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镍族金属团簇在催化加氢过程中的应用

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摘要: 贵金属纳米颗粒具有优异的催化活性, 是异相催化反应中的重要角色。作为一种理想的研究模型, 气相金属团簇被广泛应用于在原子和分子尺度探究催化反应的机理。在本专论中, 我们将本课题组近年来关于氢气在镍族金属团簇上的解离吸附进行了回顾。首先, 我们对比了不同金属团簇的结构演化规律和相对稳定性。随后, 我们系统研究了H₂分子在金属团簇上的解离吸附行为, 揭示了不同金属对H—H键的解离能力。为了表征不同金属团簇的催化活性, 我们定义了两个关键参数: 氢气的解离吸附能(ΔE_{CE})和H原子的连续脱附能(ΔE_{DE})。结果显示, 随着H覆盖度的增大, ΔE_{CE} 和 ΔE_{DE} 都呈现显著的下降。由于在实际的催化反应中, 氢气总是维持在一定的分压下, 这就意味着催化剂金属应该总是处于较高的H覆盖度下。因此, 通过处于H饱和状态下的 ΔE_{CE} 和 ΔE_{DE} 来评估金属团簇的催化能力是合理可行的。我们发现, 在饱和H吸附状态下, 每一个Pt原子可以容纳4个H原子, 而每一个Pd或Ni原子则只能吸附2个H原子。考虑到H原子在这些团簇上的脱附能力相当, Pt团簇相对较高的H吸附量将极大提高其在加氢过程中的催化活性。最后, 我们系统研究了带电状态对Pt团簇催化性能的影响规律。结果显示, 在H覆盖度较低时, H₂分子的解离以及H原子的脱附过程受Pt团簇带电状态的影响较大。在饱和H吸附时, 由于大量H原子的吸附, 电荷的影响被平均化到每个Pt—H键上, 导致 ΔE_{CE} 和 ΔE_{DE} 都收敛到一个非常小的区域。此外, 当团簇的尺寸增大时, 其所带的电荷被大量的Pt原子分摊, 每个Pt原子仅携带极少的电荷, 使得电荷的影响已经可以忽略。

关键词: 团簇; 过渡金属; 催化加氢; 饱和氢吸附; 带电状态; 密度泛函理论

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Nickel Family Metal Clusters for Catalytic Hydrogenation Processes

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Abstract: Nanoparticles of precious metals play an important role in many heterogeneous catalytic reactions due to their excellent catalytic performance. As an idealized model, gas phase metal clusters have been extensively utilized to understand catalytic mechanisms at a molecular level. Here we provide an overview of our recent studies on H₂ dissociative chemisorption on nickel family clusters. The structure evolution and the stability of the metal clusters were first compared. H₂ dissociation on the clusters was then carefully addressed to understand the capability of metal clusters to break the H-H bond. Two key parameters, the dissociative chemisorption energy (ΔE_{CE}) and the H sequential desorption energy (ΔE_{DE}),

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were employed to characterize the catalytic activity of metal clusters. Our results show that both ΔE_{CE} and ΔE_{DE} decline significantly as the H coverage increases. Since the catalyst is in general covered entirely by H atoms and H_2 molecules in a typical hydrogenation process, and maintained at a pre-determined pressure of H_2 gas, we can rationally use the calculated ΔE_{CE} and ΔE_{DE} values at full H saturation to address the activity of metal clusters. Our results suggest that at full H coverage, each Pt atom is essentially capable of adsorbing 4 H atoms, while each Ni or Pd atom can only accommodate 2 H atoms. Considering the similar values of H desorption energies on Pt and Pd clusters, the higher average H capacity per Pt atom could probably lead to a faster reaction rate because more active H atoms are produced on the Pt catalyst particles in the hydrogenation process. Finally, the charge sensitivity of the key catalytic properties of Pt clusters for hydrogenation was systematically evaluated. The results show that the dissociation of H_2 and H desorption are strongly correlated to the charge state of the Pt clusters at low H coverage. However, at high H-capacities, both ΔE_{CE} and ΔE_{DE} fall into a narrow range, suggesting that the charge can be readily dispersed and that the Pt–H bonds average the interaction between clusters and H atoms. As a result, the H-capacities on charged clusters were found to be similar as the cluster size increased; in case of sufficiently large clusters, the reactivity of a fully saturated cluster was no longer sensitive to its charge state.

Key Words: Clusters; Transition metal; Catalytic hydrogenation; Full H saturation; Charge state; Density functional theory

1 Introduction

Catalytic hydrogenation on transition metal catalysts is of great industrial interest and has been extensively used in petrochemical, agrochemical and pharmaceutical processes¹. Design and development of catalysts for effective hydrogenation of olefins under mild conditions has been a subject of intensive studies in the past few decades^{2–4}. Nickel family metals, in particular, are among the most important catalysts used in many industrial processes due to their unique catalytic activity and selectivity^{5–7}. In a typical catalytic hydrogenation process, H_2 molecules initially undergo dissociation on catalyst surfaces to form metal hydride followed by H atom desorption to attack target molecules. Therefore, the dissociative adsorption energy of H_2 (ΔE_{CE}) and the desorption energy of H atom (ΔE_{DE}) are the two most important chemical properties that dictate catalytic activity of a metal catalyst. In order to develop highly efficient and low-cost catalysts for hydrogenation, tremendous efforts have been made to understand the mechanisms of the catalytic processes on

nickel family metal surfaces^{8–13}. Experimentally, the ΔE_{CE} value on Pt(111) surface was found to be in the range between 0.70 and 0.83 eV^{14,15}. Theoretically, the calculated ΔE_{CE} on the Pt(111) surface falls in the range of 0.80 to 1.54 eV, significantly higher than the experimental values^{16–18}. For Pd(111) surface, the ΔE_{CE} was found to be much lower than the value on Pt(111) and the diffusion energies and dissociation barriers of H_2 on Pd(111) were correlated to the H_2 coverage on the substrate^{19–21}.

Since nano-sized particles are chemically more active than bulk-sized catalyst of the same element, these metal catalysts are often dispersed in a form of nanoparticles or clusters on various support materials^{22–30}. Generally, compared with the bulk form, small size metal clusters exhibit quite different physicochemical properties. The catalyst particles have more edges and corners that are responsible for catalytic reactions. Liu *et al.*^{31–33} reported a significantly enhanced H_2 chemisorption energy of 1.36 eV on a NaY zeolite supported Pt_{13} cluster³⁴. Similar results have also been reported by

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Okamoto *via* DFT calculations^{35,36}. Besides the relatively high adsorption energies of H₂ on transition metal clusters (TMCs), the desorption energies of atomic hydrogen adsorbed on the TMCs were also found to be much higher than the value on crystal surfaces. For instance, the H desorption on Pt(111) surface was found to be 2.60–2.65 eV^{37–39}. However, the desorption energy was found to increase substantially to 2.9–4.5 eV when the H atom is adsorbed on a Pt₁₃ cluster⁴⁰.

In addition to the size effect of catalyst particles, H₂ adsorption and H desorption properties are also dependent on surface coverage, which profoundly influences the catalytic activity of TMCs. Indeed, there is a significant variation on catalytic performance of metal clusters at different H loadings. Generally, at low surface coverage, H₂ dissociative chemisorption produces a strong adsorption energy, which declines gradually as coverage increases¹³. In a practical hydrogenation process, a partial pressure of hydrogen is always maintained. Therefore, surfaces of a catalyst are nearly fully saturated by the dissociated H atoms. Much attention has been paid to catalytic performance at low H coverage, relatively scarce theoretical studies on catalysis at high H coverage on TMCs have been conducted. On the other hand, a wide variety of gas phase neutral, anionic, and cationic metal clusters has been produced using techniques such as pulsed laser ablation^{41–43} and time-of flight apparatus of supersonic beams *via* electron attachment or ionization^{44–47}. It was found that there are significant differences in physicochemical properties between neutral and charged clusters. A recent combined theoretical and experimental study⁴⁸ on hydrogen dissociative chemisorption on small platinum clusters further showed that the number of hydrogen molecules adsorbed dissociatively on a cationic Pt cluster is significantly smaller than on a neutral cluster of the same size^{13,49,50}.

In this paper, we present our recent first principles studies on H₂ dissociative chemisorption on a series of nickel family metal clusters M_n (M = Ni, Pd, Pt; *n* = 2–9, 13) to address their catalytic performances. The influences of H surface coverage, metal type, and charge state of clusters on catalytic hydrogenation are systematically discussed. The results are also validated by available experimental data. The purpose of the present report is to provide useful insight into the atomistic details of the chemical processes from the electronic structure calculations.

2 Gas phase TMCs

For nickel family clusters, the stable structure and growth pathway from small cluster to bulk could undergo three typical patterns, including the close-packed pattern, the icosahedral pattern and the fcc-like pattern^{8,51,52}. Take a Pd cluster as an example. The optimized structures and the associated binding energies of Pd_n clusters (*n* = 2–15) are summarized in Fig.1, where the structures of the isomers are also included. The Pd clusters adopt a close-packed planar configuration before

tetramer, after which a 3-dimensional (3D) configuration is energetically preferred. From Pd₄ to Pd₇, the clusters exhibit bipyramid configurations with elongated Pd-Pd bond distances and higher binding energies. A previous DFT study based on a tight-binding model⁵³ suggested that the most stable structure of Pd₇ is planar (Pd₇-c), which is much less favorable than the bipyramid configuration in our calculation. From Pd₈, only slight deviation on the binding energies between different isomers is observed, suggesting that these close-packed isomers may coexist thermodynamically. Li *et al.*⁵⁴ suggested that the Pd₇ and Pd₈ should adopt a more symmetric configuration (i.e. Pd₇-b and Pd₈-d). However, our results indicate that the close-packed structure is energetically more stable. In particular, Pd₁₃-b exhibits a typical icosahedral configuration with the calculated binding energy of 2.337 eV, nearly degenerated with that of Pd₁₃-a, which adopts a close-packed pattern.

A similar growth path for Pt_n clusters to what is observed for Pd_n clusters is shown in Fig.2(a), where the associated binding energy and geometric parameters are also included. Interestingly, the Pt₆ prefers a 2-dimensional (2D) planar configuration, while Pt₄ and Pt₅ adopt a 3D close-packed pattern, in line with the results reported by Kadioglu *et al.*⁵⁵. In addition to the 2D equilateral triangular structure, we also obtained an octahedral structure for Pt₆ whose average binding energy of 2.886 eV is only slightly smaller than that of the equilateral structure (2.941 eV). It is possible that both geometries may exist for this cluster. For Ni clusters, the calculated lowest energy cluster of a given size exhibits similar structural characteristics to the same size of Pt and Pd clusters and the Ni clusters undergo a similar triangular growth pathway (Fig.2(b)).

To understand the relative stability of the clusters, the structures and binding energies of Ni_n, Pd_n and Pt_n are systematically compared, as shown in Fig.3. We note that the Ni–Ni bond lengths fall into a narrow range between 2.35 and 2.45 Å (1 Å = 10^{–10} m), which is relatively short due to the small size of nickel atom. However, the Pd clusters exhibit the longest bond lengths, although its atomic size is smaller than Pt. The long Pd–Pd distances give rise to the more relaxed packing configurations of Pd clusters, leading to weak binding strengths. Indeed, the calculated binding energies of the Pd clusters are much lower than the values of the corresponding Pt clusters which display the strongest bind strengths. The average binding energy increases with the cluster size monotonically. For the same cluster size, the binding strength of the Ni cluster is similar to that of the Pd cluster but smaller than that of the Pt cluster. The relative binding strength of small clusters shown in Fig.3 is consistent with the trend of the cohesive energies of the bulk Ni, Pd and Pt solids.

3 H₂ adsorption and dissociation on TMCs

Fig.1 Optimized structures for Pd_n clusters ($n = 2-15$)⁵².

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We next focus on the sequential H_2 dissociative chemisorption on the lowest energy TMCs. Fig.4 displays the H_2 dissociative process on the Pt_2 cluster¹³. The H_2 molecule approaches the Pt_2 dimer from one end of the dimer axis with the Pt atom vertically toward the center of mass of H_2 to form a weakly bonded species (R). Subsequently, the R undergoes a transition state (TS1) with a small energy barrier of 0.05 eV that leads to decomposition of H_2 . The dissociative chemisorption leads to the formation of a T-shaped adsorption structure (P1) with the calculated exothermic reaction energy of -0.26 eV. The adsorbed H atom may diffuse to the other side of the dimer (P2) to further stabilize the adsorption structure with an energy barrier of 0.13 eV (TS2). Overall, the calculated chemisorption energy is 1.78 eV. The strong chemisorption arises from the orbital overlaps between the 1s orbital of H atoms and the 5d orbitals of Pt atoms, resulting in charge transfer from Pt 5d to H 1s. For large cluster (Pt_{13}), similar

reaction pathway was identified with the calculated activation barriers of 0.06 and 0.34 eV for TS1 and TS2, respectively. Recently, Ignatov *et al.*⁵⁶ reported the adsorption behavior of H_2 on a Pt_{24} subnanoparticle, where the dissociation of H_2 and migration of H atom were also found kinetically favorable with moderate activation barriers (less than 0.2 eV). In fact, for Ni ⁸ and Pd ¹² clusters (Fig.5), the dissociation process is essentially barrierless, similar to the situation of H_2 dissociation on Pt clusters⁵⁷. The calculated H_2 adsorption energy on a Ni_6 cluster is 1.31 eV, slightly higher than the value on Pd_6 (1.16 eV) but considerably lower than on Pt_6 (1.61 eV). The H migration on Ni_6 requires only 0.19 eV activation energy, which is slightly higher than that on Pd_6 (0.11 eV) but slightly lower than on Pt_6 (0.23 eV). The modest difference in the calculated H migration barriers among these clusters correlates well with the relative stability of H_2 adsorption on the clusters. Our calculations suggest that the H_2 dissociative chemisorption requires very

Fig.2 Optimized configurations of (a) Pt_n clusters and (b) Ni_n clusters ($n = 2-9, 13$).

The unit of the bond distance is Å ($1 \text{ Å} = 10^{-10} \text{ m}$).^{8,51} Adapted with permission from Springer-Verlag.

Fig.3 Comparison of the calculated bond length and binding energies of small Ni, Pd and Pt clusters.⁸

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Fig.5 Energy diagram of H₂ dissociation and diffusion on the Pd₆ octahedral cluster.

The unit of the bond distance is Å.¹² Adapted with permission from Royal Society of Chemistry.

Fig.4 Energy diagram of H₂ dissociative chemisorption and diffusion on the Pt₂ cluster.

The unit of the bond distance is Å.¹³

little activation energy and the adsorbed H atoms are highly mobile.

In general, H₂ dissociative chemisorption energy (ΔE_{CE}), H sequential desorption energy (ΔE_{DE}) and H capacity are the key

factors that dictate catalytic performance of TMCs. To understand the coverage effect on the values of ΔE_{CE} and ΔE_{DE} , sequential H₂ chemisorption on Pt clusters was simulated. For Pt₂, the calculated ΔE_{CE} and ΔE_{DE} are shown in Fig.6, (a1) and (b1), respectively. The Pt₂ cluster exhibits a relatively high H capacity up to 10 H atoms, after which additional two H atoms are recombined to form a H₂ molecule. Both ΔE_{CE} and ΔE_{DE} decrease as the number of H atoms on the cluster increases. Upon saturation, the calculated chemisorption energy is 1.1 eV, about 0.3–0.4 eV higher than the experimental value for H₂ on the Pt(111) surface¹⁶. It is interesting to note that the value of H₂ dissociation energy ΔE_{CE} drops substantially from 1.78 eV at low coverage to 1.1 eV at full saturation, while the threshold H-desorption energy ΔE_{DE} at full coverage is about 0.6 eV lower than its value at low coverage. The amount of the calculated Hirshfeld charge transferred from Pt₂ to the H atoms (ΔQ) is shown in Fig.6(c1), which declines with the number of

Fig.6 Calculated (a) ΔE_{CE} , (b) ΔE_{DE} , and the loss of the Hirshfeld charges of Pt clusters with respect to H coverage¹³.

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H atoms. For the Pt_3 trimer, the calculated ΔE_{CE} , ΔE_{DE} , and ΔQ exhibit almost the same trends as for the Pt_2 dimer. The Pt_3 cluster can accommodate up to 12 H atoms. Substantial structural expansion as well as distortion of the triangular geometry of the cluster is observed upon hydrogen uptake.

To show the H_2 sequential adsorption on Pt clusters, the Pt_4 clusters with various H coverages were selected as a model system, as shown in Fig.7(a). The bare Pt_4 cluster adopts a tetrahedral configuration. Upon H loading, the cluster is distorted to a certain extent. Full saturation is realized at H capacity of 16. In contrast, loading 18 H atoms on the cluster would result in recombination of 2 H atoms to form H_2 molecule during *ab initio* MD simulations. It was observed from the MD trajectories that two H atoms are readily squeezed out from the cluster, forming a H_2 molecule that is subsequently bonded to the cluster *via* a weak interaction force. The calculated H—H bond distance distribution for Pt_4H_{16} and Pt_4H_{18} are shown in Fig.7(b). The smallest H-H distance for

Pt_4H_{16} is around 2.1 Å, indicating complete dissociation of H_2 molecules. In contrast, a peak around 0.75 Å corresponding to the formation of H_2 molecule was observed for Pt_4H_{18} . Once again, more charge flows from the Pt_4 cluster to H atoms as the H coverage increases (Fig.6(c)). or larger Pt_n ($n > 4$) clusters, the calculated ΔE_{CE} , ΔE_{DE} , and ΔQ exhibit similar features to what were found for smaller clusters (Fig.6). The general trend of these quantities is that they decline with the H coverage. However, while both ΔE_{CE} and ΔQ decrease monotonically with the number of H atoms, some fluctuation of ΔE_{DE} is observed. This is because H atoms first saturate the energetically most favorable sites. As these sites become filled, their stability decreases and the vacant sites begin to fill. The fluctuation of ΔE_{DE} is due to the difference in chemisorption energies at different adsorption sites near the saturation boundary. The full H saturation is determined by MD simulations with the same procedure as Pt_4 . We note that in all cases, the H_2 dissociative chemisorption energy fluctuates in

Fig.7 (a) Fully optimized structures of H_2 sequential dissociative chemisorption on a Pt_4 cluster; (b) calculated H-H distance distribution for Pt_4H_{16} and Pt_4H_{18} , respectively¹³.

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the range between 0.9 and 1.1 eV at the full saturation, slightly higher than the experimental value for the H_2 dissociative chemisorption on the Pt(111) surface at zero coverage by 0.2–0.3 eV. Similarly, the calculated threshold H sequential desorption energy varies in a narrow range of 2.45–2.60 eV, slightly smaller than the value for an isolated H atom on the Pt(111) surface reported in a previous study by Papoian and coworkers¹⁶. Fig.8 summarizes the calculated ΔE_{CE} and ΔE_{DE} at low and high H coverages. Both ΔE_{CE} and ΔE_{DE} are significantly reduced at high H coverage. For ΔE_{CE} , a large energy gap of 0.8 eV is observed between the low and high H coverages. Meanwhile, an energy gap of 0.5 eV is emerged in the calculated ΔE_{DE} . Our results suggest that both the H_2 dissociative chemisorption energy and H desorption energy on Pt clusters are strongly coverage dependent.

To identify the H capacity of Pt_n clusters at various size, the number of H atoms *versus* the size of clusters at full saturation is shown in Fig.9, where the optimized structures of Pt hydrides

Fig.8 Comparison of the calculated (a) ΔE_{CE} and (b) ΔE_{DE} on Pt clusters at low and full H coverages¹³.

Data collected from Ref.13.

Fig.9 (a) Number of H atoms adsorbed on Pt_n cluster at fully H coverage; (b) optimized structures of Pt hydrides¹³.

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are also included. It shows that the number of H atoms increases almost linearly with the size of clusters. We expect such a quasi-linear relationship would not hold for larger clusters since only the surface Pt atoms are accessible for H_2 .

Fig.10 Optimized structures of Pd_n and Ni_n clusters at full H coverage^{8,12}.

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Nevertheless, the catalytic efficiency of small clusters for H_2 dissociative chemisorption is still remarkable. The H-capacity could be revealed by the H : Metal ratio, which approximately gives an H:Pt ratio of 4 based on our results.

For Pd and Ni clusters, similar H_2 dissociation processes were simulated. Fig.10 shows the fully saturated hydrides of the selected Ni_n and Pd_n clusters. We note that, H atoms prefer the 2-fold edge sites on both Pd and Ni clusters. In contrast, the 1-fold on-top site is energetically more stable for Pt cluster (Fig.9(a)). Although most of the H atoms are located at the edge sites, some of the on-top sites are also populated for large clusters and at high H loadings, at which the edge sites become fully occupied. The H capacities of the selected Pt, Pd and Ni clusters are summarized in Fig.11(c). The results indicate that at a given size the maximum hydrogen capacity of a Ni cluster is virtually identical to that of the Pd cluster, despite the fact that the size of Pd cluster is considerably larger than Ni with the same metal atoms. Interestingly, the capacity of small Pd and Ni clusters to absorb H atoms is essentially half of what was found for Pt clusters, which not only have higher binding strengths with H atoms but also allow H atoms to reside at the on-top sites.

Fig.11(a) compares the calculated average H_2 dissociative chemisorption energies ($\Delta E_{\text{CE}}^{\text{T}}$) of Ni_n , Pd_n and Pt_n clusters at full saturation. Remarkably, they all vary in a small energy range between 0.6 and 1.0 eV regardless of the cluster size except for Pd_2 and Pd_3 , which exhibit considerably higher average H_2 dissociative chemisorption energies. The results imply that clusters of the three metal elements behave similarly in terms of dissociating H_2 molecules at full H coverage. The size-independence is largely due to the fact that the chemical bonding of the clusters evolves from metallic to covalent as H atoms are sequentially loaded up onto the clusters. As a

consequence, the chemical properties become localized and thus do not depend strongly on cluster size. We note that at typical catalytic hydrogenation conditions the metal catalysts are fully covered by H atoms since a given hydrogen pressure is always maintained. For a given catalyst quantity, smaller catalyst particles offer higher surface area exposed to the gas species. However, our results suggest that H_2 dissociative

Fig.11 Comparison on (a) the threshold of H_2 dissociative chemisorption energy, (b) the threshold of H desorption energy and (c) the maximum H-capacity of small Ni, Pd and Pt clusters⁸.

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chemisorption energies do not change significantly with particle size. This makes computational modeling of surface catalysis convenient because one could select a relatively small size cluster to represent catalyst particles. Similarly, we calculated H atom desorption energies ($\Delta E_{\text{DE}}^{\text{T}}$) at full H coverage of the metal clusters and the results are displayed in Fig.11(b). The desorption energy at full H coverage is an important physical quantity because it can serve as an indicator of catalytic activity. A small desorption energy indicates higher activity. For small Ni_n clusters, the H desorption energy varies in a range between 2.08 to 2.73 eV. The highest desorption energy is observed for Ni_{13} , sharply higher than the values of Pd_{13} and Pt_{13} . The results suggest that it is more difficult to pull H atoms out of the Ni catalyst than out of Pd and Pt catalysts. Fig.11(c) displays the calculated average H capacities of Ni_n , Pd_n and Pt_n clusters. Essentially, each Pt atom is capable of adsorbing 4 H atoms, while each Ni or Pd atom can only accommodate 2 H atoms. Pelzer *et al.*⁵⁸ reported a much higher H_2 uptake on small Pd_n clusters ($n < 5$), where each Pd atom could adsorb more than 4 H atoms. However, instead of dissociative chemisorption, most H_2 molecules were only physically attached on Pd atoms in there simulations. Considering the similar H desorption energies on the Pd_n and Pt_n clusters, the relatively high H capacity of Pt_n gives rise to a superior reaction rate since more active H atoms are provided with Pt catalyst particles in hydrogenation processes.

4 Charge effect

We next consider the charge effect on the catalytic activity of TMCs. It was reported that, charged clusters could exhibit significant differences in physicochemical properties, leading to substantial variation on catalytic performances^{59–62}. Indeed, these experimental observations have raised a fundamental question on whether a metal cluster in its charged state would maintain similar catalytic properties to the cluster in its charge-neutral form and, more profoundly, on whether clusters could indeed serve as a valid model for catalyst particles regardless of their charge states. Generally, metal catalysts used in practice are charge neutral, while metal clusters produced in spectroscopic experiments could be either cationic or anionic. Moreover, the charge state of a metal catalyst on a supporting material may also be affected by the interaction between the catalyst and the substrate *via* electron transfer, which in turn may influence the activity of the catalyst^{28,63,64}. Here, DFT calculations on selected Pt clusters (Pt_2 , Pt_4 , Pt_6 and Pt_8) were carried out to determine the impact of charges on the reactivity of catalysts through a systematic analysis of the key catalytic properties for hydrogenation, including ΔE_{CE} , ΔE_{DE} and H-capacity.

We first chose neutral Pt_4 , cationic Pt_4^+ and anionic Pt_4^- clusters as probes to identify the differences upon sequential H_2 dissociative chemisorption. A tetrahedral configuration with negligible structural deformation was observed for all bare Pt_4

clusters, regardless of their charge state. The average Pt–Pt bond distance is gradually elongated from 2.654 to 2.728 Å with respect to the enrichment of the electron density on Pt_4 . The calculated electron density difference of the neutral and charged states of Pt_4 and the *d*-band center of Pt clusters with various sizes and charges are shown in Fig.12. As expected, Pt_4^+ is most electron deficient, while Pt_4^- holds the highest electron density. The charge distribution on the clusters profoundly influences their capability on catalytic hydrogenation, in which the activity is highly correlated to the electron transfer from Pt to H_2 . Fig.12(b) reveals that the *d*-band center decreases gradually with the cluster size. In general, for a given cluster size, an anionic cluster exhibits a higher *d*-band center, while a cationic cluster displays a lower *d*-band center. However, the *d*-band center gradually converges as the cluster size increases, regardless of the charges on the clusters. Our results also suggest that the *d*-band center of large clusters becomes insensitive to the charge states.

To understand the influence of the charge state on catalytic dissociation of H_2 , minimal energy pathway calculations of H_2 dissociative chemisorption were carried out on the Pt_4^+ , Pt_4 and Pt_4^- clusters, respectively, and the results are shown in Fig.13. The associated energy profiles for the Pt_4^+ , Pt_4 and Pt_4^- clusters are compared in Fig.14. For the neutral Pt_4 , H_2 dissociation exhibits a reaction pathway similar to that of Pt_2 (Fig.4). Here, the H_2 molecule adsorbed on the atop-site of Pt_4 undergoes spontaneous dissociation, leading to two atomic H species adsorbed on the same Pt atom. Considering the high mobility of H atoms on TMCs, one H atom can easily diffuse to the bridge-site (P1) with a moderate activation barrier of 0.466 eV to further stabilize the hydride. The strong chemisorption is

Fig.12 (a) Calculated electron density difference of Pt_4^+ , Pt_4 and Pt_4^- ; (b) *d*-band center of the clusters with various sizes and charges⁶¹.

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Fig.13 Reaction pathway of H_2 activated by (a) the Pt_4 , (b) the Pt_4^+ and (c) the Pt_4^- cluster.

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Fig.14 Calculated energy diagram of H_2 molecule dissociative chemisorption on the Pt_4 clusters⁶¹.

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attributed to the large orbital overlap between the $1s$ orbital of H and the $5d$ orbitals of the Pt atoms, resulting in electron transfer from Pt to H. As a result, the electron rich Pt_4^- cluster exhibits a higher H_2 dissociative chemisorption energy. Indeed, our results show that H_2 dissociation on the electron rich anionic Pt_4^- cluster follows a similar reaction pathway (Fig.13(c)) but with a stronger Pt-H interaction.

Typically, dissociation of H_2 is catalyzed by electron migration from d -orbitals of the metal to the anti-bonding π^* -orbital of H_2 , as have been observed for the Pt_4 and Pt_4^- clusters. However, for the electron deficient cationic Pt_4^+ cluster, a small electron transfer from the bonding σ -orbital of H_2 to the metal cluster is observed, resulting in a considerably weaker force to break up the H—H bond. In fact, the H_2

molecule may be molecularly anchored on Pt_4^+ upon contact with the cluster (Fig.13(b)). The molecularly bonded H_2 is also chemisorbed and slightly activated with a H—H bond distance of $0.886 \text{ \AA}$. A similar phenomenon of molecular H_2 adsorption on a cationic Ni_4^+ cluster has been observed previously in a vibrational spectroscopic (IR-MPD) study by Swart and co-workers⁴³. In the present case, the calculated adsorption energy on the cationic Pt_4^+ cluster (-0.817 eV) is only half of the value on the neutral Pt_4 cluster (-1.650 eV). An energy barrier of 0.310 eV is required for dissociation of the molecularly adsorbed H_2 species (R_M) into two H atoms, which subsequently migrate to the most stable chemisorption sites on the Pt_4^+ cluster (P_1) to further enhance the dissociative chemisorption of H_2 by 0.284 eV . Our results indicate that H migration on Pt_4^+ is easier than that on Pt_4 due to the weaker binding strength on the cationic cluster. Charge distribution analysis indicates that the H atoms gain only a small fraction of electron ($0.046e$) from the Pt_4^+ cluster at the most stable binding sites (P_1). In contrast, the excess electron on Pt_4^- gives rise to significantly enhanced electron transfer from the cluster to the H atoms ($0.242e$ at P_1), which is almost twice the value found for the neutral case. As a consequence, the H_2 dissociation process on Pt_4^- becomes highly exothermic with the calculated chemisorption energy of -2.117 eV . Not surprisingly, the diffusion of H atoms on the anionic cluster is somewhat restricted due to the strong Pt-H interactions. An activation barrier of 0.554 eV , which is slightly larger than on Pt_4 and Pt_4^+ , is required to move a H atom to the most stable site (P_1).

The above results indicate that H_2 chemisorption is very sensitive to the charge state of a cluster at low H_2 loadings. While these results are consistent with experiments on small clusters, they provide limited insight into the reactivity of a realistic catalyst, in which the metal surface is often saturated with hydrogen atoms/molecules. To address the effect of H coverage on Pt clusters with different charges, the sequential dissociative chemisorption of H_2 molecules on the clusters was examined until full saturation, where all H_2 molecules were

Fig.15 Calculated H-H distance distribution function $g(r)$ of the fully H saturated structures, obtained by tabulating all the H—H distances at each step of the MD trajectories⁶¹.

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Fig.16 Calculated H₂ average dissociative chemisorption energy (a), H sequential desorption energy (b), and the loss of the Hirshfeld charges (c)⁶¹.

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completely dissociated into H atoms and adsorbed on the clusters (Fig.15). The maximum H atom loadings on the Pt₄⁺, Pt₄ and Pt₄⁻ clusters were evaluated to be 8, 16, and 18 H atoms, respectively. As mentioned in Section 3, the saturation limit for each of these clusters was tested by MD simulations, during which loading two more H atoms onto the saturated clusters yields a H₂ molecule (peak at ca 0.75 Å) weakly bonded to the clusters. These results indicate that the charge state of a Pt cluster significantly affects the H-capacity of the cluster, which increases with the number of electrons for a given cluster size. In particular, the H-capacity of the Pt₄⁺ cluster is only half of the value of the neutral cluster, in agreement with the results reported by Kerpál and co-workers⁶⁵. Since the breaking of the H₂ bond is the main process during a catalytic hydrogenation reaction, the Pt₄⁻ cluster would provide the highest catalytic reactivity, while the Pt₄⁺ cluster with the significantly reduced H-capacity would yield the lowest activity.

The high sensitivity of the H-capacity to the charge state indicates that a Pt₄ cluster is too small to effectively represent a nanoparticle catalyst. In order to gain additional insight into the variation of the H-capacity for different charge states, we calculated the values of ΔE_{CE} , ΔE_{DE} and ΔQ as a function of H coverage for the Pt₄⁺, Pt₄ and Pt₄⁻ clusters. The results are shown in Fig.16. Clearly, ΔE_{CE} decreases monotonically as H coverage increases and thus, thermodynamically, dissociation of H₂ becomes increasingly more difficult. Despite the distinctive difference in H-capacities of these clusters, the calculated average chemisorption energies at full H saturation in all cases fall into a narrow range (ca 1.05–1.15 eV). These results suggest that all 3 clusters to some extent hold the same binding strength toward H atoms at high H loadings. Likewise, all the calculated ΔE_{DE} values at full H coverage fall within a narrow range (ca 2.65–2.85 eV) despite the large energy variation observed at low H loadings. Although the chemisorption energies and H desorption energies on different charged Pt clusters are similar at full H saturation, the charge

transfer shown in Fig.16(c) is quite different. This difference is responsible for the significant variation in H-capacity for different charge states of the Pt₄ cluster.

To understand the effect of charge states on the H-capacity for different cluster sizes, we further calculated the saturated hydrogen complexes of Pt₂, Pt₆ and Pt₈ clusters with different charge states at full saturation. The H/Pt ratio vs clusters size at full saturation is shown in Fig.17. In general, we found that more H atoms are loaded onto an anionic Pt_{*n*}⁻ cluster and fewer H atoms are attached to a cationic Pt_{*n*}⁺ cluster. For anionic Pt_{*n*}⁻ cluster, the H/Pt ratio decreases from 5.00 to 4.25 as the clusters size increases from 2 to 8. For cationic Pt_{*n*}⁺ clusters, the H/Pt ratio initially decreases with cluster size before increasing from 2.00 to 3.75 as the clusters size increases from 4 to 8. The H/Pt ratio gradually converges to 4.00 as the size of clusters increases, independent of the charges on the clusters. Therefore, the charge effect would be significantly diminished for large size clusters with high H loadings. It is in this limit (H/Pt ratio equal to 4 at full H saturation) that a small cluster may be used to model catalyst particles. In this case, the cationic or anionic charge can be readily dispersed and a sufficient number of Pt–H bonds is involved to average the interaction between the cluster and H atoms. This phenomenon is consistent with the experiments for cationic Pt and Ni

Fig.17 H/Pt ratio versus cluster size at full saturation⁶¹.

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clusters, where the reactivity of metal clusters was observed to increase significantly as the cluster size increases at a subnanoscale^{43,65}. The reason for the increased catalytic reactivity is mainly attributed to the increased H-capacity for large cationic clusters in which the charge effect is effectively minimized. Our results demonstrate that H-capacities on charged clusters become similar for large size clusters, and the reactivity of a fully saturated cluster is no longer sensitive to its charge state if the cluster size exceeds a certain number of atoms (e.g. ~8 Pt atoms).

5 Conclusions

Design and development of catalysts for effective hydrogenation of olefins under mild conditions has been a subject of intense studies in the past few decades. Nickel family metals have been used as the most important catalysts in many industrial heterogeneous catalytic processes due to their unique catalytic activity and high selectivity. In this review, we summarized our recent first principles studies on H₂ dissociative chemisorption on a series of nickel family metal clusters M_n (M = Ni, Pd, Pt; n = 2–9, 13) to address their catalytic performances. We first compared the growth pathways of Ni, Pd and Pt clusters. It was found that the metal clusters prefer to grow in a 3D close-packing growth pattern. The Pd clusters exhibit the longest bond lengths, although its atomic size is smaller than Pt. The average binding energy of the metal clusters increases with the cluster size monotonically. For a given cluster size, the binding strength of a Ni cluster is similar to that of the Pd cluster but smaller than that of the Pt cluster. Subsequently, H₂ dissociative chemisorption on metal clusters was systematically addressed. It was found that H₂ dissociation is almost barrierless on the Ni, Pd and Pt clusters. A moderate activation energy is required for H atom migration to the most stable adsorption site, indicating that the H atoms are highly mobile on metal clusters. Two key energy parameters, the H₂ dissociative chemisorption energy (ΔE_{CE}) and H sequential desorption energy (ΔE_{DE}), were defined as the probe to characterize the catalytic activity of metal clusters. Both ΔE_{CE} and ΔE_{DE} decrease significantly as the number of H atoms on the cluster increases. Upon saturation, large energy gaps were observed between low and high H coverages for both ΔE_{CE} and ΔE_{DE} . However, the ΔE_{CE} value of the Ni, Pd and Pt clusters at full H saturation vary in a small energy range between 0.6 and 1.0 eV regardless of the cluster size. We found that it is more difficult to pull H atoms out from the Ni clusters than from the Pd and Pt clusters. At full H coverage, each Pt atom is essentially capable of adsorbing 4 H atoms, while each Ni or Pd atom can only accommodate 2 H atoms. Considering the similar H desorption energy on the Pt and Pd clusters, the relatively high H capacity of Pt would lead to a superior reaction rate since more active H atoms are available for a hydrogenation process. In addition, charge sensitivity of the key energy parameters for several selected Pt clusters was also

systematically evaluated. The results show that the dissociation of H₂ and H-capacity are strongly correlated to the charge state of the Pt clusters at low H coverage. However, at high H-capacity, both ΔE_{CE} and ΔE_{DE} fall into a narrow energy range, suggesting that the charge effect can be readily diminished and a sufficient number of Pt–H bonds is involved to average the interaction between cluster and H atoms for large size clusters. As a result, the H-capacities on different charged clusters become similar if the cluster size becomes sufficiently large, and the reactivity of the fully saturated cluster is no longer sensitive to its charge state. The present review provides useful insight into the reactivity of small nickel metal family clusters for catalytic hydrogenation.

Supporting Information: available free of charge *via* the internet at <http://www.whxb.pku.edu.cn>.

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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 $g(r)$.

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