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Chemical reactivity of CO and CO_2 at a Cu(110)–Cs surface

A.F. Carley, M.W. Roberts and A.J. Strutt

School of Chemistry and Applied Chemistry, University of Wales, Cardiff,
PO Box 912, Cardiff CF1 3TB, UK

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Carbon dioxide and carbon monoxide undergo reactive chemisorption with cesium modified Cu(110) and Cu(110)–O surfaces and via the anionic intermediate $CO_2^{\delta-}$(a) form a surface carbonate. The $CO_2^{\delta-}$(a) species was characterised by VEELS and XPS at low temperature (80 K) and the surface carbonate at 295 K. For cesium modified Cu(110) surfaces chemisorption of carbon monoxide gives rise to electron energy loss peaks (ν_{CO}) as low as 1450 cm^{-1} at 295 K.

Keywords: carbon dioxide; carbon monoxide; cesium; copper; electron spectroscopy

1. Introduction

Recent interest [1] in CO and CO_2 chemistry at copper surfaces has been stimulated partly by the special role that copper plays as one of the components of the ICI Cu–ZnO catalyst for methanol synthesis. Furthermore, the adsorption of carbon monoxide at metal surfaces is one of the classical model systems in the development of our understanding of chemisorption. That CO dissociatively chemisorbs at some metal surfaces was first established [2] unequivocally by XPS/UPS. However, at copper surfaces there is universal agreement for adsorption being weak (<80 kJ mol^{-1}) and molecular [3].

In contrast, the intrinsic thermodynamic stability of carbon dioxide did not make it an attractive candidate for exploring its surface chemistry. Nevertheless it was shown relatively recently that the sp-metals aluminium and magnesium participated in the reactive chemisorption of CO_2 at low temperatures [4] with a series of step-wise thermally activated events being delineated,

$$CO_2(g) \rightarrow CO_2(a) \rightarrow CO_2^{\delta-}(a) \qquad (1)$$

$$CO_2(a)\text{---}CO_2^{\delta-}(a) \rightarrow CO_3(a) + CO(g) \qquad (2)$$

$$CO_3(a) \rightarrow C^{\delta-}(a) + O^{\delta-}(a)\,, \qquad (3)$$

leading finally to carbidic and oxide species (eq. (3)). Freund and his colleagues [5] established, first theoretically and later by XPS, the possible role of CO_2 dimers as intermediates in the chemistry of CO_2 at nickel surfaces (eq. (2)). There is, therefore, apparently little distinction to be made between the reactivity of sp- and d-metals towards CO_2, a point made earlier in connection with the surface chemistry of nitric oxide [6] and emphasised more recently by Mason [7].

In this paper we address the question as to how the presence of cesium at a Cu(110) surface influences both the adsorption characteristics and chemical reactivities of carbon monoxide and carbon dioxide. A combination of in situ XPS and VEELS has been used, the former providing quantitative surface concentration data and the latter being able to discriminate between analogous, but structurally distinct, species. That alkali metal additives have a profound influence on CO bonding – mainly of transition metals studied by means of RAIRS – has been thoroughly reviewed recently by Bonzel [8]. The only previously reported studies of alkali modified Cu(110) surfaces are those of Rodriguez et al. [9] and Lackey and King [10]. Less attention has been given to CO_2, although studies with bismuth, copper and gold – with modification by sodium – have been reported from this laboratory [11]. That the anionic $CO_2^{\delta-}$(a) state could be generated at alkali (potassium) modified metal surfaces was first established with Pd(100) and Rh(111) surfaces by Solymosi [12]. More recently Solymosi and Klivényi [13] established that $CO_2^{\delta-}$ formation could be enhanced at Rh(111) by illumination with UV radiation; analogous behaviour [11] has also been observed with Al Kα radiation for CO_2 adsorbed at Cu(110).

2. Experimental

The core-level and vibrational spectra were obtained using a single spectrometer with X-ray facilities supplied by VG Scientific (now Fisons) and VEEL facilities provided by VSW. The pass energies used for the XP spectra were usually 60 eV and the binding energies calibrated against the Cu(2p) line at 932.8 eV. Electron energy loss spectra were collected in the specular mode with a beam energy of 5 eV. The spectrometer is capable of an ultimate pressure of 5×10^{-11} mbar and crystal cleaning achieved by Ar^+ sputtering followed by annealing at 700 K. The single crystal was supplied by Metal Crystals and Oxide Ltd., Cambridge.

2.1. CARBON DIOXIDE: XPS AND VEEL SPECTRA

Carbon dioxide, although chemically unreactive at an atomically clean Cu(110) surface at 298 K and below, readily forms the anionic species $CO_2^{\delta-}$ at 110 K at a Cu(110)–Cs surface (fig. 1A(i)). There are three loss peaks which we associate with adsorbed CO_2 – two of them 1460 cm^{-1} (ν_sOCO) and 1660 (ν_aOCO) characteristic of the anionic state $CO_2^{\delta-}$(a). The third at 660 cm^{-1} (δ_aOCO) is characteristic of physically adsorbed CO_2 and has been observed with Bi(0001) and

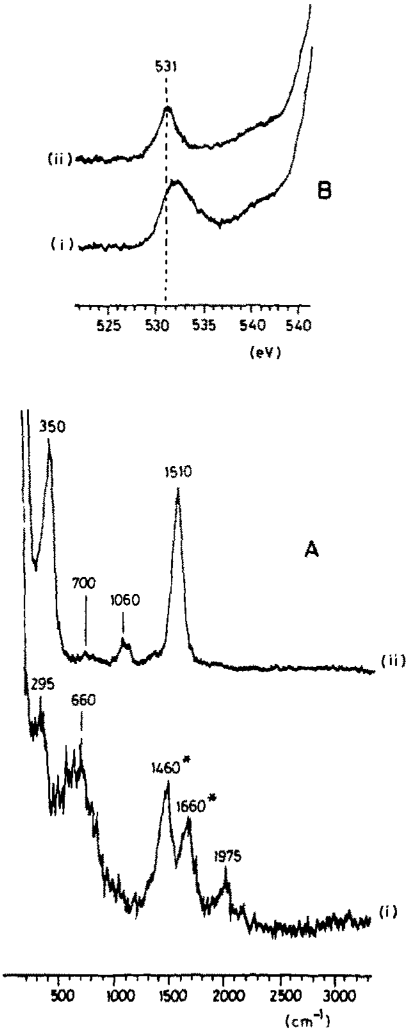

Fig. 1. (A) VEEL spectra for adsorption of CO$_2$ at a Cu(110)–Cs surface. Analysis of the Cs(3d) spectra indicates that $\sigma_{Cs} = 3.8 \times 10^{14}$ cm^{-2}. (i) Surface exposed to CO$_2$ at 80 K then warmed to 110 K (analysis of the O(1s) spectra indicates a total "oxygen" surface concentration of $\sigma_o = 1.3 \times 10^{15}$ cm^{-2}), (ii) after warming (i) to 295 K. The peaks marked with an asterisk are assigned to $CO_2^{\delta-}$(a). (B) O(1s) spectra corresponding to (A).

Cu(100) surfaces [11]. The two other features we associate with adsorbed carbon monoxide 295 cm^{-1} (ν_{Cu-CO}); 1975 cm^{-1} (ν_{CO}). The corresponding O(1s) spectrum (fig. 1B(i)) shows a weak feature at a binding energy of 536 eV, CO$_2$(a), and a highly asymmetric peak encapsulating the O(1s) region, centred at 532 eV, which we would anticipate would be characteristic of $CO_2^{\delta-}$(a). Chemisorbed oxygen has an O(1s) binding energy of ~ 530 eV.

On warming to 298 K both the VEEL (fig. 1A(ii)) and O(1s) spectra (fig. 1B(ii)) simplify and are assigned to a monodentate surface carbonate species:

350 cm^{-1} (ν_{Cu-O}); 700 cm^{-1} (δ_sOCO); 1060 cm^{-1} (ν_sOCO); and 1510 cm^{-1} ($\nu_{C=O}$). The relatively narrow O(1s) peak at 531 eV – with slight asymmetry to the low binding energy side assigned to chemisorbed oxygen – is characteristic of surface carbonate. Our experimental data are compatible with the Freund–Messmer dimer mechanism (eq. (3)) involving the two forms of adsorbed carbon dioxide – one being the anionic state $CO_2^{\delta-}$(a).

2.2. CARBON MONOXIDE: XPS AND VEEL SPECTRA

Fig. 2(i) shows the VEEL spectra for the adsorption of carbon monoxide at Cu(110) at 80 K, with the anticipated strong loss feature, ν_{CO}, at 2085 cm^{-1}. Exposing this adlayer to cesium atoms ($\sigma_{Cs} = 4.1 \times 10^{14}$ cm^{-2}) at the same temperature results in the loss feature being replaced (fig. 2(ii)) by one at some 350 cm^{-1} lower frequency (1730 cm^{-1}). On warming to 295 K two features (fig. 2(iii)) are present, one at appreciably lower frequency 1450 cm^{-1}, and a weaker one at 1950 cm^{-1} which is closer to that typical of CO adsorption at atom-

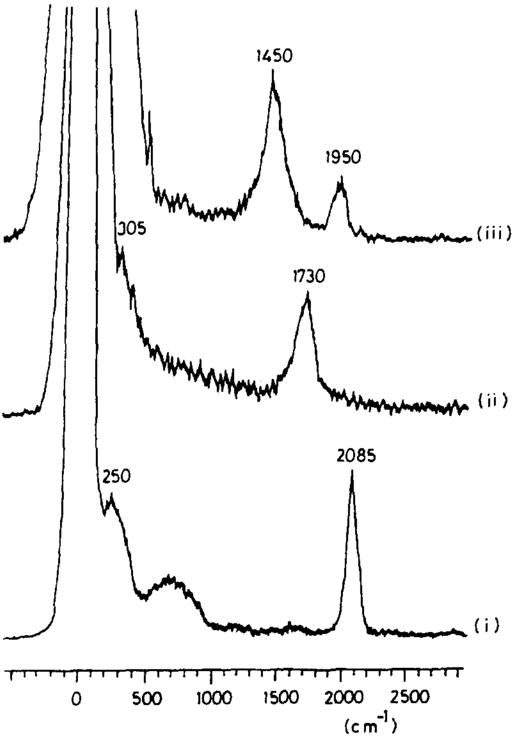

Fig. 2. VEEL spectra showing the effect of Cs on a CO adlayer at Cu(110) surface: (i) adsorption of CO at a clean Cu(110) surface at 80 K ($\sigma_{CO} \approx 3 \times 10^{14}$ cm^{-2}). The loss peak at 800 cm^{-1} is assigned to δ(H$_2$O) present at very low concentrations ($<1 \times 10^{14}$ cm^{-2}). (ii) After depositing Cs ($\sigma_{Cs} = 4.1 \times 10^{14}$ cm^{-2}) on to the adlayer (iii) after warming the adlayer (ii) to 295 K.

ically clean copper surfaces. Although we have no experimental evidence, we would anticipate considerable surface rearrangement (reconstruction) on warming the Cu(110)–Cs adlayer with the creation of sites potentially active in CO adsorption that are not present at 80 K. Reconstruction has been reported for the Cu(110)–K system [18]. In the context of the present investigation the spectra emphasise the role that cesium doping can play in the creation of sites at the Cu(110) surface which are able to chemisorb CO strongly, with considerable weakening of the carbon–oxygen bond arising from back bonding into the antibonding orbitals.

2.3. OXIDATION OF CARBON MONOXIDE: XPS AND VEEL SPECTRA

The weakening of the CO bond might be expected to be reflected in enhanced chemical reactivity and indeed evidence for this comes from recent observations of the oxidation of carbon monoxide to surface carbonate by preadsorbed oxygen adatoms present at the Cu(110)–Cs surface at 360 K [14]. The individual steps involved in the reaction mechanism and the participation of surface intermediates have been identified here by following the reaction at low temperature. Figs. 3A and 3B show the VEEL and O(1s) spectra observed when a Cu(110)–Cs surface was exposed to dioxygen at 298 K and then to CO at 80 K. In the O(1s) region (fig. 3B), exposure to CO results in the development of features to the high binding energy side of the peak corresponding to chemisorbed oxygen atoms (529.6 eV). The peak at 535.9 eV is unambiguously assigned to physically adsorbed CO_2, which is also characterised by the presence of a C(1s) peak at 292.1 eV (not shown). The O(1s) intensity in the range 531–533 eV we assign to the $CO_2^{\delta-}$ species. Both of these assignments are confirmed by the VEEL spectra (fig. 3A), and also are compatible with our earlier discussion of the adsorption of carbon dioxide at a Cu(110)–Cs surface. On warming to 298 K, changes in both the VEEL and XPS spectra (figs. 3A and 3B) indicate the formation of surface carbonate via the Freund–Messmer dimer mechanism. In the absence of cesium, chemisorbed oxygen at Cu(110) surfaces are unreactive to carbon monoxide under the same experimental conditions. The two dominant loss features at 1380 and 1500 cm^{-1} are assigned to $\nu_{C=O}$ features of two structurally different surface carbonates. The assignments of these loss peaks – by comparison with the infrared literature [19,20] – are not unambiguous with peaks at 1530 and 1330 cm^{-1} being ascribed to bidentate carbonates, peaks at 1466 and 1383 cm^{-1} to monodentate carbonates [19] and peaks at 1560 and 1380 cm^{-1} to polydentate carbonates [20]. For CO_2 interaction with the Cu(110)–Cs surface only one of these species – characterised by a loss peak at 1510 cm^{-1} – is observed at 295 K (fig. 1A(ii)).

These studies provide further evidence for the crucial role that $CO_2^{\delta-}$(a) plays in surface catalysed reactions. Coadsorption experiments with ammonia [15] and water [16] have indicated that at copper, aluminium and magnesium single crystal

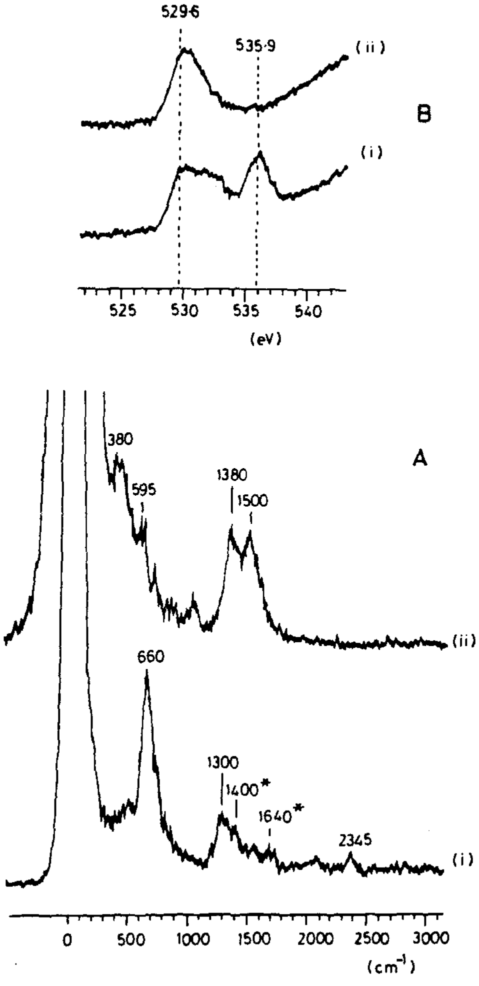

Fig. 3. (A) VEEL spectra corresponding to B. The peaks marked with an asterisk are assigned to $CO_2^{\delta-}$(a). (B) O(1s) spectra for CO adsorption at a Cu(110)–Cs surface which had been pre-oxidised at 295 K ($\sigma_o = 6.6 \times 10^{14}$ cm^{-2}) (i) after exposure of the Cu(110)–Cs–O surface to CO at 80 K (ii) after warming (i) to 295 K.

surfaces at low temperatures, where $CO_2^{\delta-}$(a) is stable, the formation of carbamate and hydrogenated forms of CO_2 ($HCOO^{\delta-}$) may occur. Analogous studies by Freund and his colleagues [17] have established that at Ni(110) surfaces acetate species are formed through the reaction of $CO_2^{\delta-}$ and methyl radicals. Again the mechanism involves a low energy pathway reaction occurring at low temperatures.

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References

[1] G.C. Chinchen, M.S. Spencer, K.C. Waugh and D.A. Whan, J. Chem. Soc. Faraday Trans. I 83 (1987) 2193.

[2] S.J. Atkinson, C.R. Brundle and M.W. Roberts, Chem. Phys. Lett. 24 (1974) 175;
R.W. Joyner and M.W. Roberts, Chem. Phys. Lett. 29 (1974) 447;
K. Kishi and M.W. Roberts, J. Chem. Soc. Faraday Trans. I 71 (1975) 1721.

[3] J. Pritchard, T. Catterick and R.K. Gupta, Surf. Sci. 53 (1975) 1.

[4] A.F. Carley and M.W. Roberts, J. Chem. Soc. Chem. Commun. (1987) 355;
R.G. Copperthwaite, P.R. Davies, M.A. Morris, M.W. Roberts and R.A. Ryder, Catal. Lett. 1 (1988) 11;
A.F. Carley, D.E. Gallagher and M.W. Roberts, Spectrochim. Acta 43 A (1987) 1447; Surf. Sci. 183 (1986) L263;
M.W. Roberts, Chem. Soc. Rev. 18 (1989) 451.

[5] H-J. Freund and R.P. Messmer, Surf. Sci. 172 (1986) 1.

[6] C.T. Au, A.F. Carley and M.W. Roberts, Phil. Trans. Roy. Soc. A 318 (1986) 3.

[7] R. Mason, Catal. Today 12 (1992) 413.

[8] H.P. Bonzel, Surf. Sci. Rep. 8 (1988) 43.

[9] J.A. Rodriguez, W.D. Glendining and C.T. Campbell, J. Phys. Chem. 93 (1989) 5238.

[10] D. Lackey and D.A. King, J. Chem. Soc. Faraday Trans. I 83 (1987) 2001.

[11] V.M. Browne, A.F. Carley, R.G. Copperthwaite, P.R. Davies, E.M. Moser and M.W. Roberts, Appl. Surf. Sci. 47 (1991) 375.

[12] A. Berko and F. Solymosi, Surf. Sci. 201 (1986) L489.

[13] F. Solymosi and G. Klivényi, Catal. Lett. 22 (1993) 337.

[14] A.F. Carley, M.W. Roberts and A.J. Strutt, J. Phys. Chem., to be published.

[15] A.F. Carley, P.R. Davies and M.W. Roberts, J. Chem. Soc. Chem. Commun. (1989) 677.

[16] A.F. Carley, S. Read, M.W. Roberts and A. Zeini-Isfahan, to be published.

[17] J. Wambach and H-J. Freund, private communication.

[18] R. Schuster, J.V. Barth, G. Ertl and R.J. Behm, Phys. Rev. B 44 (1991) 13689.

[19] J.F. Edwards and G.L. Schrader, J. Catal. 94 (1985) 175;
S.G. Neophytides, A.J. Marchi and G.F. Froment, Appl. Catal. A 86 (1992) 45.

[20] G. Busca and V. Lorenzelli, Mater. Chem. 7 (1982) 89.