Adatom bond energies and lateral interaction energies from calorimetry: NO, O₂, and N₂ adsorption on Ni{100}

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Heats of adsorption and sticking probabilities have been measured for NO and O₂ on clean and oxygen precovered Ni{100} at room temperature by single crystal adsorption calorimetry (SCAC). Adsorption is initially dissociative for both species and the initial heat of adsorption is 536 kJ/mol for O₂ and 426 kJ/mol for NO. From these data the initial heat of dissociative adsorption of N₂ on Ni{100} is estimated to be 136 kJ/mol. With increasing coverage the adsorption heat for both NO and O₂ decreases due to repulsive interactions between adsorbed adatoms; the magnitude of these pairwise repulsive interactions between oxygen adatoms is estimated to be about 40 kJ/mol by fitting the experimental data for O₂ dissociative adsorption with a Monte Carlo simulation. The pairwise repulsive interaction between nitrogen and oxygen and between nitrogen adatoms is obtained as about 100 kJ/mol. Due to the high magnitude of lateral repulsive interactions between adatoms, a critical coverage of NO is reached for which molecular adsorption is energetically favored with respect to dissociative adsorption. This coverage is ~0.16 ML for a 1:1 O:N adatom coverage decreasing to ~0.07 ML for 3:1 O:N adatom ratio. For O₂ adsorption, the lower magnitude of repulsive interactions allows dissociative adsorption to take place up to a coverage of about 0.3–0.4 ML; above this coverage the bulk oxide is more energetically favorable and an oxide layer is formed. NO dissociative adsorption is precursor mediated, whereas for O₂ the precursor plays only a limited role. © 1996 American Institute of Physics.

I. INTRODUCTION

Adsorption of NO on Ni{100} has been investigated by a large variety of techniques, including LEED, AES, UPS, and TDS. More studies exist for O₂ adsorption on Ni{100}, including an earlier study of O₂ and K coadsorption performed by single crystal adsorption calorimetry (SCAC), while NO and O₂ coadsorption have only been investigated to a limited extent, although recently detailed HREELS, ARUPS, and NEXAFS studies have been performed. Adsorption of NO on Ni{100} is particularly interesting because at room temperature it initially adsorbs dissociatively, while under the same conditions molecular chemisorption takes place on Pt{100}. On Ni{100} NO adsorbs dissociatively for exposures below 0.8 L and partly molecularly at higher exposures (0.8–100 L). When the exposure exceeds 100 L, oxide formation starts to occur. No ordered LEED pattern was observed for temperatures lower than 400 K. Oxygen behaves differently at room temperature; it adsorbs dissociatively over the whole coverage range, with the successive formation of p(2×2) and c(2×2) structures. At high exposures, the formation of an oxide layer sets in. No molecular state is reported at room temperature. The adsorption of O₂ on Ni has already been investigated by SCAC, and in particular the effect of K preadsorption has been investigated as a model for the catalytic action of alkali promoters. In this paper we focus on the role of repulsive interactions on the kinetics and the dynamics of NO and O₂ adsorption. A lattice Monte Carlo simulation of the kinetics and dynamics of adsorption is presented to quantitatively describe both the sticking probability s and the heat of adsorption in the range of coverage in which adsorption is dissociative. The role of oxygen preadsorption on NO dissociation has also been investigated. The magnitude of N–N and O–N lateral interactions for atoms in nnn sites is obtained by fitting the experimental data. The importance of obtaining metal–molecule and metal–atom bond energies has been highlighted because of its importance in explaining and predicting catalytic activity. Where the sticking probability is low or even zero, such as for the dissociative adsorption of N₂ on Ni, the bond energy—in this case Ni–N—must be obtained indirectly. Here we report a determination of the Ni–N bond energy from NO adsorption, and an estimate of the activation barrier for the dissociative adsorption of N₂ on Ni{100}.

II. EXPERIMENT

The experimental layout for SCAC has been extensively described elsewhere, only a brief description is given here. The surface is cleaned by gentle argon ion sputtering and annealing cycles until no contaminants are detected by Auger spectroscopy; the crystallinity and order of the surface are checked by LEED. Pulsed supersonic molecular beams of NO or O₂ with ~10¹² molecules for each 50 ms pulse impinge at normal incidence on a Ni{100} film which is supported on a Ni polycrystalline ring. The back face of the film, thickness about 200 nm, is coated with carbon to increase its IR emissivity. When adsorption occurs on the surface of the film an increase in the temperature of the surface is remotely
detected by monitoring the change in IR emission from the back face of the sample by a Hg–Cd–Te infrared detector. The intensity of the infrared emission is calibrated by comparison with the intensity observed when a pulsed calibrated laser beam irradiates the surface. The sticking probability is measured by the King and Wells reflection detector technique.14 The molecular beam flux is calibrated with a spinning rotor gauge, and the coverage is obtained by summing the amount of gas adsorbed during each pulse. The coverage scale eventually extends indefinitely, when a steady state is reached in which the amount of gas adsorbed in each pulse is exactly equal to the gas desorbing in the time \(\sim 2.5 \text{s} \) between pulses. Due to the limited time of detection of the IR emission (50 ms) only processes taking place on a comparable time scale affect the result of the measurement.

III. RESULTS

The variations of heat of adsorption with coverage for NO on clean and oxygen precovered Ni\(\{100\}\) are shown in Fig. 1. The initial heat of adsorption of NO on the clean Ni\(\{100\}\) surface is \(\sim 426 \text{ kJ/mol}\), decreasing with increasing coverage. At 0.16 monolayer (ML) of NO molecules (or 0.32 ML of adatoms) a plateau is reached where the adsorption heat is about 150 kJ/mol. The heat remains constant up to about 0.3 ML NO, when it drops to about 110 kJ/mol.

When NO is dosed onto an oxygen precovered surface, the initial heat of adsorption is lower and the plateau at about 150 kJ/mol is reached at a lower NO coverage. A coverage of 0.014 ML \(\mathrm{O}_2\) (or 0.028 ML O atoms) is enough to diminish the initial heat of adsorption of NO by about 80 kJ/mol and to cause the plateau in the differential heat \(\Delta q\) to begin at a coverage \(\sim 0.12 \text{ ML NO}\). When the oxygen precoverage is as high as 0.2 ML O, the initial heat of adsorption of NO is \(\sim 200 \text{ kJ/mol}\) and the plateau corresponding to a roughly constant heat of adsorption is reached almost immediately. Intermediate behavior is observed for intermediate O precoverage.

The sticking probability variation with coverage for NO on clean and oxygen predosed Ni\(\{100\}\) is shown in Fig. 2. On the clean surface, it is initially 0.8 and decreases linearly. Remarkably, at the coverage corresponding to the plateau in the heat, where the heat of adsorption has already diminished substantially, the sticking probability is still about 70% of its initial value and there is no change in the slope. On the oxygen precovered surface the initial sticking probability \(s_0\) is lower than on the clean surface and decreases linearly and slightly more rapidly with coverage to \(\sim 0.2\). As shown in the discussion to follow, this simple behavior masks the complicated kinetics involved in the dissociative adsorption up to a critical coverage, depending on the oxygen precoverage, followed by molecular adsorption.

In Fig. 3 the measured data for the sticking probability and the heat of adsorption of O\(_2\) on the clean Ni\(\{100\}\) surface are shown; the results agree with previous SCAC measurements,7 but are reproduced here because the comparison between NO and O\(_2\) data are essential to the discussion. The initial heat of adsorption of O\(_2\) is about 536 kJ/mol. It remains constant up to about 0.1 ML, falls rapidly until between 0.3 and 0.4 ML a plateau is reached at a value of about 220 kJ/mol. The initial value of the sticking probability \(s\) is about 0.36 and it decreases rapidly to a value lower than 0.05 when the plateau in the differential heat is reached.
the activation barrier for adsorption, $E_a$ may be estimated as $(E_d - q_{N_2})$, giving $E_a = 59$ kJ/mol corresponding to a kinetic energy of about 0.6 eV; this high value is consistent with a sticking probability of zero for thermal energies. The activation energy derived here is close to the value obtained for N$_2$ adsorption on polycrystalline Ni of 50.2 kJ/mol by Xi et al.\textsuperscript{15} who observed a substantial increase in the initial sticking probability from 0 to 0.03 when the N$_2$ translational energy was increased from 46.1 to 83.3 kJ/mol.

As the coverage of NO is increased to 0.16 ML NO, there is a rapid decrease in the differential heat. The measured heat at these coverages is attributed to dissociative adsorption and the rapid decrease in the differential heat must therefore be due to strong repulsive interactions between adatoms. Since the heat of adsorption starts to decrease immediately, we also argue that the adsorption is highly disordered; this is consistent with the complete absence of an ordered overlayer. If equilibration occurred, the adatoms would be ordered in such a way as to minimize the repulsive interactions. For example, a roughly constant heat of adsorption should be observed up to a total adatom coverage of 0.25 ML (N+O), when a $R(2\times2)$ overlayer would be observed by LEED. Absence of equilibration indicates low mobility of the strongly adsorbed adatoms at room temperature. This is supported by the fact that when the temperature is raised (>400 K), ordered structures are observed.\textsuperscript{1}

When the plateau at 150 kJ/mol in the differential heat of adsorption is reached at 0.16 ML NO, the sticking probability is still about 0.6 and continues to decrease; this plateau in the heat curve cannot be ascribed to steady state adsorption. Consistent with spectroscopic data, we assign this to molecular adsorption. The differential heat of adsorption is almost coverage independent in this range. This implies that repulsive interactions between adsorbed molecules are relatively weak. We note that the initial heat of adsorption for molecular NO on Pt(100)(1×1) is around 200 kJ/mol,\textsuperscript{10} about 50 kJ/mol higher than on O+N predosed Ni(100). Finally, we associate the relatively small drop in heat at 0.3 ML to the end of molecular adsorption and the onset of oxide layer formation, which requires very high exposures for its full development and is therefore not investigated in the present work. We now focus our attention on the first coverage range (0–0.16 ML).

B. Monte Carlo simulations: Lateral interaction energies and empty site arrays

Pairwise repulsive interaction between adsorbed atoms can be estimated from the decrease in the heat of adsorption of NO with coverage. At least three interaction terms are required (O–O, O–N, and N–N) for each possible configuration (nn and nnn sites), giving a large number of free parameters. The task is simplified by some qualitative considerations. First, the maximum coverage reached by the dissociated species is lower than 0.5 ML (N+O), which indicates that the pairwise repulsive interaction for nn adatoms is prohibitively high. These nn interaction terms can therefore be set at a very high value. We then include three pair-
wise interaction terms, for N–N, O–N, and O–O pairs in \( nnn \) sites. To achieve that, we first determine the O–O interaction energy by simulating the \( O_2 \) adsorption heat data, and then turn to the more complicated case of NO dissociative adsorption.

### 1. Simulation of dissociative \( O_2 \) adsorption

Inspection of Fig. 3 reveals that the lattice is better equilibrated in the case of oxygen, as revealed by the invariance of the heat of adsorption up to 0.1 ML of O atoms. In this range of coverage a \( p(2 \times 2) \) overlayer is formed, as noted by LEED. Since the equilibration is not perfect, as already proposed in the first SCAC study\(^7\) of this system, the differential heat starts to decrease at about 0.1 ML, with filling of centered sites indicated by the appearance of a \( c(2 \times 2) \) pattern. At a coverage of about 0.33 ML the process of filling centered sites is terminated, which is well below the coverage of 0.5 ML where all would be filled. Instead, beyond 0.4 ML oxide formation sets in. The sticking probability actually rises as the oxide film grows,\(^7\) although this is not shown here.

We have performed a lattice Monte Carlo simulation to model the dynamics and the kinetics of \( O_2 \) dissociative adsorption. The procedure is described as follows. A random position is chosen and the molecule enters into a precursor state at that position. If the corresponding chemisorbed site is filled, the molecule desorbs with probability \( p_{\text{des}} \) or hops to a neighboring site with probability \( 1 - p_{\text{des}} \). If the corresponding site for chemisorption is empty, the particle may adsorb with probability \( p_{\text{des}} \) and \( p_{\text{des}} \) to be equal to reduce the number of free parameters. A low desorption probability characterizes a system where the precursor state plays an important role leading to a slow decrease in the sticking probability with coverage while a higher value of \( p_{\text{des}} \) (and \( p_{\text{ads}} \)) causes the sticking probability to decrease very rapidly with coverage. Each dissociating molecule is assigned an attractive energy \( \omega_0 \) (which equals the initial heat of adsorption) and a repulsive pairwise contribution, \( \omega_1 \), is added for adatoms in \( nnn \) sites (along the diagonal of the square lattice). A second order pairwise contribution, \( \omega_2 \), due to the interaction between adatoms along rows or columns separated by an empty site (\( nnnn \) sites) is also considered. Occupation of \( nn \) sites is forbidden by assigning zero adsorption probability to precursor molecules on empty pair sites with \( nn \) sites occupied by O adatoms. If one of the pair sites occupied by the precursor is filled the probability is also zero. After dissociation the atoms may hop to nearby sites, the maximum number, \( n_{\text{hop}} \), of allowed hops being fixed. This accounts for the possibility of limited hot adatom migration before energy is dumped into the lattice, and also provides more equilibration of the adlayer. A low value of \( n_{\text{hop}} \) produces a disordered adlayer, while a reasonably high value produces some local order with a lower energy configuration. Since previously adsorbed atoms are not moved, the equilibration is still partial, an ideal situation in simulating the present system.

It was found that the best fit value for \( \omega_1 \) depends somewhat on \( n_{\text{hop}} \); for example, with \( n_{\text{hop}} = 5 \), the best fit value is about 40 kJ/mol, while for \( n_{\text{hop}} = 15 \) the best fit is obtained when \( \omega_1 = 45 \) kJ/mol. Further increasing \( n_{\text{hop}} \) does not produce any significant change in the simulated results. The difference between the best fit values is so small that \( n_{\text{hop}} = 5 \) is chosen to shorten the computing time. Lower values of \( n_{\text{hop}} \) are rejected because equilibration becomes too inefficient and the limit of completely disordered adsorption is approached. In this case the integral heat does not show an initial constant value but starts to decrease almost immediately. A 50×50 lattice with periodic boundary conditions to avoid finite size effects was used. A simulation of the coverage dependence of the differential heat requires averaging adsorption events, with some loss of coverage resolution. Integral heats are then computed as a function of coverage before a comparison is made with the integrated experiment-
with the values independently obtained from SCAC data by
and $v$ state is 0.25.

The open circles reproduce Monte Carlo results for
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Figure 5 shows a comparison of the simulated and ex-
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ternal data. The integral heat, $q_{\text{int}}$, is obtained from the differ-
ential heat $q_{\text{diff}}$ through the expression,

$$ q_{\text{int}} = \frac{1}{\theta} \int q_{\text{diff}} \, d\theta, $$

where $\theta$ is the fractional coverage.

Figure 5 shows a comparison of the simulated and ex-
perimental integral heats of adsorption, for $\omega_1 = 40$ kJ/mol
and $\omega_2 = -2$ kJ/mol. These values are in good agreement
with the values independently obtained from SCAC data by
Wartnaby$^{16}$ (35 kJ/mol and $-2$ kJ/mol, respectively). The
reliability of the second parameter is limited because it af-
facts only the very early stages of the adsorption sequence,
when no centred sites are filled and the behavior is deter-
mained by the second $nnn$ interaction.

In Fig. 6 the experimental and simulated sticking prob-
abilities are also shown, normalized to the initial value, for
both environments of Fig. 4. This best fit is obtained with
$p_{\text{des}} = 0.25$ which indicates a limited role for the precursor
state. Good agreement between experiment and model is
achieved because only dissociative adsorption takes place in
the range of coverage investigated. As expected, both our
geometry and that suggested by Brundle lead to a good fit,
with the same values of the parameters. When a coverage of
0.33 ML of O adatoms is reached, no further dissociative
adsorption is possible and oxide formation starts, as exten-
sively explained by King and co-workers$^7$ because of strong
repulsive interactions between adatoms in the overlayer,
above this coverage the adlayer is less stable than the oxide
film.

The present model has the advantage of including the
possibility of partial equilibration of the lattice and thus al-


FIG. 6. Comparison between experimental ($s/s_0$ exp) and simulated ($s/s_0$ MC) normal-
ized sticking probability for O$_2$ on Ni[100] at room temperature, for both
environments of Fig. 4. The open circles reproduce Monte Carlo results for
our empty site array, while crosses show the results if the empty site array of
Brundle is used in our program. The values of the interaction constants are
the same as in Fig. 5 and the probability for desorption from the precursor
state is 0.25.

The present model has the advantage of including the
possibility of partial equilibration of the lattice and thus al-

dows the experimental data to be fit at room temperature.
Whenever the mobility of the adsorbate is not high, as in the
present case, the possibility of partial equilibration has to be
included to fit the experimental data quantitatively. More-

2. Simulation of dissociative NO adsorption

We now consider the more complicated case of NO ad-

sorption. If a simplified simulation is performed with only
one interaction term constant, i.e., assigning the same repul-
sive interactions to O–O, N–N, and N–O pairs of $nnn$ ada-
toms, an average value for $\omega_1$ of about 60 kJ/mol is obtained.
This value is significantly higher than that obtained above for
O–O interactions alone, which suggests that N–O and or
N–N interactions are more strongly repulsive than O–O in-
teractions. This is confirmed by inspecting the decrease in
the heat of adsorption for oxygen and NO, with respect to the
initial value; at 0.3 ML, the differential heat of adsorption
has decreased by about 200 kJ/mol for oxygen and by about
250 kJ/mol for NO. For this reason a more refined fitting
procedure was followed by introducing different values for
the N–N, N–O, and O–O pairwise interaction energies. In
the simulations both an initially clean surface and a partially
oxygen-adatom-covered surface were considered with an
oxygen adatom precocurrence of 0.14 ML. The size of the
lattice was chosen to be 30×30 in order to achieve an ac-
ceptable computing time. Assuming that singleton bond en-
ergies (Ni–O and Ni–N) are coverage independent (as is
reasonable since no reconstruction takes place) and assuming
that pairwise interactions are independent of adlayer compo-
sition, an additional variable is $n_{\text{hop}}$. The role of this dy-
amic parameter, related to the mobility of hot adatoms, is
demonstrated in Fig. 7. For fixed values of all the other pa-
rameters, a very low value of $n_{\text{hop}}$ gives a lower heat of
adsorption because the adatoms are arranged without any


local minimization of the energy. On the other hand, a relatively high value allows a better local equilibration and consequently gives a higher heat of adsorption. A good fit requires \( n_{\text{hop}} \) to be 8 for NO adsorption on the clean surface and 4 on the oxygen precovered one. It appears that adatom mobility is lower on a high coverage predosed surface, than on a clean surface, which is not unreasonable. For simplicity the maximum number of allowed hops has been considered coverage independent for a fixed O precoverage.

A reasonably good fit to both the clean and the oxygen precovered data are obtained with N–N and O–N coupling of about 100 kJ/mol. This value actually corresponds to the weighted average of N–N and O–N coupling which cannot be unambiguously separated. To do that, we should extract N–N repulsive interactions from the variation of the heat of dissociative adsorption for \( N_2 \) with coverage, an impossible experiment. The error on the evaluation of these parameters is estimated to be about 10 kJ/mol, from inspection of the values of \( \omega_1 \) required to fit the data when \( n_{\text{hop}} \) is changed. The effective number of hops per atom is, however, small (0.7 on the clean surface and 0.15 on the precovered surface); the values are small and the relatively large difference is probably a statistical effect.

The best fit to the integral heats is shown in Fig. 8 and to the normalized sticking probability in Fig. 9. This simple model, including only dissociative adsorption, provides a good fit to the data up to a coverage close to the beginning of the plateau which we assign to the onset of molecular adsorption. As the plateau is approached both the sticking probability and the integral heat given by the model strongly deviate from experiment. This simply indicates the onset of molecular adsorption which is not accounted for in the model. For oxygen, where dissociative adsorption takes place up to a coverage 0.33 ML, the model provides a good description of the data over the entire coverage range over which chemisorption takes place.

C. Criterion for dissociative or nondissociative adsorption

The strength of lateral interactions between adatoms clearly determines the onset of molecular adsorption. Dissociative adsorption is energetically favored at low coverage; at higher coverages, as repulsive interactions between adatoms become involved, molecular adsorption becomes more energetically favorable, even though it is characterized by a smaller singleton (Ni–NO) energy. Clearly, molecule–adatom and molecule–molecule interactions are not important at these coverages. The magnitude of repulsive adatom...
interactions also affects the kinetics of dissociative adsorption; significantly the observed sticking probability for NO in the range where dissociative adsorption takes place is only compatible with very small values of $p_{\text{des}}$ (0.015), indicative of effective precursor behaviour. According to this model, the nearly linear fall in $s$ with coverage hides a much more complicated situation.

V. CONCLUSIONS

Our findings for the interaction of O$_2$, NO, and NO with preadsorbed O on the \{100\} surface of Ni at room temperature by SCAC may be summarized as follows:

1. The initial heats of dissociative adsorption are $\sim$426 kJ/mol for NO and $\sim$536 kJ/mol for oxygen, which yield a prediction for the heat of dissociative adsorption of N$_2$ of $\sim$136 kJ/mol. The heat of adsorption decreases with coverage due to repulsive interactions between adatoms in the adlayer. The O–O pairwise repulsive interaction energy for atoms in $nnn$ positions is estimated to be about 40 kJ/mol, while N–O and N–N interaction energies are higher, about 100 kJ/mol on average. These values may be compared with theoretical predictions by Gallagher et al., who derived an O–O $nnn$ repulsive interaction energy of about 33 kJ/mol (within a factor 3); the present values are reasonable, even if unexpectedly large.

2. Depending on oxygen precoverage, above some critical total adatom coverage, no further NO dissociation is energetically possible and molecular adsorption becomes thermodynamically favored. The heat of adsorption for the molecular state does not fall drastically, indicating that molecule–molecule interactions are relatively weak. This finding is particularly relevant for the understanding of vital catalytic phenomena. If a catalytic action requires NO dissociation, as in the NO+CO reaction, pressures producing adatom coverages above the critical value will not aid the reaction but for reactions where molecular NO is a desired product, as in NH$_3$ oxidation to NO, where N$_2$ is not the desired product, exceeding the critical adatom coverage is critical. This has been recently shown for ammonia oxidation on Pt \{100\}. The kinetics of dissociative adsorption is strongly precursor mediated for NO adsorption, but for oxygen the role of the precursor is marginal. The sticking probability for O$_2$ decreases more rapidly with coverage than that of NO.

3. The lower value of lateral repulsive interactions for O adatoms and the better equilibration allow dissociative adsorption to take place up to a coverage of about 0.33 ML with the formation of ordered $p(2\times2)$ and $c(2\times2)$ overlayers. The chemisorption regime ends at 0.33 ML, with the $c(2\times2)$ structure showing its maximum development, while a coverage close to 0.5 ML would be expected. This is consistent with STM observations by Kopatzki and Behm which show the hopping frequency for O atoms at room temperature to be only $3\times10^{-4}$ s$^{-1}$. At coverages above 0.33 ML further uptake is in the form of oxide film growth, which is more thermodynamically stable than $c(2\times2)$–O with invocation of lateral interactions. The degree of equilibration is temperature dependent; previous measurements by Wartnaby show that at 90 K the heat of adsorption of O$_2$ starts to decrease immediately, while at 300 K it is constant up to about 0.12 ML and at 400 K up to 0.25, thus supporting our explanation.

With dissociative NO equilibration of the adsorbate is not achieved and the adlayer is disordered at all coverages. As with oxygen, when the temperature is increased, better equilibration is achieved and ordered structures form.

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