The Study on the Generation of Persistent Free Radicals in the Explosive Industry Area

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Abstract: Phenolic compounds and transition metals exist in wastewater having a large number of emissions due to the discharge of polluted wastewater from the explosive industry. And these two substances are important factors that affect the generation of persistent free radicals (PFR). However, the generation of more toxic and harmful PFR is unclear in wastewater from the explosive industry. In this study, the dissociation reaction of phenol on transition metal oxides ZnO to form PFR has been explored by the density functional theory (DFT) calculation. The dissociation of phenol on the ZnO surface is an exothermic and barrierless reaction process, which indicates that PFR can be formed in the wastewater of the explosive industry. Thus, more attention should be paid to the toxicity of PFR in the wastewater produced by the explosive industry.

1. Introduction

Identifying dangerous substances quantitatively is the first step in any risk assessment.[1] Previous studies have pointed out that risk assessments are usually based on toxicity databases for individual pollutants. However, there are often inconsistencies between measured concentrations of pollutants and health risks.[2] Therefore, some unknown toxic chemicals that are not included in the monitoring should be carefully assessed in studies involving regional risk assessment, for example, PFR have attracted much attention due to their significant toxicity and risk.

The important factors for the generation of PFR are phenol and transition metal oxides. Both of these can be found in some places. For example, the discharge of phenol-containing wastewater from the explosive industry is large. The main pollutant phenol is a high-toxic substance and is difficult to be degraded, which has caused serious harm to the ecological environment and human health.[3] In addition, a lot of transition metal oxides, such as ZnO, are observed in the wastewater. However, it is not clear whether the more toxic and harmful PFR can be formed in wastewater from the explosive industry.

DFT simulations were used to study phenol dissociation on the ZnO surface in order to shed light on the production of PFR. This research is valuable for learning more about the toxicity of wastewater produced by the explosives business.

2. Methods

The Vienna Ab Initio Simulation Package (VASP)'s projector augmented-wave (PAW) technique was used to calculate the DFT[4]. Both the generalized gradient approximation (GGA) and Perdew−Burke−Ernzerhof (PBE)was examined by the electronic exchange-correlation function. The cutoff energy was 400 eV. The convergence criteria for iteration and force were set to 1×10^{-6} eV and 0.03 eV Å^{-1}, respectively. The k-points were $3\times3\times1$ and the smearing width was 0.20 eV. With a U value of 5.2 eV, the GGA + U was used. Utilizing the Climbing-Image Nudged Elastic Band method (CI-NEB), the reaction pathways were determined. Four images were used in the CI-NEB calculations between the original and final structures.

The calculated lattice constants of ZnO are compared with the experimental data to ensure the accuracy of the model and the selected calculation parameters. When optimized ZnO lattice constants are a = 3.233 Å, c=5.275Å, which are agree with experimental data (a=3.252 Å, c=5.313 Å) and theoretical data (a = 3.235 Å, c =5.205 Å). The unit cell volume, which closely resembles the experimental data, is used with the optimized lattice parameters.

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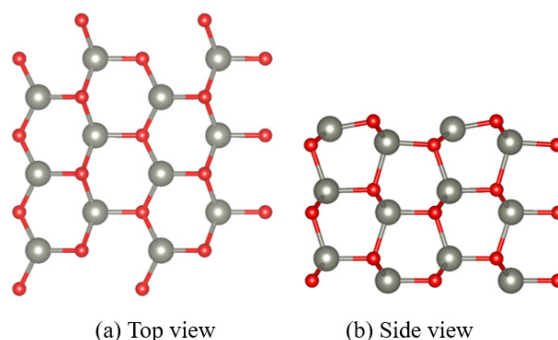
(a) Top view   (b) Side view

Figure 1. The surface morphology of ZnO surface. (a) Top view and (b) Side view. Color: Zn, gray; O, red.

The exposed ($10\bar{1}0$) surface of ZnO which had six atomic layers with (3×2) supercell and 15 Å of vacuum, was selected as a model system (Figure 1). The top four layers of the slab and molecules are relaxed, and the bottom three layers are kept fixed.

3. Results and discussions

3.1 Isolated Phenol Molecule.

The idealized representation of the phenol molecule is depicted in Figure 2. The bond lengths and angles that were calculated and are shown in Table 1 agree exactly with the available experimental data.

Furthermore, to study the potential reaction sites of phenol, molecular electrostatic potential (ESP) analyses are undertaken, as shown in Figure 2. The site with more positive ESP has a stronger ability to attract nucleophiles and the site with more negative ESP has a stronger ability to attract electrophiles. Thus, the H atom of phenol has the most positive ESP (55.80 kcal/mol) and prefers to be absorbed on the O (nucleophilic site) of ZnO surface; whereas the O atom of phenol has the most negative ESP (-27.00 kcal/mol) and prefers to be absorbed on Zn (electrophilic site) of ZnO surface.

Table 1. The molecular geometry about optimized phenol.

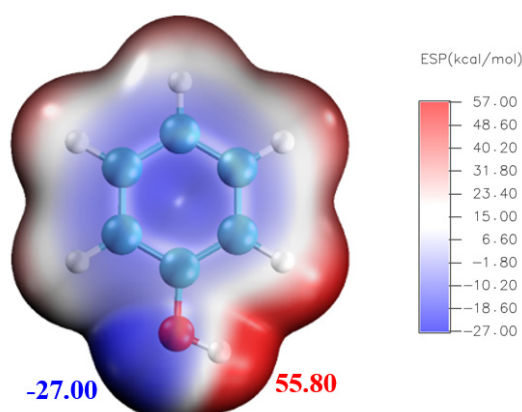| Atoms	This study	Experiment
Bond length(Å)		
C-H	1.07	1.08
C-C	1.40	1.40
O-H	0.96	0.96
C-O	1.38	1.36
Angle(°)		
C-O-H	109.11	109.00

Figure 2. The ESP mapped molecular surface of Phenol.

3.2 The dissociation of phenol to form persistent free radicals on the ZnO surface

It has been reported that there are two disruption ways of phenol: one is the direct disruption of the H atom from the hydroxyl group (Path a, C_6H_5O-H) and another is the disruption of the hydroxyl radical (Path b, C_6H_5-OH). And the disruption of phenol prefers Path a than Path b in the gas-phase or presence of a catalyst. Therefore, the disruption of phenol by direct fission of the H atom from the hydroxyl group (Path a, C_6H_5O-H) is considered in this work.

3.2.1 The adsorption of molecules

Due to the various adsorption sites on the ZnO surface, various adsorption modes have been examined to determine the most likely starting structure for the dissociation of the phenol molecule. The most stable adsorption molecules are plotted in Figure 3 with the adsorption energies and the adsorption sites summarized in Table 2. These results make it clear that phenol favors Top-Zn_{suf}, and the most stable compound with an adsorption energy of -0.86 eV.

Table 2 Lists the adsorbed compounds' adsorption energies and sites on the ZnO surface.

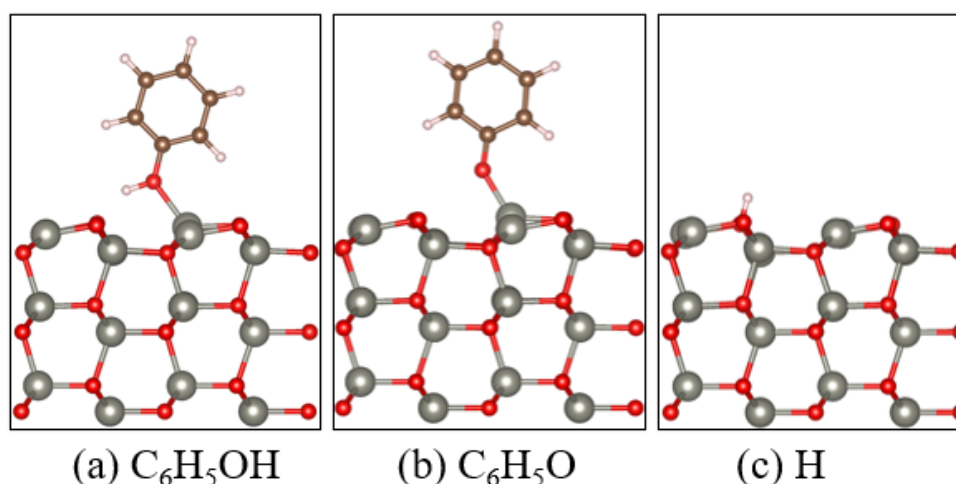| Molecules	Adsorption site	E_{ads}/(eV)
C_6H_5OH	Top-Zn_{suf}	-0.86
C_6H_5O	Top-Zn_{suf}	-2.70
H	Top-O_{suf}	-0.77

Figure 3. The most stable adsorption structures of the adsorbed molecules on ZnO surface.

Moreover, the adsorption structures of the two components from the O-H bond dissociation, the H and the phenoxyl, are investigated separately to better understand the structure following the dissociative dehydrogenation step. Figure 3 visually depicts these structures while Table 1 summarizes the precise adsorption energy data for all adsorption molecules. The Top-O_{suf} position is discovered to be the most stable among all the adsorption locations for the H, with an adsorption energy of -2.70 eV; for the phenoxyl, the Top-Zn_{suf} position is discovered to be the most stable, with an adsorption energy of -0.77 eV. Hence, it is discovered that the phenoxyl and H are the most stable on top of the Zn and O atoms on the ZnO surface, respectively.

In the next step, the co-adsorption of one H and phenoxyl is investigated to obtain the most stable structure after the rupture of the O-H bond.

3.2.2 The dissociation of phenol to form persistent free radicals

The optimal initial state and final state structures involved in the reaction processes on the ZnO surface have been taken into consideration to comprehend the O-H bond rupture phase of the phenol on the ZnO surface. As shown in Figure 4, it is evident that the phenol prefers Top-Zn_{suf} on the ZnO surface, which is thought to be the Trigger for the dissociative process. Between this starting state and the final state, four photos are taken. The phenolic O-H bond in phenol extends from 1.033 Å to 1.488 Å on the ZnO surface during the dissociative process of phenol. This result indicates that following the dissociation of phenol, the phenolic O-H bond is totally broken. The distance between the phenoxyl O and the Zn atom, which is reduced from 2.057 Å to 1.952 Å on the ZnO surface, is another notable difference between the dissociative structures and the non-dissociative structures. In the meantime, a new bond of FS with bond length (1.059 Å) is created between surface O atom and phenolic H atom.
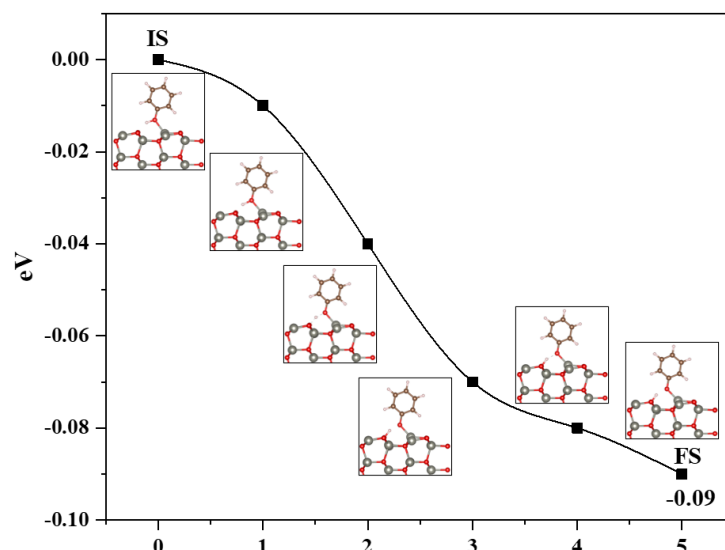
Figure 4. The energy profile for the persistent free radicals generation on the ZnO surface with the corresponding structures.

The reaction energy of phenol dissociation on the ZnO surface, as shown in Figure 4, is -0.09 eV, indicating that the reaction is exothermic on the ZnO surface. On the ZnO surface, production of PFR is thermodynamically advantageous. The phenol dissociation, nevertheless, is a barrierless process. These findings show that phenol dissociation on the ZnO surface is both kinetically and thermodynamically advantageous. Figure 4 also shows the energies of the phenol dissociation process in reverse on the ZnO surface (i.e., the recombination of H and phenoxyl). Thus, on the ZnO surface, phenol is more likely to dissociate.

4. Conclusion

Phenol-containing wastewater and transition metal produced by explosive industry have a large number of emissions, and these two substances are important factors that affect the PFR generation. However, the generation of more toxic and harmful PFR is unclear in wastewater from the explosive industry. In this study, the dissociation reaction of phenol on transition metal oxides ZnO to form PFR has been explored by the DFT calculation. The dissociation of phenol on the ZnO surface is an exothermic and barrierless reaction process, which indicates that PFR can be formed in the wastewater of the explosive industry. Thus, more attention should be paid to the toxicity of PFR in the wastewater produced by the explosive industry.

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