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Enhancing direct hydroxylation of benzene to phenol on Fe₁/PMA single-atom catalyst: a comparative study of H₂O₂ vs. O₂-assisted reactions†

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In this study, systematic first-principles calculations were carried out to ascertain the optimal single-atom catalyst (SAC) among the 3d-transition metals (TM₁ = Fe₁, Co₁, Ni₁, Cu₁, and Zn₁) anchored on a phosphomolybdic acid (PMA) cluster for efficient benzene oxidation to phenol, which is otherwise challenging at ambient temperature. Strong binding due to substantial charge transfer between Fe₁ and PMA, and the adsorption energies of H₂O₂ and O₂ oxidants enabled significant bonding within the Fe₁/PMA cluster, facilitating enhanced catalytic performance compared to that of 3d-TM₁ (Co₁, Ni₁, Cu₁, and Zn₁). The Fe₁/PMA cluster demonstrated enhanced reactivity towards H₂O₂ supported by lower activation barriers and rate-determining steps for H₂O₂ (0.84 and 0.67 eV) compared to O₂ (1.02 and 0.66 eV). The spontaneous dissociation of H₂O₂ on Fe₁/PMA, in contrast to O₂, is a crucial step to initiate iron-oxo (Fe₁-O) active site formation, easing benzene to phenol oxidation at ambient temperature. Thus, the proficient coordination environment of Fe₁ atoms as SACs adsorbed on the PMA cluster is found to influence catalytic performance, especially in the case of H₂O₂. The proposed mechanism is reminiscent of hydrocarbon hydroxylation in enzymatic processes, establishing Fe₁/PMA as an environmentally friendly, heterogeneous and non-noble metal green catalyst for electrocatalytic phenol production.

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1. Introduction

The selective transformation of hydrocarbons, such as xylene, toluene, benzene, *etc.*, into valuable compounds like phenol by the oxidation of benzene under normal working conditions is

one of the most widely researched fundamental topics in applied catalysis.^{1–3} However, high-energy benzene activation significantly reduces the production yield of phenol, increasing the conversion cost and making it challenging from the research viewpoint.^{4,5} Currently, phenol is produced by the direct H₂O₂-based oxidation of benzene as described by the three-step cumene process developed in the 1950s.⁶ Despite the considerable success of the cumene process, being energy deficient, producing a large number of by-products and pollutants, and especially low selectivity for phenol are obvious concerns regarding the efficiency of the process.⁷ To overcome the drawbacks of benzene to phenol indirect conversion, direct hydroxylation is considered a potential, economical, and environment-friendly route.^{7,8} The direct hydroxylation of benzene is carried out using different catalysts, such as mesoporous molecular sieves attached with titanium, Fe-zeolites, vanadium-substituted phosphomolybdate, palladium membranes, *etc.* by one-step phenol production.^{1,8–10} The direct hydroxylation of benzene has also been extensively studied using transition metals such as Fe, Cu, and V,^{11,12} while the Fenton reagent (Fe²⁺-H₂O₂)¹³ has been most widely used as a catalyst in processes involving benzene conversion to phenol.

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Besides, several studies have reported Fe-g-C₃N₄ and TiO₂ as being active catalysts for the benzene oxidation reaction occurring under visible or ultraviolet light.^{14,15} During the last two decades, the direct hydroxylation of benzene has been of key research interest and extensively studied for phenol production,^{16,17} which is attributed to the independence of the market price of acetone for phenol production *via* a one-step process.^{6,18,19}

Numerous researchers have adopted direct hydroxylation of benzene to phenol using different green oxidants such as molecular oxygen (O₂),^{20–22} hydrogen peroxide (H₂O₂),^{8,23,24} a mixture of oxygen (O) and hydrogen (H),^{1,25,26} and nitrous oxide (N₂O),^{27–30} *via* three main pathways. High-temperature requirements led to the over-oxidation of benzene, decreasing the phenol selectivity and the process yield.^{30,31} Among different green oxidants, N₂O has been adopted as a commercial catalytic oxidant, and it can be retrieved as a cheap by-product at the end of the process.³² In contrast to the other catalysts, the generation of water as a by-product is a clear advantage of H₂O₂ over the rest, therefore utilizing a H₂O₂ oxidant under a titanium-containing zeolite-catalyst for the direct hydroxylation of benzene to phenol offers outstanding catalytic efficiency even without provisional reaction conditions.⁹ Meanwhile, developing low-cost and green heterogeneous catalysts to produce phenol *via* one-step hydroxylation of benzene under normal working conditions is highly imperative from the industrial viewpoint.

Single-atom catalysis (SAC) is a new branch of heterogeneous catalysis in which transition metal active centers are dispersed over the surface of selective metal oxide or conducting surfaces to better utilize atoms to improve selectivity and enhance the reaction kinetics.^{33,34} Despite the atomic scale dispersion, post-use separation of catalysts is not required during industrial chemical reactions. One of the greatest advantages of the SAC is an extensive increase in catalytic efficiency and selectivity, where a catalyst present as a single atom significantly reduces the demand for costly metals and requires minimal quantity.³⁵ Significant downsizing of a catalyst from nanoparticle catalysts, nanoclusters, and dots to SAC substantially changes the bonds and coordination environments of electronic shell configurations that exclusively changes the chemical phenomena and result in an efficient catalytic response. However, the SAC structure strongly depends on the processing pressure and temperature, while the catalytic activity quenches with the formation of nanoparticles on the support. The accumulation of metal atoms occurs due to the high surface energy of the metal atoms, which results in the formation of giant clusters of metal oxide. Therefore, developing an appropriate, microscopically smooth, and efficiently active support surface is a prerequisite to understanding the true nature of SACs, especially while working under ambient conditions.^{35,36} In this regard, several computational and experimental research studies have reported stable metal oxide supports that effectively supported SACs.^{34,37,38} Whereas the broad spectrum of SAC applications such as electro-catalysis, photo-electrocatalysis, photo-catalysis, and

thermo-catalysis is evidence of the exceptional catalytic potential based on the specific electronic structure, especially for the case of C–H bond activation.^{39,40} Similarly, non-noble metal SACs are also good at benzene hydroxylation with H₂O₂, but their efficiency is very low and needs improvement.^{11–13,41} Besides, the complex composition of catalysts results in a poor understanding of their catalytic active sites and structure–activity relationship that ultimately leads to relatively low efficiencies of the catalytic reactions.

Recently, heteropolyacid oxo-anions known as polyoxometalate (POM) clusters based on their excellent catalytic characteristics and well-defined structures are being considered the most promising and highly stable metal oxide supports for SACs, and they provide coordination sites for single atom anchoring and protect leaching of active metal centers.^{42,43} Recently, researchers have highlighted the promising potential of POM-based materials and their derivatives for their application in electrocatalysis and energy storage.⁴⁴ The study is based on systematic experiments, conducted at elevated temperatures (150–400 °C), in which surface oxygen species derived from the polyoxometalate (POM) component act as the oxidizing agent for the conversion of CO to CO₂.⁴⁵ Another study explored a novel strategy for SAC creation. By employing POM cluster traps, researchers were able to disperse cobalt atoms and create highly active and stable SACs for the oxygen reduction reaction (ORR).⁴⁶ One of the distinctive features of the POM family members like H₃PMo₁₂O₄₀ and PMA is their keggin-type structure which is considered very effective in stabilizing single Pt atoms.⁴⁷ That is the reason why the POMs studied as heterogeneous catalysts offer a perfect platform to investigate the structure–activity relationship in SACs.^{48,49}

Iron-based (Fe) surfaces in catalysis have remarkably changed the world. The Haber–Bosch process is an important example in which Fe-based catalysts usually convert molecular nitrogen into ammonia which is the building block for food production with an ever-growing global population.⁵⁰ The formal oxidation states of Fe range from –II to +VI and present a wide window of redox reactions. Lewis acidity varies from moderate to high and its cations can bind with N- and O-species N-based heterocycles. Iron-based catalysts played a critical role in direct benzene oxidation to phenol on Fe-based surfaces.⁵¹ Earlier copper-based complexes were used for direct oxidation but yield was quite low.⁵² Moreover, supports are also critical in heterogeneous systems. ZSM-5 and other porous supports were used for Fe-based catalysts to perform direct oxidation of benzene to phenol.⁵³ The present study proposed a new path of using a PMA cluster as a support to avoid leaching and access abundant sites for SAC.

Based on the proposed features of the heterogeneous SAC in preceding studies, current work focuses on the extensive density functional theory (DFT) calculations of benzene oxidation to phenol using Fe₁ atoms anchored on the PMA cluster support under ambient working conditions. In addition to the electronic structure, geometry stability, and Fe₁/PMA catalytic activity calculations, the H₂O₂ and O₂ oxidant absorption is also studied. Eventually, the present study aims to investigate



the SAC mechanism dominating the benzene oxidation to phenol by H₂O₂ and O₂ as active oxidants under ambient conditions.

2. Computational details

In this study, the energy calculations and geometrical optimizations are conducted using the Vienna *ab initio* simulation package (VASP)^{54,55} through spin-polarized DFT with the GGA-PBE exchange–correlation functional.^{56,57} To explain the interactions between the ionic core and valence electrons, the projector augmented wave (PAW) method was utilized.⁵⁸ The valence electrons designated to the corresponding atoms are 3d-TMs-Fe₁, Co₁, Ni₁, Cu₁, Zn₁ (3d^x 4s^x), Mo (4d⁵ 5s¹), O (2s² 2p⁴), P (3s² 3p³), and H (1s¹). The kinetic energy cutoff was set to be 400 eV for a plane-wave basis set expansion of the electron eigenfunction. An appropriate 20 Å vacuum space was preset to avoid the interactivity among different periodic systems under study. A widely used empirical dispersion correction method, the Grimme DFT-D3 method, was used to investigate the long-range van der Waals interactions. The accuracy of the Brillouin zone integration for the PMA was enhanced by using a 1 × 1 × 1 *k* sampling point during the geometry optimization of the PMA itself, the binding of a specific TM₁, and the adsorption of H₂O₂ and O₂ oxidants on the PMA cluster for benzene oxidation to phenol, as shown in Fig. 1 (for more details, see Table S1 in the ESI†).^{33,42} Moreover, convergence for the total energy was achieved at 10^{−5} eV, and the maximum allowed relaxation force was set to less than 0.03 eV Å^{−1}. The matrix-based Bader analysis was used for the computation of electron charge exchange.⁵⁹ The binding energy of the TM₁ atom on the PMA is given as follows:

$$E_{\text{bin(TM1)}} = E_{\text{tot(TM1-PMA)}} - E_{\text{(PMA)}} - E_{\text{(TM1)}} \quad (1)$$

where $E_{\text{bin(TM1)}}$ is the total energy, and $E_{\text{tot(TM1-PMA)}}$, $E_{\text{(PMA)}}$ and $E_{\text{(TM1)}}$ denote the total energies of the complex, free PMA, and support TM₁ atoms, respectively.

The adsorption energy is defined as follows:

$$\Delta E_{\text{ads}} = E_{\text{(adsorbate+catalyst)}} - E_{\text{(adsorbate)}} - E_{\text{(catalyst)}} \quad (2)$$

where $E_{\text{(adsorbate+catalyst)}}$, $E_{\text{(adsorbate)}}$, and $E_{\text{(catalyst)}}$ are the electronic energies corresponding to the species adsorbed on the

catalyst, metal atom/non-adsorbed molecules, and the pure catalyst, respectively. The climbing image-nudged elastic band (CI-NEB)⁶⁰ and dimer methods⁶¹ were used for the determination of energy barriers and reaction pathways. The transition state (TS) was signified by the most elevated image towards the least energy barrier, while the energy barrier was taken from the difference between the initial and transition state energies. Besides, one imaginary frequency was retained for the confirmation of the transition state geometry. Moreover, the rest of the program settings were used as default, while positive and negative values of energies represent the endothermic and exothermic reactions, respectively. In the context of SAC, the electron localization function (ELF) can offer valuable information about the electronic structure and bonding properties, which are crucial for understanding catalytic activity. It provides information about the probability of finding an electron in a specific region of space.⁶² In this study, we leverage ELF to differentiate between the charge transfer reactivity and the electron delocalization occurring between the metal/support and the adsorbed molecule (benzene).

3. Results and discussion

3.1. Exploring coordination environments in PMA for SACs

Phosphomolybdic acid (PMA) establishes a kegggin-type structure where the corners of 12 MO₆ octahedrons are connected to the PO₄ tetrahedron pinned at the center. The cubic unit cell at the epicenter of the classical kegggin comprises 12 Mo atoms, 40 O atoms, and 1 P atom. The oxygen atoms present on the surface of the PMA cluster offer different coordination sites, such as the terminal (O_t), bridging (O_{bri}), and at the sides of the Keggin structure (O_c). Therefore, the PMA cluster can provide single to multifold binding sites for metal atoms such as the single corner, O_c-O_{br}-bridge, three-fold hollow (3-H_{O_c} and 3-H_{O_{br}}), and four-fold hollow (4-H) sites. The optimized structure of PMA is shown in Fig. 1, and the possible coordination sites are presented in Fig. S1 of the ESI†. The optimized key geometry parameters are presented in Table S2 (ESI†).

3.2. Screening binding energies of 3d-TMs on PMA

A series of 3d-TMs in the periodic table (3d-TMs = Fe₁, Co₁, Ni₁, Cu₁, and Zn₁) were investigated for an ideal catalytic system for benzene oxidation to phenol. As shown in Fig. S2 (ESI†), all the considered 3d-TM atoms are expected to anchor at the 4H sites on the PMA cluster, which is consistent with previous theoretical calculations.^{33,63} The effectiveness of heterogeneous catalysis relies heavily on the interaction between the adsorbed metal and its supporting material, determining the catalytic activity and stability of the catalytic system. Our study aimed to evaluate the catalytic potential of 3d-TM₁, including Fe₁, Co₁, Ni₁, Cu₁, and Zn₁, by analyzing their interactions with a PMA cluster. The computational results revealed negative binding and formation energies for the interactions between 3d-TM₁ adatoms and the PMA cluster. These negative values generally decrease as the atomic size of the adatoms increases, as

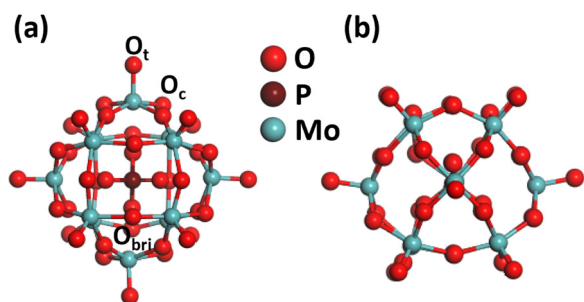


Fig. 1 Optimized structure of PMA: (a) top view; (b) side view. Color code: O_t/O_b, red; Mo, dark cyan; and P, pink.



presented in Table S3 (ESI[†]). Notably, Fe₁ exhibited the highest binding energy at -10.47 eV, while Zn₁ displayed the lowest binding energy at -5.46 eV. The substantial binding and formation energies of Fe₁ develop a robust bond with the PMA cluster, making it more stable compared to the other 3d-TMs (Co₁, Ni₁, Cu₁, and Zn₁).

Besides, Bader charge analysis was conducted for gaining deeper insights into the strong binding between the 3d-TMs and the PMA cluster. The results, outlined in Table S3 (ESI[†]), consistently showed that as the atomic size of the 3d-TMs increased, there was a decrease in the electron transfer from these metals to the PMA cluster. A strong correlation between binding energies and charge transfer was observed for transition metals adsorbed on the PMA cluster. This correlation suggests that a higher degree of charge transfer from the transition metal atoms corresponds to stronger binding energies of these atoms. In this context, the substantial charge transfer between Fe₁ and the PMA cluster played a pivotal role in establishing a strong binding energy observed, especially when compared to other 3d-TM₁ (Co₁, Ni₁, Cu₁, and Zn₁). This strong metal-cluster binding interaction, driven by significant charge transfer, suggests that the Fe₁/PMA catalyst may exhibit exceptional catalytic activity and stability in this specific reaction.

3.3. Screening 3d-TM₁/PMA clusters *via* adsorption of H₂O₂ and O₂ oxidants for unveiling active phenol catalysis

In the context of heterogeneous catalysis, the adsorption of reactant molecules plays a pivotal role. Therefore, before delving into the detailed mechanism of benzene oxidation to phenol, we initiated an individual investigation into the adsorption of H₂O₂ and O₂ molecules, which serve as oxidants, on Fe₁, Co₁, Ni₁, Cu₁, and Zn₁/PMA clusters under ambient reaction conditions. The optimized structures of H₂O₂ on the 3d-TM₁/PMA clusters are visually represented in Fig. S3 (ESI[†]), and the corresponding adsorption energies are provided in Table S4 (ESI[†]). From the outcomes of these calculations, it is

evident that H₂O₂ exhibits relatively weak adsorption on Zn₁/PMA, with an adsorption energy of merely -0.33 eV. In contrast, the most substantial interaction is observed with Fe₁/PMA, where the adsorption energy amounts to -0.53 eV.

Regarding O₂ adsorption on the 3d-TM₁/PMA surfaces, different binding configurations are observed as shown in Fig. S4 (ESI[†]). O₂ molecules tend to align in a parallel fashion over the Fe₁ and Co₁ atoms, with both oxygen atoms of O₂ forming connections with the metal atom (referred to as the side-on coordination). Conversely, for Ni₁, Cu₁, and Zn₁, only one oxygen atom establishes a connection with the metal atom (termed the end-on coordination). The most robust interaction is likewise witnessed with Fe₁/PMA, where the adsorption energy is measured at -0.41 eV, while Cu₁/PMA exhibits the least favorable adsorption energy at -0.04 eV. The results indicate that among the 3d-TM₁/PMA clusters, Fe₁/PMA demonstrates the highest adsorption energies for both H₂O₂ and O₂. Based on the computational results, Fe₁/PMA is a highly active and stable catalyst for benzene oxidation to phenol due to its strong binding interactions with both the PMA cluster and the oxidant molecules, as detailed in Table S4 (ESI[†]).

3.4. Electronic properties of Fe₁/PMA

According to the optimized geometry structure of the Fe₁/PMA cluster shown in Fig. 2(a) and (b), the Fe₁ atoms are allocated at the most stable 4-Hollow (4-H) sites of the PMA cluster, which is more favorable (Table S5 of the ESI[†]), where Fe₁ develops Fe₁-O bonding (1.84 and 1.81 Å) with the four adjacent oxygen atoms. The calculated binding energy (-10.47 eV) testifies the strong interaction between the Fe₁ atom and PMA which makes it a compelling candidate for achieving a chemically stable SAC. Based on the Bader charge analysis, there exists a charge difference between neighboring oxygen atoms ($-1.16|e|$) and Fe₁ atoms ($1.66|e|$) due to which the electron density tends to transfer from Fe₁ to PMA and the surface acts as an electron-withdrawing support, consequently, the Fe₁ single atom stabilizes and the binding energy between the Fe₁ atom and the

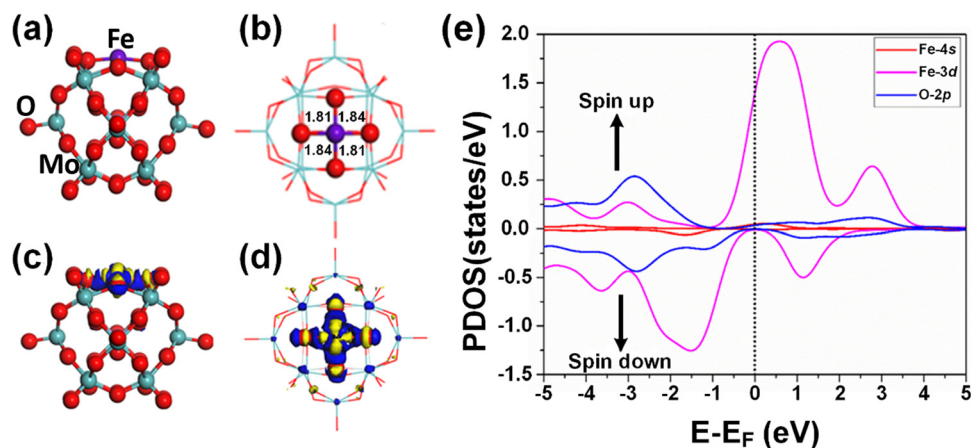


Fig. 2 Optimized geometry of Fe₁ embedded on the PMA cluster, side view (a) top view (b), charge density difference (CDD); (c) and (d) the counter value of the CDD is ± 0.05 a.u., where charge accumulation is rendered in blue and charge depletion is shown yellow in the contour plots; and (e) the spin-polarized density of states on Fe₁-3d (purple), Fe₁-4s (red), and O-2p (blue) orbitals. The Fermi level (E_F) is set to be zero.



support surface increases. Because of having a more positive charge, the Fe₁ atom not only stabilizes the adsorption of gases, which is important for a catalytic reduction but also provokes the catalytic reaction of benzene oxidation due to being in a higher oxidation state. Moreover, the charge density differences of the Fe₁/PMA cluster were also calculated to gain insights into the nature of chemical bonding between the Fe₁ atom and PMA cluster, and the results are shown in Fig. 2(c) and (d). As seen from Fig. 2(c) and (d), a significant charge density accumulates around Fe₁ and neighboring O atoms because of the Fe₁/PMA cluster assimilation, significantly reorganizing electrons. The magnetic moment of Fe₁ atoms (2.90μ_B) and oxygen atoms (−0.07μ_B) also suggests strong spin density on the Fe₁ atoms compared to O atoms. That is why the H₂O and O₂ molecules can easily activate and coordinate with free electrons on the Fe₁ atoms. Spin-polarized partial density of states (PDOS) results shown in Fig. 2(e) further confirm the preceding arguments, where the overlapping among the peaks of Fe₁ and O atoms is quite significant. The strong coupling of Fe₁ atom orbitals (3d and 4s) with O atom orbitals (2p) near the Fermi level (*E*_F) is clear evidence of the covalent metal-support interactions (CMSI) at the 4-H sites of PMA. Similar results for SAC have been reported by Qiao *et al.*⁶⁴ Despite the asymmetric spin-up and spin-down PDOS of the Fe 3d orbital, its presence near the *E*_F is evidence of the high reactivity which might be responsible for the activation of adsorbates during catalytic reactions.

3.5. Adsorption of H₂O₂ and O₂ on Fe₁/PMA

The adsorption of the reactants during heterogeneous catalysis is of key importance to proceed with the mechanism, therefore before going deep into the mechanism of benzene oxidation to phenol, at first, we individually investigate the adsorption of H₂O₂ and O₂ molecules as oxidants on the Fe₁/PMA support surface under ambient reaction conditions. The calculated value of adsorption energy *E*_{ads} = −0.53 eV of the H₂O₂ molecule on the Fe₁/PMA surface shows that the reaction is exothermic, which is important for the adsorption of the H₂O₂ molecule on the surface (Fig. 3a). The bond distance between Fe₁–O is

2.12 Å, whereas the O–O bond distance for the case of adsorbed H₂O₂ (1.47 Å) is larger than that for the free form of H₂O₂ (1.45 Å) by an amount of 0.02 Å. According to the Bader charge analysis, although the H₂O₂ molecule gained 0.79|*e*| charge from the Fe₁/PMA cluster the Fe₁ atoms remain positively charged (1.89|*e*|). The charge density difference represented in Fig. 3b shows that on the one side the charge density accumulates between the Fe₁ and O atoms, while on the other side, it decreases between the two oxygen atoms, as seen by the blue and yellow areas, respectively. A slight decrease in the magnetic moment of Fe₁/PMA from 2.90 to 2.78μ_B is observed after the H₂O₂ adsorption, which might be attributed to a large bond distance of 2.12 Å between the Fe₁ atom and the O atom from H₂O₂. In Fig. 3c, the PDOS calculations for the Fe₁/PMA surface adsorbed with H₂O₂ molecules, and Fe₁-4s/3d and O-2p orbitals further confirm the Fe₁-3d and O-2p orbital mixing. However, the orbital mixing is not very significant, which is again because of the large bond distance of 2.12 Å of Fe₁–O. Besides, the wide range overlap between the major peaks of Fe₁-3d and O-2p orbitals below the Fermi level shows significant interactions between Fe₁ and H₂O₂ molecules.

Besides, the O₂ molecules adsorbed with *E*_{ads} = −0.41 eV on the Fe₁/PMA cluster were found to be situated parallel to the Fe₁ atoms developing side-on coordination, as shown in Fig. 4a. The higher value of the O–O bond length (1.33 Å) is evidence of O₂ acting as superoxide (O₂[−]) on the Fe₁/MA cluster when compared with the free O₂ molecule bond length (1.23 Å). The O–O distance varies according to the reduction state, that is why the O–O distance for free di-oxygen is 1.21 Å, that for superoxide is 1.28 Å, and that for peroxide is 1.50 Å,⁶⁵ hence the O₂ molecule was accordingly adsorbed and activated as superoxide on the Fe₁/PMA cluster. The calculated interatomic distances for Fe₁–O are 1.84 and 1.81 Å, while 1.33 Å for O–O making it 0.12 Å longer than 1.21 Å for free O₂ molecules. The Bader charge analysis of O₂ absorbed on the Fe₁/PMA cluster shows that Fe₁ atoms gained a positive charge (+1.82|*e*|), while absorbed O₂ gained a negative charge (−0.2|*e*|) from the cluster and became activated for the proceeding reactions. Therefore,

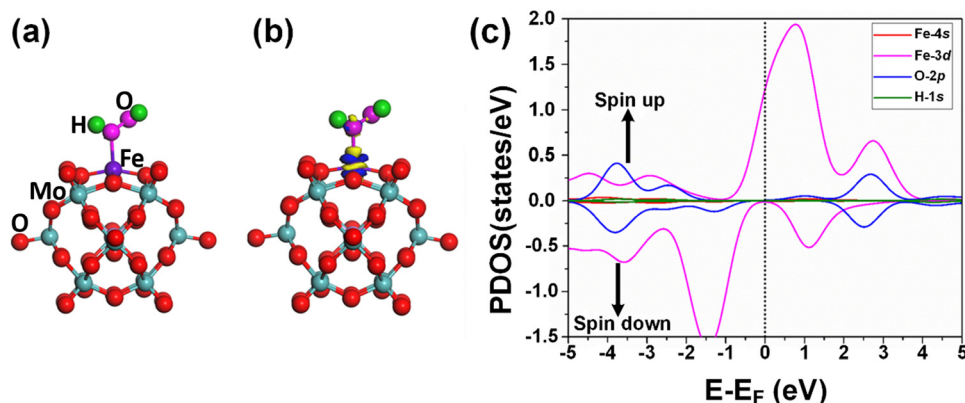


Fig. 3 (a) Top view of the optimized geometry of H₂O₂ embedded in the Fe₁/PMA cluster, CDD, for the contour plots, the electron accumulation regions are represented in blue while the electron depletion regions are shown in yellow; (b) the counter value of the CDD is ±0.05 a.u.; (c) the spin-polarized PDOS projected on Fe₁-3d (purple), Fe₁-4s (red), H-1s (green) and O-2p (blue) states. The *E*_F was set to be zero.



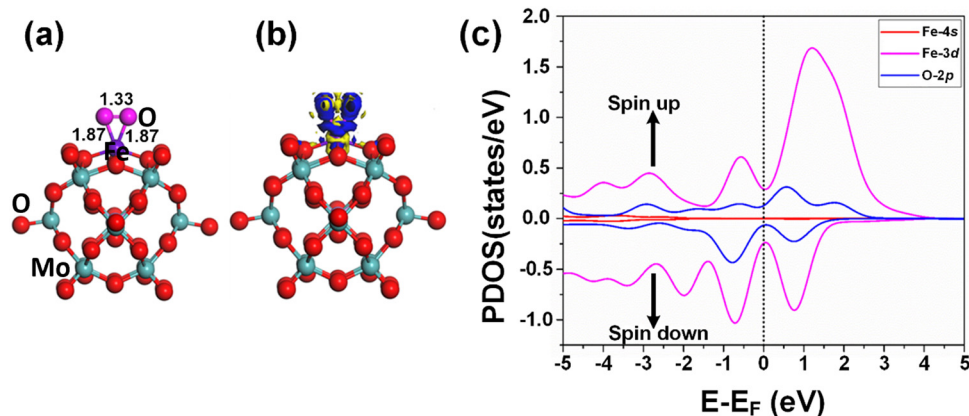


Fig. 4 (a) Top view of the optimized geometry of O_2 embedded in the Fe_1/PMA cluster; (b) CDD, for the contour plots, the electron accumulation regions are represented in blue while the electron depletion regions are shown in yellow, while the counter value of the CDD is ± 0.05 a.u.; and (c) the spin-polarized PDOS projected on $Fe_1/3d$ (red) $Fe_1/4s$ (red) and adsorbed O_2 2p (blue) states. The E_F was set to be zero.

the Fe_1 atoms act as charge donors while O_2 molecules as acceptors due to having positive and negative charges, respectively. The charge density difference results of O_2 on Fe_1/PMA , as shown in Fig. 4b, also validate the argument of charge transfer from the surface to the adsorbed O_2 . The excessive charge present on the O_2 molecule fills the $2p\pi^*$ antibonding orbital and accumulates between the O–O bond, thus the O–O bond length increases which also demonstrates the activation of the O_2 molecule by the Fe_1/PMA cluster.

After the adsorption of the O_2 molecule on Fe_1/PMA , although the magnetic moment of Fe_1/PMA decreased from 2.9 to $2.06\mu_B$, the majority of the magnetic moments were still located around the Fe_1 atom. The apparent decrease in the unpaired electrons might be attributed to the orbital mixing from Fe_1 (3d) and O (2p), as seen from the spin-polarized PDOS of $O_2/Fe_1/PMA$ in Fig. 4c. Near the Fermi level, the extreme closeness of the Fe_1 (3d) orbital with the O (2p) of the adsorbed O_2 molecule on the single Fe_1 atom is because of their relatively strong interaction that consequently influences the electron transfer from the Fe_1/PMA catalyst to the O_2 (2p) orbital. Due to the partial occupation of the O_2 (2p) antibonding orbital, on the one side the O–O bond gets undermined while on the other side, the bonding between O_2 and Fe_1/PMA strengthens. That is the reason why the O–O bond stretches because of the accumulation of charge and filling of the O_2 (2p) antibonding orbital.

Hence, despite the small difference in the adsorption energies of H_2O_2 (-0.53 eV) and O_2 (-0.41 eV), the adsorption of H_2O_2 is preferred when compared with the adsorption of the O_2 molecule on the Fe_1/PMA cluster. Therefore, it can be inferred that relatively strong adsorption between H_2O_2 and the Fe_1/PMA cluster is key to the efficient commencement of the benzene oxidation to phenol. Aiming for a better understanding, a further detailed reaction mechanism of benzene oxidation to phenol is investigated computationally *via* DFT to explore the efficiency of Fe_1/PMA SAC under ambient working conditions.

3.6. Oxidation of benzene to phenol on Fe_1/PMA using H_2O_2

The adsorption of the H_2O_2 oxidant on the active Fe_1 sites of the Fe_1/PMA cluster is shown in the potential energy profile in Fig. 5(a), where the activated H_2O_2 oxidant efficiently decomposes into a water molecule (H_2O) and active surface oxygen (O^*) by the Fe_1/PMA cluster under ambient conditions, as shown in TS1; the initial state (IS), intermediate state (IM), transition state (TS), and final state (FS) are shown in Fig. 5(b). Initially, the Fe_1 –O bond is formed due to the adsorption of the

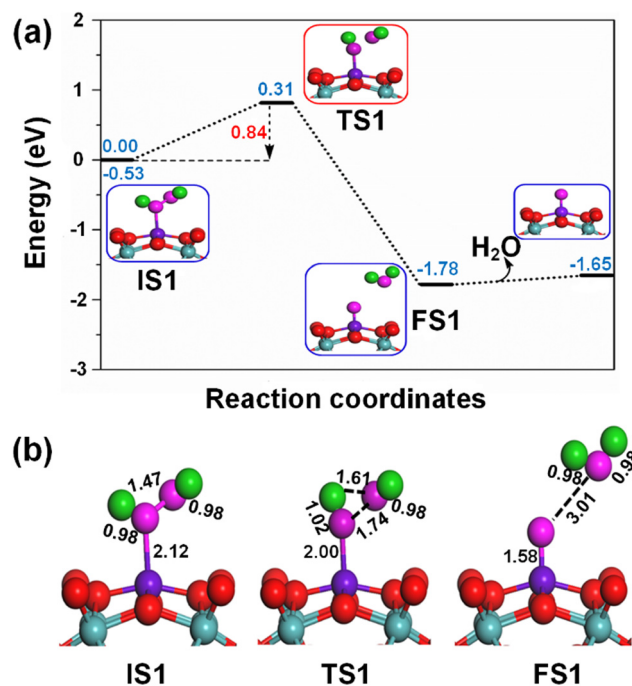


Fig. 5 (a) Potential energy profile of the efficient decomposition of H_2O_2 on Fe_1/PMA , all DFT energies are in eV; (b) the optimized geometries of IS, TS, and FS of the H_2O_2 decomposition on Fe_1/PMA , all the calculated bond lengths are given in Å.



H₂O₂ oxidant on an active Fe₁ site with a bond distance of 2.12 Å. In the meantime, the O–O bond is activated by expanding the bond length to 1.47 Å from 1.45 Å in the gas phase. Furthermore, an increase in the O–O bond length from 1.47 to 1.74 Å and a decrease in the O–H bond length from 1.92 to 1.61 Å show that the current variations in the bond lengths are associated with the dissociation of the H₂O₂ oxidant into H₂O and active O* species on the Fe₁/PMA cluster. The potential energy profile also shows that the first elementary reaction *i.e.*, the H₂O₂ decomposition into H₂O and O* *via* IS1 → FS1 (Fig. 5) having an energy barrier of 0.84 eV (TS1, imaginary frequency 470i cm⁻¹) is highly exothermic (−1.25 eV). Besides, the low adsorption energy (0.13 eV) of H₂O on OFe₁/PMA is evidence of the greater probability of forming an OFe₁/PMA catalyst. Accordingly, the H₂O molecule departs, leaving iron-oxo (Fe₁–O) species intact on the surface to form OFe₁/PMA, which further reacts as a catalyst for the oxidation of benzene. The potential energy profile including IS, IM, TS, and FS of the benzene oxidation through the OFe₁/PMA catalyst is shown in Fig. 6(a) and (b).

In our study, we also examined the performance of other investigated 3d-TM₁/PMA clusters (3d-TM₁ = Co₁, Ni₁, Cu₁, and Zn₁). Our findings revealed that the energy barriers for the initial step of the H₂O₂ decomposition reaction into H₂O and O* were notably higher for these cluster systems, specifically, 1.11 eV for Co₁, 1.21 eV for Ni₁, 2.25 eV for Cu₁, and 1.68 eV for Zn₁, when compared to the energy barriers for Fe₁/PMA (as detailed in Fig. S5, ESI†). These results strongly suggest that Fe₁/PMA is a more effective catalyst for facilitating the H₂O₂ decomposition reaction, primarily due to its significantly lower energy barrier, which can be advantageous in the direct conversion of benzene oxidation to phenol.

Fig. 6 shows the formation of a π type iron-oxo-benzene complex due to the adsorption of benzene by van der Waals interaction of C–H···O on the OFe₁/PMA cluster during the second elementary step (IS2). The adsorption energy of benzene is 0.35 eV which shows that the adsorption is of the physical type, while the C–H and O···H bond lengths in IS2 are 1.09 and 2.76 Å.

Notably, understanding chemisorption is critical for obtaining a comprehensive picture of the interaction between benzene and the metal atoms in our single-atom catalysts. To check the direct interaction (chemisorption) between benzene and the metal atoms, we also considered the adsorption energies of these systems. According to the results, the adsorption energies for the chemisorption of benzene on the studied single-atom catalysts varied significantly (See Fig. S6 and Table S6 in the ESI†). Further details regarding the chemisorption of benzene on all studied TM₁ are provided in the ESI†. And the results indicated that the adsorption energy of benzene on Fe₁/PMA is 0.35 eV for physisorption and −1.62 eV for chemisorption (Table S6 in the ESI†). Higher chemisorption energy makes it difficult for the next oxidation step to occur. The results suggest that physisorption facilitates benzene conversion to phenol on Fe₁/PMA. Subsequently, the detachment of the H atom from the benzene molecule occurs *via* a TS2 transition state reaction,

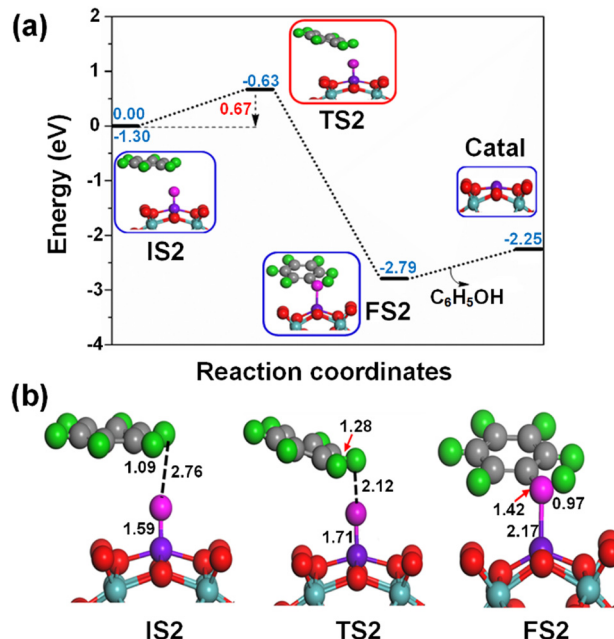


Fig. 6 (a) Potential energy profile of the efficient decomposition of direct oxidation of benzene to phenol on Fe₁/PMA (in the case of a H₂O₂ oxidant), all DFT energies are in eV; (b) optimized geometries of IS, TS, and FS of the benzene oxidation on Fe₁/PMA, all the calculated bond lengths are given in Å.

and a hydroxo intermediate is formed simultaneously by a C···H–O interaction, with the activation of the C–H bond of C₆H₆ on the surface of OFe₁/PMA. Besides, due to the C···H–O type interaction with the FeO complex, benzene appears a little distorted. The TS2 transition state having 0.67 eV activation energy and 164i cm⁻¹ imaginary frequency is responsible for the dissociation of the C–H bond from benzene and the formation of an O–H bond. Furthermore, the iron-oxo-benzene complex connects the hydroxo complex during the TS2 transition state. An increase in the C–H bond distance from 1.09 to 1.28 Å in C₆H₆ and a decrease in the O–H bond distance from 2.76 to 2.12 Å are also evidence for the feasible transition state structure which is responsible for the cleavage of C–H and the bifurcation of the O–H bond. Eventually, the phenol complex [Fe₁(C₆H₅OH)] is formed which results in the dissociation of the Fe₁–O bond and the association of the O–H bond. Therefore, the phenol complex and the hydroxo intermediate are connected to the OFe₁/PMA cluster during the FS2 reaction. Similarly, the C–H bond length in C₆H₆ increased to 1.42 Å while the O–H bond length decreased to 0.97 Å. Finally, the phenol desorption from the surface occurred with the restoration of the Fe₁/PMA cluster at the last step of the reaction. The progression from IS1 to FS2 is highly exothermic as evident from ΔE = −2.26 eV. The low adsorption energy (E_{ads} = 0.54 eV) between phenol and the Fe₁–PMA surface during FS2 is suitable for the desorption of phenol from Fe₁(C₆H₅OH)/PMA leaving behind the Fe₁/PMA catalyst. It should be noted that the phenol moiety in the complex structure is quite similar to that of free phenol. Besides, a comparison of the energy barriers in the first



and second steps shown, respectively, in Fig. 5a and 6a define the decomposition of H_2O_2 in the first elementary reaction as the rate-limiting step.

The spin magnetic moment calculated for the elementary steps in the benzene oxidation to phenol provides valuable insights about the IS, TS, and species description. The spin magnetic moment calculated at the initial stage of the mechanism shows that $\text{Fe}^{\delta+}$ is an active center of the Fe_1/PMA cluster. When H_2O_2 is adsorbed on the Fe_1/PMA cluster, the magnetic moment of $\text{Fe}^{\delta+}$ changed slightly from 2.90 to $2.78\mu_{\text{B}}$ (see **IS1** in Fig. 5a). A small change in the magnetic moment of $\text{Fe}^{\delta+}$ might be related to the large separation of 2.12 Å between Fe_1 and adsorbed H_2O_2 , which results in a very weak interaction between them. With the physisorption of H_2O_2 on the Fe_1/PMA cluster (see **TS1** in Fig. 5) $\text{Fe}^{\delta+}$ is reduced having a spin magnetic moment of **FS1** to $0.53\mu_{\text{B}}$. However, decreasing the spin magnetic moment of **FS1** to $0.53\mu_{\text{B}}$ indicates a reduction in $\text{Fe}^{\delta+}$, as shown in Fig. 5. The reduction in the magnetic moment is related to the interaction of the surface oxygen with the Fe_1 atom of the Fe_1/PMA cluster.

During **IS2** and **TS2**, with the introduction of benzene on OFe_1/PMA , a hydroxo complex forms, and the magnetic moments for **IS2** and **TS2** are $0.66\mu_{\text{B}}$ and $0.77\mu_{\text{B}}$, respectively, as shown in Fig. 6. Therefore, due to the $\text{C}\cdots\text{H}-\text{O}$ type interaction with the Fe_1O complex, benzene gets a little distorted, as discussed earlier. With the formation of the phenol complex on the Fe_1/PMA cluster, $\text{Fe}^{\delta+}$ is oxidized, and the magnetic moment is increased to $1.63\mu_{\text{B}}$. Similarly, the magnetic moment increases to $3.56\mu_{\text{B}}$ with the desorption of phenol from the Fe_1/PMA cluster, indicating re-oxidation of $\text{Fe}^{\delta+}$.

When examining the PDOS of Fe 3d-orbitals for each elementary step in the reaction a strong correlation emerges between the changes in the magnetic moment of Fe and the behavior of the Fe 3d orbital near the Fermi level, as shown in Fig. S8 of the ESI.† Specifically, after the initial adsorption of benzene (**IS2**), there seems to be a decrease in the availability of states for Fe 3d-orbitals near the Fermi level compared to the initial state. As the reaction progresses up to the formation of phenol, the PDOS near the Fermi level indicate an increase in the available states. Fig. S8 of the ESI† reveals a significant discrepancy between the spin-up and spin-down PDOS of Fe 3d-orbitals. This asymmetry suggests a non-zero magnetic moment for Fe, with the magnitude potentially proportional to the degree of separation between the spin-up and spin-down peaks. The large asymmetry in the Fe_1/PMA PDOS, with a dominant contribution from spin-down states, indicates a strong magnetic moment for the reference material. The minimal change in the asymmetry for the initial state (**IS1**) compared to Fe_1/PMA suggests a relatively small variation in the magnetic moment during the initial stage of the reaction. The higher spin-up contribution might be linked to a decrease in the net spin magnetic moment of the final state (**IF1**). A less pronounced asymmetry in **IS2** compared to **IS1** could imply a less magnetic moment on Fe_1 at this stage. The formation of the phenol complex on the Fe_1/PMA cluster in **FS2** might lead to the observed discrete molecular levels in the Fe_1 PDOS. The

increased contribution from spin-down states in this final state could indicate a change in the magnetic moment compared to the initial state. Overall, the analysis of the PDOS plots provides valuable qualitative information about the magnetic properties of Fe_1 during the reaction. Furthermore, the shifting and broadening of the high valence bands around the Fermi level across the elementary steps suggest a change in the overall electronic structure of the catalyst surface (OFe_1/PMA). This shift in the d-band center, as reflected in the PDOS plots, aligns with the reactivity of the catalyst for benzene oxidation.⁶⁶

The foregoing discussion reveals that the H_2O_2 molecule can be dissociated with an activation energy of 0.84 eV on the confined Fe sites, subsequently forming a Fe_1-O active center by releasing the H_2O molecule from the surface. Fe_1-O having active surface oxygen (O^*) successfully absorbs the benzene molecule and forms C–O and O–H bonds at low temperatures with 0.67 eV activation energy. Therefore, it can be concluded that benzene oxidation to phenol is a direct process rather than being controlled by species or ionic intermediates.

3.7. Oxidation of benzene to phenol on Fe_1/PMA using O_2

When oxygen is an oxidant, at first place the Fe_1/PMA cluster activates the O_2 molecule as superoxide, and then it is activated as an oxidizing catalyst, as shown in Fig. 4. As described previously, the O_2 while staying on the Fe_1 atom in PMA is activated as superoxide and prefers to develop side-on coordination. The calculated potential energy landscape of benzene oxidation mediated by the $\text{O}_2\cdots\text{Fe}_1/\text{PMA}$ catalyst (**IS**), intermediate (**IM**), (**TS**), and (**FS**) is shown in Fig. 7. The calculated adsorption energy of benzene attacking the adsorbed O_2 molecule on Fe_1/PMA is -0.05 eV, which is higher than that of the initial state of $\text{O}_2\cdots\text{Fe}_1/\text{PMA}$ (**IS3**), and the reaction is thermodynamically feasible as described by the highly exothermic (-0.78 eV) adsorption of O_2 on Fe_1/PMA . The iron-oxo-benzene complex (**IS3**) is formed between $\text{O}_2\text{Fe}_1/\text{PMA}$ and benzene because of the van der Waals interactions between $\text{C}-\text{H}\cdots\text{O}-\text{O}$, where the bond lengths of C–H and $\text{O}\cdots\text{H}$ of **IS3** are 1.09 and 2.80 Å. Afterward, one of the oxygen atoms from adsorbed O_2 molecules on the Fe_1/PMA cluster transfers to benzene and forms a new hydroxo-intermediate complex by a $\text{C}\cdots\text{H}-\text{O}-\text{O}$ interaction along with the activation of the C–H bond of C_6H_6 on the surface of $\text{O}_2\text{Fe}_1/\text{PMA}$. It can be inferred that during the transition state (**TS3**) when benzene is connected with one of the O atoms, the side-on configuration of O atoms transmuted to an end-on configuration.

Ranging from the dissociation of the C–H bond from benzene and the formation of the O–H bond, the **TS3** transition state having 1.02 eV activation energy and one imaginary frequency of $209i\text{ cm}^{-1}$ is responsible for many electronic processes. Furthermore, the iron-oxo-benzene complex connects the hydroxo complex during the **TS3** transition state. Besides, an increase in the C–H bond distance from 1.09 to 1.22 Å in C_6H_6 and a decrease in the O–H bond distance from 2.8 to 2.08 Å are quite appropriate for the **TS3** structure to cleavage the C–H bond and to bifurcate the O–H bond. Whereas the formation of a hydroxo intermediate is of key importance in



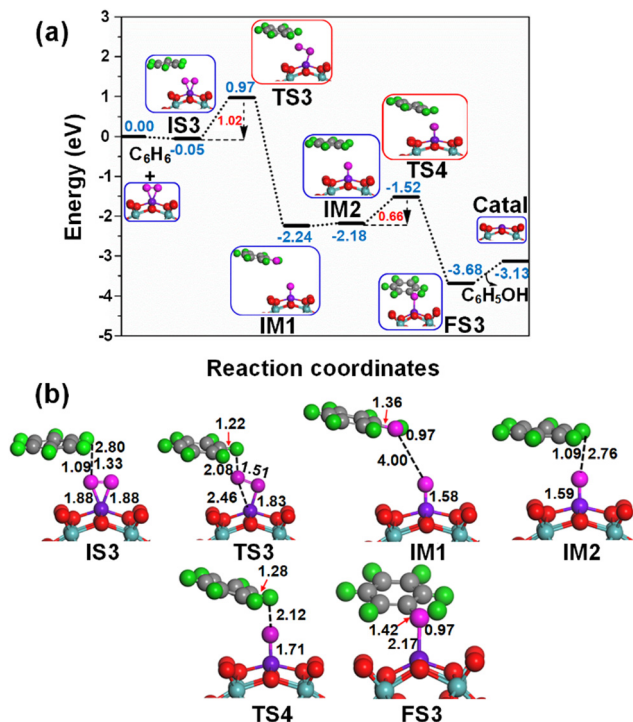


Fig. 7 (a) Potential energy profile of the efficient decomposition of direct oxidation of benzene to phenol on Fe_1/PMA in the case of an O_2 oxidant, all DFT energies are in eV; (b) optimized geometries of IS, IM, TS, and FS of the benzene oxidation on Fe_1/PMA , all the calculated bond lengths are given in Å.

the process of benzene oxidation to phenol, which is associated with the breakage of the O–O bond and the formation of the O–H bond occurring between **TS3** and **IM1**. Eventually, the phenol complex $[\text{Fe}_1\text{O}\cdots(\text{C}_6\text{H}_5\text{OH})]$ is formed which results in the dissociation of the $\text{Fe}_1\text{–O}\cdots\text{O}$ bond and the association of the O–H bond. Therefore, the phenol complex and the hydroxo intermediate are connected to the OFe_1/PMA cluster during the **IM1** reaction. Similarly, the C–H bond length in C_6H_6 increased to 1.42 Å while the O–H bond length decreased to 0.97 Å. Finally, the phenol desorption from the surface occurred with the restoration of the PMA cluster at the last step of the reaction. The progression from **IS3** to **IM1** is highly exothermic as evident from $\Delta E = -2.19$ eV. Due to the weak adsorption energy ($E_{\text{ads}} = 0.06$ eV), the phenol leaves the surface making Fe_1/PMA covered with the O atom and being available for another cycle of oxidation of benzene.

Successively, the oxygen atom pre-adsorbed on the Fe_1/PMA cluster reacts with the benzene during **IM2**, and the benzene molecule physisorbed at 2.76 Å away from the surface O atom is taken as an underlying structure in **IM3**. The reaction between the surface O atom and benzene at the Fe_1/PMA cluster produces a second phenol during **FS3** through **TS4**, while the catalyst is recovered as the cluster. The **TS4** having 0.66 eV of activation energy and $164i\text{ cm}^{-1}$ imaginary frequency is responsible for the dissociation of the C–H bond and the formation of the O–H bond. However, the formation of new C–O and O–H bonds with 1.42 and 0.97 Å bond lengths, respectively, is

responsible for the arising of the final state (FS). The progression from **IM2** to **FS3** is highly exothermic as evident from $\Delta E = -1.50$ eV. Due to the weak adsorption energy ($E_{\text{ads}} = 0.55$ eV), the phenol leaves the surface thus regenerating the Fe_1/PMA catalyst, whereas the phenol moiety in the complex structure is quite similar to that of free phenol. Moreover, the formation of the first phenol during **IS3** to **IM1** (see Fig. 7) on the Fe_1/PMA cluster and the activation of C–H bond are the rate-limiting steps having an activation energy of 1.02 eV in phenol production from benzene oxidation.

According to the spin magnetic moment calculations, the Fe_1/PMA cluster has a $\text{Fe}^{\delta+}$ active center at the start of the mechanism, which is the same as that of the Fe_1/PMA catalyst. However, with the physisorption of O_2 on Fe_1/PMA during **IS1** (see Fig. 4 for benzene oxidation), the oxidation state of $\text{Fe}^{\delta+}$ was reduced having a spin magnetic moment of $2.06\mu_{\text{B}}$. The introduction of benzene on $\text{O}_2\text{Fe}_1\text{–PMA}$ during **IS3** and **TS3** (see Fig. 7) forms a hydroxo complex while Fe_1 has spin magnetic moments of $2.05\mu_{\text{B}}$ and $1.88\mu_{\text{B}}$ during **IS3** and **TS3**, respectively. However, $\text{Fe}^{\delta+}$ further reduced after the formation of the phenol complex during **IM1**, while having a magnetic moment of $0.65\mu_{\text{B}}$. In **IM2** and **TS4** (see Fig. 7), when the second benzene is introduced on $\text{OFe}_1\text{–PMA}$, the magnetic moments of $\text{Fe}^{\delta+}$ changed to $0.66\mu_{\text{B}}$ and $0.77\mu_{\text{B}}$, respectively. In conclusion, the benzene and hydroxo complex was distorted because of their interaction with the O atom present on the surface of OFe_1/PMA .

During **FS3**, with the formation of the phenol complex on the surface of the Fe_1/PMA cluster, $\text{Fe}^{\delta+}$ oxidized with the increase of the magnetic moment to $1.63\mu_{\text{B}}$. Besides, $\text{Fe}^{\delta+}$ is re-oxidized as the magnetic moment increased to $3.56\mu_{\text{B}}$ after the desorption of phenol from the surface. According to the PDOS calculation shown in Fig. S9 of the ESI,† the Fe_1 3d orbital near the Fermi level is a key factor behind changes in the magnetic moment of the Fe_1 atom during all the fundamental steps. In Fig. S9 of the ESI,† the Fe 3d-orbitals exhibit significant asymmetry between the spin-up and spin-down PDOS, indicating a non-zero magnetic moment for Fe_1 . In **IS3**, PDOS displays a strong magnetic moment of Fe_1 , with spin-down states dominating, while **IM1** and **IM2** exhibit less asymmetry, suggesting a low magnetic moment. In **FS3**, the phenol complex formation results in discrete molecular levels in Fe_1 PDOS, with increased spin-down contribution indicating a change in the magnetic moment. In summary, PDOS analysis offers valuable qualitative insights into the magnetic properties of Fe_1 during the reaction. Furthermore, a gradual change in the d-band center with the shifting of high and broad valence bands around Fermi energy indicates the reactivity of the $\text{O}_2\text{Fe}_1/\text{PMA}$ surface for benzene oxidation (Fig. S9 of the ESI†). We also investigated the spin configuration of the Co_1/PMA cluster, detailed in Fig. S10 of the ESI.†

The preceding discussion reveals that it is easy to activate the O_2 molecule on the confined Fe_1 sites by forming iron-superoxide species (Fe_1O_2) as an active center. Still, it offers comparatively weak adsorption of benzene molecules for the formation of C–O and O–H bonds with a 1.02 eV activation



Table 1 Rate constants k (s^{-1}) of all the primary phases elaborate in three reaction pathways: decomposition of H_2O_2 and direct oxidation of benzene to phenol *via* the H_2O_2 oxidant and the O_2 oxidant on the Fe_1/PMA catalyst at various temperatures

	T (K)	100	200	298.15	400	500	600
H_2O_2 Decomposition	$H_2O_2^* \rightarrow H_2O + O^*$	6.06×10^{-30}	1.78×10^{-8}	0.24×10^0	1.36×10^3	2.23×10^5	6.91×10^6
H_2O_2 Oxidant	$O^* + C_6H_6 \rightarrow C_6H_5OH + ^*$	2.24×10^{-21}	0.00	1.84×10^2	1.89×10^5	1.15×10^7	1.85×10^8
O_2 Oxidant	$C_6H_6 + O_2^* \rightarrow C_6H_5OH + O^*$	5.14×10^{-39}	5.19×10^{-13}	0.000	7.31×10^0	3.42×10^3	2.12×10^5
	$C_6H_6 + O^* \rightarrow C_6H_5OH + ^*$	7.21×10^{-21}	0.000	2.72×10^2	2.53×10^5	1.45×10^7	2.24×10^8

energy barrier of the rate-limiting step. The above results indicate that the Fe_1O active center plays an important role in improving benzene oxidation activity as compared to the Fe_1O_2 active center.

3.8. Microkinetic study for oxidation of benzene to phenol on Fe_1/PMA

To better understand the catalytic benzene oxidation reaction on the Fe_1/PMA cluster, the rate constants k (s^{-1}) for each fundamental step in the decomposition of H_2O_2 , oxidation of benzene to phenol *via* the H_2O_2 oxidant, and the O_2 oxidant can be calculated using the transition state theory (TS).

$$k = \frac{k_B T}{h} \frac{q_{TS}}{q_R} \exp\left[-\frac{E_a}{k_B T}\right] \quad (3)$$

where q_R and q_{TS} are the vibrational partition functions for the primary phase's reactants and TS, k_B is the Boltzmann constant ($k_B = 1.3806452 \times 10^{-23} \text{ J K}^{-1}$), T is the temperature (298.15 K), h is Planck's constant ($6.626 \times 10^{-34} \text{ Js}$), and E_a is the activation energy.

$$q = \frac{1}{\prod_{i=1}^{\text{vibrations}} \left[-\exp\left(-\frac{h\nu_i}{k_B T}\right) \right]} \quad (4)$$

In this context, ν_i signifies the vibrational frequency. It is important to remember that imaginary frequencies are omitted for TS. Table 1 shows the rate constants for all the rate-determining steps elaborated in the aforementioned mechanisms at various temperatures. The rate constants (k) of the rate-determining step in the oxidation of benzene to phenol *via* the H_2O_2 oxidant are considerably higher than those for the decomposition of H_2O_2 and oxidation of benzene to phenol *via* the O_2 oxidant. The results are consistent with the DFT calculations that predicted benzene to phenol oxidation *via* the H_2O_2 oxidant would progress more efficiently than other mechanisms. In contrast, rate constants for many reactions increase as temperature increases, suggesting that Fe_1/PMA can accelerate benzene oxidation. The cryogenic atmosphere inhibits the oxidation of benzene to phenol with H_2O_2 , while using the O_2 oxidant the reaction rate becomes even slower at 100 K.

3.9. Intrinsic electronic features of Fe_1O and Fe_1O_2 active centers

The electronic features of Fe_1O and Fe_1O_2 are further investigated regarding their reactivity to influence the benzene oxidation because different coordination environments of SAC result in distinct catalytic performance as suggested by Gao *et al.*⁶⁷

Fe_1O is a coordinatively oxygen-unsaturated iron center having a coordination number of 5 around the Fe_1 metal, which is less than that of Fe_1O_2 having a coordinatively oxygen-saturated iron center due to a coordination number of about 6 around the Fe_1 metal. Moreover, the interaction of benzene with coordinatively oxygen-saturated iron center Fe_1O_2 (0.05 eV) is weaker than that with coordinatively oxygen-unsaturated iron center Fe_1O (0.35 eV), which may result in a higher C–H bond activation barrier of benzene for coordinatively oxygen-saturated Fe_1O_2 (1.01 eV) than its oxygen-unsaturated counterpart (0.84 eV). Therefore, the probability of Fe_1O_2 coordinatively oxygen-saturated iron center to activate the C–H bond is relatively lower than the coordinatively oxygen-unsaturated iron center Fe_1O , which is important for the benzene oxidation to phenol at ambient temperature.

Besides, the electron localization function (ELF) is an important parameter to differentiate the charge transfer reactivity, electron delocalization in molecules and solids, and bond classification.^{62,68} According to the ELF of Fe_1O shown in Fig. 8a, the Fe_1 –O bond exhibits covalent characteristics. At the same time, the lone pair electron property of oxygen becomes more significant due to the surrounding non-spherical charge distribution, whereas a significant charge transfer occurs from Fe_1 to O thus reducing Fe_1 (II) to Fe_1 (I) as described by the **IS1** to **FS1** in Fig. 5. Consequently, the reactivity of surface O atoms is enhanced due to the development of radical-like characteristics. After the formation of the iron–oxo–benzene complex (see Fig. 6, **IS2**), benzene appears a little distorted due to the C–H...O interaction on the OFe_1/PMA cluster (see Fig. 8b). Therefore, the adsorption of benzene on the O site of Fe_1 –O is more promising (0.35 eV). These results are also consistent with the charge density difference calculation results shown in Figure S11 of the ESI.†

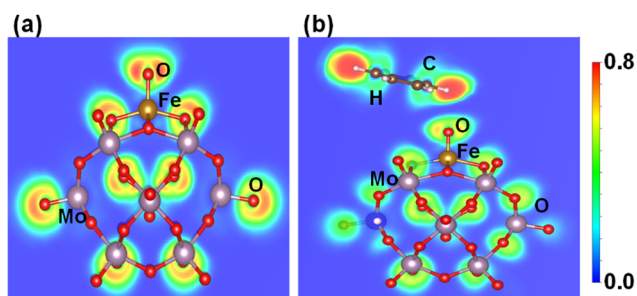


Fig. 8 Electron localization functions after geometry optimization for (a) OFe_1/PMA and (b) $C_6H_6-OFe_1/PMA$.



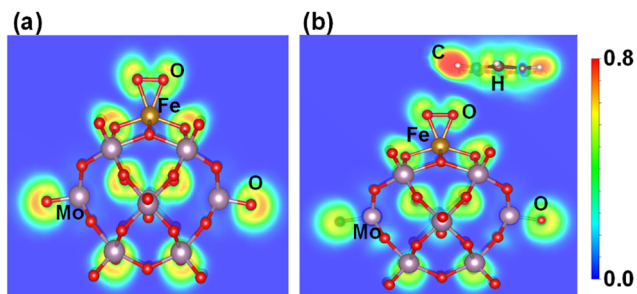


Fig. 9 (a) Electron localization functions after geometry optimization for (a) $\text{O}_2\text{Fe}_1/\text{PMA}$ and (b) $\text{C}_6\text{H}_6\text{-OfFeO}_1/\text{PMA}$.

Similarly, the ELF of Fe_1O_2 shows that the charge density is localized between the O_2 molecules, while $\text{Fe}_1\text{-O}$ has covalent bond characteristics where the strong localization of orbitals increases its polarizability, as shown in Fig. 9a. Consequently, the interaction between the benzene and Fe_1O_2 becomes very weak (0.05 eV) due to the very poor charge transfer from the O site to the benzene (see Fig. 9b). These results also agree with the CDD calculation results shown in Fig. S12 of the ESI.† Besides, the higher Bader charge population of O atoms in $\text{Fe}_1\text{-O}$ ($-0.51|e|$) as compared to that of Fe_1O_2 ($-0.20|e|$) also indicates better catalytic activity for benzene oxidation in the case of the Fe_1O active center.

4. Conclusions

In this study, density functional theory was used to investigate the mechanism of direct benzene oxidation to phenol under ambient conditions, focusing on a non-noble metal Fe_1 SAC dispersed on a PMA support (Fe_1/PMA) compared to other 3d-TM₁ (Co_1 , Ni_1 , Cu_1 , and Zn_1). The results demonstrate that Fe_1/PMA exhibits strong binding interactions with both the PMA cluster and the oxidant molecules (H_2O_2 and O_2), making it a highly active and stable catalyst for benzene oxidation to phenol. Based on the theoretical calculations, the key conclusions obtained are as follows:

(1) The comparable adsorption energies -0.53 and -0.41 eV on the Fe_1/PMA cluster and low energy barriers 0.84 and 1.02 eV for rate-limiting steps of H_2O_2 and O_2 molecules, respectively, make them ideal oxidants for the oxidation of benzene to produce phenol under ambient conditions.

(2) H_2O_2 , having a relatively low energy barrier, adheres to spontaneous dissociation on the Fe_1/PMA surface to initiate the active site $\text{Fe}_1\text{-O}$, which is responsible for the catalytic activity. Meanwhile, the adsorption of benzene on the surface O site of the $\text{Fe}_1\text{-O}$ active center is more promising because of the coordinative oxygen unsaturated Fe_1 center. While for the O_2 oxidant, the O atoms from the Fe_1 -superoxide ($\text{Fe}_1\text{-O}_2$) are comparatively less active to support benzene adsorption because of the coordinative oxygen-saturated Fe_1 center. It was observed that the interaction of benzene with the oxygen-saturated iron center $\text{Fe}_1\text{-O}_2$ (0.05 eV) is weaker than that with the oxygen-unsaturated iron center $\text{Fe}_1\text{-O}$ (0.35), which may

result in a higher C–H bond activation barrier of benzene for oxygen-saturated $\text{O-Fe}_1\text{-O}$ (1.01 eV) than its oxygen-unsaturated counterpart (0.67 eV).

(3) Besides, the reactivity of Fe_1O and Fe_1O_2 (oxo and super oxo active centers) was also explored through coordination states of the Fe_1 metal atom on the PMA surface. It was found that the probability of the coordinative unsaturated (CUS) Fe_1 atom to activate H_2O_2 for the formation of $\text{Fe}_1\text{-O}$ is relatively higher than that to activate the O_2 molecule, which is important for the benzene oxidation to phenol. In summary, the results demonstrate that coordination patterns influence not only the structure and electronic features but also the catalytic reaction pathway and the formation of key oxidative species.

(4) Finally, the energy barrier of 0.84 eV for the rate-limiting step of Fe_1O is lower than that (1.01 eV) for the rate-limiting step of Fe_1O_2 , suggesting that Fe_1O_2 species is relatively less active for the oxidation of benzene to phenol.

In the future perspective, the current study might flag the new structure–reactivity descriptors contributing to the next generation of functional condensed phase catalysis at a molecular level.

Conflicts of interest

The authors declare no competing financial interests.

Acknowledgements

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