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A density functional theory study of the reaction of C+O, C+N, and C+H on close packed metal surfaces

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Density functional theory (DFT) has been used to determine reaction pathways for several reactions taking place on Pt(111) and Cu(111) surfaces. On Pt(111), the reactions of C+O and C+N were studied, and on Cu(111) we investigated the reaction of C+H. The structures of the transition states accessed in each reaction are similar. An equivalent distance separates the reactants with the first located at a three-fold hollow site and the second close to a bridge site. Previous DFT studies have, in fact, often identified transition states of this type and in every case it is the reactant with the weaker chemisorption energy that is located close to the bridge site. An explanation as to why this is so is provided. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1352731]

An understanding of the detailed microscopic mechanisms of chemical reactions is fundamental and yet elusive. Reactions that occur at the gas–solid interface are especially important since these form the basis of the heterogeneous catalysis industry.[1–3] Therefore, to understand catalytic reactions, in particular reaction pathways, is one of the ultimate goals of chemistry. In this paper we report microscopic reaction pathways determined using density functional theory (DFT) for certain catalytic reactions taking place on Pt(111) and Cu(111) surfaces. Insight into the pathways of the specific reactions studied is provided.

Recently on Pt(111) we performed a systematic study of nine different hydrogenation reaction pathways.[4] All the elementary steps in the hydrogenation of carbon to methane, nitrogen to ammonia and oxygen to water were investigated. We found that the pathways followed in each reaction depended upon the valency of the reactants involved. This relationship is best observed by a consideration of the transition states of each reaction. As the valency of a reactant decreases, so too does the coordination number of the site at which the transition state is located: Monovalent adsorbates (for example, CH_3, NH_2, and OH) tend to make transition states close to top sites; divalent adsorbates (CH_2, NH, and O) near bridge sites; and tri and tetra-valent adsorbates (CH, N, and C) near three-fold hollow sites. The reactions reported, however, were all hydrogenation reactions and chemisorbed H was, therefore, a reactant in each case. It was found that in each reaction the chemisorbed H atoms had a large degree of freedom with their location at transition states determined by their reaction counterpart. This is due, in part, to an exceptionally smooth potential energy surface for H diffusion on Pt(111).[5,6] Reactions in which *both* reactants exhibit a corrugated potential energy surface are more common and encompass a wider variety of chemical processes. An obvious question is therefore: what principles govern the pathways of these common types of reaction? In

the present study we use the following prototype systems to model this variety of reaction: (i) chemisorbed carbon and oxygen yielding chemisorbed CO on Pt(111); (ii) chemisorbed carbon with chemisorbed nitrogen to form chemisorbed CN, also on Pt(111); and (iii) on Cu(111), the reaction of chemisorbed carbon and chemisorbed hydrogen yielding chemisorbed CH. Through a determination of the microscopic reaction pathways of these prototype reactions, we aim at a deeper understanding of the factors that govern catalytic reaction pathways in general.

First-principle total energy calculations within the DFT framework were performed.[7] Ultrasoft pseudopotentials[8] were expanded within a plane wave basis set up to a cutoff of 300 eV. Electron exchange and correlation effects were described by the generalized gradient approximation of Perdew and Wang.[9] A Fermi smearing of 0.1 eV was utilized and the corrected energy extrapolated to zero Kelvin. The Pt(111) and Cu(111) surfaces were modelled by a periodic array of slabs. Each slab consisted of three layers of metal atoms fixed at bulk truncated positions. The vacuum region between adjacent slabs was in excess of 12 Å. Calculated Pt and Cu lattice constants of 3.9711 Å (expt. 3.9239 Å) and 3.6310 Å (3.6147 Å) were used throughout. A $p(3 \times 2)$ surface unit cell was used. This cell is large enough to avoid bonding competition in the initial states of the reactions by allowing each reactant to chemisorb in three-fold hollow sites which do not ''share'' metal atoms, with each other. A Monkhorst-Pack mesh[10] with $2 \times 2 \times 1$ **k**-point sampling within the surface Brillouin zone, was found to offer sufficient accuracy. Previous studies using this[4,11] and similar models[12,13] have shown that this approach provides a satisfactory description of the adsorbate–substrate interface. In addition, testing calculations were conducted using a denser **k**-point mesh ($4 \times 3 \times 1$), a four layer metal slab in which the top layer of metal atoms were allowed to relax and a higher cutoff energy (350 eV). Reaction barriers between this and the chosen model differed by <0.2 eV and pathways and transition states were qualitatively similar. The surface

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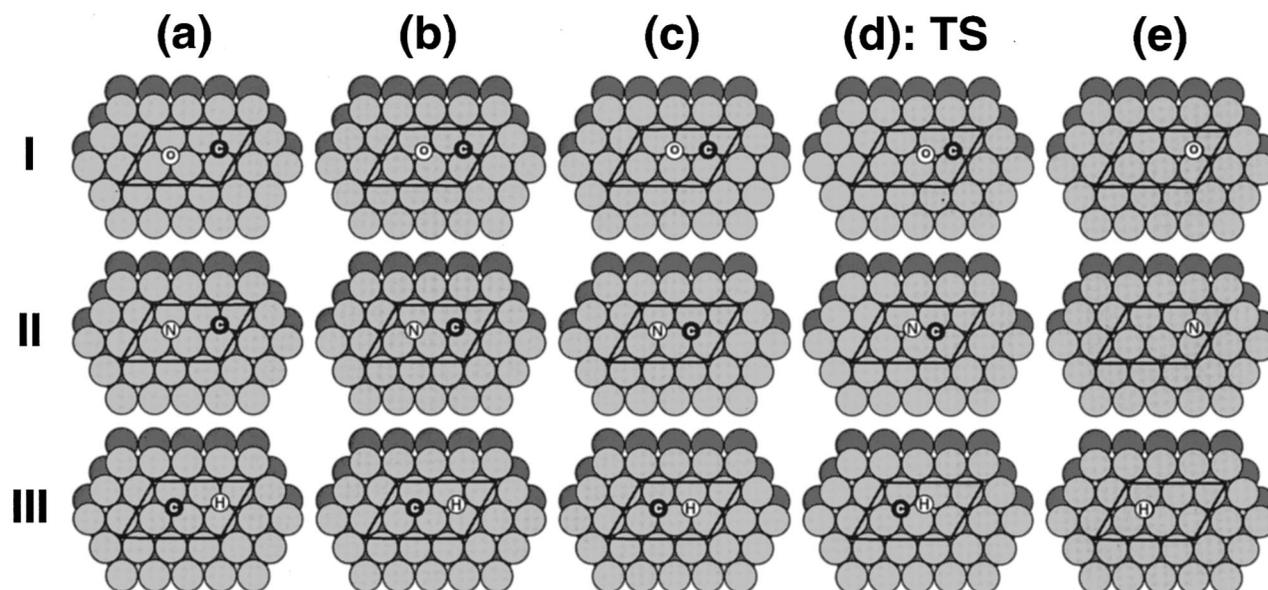
FIG. 1. Reaction pathways for: (I) C+O to CO on Pt(111); (II) C+N to CN on Pt(111); and (III) C+H to CH on Cu(111). The large gray circles are surface atoms, black circles are C. The white circles are O, N, and H atoms in I, II, and III, respectively. The solid lines indicate the surface unit cell. For clarity, the periodic nature of the systems is not shown and only two layers of surface atoms are displayed.

degrees of freedom were found to play only a minor role in the overall reactivity.

Reaction pathways and transition states were searched with a constrained minimisation technique.[14] The approach employed was to fix the distance between the two reactants and minimize the total energy with respect to all remaining degrees of freedom. Through a series of such constrained structure optimisations, with a different reactant separation in each case we determine an energy profile for the reaction. Since the only constraint is the distance between the reactants, the reactants are free to rotate and translate subject to the above constraint. The transition state is identified when (i) the forces on the atoms vanish and (ii) the energy is a maximum along the reaction coordinate but a minimum with respect to all remaining degrees of freedom.

The pathways and energy profiles for each of the three reactions investigated are displayed in Figs. 1 and 2. Figure 1(a) displays the initial states of each reaction, each of which are the most stable coadsorption of the reactants in $p(3 \times 2)$ unit cells. In the coadsorption states shown in Fig. 1(a),
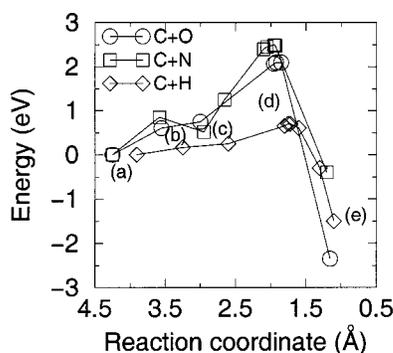
and when chemisorbed independently, all the reactants chemisorb preferentially at three-fold hollow sites. In the initial states of the C+O and C+N reactions, C atoms are at hcp three-fold hollow sites and O or N atoms are at fcc sites. In the C+H reaction it is most stable to have C atoms at fcc sites and H atoms at hcp sites. From Fig. 1 it can be seen that the transition states of each reaction are *similar*. The separation of the reactants is about 1.8–2.0 Å and one adsorbate is close to a threefold hollow site while the other has been activated from their favored (hollow) site to a bridge site. Indeed, this represents a very common structure for a transition state on a (111) metal surface. Transition states with this structure are often observed in the dissociation of diatomic molecules—reactions which are the reverse of those currently under discussion. DFT calculations have shown that the dissociation of N_2,[15] CO,[16,17] and NO[18,19] on a variety of transition metal surfaces all proceed via this type of transition state. Furthermore, we report that the transition state for the N+N recombination reaction on Pt(111) is also of this type.

In order to understand the structure of this important class of transition state it is beneficial to consider the geometry of the Pt(111) and Cu(111) surfaces. A plan view of a segment of a (111) surface of an fcc metal is shown in Fig. 3(a). On both Pt(111) and Cu(111) the distance between hollow sites a and b, in Fig. 3(a), is approximately 1.6 Å and the distance between hollow sites a and c is approximately 2.7 Å. Since the distance between two reactants in this type of transition state is about 1.8–2.0 Å it is clear that if one reactant is at hollow site a (for example, C and N are both reactive at hollow sites)[4] then both hollow sites b and c are unsuitable locations for the other reactant. Hollow site b is too close at 1.6 Å and hollow site c is too far away at 2.7 Å. Naturally, the bridge site or near to the bridge site between these two hollow sites is a suitable location for the second

FIG. 2. Energy profiles of the three reactions studied. The points (a)–(e) of each reaction correspond to the points (a)–(e) of Fig. 1.
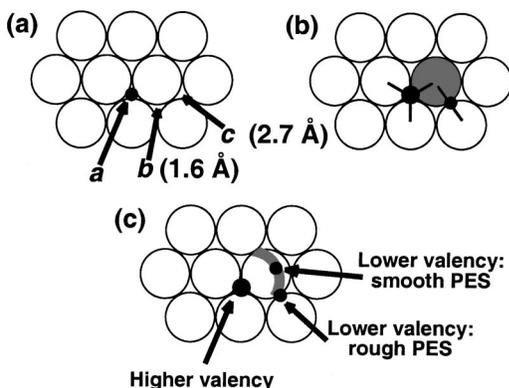
FIG. 3. Illustrations of: (a) typical distances between adsorbates when chemisorbed at neighboring threefold hollow sites on Pt(111) and Cu(111); (b) bonding competition in a transition state. Both reactants compete for bonding with the shaded surface atom; (c) the structure of two common types of transition state on a (111) metal surface. In (a) to (c) the large white circles represent surface atoms, and the small black circles reactants.
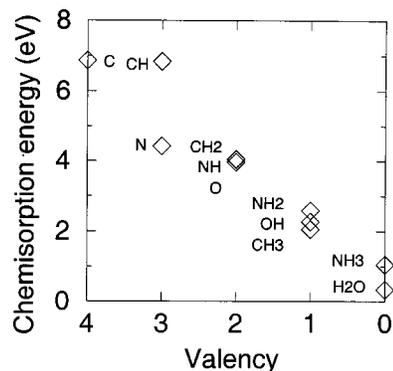

FIG. 4. Calculated chemisorption energies (eV) for a number of important species in heterogeneous catalysis at their most stable adsorption sites on a fixed three layer Pt(111) slab. It can be seen that as the valency of the adsorbate decreases so too does the chemisorption energy.

reactant. With one reactant close to a hollow site and the other to a bridge site then the transition state for the C+O reaction can be readily understood. Carbon which is reactive at hollow sites is located at the hollow site. Oxygen which is reactive at bridge sites is located at the bridge site. In the C+N reaction, however, since both C and N are reactive at hollow sites then there are two possible transition state structures: (i) C is at the hollow site and N is at the bridge site; and (ii) C is at the bridge site and N is at the hollow site. We find that the former is favored (Fig. 1). We have attempted but could not locate a transition state with N near a hollow site and C near a bridge site. In the C+H reaction, C is again at a three-fold hollow site and H is at a bridge site. This leads to an important suggestion. In these three atomic recombination reactions it is the reactant with the higher valency that is located close to the high coordination site while the reactant with the lower valency is close to the low coordination site. We believe that this may be a general finding since it holds, not only for the current reactions, but also for the dissociation reactions from the literature mentioned above.[15–19]

It must be emphasised that in the transition state of the C+N reaction the observation that N resides at a bridge site was initially surprising because the calculated energy difference between a N atom chemisorbed at a three-fold hollow and bridge site of Pt(111) is 0.87 eV, whilst in the case of C, this difference is only 0.78 eV. In other words, the potential energy surface for diffusion of N is more corrugated than that of C.[20] Thus one may expect that C rather than N should be activated from the hollow site to a bridge site in order to achieve a transition state. This is clearly not the case and it shows, as with the hydrogenation reactions mentioned in the introduction,[4] that an important factor in determining the structure of a transition state is the valency of the reactants involved.

An obvious question is therefore: *why, in a transition state of this type, is the lower valency adsorbate activated to the bridge site*? The answer relates to the fact that this arrangement minimizes repulsion between the adsorbates. In a transition state of this type, the adsorbates can be arranged in

two ways: (i) the lower valency adsorbate is close to the bridge site with the other close to the hollow site; or (ii) the lower valency adsorbate is close to the hollow site with the other close to the bridge site. In either case there is one surface atom that is bonded to both adsorbates [the shaded atom in Fig. 3(b)]. The shared surface atom is one of three atoms of the hollow site, but one of two of the bridge site [Fig. 3(b)]. The bonding of each adsorbate to this particular surface atom is weakened considerably. Consequently, a greater proportion of the adsorbate-surface bond is weakened for the bridge site adsorbate than the hollow site adsorbate. We know that absolute chemisorption energy decreases with valency, i.e., low valency adsorbates bind more weakly to a surface than high valency adsorbates, as shown in Fig. 4 for a variety of small molecules on Pt(111). It is, therefore, preferable to have the lower valency adsorbate, the one with the weaker chemisorption energy, on the bridge site. Clearly, it is better to lose a greater proportion of the chemisorption energy of the weaker adsorbate rather than the stronger adsorbate.

Further insight into the structure of transition states can be gained by comparing the transition state of the C+H reaction on Cu(111) with those of the C+H, CH+H and N+H reactions on Pt(111).[4] As we have seen in the transition state of the C+H reaction on Cu(111), C is at a hollow site and H is close to a bridge site (Fig. 1). In the transition states of the three reactions on Pt(111) C, CH, and N are close to a hollow site whilst H in each case is close to a *top* site. This difference in the location of H can be traced back to the individual potential energy surfaces for diffusion of H. On Pt(111) both experimental and theoretical studies reveal that H has a very smooth potential energy surface.[5,6] In agreement with this, we find that H binds at each of the four high symmetry sites of Pt(111) to within a 0.1 eV energy difference. When H reacts with another adsorbate on Pt(111) it, therefore, approaches in the most reactive direction (the $p-d$ bonding direction) about the chemisorbed reactant, which is over the top site of a metal atom. The potential energy surface for H diffusion on Cu(111) is, however, much more corrugated. H exhibits quite a strong preference for adsorption at three-fold hollow sites. We find, in fact, in agreement with the recent DFT calculations of Stromquist *et al.*[21] that

there is approximately a 0.5 eV difference between H adsorption at the fcc and top sites. It is this dislike for H adsorption at top sites that prevents H from making transition states at these sites on Cu(111). Similarly, in the C+O and C+N reactions on Pt(111) the strong dislike for O and N adsorption at top sites prevents these adsorbates from accessing transition states at top sites. In general, therefore, as illustrated in Fig. 3(c), if the potential energy surface of the activated adsorbate is quite smooth then it will be located close to a top site. If, on the other hand, the potential energy surface of the activated adsorbate is corrugated and it has a strong dislike for the top site then it will be located at a bridge site.

In conclusion, DFT has been used to determine reaction pathways for catalytic reactions on Pt(111) and Cu(111). We find that the structures of the transition states accessed in each reaction are similar. An equivalent distance separates the reactants with the first located at a three-fold hollow site and the second close to a bridge site. Indeed, previous DFT studies have also identified transition states of this type and in every case it is the reactant with the lower valency that is located close to the bridge site. It has been shown that this is because of the weaker chemisorption energy of the lower valency adsorbates.

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