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Article

Reveal the nature of particle size effect for CO₂ reduction over Pd and Au

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ABSTRACT

Small cluster and periodic surface models with low coverages of intermediates are frequently employed to investigate reaction mechanisms and identify active sites on nanoparticles (NPs) in density functional theory (DFT) studies. However, diverse active sites on NPs cannot be sufficiently represented by these simple models, hampering the in-depth insights into the catalytic behavior of NPs. This paper describes the crucial roles of both model and coverage effect on understanding the nature of active sites for CO₂ reduction over Au and Pd NPs using DFT calculations. Terrace sites exhibit higher selectivity for CO than edge sites on Au NPs, which is opposite to the results on Au periodic surfaces. This contradiction reveals the computational model effect on clarifying active site properties. For Pd catalysts, the coverage effect is more significant. On bare Pd NPs and periodic surfaces, the selectivity for CO at edge sites is nearly identical to that at terrace sites, whereas edge sites display higher selectivity for CO than terrace sites in the case of high CO coverages. Through considering the more realistic models and the coverage effect, we successfully describe the size effect of Au and Pd NPs on CO selectivity. More importantly, this work reminds us of the necessity of reasonable models in DFT calculations.

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1. Introduction

The (photo-)electrochemical conversion of CO₂ to chemicals and fuels is a sustainable pathway for the storage of renewable energy with a concomitant mitigation of global warming [1–4]. One major hurdle for the commercial utilization of CO₂ electrochemical reduction (CO₂ER) is the poor selectivity for the carbonaceous products due to the prevalent hydrogen evolution reaction (HER) [5]. Therefore, it is of great significance to

develop catalysts for CO₂ER with high selectivity. To fabricate advanced catalysts for CO₂ER, plentiful studies have focused on optimizing the size of nanoparticles (NPs) according to the size effect of nanocatalysts [6–10]. It is found that larger Au NPs exhibited improved CO selectivity than small Au NPs. In contrast to the performance of Au NPs, Pd NPs showed the increasing selectivity for CO selectivity with the decreasing particle size. In order to get insights into the relationship between CO selectivity and the size of NPs, density functional theory

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(DFT) calculations were performed in these studies where the various sites on NPs were represented by small metal clusters and periodic slab models. For example, a previous study which employed Au₁₃ cluster to depict the corner site on NPs indicated that corner site could accelerate HER due to the strong binding of H*. However, a recent study using Au₃₀₉ particle model revealed that the binding of H* at corner site was weaker than that at other sites [11]. This contradiction could stem from the excessively strong binding of adsorbates on the small clusters caused by the quantum size effect [12]. Additionally, the generalized coordination number of edge sites on NPs are different from that on periodic Au(211) slab model, leading to discrepant adsorption energies of intermediates [13]. Thus, the nature of active sites on NPs and their catalytic behavior were incorrectly described by these simple models, which impedes the rational design of catalysts [14–16]. In this regard, the establishment of nanoparticle model with more realistic size is crucial to gain a deeper understanding of the size effect.

Apart from the influence of catalyst models, the coverage effect also plays a profound role on the clarification of active sites and interpretation of reaction mechanism [17]. In the case of high coverages, the adsorption of intermediates could be weakened owing to the change of adsorption configurations and electronic properties of active sites, which could alter the reaction pathways [18,19]. Effects of CO* coverages on the activity and selectivity of CO₂ER have been investigated by some theoretical researches [20,21]. It is found that the adsorption of COOH* and H* are weakened by the CO* co-adsorption, resulting in the different CO selectivity on the CO* covered models and the originally clean models. Thus, it is essential to consider the coverage effect on the selectivity of CO₂ER at different sites on catalysts, particularly on materials with strong binding of adsorbates.

Here, by DFT calculations on a set of Au and Pd NPs and periodic slab models, we explicate that more realistic catalyst models and coverage effect are indispensable to elucidate the size effects of Au and Pd NPs. We find that CO selectivity is higher at (100) sites than that at edge sites on Au NPs, but lower at periodic Au(100) slab model than that at periodic Au(211) slab model. The opposite trend is mainly originated from the underestimation of H* adsorption at edge site using Au(211) periodic slab model, which reflects the rigorous requirements for models in DFT studies. Based on the more realistic Au nanoparticle models, the Faradaic efficiency for CO is enhanced with the increasing size of NPs. For Pd catalysts, the coverage effect on CO selectivity is more remarkable. We propose a simple approach to predict the adsorption energies of intermediates on Pd NPs with high CO* coverages. In the case of high CO* coverages, edge site shows the stronger COOH* adsorption than (100) site, contributing to the better CO selectivity. Furthermore, the Faradaic efficiency for CO increases with the decreasing size of NPs, which corrects the nearly identical Faradaic efficiency for CO on bare Pd NPs with different sizes. The electronic and adsorption structures analysis indicates that the flexible COOH* adsorption structures at edge sites mitigate the repulsion from adjacent CO*, resulting in a more stable COOH* adsorption and higher CO selectivity.

2. Models and methods

DFT calculations were performed with the Vienna Ab initio Simulation Package code [22]. The BEEF-vdW exchange correlation functional [23] is used here to properly represent adsorbate interactions. The interaction between atomic cores and electrons was described by the projector augmented wave (PAW) method [24]. Au NPs of cuboctahedra were built by Wulff construction based on the surface energies of (100) and (111) facets ($\gamma_{100}/\gamma_{111} = 1.06$). The cuboctahedra NPs include various sites analogous to the slab model (Scheme 1), which provides a convenient model to study the correspondence of properties between NPs surface and slab surface. In order to make a direct comparison with the results on Au NPs, the Pd NPs were built with the same shapes [12]. Therefore, the cuboctahedra NPs models of 55, 147, 309 and 561 atoms (denoted by M₅₅, M₁₄₇, M₃₀₉ and M₅₆₁, respectively) and the periodic five-layer (4×4)-M(100) and (3×4)-M(211) slab models were constructed in this work (M = Au and Pd). For NPs models, the Brillouin zone was sampled by the gamma point only. As calculations of NPs models are highly expensive, a stepwise optimization procedure was carried out. First, geometry optimizations were conducted with a plane-wave cutoff of 250 eV. All atoms were optimized until the forces between atoms were lower than 0.02 eV/Å. Single-point calculations with a plane-wave cutoff of 400 eV were then performed for more reliable adsorption energies. The adsorption energies obtained by this method achieved the similar accuracy with those calculated under full relaxation with a plane-wave cutoff of 400 eV (Table S1). For periodic models, the Brillouin zone was sampled with a (3×3×1) Monkhorst-Pack *k*-points grid. The upper two layers were allowed to relax, while the bottom three layers were fixed to the bulk positions. Geometry optimizations were considered converged when the residual forces were smaller than 0.02 eV/Å.

As shown in Scheme 1, the corner site, edge site and terrace site of NPs models are noted by Corner, Edge, (100) and (111), respectively. It is worth noting that edge sites, such as E₁, E₂ and E₃ on NPs models of 561 atoms, are not equivalent on the NPs models due to the absence of translational symmetry

Scheme 1. Cuboctahedra Au and Pd NPs used in this work, ranging from 1.3 to 2.7 nm (55 to 561 atoms).

compared with the bulk system. According to the number of different active sites of NPs models (Table S2), edge sites and terrace sites of (100) are major sites while corner sites are minor, especially for the larger NPs. Thus, we mainly considered edge sites and terrace sites rather than corner sites in this work.

3. Results and discussion

The mechanism of CO₂ER has been investigated by a large number of experimental and theoretical studies [25–27]. On the basis of previous studies, it is known that CO₂ER to CO involves the following elementary steps: (1) the activation of CO₂ to COOH*; (2) the protonation of COOH* to CO*; (3) the desorption of CO* from the reaction site. In this reaction pathway, the activation of CO₂ which could follow a PCET (Proton Coupled Electron Transfer) mechanism or a stepwise mechanism of forming CO₂* before COOH* [25], is a key step for improving CO₂ reduction efficiency [28,29]. The widely perceived limiting step of CO₂ER to CO on Au catalysts is the initial CO₂ activation that entails high overpotential to form the adsorbed COOH* [30,31]. The stronger COOH* adsorption indicates the higher activity for CO₂ER, while the catalytic selectivity for CO₂ER is dependent on the competition between the adsorption of COOH* and H*, the intermediate of the prevalent HER in the aqueous solution [32].

We first compare the adsorption energies of COOH* (E_{adsCOOH^*}) and H* (E_{adsH^*}) at terrace sites of (100) and edge sites on Au NPs and those on periodic slab models (Table S3). The small Au₅₅ cluster exhibits the stronger binding of COOH* and H* than other larger Au NPs as well as Au slab models, in agreement with an earlier study [8]. We focus on edge site of E₂ since E₁ site which is composed of not only the edge atom but also the corner atom cannot reflect the nature of edge site. Generally, E_{adsCOOH^*} at (100) sites are hardly different from that at E₂ sites on NPs except for Au₁₄₇. However, Au(211) slab model manifests stronger COOH* adsorption than Au(100) slab model (Fig. 1(a)). On the other hand, the adsorptions of H* at E₂ sites are significantly stronger than that at (100) sites on NPs, especially on Au₁₄₇, whereas they are almost equivalent on Au(100) and Au(211) slab models (Fig. 1(b)). In addition, the E₂ sites of Au NPs shows stronger adsorption of H* than Au(211) but binds COOH* similarly to Au(211), which is consistent with the previous report [13]. These contrasts clearly reveal the differences between the active sites on Au NPs and corresponding sites on Au slab models in terms of adsorption of COOH* and H*.

The free energy diagrams for CO₂ER to CO and HER are summarized in Fig. S1. On E₂ site of Au₁₄₇, the free energy required to generate the COOH* is lower compared to that on (100) site as a result of stronger COOH* adsorption, suggesting the higher activity of CO₂ER. On the other hand, the activity of HER on E₂ site of Au₁₄₇ is also higher than that on (100) site since free energy of H adsorption are closer to 0 eV. This correlation between the activity of CO₂ER and HER were also observed by the previous study [8]. Hence, the selectivity of CO₂ER to CO on different sites cannot be determined by the

Fig. 1. (a) Adsorption energies of COOH*; (b) Adsorption energies of H*; (c) The predicted selectivity for CO on Au nanoparticles (Au₁₄₇, Au₃₀₉ and Au₅₆₁) and periodic slab models; (d) The predicted Faradaic efficiency for CO on Au nanoparticles with different sizes..

adsorption of COOH* alone. In order to evaluate the selectivity of CO₂ER over unwanted HER, the difference between E_{adsCOOH^*} and E_{adsH^*} can be regarded as an approximate measure and more positive difference indicates less selectivity [33].

For the periodic slab models, Au(211) indeed exhibits the higher selectivity for CO than Au(100) (Fig. 1(c)). In contrast, E₂ sites show no superiority over (100) sites on NPs, even more poor selectivity on smaller NPs (Fig. 1(d)). The reason for the discrepancy lies mainly in the stronger binding of H* at E₂ site of Au NPs compared to that on Au(211). These results expose the different nature of edge sites on Au NPs and periodic Au(211) slab model and imply the decisive effect of model selection on predicting CO selectivity on NPs. On the basis of more reasonable NPs models, we calculated the theoretical Faradaic efficiency (FE) [34] for CO on Au NPs with different sizes at −1.2 V vs. RHE. Calculation details can be found in Supporting Information. It is observed that FE for CO on Au NPs rises with the increase of particle size, in agreement with the trend of experiments [8].

In addition to the Au catalysts, we also explore the size effect of Pd catalysts as shown in Fig. 2. According to the calculated E_{adsCOOH^*} and E_{adsH^*} on Pd NPs and slab models (Table S4), neither E₂ and (100) site on Pd NPs model nor the Pd(211) and Pd(100) slab models exhibit obviously discrepant E_{adsCOOH^*} and E_{adsH^*} , leading to indistinguishable CO selectivity at various sites on Pd NPs and slab models. Furthermore, FE for CO remains almost constant on Pd NPs with various size, which is not coincident with the experimental observations [9,35].

Given the strong binding of CO* on Pd surfaces, we suppose that high coverages of CO* will contribute to the diverse CO₂ER performances at different sites. To verify the existence of high CO* coverages on Pd NPs, we first choose the (100) site as the representation of terrace site due to the similar adsorption energies of CO* at (100) and (111) sites on NPs (Table S6) and the higher proportion of (100) sites. We then estimate CO* coverages on a surface composed by (100) sites and edge sites

Fig. 2. (a) Adsorption energies of COOH*; (b) Adsorption energies of H*; (c) The predicted selectivity for CO on Pd nanoparticles (Pd₁₄₇, Pd₃₀₉ and Pd₅₆₁) and periodic slab models with low CO* coverages; (d) The predicted Faradaic efficiency for CO on Pd nanoparticles with different sizes.

(Fig. S2). At high CO* coverages where CO* begins to co-adsorb with adjacent CO* at the same Pd atoms, $E_{\text{ads}}\text{CO}^*$ at edge sites will decrease to -1.27 eV. According to the CO partial pressure of 1 mbar, CO* is expected to adsorb on Pd surface with adsorption energies more negative than -0.75 eV [36]. Based on the above analysis, we can infer that the high coverages of CO* can form on the Pd NPs. Next, we test the $E_{\text{ads}}\text{COOH}^*$ on Pd NPs with moderate and high CO* coverages defined by whether COOH* and CO* will co-adsorb at the same Pd atom.

When CO* coverages on Pd₁₄₇ are moderate in which COOH* and CO* will not bind to the same Pd atom (Fig. S3(a)), the $E_{\text{ads}}\text{COOH}^*$ remains relatively constant with an error of 0.14 and 0.11 eV at edge sites and (100) sites, respectively (Fig. 3(a)). In the case of high CO* coverages, COOH* and CO* begin to adsorb at the same Pd atom (Fig. S3(b)) and the $E_{\text{ads}}\text{COOH}^*$ weakens to 0.43 eV (Fig. 3(b)). Intriguingly, we find that $E_{\text{ads}}\text{COOH}^*$ at exactly high CO* coverages almost equals to that a simple model on which only includes two adjacent CO* species (Fig. 3(b)).

Fig. 3. Adsorption energies of COOH* on Pd₁₄₇ at moderate CO* coverages (a) and high CO* coverages (b); Adsorption energies of COOH* on Pd₃₀₉ at moderate CO* coverages (c) and high CO* coverages (d).

Therefore, we speculate that the weakened $E_{\text{ads}}\text{COOH}^*$ at high CO* coverages greatly depends on adjacent CO* species rather than nonadjacent CO* species. We also examine the impacts of nonadjacent and adjacent CO* species on the $E_{\text{ads}}\text{COOH}^*$ on Pd₃₀₉ using a simple model (shown in Fig. S4), and obtain similar conclusions (Figs. 3(c)–(d)). Thus, we suppose that $E_{\text{ads}}\text{COOH}^*$, even the adsorption energies of other intermediates at high CO* coverages can be predicted by some simple models containing adjacent CO* species, which will greatly alleviate the expensive calculations, especially for large NPs.

In order to further simplify the co-adsorption model, some elementary structures are established to represent the influence of adjacent CO* on the adsorption of COOH* and H* (Fig. S5). The fitted adsorption energy of an adsorbate i (E_{ads}^i) takes the form:

$$E_{\text{ads}}^i = \Delta E_{\text{ads}}\text{CO}_i^* + \Delta E_{\text{ads}} i^*_{\text{CO}} + E_{\text{ads}}^i$$
 (1)

For COOH*, $\Delta E_{\text{ads}}\text{CO}_i^*$ and $\Delta E_{\text{ads}}\text{COOH}^*_{\text{CO}^*}$ are the decreased adsorption energies of COOH* when CO* species share Pd atom with O and C atom of COOH*, respectively. E_{ads}^i represents the original adsorption energy of adsorbate i on the clean surface. Actually, the adsorption energies of COOH* and H* fitted by Eq. (1) ($E_{\text{ads}}^{\text{COOH}^*}$ and $E_{\text{ads}}^{\text{H}^*}$) and those obtained by the full DFT calculations ($E_{\text{ads}}\text{COOH}^*$ and $E_{\text{ads}}\text{H}^*$) are generally comparable, with a minimum error of 0.01 eV and a maximum error of 0.14 eV (Figs. 4(a) and (b)). Hence, $E_{\text{ads}}\text{COOH}^*$ and $E_{\text{ads}}\text{H}^*$ at realistic high CO* coverages can be evaluated by Eq. (1), further simplifying the calculations for NPs.

Based on the discussions above, we calculate the $E_{\text{ads}}^{\text{COOH}^*}$ and $E_{\text{ads}}^{\text{H}^*}$ at high CO* coverages using this method and evaluate CO selectivity at various sites of Pd NPs again. It is evident that E₁ sites exhibit higher CO selectivity than (100) sites (Fig. 5(c)). The reason lies in the stronger adsorption of COOH* and simultaneous weaker adsorption of H* at E₁ sites than those at (100) sites (Figs. 5(a) and (b)). It is worth noting that both adsorption of COOH* and adsorption of H* are stronger at E₂ sites than those at (100) sites, leading to less obvious difference of CO selectivity. On the whole, edge sites display better CO selectivity compared with (100) sites. In addition, the free energy diagrams for CO₂ER to CO and HER on Pd NPs with high CO* coverages are shown in Fig. S6. It is found that edge sites also exhibit higher activity of CO₂ER due to the lower free energy for the generation of COOH*. Faraday efficiencies (FEs) for CO at -0.8 V vs. RHE on Pd NPs with different sizes were calculated based on the experimental results [9]. It is found that FE for CO decreases gradually with increasing size of Pd NPs, consistent

Fig. 4. Comparison of adsorption energies of COOH* (a), and H* (b) fitted by Eq. (1) and those obtained by the full DFT calculation.

Fig. 5. (a) Adsorption energies of COOH^{*}; (b) Adsorption energies of H^{*}; (c) The predicted selectivity for CO on Pd nanoparticles (Pd₁₄₇, Pd₃₀₉ and Pd₅₆₁) and periodic slab models with high CO^{*} coverages; (d) The predicted Faradaic efficiency for CO on Pd nanoparticles with different sizes.

with the experimental trend [9,35]. Additionally, we preliminarily investigate the role of Pd hydride on understanding the size effect of Pd NPs by constructing a simplified model of Pd₁₄₇ hydride (Fig. S7). The E₂ site manifests significantly higher CO selectivity compared to (100) site on Pd₁₄₇ hydride, suggesting that the formation of Pd hydride could have an impact on the performance of different active sites [37]. It is worthwhile to confirm this speculation by further calculations on larger Pd NPs.

To gain insights into the improved CO selectivity at edge sites, the analysis of electronic and adsorption geometries are performed. Compared with that on clean Pd NPs, $E_{\text{ads}}^{\text{COOH}^*}$ on Pd NPs with high CO^{*} coverages become weaker at both E₁ site and (100) site due to the lower *d*-band, center of Pd atom (Fig. 6). In the case of high CO^{*} coverages, there are no apparent differences between the *d*-band centers of Pd atoms at E₁ sites and (100) sites. However, the adsorption of COOH^{*} is stronger at E₁ site. Through the analysis of COOH^{*} adsorption configuration, we find that COOH^{*} and CO^{*} adsorbed at the (100) site are in the same plane which is perpendicular to the (100) surface,

Fig. 6. The adsorption energies of COOH^{*} against the *d*-band center of Pd atoms on Pd₃₀₉.

whereas a certain angle that exists between COOH^{*} and CO^{*} at E₁ site increases the distance between the two O atoms of COOH^{*} and CO^{*}. Therefore, we propose that the more flexible adsorption structure of COOH^{*} weakens the repulsion from CO^{*} at high CO^{*} coverages and stabilize COOH^{*} species.

4. Conclusions

In summary, we expound the decisive role of more realistic models and coverage effects on understanding active sites for CO₂ER by DFT calculations via a set of Au and Pd NPs. The edge sites on Au NPs show similar adsorption of COOH^{*} compared to Au(211) periodic slab model, whereas the adsorption of H^{*} is weaker at edge sites on Au NPs. This further results in misunderstanding the CO selectivity at edge sites on Au NPs, which reflects the rigorous requirements for models in DFT studies. Furthermore, we analyze the influence of CO^{*} coverages on the adsorption energies of intermediates at different sites and use a reliable approach to simplify the adsorption energy calculations on Pd₁₄₇ and Pd₃₀₉ with high CO^{*} coverages. Importantly, the CO selectivity predicted by this simple method reveals the higher selectivity at edge sites compared to that at (100) sites on Pd NPs. The electronic and adsorption geometries analysis indicate that the higher CO selectivity at edge sites can be ascribed to the flexible COOH^{*} adsorption structure. In conclusion, we suggest that both more accurate models and coverage effects are essential to understand the property of active sites in DFT calculations.

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Graphical Abstract

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Reveal the nature of particle size effect for CO₂ reduction over Pd and Au

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The realistic nanoparticle models and coverage effects play critical roles in understanding the properties of active sites on Au and Pd nanoparticles and revealing the size effect on the selectivity of CO₂ reduction to CO.

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纳米Pd和Au催化CO₂还原粒径效应的密度泛函理论计算研究

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摘要: 以可再生能源为能量来源, 在水溶液中进行的光(电)催化CO₂还原生成高附加值化学品和燃料是解决能源危机与环境污染的有效途径之一。CO是一种简单却很重要的CO₂还原产物, 它可以作为水煤气变换反应与费托合成的重要原料。具有较高CO选择性的贵金属纳米颗粒催化剂(如Au和Pd)一直受到研究者的广泛关注。一般来说, 金属颗粒催化剂的催化性能与粒径大小密切相关, 即所谓的粒径效应。然而在实际的理论计算研究中, 由于受到计算能力的限制, 催化剂模型都仅局限于简单的周期性模型或小的金属团簇模型, 无法准确描述真实颗粒上复杂的反应位点的性质, 导致了对催化行为的误解。因此, 建立更加真实的颗粒模型对探究纳米颗粒催化剂上活性位点的性质, 解释其粒径效应至关重要。本文旨在阐述Au与Pd纳米颗粒催化剂不同活性位点上CO₂还原反应与产H₂副反应的竞争机制, 并解释Au与Pd纳米颗粒催化剂在CO₂电还原中表现出不同粒径效应的原因。本文基于密度泛函理论, 采用VASP软件, BEEF-vdW泛函进行计算。分别建立了原子数为55, 147, 309和561的颗粒模型和高CO*覆盖度模型, 避免了传统周期性模型的局限性, 探究了金属颗粒催化剂不同反应位点上的CO选择性。结果表明, 对于颗粒模型来说, (100)位点对CO的选择性优于边缘位点; 但对于周期性模型来说, Au(211)对CO的选择性则优于Au(100)。产生这种反差的主要原因在于Au颗粒的边缘位点对H*的吸附过强。通过对比, 我们直观地展现了颗粒模型上平面位点和Edge位点与相对应的周期性模型上CO选择性的区别, 突出了模型选择对揭示活性

位点性质的重要性. 在此基础上, 通过计算理论CO法拉第效率, 发现Au颗粒随着粒径的减小, CO选择性降低, 与实验的趋势一致. 对于Pd催化剂来说, 低覆盖度模型无法正确预测活性位点的性质; 而高CO覆盖度的情况下, Pd颗粒的边缘位点对COOH*吸附能更强, 这是导致边缘位点上CO选择性更高的主要原因. 同样通过计算理论CO法拉第效率, 发现随着粒径的减小, Pd颗粒上CO选择性升高. 本文不仅成功揭示了Au与Pd颗粒催化剂上活性位点的性质, 对粒径效应做出了合理解释, 也强调了合理的计算模型是理论研究的基础.

关键词: 密度泛函理论; CO₂还原; 覆盖度效应; 催化剂模型; 纳米颗粒

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