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IR STUDY OF CO CHEMISORBED ON METALLIC Cu DISPERSED IN ZnO

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Abstract. The adsorption of CO on Cu/ZnO has been studied by i.r. transmission spectroscopy. The CO stretching vibrations are observed at 2103 and 2080 cm$^{-1}$; the first identified with an "on top" chemisorbed species, the second with a species lying"flat" on the surface.

Adsorption studies of some simple molecules on different single-crystal Cu surfaces have been performed by several combined techniques (IRAS, ELS, LEEDS, UPS). As a result there is now a rather detailed description of such adsorption and therefore it seemed interesting to study the adsorption on small Cu metal particles using the insight gained on single-crystals.

The Cu/ZnO supported samples were prepared and characterized by Petrini et al. (1). The copper content is 3% in Cu atoms. The mean particle size, determined by O$_2$ adsorption at 150K (2), is ~20 Å, if a spherical shape of the particles and a O/Cu ratio of 1/2 are assumed.

In this work we have studied by i.r. transmission spectroscopy the CO adsorption at 77 and 300K on clean Cu/ZnO surfaces and on O$_2$ or N$_2$O pretreated ones. Preadsorption of O$_2$ has been performed at 77 K and that of N$_2$O at 300 K, these being the conditions that allow an oxygen extended surface coverage without bulk oxidation. The sample discs were inserted in a cell which allows to perform thermal treatments in controlled atmosphere or in vacuum and to obtain spectra at different temperatures. The spectra were recorded with a 580 B Perkin-Elmer spectrophotometer connected with a 3600 Kata Station.

Results and discussion. CO adsorption at 300 K on clean surface is slightly pressure dependent: only one band grows at increasing equilibrium pressure ($P_{eq}=2100$ cm$^{-1}$, FWHM=12 cm$^{-1}$), no shift was observed with increasing coverage.

CO adsorption at 77 K on clean surface gives rise to a more complex spectrum: three bands are present at 2180, 2103, and 2080 cm$^{-1}$. The first one is slightly pressure dependent ($P_{eq}=3$ torr) and its frequency shows a red shift with increasing coverage and can be assigned to a CO chemisorbed on Zn ions(3). The other two are irreversible under outgassing at 77 K: the 2103 cm$^{-1}$ is sharp and strong (FWHM =10 cm$^{-1}$), the 2080 cm$^{-1}$ broad and weak (FWHM =40 cm$^{-1}$). Under outgassing at 200 K the 2080 cm$^{-1}$ component completely disappears and at the same time the 2103 cm$^{-1}$ one shifts to 2100 cm$^{-1}$. 


Fig. 1 shows the comparison between CO adsorbed at 300 and 77 K (a and b curves respectively) for the maximum coverage and the difference spectrum b-a (curve c).

Infrared reflection experiments on Cu monocrystals (4) indicate that, at saturation, the CO stretching mode on Cu stepped surfaces (755), (311), (211) fall at 2103-2110 cm\(^{-1}\), while the low-index planes give CO bands at 2070-2088 cm\(^{-1}\) and have been ascribed to "on top" bounded CO. The two bands of CO adsorbed on our samples fall in these two regions. As regard to the 2103 cm\(^{-1}\) band, its position, intensity and FWHM are characteristic of an "on top" CO chemisorption. Moreover the pressure and temperature ranges of its existence on the surface are the same as shown by the on top species adsorbed on monocrystals. As far as the 2080 cm\(^{-1}\) band is concerned, its FWHM, intensity pressure, and temperature dependence suggest an alternative binding mode.

Angle-resolved photoemission experiments (5) on the stepped Cu (311) plane have demonstrated the existence of a CO species in which the molecule lies "flat" on the surface, parallel to the step direction, the range of pressure and temperature of its existence being the same as for our species related to the 2080 cm\(^{-1}\) band. Measurements of surface potential changes (4) with CO coverage at 77 K show the existence at this temperature of two adsorption stages, which can be correlated with changes in the LEED patterns (4). The second stage was discussed in terms of additional CO molecules bound bridged or tilted. Neither hypothesis was supported by IRAS experiments (4).

The presence of "flat" CO molecules could be the reason of this discrepancy. In fact molecules lying flat on the surface would not be seen in i.r. as the dipole would be effectively screened by the metal. It was however suggested that the "metal selection rule" should apply only at metal particles larger than 20 Å (6). In our case the dispersion of the metal particles is sufficient to weaken the selection rule.

We propose to assign the 2080 cm\(^{-1}\) band to a species of this type.

The two species show a different behaviour with respect to the two different oxidation treatments.
Fig. 2 shows the comparison between the i.r. spectra of the CO adsorbed at 77 K on a clean sample (curve a) and on a sample previously contacted with O₂ at 77 K and subsequently evacuated (curve b); curve c is the difference spectrum (a-b).

Two effects are produced by the preadsorption of oxygen: i) the broad band at 2080 cm⁻¹ is missing; ii) the band at 2103 is shifted to higher frequency (2116 cm⁻¹), its FWHM and intensity being almost unaffected.

The N₂O preadsorption at 300 K (not shown for brevity) produces the depletion of the 2080 cm⁻¹ band and a very small effect on the 2103 cm⁻¹ one (a shift from 2103 to 2105 cm⁻¹ without changes in its intensity).

The "flat" species is destroyed by the two oxidation processes illustrated, while the "on top" species is strongly perturbed by O₂ interaction at 77 K and only slightly perturbed by N₂O interaction.

A scheme which allows to explain all the above data is:
In the scheme, the "on top" species have been assumed to be coordinated to a Cu atom located at the external edge of a step, the "flat" species coordinated to the first uncoordinated Cu atom on the internal edge.

In fact theoretical calculations(7) predict that atoms at the external edge of metal surfaces are relatively electropositive if compared with those of non stepped surfaces. On the contrary the atoms at the internal edges are relatively electronegative if compared with those of non stepped faces. Therefore the first would be the most suitable to give "on top" species, while the second would better stabilize a flat lying geometry, being more efficient in donating electrons to the CO $2\pi$ orbital.

This scheme allows us to explain the different effect of the two oxidization interactions. When an O$_2$ interaction is performed the more active sites, i.e. the external edge atoms, decompose the O$_2$ molecule and the oxygen atoms remain chemisorbed on these sites; the subsequent CO "on top" chemisorption reveals a Cu site strongly modified as a consequence of a charge transfer from the copper to the oxygen(8).

When the oxidization interaction is performed with the N$_2$O, if the decomposition occurs as shown in the scheme, the oxygen atom is left on the first Cu atoms of the internal edge and therefore the subsequent CO chemisorption on the external edge atoms is only slightly perturbed.

In either case the oxygen does not allow the formation of the flat species. Since all the spectroscopic evidences of CO on Cu can be interpreted with the proposed scheme, we can infer that almost all the Cu exposed atoms are present as external edge atoms or as internal edge atoms. This fact can be a consequence of the very mild condition of preparation that produces rough or "incomplete" microcrystals.

References.