

THEORETICAL STUDY OF THE ADSORPTION OF CO MOLECULES
ON STEPPED SINGLE CRYSTAL PT SURFACES

(Preliminary communication)

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(Received November 20, 1990)

BY EMPLOYING THE SEMIEMPIRICAL QUANTUM CHEMICAL ASEd-MO METHOD, ADSORPTION OF CARBON MONOXIDE MOLECULES ON STEPPED PT SURFACES BASED ON (111) TERRACES OF FCC (775), (755) AND (533) STRUCTURES HAS BEEN INVESTIGATED AND, ON BASIS OF THE CALCULATED ELECTRONIC DATA, FAVOURABLE SITES OF ADSORPTION HAVE BEEN PREDICTED.

To understand the elementary steps of heterogeneous catalysis it is important to investigate the chemisorption of small molecules on single crystal surfaces of metals. Theoretical studies promote such investigations and support the explanations of experimental observations. The adsorption of carbon monoxide on a Pt surface is one of the best model both for experimental [1-5] and theoretical [6-10] examinations. Most of the studies are concerned with smooth surfaces, and only a limited number of theoretical works has been dealing with surfaces having terraces, steps, kinks, *etc.* on them. By the present paper, our aim is to calculate the electronic properties of carbon monoxide molecules chemisorbed on stepped Pt(111) surfaces so being able to predict the most favourable adsorption sites and orientations for CO molecules. Another aim

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of our work is to determine the minimum size of the substrate-adsorbate system and especially that of the metal cluster which should be used for such model calculations.

Three relatively simple types of stepped surfaces, based on (111) terraces, have been chosen. One of them has step faces of (111) orientation, as with fcc(775), and the other two have step faces of (100) orientation, as with fcc(755) and fcc(533). The bulk cubic Pt lattice parameter of 392.39 pm (nearest-neighbour distance of 277.46 pm) has been used [11] in all the electronic structure calculations by employing the atom superposition and electron delocalization (ASED-MO) method [12] with its modified parameter sets [13]. One-fold top-site positions have been assumed for the CO molecules, preferentially chemisorbed with a constant Pt-C bond length of 198 pm from the surface (carbon end down), with a frozen C-O distance of 115 pm, being based on a structure determination by LEED of CO on Pt(111) [14]. The geometries of the system composed of the substrate and the adsorption overlayer were determined by the computer program PSD [15]. Predictions based on electronic properties could be compared and checked with experimental data available so far only for the orientation of CO molecules on stepped Pt(533) surface, obtained by a NEXAFS study [16]. However, it should be mentioned that the surface structures and so the electronic structures of fcc(533) and fcc(755) are similar therefore it is expected that the corresponding experimental observations would be nearly the same for fcc(755).

By the program PSD, first a metal cluster was separated from the appropriate crystal lattice having the characteristic features: terraces and steps. The size of the cluster was chosen so that it could easily be handled by the ASED-MO method, not consuming too much computing time. In the starting computations a maximum of 45 Pt atoms in three layers (beneath each other) and 6 CO molecules in predetermined arrays were included. Then the numbers of Pt atoms and CO molecules were reduced

systematically to the point when relative values of electronic properties (net charges, overlap populations, sum of one-electron energies, *etc.*), and trends in them, began to change substantially. The determination of the smallest possible cluster size to be used in the calculations, employing the same model, allows us the later use of more sophisticated quantum chemical (*e.g.* "ab initio") methods. When doing calculations on any of the three stepped surfaces it was found [17] that a cluster composed of 15 Pt atoms (three Pt atoms in rows) placed in one layer and 3 CO molecules on top of the Pt atoms in a row supplied the same overall electronic picture (relative values and trends) as the much larger system. Therefore the detailed calculations were carried out with the reduced size metal cluster having the characteristic features of the fcc(775), fcc(755) and fcc(533) structures, respectively. The 3 CO molecules with collinear Pt-C-O axis were placed on one row of Pt atoms parallel to the step edges in different specified positions (on terrace atoms, or at the outside and inside step sites, respectively), and the differences in total electronic energies (the sums of one-electron energies) of the whole substrate-adsorbate system and that of the metal cluster and the 3 COs separately were considered and compared. The dependence of the electronic data on the tilting angle of the CO molecules (the collinear Pt-C-O axis) to the terrace normal has also been investigated, by gradually tilting the CO molecules by the same polar angle at zero azimuth (parallel and zig-zag or fish-bone tilting regarded).

It has been found [17] that layers lying deeper beneath the top layer Pt atoms do not modify significantly the overall electronic picture of the system in any of the three stepped structures, at the approximation level used. In other cases —*e.g.* when calculating fcc(110) crystal lattice [10]— even the presence of third layer atoms in addi-

tion to the top layer ones are quite important for the CO orientation. CO bonding to the surfaces is predominantly a result of 5σ stabilization due to mixing with the metal orbitals having s and d character and back-donation to the CO π^* orbitals from the metal d -orbitals. Our calculations give the orientation of adsorbed CO at both step and terrace sites on stepped Pt(533) surface in accordance with the experimental study of SOMERS et al. [16]. The angular dependence of both the 2π intensity and the $\sigma/2\pi$ intensity ratio indicates that the terrace CO is bonded essentially normal to the terrace and that the step CO is tilted away by only a few degrees towards the macroscopic surface normal. A dramatically large angle of tilt for CO on step/kink sites as observed in the system CO/Pt(321) [18] was not found. The energy of the σ -resonance is identical for both step and terrace CO indicating that there is little change in the C-O overlap population (bond order) even though temperature programmed desorption shows that the step species is more strongly bonded by ~ 20 kJ mol⁻¹ (~ 0.2 eV molecule⁻¹) than terrace COs. This means that the carbon-to-metal bond strength is ~ 20 kJ mol⁻¹ higher for CO adsorbed at the steps than at terrace sites.

The lowest total energies in any of the three stepped substrate-adsorbate systems investigated are related always with COs in "outside" step (i.e. step-edge) positions, at any angles. In "inside" step (step-bottom) positions a tilting angle of 45 degree (off the step) is favoured. Almost exactly the same energies have been found in positions at the ends of the metal cluster. The terrace COs are bonded essentially normal to the terrace. Except "outside" and "inside" step sites the energies are at maximum when the tilting angle is nearly 30°. The lowest energies can always be attributed to the fish-bone (zig-zag) tilting of COs, in any location of them, on the surface. At tilting angles between 60-70 degrees the energy of the system has been found to be almost exactly the same whatever are the positions of COs and it approached the minimum.

When the three CO molecules have been placed at random on the surface the total energy is always larger than at row positions. In accordance with those discussed above, in view of heterogeneous catalysis the adsorption sites on step edges (at any angles) and any sites on terraces of the structures examined (at tilting angles 60–70° to the terrace normal) are favoured and preferred to other sites and angles.

Geometry data, numerical results and details of the calculations are available on request.

Acknowledgement

Thanks are due to Prof. M. A. Van Hove (Berkeley, USA) for suggesting the problem and to Prof. A. B. Anderson (Cleveland, USA) for his advice concerning the parameterization and lending and permitting the use of his program ASED-MO. The support of this work is acknowledged to the Hungarian Academy of Sciences (OTKA Grant No. 393/1988).

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