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INTERMOLECULAR CHARGE-TRANSFER AND THE CLEAVAGE OF THE DIOXYGEN BOND AT METAL SURFACES: OXYGEN AT Zn(0001)

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Evidence is provided for the participation of surface pyridine-dioxygen charge transfer complexes in the pyridine accelerated cleavage of the dioxygen bond at Zn(0001) surfaces.

The recent observation that the rate of dissociative chemisorption of dioxygen at Zn(0001) surfaces was enhanced in the presence of ammonia led to the conclusion that a dioxygen-ammonia complex was involved as a precursor state [1]. The mechanism by which the rate of $O^{2-}(a)$ formation is enhanced by a factor of almost 10^3 was suggested to arise as follows (see below) with the role of ammonia being to decrease the activation energy for dioxygen dissociation and also to increase the effective surface concentration of dioxygen through an increase in the term

$$\exp\left(\frac{\Delta H \text{ complex}}{RT}\right)$$

where ΔH complex is the heat of adsorption of $(O_2^- \text{---} NH_3)(s)$.

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

$$O_2^-(s) + NH_3(s) \rightarrow (O_2^- \text{---} NH_3)(s)$$

$$(O_2^- \text{---} NH_3)(s) \rightarrow NH_2(a) + OH(a) + O^{2-}(a).$$

It is important to recall that ammonia itself is only weakly adsorbed at the Zn(0001) surface and no 'nitrogen' containing (NH_x) species were observed in the absence of dioxygen [1] at low temperature. In order to explore whether the stability of the surface precursor complex $(O_2^- \text{--} NH_3)$ could be attributed to just a H-bonding component or whether the electron donor (Lewis base) property of NH_3 was more important, we investigated whether or not the rate of dioxygen dissociation at a Zn(0001) surface could be influenced by coadsorbing with pyridine where H-bonding would not play any role.

Photoelectron spectroscopy (XPS) was used to determine the surface concentrations of oxygen and pyridine through monitoring the O(1s), C(1s) and

N(1s) spectral regions while ultraviolet photoelectron spectroscopy (UPS) provided information on the bonding of pyridine to the surface.

Figure 1 shows a set of O(1s), C(1s) and N(1s) spectra observed when a

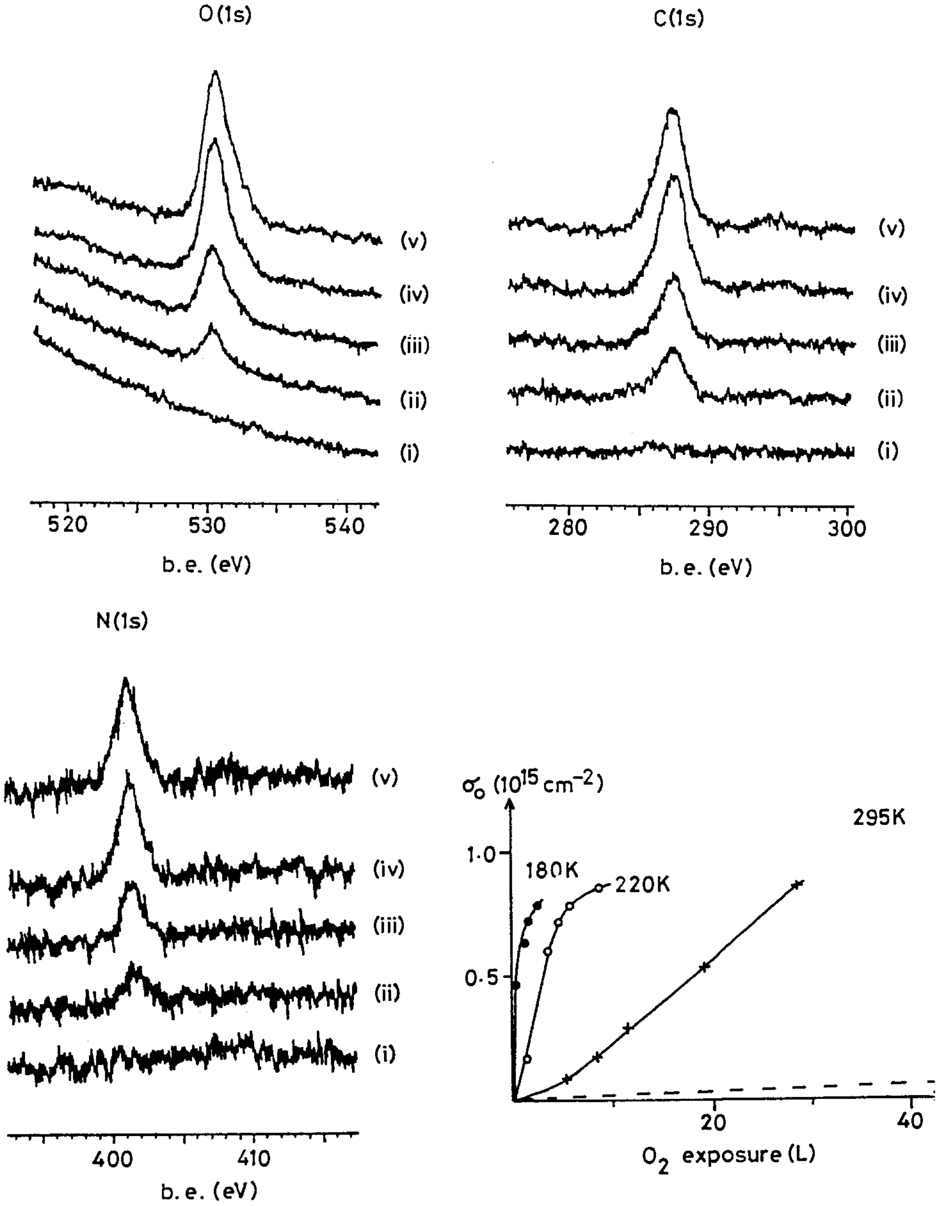

Fig. 1. O(1s), C(1s) and N(1s) spectral regions for (i) clean Zn(0001) and after various exposures to dioxygen-pyridine mixtures (1 : 9) at 220 K. The exposures are given in terms of dioxygen: (ii) 1.4L, (iii) 2.4L, (iv) 4.7L and (v) 9L. Also shown is the calculated surface oxygen concentration at 220 K (based on the O(1s) intensity data) and two other temperatures (180 K and 295 K). The surface concentration data for "pure dioxygen" at 220 K are also shown (dotted line).

mixture of oxygen and pyridine is coadsorbed at an atomically clean Zn(0001) surface at 220 K. It can be seen that cleavage of the dioxygen bond is facile leading to a surface concentration of chemisorbed oxygen. $O^{2-}(a)$, of 0.8×10^{15} cm^{-2} for an effective exposure to dioxygen of 8L. (The exposure to the mixture was about 80L and the composition of the pyridine-dioxygen gas mixture was approximately 10 : 1.) Surface oxygen concentrations are also shown for similar studies at 180 K and 295 K, the lower the temperature the more effective is the role of pyridine in inducing the cleavage of the dioxygen bond leading to $O^{2-}(a)$ formation. At 180 K the efficiency of oxygen dissociation per molecular impact with the surface is close to unity whereas in the absence of pyridine it is about 10^{-3}.

With atomically clean Zn(0001) surfaces an impinging dioxygen molecule will exchange energy and momentum with the surface atoms, after which it may scatter or become trapped (see scheme below). Trapped molecules may return to the gas phase or undergo dissociative chemisorption. The coadsorption of dioxygen with pyridine provides a more efficient route for dioxygen dissociation than does dioxygen alone (k_3, $k_4 \gg k_1$, k_2), and this we suggest is due to ability of pyridine to form donor-acceptor complexes with diatomic molecules.

Dissociative chemisorption of dioxygen at a Zn(0001) surface:

$O_2(g) \rightleftarrows O_2(s)$	Accommodation at the surface
$O_2(s) + Zn \xrightarrow{k_1} O_2^-(s)$	1st stage of chemisorption
$O_2^-(s) \xrightarrow{k_2} O^{2-}(a)$	Dissociative chemisorption

Coadsorption of dioxygen + pyridine at a Zn(0001) surface:

$O_2(s) + Py(s) \xrightarrow{k_3} (O_2^- - Py^*)(s)$	Oxygen C–T surface complex with pyridine coadsorbate
$(O_2^- - Py^*)(s) \xrightarrow{k_4} O^{2-}(a) + Py^+(a)$	Dissociation of transient C–T complex.

Such C–T complexes between pyridine and diatomic molecules have been recognised (in solution) through characteristic shifts in their infrared absorption spectra [2] and interpreted as reflecting bond weakening in the diatomic molecule. We can, however, only speculate on the nature of the electronic interactions involved in the C–T dioxygen-pyridine surface complex (see reaction scheme). There are two possibilities, either the nitrogen lone-pair electrons are involved (pyridine acting as a Lewis base) or alternatively there is delocalization of the negative charge on the $O_2^-(s)$ into the pyridine ring. While studies in this laboratory of the coadsorption of dioxygen with benzene [3] provided no evidence for the catalysis of dioxygen bond cleavage at Zn(0001) surfaces, suggesting no

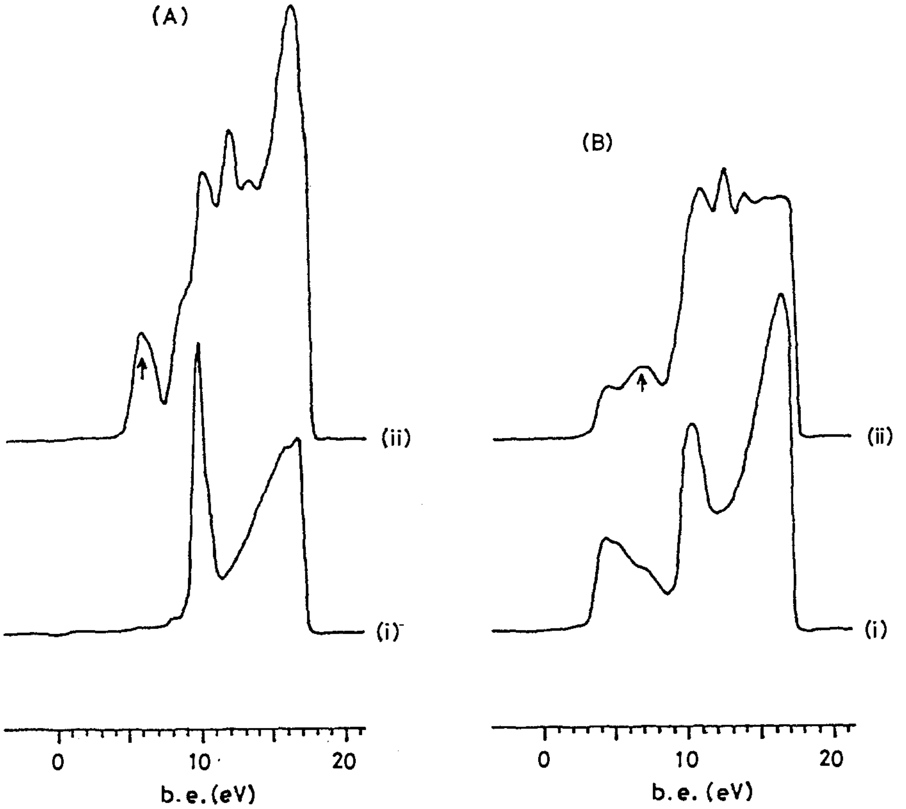

Fig. 2. HeI spectra obtained after exposure of a clean (A) and pre-oxidised (B) Zn(0001) surface to pyridine: A (i) clean Zn(0001) surface, A (ii) exposed to pyridine at 120 K, B (i) Zn(0001)–O surface, B (ii) exposed to pyridine at 220 K. The feature indicated with an arrow is sensitive to the nature of the bonding of the adspecies to the substrate (see text).

π^*-electron involvement, Slough [4] has reported ESR and visible and ultraviolet absorption spectra of O_2^--pyridine complexes in solution which are consistent with delocalization of the negative charge on to the pyridine ring.

We turn now to the fate of the pyridine fragment of the ($Py^* - O_2^-$) surface complex. In the co-adsorption experiment at 220 K. It was established that there is a clear parallelism between the variation of the pyridine and oxygen surface concentrations with exposure, five oxygen adatoms being formed per ‘nitrogen’ adsorbed. Since there is no detectible adsorption of pyridine on the clean surface at this temperature, this is indicative of a pyridine-Zn^{2+} or pyridine-O^{2-} interaction *subsequent to the dissociation of the C–T complex*. UPS data from pyridine adsorbed on a clean Zn(0001) surface at 120 K and on an oxidised surface at 220 K are shown in fig. 2. The identification of adsorbate geometry, that is the discrimination between a perpendicular (N-bonded) and flat (π-bonded) species, from UPS data is not straightforward. The same angle-resolved data for pyridine adsorption on copper, for example, have been interpreted [5,6] in different ways.

However, differences between HeI spectra from the same adsorbate are more amenable to analysis. The lowest binding energy peak, at ca 6 eV binding energy, (fig. 2) consists of contributions [5] from π orbitals ($1a_2 + 2b_1$) and the nitrogen lone pair orbital ($7a_1$). For adsorption at the preoxidised surface, this feature is shifted to higher binding by about 0.9 eV compared with adsorption at the clean surface, and is broadened. We ascribe this to the involvement of the N-lone pair electrons in bonding to the oxidised surface, presumably via donation to Zn^{2+} sites. A similar explanation has been given for comparable data for pyridine adsorption at oxidised nickel surfaces [7]. Although we cannot rule out the formation of pyridine 1-oxide bonded to a surface Zn^{2+}, we would then have anticipated two distinct components to the O(1s) spectrum; this is not observed.

These conclusions prompt us to recall that there is observed frequently a correlation between activation energy (reaction rates) and the thermodynamic stability of the products – the Polanyi relationship – which (for surfaces) can be discussed in terms of a Lennard-Jones potential diagram [1]. The reaction pathway – involving the transient pyridine-dioxygen complex – will depend on the potential energy profile along the reaction coordinate which will in turn reflect the decomposition of the intermediate complex to give O^{2-}(a) and a strongly chemisorbed pyridine molecule bonded at an electron deficient Zn^{2+} site.

To summarise, these results lead to the conclusion that the rate determining step in the dissociative chemisorption of dioxygen to give O^{2-}(a) involves the formation of O_2^-(s). In the gas phase the formation of O_2^- is exothermic to the extent of about 42 kJ. It is the ability of pyridine through the formation of a complex with dioxygen, $(O_2^- - Py^*)$(s), resulting in an increase in the rate of O^{2-}(a) formation, that is emphasised in this paper. Such intermolecular induced cleavage of dioxygen is likely to be most significant for metal-oxygen systems where the sticking probability for dioxygen dissociation is low (e.g. 10^{-3}) which is indeed the case for Zn(0001). These results emphasise the need to explore whether transient C–T complexes are of more general significance in determining chemical specificity and the kinetics of surface reactions.

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