THE REACTIVITY OF METAL SURFACES

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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.
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 \( \text{H}_2 \) 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 \( \text{H}_2 \) dissociation process

Fig. 1 shows the sticking probability for \( \text{H}_2 \) 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 \( \text{H}_2 \) 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