SPECIAL TOPIC: Single-atom Catalysts

Catalytic mechanism and bonding analyses of Au–Pd single atom alloy (SAA): CO oxidation reaction

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ABSTRACT Single-atom catalysts (SACs), including metal-metal-bonded bimetallic ones named single-atom alloys (SAAs), have aroused significant interest in catalysis. In this article, the catalytic mechanism and bonding analysis of CO oxidation reaction on bimetallic gold–palladium (Au–Pd) model of single atom alloy Au₃₇Pd₁ are investigated by using quantum chemical calculations. The molecular geometries and adsorbate/substrate binding energies of CO@Au–Pd, O₂@Au–Pd and CO/O₂@Au–Pd configurations are identified. The core-shell structure is confirmed to be the most stable structure for Au–Pd SAA, where the Pd atom prefers to situate at the core site. Charge transfer from the Pd atom to the Au atoms has been confirmed to stabilize the structure. According to the binding energy and chemical bonding analysis, both CO and O₂ prefer to bind to the Pd atom at the hex site with low coordination number. The formation of new co-adsorption species is identified, in which vertical and parallel bridging adsorptions of CO and O₂ on the Au–Pd bonds are observed. CO oxidation on Au–Pd SAA is found to be feasible with low energy barriers and follows the Langmuir-Hinshewood (L-H) mechanism. Our work offers insights into the significant role of single atom of the SAAs in catalytic reactions and can provide evidence for designing new SAAs with high-performance catalytic activities.

Keywords: single-atom catalyst, CO oxidation, Au–Pd alloy, bonding analysis, reaction mechanism

INTRODUCTION

Single-atom catalysts (SACs) have received much attention in recent years since it was first proposed in 2011 by Qiao and coworkers [1]. SACs have found significant applications in catalytic reactions such as CO oxidation

[1], water-gas shift (WGS) [2,3] and 1,3-butadiene hydrogenation reactions [4]. A huge number of reactions have been studied with SACs where single metal atoms anchored on oxide supports or metal surfaces act as the active sites [1,3,5–14]. Bimetallic nanoalloys have revealed superior catalytic activities and selectivities towards different catalytic reactions, when compared with monometallic nanoparticles (NPs) [13,15–26]. In this regard, great efforts have been devoted to the synthesis of nano-sized bimetallic NPs with controllable particle size, structure and property. Previous studies reported that the structure, stability and activity of gold (Au) NP catalysts strongly depend on the size, shape and properties of the supports [27–39]. In recent years, gold based bimetallic nanoalloy catalysts were synthesized by introducing transition metals (Pd, Pt, Ir) to improve the catalytic efficiency [40–43]. Among them, gold–palladium (Au–Pd) bimetallic NPs were applied as potential catalysts in a wide range of catalytic reactions, such as oxidation of CO [43–45], hydrogen peroxide (H₂O₂) synthesis from H₂ and O₂ [44,46–51], hydrocarbon and methanol oxidation [15,52–55], vinyl acetate (VA) synthesis [56,57], dehydration of formic acid [58], decomposition of N₂O [13] and other transformations [59–64]. Pd–Cu single atom alloy (SAA) was found to be active for selective hydrogenation of styrene [65], acetylene [65], and phenylacetylene [66] by Flytzani-Stephanopoulos's group. Therefore, alloying the single palladium atom at gold clusters is an effective approach to investigate the functions of single Pd atom on the activity and selectivity of chemical reactions.

Several experimental studies were reported on Au–Pd based bimetallic NP catalysts for CO oxidation reaction.

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Scott *et al.* [45] proposed that TiO₂ supported Au–Pd bimetallic catalysts prepared using dendrimer-encapsulated NPs show the utmost catalytic activity towards the CO oxidation compared with the supported Au and Pd monometallic catalysts. Yang and co-workers [67] reported the vapor phase synthesis and characterization of supported Pd, Au and unsupported bimetallic NP catalysts for CO oxidation, where excellent activity of unsupported Au–Pd bimetallic NPs for CO oxidation was observed. In 2010, Xu and co-workers [43] reported low temperature CO oxidation over SiO₂ supported Au–Pd bimetallic nanoalloy exhibiting remarkable activity. Gao *et al.* [68] also identified the superior activity of TiO₂ supported Au–Pd bimetallic nanoalloys for CO oxidation at low-temperature through reaction kinetics and spectroscopic investigations. Besides, numerous theoretical calculations were performed to study the properties and activities of Au–Pd bimetallic NPs in catalytic reactions. Density functional theory (DFT) studies on distributions of Pd atoms on Au NP by Yuan and co-workers [69] showed that Pd atoms might only prefer to locate at the face-centered cubic (fcc) (111) facets while leaving the fcc (100) facets for free. Structural rearrangement and catalytic performance are highly dependent on the reaction conditions such as gas molecule adsorptions. Previous DFT studies by Henkelman and co-workers [70] observed CO-adsorption-induced surface segregation of Pd on Au/Pd bimetallic surfaces. Our *ab initio* molecular dynamics (AIMD) simulations showed that the Pd atoms migrated from the core to the surface of the Au₃₂Pd₆ cluster with H₂ adsorptions [71]. Zhu and co-workers [72] reported that Pd atoms would segregate and stabilize at edges of Au–Pd NP under CO exposure.

Although earlier studies found that the Au₃₈ NP with truncated octahedron (TO) was not the global minimum geometry [73,74], it was chosen as the theoretical model cluster to mimic the larger NPs, because this model owns all the vital sites and surfaces of the nanocrystal. Moreover, 38 is a magic number for the TO structure and this is the typical model for the large-size NPs [72,75–79]. Our group recently also investigated Au₃₈ and Au–Ag, Au–Pd bimetallic NPs exhibiting highly symmetric structure (O_h), with all six Ag and Pd atoms located in the core site [18,71,80]. Thus we chose Au₃₇Pd₁ as a characteristic model to better understand the active site and catalytic mechanism of Au–Pd SAA. As the typical reaction mechanisms of CO oxidation have been well-established, investigations on the catalytic performance of Au₃₇Pd₁ SAA for CO oxidation can provide insights into the significant role of single atom on the catalytic activities. We

examined the most stable structure, various adsorption patterns and reaction pathway for the selected Au–Pd SAA through DFT calculations. Bonding analyses were also performed to better understand the electronic structure and the catalytic property. The findings here are helpful in predicting the structures and catalytic properties of other relevant SACs, SAAs, and even surface systems for related reactions.

THEORETICAL METHODS

Geometry optimizations and energy calculations were performed using spin-polarized DFT calculations as implemented in the Vienna *ab initio* simulation package (VASP) [81–83]. Projector augmented wave (PAW) method was employed to describe the interactions between the atomic cores and valence electrons [84]. The exchange-correlation energies were calculated *via* the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) functional [85]. The valance electrons were described by 5d¹⁰6s¹ for Au, 4d⁹5s¹ for Pd, 2s²2p⁴ for O and 2s²2p² for C. We used a 25 Å×25 Å×25 Å cubic supercell for all the calculations, as reported by Lin *et al.* [86,87]. An energy cutoff of 400 eV was chosen for the plane wave expansion of the electronic eigenfunctions. The Brillouin zone was sampled at the Γ point. All the atoms were allowed to relax until the maximum force decreases below 0.03 eV Å^{−1}. Atomic charge was calculated by Bader analysis [88,89]. The transition states (TSs) were determined using the dimer method [90–92]. Vibrational frequency calculations were performed to confirm that all stationary points were local minima (zero imaginary frequency) or TSs (one imaginary frequency).

The adsorption energy was calculated as $\Delta E_{\text{ads}} = E_{\text{total}} - E_{\text{Au-Pd}} - E_{\text{adsorbate}}$, where E_{total} , $E_{\text{Au-Pd}}$ and $E_{\text{adsorbate}}$ are the energy of the Au–Pd bimetallic NP with adsorbed gas species, bare Au–Pd and free adsorbates, respectively. Furthermore, the co-adsorption energy of CO and O₂ was defined as $\Delta E_{\text{coads}} = E_{\text{total}} - E_{\text{Au-Pd}} - E_{\text{CO}} - E_{\text{O}_2}$.

Energy decomposition analysis (EDA) was performed using DFT methods as implemented in the Amsterdam Density Functional (ADF 2016.101) program [93,94]. The PBE functional was used [85], together with the triple-zeta plus polarization (TZP) Slater-type basis sets [95]. Frozen core approximations were applied to the inner shells [1s²] for C and O, [1s²-3d¹⁰] for Pd and [1s²-4d¹⁰] for Au. The scalar relativistic (SR) effects were taken into account by the zero-order-regular approximation (ZORA) [96,97]. To understand the bonding nature between Au–Pd SAA and the adsorbates, we performed

natural bond orbital (NBO) analysis using NBO 6.0 package [98–100]. All-electron basis sets 6-311G* [101] were used for C and O atoms. LANL2DZ [102,103] basis sets and the corresponding effective core potentials (ECPs) were employed for Au and Pd atoms. These computational procedures were accomplished by using Gaussian 09 software package [104].

RESULTS AND DISCUSSION

Stability, geometry and bonding analysis of Au–Pd SAA

Same as classified in our previous paper, three sites of the NP are defined as: core site at the core of the NP, cent site at the centroid of the fcc (111) facet and hex site at the (100) facet. Thus, as shown in Fig. S1, three isomers are found for gas phase $\text{Au}_{37}\text{Pd}_1$ SAA, where Pd atom locates at three distinct sites, respectively. Au–Pd bond is stronger than Au–Au bond [69] in the bimetallic NP because of its ionic feature. Consequently, the core structure is the most stable one, with the largest coordination number of Pd atom (CN_{Pd}) in the core. The hex structure is the least stable isomer due to the weak Au–Pd interactions caused by small CN_{Pd} . Our results reveal similar trend as Yuan and co-workers reported [69].

Various methods were applied to calculate the net charge of Pd atom in the Au–Pd isomers, as shown in Table S1. Mulliken charge could not describe this bimetallic NP system very well, which has been mentioned in other work [105]. All the other methods indicate that Pd is positively charged due to the stronger electronegativity of Au atom. The largest electron transfer from Pd to Au occurs in the core structure, further confirming its strong Au–Pd interaction and stability. We compared average bond lengths and bond orders of Au–Pd and $\text{Au}_{\text{core}}\text{--Au}_{\text{core}}$ bonds in the core structure of Au–Pd NP, as shown in Table S2. Bond lengths of Au–Pd and Au–Au are all larger than the sum of the corresponding Pyykkö covalent radii (2.44 Å, 2.48 Å) [106]. $\text{Au}_{\text{core}}\text{--Pd}$ bond distance is smaller than $\text{Au}_{\text{core}}\text{--Au}_{\text{core}}$ as Pd atom presents smaller atomic radius. Besides, bond length and bond order of $\text{Au}_{\text{hex}}\text{--Pd}$ are both similar to that of $\text{Au}_{\text{core}}\text{--Pd}$ while $\text{Au}_{\text{cent}}\text{--Pd}$ shows apparent weak strength.

Adsorption of Gas molecules

To study the CO oxidation reaction on bimetallic Au–Pd SAA, we first consider the stable adsorption structures of CO and O_2 molecules on the Au–Pd SAA, as shown in Figs S2 and S3. As can be seen from Fig. S2, CO prefers to adsorb on the Au–Pd SAA by “end-on” configuration,

where C atom binds to Au or Pd atom. Among all the optimized conformations, the most favorable CO adsorption structure is an “end-on” structure at the Pd site of the hex structure (STRA_1), with the adsorption energy of -1.40 eV. The adsorption strength of CO is stronger at the Pd site than at the Au site. Compared with STRA_5 with CO adsorbed at the Au site, STRA_1 shows a shorter Pd–C bond length (1.91 Å) and stronger adsorption energy of 0.54 eV. Pd and Au coordinated C–O bond is slightly elongated by about 0.02 and 0.01 Å than free CO (C–O, 1.14 Å), respectively. Meanwhile, the Pd_{cent} site with larger CN of STRA_3 shows less favorable adsorption than Pd_{hex} site of STRA_1. These results suggest that the CN of Pd at the surface of the bimetallic nanoalloy has great influence on the CO adsorption. Previous studies by Zhu and co-workers [72] also demonstrated that Pd atoms would migrate toward the edge positions of bimetallic AuPd NPs in the presence of adsorbed CO.

In addition, we performed the Bader charge analysis for STRA_1 and STRA_5. The coordinated CO molecules are positively charged by $0.04|e|$ for STRA_1 and negatively charged by $-0.03|e|$ for STRA_5. The electron density difference (EDD) analysis shown in Fig. 1a and b indicates obvious charge transfer from the adsorption site of the SAA to CO molecule. To gain better understanding of the interaction between CO and Au–Pd SAA, we carried out spin-polarized partial density of states (PDOS), as displayed in Fig. 1c and d. The Pd-4d orbitals strongly mix with $2\pi^*$ orbitals of CO below the Fermi level (Fig. 1c) and there is no strong overlap between the Au-5d, 6s orbital with $2\pi^*$ states of CO (Fig. 1d).

To investigate why CO adsorption is stronger at the Pd site than at the Au site, we performed the EDA for CO + Au–Pd $\rightarrow$ CO@Au–Pd process. The total energy shows that CO adsorption at the Pd site is 0.58 eV lower in energy than at the Au site, consistent with the adsorption energy shown in Fig. S2. The steric interaction is the dominated term in the total energy and Pauli repulsion is the main component in the steric term (Table S3). Therefore, compared with Au site, CO adsorption at the Pd site with weaker electronegativity is more favorable because of easier electron transfer from Pd to C atom.

The Mayer bond orders and NBO population analysis of Pd–C and Au–C bonds in STRA_1 and STRA_5 are listed in Table S4. It is found that Pd–C bond order is larger than Au–C, indicating that Pd–C bond is stronger than Au–C. The NBO population analysis shows that the major contributions of the M–C bond are from C atom, illustrating a $\text{OC} \rightarrow \text{Pd--Au}$ donation pattern. The s-d

Figure 1 EDD for (a) STRA_1, (b) STRA_5 and the spin-polarized PDOS projected on (c) Pd-4d (red), Pd-5s (wine) and C-2sp (blue) for STRA_1, (d) Au-5d (black), Au-6s (green) and C-2sp (blue) states for STRA_5. For the contour plots, the charge accumulation regions are rendered in blue while the charge depletion regions are shown in green. The contour value of the electron difference density is 0.005 a.u. The Fermi level is set to zero, as shown by the dashed line.

hybridization of Pd and Au as well as the s-p hybridization of C is also clearly described. In Fig. S3, we can visualize the bonding orbitals of Pd-CO and Au-CO, where the primary interactions result from overlaps of s-d hybridization of M and 5 σ orbital of CO.

Various isomers of O₂ adsorption on Au-Pd SAAs are shown in Fig. S4, which reveals that O₂ can easily adsorb on two metal atoms of the SAA *via* the bridge binding mode. Unlike CO adsorption, “end-on” adsorption of O₂ on Au-Pd SAA is difficult. The strongest O₂ adsorption is observed in the hex Au-Pd structure (STRB_1) with the adsorption energy of −0.84 eV, where two O atoms adsorb on the parallel bridging site of one Au-Pd bond (i.e., side-on adsorption). The O–O bond length of STRB_1 is 1.35 Å, much longer than that of the free O₂ (1.23 Å), indicating that O₂ can be viewed as superoxide (O₂[−]).

The Bader charge analysis suggests that O₂ is negatively charged (−0.32|e|), while the connected Pd and Au atoms

are positively charged (0.33|e|, 0.18|e|). Therefore, O₂ acts as the electron acceptor and Au-Pd SAA acts as the electron donor. The large amount of electron transfer to the partially occupied 2 π^* orbital of O₂ leads to the elongation of the O–O bond length. This result agrees well with the EDD analysis as shown in Fig. 2a, where the electron depletion region (green) is mainly localized around the Pd and Au atoms and the electron accumulation region (blue) around O₂. Strong orbital overlaps are found between the 2 π^* orbital of O₂ and Pd-4d, Au-5s, Au-5d orbitals in the PDOS graph (Fig. 2b).

In summary, CO and O₂ both prefer to adsorb at the Pd site of the hex Au-Pd SAA because of its sufficient space for adsorbates and the weak interactions of the vertex atoms with the neighboring metal atoms. Easier charge transfer from Pd to CO or O₂ also contributes to its stability. Besides, O₂ adsorption is less favorable than CO adsorption on Au-Pd SAA.

Figure 2 (a) EDD and (b) PDOS projected on Pd-4d (red), Au-5d (black), Au-6s (green), O_{Au} -2p (blue) and O_{Pd} -2p (magenta) states for STRB_1. For the contour plots, the charge accumulation regions are rendered in blue while the charge depletion regions are shown in green. The contour value of the electron difference density is 0.01 a.u. The Fermi level is set to zero, as shown by the dashed line.

Co-adsorption of CO and O_2 on bimetallic Au-Pd (hex) NPs

In this section, co-adsorption of CO and O_2 on the Au-Pd SAA is discussed to study the CO oxidation reactions. As shown in Fig. 3, several possible co-adsorption structures are considered and named as STRC_ n ($n = 1-7$), respectively. The most beneficial co-adsorption configuration is STRC_1 ($\Delta E_{ads} = -1.94$ eV), in which the O_2 molecule adsorbs on the parallel bridging site of the Au-Pd bond and the CO molecule adsorbs on the vertical bridging site of the adjacent Au-Pd bond. The bond lengths of the co-adsorbed C-O and O-O are 1.17 and 1.35 Å, respectively, similar to those of the single molecule adsorptions. As the adsorption strength of STRC_1 is stronger than STRA_1 and STRB_1, we can conclude that the co-adsorption structure is the most favorable intermediate in the reaction pathway.

Reaction mechanism of CO oxidation on bimetallic Au-Pd NPs

In general, CO oxidation reaction mainly proceeds *via* Langmuir-Hinshelwood (L-H), Eley-Rideal (E-R) or Mars-van Krevelen (MvK) mechanism. As there is no surface lattice non-metal atom in the Au-Pd SAA, MvK mechanism is unlikely. For the E-R mechanism, the surface of Au-Pd SAA will be predominantly covered by CO molecule as the adsorption energy of CO (−1.40 eV) is much larger than O_2 (−0.86 eV). Then the E-R mechanism that gaseous O_2 adsorbs at the CO pre-adsorption configuration does not seem to be reasonable due to unfavored energetics. As O_2 adsorption at the Pd atom with the pre-adsorbed CO is exothermic (−0.54 eV), the Pd site will be covered by CO and O_2 with the co-ad-

sorption structure instantly under CO oxidation conditions. Accordingly, we focus on the well-accepted L-H mechanism in this article.

For the L-H mechanism, the structures of intermediates (IMs), TSs and the potential energy profile for CO oxidation reaction are summarized in Figs 4 and 5. As co-adsorption is the strongest adsorption pattern, we take STRC_1 as the initial configuration for the further CO oxidation reactions. Then the adsorbed O_2 molecule interacts with the adsorbed CO to yield peroxo-type (OOCO) complex intermediate (IM2) through an energy barrier of 0.73 eV. Afterwards, the cleavage of O-O bond of OOCO intermediate occurs immediately, resulting in the subsequent elimination of a CO_2 molecule and an oxygen atom on the Au-Pd SAA. Then a new CO molecule adsorbs on the Pd site and reacts with the remaining O atom, forming another CO_2 molecule with an energy barrier of 0.84 eV. All fundamental steps of the catalytic cycle are exothermic and the energy barriers for the TSs (TS1 and TS2) are reasonable for the CO oxidation reaction under ambient experimental conditions.

We used Bader charges (see Table 1), EDD and PDOS to further analyze the electronic structures of the Au-Pd SAA during the CO oxidation reaction. It can be seen from the co-adsorption superoxo structure IM1 that there is obvious charge transfer from Au-Pd SAA to the adsorbates, where the Bader charges of the adsorbed O_2 and CO molecules are $-0.63|e|$ and $-0.19|e|$, respectively. This result reveals that there are more charge transfers from the SAA to O_2 adsorption and the Bader charge of the SAA increases significantly to $0.82|e|$. The charge transfer is also observed in the EDD analysis shown in Fig. S5a, where obvious electron accumulations at $2\pi^*$ orbitals of

Figure 3 Co-adsorption structures and adsorption energies of CO and O₂ on Au-Pd bimetallic NPs. Selected bond lengths are marked in Å.

Figure 4 The structures of initial state (IS), TSs, IMs and final state (FS) in CO oxidation reaction on Au-Pd SAA. Selected bond lengths are marked in Å.

Figure 5 Schematic potential energy profile for the CO oxidation reaction on Au-Pd SAA via the L-H mechanism. IM1 and IM2 feature activated superoxo and peroxy O₂ species, respectively.

O₂ and CO molecules mainly contribute to the enlarged O–O and C–O bond lengths. Besides, strong interactions

between CO, O₂ and SAA are shown in PDOS (see Fig. S5b and c), with apparent $2\pi^*(O_2)$ orbitals located near the Fermi level and partially occupied $2\pi^*$ orbitals of CO.

When one O atom of the O₂ molecule approaches to the CO molecule to form TS1, less charge transfers from SAA to the adsorbates and apparent charge transfer from CO to O₂ molecule is observed, as shown in Table 1 and Fig. S6a. PDOS in Fig. S6b also reveals that the O atom dissociated from O₂ interacts with CO and contributes to remarkably enhanced C-2sp distributions below the Fermi level. After the formation of the first CO₂ molecule, a negatively charged O^{x-} ($x = 1, 2$) ion is left on the SAA, resulting in an increase of the positive charge of the SAA in IM3. Then the adsorption of the second CO molecule at the Pd site causes more charges transfer from the SAA. Finally, charge transfers back to the SAA with the release of the second CO₂ molecule.

CONCLUSIONS

In the present study, we have probed the catalytic me-

Table 1 Bader charges of IS, IMs, TSs and FS in the reaction pathway^a

Systems	[Pd]	[Au-Pd]	[CO_1]	[O ₂]	[OOCO]	[CO_2]	[O]	[OCO]
STRA_1	0.23	0.16	-0.16	—	—	—	—	—
IM1	0.43	0.82	-0.19	-0.63	-0.82	—	—	—
TS1	0.22	0.58	-0.09	-0.49	-0.58	—	—	—
IM2	0.24	0.67	0.75	-1.42	-0.67	—	—	—
IM3	0.37	0.79	—	—	—	—	-0.79	—
IM4	0.40	0.97	—	—	—	-0.16	-0.81	-0.97
TS2	0.39	0.78	—	—	—	-0.03	-0.76	-0.79
FS	0.13	0.00	—	—	—	—	—	—

a) [Pd] and [Au-Pd] refer to the charge of the Pd atom and total charge of Au-Pd SAA, [CO_1], [CO_2] and [O₂] refer to the charge of the first, second adsorbed CO and O₂ molecules, while [OOCO], [O] and [OCO] refer to the charges of the adsorbates at the surfaces SAA.

chanism of CO oxidation reaction on Au-Pd single atom alloy Au₃₇Pd₁ via DFT calculations. The relative energies and electronic structures of Au-Pd SAAs reveal that Pd atom at the core site is more favored than the cent and hex sites. CO prefers terminal adsorption at the Pd site of Au-Pd SAA while O₂ tends to form a bridging bond with Pd and its adjacent Au atom. The co-adsorption structure of CO/O₂@Au-Pd is found to be the most beneficial adsorption configuration, where CO and O₂ molecules adsorb on the vertical (end-on) and parallel bridging (side-on) sites of Au-Pd bonds, respectively. The calculated energy profile indicates that CO oxidation reaction on Au-Pd SAA follows the L-H mechanism and is feasible at relatively low temperature due to the low activation energy barriers (0.73 and 0.84 eV). This work yields guidelines for understanding the active sites and catalytic mechanisms of Au-Pd NPs, which may also provide evidence for designing new SAAs with high-performance catalytic activities.

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Author contributions Li J conceived the project. Baskaran S and Xu CQ carried out the theoretical calculations and co-wrote the paper. All authors discussed the results and commented on the manuscript.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Experimental details are available in the online version of the paper. Additional information on the optimized geometries, charges, bond lengths and bond orders of Au–Pd nanoparticle as well as the structures, adsorption energies and bonding analyses including the EDA and NBO analyses of CO@Au-Pd and $\text{O}_2\text{@Au-Pd}$ is provided.

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Au–Pd单原子合金(SAA)催化剂的催化机理和成键分析: CO氧化反应

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摘要 单原子催化剂(SACs)在催化科学领域引起了人们的广泛关注, 包括被称为单原子合金(SAAs)的包含金属-金属键合的双金属催化剂. 本文通过量子化学计算方法研究了Au–Pd单原子合金模型 $\text{Au}_{37}\text{Pd}_1$ 上CO氧化反应的催化机理和成键分析, 确定了 CO@Au-Pd , $\text{O}_2\text{@Au-Pd}$ 和 $\text{CO/O}_2\text{@Au-Pd}$ 等吸附构型的几何结构以及吸附物与底物间的结合能. Pd原子位于核芯位置的核-壳结构被证实为Au–Pd单原子合金的最稳定构型, 该结构的稳定性来源于Pd原子向Au原子的电荷转移. 根据结合能和化学成键分析, CO和 O_2 分子均优先吸附在配位数低且位于顶点位置的Pd原子上. 本文报道了一种新的CO和 O_2 共吸附结构, 其中CO和 O_2 分别在两个相邻Au–Pd键上以垂直和平行桥联方式吸附, 该Au–Pd单原子合金的CO氧化反应具有低能垒且遵循Langmuir-Hinshewood (L-H) 机理. 本文探讨了单原子合金催化剂中单原子在催化反应中的重要作用, 可以为设计具有优异催化活性的新型单原子合金催化剂提供依据.