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Investigation of water adsorption and dissociation on Au₁/CeO₂ single-atom catalysts using density functional theory

Yan Tang^a, Yang-Gang Wang^{a,#}, Jin-Xia Liang^{a,b}, Jun Li^{a,*}^a Department of Chemistry and Key Laboratory of Organic Optoelectronics & Molecular Engineering of Ministry of Education, Tsinghua University, Beijing 100084, China^b Guizhou Provincial Key Laboratory of Computational Nano-Material Science, Guizhou Normal College, Guiyang 550018, China

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ABSTRACT

We examined the water adsorption and dissociation on ceria surfaces as well as ceria-supported Au single-atom catalysts using density functional theory calculations. Molecular and dissociative water were observed to coexist on clean CeO₂ and reduced Au₁/CeO_{2-x} surfaces because of the small difference in adsorption energies, whereas the presence of dissociative water was highly favorable on reduced CeO_{2-x} and clean Au₁/CeO₂ surfaces. Positively charged Au single atoms on the ceria surface not only provided activation sites for water adsorption but also facilitated water dissociation by weakening the intramolecular O–H bonds. In contrast, negatively charged Au single atoms were not reactive for water adsorption because of the saturation of Au 5d and 6s electron shells. This work provides a fundamental understanding of the interaction between water and single-atom Au catalysts.

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1. Introduction

Supported Au nanoparticles have attracted extensive attention in heterogeneous catalysis since Haruta et al. [1] and Hutchings [2] first observed that nanosized Au was highly reactive for various important chemical reactions. Although small Au nanoparticles (2–5 nm) appear to be significant for high catalytic activity [3–9], it has recently been reported that a Au single atom can catalyze various reactions with remarkable reactivity, such as CO oxidation [10–13], water-gas shift [14–16], methanol reforming [17], and ethanol dehydrogenation [18]. It is suggested that the strong metal-support interaction plays an important role in promoting both the stability and reactivity of Au single-atom catalysts (SACs) on oxide supports. In particular, the single atoms on the oxide surfaces exhibit

significant covalent bonding with the oxide surface atoms, which is termed *covalent metal-support interaction* [11]. We further studied a series of SACs with MO₂ supports (M = Ti, Zr, Hf, Ce, and Th) and attributed the promoting role of the oxide support in single-atom Au catalysts to the *quantum primogenic effect* [19]. Using *ab initio* molecular dynamics (AIMD) simulations, we also observed that single-atom Au catalysts can even be formed dynamically in the interfacial area on titania- and ceria-supported Au nanoparticles under certain reaction conditions. We termed these dynamically formed surface-supported single atoms *dynamic single-atom catalysts* [20–22] as an extension of static surface-supported single-atom catalysts [10, 23–26].

As the most ubiquitous molecule in the environment, water is vital in various chemical reactions in heterogeneous cataly-

* Corresponding author. Tel: +86-10-62795381; Fax: +86-10-62797472; E-mail: junli@tsinghua.edu.cn

Corresponding author. E-mail: wangygtcl@gmail.com

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sis, especially Au catalysis [27–35]. Water can exist in catalysis as moisture and a solvent as well as a reactant, intermediate, and product. In practice, it is extremely challenging to remove water molecules from the surface of catalysts on the microscale. The essential role of water is generally reflected in [34–36]: (1) the solvation effect, (2) water-mediated H-transfer, (3) the promotional role of hydroxyls, and (4) other miscellaneous effects, such as surface reconstruction and active site blocking. For example, on Au nanoparticles, it has been suggested that H₂O protonates O₂ to form an activated hydroperoxyl *OOH complex, which can easily oxidize CO [37,38]. The dissociation of water into hydroxyls is generally believed to be a critical step for hydrogen production and CO₂ formation during the water-gas shift (WGS) reaction, and significant attention has been paid to where and how the water is dissociated for oxide-supported Au catalysis. Rodriguez et al. [39] observed that ceria-supported Au nanoparticles and Cu nanoparticles could facilitate the water dissociation and result in high catalytic performance toward the WGS. Bruix et al. [40] noted that the Pt/CeO₂(111) surface has the unique property that the ad-metal can adsorb and dissociate water in an efficient manner because of a new type of “strong metal-support interaction” that produces large electronic perturbations for small Pt particles in contact with ceria. Despite the increasing experimental and theoretical efforts on the role of water in supported nanocatalysts, an understanding of the effects of water in single-atom catalysts remains elusive.

In this work, we elucidate the interaction of water and ceria-supported Au SACs to better understand (1) the use of single-atom Au catalysts for water dissociation when water is a reactant species and (2) the effect of water on single-atom Au catalysts when water works as a co-catalyst during a catalytic process. We performed density functional theory (DFT) calculations corrected by on-site Coulomb interactions (DFT+U) to investigate the water adsorption and dissociation on Au₁/CeO₂ SAC as well as on the CeO₂ surface with or without an oxygen vacancy. In addition, Grimme’s empirical three-body dispersion correction in the scheme of Becke-Johnson damping, namely DFT-D3 (BJ) [41,42], was also adopted to consider the effect of dispersion on the adsorption of water.

2. Methods

All the calculations were performed using periodic DFT methods as implemented in the Vienna ab initio simulation package (VASP) [43,44]. The projector augmented wave method [45] was used for the interaction between the atomic cores and valence electrons. The valence orbitals of Ce (4*f*, 5*s*, 6*s*, 5*p*, 5*d*), Au (5*d*, 6*s*), O (2*s*, 2*p*), and H (1*s*) were described by plane-wave basis sets with cutoff energies of 400 eV. The exchange-correlation energies were calculated via the generalized gradient approximation with the Perdew-Burke-Ernzerhof (PBE) functional [46]. Spin-polarized DFT+U calculations [47,48] with a value of $U_{\text{eff}} = 5.0$ eV [49,50] for the Ce 4*f* state were applied to correct the strong electron-correlation properties of CeO₂. The CeO₂(111) surface was modeled by $p(3 \times 3)9$ atomic layer supercells with the bottom three layers fixed. The

vacuum gap was set at 1.5 nm to avoid the interaction between periodic images. The Brillouin zone was sampled at the Γ -point only. The effects of *k*-points were tested in our previous studies [19]. The convergence criteria for the energy and force were set to 10^{−5} eV and 0.2 eV/nm, respectively. The search for the transition state (TS) of the surface reaction was performed using the dimer method [51]. Vibrational analysis was further used to confirm the TSs with only one imaginary frequency.

The energy barrier (E_a) was defined as the energy difference between the corresponding transition and initial states. The *adsorption energies* were calculated according to the following equation:

$$E_{\text{ads}} = E_{(\text{slab} + \text{adsorbate})} - E_{(\text{slab})} - E_{(\text{adsorbate})}$$

where $E_{(\text{slab} + \text{adsorbate})}$, $E_{(\text{slab})}$, and $E_{(\text{adsorbate})}$ are the energies of species adsorbed on the surface, bare surface, and gas-phase molecule, respectively. Similarly, the *reaction energy* was estimated using $\Delta E = E_{(\text{products})} - E_{(\text{reactants})}$. Atomic charges were computed using the atom-in-molecule (AIM) scheme proposed by Bader [52]. The charge density differences were evaluated using the formula $\Delta\rho = \rho_{\text{A+B}} - \rho_{\text{A}} - \rho_{\text{B}}$, where ρ_{X} is the electron density of X.

3. Results and discussion

3.1. Water adsorption and dissociation on CeO₂(111) surface

It is essential to determine whether water is molecularly adsorbed or dissociatively adsorbed in heterogeneous catalysis. The potential energy diagram for water dissociation on clean CeO₂(111) is presented in Fig. 1, and the structures of the surface intermediates and TSs are presented in Fig. 2. It is observed that water can molecularly adsorb on a clean CeO₂(111) surface with an adsorption energy of −0.51 eV. The distance between O_w in water and the surface Ce atom is 0.262 nm. One hydrogen in water also forms a hydrogen bond with the nearest lattice oxygen (bond length ~0.172 nm). Water adsorbed on a clean CeO₂(111) surface can also dissociate into one terminal hydroxyl and one bridged hydroxyl. The dissociation barrier and reaction energy were calculated to be only 0.11 and 0.02 eV, respectively, suggesting that kinetically this process occurs easily; however, both the molecular and dissociated species can

Fig. 1. Potential energy diagram of water dissociation on clean CeO₂(111) (red line) and reduced CeO_{2-x}(111) (blue line). The numbers in parentheses indicate the barriers of the elementary steps. MA and DA denote the molecular adsorption and dissociative adsorption, respectively.

Fig. 2. Geometric configurations of MA (a); TS (b); and DA for water dissociation on clean CeO₂(111) (c). Color codes: blue (H), red (O), white (Ce).

coexist to an equilibrium under realistic conditions. This result is consistent with experimental scanning tunneling microscopy images and previous theoretical results [53–57]. Bader charge analyses indicate that this dissociation process does not significantly affect the electronic structure of the CeO₂ surface, indicating that O–H bond breaking is a heterolytic process (i.e., through proton transfer). This heterolytic dissociation of O–H on the CeO₂ surface is reminiscent of the dissociation of the inert C–H bond on the ion-pair active center on the surface of Co₃O₄ nanocrystals [58,59].

Water dissociation on a reduced CeO_{2-x}(111) surface has been explored in previous work by us and others [60]. AIMD simulations have indicated that the water molecule can easily dissociate into two surface-bound hydroxyls at the nearest Ce⁴⁺ site associated with an oxygen vacancy (O_v) site. In this work, we recalculate the potential energy diagram on a reduced CeO_{2-x}(111) surface using VASP code and compare the results with those for a stoichiometric CeO₂(111) surface, as shown in Fig. 1. The structures of the surface intermediates and transition states are presented in Fig. 3. The energies of molecular adsorption (MA) and dissociative adsorption (DA) are –0.81 and –1.95 eV, respectively. Water dissociation is highly active with a low energy barrier (0.04 eV) and highly exothermic reaction energy (–1.14 eV). It is clear that the presence of the oxygen vacancy strengthens the adsorption energies of water, especially for DA. Therefore, DA is much more favorable than MA. In addition, the presence of the oxygen vacancy also facilitates the dissociation of water by lowering its barrier. Notably, Bader charge analyses confirm that the dissociation process on the reduced surface does not affect the electronic structure of the CeO_{2-x} surface, such as on a stoichiometric surface. Finally, we should emphasize that the occupancy of the oxygen vacancy by water dissociation is irreversible, leading to the deactivation of the surface for further water activation. Water can also adsorb on the second-nearest Ce³⁺ site with an adsorption energy of –0.59 eV; however, this result shows no distinct difference from that on the clean CeO₂ surface.

Fig. 3. Geometric configurations of MA (a), TS (b), and DA for water dissociation on reduced CeO_{2-x}(111) (c). The purple balls represent Ce³⁺ atoms.

3.2. Water adsorption and dissociation on Au₁/CeO₂(111) surface

The geometric and electronic structures of Au₁/CeO₂(111) with or without the oxygen vacancy were identified in our previous study [19]. In this work, we use the Au₁/CeO₂(111) and Au₁/CeO_{2-x}(111) models in Ref. [19] to directly investigate the interaction between water and single-atom Au catalysts. We first explore both water adsorption and dissociation on Au₁/CeO₂(111). All possible sites for water adsorption, including surface sites and the single Au atom site have been tested. For molecular adsorption, it is observed water prefers to adsorb at the Au site. Upon water adsorption, the Au adatom spontaneously diffuses from the bridge site to the top site, which is similar to the process for CO adsorption [19,61]. The adsorption energy is calculated to be –0.81 eV, which is much lower than that on a clean CeO₂(111) surface. For dissociative adsorption, the configuration with one hydroxyl at the single Au site and one hydrogen bonded to the adjacent lattice oxygen (i.e., a bridged hydroxyl) is calculated to be most stable. The dissociative adsorption energy is calculated to be –1.87 eV. The potential energy diagram of water dissociation on clean Au₁/CeO₂(111) is shown in Fig. 4. The structures of the surface intermediates are presented in Fig. 5. The water dissociation process on Au₁/CeO₂(111) is nearly barrierless and is highly exothermic by 1.06 eV, suggesting that water dissociation is highly favorable on Au₁/CeO₂(111) both kinetically and thermodynamically. Compared with the energetics on the clean CeO₂ surface, our results indicate that the presence of the Au SACs can strongly strengthen water adsorption, especially dissociative adsorption to form hydroxyls. In addition, we observed that the molecular and dissociative adsorption energies and the reaction barrier on the second-neighbor Ce⁴⁺ site are –0.50, –0.49, and 0.12 eV, respectively, similar to those on the clean surface. These results suggest that the presence of single-atom Au has no significant effect on the adsorption of water on the surface Ce⁴⁺ site; however, the water adsorption at the second-neighbor Ce³⁺ site is indeed observed to increase to –0.72 eV.

The electronic structures of molecularly and dissociatively adsorbed water on Au₁/CeO₂(111) were further investigated. The Bader charge of single-atom Au in MA/Au₁/CeO₂(111) was determined to be +0.37 |e|, which is similar to the Au charge on

Fig. 4. Potential energy diagram of water dissociation on clean Au₁/CeO₂(111) (red line) and reduced Au₁/CeO_{2-x}(111) (blue line).

Fig. 5. Geometric configurations of MA (a) and DA for water dissociation on clean $\text{Au}_1/\text{CeO}_2(111)$ (b). Color codes: blue (H), red (O), white (Ce), yellow (Au).

a clean $\text{Au}_1/\text{CeO}_2(111)$ surface (+0.35 |e|), indicating that the charge state of the single-atom Au is not greatly affected. The charge density differences for the MA/ $\text{Au}_1/\text{CeO}_2(111)$ surface (Fig. 6(a) and (b)) also reveal the existence of one Ce^{3+} ion on the surface. Similar results were also observed for DA/ $\text{Au}_1/\text{CeO}_2(111)$. Therefore, we conclude that O–H bond breaking during water dissociation is a nonredox and heterolytic process (i.e., through proton transfer) on $\text{Au}_1/\text{CeO}_2(111)$, which does not induce any electron transfer from the substrate to the reactant species.

We now turn to investigate the water adsorption and dissociation on a reduced $\text{Au}_1/\text{CeO}_{2-x}(111)$ surface, where the single Au is located at the oxygen vacancy. Unlike stoichiometric $\text{Au}_1/\text{CeO}_2(111)$, the single Au on reduced $\text{CeO}_{2-x}(111)$ surface only weakly binds to molecular water (Fig. 7(b)). The adsorption energy is calculated to be only -0.03 eV. In particular, the water adsorption at the adjacent Ce^{4+} site (Fig. 7(a)) is also increased to -0.31 eV. These decreases of adsorption energies are due to the presence of the oxygen vacancy, which alters the surface chemical potentials of ceria, forcing the Au to exist in a negative-charge state (i.e., in the $\text{Au}(-\text{I})$ oxidation state or Au^-). In Au^- , all the 5d and 6s orbitals are fully occupied, leading to the deactivation of the single Au site. In addition, water adsorption at the second-neighbor Ce^{4+} site and third-neighbor Ce^{3+} are -0.44 and -0.45 eV, respectively. The Bader charge analyses indicates that the molecular adsorption of water on both Ce and Au sites has no effect on the oxidation state of Au.

All the possible dissociative adsorption configurations of water have also been considered, as shown in Fig. 7(c) and (d). Fig. 7(c) shows the water dissociative adsorption on the adjacent Ce^{4+} site with the adsorption energy of -0.28 eV, which is higher than that on the Ce site in clean $\text{CeO}_2(111)$ and $\text{Au}_1/\text{CeO}_2(111)$ surfaces. The distance between O_w and the sur-

Fig. 6. Calculated charge density differences for molecular (a,b) and dissociative water adsorption on $\text{Au}_1/\text{CeO}_2(111)$ surface (c,d): (a, c) top view and (b, d) side view. The yellow and blue areas represent charge increase and reduction, respectively. The cutoff of the density-difference isosurfaces is 5 electrons/ nm^3 .

Fig. 7. Geometric configurations of MA (a,b) and DA for water dissociation on reduced $\text{Au}_1/\text{CeO}_{2-x}(111)$ surface (c,d).

face Ce atom is 0.227 nm. The Bader charge of single-atom Au is -0.53 |e|, indicating that Au exhibits oxidation states of $\text{Au}(-\text{I})$. Fig. 7(d) displays the water dissociative adsorption on the Au site with the adsorption energy of -0.35 eV. The bond lengths of Au–H and Au– O_w are 1.56 and 0.209 nm, respectively. The Bader charge of the H atom close to Au is +0.12 |e|, suggesting the formation of a surface-bound H radical. As the single-atom Au is oxidized from $\text{Au}(-\text{I})$ to $\text{Au}(0)$, we speculate that the O–H bond breaking in this system occurs via a homolytic process. To further understand the effect of single-atom Au in $\text{Au}_1/\text{CeO}_{2-x}(111)$ on H_2O dissociation, we calculated the potential energy diagram of water dissociation on the adjacent Ce^{4+} site, as shown in Fig. 4. The barrier of water dissociation was determined to be 0.14 eV, which is slightly larger than that of clean $\text{CeO}_2(111)$. Compared with the reduced $\text{CeO}_{2-x}(111)$, the single-atom Au at the oxygen vacancy does not promote water adsorption or dissociation.

3.3. Electronic interaction between H_2O and $\text{Au}_1/\text{CeO}_2(111)$

We have demonstrated the excellent performance of Au single atoms in H_2O adsorption and dissociation on clean ceria supports. We now examine the electronic structures to understand the key role of single-atom Au in these processes. The calculated projected density of states (PDOS) for molecular or dissociative H_2O on $\text{Au}_1/\text{CeO}_2(111)$ surfaces are presented in Fig. 8 and Fig. 9, respectively. In Fig. 8, the Au 5d and lone pair states of O 2p exhibit a distinct overlap between -5 and -6 eV below the Fermi level, leading to the strong molecular adsorption of H_2O . The anti-bonding of O–H in MA/ $\text{Au}_1/\text{CeO}_2(111)$ is filled through interaction with the Au-5d orbital, thus weakening the intermolecular O–H bond of water and facilitating the subsequent water dissociation. Similarly, in Fig. 9, it is observed that for water dissociative adsorption, the interactions between Au 5d and O 2p states become quite strong across a wide range of energy levels from -8 to 0 eV below the Fermi energy, implying that the O 2p states are well activated because of water dissociation. In addition, the hybridizations between Au 6s and 5d states near -2 eV below the Fermi level suggest charge redistribution among the states of Au because of the formation of

Fig. 8. Calculated density of states (DOS) for free H₂O (a) and H₂O on Au₁/CeO₂(111) surfaces (b). The energies are referenced to the Fermi level (E_F).

strong chemical bonding. Overall, the presence of single-atom Au(+I) can strongly correlate with the O 2p states in water, which not only provides the active site for water adsorption but also activates water molecules, promoting the water dissociation process. Han et al. [57] also systematically investigated the interaction of water with M₁/CeO₂ (M = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn) and observed that dissociative adsorption is more favorable than molecular adsorption on all these SACs, which is similar to our observations for Au₁/CeO₂. In addition, we find that Au₁/CeO₂ exhibits distinctly higher reactivity (i.e., lower barrier and higher exothermic reaction energy) than Cu₁/CeO₂, Au nanoparticles or surfaces, and some other metal nanoparticle catalysts supported on ceria (such as Cu₄/CeO₂, Pt₈/CeO₂) [39,40,62,63]. Thus, we can conclude that SACs, especially Au₁/CeO₂, are potential catalysts for reactions in which the dissociation of water plays an important role. However, the

stability of the SACs may be affected at high temperature and in a reducing environment, leading to aggregation under severe conditions.

We also investigated H₂O dissociation on Au₁/CeO_{2-x}(111) and observed that the single-atom Au(-I) cannot provide the adsorption site for molecular water because of the lack of an unoccupied orbital. The most stable adsorption site for molecular water is the Ce site with the adsorption energy of -0.31 eV. Song et al. [64] studied the water dissociation on Au₁/CeO_{2-x}(110) and observed that water can only adsorb at the Ce site with an energy of 61 kJ/mol (i.e., 0.63 eV). The barrier of water dissociation on Au₁/CeO_{2-x}(110) is 45 kJ/mol. Comparison of the Au₁/CeO_{2-x}(110) and Au₁/CeO_{2-x}(111) surfaces indicates that H₂O molecular adsorption is hindered on a negatively charged single Au atom, independent of the surface structures. It is also reported that water can readily dissociate at the interface between Au and CeO₂ in Au₃/CeO_{2-x}(111), Au₃/CeO_{2-x}(110), and Au_n/CeO_{2-x}(110) systems [64,65], and these systems exhibit high activity for the WGS, indicating that Au clusters might be much more reactive than a single-site Au atom for reduced ceria surfaces.

3.4. Effect of van der Waals forces

Thus far, we have discussed the results of PBE calculations that do not include van der Waals (vdW) forces. However, the vdW interaction should be considered to accurately describe the interaction between H₂O and supports. Here, the DFT-D3 (BJ) approach [41,42] was adopted to consider the effect of dispersion on the adsorption of water. As expected, the molecular and dissociative adsorption energies both increased (in absolute values) when the long-range terms were included (Table 1). However, even with consideration of the vdW forces, the stability order of molecular adsorption and dissociative

Fig. 9. Calculated projected density of states (PDOS) for dissociative H₂O on Au₁/CeO₂(111) surfaces. The energies are referenced to the Fermi level (E_F).

Table 1Molecular and dissociative adsorption energies of water on CeO₂ and Au₁/CeO₂ surfaces with and without van der Waals forces.

Surface	DFT+U			DFT+U/D3		
	E_{MA} (eV)	E_a (eV)	E_{DA} (eV)	E_{MA} (eV)	E_a (eV)	E_{DA} (eV)
CeO ₂ (111)	−0.51	0.11	−0.49	−0.70	0.10	−0.67
CeO _{2-x} (111)	−0.81	0.04	−1.95	−0.97	0.04	−2.15
Au ₁ /CeO ₂ (111)	−0.81	0.00	−1.87	−0.82	0.00	−1.98
Au ₁ /CeO _{2-x} (111)	−0.31	0.14	−0.28	−0.59	0.12	−0.57

adsorption remained the same as the results using DFT+U. In addition, the reaction barriers using the DFT+U/D3 approach are similar to those obtained using the DFT+U approach, and the geometric structures and electronic structures (Bader charges) only changed slightly when the vdW interactions were included. In other words, the DFT+U/D3 approach does not affect the conclusions drawn using DFT+U, although the adsorption energies were increased.

4. Conclusions

In this work, we performed a systematic study of the water adsorption and dissociation on Au₁/CeO₂ single-atom catalysts as well as CeO₂ surfaces with or without an oxygen vacancy using DFT+U and DFT+U-D approaches. The following conclusions can be drawn from this work: (1) Dissociative adsorption is highly favorable on a stoichiometric Au₁/CeO₂ surface. In contrast, upon the formation of an oxygen vacancy, molecular and dissociative water may coexist on the reduced Au₁/CeO_{2-x} surface because of the small difference in the adsorption energies; this situation is reversed for pure ceria. (2) On a clean Au₁/CeO₂ surface, the positively charged Au single atoms not only provide activation sites for water adsorption but also facilitate water dissociation by weakening the intramolecular O–H bonds. (3) On a reduced Au₁/CeO_{2-x} surface, the negatively charged Au single atom is not reactive for water adsorption because of the saturation of the Au 5d and 6s shell in an Au(−I) oxidation state. (4) Despite increasing the adsorption energies of water, the DFT+U approach with dispersion corrections does not change the conclusions drawn using the DFT+U approach.

These findings provide an understanding of the interaction between water and ceria-supported Au SACs and can help to design efficient single-atom Au catalysts for reactions in which the dissociation of water plays an important role.

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Graphical Abstract

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Investigation of water adsorption and dissociation on Au₁/CeO₂ single-atom catalysts using density functional theory

Yan Tang, Yang-Gang Wang*, Jin-Xia Liang, Jun Li*
Tsinghua University; Guizhou Normal College

Positively charged single-atom Au on ceria support is a potential catalyst for water dissociation. It can not only provide the activation site for water adsorption but also facilitate water dissociation by weakening the intramolecular O–H bond.

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水在Au₁/CeO₂单原子催化剂上吸附与解离的理论研究

汤 妍^a, 王阳刚^{a, #}, 梁锦霞^{a, b}, 李 隽^{a, *}

^a清华大学化学系有机光电子与分子工程教育部重点实验室, 北京100084

^b贵州省纳米材料模拟与计算重点实验室, 贵州贵阳550018

摘要: 自Haruta和Hutchings发现负载的纳米金催化剂的催化活性后, 负载型金催化剂一直是非均相催化的研究重点之一。近年来, 单原子催化剂因其优异的活性、选择性, 超高的原子利用效率, 引起了科学家们的广泛关注。越来越多的单原子金催化剂被成功制备, 并被证实具有很好的催化活性。水, 作为环境中最常见的物质, 在实际的催化体系中往往难以避免, 即使在超高真空环境中也会有痕量的水气存在。水的解离不仅是水煤气反应的重要步骤之一, 而且对别的反应也有一定的

促进作用。尽管水和纳米团簇催化剂之间的研究已经颇有成效,但水和单原子金催化剂之间的作用还不是非常清晰。因此,我们采用密度泛函理论从原子尺度研究了水和 Au_1/CeO_2 单原子催化剂的相互作用。

我们首先研究了水在完美 CeO_2 表面和含有一个氧空位的 CeO_{2-x} 表面上的解离过程,研究发现分子态的水和解离态的水在完美 CeO_2 表面可以共存,而一旦在表面形成氧空位后,由于较低的能垒和极大的放热,解离态的水将占据绝对优势。接下来探索了水在完美 Au_1/CeO_2 表面和含有一个氧空位的 $\text{Au}_1/\text{CeO}_{2-x}$ 表面上的解离过程,发现结论恰好和 CeO_2 表面相反。水的解离过程在完美的 Au_1/CeO_2 表面几乎是一个无能垒的过程,并且解离会放出大量的热量。而一旦在表面形成氧空位后,单原子 Au 的轨道处于满占状态,无法提供水的吸附位点。水的解离过程在 Ce 位点进行,分子吸附能与解离吸附能相当,分子态与解离态共存。

为了进一步理解单原子金在水的解离过程中起到的作用,我们分析了水和 Au_1/CeO_2 之间的电子相互作用。研究结果表明,单原子金不仅为水的吸附提供了位点,金的 $5d$ 轨道和水的 $2p$ 轨道之间的相互作用还有效减弱了水中氧氢键的强度,使水的解离更容易进行。由此可见,在涉及到水解离的反应中,以 Au_1/CeO_2 为代表的单原子催化剂有望带来新的突破。

最后,我们还测试了范德华力对研究体系的影响。研究发现尽管范德华力会使吸附能的绝对值增加,但是并不影响我们得到的结论。

关键词: 单原子催化剂; 金单原子; 二氧化铈; 水解离

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*通讯联系人. 电话: (010)62795381; 传真: (010)62797472; 电子信箱: junli@tsinghua.edu.cn

#通讯联系人. 电子信箱: wangygtccl@gmail.com

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