A new approach to the mechanism of heterogeneously catalysed reactions: the oxydehydrogenation of ammonia at a Cu(111) surface

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Received 30 July; accepted 27 August 1992

The oxydehydrogenation of ammonia at a Cu(111) surface is a highly efficient process at 295 K, with the selectivity sensitive to the dioxygen–ammonia ratio. However, there is no evidence from either XPS or HREELS for surface oxygen being present during the reaction and, in effect, catalysis occurs at a clean Cu(111) surface. The rate of NH_x(a) formation is indistinguishable from the rate of the dissociative chemisorption of oxygen at close to zero coverage suggesting that the reactive oxygen species are the hot transients O^-(s). The chemisorbed oxygen overlayer, the O^{2-}(a)-like species are, by comparison, unreactive. The reaction is, therefore, not characteristic of either Eley–Rideal or Langmuir–Hinshelwood mechanisms but involves the interaction of rapidly diffusing ammonia molecules and hot transient O^-(s)-like species. Models for this type of reaction have been discussed previously, while very recent studies by scanning tunnelling microscopy have provided further evidence for such oxygen transients.

Keywords: Oxydehydrogenation; surface oxygen transients; copper; ammonia

In a recent study [1] of the coadsorption of dioxygen and ammonia at a Cu(110) surface a highly selective and efficient oxydehydrogenation reaction was shown to occur at 295 K with the formation of a bent imide species. The $NH_3:O_2$ ratio was 36:1. No surface oxygen was present during most of the reaction i.e. *catalysis occurred at essentially a clean Cu(110) surface*. By comparison, the chemisorbed oxygen overlayer at the Cu(110) surface underwent a relatively slow and somewhat restricted chemisorptive replacement reaction when exposed to ammonia under the same conditions. The evidence therefore pointed to a highly reactive oxygen species being involved in the dehydrogenation reaction. We considered two possibilities; O^-(s), a hot oxygen transient

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shown [2] to be very efficient in H-abstraction at a Mg(0001) surface, and $O_2^-(s)$ known to form a dioxygen–ammonia transient surface complex at a Zn(0001) [3] surface which decomposes to form the chemisorbed amide $NH_2(a)$ species. Distinguishing between $O^-(s)$ and $O_2^-(s)$ as the active oxygen species was not unambiguous with the Cu(110) surface since the rates of imide formation and dissociative chemisorption of dioxygen were both very similar and fast. Although the experimental evidence favoured the involvement of a dioxygen precursor, it was recognised [1] that an error of only ≈ 1 L (langmuir $= 10^{-6}$ Torr s) in estimating the exposure would lead to uncertainty in the conclusions.

We suggested [1] that the Cu(111) surface would provide more scope for distinguishing unambiguously between the two possibilities and in the present study we report data for the Cu(111) surface, where the dissociative chemisorption of dioxygen is much slower at 295 K (sticking probability ≈ 0.001 compared with 0.2 for the Cu(110) surface). There is therefore available a kinetic window which should allow a distinction to be made between reaction steps (2), (4), (5) and (6), where (a) represents a strongly chemisorbed species and (s) a surface transient:

$$O_2(g) \xrightarrow{e} O_2^-(s), \tag{1}$$

$$O_2^-(s) + 2NH_3(s) \rightarrow 2NH(a) + 2H_2O(s), \tag{2}$$

$$O_2^-(s) \xrightarrow{e} 2O^-(s), \tag{3}$$

$$O^-(s) + NH_3(s) \rightarrow NH(a) + H_2O(g), \tag{4}$$

$$O_2(g) \xrightarrow{e} 2O^-(s) \xrightarrow{e} 2O^{2-}(a), \tag{5}$$

$$O^{2-}(a) + NH_3(g) \rightarrow NH(a) + H_2O(g). \tag{6}$$

We also explore with the Cu(111) surface whether there is any dependence of the dehydrogenation selectivity on the $NH_3:O_2$ ratio. We know [4] that for both Cu(110)–O and Cu(111) adlayers, when $\theta_{O^{2-}(a)} \rightarrow 1.0$, the chemisorptive replacement reaction (6) is both very slow and restricted by comparison with the rate of imide formation through coadsorption of $NH_3(g)$ and $O_2(g)$ and involving either reaction (2) or (4).

In fig. 1 are shown a set of N(1s) spectra for three separate experiments using different $NH_3:O_2$ ratios. The N(1s) FWHM values are substantially greater (≈ 3 eV) than those observed in analogous experiments with Cu(110) surfaces (≈ 2 eV) and it is clear that, as the gas mixture becomes richer in ammonia, a second component emerges to the N(1s) profile at a binding energy of 398.2 eV. We assign that with a binding energy of 397.2 eV to the imide NH(a) species [1] and that at 398.2 eV to the amide $NH_2(a)$ species [3]. As with the Cu(110) surface no intensity was observed in the O(1s) spectrum until the N(1s) intensity for any particular $NH_3:O_2$ ratio was close to its maximum; the peak in the O(1s) spectrum was at a binding energy of 529.6 eV and characteristic of

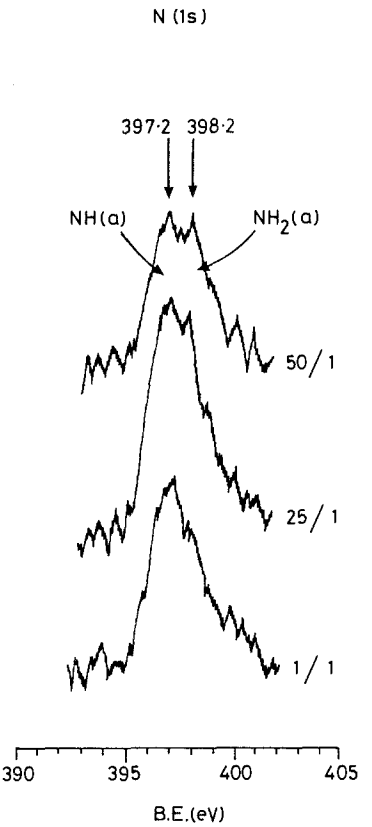

Fig. 1. N(1s) spectra for the coadsorption of ammonia and dioxygen at a Cu(111) surface at 295 K for three different $NH_3:O_2$ ratios 1:1, 25:1 and 50:1. The corresponding oxygen exposures in each case are 100, 75 and 20 L respectively.

chemisorbed oxygen and which we designate as O^{2-}(a). On heating the adlayer, further dehydrogenation to generate nitrogen adatoms occurs.

In fig. 2 is shown the electron energy loss spectrum corresponding to a Cu(111) surface that has been exposed to an ammonia–dioxygen mixture (8:1) at 220 K and then warmed to 250 K. There are three obvious loss peaks at 610, 1100 and 3350 cm^{-1} which are assigned to ν_{Cu-NH}, δ_{NH} and ν_{NH} respectively. Under these conditions the dominant chemisorbed species is the imide (bent) NH(a) with no evidence from electron energy loss spectroscopy for NH_2(a) which would be expected to have a characteristic peak $\delta_s(NH_2)$ at ≈ 1500 cm^{-1}. Only when the ammonia–dioxygen mixture becomes very much richer in ammonia does the N(1s) spectra indicate the presence of significant concentrations of NH_2(a) at 295 K (fig. 2). These loss-peaks are at somewhat higher values than those observed for the NH(a) generated at a Cu(110) surface, the ν_{Cu-NH} in the latter case being at 430 cm^{-1} in keeping with a greater ligancy expected for NH(a) at Cu(110) compared with the atomically smoother Cu(111) surface.

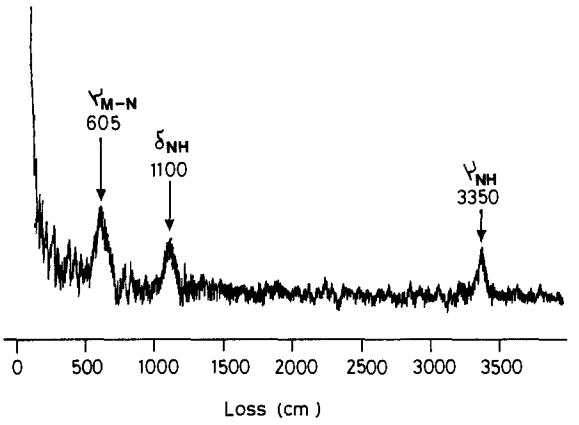

Fig. 2. Electron energy loss spectrum after the exposure of a Cu(111) surface to an 8:1 ammonia–oxygen mixture at 220 K and the spectrum taken at 250 K.

Fig. 3 shows the total concentration of the nitrogen containing species (NH_x, where $x = 1, 2$) formed as a function of the oxygen exposure in a series of experiments with Cu(111) at 295 K using different $NH_3 : O_2$ ratios; also shown is the oxygen adatom concentration $O^{2-}(a)$ when the surface is exposed to dioxygen at 295 K. The latter has an O(1s) binding energy of 529.6 eV and a

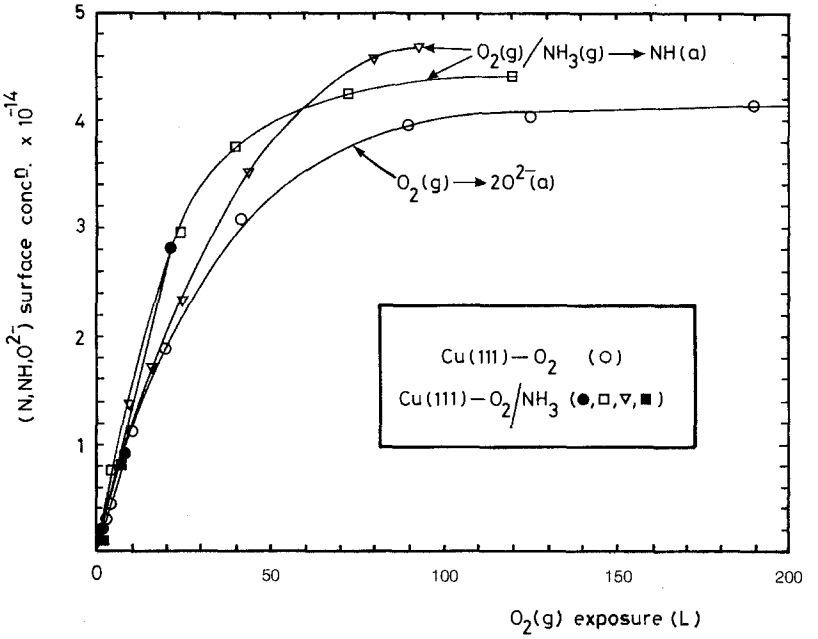

Fig. 3. Concentration of $NH_x(a)$ formed for four different $NH_3 : O_2$ ratios at a Cu(111) surface at 295 K, (●) 50:1; (□) 10:1; (▽) 25:1; (■) 1:1. Also shown (○) is the formation of $O^{2-}(a)$ in the dissociative chemisorption of dioxygen for Cu(111) at 295 K as a function of oxygen exposure.

characteristic single loss peak at 255 cm^{-1} corresponding to ν_{Cu-O}. The interesting and significant feature of these data is that the rate of NH_x formation is indistinguishable from *the rate of dioxygen dissociation when* $\theta_{O^{2-}(a)} \rightarrow 0$. *Furthermore the rate of* NH_x *formation remains virtually constant up to an* NH_x *surface concentration of* $\approx 3 \times 10^{14}$, *i.e. close to complete surface coverage*, the maximum $O^{2-}(a)$ concentration being $\approx 4 \times 10^{14}$ cm^{-2}.

The simplest interpretation of these results is that dissociative chemisorption of dioxygen generating the hot oxygen atom $O^{-}(s)$ (eqs. (3) or (5)) also determines the rate of NH_x formation through the highly efficient hydrogen abstraction reaction (eq. (4)). Throughout this reaction the *surface Cu(111) remains free of chemisorbed oxygen* $O^{2-}(a)$, i.e. step 5 is blocked until the efficiency of reaction (4) decreases at high NH(a) coverage.

We first drew attention to the distinctive surface chemistry associated with oxygen transients generated by the dissociative chemisorption of dioxygen at a Mg(0001) surface using ammonia as the probe molecule [2]. These oxygen transients designated $O^{-}(s)$, characterised by finite surface lifetimes, underwent rapid surface diffusion before being finally chemisorbed as the stable and unreactive chemisorbed $O^{2-}(a)$ species. Assuming the activation energy of surface diffusion of the probe molecule $NH_3(s)$ to be close to zero then the $O^{-}(s)$ residence time in reaction (4) is estimated to be about 10^{-8} s [5]. We had therefore evidence through the "probe-molecule" approach for (a) the existence of oxygen transients, and (b) their distinctive and high chemical reactivities compared with the final chemisorbed state. Recently Ertl and co-workers [6] have provided more direct experimental evidence for such oxygen transients in scanning tunnelling microscopic studies of oxygen chemisorption at Al(111) surfaces. The significant conclusion of relevance to our studies of oxygen transients is that the two oxygen atoms of a dissociating dioxygen molecule come to rest some 100 Å apart on the aluminium surface at 300 K, i.e. the oxygen atoms $O^{-}(s)$ undergo rapid surface diffusion before being finally chemisorbed. That such oxygen atoms possess high chemical reactivities relevant to the mechanism of metal catalysed reactions is already well documented through their reactions with ammonia [2], carbon monoxide [7], propene and water [7]. In the oxydehydrogenation of ammonia at the Cu(111) surface the richer in oxygen is the mixture the more favourable becomes NH(a) formation compared with $NH_2(a)$ at 295 K. This supports a mechanism where dehydrogenation involves ammonia molecules present at very low surface coverage undergoing rapid surface diffusion interacting with the transient $O^{-}(s)$ and resulting in the step-wise process $NH_3 \rightarrow NH_2 \rightarrow NH \rightarrow N$, the extent of dehydrogenation being a function of the $NH_3 : O_2$ ratio and temperature. At some critical value of the $NH_3 : O_2$ ratio – in the oxygen rich regime – step 5 will dominate and the formation of chemisorbed oxygen will be the major pathway. With the formation of $O^{2-}(a)$ the oxydehydrogenation reaction is poisoned. It is therefore neither an Eley–Rideal nor a Langmuir–Hinshelwood mechanism and is more akin to a

reaction of two transient species within a two-dimensional gas with the metal surface providing a strong thermodynamic sink for the chemisorbed products of the reaction. In the absence of this thermodynamic sink we would expect desorption of the products of the radical-type two-dimensional gas reaction.

We should emphasise that the formation of the less reactive O^{2-}(a) species requires a significant contribution from the Madelung potential term so that O^{-}(s) can be thought of as an oxygen surface atom that has not developed the electronic charge associated with a "fully coordinated" oxygen.

We raised recently [8] the issue as to whether isolated chemisorbed oxygen adatoms, present at very low coverage, exhibited high reactivity compared with those at higher coverage and have now shown [9] that, for *very low coverages ($\theta \approx 0.1$) of preadsorbed oxygen*, two distinctly different oxygen species are present. A fraction ($\theta = 0.05$) are reactive to NH_3(g) whereas the remainder are not, suggesting that under these conditions both O^{-} and O^{2-}-like species are present. With increasing oxygen coverage the fully coordinated and unreactive O^{2-}-like species, stabilised through a Madelung energy term, dominate. To sustain high catalytic activity there are, therefore, distinct advantages in preventing reconstruction leading to oxide nucleation-growth of O^{2-}(a), or, in the language of cluster-chemistry, maintaining small cluster sizes so that the Madelung energy term is of no real significance so that the highly reactive O^{-}-like species are favoured. Kinetic models for reactions involving O^{-}(s) transients have been considered elsewhere [2,5] and their relevance to the chemistry of coadsorbed molecules emphasised [7].

Acknowledgement

AB and AP acknowledge gratefully awards from the Royal Society.

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