

# The Bonding of Adsorbed Species at Catalyst Surfaces

## APPLICATION OF MOLECULAR ORBITAL THEORY

By G. C. Bond, D.Sc., F.R.I.C.

Research Laboratories, Johnson Matthey & Co Limited

*The nature of the bonds between catalyst surfaces and the adsorbed intermediates formed during catalytic reactions is still a matter for discussion. A recent symposium organised by the American Chemical Society was devoted to this subject, as well as a General Discussion of the Faraday Society held in Liverpool in April. Although many new techniques have become available and have been exploited during the past decade, they have only served to reveal a multiplicity of adsorbed states whose relevance to catalysis is uncertain, and there has been no corresponding advance in basic theory. The purpose of this article is to present a sketch of a possible new approach to the bonding of adsorbed species on metal surfaces.*

The catalytic properties of metals should be regarded as only one of the physical and chemical properties of metals requiring theoretical interpretation. The difficulties encountered in developing a satisfactory theory of the metallic state are well known. Two extreme types of theory have been proposed: in the Electron Band or Collective Electron Theory, electrons are assumed to be delocalised over the whole metallic crystal, but at least in its simplest form this theory cannot account for the regular variation in crystal structure across the Transition Series. The Valence Bond

Theory, in which the cohesive properties of metals are described in terms of localised bonds between atoms, has been extended to describe this phenomenon (1). Both theories have been of some assistance in accounting for catalytic properties, but both have their limitations. It is therefore worth examining whether the description of metallic behaviour in terms of molecular orbitals is fruitful when applied to surface phenomena.

It is worth emphasising that this new approach, due especially to Goodenough (2), is not a completely new theory (3) but rather an attempt to unify the two theories mentioned above in one satisfying picture which is in accord with the latest thinking in solid state physics. It uses the language of molecular orbital theory: it is best described in relation to the face-centred cubic metals to which family belong most of the metals of catalytic interest.

In these metals each atom is in contact with twelve others, four in each of three planes mutually at right angles, while six

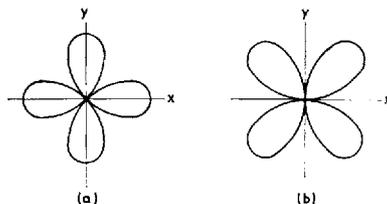
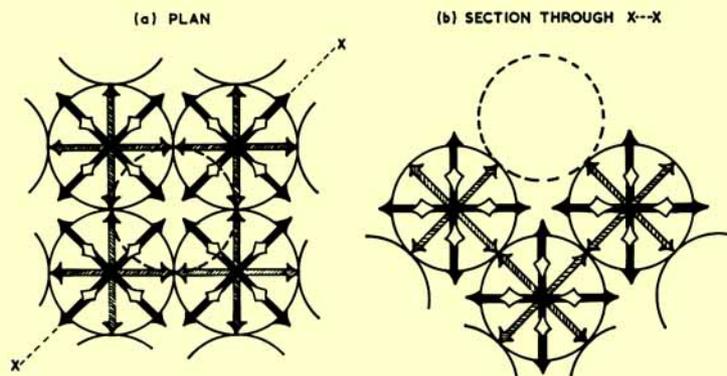


Fig. 1 Representation of (a) the  $d_{x^2-y^2}$  orbital and of (b) the  $d_{xy}$  orbital, examples respectively of the  $e_g$  and  $t_{2g}$  families of orbitals in an octahedral complex

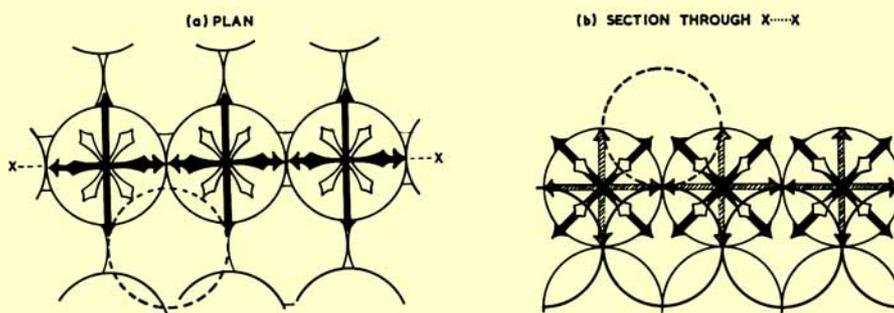


**Fig. 2** The emergence of orbitals from the (100) face of a face-centred cubic metal : (a) plan; (b) section

Filled arrows :  $e_g$  orbitals in plane of paper  
 Hatched arrows :  $t_{2g}$  orbitals in plane of paper  
 Open arrows :  $t_{2g}$  orbitals at  $45^\circ$  to plane of paper

others octahedrally disposed lie at a slightly greater distance. Now according to the Crystal Field Theory the five  $d$ -orbitals are split in an octahedral environment into two groups. The two higher energy orbitals are taken to lie along the Cartesian axes (Fig. 1a) and are designated  $d_{x^2 - y^2}$  and  $d_{z^2}$ , or collectively in the language of group theory as  $e_g$ . The three lower energy orbitals then lie between the Cartesian axes (Fig. 1b) and so are designated  $d_{xy}$ ,  $d_{yz}$  and  $d_{zx}$  or collectively

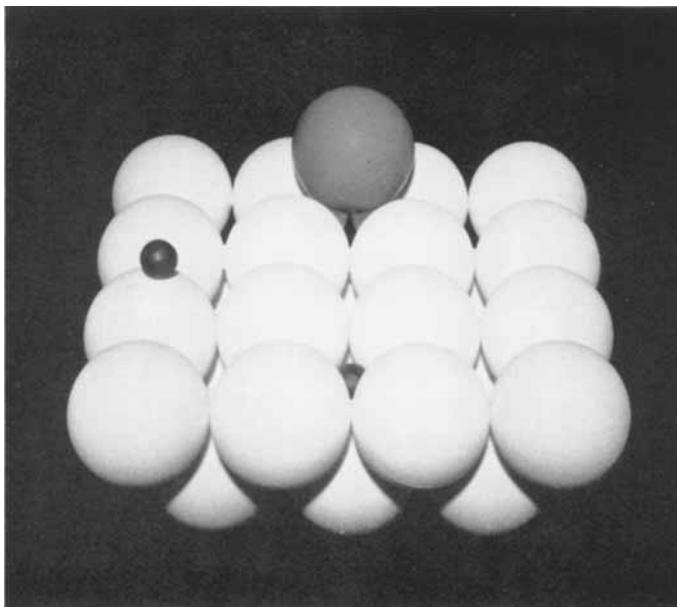
as  $t_{2g}$ . As each of these orbitals has four lobes, it is reasonable to say that the twelve near neighbours in the face-centred cubic crystal are bonded to the central atom by  $t_{2g}$  orbitals which overlap to form a broad collective  $t_{2g}$  band, while the six next nearest neighbours are bonded by  $e_g$  orbitals. In fact, however, these latter orbitals do not overlap significantly because the next nearest neighbours are too far apart, so that electrons in the  $e_g$  orbitals occupy localised states around each atom.



**Fig. 3** The emergence of orbitals from the (110) face of a face-centred cubic metal : (a) plan; (b) section

Filled arrows :  $e_g$  orbitals in plane of paper or emerging at  $45^\circ$   
 Hatched arrows :  $t_{2g}$  orbitals in plane of paper  
 Open arrows :  $t_{2g}$  orbitals at  $30^\circ$  to plane of paper

Fig. 4 Model of the (100) face, showing one metal atom in the next layer, and two locations for hydrogen atoms



It is now an easy matter to evaluate the manner in which the two groups of orbitals emerge from the three low index planes. This is illustrated in Figs. 2 and 3 for the (100) and (110) planes respectively. The former consists of a square array of atoms (Fig. 2a): the non-bonding  $e_g$  orbitals in the plane of the surface are shown in black while the bonding  $t_{2g}$  orbitals are hatched. Furthermore, there are four  $t_{2g}$  orbitals emerging from each atom at  $45^\circ$  to the plane of the surface, and these are shown in white: one of these from each of four atoms is directed towards the position occupied by an atom in the next layer (broken circle: see also Fig. 4). Fig. 2b shows a section normal to the surface.

Fig. 3a shows the plan of the (110) plane: this consists of parallel rows of next nearest neighbours bonded as usual by shaded  $t_{2g}$  orbitals. Other  $t_{2g}$  orbitals emerge, four from each atom (shown in white) at  $30^\circ$  to the plane of the surface and are directed towards the sites of atoms in the next layer, again indicated by a broken circle (see also Fig. 5). Fig 3b shows a section normal to the surface: this plane differs from the (100) in that it is a  $t_{2g}$  orbital which emerges normal to the surface from each atom.

Having obtained the direction of emergence of the  $t_{2g}$  and  $e_g$  orbitals from the low index planes of the crystal, it is now necessary to try to decide on the extent to which they are occupied by electrons. If we confine our consideration to Group VIII<sub>3</sub> (nickel, palladium and platinum), we find, following Goodenough (2), that the 0.55  $d$ -band holes are distributed between the two bands as follows:  $t_{2g}$  band, 0.41 holes:  $e_g$  band, 0.14 holes. Both bands are therefore substantially filled, and we will suppose that both can participate in forming covalent bonds with adsorbed species.

For the purpose of this article we consider only the new light which this approach throws on the location of adsorbed hydrogen atoms. Fig. 4 shows two possible locations for these atoms on the (100) plane. The atom in the centre foreground is deeply imbedded in the surface: it is bonded by overlap of its spherical 1s orbital with four  $e_g$  orbitals from the surrounding metal atoms and by a further  $e_g$  orbital from the metal atom below it. This must therefore be quite a strongly bound state. The atom on the left is bonded only by this latter  $e_g$  orbital and is likely to be much more weakly bound.

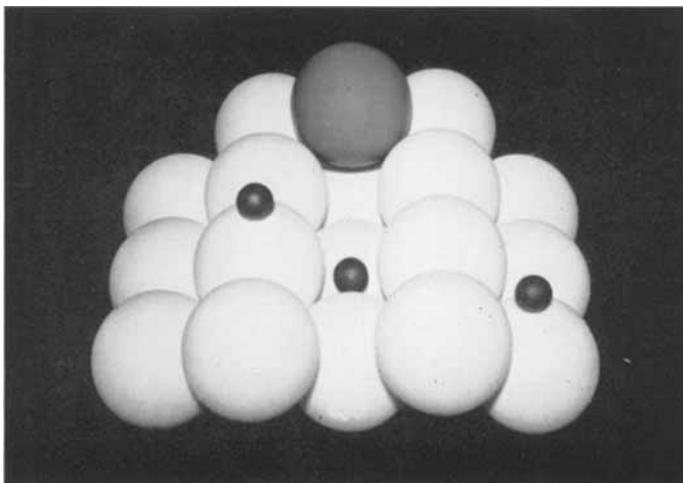


Fig. 5 Model of the (110) face, showing one metal atom in the next layer, and three locations for hydrogen atoms

Fig. 5 shows three locations for hydrogen atoms on the (110) plane. The atoms on the left and right are bonded simply by the normal-emergent  $t_{2g}$  orbitals: the one on the right is, however, bonded to a metal atom in a layer one below the surface, but both should be weak states of binding. The position of the atom in the centre is more complicated: it is bonded by two  $t_{2g}$  orbitals emerging from the atoms below it and by two  $e_g$  orbitals emerging from the atoms below it and by two  $e_g$  orbitals from the atoms on either side of it. This should therefore be a strongly bound state.

Space does not permit the elaboration of these ideas to the adsorption of other atoms and molecules. The same basic concept can also be applied to metals crystallising in other habits, but this development has not yet been fully exploited.

#### References

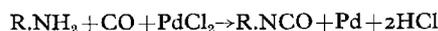
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- 2 J. B. Goodenough, *Magnetism and the Chemical Bond*, (Interscience, New York, 1963)
- 3 D. A. Dowden, in *Coloquio sobre Química Física de Processos en Superficies Sólidas*, (Liberia Científica Medinaceli, Madrid, 1965), p. 177

## Isocyanate Preparation with Palladium Chloride

The manufacture of numerous plastics and synthetic surface coatings involves the production on a large scale of several important isocyanates. These are generally produced by treating a primary amine or its salt with phosgene, resulting in the intermediate formation of a carbonyl chloride from which HCl is eliminated to yield the isocyanate.

Research carried out by E. W. Stern and M. L. Spector of the M. W. Kellogg Company, New Market, New Jersey (*J. Org. Chem.*, 1966, **31**, (2), 596), has yielded a new route to isocyanates that is unusual in that it employs palladium chloride as a reactant. In this method, the primary aliphatic or aromatic amine reacts with carbon monoxide in the presence of palladium

chloride at, or very slightly above, atmospheric pressure and in the temperature range 65 to 85°C, yielding the isocyanate while the salt is reduced to metallic palladium:



A detailed mechanism of the reaction has not yet been worked out; the *in situ* formation of phosgene from  $PdCl_2$  and the carbon monoxide, however, has been ruled out, since no reduction of the salt to metal occurs in the absence of the amine. It seems possible that both the amine and the carbon monoxide combine with the palladium chloride to form a complex that leads to isocyanate formation on decomposition.

H. C.