The formation of N_2O during the chemisorptions of nitric oxide at platinum surfaces at low temperature: a comment on the mechanism

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An alternative mechanism by which nitrous oxide is formed during both the catalytic reaction of nitric oxide and the oxidation of ammonia at platinum surfaces is suggested.

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At the meeting held at the Royal Institution in London in September 2002 to celebrate John Meurig Thomas' 70th birthday the mechanism of the formation of N_2O during the interaction of nitric oxide with a platinum catalyst was discussed by Burch [1]. Both kinetic data and density functional theory calculations were presented. The calculations carried out for a Pt(111) surface were reported for two possible mechanisms for the formation of $N_2O(a)$ (equations (1) and (2))

$$\mathrm{N(a) + NO(a) \rightarrow N_2O(a)} \quad (1)$$

$$\mathrm{NO(g) \rightarrow (NO)_2(a) \rightarrow N_2O(a) + O(a)} \quad (2)$$

Although the kinetic studies were not able to distinguish between these two possibilities, density functional theory provided very different values for the energy barriers for the formation of N_2O by these mechanisms. For the reaction between chemisorbed nitrogen atoms, N(a), and adsorbed nitric oxide, NO(a), (equation (1)) the activation energy barrier was 1.8 eV. This was considered to be "too high to account for N_2O formation at temperatures well below 373 K". For the formation of N_2O via the dimer $(NO)_2(a)$ (equation (2)), the barrier is however much lower, 0.46 eV, and on this basis was considered to be the favoured mechanism of N_2O formation at low temperatures.

In the ensuing discussion I drew attention to the possibility of an alternative mechanism based on our earlier photoelectron studies of nitric oxide chemisorption at metal surfaces at low temperatures [2]. These were discussed further at a Discussion Meeting of the Royal Society in 1986 [3]. Central to the mechanism proposed was the participation of mobile nitrogen adatoms N(s) generated by the dissociative chemisorption of nitric oxide at 80 K by an oxygen abstraction process (equation (3)) the mobile nitrogen atoms N(s) could either desorb (equation (4)), undergo an addition reaction (equation (5)) to form N_2O or become chemisorbed N(a), (equation (6)).

$$\mathrm{NO(g) \rightarrow N(s) + O(a)} \quad (3)$$

$$\mathrm{2N(s) \rightarrow N_2(g)} \quad (4)$$

$$\mathrm{N(s) + NO(a) \rightarrow N_2O(a)} \quad (5)$$

$$\mathrm{N(s) \rightarrow N(a)} \quad (6)$$

The fate of the nitrogen transient, N(s), is both metal specific and temperature sensitive. For example at Cu(1 0 0) and Cu(1 1 1) surfaces [2] there is no evidence at 80 K, for chemisorbed nitrogen atoms N(a) with a characteristic photoelectron N(1s) binding energy at 397 eV, all the "nitrogen" arising from the dissociation of NO being accounted for by the N_2O formed (equation (5)). In addition two molecular states NO(a) of nitric oxide are present with N(1s) binding energies which are compatible with linear and bridged bonding states. At 295 K, however, chemisorbed nitrogen adatoms N(a) and chemisorbed oxygen O(a) are the only surface species present when Cu(1 0 0) is exposed to nitric oxide [2]. With polycrystalline aluminium surfaces at 80 K chemisorbed nitrogen atoms N(a) are observed at low surface coverage with evidence for $N_2O(a)$ only appearing with further exposure to nitric oxide. In this case the probability of reaction (6) occurring is initially greater than the addition reaction (equation (5)) and only at higher coverage does N_2O formation occur [4]. A correlation was tentatively drawn [3] between the propensity for the formation of chemisorbed nitrogen adatoms N(a) and the heats of formation of the corresponding bulk nitrides, high heats of formation favouring N(a) rather than $N_2O(a)$.

The mechanism by which N_2O is generated during the catalytic oxidation of ammonia at platinum surfaces has also not been successfully resolved. However, what has been established [5] is that when oxygen and ammonia are coadsorbed at a Pt(1 1 1) surface at 295 K oxydehydrogenation is very efficient and facile, leading to the formation of a well ordered $N(2 \times 2)$ adlayer, with a characteristic N(1s) binding energy of 397.6 eV. Since nitric oxide is the major product in the catalytic

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oxidation of ammonia then a simple radical type addition reaction of the transient N(s) to nitric oxide is a possible mechanism by which N_2O is formed as a byproduct (equation (5)).

There is now more direct evidence from scanning tunneling microscopy (STM) for the mobility of surface adatoms at low temperatures and in some cases, where the adsorption process is highly exothermic, ejection of atoms (e.g. oxygen) into the gas phase occurs [6]. That oxygen transients can provide low energy pathways in heterogeneously catalysed reactions is well established [7] with ammonia oxidation at metal surfaces studied in some detail. For ammonia rich mixtures a highly selective oxidation reaction to generate chemisorbed imide species NH(a) occurs with Cu(1 1 0) at 295 K but with no evidence from either XPS or STM for any surface oxygen state being present during the catalysis. A transient O^- like species was proposed to be the active oxidant. In this context it is significant that in a very recent study Wang and Barteau [8] using a novel oscillating microbalance reactor established that in the catalytic oxidation of butane over vanadyl pyrophosphate the traditional Mars-vanKrevelen mechanism, involving the lattice oxygen O^{2-}, accounted for only 5% of the maleic anhydride formed. The catalytically active oxygen accounting for the major reaction pathway is suggested to be O^-, present in very low concentrations at the catalyst surface. It is what we have designated in our studies of oxidation catalysis [7] as a transient state and the precursor to the formation of the final relatively unreactive oxide state, O^{2-}(a). There is clearly an argument for also exploring whether nitrogen transients have a wider role in heterogeneous catalysis than previously recognised.

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