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COMPUTER MODELLING OF THE KINETICS OF THE COADSORPTION OF AMMONIA AND DIOXYGEN AT A Mg(0001) SURFACE *

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The activity of a surface oxygen transient, $O^-(s)$, for H-abstraction from an ammonia molecule undergoing surface diffusion at a Mg(0001) surface at 298 K has been simulated by computer modelling. The time dependence of the chemisorbed products, $NH_2(a)$, OH(a) and $O^{2-}(a)$, has been determined making reasonable assumptions of the activation energy for the surface diffusion of physisorbed ammonia, the surface life-time of $O^-(s)$ and the surface stoichiometry determined from XPS studies.

1. Introduction

We have drawn attention to the specific chemistry associated with surface oxygen transients at metal surfaces under circumstances where the stable chemisorbed oxygen species show no reactivity [1]. The studies are of necessity at low temperatures so that spectroscopic identification of the reaction products can be achieved and mechanistic aspects explored. In this paper we consider further the conclusions of Au and Roberts [1] who investigated the reaction of coadsorbed ammonia and oxygen on Mg(0001) surfaces as part of a study of the activation of N–H bonds by surface oxygen transients, suggested to be $O^-(s)$ species. ** In this system $O^-(s)$ either abstract hydrogen from the physisorbed ammonia undergoing diffusive hopping, yielding strongly chemisorbed $NH_2(a)$ and OH(a) species, or are transferred to $O^{2-}(a)$, surface oxide species which are unreactive to ammonia under the experimental conditions of the investigation. By 'monitoring' the surface amide-oxide ratio by photoelectron spectroscopy and using steady-state assumptions for the concentrations of $NH_3(s)$ and $O^-(s)$ it was possible to estimate the natural surface lifetime of the latter as being about 10^{-8} s assuming that the hopping frequency of $NH_3(s)$ was 10^{13} s^{-1} i.e. taking E_{diff} the activation energy for hopping as close to zero.

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** Note: (s) and (a) represent weakly adsorbed surface transients and stable chemisorbed species respectively.

In view of the significance and apparent generality of these reactions we have examined the kinetic model more quantitatively by solving the relevant differential equations, without making any assumptions concerning the steady-state concentrations of surface species. It thus enables us to determine whether the steady-state kinetic model *assumed* by Au and Roberts [1] was firmly based and could account both qualitatively and quantitatively for both the chemisorption states observed and the estimated surface residence time of $O^-(s)$.

2. The kinetic model

The mechanism proposed was as follows:

1.	$O_2(g) \rightarrow 2O^-(s)$	: Dioxygen dissociation: formation of surface transients
2.	$O^-(s) \overset{e}{\rightarrow} O^{2-}(a)$	: Chemisorption: formation of unreactive $O^{2-}(a)$
3.	$NH_3(g) \rightleftarrows NH_3(s)$	: Physical adsorption of ammonia
4.	$NH_3(s) + O^-(s) \rightarrow NH_2(a) + OH(a)$	: H-abstraction: amide and hydroxyl formation
5.	$OH(a) \rightarrow O^{2-}(a) + H(s)$	: Dehydrogenation of surface hydroxyls

The surface was exposed [1] to an ammonia-dioxygen (5 : 1) gas mixture at a total pressure of 10^{-6} Torr so that the following rate expressions apply to each of the above steps under the experimental conditions used:

$R_1 = 2N_{O_2}\alpha_{O_2}S/S_0 = 0.2S$ cm^{-2}s^{-1}.

The impact rate, N_{O_2} is 10^{14} cm^{-2} s^{-1}, α, a term incorporating both surface accommodation and dissociation of dioxygen, is assumed to be unity, and S_0 and S represent the number of Mg^0 sites cm^{-2} at zero time and time t respectively, with $S_0 = 10^{15}$ cm^{-2}. $O^-(s)$ species are formed and present only at Mg^0 sites while the surface sites occupied by $O^{2-}(a)$, $NH_2(a)$ and $OH(a)$ are all inactive in $O^-(s)$ formation.

$R_2 = \sigma_{O^-}/\tau_{O^-}$ i.e. the ratio of the surface concentration and intrinsic lifetime of $O^-(s)$.

$R_3 = N_{NH_3}\alpha_{NH_3} = 5 \times 10^{14}$ cm^{-2}s^{-1} (α_{NH_3} the sticking probability of NH_3 is assumed to be unity)

$R_{-3} = \nu_{des}\, e^{-E_{des}/RT}\sigma_{NH_3}$

where $\nu_{des} = 10^{13}$ s^{-1} and E_{des} is assumed to be the same as the heat of adsorption of ammonia estimated experimentally to be 40 kJ mol^{-1}.

H-abstraction occurs through a mechanism involving the interaction of $O^-(s)$ and the surface diffusing (hopping) $NH_3(s)$ species.

Therefore, $R_4 = \nu_{dif}\, e^{-E_{dif}/RT}\sigma_{NH_3}\sigma_{O^-}/S_0$

where $\nu_{dif} = 10^{13}$ s^{-1} and E_{dif} was varied from 0–14 kJ i.e. the maximum activation energy of NH_3 surface diffusion was assumed to be $E_{des}(NH_3)/3$ so that $R_4 = 10^{-2}\ e^{-E_{dif}/RT} \sigma_{NH_3} \sigma_{O^-}$.

We assume a zero activation energy for the H-abstraction step for which there is good evidence from gas phase studies.

Step 5 requires a free Mg site so that $R_5 = k_5 \sigma_{OH} S$.

The six differential equations arising from the model are:

$$-dS/dt = 0.2S + 10^{-2}\ e^{-E_{dif}/RT} \sigma_{O^-} \sigma_{NH_3}$$

$$d\sigma_{O^-}/dt = 0.2S - \sigma_{O^-}/\tau_{O^-} - 10^{-2}\ e^{-E_{dif}/RT} \sigma_{O^-} \sigma_{NH_3}$$

$$d\sigma_{O^{2-}}/dt = \sigma_{O^-}/\tau_{O^-} + k_5 \sigma_{OH} S$$

$$d\sigma_{NH_3}/dt = 5 \times 10^{14} - 10^{13}\ e^{-E_{des}/RT} \sigma_{NH_3} - 10^{-2}\ e^{-E_{dif}/RT} \sigma_{O^-} \sigma_{NH_3}$$

$$d\sigma_{NH_2}/dt = 10^{-2}\ e^{-E_{dif}/RT} \sigma_{O^-} \sigma_{NH_3}$$

$$d\sigma_{OH^-}/dt = 10^{-2}\ e^{-E_{dif}/RT} \sigma_{O^-} \sigma_{NH_3} - k_5 \sigma_{OH} S.$$

These were solved for *each species* using Heun's prediction-corrector method. Most solutions were obtained using the Cardiff Multics computer; however very small step sizes were often necessary in order to obtain stable behaviour and the University of London Cray computer was used for some longer runs.

Various computations (experiments) were performed, corresponding to *different activation energies for step 4* and a value of the intrinsic lifetime $\tau_{O^-(s)}$ of $O^-(s)$ chosen to yield the experimentally-obtained value of β the fraction of $O^-(s)$ diverted to generate surface amide $NH_2(a)$ species [1] at 298 K.

3. Results

We consider first the validity [1] of the steady-state assumptions for ammonia and the surface transient $O^-(s)$.

$NH_3(a)$

The results (fig. 1) show that this assumption is totally justified for NH_3, a steady-state value being established in a few microseconds. This value, typically $\sigma_{NH_3} = 4.8 \times 10^8\ cm^{-2}$, at 298 K, is some 15% below the equilibrium concentration obtained from step 3 alone, the difference corresponding to the effect of amide formation (step 4) on the surface concentration term σ_{NH_3}. As the reaction proceeds, amide formation becomes less significant and σ_{NH_3} rises very slowly to reach the equilibrium concentration as θ the total surface coverage approaches unity.

$O^-(s)$

A steady value is reached in about 10 μs, typically $\sigma_{O^-(s)} = 10^7\ cm^{-2}$, which thereafter declines in proportion to the concentration of free Mg sites (S). After

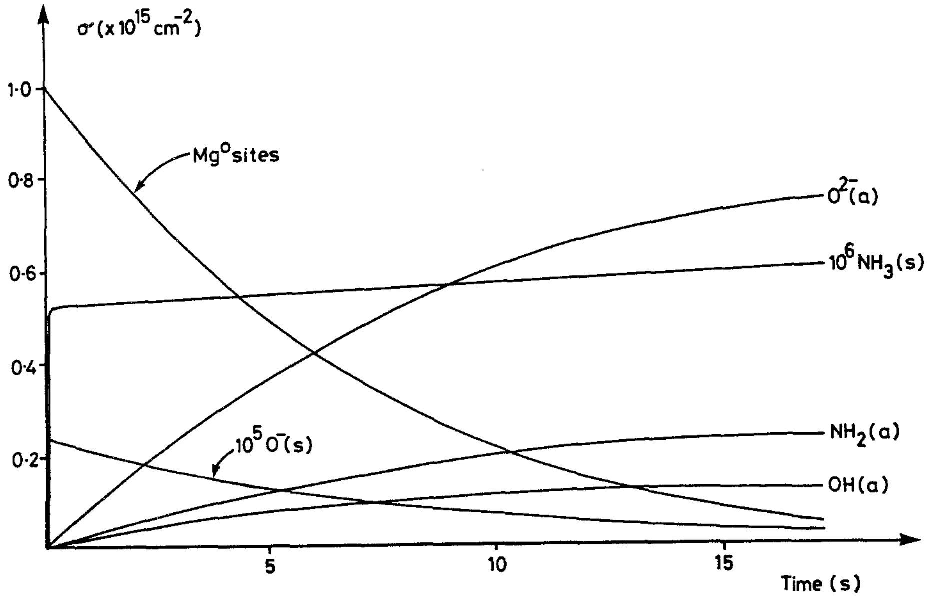

Fig. 1. Variation of the concentration of surface species with time calculated from the differential equation describing the model for H-abstraction. The activation energy of surface diffusion of ammonia is assumed to be 14 kJ mol^{-1} at 298 K, $\tau_{O^-(s)}$ is adjusted to 1.5×10^{-5} s to fit the experimental value of β i.e. $NH_2(a)/O^{-2}(a)+NH_2(a) = 0.21$ and k_5 is taken to be 5×10^{-16}.

10% reaction $d\sigma_{O^-}/dt = -3 \times 10^6$ cm^{-2}s^{-1}. In the steady-state approximation for σ_{O^-},

$$d\sigma_{O^-}/dt = 0.2S - \sigma_{O^-}/\tau_{O^-} - 10^{-2}\, e^{-E_{\text{dif}}/2.47}\sigma_{O^-}\sigma_{NH_3}$$

is assumed to equal zero. Substituting the computed values into this equation we have $-3 \times 10^{-6} = 2.0 \times 10^{14} - 1.5 \times 10^{14} - 0.5 \times 10^{14}$. Thus the degree to which the actual value of $d\sigma_{O^-}/dt$ differs from the assumed steady-state value of zero is quite negligible compared with the other rate terms in the equation. Consequently the previous use by Au and Roberts of the steady-state approximation in this system is fully justified.

4. General comments on the modelling results

Figure 1 shows the concentration/time data obtained at 298 K when E_{dif} (or E_4) is set at 14 kJ mol^{-1}, $\tau_{O^-(s)}$ is adjusted to 1.5×10^{-5} s to fit the experimental value of β, and $k_5 = 5 \times 10^{-16}$.

The experimental observation [1] that about 20% of the O$^-$(s) species is removed through the amide-producing reaction pathway sets the relative rate of R_4 and R_2. Thus a decrease in the rate R_4 due to an increasing activation energy for the surface diffusion process (or the H-abstraction step) must be associated with a lower value of R_2 due to a longer $O^-(s)$ intrinsic lifetime. The table shows some results for a number of different parameter values, where θ is the fraction of the surface covered by a species.

DEPENDANCE OF SURFACE COVERAGES AND O^- LIFETIMES ON AMMONIA DIFFUSIVE (HOPPING) ENERGY

E_{dif}/kJ	τ_{O^-}/sec	θ_{O^-}	θ_{NH_3}
0	5×10^{-8}	10^{-8}	4.9×10^{-7}
7	1×10^{-6}	1.5×10^{-7}	4.9×10^{-7}
14	1.5×10^{-5}	2×10^{-6}	5.0×10^{-7}

The values assumed for E_{dif} i.e. up to a maximum of one third of E_{des} (or ΔH_{ads}) of NH_3 (40 kJ mol^{-1}) are physically realistic from surface diffusion data for other systems.

5. Conclusions and mechanism

It is assumed in the model that the rate of formation of $O^-(s)$ is equal to twice the rate of impact of dioxygen on free Mg sites (2×10^{14} $cm^{-2}s^{-1}$). If this is correct it follows that the rate of hydrogen abstraction from NH_3 by $O^-(s)$ must be about 5×10^{13} cm^{-2} s^{-1}, and so the steady-state $\theta_{O^-(s)}$ is calculated to be about 10^{-7}. This rules out a simple Eley-Rideal mechanism for H-abstraction, step 4, for which the maximum rate ($E = O$) would be given by $R_4 = N_{NH_3} \theta_{O^-(s)} e^{-E/RT} = 5 \times 10^{14} \times 10^{-7}$ i.e. 5×10^7 cm^{-2} s^{-1}. If this mechanism was valid the formation of the chemisorbed reaction products would take 10^7 sec i.e. a factor of about 10^6 greater than what is observed experimentally. To match the rate of the Eley-Rideal process would require $\theta_{O^-(s)} > 0.1$ and a consequent $\tau_{O^-(s)}$ of > 0.5 s. Experimentally there is no XPS evidence in this system for such coverages, and the surface lifetime $\tau_{O^-(s)}$ is unrealistically high.

Thus the mechanism proposed, and evaluated in the computer analysis, involving the sampling of the surface transient chemisorbed $O^-(s)$ species by ammonia molecules undergoing surface diffusion resulting in H-abstraction has been both qualitatively and quantitatively confirmed. Clearly the mechanism will only be valid for metal-oxygen systems where the sticking probability, and in particular the efficiency of dioxygen bond cleavage per molecular oxygen impact with the surface is high. This is the case for dioxygen at Mg(0001) surfaces. In other metal-oxygen systems such as the dissociative chemisorption of dioxygen at Zn(0001) surfaces [2] cleavage of the dioxygen bond is very inefficient - the reactive sticking probability being about 10^{-3} and coadsorption (with for example ammonia) catalyses bond cleavage through interacting with a *molecular dioxygen surface transient in a predissociation step.* In other words there is an enhancement of the efficiency of the dioxygen accommodation step, $O_2(g) \rightarrow$

O_2^-(s), through a three centre mechanism involving the surface intermediate or transition state complex $Zn^{\delta+}O_2^- - NH_3$. The latter dissociates to generate O^{2-}(a), OH(a) and NH_2(a) in stoichiometric proportions. It is the characteristics of the three centre zinc complex that determines the kinetic characteristics in the Zn(0001)-dioxygen-ammonia system [2].

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References

[1] C.T. Au and M.W. Roberts, J. Chem. Soc. Faraday Trans. I 83 (1987) 2047; Nature 319 (1986) 206.

[2] A.F. Carley, M.W. Roberts and Song Yan, J. Chem. Soc. Chem. Comm. (1988) 267.