Establishing and Understanding Adsorption−Energy Scaling Relations with Negative Slopes

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Abstract: Adsorption−energy scaling relations are widely used for catalyst design. To date, only linear scaling relations are known where slopes are positive. Considering adsorption energies of F, O, N, C, and B on transition metals, we show for the first time that scaling relations with negative slopes also exist between certain adsorbates[1]. Conventional scaling relations are formed between adsorbates such as F, O, etc, which create ionic-like bonds with surfaces. Conversely, anomalous relations are established between those and covalently bound adsorbates such as B. This widens the theory of adsorption−energy scaling relations and opens new avenues in physical chemistry and catalysis.

Keywords: Adsorption−energy scaling relations, Ionic adsorption bond, Covalent adsorption bond.

1. Introduction

It is widely accepted that the adsorption properties of transition-metal surfaces are determined by their geometric and electronic structures. Such extended agreement came after numerous works reporting correlations between structural parameters, adsorption energies, and catalytic activities.[2] Those "structure−energy" relations are complemented by a variety of "energy−energy" relations, such as Brønsted−Evans−Polanyi relations, bulk−surface relations, and adsorption−energy scaling relations,[3] which have enormously facilitated the in silico design of new materials because of their simplicity. The adsorption energies of species 2 scale with those of species 1 as follows

$$\Delta E_1 = m\ \Delta E_2 + b \qquad (1)$$

where b is a constant that depends on surface coordination. So far, m has always been found to be positive, as in some approaches it is estimated as the ratio between the lack of bonds of species 1 and 2 to reach the octet or as the ratio of the bond orders in other approaches. Analyzing the density functional theory (DFT) adsorption energies of F, O, N, C, and B on the close-packed surfaces of 4d and 5d transition metals, we will show that negative slopes are possible in scaling relations. This intriguing phenomenon is related to significant differences in the metal−adsorbate bonds made by species 1 and 2 in eq 1.

2. Theoretical

All adsorption energies (ΔE_{ADS}) were calculated using VASP with PBE.[4] (2 × 2) 5-layer (111), (0001), and (110) slabs for fcc, hcp, and bcc transition metals were used, separated by 15 Å of vacuum. The two bottommost layers were fixed at the bulk distances, and the three topmost layers and the adsorbates were fully relaxed. The Brillouin zones were sampled with 5 × 5 × 1 Monkhorst−Pack grids. The plane-wave cutoff was 400 eV. ΔE_{ADS} was calculated using the most stable adsorption configurations relative to the clean surfaces and the isolated atoms.

3. Results and discussion

Figure 1 shows the scaling relations between the most stable adsorption energies of N and the other adsorbates under study on the closest-packed surfaces of 4d and 5d metals. While the scaling between F, O, C, and N is normal ($m > 0$), B and N exhibit an atypical negative slope. Hence Figure 1 raises an important question: How can one rationalize negative slopes in adsorption−energy scaling relations?

We resort to the qualitative explanations of molecular-orbital theory.[4] The interaction between adsorbate A and metal M can be classified in the four categories in Figure 2a−d. If the orbital energy levels of A and M are largely different (Figure 2a), then the interaction is ionic. As the energy-level difference between A and M decreases (Figure 2b), covalent interactions are strengthened. However, the bonding is still mainly ionic, corresponding to the interaction between transition metals and electronegative atoms (e.g., F, O). The differential charge density maps (Figure 2e) show considerable charge withdrawal from Zr or Rh by F and O, indicative of mostly ionic bonds. When the energy-level difference decreases (Figure 2c), the orbital mix is larger, leading to stronger covalent interactions. This is the case of bonds between transition metals and less electronegative atoms (e.g., B). Figure 2e shows that considerable charge builds up between Zr or Rh and B, meaning that their bonds are largely covalent. For N and C, both ionic and covalent bonding contribute significantly. Finally, for A and M at the same energy level, the orbital mixture is maximal and the bonding is purely covalent (Figure 2d).

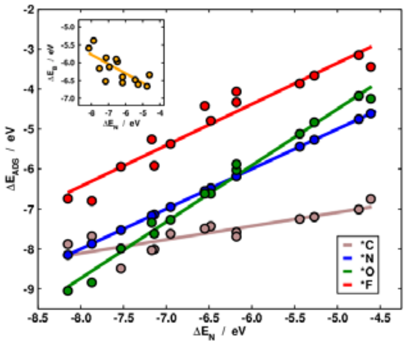

Figure 1. Normal scaling relations between the adsorption energies (ΔE_{ADS}) of N and F, O and C. Inset: anomalous scaling relationship between ΔE_B and ΔE_N.

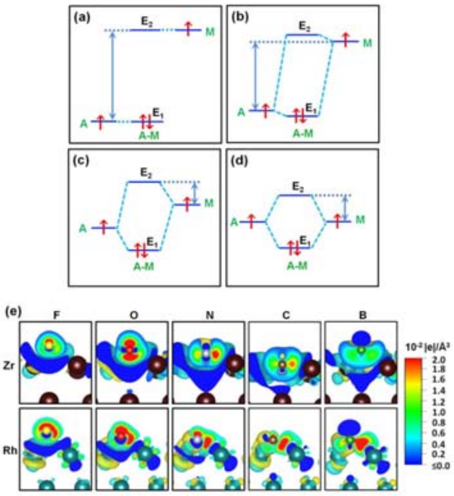

Figure 2. (a-d) Interactions between adsorbate A and metal M based on Hoffmann's model. (e) Differential charge density map for F, O, N, C, and B adsorption on Zr(0001) and Rh(111). Blue and yellow-red isosurfaces indicate charge depletion and accumulation. The 2D profile is a cut along a Rh/Zr–adsorbate bond.

4. Conclusions

In conclusion, classifying metal−adsorbate bonds into ionic and covalent helps rationalize conventional and unconventional adsorption-energy scaling relations. Conventional relations are observed between highly electronegative adsorbates such as F, O, N, and C. The covalence of B-metal bonds introduces negative slopes in its scaling relations with those adsorbates. These results and others widen the state of the art in scaling relations and open new avenues, for instance, in the design of better catalysts for direct borohydride fuel cells.

References

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