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# A reactive oxygen state at a barium promoted Au (100) surface: the oxidation of ethene at cryogenic temperatures

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Although Au (100) does not adsorb oxygen at either 295 K or 80 K, a barium modified Au(100) surface is active in oxygen dissociation resulting, through surface diffusion of oxygen adatoms, in the formation of a chemisorbed oxygen adlayer. This oxygen species is inactive for ethene oxidation, as is the oxygen species pre-adsorbed at an Au(100)–Ba surface at 80 K, and the clean Au(100)–Ba surface. However, when molecularly adsorbed ethene present at a Au(100)–Ba surface at 80 K is exposed to dioxygen and warmed to 140 K, surface carbonate is observed. We conclude that a transient oxygen species is the oxidant.

**KEY WORDS:** gold; barium; oxygen transients; ethene.

Much of our understanding of oxidation catalysis at metal surfaces is based on the spectroscopic characterisation of oxygen states under static experimental conditions, although in the case of oxidation catalysis on gold, more attention has been given to the structural characteristics of the surface [1]. However, it is now well established that oxygen adsorbed at low temperatures (80 K), or transiently present under dynamic co-adsorption conditions, can activate (oxidise) molecules under conditions where the stable chemisorbed oxygen overlayer at metal surfaces is unreactive, and this has led to new insights into oxidation catalysis [2–4]. In this paper, we establish that a transient oxygen state present at a barium modified Au (100) surface is effective in the facile oxidation of ethene at low temperatures.

The X-ray photoelectron spectra were obtained using a VG ESCA3 spectrometer and the surface concentration data determined from an analysis of the O(1s), Au(4f) and Ba(3d) spectra using the method of Carley and Roberts [5]. The barium was deposited on the Au(100) crystal by means of an electrically heated getter (SAES).

Although the clean Au (100) surface is unreactive to dioxygen [6], extensive adsorption occurs when the surface doped with barium ($\sigma_{Ba} = 0.610^{15}$ cm$^{-2}$) is exposed to dioxygen (figure 1), characterised by an O(1s) binding energy of 531.0 eV; the surface oxygen adatom concentration is calculated to be $3 \times 10^1$ cm$^{-2}$. This is analogous to what was observed in previous studies of the Zn(0001)–Ba surface ($\sigma_{Ba} = 0.06 \times 10^{15}$ cm$^{-2}$), where the rate of dioxygen dissociation was increased by a factor of nearly $10^3$ compared with that at the atomically clean Zn(0001) surface [7] and resulted in the formation of the complete "final state" chemisorbed layer. In both cases, Au(100) and Zn(0001), the oxygen uptake is significantly greater than that expected for the formation of an oxygen state associated directly with the dopant Ba atoms: following oxygen dissociation at barium sites, the adatoms undergo surface diffusion resulting in a high concentration of surface oxygen atoms ("spillover").

Both the Au(100) and Au(100)–Ba surfaces are unreactive towards ethene, the molecularly adsorbed species observed after exposure at 80 K desorbing on warming to 130 K (figure 2). The oxygen adatoms generated at the Au (100)–Ba surface at 295 K are also unreactive to ethene at both 295 K (figure 3) and 80 K. However, when ethene is present in a molecularly adsorbed state at 80 K (C(1s) binding energy = 286 eV) and is exposed to dioxygen at low temperature (figure 4), there is a distinct change in the C(1s) binding energy and the development of an O(1s) peak which is significantly broader than that observed after the adsorption of oxygen on the Au(100)–Ba surface. Warming this surface to 295 K leads to an increase in C(1s) intensity in the range 287–290 eV at the expense of that associated with the molecularly adsorbed state of ethene. At 140 K virtually all the C(1s) intensity is centred at 290.5 eV, and is accompanied by a shift in the O(1s) peak to 532 eV, both features (figure 4) being characteristic of a surface carbonate species. It is significant that we observe no reaction between ethene and the oxygen species formed by prior adsorption of dioxygen at Au(100)–Ba at 80 K, nor between dioxygen gas and ethene physisorbed at an undoped Au(100) surface at 80 K.

It is clear that a reactive oxygen species is formed at 80 K at the Au(100)–Ba surface, which reacts with pre-adsorbed ethene, but in the absence of ethene forms an unreactive surface state. In the former case the reaction leads to some carbonate formation even at 80 K, the

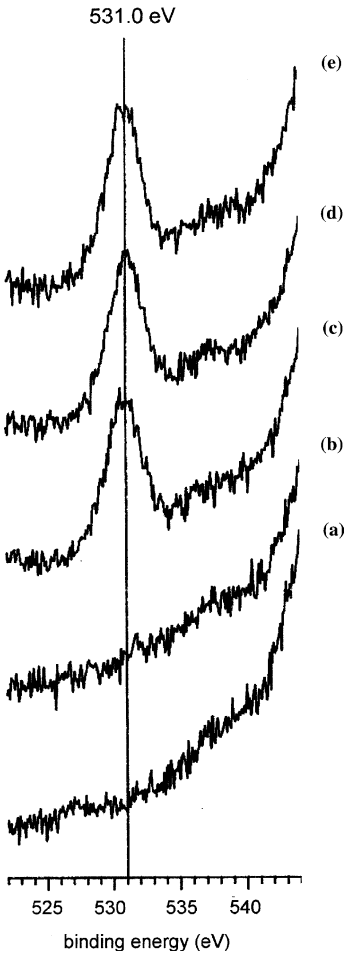


Figure 1. O(1s) spectra for oxygen chemisorption at 298 K at a Au(100)–Ba surface: (a) clean Au(100), (b) after Ba deposition ($\sigma_{Ba} = 0.6 \times 10^{15}$ cm$^{-2}$), (c) 10 L exposure to oxygen, (d) 100 L oxygen, (e) 1000 L oxygen (1 L $\equiv$ $10^{-6}$ Torr-sec).

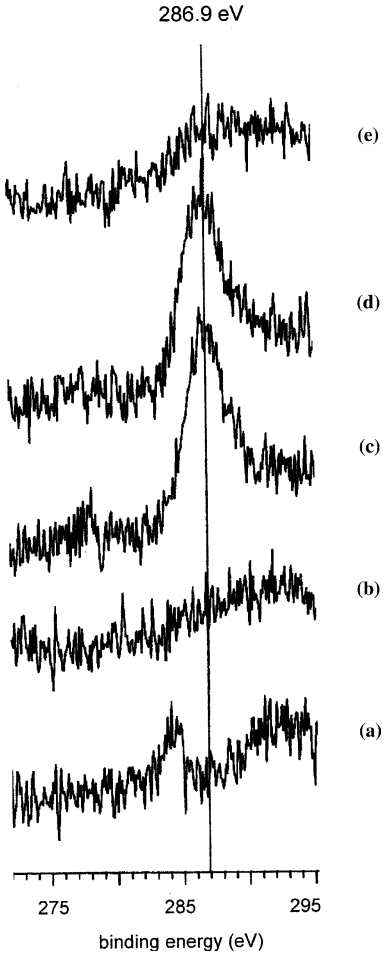


Figure 2. C(1s) spectra for ethene adsorption at a Au(100)–Ba surface: (a) clean Au(100), (b) after Ba deposition ($\sigma_{Ba} = 0.6 \times 10^{15}$ cm$^{-2}$), (c) 100 L exposure to ethene at 80 K, (d) 1000 L exposure to ethene at 80 K, (e) after warming to 130 K.

reaction being almost complete by 140 K (figure 4). There are strong similarities with our earlier studies of Zn(0001)–Ba and also of other systems, including the oxidation of propene at Ag(100)–Cs surfaces at low temperatures [8]. We are unable distinguish spectroscopically between the involvement of a molecular transient $O_2^{\delta-}$ (s) (equation 1, below) and an atomic transient $O^{\delta-}$ (s) (equation 2), but the XPS data are consistent with the formation of surface carbonate which partially forms at 80 K, which is essentially complete after warming to 140 K. In the absence of co-adsorbed ethene these transients would form unreactive $O^{\delta-}$ (a) species (equation 3).

$$O_2(g) \Rightarrow O_2^{\delta-}(s) \quad (1)$$

$$O_2^{\delta-}(s) \Rightarrow O^{\delta-}(s) + O^{\delta-}(s) \quad (2)$$

$$O^{\delta-}(s) \Rightarrow O^{\delta-}(a) \quad (3)$$

In the case of the oxidation of ammonia at a Zn(0001) surface [9], where dioxygen bond cleavage is very slow and precursor kinetic behaviour is observed, the evidence is for a dioxygen–ammonia complex ($O_2^{\delta-}$–$NH_3$) as the transition state, whereas at a Cu(110) surface isolated disordered oxygen adatoms $O^{\delta-}$ (s) were shown to be the active species in ammonia oxidation, resulting in complete oxidation to give nitrogen adatoms at about 100 K [10]. Similarly, methane was completely oxidised to surface carbonate at lithium and magnesium surfaces at low temperatures; in the latter case, oxygen adatoms were established unequivocally to be the oxidising species, having been formed *in situ* by the dissociative chemisorption of nitric oxide [11]. Similar conclusions were reached for the mechanism of the oxidation of carbon monoxide at an aluminium surface at 80 K [3], a reaction central to the current interest in gold as a low temperature catalyst. It is also relevant to mention that when oxygen adatoms are generated *in situ via* a hot filament then complete oxidation of propene occurs at Au(111) and Au(100) surfaces when the oxygen cover-

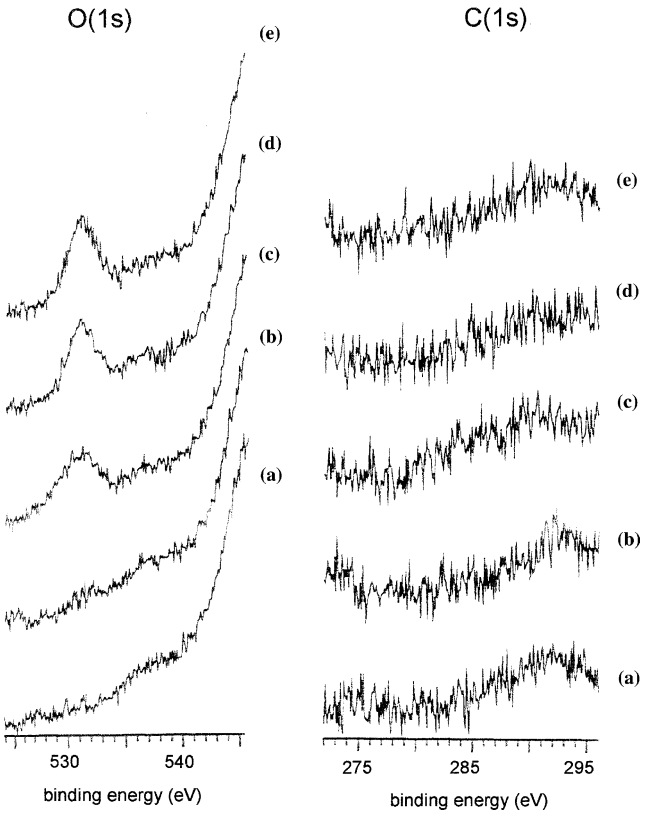


Figure 3. O(1s) and C(1s) spectra for ethene adsorption on a preformed chemisorbed oxygen adlayer at a Au(100)–Ba surface: (a) clean Au(100), (b) after Ba deposition ($\sigma_{Ba} = 0.3 \times 10^{15}$ cm$^{-2}$), (c) 0.25 L exposure to oxygen at 295 K, (d) 100 L exposure to ethene at 295 K, (e) 1000 L exposure to ethene at 80 K.

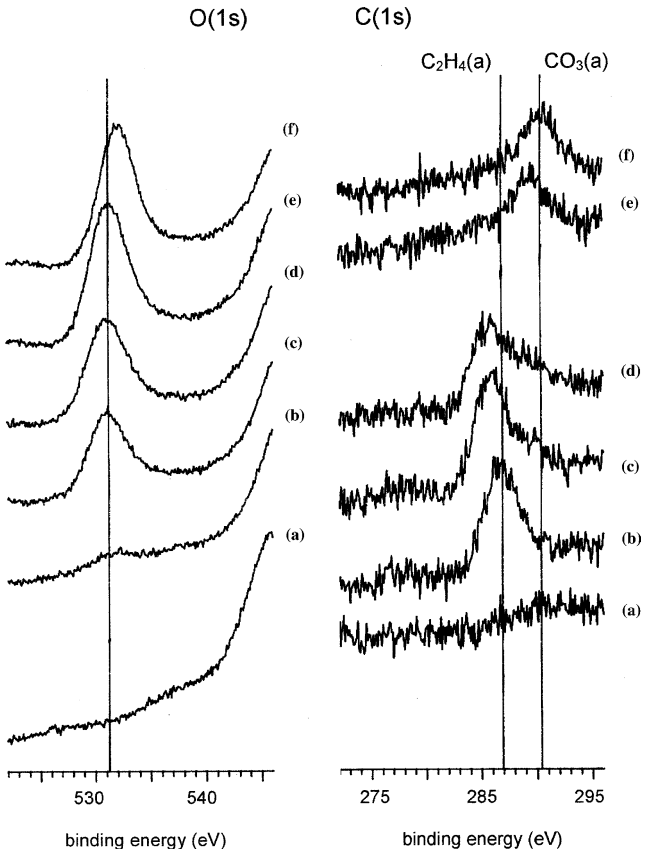


Figure 4. O(1s) and C(1s) spectra for the low temperature interaction of oxygen with ethene adsorbed at a Au(100)–Ba surface: (a) Au(100)–Ba surface ($\sigma_{Ba} = 0.6 \times 10^{15}$ cm$^{-2}$), (b) 100 L exposure to ethene at 80 K, (c) 100 L exposure to $O_2$ at 80 K, (d) 1000 L exposure to $O_2$ at 80 K, (e) warmed to 140 K, (f) warmed to 295 K.

age $\theta_0 = 1$; for smaller coverages ($\theta_0 = 0.4$) there is evidence for partial oxidation products [12]. In view of these analogous observations, and no evidence for precursor-type kinetics, we suggest that the reactive oxygen is the atomic $O^{\delta-}$ (s) transient state (equation 2).

## 1. Conclusions

In a critical comprehensive review [1] from Freund's group at the Fritz-Haber Institute in Berlin, concerning catalysis at gold surfaces, attention is drawn to the "unsystematic manner" in which experiments have been carried out with "contradictory results", "the mechanism and active sites remaining unknown" and "the nature of the reactive oxygen still a mystery." In this paper, we have established that a metastable oxygen state provides a low energy pathway to the oxidation of ethene at a Au(100)–Ba surface.

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