Angewandte Chemie

DOI: 10.1002/anie.200705739

Surface Adsorption

Scaling Relationships for Adsorption Energies on Transition Metal Oxide, Sulfide, and Nitride Surfaces**

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There has been substantial progress in the description of adsorption and chemical reactions of simple molecules on transition-metal surfaces. Adsorption energies and activation energies have been obtained for a number of systems, and complete catalytic reactions have been described in some detail.[1–7] Considerable progress has also been made in the theoretical description of the interaction of molecules with transition-metal oxides,[8–19] sulfides,[20–25] and nitrides,[26–29] but it is considerably more complicated to describe such complex systems theoretically. Complications arise from difficulties in describing the stoichiometry and structure of such surfaces, and from possible shortcomings in the use of ordinary generalized gradient approximation (GGA) type density functional theory (DFT).[30]

Herein we introduce a method that may facilitate the description of the bonding of gas molecules to transition-metal oxides, sulfides, and nitrides. It was recently found that there are a set of scaling relationhips between the adsorption energies of different partially hydrogenated intermediates on transition-metal surfaces.[31] We will show that similar scaling relationships exist for adsorption on transition metal oxide, sulfide, and nitride surfaces. This means that knowing the adsorption energy for one transition-metal complex will make it possible to quite easily generate data for a number of other complexes, and in this way obtain reactivity trends.

The results presented herein have been calculated using self-consistent DFT. Exchange and correlation effects are described using the revised Perdew–Burke–Ernzerhof (RPBE)[32] GGA functional. It is known that GGA functionals give adsorption energies with reasonable accuracy for transition metals.[32,33] It is not clear, however, whether a similar accuracy can be expected for the oxides, sulfides, and nitrides, although there are examples of excellent agreement between DFT calculations and experiments, for example, with RuO_2 surfaces.[9] In our study we focused entirely on variations in the adsorption energies from one system to another, and we expected that such results would be less dependent than the absolute adsorption energies on the description of exchange and correlation.

For the nitrides, a clean surface and a surface with a nitrogen vacancy were studied. For MX_2-type oxides or sulfides, an oxygen- or sulfur-covered surface with an oxygen or sulfur vacancy was studied. The structures of the clean surface considered in the present work and their unit cells are shown in Figure 1. The adsorption energies given below are for the adsorbed species in the most stable adsorption site on the surface.

By performing calculations for a large number of transition-metal surfaces of different orientations,[31] it was found that the adsorption energy of intermediates of the type AH_x is linearly correlated with the adsorption energy of atom A (N, O, S) according to Equation (1):

$$\Delta E^{AH_x} = \gamma(x)\Delta E^{A} + \xi \tag{1}$$

Here the scaling constant is given to a good approximation by Equation (2) where x_{max} is the maximum number of H atoms that can bond to the central atom A ($x_{max} = 3$ for A = N, and $x_{max} = 2$ for A = O, S), that is, the number of hydrogen atoms that the central atom A would bond to in order to form neutral gas-phase molecules.

$$\gamma(x) = (x_{max} - x)/x_{max} \tag{2}$$

We have performed similar calculations for the adsorption of oxygen, sulfur, and nitrogen on a series of transition metal oxide, sulfide, and nitride surfaces (Figure 2). We find that scaling relationhips also exist for these systems, which are considerably more complex than the transition-metal surfaces. Such a correlation between the adsorption energies of O and OH has previously been found for the MO_2 oxides.[12] Furthermore, it can be seen that the scaling constant $\gamma(x)$ is given to a good approximation by the same expression [Eq. (2)] as for adsorption on the transition metals. We find that the mean absolute error (MAE) is lower than 0.19 eV for all the species considered here. The nitride surfaces present a poorer correlation than the others, mainly because TiN(100) is a clear outlier.

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[**] The Center for Atomic-scale Materials Design is funded by the Lundbeck Foundation. We wish to acknowledge additional support from the Danish Research Agency through grant 26-04-0047 and the Danish Center for Scientific Computing through grant HDW-0107-07.

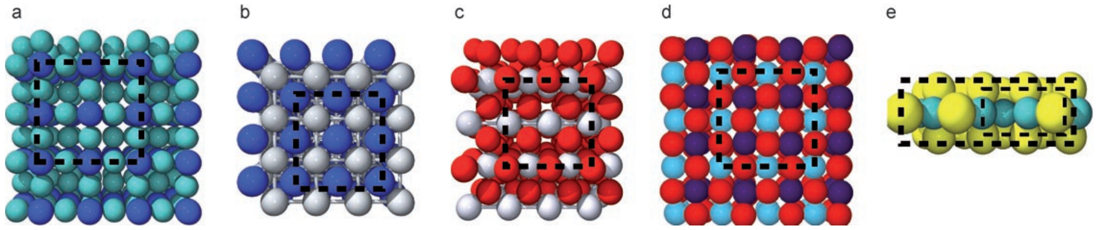

Figure 1. Structures used to describe the surfaces of the transition-metal nitrides, oxides and sulfides. a) Fcc-like structure for the M_2N (100) surface, M = Mo and W. Dark and light blue spheres represent metal and N atoms, respectively. b) Fcc-like rock-salt structure for the TiN (100) surface. Dark blue and gray spheres represent Ti and N atoms, respectively. c) Rutile-like (110) surface for the PtO_2 surface. Red and white spheres represent O and metal atoms, respectively. d) Perovskite structure for the $LaMO_3$ (100) surface, with M = Ti, Ni, Mn, Fe, and Co. Red, purple, and violet spheres represent O, La, and metal atoms, respectively. e) Hcp-like (−1010) surfaces for NbS_2, TaS_2, MoS_2, WS_2, Co-Mo-S, Ni-Mo-S, and Co-W-S. Yellow and green spheres represent S and metal atoms, respectively. The black dashed boxes indicate the unit cell.

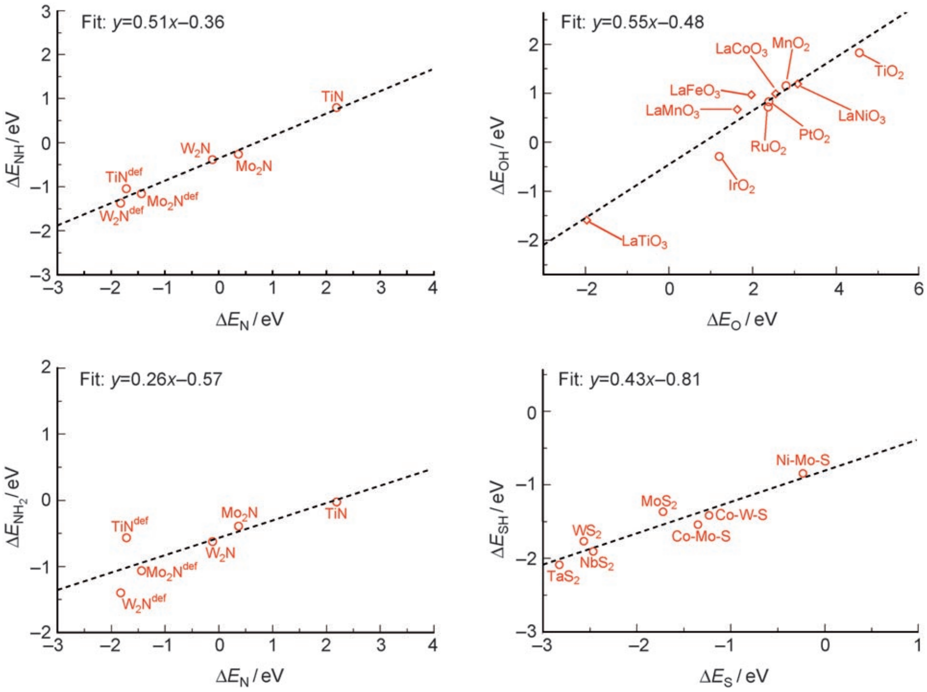

Figure 2. Adsorption energies of NH and NH_2 intermediates over nitrides, an OH intermediate over oxides, and an SH intermediate over sulfides plotted against adsorption energies of N over nitrides, O over oxides, and S over sulfides, respectively. The adsorption energy of AH_x is defined as: $\Delta E^{AH_x} = E(AH_x{*}) + (x_{max}-x)/2\,E(H_2) - E({*}) - E(AH_{x_{max}})$ where $E(AH_x{*})$ is the total energy of an AH_x intermediate adsorbed on the most stable adsorption site, $E({*})$ is the total energy of the surface without the A atom adsorbed, and $E(H_2)$ and $E(AH_{x_{max}})$ are the total energies of the hydrogen molecule and the $AH_{x_{max}}$ molecule in a vacuum, respectively.

It is interesting to compare the results of Figure 2 with the equivalent results for adsorption on the transition metals (Figure 3). It is found that the linear relationships for the nitrides are essentially the same for the two classes of systems. For the oxides, and partially for the sulfides, the results for the compounds are shifted from those on the transition metals. We trace this difference to a difference in the adsorption sites on the two kinds of systems. On the transition-metal surfaces, O and OH are generally found to coordinate with more than one metal neighbor. On the other hand, on the oxide surfaces the O atoms are generally coordinated to a single metal atom. If we use the adsorption energies for O and OH on the transition metals, where they are forced to adsorb in an on-top manner, the results now fall on the same line as for the oxides (Figure 3). For the sulfides, the S atom also adsorbs at a different site than on the transition metal. If the same adsorption site on the metal is considered the data agree, as for the oxides, with the results obtained for adsorption onto the sulfide surface.

The results of Figures 2 and 3 are remarkable and indicate that the nature of the adsorption bond is similar for the transition metals and the compounds. For the transition-metal surfaces, the scaling relationships can be understood within the d-band model.[34–39] The variation in adsorption energies for a given atom or molecule among the transition metals is mainly given by the variations in the strength of the coupling of the valence states of the adsorbate with the d states of the transition metal. The variations in the adsorption energy of an atom A from one transition-metal surface to the next reflect this. If H atoms are now added to atom A, the ability of A to couple to the metal d states decreases, either because the modified A states can couple to fewer d states or because the bonds become longer.[31] The principle of bond-order conservation would indicate that the weakening of the bond strength is proportional to the number of H atoms added, which corresponds to Equation (2).[31] The scaling behavior observed in Figures 2 and 3 indicates that similar arguments should hold for adsorption on transition-metal oxides, sulfides, and nitrides. The key to understanding this can be found in recent work by Ruberto and Lundqvist,[40] in which they show that a suitably modified d-band model can be used to understand trends in adsorption energies on transition-metal carbides and nitrides.

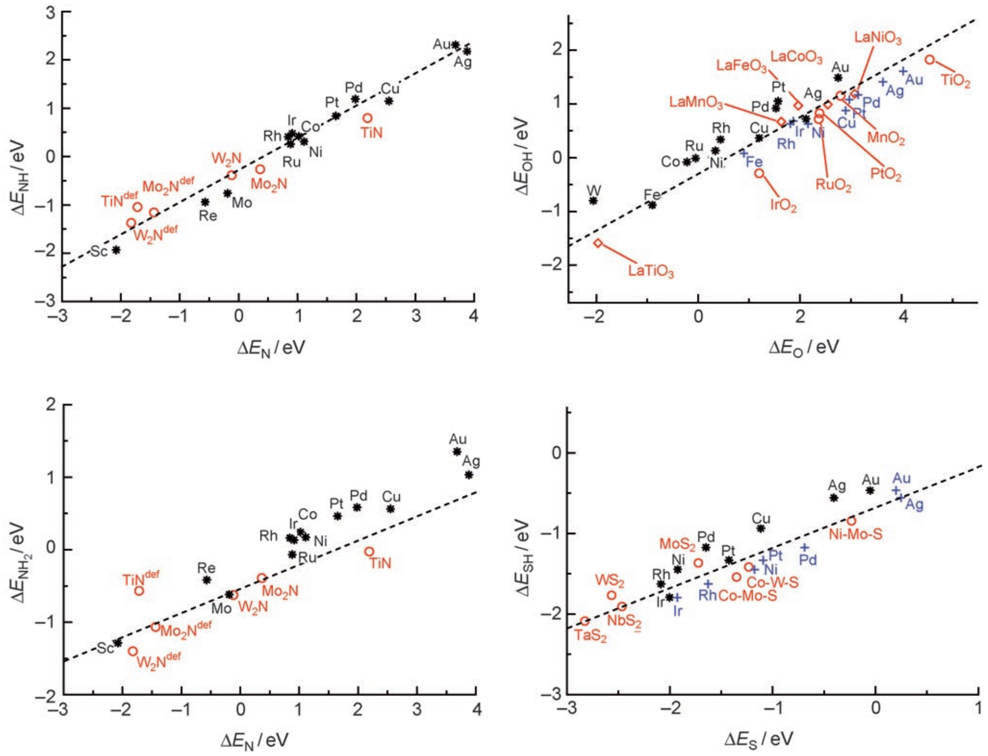

Figure 3. Adsorption energies of NH and NH_2 intermediates on transition metal nitride and transition-metal surfaces, the OH intermediate on transition metal oxide and transition metal surfaces, and the SH intermediate on transition metal sulfide and transition metal surfaces are plotted against the adsorption energies of N, O, and S, respectively. Close-packed surfaces for NH_x and OH_x intermediates, and the stepped surface for SH_x intermediates are considered. The adsorption energies for the OH intermediate on a top site and S intermediates on a bridge site over transition metal centers are included (blue points). The dashed line is the slope $\gamma(x)$ obtained from Equation (2).

The strength of the scaling relationships is shown by the following example. If one has a calculated or an experimental adsorption energy of an adsorbate AH_x ($\Delta E^{AH_x}_{M1}$) for one transition metal or transition-metal compound M1, we can estimate the energy $\Delta E^{AH_x}_{M2}$ of the same intermediate on another system M2 from the adsorption energies of atom A on the two systems, by using Equation (3).

$$\Delta E^{AH_x}_{M2} = \Delta E^{AH_x}_{M1} + \gamma(x)(\Delta E^{A}_{M2} - \Delta E^{A}_{M1}) \qquad (3)$$

$\gamma(x)$ is a rational number given by Equation (2). If we have a database of atomic adsorption energies for a number of systems, we may then estimate the adsorption energy of a number of intermediates. This opens the possibility of obtaining an overview of adsorption energies on oxides, sulfides, and nitride surfaces on the basis of a few calculations.

In summary, density functional theory calculations on the adsorption of O, OH, S, SH, N, NH, and NH_2 on a range of transition metal oxide, sulfide, and nitride surfaces have been presented. It is shown that the adsorption energies ΔE^{AH_x} of AH_x intermediates scale with the adsorption energies ΔE^{A} of the A atoms according to the equation $\Delta E^{AH_x} = \gamma(x)\Delta E^{A} + \xi$, where the proportionality constant $\gamma(x)$ is independent of the metal and only depends on the number of H atoms in the molecule.

Experimental Section

The results presented herein were calculated using self-consistent DFT. The ionic cores and their interaction with the valence electrons are described by ultrasoft pseudopotentials (soft pseudopotential for S),[41] and the valence wave functions are expanded in a basis set of plane waves with a kinetic energy cut-off of 350–400 eV. The electron density of the valence states was obtained by a self-consistent iterative diagonalization of the Kohn–Sham Hamiltonian with Pulay mixing of the densities.[42] The occupation of the one-electron states was calculated using an electronic temperature of $k_B T = 0.1$ eV (0.01 eV for the molecules in a vacuum); all energies were extrapolated to $T = 0$ K. The ionic degrees of freedom were relaxed using the quasi-Newton minimization scheme, until the maximum force component was smaller than 0.05 eV Å^{-1}. Spin magnetic moments for the oxides, Co-Mo-S, Ni-Mo-S, and Co-W-S were taken into account. Exchange and correlation effects are described using the RPBE[32] GGA functional.

We used the periodic slab approximation, and the unit cells considered were modeled by a (2×2) unit cell for the nitrides and perovskite-type oxides, a (2×1) unit cell for PtO_2, a (2×1) unit cell for Co-W-S and MS_2 surfaces with M = Mo, Nb, Ta, and W, and a (4×1) unit cell for the M-Mo-S surface with M = Ni and Co. A four-layer slab for the nitrides and perovskite-type oxides, a four trilayer slab for PtO_2-type oxides, and an 8 or 12 layer slab for sulfides were employed in the calculations. Neighboring slabs were separated by more than 10 Å of vacuum. The results for the MO_2 surfaces with M = Ir, Mn, Ru, and Ti are taken from Refs. [12,15] The adsorbate together with the two topmost layers for the nitrides and perovskite-type oxides, the two topmost trilayers for MO_2 oxides, and all layers for the sulfides were allowed to fully relax. The Brillouin zone of the systems was sampled with a $4\times4\times1$ Monkhorst-Pack grid for the nitride and oxide surfaces and with a $6\times1\times1$ $(4\times1\times1)$ grid for the 2×1 (4×1) supercell of the sulfide surfaces.

Received: December 14, 2007
Revised: March 28, 2008

Keywords: adsorption · density functional calculations · surface chemistry · transition metals

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