Lateral interactions as the determinant in the switch from dissociative to molecular chemisorption: NO on Ni{100}

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Lateral interactions between adatoms on a solid surface play a key role in determining whether adsorption takes place dissociatively or non-dissociatively, as revealed by single crystal adsorption calorimetry. With NO on Ni{100}, adsorption occurs dissociatively at low coverage, while at higher coverage strong interatomic repulsions reverse the relative stability and the molecularly adsorbed state is then more stable than the dissociated state. Essentially, above a critical adatom coverage the adsorption heat for further dissociative adsorption is *lower* than that for non-dissociative adsorption, due to strong repulsive interactions between adatoms on the surface. By changing the oxygen adatom precoverage it is possible to control the relative amounts of dissociated and molecularly adsorbed NO. This result has important general consequences for the control of catalytic reactions.

Keywords: models of surface chemical reactions; catalysis; chemisorption

It has been known for some time that for many molecule/metal surface systems, dissociative adsorption occurs at low fractional coverage θ, but as θ increases adsorption occurs into a molecularly adsorbed state. Examples are CO on tungsten [1–3][#1], HCOOH on Ni{110} [4] and NO on Ni{110} [5]. Invariably this is attributed to the partial blocking of the empty site array required for the dissociation products on the surface. The recent availability of single crystal adsorption calorimetry (SCAC) [6,7] has opened up the possibility of directly measuring adsorption heats for reversible and irreversible systems, and hence of obtaining interaction energies between adsorbed species. Here we provide calorimetric and kinetic evidence for NO on Ni{100} which demonstrates for the first time that surprisingly large repulsive interactions between adatoms *and* small interactions between molecules control the relative stabilities of the dissociated and non-dissociated states. This new model has important implications for catalytic properties, which are discussed.

The heat of adsorption (defined as the negative of the enthalpy change) of NO on clean and on oxygen-predosed Ni{100} has been measured as a function of coverage [8]. Gas dosing is achieved by a pulsed molecular beam. The sticking probability is measured by the King and Wells method [9] and the flux is determined by a spinning rotor gauge. The temperature change is measured by monitoring the change in black body radiation from the back face of a Ni{100} single crystal film of 200 nm thickness by a Hg–Cd–Te infrared detector. The quality of these single crystal films, epitaxially grown on Ni{100}, is comparable to the usual bulk sample crystals, as demonstrated by meV ion channelling and LEED. Calibration of the calorimeter is carried out in situ by comparison with the signal recorded when a laser beam with the same spatial and temporal profile as the molecular beam and of known power strikes the sample. Simultaneous recording of the sticking probability and the differential heat of adsorption is then obtained as a function of coverage. Each experiment is repeated six times, and the results are shown as the average of all sets of data. All results refer to a crystal temperature of 300 K.

Results are shown in fig. 1 for both the initially clean surface and also for an oxygen predosed surface (oxygen coverage = 0.14 ML). On the clean surface the heat of adsorption decreases rapidly from an initial value of 426 kJ/mol to about 150 kJ/mol at 0.15 ML of NO, when a plateau is reached. Each gas pulse arriving at the surface is 50 ms duration, with a 2 s delay between pulses. When the heat of adsorption is sufficiently low ($\leqslant$80 kJ/mol at 300 K) some adsorption occurs between pulses, which is difficult to quantify. Hence at high exposures the coverage obtained by summing the amount adsorbed during pulses is an overestimate. The plateau above 0.15 ML cannot, however, be ascribed to reversible adsorption because the sticking probability at 0.15 ML is still high and decreases with coverage over the whole range investigated and the adsorption heat is too high. The true coverage is still increasing when the heat of adsorption reaches its plateau.

Spectroscopic considerations allowed other researchers [5] to unambiguously deduce that adsorption of NO on Ni{100} is dissociative initially and molecular at high coverage. This is perfectly consistent with the present calorimetric data; the high initial adsorption heat is

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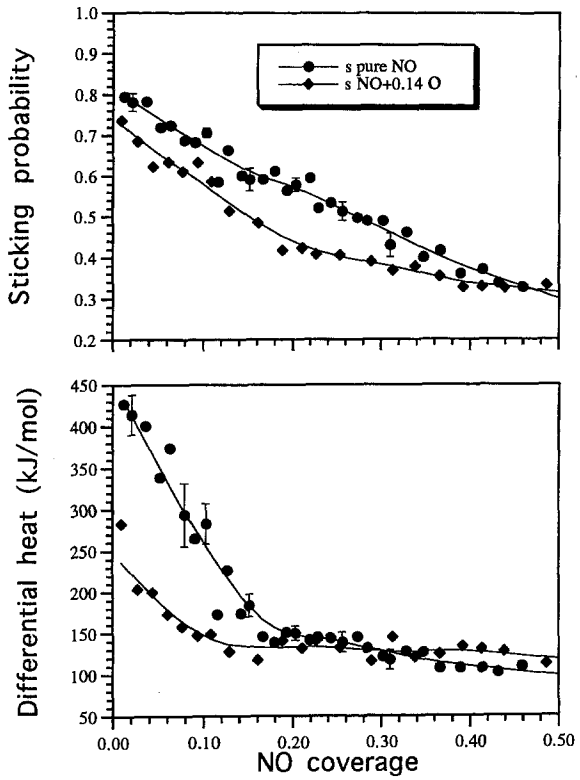

Fig. 1. (a) The sticking probability for NO on the clean (s pure NO) and oxygen precovered Ni{100} surface (s NO + 0.14 O) is plotted as a function of coverage. (b) The corresponding differential heats are shown. Since molecular and dissociative adsorption coexist, the coverage is expressed in ML of NO molecules. The oxygen precoverage is 0.14 ML of O adatoms. The coverage scale is expressed relative to a monolayer of Ni surface atoms, equivalent to 1.62×10^{15} atoms/cm^2.

attributable to dissociative adsorption, and the plateau above a critical coverage of 0.15 ML (fig. 1b) to molecular chemisorption with an adsorption heat of $\sim$ 150 kJ/mol. The sharp fall in adsorption heat between zero and 0.15 ML is attributed to repulsive interactions between N and O atoms formed by the dissociation of the NO molecule, but the invariance of the adsorption heat in the molecular state shows that molecule–molecule interactions in the adlayer are, at these coverages, relatively weak.

When NO is dosed on a surface precovered with 0.14 ML of O adatoms, the behaviour of the heat of adsorption is different. Firstly, the initial heat of adsorption is lowered significantly and, secondly, the critical coverage at the start of molecular adsorption is decreased. The heat of adsorption into the molecular state is, however, hardly affected, indicating that molecule–adatom interactions are weak at these coverages, in addition to molecule–molecule interactions. Measurements performed at different oxygen precoverages show that both the coverage corresponding to the plateau and the initial value of the differential heat decrease rapidly with increasing oxygen precoverage.

The sticking probability is relatively insensitive to the presence of predosed O adatoms; it is only slightly decreased. The results indicate that over the range where dissociative adsorption occurs the sticking probability is higher (0.8 to 0.6) than over the range where the molecular state is formed ($\leqslant$0.6).

The data can be explained in toto if the role of lateral interactions between adsorbed atoms is considered. NO adsorption is disordered at all coverages at room temperature [5]. In accordance with this, the heat of adsorption decreases continuously with coverage during dissociative adsorption ($\theta < 0.15$ ML). When NO is dosed on the oxygen precovered surface the initial value is about 280 kJ/mol and rapidly decreases, reaching the plateau at a coverage of only about 0.08 ML. Monte Carlo simulations were conducted to determine the lateral interactions by fitting to the experimental data. The maximum coverage reached by the dissociated species is lower than 0.5 ML (N + O), which indicates that the pairwise repulsive interaction for *nearest* neighbour (nn) adatoms is prohibitively high. These nn interactions are therefore set at a very high value to completely block nn occupation. We then include three pairwise interaction terms for N–N, N–O and O–O pairs in second nn sites; different values for these pairwise interactions energies [8] are introduced into the procedure. In the simulations both the initially clean surface and a partially oxygen-adatom-covered surface were considered. The size of the lattice was chosen to be 30 × 30 in order to achieve an acceptable computing time. We assume that the singleton bond energies (Ni–O and Ni–N) are coverage independent (as is reasonable since no reconstruction takes place), and that the pairwise interactions are independent of adlayer composition. An additional variable n_{hop} is introduced into the procedure. This dynamic parameter is related to the mobility of "hot" adatoms. For fixed values of all the other parameters, a very low value of n_{hop} gives a lower heat of adsorption because the adatoms are arranged without any local minimisation of the energy. On the other hand, a relatively high value allows better local equilibration and yields a higher heat of adsorption. A good fit to the data required n_{hop} to be 8 for NO adsorption on the clean surface and 4 on the oxygen covered one. Hot adatom mobility is lower on a high coverage predosed surface, than on a clean surface, which is reasonable.

By fitting the experimental data both for O_2 and NO adsorption [8], the second-nearest neighbour (nnn) pairwise lateral interaction energy between O atoms is estimated to be about 40–50 kJ/mol, while that for O–N and N–N averages to about 100 kJ/mol.

Fig. 2 shows a comparison between the simulated differential heat for dissociative adsorption and the experimental results. We note that above $\sim$ 0.12 ML the heat of adsorption estimated for *dissociative* adsorption falls well below the experimental value, due to the increased occupancy of nnn pairs. Above this coverage molecular chemisorption is *energetically* favoured over the disso-

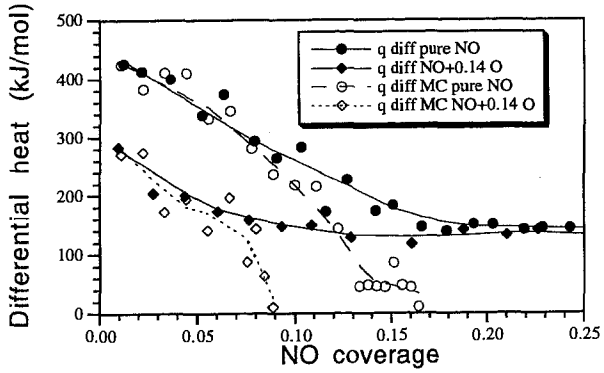

Fig. 2. Comparison between simulated and experimental differential heat of adsorption for NO on the clean and oxygen predosed (0.14 ML of O) Ni{100} surface. The model includes only dissociative adsorption, so that the simulations deviate from the experimental points when the coverage corresponding to the onset for molecular chemisorption is approached.

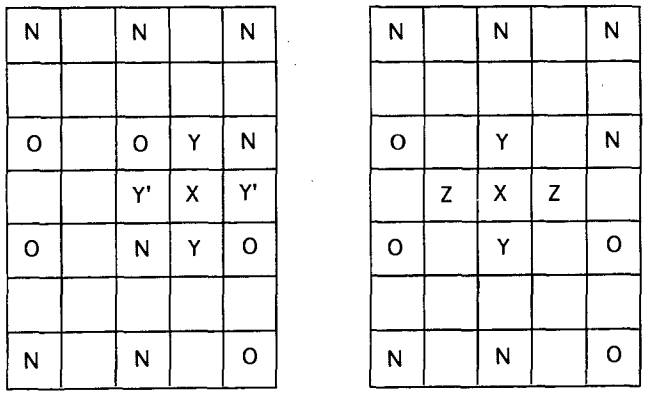

Fig. 3. Schematic illustration of the site arrays required for dissociative adsorption to be more energetically favourable than non-dissociative adsorption. N and O represent adatoms, X is the site where a NO molecule is adsorbed, and Y, Y' and Z are possible destinations for its constituent adatoms. Only adatoms in the pair of Y sites in (b) would be more stable than the molecule at X.

ciated state. Molecular chemisorption is not included in the model, since this is trivially achieved and adds nothing to the analysis. When NO is dosed onto a surface where oxygen adatoms are already present, the heat of adsorption is initially smaller than on a clean surface due to contributions from repulsive interactions with preadsorbed atoms.

In the literature to date, it has been almost invariably assumed that for a given gas/single crystal metal system dissociation is prevented at high coverages of adatoms due to a *kinetic* constraint [9–12] [#2]. An example is the dissociative adsorption of N_2 on W{100}, where "saturation" coverage at half monolayer coverage was attributed to two factors, the need for an empty pair of nearest neighbour (nn) sites at the collision point and the existence of strong repulsive pairwise nn lateral interaction energies which produces a double-spaced c(2 × 2)-N structure at $\theta \approx 0.5$ with no empty nn pair sites [9,13]. This model was extended by Brundle, Behm and Barker [14] to the case of O_2 on Ni{100}, where a sharp fall in s towards zero at $\theta \approx 0.2$ was attributed to a kinetic requirement that dissociative adsorption would only occur if an empty array of *eight* sites exists at the point of impact. Subsequently, Wartnaby et al. [15] also fitted s and adsorption heat data for this system with a *nine* empty site array requirement for dissociative adsorption. However, it is now apparent that the peculiarly large size of the empty site array for O_2 and also for NO on Ni{100} has a simple explanation as a local energy, and not a kinetic, constraint. For example, fig.3a depicts a (2 × 2) array of N and O atoms (with random occupancy). If the impact site for a molecule is X, local dissociation would produce adatoms at two of the four Y sites, which would invoke prohibitively large pairwise repulsion with nn N and/or O adatoms. The singleton (zero coverage) dissociative adsorption energy ε_d would be reduced to $[\varepsilon_d - 4\omega_1]$, where ω_1 is the nn pairwise repulsive interaction energy, and this would be less than the non-dissociative adsorption energy ε_{nd}; dissociation would not occur. On the other hand, with the N and O adatom occupancy shown in fig. 3b impact at X would lead to dissociation into the two Y sites without significant reduction in dissociative adsorption energy ε_d, which is therefore favoured since $\varepsilon_d \gg \varepsilon_{nd}$. Occupancy of the two Z sites, however, would lead to an adsorption energy $[\varepsilon_d - 4\omega_2]$, where ω_2 is the nnn pairwise interaction energy estimated here as 100 kJ/mol. Since $\varepsilon_d = 426$ kJ/mol and $\varepsilon_{nd} \approx 150$ kJ/mol, we see that occupancy of the two Z sites is energetically unfavourable: dissociation can only occur into the Y sites. Occupancy of one Y and one Z site will give an adsorption energy $[\varepsilon_d - 3\omega_2] \approx 126$ kJ/mol, which is again less favourable than non-dissociative adsorption. It is therefore evident that the empty site array required for dissociative adsorption to be energetically favoured over non-dissociative adsorption can be very extensive if repulsive interactions are large. Kinetics alone would restrict the array requirement to a pair of nn sites, as appears to be the case for N_2 dissociation on W{100} [9].

These findings are essentially independent of the details of the model chosen to fit the experimental data and used to estimate the pairwise interaction energies. It is possible to obtain the total contribution, U_{rep}, of lateral interactions to the energy of the Ni{100}–NO system directly from the measured $q_{diff}(\theta)$:

$$U_{rep} = \int_0^{\theta_{atoms}} [q_{diff}(0) - q_{diff}(\theta)]\, d\theta . \qquad (1)$$

[#2] Ref. [12] contains reviews of kinetics of dissociative adsorption.

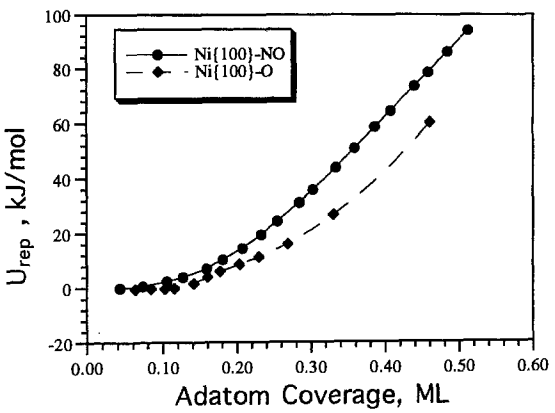

Fig. 4. Total contribution of repulsive interactions to the energy of the Ni{100}–NO and Ni{100}–O_2 system as a function of the total adatom (N + O or O) coverage. The data for O are taken from ref. [8] and the energy is evaluated using eq. (1).

Such a contribution is plotted in fig. 4 and compared to the total contribution of the repulsive interaction to the energy of the Ni{100}–O system, as obtained from the data reported in ref. [8]. It is apparent that repulsive interactions are larger in a mixed N and O adlayer than in an O adlayer.

We have therefore demonstrated that lateral interactions are a key factor in the occurrence of dissociative or molecular chemisorption, thus explaining both the coverage dependence of the heat of adsorption and the influence of oxygen preadsorption in a simple and straightforward way. The result is particularly relevant to catalysis: as is well-known oxygen may act as a promoter or as a poison depending on the reaction involved [16,17]. For the specific case under discussion, when molecules of NO are desired in a catalytic process, oxygen is expected to be a promoter, but when N or O atoms are required on the surface for the catalytic reaction to proceed, oxygen preadsorption should have a poisoning effect. It is moreover possible to predetermine the amount of NO which will dissociate by changing the O predose. The mechanism presented in this study is pertinent to NO chemisorption on Ni{100}, but it is clear that similar conclusions may be valid for any species which coexists in both dissociated and molecular state on a surface at the same temperature.

A recent investigation of ammonia oxidation on Pt{100} [18] has provided direct experimental evidence for the role of O preadsorption in determining the catalytic activity. This reaction is used in the industrial synthesis of NO, at temperatures of $\sim$ 1300 K. Under reaction conditions NO is produced in a rapid surface reaction between adsorbed NH_3 and O adatoms, but if the O adatom coverage is below a critical value the molecularly adsorbed NO is rapidly converted to N and O adatoms; this is then followed by N adatom recombination to gaseous N_2, the undesired product. It was shown that this undesired product could be completely eliminated, even at temperatures as low as 450 K, if the O adatom coverage was kept above the critical value of 0.2 ML during the reaction [18]. This is a concrete example of the application of the conclusions of the present paper to an important catalytic process. We suggest that the long-range influence of several known catalytic poisons [16,19], such as sulphur adatoms, which has been extensively discussed in the literature, may have a similar origin in inhibiting the dissociation of molecular species. Here, the repulsive interaction between dissociated adsorbed product and the inhibitor adatom would play the critical role in destabilising the dissociated species, with respect to the non-dissociated species.

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