Spectroscopic Evidence for a New Surface Carbonyl Species on a Cu/ZnO Catalyst

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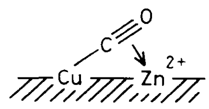
CO chemisorption on reduced Cu/ZnO catalysts gives an isolated band at 1580 cm^{-1} assigned to the CO stretching frequency of an unusual four-electron donor carbonyl species.

Catalysts for methanol synthesis must be able to activate the molecule so that the CO triple bond is weakened in order to facilitate hydrogen attack, but without bond breaking.

Although one of the precursors hypothesized[1] is a molecule of CO bonded to a surface by both the carbon and oxygen atoms, no spectroscopic evidence for its formation has been



(1)

reported till now. We report here evidence that a CO species, bonded in a novel bridging mode to the surface, is formed on a reduced Cu/ZnO catalyst. I.r. spectra were recorded on a Perkin-Elmer 580B spectrometer equipped with a Data Station 3600.

Samples with a different copper content (3—10 Cu atom %) have been prepared and characterized as described elsewhere.[2] The characterization of the reduced samples[3,4] leads to the conclusions that the catalyst is composed of flat copper metal particles, epitaxially grown on ZnO microcrystals. CO adsorption at 77 K produces bands in the 2200—2000 cm^{-1} range as reported in Figure 1, curve (a). The bands have been previously assigned[3—5] as follows: the band at 2178 cm^{-1} to CO adsorbed linearly on zinc ions, the 2098 cm^{-1} one to CO linearly adsorbed on Cu(0) extended surface areas, and the 2070 cm^{-1} one to CO linearly bonded to Cu(0) borderline atoms.

On outgassing at 77 K the band at 2178 cm^{-1} gradually decreases and blue-shifts to 2198 cm^{-1}, and finally disappears after 30 min outgassing, Figure 1, curve (b). Outgassing at increasing temperature gives rise to a gradual decrease in intensity of the 2098 and 2070 cm^{-1} bands, while a new band at 1580 cm^{-1} increases in intensity. At 298 K this band dominates the spectrum, Figure 1, curve (c). No bands are detected in the C–H stretching region.

A band at 1580 cm^{-1} is characteristic of a CO double bond stretching mode. However, its assignment to the asymmetric CO stretching of a carbonate-like or a formate species, or to the stretching of a formyl species, can be excluded because of the absence of other correlated bands at lower frequency or in the C–H stretching region. Therefore this species must be a carbonyl ligand.

An homogeneous complex $Mn_2(CO)_5(Ph_2PCH_2PPh_2)_2$ is known.[6] It shows a CO stretching mode at 1645 cm^{-1} assigned to a carbonyl group bonded to both the Mn atoms, but not by the usual symmetrical bridging mode. It is bonded through the carbon to one Mn atom and strongly interacts with the other one *via* the π-orbital of the CO bond. The CO molecule is acting as a four-electron donor ligand, with two electrons donating to each Mn atom.

We propose a similar structure for the carbonyl group absorbing at 1580 cm^{-1}, as illustrated in (**1**).

Our i.r. experiments also provide evidence for the structure as follows. In Figure 2 spectra obtained after CO–O_2 interaction in two different ways are compared: curve (a) is the spectrum obtained after contact at 77 K with CO on a preoxidized sample; curve (b) is the spectrum obtained after oxidizing at 77 K a sample previously covered with CO. In curve (a) the band at 2198 cm^{-1} is present, while the bands at 2070 and 2098 cm^{-1} on the reduced samples are shifted to 2140

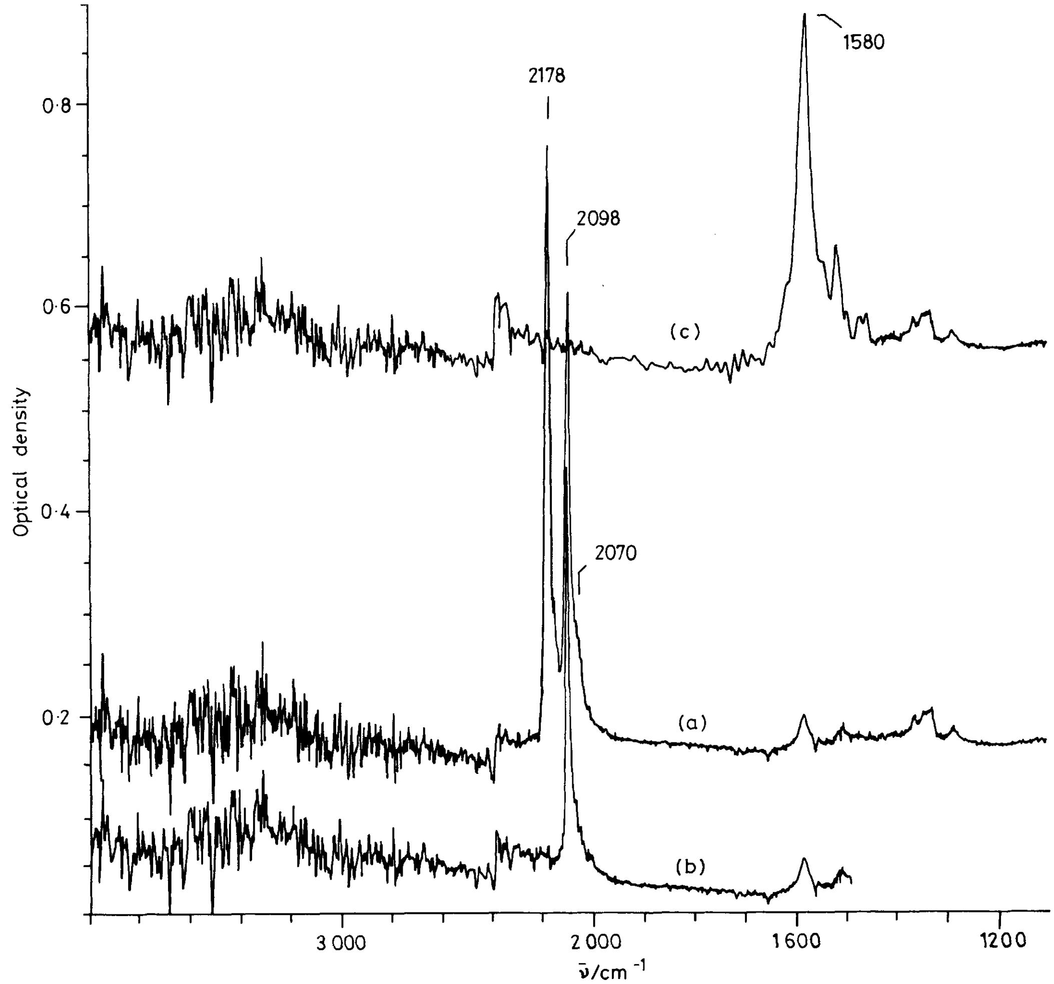


Figure 1. I.r. spectra of CO adsorption on a Cu/ZnO reduced sample. Curve (a), 0.5 Torr (1 Torr = 133.32 N m^{-2}) at 77 K; curve (b), after 30 min outgassing at 77 K; curve (c), after 10 min outgassing at 298 K.

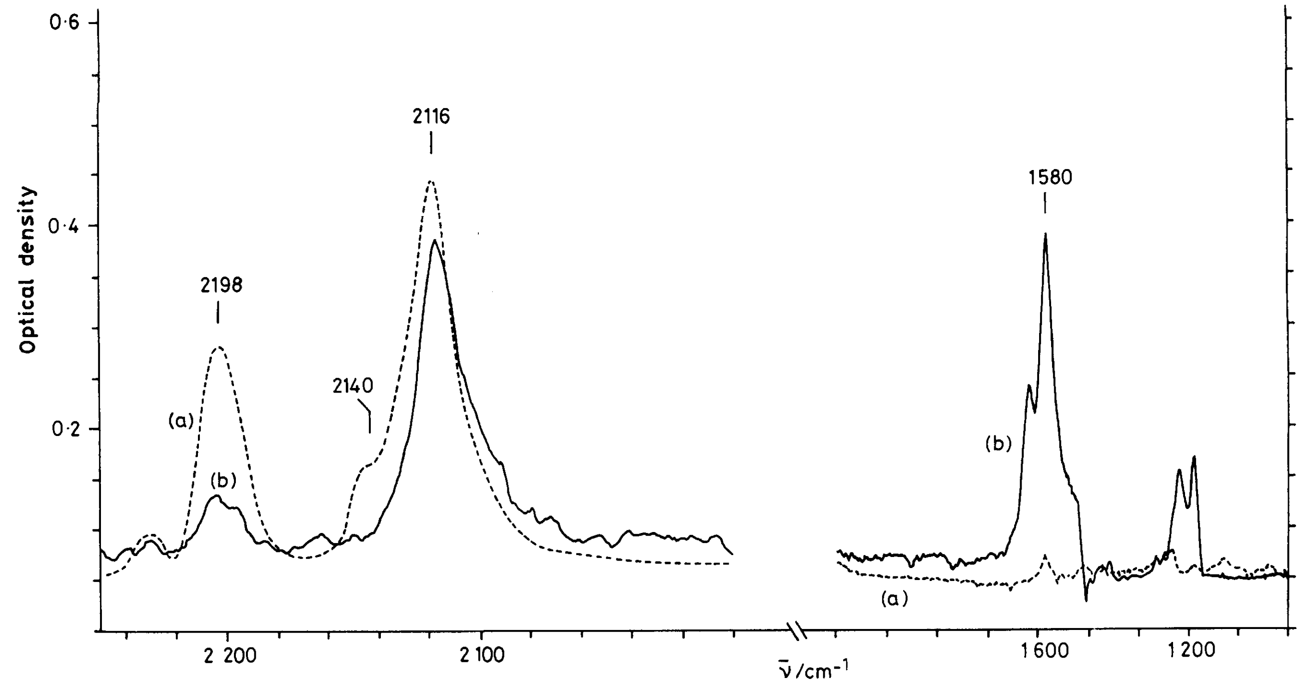


Figure 2. I.r. spectra of CO–O_2 interaction at 77 K on a reduced Cu/ZnO sample; curve (a) CO on a preoxidized sample; curve (b), 5 Torr of O_2 on a sample previously covered with CO (the CO coverage corresponds to 5 min of outgassing).

and 2116 cm^{-1} repectively. In curve (b) the band at 2198 cm^{-1} has a lower intensity, the 2140 cm^{-1} one does not appear, while the bands at 2116 and 1580 cm^{-1} immediately appear, accompanied by minor absorptions at 1620, 1520, 1330, and 1290 cm^{-1} assigned to carbonate-like species.[7]

The bands at 2140 and 2116 cm^{-1} have previously been assigned to CO adsorbed on borderline oxidized Cu atoms and on oxidized Cu atoms of extended surface areas respectively.[2]

On the basis of the contemporaneous lack of the 2198 and 2140 cm^{-1} bands when the 1580 cm^{-1} one is present, we can infer that the 1580 cm^{-1} related species is bonded to both a zinc ion and a Cu borderline site; the oxidation of the CO-precovered surface makes the formation of this species easier as a consequence of electron withdrawal from the surface, favouring the formation of the four-electron donor species.

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