

1 + 1' > 2: Heteronuclear Biatom Catalyst Outperforms Its Homonuclear Counterparts for CO Oxidation

Fengyu Li,* Xinying Liu, and Zhongfang Chen*

By means of density functional theory (DFT) computations, the CO/O₂ adsorption and CO oxidation pathways on the biatom catalyst, namely the heteronuclear Fe₁Cu₁@C₂N, in comparison with its homonuclear counterparts Fe₂@C₂N and Cu₂@C₂N are systemically investigated. The reactions of O₂ dissociation and CO oxidation with preadsorbed CO or O₂ are comparably studied. The computations find that the heteronuclear species Fe₁Cu₁@C₂N possesses high stabilities and is feasible to be synthesized experimentally. More importantly, the heteronuclear Fe₁Cu₁@C₂N catalyst has even better catalytic activity toward CO oxidation than its homonuclear counterparts, especially, without suffering the CO-poisoning problem. Considering the myriad of unexplored heteronuclear dimers that can be potentially anchored at appropriate supports, this work opens a new avenue and provides a useful guideline for further developing biatom-based nanocatalysts.

1. Introduction

The oxidation of CO plays a very important role in reducing the environmental CO emission and removing CO contaminations from H₂-rich fuel gases for polymer electrolyte fuel cells (PEFC).^[1] Typically supported metal clusters, especially those made of noble metals, e.g., Pt, Pd, Au, Rh, and Ru, exhibit high activity for CO oxidation. The cooperation between the support and the metal clusters can promote the O₂ activation and CO oxidation, for example, the activation barriers for O₂ dissociation and CO oxidation on the TiO₂ supported Au and Pd clusters are very low (nearly barrierless).^[2–4] However, the catalytic activities of the supported metal nanoparticles are size- and

shape-dependent;^[5–7] moreover, the large-scale applications are restrained by the high costs and the limited storage of these metals on earth.

The recently developed single-atom catalysts (SACs)^[8–18] are promising to reduce the metal usage in catalysis and enhance the catalytic efficiency. In SACs, isolated individual atoms are dispersed on, and/or coordinated with, the surface atoms of an appropriate support, which maximizes the metal atom efficiency. Since the first SAC, single Pt atoms on FeO_x,^[8] was reported in 2011, various SACs with metal oxide supports have been successfully fabricated, such as single Au/Pt/Ir/Ni/Os atoms on FeO_x,^[19–25] CO₃O₄,^[26] CeO₂,^[27] Al₂O₃,^[28] and MnO₂^[29] surfaces. At the same time, the SACs could be accessed by thermal atomization of supported metal nanoparticles^[30] and direct atoms emitting from bulk metals.^[31] These experimental explorations also inspired many theoretical efforts. For example, various FeO_x-supported single metal atom catalysts for CO oxidation were systemically investigated by means of density functional theory (DFT) computations.^[32,33]

Besides metal-oxides, a variety of porous graphene-like materials have been used as the substrates to anchor metal atoms/clusters for catalysis. For example, it has been experimentally demonstrated that single metal atoms (Pt, Pd, Ag, Ir, Au) embedded in g-C₃N₄ are highly active for the semihydrogenation of 1-hexyne^[34] and electrochemical synthesis of ammonia.^[35] Theoretical studies suggested that single transition metal atoms anchored on C₂N could serve as low-cost but highly efficient catalysts for oxygen evolution reaction,^[36] CO oxidation,^[37] nitrogen reduction reaction,^[38] HCOOH dehydrogenation,^[39] and CO₂ electrochemical reduction,^[40] and the noble metal atoms anchored on graphyne are very promising for low-temperature CO oxidation.^[41]

Beyond SACs, biatom catalysts, in which metal dimers are anchored on an appropriate substrate, have recently emerged as extended family members. Experimentally Yan et al. synthesized the stable platinum dimers (but dominantly in the oxidized form of Pt₂O_x without Pt–Pt bond) on graphene using atomic layer deposition, and demonstrated that Pt₂ dimers exhibit higher activity toward hydrolytic dehydrogenation of ammonia borane than that of graphene supported Pt₁ single atoms and nanoparticles.^[42] Theoretically, Luo et al. predicted that the Pd dimer embedded in graphene can effectively and selectively catalyze formic acid dehydrogenation;^[43] Sun and co-workers proposed that Cu dimer on graphene or Mn dimer

Prof. F. Li
School of Physical Science and Technology
Inner Mongolia University
Hohhot 010021, China
E-mail: fengyuli@imu.edu.cn

Prof. X. Liu
Institute for the Development of Energy for African Sustainability
University of South Africa
Johannesburg 1710, South Africa

Prof. Z. Chen
Department of Chemistry
University of Puerto Rico
Rio Piedras Campus, San Juan, PR 00931, USA
E-mail: zhongfang_chen@gmail.com

The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/smt.201800480>.

DOI: 10.1002/smt.201800480

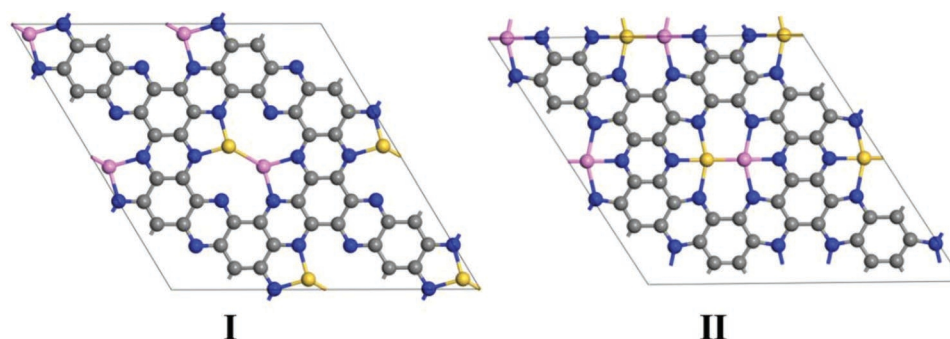


Figure 1. The two possible configurations of two metal atoms anchored C₂N (I and II). Color scheme: C, gray; N, blue; gold, M¹; pink, M².

on a phthalocyanine sheet exhibit higher catalytic activity for CO₂ reduction;^[44–46] Compared with their single-atom counterparts, several double transition metal (TM) atoms supported by 2D crystal C₂N were predicted to have better catalytic performance for oxygen reduction reaction^[47] and CO oxidation than their single-atom counterparts;^[48] Several other transition metal dimers anchored on C₂N monolayers were also expected to exhibit high activity for some important chemical reactions, e.g., carbon dioxide electrochemical reduction (Cu₂@C₂N),^[49] hydrogen evolution reaction (Co₂@C₂N, Ni₂@C₂N, Cu₂@C₂N, Ru₂@C₂N),^[50] and nitrogen fixation (Mo₂@C₂N,^[51] Mn₂@C₂N).^[52]

Note that the metal dimers in the above mentioned biatom catalysts are all homonuclear. In principle, there are even more possibilities for heteronuclear dimers awaiting our explorations. In this work, by means of systematic DFT computations, we explored the potential of heteronuclear metal dimer Fe₁Cu₁ anchored on the porous C₂N monolayer^[53] as biatom catalyst for CO oxidation, in comparison with its homonuclear counterparts Fe₂@C₂N and Cu₂@C₂N. Our computational results demonstrated that the heteronuclear metal dimer system Fe₁Cu₁@C₂N has high stabilities and superior performance toward CO oxidation compared to the homonuclear counterparts, especially Fe₁Cu₁@C₂N does not suffer the CO-poisoning issue. This work not only further spans the homonuclear biatom catalysts to heteronuclear biatom catalysts, but also provides insights and guidelines to future experimental and computational studies, and help promote the design and production of novel low-cost and efficient nanocatalysts.

2. Results and Discussion

2.1. Geometries and Thermodynamic Stabilities of the M¹M²@C₂N Monolayers (M¹/M² = Cu or Fe)

Previous theoretical studies showed that the single-atom catalyst Fe₁@C₂N^[54] and biatom catalyst Cu₂@C₂N possess good performance for CO oxidation.^[48] Thus, we constructed the homonuclear biatom species Fe₂@C₂N and the heteronuclear analogue Fe₁Cu₁@C₂N in this study.

We first examined the energetically most favorable anchoring site of Fe on the C₂N monolayer, for which three possible anchoring sites^[48] were considered. In the lowest energy configuration of Fe₁@C₂N, the Fe atom forms three bonds with

N atoms, while for the case of Cu₁@C₂N, the Cu atom prefers coordinating with two N atoms^[48] (Figure S1, Supporting Information). These results are in line with previous theoretical findings.^[50,54] For these two single metal atom complexes, Fe has the larger binding energy (E_b^1) of 4.56 eV, Cu has the much smaller E_b^1 value of 3.25 eV.

For the biatom catalysts examined in this study (homonuclear: Fe₂@C₂N and Cu₂@C₂N; heteronuclear: Fe₁Cu₁@C₂N), we only considered two configurations (I and II in Figure 1), in which two metal atoms are located in the porous region of C₂N, since the binding energies at other sites are less favorable.^[37,48,50] Both homo- and heteronuclear metal dimers prefer adopting Configuration II, in which two metal atoms coordinate with three N atoms of the C₂N substrate (Figure 1; Table S1, Supporting Information). The distance between the two metal atoms in II is slightly longer than that in Configuration I (Table S1) for the three examined biatom catalysts. The binding energies of the second metal atoms (E_b^2) in biatom catalysts, 2.69/4.31, and 2.48/3.79 eV for Cu₂, Fe₂, and Cu₁Fe₁@C₂N monolayers, are slightly lower than the binding energies in the corresponding single-atom catalysts (E_b^1) (3.25 and 4.56 eV for Cu₁@C₂N and Fe₁@C₂N, respectively). The preference of configuration II is accompanied by the more charge transfer between the metal atoms and the C₂N substrate (Table S1, Supporting Information). These highly favorable binding energies indicate the good thermodynamic stabilities of these biatom catalysts under investigation. Note that the Bader charge of Cu/Fe in the dimer M¹M²@C₂N of II configuration is smaller than monomer Cu₁@C₂N or Fe₁@C₂N, except that the value of Fe in Fe₁Cu₁@C₂N (+1.10 |e|) is larger than that of Fe₁@C₂N (+1.02 |e|), which could be assigned to electron transfer from Fe to Cu in the Fe₁Cu₁@C₂N, since 0.18 |e| charge transfer was found in the isolated Fe₁Cu₁ dimer from our calculations.

Note that the aggregation to metal atoms to larger clusters is a big concern.^[40] To examine the resistance of the biatom species M¹M²@C₂N against aggregation into trimer or larger metal clusters, we compared the relative stability of the biatom species and the single-triatom systems using a 2 × 1 × 1 supercell. For the homonuclear case, biatom species Cu₂–Cu₂ and Fe₂–Fe₂ are lower in energy than their single-triatom counterparts (Cu₁–Cu₃ and Fe₁–Fe₃) by 2.46 and 3.18 eV, respectively (Figure S2, Supporting Information). For the heteronuclear Fe₁Cu₁@C₂N (in the form of Fe₁Cu₁–Fe₁Cu₁ in 2 × 1 × 1 supercell), its single-triatom counterparts could be the combination of Cu₁ and Cu₁Fe₂ (Cu₁–Cu₁Fe₂) or Fe₁ and Fe₁Cu₂ (Fe₁–Fe₁Cu₂); these

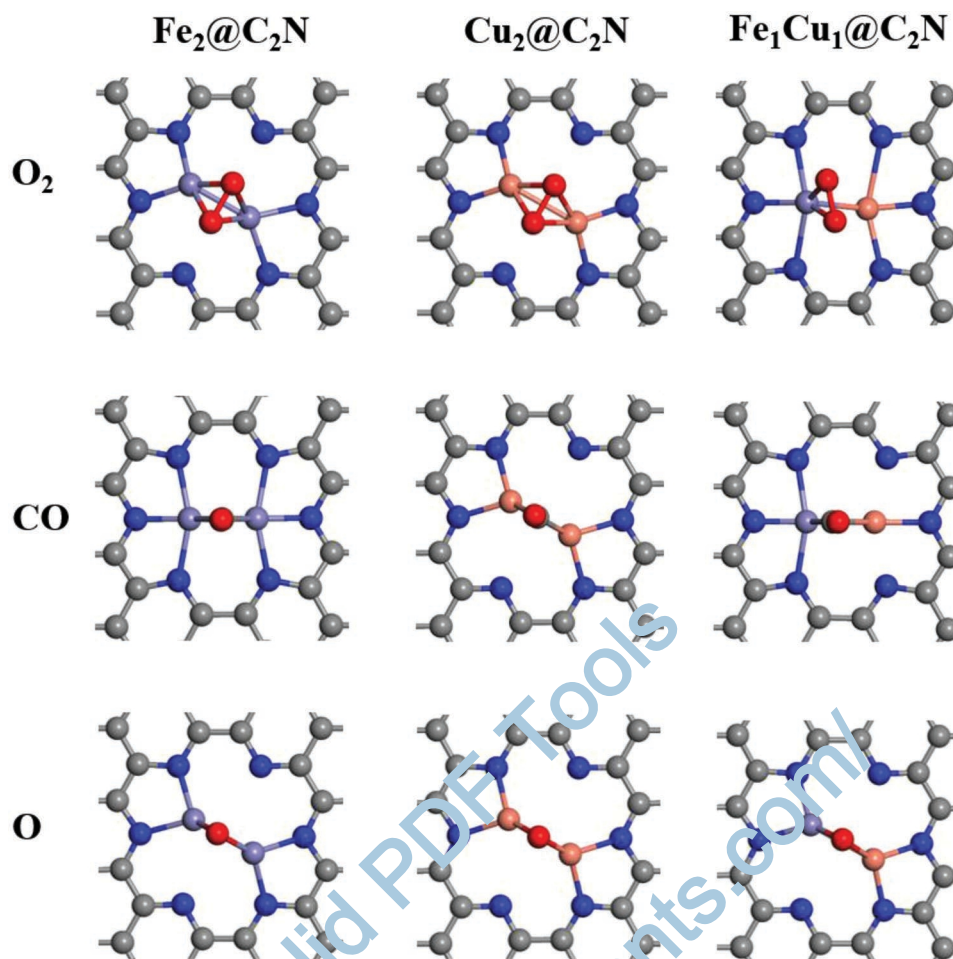


Figure 2. Top views of O_2 (top panel), CO (middle panel) and O (bottom panel) adsorption on the three $M^1M^2@C_2N$ monolayers. Color scheme: C, gray; N, blue; purple, Fe; orange, Cu; red, O.

two configurations are not only higher in energy than their corresponding biatom structures (by 0.51 and 0.95 eV, respectively), but also have rather high transition barriers (4.44 and 3.98 eV, respectively) for their transition to biatom counterparts (Figure S2, Supporting Information). Thus, the Cu_1Fe_1 dimers anchored on C_2N are expected to be stable without aggregation to larger clusters.

2.2. Adsorption of CO and O_2 on the $M^1M^2@C_2N$ Monolayers

Before investigating the detailed reaction pathways of CO oxidation, we examined the adsorption of CO and O_2 molecules on the energetically most favorable configurations of the three $M^1M^2@C_2N$ monolayers.

Many adsorption sites and configurations were considered, for example, four adsorption sites of O_2 with side-on configuration were explored (Figure S3, Supporting Information): the $O-O$ bond perpendicular to the metal bond (A), crossing to the metal bond (B), unilateral to the metal bond (C), and over the metal bond (C'). For the homonuclear $Fe_2@C_2N$ and $Cu_2@C_2N$ monolayers, O_2 adsorption with Configuration A is energetically

most favored, and the structure of substrate will change from II to I upon O_2 adsorption for both cases (Figure 2); in contrast, for the heteronuclear $Fe_1Cu_1@C_2N$, the adsorbed O_2 is close to the Fe atom instead of over the metal bond center due to the much stronger interaction between Fe and O_2 , which can be reflected by the more enhanced O_2 adsorption energy on $Fe_1@C_2N$ ($E_{ad} = 2.41$ eV) than that on $Cu_1@C_2N$ ($E_{ad} = 0.59$ eV) (Table S3, Supporting Information). Compared to the single-metal-atom counterparts $Fe_1@C_2N$ and $Cu_1@C_2N$, the O_2 adsorption strengths on homonuclear $Fe_2@C_2N$ and $Cu_2@C_2N$ (2.62 and 1.33 eV, respectively) are enhanced (by 0.21 and 0.74 eV), and the $O-O$ bond lengths are further elongated (by 0.05 and 0.17 Å, see Table 1 and Table S3, Supporting Information). When compared to the homonuclear counterparts (Table 1), the O_2 adsorption strength on heteronuclear $Fe_1Cu_1@C_2N$ ($E_{ad} = 2.45$ eV) is in between $Fe_2@C_2N$ ($E_{ad} = 2.62$ eV) and $Cu_2@C_2N$ ($E_{ad} = 1.33$ eV).

For CO adsorption, in the lowest energy structure, CO adopts an end-on configuration for all these three metal dimer systems, and only $Cu_2@C_2N$ will transform from configuration II to I upon CO adsorption (Figure 1). The CO adsorption strengths on the three biatom species are very comparable: the CO adsorption

Table 1. The CO, O₂, and O adsorption energies (E_{ad} , in eV) on $\text{M}^1\text{M}^2\text{@C}_2\text{N}$, their corresponding bond lengths ($d_{\text{C-O}}/d_{\text{O-O}}$, in Å), as well as the Bader charge (q , in $|e|$) of CO/O₂/O and M^1/M^2 .

	$\text{Fe}_2\text{@C}_2\text{N}$	$\text{Cu}_2\text{@C}_2\text{N}$	$\text{Fe}_1\text{Cu}_1\text{@C}_2\text{N}$
$E_{\text{ad}}(\text{O}_2)$	2.62	1.33	2.45
$d_{\text{O-O}}$	1.46	1.45	1.44
$q(\text{O}_2)$	−1.08	−0.90	−0.92
$q(\text{M})$	+1.22	+0.99	+1.23
	+1.30	+0.99	+0.77
$E_{\text{ad}}(\text{CO})$	2.24	2.14	2.20
$d_{\text{C-O}}$	1.19	1.18	1.18
$q(\text{CO})$	−0.66	−0.34	−0.50
$q(\text{M})$	+1.18	+0.78	+1.13
	+1.18	+0.75	+0.70
$E_{\text{ad}}(\text{O})$	3.32	1.82	2.72
$q(\text{O})$	−1.10	−0.85	−0.97
$q(\text{M})$	+1.28	+0.86	+1.36
	+1.35	+0.87	+0.85

energy on $\text{Fe}_1\text{Cu}_1\text{@C}_2\text{N}$ ($E_{\text{ad}} = 2.20$ eV) is between the values on $\text{Fe}_2\text{@C}_2\text{N}$ ($E_{\text{ad}} = 2.24$ eV) and $\text{Cu}_2\text{@C}_2\text{N}$ ($E_{\text{ad}} = 2.14$ eV).

Interestingly, the O₂/CO adsorption strength well correlates with the amount of charge transfer from the metal dimers to the adsorbate (Table 1; Table S3, Supporting Information): the more charge transfer from the metal dimers to the O₂/CO, the stronger adsorption strength of O₂/CO. Notably, except $\text{Cu}_2\text{@C}_2\text{N}$, both $\text{Fe}_2\text{@C}_2\text{N}$ and $\text{Fe}_1\text{Cu}_1\text{@C}_2\text{N}$ have larger adsorption energies of O₂ than those of CO. The preferable O₂ adsorption over CO is beneficial to these two catalysts for excluding the CO poisoning issue.

Jiang and co-workers' very recent theoretical studies revealed that spin transition of single metal atom could be induced by CO adsorption.^[55] Thus, we examined the magnetic configurations of the bare $\text{Fe}_1\text{Cu}_1\text{@C}_2\text{N}$ and with 1–4 CO adsorption in a $2 \times 1 \times 1$ supercell using the DFT + U method ($U = 4$ eV for the d electrons of Fe and Cu atoms). The bare $\text{Fe}_1\text{Cu}_1\text{@C}_2\text{N}$ is ferromagnetic with the magnetic moment of $7.36 \mu_{\text{B}}$, of which Fe atoms contribute dominantly (Figure S4a, Supporting Information). With one CO adsorption, the ferromagnetism of the $\text{Fe}_1\text{Cu}_1\text{@C}_2\text{N}$ will not change (Figure S4b, Supporting Information), but the magnetic moment is reduced to be $4.74 \mu_{\text{B}}$. However, two CO adsorption on the $\text{Fe}_1\text{Cu}_1\text{@C}_2\text{N}$ in either the symmetric (Figure S4c, Supporting Information, the magnetic moment: $0.00 \mu_{\text{B}}$) or the asymmetric configuration (Figure S4d, Supporting Information, the magnetic moment: $2.91 \mu_{\text{B}}$) induces the spin transition from ferromagnetism to antiferromagnetism. The antiferromagnetism remains with more (three and four) CO adsorption, and the magnetic moments are 0.85 and $0.00 \mu_{\text{B}}$, respectively (Figure S4e,f, Supporting Information). Note that the energy differences between the spin configuration of antiferromagnetism and ferromagnetism are all less than 0.01 eV for the considered systems of the $\text{Fe}_1\text{Cu}_1\text{@C}_2\text{N}$ with 0–4 CO molecules. The magnetic moment of each metal atom with 0–4 CO adsorption was listed in Table S4 (Supporting Information).

2.3. Mechanisms of CO Oxidation on the $\text{M}^1\text{M}^2\text{@C}_2\text{N}$ Monolayers

Since both O₂ and CO can be adsorbed on the $\text{M}^1\text{M}^2\text{@C}_2\text{N}$ monolayers with reasonable strength, we considered two possible conditions, the catalyst is preadsorbed by either O₂ or CO, when investigating CO oxidation on these biatom catalysts.

2.3.1. CO Oxidation on the O₂-Preadsorbed Catalyst Surface

We first examined the O₂ dissociation reactions on the three $\text{M}^1\text{M}^2\text{@C}_2\text{N}$ monolayers by taking the lowest-energy configurations of O₂ adsorbed $\text{M}^1\text{M}^2\text{@C}_2\text{N}$ monolayers as the initial structures. Our previous study revealed that the O₂ dissociation on the $\text{Cu}_2\text{@C}_2\text{N}$ is endothermic by 0.27 eV, and the corresponding reaction barrier is 0.50 eV.^[48] However, the O₂ dissociations on $\text{Fe}_2\text{@C}_2\text{N}$ and $\text{Fe}_1\text{Cu}_1\text{@C}_2\text{N}$ monolayers are both barrierlessly, and exothermic by 1.48 and 1.56 eV, respectively (Figure S5, Supporting Information). These findings are reminiscent of the extremely low O₂ dissociation barriers on the C₂N monolayer supported transition metal dimers (Co₂, Ni₂, and Cu₂).^[47]

Considering preferable adsorption of O₂ over CO (except $\text{Cu}_2\text{@C}_2\text{N}$) and the low barriers of O₂ dissociation on these bimetal systems, we started the CO oxidation over $\text{Fe}_2\text{@C}_2\text{N}$, and $\text{Fe}_1\text{Cu}_1\text{@C}_2\text{N}$ monolayers with preadsorbed and dissociated O₂. In this process, CO will react with the dissociated O atoms on the catalyst surface, followed by the regeneration of the original catalyst surface. Providing that the first chemisorbed O could be removed by the first CO easily, the removal of the second chemisorbed O will be crucial for the recovery of the pristine biatom catalysts. Therefore, we first evaluated the feasibility of removing the second atomic O on the metal dimers.

According to the Sabatier principle,^[56] a moderate adsorption strength between the reactants and the catalyst is a key factor for the catalytic performance. As shown in Table 1, the homonuclear $\text{Fe}_2\text{@C}_2\text{N}$ ($E_{\text{ad}} = 3.32$ eV) and $\text{Cu}_2\text{@C}_2\text{N}$ ($E_{\text{ad}} = 1.82$ eV) monolayers have the largest and smallest adsorption energy of the atomic O species, respectively; compared with their homonuclear analogs, the O adsorption energy on the heteronuclear $\text{Fe}_1\text{Cu}_1\text{@C}_2\text{N}$ catalyst ($E_{\text{ad}} = 2.72$ eV) is between $\text{Fe}_2\text{@C}_2\text{N}$ (3.32 eV) and $\text{Cu}_2\text{@C}_2\text{N}$ (1.82 eV). These data suggest that the heteronuclear complex $\text{Fe}_1\text{Cu}_1\text{@C}_2\text{N}$ might outperform the homonuclear counterparts for the removal of the second atomic O.

We then computed the reaction energies and activation barriers of the CO oxidation by the second atomic O on these metal dimers. This process is expected to proceed via the Eley–Rideal (E–R) mechanism, in which the reactant CO directly reacts with the O atom from the gas phase passing a transition state, and the CO₂ product is released. On $\text{Fe}_1\text{Cu}_1\text{@C}_2\text{N}$, the reaction energy is -0.16 eV and the barrier of removing the second atomic O to form the second CO₂ is 0.69 eV (Figure 3). As we reported before, on $\text{Cu}_2\text{@C}_2\text{N}$, the removal of O by CO via E–R mechanism to form the second CO₂ is kinetically more favorable (with an activation barrier of 0.29 eV) and this E–R reaction step is exothermic (1.28 eV).^[48]

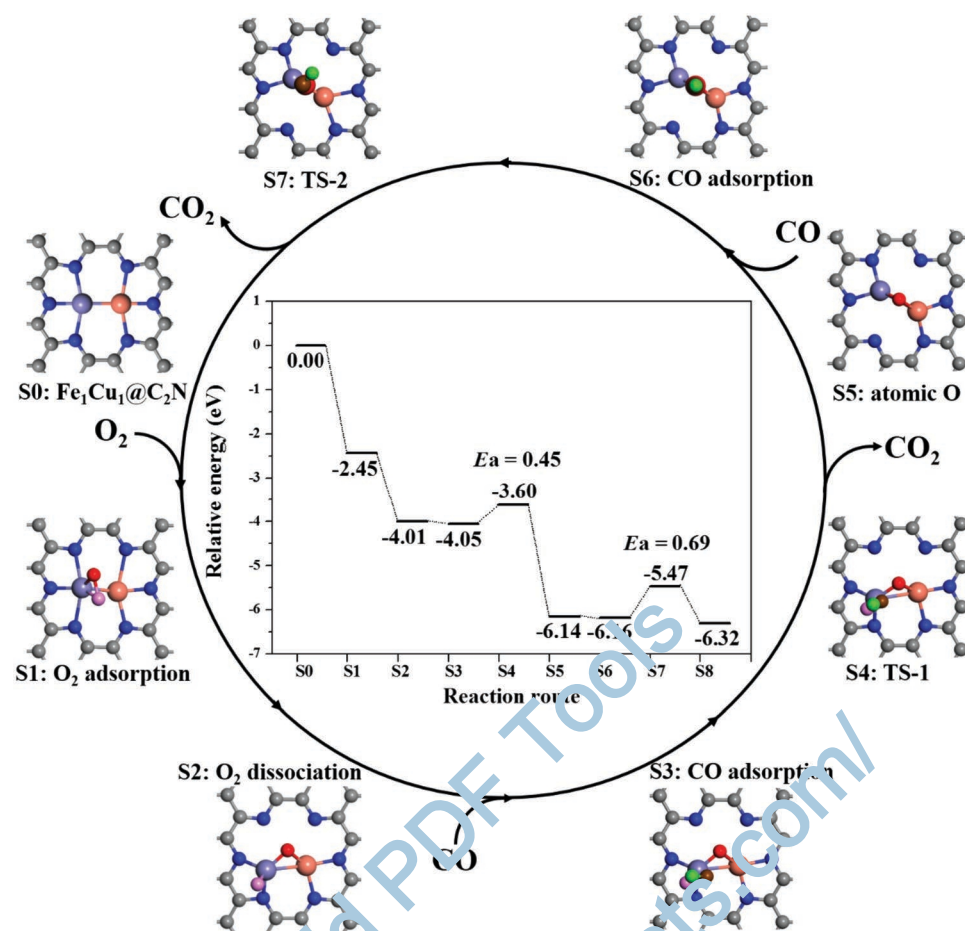


Figure 3. The reaction pathways (E–R) and energy profile for CO oxidation on the heteronuclear $\text{Fe}_1\text{Cu}_1@\text{C}_2\text{N}$ monolayer. The corresponding side views were given in Figure S7 (Supporting Information). Color scheme: N, blue; Fe, purple; Cu, orange; C in C_2N , gray; C in CO, brown; O in CO, green; O in O_2 , pink (first removed by CO) and red (second removed by CO).

However, the E–R process is slightly endothermic on $\text{Fe}_2@\text{C}_2\text{N}$ (0.05 eV), and the reaction barrier is as high as 1.53 eV. As expected by the Sabatier principle, the reaction barrier of removing O from the catalyst surface and the atomic O adsorption energy have a quasilinear relationship (Figure S6, Supporting Information). The overwhelming strong O adsorption and the difficulty in removing the atomic O on the $\text{Fe}_2@\text{C}_2\text{N}$ surface rule out its capacity to catalyze CO oxidation since the strongly bound atomic O will block the catalytically active sites. Previous studies already confirmed the activity of $\text{Cu}_2@\text{C}_2\text{N}$ toward CO oxidation,^[48] thus we will not further discuss it in the following sections.

The above analyses showed that heteronuclear $\text{Fe}_1\text{Cu}_1@\text{C}_2\text{N}$ can well catalyze the CO oxidation by the second atomic O, as indicated by the small reaction barrier and the exothermic process of removing the atomic O from the catalyst surface. Then, we checked if the CO oxidation with the first atomic O is also facile on $\text{Fe}_1\text{Cu}_1@\text{C}_2\text{N}$. Excitingly, our computations revealed that this reaction is exothermic by 2.09 eV via overcoming a barrier of 0.45 eV.

Figure 3 (Figure S7, Supporting Information) illustrates the reaction profile of O_2 adsorption, dissociation, and CO oxidation on the $\text{Fe}_1\text{Cu}_1@\text{C}_2\text{N}$. Starting from the clean $\text{Fe}_1\text{Cu}_1@\text{C}_2\text{N}$

(S0) with the most stable configuration II, the O_2 molecule is adsorbed (S1) on the Fe atom, and then dissociates spontaneously (S2) to form an atomic O only attached to Fe and another O atom bridging Fe and Cu atoms. Subsequently, the singly bonded O atom will be approached by the first CO (S3), by passing over the transition state (S4) with the activation energy (E_a) of 0.45 eV, the first CO_2 molecule is produced accompanying with the reaction energy of 2.09 eV released. With the first CO_2 released, only the second atomic O is bridge-bonded with Fe and Cu atoms (S5). When the second CO approaches to the bridged O (S6), by passing over the transition state (S7) with the activation energy of 0.69 eV, the second CO_2 is formed (S8) with the exothermicity of 0.16 eV. Thus, the heteronuclear $\text{Fe}_1\text{Cu}_1@\text{C}_2\text{N}$ exhibits good performance for CO oxidation on the O_2 -preadsorbed catalyst surface among the examined dimer systems.

2.3.2. CO Oxidation on the CO-Preadsorbed Catalyst Surface

We then examined the CO oxidation over the CO preadsorbed $\text{Fe}_1\text{Cu}_1@\text{C}_2\text{N}$ following the bimolecular Langmuir–Hinshelwood (BLH) mechanism. As mentioned before, the

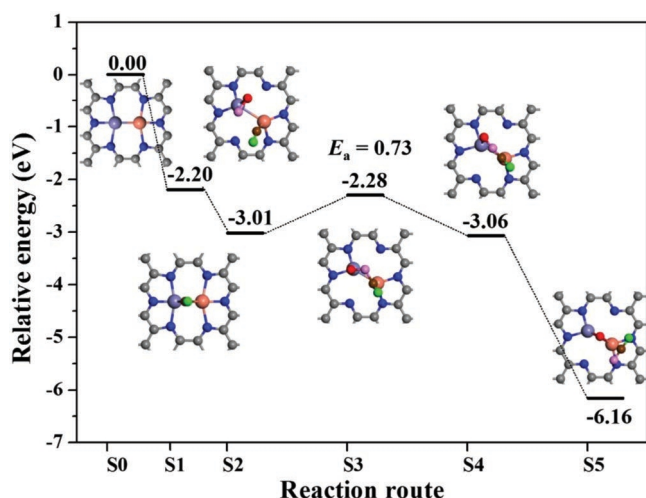


Figure 4. The reaction pathways (BLH) based on the coadsorption of CO and O₂ and energy profile for CO oxidation on the heteronuclear metal-dimer Fe₁Cu₁@C₂N monolayer. The corresponding side views were given in Figure S8 (Supporting Information). Color scheme: N, blue; Fe, purple; Cu, orange; C in C₂N, gray; C in CO, brown; O in CO, green; O in O₂, pink and red.

adsorption energy of CO on the Fe₁Cu₁@C₂N is 2.20 eV. Our computations showed that the O₂-coadsorption is energetically favored by 0.81 eV. The coadsorbed O₂ (O–O*) and CO (OC*) adopt side-on and end-on configurations (S2 in Figure 4), respectively. The ability for the coadsorption of CO and O₂ indicates the feasibility of the bimolecular L–H mechanism. Figure 4 presents the reaction pathway and energy profile for CO oxidation following L–H mechanism, and Figure S8 (Supporting Information) gives the side views and key geometric parameters of intermediates. Following this mechanism, first OC* approaches to O–O*, passing over the transition state (S3 in Figure 4, the intermolecular C...O distance of 2.33 Å in S2 becomes to 1.50 Å in S3) with a barrier of 0.73 eV to form the intermediate OOCO* (S4 in Figure 4). For the intermediate S4, the O–O and C–O bonds are elongated to be 1.46 and 1.22 Å, respectively, and the newly formed intermolecular C–O bond is 1.37 Å. Then, a CO₂ molecule is produced barrierlessly (S5 in Figure 4, the OO distance is 3.00 Å) accompanied by a release of 3.10 eV of energy (Figure 4; Figure S6, Supporting Information).

Furthermore, we studied the situation with two CO molecules preadsorbed on the Fe₁Cu₁@C₂N, which can occur under high concentration of CO. To well simulate such a condition, we explored the trimolecular ER (TER) mechanism proposed by Li and co-workers when investigating the CO oxidation over the single Au atom supported by B and N doped single-walled carbon nanotube,^[57] where O₂ reacts with two adsorbed CO. On Fe₁Cu₁@C₂N, the adsorption energy of the second CO (1.00 eV) is lower than the individual CO adsorption energy (i.e., 2.20 eV for the first CO), thus the CO coadsorption will be in competition with the adsorption of two individual CO molecules. Both adsorbed CO (OC*) adopt the end-on configuration with the intermolecular C...C distance of 2.30 Å, and the coadsorption energy is 3.20 eV (S1 in Figure 5). Following TER mechanism, the reaction starts with the two adsorbed

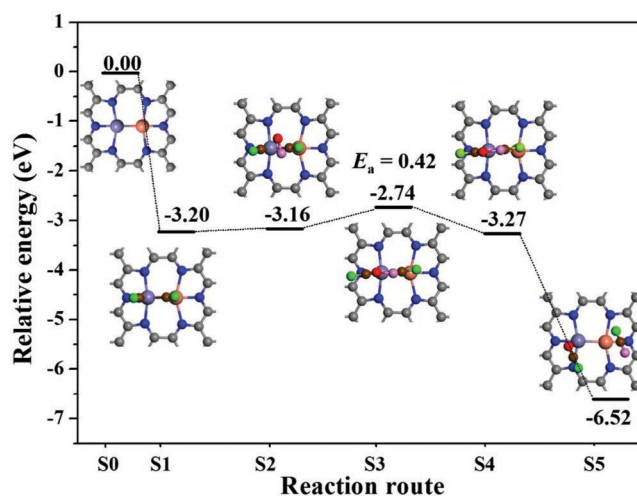


Figure 5. The reaction pathways based on the TER mechanism and the energy profile on the heteronuclear metal-dimer Fe₁Cu₁@C₂N monolayer. The corresponding side views were given in Figure S9 (Supporting Information). Color scheme: N, blue; Fe, purple; Cu, orange; C in C₂N, gray; C in CO, brown; O in CO, green; O in O₂, pink and red.

CO (OC*) and an O₂ approaching to the two adsorbed CO (S2 in Figure 5), and the O₂ is activated by the two adsorbed CO instead of the Fe₁Cu₁ dimer. In the transition state S3 (Figure S9, Supporting Information), the O–O bond is elongated to 1.34 Å, and the distances between the two O atoms and the two C atoms of OC* are 1.78 and 1.97 Å, respectively. The activation barrier (0.42 eV) is significantly lower than that of the BLH mechanism (0.73 eV). Surpassing the transition state S3, a pentagonal ring intermediate OCOOCO (S4 in Figure 5), 0.11 eV lower in energy than S2, is formed, in which the O–O bond is further stretched to 1.46 Å, and the two newly formed C–O bonds are 1.36 and 1.38 Å, respectively. Then, the intermediate S4 dissociates into two CO₂ molecules (S5 in Figure 5) spontaneously, and at the same time, 3.25 eV of heat is released.

To sum up, we examined the CO oxidation on Fe₁Cu₁@C₂N monolayer following three different mechanisms, namely ER mechanism with O₂-preadsorbed catalyst surface, BLH mechanism with CO-preadsorbed catalyst surface (low CO partial pressure), and TER mechanism with two CO molecules preadsorbed on catalyst surface (high CO partial pressure). Comparing the E–R, BLH, and TER routes discussed above, we could easily find the TER mechanism is the most favored pathway, since it has the lowest activation energy of 0.42 eV, thus it is recommended to perform CO oxidation at high CO partial pressure since it will favor TER mechanism. Notably, the largest activation energies of all the examined mechanisms (TER: 0.42 eV; ER: 0.69 eV; BLH: 0.73 eV) are less than 0.8 eV, indicating that the CO oxidation process could occur at room temperature.^[58] Interestingly, the notorious CO-poisoning problem could be avoided on Fe₁Cu₁@C₂N: O₂ and CO have comparable adsorption strengths (2.45 and 2.20 eV, respectively) on the catalyst surface, and O₂ could react with the preadsorbed CO by surpassing moderate barriers (0.73 and 0.42 eV for the preadsorption of one and two CO, respectively). Thus, the hetero-nuclear Fe₁Cu₁@C₂N is quite promising as

low-cost catalyst for CO oxidation at room temperature without suffering the CO-poisoning problem.

Notably, the heteronuclear $\text{Fe}_1\text{Cu}_1@\text{C}_2\text{N}$ outperforms its homonuclear counterparts ($\text{Fe}_2@\text{C}_2\text{N}$ and $\text{Cu}_2@\text{C}_2\text{N}$) as a catalyst for low-temperature CO oxidation: it is much easier to remove the chemisorbed atomic O on the $\text{Fe}_1\text{Cu}_1@\text{C}_2\text{N}$ than the $\text{Fe}_2@\text{C}_2\text{N}$ (reaction barrier 0.69 eV vs 1.53 eV); the O_2 dissociation on the $\text{Fe}_1\text{Cu}_1@\text{C}_2\text{N}$ is barrierlessly, while a barrier of 0.50 eV should be surpassed on the $\text{Cu}_2@\text{C}_2\text{N}$;^[48] CO-poisoning will not be the limited issue for the $\text{Fe}_1\text{Cu}_1@\text{C}_2\text{N}$, but $\text{Cu}_2@\text{C}_2\text{N}$ is prone to be poisoned by CO molecules due to the higher CO adsorption energy compared with that of O_2 (2.14 eV vs 1.33 eV).

2.4. Origin of the Superior Catalytic Performance of $\text{Fe}_1\text{Cu}_1@\text{C}_2\text{N}$

To understand the much enhanced catalytic performance of $\text{Fe}_1\text{Cu}_1@\text{C}_2\text{N}$ over its homonuclear counterparts ($\text{Fe}_2@\text{C}_2\text{N}$ and $\text{Cu}_2@\text{C}_2\text{N}$), we examined the density of states of the d electrons and analyzed the d-band centers of these three dimer species (Figure S10, Supporting Information). According to the d-band center theory, the position of the d-band center can differentiate the adsorption strength with adsorbates. Checking the relationship between the d-band centers, including the d-band centers of the spin-up channel (d-up) and spin down channel (d-down) and the adsorption energies of CO, O_2 , and O (Figure 6), we found that the adsorption energy change well correlates with the d-band center position: the adsorption strength of CO/ O_2 /O on the $\text{Fe}_1\text{Cu}_1@\text{C}_2\text{N}$ is between them on the $\text{Fe}_2@\text{C}_2\text{N}$ and $\text{Cu}_2@\text{C}_2\text{N}$, and the d-band center of spin-down channel for the $\text{Fe}_1\text{Cu}_1@\text{C}_2\text{N}$ is placed between the d-down of the $\text{Fe}_2@\text{C}_2\text{N}$ and $\text{Cu}_2@\text{C}_2\text{N}$. Thus, the dependence of the adsorption strength and the d-band center is in line with the d-band center theory proposed by Hammer and Nørskov.^[59]

We also noted that the CO/ O_2 /O adsorption in the lowest-energy structures can induce the structural transformation of metal dimer from II to I, as shown in Figure 1. Thus, we further compared the d-band centers of the $\text{Fe}_1\text{Cu}_1@\text{C}_2\text{N}$ in

different configurations with those of $\text{Fe}_2@\text{C}_2\text{N}$ and $\text{Cu}_2@\text{C}_2\text{N}$. For $\text{Fe}_1\text{Cu}_1@\text{C}_2\text{N}$, in either configuration I or II, the d-band centers of the spin-down channel are located between the corresponding values of $\text{Fe}_2@\text{C}_2\text{N}$ and $\text{Cu}_2@\text{C}_2\text{N}$ (Figure S10, Supporting Information and Figure 6); while the spin-down channel of the d-band centers of $\text{Fe}_2@\text{C}_2\text{N}$ in both I and II configurations are quite close to the Fermi level, leading to the strong interaction with the adsorbates (CO, O_2 , and O) and the concomitant high activation energy to remove the atomic O (as high as 1.53 eV). The cooperation of Fe and Cu endows the $\text{Fe}_1\text{Cu}_1@\text{C}_2\text{N}$ possessing the moderate d-band centers in configurations I and II, and thus leads to the heteronuclear species outperforming its homonuclear counterparts, consisting with previous theoretical results that catalysts with moderate d-band centers exhibit good catalytic performance.^[58–61]

2.5. The Feasibility for Experimental Realization of $\text{Fe}_1\text{Cu}_1@\text{C}_2\text{N}$

So far single metal atom on C_2N has not been synthesized yet, instead the Pt nanoparticles dispersed within the nitrogenated holes of C_2N ^[42] and Fe nanoparticles supported on C_2N ^[63] were obtained by Baek and co-workers. Previously we proposed a synthetic route and simulated the synthesis process for experimental realization of $\text{Cu}_1@\text{C}_2\text{N}$ and $\text{Cu}_2@\text{C}_2\text{N}$ using CuCl_2 as the metal precursor, and found that both catalysts are quite easy to be obtained.^[48] Since the E_b^0 value of Fe (3.79 eV) is much larger than that of Cu (2.61 eV) for $\text{Fe}_1\text{Cu}_1@\text{C}_2\text{N}$ (Table S1, Supporting Information), we then examined the feasibility for experimental realization of $\text{Fe}_1\text{Cu}_1@\text{C}_2\text{N}$ based on $\text{Cu}_1@\text{C}_2\text{N}$ and FeCl_2 by computing the energy profile of the proposed synthetic route (Figure S11, Supporting Information) and simulating the synthesis process by first principles molecular dynamics (FPMD) at 350 K in an NVT canonical ensemble. All the reaction steps can easily occur since they are either spontaneous (barrierless) or only slightly endothermic (Figure S12, Supporting Information). In our FPMD simulations, the FeCl_2 in the solution is observed to adsorb on the $\text{Cu}_1@\text{C}_2\text{N}$, afterward the Cl^- ions is desorbed. Within 0.5 ps, $\text{Fe}_1\text{Cu}_1@\text{C}_2\text{N}$ is formed (Figure S13, Supporting Information). The FPMD simulation (5 ps at 800 K) revealed that the $\text{Fe}_1\text{Cu}_1@\text{C}_2\text{N}$ system has very good thermal stability (Figure S14, Supporting Information). Note that during the period of revision, the $\text{Cu}_1^0\text{--Cu}_1^{x+}$ pair anchored on $\text{Pd}_{10}\text{Te}_3$ alloy nanowires have been developed for selective and efficient electrochemical reduction of CO_2 ^[64] the Zn–Co atomic pairs on N-doped carbon support was experimentally achieved and the high activity toward oxygen reduction reaction was demonstrated.^[65] Thus, we believe that the highly stable and efficient $\text{Fe}_1\text{Cu}_1@\text{C}_2\text{N}$ catalysts could be synthesized by using CuCl_2 and FeCl_2 as the metal precursors.

3. Conclusions

In summary, by means of DFT computations, we explored the potential of using C_2N monolayer to anchor heteronuclear metal dimer, i.e., $\text{Fe}_1\text{Cu}_1@\text{C}_2\text{N}$, as the biatom catalyst for CO oxidation, in comparison with its the homonuclear counterparts $\text{Fe}_2@\text{C}_2\text{N}$ and $\text{Cu}_2@\text{C}_2\text{N}$. The heteronuclear $\text{Fe}_1\text{Cu}_1@\text{C}_2\text{N}$

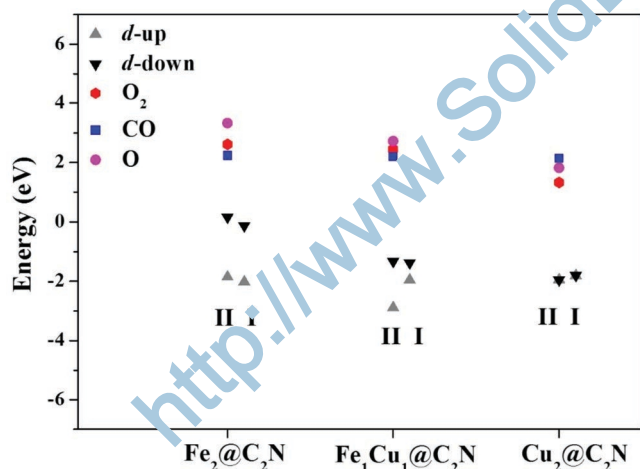


Figure 6. The d-band centers of configuration II and I, and the adsorption energies of CO, O_2 , and O for the $\text{Fe}_2@\text{C}_2\text{N}$, $\text{Fe}_1\text{Cu}_1@\text{C}_2\text{N}$ and $\text{Cu}_2@\text{C}_2\text{N}$.

has good thermodynamic and thermal stabilities, and exhibits superior performance toward CO oxidation compared to the homonuclear catalysts $\text{Fe}_2\text{@C}_2\text{N}$ and $\text{Cu}_2\text{@C}_2\text{N}$, and especially does not suffer the notorious CO oxidation problem. The heteronuclear $\text{Fe}_1\text{Cu}_1\text{@C}_2\text{N}$ species is feasible to be synthesized according to our proposed synthetic route and MD simulations. Our comparative study suggests that the heteronuclear biatom catalyst, namely the iron copper dimer anchored on suitable substrate, is highly active for CO oxidation.

Heteronuclear dimers provide a simple means of modulating the d-band centers, so that the optimal interactions with the intermediates can be achieved, thus enhancing the catalytic performance. Note that this work is the first attempt to investigate heteronuclear biatom catalysts, and there might be some metal dimers exhibiting even better performance than $\text{Fe}_1\text{Cu}_1\text{@C}_2\text{N}$ for CO oxidation, considering the vast number of possible combinations of heteronuclear dimers. This work not only spans the single-atom catalysts, but also provides useful insights and guidelines to future theoretical and experimental investigations, and help promote the design and development of novel low-cost and efficient nanocatalysts for many other important reactions.

4. Computational Details

Our spin-polarized DFT computations were based on the generalized gradient approximation (GGA) in the form of the Perdew–Burke–Ernzerhof exchange–correlation functional (PBE).^[66] Frozen-core all-electron projector augmented wave (PAW) method^[67] was used as implemented in the Vienna ab initio simulation package (VASP).^[68] The Monkhorst–Pack scheme^[69] of $(5 \times 5 \times 1)$ k -points mesh was applied to carry out the numerical integrations in the reciprocal space. The kinetic energy cutoff for the plane-wave basis set was chosen to be 500 eV. The optimized lattice parameter of the 2D C_2N unit cell (C_{12}N_6) is 8.33 Å, which agrees well with both experimental value^[53] and previous theoretical results.^[37] The computations on the isolated molecules and atoms were carried out in a $(10 \text{ Å} \times 10 \text{ Å} \times 10 \text{ Å})$ unit cell with the Γ -point only for the k -point sampling. The reaction pathways were investigated by using the climbing image nudged elastic band method (CI-NEB),^[70] and for each reaction, 5–9 images were inserted between the reactant and the product. Bader charge analysis^[71] was used to evaluate the charge transfer. Unless stated otherwise, the unit cell was used in our computations.

The binding energy (E_b) of a metal atom or the adsorption energy (E_{ad}) of an adsorbate (O_2 , CO, etc.) on the substrate was defined as $E_b/E_{\text{ad}} = E + E' - E_{\text{tot}}$, where E , E' , and E_{tot} represent the total energies of the clean slab, the isolated adsorbed atom/molecule, and the slab after adsorption, respectively. In the case of the coadsorption of two species A and B, E' is the sum of the total energies of isolated A and B. According to this definition, a positive (negative) value of E_b/E_{ad} indicates that the adsorption is exothermic (endothermic).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This work was supported in China by the National Natural Science Foundation of China (No. 11704203) and the Startup Project of Inner Mongolia University in China, and in USA by NSF-CREST Center for Innovation, Research and Education in Environmental Nanotechnology (CIREDN) (Grant Number HRD-1736093). All the computations were performed on PARATEAR at Guangzhou Supercomputer Center.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

biatom catalysis, CO oxidation, density functional calculations, heteronuclear, single-atom catalysis

Received: November 22, 2018

Revised: February 2, 2019

Published online:

- [1] K. Liu, A. Wang, T. Zhang, *ACS Catal.* **2012**, 2, 1165.
- [2] L. M. Molina, M. D. Rasmussen, B. Hammer, *J. Chem. Phys.* **2004**, 120, 7673.
- [3] L. Li, Y. Gao, H. Li, Y. Zhao, Y. Pei, Z. Chen, X. C. Zeng, *J. Am. Chem. Soc.* **2013**, 135, 19356.
- [4] W. An, P. Liu, *Phys. Chem. Chem. Phys.* **2016**, 18, 30899.
- [5] M. Haruta, N. Hamada, T. Kobayashi, S. Iijima, *J. Catal.* **1989**, 115, 301.
- [6] K. Judai, S. Albet, A. S. Wörz, U. Heiz, C. R. Henry, *J. Am. Chem. Soc.* **2003**, 126, 2732.
- [7] T. Schadow, B. Brandt, D. E. Starr, M. S. Laurin, K. Shaikhutdinov, S. Hauermann, J. Libuda, H.-J. Freund, *Angew. Chem., Int. Ed.* **2006**, 45, 3693.
- [8] B. Qiao, A. Wang, X. Yang, L. F. Allard, Z. Jiang, Y. Cui, J. Liu, J. Li, T. Zhang, *Nat. Chem.* **2011**, 3, 634.
- [9] X. Yang, A. Wang, B. Qiao, J. Li, J. Liu, T. Zhang, *Acc. Chem. Res.* **2013**, 46, 1740.
- [10] W. Zhang, W. Zheng, *Adv. Funct. Mater.* **2016**, 26, 2988.
- [11] J. Liu, *ACS Catal.* **2017**, 7, 34.
- [12] B. Bayatsarmadi, Y. Zheng, A. Vasileff, S.-Z. Qiao, *Small* **2017**, 13, 1700191.
- [13] L. Wang, L. Huang, F. Liang, S. Liu, Y. Wang, H. Zhang, *Chin. J. Catal.* **2017**, 38, 1528.
- [14] F. Chen, X. Jiang, L. Zhang, R. Lang, B. Qiao, *Chin. J. Catal.* **2018**, 39, 893.
- [15] C. Zhu, S. Fu, Q. Shi, D. Du, Y. Lin, *Angew. Chem., Int. Ed.* **2017**, 56, 13944.
- [16] J.-C. Liu, Y. Tang, Y.-G. Wang, T. Zhang, J. Li, *Natl. Sci. Rev.* **2018**, 5, 638.
- [17] a) Z. Li, D. Wang, Y. Wu, Y. Li, *Natl. Sci. Rev.* **2018**, 5, 673; b) J. Wang, Z. Li, Y. Wu, Y. Li, *Adv. Mater.* **2018**, 30, 1801649.
- [18] L. Zhang, M. N. Banis, X. Sun, *Natl. Sci. Rev.* **2018**, 5, 629.
- [19] J. Lin, A. Wang, B. Qiao, X. Liu, X. Yang, X. Wang, J. Liang, J. Li, J. Liu, T. Zhang, *J. Am. Chem. Soc.* **2013**, 135, 15314.
- [20] J. Liang, J. Lin, X. Yang, A. Wang, B. Qiao, J. Liu, T. Zhang, J. Li, *J. Phys. Chem. C* **2014**, 118, 21945.
- [21] H. Wei, X. Liu, A. Wang, L. Zhang, B. Qiao, X. Yang, Y. Huang, S. Miao, J. Liu, T. Zhang, *Nat. Commun.* **2014**, 5, 5634.

- [22] B. Qiao, J. Liang, A. Wang, C. Xu, J. Li, T. Zhang, J. Liu, *Nano Res.* **2015**, *8*, 2913.
- [23] J. Lin, B. Qiao, N. Li, L. Li, X. Sun, J. Liu, X. Wang, T. Zhang, *Chem. Commun.* **2015**, 51, 7911.
- [24] B. Qiao, J. X. Liang, A. Wang, J. Liu, T. Zhang, *Chin. J. Catal.* **2016**, *37*, 1580.
- [25] J. Liang, X. Yang, A. Wang, T. Zhang, J. Li, *Catal. Sci. Technol.* **2016**, *6*, 6886.
- [26] B. Qiao, J. Lin, A. Wang, Y. Chen, T. Zhang, J. Liu, *Chin. J. Catal.* **2015**, *36*, 1505.
- [27] B. Qiao, J. Liu, Y. Wang, Q. Lin, X. Liu, A. Wang, J. Li, T. Zhang, J. Liu, *ACS Catal.* **2015**, *5*, 6249.
- [28] M. Moses-DeBusk, M. Yoon, L. F. Allard, D. R. Mullins, Z. Wu, X. Yang, G. Veith, G. M. Stocks, C. K. Narula, *J. Am. Chem. Soc.* **2013**, *135*, 12634.
- [29] D. Yang, S. Zhang, P. Xu, N. D. Browning, D. A. Dixon, B. C. Gates, *Chem. - Eur. J.* **2017**, *23*, 2532.
- [30] J. Yang, Z. Qiu, C. Zhao, W. Wei, W. Chen, Z. Li, Y. Qu, J. Dong, J. Luo, Z. Li, Y. Wu, *Angew. Chem., Int. Ed.* **2018**, *57*, 14095.
- [31] Y. Qu, Z. Li, W. Chen, Y. Lin, T. Yuan, Z. Yang, C. Zhao, J. Wang, C. Zhao, X. Wang, F. Zhou, Z. Zhuang, Y. Wu, Y. Li, *Nat. Catal.* **2018**, *1*, 781.
- [32] F. Li, Y. Li, X. C. Zeng, Z. Chen, *ACS Catal.* **2015**, *5*, 544.
- [33] J. Liang, Q. Yu, X. Yang, T. Zhang, J. Li, *Nano Res.* **2018**, *11*, 1599.
- [34] a) G. Vilé, D. Albani, M. Nachtegaal, Z. Chen, D. Dontsova, M. Antonietti, N. López, J. Pérez-Ramírez, *Angew. Chem., Int. Ed.* **2015**, *54*, 11265; b) Z. Chen, S. Mitchell, E. Vorobyeva, R. K. Leary, R. Hauert, T. Furnival, Q. M. Ramasse, J. M. Thomas, P. A. Midgley, D. Dontsova, M. Antonietti, S. Pogodin, N. López, J. Pérez-Ramírez, *Adv. Funct. Mater.* **2017**, *27*, 1605785.
- [35] X. Wang, W. Wang, M. Qiao, G. Wu, W. Chen, T. Yuan, Q. Xu, M. Chen, Y. Zhang, X. Wang, J. Wang, J. Ge, X. Hong, Y. Li, Y. Wu, Y. Li, *Sci. Bull.* **2018**, *63*, 1246.
- [36] X. Li, P. Cui, W. Zhong, J. Li, X. Wang, Z. Wang, J. Jiang, *Chem. Commun.* **2016**, 52, 13233.
- [37] D. Ma, Q. Wang, X. Yan, X. Zhang, C. He, D. Zhou, L. Tang, Z. Lu, Z. Yang, *Carbon* **2016**, *105*, 463.
- [38] Z. Wang, Z. Yu, J. Zhao, *Phys. Chem. Chem. Phys.* **2018**, *20*, 12835.
- [39] W. Zhong, Y. Liu, M. Deng, Y. Zhang, C. Jia, D. V. Prezhdov, J. Yuan, J. Jiang, *J. Mater. Chem. A* **2018**, *6*, 11105.
- [40] X. Cui, W. An, X. Liu, H. Wang, Y. Men, J. Wang, *Nanoscale* **2018**, *10*, 15262.
- [41] D. Ma, T. Li, Q. Wang, G. Yang, C. He, B. Ma, Z. Lu, *Carbon* **2017**, *95*, 756.
- [42] H. Yan, Y. Lin, H. Wu, W. Zhang, Z. Sun, H. Cheng, W. Lin, C. Wang, J. Li, X. Huang, T. Yao, J. Yang, S. Wei, J. Lu, *Nat. Commun.* **2017**, *8*, 1070.
- [43] Q. Luo, W. Zhang, C.-F. Fu, J. Yang, *Int. J. Hydrogen Energy* **2018**, *43*, 6997.
- [44] Y. Li, H. Su, S. H. Chan, Q. Sun, *ACS Catal.* **2015**, *5*, 6658.
- [45] G. Zhu, Y. Li, H. Zhu, H. Su, S. H. Chan, Q. Sun, *Nano Res.* **2017**, *10*, 1641.
- [46] H. Shen, Y. Li, Q. Sun, *J. Phys. Chem. C* **2017**, *121*, 3963.
- [47] X. Li, W. Zhong, P. Cui, J. Li, J. Jiang, *J. Phys. Chem. Lett.* **2016**, *7*, 1750.
- [48] F. Li, Z. Chen, *Nanoscale* **2018**, *10*, 15696.
- [49] J. Zhao, J. Zhao, F. Li, Z. Chen, *J. Phys. Chem. C* **2018**, *122*, 19712.
- [50] X. Zhang, A. Chen, Z. Zhang, M. Jiao, Z. Zhou, *J. Mater. Chem. A* **2018**, *6*, 11446.
- [51] X. Zhang, A. Chen, Z. Zhang, Z. Zhou, *J. Mater. Chem. A* **2018**, *6*, 18599.
- [52] Z. W. Chen, J.-M. Yan, Q. Jiang, *Small Methods* **2018**, *2*, 1800291.
- [53] J. Mahmood, E. K. Lee, M. Jung, D. Shin, I.-Y. Jeon, S.-M. Jung, H.-J. Choi, J.-M. Seo, S.-Y. Bae, S. D. Sohn, N. Park, J. H. Oh, H.-J. Shin, J.-B. Baek, *Nat. Commun.* **2015**, *6*, 6486.
- [54] B. L. He, J. S. Shen, Z. X. Tian, *Phys. Chem. Chem. Phys.* **2016**, *18*, 24261.
- [55] Q.-K. Li, X.-F. Li, G. Zhang, J. Jiang, *J. Am. Chem. Soc.* **2018**, *140*, 15149.
- [56] P. Sabatier, *La Catalyse en Chimie Organique*, Librairie Polytechnique, Paris et Liège **1920**.
- [57] S. Ali, T. Liu, Z. Lian, B. Li, D. S. Su, *J. Mater. Chem. A* **2017**, *5*, 16653.
- [58] J. Liang, Q. Y. X. Yang, T. Zhang, J. Li, *Nano Res.* **2018**, *11*, 1599.
- [59] B. Hammel, J. K. Nørskov, *Advances in Catalysis*, Vol. 45, Academic Press Inc, San Diego, **2000**, p. 71.
- [60] L. Li, H. Shu, C. Hu, Z. Shi, X. Liu, P. Liang, X. Chen, *ACS Appl. Mater. Interfaces* **2015**, *7*, 27405.
- [61] G. Zhu, Y. Li, H. Zhu, H. Su, S. H. Chan, Q. Sun, *ACS Catal.* **2016**, *6*, 6294.
- [62] J. Mahmood, F. Li, C. Kim, H.-J. Choi, O. Gwon, S.-M. Jung, Jeong-MinSeo, S.-J. Cho, Y.-W. Ju, H. Y. Jeong, G. Kim, J.-B. Baek, *Nat. Nanotechnol.* **2017**, *12*, 441.
- [63] J. Mahmood, F. Li, S.-M. Jung, M. S. Okay, I. Ahmad, S.-J. Kim, N. Park, H. Y. Jeong, J.-B. Baek, *Nano Energy* **2018**, *44*, 304.
- [64] J. Jiao, K. Lin, S. Liu, W. C. Cheong, C. Zhang, Z. Chen, Y. Pan, J. Tang, K. Wu, S. F. Hung, H. M. Chen, L. Zheng, Q. Lu, X. Yang, R. Xu, H. Xiao, J. Li, D. Wang, Q. Peng, C. Chen, Y. Li, *Nat. Chem.* **2017**, *11*, 222.
- [65] Z. Lu, B. Wang, Y. Hu, W. Liu, Y. Zhao, R. Yang, Z. Li, J. Luo, B. Chi, Z. Jiang, M. Li, S. Mu, S. Liao, J. Zhang, X. Sun, *Angew. Chem., Int. Ed.* **2019**, *58*, 2622.
- [66] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865.
- [67] P. E. Blöchl, *Phys. Rev. B* **1994**, *50*, 17953.
- [68] G. Kresse, J. Furthmüller, *Phys. Rev. B* **1996**, *54*, 11169.
- [69] H. J. Monkhorst, J. D. Pack, *Phys. Rev. B* **1976**, *13*, 5188.
- [70] G. Henkelman, B. P. Uberuaga, H. Jónsson, *J. Chem. Phys.* **2000**, *113*, 9901.
- [71] G. Henkelman, A. Arnaldsson, H. Jónsson, *Comput. Mater. Sci.* **2006**, *36*, 354.