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Activation Barrier for Adsorbate Surface Diffusion, Heat of Chemisorption, and Adsorbate Registry: Theoretical Interrelations

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Abstract: For transition-metal M/adsorbate X chemisorption, interrelations between the surface diffusion barrier ΔE^* and the heat of chemisorption Q are analyzed by using Morse-type potentials. For a multicenter M_n–X site, it is assumed that the two-center M–X contributions (limited to nearest neighbors) are additive and the total M_n–X bond order is normalized to unity and conserved along the diffusion path. It is proved that, for adatoms A, the highest symmetry site is preferable and represents the only total energy minimum, the values of ΔE^* comprising the range of $0.1Q$–$0.3Q$. For admolecules AB, however, there can be more than one total energy minimum, and the ground chemisorption state may correspond to both hollow (bridge) and on-top sites, the latter being more probable for an acceptor AB, say CO. In such cases, ΔE^* will be larger than ΔQ between the minima. The model conclusions are in encouraging agreement with experiment. Some model extensions (in particular, interrelations among ΔE^*, Q, and vibrational frequencies) are also discussed.

Surface-diffusion processes (as an adsorbate moves laterally along a surface) govern annealing and order–disorder transformations and may be rate limiting in desorption of a dissociated species, in bimolecular reactions, and in bifunctional catalysis.[1] Measurements of surface-diffusion rates on single-crystal planes are exceedingly difficult,[1-7] and reliable data have been reported only for a few cases.[8] Empirical observations show that the activation barrier ΔE^* for surface diffusion typically varies within 10–30% of the heat of chemisorption Q for transition-metal/gas systems.[1-7] To our knowledge, there are no specific theoretical arguments explaining this empirical range of $\Delta E^*/Q$. The primary purpose of this work is to explore theoretical interrelations between ΔE^* and Q. We will consider both atomic A and molecular (diatomic) AB adsorbates and will use general Morse-type functions to describe the relevant potential energy profiles. Assuming the additivity of the M–A (M–AB) interactions and the conservation of the M–A (M–AB) bond order, we will obtain analytical expressions relating ΔE^* to Q. We will show that the atomic diffusion patterns may differ greatly from the molecular patterns and briefly discuss some conceptual ramifications of our model findings.

Description of the Model. Consider surface diffusion (migration) of an adsorbate X (an atom A or a diatomic molecule AB) between metal sites M_n of different geometries such as hollow, bridge, or on-top, where n is the number of surface metal atoms interacting with X. We want to know how the M_n–X bonding energy depends on n, what site (what value of n) will correspond to the maximum value of Q (to the global energy minimum), and how ΔE^* relates to the differences ΔQ on the diffusion path. Our model assumptions are as follows. (1) Each two-center M–X interaction is described by the Morse-type potential (eq 1), the

$$E(\chi) = Q_0(\chi^2 - 2\chi) \qquad (1)$$

$$\chi = \exp[-(r - r_0)/a] \qquad (2)$$

simplest general function relating the total energy $E(\chi)$ to the bond order χ (eq 2) which, in turn, relates to the internuclear distance r. Here, a is some empirical constant (e.g., the Pauling value is $a = 0.26$ Å[9]), and r_0 and Q_0 are the equilibrium distance and bond energy, respectively, when $\chi = 1$, by definition.[10a] (2) The M_n–X interactions are limited to n nearest-neighbor metal atoms. In particular, for the fcc(111) surface, n = 3, 2, and 1 for the hollow (C_{3v}), bridge (C_{2v}), and on-top positions. (3) For a given M_n–X, n two-center M–X interactions are additive. (4) The total bond order χ for the M_n–X interactions is normalized to unity and conserved along the diffusion path regardless of the values of n (eq 3). Conservation of χ for various gas-phase

$$\sum_{i=1}^{n} \chi_{Xi} = 1 \qquad (3)$$

three-center A···B···C interactions ($\chi_{AB} + \chi_{BC} = 1$) has been found to be a very accurate criterion.[10b]

Table I. Q_0 vs. Q_n vs. ΔE^* Interrelations

n	Q_n/Q_0[a]	$\Delta E^*/Q_n$[b]	surface
1	1.00		
2	1.50		
3	1.67	0.10	hcp(001) fcc(111) bcc(110)[c]
4	1.75	0.14	fcc(100)
5	1.80	0.17	bcc(100)
6–9[d]	1.83–1.89	0.18–0.21	stepped, kink
12	1.92	0.22[e]	

[a] Equation 5. [b] Equation 6b. [c] Here the C_{2v} "center" site has the effective coordination number larger than the regular C_{2v} bridge site, so that the ratio of $\Delta E^*/Q_n$ may be smaller than 0.10.[11,14] [d] Possible high coordinations on rough surfaces. [e] The hypothetical upper limit of diffusion through the C_{2v} bridge point.

Results

Atomic Adsorbates. We begin with an atom A chemisorbed on a surface with a C_{nv} unit mesh M_n, for example, C_{3v} (n = 3) for fcc(111) and C_{4v} (n = 4) for fcc(100). Clearly, all surfaces may have the on-top positions with n = 1 and the bridge (C_{2v}) ones with n = 2. For some instant position of A within the M_n site, corresponding to the instantaneous bond orders χ_{Ai} (i = 1, 2, ..., n), the M_n–A bond energy $Q_n(i)$ reads as (cf. eq 3)

$$Q_n(i) = Q_0 \sum_{i=1}^{n} (2\chi_{Ai} - \chi_{Ai}^2) = Q_0(2 - \sum_{i=1}^{n} \chi_{Ai}^2) \qquad (4)$$

From eq 3 and 4, it *strictly* follows that, for a given n, the maximum M_n–A bonding energy Q_n (the minimum total energy $E_n = -Q_n$) will correspond to the equivalent two-center M–A

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interactions having the *same* bond order $1/n$. It also means that the larger n, the larger Q_n. More specifically, if Q_0 is the maximum M–A bond energy in the on-top position (cf. eq 1), the maximum M_n–A bond energy Q_n will be (cf. eq 4)

$$Q_n = Q_0(2 - 1/n) \qquad (5)$$

Table I lists the ratios of Q_n/Q_0 for the typical values of $n = 1$–5 (and some others). We conclude that the M_n–A bonding energy *monotonically* increases as n increases and there is only *one* (global) total energy minimum corresponding to the highest coordination number (hollow) site, so that the observed heat of chemisorption Q can be identified with Q_n. In other words, for the surfaces with C_{nv} unit meshes such as fcc(111) or fcc(100), the bridge (C_{2v}) sites are *not* stationary points and the on-top site is always the total energy maximum. Thus, for such surfaces, the low-energy pathway for atomic diffusion should always be confined to the twofold axis path, namely from the hollow C_{nv} site to the bridge C_{2v} site and then to the hollow C_{nv} site (of the adjacent unit mesh). The total energy along this path $C_{nv} \rightarrow C_{2v} \rightarrow C_{nv}$ first monotonically increases up to the C_{2v} point and then monotonically decreases. Thus, the diffusion barrier ΔE^* (eq 6a)

$$\Delta E^* = \Delta Q = Q_n - Q_2 \qquad (6a)$$

can be identified with ΔQ, the difference between the M_n–A (Q_n) and M_2–A (Q_2) bonding energies. For a given C_{nv} unit mesh, we can immediately express Q_2 via Q_n and thus estimate ΔE^*, namely

$$\Delta E^* = \frac{n-2}{4n-2}Q_n \qquad (6b)$$

For example, for fcc(111), C_{3v}, we have $\Delta E^* = 0.10Q_3$. For fcc(100), C_{4v}, we find $\Delta E^* = 0.14Q_4$. For bcc(100), C_{4v} (assuming effective M_5–A coordination), we estimate $\Delta E^* = 0.17Q_5$. The results are summarized in Table I.

For the surfaces considered in Table I, the ratio $\Delta E^*/Q_n$ is a structural constant (independent of A) which *increases* as the surface becomes more open. So far, our basic premise was the validity of eq 3 for the hollow sites. If, however, the metal–metal distances impose steric constraints, when eq 3 (via eq 2) cannot be satisfied for high coordination sites, an adatom will prefer to occupy the site of lower coordination (see below). Presumably, the bridge sites can always satisfy eq 2 and 3. So, we can get an idea of what might be the *upper* limit of $\Delta E^*/Q$ if we consider the hypothetical diffusion strictly along the M_2 bridge, from the minimum on the C_{2v} site to the maximum on the on-top site. In this case, we have (see Table I) $\Delta E^* = Q_2 - Q_1 = 0.33Q_2$. Summing up, the surface diffusion barrier ΔE^* (eq 7) is directly

$$\Delta E^* = kQ \qquad (0.1 \leq k < 0.3) \qquad (7)$$

proportional to the heat of chemisorption Q. The coefficient k may be a constant or some parameter with values typically in the range 0.10–0.25. Because our model does not take into account the adsorbate–adsorbate interactions, the above values of $k = \Delta E^*/Q$ should be assigned to the extreme case of zero coverage (of single isolated adatoms).

Our model approach also allows one to estimate, for a given A, the anisotropy of Q on different surfaces. For example (see Table I), we have $Q_3 = 1.67Q_0$ for fcc(111) and $Q_4 = 1.75Q_0$ for fcc(100), so that $\Delta Q = 0.08Q_0 \simeq 0.05Q_3 \simeq 0.04Q_4$. In other words, from fcc(111) to fcc(100), the value of Q will increase but by less than 5%. Similar estimates can be done easily for other surfaces. As said above, the M–M spacing can make eq 3 (via eq 2) incompatible with some high-coordination sites, especially on open surfaces and for small atoms, especially for hydrogen. This incompatibility may lead to surface reconstruction. In such cases, the data in Table I should be assigned to the *observed* coordination numbers n. This is the reason why the values of Q may show a complicated dependence on the number of metal atoms in the unit mesh M_n–A.

Molecular Adsorbates. Consider the surface diffusion of a diatomic molecule AB such as H_2 or CO. Again, we want to know what metal site M_n will be preferable and how the activation barrier ΔE^* will change along the diffusion path. By logic, our model assumptions and conclusions for admolecules must be reduced to those for adatoms if we neglect the *internal* structure of an admolecule and treat it as a quasiatom. So, the general assumptions such as pairwise additivity (limited to nearest neighbors) and conservation of the bond order (normalized to unity) are preserved in the molecular case. The new assumptions, specific for molecular diffusion, are as follows. (1) The A–B distance and thus the A–B bond order (bond energy) are the same for different chemisorption sites,[11,14] so that the M–AB (Q_{AB}) bond energy is a function of two contributions, M–A(Q_A) and M–B(Q_B). Their interrelations are given by eq 8, where the donor AB →

$$\begin{aligned} &Q_A > 0,\ Q_B > 0 \text{ for donor AB} \\ &Q_A > 0,\ Q_B < 0 \text{ for acceptor AB} \end{aligned} \qquad (8)$$

M vs. acceptor AB ← M bonding (related to the in-phase vs. out-of-phase LCAO MO's of AB[12]) is reflected by the sign of Q_B. Regarding the conserved M–AB bond order (cf. eq 3), now the sum of $\chi_A + \chi_B$ is normalized to unity and conserved along the surface (eq 9). (2) For the sake of argument, the starting geometry corresponds to an upright AB (with the A end down) in the on-top metal site. While AB, remaining normal to a surface, moves to a multicenter M_n site, by obvious geometrical reasons, the M–A distance will increase and the bond order χ_{Ai} will decrease more significantly than the M–B counterparts will.[13] Thus, if $\chi_A = \chi_0$ and $\chi_B = 1 - \chi_0$ for the starting (upright on-top) geometry, then, introducing the redistribution parameter $\delta > 0$ for the M_n site, eq 9 transforms into eq 10. [Obviously, if $\chi_B = 0$, then $\delta = 0$, and the molecular case (eq 10) reduces to the atomic case (eq 3)].

$$\sum_{i=1}^{n}(\chi_{Ai} + \chi_{Bi}) = 1 \qquad (9)$$

$$\sum_{i=1}^{n}\chi_{Ai} = \chi_0 - \delta \qquad \sum_{i=1}^{n}\chi_{Bi} = 1 - \chi_0 + \delta \qquad (10)$$

$$\delta > 0 \text{ if } n > 1$$

With the assumptions in eq 8–10, the following results are straightforward. For the upright on-top geometry, the M–AB bond energy is

$$Q_0 = Q_A(2\chi_0 - \chi_0^2) + Q_B(1 - \chi_0^2) \qquad (11)$$

For some instant position of AB within the M_n site, the M_n–AB bond energy Q_n (eq 12) is (neglecting the δ^2 terms) the sum of Q_0 (eq 11) and two other terms, $\Delta Q^{(1)}$ (eq 13) and $\Delta Q^{(2)}$ (eq 14). Since $\chi_A \gg \chi_B$ ($\chi_0 \gg 1 - \chi_0$), $\Delta Q^{(1)}$ is positive for both donor and acceptor admolecules AB (assuming Q_A and Q_B are comparable in absolute value). At the same time, $\Delta Q^{(2)}$ is always negative for an acceptor AB ($Q_B < 0$) but may be either positive (typically) or negative (rarely) for a donor AB ($Q_B > 0$). The positive $\Delta Q^{(1)}$ term increases as n increases and, for a given n, is maximum for the most symmetric site ($\chi_{Ai} = \chi_{Aj}$, $i \neq j$). Thus, $\Delta Q^{(1)}$ is the atom-like term (cf. eq 4) favoring the multicenter sites, and their attractiveness should be more pronounced for a donor AB ($Q_B > 0$) than for an acceptor AB ($Q_B < 0$). On the contrary, the negative $\Delta Q^{(2)}$, being of specifically molecular origin,

$$Q_n = Q_0 + \Delta Q^{(1)} + \Delta Q^{(2)} \qquad (n > 1) \qquad (12)$$

$$\Delta Q^{(1)} = 2\sum_{i<j}^{n}(Q_A\chi_{Ai}\chi_{Aj} + Q_B\chi_{Bi}\chi_{Bj}) \qquad (n > 1) \qquad (13)$$

$$\Delta Q^{(2)} = -2\delta[Q_A(1 - \chi_0) - Q_B\chi_0] \ (n > 1) \qquad (14)$$

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(10) (a) The Morse function (eq 1) includes both attractive and repulsive terms such that it has a minimum at $\chi = 1$. This is the principal advantage over the power function $E(\chi) = E_0\chi^p$ commonly used to describe the migration barrier and limited, so far, to three-center interactions.[10b] (b) For a discussion, see, for instance: Murdoch, J. R. *J. Am. Chem. Soc.* **1983**, *105*, 2667.

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(13) Moreover, the M–B distances (e.g., for the M–CO interactions) will typically decrease, and thus χ_{Bi} may significantly increase.[11]

always favors the on-top site, especially for an acceptor AB ($Q_B < 0$). Also, as it follows from eq 13, for an acceptor AB, say CO, the attractiveness of the bridge or hollow positions may be enhanced by tipping (toward the on-top site), making $\chi_{Bi} \neq \chi_{Bj}$ and thus decreasing the destabilizing (negative) contribution to $\Delta Q^{(1)}$ from the $Q_B\chi_{Bi}\chi_{Bj}$ terms. Finally, because of such an opposing behavior of $\Delta Q^{(1)}$ and $\Delta Q^{(2)}$, the total energy along the migration path can change *non*monotonically. Thus, for molecular (unlike atomic!) chemisorption, it can happen that the M–AB energy surface has more than one minimum, and therefore the migration barrier ΔE^* is larger than ΔQ between the minima (which do not always correspond to the symmetric sites). In other words, adatoms and acceptor admolecules will typically prefer different chemisorption sites. Because most admolecules behave as acceptors,[12] this model conclusion is quite practical and may be of special interest for various coadsorption processes, in particular for associative–dissociative chemisorption (say, $CO \rightleftarrows C + O$).[11,14]

Discussion

Let us restate our major conclusions. (1) For atomic adsorbates (if there are no steric constraints), the highest symmetry site is preferable and represents the only total energy minimum. The diffusion barrier ΔE^* may be identified with the energy difference between the hollow and bridge positions. Typically, $\Delta E^* = 0.10Q$–$0.25Q$ and, for different surfaces, $\Delta Q \leq 0.05Q$. (2) For molecular (diatomic) adsorbates, the ground chemisorption state may correspond to both bridge (hollow) and on-top positions; the former is more probable for donor adsorbates, the latter for the acceptor ones. There can be more than one total energy minimum (not necessarily in symmetric sites), and the diffusion barrier ΔE^* may not typically be identified with ΔQ between the minima. Tipping of acceptor molecules in hollow (bridge) sites may be energetically favorable.

The above conclusions are in very encouraging agreement with experiment and straightforward calculations, which will be discussed in detail elsewhere.[14] Here we just mention a few of the most relevant facts. (1) The experimental ratios of $\Delta E^*/Q$ lie within 0.1–0.3.[1-7] At low coverages, these ratios are very close to the low limit of 0.10.[7] (2) On the most symmetric surfaces such as fcc(111), fcc(100), or bcc(100), atomic adsorbates, even H[15a] (except H/W(100)[15b]), have invariably been found in the hollow sites.[1-3,15] (3) The anisotropy ΔQ for different surfaces (if any) never exceeds a few percent of Q.[1-3] (4) At low coverages, the prevailing registry of CO on flat metal surfaces is on-top (upright, the C end down).[16] For CO/Pt(111), the diffusion activation barrier ΔE^* (7 kcal/mol[6]) is ostensibly larger than the differences in Q among possible chemisorption sites ($\Delta Q < 1$ kcal/mol[17]).

The crucial model assumption is, of course, the conservation of the bond order (eq 3 and 9). From eq 2 and 3, within the nearest-neighbor approximation, we can define the "normal" M–A distance r_n for the C_{nv} site and the ratios of $\Delta r_n = r_n - r_0$ (eq 15).

$$r_n = r_0 + a \ln n \qquad \Delta r_2:\Delta r_3:\Delta r_4 = 0.69:1.10:1.39 \tag{15}$$

If experimental data on r_n are available, eq 15 allows one to estimate the parameter a. On the other hand, the value of a can be found from vibrational frequencies ω_n of the M_n–A bonds. Indeed, for a vibration perpendicular to the surface, we have[11,14] eq 16, where ψ_n is the angle between the M–A vector and the

$$a = \frac{\cos \psi_n}{\omega_n}\left(\frac{2Q_n}{\mu}\right)^{1/2} \tag{16}$$

surface normal and μ is the mass of an adatom A. Because a is constant for a given A/M system, the interrelation ω_n vs. ω_m for the M_n–A vs. M_m–A sites will be (cf. eq 5)

$$\omega_n = \omega_m \frac{\cos \psi_n}{\cos \psi_m}\left(\frac{Q_n}{Q_m}\right)^{1/2} = \omega_m \frac{\cos \psi_n}{\cos \psi_m}\left(\frac{2 - 1/n}{2 - 1/m}\right)^{1/2} \tag{17}$$

For the on-top site ($\psi = 0$), eq 16 reduces to the standard form of $a = (2Q_0/\omega_0^2\mu)^{1/2}$, and eq 17 may be rewritten as eq 18, where

$$\omega_n = \omega_0 \cos \psi_n \cdot t_n \qquad t_n = (2 - 1/n)^{1/2} \tag{18}$$

Q_0 and ω_0 are the relevant "on-top" quantities. Because of inequality 19, our model describes the situation intermediate between two model extremes, the "weak bonding" when t_n = constant = 1[18,19] and the "strong bonding" when $t_n = n^{1/2}$.[19,20] As a matter

$$1 \leq (2 - 1/n)^{1/2} \leq n^{1/2} \qquad (n \geq 1) \tag{19}$$

of fact, our projections for the bridge and hollow sites (from eq 18, $t_2:t_3:t_4 = 1.22:1.29:1.32 = 1:1.06:1.08$) are very close to those by the "weak bonding" model.[18] (Obviously, all three models are indistinguishable for $n = 1$, but, as shown above, this "on-top" registry for atomic adsorbates can hardly be realized.)

Our analysis of experimental data has shown[11,14] that the values of a estimated from eq 15–18 are coherent and persistently larger than the Pauling value of 0.26 Å.[9] This increase in a seems to be partly related to a contribution from nonnearest neighbors. Though the relevant nonnearest-neighbor corrections are useful for quantitative calculations,[14,21] they appear not to change the qualitative model conclusions discussed.

Certainly, our model further simplifies the problems by neglecting other factors such as surface defects and adsorbate–adsorbate interactions. However, within the model assumptions, the results described are *rigorous*, so that the model has good potential to be scrutinized both experimentally and theoretically. Summing up, our model approach may provide a conceptual framework for interrelating the diffusion barrier, the heat of chemisorption, the vibrational frequency, and the preferred adsorbate registries and geometries (including tipping, which is crucial for bond cleavage[12]). We hope that our consideration will shed new light on the problems and stimulate further experimental and theoretical developments.

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