

Understanding the effect of steps, strain, poisons, and alloying: Methane activation on Ni surfaces

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It is shown that a single parameter characterizing the electronic structure of a transition metal surface, the d-band center (ϵ_d), can be used to provide a unified description of a range of phenomena in heterogeneous catalysis. Using methane activation on Ni surfaces as an example, we show that variations in ϵ_d can be used to quantitatively describe variations in the activation energy when the surface structure is changed, when the coverage of carbon is changed, when the surface is strained, when the surface is alloyed, and when the surface is poisoned by sulfur. The d-band center is, therefore, a very general descriptor of the reactivity of a surface.

KEY WORDS: Density Functional Theory; steps; strain; defects; promoters; surface alloys; d-band center; methane; nickel.

1. Introduction

One of the principal goals of surface science has long been to develop a fundamental understanding of the reactivity of transition metal surfaces [1–4]. The realization of such an understanding could potentially provide concepts for the interpretation of kinetic data on heterogeneous catalysts. Unfortunately, given the immense complexity of catalytic systems, these types of principles have proven extremely difficult to develop.

The d-band model of Hammer and Nørskov [5,6] has recently been shown to have significant explanatory power for the analysis of adsorbate binding energies and transition state energies on a variety of well-defined metal surfaces. One of the fundamental descriptors of the theory, the surface d-band center (ϵ_d), correlates well with these reactivity parameters for a variety of systems, including pure metals and surface alloys with homogeneous overlayers [7–13], alloys with heterogeneous surface layers [14,15], distorted surfaces (with, e.g., steps and strain) [16,17], and surfaces with poisons and promoters [18]. However, to our knowledge, no single study that simultaneously correlates a significant number of these effects has been undertaken. In the present work, we report on the results of just such a study. We show that, when it is properly defined, ϵ_d can be used to quantitatively predict trends in methane activation energies on a variety of surfaces with different geometries, strain levels, promoters, poisons, and alloy compositions. Thus, we demonstrate that ϵ_d has a more general descriptive power than was previously known.

2. Computational methods

Using the Dacapo total energy code [19], we perform periodic, self-consistent, Density Functional Theory (DFT) calculations of the dissociative adsorption of methane on pure and modified nickel surfaces. On the (111) surfaces, we use a 3-layer, (2×2) unit cell with the top layer relaxed, and on the (211) surfaces, we use a 9-layer, (2×1) unit cell with the top (111) layer relaxed. In all cases, adsorption is allowed on only one of the two exposed surfaces of the metal slabs, and the electrostatic potential is adjusted accordingly [20]. Ionic cores are described by ultrasoft pseudopotentials [21], and the Kohn-Sham one-electron valence states are expanded in a basis of plane waves with kinetic energy below 340 eV; a density cutoff of 500 eV is used. The surface Brillouin zone is sampled with a 4×4×1 Monkhorst-Pack \mathbf{k} -point grid. In all cases, convergence of the total energy with respect to the cutoff energies and the \mathbf{k} point set is confirmed. The exchange-correlation energy and potential are described by the generalized gradient approximation (GGA-RPBE98) [19]. The self-consistent RPBE98 density is determined by iterative diagonalization of the Kohn-Sham Hamiltonian, Fermi population of the Kohn-Sham states ($k_B T = 0.1$ eV), and Pulay mixing of the resulting electronic density [22]. All total energies have been extrapolated to $k_B T = 0$ eV. The calculations are performed fully spin-polarized.

3. Results and discussion

Figure 1 illustrates the relationship between the transition state energy for CH₃–H bond scission and the clean slab d-band center on a variety of surfaces. Systems analyzed include flat(111) and stepped (211) nickel

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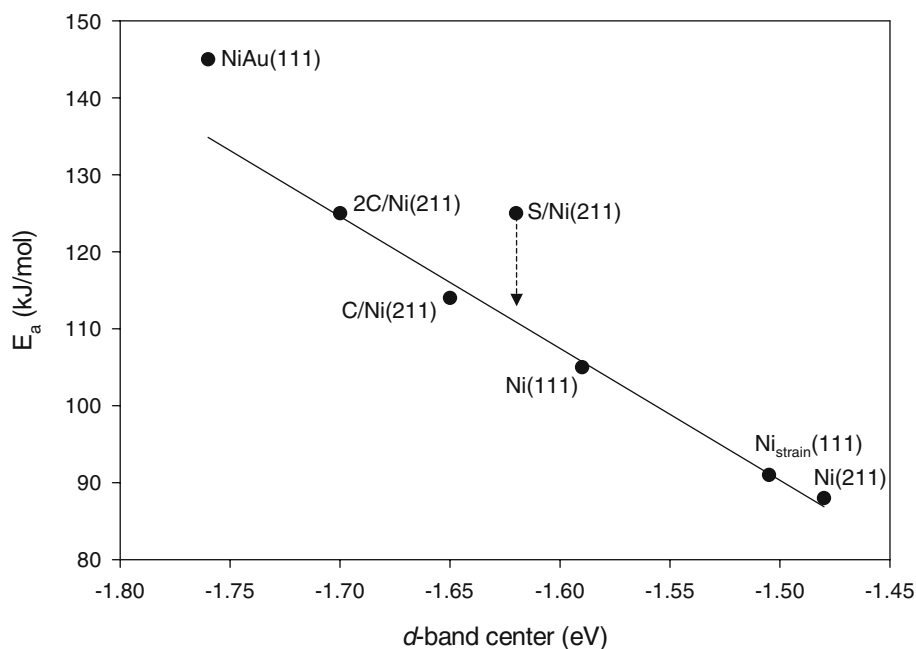


Figure 1. Transition state (T.S.) energy for $\text{CH}_3\text{-H}$ bond scission as a function of the surface d-band center. The T.S. energy is referenced to gaseous CH_4 and a slab with no methane complexes present (a “clean” slab – note, however, that preadsorbed S and C species are present on the “clean” slabs). The dashed arrow indicates the qualitative shift of the S/Ni(211) transition state energy when direct S-transition state interactions are corrected for. The d-band center is as defined in the text. The indicated solid line is intended as a guide to the eye only.

surfaces, stretched nickel surfaces, nickel poisoned with both carbon and sulfur atoms, and a surface alloy (NiAu); schematics of these surfaces and the calculated transition states can be found in figure 2, and geometrical information for the transition states is reported in Table A1 of the Appendix. The d-band centers for each system are computed by first projecting the total metal

density of states onto d-orbitals centered on each atom in the respective surface layers and then taking a weighted average of the resulting ϵ_d 's:

$$\epsilon_d = \frac{\sum_{i=\text{atoms}} V_i(r_{ia})^2 \epsilon_{d,i}}{\sum_{i=\text{atoms}} V_i(r_{ia})^2} \quad (1)$$

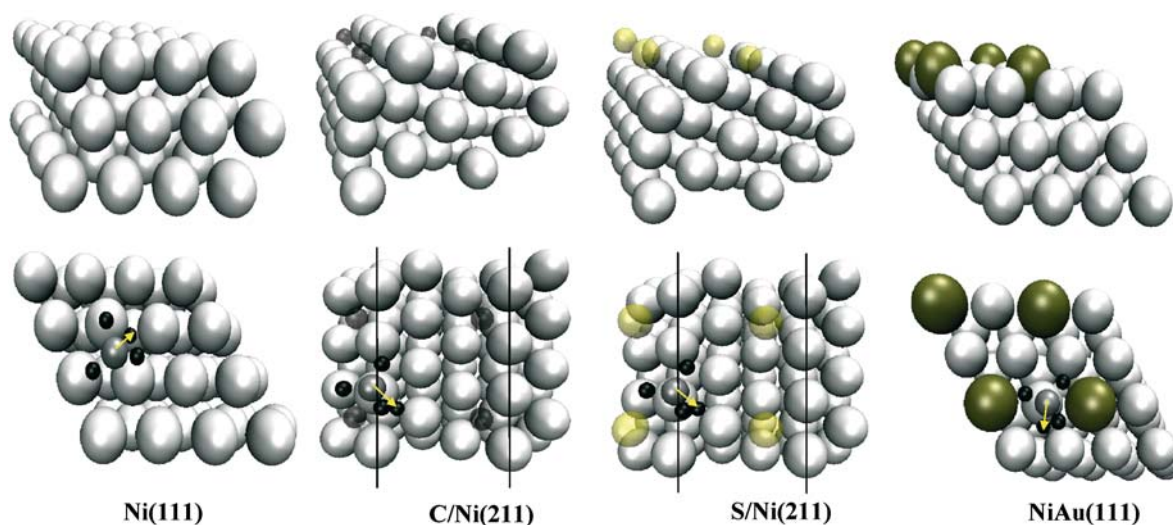


Figure 2. Side and top views of selected Ni slabs. The side views are drawn without the transition state complexes while the top views include the transition states. The dashed lines in the top views indicate the location of the step edges. All images contain four repetitions of the surface unit cell, but the transition states themselves are shown only once. The yellow arrows in the top views indicate the particular C–H bond that is cleaved at the respective transition states. The graphics were produced with VMD [25].

Table A1
Geometrical data for transition states

System	C–Ni bond length (Å)	C–H bond length (Å)
Ni(111)	2.00	1.60
Ni(211)	2.06	1.58
C/Ni(211)	2.10	1.59
2C/Ni(211)	2.12	1.59
S/Ni(211)	2.11	1.59
Ni _{strain} (111) (4.5% lattice expansion)	2.03	1.74
NiAu(111)	2.02	1.56

References for Appendix

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In this expression, the coupling matrix elements have been taken to vary with the distance r_{ia} between the carbon atom of the transition state and the i th metal atom as

$$V_i(r_{ia})^2 = \frac{V_{0,i}^2}{r_{ia}^\alpha}, \quad (2)$$

where $V_{0,i}^2$ is a characteristic value of the coupling matrix element between the transition state frontier orbitals and the d-band of the i th metal atom (these parameters are tabulated and discussed in detail in [23]). A value of 7.3333 was used for the exponent α ; this value was determined by noting that overlap matrix elements are proportional to $1/r_{ia}^{l_a+l_d+1}$ [23]. In this expression, l_a and l_d are the angular momentum quantum numbers of the adsorbate and metal states. An effective sp^2 hybridization is assumed for the $\text{CH}_3\text{-H}$ transition state (corresponding to $l_a = \frac{2}{3}$), and a value of $l_d = 2$ is taken for the metal d-states. We note that an alternative definition of the coupling matrix elements could involve the distance between the *center* of the carbon–hydrogen bond and the appropriate metal atoms. This approach does not change the trends shown in figure 1; the alternative definition only decreases the d-band center of the NiAu system by ~ 0.1 eV, for example. The physical principle underlying equation (1) is simply that the importance of different surface metal atoms in determining the interaction energy with an adsorbate is given by the strength of the coupling (measured by the square of the coupling matrix element [23]) between the adsorbate and the metal d-states; a derivation of this equation is given in the Appendix. We note that heuristic versions of this expression have been used in previous work [15, 24].

Clearly, a remarkably good correlation exists between the weighted d-band center and the $\text{CH}_3\text{-H}$ transition state energy. The quality of the relationship is even more impressive given that it includes data for clean (111) and (211) surfaces, strained (111) surfaces, (211) surfaces with preadsorbed poisons (carbon and sulfur), and a heterogeneous surface alloy. We stress, however, that for the simple, intuitive, relationship shown in figure 1 to hold, it is important both that the d-band center be appropriately defined (by accounting for the geometry of the system in the manner described in equation (1)). If a simple arithmetic average of the d-band centers of all four surface atoms of the (2×2) NiAu alloy is used, for example, the NiAu data point in figure 1 is shifted to the left by ~ 0.4 eV (corresponding to a lower effective d-band center), leading to a significant deviation from the trend line.

The interaction between the adsorbate states and the metal d-states clearly dominates the trends in transition state energies. There are, however, additional terms that contribute, to a lesser extent, to these energies. In cases where the different surfaces have widely different dipole moments and the adsorbate (in this case the transition state complex) also has a significant dipole moment, the direct electrostatic interaction between the surface and the adsorbate must be included [26]. For the systems under consideration here, however, we find that such electrostatic corrections are not significant (less than 0.1 eV).

Additional corrections that might, in some circumstances, be important, include Pauli repulsion effects and corrections from direct adsorbate–adsorbate interactions. Based on the analysis by Mortensen *et al.* [27], we suggest that the anomalously high value of the transition state energy for the S/Ni(211) system is due to a direct interaction (Pauli repulsion) between the transition state complex and the large S atom (ion). That analysis determined a direct repulsion of ~ 0.2 eV between nitrogen and sulfur at a separation of 3.25 Å (the same as the carbon–sulfur separation in the present study) on Ru(0001); although the chemical identity of the species in the present system is clearly different from the corresponding identity in the referenced system, the magnitude of the repulsive effects is probably similar. We note, in passing, that there is little direct adsorbate–adsorbate repulsion for the C/Ni(211) systems because the carbon here sits deep in the surface, and the C orbitals are considerably less extended than the corresponding valence S orbitals.

The present study demonstrates that, when properly defined, the surface d-band center determines trends in transition state energies for stepped, planar, and strained surfaces, for surfaces with poisons and promoters, and for systems that include surface alloys. As such, this clean-surface parameter has very broad explanatory power for reaction kinetics, and it is expected to become an important unifying principle in the field of heterogeneous catalysis.

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Appendix

A theoretical basis for weighted d-band centers

The Newns–Anderson model has been used for many years to obtain qualitative (and sometimes quantitative) insight into the interaction of adsorbates with metal surfaces. It is essentially a tight-binding model of adsorbate/metal interactions that assumes minimal direct overlap between adsorbate and metal states [1,2]. A key quantity that emerges in the Newns–Anderson analysis is the weighted density of states (DOS) of the adsorbate/metal system [3,4]. This function provides a compact and convenient way to characterize the interactions of the adsorbate with the electronic states of the metal, and it can be used to obtain an estimate of the interaction energy between the adsorbate and the metal surface [4]. In many cases involving metals with localized d-states and narrow d-bands, the behavior of the weighted DOS is governed largely by a single parameter, the first moment of the DOS. Below, we show that, if the bands are sufficiently narrow, then the first moment of the weighted DOS is directly related to the sum of the first moments of metal states projected onto d-orbitals centered on individual metal atoms.

The weighted DOS can be written as:

$$\Delta(\varepsilon) = \sum_k \langle a | \tilde{H} | k \rangle^2 \delta(\varepsilon - \varepsilon_k),$$

where \tilde{H} is the combined Hamiltonian of the adsorbate-plus-metal system, $|k\rangle$ is a metal electronic state, and $|a\rangle$ is an adsorbate state. This expression can be expanded in localized basis sets $|j\rangle$ and $|j'\rangle$ to give

$$\Delta(\varepsilon) = \sum_{j,j'} \sum_k \langle a | \tilde{H} | j \rangle \langle j | k \rangle \langle k | j' \rangle \langle j' | \tilde{H} | a \rangle \delta(\varepsilon - \varepsilon_k).$$

The basis sets are taken to consist of localized metal d-states. The assumption that these states form complete sets for the metal states is consistent with the tight-binding approximation [5]. We note that this assumption should be sufficiently accurate for the determination of qualitative trends on Group VIII transition metals.

The definition of the first moment of the weighted density of states is

$$\varepsilon_d = \frac{\int \varepsilon \Delta(\varepsilon) d\varepsilon}{\int \Delta(\varepsilon) d\varepsilon}.$$

Substituting and contracting the delta functions gives

$$\varepsilon_d = \frac{\sum_{j,j'} \sum_k \langle a | \tilde{H} | j \rangle \langle j | k \rangle \langle k | j' \rangle \langle j' | \tilde{H} | a \rangle \varepsilon_k}{\sum_{j,j'} \sum_k \langle a | \tilde{H} | j \rangle \langle j | k \rangle \langle k | j' \rangle \langle j' | \tilde{H} | a \rangle}.$$

Noting that

$$H|k\rangle = \varepsilon_k|k\rangle,$$

where H is the metal Hamiltonian, we have

$$\varepsilon_d = \frac{\sum_{j,j'} \sum_k \langle a | \tilde{H} | j \rangle \langle j | k \rangle \langle k | H | k \rangle \langle k | j' \rangle \langle j' | \tilde{H} | a \rangle}{\sum_{j,j'} \sum_k \langle a | \tilde{H} | j \rangle \langle j | k \rangle \langle k | j' \rangle \langle j' | \tilde{H} | a \rangle}.$$

Since the states $|k\rangle$ form a complete set, $\sum_k |k\rangle\langle k| = 1$, and

$$\varepsilon_d = \frac{\sum_{j,j'} \langle a | \tilde{H} | j \rangle \langle j | j' \rangle \langle j' | \tilde{H} | a \rangle}{\sum_{j,j'} \langle a | \tilde{H} | j \rangle \langle j | j' \rangle \langle j' | \tilde{H} | a \rangle}.$$

We note that $\langle j | H | j \rangle$ is equivalent to $\int \varepsilon \sum | \langle j | k \rangle |^2 \delta(\varepsilon - \varepsilon_k) d\varepsilon$, the first moment of the metal density of states projected onto the localized d-states. Calling these projections ε_j , we have

$$\varepsilon_d = \frac{\sum_j |V_{aj}|^2 \varepsilon_j + \sum_{j,j' \neq j} \langle a | \tilde{H} | j \rangle \langle j | H | j' \rangle \langle j' | \tilde{H} | a \rangle}{\sum_j |V_{aj}|^2 + \sum_{j,j' \neq j} \langle a | \tilde{H} | j \rangle \langle j | j' \rangle \langle j' | \tilde{H} | a \rangle},$$

where

$$|V_{aj}|^2 = \langle a | \tilde{H} | j \rangle \langle j | \tilde{H} | a \rangle.$$

Since the metal d-states are assumed to be localized, the second terms in both the numerator and denominator are small, and we have

$$\varepsilon_d \approx \frac{\sum_j |V_{aj}|^2 \varepsilon_j}{\sum_j |V_{aj}|^2}$$

Thus, we obtain the interesting result that, if the metal d-states are reasonably localized, the first moment of the weighted DOS can be written as a sum of overlap matrix elements multiplied by the first moments of the metal DOS projected onto localized d-states and appropriately normalized. The selection of the particular metal d-states used in the expansion is somewhat arbitrary, but a reasonable choice would be d-orbitals centered on each metal atom. Thus, equation (1) of the main text is recovered.

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