

Evidence from Coadsorption Studies for a Molecular Precursor State in the Oxidation of Zn(0001)

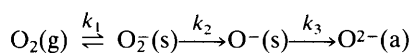
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The rate of dissociative chemisorption of dioxygen at a Zn(0001) surface at 110 K increases by a factor of nearly 10^3 when coadsorbed with ammonia; a model based on a precursor state involving an ammonia-dioxygen complex is suggested.

The role of surface oxygen in the activation of inherently unreactive adsorbate molecules at metal surfaces is now well established.¹ The distinction has been made between the influence of preadsorbed and coadsorbed oxygen, with the proposal that in the coadsorption of dioxygen and ammonia at a Mg(0001) surface a transient surface oxygen species, designated O⁻(s) in Scheme 1, was responsible for the activation.² In this Communication we report an X-ray photoelectron spectroscopic study of the coadsorption of ammonia and dioxygen at a Zn(0001) surface. Although activation of the ammonia occurs leading, *via* hydrogen abstraction, to surface amide, data which are analogous to those reported for the Mg-NH₃-O₂ system, the most significant observation is a remarkable enhancement of the rate of surface oxidation, *i.e.* O²⁻(a) formation, by a factor of nearly 10^3 at 110 K, compared with the rate of oxidation in pure dioxygen.

Figure 1 shows the O(1s) spectra for an atomically clean Zn(0001) surface exposed to dioxygen at 110 K. A peak develops at a binding energy of 530.4 eV, assigned to O²⁻(a), and is accompanied by a very weak shoulder at *ca.* 532 eV.



Scheme 1

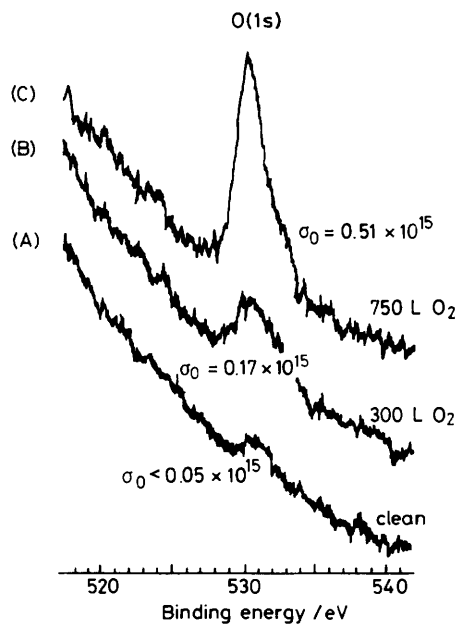
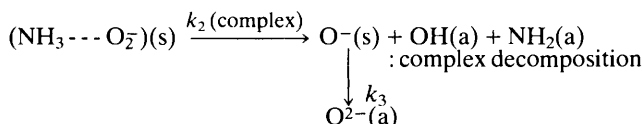
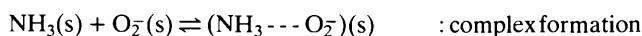
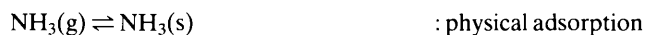


Figure 1. O(1s) spectra for (A) clean Zn(0001) surface and after exposure to dioxygen at 110 K for total exposures of (B) 300 L and (C) 750 L.

When a clean Zn(0001) surface is exposed to an ammonia-dioxygen mixture (NH₃:O₂ = 7:1) at 110 K, the striking feature (Figure 3a) is that an exposure of only 40 L (1 L = 10^{-6} torr s) gives an oxygen surface concentration, 0.63×10^{15} , comparable with that obtained after 750 L exposure to dioxygen, $0.51 \times 10^{15} \text{ cm}^{-2}$, the effective exposure to dioxygen in the mixture being only 5 L (Figure 2). The O(1s) spectrum in the case of the mixture consists of two components of about equal intensities, one at 530.4 eV and one at 532.4 eV. In keeping with other studies^{2,3} we assign the latter to surface hydroxyl species OH⁻(a), generated by hydrogen abstraction from coadsorbed ammonia. This is supported by the observation of an N(1s) feature at 399 eV characteristic of surface amide NH₂(a) (Figure 3b). The N(1s) peak at 401 eV is due to physically adsorbed ammonia NH₃(a). It should be noted that both the clean and pre-oxidised surface are chemically unreactive towards NH₃(g) under the same experimental conditions.

In the presence of the ammonia-dioxygen gas mixture we suggest that the following molecular events are involved, Scheme 2. We designate a weakly adsorbed or surface transient species by (s) and a strongly chemisorbed species by (a). The model involves the formation of an ammonia-dioxygen surface complex (NH₃---O₂)(s) as an intermediate



Scheme 2

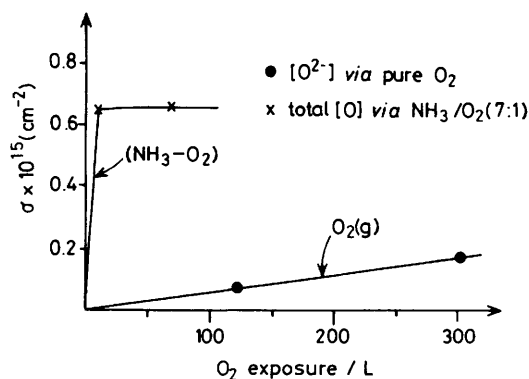


Figure 2. Plot of surface oxygen concentration vs. exposure for the interaction of Zn(0001) with dioxygen (●) and an ammonia:dioxygen (7:1) mixture (×) at 110 K. In the latter case the exposure used is that for the oxygen partial pressure in the mixture (*i.e.* *ca.* 5 L for a mixture exposure of 40 L).

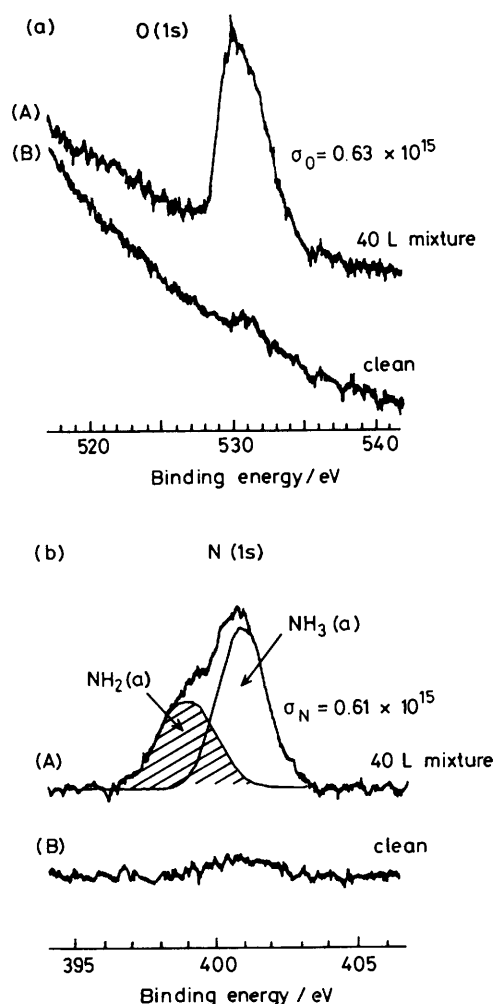


Figure 3. (a) and (b): O(1s) and N(1s) spectra for (A) a Zn(0001) surface after exposure (40 L) to a mixture of ammonia and dioxygen ($\text{NH}_3:\text{O}_2 = 7:1$) at 110 K and (B) a clean Zn(0001) surface.

or precursor state which decomposes to give chemisorbed $\text{O}^{2-}(\text{a})$, $\text{OH}(\text{a})$, and $\text{NH}_2(\text{a})$. Two factors will contribute to the observed increase in $d[\text{O}^{2-}(\text{a})]/dt$: first a higher heat of adsorption of the surface complex compared with $\text{O}_2(\text{s})$ through the term $\exp(\Delta H_{\text{complex}}/RT)$ which determines its surface concentration, and second a lowering of the activation

energy barrier for decomposition, *i.e.* leading to $k_2(\text{complex}) \gg k_2$. A description based on a Lennard-Jones potential energy profile would suggest that an increase in the thermodynamic term ΔH would be expected to be accompanied by a lowering of the activation energy term for complex dissociation. The rate determining step is therefore decomposition of the precursor complex, k_3 being fast compared with $k_2(\text{complex})$. Support for this model comes from detailed kinetic studies over a wide range of temperature, with $d[\text{O}^{2-}(\text{a})]/dt$ decreasing with increasing temperature.

Furthermore, analysis of the composite O(1s) and N(1s) spectra, using curve-fitting and spectral subtraction techniques, enables the development of individual surface species to be studied. For an experiment at 160 K, where the reaction with the mixture is slow enough to follow the early stages of the oxidation, we find that the relative concentrations of the $\text{O}^{2-}(\text{a})$, $\text{OH}^-(\text{a})$, and $\text{NH}_2^-(\text{a})$ are initially close to 1:1:1, consistent with oxygen dissociation and H-abstraction being concerted events *i.e.* $k_3 \gg k_2(\text{complex})$.

In summary, this Communication shows how an inherently unreactive molecule (ammonia) can influence the rate of a surface reaction (oxidation) through a weak interaction (possibly hydrogen bonding) in a precursor state. It also emphasises: (i) the advantages of using dynamic coadsorption to study the mechanisms of surface reactions (catalysis), (ii) the role of short-lived intermediates (precursors), (iii) the limitations of the more classical, post-reaction type analysis, and (iv) the need for high-pressure studies, when such precursor states are likely to be most important. The latter was established in the present work by study at very low temperatures and low pressures, under which conditions surface life-times may be comparable to those at much higher pressures and temperatures.

We are grateful to the S.E.R.C. and VG Scientific for their support of this work.

Received, 13th October 1987; Com. 1493

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