Oxygen states present at a Ag(111) surface in the presence of ammonia: evidence for a $NH_3–O_2^{\delta-}$ complex

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Molecular oxygen states present at Ag(111) surfaces when dioxygen is coadsorbed with ammonia at 80 K are characterised by vibrational loss features at 1488 and 1640 cm^{-1}. The former is suggested to be associated with the $NH_3{\cdots}O_2^{\delta-}$ complex, a key intermediate in the oxidation pathway.

There is now incontrovertible experimental evidence for the role of specific oxygen states present at single crystal metal surfaces (*e.g.* zinc, copper, nickel) as the active sites in oxydehydrogenation of ammonia.[1–4] In the case of Cu(110)O surfaces the isolated oxygen adatoms, or oxygens at the ends of Cu–O–Cu–O– chains, are the most active[5] but for atomically clean Cu(110) surfaces there is evidence during the coadsorption of oxygen–ammonia mixtures for a dioxygen–ammonia complex being the key intermediate. Both experimental and theoretical[6] work have supported this view and there are strong analogies with the model developed for the oxidation of ammonia when coadsorbed with dioxygen at a Zn(0001) surface at low temperatures.[2] The Ag(111)–dioxygen/ammonia system shows very similar precursor kinetics to that observed with Zn(0001) and for this reason we have searched for spectroscopic evidence, using both X-ray and vibrational electron energy loss spectroscopies (XPS and VEELS), for the presence of dioxygen states present at low temperatures when dioxygen–ammonia mixtures are coadsorbed at Ag(111) at 100 K.

The sticking probability of pure dioxygen at clean Ag(111) surfaces at 120 K is very low (*ca.* 10^{-4}); a peroxo species is observed after 3000 L exposure,[7] as evidenced by VEELS bands at 220 cm^{-1} [$\nu(AgO_2)$] and 670 cm^{-1} [ν(O–O)]. However, when dioxygen and ammonia are coadsorbed the reactivity to dissociative oxygen chemisorption is increased and the chemistry, as reflected by the O 1s and N 1s spectra, indicate that dehydrogenation has occurred. A typical set of kinetic data for the coadsorption of an ammonia–dioxygen mixture is shown in Fig. 1. The 'oxygen' uptake, calculated from the total O1s intensity data, is shown as a function of oxygen exposure in four different experiments at four different temperatures (220, 180, 150 and 120 K) using an O_2–NH_3 (1 : 3) mixture. As well as demonstrating the much increased sticking probability for oxygen adsorption [as observed at Zn(0001) surfaces[2]], these results provide strong circumstantial evidence for dioxygen–ammonia complexes participating in the oxidation pathway; this was the impetus for the VEELS investigation.

Fig. 2 shows a set of VEEL spectra when an atomically clean Ag(111) surface was exposed to an ammonia–dioxygen mixture at 100 K [Fig. 2(*a*)] and then warmed to 210 K [Fig. 2(*b*)]. The main loss features at 100 K are at 250, 700, 1120, 1480, 1640 and 3390 cm^{-1}. The assignments [Fig. 2(*a*)] are as shown; the 250 cm^{-1} feature is attributed to Ag–adsorbate stretch frequencies. A similar experiment, but replacing NH_3 with ND_3, gave rise to the spectra in Fig. 2(*c*), curves (*ii*) and (*iii*); for

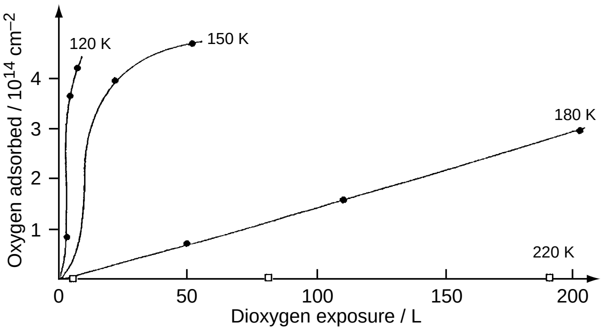

Fig. 1 Exposure of a Ag(111) surface to an O_2–NH_3 (1 : 3) mixture at four different temperatures. The graphs are plots of total concentration of oxygen adsorbed (expressed as atoms) *vs.* equivalent dioxygen exposure. The reaction of pure dioxygen leads to negligible adsorption in this exposure and temperature range.

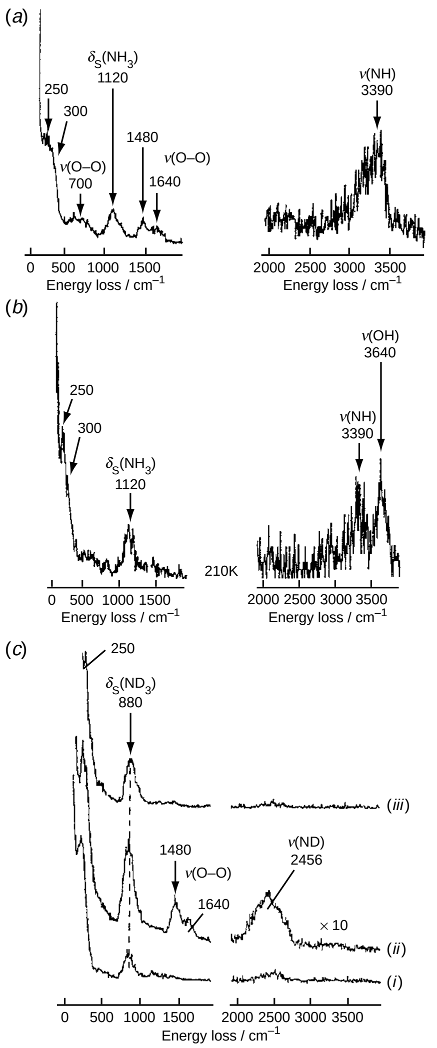

Fig. 2 VEELS spectra for (*a*) exposure of a clean Ag(111) surface to a dioxygen–ammonia mixture at 100 K; (*b*) surface in (*a*) warmed to 210 K and (*c*) VEELS spectra for (*i*) adsorption of ND_3 at Ag(111) at 100 K, (*ii*) adsorption of an O_2–ND_3 mixture at Ag(111) at 100 K and (*iii*) surface in (*ii*) warmed to 210 K

comparison curve (*i*) shows the adsorption of pure ND_3 at Ag(111) at 100 K. The spectra for deuterated ammonia confirm the assignments of the 1480 and 1640 cm^{-1} features in Fig. 2(*a*) for the ammonia–dioxygen mixture as arising from adsorbed dioxygen states. The unusually strong and broad ν(ND) feature at 2456 cm^{-1} [Fig. 2(*c*), curve (*ii*)] is the consequence of hydrogen bonding in the dioxygen–ND_3 complex.

On warming the Ag(111) surface exposed to the dioxygen–NH_3 mixture [spectrum (*a*)] to 210 K [Fig. 2(*b*)] the features assigned to the dioxygen states were not present. There was however spectroscopic evidence, from the loss feature characteristic of $\delta_s(NH_3)$ at 1120 cm^{-1}, for adsorbed ammonia present at low coverage. Also there had developed two features in the high frequency loss region, one at 3390 cm^{-1} assigned to ν(NH) and the other at 3640 cm^{-1} assigned to ν(OH).

The correlation shown to exist[8] between the O–O stretch frequencies and the electronic state of oxygen, suggests that the VEEL spectra for the coadsorbed dioxygen–ammonia system reflect the presence of two different molecular oxygen species [ν(O–O) at 1488 and 1640 cm^{-1}]. One of these (1488 cm^{-1}) is involved in a $NH_3\cdots O_2^{\delta-}$ charge transfer type complex while the other characterised by the higher frequency (1640 cm^{-1}) is a more isolated physisorbed species. There is very little charge associated with this state, its vibrational frequency being close to that reported for the gas phase molecule. It is the former that opens up a low energy oxidation pathway leading to surface OH and NH species [Fig. 2(*b*)]; in contrast, the peroxo state [ν(O–O) at 670 cm^{-1}] observed after the adsorption of pure dioxygen at a Ag(111) surface is unreactive towards ammonia. It is interesting to note that at a Cu(111) surface, exposure of an ND_3 adlayer to dioxygen at 100 K gives rise to a molecularly adsorbed oxygen species[9] characterised by a loss feature at 1500 cm^{-1}.

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Footnote and References

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1 A. Boronin, A. Pashusky and M. W. Roberts, *Catal. Lett.*, 1992, **16**, 345; B. Afsin, P. R. Davies, A. Pashusky, M. W. Roberts and D. Vincent, *Surf. Sci.*, 1993, **284,**, 109.
2 A. F. Carley, M. W. Roberts and S. Yan, *J. Chem. Soc., Chem. Commun.*, 1988, 267; *J. Chem. Soc., Faraday Trans.*, 1990, **86**, 2701.
3 G. U. Kulkarni, C. N. R. Rao and M. W. Roberts, *J. Phys. Chem.*, 1995, **99**, 3310.
4 M. W. Roberts, *Chem. Soc. Rev.*, 1996, 437.
5 A. F. Carley, P. R. Davies, M. W. Roberts and D. Vincent, *Top. Catal.*, 1994, **1**, 35; W. W. Crew and R. J. Madix, *Surf. Sci.*, 1996, **356**, 1.
6 M. Neurock, R. A. van Santen, W. Biemolt and A. P. J. Jansen, *J. Am. Chem. Soc.*, 1994, **116**, 6860.
7 A. F. Carley, P. R. Davies, M. W. Roberts and K. K. Thomas, *Surf. Sci.*, 1990, **238**, L467.
8 C. Pettenkoefer, I. Pockrand and A. Otto, *Surf. Sci.*, 1983, **135**, 1.
9 P. R. Davies, M. W. Roberts, N. Shukla and D. J. Vincent, *Surf. Sci.*, 1995, **325**, 50.

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