The Role of Water Vapour in the Hydrogenation of Nitric Oxide at a Zn(0001) Surface

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Nitric oxide is dissociatively chemisorbed at a Zn(0001) surface at 80 K, both the chemisorbed nitrogen and oxygen are stable up to 470 K; in the presence of coadsorbed water, hydrogenation of the adsorbed nitrogen occurs at 200 K by hydroxyl species formed as a result of the activation of molecularly adsorbed water by chemisorbed oxygen generated in the dissociative chemisorption of NO.

In this communication we delineate, through the use of time and temperature dependent photoelectron spectroscopy, the reaction pathway and individual steps involved in the reduction of nitric oxide by water vapour at a Zn(0001) single crystal surface. We have made use of both *X*-ray and u.v.-induced spectra to provide the experimental evidence on which the molecular mechanism is established. The intensities of the O(1s) and N(1s) spectra enable the concentration of surface species to be calculated as described previously[1,2] and from the characteristic binding energies the molecular nature of the surface species identified. Helium induced spectra provide[3] complementary information on the valence level molecular orbitals. Our earlier studies of the interaction of nitric oxide with Cu, Fe, and Ni[4—6] surfaces and also of water vapour with a Zn(0001) surface[7] are relevant to the spectral assignments and hence to establishing the proposed mechanism.

The spectra enable us to distinguish between molecularly adsorbed NO, dissociatively chemisorbed NO, incorporated oxygen O^{2-}(b), molecularly adsorbed water, adsorbed N_2O, chemisorbed nitrogen adatoms, and hydrogenated nitride species NH and NH_2. We cannot distinguish from the core-level O(1s) spectra between NO(a), O^-(a), and OH(a) but information from N(1s) and He(I) spectra enables us to distinguish between these three species. The O(1s) spectra were curve-fitted[3] and when taken in conjunction with the N(1s) spectra, surface concentrations calculated. Figure 1(a) shows N(1s) spectra for the interaction of nitric oxide with an atomically clean Zn(0001) surface in the temperature range 80—470 K. After exposure (130 L) to nitric oxide at 80 K there are three distinct N(1s) peaks at binding energies of 396, 402, and 406 eV. There is also intensity present at *ca.* 403 eV resulting from the overlap of the 401.5 and 403 eV peaks. On warming to 130 and 200 K, intensity in the higher binding energy spectral region (403—406 eV) diminishes and two distinct N(1s) peaks remain at 396 and 401.5 eV. These last peaks are assigned to N(a) and NO(a) surface species. The N(1s) intensity at 403 and 406 eV is attributed to the catalytic formation of N_2O(a) within the chemisorbed layer at 80 K; on warming to 130 K desorption of N_2O occurs as indicated by both the N(1s) and O(1s) spectra.[4] At 273 K most of the molecularly adsorbed nitric oxide had desorbed and at 360 K and above only the chemisorbed nitride species remain.

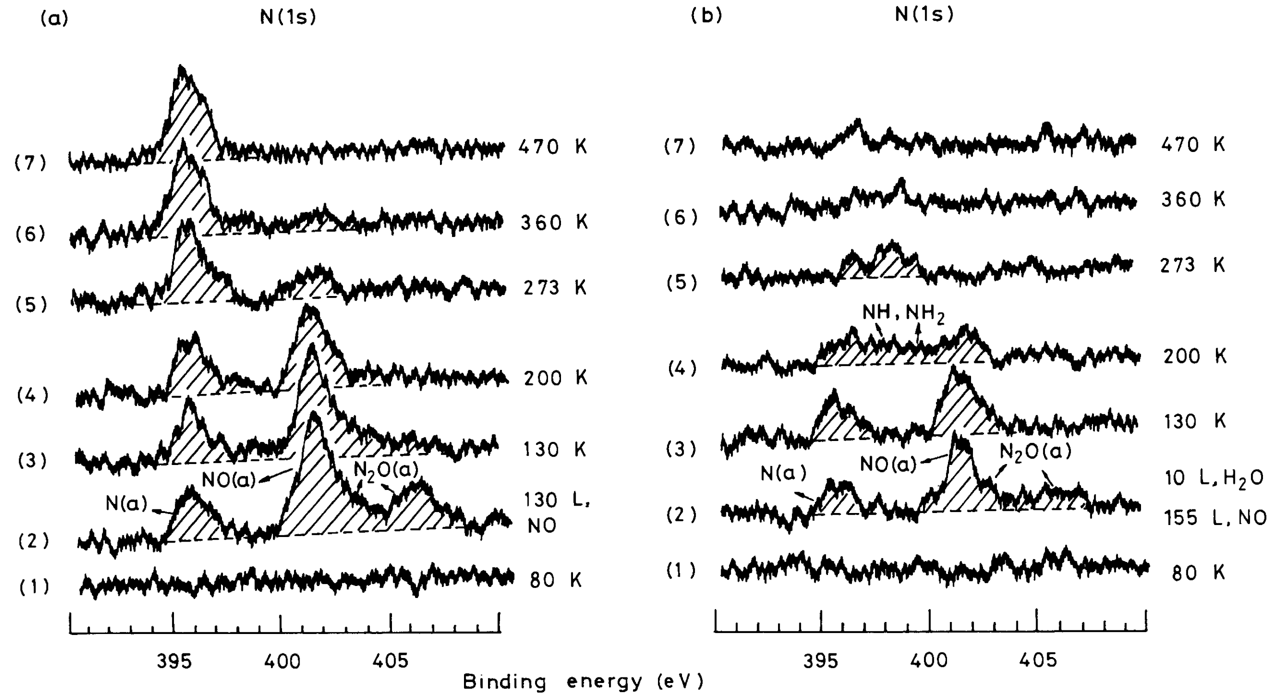

Figure 1. (a) N(1s) spectra for a Zn(0001) surface exposed to nitric oxide (1×10^{-6} Torr) at 80 K. 1 L $\equiv 10^{-6}$ Torr. (b) N(1s) spectra for a Zn(0001) surface exposed first to water vapour (1×10^{-6} Torr) and then nitric oxide (1×10^{-6} Torr) at 80 K. The spectra were recorded with a pass energy of 20 eV.

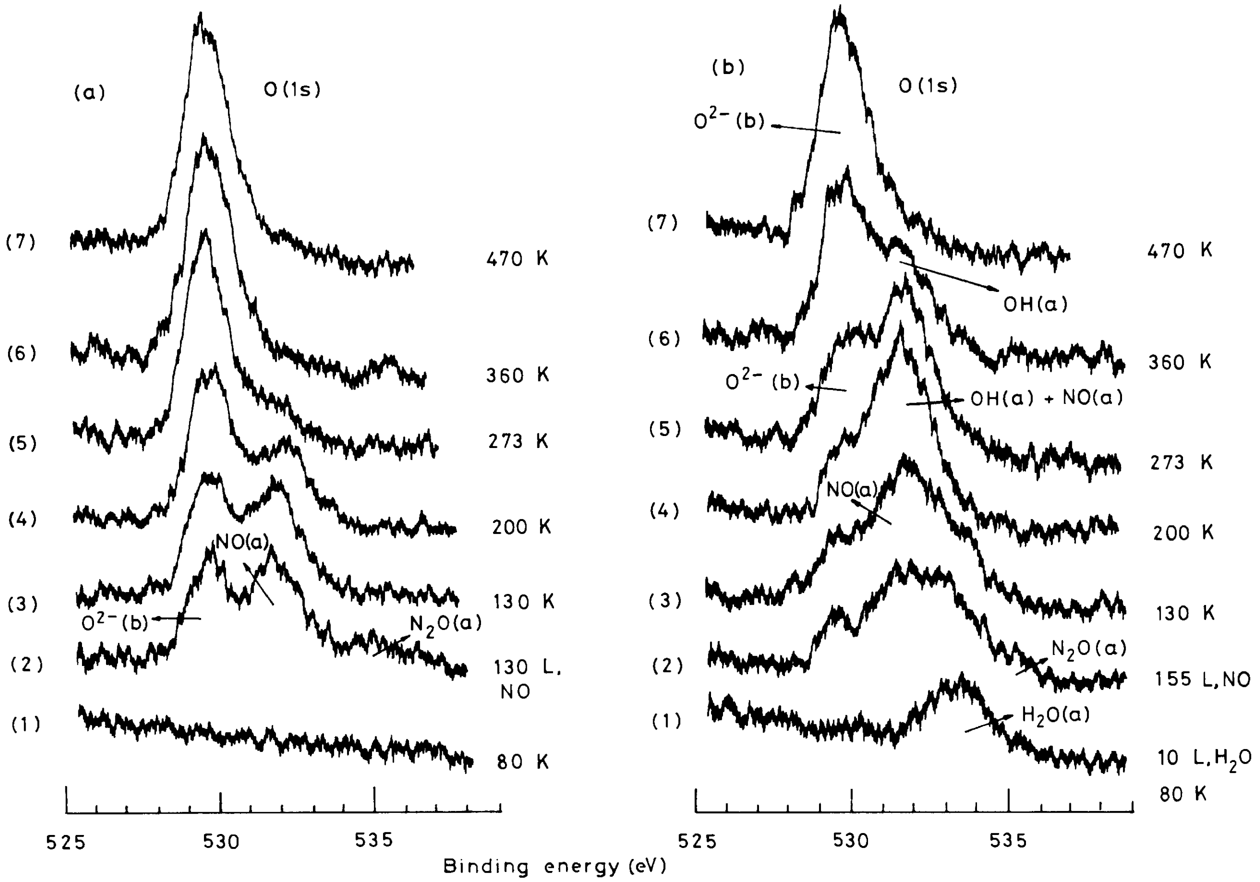

Figure 2. (a) O(1s) spectra corresponding to Figure 1(a). (b) O(1s) spectra corresponding to Figure 1(b).

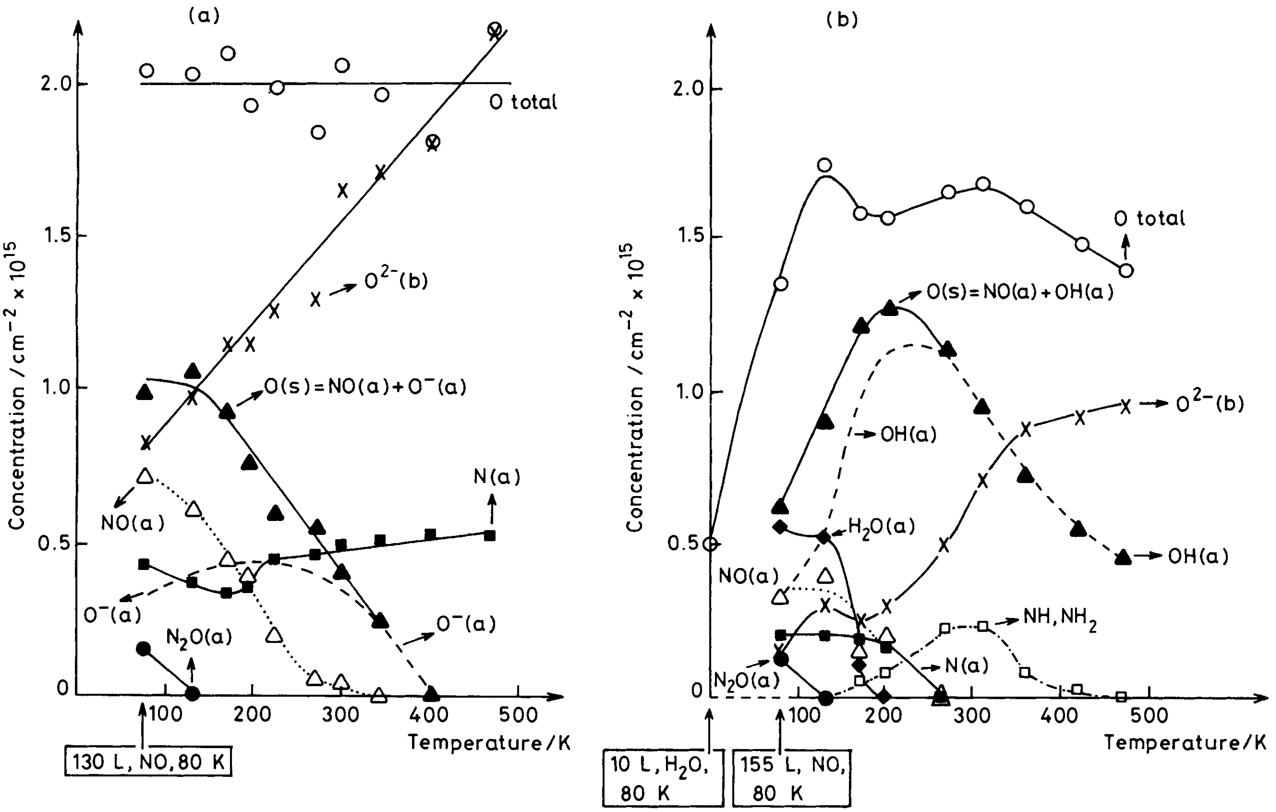

Figure 3. Concentrations of the various surface species as a function of temperature. (a) The Zn(0001) + NO system. (b) The Zn(0001) + H_2O + NO system. Symbols: ○ total oxygen; X O^{2-}(b); ● N_2O(a); ◆ H_2O(a); ▲ O(s) = NO(a) + O^-(a) + OH(a); ----- O^-(a) or OH(a); △ NO(a); ■ N(a); □ NH, NH_2.

Figure 2(a) shows the corresponding O(1s) spectra with the assignments of the peaks. From He(I) spectra taken at each temperature, difference spectra were generated[3] which confirm the assignments and surface chemistry deduced from the core-level spectra.

In Figure 3(a) are shown the concentrations of the individual surface species calculated from the curve-fitted spectra;[3] we draw particular attention to the essentially invariant temperature dependence of the surface nitride N(a) species and with increasing temperature the transfer of surface O^-(a) species into the subsurface O^{2-}(b). The total oxygen and nitride concentration at 450 K is 2.6×10^{15} atoms cm^{-2} which compares with 1.5×10^{15} Zn atoms cm^{-2} in the monolayer of a Zn(0001) surface.

Figure 1(b) shows the N(1s) spectra observed when coadsorbed molecular water and nitric oxide at 80 K are subjected to a similar temperature cycle. O(1s) and He(I) spectra were also obtained at each temperature. At 80 K the N(1s) spectra show identical features to those observed with nitric oxide above. As the temperature is increased, desorption of N_2O first occurs (130 K), and the N(1s) spectrum is very similar to that observed with nitric oxide alone. At 200 K the two distinct N(1s) peaks at 396 and 401.5 eV are no longer obvious, the N(1s) intensity being spread out as a continuous band. Previous studies[8,9] of both the chemisorption of hydrazine and ammonia have established the incremental decrease in N(1s) binding energy of *ca.* 1 eV per hydrogen removed that occurs as ammonia is dehydrogenated to chemisorbed nitrogen. At 273 K the intensity of the peak at 401.5 eV, due to NO(a), is negligible; two peaks of comparatively small intensities one at 398 eV and the other at 396 eV are present. At 360 K the N(1s) intensity, mainly at 398 eV, is close to the noise level. The O(1s) spectra corresponding to these N(1s) spectra are shown in Figure 2(b). In Figure 3(b) the surface concentrations are shown, these are estimated from the corresponding curve-fitted spectra.[3]

A particularly significant point to note, and qualitatively obvious from the raw N(1s) spectra, is that in the presence of 0.5×10^{15} molecules cm^{-2} of coadsorbed water at 80 K the surface nitride species are readily hydrogenated at 200 K to NH and NH_2 species. The concentration of nitrogen species present at 360 K is very small which contrasts with the chemisorption of nitric oxide at a Zn(0001) surface in the absence of coadsorbed water [Figure 1(a)]. It is important to recall at this stage that molecular water does not exhibit any chemical reactivity[7] with an atomically clean Zn(0001) surface being only weakly adsorbed at 80 K followed by desorption at 150 K. However, activation of molecularly adsorbed water can be effected by the presence of chemisorbed oxygen leading to surface hydroxylation. This has been discussed and the mechanism of the process occurring over the temperature range of the present work delineated.[7]

It is, therefore, the surface oxygen produced in the dissociative chemisorption of nitric oxide that 'catalyses' the decomposition of the molecularly adsorbed water leading to surface hydroxyl species in the temperature range 100—200 K. Hydrogenation of the surface nitride species then occurs to generate at 273 K mainly NH and NH_2 species with N(1s) intensity in the range 397—399 eV.

We have, therefore, direct spectroscopic evidence for the role that surface hydroxyls play in the hydrogenation of nitrogen adatoms leading to NH(a), NH_2(a), and presumably

$$\left.\begin{array}{l} \mathrm{N(a) + OH(a) \rightarrow NH(a) + O(a)} \\ \mathrm{NH(a) + OH(a) \rightarrow NH_2 + O(a)}, \textit{etc.} \end{array}\right\} \text{Scheme (A)}$$

$$\left.\begin{array}{l} \mathrm{OH(a) \rightarrow O^-(a) + H(a)} \\ \mathrm{H(a) + N(a) \rightarrow NH(a)} \\ \mathrm{NH(a) + H(a) \rightarrow NH_2(a)} \\ \mathrm{NH_2(a) + H(a) \rightarrow NH_3(a)} \\ \mathrm{NH_3(a) \rightarrow NH_3(g)} \\ \mathrm{O^-(a) \xrightarrow{c} O^{2-}(b)} \end{array}\right\} \text{Scheme (B)}$$

$NH_3(a)$, the last species desorbing at 360 K and above, and, therefore, not observed spectroscopically. Whether hydrogenation is effected directly, *i.e.* Scheme (A), the oxygen being incorporated into the sub-surface or whether it occurs as a sequence of events [Scheme (B)] involving first, hydroxyl dissociation, is not known. What is clear from the surface concentration–temperature profile is that when there is little or no evidence for any nitrogen species the decrease in hydroxyl concentration corresponds to about three times that of the nitrogen which has disappeared which is compatible with complete hydrogenation of N(a) to $NH_3(g)$. We have established[7] that surface hydroxyls form $O^{2-}(b)$ during dehydroxylation over the same temperature range but the presence of N(a) species may, however, provide a single-step and kinetically more favourable mechanism, the chemisorbed nitrogen adatoms acting as strong nucleophiles. These conclusions have important implications for the mechanism of ammonia synthesis particularly in the context of the possible role played by alkali oxides in hydrogen transfer.

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References

1 A. F. Carley and M. W. Roberts, *Proc. R. Soc. London, Ser. A*, 1978, **363**, 403.
2 M. W. Roberts, *Adv. Catal.*, 1980, **29**, 55.
3 C. T. Au and M. W. Roberts, unpublished results.
4 D. W. Johnson, M. H. Matloob, and M. W. Roberts, *J. Chem. Soc., Chem. Commun.*, 1978, 40; *J. Chem. Soc., Faraday Trans. 1*, 1979, **75**, 2143.
5 K. Kishi and M. W. Roberts, *Proc. R. Soc. London, Ser. A.*, 1976, **352**, 289.
6 A. F. Carley, S. Rassias, M. W. Roberts, and Wang-Tang-Han, *J. Catal.*, 1979, **60**, 385.
7 C. T. Au, M. W. Roberts, and A. R. Zhu, *Surf. Sci.*, 1982, **115**, L117.
8 M. A. Matloob and M. W. Roberts, *J. Chem. Res. (S)*, 1977, 336.
9 D. W. Johnson and M. W. Roberts, *J. Electron Spectrosc. Relat. Phenom.*, 1980, **19**, 185.