1 eV; simultaneously the structure of the spectrum in the near-edge region is significantly altered, revealing the modification of the coordination symmetry of Cu⁺ ions. Similar comments apply also to the XANES spectrum of Ag⁺-ZSM-5, shown in Fig. 5b, and to its modification upon adsorption of CO. Note, however, that the 1s → 5p transition of Ag⁺ appears at ca. 25518 eV (inflection point) and is less sharp than the 1s → 4p peak of Cu⁺. This is a consequence of

a considerable reduction of the 1s core-hole lifetime, which also makes the 1s → 5p transition of Ag⁺ not distinguishable from the photo-electron edge of the spectrum.

Fig. 6 shows the k³-weighted FT radial functions of the EXAFS spectra for CO/Cu⁺-ZSM-5 and CO/Ag⁺-ZSM-5 (50 Torr of CO). No phase correction was applied, since simultaneous contributions from metal-framework oxygen, metal-carbon and metal-carbonyl oxygen are present, thus rendering a quantitative analysis of the spectra very difficult to carry out. However, it is clear that the first and second significant maxima in the spectra are due to metal-framework oxygen and metal-carbon contributions, while the third maximum corresponds to the metal-carbonyl oxygen contribution. It is, however, well noted that the two first contributions strongly overlap, giving rise to interference effects as detailed in Ref. [5] for Cu⁺-ZSM-5. For the CO/Ag⁺-ZSM-5 system, this third peak goes from ca. 2.2 to 3.4 Å and covers an area significantly larger than that occupied by the corresponding peak of the CO/Cu⁺-ZSM-5 system. This fact provides further evidence that Ag⁺(CO)₂ carbonyls, which were considered when discussing IR data, are nearly linear. Note that this geometry would lead to near co-linear-

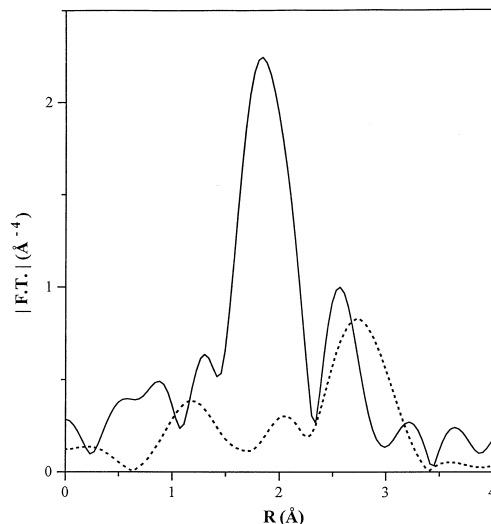


Fig. 6. k³-weighted FT radial functions for CO/Cu⁺-ZSM-5 (continuous line) and CO/Ag⁺-ZSM-5 (dotted line).

ity of five atoms, thus enhancing multiple scattering contributions to the EXAFS signal.

3.4. Comparison with homogeneous species

As discussed in Section 3.3, extra framework Cu^+ ions in Cu^+ -ZSM-5 form mono-, di- and tricarbonyls, depending on the CO equilibrium pressure. For the monocarbonyl a single C–O stretching band (at 2157 cm^{-1}) was found. However, we remark the fact that this band (Fig. 3) is strongly asymmetric, which suggests that Cu^+ ions are situated in (at least two) different local environments inside the zeolite channels. This is in agreement with EXAFS results, since a coordination number of 2.5 for the Cu^+ ion strongly suggests the present of two- and three-coordinated extra framework cations when the zeolite is in vacuo. Iwamoto and Hoshino [59] have recently given more details on the asymmetry of the 2157-cm^{-1} band.

Homogeneous Cu^+ compounds containing one CO ligand are known, and relevant examples are summarized in Table 1. Reported values of the C–O stretching frequency range from 2080 to 2178 cm^{-1} . Values smaller than 2143 cm^{-1} (the stretching frequency of free CO) clearly indicate a substantial contribution of π -back-bonding (to empty antibonding 2π orbitals of CO) which lowers the stretching frequency, while values over 2143 cm^{-1} can be explained in terms of a predominance of σ -bonding. Careful inspection of the compounds in Table 1 shows that $\nu(\text{C–O})$ increases with increasing ionicity, which reflects the fact that

less electron density is available (in the copper atom) for π -back-bonding. The value of 2157 cm^{-1} found for $\text{Cu}^+ \cdots \text{CO}$ adducts in Cu^+ -ZSM-5 is consistent with the ionic character of extra framework cations (note that otherwise they would not be easily exchangeable). However, it should be remarked that $\text{Na}^+ \cdots \text{CO}$ adducts formed in Na^+ -ZSM-5 show a C–O stretching wavenumber of 2178 cm^{-1} , being the hypsochromic shift (from 2143 cm^{-1}) due solely to electrostatic effects [37,49,50]. Since the ionic radii of Cu^+ and Na^+ are approximately the same, the 2157-cm^{-1} value found for $\text{Cu}^+ \cdots \text{CO}$ adducts seems to suggest a small degree of π -back-bonding. This back-bonding (which strengthens the metal-carbon bond) can also explain the high stability shown by these adducts.

Copper dicarbonyls formed inside the channels of Cu^+ -ZSM-5 show IR-absorption bands at 2178 and 2151 cm^{-1} . The only well characterized Cu^+ -dicarbonyl in a homogeneous phase seems to be $[\text{Cu}(\text{CO})_2]^+[\text{AsF}_6]^-$ for which a single band, at 2164 cm^{-1} , was observed (Table 1). Rack et al. [8] proposed, on account of this fact, that the homogeneous dicarbonyl has a linear structure. In contrast, the dicarbonyl formed inside the channels of Cu^+ -ZSM-5 must be angular. This can be easily explained in terms of geometrical constraints imposed by the channel wall. Note, however, that the actual value of the angle between CO ligands can be a result of a delicate balance between steric hindrance and orbital hybridization. Similarly, $\text{Cu}^+(\text{CO})_3$ species formed inside the channels of Cu^+ -ZSM-5 were found to have three IR-ac-

Table 1
Infrared data for some well-characterized (homogeneous) Cu^+ carbonyls

Complex	νCO (cm^{-1})	Reference	Remarks
$[\text{Cu}(\text{dien})\text{CO}](\text{BPh}_4)$	2080	[46]	(Diethylenetriamine)copper(I)carbonyl tetraphenylborate. White crystalline solid
$[\text{Cu}(\text{en})\text{CO}](\text{BPh}_4)$	2117	[60]	White crystals
$[\text{Cu}(\text{en})_2\text{CO}]$	2060	[60]	White crystals
$[\text{Cu}(\text{CO})]^+[\text{TFA}]^-$	2155	[61]	Copper(I)trifluoroacetate carbonyl. Ionic compound forming colorless crystals
$[\text{Cu}(\text{CO})]^+[\text{AsF}_6]^-$	2178	[8]	Brown solid
$[\text{Cu}(\text{CO})_2]^+[\text{AsF}_6]^-$	2164	[8]	Colorless, glassy solid
$[\text{Cu}(\text{CO})_3]^+[\text{AsF}_6]^-$	2183, 2206	[8]	Bright white solid

tive modes (at 2192, 2167 and 2140 cm^{-1}). They can be compared with the compound $[\text{Cu}(\text{CO})_3]^+[\text{AsF}_6]^-$ (Table 1) which only shows bands at 2183 and 2206 cm^{-1} , and was proposed to be triangular [8]. It is clear that the zeolite host imposes a distortion of the (optimum) geometry of the tricarbonyl.

A few cationic silver monocarbonyls have been described in the literature [52,62], among them $[\text{Ag}(\text{CO})]^+[\text{OTeF}_5]^-$, $[\text{Ag}(\text{CO})]^+[\text{B}(\text{OTeF}_5)_4]^-$ and $[\text{Ag}(\text{CO})]_2[\text{Zn}(\text{OTeF}_5)_4]^{2-}$; reported $\nu(\text{C}-\text{O})$ wavenumbers for these compounds are 2189, 2204 and 2203 cm^{-1} , respectively. $[\text{Ag}(\text{CO})]^+[\text{B}(\text{OTeF}_5)_4]^-$ was isolated as a pure compound, and structure determination by X-ray crystallography [62] showed a nearly linear $\text{Ag}-\text{C}-\text{O}$ linkage (176°) and an $\text{Ag}-\text{C}$ bond length of 2.10 Å. The $\text{C}-\text{O}$ stretching frequency (2204 cm^{-1}) compares well with that of 2192 cm^{-1} found for the monocarbonyl formed on Ag^+ -ZSM-5 at low CO pressure (Fig. 4). In both cases, the high value of $\nu(\text{C}-\text{O})$ provides clear evidence that CO exhibits no π -acidity in these compounds, which is also in agreement with results from recent quantum chemical ab initio calculations [63].

Cationic silver dicarbonyls containing the $[\text{Ag}(\text{CO})_2]^+$ cation and the weakly coordinating anions $[\text{B}(\text{OTeF}_5)_4]^-$, $[\text{Zn}(\text{OTeF}_5)_4]^{2-}$, $[\text{Ti}(\text{OTeF}_5)_6]^{2-}$ or $[\text{Nb}(\text{OTeF}_5)_6]^-$ have been described [52]; the corresponding $\nu(\text{C}-\text{O})$ wavenumbers are all included in the narrow range of 2196 to 2198 cm^{-1} , which is to be compared with the values of 2190 and 2184 cm^{-1} found for $\text{Ag}(\text{CO})_2$ species formed inside Ag^+ -ZSM-5 channels. $[\text{Ag}(\text{CO})_2]^+[\text{B}(\text{OTeF}_5)_4]^-$ was isolated and reported to be a hygroscopic and thermally labile compound [7,52]; the unit cell is monoclinic. The cations are located at inversion centres and have $\text{Ag}-\text{C}-\text{O}$ bond angles of 174 and 179°; i.e., the $[\text{Ag}(\text{CO})_2]^+$ moiety is roughly linear [7]. For the dicarbonyl species formed inside Ag^+ -ZSM-5 channels, the already discussed IR and EXAFS data suggest an angular structure, although the angle should not depart much from 180°. We performed computer

modelling studies which showed that, because of geometrical constraints, the zeolite encaged dicarbonyl cannot be linear. The maximum value of the $(\text{CO})-\text{Ag}-(\text{CO})$ angle could not be precisely determined, because the exact extent till which Ag^+ ions are displaced from their original position when they coordinate CO ligands is not known. However, we found that an angle of at least 165° would be tolerated.

In conclusion, comparison of our studies on carbonyl species formed upon adsorption of CO by Cu^+ -ZSM-5 and Ag^+ -ZSM-5 with data for analogous homogeneous compounds shows that the chemical and structural principles involved are very alike. However, some structural differences exist between both types of carbonyl species. These differences, which are mainly due to steric constraints imposed by the zeolite host can affect chemical reactivity, including catalytic activity. More knowledge has yet to be gained on the details of intrazeolite chemistry in order to boost technical applications of zeolite encaged chemical species.

Acknowledgements

We are indebted to F. Villain and A. Filipponi for providing helpful and important assistance during the EXAFS experiment at LURE (proposal CK 007), and at the ESRF (proposal CH-377) respectively. The European Community is gratefully acknowledged for a TMR grant to G.T.P.

References

- [1] G.A. Ozin, A. Kuperman, A. Stein, *Angew. Chem. Int. Ed. Engl.* 28 (1989) 359.
- [2] T. Bein, P. Enzel, *Angew. Chem. Int. Ed. Engl.* 28 (1989) 1692.
- [3] A.E. Aliev, K.D.M. Harris, R.C. Mordi, *J. Chem. Soc., Faraday Trans.* 90 (1994) 1323.
- [4] S. Hashimoto, *Chem. Phys. Lett.* 262 (1996) 292.
- [5] A. Zecchina, S. Bordiga, G. Turnes Palomino, D. Scaromo,

- C. Lamberti, M. Saholaggio, *J. Phys. Chem. B* 103 (1999) in press.
- [6] K. Maruszewski, D.P. Strommen, K. Handrich, J.R. Kincaid, *Inorg. Chem.* 30 (1991) 4579.
- [7] P.K. Hurlburt, J.J. Rack, S.F. Dec, O.P. Anderson, S.H. Strauss, *Inorg. Chem.* 32 (1993) 373.
- [8] J.J. Rack, J.D. Webb, S.H. Strauss, *Inorg. Chem.* 35 (1996) 277.
- [9] C. Lamberti, G. Spoto, D. Scarano, C. Pazé, M. Salvalaggio, S. Bordiga, A. Zecchina, G. Turnes Palomino, F. D'Acapito, *Chem. Phys. Lett.* 269 (1997) 500.
- [10] H. Willner, F. Aubke, *Angew. Chem. Int. Ed. Engl.* 36 (1997) 2403.
- [11] M. Iwamoto, H. Hamada, *Catal. Today* 10 (1991) 57.
- [12] Y. Li, W.K. Hall, *J. Phys. Chem.* 94 (1990) 6145.
- [13] M. Shelef, *Chem. Rev.* 95 (1995) 209, and references therein.
- [14] C. Lamberti, S. Bordiga, M. Salvalaggio, G. Spoto, A. Zecchina, F. Geobaldo, G. Vlaic, M. Bellatreccia, *J. Phys. Chem. B* 101 (1997) 344.
- [15] A. Zecchina, S. Bordiga, M. Salvalaggio, G. Spoto, D. Scarano, C. Lamberti, *J. Catal.* 173 (1998) 500.
- [16] G. Spoto, S. Bordiga, G. Ricchiardi, D. Scarano, A. Zecchina, F. Geobaldo, *J. Chem. Soc., Faraday Trans.* 91 (1995) 3285.
- [17] G. Spoto, S. Bordiga, D. Scarano, A. Zecchina, *Catal. Lett.* 13 (1992) 39.
- [18] G. Spoto, A. Zecchina, S. Bordiga, G. Ricchiardi, G. Martra, G. Leofanti, G. Petrini, *Appl. Catal. B* 3 (1994) 151.
- [19] T. Sun, K. Seff, *Chem. Rev.* 94 (1994) 857.
- [20] P.A. Jacobs, J.B. Uytterhoeven, H.K. Beyer, *J. Chem. Soc. Chem. Commun.* (1977) 128.
- [21] G. Calzaferri, S. Hug, T. Hugenotbler, B. Sulzberger, *J. Photochem.* 26 (1984) 109.
- [22] T. Baba, Y. Ono, *Zeolites* 7 (1987) 292.
- [23] D. Lai, J. Li, P. Huang, D. Wang, *J. Mater. Gas Chem.* 3 (1994) 211.
- [24] Y. Ono, K. Osako, G.-J. Kim, Y. Inoue, *Stud. Surf. Sci. Catal.* 84 (1994) 1773.
- [25] Y. Inoue, K. Nakashiro, Y. Ono, *Microporous Mater.* 4 (1995) 379.
- [26] S. Sato, Y. Yu-u, H. Yahiro, N. Mizuno, M. Iwamoto, *Appl. Catal.* 70 (1991) L1.
- [27] M. Matsuoka, E. Matsuda, K. Tsuji, H. Yamashita, M. Anpo, *Chem. Lett.* (1995) 375.
- [28] M. Matsuoka, E. Matsuda, K. Tsuji, H. Yamashita, M. Anpo, *J. Mol. Catal. A* 107 (1996) 399.
- [29] K. Masuda, K. Tsujimura, K. Shinoda, T. Kato, *Appl. Catal. B* 8 (1996) 33.
- [30] M. Anpo, M. Matsuoka, H. Yamashita, *Catal. Today* 35 (1997) 177.
- [31] M. Anpo, G.Z. Shu, H. Mishima, M. Matsuoka, H. Yamashita, *Catal. Today* 39 (1997) 159.
- [32] M. Flytzani-Stephanopoulos, Z. Li, *Appl. Catal. A* 165 (1997) 15.
- [33] F.W. Lytle, D.E. Sayers, E.A. Stern, *Physica B* 158 (1989) 701.
- [34] A. Michalowicz, *J. Phys. IV (France)* 7 (1997) C2–235.
- [35] Y. Huang, *J. Am. Chem. Soc.* 95 (1973) 6636.
- [36] M. Iwamoto, H. Yahiro, K. Tanda, N. Mizuno, Y. Mine, S. Kagawa, *J. Phys. Chem.* 95 (1991) 3727.
- [37] A. Zecchina, C. Otero Areán, *Chem. Soc. Rev.* 25 (1996) 187.
- [38] Y. Kuroda, H. Maeda, Y. Yoshikawa, R. Kumashiro, M. Nagao, *J. Phys. Chem. B* 101 (1997) 1312.
- [39] Y. Kuroda, Y. Yoshikawa, S. Konno, H. Hamano, H. Maeda, R. Kumashiro, M. Nagao, *J. Phys. Chem.* 99 (1995) 10621.
- [40] C. Lamberti, S. Bordiga, A. Zecchina, M. Salvalaggio, F. Geobaldo, C. Otero Areán, *J. Chem. Soc., Faraday Trans.* 94 (1998) 1519.
- [41] Y. Huang, *J. Am. Chem. Soc.*, 95 (1973) 6636.
- [42] H. Miessner, H. Landmesser, K. Richter, *J. Chem. Soc., Faraday Trans.* 93 (1997) 3417.
- [43] D. Scarano, S. Bordiga, C. Lamberti, G. Spoto, G. Ricchiardi, A. Zecchina, C. Otero Areán, *Surf. Sci.* 411 (1998) 272.
- [44] P.S. Braterman, *Metal Carbonyl Spectra*, Academic Press, London, 1975, p. 43.
- [45] E. Garrone, C. Morterra, A. Zecchina, *Z. Naturforsch.* 42B (1987) 728.
- [46] Y. Huang, *J. Catal.* 32 (1974) 482.
- [47] J. Baumann, R. Beer, G. Calzaferri, B. Waldeck, *J. Phys. Chem.* 93 (1989) 2292.
- [48] S. Bordiga, E. Escalona Platero, C. Otero Areán, C. Lamberti, A. Zecchina, *J. Catal.* 137 (1992) 179.
- [49] A. Zecchina, S. Bordiga, C. Lamberti, G. Spoto, L. Carnelli, C. Otero Areán, *J. Phys. Chem.* 98 (1994) 9577.
- [50] C. Lamberti, S. Bordiga, F. Geobaldo, A. Zecchina, C. Otero Areán, *J. Chem. Phys.* 103 (1995) 3158.
- [51] K. Fajans, *Naturwissenschaften* 11 (1923) 165.
- [52] P.K. Hurlburt, J.J. Rack, J.S. Luck, S.F. Dec, J.D. Webb, O.P. Anderson, S.H. Strauss, *J. Am. Chem. Soc.* 116 (1994) 10003.
- [53] K.I. Hadjiivanov, *Microporous Mesoporous Mater.* 24 (1998) 41.
- [54] S. Bordiga, C. Lamberti, G. Turnes Palomino, F. Geobaldo, D. Arduino, A. Zecchina, *Microporous Mesoporous Mater.*, 1999, in press.
- [55] L.S. Kau, D.J. Spira-Solomon, J.E. Penner-Hajin, K.O. Hodgson, E.I. Solomon, *J. Am. Chem. Soc.* 109 (1987) 6433.
- [56] N.J. Blackburn, R.W. Strang, J. Reedijk, A. Volbeda, A. Farooq, K.D. Karlin, J. Zubieta, *Inorg. Chem.* 28 (1989) 1349.
- [57] W. Grünert, N.W. Hayes, R.W. Joyner, E.S. Shpiro, M. Rafiq, H. Siddiqui, G.N. Baeva, *J. Phys. Chem.* 98 (1994) 10832.
- [58] J.M. Tranquada, S.M. Heald, A.R. Moodenbaugh, *Phys. Rev. B* 36 (1987) 5263.
- [59] M. Iwamoto, Y. Hoshino, *Inorg. Chem.* 35 (1996) 6918.
- [60] M. Pasquali, C. Floriani, A. Gaetani-Manfredotti, *Inorg. Chem.* 19 (1980) 1191.
- [61] A.F. Scott, L.L. Wilkening, B. Rubin, *Inorg. Chem.* 8 (1969) 2533.
- [62] P.K. Hurlburt, O.P. Anderson, S.H. Strauss, *J. Am. Chem. Soc.* 113 (1991) 6277.
- [63] A. Veldkamp, G. Frenking, *Organometallics* 12 (1993) 4613.