Catalytic Cleavage of Dioxygen Bond at a Zn(0001)–Ba Surface: the Role of a Dioxygen Surface Transient

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The presence of barium (θ *ca.* 0.1) at a Zn(0001) surface is shown to increase the rate of dioxygen bond cleavage by *ca.* 10^3 at 295 K; this provides further evidence for a mobile molecular precursor O_2^-(s) participating in the dynamics of the dissociative chemisorption of oxygen and first suggested by the probe-molecule approach used to search for transient surface oxygen states.

The Zn(0001)–dioxygen system offered[1] distinct advantages for exploring whether or not oxygen surface transients, O_2^-(s) or O^-(s) could exist at metal surfaces since dioxygen bond cleavage at the atomically clean surface is highly inefficient with a reaction sticking probability of *ca.* 10^{-3} at 295 K. The rate determining step in the following sequence (1) is considered to be the formation of the superoxo O_2^-(s) surface species. Support for this view came from the observation that when dioxygen is coadsorbed with ammonia the reaction rate is increased at low temperatures by up to a factor of *ca.* 10^3, with the transient O_2^-(s) clearly implicated in the mechanism through the formation of a dioxygen–ammonia charge-transfer type complex.[1,2] The latter dissociates to surface oxide, hydroxide and amide species, their presence being established by both X-ray photoelectron and vibrational spectroscopies.

$$O_2(g) \rightleftarrows O_2(s) \xrightarrow{e} O_2^-(s) \rightarrow O^-(s) \xrightarrow{e} O^{2-}(a) \qquad (1)$$

$$O_2(g) \rightarrow O_2^-(s) \qquad (2)$$

$$NH_3(g) \rightarrow NH_3(s) \qquad (3)$$

$$(O_2^- \cdots NH_3)(s) \rightarrow NH_2(a) + OH(a) + O^{2-}(a) \qquad (4)$$

We explore in this paper whether further evidence for O_2^-(s) can be obtained from studies of alkali metal activation of the Zn(0001) surface. In Fig. 1(*a*) is shown the extent of dissociative chemisorption of dioxygen at a Zn(0001) surface as a function of exposure at 295 K, the surface oxygen O^{2-}(a) concentration being assessed from the intensity of the O(1s) spectra. The rate of dioxygen bond cleavage is small with a sticking probability of *ca.* 10^{-3}. The clean Zn(0001) surface was then exposed to a source of barium and a coverage of *ca.* 10^{14} cm^{-2} atoms of barium obtained, the latter being calculated from the Ba(3d) intensity. When the Zn(0001)–Ba surface was exposed to dioxygen at 295 K the O(1s) intensity increased rapidly [Fig. 1(*b*)] with oxygen exposure and the monolayer [*ca.* 10^{15} O^{2-}(a) cm^{-2}] was completed within an exposure of less than 10 L. The rate of dioxygen dissociation has been increased by a factor of nearly 10^3 through the presence of *ca.* 10^{14} atoms per cm^2 of barium.

Clearly the barium-modified Zn(0001) surface not only catalyses dioxygen bond cleavage but also and significantly so, generates reactive oxygen species which are mobile in that they are available for forming O^{2-}(a) species at all the surface zinc atoms. We conclude that this is good evidence for O_2^-(s) having an appreciable surface lifetime and therefore providing support for the conclusions from the coadsorption studies where O_2^-(s) is suggested to form the complex $(O_2^- \cdots NH_3)$(s).[2,3]

The role of barium (and similar results have also been obtained with caesium[6]) is therefore to provide a low-work-function surface site where electron transfer to a dioxygen O_2(s) species is facile. Alkali metal promotion, or harpooning-type mechanisms, leading to O_2^- species in oxygen-scattering studies from metal surfaces also provide general support for this view.[4] Whether or not we are justified in designating a full electronic charge to the dioxygen transient is not known, and designating the dioxygen species as $O_2^{\delta-}$(s) may be more correct. This is a viewpoint we have expressed in earlier discussions of the role of surface oxygen in the activation of

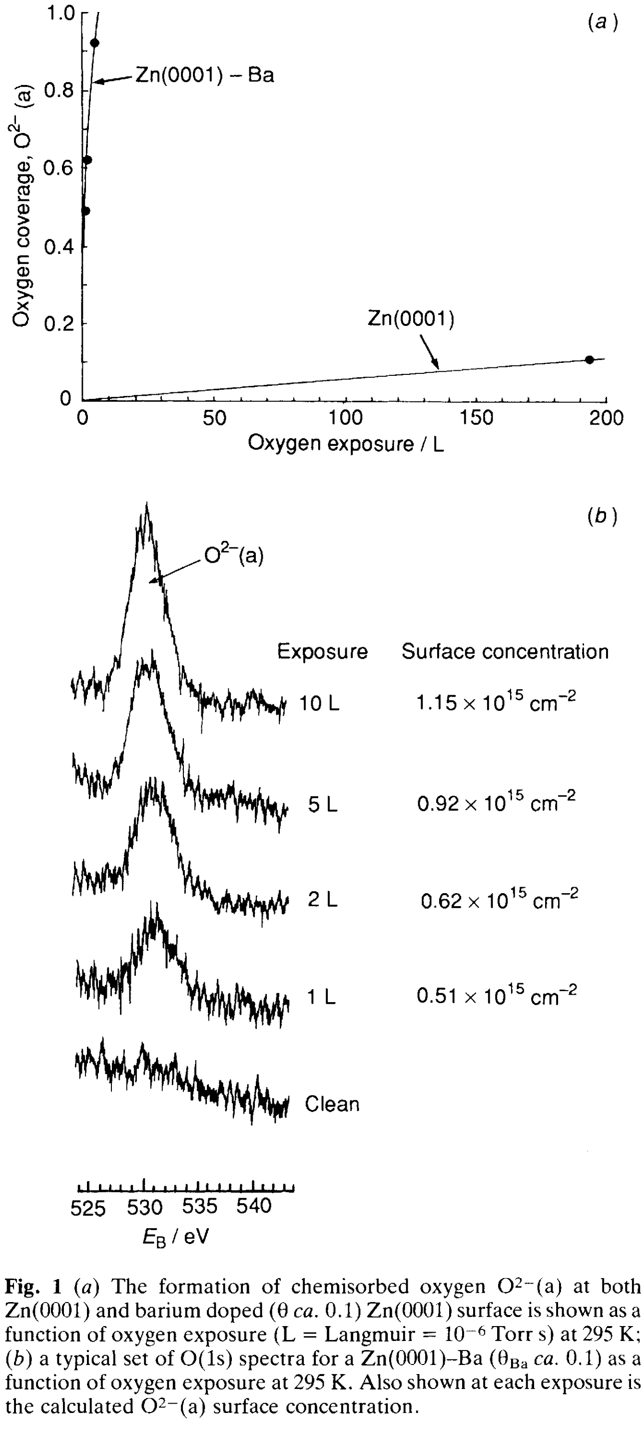

Fig. 1 (*a*) The formation of chemisorbed oxygen O^{2-}(a) at both Zn(0001) and barium doped (θ *ca.* 0.1) Zn(0001) surface is shown as a function of oxygen exposure (L = Langmuir = 10^{-6} Torr s) at 295 K; (*b*) a typical set of O(1s) spectra for a Zn(0001)–Ba (θ_{Ba} *ca.* 0.1) as a function of oxygen exposure at 295 K. Also shown at each exposure is the calculated O^{2-}(a) surface concentration.

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adsorbates.[5] The formation of the negative ion then gives rise to a coulombic interaction term resulting in bond cleavage and oxide O^{2-}(a) formation, for which there is a strong thermodynamic driving force.

An aspect not addressed in the investigation is the possibility that the Zn(0001) surface undergoes reconstruction in the presence of 0.1 or less of a monolayer of barium; whether this contributes to the facile energetics of electron transfer to dioxygen is being investigated.

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