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STRUCTURE AND FUNCTION AT CATALYST SURFACES

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New advances in theory and experiment have greatly increased our ability to study structure at surfaces. Not only can complex ordered structures of adsorbates be determined, but we can bring the same high precision techniques to disordered systems, and the methodology is available to find probability distributions of atoms, and hence dynamics of anharmonic vibrations and of diffusion. These advances are reminiscent of the contribution that protein crystallography has made to our understanding of complex biological systems, and of the impact that has had on the design of drugs by computer. Design of heterogeneous catalysts by computer remains a long term goal, but surface studies are on the move in that direction.

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Electronic structure dominated early theories of heterogeneous catalysis for some years. In the 1960's theorists spoke in terms of surface states and their interpretation as dangling bonds ready to bind any passing atom or molecule. In the 1970's Nørskov and co-workers introduced some radical new ideas: surface states were now only one ingredient in the surface picture and what mattered was the total electron density at the surface. To first order this theory said that if a surface site has the right density to suit a particular atom, then that is where the atom would attach itself. Certainly the surface state concept, although very relevant to covalent materials, seems to have had limited impact on bonding at transition metal surfaces. The new density-based ideas went a long way to explaining some gross properties of surface bonding.

As these electronic concepts were being developed, other studies, joint theory and experiment, were slowly building a picture of the crystallography of surfaces. During the 1980's surface crystallography came of age as a discipline and now enough is known to give a more sophisticated picture of bonding at surfaces. The old view, of the substrate as a passive template whose role is confined to providing some electrons for binding purposes, is being replaced by a more subtle picture. Numerous experimental studies, particularly in the Somorjai group, have exploited theoretical advances to show that adsorption at surfaces nearly always results in some reconstruction of the substrate [1]. Transition metals are certainly not passive spectators of the catalytic process: as the adsorbate configuration changes, the underlying atoms move to accommodate. Often many atoms are involved in the reconstruction and, although there have been very few total energy calculations on these complex systems, it can safely be assumed that these reconstructions play a vital role in deciding whether a given configuration is stable, and thus control the outcome of the reaction. Just as we expect a metal to screen *electronic* disturbances at a surface, so it would seem that there are *mechanical* screening processes at work, screening the stresses created by bond rearrangements in adsorbed species.

Now in the 1990's even more powerful methodologies are emerging in surface crystallography that will enable us to go beyond studies of static configurations at surfaces, and examine the dynamics of atoms migrating across the surface, and of molecules on the point of fragmenting.

To put the issue bluntly: what matters in heterogeneous catalysis,

where the electrons are?
or, where the atoms are?

Of course, both questions are relevant, and trying to answer the first question has shed much light on catalytic processes. However, now is the time for the balance to tip towards structural studies. With the availability of reliable structures for many catalysts we have the tools to hand. We can draw an analogy with the design of drugs where,

structure a dynamics are crucial to the function of drugs.
If we know the structure from protein crystallography we can calculate the dynamics and determine the function.
Drugs can be designed by computers, catalysts cannot.
Is there something missing from our picture of catalysis at surfaces?

Biochemical reactions are controlled by *steric phenomena* described by simple force fields which are within the reach of current computer power. The problem in heterogeneous catalysis is that the reactions involve the breaking of strong bonds and computers struggle to handle the complex quantum mechanical calculations. However there is a class of reactions, in zeolites, where the outcome is determined by simple steric considerations of access to the reaction site. The reaction itself is complex but largely irrelevant: if it produces the wrong molecules they will not get out and are sent back to try again. By concentrating on structural aspects, theorists have made valuable progress in predicting the course of reactions in zeolites. This understanding of reactions was preceded by a systematic attack on the structure of proteins in the one case, and on zeolites in the other. This structural work attracted some of the best brains in their subjects and has proved to be the backbone of subsequent exploitation.

I believe that there is a message here for catalysis at surfaces: it is time for a concentrated blitz on the crystallography of surfaces with a view to extracting unifying concepts in the field of catalysis.

In this paper I shall tell about the new techniques available for surface structure determination, present some of the new results that they have achieved, and discuss prospects for the future.

One concept that has stimulated many new ideas is diffuse low energy electron diffraction, or DLEED [2]. The main work horse of surface crystallography is LEED, but to bring this technique to bear the surface has to be in a well ordered state so that data are well characterised and the established theory can get to work and interpret them to give the structure. Experimentalists labour long and hard to get a sharp diffraction pattern on there screens, free of the tell tale diffuse scattering which reveals disorder on the surface. But some structures refuse to order, and certainly under reaction conditions we can hardly expect anything like perfect order to exist. Is this not rather dangerous if we are trying to establish the point that structure matters? Fortunately it has been realised that we can study crystallography on disordered surfaces, provided that the disorder is of a special kind: if each adsorbed molecule has the same local chemical environment, but is lacking in any long range correlation with other molecules on the surface, then we should see a diffuse diffraction pattern, but one which we can easily interpret to find the local environment. The theoretical concepts behind this idea have been confirmed in many instances now, and in fig. 1 we see the first structure resulting from interpretation of DLEED data [2]. It consists of oxygen randomly adsorbed on the tungsten (100) surface at low temperatures and reveals some of the features we discussed above. Note that the surrounding tungsten atoms are drawn in towards the oxygen. Two influences are at work here: bonding to oxygen, and bonding between the tungsten atoms themselves. The (100) surface of a body centred material is a very open one with no in-surface bonds. The reconstruction provides two metal-metal bonds for every tungsten, as well as a metal-oxygen bond. Imagine how dramatically this W_4O unit can be expected to affect the binding energy, not to mention migration of oxygen across the surface, and its accessibility to reaction.

Surfaces have a unique flexibility to rearrange, and to allow atoms to diffuse across them. In the bulk atoms are heavily confined by the geometry. Any weakening of bonds is generally followed by breakdown of the structure and melting or evaporation. At the surface, the integrity of the bulk and of the surface can be preserved whilst the more open geometry allows reconstruction, diffusion, and rearrangements in directions parallel to the surface. It is precisely these properties which we exploit in catalytic reactions, and the study of these properties is the objective of the next phase of surface crystallography.

The realisation that DLEED experiments could be interpreted opened some new possibilities in surface structural studies. Now that surfaces with some degree of disorder can be studied, we have realised that our concept of "determining the structure" must be broadened. In the past this has been implicitly defined as finding where on average the centres of the atoms were. In a disordered surface there is much more information available: we must instead seek the *probability*

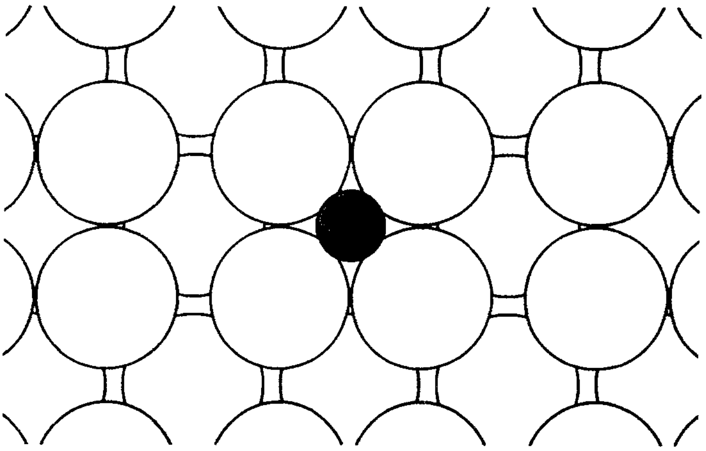

Fig. 1. The structure of oxygen adsorbed on a tungsten (100) surface, as determined by DLEED. Note the distortion of the first layer of tungsten atoms as the oxygen draws in the four neighbouring tungstens.

distribution of the adsorbed atoms. How $P(\boldsymbol{R})$ could be found in practice was first outlined in a paper by Klaus Heinz and myself [3] and applied to a simple structure: $P(2\times 2)$O/(Rh(100). Access to $P(\boldsymbol{R})$ is very exciting because it moves the whole subject forwards into a study of *dynamics* rather than of simply the static location of atoms. How does it do this? If we assume that the atoms at the surface are in thermodynamic equilibrium, then the probability distribution is

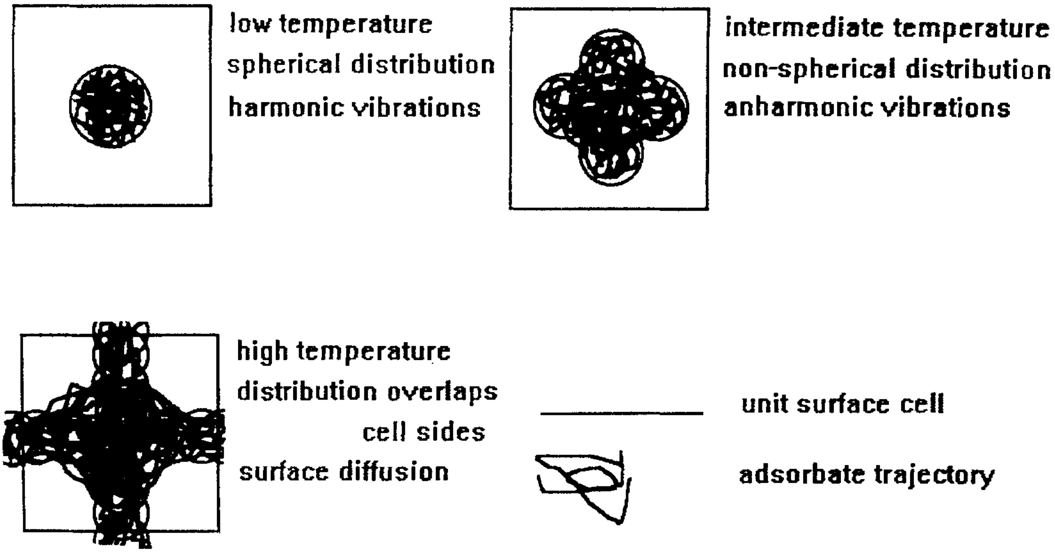

Fig. 2. Diffusion of an adsorbed atom around the unit cell of a surface. Note how the motion can be expected to change in character as the amplitude increases, first becoming anharmonic, and then diffusive, as the atom breaks loose from its site.

determined by the potential energy field in which atoms move as they migrate across the surface,

$$P(\boldsymbol{R}) = \text{constant} \exp(-V(\boldsymbol{R})/k_B T).$$

If we can find $V(\boldsymbol{R})$, then a relatively simple computer simulation will reveal the dynamics of diffusion at the surface.

Of course we do have available powerful techniques for study of vibrations at surfaces, but these are largely concerned with the high frequency vibrations about strong bonds. These are harmonic vibrations and characterise those bonds which retain their integrity during a reaction. In contrast diffraction studies will be most sensitive to those motions with the largest amplitude: bonds that are about to break, anharmonic motion, and diffusion across the surface. These are areas that are currently virtually untouched in surface studies. Fig. 2 shows an instance of what we might see as a surface warms up. At very low temperatures an adsorbed atom will execute harmonic vibrations about the bonding site. The probability distribution will be Gaussian, and its effect on diffraction accounted for by Debye-Waller theory. At higher temperature anharmonic terms will become important and the probability distribution becomes more interesting as it explores details of the potential energy surface. At higher temperatures still the adsorbate atom breaks loose from the original adsorption site and migrates across the surface. Even though migration is clearly a crucial step in catalysis, we have very few techniques that can study it. Certainly no one is able to say by what route an adsorbed atom diffuses across a surface. This state of ignorance is rather like trying to figure out how a zeolite catalyst works without knowing the channels available to reacting atoms.

One of the more imaginative developments is the possible interpretation of diffuse LEED experiments as holograms of the surface suggested by Saldin and de Andres [4]. Fig. 3 shows the diffraction process in the neighbourhood of an adsorbed atom and reveals that the atom plays the role of the beam-splitter in an holography experiment: electrons can either scatter directly from the adsorbate to the screen, or they can first scatter off the surface. Interference between these

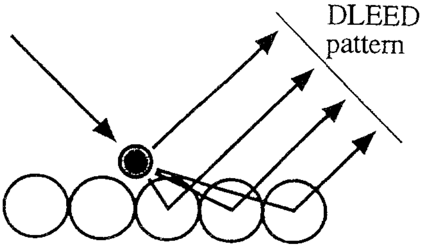

Fig. 3. A randomly adsorbed atom scatters incident electrons to all points of the screen, but some of the electrons collide with the surface before arriving at the screen. The adsorbed atom is behaving like a beam-splitter in a holography experiment, and we can think of the diffuse low energy electron diffraction pattern as an electron hologram of the surface.

processes generates the hologram. Others have made similar suggestions based on photoemission [5]. Unfortunately there are other processes which may spoil this simple picture, but in principle the DLEED pattern contains holographic information and impressive strides are being made in extracting that information.

Surface studies are poised ready to enter a new phase of studies which have the potential to change the way we think about heterogeneous catalysis. If we are lucky, a rigorous study of the structural and vibrational aspects of surfaces will bring benefits comparable with those brought by protein crystallography to the field of drug design. At the very least we can expect a fascinating period during which surface studies make rapid advances.

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