Oxygen-induced Dissociation of Carbon Monoxide at an sp-Metal (Aluminium) Surface

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The dissociation of carbon monoxide is induced at low temperatures by an oxygen transient present at aluminium surfaces in carbon monoxide–dioxygen (100 : 1) mixtures; a metastable surface carbonate is first formed which is deoxygenated in the temperature range 120—295 K.

The chemisorption and reactivity patterns for carbon monoxide at metal surfaces have been studied extensively by both i.r.[1] and photoelectron (x.p.s.) spectroscopies[2] and explained in terms of the nature of the surface bonding making recourse to the Blyholder or Dewar–Chatt models. In general, bonding is weak for sp-metals ($\Delta H \leqslant 40$ kJ mol^{-1}) whereas transition metals chemisorb carbon monoxide, in some cases dissociatively, with a high heat of adsorption ($\Delta H > 120$ kJ mol^{-1}).

The present photoelectron spectroscopic study received impetus from three different but recent aspects of our work: (a) the facile nature of oxygen activation of molecules and in particular the role of the O^-(s) species in N–H bond activation;[3] (b) the observation that carbon dioxide adsorption at an aluminium surface is dissociative leading to the formation of a surface carbonate which subsequently decomposes (deoxygenates) in the temperature range 120—295 K, the C(1s) photoelectron spectra[4] providing clear evidence for surface carbonate, two different carbon species one of which is carbidic, and oxide; (c) addition reactions involving nitrogen adatoms, exemplified by N_2O being formed at 80 K at Cu(100) surfaces as a result of the dissociative chemisorption of nitric oxide.[5] This is formally analogous to the formation of carbonate by the dissociative chemisorption of carbon dioxide which has also been observed at low temperature at magnesium surfaces.[6] Central to the mechanisms of these reactions is the preferential participation of an adatom (N or O) in an addition reaction rather than forming stable metal–adsorbate bonds, N(a) or O(a).

$$
\begin{array}{lll}
\mathrm{CO(g)} & \rightleftarrows \mathrm{CO(s)} & (1)\\
\mathrm{O_2(g)} & \rightarrow \mathrm{O^-(s)} & (2)\\
\left.\begin{array}{l}\mathrm{O^-(s) + CO(s)}\\ \mathrm{CO_2(s) + O^-(s)}\end{array}\right. & \left.\begin{array}{l}\rightarrow \mathrm{CO_2(s)}\\ \rightarrow \mathrm{CO_3(a)}\end{array}\right\} & (3)\\
\mathrm{O^-(s)} & \rightarrow \mathrm{O^{2-}(a)} & (4)\\
\mathrm{CO_3(a)} & \rightarrow \mathrm{C^0(a) + C^{\delta-}(a)} & (5)
\end{array}
$$

Scheme 1

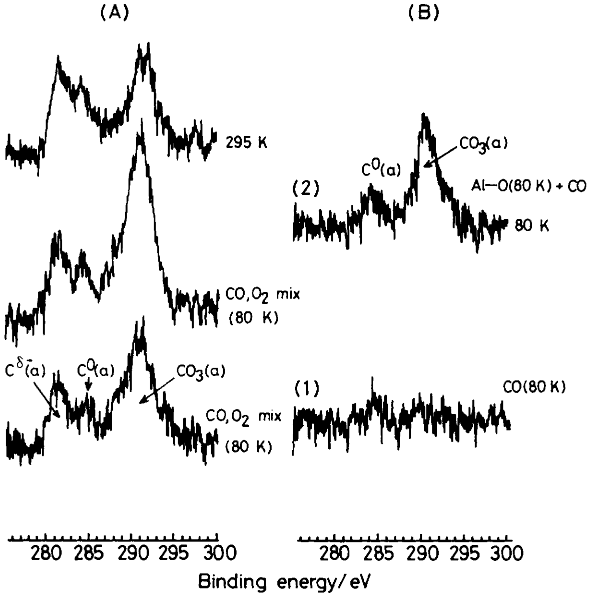

Figure 1. C(1s) spectra; (A) spectrum 1, exposure of aluminium surface at 80 K to carbon monoxide–dioxygen mixture (100 : 1) at a pressure of 3×10^{-6} Torr for 5 min; spectrum 2, further exposure to the mixture (1×10^{-5} Torr, 5 min); spectrum 3, after warming 2 to 295 K. (B) spectrum 1, exposure of aluminium surface to carbon monoxide (3×10^{-6} Torr for 20 min) at 80 K; spectrum 2, aluminium surface pre-exposed to oxygen at 80 K (1×10^{-8} Torr for 5 min at 80 K) followed by carbon monoxide at 80 K (1×10^{-6} Torr for 5 min, followed by 5×10^{-6} Torr for 5 min).

In this communication we explore whether the dissociative chemisorption of carbon monoxide may be induced at an aluminium surface through oxygen activation. We establish first that an atomically clean aluminium surface does not adsorb carbon monoxide at low pressures in the temperature range 80—295 K (Figure 1B, spectrum 1). A surface preoxidized at 295 K is also unreactive. This also is entirely in keeping with earlier studies in this laboratory of the lack of reactivity of atomically clean aluminium surfaces to carbon monoxide. The heat of adsorption is obviously small (<20 kJ mol^{-1}) and the surface coverage even at 80 K undetectable by x.p.s. We designate these species as CO(s) in Scheme 1, the symbol (s) reflecting its transient or short-lived nature. Carbon monoxide–dioxygen mixtures were then investigated under dynamic conditions using a $CO:O_2$ ratio of 100:1.

Steps (1)—(5) are suggested to occur at 80 K with step (5) becoming more significant as the temperature is increased to 295 K. The C(1s) spectra (Figure 1A) indicate that three different 'carbon' species, with binding energies of 291.2, 284.5, and 282 eV, are present at 80 K. These are assigned to surface carbonate (291.2 eV) and two other carbon species one of which (282 eV) is carbidic. The corresponding O(1s) spectra confirm the presence of oxide, O^{2-}(a), and carbonate. When the temperature is raised from 80 to 295 K the carbonate intensity decreases; this is accompanied by an increase in the intensities attributed to the carbidic and carbon (C^0) species (Figure 1A, spectrum 3). Clearly the surface carbonate is decomposing (equation 5).

This reaction scheme also finds support from other studies with aluminium where we have established that carbon dioxide deoxygenates readily, the process occurring *via* a metastable carbonate.[4] In this case the carbonate develops at slightly higher temperature (100 K) than is observed under the present 'forced conditions' where the O^-(s) species are generated by the dissociative chemisorption of coadsorbed dioxygen. In the absence of dioxygen the active oxygen species are formed by the dissociative chemisorption of CO_2(a) and this is a slightly activated process at the aluminium surface.

When the carbon monoxide : dioxygen ratio is decreased there is no evidence for the formation of any surface carbon species. The rate of oxide overlayer formation (k_4) is under these conditions fast while the rate of carbonate formation is, by comparison, insignificant, *i.e.* $k_4 \gg k_3$. When the coverage approaches unity, the rate (k_2) of generation of the electrophilic O^-(s) species becomes negligible so that carbonate formation ceases. For CO activation to take place specific interaction with O^-(s) must occur, the thermodynamically stable oxide formed at 295 K, *i.e.* O^{2-}(a) species, being inactive.

Carbon monoxide interaction with an aluminium surface pre-oxidised at 80 K leads to the formation of carbonate, and C^0, but not carbidic species, (Figure 1B, spectrum 2) showing that under these specific conditions O^-(s) is trapped as a metastable active surface oxygen. These species are absent in the oxide overlayer formed at 295 K. Evidence for analogous low temperature oxygen species has been reported previously for both sp and transition metals.[7,8]

In summary the dissociation of carbon monoxide depends critically on diverting the O^-(s) species, generated by the dissociative chemisorption of the coadsorbed dioxygen, away from oxide overlayer formation and to participate preferentially in a stepwise addition reaction to give in turn CO_2(s) and CO_3(a) (equation 3). The carbon–oxygen bond energy decreases from about 1050 kJ mol^{-1} for carbon monoxide to 500 kJ mol^{-1} for carbon dioxide leading to the metastable carbonate which readily deoxygenates at the aluminium surface, oxide overlayer formation being thermodynamically very favourable.

These results have obvious implications for catalytic reactions involving the activation of carbon monoxide. The molecule itself may be only weakly adsorbed and of negligible surface coverage but in the presence of other molecules, dioxygen in this case, cleavage of the carbon–oxygen bond occurs, making the distinction between the potential catalytic activity of transition and sp metals of less significance than hitherto supposed.

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