

Insight into Microscopic Reaction Pathways in Heterogeneous Catalysis

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Received April 5, 2000

Revised Manuscript Received August 18, 2000

A sound understanding of the chemical reaction is a fundamental aim of chemistry. This is not an easy task, however, as high spatial (atomic) and temporal (subpicosecond) resolution is required. Catalytic reactions are particularly challenging. By far the most common type of reaction in heterogeneous catalysis is the Langmuir–Hinshelwood reaction.^{1–2} The practical desire to understand such reactions stems from the long held belief that a microscopic understanding may facilitate the design of more efficient, more selective, less expensive catalytic substrates. Density functional theory (DFT)^{3–8} has been helpful in this regard and the pathways of certain catalytic reactions have recently been determined, providing a clear indication as to how these reactions are likely to take place. However, a general explanation as to how chemical reactions proceed on catalyst surfaces is lacking.

In this paper we present the results of extensive DFT calculations for nine catalytic reactions taking place on a Pt{111} surface. Specifically, we have determined microscopic reaction pathways for all the elementary steps in the hydrogenation of carbon to methane, nitrogen to ammonia, and oxygen to water. Clearly, these are all very important reactions as C, N, O, and H are the principal building blocks of most of the species involved in the fundamental processes of heterogeneous catalysis. On the basis of our results, we have devised a framework that may have a predictive nature for catalytic reaction pathways.

DFT calculations within a plane wave basis set were carried out in this study.⁹ Exchange and correlation effects are described by the generalized gradient approximation of Perdew and Wang.¹⁰ A three-layer platinum slab fixed at bulk truncated positions with a $p(3 \times 2)$ unit cell was used to model periodic geometries. $2 \times 2 \times 1$ k -point sampling, within the surface Brillouin zone, was found to offer sufficient accuracy (also see refs 11 and 12). Previous studies^{11–13} and tests concerning various aspects of the chosen model¹⁴ confirmed that this approach accurately models the adsorbate–substrate interface. Reaction pathways were determined using a method similar to one previously reported.¹⁵ For each reaction several possible reaction channels were searched, and only the results of the lowest energy pathway, i.e., that which accesses the lowest energy transition state (TS), are presented

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(14) In particular, calculations were conducted using a four-layer slab in which the top layer was allowed to relax. Reaction barriers between this and the chosen model differed by about 0.1 eV and the surface degrees of freedom were found to play only a minor role.

Table 1. Reaction Barrier (E_{act}) and Enthalpy Change (ΔH) for the Nine Hydrogenation Reactions^a

reaction	E_{act} (eV)	ΔH (eV)	reaction	E_{act} (eV)	ΔH (eV)
C+H \rightarrow CH	0.78	-0.75	NH+H \rightarrow NH ₂	1.31	0.01
CH+H \rightarrow CH ₂	0.72	0.58	NH ₂ +H \rightarrow NH ₃	0.74	-0.62
CH ₂ +H \rightarrow CH ₃	0.63	-0.19	O+H \rightarrow OH	0.87	-0.07
CH ₃ +H \rightarrow CH ₄	0.74	0.08	OH+H \rightarrow H ₂ O	0.22	-0.56
N+H \rightarrow NH	0.94	-0.42			

^a E_{act} and ΔH are determined by calculating the energy differences between the most stable initial and the lowest transition states and between the initial and final states, respectively. The final state for each of the reactions, except CH₃ + H, is a species chemisorbed upon the surface. All values are in electron volts per atom. A negative ΔH corresponds to an exothermic reaction.

here. Reaction barriers and enthalpy changes have been calculated for each reaction; these are shown in Table 1.

Clear periodic trends in the microscopic pathways of each reaction have been identified. These are best observed by an examination of the TS of each reaction. A simple representation of these is shown in Figure 1a–i, a consideration of which yields the following interesting features.

1. There are only a limited number of classes of TS. Class I: The “heavier fragment”, i.e., CH_x, NH_x, OH_x, is located close to a 3-fold *hollow site* [Figure 1a,b,e]. Class II: The heavier fragment is located close to a *bridge site* [Figure 1c,f,h]. Class III: The heavier fragment is located close to a *top site* [Figure 1d,g,i]. The hydrogenating hydrogen atoms have a large degree of freedom and appear at several positions due to a flat potential energy surface on Pt{111}.

2. Heavier fragments that are isoelectronic access similar TSs. Both CH and N, for example, are located at a hollow site in the TS of their reaction with H. The most noteworthy aspect of this phenomenon probably arises upon consideration of the reverse of these reactions, i.e., dehydrogenation: The TSs for the removal of the first hydrogen from CH₄ (Figure 1d), NH₃ (Figure 1g), and H₂O (Figure 1i), respectively, are alike. The TSs for subsequent H removal are also similar.

3. There is a clear relationship between the valency of the heavier adsorbates and the location of the TS. The higher the valency of the adsorbate, the higher the coordination number (the coordination number of a surface site equalling the number of surface atoms at that site) of the site upon which the TS is located. This is illustrated in Figure 1j. Monovalent adsorbates favor TSs at top sites, divalent adsorbates at bridge sites, and trivalent and tetravalent adsorbates at hollow sites. This relationship is rigorously followed, except for the NH + H reaction in which a hollow site TS of similar energy to that on the bridge site has also been identified. A consequence of this relationship is that if the coordination number of the site at which an adsorbate is initially chemisorbed is greater than the adsorbate's valency, then it must diffuse to a site of lower coordination to form a TS. For example, the O atom must move from a hollow site (initial chemisorption site) to a bridge site in order to react.

4. The directions in which the hydrogenating hydrogen atoms approach the heavier fragments are determined by the symmetries of the molecular orbitals of the heavier fragments (compare for example the location of H in the CH₂ + H (Figure 1c) and NH + H (Figure 1f) TSs). If the hydrogenating H atoms approach

(15) See: Michaelides, A.; Hu, P.; Alavi, A. *J. Chem. Phys.* **1999**, *111*, 1343. Transition states were searched by constraining the distance between the two reactants in each reaction and minimizing the total energy with respect to all remaining degrees of freedom. This method allows the molecules to rotate and translate subject to the above constraint. The TS 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.

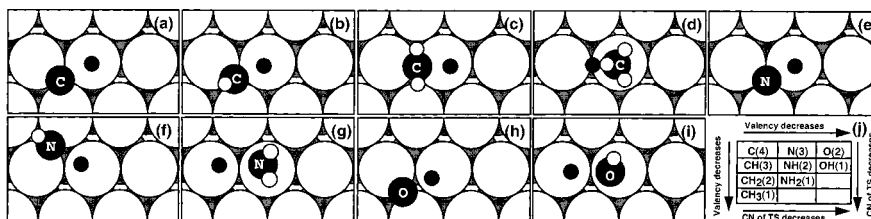


Figure 1. (a–i) Basic structure of each of the transition states (TSs) for the nine reactions studied: (a) C + H; (b) CH + H; (c) CH₂ + H; (d) CH₃ + H; (e) N + H; (f) NH + H; (g) NH₂ + H; (h) O + H; and (i) OH + H. The large white (gray) circles represent Pt atoms. The small white circles are hydrogen atoms that are bonded to an adsorbate and the small black circles are the hydrogenating hydrogens. (j) Relationship between the valency of an adsorbate and the location of the TS when it reacts with a chemisorbed H. As the valency decreases, the coordination number (CN) of the site upon which the TS is located decreases. The values in brackets refer to both the valency of the adsorbate and the coordination number of the site upon which the TS is located, except for C, where this value refers to valency alone.

the heavier fragments from completely different directions to those shown then the reaction barriers will be much higher and the reactions may not even occur.

Perhaps the most important result in this study is the identification of the relationship between the valency of the heavier adsorbate and the location of the TS. By comparing the present results on Pt with those from the literature we find that this relationship holds on a variety of transition metal surfaces. Further, it is independent of the preferred chemisorption site of the reactants. Considering Ni{111}, for example, the TSs for both the CH₂¹⁶ and CH₃¹⁵ hydrogenation reactions are located at the same sites as on Pt{111} despite the fact that both CH₂ and CH₃ initially chemisorb at hollow sites on Ni{111}, compared to bridge and top sites, respectively, on Pt{111}. In addition, TSs determined for the oxidation of CO [3,4] and the dissociation of CO^{5,17} and NO^{18,19} on Ru, Ni, Pd, and Pt surfaces are also consistent with this result.

What is the physical origin of the transition-state valency relationship? An analysis of the electronic structures of the initial, transition, and final states reveals that an answer to this question lies in the p orbitals of the adsorbates (except chemisorbed H). We find that the 2s orbitals of the adsorbates are localized and not involved in adsorbate–surface bonding.¹³ The 2p orbitals, however, mix significantly with metal states before reaction and also with metal states and H in the transition states. In other words, the 2p orbitals are involved in the bond formation and bond breakage processes and are thus strongly related to the reactivity of an adsorbate. It is found that an adsorbate is not reactive at a particular site, i.e., it cannot form a TS at this site and must be activated to a site of lower coordination to achieve a TS, if a large proportion of the p electrons around the adsorbate are at low energies. In contrast, an adsorbate is reactive at a site if a small proportion of its p electrons are at low energies. An example is shown in Figure 2a which displays the local densities of states (LDOS) for the valence electrons projected onto C, N, and O for these species chemisorbed on hollow sites. An examination of the real space distribution of the individual quantum states reveals that states between –8 eV and the Fermi level are mostly mixing states between adsorbate p and Pt d orbitals. It is clear that a greater proportion of the p electrons around O (not reactive at hollow sites) are at lower energies (about –7 eV) than those around C or N (reactive at hollow sites). This result can be rationalized as follows. If an adsorbate is to be reactive at a certain site, i.e., capable of forming a TS, it is essential that it has available p orbitals with which another species can form a new bond. If all the p orbitals of the adsorbate at a surface site are at low energies, i.e., bonding with surface atoms, and none are available for new bond formation, then the adsorbate is unreactive and this is not a suitable site for a TS. The large proportion of p electrons at low energies around the hollow site O (Figure 2a)

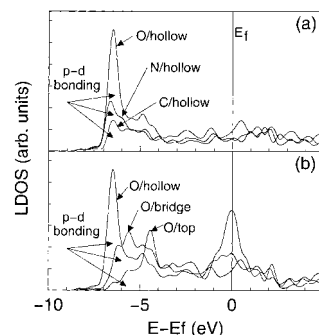


Figure 2. Local densities of states (LDOS) projected on to (a) C, N, and O on a hollow (fcc) site of Pt{111} and (b) O at hollow, bridge, and top sites. The almost purely localized 2s derived states which occur at >10 eV below the Fermi level (E_f) are not shown.

indicates that at this site oxygen p orbitals are fully or nearly fully used up in bonding with metal d states. There are insufficient p orbitals for new bond formation thus rendering O unreactive. Oxygen, at the hollow site, can be considered to be “saturated”. Consequently, it was not possible to identify an O TS on or near a hollow site. In contrast, the smaller proportion of p electrons at low energies (centered at –7 eV) around C and N, as a result of their increased valency, suggest that these adsorbates are not “saturated”. Therefore, unlike O, C and N are reactive at hollow sites and TSs could be found on hollow sites (Figure 1a,e). Another example is shown in Figure 2b, which displays LDOS plots for O chemisorbed at various sites. When O is on the bridge site (reactive), the peak of p–d bonding states is much smaller than that which is observed when O is on the hollow site. Similar findings have been found for all other adsorbates studied.

Consistently throughout we see that two factors determine the proportion of low-energy p electrons around an adsorbate and ultimately the reactivity of the adsorbates. The first is the valency of the adsorbate; as the valency increases, the proportion of low-energy p electrons decreases (Figure 2a). The second is the adsorption site; the proportion of low-energy p electrons increases as the coordination of an adsorption site increases (Figure 2b). It is the combination of these two trends that yields the important relationship between valency and the location of the TS.

On the basis of these results, we can extract the following simple rules for catalytic reaction pathways on transition metal surfaces: (i) isoelectronic adsorbates tend to go to similar sites to form TSs and (ii) the higher the valency of the adsorbate, the greater its tendency to access a TS close to a high coordination site. It remains to be seen how far this framework can be extended, but given its solid foundation we are optimistic that the two rules will be followed for many catalytic reactions and may make it possible to predict TS structures and reaction pathways for a wide variety of reactions in heterogeneous catalysis.

Acknowledgment. Sincere thanks are expressed to The Super-Computing Centre for Ireland for computer time. A.M. is grateful to EPSRC for a studentship.

JA0011919

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