Catalysis Letters 9 (1991) 173–182

THE REACTIVITY OF METAL SURFACES

J.K. NØRSKOV, P. STOLTZE

Laboratory of Applied Physics, Technical University of Denmark, DK 2800 Lyngby, Denmark and Haldor Topsøe Research Laboratories, Nymøllevej 55, DK 2800 Lyngby, Denmark

U. NIELSEN

Institute of Physics, University of Århus, DK 8000 Århus, Denmark

The relations between the microscopic description of the dynamics of chemical reactions at metal surfaces and our understanding of the activity of heterogeneous catalysts is discussed. It is shown that in some cases we start understanding some of the factors determining the catalytic activity of a given surface. Examples will be given, ranging from detailed reaction dynamics studies of simple adsorption reactions to a prediction of the trends in the ammonia synthesis rate along the transition metal series.

Keywords: Heterogeneous catalysis, reactivity trends theory on metal surfaces, ammonia synthesis model, d-electron contribution to surface bonding

1. Introduction

One of the main ambitions of surface science is to provide an increased understanding of heterogeneous catalysis. The hope is that by understanding the details of adsorption, dissociation, diffusion, reactions and desorption at surfaces we will be able to understand why a given surface catalyzes a given chemical reaction and we will eventually be in a position to help designing new catalysts.

The detailed microscopic description of a chemical reaction in terms of the motion of the individual atoms taking part in the event is known as the *reaction dynamics*. The study of reaction dynamics at surfaces is progressing rapidly these years, to a large extent because more and more results from detailed molecular beam scattering experiments are becoming available. Mono-energetic beams of molecules often in a known quantum state are scattered from well defined single crystal surfaces, and the dissociation probability or reaction probability can be measured as a function of the kinetic energy of the molecules, their angle of incidence, the degree of excitation of the internal degrees of freedom of the molecule, and as a function of the geometry and temperature of the surface. By combining with theoretical models or computer simulations it is often possible to extract knowledge of the so called potential energy surface on which the atoms move during the process, including the activation barriers in the reaction. In

addition one can get information about the coupling of the reaction to the other degrees of freedom in the system and in particular about the transfer of energy in the process.

The link between the microscopic description of the *reaction dynamics* and the *macroscopic kinetics* that can be measured in a catalytic reactor is a *micro-kinetic model*. Such a model will start from binding energies and reaction rate constants deduced from surface science experiments on well defined single crystal surfaces and relate this to the macroscopic kinetics of the reaction. There are now a number of examples in the literature where such a model has been deduced [1–4].

If one can understand what are the basic parameters of the reactants and the surface that determine the *reaction dynamics* (activation barriers etc.) then given a micro-kinetic model one has a knowledge of the factors determining the catalytic activity of the catalyst.

In the present very short review, we will try to illustrate this approach. Choosing the H_2 dissociation process, a particularly well studied example, we illustrate the dependence of the *dynamics* on the crystal face of the metal and on the position of the metal in the periodic table. Using a simulation of the dynamics based on a model potential, we show how these differences can be traced back to differences in various parameters characterizing the metal surfaces, such as work function, metal coordination number in the surface, and the number of d-electrons. This picture is then generalized to describe trends in activation energies for dissociation and binding energies for different molecules over the transition metal series. It is shown how a combination of these trends with a *micro-kinetic model* for a particular reaction, the ammonia synthesis, leads to a description of the catalytic activity of the transition metals for this reaction (the *volcano curve*) in excellent agreement with observations.

2. Dynamics of the H_2 dissociation process

Fig. 1 shows the sticking probability for H_2 on two different faces of Ni as a function of the kinetic energy of the incoming molecule [6]. On the open (110) surface the sticking probability is essentially unity over the range of incoming energies investigated indicating no barrier for dissociation. On the close packed (111) surface, on the other hand, the sticking probability increases with impact energy indicating a barrier for dissociation which is overcome when the energy increases. The H_2 dissociation process is in other words very *structure sensitive*.

The results of fig. 1 illustrate a generally observed trend that open faces like the (110) on fcc metals and (111) on bcc metals are more reactive for most adsorption processes than the more close packed ones.

When the Ni surface is substituted by a Cu surface the picture changes completely as shown in fig. 2. The sticking probability is much smaller on Cu than on Ni and it starts rising at considerably larger energies indicating a larger

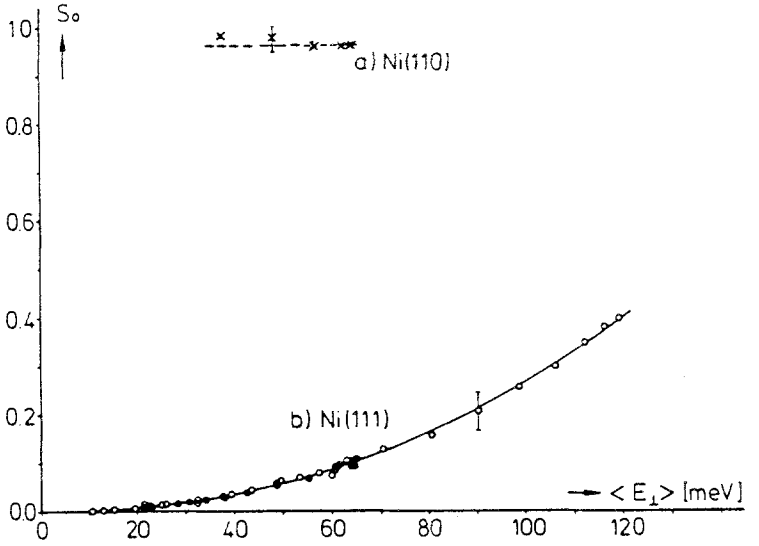

Fig. 1. The sticking probability of H_2 on Ni(110) and Ni(111) measured as a function of the kinetic energy component perpendicular to the surface of the incoming molecule. From ref. [6].

activation energy for dissociation. The figure also shows results for H_2 molecules that are vibrationally excited, and they have a considerably larger reactivity. This result indicates that it is not just a matter of having enough translational energy to surmount the energy barrier between the gas phase molecule and the dissoci-

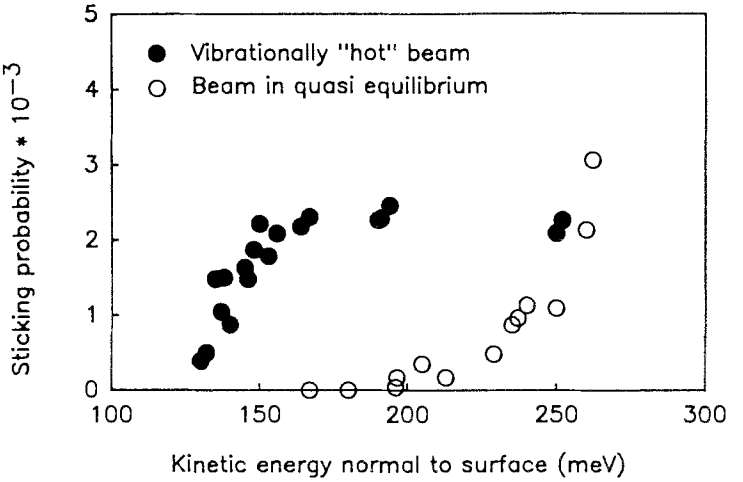

Fig. 2. The sticking probability of H_2 on Cu(110) measured as a function of the kinetic energy component perpendicular to the surface of the incoming molecule. For a beam in quasi equilibrium the translational and vibrational energy of the incoming molecules are varied simultaneously. A vibrationally 'hot' beam where the degree of vibrational excitation is kept fixed (and high) as the transitional energy is varied can be obtained by 'seeding techniques'. From ref. [7].

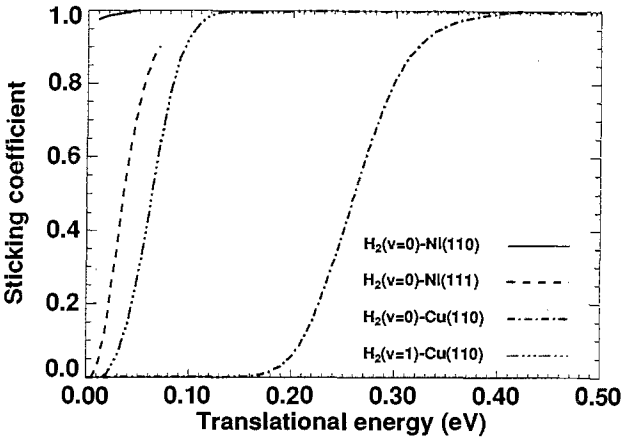

Fig. 3. The calculated sticking probability of H_2 on Ni(111) and (110) and on Cu(110) as a function of the kinetic energy component perpendicular to the surface of the incoming molecule. For the Ni surfaces only molecules in the vibrational ground state ($v = 0$) are shown, but for Cu(110) also results for $v = 1$ are included. All calculations are done in the two-dimensional potential energy cuts shown in fig. 4. From ref. [8].

ated state on the surface. It also helps if there is more energy in the relative motion of the two H atoms.

To interpret the experiments one makes computer simulations of the reaction event. The motion of the H atoms outside the surface is followed by solving the equations of motion. For heavier atoms these are just Newtons equations, but hydrogen is so light that it is necessary to solve the time dependent Schrödinger equation. The starting point is the potential energy surface, that is, the total energy of the H_2-surface system as a function of the nuclear coordinates of the two H atoms (and, in principle all the surface atom coordinates since they also move slightly during the process, but that is neglected here). To calculate this is an enormous task, and usually a simplified model is used.

Fig. 3 shows the result of a quantum simulation of the sticking process of H_2 on Ni(111) and (110) and on Cu(110). In the last case the sticking probability is calculated both for the molecule in the vibrational ground state and in the first excited state. The trends from the experimental curves in figs. 1 and 2 are seen to be well described by the simulation.

The potentials that the H_2 molecule moves in outside the different surfaces are shown in fig. 4. Here the potential energy surface is shown as a function of the distance of the molecule from the surface and the H–H distance. As anticipated, the Ni(111) potential has a small barrier for dissociation which is completely absent on the (110) face. The barrier on Cu(110) is substantially larger, and lies in the 'elbow' where both translational energy perpendicular to the surface and vibrational energy in the H–H stretch can be used to get over the barrier.

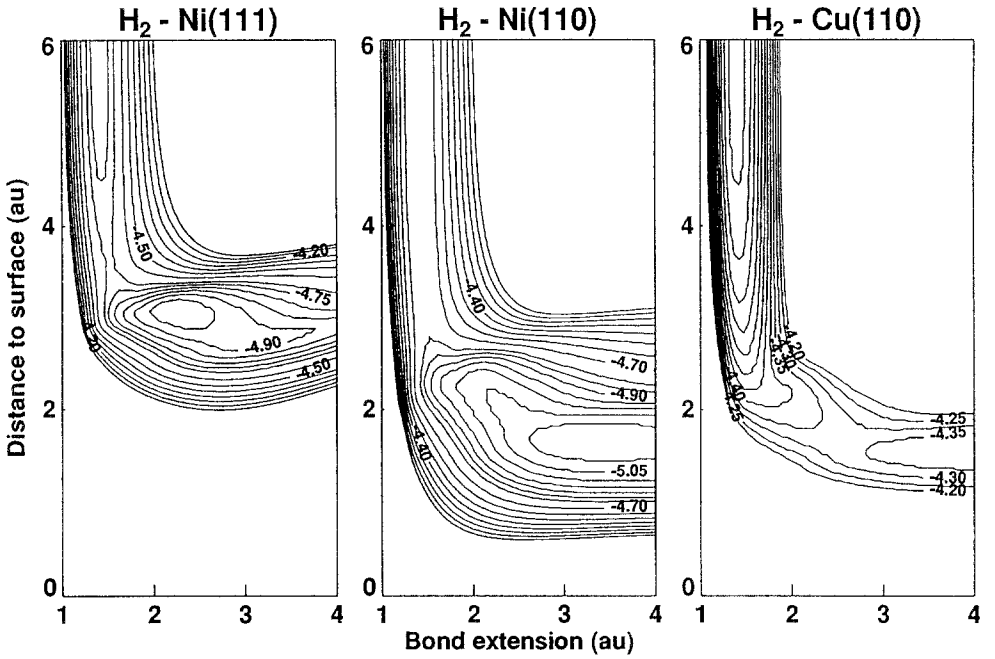

Fig. 4. Contours of constant potential energy for two H atoms outside a Ni(111), Ni(110) and Cu(110) surface calculated using the effective medium theory. The molecules approach the surface with the molecular axis parallel to the surface and over a two fold bridge site dissociating into the adjacent center sites. From ref. [8].

The model potential calculation gives a clear answer to the question why the barrier for H_2 dissociation is lower on Ni(110) than on Ni(111) and why Cu(110) is less reactive than Ni(110). The answer is that there are three main factors: the metal work function, the metal coordination number of the surface atoms, both of which contribute to the difference between different faces of the same metal, and finally the number of d-electrons, which is the main difference between Cu and Ni. In the next section we discuss the physics behind this in a little more detail. For a more thorough discussion see for instance the review in ref. [9].

3. Trends in adsorption energies and activation energies

It is generally found that the activation energy for dissociation of simple diatomic molecules decreases when going left from the noble metals in the periodic table. This can be described most simply in terms of an increased interaction between the anti-bonding adsorbate states and the metal d-states [9,10]. During the adsorption of simple diatomic molecules the anti-bonding molecular orbitals are gradually filled. For CO, for instance, the anti-bonding $2\pi^*$ states are partly filled for the chemisorbed molecule and fills even more

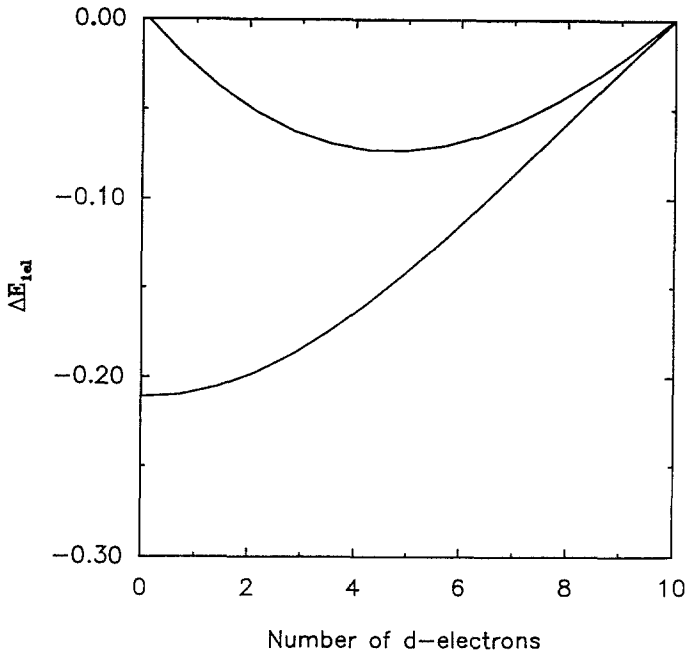

Fig. 5. A Newns-Anderson model calculation of the one-electron energy E_{1el} for an adsorbate state interacting with a d-band as a function of the d-band filling. The hopping matrix element is kept fixed and so is the d-band width. Two cases are shown. One is for an adsorbate level well below the d-band ('atomic chemisorption') and one where it is at the Fermi level ('molecular adsorption'). From ref. [10].

during the dissociation process, and a similar picture holds for the other simple gas molecules.

The transfer of electrons to the anti-bonding molecular orbitals is in general most facile when the metal work function is small. This explains why a low work function generally contributes to a small barrier for dissociation [11]. Low work functions are found for the most open surfaces. The work function can also be lowered locally by adsorbed electropositive species like alkali atoms [11].

During the electron transfer the anti-bonding molecular states must be close to the Fermi-level of the metal, and when the metal has d-states around the Fermi level, there will be a strong covalent interaction between the antibonding states and the metal d-states. Model calculations based on the Newns-Anderson model of this effect are shown in fig. 5 [10]. The interaction tends to stabilize the adsorbing molecule more for metals towards the left in the transition metal series which have fewer d electrons than ten, the largest effect being around the middle of the series where the number of d electrons is around five.

Also included in fig. 5 is a similar model calculation for the case of an atomic adsorbate. Restricting again the discussion to the simple gas atoms like H, O, C, Cl or N the main difference between the molecular case and the atomic chemiso-

rption case is that in the latter the adsorbate valence level is not at the Fermi level, but well below it, as evidenced by numerous photoemission experiments and calculations [9]. This gives rise to a different functional form of the dependence of the binding energy with the number of d-electrons. The general trend is that the binding increases as one goes to the left in the periodic table.

These model calculations have treated all the transition metals as equivalent except for the d-band occupancy. This is of cause a gross oversimplification and much more detailed calculations are needed for a detailed picture. The simple description does, however, give a physical picture of the *main trend*. Going to the finer details the interaction energy does, for instance, depend on the d-band width, even in the simple Newns-Anderson model. The main effect is that the narrower the band the stronger the interaction. This is an additional reason why, in the calculations described in the previous section, the open surfaces have lower activation energies than the more close packed ones. The surface atoms in an open surface have a lower metal coordination number and since the band width is roughly proportional to the square root of the coordination number, the band width is smaller.

We are thus beginning to have a consistent picture of the *overall trends* in the adsorbate-surface interaction energies even though many (chemically very inter-

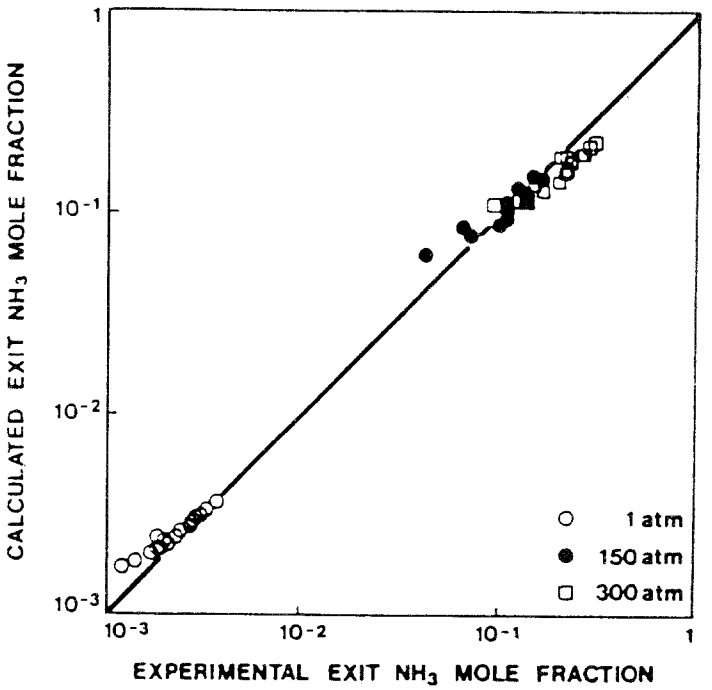

Fig. 6. Comparison of the calculated and measured ammonia production over an iron based catalyst (Topsøe KMI). The results span the entire experimentally accessible range of pressures, temperatures, gas flow, and nitrogen/hydrogen ratios. From ref. [1].

esting) details are only describable in much more sofisticated calculations. We saw in the previous section that model calculations including these (and other) effects can actually describe some of the *dynamics* of the adsorption process, indicating again that the physical picture is valid. The question then arises if this picture can be used to say something about catalytic activity.

4. The activity of the transition metals for the ammonia synthesis

As stated in the introduction the link between the microscopic description of a surface reaction and the performance of the surface as a catalyst is a micro-kinetic model. In the following we shall restrict ourselves to a system where such a model has been developed; the ammonia synthesis over iron [1].

Fig. 6 shows a comparison between the measured output from a commercial iron-based ammonia catalyst and predictions based solely on measured binding energies, sticking coefficients and vibrational frequencies of adsorbed N_2, H_2, and NH_3 on Fe single crystal surfaces with preadsorbed K to simulate the potassium promotion of the catalyst [1]. It turns out that there are two factors that control the synthesis rate. One is the N_2 sticking probability. Since the N_2 dissociation is the rate limiting step in this reaction this is not so strange. The other is the N (and to a lesser extend H) chemisorption energies. Adsorbed atomic nitrogen is the most abundant species on the surface and its binding energy therefore controls the coverage of free sites on the surface where the N_2 dissociation can take place.

We can now combine the understanding of the trends in the activation energy for dissociation and the atomic chemisorption energies with the number of d electrons, or position in the periodic table, with the micro-kinetic model to get a prediction of the variation of the catalytic activity with the number of d electrons N_d. From fig. 5 we know that the activation energy for N_2 dissociation should vary roughly parabolically with N_d and the chemisorption energies of N and H should depend linearly on N_d:

$$E_a(N_d) = E_A^0 + c_1 N_d(10 - N_d)$$

$$E_{chem}(N_d) = E_{chem}^0 + c_2 N_d. \qquad (1)$$

The four parameters E_A^0, E_{chem}^0, c_1, and c_2 can be determined from experiment. Two of them we know from the experiments on Fe ($N_d = 7$) and the others are determined from experiments on Ni and W [12].

With these assumptions we can make a prediction of the catalytic activity for the ammonia synthesis as a function of the number of d electrons. This is shown in fig. 7 together with a compilation of experimental results. Clearly activity maximum around the Fe group is thus a compromise between low sticking probability and few free sites on the surface.

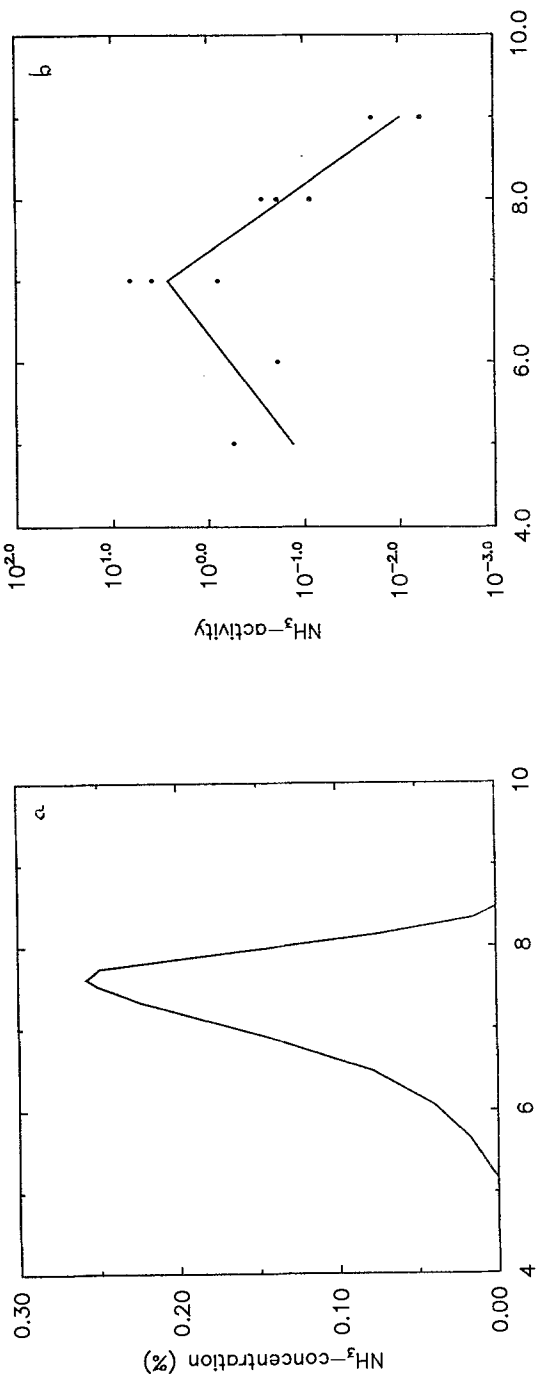

Fig. 7. Calculated (a) and measured (b) activity of an ammonia catalyst as a function of the number of d electrons. From ref. [12].

5. Concluding remarks

In this short review we have discussed the connection between the *reaction dynamics* and the macroscopic *catalytic activity* of a metal surface. We have given an example of a quite detailed understanding of the dynamics of simple reactions outside surfaces. We have also shown how general *trends* in the variation of activation energies and binding energies from one metal to the next and from one metal face to the next can be described in rather simple models. And finally we have shown how this understanding can be used to understand trends in catalytic activity among the transition metals.

A detailed atomistic description of chemical reactions outside metal surfaces is still in its infancy, but some simple notions are beginning to appear. Much more experimental and theoretical work will be needed for a more complete description of the complex phenomena that are known as heterogeneous catalysis. We have tried to illustrate how such an understanding is most likely to be achieved via a close coupling between surface science experiments, catalytic and structural measurements on real catalysts, and theoretical modeling.

Acknowledgements

Financial support from the Danish Research Councils through the *Center for Surface Reactivity* and EEC twinning grant No. ST2J-0286-C(TT) is gratefully acknowledged.

References

[1] P. Stoltze and J.K. Nørskov, Phys. Rev. Lett. 55 (1985) 2502; J. Catal. 110 (1988) 1.
[2] S.H. Oh, G.B. Fisher, J.E. Carpenter and D.W. Goodman, J. Catal. 100 (1986) 360.
[3] J.A. Dumesic and A.A. Trivino, J. Catal. 116 (1989) 119.
[4] B. Hellsing, B. Kasemo, S. Ljungström, A. Rosen and T. Wahnström, Surf. Sci. 189/190 (1987) 851.
[5] J.K. Nørskov and P. Stoltze, Surf. Sci. 189/190 (1987) 91.
[6] H.J. Robota, W. Vielhaber, M.C. Lin, J. Segner and G. Ertl, Surf. Sci. 155 (1985) 101.
[7] B.E. Hayden and C.A. Lamont, Phys. Rev. Lett. 63 (1989) 1823.
[8] U. Nielsen and J.K. Nørskov, to be published.
[9] J.K. Nørskov, Rep. Prog. Phys. 53 (1990) 1253.
[10] S. Holloway, B.I. Lundqvist and J.K. Nørskov, *Proc. Int. Congress on Catalysis*, Berlin 1984, Vol. 4, p. 85.
[11] J.K. Nørskov, S. Holloway and N.D. Lang, Surf. Sci. 137 (1984) 65; ibid. 150 (1985) 24.
[12] J.K. Nørskov and P. Stoltze, Surf. Sci. 189/190 (1987) 91.