

Supporting Information for *Acta Phys. -Chim. Sin.* 2017, 33 (7), 1310–1323

doi: 10.3866/PKU.WHXB201704172

镍族金属团簇在催化加氢过程中的应用

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Nickel Family Metal Clusters for Catalytic Hydrogenation Processes

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Computational methods

All calculations were carried out using density functional theory (DFT) with the Perdew and Wang (PW91) exchange-correlation functional¹ as implemented in the DMol³ package². The valence electrons were modeled by a double numerical basis set augmented with polarization functions (DNP), while the core electrons were treated by an effective core pseudopotential (ECP). To deal with the electronically open-shell situations of d orbitals of metals clusters, a spin-polarized scheme was employed with the formal spin as initial. Charge transfer was calculated using the Hirshfeld population scheme.³ These parameters and basis set have shown to be capable of describing transition metal clusters with sufficient accuracy.

Before analysis, all structures were fully optimized without symmetry constraints. In most cases, the ground state structure was identified by comparing at least 3 isomer configurations to locate the global energy minimum. The linear synchronous transit (LST) in combination with quadratic synchronous transit (QST) method was utilized to locate the transition state (TS) structure for H₂ dissociation on TMCs.⁴ The energy tolerance was set to be 1.0×10^{-5} Ha. The TS configuration was further confirmed by normal mode analysis that only one imaginary frequency was identified to connect reactant and product.

The binding energy of metal cluster is evaluated by $E_{\text{bind}} = -[E(M_n) - nE(M)]/n$, where $E(M_n)$, $E(M)$ and n represents the energy of metal cluster, energy of metal atom, and number of metal atoms, respectively. For the metal hydrides, the H₂ dissociative chemisorption energy ΔE_{CE} and the H sequential desorption energy ΔE_{DE} are defined by $\Delta E_{\text{CE}} = -[E(M_n\text{H}_{2x}) - E(M_n) - xE(\text{H}_2)]/x$ and $\Delta E_{\text{DE}} = -[E(M_n\text{H}_{2x}) - E(M_n\text{H}_{2x-2}) - 2E(\text{H})]/2$, respectively, where x is the number of H₂ molecules. $E(M_n\text{H}_{2x})$ and $E(M_n\text{H}_{2x-2})$ are the total energy of metal hydrides with different H atom loading. $E(\text{H}_2)$ and $E(\text{H})$ represent the energy of H₂ molecule and H atom, respectively.

To determine the H capacity on metal clusters, *ab initio* molecular dynamics (MD) simulations were conducted at room temperature (300 K) to ensure that all H atoms are stably chemisorbed. The MD simulations were performed for 2 ps with a time step of 1 fs in a NVT canonical ensemble using the Nosé-Hoover thermostat. The H-H distance distribution function $g(r)$ is obtained by tabulating all the H-H distances at each step of the MD trajectories excluding the initial 500 steps to identify the fully saturation of H on metal clusters. An excess of H atoms on the cluster would generally results in recombination of surface H atoms into H₂ molecules, leading to the emergence of a peak around 0.75 Å in the $g(r)$.

References

- (1) Perdew, J. P.; Wang, Y. *Phys. Rev. B* **1992**, *45*, 13244.
- (2) Delley, B. *J. Chem. Phys.* **2000**, *113*, 7756. doi: 10.1063/1.1316015
- (3) Hirshfeld, F. L. *Theor. Chim. Acta* **1977**, *44*, 129. doi: 10.1007/bf00549096
- (4) Halgren, T. A.; Lipscomb, W. N. *Chem. Phys. Lett.* **1977**, *49*, 225. doi: 10.1016/0009-2614(77)80574-5