A TOPOLOGICAL MODEL FOR THE ADSORPTION OF POLYCYCLIC AROMATIC HYDROCARBONS ON LATE-TRANSITION METAL SURFACES

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Abstract

We introduce and validate by first-principles calculations an analogy between metal coordination chemistry and the adsorption of polycyclic aromatic hydrocarbons (PAHs) at metal surfaces for the derivation of a model for predicting the PAH adsorption energies. We find that the adsorption energies of PAHs depend only on topological parameters including the number of metal-PAH bond and the number of rings. Moreover, when the lattice of the metal surface is commensurate with the size of benzene rings, the contribution to the adsorption energy from η^2-coordination is about twice of that from η^1-coordination. This is in analogy with the formation enthalpy of the metal-organic complex that is only determined by the number atoms bound to the metal atom. This work provides a deep understanding of PAH adsorption, and therefore facilitates the modeling of the processes involving carbonaceous species at metal surfaces.

Keywords

PAH, TOPOLOGICAL ADSORPTION ENERGY MODEL, METAL-ORGANIC COMPLEX

Introduction

Understanding the kinetics of polycyclic aromatic hydrocarbons (PAH) formation on metal surfaces is of utmost importance for controlling both the coke formation and the graphene growth. The first key step to model the kinetics of PAH formation is to systematically investigate the general adsorption mechanism of PAHs on metal surfaces. Screening the adsorption of a full set of PAHs on different surfaces is significantly hindered by both the broad variety of PAH structures and the adsorption configurations, which makes the first-principles investigation unaffordable. To overcome this complexity, here we propose an approach to systematically model the adsorption of PAH on metal surfaces on the basis of the topology of the adsorbed molecule (Ding, et al., 2018). Our model makes use of an analogy between the metal-organic compound interaction in both the metalorganic complex and the surface adsorption,

such as the same π-back-donation mechanism in both ferrocene and the cyclopentadienyl on Pt(111) (Avery, 1984). Here systematic density functional theory (DFT) investigation on the adsorption of five selected PAHs on four close-packed metal surfaces is performed to validate such analogy and the model. Our findings allow for describing the PAH adsorption only on the basis of the topological features of PAHs, and then they significantly facilitate modeling the kinetics of the processes that involve complex aromatic adsorbates on surfaces.

Models and Methods

Benzene, naphthalene, tetracene, phenanthrene and pyrene adsorbed in different configurations on Ni(111), Rh(111), Pd(111) and Pt(111) surfaces are calculated using

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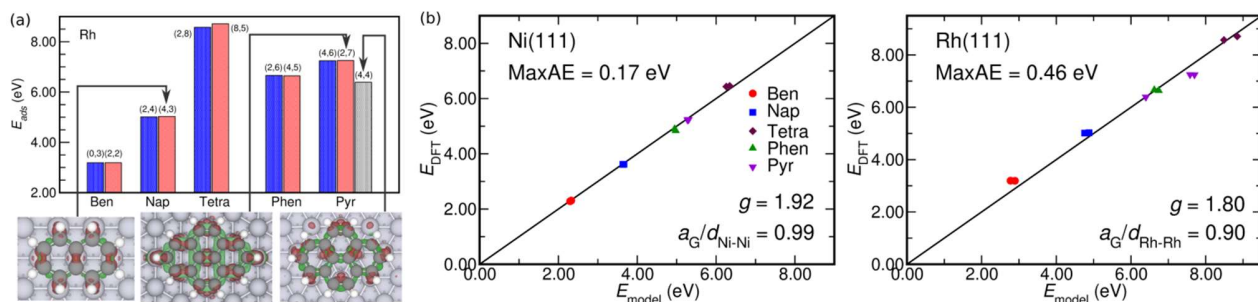
Figure 1 a) Adsorption energies of all PAHs on Rh(111) surfaces, and the charge density difference maps of selected PAHs on Rh(111) surface. The darker region around the bound metal atoms show the electron gaining, and the lighter region all over the rings show the electron depletion. b) Accuracy of adsorption energy estimated by Eq.(1).

Perdew-Burke-Ernzerhof (PBE) functionals with introducing van der Waals interaction by using Grimme D2 correction (Grimme, 2006). A tight force threshold, 2.57×10^{-3} eV/Å, is applied to guarantee the identification of true local minima on the relatively flat potential energy surface. All the calculations are performed using Quantum Espresso.

Results and Discussion

Figure 1a listed the adsorption energy of PAHs on Rh(111) surfaces. We find that the adsorption energy monotonically increases along with the number of metal-bound carbon atoms. Such correlation is explained by analyzing the electron redistribution by adsorbing PAH on Rh(111) surfaces which are plotted in Figure 1a. We observe that for all the PAHs, electron gain is always related to the metal-carbon (M-C) chemical bonding (η^n denotes the number of C atoms coordinate with a metal atom), and electron on the PAH rings always depletes Therefore, the formation of more M-C bonds induces a larger electron transfer from the orbitals on the PAH to the metal-PAH bond, thus strengthens the adsorption. Such bonding mechanism is analogous to the orbital interactions between the metal atom and the C=C bond in metal-alkene complexes (Dewar, 1951). Because of such analogy, inspired by the fact that the formation enthalpy of the metal-organic complex is only determined by the number of metal-ligand bonds (Spike and Parry., 1953), here we propose a model to relate the adsorption energy of PAHs to the topology of the PAH-metal binding (namely the number of η^1 coordinations (n_1) and the number of η^2 coordinations (n_2)). The model can be expressed as:

$$E_{bind} = E_{Ph} n_{Ph} + E_{M-C} n_1 + g E_{M-C} n_2 \qquad (1)$$

where E_{M-C} is the contribution from each η^1 M-C bond, n_{ph} is the number of the rings on PAH and E_{ph} is the energy contribution of the non-chemical interaction between the rings and the metal from each ring. Figure 1b shows that this model well describes the adsorption energies of all the PAHs on each M(111) surfaces with the linear correlation

coefficients all higher than 0.99. Furthermore, Figure 1b makes it evident that the ratio between the adsorption energy contributions from each η^2 M-C bond and that from each η^1 M-C bond, g, approaches to 2 when the lattice mismatch between the aromatic rings and the metal surface decreases. This indicates that the adsorption energy of PAH is only determined by its topological feature of adsorption, which further confirms the analogy between the formation enthalpy of the metal-organic complex and the adsorption energy of PAH.

Conclusions

A topological model for predicting adsorption energies of PAHs on transition-metal surfaces is proposed based on the analogy in the coordination mechanism of both the metal-organic complex and the PAH adsorptions. This model lays a foundation of both describing adsorption of more complex aromatic molecules and investigating thermodynamic properties of PAH adsorption. As such, this approach paves the way to systematically model the kinetics of surface processes that involve carbonaceous species.

Acknowledgment

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