THE REACTIVE CHEMISORPTION OF CARBON DIOXIDE AT MAGNESIUM AND COPPER SURFACES AT LOW TEMPERATURE

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X-ray photoelectron spectroscopic studies reveal that the following species are present when carbon dioxides reactively chemisorbed at magnesium and copper surfaces: CO_2(phys) CO_3(a), CO_2^-(a) CO(a) and C(a). At Mg(0001) surfaces, it has been shown that there is a step-wise process, with a whole range of metastable species formed above 80 K. By contrast, at copper surfaces the chemistry is less complex, the most significant species being CO_2^-(a); these form preferentially under conditions which favour high surface concentrations of CO_2(a) and therefore co-operative effects within the adlayer. The need to develop experimental methods for studying surface processes at high pressures is well recognised, however the present work shows that for some systems low temperatures (and pressures) offer a possible alternative strategy for delineating the step-wise nature of the reaction.

1. Introduction

Interest in the use of carbon dioxide as a raw material in the synthetic chemical industry has increased over the last decade, with further momentum being provided from the recent discovery by the Catalysis group of Imperial Chemical Industries that it is the main source of 'carbon' in the synthesis of methanol from CO-CO_2-hydrogen mixtures [1]. CO_2 is also an important component of the water gas shift reaction. Much effort has also been made to explore the possibility of the photocatalytic reduction of carbon dioxide and thus the opportunity of using solar energy for its conversion to useful chemicals [2].

As for chemisorption of carbon dioxide at 'clean' metal surfaces, the early classical work of Trapnell [3] suggested little reactivity with copper, rhodium, platinum and palladium but some evidence for dissociative chemisorption with aluminium. Nickel and zirconium also were reported to react dissociatively [4] while Eischens [5], in one of the earliest infrared studies, reported carboxylate-type surfaces species with nickel. With aluminium, photoelectron spectroscopy has established recently [6] that at very low temperatures, which favour cooperative interactions between physically adsorbed molecules, facile dissociation of CO_2 occurs. There have also been reported electron spectroscopic studies by Madix [7] and Bradshaw [8] with silver and controversy over whether CO_2 chemisorption is dissociative at rhodium surfaces [9]. A combined theoretical/experimental approach has also been reported recently by Freund and Messmer for CO_2-metal interactions [10].

This paper brings together data derived from a number of distinct projects each with quite different objectives. When the spectra are compared a general picture of the molecular events involved in CO_2 chemisorption at metal surfaces emerges. In some cases the chemistry is relatively simple with evidence for just associative adsorption; with others a whole range of metastable carbon and oxygen surface species may co-exist arising from dissociative reactive-chemisorption of CO_2. It is important to emphasise that bond-cleavage can be facile and occurs at very low temperatures (80 K–150 K) so that with the atomically clean metal, dissociation of carbon dioxide occurs via a route of low activation energy. We shall also see that the pressure, or more precisely the surface concentration of carbon dioxide, has important implications for the reaction pathway followed. The facile formation of 'carbon' also raises the issue of whether it may be hydrogenated to hydrocarbons and whether this is a possible route to Fischer-Tropsch type chemistry.

The advantage of using photoelectron spectroscopy at various temperatures for studying the molecular events occuring at surfaces are now well recognised. In this paper we report data derived from X-ray induced photoelectron spectroscopy (XPS) of CO_2 interactions with atomically clean Mg(0001), Cu(211) and polycrystalline copper surfaces in the temperature range 80 K to 300 K. Comparisons are also made with other metals such as aluminium and gold. We have taken a broad view of CO_2 surface chemistry since it was necessary to generate our own in-house data base in order to ensure that the assignments of features in the photoelectron spectra are well founded. There are no model compounds available and very often we observe surface species (metastable) that have no counterpart in the bulk. The importance of these species is that they may participate as intermediates in a catalytic reaction at much higher temperatures but would not be observed by any spectroscopic post-reaction type study. The isothermal methods used here give quantitative surface concentrations of individual surface species over a wide temperature range and are a pre-requisite for mechanistic surface studies.

2. Carbon dioxide interaction with magnesium and copper surfaces

We consider how the sequence of molecular steps (1 to 6) outlined below were derived from photoelectron spectroscopic studies. They provide a comprehensive model not only for carbon dioxide interactions with Mg(0001) surfaces but also form the basis for understanding the observed chemical specificity of the CO_2 interaction with other metals such as copper, aluminium and gold. Such a model enables the catalytic chemistry of carbon dioxide to be understood more comprehensively and provides the appropriate fundamental background for catalyst design.

1. Physical adsorption: essentially an isolated molecule weakly held at the metal surface

$CO_2(g) \rightarrow CO_2(phys)$.

2. Formation of a chemisorbed surface anionic species: the removal of an oxygen as O^- is energetically easier from bent $CO_2^-(a)$ than a 'neutral oxygen' from linear $CO_2(a)$.

$CO_2(phys) \rightarrow CO_2^-(a)$.

Measurements of electron attachment energies in CO_2 molecular beams show that the CO_2^- species is unstable; however, it can be stabilised by solvation with other CO_2 molecules. This solvated species is suggested to be a dimer [11] and has a proposed structure akin to solid CO_2 [12].

3. Disproportionation of dimer: intermolecular oxygen transfer leading to carbonate formation. The presence of carbonate species with Mg(0001) surfaces has been reported by us previously [13] from O(1s) and EEL spectra.

$CO_2^- – CO_2(a) \rightarrow CO_3(a) + CO(a)$.

4. Desorption of carbon monoxide: CO exhibits very low adsorption energies on sp-metal surfaces.

$CO(a) \rightarrow CO(g)$.

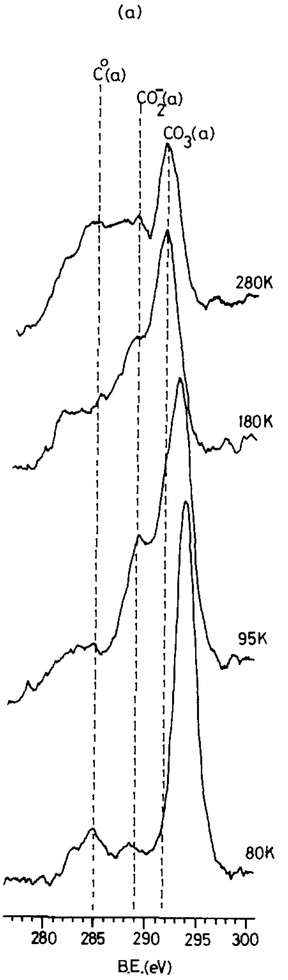
5. Deoxygenation or reduction of surface carbonate

$CO_3(a) \rightarrow C(s) +$ 'oxide'.

6. Surface carbide formation

$C(s) \rightarrow C^0(a) \rightarrow C^{\delta-}(a)$

We consider next the photoelectron spectra, including previously published data with aluminium surfaces [6], that provide the basis of the proposed model. Figure 1(a) shows a selection of smoothed C(1s) spectra taken sequentially of the interaction of carbon dioxide with a Mg(0001) surface in the temperature range 80 K to 280 K. At 80 K, carbon dioxide, present as physically adsorbed multilayers, has a C(1s) binding energy of 293.5 eV. As the temperature is increased a very significant feature develops at 95 K with a binding energy of 289



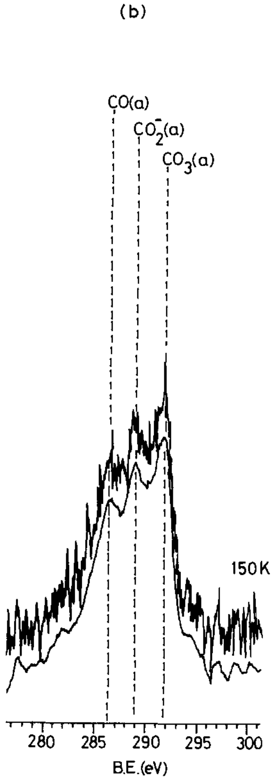


Fig. 1(a). C(1s) region of the photoelectron spectrum of a Mg(0001) surface initially exposed to 100 L CO_2 at 80 K, and then allowed to warm to the temperatures indicated (smoothed data; pass energy 50 eV).

Fig. 1(b). A comparison of a raw and smoothed C(1s) spectrum from a similar experiment taken at 150 K and higher resolution (pass energy 20 eV). Derived surface stoichiometries (O : C ratios) are estimated (see ref. [6]) to be: CO peak = 0.9: 1.0; CO_2^- peak = 1.6: 1.0 and CO_3 peak = 2.75 : 1.0.

eV. A signal also grows in the 292 eV region at the expense of the 293.5 eV peak. Until at 180 K, and also at 280 K, it is the predominant feature at 292 eV. With increasing temperature there is a gradual development of intensity at 285 eV and also a plateau between 285 eV and 289 eV. In fig. 1(b) is shown a high resolution raw and smoothed spectrum for a temperature of 150 K in a different experiment. If we compare this spectrum with that at 95 K (fig. 1a) then intensity has clearly developed at 286.5 eV, and the 292 eV peak has emerged as the dominant peak, but at the expense of the higher binding energy feature (293.5 eV) assigned to

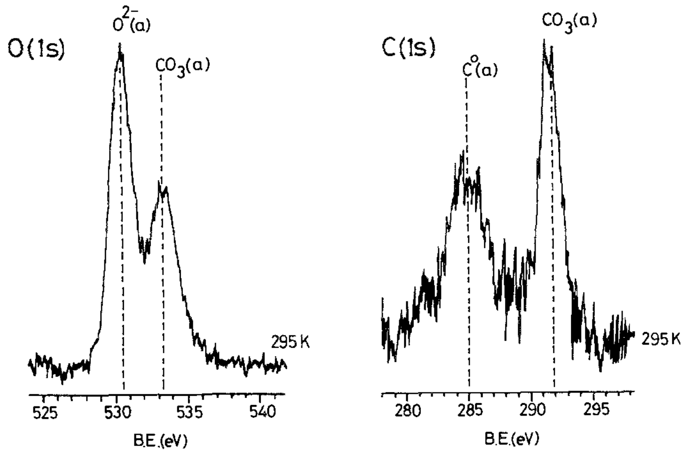


Fig. 2. O(1s) and C(1s) regions of the photoelectron spectrum of a Mg(0001) surface exposed to 100 L CO_2 at 295 K; the O : C atom ratio is 2.75 : 1 for the CO_3 species.

multilayers of physically adsorbed CO_2. We assign the three peaks observed at 150 K (fig. 1b) to CO(a), CO_2(a) and CO_3(a). We therefore can understand the plateau observed between 285 eV and 289 eV at 280 K as arising from three surface species C^0(a), CO(a) and CO_2^-(a) (reactions 2 to 6). O(1s) spectra were also obtained at each stage and provided evidence for the formation of surface oxide by the reduction of the metastable carbonate (reaction 5). There is little evidence for carbide, $C^{\delta-}$(a), formation with Mg(0001) surfaces in contrast to aluminium where both $C^{\delta-}$(a) and C^0(a) develop, the carbidic species preferentially (reaction 6).

C(1s) and O(1s) spectra after a single CO_2 exposure (3200 L) at 295 K are shown in fig. 2. The dominant species are C^0(a), CO_3(a) and oxide. There is no

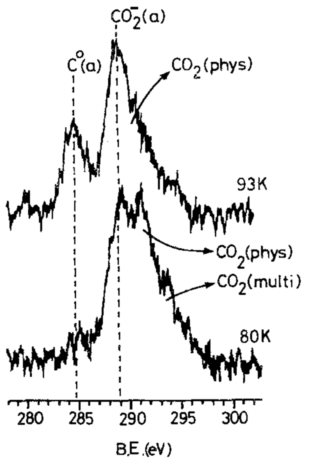


Fig. 3. C(1s) region of the photoelectron spectrum of a polycrystalline copper surface exposed to 115 L CO_2 at 80 K and then warmed to 93 K (pass energy, 50 eV). The O : C atom ratio is 1.85 : 1.

plateau evident in the intensity between 286 eV and 290 eV which indicates the *absence of both CO(a) and* CO_2^-*(a) species. This contrasts with what is observed when the adlayer at 80 K is warmed to room temperature* (fig. 1).

A polycrystalline copper surface when exposed to CO_2(g) at 80 K (fig. 3) exhibits in the C(1s) spectrum two main features, one at 289 eV and the other at 291 eV. These we assign to CO_2^-(a) and CO_2(phys) respectively, the latter species being bonded (dispersion forces) to the surface copper atoms whereas the small intensity at 293.5 eV is due to CO_2 multilayers. At 93 K the major intensity is at 289 eV, CO_2^-(a), (reaction 2), with also a substantial intensity at 285 eV due to C^0(a). When a single crystal Cu(211) surface was first preoxidized until $\theta_0 = 1.0$, (the chemisorbed oxygen being characterised by an O(1s) binding energy at 529.5 eV (fig. 4)), and then exposed to carbon dioxide to give multilayer adsorption at

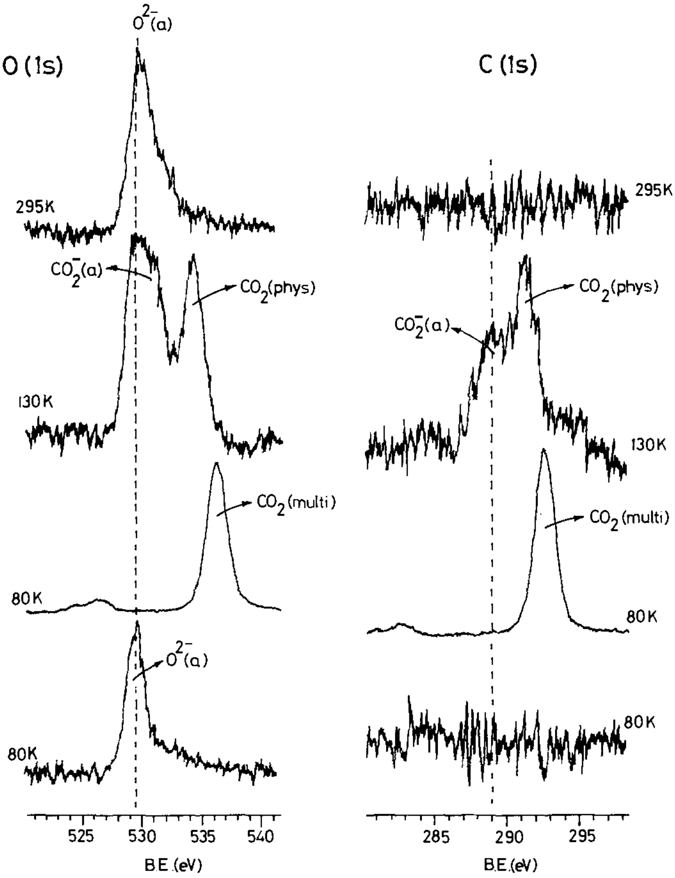


Fig. 4. O(1s) and C(1s) regions of the photoelectron spectrum of a Cu(211) surface: initially clean, preoxidised (50 L, O_2), exposed to 100 L CO_2 at 80 K, and then subsequently warmed to the temperatures indicated (pass energy 50 eV). At 130 K the surface coverage of CO_2^- (a) is estimated to be 0.75 monolayers of C. The derived O1s to C1s photoelectron peak intensities indicate an O : C atom ratio of 1.7 : 1.

80 K, an O(1s) peak at 536 eV and a C(1s) peak at 293.5 eV was observed. (Note the O^{2-}(a) species is 'buried' under the multilayers, so that no characteristic peak at 529.5 eV is visible at 80 K due to the short $\simeq 10$ Å photoelectron escape depth). On warming to 130 K the CO_2 multilayers are desorbed, leaving at the copper surface physically adsorbed carbon dioxide CO_2(phys). There are now present O(1s) and C(1s) features at 531.5 eV and 289 eV respectively; these are assigned to CO_2(a) the concentration of which decreases as the surface is warmed to 295 K. Clearly the chemisorbed anionic species is not strongly adsorbed at the Cu(211) surface. Furthermore, we draw attention to it being at its maximum surface concentration in the presence of CO_2(phys) at low temperature (eg 130 K); under these conditions its formation is kinetically fast. If, however, the copper surface is exposed to carbon dioxide at the same pressure (10^{-6} torr) at 295 K, very high exposures are necessary ($\simeq 3000$ L) before there is any evidence in the photoelectron spectrum for either a 'carbon' or 'oxygen' containing species. When they are observed, the binding energies suggest that mainly dissociated species are formed. We believe the reason for the significant difference between the chemistry observed at 295 K and low temperature is the absence of cooperative effects within the molecular CO_2 adlayer. The chemistry observed at low temperature (reaction 1 to 5) could however be simulated at 295 K by increasing the CO_2 pressure. This has been confirmed with aluminium [6].

A significant point which also emerges is that for preoxidized copper surfaces, CO_2^-(a) species which are present at low temperature (130 K) do not dissociate to give C^0(a) in contrast to that observed with atomically clean copper (cf for example the C(1s) spectra in figs. 3 and 4). This is understandable in that free copper surface atoms would be necessary to provide the necessary thermodynamic driving force for reduction through the formation of copper-oxygen bonds. On the other hand dissociation is a major pathway with both aluminium and magnesium, in both cases being driven by the formation of the thermodynamically stable metal-oxygen bonds.

3. Comments on spectral assignments

The assignments of features in the C(1s) spectra to CO_2(multilayers), CO_2(phys), CO_2^-(a), CO_3(a), C^0(a) and $C^{\delta-}$(a) are also firmly established from other studies with aluminium, zinc and gold. The carbon: oxygen atom ratios calculated from the C(1s) and O(1s) intensities further confirm the assignments in that the stoichiometries of the species can be determined. These derived values are shown in the figure captions. We stress in particular the advantages of following step by step how the surface reaction progresses; for example, we established that the facile reduction of the metastable carbonate at an aluminium surface leads to loss of intensity at 291.5 eV and an equal gain of intensity at 282 eV, $C^{\delta-}$(a), and 285 eV, C^0(a). With Zn(0001) and Au(001) only physical adsorption is observed, furthermore there are no significant X-ray induced effects. Although in all cases complementary valence-level spectra UPS were obtained we did not find them informative for discriminating between the several surface species generated in the reactive chemisorption of carbon dioxide. UPS is of course admirable for establishing the presence of CO_2(phys) or CO_2(multi) through their characteristic molecular orbital peaks.

Our assignment of a C(1s) peak at 289 eV and an O(1s) peak at 531.4 eV to the anionic CO_2^-(a) species (see for example fig. 4), requires further comment in view of its likely significance as an important surface intermediate in catalysis. We have relied, firstly, on the correlation between charge on the carbon and oxygen atoms and their binding energies; secondly, the model compound data for discrete 'CO_2' moieties in polymers; thirdly the carbon: oxygen atom ratios calculated from spectral intensities; fourthly the anticipated chemistry of the suspected CO_2^- species and fifthly recent theoretical calculations which suggest that it is stabilised as solvated clusters of carbon dioxide [10]. That a carbonyl carbon, CO(a), should have a C(1s) binding energy of 286 eV at metal surfaces is generally accepted and this is again supported by photoelectron spectra of carbonyl ligands in polymer systems. Disproportionation, (reaction 3), is the source of CO(a) which is only observed in low-temperature studies of CO_2 interactions with Mg(0001) surfaces. Under these low temperature conditions we suggest that, as the surface reaction proceeds, the charge on the magnesium atom varies, resulting in the magnesium exhibiting specific chemisorption reactivities to carbon monoxide which are not characteristic of either Mg^0 nor the final Mg^{2+} state of the thermodynamically stable MgO overlayer (modified by the presence of "carbon" species). The stability of CO(a) is also compatible with the theoretical views of Bagus et al. [14] who showed that if σ electrons could be removed from an sp-metal, destabilisation arising from interaction with CO σ-orbitals could be reduced and favourable π-orbital interactions become more important. This we suggest is the reason for the observation of CO(a) at 95 K resulting from the disproportionation of the dimer (reaction 4); it is a metastable adsorption state.

4. Relevance to methanol synthesis

A distinctive feature of the spectroscopic aspects of the chemistry of carbon dioxide interaction with copper surfaces is its relative simplicity compared with aluminium and magnesium; other than physical adsorption, the only other significant surface species is the anionic state CO_2^-(a). This is formed preferentially at low temperatures and we *estimate* (from the Frenkel equation) its heat of adsorption to be no more than 60 kJ $mole^{-1}$. This species is also present with magnesium but is more readily transformed (reduced) to surface carbon, C^0 and $C^{\delta-}$, CO_3^{2-}, CO and 'oxide'. Both low temperatures and high surface concentrations of $CO_2(a)$ favour the formation of $CO_2^-(a)$ which support the view that co-operative effects within the adlayer are important. One would expect intuitively that this species would readily add 'hydrogen' to give a formate type species, known to be an important intermediate in CH_3OH synthesis Formate and CO_2^- would probably be indistinguishable by XPS.

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