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Article

Mn-corrolazine-based 2D-nanocatalytic material with single Mn atoms for catalytic oxidation of alkane to alcohol

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ABSTRACT

Heterogenization of organic-macrocyclic metal catalysts is one of the simplest and most efficient methods for effective separation of products and cyclic application of a catalyst. By using an environmentally friendly Mn-corrolazine catalyst as the building unit, which can directly oxidize organic substrates under oxygen atmosphere and mild conditions, we theoretically constructed a novel two-dimensional (2D) Mn-corrolazine nanocatalytic material with high catalytic activity. In this material, each Mn atom maintains its electronic configuration in the monomer and can directly activate O₂ as the single-atom catalyst (SAC) center to form a radical-like [Mn]-O-O under mild visible-light irradiation conditions. The newly generated [Mn]-O-O can efficiently and selectively oxidize C–H bonds to form alcohol species through H-abstraction and the rebound reaction. Moreover, the catalytic reaction is easily regulated by an external electric field along its intrinsic Mn–O–O reaction axis. The current study provides a theoretical foundation for further experimental studies and practical applications of the Mn-corrolazine-based SAC.

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1. Introduction

Corrole [1–4], a porphyrinoid aromatic macrocyclic system constructed by four conjugated pyrrole rings, has entered a new stage after the breakthrough advances to address synthetic technology bottlenecks [5], and has attracted significant research interest owing to its superior photoelectric properties and its increasing applications in catalysis, dye-sensitized solar cells (DSSCs), sensors, and medicines. Several reviews [1,2,6–9]

present recent advances in the synthesis of corrole derivatives and strategies for corrole functionalization. It is well-known that corrole has one *meso*-carbon atom less than porphyrins, which leads to a smaller cavity of the corrole ring [10,11] in favor of stabilizing high-valent transition metals [M(III), M(IV), M(V), or M(VI); M = Cr, Mn, Fe, Co, Ni, Cu, Y, Rh, Ag, La, Au, Ga] [8,12–20]. The structural and spectroscopic properties of corrole derivatives have been extensively investigated, both experimentally and theoretically. Among these metal corroles,

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manganese corroles have received considerable attention because of their excellent photoelectric properties. Many studies have been conducted to investigate the oxidation state changes from +III to +IV and +V of manganese at the center of corrole and the effect of substituents mainly residing on the *meso*- (5,10,15) and β - (2,3,7,8, 12,13,17,18) positions of corrole [1,21,22]. In recent years, the formation of corrolazine through structural modification with the substitution of N atoms for the *meso*-C atoms of corrole has further increased the progress in the chemistry of the corroles.

High-valent metal-oxo species have been identified as key reactive intermediates in catalytic-selective oxidation reactions. Manganese corrolazines have the most common and stable pentavalent oxidation state of Mn(V), and are conveniently prepared by oxidation of Mn(III) corrolazines. It is important to develop transition-metal complexes that can directly utilize O₂ in catalytic oxidations as an ideal oxidant because of its cost-effectiveness and cleanliness. To the best of our knowledge, this is the first report of the direct conversion of Mn(III)- to Mn(V)-oxo corrolazine complex with O₂ under visible-light irradiation [23]. Prokop and Goldberg [23] and our density functional theory (DFT) calculations [24] showed that a free-radical-like Mn-O-O is generated during the reaction of Mn-corrolazine with O₂ under visible light irradiation, which exhibits excellent activity to the formation of a high-valent Mn(V)-oxo active oxidant by abstracting hydrogen from the substrate followed by a rebound reaction [25]. Furthermore, a new activation mechanism of O₂ was proposed, in which the d_{xz} and d_{yz} orbitals of Mn with a single electron can couple with $\pi_{xz_2}^3$ and $\pi_{yz_2}^3$ of O₂, respectively, to form two new extended π bonds perpendicular to each other, $\pi_{xz_3}^4$ and $\pi_{yz_3}^4$ leading to an increase in the O-O bond length and the weakening of the O-O bond strength.

Two-dimensional (2D) nanomaterials have attracted significant interest in catalytic and photoelectric fields owing to their unique physical and chemical properties [26–30]. However, there is no report on the heterogeneous formation of homogeneous metal corrole catalysts into 2D nanocatalytic materials to expand their practical applications. Thus, to construct 2D nanocatalytic materials with high catalytic activity in which each metal atom acts as a single-atom catalyst (SAC) center [31–49], we selected linear ethynes as bridging groups to construct *meso*- and β -linked corrolazine dimers and tetramer [50]. Furthermore, a two-dimensional (2D) planar Mn-corrolazine nanocatalytic material can be constructed by extending the basic units of the Mn-corrolazine dimer along its two axes direction. Extensive first-principle calculations were performed to investigate their electronic properties, structural stabilities, energy density of states (DOS), and the possible activation mechanism for the selective oxidation process: $C_nH_{2n+2} + [Mn(III)]-O-O \rightarrow Mn(V)-oxo + C_nH_{2n+1}OH$ as well as its external electric field regulation mechanism. The present study theoretically designed and predicted a novel class of Mn-corrolazine-based 2D nanocatalytic materials with excellent catalytic properties that are easily regulated by the external electric field, and provides the fundamental basis for further experimental studies and practical applications of the

Mn-corrolazine in heterogeneous catalysis.

2. Computational details

Calculations of the structural and electronic properties of Mn-corrolazine polymers were performed using the Gaussian 09 package [51]. The B3LYP hybrid functional [52,53] in combination with the effective core potential coupled with the LANL2DZ basis set for manganese and the all-electron 6-31G(d) basis set for other atoms has been used for DFT calculations [51]. Frequency calculations were used to assess the nature of the stationary points on the potential-energy surfaces (PESs) and estimate their thermodynamic properties.

The structural and electronic properties of the 2D Mn-corrolazine nanomaterial were calculated using the Vienna *ab initio* simulation package (VASP) [54,55]. The generalized gradient approximation (GGA) with the PBE functional was employed to describe the electron-exchange-correction potential in all calculations. The projector augmented wave (PAW) method was used to describe the electron-ion interaction, and the cutoff energy was set to 500 eV. The calculations were carried out with the DFT+U method, using the formalism suggested by Dudarev et al. [56]. The parameters were set at $U = 4.0$ eV and $J = 1.0$ eV. All atomic positions were optimized by the conjugated gradient method with a converging tolerance of 0.02 eV/Å for the force on all atoms. Periodic boundary conditions are considered along with the growth directions of the nanomaterials. A vacuum distance over 15 Å was set to maintain the negligible interaction between the periodic nanostructures in the adjacent cells. A 5×5×1 Monkhorst-Pack grid was used for geometry optimization. The Brillouin zone was sampled by 21 *k*-points using Heyd-Scuseria-Ernzerhof (HSE06) screened Coulomb hybrid density functional [57–59] to calculate the electronic band structures and DOS of 2D Mn-corrolazine nanomaterials. The activation energy of C-H bonds was also corrected by the dispersion correction using the approach of the DFT-D3 method as implemented in VASP 5.3.5 [60], and further external electric field effects on the C-H bond activation were investigated at the same level of theory based on the optimized structures.

3. Results and discussion

3.1. Structural and electronic properties of the Mn-corrolazine polymers

Considering that the β - positions of corrolazine and metallocorrolazines are the active sites and the structures with substituents at these sites are much more stable and robust, a series of β -to- β ethyne-linked Mn-corrolazine polymers and 2D Mn-corrolazine nanocatalytic materials (2D-Mn_{cor}) were constructed herein (Scheme 1). As shown in Scheme 1, the order of Mn-corrolazine rings is marked as Mn₁ and Mn₂ in the Mn-corrolazine dimer (di-Mn_{cor}), and it is clockwise marked by Mn_N ($N = 1, 2, \dots$) in the Mn-corrolazine tetramer (tetra-Mn_{cor}). The optimized stable geometries without any imaginary frequency, selected bond lengths, and Mulliken charges of Mn of

Scheme 1. Manganese corrolazine dimer (di-Mn_{cor}), tetramer (tetra-Mn_{cor}) and their extended two-dimensional nanocatalytic material (2D-Mn_{cor}) constructed by combining Mn-corrolazines and ethynes.

the lowest singlet and nonet states for the Mn-corrolazine dimer and the singlet and 17-et states for the Mn-corrolazine tetramer are displayed in Fig. 1 and Fig. S1, and Table S1, respectively. As shown in Fig. 1(a) and (b), the optimized geometries of the dimer in the singlet (C_s symmetry) and nonet (D_{2h} symmetry) states are quite similar. The singlet state is higher in energy than the nonet state by 98.65 kcal/mol, and the nonet state is thus the ground state. Furthermore, the optimized geometries of the tetramer in the singlet (C_1 symmetry) and 17-et (C_1 symmetry) states are slightly distorted, as shown in Figs. 1(c) and (d). The singlet state of the tetramer is higher in energy than the 17-et states by 194.38 kcal/mol, and thus the 17-et state is the ground state. These results are in agreement with those of previous studies [24,61] in the fact that Mn-corrolazine exhibits a paramagnetic ground state, suggesting that the polymerization of corrolazine rings does not affect the electronic configuration of the central Mn atom, which is very favorable for constructing 2D materials with enhanced catalytic activity.

As seen in Table 1, the bond lengths of Mn-N in the nonet ground state of di-Mn_{cor} and 17-et ground state of tetra-Mn_{cor} complexes are 1.860–1.864 and 1.865–1.880 Å, respectively. To evaluate the stability of the nonet state of di-Mn_{cor}, 17-et state of tetra-Mn_{cor}, the binding energies (BE s) were calculated as:

$$BE_{\text{di-Mn}_{\text{cor}}} = 2E_{\text{HC}\equiv\text{CH}} + 2E_{\text{Mn-cor}} - E_{\text{di-Mn}_{\text{cor}}} - 4E_{\text{H}_2} \quad (1)$$

Fig. 1. Optimized geometries and relative energies (kcal/mol) of di-Mn_{cor} in (a) singlet and (b) nonet states; tetra-Mn_{cor} in (c) singlet and (d) 17-et states (top view).

Table 1

Selected optimized bond lengths (Å), Mulliken spin densities (ρ_{spin}) of Mn, magnetic moment (μ_B), and relative energies (ΔE , kcal/mol) of Mn(III)-corrolazine in di-Mn_{cor} in the singlet and nonet states, tetra-Mn_{cor} in the single and 17-et states, 2D-Mn_{cor} with ferromagnetism (FM) and antiferromagnetism (AFM).

Polymer (State)	$d_{\text{Mn-N1}}$ $d_{\text{Mn-N2}}$	$d_{\text{Mn-N3}}$ $d_{\text{Mn-N4}}$	$d_{\text{C}\equiv\text{C}}$	ΔE	ρ_{spin}/μ_B Mn
Di-Mn _{cor} (nonet)	1.864, 1.864	1.860, 1.861	1.218, 1.218	0.0	3.77, 3.77
Di-Mn _{cor} (singlet)	1.848, 1.848	1.863, 1.863	1.218, 1.218	98.65	—
Tetra-Mn _{cor} (17-et)	1.865, 1.878	1.868, 1.867	1.215, 1.222	0.0	3.77, 3.77
	1.866, 1.879	1.868, 1.867	1.215, 1.223		
	1.866, 1.880	1.868, 1.867	1.216, 1.224		
	1.866, 1.878	1.868, 1.866	1.216, 1.224		
Tetra-Mn _{cor} (singlet)	1.847, 1.856	1.865, 1.865	1.216, 1.222	194.38	—
	1.847, 1.856	1.865, 1.865	1.216, 1.222		
	1.847, 1.856	1.865, 1.865	1.216, 1.222		
	1.848, 1.856	1.865, 1.865	1.217, 1.224		
2D-Mn _{cor} (FM)	1.903, 1.904	1.885, 1.886	1.230, 1.231	13.34	3.57, 3.57
2D-Mn _{cor} (AFM)	1.903, 1.904	1.885, 1.886	1.231, 1.231	0.0	3.65, -3.65

$$BE_{\text{tetra-Mn}_{\text{cor}}} = 8E_{\text{HC}\equiv\text{CH}} + 4E_{\text{Mn-cor}} - E_{\text{tetra-Mn}_{\text{cor}}} - 16E_{\text{H}_2} \quad (2)$$

where $E[\cdot]$ are the total energies of the ethyne bridges, the Mn-corrolazine ring, the di-Mn_{cor}, tetra-Mn_{cor}, and the hydrogen molecules.

The calculated BE of 0.42 eV suggests that the formation of the ground state di-Mn_{cor} is exothermic and energetically stable. With the increase of Mn-corrolazine rings in the ground state tetra-Mn_{cor}, the BE is 1.11 eV, suggesting that the structure becomes more stable with an increase in the number of Mn-corrolazine rings and the ethyne bridges. Furthermore, in the dimer, two Mn-corrolazine rings linked by ethyne at the β -(2, 18) positions form a planar 12-numbered conjugated ring, which benefits the stabilization of the dimer according to previous studies [62,63]. In tetra-Mn_{cor}, there are multiple macrocycles without the metal center, including two 12-membered C_{12} rings, one 16-membered C_{16} ring, and two 14-membered $C_{12}N_2$ rings. The $C_{12}N_2$ ring is composed of β -C atoms, β -CH groups, *meso*-N atoms of corrolazine, and $-\text{C}\equiv\text{C}-$ bridging groups. The areas defined by the lengths and widths of C_{12} , C_{16} , and $C_{12}N_2$ rings in the complex are *ca.* 5.79×3.66 , 6.14×5.27 , and $5.41 \times 3.87 \text{ \AA}^2$, respectively. Because these polymers have pores with different sizes to accommodate numerous suitable reactive species, it is highly likely to construct an excellent platform for chemical reactions [64]. Mulliken population analysis revealed that the spin densities of the single Mn atoms in the nonet state (see Table 1) of di-Mn_{cor} and the 17-et state of tetra-Mn_{cor} are approximately 3.77, which indicates that all Mn atoms have nearly all of the unpaired four electrons, respec-

tively. Mn atoms in these polymers remain in their single-atom catalytic center for the reaction as in the monomer.

As shown in Fig. 2, similar to the monomer of Mn-corrolazine [24], the energy level of the d_{xy} orbital of central Mn in the ground state di-Mn_{cor} is the highest among all d orbitals of manganese because of the strong repulsion originating from the direct coordination interaction of four N atoms of the corrolazine ring. The lowest orbital is the $d_{x^2-y^2}$ orbital owing to weak coordination interactions because its stretching direction comes from the four N atoms of the corrolazine ring. The energy levels of the d_{z^2} , d_{xz} , and d_{yz} orbitals are between the two orbitals mentioned above, resulting from no direct interaction with the atoms of the corrolazine ring. The energy level of d_{z^2} is slightly higher owing to its small distribution in the corrolazine ring plane, and both d_{xz} and d_{yz} are approximately degenerate because of the only difference in their directions of space extension. Thus, the trivalent Mn atoms in these ground-state polymers still remain in the $d_{x^2-y^2}^1 d_{xz}^1 d_{yz}^1 d_{z^2}^2$ configuration as in the monomer.

3.2. Activation of O₂ on Mn-corrolazine polymers

From the above results, the single electrons of di-Mn_{cor} in its nonet ground state mainly reside in two individual Mn atoms, and thus can form weak interaction complexes with the ground state ³[O₂] through two spin alignments, respectively, as shown in Figs. 3(b) and (c). The spin reverse combination between the nonet di-Mn_{cor} and two triplet ³[O₂] forms a quintet di-O-Mn_{cor} with four spin-up single electrons, in which the spin densities are 3.74 in two Mn atoms and −0.92–(−1.03) in four oxygen atoms of the two adsorbed O₂ (see Table 2). The bond lengths of Mn–N and O–O in quintet di-O-Mn_{cor} are 1.871–1.874 and 1.216 Å, respectively. The distance between the Mn and O atoms is elongated up to 2.502–2.503 Å. The other spin parallel combination between the nonet di-Mn_{cor} and two triplet ³[O₂]

Fig. 2. Selected Mn-dominated molecular orbitals of the di-Mn_{cor} in the nonet state.

Fig. 3. Optimized geometries of di-O-Mn_{cor} complexes consisting of O₂ and di-Mn_{cor} in (a) singlet, (b) quintet, and (c) 13-et states. (d) Tetra-O-Mn_{cor} in the singlet state consisting of O₂ and tetra-Mn_{cor} with specific bond lengths (Å).

forms a 13-et di-O-Mn_{cor} with net 12 spin-up single electrons, in which the spin densities are 3.77 in two Mn atoms and 0.98–1.03 in four oxygen atoms of the two adsorbed O₂, and the bond lengths of Mn–N and O–O are 1.864–1.868 and 1.214 Å, respectively. The distance between Mn and O atoms is even longer, up to 3.015–3.057 Å. As the di-Mn_{cor} and O₂ moieties are far apart in both quintet and 13-et complexes, their interactions are very weak and they are almost isoenergetic with only an energy difference of 2.98 kcal/mol. The corresponding spin densities of the individual Mn atoms (see Table 2) are also similar, 3.74 and 3.77, respectively. The interconversion of both configurations is almost barrier-free, and these may act as precursors for the reaction of di-Mn_{cor} and O₂.

As shown in Fig. 3(a), the bond length of Mn–O in the singlet

Table 2

The bond lengths of Mn–N (Å), the relative energies (ΔE , kcal/mol) and Mulliken spin densities (ρ_{spin}), selected atoms' magnetic moments (μ_B) of the complexes of O₂ and Mn(III)-corrolazine in different states of di-O-Mn_{cor}, tetra-O-Mn_{cor} and 2D-Mn_{cor}.

Polymer (State)	$d_{\text{Mn-N1}}$ $d_{\text{Mn-N2}}$	$d_{\text{Mn-N3}}$ $d_{\text{Mn-N4}}$	$d_{\text{O-O}}$	ΔE	ρ_{spin}/μ_B		
					^a O	^b O	Mn
Di-O-Mn _{cor} (13-et)	1.867, 1.868	1.865, 1.864	1.214	0.0	1.03	0.98	3.77
	1.867, 1.868	1.864, 1.864					
	1.874, 1.874	1.871, 1.871	1.216	2.98	−1.03	−0.92	3.74
	1.874, 1.873	1.871, 1.871	1.216		−1.03	−0.92	3.74
Di-O-Mn _{cor} (singlet)	1.871, 1.877	1.899, 1.894	1.256	84.14	—	—	—
	1.873, 1.876	1.896, 1.894	1.256				
	1.858, 1.897	1.886, 1.894	1.254	—	—	—	—
	1.897, 1.865	1.894, 1.893	1.255				
Tetra-O-Mn _{cor} (singlet)	1.894, 1.858	1.898, 1.886	1.256	—	—	—	—
	1.897, 1.865	1.894, 1.893	1.255				
	1.894, 1.894	1.898, 1.898	1.255				
	1.894, 1.921	1.898, 1.903	1.255				
2D-O-Mn _{cor} (spin-polarized)	1.921, 1.923	1.903, 1.902	1.262	0.0	−0.73	−0.58	3.58
	1.920, 1.921	1.903, 1.904	1.262		0.73	0.57	−3.58
	1.925, 1.929	1.917, 1.918	1.267	74.53	—	—	—
	1.927, 1.928	1.917, 1.918	1.267				

state of di-O-Mn_{cor} is shorter than those in the quintet and 13-et states of di-O-Mn_{cor} by 0.885–0.886 and 1.398–1.440 Å, respectively. This result suggests that there is a strong bonding interaction between Mn and O₂ in the direction perpendicular to the corrolazine plane in the singlet complex, leading to the high-energy singlet complex. This structure is less stable than the quintet and 13-et states of di-O-Mn_{cor} by 40.58 and 42.07 kcal/mol per unit, respectively. Such energy differences are in the visible range and are compatible with the mild Mn-corrolazine-catalyzed reaction condition of visible-light irradiation. Furthermore, the energy levels of d_{z^2} Mn orbitals in the singlet state of di-O-Mn_{cor} significantly increase due to the strong interaction arising from the O₂ ligand in the z direction. Thus, the reaction of di-O-Mn_{cor} with O₂ would undergo the electron spin-reverse process, where the weak interaction of the precursors, di-O-Mn_{cor} complexes in the quintet and 13-et states, may evolve into strong interactions by the spin-flip of electrons in high-energy d_{z^2} orbitals and transfer to low-energy $d_{x^2-y^2}$ orbitals under visible-light irradiation, and the electronic configuration of Mn(III) changes from $d_{x^2-y^2}^1 d_{xz}^1 d_{yz}^1 d_{z^2}^1$ to $d_{x^2-y^2}^2 d_{xz}^1 d_{yz}^1$ (as shown in Fig. 4).

In addition, similar to the Mn-corrolazine monomer, the Mn-O-O in the singlet di-O-Mn_{cor} forms a linear structure so that two extended π bonds π_{xz}^4 and π_{yz}^4 featuring free radicals are formed originating from d_{xz} and d_{yz} orbitals of Mn coupled with the π_{xz}^3 and π_{yz}^3 of O₂. Moreover, with an increase in the Mn(III)-corrolazine rings, the O-O and Mn-O bond lengths of the singlet tetra-O-Mn_{cor} complex consisting of the adsorbed O₂ and the tetra-polymer (as shown in Fig. 3(d)) are almost the same as those of the singlet di-O-Mn_{cor}. The Mn-O-O moieties also form extended linear π bonds with free radical characteristics, indicating that the increase of Mn(III)-corrolazine rings has little effect on the electronic properties of the polymers composed of Mn(III)-corrolazine rings and ethyne bridges. These results suggest that the reaction process between Mn-corrolazine polymers and O₂ did not change with the increase in the number of Mn(III)-corrolazine rings.

Fig. 4. The optimized structures of quintet-, triplet- and singlet-state complexes of Mn(III)-corrolazine and ³[O₂] and the energy difference between corresponding two complexes with different spin multiplicities.

3.3. Structural, electronic properties, and stability of the 2D Mn-corrolazine catalyst

As discussed above, Mn-corrolazine polymers become more stable with increasing β -to- β -ethyne-linked Mn-corrolazine rings. These polymers have a highly ordered pore structure, which allows us to further extend the polymers explanation to two-dimensional (2D) nanomaterials. We use ethyne to link the units of di-Mn_{cor} by β -to- β along its x - and y -axial directions (as shown in Fig. 5(a)). The optimized stable structure and selected bond lengths of 2D-Mn_{cor} are presented in Fig. 5(a) and Table 1. As seen in Fig. 5(a) and Table 1, the optimized structure of 2D-Mn_{cor} is planar, and the bond lengths of Mn-N (1.885–1.905 Å) and -C≡C- (1.231 Å) in 2D-Mn_{cor} are quite similar to those of di-Mn_{cor}, suggesting that the 2D-Mn_{cor} maintains the structural properties of the Mn-corrolazine polymers. Moreover, the electronic spin densities of the 2D-Mn_{cor} (Fig. S2) are mainly distributed on the individual Mn atoms, in which the calculated magnetic moments of two individual Mn atoms in the unit cell of 2D-Mn_{cor} are 3.65 and -3.65 μ_B (Table 1). This indicates that Mn atoms in the 2D nanomaterial still remain in the active center for the reaction as in the monomer.

Similar to the di-Mn_{cor} and tetra-Mn_{cor} complexes, there are also many pores of 12-membered C₁₂, 16-membered C₁₆, and

Fig. 5. (a) Optimized geometry and (b) the electronic band structure of 2D-Mn_{cor} nanomaterial

14-membered $C_{12}N_2$ in the 2D- Mn_{cor} nanomaterial, with sizes of *ca.* 5.65×4.13 , 6.57×5.42 , and $5.28 \times 4.11 \text{ \AA}^2$, respectively. These pores with different sizes allow the corresponding molecules to cross the plane of this novel 2D- Mn_{cor} nanomaterial, which may facilitate the reaction of molecules on its surface. In addition, the 2D- Mn_{cor} nanomaterial is actually a semiconductor with a precise band gap of 0.14 eV predicted by HSE06 in Fig. 5(b) and by pure PBE in Fig. S3, in which each Mn center retains its independent single-atom catalytic activity during the reaction. Thus, the 2D- Mn_{cor} nanomaterial is likely to be an excellent platform for catalytic reactions.

3.4. Activation of the C-H bond on the 2D Mn-corrolazine catalyst

Fig. S4 shows that once O_2 is adsorbed on the 2D- Mn_{cor} , stable spin-polarized 2D-O- Mn_{cor} is formed. The 2D- Mn_{cor} moiety in the optimized 2D-O- Mn_{cor} remains approximately planar, except for the slightly upward out-of-plane distortion of Mn atoms due to their interactions with the adsorbed O_2 . As shown in Table 2, the calculated magnetic moments of the two Mn atoms in 2D-O- Mn_{cor} are 3.58 and $-3.58 \mu_B$, respectively, and the electronic spin densities of 2D-O- Mn_{cor} (Fig. S2) are mainly distributed on the Mn atoms and adsorbed O_2 .

Similar to di-O- Mn_{cor} , 2D-O- Mn_{cor} also has a high-energy spin-unpolarized state in which the O_2 molecule can form the radical-like [Mn]-O-O with the central Mn atom of 2D- Mn_{cor} , as shown in Fig. S4. The O-O bond length increases from 1.205 Å in the free oxygen molecule to 1.267 Å in its adsorbed state, indicating that the O_2 molecule is significantly activated and the Mn atoms in the 2D nanomaterial can act as catalytic centers for the activation of O_2 . Moreover, as shown in Table 2, the energy of the spin-unpolarized state is higher than that of the spin-polarized state by 37.27 kcal/mol per [Mn]-O-O unit, which is again in the visible-light range (accessible with visible light irradiation). This suggests that the Mn-corrolazine catalyst is photo-triggered under mild conditions.

Here, we investigated the catalytic performance of the [Mn]-O-O moiety of 2D-O- Mn_{cor} in the spin-unpolarized state towards the activation of C-H bonds [65–67], which is one of the most important topics in catalysis. We first explored the selective conversion of cyclohexane into cyclohexanol, in which

one C-H bond is converted by oxidation. Similar to the Mn-corrolazine monomer, the [Mn]-O-O moiety of 2D-O- Mn_{cor} selectively converts cyclohexane to cyclohexanol through H-abstraction and rebound reaction processes [25,68]. Fig. 6 presents the relative energy profiles for the reaction steps (3) and (4), along with the optimized structures of reactant (R), transition state (TS), and product (P). Since the rebound step from the newly generated radical is very fast, it will merge into the H-abstraction process, and the selective oxidation of cyclohexane to cyclohexanol is similar to the oxygen insertion reaction. As shown in Fig. 6, the selective oxidation process is remarkably exothermic by 63.5 kcal/mol with an activation energy of 26.72 kcal/mol, which indicates that the [Mn]-O-O moiety of the 2D-O- Mn_{cor} nanomaterial maintained a high catalytic activity, similar to its monomer.

Considering the high activity of the [Mn]-O-O moiety of the 2D-O- Mn_{cor} nanomaterial, we further investigated its catalytic performance in the direct conversion of methane into methanol [69–71]. The reaction pathway for the activation and oxidation of CH_4 by the 2D-O- Mn_{cor} nanomaterial through the H-abstraction and rebound steps (5) and (6) is proposed; the predicted relative energies and the optimized structures of reactant (R), transition state (TS), and product (P) are shown in Fig. 7. In the first step of CH_4 activation from the initial structure (Fig. 7), the H abstraction from CH_4 by the terminal O of the radical-like [Mn]-O-O species leads to the [Mn]-O-OH intermediate (Int) and the $CH_3 \cdot$ free radical, with an activation energy of 34.96 kcal/mol. The distance between the terminal O and the abstracted H varies from 2.643 to 1.198 Å, and the O-O bond length of the adsorbed O_2 increases from 1.271 to 1.674 Å at the same time, resulting in the formation of OH between the free radical $CH_3 \cdot$ and [Mn(V)]-O. Thereafter, the rebound reaction [25,68] immediately occurs in the second step, which is essential in the formation of methanol; the OH species rapidly rebounds to $CH_3 \cdot$, which produces the Mn(V)-oxo corrolazine nanomaterial and CH_3OH . Because of the high reaction rate of OH rebounding to the substrate radical $CH_3 \cdot$, the $CH_3 \cdot$ radical has insufficient time to leave the Mn-O-OH moiety, selectivity leading to a highly specific and stable methanol product. Similarly, the facile rebound step initiates the H-abstraction process, as for the selective oxidation of cyclohexane. Moreover,

Fig. 6. The predicted reaction pathway for the generation of cyclohexanol and the Mn(V)-oxo unit catalyzed by the 2D-O- Mn_{cor} nanomaterial in the spin-unpolarized state (relative energies and selected bond lengths are in kcal/mol and Å, respectively).

Fig. 7. Proposed reaction pathway for CH_4 activation on the 2D-O- Mn_{cor} nanomaterial in the spin-unpolarized state (relative energies and selected bond lengths are in kcal/mol and Å, respectively).

Fig. 8. Predicted barriers for the conversion of CH₄ to CH₃OH under various external electric fields.

the energy released in the OH formation and rebound reaction is as high as 57.55 kcal/mol with respect to the initial reactants, which provides the driving force for the overall reaction to the selective formation of methanol. Additionally, the rationality of the catalytic oxidation of alkanes to alcohol through the singlet potential energy surface and the possibility that the left oxygen atom on the catalyst further oxidizes the alkane to the alcohol is discussed in the supporting information, as shown in Figs. S5, S6, and S7.

Overall, the Mn-corrolazine 2D nanomaterial can maintain the catalytic activity of the Mn-corrolazine molecular unit, where each Mn atom of the Mn-corrolazine rings can act as the SAC center to efficiently catalyze the direct conversion of highly stable methane to methanol by O₂, which may possibly expand the applications of Mn-corrolazine-based catalysts in the industry.

3.5. Effect of external electric field on the catalytic activity of 2D Mn-corrolazine

In comparison with the conversion of cyclohexane into cyclohexanol catalyzed by the Mn-corrolazine 2D nanomaterial, the activation energy for the catalytic conversion of methane into methanol has a higher activation energy of 34.96 kcal/mol. To reduce the activation energy, the effect of an external electric field on the reaction was investigated.

External electric fields [72,73] have a great potential to regulate the reaction activity of various molecules, few-layer graphene (FLG), and ferromagnetism in thin-film semiconducting alloys. However, they need to achieve the difficult task of orienting the reactants and the external electric field along the reaction axis. The electronic reorganization from reactants to products results in enhancing the stability of ionic structures to facilitate catalytic reactions. For the 2D-Mn_{cor} nanomaterial with high stability, its intrinsic reaction axis is always found to be along the Mn-O-O bond. Thus, it was quite easy to orient the reactants and the electric field along the reaction axis simultaneously, by aligning the external electric field with the Mn-O-O

bond. Based on the optimized structures of *R* and *TS* in Fig. 7, the external electric field effects on the *R* and *TS* energies were investigated theoretically. Fig. S8 shows that for $F_z > 0$, the energy changes for *R* and *TS* are similar, while for $F_z < 0$, the energy of *TS* decreases more rapidly than that of *R*. Such discrepancies might be used for activity regulation with the aid of an external electric field. Accordingly, the electric field is oriented to the *z*-axis which is the reaction axis Mn-O-O, as shown in Fig. 8. For $F_z > 0$, the reaction barrier increases slightly, while for $F_z < 0$, the reaction barrier decreases from 34.96 to 14.23 kcal/mol when F_z changes from 0 to -1.0 V/Å. Clearly, the oriented external electric field, along with its intrinsic reaction in the axis perpendicular to the material plane, can significantly decrease the activation energy and enhance the catalytic conversion of CH₄.

4. Conclusions

In summary, we designed and systematically studied the Mn-corrolazine-based polymer and its 2D monolayer material for the catalytic conversion of alkanes to alcohols using *ab initio* calculations. The results show that the stability of these polymers increases with the integration of the Mn-corrolazine rings from di-Mn_{cor} to tetra-Mn_{cor}. Based on the Mn-corrolazine and -C≡C- building blocks, a 2D nanocatalytic material, 2D-Mn_{cor}, was constructed. Moreover, in these polymers and 2D-Mn_{cor}, there is a central Mn atom in each corrolazine ring, and the individual Mn atom maintains its electronic configuration with four single electrons, which can act as an excellent catalytic center. There are numerous pores with different sizes in 2D-Mn_{cor} to allow suitable molecules to pass through the 2D framework. Thus, 2D-Mn_{cor} can be an excellent reaction platform where each central Mn atom acts as a SAC center and activate O₂ to form the radical-like [Mn]-O-O intermediate. The [Mn]-O-O free radical can activate the C-H bond, which catalyzes the direct conversion of cyclohexane to cyclohexanol or methane to methanol through the H-abstraction of CH₄, followed by the rebound reaction. This selective oxidation of CH₄ can be easily regulated by the external electric field along its intrinsic Mn-O-O reaction axis. The present study opens an alternative to heterogenize homogeneous catalysts and to improve their catalytic performance.

Electronic supporting information

Supporting information is available in the online version of this article.

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Graphical Abstract

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Mn-corrolazine-based 2D-nanocatalytic material with single Mn atoms for catalytic oxidation of alkane to alcohol

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Novel two-dimensional (2D) Mn-corrolazine nanocatalytic materials bearing Mn atoms as single-atom catalyst centers can efficiently and selectively oxidize C–H to C–OH bonds through the regulation of an external electric field.

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基于氮杂Mn卟咯二维纳米材料的单原子Mn中心催化氧化烷烃制醇

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摘要: 卟咯是由四个吡咯共轭相连而形成的具有芳香性的新型卟啉类大环化合物, 但卟咯分子中存在一个直接连接两个吡咯环的C–C键, 与卟啉相比, 仅仅是少了一个“meso”位置的C原子。因此, 在结构上, 卟咯含有三个“吡咯型”氮原子和一个“吡啶型”氮原子, 当卟咯失去三个内氢原子后变成了三价阴离子, 易与金属形成高价态的稳定配合物。氮杂卟咯是一种卟咯的meso位上的C被取代为N的卟咯衍生物。与正常的卟咯相比, 它更易于与过渡金属形成稳定配合物。正是由于这些独特的结构特点, 使其在金属催化、染料敏化太阳能电池、光敏剂、金属传感器、甚至在医学上都有很好的应用前景。

金属有机大环均相催化剂的非均相化, 是改进反应产物分离和实现催化剂循环使用的最简单有效方法之一。环境友好的Mn氮杂卟咯催化剂, 在温和条件下可以利用氧气直接将有机底物氧化。本文选用Mn氮杂卟咯催化剂作为基本构建单元, 通过理论计算, 构建了一种新型的具有高催化活性的含Mn氮杂卟咯环结构单元的二维纳米催化材料。我们分别使用高斯软件(Gaussian 09)和维也纳从头算模拟软件包(VASP)对孤立分子和周期性体系进行结构优化以及性质的计算。在这种

二维材料中, 每一个Mn原子作为相对独立的金属单原子中心(SAC), 保留了单环中Mn金属中心的高催化活性. 在温和的光照条件下, Mn金属中心可以直接活化氧气生成类自由基[Mn]-O-O中心, 随后[Mn]-O-O中心可以有效地通过夺取有机底物中的H和紧接着新生自由基的偶合反应, 选择性氧化C-H键为C-OH键. 另外, 通过沿[Mn]-O-O反应轴施加不同强度的外电场, 可对此二维纳米材料的催化反应活性进行精细调控. 本文为实验上制备基于Mn氮杂咕咯的非均相催化剂以及单原子Mn基催化剂提供了理论依据.

关键词: 单原子催化剂; 非均相化; 二维纳米材料; 第一性原理计算; C-H键的活化

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