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Understanding the CH₄ Conversion over Metal Dimers from First Principles

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Abstract: Inspired by the advantages of bi-atom catalysts and recent exciting progresses of nanozymes, by means of density functional theory (DFT) computations, we explored the potential of metal dimers embedded in phthalocyanine monolayers (M₂-Pc), which mimics the binuclear centers of methane monoxygenase, as catalysts for methane conversion using H₂O₂ as an oxidant. In total, 26 transition metal (from group IB to VIIIB) and four main group metal (M = Al, Ga, Sn and Bi) dimers were considered, and two methane conversion routes, namely *O-assisted and *OH-assisted mechanisms were systematically studied. The results show that methane conversion proceeds via an *OH-assisted mechanism on the Ti₂-Pc, Zr₂-Pc and Ta₂-Pc, a combination of *O- and *OH-assisted mechanisms on the surface of Sc₂-Pc, respectively. Our theoretical work may provide impetus to developing new catalysts for methane conversion and help stimulate further studies on metal dimer catalysts for other catalytic reactions.

Keywords: metal dimers; nanozymes; methane conversion; density functional theory

1. Introduction

Global warming is gaining increasing concern worldwide. Greenhouse gases include carbon dioxide, methane, nitrous oxides, and other gases. According to EPA, carbon dioxide accounted for ca. 80% of all greenhouse gas emissions from human activities in the USA in 2019. Though methane has a lower emission (10%), it is also a major greenhouse gas since its greenhouse effect is 21 to 23 times that of carbon dioxide [1]. Therefore, the effective conversion of methane into value-added chemicals (instead of direct burning) is of both environmental and commercial importance [2–4].

The direct conversion of methane mainly associates with the high C—H bond strength (~434 kJ/mol) in the non-polar and highly symmetric methane [5–8]. In traditional industries, methane is first converted into syngas, then transferred to liquid hydrocarbons by Fischer–Tropsch process, which not only causes waste of resources, but also requires a high equipment maintenance cost [9–14]. Biological enzyme catalysis may be a good alternative since it has the advantages of high product selectivity and mild reaction conditions: compared with the current industrial process, the direct conversion of methane to methanol that occurs in the methane monoxygenase (MMO) from Methylococcus capsulatus is much more efficient [15–18]. Due to their high catalytic efficiency, biological enzymes can greatly increase the rate of chemical reactions, saving time and cost. Unfortunately, structural instability and sensitivity to the environment greatly limit their performance in industrial applications. A promising way to conquer such challenges is to mimic the MMO with the binuclear active sites [19–21]. Zeolites such as ZSM-5 are able to form stable binuclear centers (diiron or dicopper) in similar enzymes, and exhibit unprecedented high performance in methane conversion, but their catalytic mechanism and structure–property...
relationship remain unclear. The direct conversion of methane at room-temperature and atmopheric pressure is still an unsolved but high-rewarding challenge [22,23].

Nanozymes are a class of nanomaterials with unique enzyme-like properties, which have very similar active sites and catalytic mechanisms to biological enzymes. The first nanozymes were discovered in 2007, since then more than 300 nanomaterials have been found to have enzymatic activity [24–26]. Since “single-atom catalysis” was proposed in 2011, the concept of single-atom nanozymes (SAzymes) has also emerged as a research hotspot [27–30]. Compared with single-atom catalysts, bi-atom catalysts may possess improved catalytic performance [31,32]. For example, Yan et al. showed that Pt dimers embedded in graphene have 17-fold and 45-fold higher catalytic activity for the hydrolytic dehydrogenation of ammonia borane than its corresponding single-atom and nanoparticle counterparts [33]. Li et al. demonstrated that Cu dimers supported on C$_2$N layers exhibited superior performance for CO oxidation compared to Cu$_1$@C$_2$N [34], and showed excellent performance with a small confinement potential of $-0.23$ V for electrochemical CO$_2$ reduction [35]. However, to date, few studies have been reported on the catalytic performance of supported metal dimers for methane conversion. Inspired by the advantages of nanozymes and bi-atom catalysts, we designed a series of supported metal dimer catalysts for methane conversion by mimicking the binuclear centers in biological enzymes based on density functional theory computations.

The two-dimensional (2D) phthalocyanine-based (Pc) catalysts have a high surface area to volume ratio, abundant binding sites for anchoring metal atoms and the ability to prevent these metal atoms from aggregating into clusters. In 2011, Abel et al. [36] successfully prepared FePc complex and characterized the samples using scanning tunneling microscope (STM) at room temperature. Later on, Matsushita et al. [37] synthesized a rectangular phthalocyanine with two adjacent transition metal sites. Since Pc and transition metals are of low-cost, environmentally benign, more readily available than precious metals, the Pc-supported transition metal catalysts can be produced in a low-cost manner. Note that DFT calculations have been widely used to provide guidance in conversion/bonding/adsorption of molecules/clusters and reactions [38,39]. Here, first-principles calculations were conducted to explore the potential of all the 3d, 4d, and 5d non-toxic transition metals and the four main group metal (M = Al, Ga, Sn and Bi) dimers supported on the Pc (M$_2$-Pc) for methane conversion.

2. Computational Methods

All the computations were carried out by spin-polarized density functional theory (DFT) calculations including van der Waals (vdW) corrections (DFT-D2) [40], as implemented in Vienna Ab initio Simulation Package (VASP) using the projector augmented wave (PAW) method [41]. The generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional was adopted [42]. The energy cutoff for the plane-wave basis set was chosen as 550 eV, the systemic energy tolerance and the remaining total force were set as $1 \times 10^{-5}$ eV and 0.01 eV Å$^{-1}$, respectively. The Brillouin zone was sampled with a $5 \times 5 \times 1$ k-points grid of the Monkhorst–Pack scheme [43] for geometry optimization, and a denser k-mesh of $15 \times 15 \times 1$ for electronic structure computations. To avoid interactions between periodic images, a vacuum space of 15 Å was used in the perpendicular direction of the 2D layer. The reaction energy barriers were estimated using the climbing-image nudged elastic band (CI-NEB) method [44,45], and the transition states were obtained by relaxing the force below 0.05 eV/Å. The entropic effects were not included in estimating reaction barriers. The binding energy ($E_b$) of a metal atom was computed from the following equation.

$$E_b = \frac{(E_{tot} - E_{sub} - 2 \times E_M)}{2}$$

where $E_{tot}$, $E_{sub}$, and $E_M$ represent the total energy of the complex of substrate and metal atoms, the energy of the substrate, and the energy of a free M atom, respectively. According
to this definition, a more negative $E_b$ value indicates a higher thermodynamic stability. The adsorption energy ($E_{ads}$) of an adsorbate was computed according to the following equation:

$$E_{ads} = E_{tot} - E_{cat} - E_{adsorbate}$$

where the $E_{tot}$ is the total energy of an adsorbate adsorbed on the catalyst, $E_{cat}$ and $E_{adsorbate}$ represent the energies of the catalyst and a free adsorbate, respectively. The reaction energy ($E_{rec}$) and activity energy barrier ($E_{act}$) were calculated using the following expressions:

$$E_{rec} = E_{FS} - E_{IS}$$
$$E_{act} = E_{TS} - E_{IS}$$

in which $E_{FS}$, $E_{IS}$, and $E_{TS}$ denote the energies of the final, initial, and transition states, respectively. The reaction mechanism can also be effectively modeled by ab initio molecular dynamics (AIMD) simulations at specific temperatures \[46\].

3. Results and Discussion

This work describes our efforts to study the catalytic activity of $M_2$-Pc on the conversion of methane. In this paper, we use $H_2O_2$ as the oxidant, because its reaction by-product is only water, which is a green catalyst \[47\]. Moreover, $H_2O_2$ has been widely used as an oxidant to study the conversion of methane \[48–52\]. The $CH_4$ oxidation with $H_2O_2$ via both $^*OH$- and $^*O$-assisted mechanisms was investigated in detail \[48\].

3.1. Geometric Structure and Stability of $M_2$-Pc

First, the geometric structure of the Pc monolayer was optimized, and the lattice parameters $a$ and $b$ in the Pc monolayer of 14.13 Å were used. As shown in Figure S1a, the unique cavity structure of Pc can provide ideal anchoring sites for the metal atoms to be connected, to four isoindole rings, preventing their migrating and aggregating. The computed energy band gap of Pc sheet is 0.94 eV (in Figure S1b,c). The geometric structures and related information of the optimized $M_2$-Pc are shown in Figure S2 and Table S1. Obviously, due to the different radii of the metal atoms, the structures of $M_2$-Pc are slightly different. The anchored metal atoms with smaller atomic radii form an in-plane configuration in the Pc cavity (Al, Mn, Fe, Co, Ni, Cu, Ga, Ru, Rh, Re, Os, and Ir), while others with larger atomic radii are pulled out of the Pc plane and lead to a buckled structure.

To confirm the stability of metal dimers embedded in the Pc sheet, the binding energy ($E_b$) was calculated. Meanwhile, the corresponding metal bulk cohesive energy ($E_{bulk}$) were compared (Table S1), which are less negative than $E_b$, indicating that the interaction between the metal atoms and Pc monolayer is very strong, i.e., the anchoring of metal dimers on the Pc has strong coupling and good stability. We also performed AIMD simulations of the Ag$_2$-Pc monolayer, whose binding energy is the least favorable ($-4.13$ eV) among the considered systems ($-13.47$ to $-4.13$ eV), and found that the monolayer structure was well kept during 5 ps’s annealing at 300, 800, 1000, 1300, and 1500 K, respectively, and bond breakage occurred at 1500 K (Figure S3). Therefore, all the models in our work have high thermal stability, and in the next section, we will study the catalytic mechanism for methane conversion on these $M_2$-Pc catalysts.

3.2. Decomposition of $H_2O_2$ on $M_2$-Pc

Since the adsorption and dissociation of oxidants are important in methane oxidation, we considered both side-on and end-on configurations of the $H_2O_2$ adsorption (Figure S4) on the examined 30 $M_2$-Pc, including 26 transition metals from IB to group VIIIIB and four main group metals (M = Al, Ga, Sn and Bi).

Upon adsorption, $H_2O_2$ will spontaneously decompose on the surface of the nine $M_2$-Pc (M = Sc, Ti, V, Y, Zr, Nb, Hf, Ta, and W), all of which are highly exothermic (as shown in Table S2). As shown in Figure 1, $H_2O_2$ can be dissociated when the electronic state of...
the embedded atoms is a semi-occupied state. Among them, a H₂O₂ is spontaneously decompose into a H₂O and an adsorbed oxygen (H₂O₂ → *O + H₂O) on the Nb₂-Pc with the energy release of −6.08 eV, and into two adsorbed hydroxy groups (H₂O₂ → 2 *OH) on the five M₂-Pc (M = Ti, V, Y, Hf, and Ta) with the exothermic energy of −7.51, −6.70, −5.03, −8.71, and −9.04 eV, respectively), while into either a water molecule and an atomic oxygen (by releasing the heat of −3.75, −6.29, and −4.78 eV, respectively), or two OH species (by releasing the heat of −5.19, −8.16, and −7.41 eV, respectively) on the Sc₂-Pc, Zr₂-Pc, and W₂-Pc. All the surface-adsorbed oxo species (*O) occupy the bridge position of the metal dimers. We also examined the magnetic moments and Bader charges on the metal atoms of these nine M₂-Pc monolayers (M = Sc, Ti, V, Y, Zr, Nb, Hf, Ta, W) (Table S3), among which the Sc₂-Pc, Ta₂-Pc, Y₂-Pc, and W₂-Pc have spin states in singlet, the Nb₂-Pc, Ti₂-Pc, Zr₂-Pc, and Hf₂-Pc are triplet, while V₂-Pc is in quintet spin state. According to the dissociation structure and energy, H₂O₂ dissociation on these nine catalysts (Figure S5 and Table S2) are much more exothermic than the previously reported dissociation reaction of H₂O₂ on Pd(111) and Au/Pd(111) surfaces (−1.76 and −1.58 eV for two adsorbed hydroxy groups, and −2.27 and −2.06 eV for absorbed oxygen) [53]. Therefore, it is believed that the decomposition of H₂O₂ on these nine catalysts is likely to occur under environmental conditions. Unexpectedly, Fe₂ and Cu₂ metal centers, very common active center in biological systems and some biomimetic compounds [54], cannot decompose H₂O₂ to form reactive intermediates on Pc sheet.

Figure 1. (a) Top view of M₂-Pc sheet. (b) The metals examined in this work. The poisonous metals were indicated in gray; the metals assist H₂O₂ decomposition into 2*OH or *O and H₂O are highlighted in yellow and orange, respectively; the metals could decompose H₂O₂ into either 2*OH or *O and H₂O are represented in blue; metals in white cannot spontaneously decompose H₂O₂.

3.3. Catalytic Conversion of Methane on the M₂-Pc

Previous theoretical studies by Yoo et al. [53] showed that when *OH and *O species exist on the surface, the activation energy barrier of the C−H bond on the precious metal will be decreased [48,55,56]. Based on the spontaneous decomposition of H₂O₂ on M₂-Pc, two mechanisms of CH₄ conversion will be examined: the *OH-assisted mechanism on Sc₂-Pc, Ti₂-Pc, V₂-Pc, Y₂-Pc, Zr₂-Pc, Hf₂-Pc, Ta₂-Pc, and W₂-Pc, the *O-assisted mechanism on Nb₂-Pc, Sc₂-Pc, Zr₂-Pc, and W₂-Pc.

3.3.1. OH-Assisted Methane Conversion

We first examined the methane conversion over Sc₂-Pc, Ti₂-Pc, V₂-Pc, Y₂-Pc, Zr₂-Pc, Hf₂-Pc, Ta₂-Pc, and W₂-Pc via *OH-assisted mechanism. The two quenching reactions of *OH, namely the disproportionation of two OH groups to H₂O and O (2(*OH) → *O + H₂O) [57] and the self-reaction of H₂O₂ (H₂O₂ + 2(*OH) → O₂ + 2H₂O) [58], will result in a low reaction efficiency, thus the quenching reactions were investigated before the calculation.

The disproportionation of two *OH groups to H₂O and *O on the Ti₂-Pc, V₂-Pc, Y₂-Pc, Hf₂-Pc, and Ta₂-Pc were firstly evaluated. As shown in Table S4, the reaction on Y₂-Pc, Hf₂-Pc, and Ta₂-Pc are difficult (Gibbs free energies are 1.83, 1.72, and 1.63 eV, respectively),
in comparison, the free energy change on Ti$_2$-Pc and V$_2$-Pc are both less than 1 eV. However, the energy barriers on Ti$_2$-Pc and V$_2$-Pc are as high as 1.95 and 2.59 eV, respectively (Figure S6), indicating that the reaction is also difficult to proceed on these two catalysts. Though on Sc$_2$-Pc, Zr$_2$-Pc, and W$_2$-Pc catalysts, the decomposition of H$_2$O$_2$ into a H$_2$O and an adsorbed oxygen are more energy-efficient than the splitting into two *OH, considering that the splitting into two *OH on these three catalysts is spontaneous, we also calculated the methane conversion via *OH-assisted mechanism on these three catalyst surfaces.

The formation of O$_2$ is also a competitive reaction, which means that H$_2$O$_2$ may become its own scavengers. The energy parameters for the self-reaction on the six M$_2$-Pc (M = Ti, V, Zr, Sc, Y, and Hf) are given in Table S5, the rather high Gibbs free energies for the reaction on the Ti$_2$-Pc, V$_2$-Pc, and Zr$_2$-Pc (2.61, 2.69, and 3.08 eV, respectively) indicate that the self-reaction on these three catalysts is not thermodynamically favorable. No matter what initial structure is built on the Ta$_2$-Pc and W$_2$-Pc, they will become two adsorbed hydroxy groups after relaxation, i.e., the reaction will not proceed on either Ta$_2$-Pc or W$_2$-Pc. The calculated reaction energies over the Sc$_2$-Pc, Y$_2$-Pc, and Hf$_2$-Pc are 0.54, 0.65, and −0.18 eV, respectively; however, the activation energy barriers are 2.27, 1.66, and 1.36 eV, respectively (Figure S7), which means that the *OH is also difficult to quench on these three catalysts.

The above results showed that *OH will not be quenched on the eight catalysts examined in this section. Based on this finding, we investigated the methane conversion reaction via *OH-assisted mechanism.

First, CH$_4$ is weakly adsorbed on the catalyst covered by OH, and the C−M bond lengths are 2.59, 2.42, 2.37, 2.81, 2.51, 2.45, 2.64, and 2.42 Å on the Sc$_2$-Pc, Ti$_2$-Pc, V$_2$-Pc, Y$_2$-Pc, Zr$_2$-Pc, Ta$_2$-Pc, W$_2$-Pc, and Hf$_2$-Pc, respectively. The adsorption energies are −0.15, −0.53, −0.52, −0.41, −0.49, −0.51, 0.28, and −0.22 eV, respectively. The reaction energies of surface *OH groups attracting H from CH$_4$ are 0.76, 0.81, 0.59, 0.95, −0.14, 0.58, and 0.83 eV on Sc$_2$-Pc, Ti$_2$-Pc, V$_2$-Pc, Y$_2$-Pc, Zr$_2$-Pc, Ta$_2$-Pc, and Hf$_2$-Pc, respectively; the corresponding activation energy barriers are 1.09, 0.85, 1.41, 1.35, 0.86, 0.62, and 1.22 eV. The reaction of extracting H from CH$_4$ on the W$_2$-Pc is not considered because its repulsiveness to CH$_4$ (Figure S8). These analyses suggested that Ti$_2$-Pc, Zr$_2$-Pc, and Ta$_2$-Pc can catalyze the C-H breakage due to favorable reaction energies and relatively small activation barriers (0.85, 0.86 and 0.62 eV). Note that though the activation barrier on Sc$_2$-Pc is slightly high (1.09 eV), considering that the O-assisted methane conversion on this catalyst benefits from the assistance of *OH (see Section 3.3.2), we also investigated the the *OH-assisted mechanism on Sc$_2$-Pc. Thus, four catalysts which are feasible to break the C-H bonds, namely, Sc$_2$-Pc, Ti$_2$-Pc, Zr$_2$-Pc, and Ta$_2$-Pc, will be further investigated.

Then, we calculated the subsequent reactions over Sc$_2$-Pc, Ti$_2$-Pc, Zr$_2$-Pc, and Ta$_2$-Pc. Figure 2a–d summarizes the corresponding potential energy profile and the optimized geometries along the reaction path on these four M$_2$-Pc. After the cleavage of the C−H bond, CH$_3$ and H$_2$O are adsorbed on the four catalyst surfaces. Next, the desorption of *CH$_3$, the desorption of *H$_2$O, and the reaction with OH in the solution to generate CH$_3$OH were considered, respectively. The best path for all these four catalysts is to react with OH in the solution. Note that *CH$_3$ will react with ·OH in the solution to form CH$_3$OH on Sc$_2$-Pc and Ti$_2$-Pc, the reaction proceeds spontaneously on Sc$_2$-Pc, and the energy barrier on Ti$_2$-Pc is only 0.08 eV. While on Zr$_2$-Pc and Ta$_2$-Pc, OH will combine with the H atom of *OH to generate H$_2$O instead of reacting with *CH$_3$ (this process occurs spontaneously on both catalysts). After desorbing H$_2$O, *CH$_3$, and *OH will remain on the surface. Unexpectedly, on both Zr$_2$-Pc and Ta$_2$-Pc catalysts, *CH$_3$ will not combine with *OH on the surface to form CH$_3$OH, but will combine with ·OH in the solution to generate CH$_3$OH (the energy barriers are 0.84 and 0.08 eV, respectively, as shown in Figure 2c,d).
Note that though the activation barrier on the Nb2-Pc, W2-Pc, Zr2-Pc, and Sc2-Pc catalysts is significantly higher than on the other catalysts, we considered all catalysts. The activation barriers on these four catalysts are 0.84, 0.62, 0.86, and 0.85 eV, respectively, as shown in Figure S9. Figure S9 shows the energy diagram of methane conversion on these four O-adsorbed catalysts following the surface-stabilized or radical-like mechanism, and the competition reaction pathway of the *CH3 dehydrogenation is also considered (*CH3 + *OH → *CH2 + *H2O). In contrast to the quintet state of Fe(IV)(oxo) in Fe(IV)O/MOF-74 [61], the M-O-M moiety (M = Sc, Zr, Nb, W) is singlet in the ground state, since the magnetic moment on either M or O is zero. Accordingly, the oxidation state of O and Sc/Zr/Nb/W could be assigned as −2 and +3/+4/+4/+4, respectively, which is quantitatively in line with our Bader charge analysis (Table S6). Notably, the spin state of Nb2-Pc and Zr2-Pc switches from the triplet to the singlet when forming M-O-M moiety, agreeing well with our recent theoretical observations in metal dimer-related catalysis [62]. The partial density of states (PDOS) of CH4 adsorption on M-O-M moiety (Figure S10) shows that there is orbital hybridization between M-O-M and CH4.

Among these examined catalysts, *O-assisted conversion of methane is energetically more favorable on the Sc2-Pc monolayer through a surface-stabilized mechanism (Figure S9). This is different from the traditional single-site catalyst, which prefers the

![Figure 2. Reaction pathway of *OH-assisted CH4 decomposition on the Sc2-Pc (a), Ti2-Pc (b), Zr2-Pc (c), and Ta2-Pc (d) monolayers. Blue, black, and red lines represent the reaction paths for *CH3 desorption, *H2O desorption, and the reaction with OH in the solution, respectively.](image-url)
free radical mechanism [60–65]. The potential energy profile and the reaction path of *O-assisted methane C—H bond cleavage on the Sc2-Pc surface are illustrated in Figure 3, in which the C—H bond activation is found as the rate-determining step for the first methanol formation. The reaction begins with the adsorption of CH4, which is physically adsorbed on the O-preadsorbed Sc2-Pc through van der Waals interaction as the initial state with the adsorption energy of 0.09 eV, where the C—H bond length is 1.10 Å, slightly longer than that in the free CH4 molecule (1.07 Å), and the distance between O and H is 1.84 Å. In the transition state, the distance between C and H is elongated to 1.47 Å, and the distance between O and H is shortened to 1.21 Å, both of which are between the initial state and the final state. In the final state, *OH and *CH3 will form one Sc—C (bond distance of 2.25 Å) and two Sc—O bonds (bond lengths 1.97 and 2.37 Å) on surface. In other words, the *O-assisted methane activation on the Sc2-Pc catalyst follows the surface-stabilized mechanism, and the energy barrier for activation of the first C—H bond is 0.63 eV, which is much lower than the *O-assisted Au (111) surface (1.33 eV) [53].

![Reaction pathway](image)

**Figure 3.** Reaction pathway of *O-assisted CH4 decomposition on the Sc2-Pc monolayer. Blue, black, and red lines represent the three paths of *CH3 reacting with *OH, *CH3 reacting with -OH in solution, and the migration of *OH from bridge to top site, respectively.

After the C-H bond cleavage on Sc2-Pc, the position of *O is transferred from the bridge site of two Sc atoms to the top of one Sc atom, and *CH3 is adsorbed on the other Sc atom. Unlike single-site active center catalysts, bi-atom active centers increase the adsorption strength of the intermediates, thereby preventing the combination of *CH3 and *OH, which can be seen from the very high energy barrier (1.65 eV) in Figure 3.

We also considered that *CH3 reacts with -OH in the solution to form *CH3OH. This reaction proceeds spontaneously (the initial state structure and the final state structure are shown in Figure S11) by releasing energy of 0.54 eV (the blue line in Figure 3). The desorption of *CH3OH requires 0.13 eV of energy. After desorbing CH3OH, *OH remains being adsorbed on the surface occupying the bridge position of Sc dimers. Subsequently, we investigated two reaction paths: *OH moves to the top site of Ta atom, and *OH on the bridge position continues to activate CH4. As shown in Figure 3, the C—H bond cleavage assisted by the *OH on the bridge site is endothermic by 0.87 eV, while the migration of the *OH on the bridge site to the top site is slightly endothermic by 0.23 eV. Therefore, the *OH prefers moving to the top site, and the subsequent reaction is the same as discussed in Section 3.3.1. Noted that the active site motif for H2O2-converting methane is M-O-M (where M is a metal center), different from the biological MMOs containing binuclear Fe
centers for the oxidation of CH$_4$ to CH$_3$OH by O$_2$, where the reaction involves the formation of a pair of highly active iron(IV)oxo groups in a “diamond core” arrangement [61].

Note that the DFT self-interaction errors can have significant effects on the reactivity of high-valent Fe species during the oxidation of methane in metal-organic frameworks [66]. Thus, we tested the reaction of the first C–H bond cleavage using the HSE06 functional [67] and compared with the PBE result, Ti$_2$-Pc was taken as a representative due to its best catalytic performance among the catalysts examined in this work. We found that reaction barriers (0.84 vs 0.85 eV) and reaction energies (0.78 vs 0.81 eV) are very close from the two methods (Figure S12). Thus, we conjecture that PBE results are reliable for our systems, and we adopted PBE functional through our calculations.

4. Conclusions

To sum up, we designed low-cost bi-atom (M$_2$-Pc) catalysts for CH$_4$ conversion using a two-dimensional material Pc to support the metal dimers. Two methane conversion routes, namely *O-assisted and *OH-assisted mechanisms, over M$_2$-Pc were systematically studied by means of density functional theory computations. Our computations identified four high-performance catalysts for methane conversion: the Sc$_2$-Pc surface following a combined *O-assisted and *OH-assisted mechanism with the C–H bond breaking energy barrier of 0.63 eV, and Ti$_2$-Pc, Zr$_2$-Pc, and Ta$_2$-Pc following *OH-assisted mechanism with energy barriers of 0.85, 0.86, and 1.11 eV, respectively, all these activation barriers are lower than that on the Au(111) surface (1.33 eV) [53]. This work clearly demonstrated that the M$_2$-Pc monolayers can serve as low-cost and efficient bi-atom catalysts for methane conversion, which not only enrich the family of bi-atom catalysts, but also provides new strategy to design effective bi-atom catalysts for methane conversion and related reactions.

Supplementary Materials: The Supporting Information is available free of charge at https://www.mdpi.com/article/10.3390/nano12091518/s1. Table S1. The lattice parameters ($a/b$, in Å) of M$_2$-Pc catalysts, their corresponding bond lengths (the bond lengths of metal to metal, metal to nitrogen, $d_{M-M}$, $d_{M-N}$, $d_{M-Nc}$, where Nc represents the N atom adjacent to the C atom, in Å), and the binding energy ($E_b$, in eV) of metal dimer anchoring at Pc monolayer, as well as the cohesive energy ($E_{built}$, in eV) of metal in bulk, Table S2. (a) The reaction energy for H$_2$O dissociation into *O + H$_2$O on M$_2$-Pc (M = Sc, Zr, Nb, W), bond lengths ($d_{M1-O}$/$d_{M2-O}$, in Å) (M1 = M2 = M), as well as the H$_2$O binding energies ($E_{ads}$ (H$_2$O), eV), (b) The reaction energy for H$_2$O dissociation into *OH + *OH on M$_2$-Pc (M = Sc, Ti, V, Y, Zr, Hf, Ta, W), as well as the bond lengths ($d_{M1-O}$/$d_{M2-O}$, $d_{O1-O2}$, $d_{O1-H}$/$d_{O2-H}$, Å) (M1 = M2 = M), O1 and O2 represent the two O atoms bonded to M1 and M2, respectively, Table S3. The total magnetic moments and magnetic moment (in μB) of two metal atoms of M$_2$-Pc (M = Sc, Ti, V, Y, Zr, Nb, Hf, Ta, W) (structures as shown in Figure S2), and the Bader charge (q, in e$^{-}$) of the two atoms. Table S4. The calculated zero-point energy, entropy, and free energy change of the reaction of the abstraction of a hydrogen from one of the *OH groups to the formation of water and oxo species (*OH + *OH → *O + H$_2$O) on M$_2$-Pc (M = Ti, V, Y, Hf, Ta), Table S5. The calculated zero-point energy, entropy, and free energy change of the self-reaction of H$_2$O$_2$ (2*OH + H$_2$O$_2$ → O$_2$ + 2H$_2$O) on M$_2$-Pc (M = Sc, Ti, V, Y, Zr, Hf) Table S6. The partial charges of O (O) and M (M$_1$/M$_2$) for M$_1$-O-M$_2$ (in q) (M1 = M2 = Sc, Zr, Nb, W). Values were obtained from Bader charge analysis, Figure S1. Top and side view of the structure of Pc in a 2 × 2 × 1 supercell (a), and its band structure (b) and projected density of state (DOS) (c). The Fermi lever is set to zero, Figure S2. Top and side views of the optimized M$_2$-Pc monolayers, Figure S3. The energy evolution with time progress of the 5 ps MD simulation of the Ag$_2$-Pc at 300 K, 800, 1000, 1300, and 1500 K, as well as the snapshot of structure at the end of 5 ps, respectively, Figure S4. Two adsorption configurations of H$_2$O$_2$ on the M$_2$-Pc, Figure S5. The structures of spontaneously dissociated H$_2$O$_2$ on the M$_2$-Pc monolayers, Figure S6. Transformation process of *OH + *OH → *O + H$_2$O on Ti$_2$-Pc (a) and V$_2$-Pc (b) surfaces. The inset was the atomic structure model of each step, Figure S7. Transformation process of H$_2$O$_2$ + 2*OH → O$_2$ + 2H$_2$O on the Sc$_2$-Pc, Y$_2$-Pc and Hf$_2$-Pc surface. The inset was the atomic structure model of each step, Figure S8. The initial state structure (a) and the final state structure (b) of methane adsorption on W$_2$-Pc surface, Figure S9. The corresponding energy profile of methane conversion via *O-assisted mechanism, Figure S10. Partial density of states (PDOS) of CH$_4$ adsorption on M-O-M moiety. The Fermi level was set to zero. Figure S11. The initial state structure (a) and the final state structure (b) of
the reaction between *^{13}CH_3 and OH in solution on Sc$_2$-Pc, Figure S12. Energy diagram of the C−H bond cleavage on Ti$_2$-Pc surface calculated by PEB and HSE06 functional.

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