Triazine COF-supported single-atom catalyst (Pd₁/trzn-COF) for CO oxidation

Yin-Juan Chen^{1,2}, Hong-Ying Zhuo², Yuan Pan¹, Jin-Xia Liang^{3*}, Chen-Guang Liu^{1*} and Jun Li^{2,3*}

ABSTRACT Single-atom catalysts (SACs) with well-defined and specific single-atom dispersion on supports offer great potential for achieving both high catalytic activity and selectivity. Covalent organic frameworks (COFs) with tailor-made crystalline structures and designable atomic composition is a class of promising supports for SACs. Herein, we have studied the binding sites and stability of Pd single atoms (SAs) dispersed on triazine COF (Pd₁/trzn-COF) and the reaction mechanism of CO oxidation using the density functional theory (DFT). By evaluating different adsorption sites, including the nucleophilic sp² C atoms, heteroatoms and the conjugated π -electrons of aromatic ring and triazine, it is found that Pd SAs can stably combine with trzn-COF with a binding energy around -5.0 eV, and there are two co-existing dynamic Pd₁/trzn-COFs due to the adjacent binding sites on trzn-COF. The reaction activities of CO oxidation on Pd₁/trzn-COF can be regulated by the anion- π interaction between a $+\delta$ phenyl center and the related $-\delta$ moieties as well as the electron-withdrawing feature of imine in the specific complexes. The Pd₁/trzn-COF catalyst is found to have a high catalytic activity for CO oxidation *via* a plausible tri-molecular Eley-Rideal (TER) reaction mechanism. This work provides insights into the d- π interaction between Pd SAs and trzn-COF, and helps to better understand and design new SACs supported on COF nanomaterials.

Keywords: single-atom catalysts, Pd loading, covalent organic frameworks, CO oxidation

INTRODUCTION

Heterogeneous single-atom catalysis has aroused great interest in catalysis science since this concept was proposed a decade ago [1]. Significant progress has been

made in this field in recent years [2–16]. Single-atom catalysts (SACs) with well defined, atomically distributed metal active centers are the ultimate goal of fine dispersion [17–19] and are particularly important for the supported noble metal catalysts [1,20]. SACs offer great potential for gaining insight into the electronic structures of active centers and the catalytic reaction mechanisms for their activity and selectivity [5]. As is well known, the support plays a vital role in dictating the catalytic properties and performance of SACs. Usually, oxides are the most widely used supports for metal catalysts, where the defects on surface are specifically used to stabilize metal single atoms (SAs) [1,20–24]. Besides, carbon-based supports doped with other heteroatoms also offer important donor sites for metal atoms, especially for N-doped carbon materials and mesoporous polymeric graphitic carbon nitride (e.g., mpg-C₃N₄), which can not only strongly anchor metal atoms but also regulate the electronic properties of the prepared SACs [25–29]. Currently, among the challenges of SACs, the amount of loading and the stability of metal SAs on the surface are the bottleneck for practical application of SACs [30,31]. Therefore, the deliberately chosen supports may be one of the important ways to balance the loading amount and the stability of SAs.

Covalent organic frameworks (COFs) are a type of porous and crystalline materials, which are constructed solely from light elements (H, B, C, N, and O) that are known to form strong covalent bonds [32–36]. As an emerging class of porous materials, COFs represent one kind of catalyst supports with designable periodic structures, which can interact with active metal nanoparticles or SAs to form excellent heterogeneous catalysts [37–39].

¹ State Key Laboratory of Heavy Oil Processing, College of Chemical Engineering, China University of Petroleum (East China), Qingdao 266580, China

² Department of Chemistry, Key Laboratory of Organic Optoelectronics & Molecular Engineering of Ministry of Education, Tsinghua University, Beijing 100084, China

³ Department of Chemistry, Southern University of Science and Technology, Shenzhen 518055, China

* Corresponding authors (emails: liangjx2009@163.com (Liang JX); cgliu@upc.edu.cn (Liu CG); junli@tsinghua.edu.cn (Li J))

Among many examples, the Pd/COF-LZU1 with the singly dispersed Pd(OAc)₂ was reported, and its excellent catalytic activity was confirmed by the Suzuki-Miyaura coupling reaction [37–39]. COF-367-Co (1%) with separated cobalt atoms in an extended COF gives rise to electrocatalysts that promote CO₂ reduction to CO with exceptionally high activity and selectivity [40], and the spin-state manipulation of cobalt in COF-367-Co can regulate the photocatalytic performance of such materials [41]. Recently, Co-TpBpy, Ni-TpBpy and Cu-TpBpy with 2,2'-bipyridine used as atomic metal anchors are established for robust water oxidation electrocatalysts, CO₂ photoreduction and cycloaddition reactions, respectively [42–44]. Triazine and its derivatives are typical building blocks for two-dimensional (2D) COFs, which are widely used as catalysts as well as gas adsorption and separation [45–48]. In fact, sp² carbon or heteroatom-rich monomers such as graphene and triazine derivatives could serve as strong doping sites for the transition metal atoms [49]. Trzn-COF built by *p*-phenylenediamine, *s*-triazine and *p*-phthalaldehyde is an ideal scaffold, and the loaded palladium atoms or nanoparticles provide catalytic active sites for multi-fold Heck, C–C couplings and CO oxidation reactions [50]. Actually, the efficient active centers in some supported metal nanoparticles are demonstrated experimentally and theoretically to be SA moiety [51–53], and the dynamic single-atom catalytic mechanism was proposed in our previous study [18,54,55]. At present, there are a number of experimental investigations on the assembling and performance of the COF catalysts [56]. However, in-depth theoretical understanding of the stability, activity and selectivity of these catalysts remains elusive.

In this work, density functional theory (DFT) investigations are carried out to study the stability of Pd₁/trzn-COF catalyst and its catalytic mechanism of CO oxidation. The binding sites of Pd SAs on the skeleton, side-wall, surface as well as interlayers [56] of trzn-COF are systematically studied. It turns out that there are strong interactions between Pd SAs and the wall of the main channel of trzn-COF, with the calculated binding energy of Pd SAs greater than –5.00 eV. The differential electron density of Pd₁/trzn-COF indicates that Pd atoms can be stably anchored on the surface of trzn-COF due to the strong interaction between the conjugated π -electrons of trzn-COF and the d orbitals of Pd SAs. It is difficult for Pd SAs to penetrate the interlayer conjugation and migrate on the wall of the straight channels in the *c*-axis orientation of Pd₁/trzn-COF. To explore the catalytic properties of the Pd₁/trzn-COF, the CO oxidation to CO₂

is studied as a probe reaction. Furthermore, both Langmuir-Hinshelwood (L-H) and tri-molecular mechanisms [57–59] for CO oxidation on Pd₁/trzn-COF SAC are taken into consideration. Based on our theoretical calculations, we demonstrate that the Pd SAs can be stably anchored on the side-wall of trzn-COF through a strong interaction between the conjugated π electrons/lone-pair electrons of trzn-COF and the d orbitals of Pd SAs, and Pd₁/trzn-COF SAC shows relatively high catalytic activity for CO oxidation.

COMPUTATIONAL MODEL AND METHODS

The first-principles DFT calculations were carried out using Dmol³ module in the Materials Studio software package. The Perdew-Wang functional (PW91) [60,61] within the formulation of generalized gradient approximation (GGA) was used to handle the electron exchange and correlations. The Ortmann, Bechstedt and Schmidt (OBS) [62] parameters for van der Waals (vdW) dispersion correction were also used for all the calculations. The electrons of the metal atoms were described by semi-core pseudopotentials (DSPPs) and a double numerical plus polarization (DNP) basis set [63]. The light elements including C, H, O, N atoms were treated with full-electron basis sets. A 3 × 3 × 5 *k*-point mesh (see computational details S1 in the Supplementary information (SI)) and a Gaussian smearing finite temperature broadening method ($\sigma = 0.005$ Hartree) were used and the real space atomic cutoff radius was chosen as 4.0 Å. All geometry optimizations and self-consistent field calculations were performed with the threshold of 2 × 10^{–5} a.u. for energy change and 1 × 10^{–5} a.u. for self-consistent-field (SCF) density convergence.

The trzn-COF unit cell was obtained from the work of Mullangi's group [50]. The lattice parameters of primitive cell were fully relaxed within the aforementioned computational scheme. A two-layer trzn-COF (001) surface was built with the vacuum slab thickness of 15 Å. Binding sites locating between two layers as well as in the wall of COF pore were considered [64]. The transition states were located using the synchronous method with conjugated gradient refinements [65], which involved a linear synchronous transit (LST) maximization, followed by repeated conjugate gradient (CG) minimizations and quadratic synchronous transit (QST) maximizations until a transition state was located, and further confirmed by the vibrational frequency analysis. More calculational details and theoretical analysis strategy are listed in the computational details of SI.

RESULTS AND DISCUSSION

Structural and electronic properties of trzn-COF primitive cell

The optimized lattice parameters (space group $P6/mcc$, $a = 36.3667 \text{ \AA}$, $c = 6.8003 \text{ \AA}$) of trzn-COF primitive cell (Fig. 1) are consistent with the previous results [50]. The calculated charges of trzn-COF from Mulliken and Hirshfeld population analyses (abbreviated as MPA and HPA, respectively) are listed in Table S1. As shown in Table S1, both HPA and MPA show that the selected atomic charges of sp^2 phenyl C atoms (C_5 , C_6 , C_8 , C_9 , C_{13} , and C_{19}), N_1 , N_{11} and O_3 atoms in trzn-COF are of negative values; the HPA and MPA charge values are -0.076 and -0.043 for C_5 , -0.085 and -0.024 for C_6 , -0.041 and -0.022 for C_8 , -0.064 and -0.058 for C_9 , -0.057 and -0.038 for C_{13} , -0.045 and -0.028 for C_{19} , -0.390 and -0.151 for N_1 , -0.349 and -0.169 for N_{11} , -0.425 and -0.072 for O_3 , respectively. Although the atomic charge populations of the phenyl C atoms have an order of magnitude difference compared with those of N and O atoms that contain lone-pair electrons, the atomic Fukui indices (Table S1) of those atoms share the same magnitude. These data illustrate that these sites of sp^2 phenyl C atoms and imine ($C=N$ linker) nitrogen and oxygen atoms have electronegativity and the nucleophilic attack sensibility, which is further addressed by electrostatic potential (ESP) mapped vdW surface and local minima of average local ionization energy (ALIE) on vdW surface of the trzn-COF primitive cell (as shown in Fig. S1a and b). Thus, we choose all of these different sites of trzn-COF and also the small clefts (Fig. S2) around the triazine core composed of the ether, N and C atoms of the triazine

rings suggested by Mullangi *et al.* [50] to investigate the adsorption stability of Pd atoms on trzn-COF.

Depiction of Pd_1 /trzn-COF

According to the charge population analysis of the ESP mapped vdW surface and local minima of ALIE on vdW surface, nine Pd atomic adsorption sites are chosen. Based on the metal adsorption target sites (Fig. 1b), the top view of 3D tran-COF (Fig. 1c) and the optimized structures of Pd_1 /trzn-COF (Fig. 2), the nine Pd atomic adsorption sites are divided into three surface sites (on the surface layer of the 3D tran-COF, S_n , $n = 1, 2, 3$), three interlayer sites (in the crevice of the two-layer trzn-COF slab, L_n , $n = 1, 2, 3$) and the other three wall sites along the c -direction circular channel of the trzn-COF (W_n , $n = 1, 2, 3$). The optimized structures of the Pd_1 /trzn-COF are displayed in Fig. 2, and the calculated binding energies (E_b) (Equation (S5) in SI) of Pd SA adsorption on trzn-COF, the distances between Pd and N, C or O atoms, and the amount of Hirshfeld charge population transferred from the Pd SAs to trzn-COF in S_n , L_n and W_n sites are listed in Table S2. As seen from Table S2 and Fig. 2, the binding energies of Pd SAs on L_1 and L_3 structures are 0.11 and 0.07 eV, respectively, indicating that the two structures are thermodynamically unstable. In other words, the relative strong π - π interaction can block the penetration of Pd SAs into the layers of the eclipsed triazine and p -phenylenediamine groups with a layer-distance of $3.4 \text{ \AA}$ in L_1 and L_3 . Conversely, the adsorption of Pd SAs on the different sites of S_n and W_n are thermodynamically favorable because of their negative binding energies ranging from -1.17 to -5.83 eV, and the strength order of the binding energies is $W_2 > W_3 > S_3 > S_2 > S_1 >$

Figure 1 Schematic representation of the monomeric units and the COF structure. (a) 2,4,6-tris(p -formylphenoxy)-1,3,5-triazine reacting with benzene-1,4-diamine to form triazine COF (trzn-COF). (b) Target sites for metal adsorption are marked with different numbers, in which, the red numbers 1, 2, 3 represent the triazine group, phenyl, p -phenylenediamine group, respectively; the minimal build unit of trzn-COF are marked with atomic symbols and indexes. (c) The top view of 3D framework formed by the stacking of the hexagonal layers in a $P6/mcc$ setting. The 1D channels extend along the c -axis (with the diameter of $29 \text{ \AA}$).

Figure 2 The optimized structures of Pd₁/trzn-COF with different adsorption sites of Pd SAs (S_n , L_n and W_n ; $n = 1, 2, 3$). The letters of S, L and W represent the surface, interlayer and wall of the straight channel in the c -direction of Pd₁/trzn-COF, respectively. The Pd SAs are marked with fluorescent green balls.

$L_2 > W_1$. Among these stable structures, W_2 represents one of the most stable structures due to its strongest binding energy (-5.83 eV), leading to the strong interaction between Pd SA and trzn-COF. The calculated Hirshfeld charge population ($+0.32|e|$) of Pd SA in W_2 shows that there are some electrons transferred from Pd SA to trzn-COF. For the structure of W_2 , the Pd SA adsorbs on the bridge site of C–C bond, and the bond lengths (2.15 and 2.36 Å) of Pd–C (sp^2 C atom) are very close to that (2.05 – 2.32 Å) in the typical chemical bonds of Pd–C observed in various Pd-based complexes [66].

It is worth noting that even though the structural parameters apparently (Table S2) display that the distances (2.48 – 2.79 Å) between Pd and C or N atoms in S_n ($n = 1, 2, 3$) are longer than the normal chemical bonding distances of Pd–C and Pd–N [67], the binding energies of Pd₁/trzn-COF of S_n ($n = 1, 2, 3$) are still high (-4.74 to -5.44 eV), indicating that there are relative strong interactions between Pd SAs and the surface of trzn-COF in S_n ($n = 1, 2, 3$). To further investigate this type of interaction between Pd SAs and trzn-COF in S_n ($n = 1, 2, 3$), the differential electron density of Pd₁/trzn-COF for S_n ($n = 1, 2, 3$) is calculated and displayed in Fig. 3a (more details are given in computational details S2 in SI) [68,69]. As seen from Fig. 3a, the blue areas show where the electron density has been enriched with respect to the fragments,

whereas the yellow areas show where the density has been depleted. The relatively enriched electron densities are delocalized between Pd SAs and the π -electron zones of six-membered rings, while the densities decrease on the d-electron zone of Pd and the planes of all six-membered rings in S_n ($n = 1, 2, 3$), especially in S_2 and S_3 . Accordingly, the strong interaction results from the d-electrons of the adsorbed Pd SAs and the conjugate π -electron of six-membered rings in S_n ($n = 1, 2, 3$). Here the calculated Hirshfeld charges of Pd SAs in S_n ($n = 1, 2, 3$) are $+0.14|e|$, $+0.21|e|$ and $+0.20|e|$, respectively, which also show that there are some electrons transferred from Pd SAs to trzn-COF.

In comparison, the binding energy (-3.80 eV) of Pd SA and trzn-COF in L_2 site is lower than that in S_n ($n = 1, 2, 3$) and W_n ($n = 2, 3$) sites, possibly attributed to the staggered phenyl groups between layers of L_2 , which can weaken the π – π interaction between layers. The Pd SA is on the plane of four C atoms from the eclipsed C–C bonds of two staggered phenyl groups with two Pd–C bonds (1.86 Å) and two Pd–C bonds (1.96 Å) in L_2 . In order to analyze the bonding interaction of Pd and C, N, O atoms of trzn-COF, the projected density of states (PDOS) of L_2 and W_n ($n = 1, 2, 3$) are shown in Fig. 3b. As seen from Fig. 3b, we note that there are more overlap levels between Pd 4d and C/N/O 2p states near Fermi level, illustrating that there is relatively strong interaction among these atoms, which agrees with the calculated binding energies (-1.17 to -5.83 eV) of Pd SAs on trzn-COF. Furthermore, the strength of the binding energies increases with the decrease of the d-band center (E_{dbc}) of Pd SAs, showing an obvious linear relationship (Fig. 3c).

Adsorption of gas molecules

For CO oxidation over Pd₁/trzn-COF, the adsorption strength of CO, the adsorption state of O₂ on the Pd₁/trzn-COF, and the desorption of CO₂ are the key factors in determining the catalytic mechanism and activity of CO oxidation reaction. Thus, the adsorption of reactants and products are considered here.

CO and O₂ adsorption

Based on the most stable structure (W_2) of Pd₁/trzn-COF, we here consider the CO and O₂ independent adsorption and co-adsorption on Pd SA of W_2 . Firstly, the calculated differential electron densities based on the optimized structures of CO and O₂ adsorption on Pd SA are displayed in Fig. 4a and b, respectively. And the selected bond lengths of Pd–C and Pd–O as well as adsorption energies of CO and O₂ are collected in Table S3. As seen

Figure 3 (a) The isosurfaces of differential electron densities of Pd₁/trzn-COF for S_n ($n = 1, 2, 3$) between the different two fragments of Pd SAs and trzn-COF (blue and yellow refer to the increase and decrease of the electron density, respectively; isosurface value = 0.01 a.u.). (b) PDOS of the Pd SAs of Pd₁/trzn-COF. The Fermi energy level is plotted with green short-dash line. (c) Linear fitting of binding energy (E_b) to the d -band center energy (E_{dbc}) of Pd SAs.

from Fig. 4a and b, CO “end-on” adsorbs on Pd SA with a Pd–C bond length of 1.88 Å that is between the Pd–C single and double bond lengths estimated from the atomic covalent radii of Pyykkö [67], which leads to a relatively strong CO adsorption energy (E_{ad} , −2.13 eV) on W₂, which is consistent with the calculated differential electron densities of CO and Pd₁/trzn-COF. As shown in Fig. 4a and b, the larger electron densities on Pd–C bonds clearly demonstrate the formation of strong covalent bonding after CO adsorption on Pd SA. However, O₂ prefers to bind to Pd SA “side-on” and the distances between Pd and O atoms are 2.04 and 2.22 Å, respectively. These distances are longer than the single bond length (1.91 Å) of Pd–O [52], and thus the adsorption (−1.00 eV) of O₂ on W₂ is relatively weak. And the electron densities between Pd and two O atoms of O₂ are also lower than those on Pd–C bonds. Moreover, the PDOS analyses are displayed in Fig. 4e. The CO 2 π^* and O₂ 2 π^* orbitals are partially charged and redistributed below the Fermi level and the CO 5 σ orbitals are pushed down and merged with the 1 π orbitals after CO and O₂ adsorption on Pd₁/trzn-COF, and partially Pd 4d states are expanded across the Fermi level, which indicates that there is possibly some electron transfer between Pd SAs and the

adsorbed CO and O₂ (Fig. 4e). The Hirshfeld charge population Δq^c (e) of Pd SAs in W₂ is +0.32| e |. The transferred Hirshfeld charge population (Δq^d (e)) from Pd₁/trzn-COF to adsorbed specific species listed in Table S3 shows that Δq^d (e) of the adsorbed CO and O₂ on Pd₁/trzn-COF are −0.09| e | and −0.35| e |, respectively. The current Δq^e (e) of Pd after O₂ and CO adsorption are 0.44| e | and 0.26| e |, respectively. Compared with Pd SAs on clean Pd₁/trzn-COF, the Pd SAs loses charge (0.12| e |) after O₂ adsorption, and obtains charge (0.06| e |) after CO adsorption due to the CO 5 σ donation.

Besides, we also explore the CO and O₂ co-adsorption on Pd₁/trzn-COF and the optimized structures are shown in Fig. 5. As shown in Fig. 5a and b, the adsorbed O₂ is pushed aside by the co-adsorbed CO and the adsorption energies of the adsorbed O₂ towards C=N bond (Fig. 5a, CO–O₂*-1) and phenyl (Fig. 5b, CO–O₂*-2) are −2.21 and −2.56 eV, respectively. By comparing the electron localization function (ELF) map, the differential electron densities and PDOS (Fig. 5a–d, g), no distinguishable shifts are found. However, the ESP mapped isosurface shows the typical anion– π interaction fingerprint with the $-\delta$ oxygen and $+\delta$ phenyl center in CO–O₂*-2 (Fig. 5e, f). Accordingly, the distance of oxygen to phenyl center is

Figure 4 The differential electron densities of the structures of the adsorbed species (a) CO, (b) O₂, (c) CO₂ “side-on” (CO₂*-1) and (d) CO₂ “end-on” (CO₂*-2) absorption on Pd₁/trzn-COF (blue: zone of charge increased, yellow: zone of charge decreased, isosurface value = 0.05 a.u.). (e) The PDOS of CO, O₂ and CO₂ adsorbed on Pd₁/trzn-COF, where the states of all Pd 4d are blue, and the Pd₁/trzn-COF without and with the adsorbed species are green and red, respectively. The Fermi level is plotted by green short-dash line.

3.53 Å with energetic preponderance for CO-O₂*-2 of -0.34 eV (the typical anion- π interaction energies are in the range of -0.21 to -0.52 eV) [70], which is mainly attributed to the electrostatic energy according to the energy components (Table S4) and electronic features. Therefore, the sp² C not only provides the binding site to Pd SA, but also adjusts the adsorption features of intermediates.

Considering the strong adsorption of CO molecule on Pd₁/trzn-COF, co-adsorption of two CO molecules is further investigated. The optimized structure and the calculated isosurface map of differential electron densities and PDOS of two CO molecules adsorbed on Pd₁/trzn-COF are displayed in Fig. 6. The adsorption energy of two CO molecules is -3.88 eV, and the Pd-C distances in CO*-1 and CO*-2 are 1.92 and 1.96 Å, respectively (Fig. 6a). ELF map shows obvious valence bonding of Pd-C and lone-pair electron feature on O atoms of CO*. From PDOS, the interaction of Pd 4d with CO 2 π * and CO 5 σ states results in the CO 2 π * orbital close to the Fermi level, while the CO 5 σ orbital is far away from the Fermi level.

CO₂ adsorption

As shown in Fig. 4c and d, the adsorption states of CO₂ are “side-on” and “end-on” on W₂ of the Pd₁/trzn-COF, and the two adsorption energies of CO₂ are -0.63 and -0.42 eV, respectively, showing that the “side-on” adsorption is more stable than the “end-on” state. Actually,

the “side-on” adsorbed CO₂ is slightly bending (150.8°) on the Pd SA similar to that of the CO₂ anion in the previous study [71], indicating that there is some electron transfers from Pd SA to the “side-on” adsorbed CO₂. The calculated PDOS (Fig. 4e, CO₂*-1) shows that the CO₂ 5 σ * orbitals are partially charged and cross over the Fermi level. That is due to the lone pair of CO₂ that provides electrons to the Pd 4d orbitals, while the Pd 4d electrons back donate to the CO₂ orbitals. In contrary, when CO₂ “end-on” approaching Pd atom, there is almost no electron transfer from the lone-pair electron to the 4d orbitals, with the net charge on CO₂ of 0.07|e| only (Fig. 4e, CO₂*-2).

CO oxidation mechanism on Pd₁/trzn-COF

According to the previous reports [57–59], CO oxidation with strongly associated support generally occurs through E-R or L-H mechanisms, depending on the type of catalyst and the state of adsorbates. On the basis of the calculated properties of CO, O₂ and their co-adsorption configurations, the adsorption of CO ($E_{\text{ad}} = -2.13$ eV) on Pd₁/trzn-COF is significantly stronger than O₂ ($E_{\text{ad}} = -1.00$ eV). The recently proposed new Eley-Rideal (NER) mechanism is unlikely to occur because of dominant CO adsorption compared with O₂ adsorption [72]. Comparing co-adsorption of CO and O₂, the adsorption energy (-3.88 eV) of two CO molecules is energetically more favorable. Thus, both the L-H mechanism and tri-molecular L-H (TLH) or tri-molecular E-R (TER) mechanism

Figure 5 The co-adsorption of CO and O₂. (a, b) Electron localization function maps, (c, d) isosurface maps of differential electron densities of CO-O₂*-1 and CO-O₂*-2 (blue: zone of charge increased, yellow: zone of charge decreased, isosurface value = 0.05 a.u.). (e, f) Top and side views of ESP mapped isosurface of CO-O₂*-2 (isosurface value = 0.08 a.u.). (g) The PDOS with Pd 4d states in blue, the CO and O₂ states in green and pink, respectively. The Fermi level is plotted with green short-dash line.

Figure 6 The co-adsorption of two CO molecules. (a) Isosurface map of differential electron densities (blue: zone of charge increased, yellow: zone of charge decreased, isosurface value = 0.05 a.u.). (b) Electron localization function map. (c) The PDOS with Pd 4d states in blue, the free CO 2p and CO*-1 2p states in green, CO*-2 2p states in red, respectively. The Fermi level is plotted with green short-dash line.

[19,73–75] are considered here.

L-H mechanism on W₂ site

For CO oxidation following the L-H mechanism, the initial states can start from CO-O₂*-1 (Fig. 7a, IS2-1) and CO-O₂*-2 (Fig. 7a, IS2-2). The reaction triggered from CO-O₂*-2 is energetically more favorable due to the electrostatic interaction between + δ phenyl and related - δ moiety. PDOS analysis presents similar variations for

both CO-O₂*-1 and CO-O₂*-2, except the slight shift of intermediate (IM1) Pd 4d states (Fig. S3a). In IM1-2, the distance of Pd-C is shorter (2.34 Å) than that in IM1-1 (2.58 Å), which makes IM1-2 more stable. While the C-O bond forms in the first transition state (TS1), the 5 σ +1 π and 4 σ states merge with sufficient overlap. Similarly, the analogous trend also exists in the process of O-O bond cleavage (TS2). Additionally, the O₂ splits to form the first CO₂ and the atomically adsorbed O on the Pd SA. For the

Figure 7 (a) Calculated energy profiles of CO oxidation along the L-H mechanism with zero-point vibrational energy (ZPVE) included. Optimized geometries of CO-O₂*-2 triggered pathway are in red (b) and CO-O₂*-1 ones are in green (c), the selected bond distances (Å) of transition states are marked in red and the related bonding details are listed in Tables S5 and S6.

pathway starting from CO-O₂*-1, the energy barriers for the formation of C-O bond and the cleavage of O-O bond are 1.16 and 0.20 eV, respectively. While for the pathway starting from the CO-O₂*-2, the energy barriers of above two steps are 1.27 and 0.10 eV, respectively. Thus, compared with the energy barriers in the pathway of CO-O₂*-1, the anion- π interaction between $+\delta$ phenyl center and $-\delta$ oxygen in CO-O₂*-2 can stabilize the CO and O₂ co-adsorption state and facilitate the O-O bond cleavage. As shown in Fig. 7a and b, the formation of the second CO₂ is much easier with an energy barrier of 0.28 eV (TS3). Finally, the bent CO₂⁻ (FS2) can lose one electron, leading to the formation and desorption of a neutral CO₂ molecule.

Tri-molecular mechanism on W₂ site

For the CO oxidation *via* the tri-molecular mechanisms, as shown in Fig. 8, the reaction progress of the TER can

be characterized by an equation: $2\text{CO}^* + \text{O}_2 \rightarrow \text{OCO-OCO}^* \rightarrow 2\text{CO}_2^*$, in which an additional O₂ is weakly adsorbed between the two adsorbed CO on Pd SA and then the OCOO-CO* intermediate forms. In contrast, for the TLH, the O₂ is actively adsorbed on Pd SA directly after adsorption of two CO molecules. As seen from Fig. 8a, the rate-limiting steps of CO oxidation following TER (TS4-1) and TLH (TS4-2) on W₂ site are also the formation of C-O bond with the apparent activation energy of 1.03 and 1.19 eV, respectively. And O-O bond cleavage is easy for TER mechanism due to the very low energy barrier of 0.13 eV (TS5-1). However, the cleavage of O-O bond followed by the formation of C2-O4 bond (TS5-2) is a little bit difficult with the energy barrier of 0.69 eV, due to the strong interaction between Pd-O4 (the distance of Pd-O4 is 2.02 Å). Therefore, the CO oxidation through the TER mechanism with O₂ molecule activated by two pre-adsorbed CO molecules with the formation of OCO-

Figure 8 (a) Calculated energy profiles of CO oxidation on W_2 site through the tri-molecular mechanism with ZPVE included. Optimized geometries along the TER mechanism (b) and TLH mechanism (c). The selected bond distances (in the unit of Å) of transition states are marked in red and the related bonding details are listed in Tables S7 and S8.

OCO* peroxide is energetically most favorable.

The dynamic co-existence of W_2 and W_3

Inasmuch as W_3 is adjacent to W_2 , as shown in Figs 2 and 3c, the diffusion of Pd SA from the W_2 site to the adjacent imine-bonded W_3 site is not impossible. The calculated diffusion energy barrier of Pd SA is only 0.27 eV. Moreover, as CO will likely facilitate the mobility of metal atoms [18,54,55], the migration of Pd-CO is calculated to have the diffusion energy barrier of 0.23 eV. Thus, the diffusion of Pd SAs on the W_2 and W_3 sites of $Pd_1/trzn-COF$ is possible. The second Pd SA is added on both the closed W_3 site and the pre-established Pd SA of W_2 site, the adsorption energy of the second Pd SA on each site is -0.84 and -1.04 eV, respectively. Compared with Pd dispersed by the single-atom state in different loading sites of COF, the co-adsorption configurations of Pd_2 are not dominant and energetically unfavorable. Presumably, Pd SA anchored on the adjacent W_2 and W_3 sites can dynamically coexist in $Pd_1/trzn-COF$. Therefore, CO oxidation on W_3 site is also investigated.

CO oxidation mechanism on W_3

The predicted energy profiles of partial CO oxidation pathways on W_3 with the rate-determining step of L-H mechanism on W_2 are displayed in Fig. 9. As seen from Fig. 9a, the electron-withdrawing function of Schiff bond

nitrogen on W_3 site enhances the interaction of both reactants and intermediate, and the C–O bond is elongated from 1.80 Å on W_2 to 1.98 Å in the transition state with the formation of C–O bond on W_3 (Fig. 9b, TS1'). Consequently, the barrier energy increased from 1.27 eV on W_2 (TS1-1) to 1.49 eV (TS1') on W_3 in the L-H pathway. Here we also considered the tri-molecular mechanisms (TLH and TER) on W_3 and the predicted reaction pathway of CO oxidation; the optimized structures are displayed in Fig. 10. As shown in Fig. 10, although the formation of C–O bond on W_3 site along TLH mechanism has the relatively low energy barrier of 0.83 eV (TS4-2'), O–O scission along this pathway is very difficult with the high energy barrier of 1.89 eV (TS5-2'), which indicates that CO oxidation along TLH mechanism is energetically unfavorable. However, for the TER mechanism on W_3 , the apparent activation energy of CO-promoted O_2 activity is only 0.53 eV (W_3 -TER, TS4-1'), and the barrier energy of O–O scission is 0.60 eV (W_3 -TER, TS5-1'). This $Pd_1/trzn-COF$ catalyst has high catalytic activity for CO oxidation occurring on W_3 site following the TER mechanism. And the rate-limiting step is the O–O scission step with the energy barrier of 0.60 eV, and the calculated reaction rate constant is $4.07 \times 10^8 \text{ s}^{-1} \text{ mol}^{-1} \text{ L}$, as detailed in the SI. In addition, the first CO_2 desorption energy barrier is only 0.42 eV, and the second CO_2 can easily desorb *via* a CO-promoted route with an exother-

Figure 9 (a) Calculated energy profiles of the rate-limiting CO oxidation steps on W_3 with ZPVE included. (b) Optimized geometry configurations of L-H mechanism. The selected bond distances (in the unit of Å) of transition states are marked in red and the related bonding details are listed in Table S9.

Figure 10 (a) Calculated energy profiles of CO oxidation on W_3 site through the tri-molecular mechanism with ZPVE included. Optimized geometries along the TER mechanism (b) and TLH mechanism (c). The selected bond distances (in the unit of Å) of transition states are marked in red and the related bonding details are listed in Tables S10 and S11.

micity (-0.37 eV) (Fig. S4), then retriggering the reaction cycle by adsorption of another CO molecule. Therefore, instead of the reaction running on an onset temperature of 100°C as discussed on trzn-COF supported nanoparticles, CO oxidation can be catalyzed by this new SACs $\text{Pd}_1/\text{trzn-COF}$ at room temperature [50].

Comparing the energy profiles of W_2 -TER and W_3 -TER for CO oxidation, the variation of the barrier energies comes from the difference between the structures of the co-adsorption of two CO molecules (IS_4 on W_2 and IS_4' on W_3) and the OCO-OCO^* intermediates (IM_2 -1 on W_2 and IM_2 -1' on W_3). The calculated PDOS of these

structures are displayed in Figs S5 and S6. As shown in Fig. S5, the stronger interaction of Pd-C causes the $\text{Pd } 4d$ shift towards the Fermi level and occupation of $\text{CO-}2\pi^*$ states on IS_4' when compared with IS_4 (Fig. S5e), while CO to metal σ -donation leads to the accumulation of electron density on the top zone of Pd (Fig. S5b). Therefore, IS_4' is more flexible to approach O_2 molecule and activates it simultaneously. As for the stronger Pd-C interaction in IM_2 -1', the distances of Pd-C are shorter (1.935 and 1.955 Å) than that in IM_2 -1 (1.961 and 1.974 Å) combining with the Pd-N interaction in IM_2 -1' (Fig. S6a and b), which is beneficial for the stabilizing of

the OCO-OCO* intermediate and the increase of the barrier energy of O–O bond scission.

CONCLUSIONS

In this work, we have studied different adsorption sites of Pd SAs on trzn-COF and the different reaction mechanisms of CO oxidation over Pd₁/trzn-COF using density functional calculations. Our studies indicate that the N atom with a lone-pair electron, the sp² C atom along the linker of trzn-COF and the six-member ring on the trzn-COF slab can provide sufficient adsorption sites for Pd SAs. And the calculated order of stability of Pd SAs on these sites is: W₂ > W₃ > S₃ > S₂ > S₁ > L₂ > W₁. In addition, the dynamic co-existence of single-atom sites are investigated on this new designed Pd₁/trzn-COF SAC, where the diffusion barrier energy of Pd SAs between W₂ and W₃ is as low as 0.27 eV. The CO reaction can be regulated by anion-π electrostatic interaction between the +δ phenyl center and related –δ moieties in the specific progresses as well as the electron-withdrawing interaction of Schiff bond nitrogen on the COF skeleton. Furthermore, a plausible TER reaction mechanism for CO oxidation on W₃ is elucidated. The rate-determining step is the scission of O–O bond and the barrier energy is only 0.60 eV. This predicted new noble-metal SAC of Pd₁/trzn-COF shows high catalytic activity in CO oxidation at room temperature. These results can help to better understand and design new SACs supported on COF nanomaterials.

Received 10 January 2021; accepted 5 March 2021;
published online 18 May 2021

- Qiao B, Wang A, Yang X, *et al.* Single-atom catalysis of CO oxidation using Pt₁/FeO_x. *Nat Chem*, 2011, 3: 634–641
- Yang XF, Wang A, Qiao B, *et al.* Single-atom catalysts: A new frontier in heterogeneous catalysis. *Acc Chem Res*, 2013, 46: 1740–1748
- Liang JX, Wang YG, Yang XF, *et al.* Recent Advances in Single-Atom Catalysis. *Encyclopedia of Inorganic and Bioinorganic Chemistry*. New York: John Wiley & Sons, Ltd., 2017
- Liu JC, Tang Y, Wang YG, *et al.* Theoretical understanding of the stability of single-atom catalysts. *Natl Sci Rev*, 2018, 5: 638–641
- Wang A, Li J, Zhang T. Heterogeneous single-atom catalysis. *Nat Rev Chem*, 2018, 2: 65–81
- Jiao J, Lin R, Liu S, *et al.* Copper atom-pair catalyst anchored on alloy nanowires for selective and efficient electrochemical reduction of CO₂. *Nat Chem*, 2019, 11: 222–228
- Li Z, Chen Y, Ji S, *et al.* Iridium single-atom catalyst on nitrogen-doped carbon for formic acid oxidation synthesized using a general host-guest strategy. *Nat Chem*, 2020, 12: 764–772
- Li J, Stephanopoulos MF, Xia Y. Introduction: Heterogeneous single-atom catalysis. *Chem Rev*, 2020, 120: 11699–11702
- Zhuo HY, Zhang X, Liang JX, *et al.* Theoretical understandings of graphene-based metal single-atom catalysts: stability and catalytic performance. *Chem Rev*, 2020, 120: 12315–12341
- Li J, Li Y, Zhang T. Recent progresses in the research of single-atom catalysts. *Sci China Mater*, 2020, 63: 889–891
- Pan Y, Zhang C, Lin Y, *et al.* Electrocatalyst engineering and structure-activity relationship in hydrogen evolution reaction: From nanostructures to single atoms. *Sci China Mater*, 2020, 63: 921–948
- Liu K, Tang Y, Yu Z, *et al.* High-loading and thermally stable Pt₁/MgAl_{1.2}Fe_{0.8}O₄ single-atom catalysts for high-temperature applications. *Sci China Mater*, 2020, 63: 949–958
- Ren S, Yu Q, Yu X, *et al.* Graphene-supported metal single-atom catalysts: A concise review. *Sci China Mater*, 2020, 63: 903–920
- Yang F, Ding S, Song H, *et al.* Single-atom Pd dispersed on nanoscale anatase TiO₂ for the selective hydrogenation of phenylacetylene. *Sci China Mater*, 2020, 63: 982–992
- Xu Q, Guo CX, Tian S, *et al.* Coordination structure dominated performance of single-atomic Pt catalyst for anti-Markovnikov hydroboration of alkenes. *Sci China Mater*, 2020, 63: 972–981
- Baskaran S, Xu CQ, Wang YG, *et al.* Catalytic mechanism and bonding analyses of Au-Pd single atom alloy (SAA): CO oxidation reaction. *Sci China Mater*, 2020, 63: 993–1002
- Wang WL, Santos EJG, Jiang B, *et al.* Direct observation of a long-lived single-atom catalyst chiseling atomic structures in graphene. *Nano Lett*, 2014, 14: 450–455
- Wang YG, Mei D, Glezakou VA, *et al.* Dynamic formation of single-atom catalytic active sites on ceria-supported gold nanoparticles. *Nat Commun*, 2015, 6: 6511–6517
- Mao K, Li L, Zhang W, *et al.* A theoretical study of single-atom catalysis of CO oxidation using Au embedded 2D h-BN monolayer: A CO-promoted O₂ activation. *Sci Rep*, 2015, 4: 5441
- Zhuo HY, Yu X, Yu Q, *et al.* Selective hydrogenation of acetylene on graphene-supported non-noble metal single-atom catalysts. *Sci China Mater*, 2020, 63: 1741–1749
- Liang J, Yu Q, Yang X, *et al.* A systematic theoretical study on FeO_x-supported single-atom catalysts: M₁/FeO_x for CO oxidation. *Nano Res*, 2018, 11: 1599–1611
- Zhao S, Chen F, Duan S, *et al.* Remarkable active-site dependent H₂O promoting effect in CO oxidation. *Nat Commun*, 2019, 10: 3824–3832
- Huang ZQ, Liu LP, Qi S, *et al.* Understanding all-solid frustrated-Lewis-pair sites on CeO₂ from theoretical perspectives. *ACS Catal*, 2018, 8: 546–554
- Liu P, Zhao Y, Qin R, *et al.* Photochemical route for synthesizing atomically dispersed palladium catalysts. *Science*, 2016, 352: 797–800
- Liu W, Zhang L, Liu X, *et al.* Discriminating catalytically active FeN_x species of atomically dispersed Fe–N–C catalyst for selective oxidation of the C–H bond. *J Am Chem Soc*, 2017, 139: 10790–10798
- Liu W, Zhang L, Yan W, *et al.* Single-atom dispersed Co–N–C catalyst: Structure identification and performance for hydrogenerative coupling of nitroarenes. *Chem Sci*, 2016, 7: 5758–5764
- Pan Y, Chen Y, Wu K, *et al.* Regulating the coordination structure of single-atom Fe–N_xC_y catalytic sites for benzene oxidation. *Nat Commun*, 2019, 10: 4290–4300
- Chen Z, Chen Y, Chao S, *et al.* Single-atom Au^I–N₃ site for acetylene hydrochlorination reaction. *ACS Catal*, 2020, 10: 1865–1870
- Nie G, Li P, Liang JX, *et al.* Theoretical investigation on the photocatalytic activity of the Au/g-C₃N₄ monolayer. *J Theor Comput Chem*, 2017, 16: 1750013

- 30 Kyriakou G, Boucher MB, Jewell AD, *et al.* Isolated metal atom geometries as a strategy for selective heterogeneous hydrogenations. *Science*, 2012, 335: 1209–1212
- 31 Yin P, Yao T, Wu Y, *et al.* Single cobalt atoms with precise N-coordination as superior oxygen reduction reaction catalysts. *Angew Chem Int Ed*, 2016, 55: 10800–10805
- 32 Côté AP, Benin AI, Ockwig NW, *et al.* Porous, crystalline, covalent organic frameworks. *Science*, 2005, 310: 1166–1170
- 33 Colson JW, Dichtel WR. Rationally synthesized two-dimensional polymers. *Nat Chem*, 2013, 5: 453–465
- 34 Colson JW, Mann JA, DeBlase CR, *et al.* Patterned growth of oriented 2D covalent organic framework thin films on single-layer graphene. *J Polym Sci Part A-Polym Chem*, 2015, 53: 378–384
- 35 Medina DD, Rotter JM, Hu Y, *et al.* Room temperature synthesis of covalent-organic framework films through vapor-assisted conversion. *J Am Chem Soc*, 2015, 137: 1016–1019
- 36 Yoo JT, Lee SH, Hirata S, *et al.* *In situ* synthesis of covalent organic frameworks (COFs) on carbon nanotubes and graphenes by sonochemical reaction for CO₂ adsorbents. *Chem Lett*, 2015, 44: 560–562
- 37 Pachfule P, Panda MK, Kandambeth S, *et al.* Multifunctional and robust covalent organic framework-nanoparticle hybrids. *J Mater Chem A*, 2014, 2: 7944–7952
- 38 Pachfule P, Kandambeth S, Díaz Díaz D, *et al.* Highly stable covalent organic framework–Au nanoparticles hybrids for enhanced activity for nitrophenol reduction. *Chem Commun*, 2014, 50: 3169–3172
- 39 Ding SY, Gao J, Wang Q, *et al.* Construction of covalent organic framework for catalysis: Pd/COF-LZU1 in Suzuki-Miyaura coupling reaction. *J Am Chem Soc*, 2011, 133: 19816–19822
- 40 Chao S, Guan Q, Li W. Study of the active site for acetylene hydrochlorination in AuCl₃/C catalysts. *J Catal*, 2015, 330: 273–279
- 41 Gong YN, Zhong W, Li Y, *et al.* Regulating photocatalysis by spin-state manipulation of cobalt in covalent organic frameworks. *J Am Chem Soc*, 2020, 142: 16723–16731
- 42 Aiyappa HB, Thote J, Shinde DB, *et al.* Cobalt-modified covalent organic framework as a robust water oxidation electrocatalyst. *Chem Mater*, 2016, 28: 4375–4379
- 43 Zhong W, Sa R, Li L, *et al.* A covalent organic framework bearing single Ni sites as a synergistic photocatalyst for selective photo-reduction of CO₂ to CO. *J Am Chem Soc*, 2019, 141: 7615–7621
- 44 Sun Q, Aguila B, Perman J, *et al.* Flexibility matters: Cooperative active sites in covalent organic framework and threaded ionic polymer. *J Am Chem Soc*, 2016, 138: 15790–15796
- 45 Stegbauer L, Schwinghammer K, Lotsch BV. A hydrazone-based covalent organic framework for photocatalytic hydrogen production. *Chem Sci*, 2014, 5: 2789–2793
- 46 Puthiaraj P, Lee YR, Zhang S, *et al.* Triazine-based covalent organic polymers: design, synthesis and applications in heterogeneous catalysis. *J Mater Chem A*, 2016, 4: 16288–16311
- 47 Gomes R, Bhanja P, Bhaumik A. A triazine-based covalent organic polymer for efficient CO₂ adsorption. *Chem Commun*, 2015, 51: 10050–10053
- 48 Xu N, Wang RL, Li DP, *et al.* A new triazine-based covalent organic polymer for efficient photodegradation of both acidic and basic dyes under visible light. *Dalton Trans*, 2018, 47: 4191–4197
- 49 Miroshnikov M, Divya KP, Babu G, *et al.* Power from nature: Designing green battery materials from electroactive quinone derivatives and organic polymers. *J Mater Chem A*, 2016, 4: 12370–12386
- 50 Mullangi D, Nandi S, Shalini S, *et al.* Pd loaded amphiphilic COF as catalyst for multi-fold Heck reactions, C-C couplings and CO oxidation. *Sci Rep*, 2015, 5: 10876–10887
- 51 He Y, Liu JC, Luo L, *et al.* Size-dependent dynamic structures of supported gold nanoparticles in CO oxidation reaction condition. *Proc Natl Acad Sci USA*, 2018, 115: 7700–7705
- 52 Parkinson GS, Novotny Z, Argentero G, *et al.* Carbon monoxide-induced adatom sintering in a Pd–Fe₃O₄ model catalyst. *Nat Mater*, 2013, 12: 724–728
- 53 Wang J, McEntee M, Tang W, *et al.* Formation, migration, and reactivity of Au–CO complexes on gold surfaces. *J Am Chem Soc*, 2016, 138: 1518–1526
- 54 Wang YG, Yoon Y, Glezakou VA, *et al.* The role of reducible oxide-metal cluster charge transfer in catalytic processes: New insights on the catalytic mechanism of CO oxidation on Au/TiO₂ from *ab initio* molecular dynamics. *J Am Chem Soc*, 2013, 135: 10673–10683
- 55 Tang Y, Asokan C, Xu M, *et al.* Rh single atoms on TiO₂ dynamically respond to reaction conditions by adapting their site. *Nat Commun*, 2019, 10: 4488–4497
- 56 Guo J, Jiang D. Covalent organic frameworks for heterogeneous catalysis: Principle, current status, and challenges. *ACS Cent Sci*, 2020, 6: 869–879
- 57 Pinchuk VM, Kotlyarova ES, Parkhomenko NV, *et al.* Quantum chemical analysis of the Eley-Rideal and Langmuir-Hinshelwood mechanisms of the catalytic oxidation of carbon monoxide on the nickel surface. *J Struct Chem*, 1996, 37: 544–556
- 58 Lopez-Acevedo O, Kacprzak KA, Akola J, *et al.* Quantum size effects in ambient CO oxidation catalysed by ligand-protected gold clusters. *Nat Chem*, 2010, 2: 329–334
- 59 Wang Y, Wu G, Yang M, *et al.* Competition between Eley-Rideal and Langmuir-Hinshelwood pathways of CO oxidation on Cu_n and Cu_nO (n = 6, 7) clusters. *J Phys Chem C*, 2013, 117: 8767–8773
- 60 Perdew JP, Yue W. Accurate and simple density functional for the electronic exchange energy: Generalized gradient approximation. *Phys Rev B*, 1986, 33: 8800–8802
- 61 Perdew JP, Wang Y. Accurate and simple analytic representation of the electron-gas correlation energy. *Phys Rev B*, 1992, 45: 13244–13249
- 62 Ortmann F, Bechstedt F, Schmidt WG. Semiempirical van der Waals correction to the density functional description of solids and molecular structures. *Phys Rev B*, 2006, 73: 205101
- 63 Delley B. Hardness conserving semilocal pseudopotentials. *Phys Rev B*, 2002, 66: 155125
- 64 Yaghi OM, O’Keeffe M, Ockwig NW, *et al.* Reticular synthesis and the design of new materials. *Nature*, 2003, 423: 705–714
- 65 Halgren TA, Lipscomb WN. The synchronous-transit method for determining reaction pathways and locating molecular transition states. *Chem Phys Lett*, 1977, 49: 225–232
- 66 Ananikov VP, Musaev DG, Morokuma K. Theoretical insight into the C–C coupling reactions of the vinyl, phenyl, ethynyl, and methyl complexes of palladium and platinum. *Organometallics*, 2005, 24: 715–723
- 67 Pyykkö P, Atsumi M. Molecular single-bond covalent radii for elements 1–118. *Chem Eur J*, 2009, 15: 186–197
- 68 Lu T, Chen F. Multiwfn: A multifunctional wavefunction analyzer. *J Comput Chem*, 2012, 33: 580–592
- 69 Humphrey W, Dalke A, Schulten K. VMD: Visual molecular dynamics. *J Mol Graphics*, 1996, 14: 33–38
- 70 Schottel BL, Chifotides HT, Dunbar KR. Anion- π interactions.

- Chem Soc Rev, 2008, 37: 68–83
- 71 Yoshioka Y, Schaefer III HF. Theoretical investigation of the electron affinity of CO₂. *J Chem Phys*, 1981, 75: 1040–1041
 - 72 Xu G, Wang R, Ding Y, *et al.* First-principles study on the single Ir atom embedded graphdiyne: An efficient catalyst for CO oxidation. *J Phys Chem C*, 2018, 122: 23481–23492
 - 73 Liu C, Tan Y, Lin S, *et al.* CO self-promoting oxidation on nanosized gold clusters: Triangular Au₃ active site and CO induced O–O scission. *J Am Chem Soc*, 2013, 135: 2583–2595
 - 74 Talib SH, Hussain S, Baskaran S, *et al.* Chromium single-atom catalyst with graphyne support: A theoretical study of NO oxidation and reduction. *ACS Catal*, 2020, 10: 11951–11961
 - 75 Talib SH, Yu X, Yu Q, *et al.* Non-noble metal single-atom catalysts with phosphotungstic acid (PTA) support: A theoretical study of ethylene epoxidation. *Sci China Mater*, 2020, 63: 1003–1014

Acknowledgements This work was supported by the National Natural Science Foundation of China (22033005, 21590792 and 21763006), and Guangdong Provincial Key Laboratory of Catalysis (2020B121201002). The calculations were performed using supercomputers at SUSTech and Tsinghua National Laboratory for Information Science and Technology. We thank Professor Xufeng Lin (hattrick2009@upc.edu.cn) for helpful discussion during the preparation of the manuscript.

Author contributions Li J directed the research. Liang JX, Liu CG and Chen YJ conducted the DFT calculations. Chen YJ, Zhuo HY, and Pan Y analyzed the data. All the authors discussed the results and co-wrote the manuscript.

Conflict of interest The authors declare no competing financial interest.

Supplementary information Supporting data is available in the online version of the paper.

Yin-Juan Chen is currently a PhD candidate in Prof. Chen-Guang Liu's group at China University of Petroleum (East China), and also a visiting student in Prof. Jun Li's group, Department of Chemistry, Tsinghua University (Beijing, China). Her current research interests focus on theoretical investigations on heterogeneous single-atom catalysts (SACs).

Jin-Xia Liang received her BSc degree from the Department of Chemistry at Shaanxi University of Technology in 2004, MS degree from the School of Chemistry and Chemical Engineering at Shaanxi Normal University in 2009, and PhD degree from the College of Chemistry and Chemical Engineering at Xiamen University in 2012. She did her postdoctoral research at the Department of Chemistry, Tsinghua University. She joined the faculty of Guizhou Provincial Key Laboratory of Computational Nano Material

Science, Guizhou Education University in 2014. She is currently a research associate professor at the Department of Chemistry, Southern University of Science and Technology. Her research interests focus on the theoretical design of functional nanomaterials and investigation of catalytic mechanisms of SACs.

Chen-Guang Liu received his PhD degree in 1991 in applied chemistry at China University of Petroleum. He is now a professor in the State Key Laboratory of Heavy Oil Processing and College of Chemical Engineering at China University of Petroleum. His current research interests include petrochemistry, petroleum refining and chemical engineering, green fine chemical technology and renewable energy and oxygen-containing fuel applications.

Jun Li received his PhD degree from Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences in 1992. He did postdoctoral research at the University of Siegen (Germany) and The Ohio State University (USA) from 1994 to 1997. He worked as a Research Scientist at The Ohio State University and a Senior Research Scientist and Chief Scientist at the Pacific Northwest National Laboratory from 1997 to 2009. He is now a full professor at Tsinghua University. His research involves theoretical chemistry, relativistic heavy-element chemistry, and computational catalysis science.

oretical chemistry, relativistic heavy-element chemistry, and computational catalysis science.

三嗪-共价有机框架材料负载的单原子催化剂Pd₁/trzn-COF催化CO氧化的理论研究

陈银娟^{1,2}, 卓红英², 潘原¹, 梁锦霞^{3*}, 刘晨光^{1*}, 李隽^{2,3*}

摘要 共价有机框架材料(COF)是一类新兴的可裁剪、原子组成可控的催化剂载体。单原子催化剂(SACs)具有明确的活性中心结构和原子组成,为同时满足催化剂的高活性和高选择性提供可能,并为催化剂的实验和理论的高契合度研究提供桥梁。因此,本论文采用密度泛函理论(DFT),系统研究了以典型三嗪-共价有机框架材料为载体的钯单原子催化剂(Pd₁/trzn-COF)的金属负载位点、稳定性和反应活性。基于sp² C原子、N/O杂原子和芳香环与三嗪环的共轭π电子的亲核性,一系列不同的吸附位点被用于负载Pd原子,研究表明Pd原子以约−5.0 eV的结合能稳定地结合在该COF材料上;基于两个最稳定构型间的位置毗邻性、能量相近性及其温和的迁移能垒,可以预测该体系中存在动态共存的单原子催化位点。此外,CO氧化机理研究表明, Pd₁/trzn-COF的催化活性可通过特定−δ基团与+δ苯环中心的阴离子−π相互作用以及亚胺基团的吸电子特性进行调控。我们设计了一种新型的单原子催化剂Pd₁/trzn-COF,并预测了其可能的CO氧化反应机理为三分子Eley-Rideal机理。该工作揭示了Pd原子与trzn-COF之间的d−π相互作用模式对于单原子催化剂Pd₁/trzn-COF的稳定性和反应活性的影响,其研究结果有助于理解和设计基于COF的新型单原子催化剂。