Highly Efficient Degradation of Phenol via Metal Sulphides

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Abstract. The development of highly efficient electrode materials for the electro-catalytic oxidation of phenol from waste-water is a primary goal of environmental protection. In the present work, we have studied different metal sulphides (CoS, FeS, NiS, CuS) for phenol degradation. Using the density functional theory (DFT) based approach, we have studied the performance of these metal-sulphides for the electro-Fenton like processes and argue that NiS to be the best candidate, as seen in the recent experiment. From the calculated adsorption energies and activation barriers for the desorption of various important intermediates such as H$_2$O$_2$, OH, 2OH etc., the Bader surface charges that can be directly related to Lewis acidic behaviour, we conclude that NiS shows the optimal catalytic behavior required for the degradation of phenols.

INTRODUCTION

Industrial waste-water contains many hazardous pollutants due to phenol or phenolic compound [1]. Several methods adopted to remove phenol from wastewater such as physical adsorption [2], coagulation [3], biological treatment [4], chemical oxidation [5] and electro-catalytic oxidation technology [6]. There are many advantages in the electrocatalytic oxidation technology such as electro-Fenton process has low cost and no serious secondary pollutant [7]. In a typical electro-Fenton process the hydroxyl radical (•OH) is generated due to the electron transfer between hydrogen peroxide(H$_2$O$_2$) and metal catalyst (M$^{6+}$) [8]. The hydroxyl radical (•OH) attacks the organic pollutants to form harmless compounds (e.g.,CO$_2$ and/or H$_2$O) [9, 10]. The typical electro-Fenton process involves,

$$M^{6+} + H_2O_2 \rightarrow M^{(6+1)} + OH^- + (\cdot OH) \quad (1)$$

Hydrogen peroxide H$_2$O$_2$ has capability of carrying various oxidizers such as •O$_2^-$, •OOH, and •OH which can degrade the organic contaminants from water-bodies and aquifer solids [11]. By application of catalytic scissors, H$_2$O$_2$ dissociation can be achieved as shown in Eq.(1), which has high •OH productivity. S-modified, Fe-bearing surfaces are promising candidates for catalysing H$_2$O$_2$ cleavage, contains rapidly and heterogeneously nature [12]. The FeS$_2$ contains unique Lewis acidic feature, which is capable to cleave H$_2$O$_2$ via Fe$^{5+}$ redox-mediated heterogeneous catalysis [12]. In above described literature, for H$_2$O purification, there are applications of S-doped Fe oxides [13], FeS$_2$ [12] and their analogues [14] as catalysts. Therefore, it is worth to study the catalytic nature in other metal sulphides which can even enhance the H$_2$O$_2$ scission performance over FeS. So we have chosen simplest yet synthetically viable metal sulphide structure (M: metal (Fe, Co, Ni, Cu); S: sulphur) [15]. The reason behind the selection of these metal sulphides is, they can be easily obtained via hydrothermal or solvothermal synthesis, due to hexagonal crystal system are able to circumvent the inclusion of any geometrical effect on their catalytic performance [15]. These metal sulphides are also barely porous, so they can easily minimize any textural effect comes due to catalytic consequences [15].

We have considered the identical crystal systems for fair comparison among MS catalysts, but their atom connectivities play a major role in finding the periodic trend of MS catalysts to cleave H$_2$O$_2$. The reason behind it is, the amount of Lewis acidic sites have a strong dependency on the coordination geometry of metal species innate to MS catalysts [14]. The electronegativity of metal species included in metal sulphide is an important factor. In a recent experimental study [16], it was shown that, NiS shows the best performance among all the above mentioned metal sulphides. The present study focuses on the theoretical understanding of the periodic trend of MS catalysts in
their ability to fragment the H$_2$O$_2$, (•OH) production and subsequent desorption of (•OH). We present our results after a brief description of the computational details below.

**COMPUTATIONAL DETAIL**

The first-principles calculations have been performed in the framework of the density functional theory (DFT) with help of Vienna ab initio simulation package (VASP) [17]. The projector augmented wave (PAW) method is applied in whole calculation [18]. The Perdew-Burke Ernzerhof functional is taken for exchange-correlation energy [19]. The PAW-PBE potentials are considering 3d and 4s valence electrons for Fe, Co, Ni and Cu, 3s and 3p valence electrons for S, 2s and 2p valence electrons for O and 1s electron for H. There is a consideration of hexagonal (0001) surfaces of metal sulphides (MS) for the calculations with H$_2$O$_2$ and OH molecules adsorbed on the MS surfaces. The MS unit cell crystal structures are taken from “Materials Project” database and IDs are FeS (MP-2099), CoS (MP-1274), NiS (MP-594) and CuS (MP-504), respectively. There is adsorption of top four atomic layers with OH molecule on the hollow sites and remaining bottom atomic layers are assumed as bulk. The Monkhorst pack 5×5×1 k-points was used for Brillouin zone integration. The plane wave kinetic energy cut-off of 500 eV is taken. There is selection of Methfessel-Paxton smearing with smearing width of 0.2 eV. The conjugate gradient algorithm method is used for ionic relaxation and the ionic iterations convergence are fixed to be 0.05 eV/Å. The dipole corrections are applied perpendicular to the surface slabs for the correction of the electric fields due to the periodicity and asymmetry in the structure. The formula for adsorption energy ($\text{E}_{\text{ads}}$) is following,

$$\text{E}_{\text{ads}} = \text{E}_{\text{S+A}} - (\text{E}_\text{S} + \text{E}_\text{A}).$$

Where $\text{E}_{\text{S+A}}$ is belong to total energy of surface and adsorbed OH molecule, $\text{E}_\text{S}$ and $\text{E}_\text{A}$ are the total energies of clean MS surface and free OH molecule respectively.

**RESULTS AND DISCUSSIONS**

The relaxed bulk structures of FeS, CoS, NiS and CuS are shown in Fig.(1). The vacuum between slab and surfaces is taken 15Å to avoid any spurious interactions between the surfaces. Adsorption energies of different reactant species such as H$_2$O$_2$ and OH are calculated on top, bridge and the hollow sites respectively. It was found that these reaction intermediates are most stable on the hollow sites.

**FIGURE 1.** Relaxed bulk structures of metal sulphides used in our calculations (a) CoS(Co-red, S-green) (b) FeS (Fe-black, S-green) (c) NiS (Ni-yellow, S-green) (d) CuS (Cu-blue, S-green).

We discuss about the trend of the MS in (1) H$_2$O$_2$ adsorption, (2) surface reaction to form OH and (3) the desorption of OH. The adsorption energies of H$_2$O$_2$ molecule, on the various MS surfaces are shown in Fig.2(a). It can be seen that H$_2$O$_2$ has largest adsorption energy for FeS, while it has lowest value for the CuS surface. The higher value of adsorption energy means, the stronger binding of H$_2$O$_2$ molecules in FeS surface, so the rate of desorption for OH molecules from the FeS surface is very small, which is a primary active species for attack on the phenol molecule towards its subsequent degradation. On the other hand, very small adsorption energy of H$_2$O$_2$ molecule in CuS surface indicates a large adsorption barrier, and therefore the adsorption of H$_2$O$_2$ is the rate
determining step in this case. Moderate values of adsorption energies are seen for the CoS and NiS which make them better candidates for such process. In the Fig.2(b), we show the adsorption energies of OH and 2OH molecules on different MS surfaces. In all cases, we can see that the adsorption energies of single OH is higher than that of 2OH, except in the case CuS, for which 2OH has slight higher adsorption energy indicating a weak tendency of clustering in that case. It is therefore expected that all the MS except CuS will not show any OH clustering on their surfaces or formation of M─OH complexes. By comparing the adsorption energies of H₂O₂ and OH in the Fig.2(a) & 2(b), we can see that the adsorption of H₂O₂ and the desorption of OH should be close to equilibrium in the case of NiS. Also, comparable adsorption energies of H₂O₂ and OH suggests a higher OH production rate in NiS.

FIGURE 2. Plot of adsorption energies (E_{ads}) in eV (a) for H₂O₂ (b) for OH and 2OH, on various metal sulphides.

Sulphur possess larger electro-negativity than metal species used in catalysis, therefore, it has capability to extract e⁻ from metals. The metal sulphide, which has greater electro-negativities of metal, provide smaller Lewis acidic strengths [23] and makes weakest interactions of metals with H₂O₂. Ni contains highest value of electro-negativity among all other selected metals, so there will be weakest interactions between Ni⁺⁺ sites and H₂O₂, when forming NiS. Similarly in the case of FeS, as Fe has the lowest value of electro-negativity, it should show the highest interactions between metal M⁺⁺ sites and H₂O₂ molecules. Such charge transfer from metal to sulphur for FeS, NiS, CoS and CuS surfaces have been studied by Bader charge analysis method [24]. The charge transfer between S to Metal was calculated by considering only the top four layers. We find that, sulphur extracts maximum electron in FeS (0.61e) and least amount of electrons in NiS (0.44e). Moderate charge transfer is observed in the CoS (0.47e) and CuS (0.49e). Considering the best performance shown by NiS as seen in the experiment [16], it can be said that the best catalytic performance is obtained for the metal Mδ⁺ having smallest δ⁺.

In the Fig.(3), we show the site projected density of states (DOS) for M, S and OH for the various OH adsorbed MS surfaces. For FeS, we can see that there is a large bonding peak around -6 eV for the minority spin channel resulting a strong FeS-OH binding [Fig.3 (a)]. Also, absence of any OH states near Fermi energy suggest absence of antibonding states involving OH, and OH is therefore quite stable on FeS surface. While as we move from Fe to Cu, we can see the OH states near Fermi energy progressively increases and for the CuS, there is a clear visible OH peak at Fermi energy [Fig.3 (d)]. Movement of OH-states towards higher energies as we move from FeS to CuS is consistent with the trend of the adsorption energy and can be understood in terms of metal d-band filling. Finally, we calculate the energy barrier for the adsorption of OH from different MS surfaces. Activated energies are calculated by nudged elastic band (NEB ) method as already mentioned in Table 1.

The OH adsorbed from the hollow sites in different MS are desorbed to gas phase:

\[ \text{OH}^+ + * \rightarrow * + \text{OH(g)} \quad (3) \]

Where * is the adsorption site on the MS. Respective activation barrier and heat of the reaction for different surfaces are shown in Table(I). Moderate value of heat of reaction ΔH(eV ) and activation energy for the NiS makes it a good candidature of phenol degradation.
FIGURE 3. Site projected density of states for M sulphides with OH adsorbed on it.

TABLE 1. Table describing heat of reaction $\Delta H\,(eV)$ and activation energy $E_a\,(eV)$ in various metal sulphide.

<table>
<thead>
<tr>
<th>Metal Sulphide</th>
<th>$\Delta H,(eV)$</th>
<th>$E_a,(eV)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoS</td>
<td>3.77</td>
<td>3.73</td>
</tr>
<tr>
<td>NiS</td>
<td>3.38</td>
<td>3.50</td>
</tr>
<tr>
<td>CuS</td>
<td>0.24</td>
<td>1.64</td>
</tr>
</tbody>
</table>

CONCLUSIONS

Phenol degradation using different metal sulphide catalysts MS, (M=Fe,Co,Ni,Cu) are studied using the first principles based approach with the framework of the density functional theory. From the adsorption behaviour of different reaction intermediate species such as $H_2O_2$, OH and the Lewis acidic strengths of different metals used we have provided the explanation of the trend of the catalytic activity of these metals sulphides as observed in the recent experiment.

REFERENCES