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Notes

Molecular Orbital Study of Formate Chemisorption on a Pt(111) Surface

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A molecular orbital study, using atom superposition electron delocalization (ASED) technique, has been made of the structures and energy levels of formate species on a clean Pt(111) surface. Formate species is predicted to be preferentially adsorbed at a bridge position in a highly symmetric C_{2v} configuration with its two-fold axis perpendicular to the image plane of the Pt(111) surface. This is in good agreement with the recent high resolution electron-energy loss spectroscopic studies of Avery [*Appl Surf Sci*, **11/12** (1982) 774]. The two oxygen atoms are predicted to be symmetrically placed above a bridge position at a height of 1.81 Å.

The decomposition of formic acid over many catalytic surfaces has drawn considerable attention in recent years. Many workers have studied the chemisorption and decomposition of HCOOH on Ni(110)[1,2], W(001)[3], Cu(001)[4], Ag(110)[5], Pt(110)[6] and Pt(111)[7] surfaces. Recently Avery[8] has shown that the chemisorbed species on Pt(111) surface is the formate. In our laboratory, we have started a theoretical study of the electronic structure of chemisorbed formate species on various metal surfaces and in this note we report the results of our study for HCOO/Pt(111) system.

We have used atom superposition electron delocalisation technique (ASED), which combines one-electron orbital energies with atom-atom repulsion energies[9]. Here the total energy consists of two parts. The binding part due to electron delocalization is given by the extended Hückel one-electron energy, and the atom superposition part is a sum of repulsive interatomic interactions. Although this method is not sophisticated as compared to other quantum mechanical methods (i.e. X_α and ab-initio), it is useful in predicting trends and general conclusions; precise energy values are not obtainable by this method. The method has been found useful for determining structures, binding energies and electronic energy levels for numerous transition metal complexes and surface systems, including studies of structures and reaction of water[10], carbon monoxide[11-13] and acetylene[14] on Pt(111) surface.

A Pt_4 model (see Fig. 1) of Pt(111) surface is used in the present study. This cluster is bulk superimposable and has four unpaired electrons[11-13] at the top of the *d*-band. Theory parameters are given in Table 1. Geometry optimization have been carried out by keeping the cluster distance (Pt-Pt) and geometry of HCOO fixed at experimental distances.

Calculations are made for both horizontal and vertical orientations (Fig. 1) of HCOO over Pt(111)

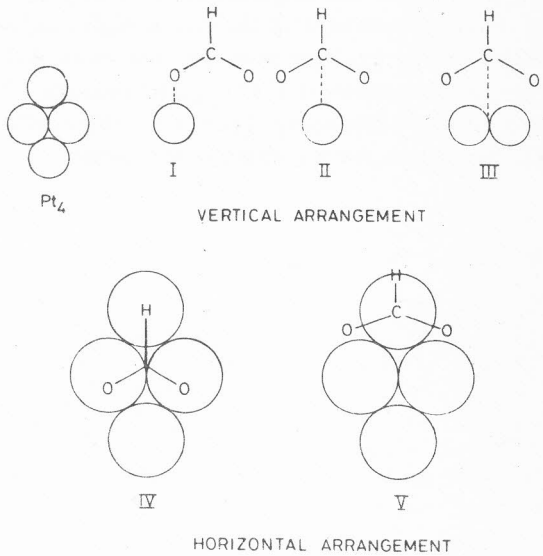

Table 1—Principal Quantum Number, Ionization Potential, Orbital Exponents and Respective Coefficients (*d* only) Used in Present Study

[For all adsorption studies Pt ionization potentials are increased 1.5 eV, H, C and O ionization potentials are decreased by 1.5 eV and O and H exponents are decreased by 0.1; all to mimic self-consistency (see ref. 11)]

Atom	*s*			*p*			*d*
Pt	6	9.0	2.55	6	4.96	2.25	5 9.6, 2.39, 6.013, 0.5715, 0.6567
H	1	13.6	1.30				
C	2	20.00	1.658	2	11.26	1.618	
O	2	28.48	2.246	2	13.62	2.227	

Table 2—Formate Chemisorption on Pt(111) Surfaces: Optimized Distances and Corresponding Energies of the System

Structure (Fig. 1)	Distance (Å)	Energy (eV)
(Vertical approach)		
(I)	Pt – O = 1.83	– 738.33
(II)	Pt – C = 2.41	– 737.38
(III)	Pt(111) plane to C distance = 2.38	– 738.95
(Horizontal approach)		
(IV)	Pt(111) plane to C distance = 2.00	– 736.73
(V)	Pt – C = 3.10	– 736.93

surface. The vertical (I, II, III) arrangements are all the time predicted to be more stable than the horizontal ones (IV, V). In coordination chemistry, three types of carboxylate ligands have been recognised[15], i.e. monodentate (I), bidentate (II) and bridged (III) (Fig. 1). Energy minimizations for all three vertical configurations have been made and results of these calculations are summarised in Table 2. It can be seen that HCOO is predicted to be preferentially adsorbed at a bridge position (configuration III). This prediction is in good agreement with the recent high resolution electron energy loss spectroscopic studies of Avery[8].

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