

I.R. Spectroscopic Evidence of Formyl Species formed by CO and H₂ Co-adsorption on ZnO and Cu-ZnO

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The i.r. spectrum of a mixture of CO and H₂ adsorbed on ZnO or Cu-ZnO shows a pair of weak bands at 2770 and 2661 cm⁻¹ while a mixture of CO and D₂ gives rise to a corresponding single band at 2020 cm⁻¹; these bands are assigned to vibrations of surface formyl species.

In homogeneous catalysis, metal formyl complexes have been proposed as important intermediates in the metal-catalysed reduction of CO by H₂.¹ In heterogeneous catalysis, Henric-Olivé and Olivé suggested that the first step in the reduction also gives rise to formyl species.² Deluzarche *et al.*³ claimed to have identified, by chemical trapping, such species on nickel. In i.r. spectroscopy, Blyholder and Neff⁴ interpreted a band around 1700 cm⁻¹ as indicating decomposition of C_xH_yO compounds on nickel to form an acyl structure. However in our opinion, i.r. spectroscopic evidence for formyl species resulting from the interaction of CO and H₂ in heterogeneous catalysis has not previously been reported.

We show herein that such species are formed on zinc oxide and on zinc oxide which contains copper.

The zinc oxide powder used was Kadox 15 from the Asturienne New Jersey Zinc Co. The Cu-ZnO catalyst was prepared by impregnation of the ZnO Kadox 15 as support with an alcoholic solution of Cu(MeCO₂)₂·H₂O. The samples were pretreated with oxygen at 723 K as described in reference 5. The hydrogen (N55) and carbon monoxide (N45) were obtained from 'Air Liquide'. I.r. spectra were recorded on a Nicolet FT-MX-1 spectrometer at *ca.* 273 K.

Hydrogen adsorption on ZnO has been shown to be mainly reversible and dissociative; in agreement with reference 6, we

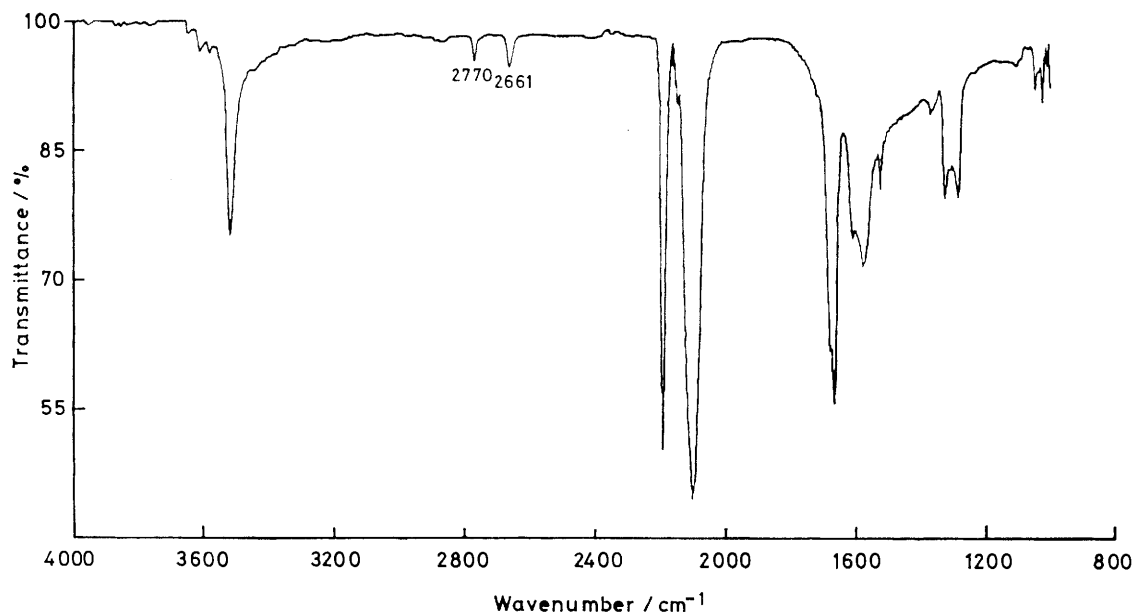


Figure 1. I.r. spectrum of CO + H₂ [$p(\text{CO})/p(\text{H}_2) = 0.5$; $p(\text{H}_2) = 200$ Torr] adsorbed on Cu-ZnO (0.1 wt. % Cu) at *ca.* 270 K (the background absorbance and the spectrum of CO gas have been subtracted).

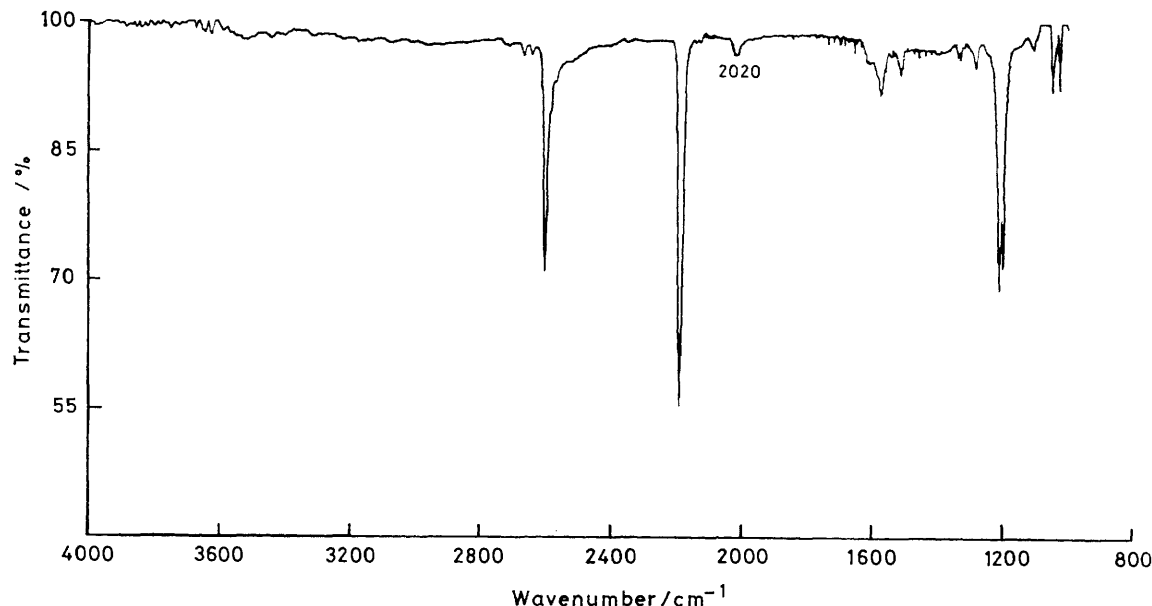


Figure 2. I.r. spectrum of CO + D₂ adsorbed on ZnO at ca. 270 K.

observed the following sharp bands for a hydrogen-saturated surface: 3491, $\nu(\text{OH})$; 1707, $\nu(\text{ZnH})$; 842 and 817 cm^{-1} , deformation modes. The same bands also appear in the spectrum of hydrogen adsorbed on Cu-ZnO, showing adsorption at the Zn-O pair sites.

CO reversibly adsorbed on ZnO is associated with a band at 2187 cm^{-1} .^{7,8} On Cu-ZnO, an additional broad band appears centred at about 2100–2120 cm^{-1} , corresponding to CO bound to co-ordinatively unsaturated copper ions. This broad band will be analysed elsewhere.⁹

The co-adsorption of H₂ and CO modifies the $\nu(\text{ZnH})$ band due to reversibly adsorbed hydrogen, as already reported for ZnO.⁷ Under our conditions [$p(\text{CO})/p(\text{H}_2) = 0.5$; $p(\text{H}_2) = 200$ Torr] we observe a doublet at 1675 and 1662 cm^{-1} , and, in addition, the spectra show two weak bands at 2770 and 2661 cm^{-1} , not reported in reference 7. The latter bands appear as soon as the mixture of CO and H₂ is introduced at ca. 273 K and seem more intense when using Cu-ZnO (Figure 1). With ZnO, additional weak bands appear in the 2800–3100 cm^{-1} range. The 2770 and 2661 cm^{-1} bands tend to disappear with time at room temperature, while others appear in the 2800–3100 cm^{-1} range. This observation will be discussed elsewhere.⁹

The 2770 and 2661 cm^{-1} bands result from an interaction between CO and H₂. Their very low wavenumber suggests that they are due to the $\nu(\text{CH})$ vibration of an aldehydic group.¹⁰ Moreover, it is well known that this vibration generally corresponds to two bands caused by a strong Fermi resonance between the $\nu(\text{CH})$ and $2\delta(\text{CH})$ levels.¹¹ This perturbation does not affect the $\nu(\text{CD})$ mode of the $-\text{C}(\text{O})-\text{D}$ group¹² and hence a mixture of CO and D₂ leads only to a single corresponding $\nu(\text{CD})$ band at 2020 cm^{-1} (Figure 2).

After a short time of contact (ca. 1 min) on Cu-ZnO, no band other than those at 2770 and 2661 cm^{-1} appears in the 2500–3100 cm^{-1} range. This allows us to disregard the formation of aldehydes with CH₂ or CH₃ groups. Experiments carried out with formaldehyde itself do not lead to the 2770 and 2661 cm^{-1} doublet,⁹ so we deduce that this doublet is due to formyl species. This assignment is confirmed by comparison with organometallic complexes: for instance, the i.r. spectrum

of the formyl-hydrido complex Os(CHO)H(CO)₂(PPh₃)₂ shows three bands between 2800 and 2500 cm^{-1} ,¹³ the two highest wavenumber ones, at 2760 and 2680 cm^{-1} , being similar to those observed in the present study. In this complex,¹³ the $\nu(\text{C}=\text{O})$ band appears at 1601 cm^{-1} . This could explain why we are not able to distinguish the band corresponding to this mode in the present study, as bands due to carbonate species also occur in the 1500–1650 cm^{-1} range. However, from Figure 2, we can deduce that its intensity is certainly very weak.

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