

The oxygen state active in the catalytic oxidation of carbon monoxide at a caesium surface: isolation of the reactive anionic $\text{CO}_2^{\delta-}$ species

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Analysis of X-ray photoelectron spectra taken as a function of oxygen exposure shows that at a caesium surface at 80 K the $\text{O}^{\delta-}$ state develops first as a precursor to the oxide O^{2-} and peroxy $\text{O}_2^{\delta-}$ states; the $\text{O}^{\delta-}$ species are reactive to $\text{CO}(\text{g})$ at 80 K giving the anionic form of adsorbed carbon dioxide $\text{CO}_2^{\delta-}$; the latter is readily converted to surface carbonate on exposure to dioxygen.

The role of alkali metals as promoters in heterogeneous catalysis is well recognised¹ with various oxygen species, including peroxy, being proposed as participating in selective oxidation reactions. In this communication we provide experimental evidence for the emergence of four different oxygen species at low temperature (≈ 80 K) through a quantitative analysis of the exposure-time dependent X-ray photoelectron O(1s) spectra. Using carbon monoxide as a probe we isolate one of these as active in CO oxidation to give adsorbed $\text{CO}_2^{\delta-}$ species.

There have been previous studies² of oxygen interaction with Cs present at both the monolayer and as multilayers on various metal substrates but only one, that of Hrbek, Yang and Rodriguez,³ is of the oxidation of multilayers of caesium at 80 K using XPS.

In the present work caesium was evaporated from an SAES getter on to a Ni(110) surface; after evaporation the Ni(2p) intensity was strongly attenuated a typical value of the Cs(3d):Ni(2p) ratio being $> 12:1$ indicating the presence of multilayers of caesium.

Fig. 1 shows the development of intensity in the O(1s) spectra region upon oxygen exposure at 80 K. After 0.5 L the O(1s) profile clearly consists of more than just the two obvious components with binding energies of ≈ 528 and 531.3 eV. At higher exposures (2, 10 and 20 L, Fig. 1) and greater O(1s) intensities we have curve-fitted the spectra using a maximum of four gaussian peaks, by floating the FWHM values, the intensities and the energy positions from a set of initial values. The best fits are shown in Fig. 1 revealing O(1s) peaks at ≈ 527.5 , 530.2, 531.3 and 533.4 eV. After an exposure of 10 L the calculated concentrations of oxygen species with binding energies of 527.5, 530.2, 531.3 and 533.4 eV are $\approx 1 \times 10^{14}$, 5×10^{14} , 4×10^{14} and $5 \times 10^{14} \text{ cm}^{-2}$ respectively. At high exposure (20 L) only two peaks are present, those at 530.3 and 533.4 eV. In the only previous analogous XPS investigation,³ O(1s) intensities were observed at 526.5, 530.3 and 533.65 eV, but no attempt was made either to curve-fit the O(1s) spectra or to extract quantitative oxygen concentration data as a function of exposure. As in the present investigation, the lowest binding energy component (526.5 eV) was a very small fraction of the total O(1s) intensity present after an exposure of 4.5 L, with that at 530.3 eV dominant.³ The inherently large FWHM value (≈ 3 eV) of the latter peak suggests that after an oxygen exposure of 4.5 L it could reflect a composite peak. This is indeed compatible with the present analysis of the present spectra (Fig. 1). We also monitored the Cs(3d) spectral region and observed shifts in binding energy with increasing oxygen exposure analogous to those reported by Hrbek *et al.*³

The oxygen species characterised by the very low binding energy (≈ 527.5 eV) can be assigned to a highly electronegative species associated with a highly electropositive defective

caesium site. A significant aspect of the curve-fitting analysis of the O(1s) spectra is that at low oxygen exposure (0.5 and 2 L, Fig. 1) it is the 531.3 eV component that dominates the spectrum, this we assign to oxygen species $\text{O}^{\delta-}(\text{a})$ that have not acquired the full 2e charge associated with the development of a true oxide species where the contribution from the Madelung term allows the oxygen species to develop its maximum charge. As the oxygen coverage increases this becomes less significant and we assign the O(1s) peak at 530.3 eV to the $\text{O}^{2-}(\text{a})$ species and that at 533.4 eV to a peroxy-like oxygen $\text{O}_2^{\delta-}(\text{a})$. These species are compatible with the discrete steps shown to be involved⁴ in the dissociative chemisorption of oxygen at metal surfaces where (s) represents a transient and (a) stable or metastable chemisorbed oxygen species respectively (Scheme 1). The evidence for these transient species has been discussed elsewhere and their participation in specific catalytic chemistry established.⁴

That the O(1s) peak at 531.3 eV is correctly assigned to 'isolated' $\text{O}^{\delta-}(\text{a})$ -like species was pursued further by using carbon monoxide as a probe molecule. Carbon monoxide is

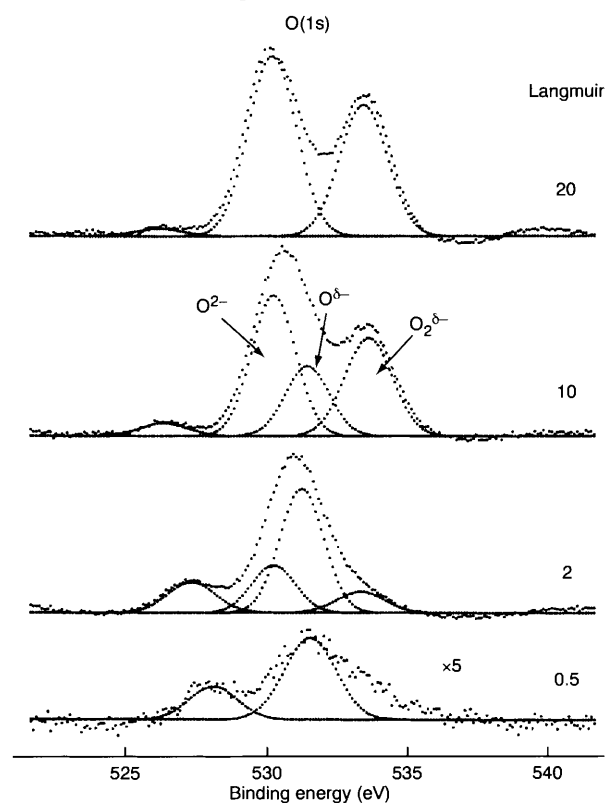
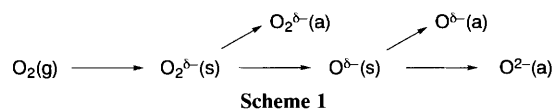


Fig. 1 O(1s) spectra as a function of oxygen exposure to caesium multilayers at 80 K; assignments of the three curve-fitted peaks after an exposure of 10 L are shown. The total oxygen atom concentration at 20 L exposure is $15 \times 10^{14} \text{ cm}^{-2}$.



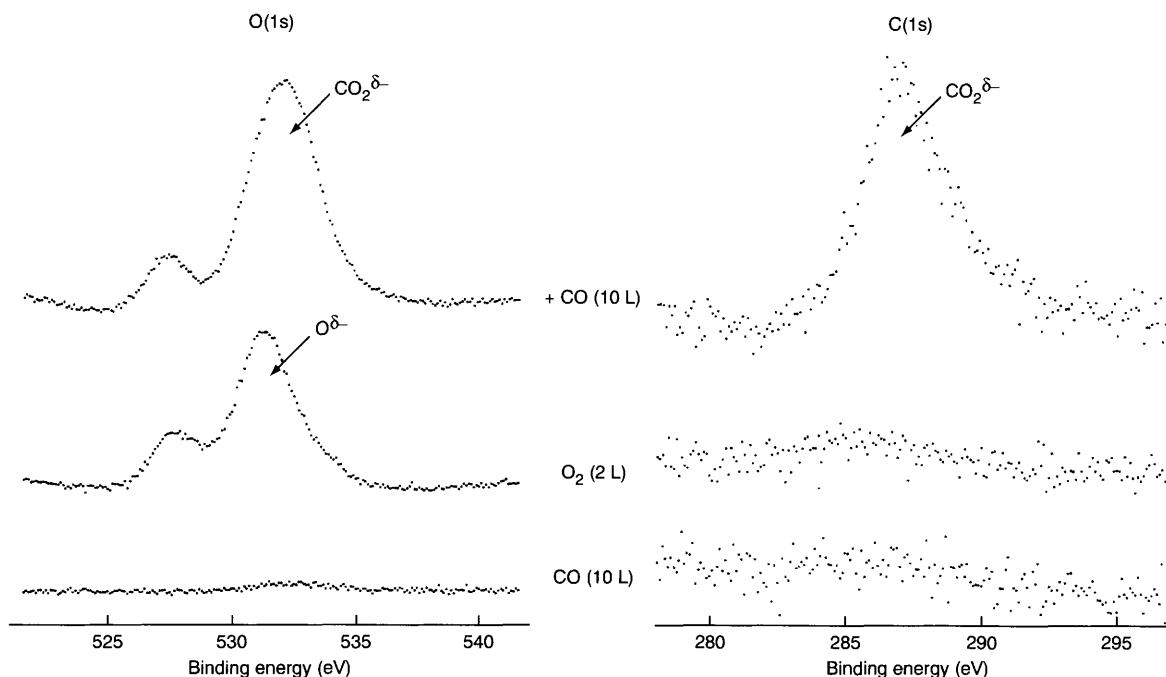


Fig. 2 O(1s) and C(1s) spectra for the interaction of carbon monoxide with caesium multilayers at 80 K indicate no adsorption; the O(1s) spectrum characteristic of the $O^{\delta-}$ state after low oxygen exposure (2 L) at 80 K has a binding energy of 531.3 eV, and a calculated concentration of 5×10^{14} atoms cm^{-2} . There is also present a highly electronegative oxygen state [$O(1s) \approx 527.5$ eV] at a concentration of $\approx 1 \times 10^{14}$ atoms cm^{-2} . On exposure of this oxidised surface to carbon monoxide at 80 K there is an increase in the O(1s) intensity and a corresponding shift to higher binding energy (532 eV). This state has associated with it a C(1s) peak at 290.1 eV and is assigned to $CO_2^{\delta-}$ species. The calculated concentration is 5×10^{14} cm^{-2} and a C:O ratio of 1:2.

particularly suitable since it does not adsorb at a caesium surface at 80 K [see O(1s) and C(1s) spectra, Fig. 2]. After exposing multilayers of caesium to oxygen (2 L) at 80 K, the O(1s) profile indicated the presence of the defective highly electronegative oxygen species present at a concentration of $\approx 1 \times 10^{14}$ atoms cm^{-2} *i.e.* less than 10% of a monolayer and the $O^{\delta-}$ (a) species at a concentration of $\approx 5 \times 10^{14}$ atoms cm^{-2} . There was no intensity in the C(1s) region at this stage (Fig. 2). However, on exposing this Cs- $O^{\delta-}$ (a) adlayer to carbon monoxide at 80 K the intensity of the O(1s) increased and a C(1s) peak emerged (Fig. 2) with a binding energy (287 eV) characteristic of $CO_2^{\delta-}$ (a). The concentration of the carbon atoms estimated from the C(1s) intensity was $\approx 5 \times 10^{14}$ atoms cm^{-2} and the carbon: oxygen atom ratio was close to 1:2 in keeping with our assignment of the surface species to $CO_2^{\delta-}$ (a). The O(1s) peak characteristic of $CO_2^{\delta-}$ (a) is at a binding energy of 532.0 eV. The $CO_2^{\delta-}$ species are converted,⁶ on exposure to further oxygen at 80 K, to carbonate and characterised by a C(1s) binding energy of 290.1 eV. The $CO_2^{\delta-}$ species has been central to the understanding of the surface chemistry of carbon dioxide at metal surfaces⁵ and the O(1s) and C(1s) binding energies (Fig. 2) are identical to those reported by Wambach and Freund⁵ for $CO_2^{\delta-}$ (a). The O(1s) and C(1s) binding energies of physically adsorbed CO_2 are at substantially higher values, 536 and 292 eV, respectively.^{5,6}

At higher oxygen exposures (20 L) when only O^{2-} (a) and $O_2^{\delta-}$ (a) are present (see Fig. 1) exposure to carbon monoxide under the same conditions leads to the formation of a carbonate species characterised by C(1s) and O(1s) binding energies of 290.6 and 533 eV respectively⁷ and a calculated oxygen: carbon atom ratio of 2.6:1. The intensity of the 530 eV characteristic of O^{2-} (a) did not change after exposure to carbon monoxide, compatible with its inactivity, the reactive surface species leading directly to carbonate being the peroxy $O_2^{\delta-}$ (a) species.

There are two aspects of this work that have significant implications to other studies—first that the $O^{\delta-}$ -like species, the predominant species present at low oxygen coverage, are the

active sites for carbon monoxide oxidation with a low-energy pathway to $CO_2^{\delta-}$ species. The latter are the species isolated in studies⁶ of the coadsorption of carbon monoxide and dioxygen at magnesium and caesium promoted Cu(110)-O surfaces and intermediates in carbonate formation.⁷ The $O^{\delta-}$ -like species are also those reported^{4,8} to be active as transients in oxydehydrogenation reactions. Secondly, Greber *et al.*⁹ have reported the ejection of O^- ions during the first stages of the dissociative chemisorption of dioxygen at caesium surfaces. This coincides with the oxygen exposure (≈ 2.5 L) when the $O^{\delta-}$ (a) concentration is at its maximum at a caesium (multilayer) surface (Fig. 1). At higher exposures⁹ the O^- emission falls to zero when the predominant species present are O^{2-} (a) and $O_2^{\delta-}$ (a) (Fig. 1).

The authors are grateful to EPSRC for a ROPA Award (to M. W. R. and S. L.) and to Unilever for a Research Assistantship to G. U. K. who also acknowledges the encouragement of Professor C. N. R. Rao.

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Received, 4th October 1995; Com. 5106550J