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Research paper

Theoretical exploration of VOCs removal mechanism by carbon nanotubes through persulfate-based advanced oxidation processes: Adsorption and catalytic oxidation

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ABSTRACT

Carbon-catalyzed persulfate activation for the removal of gaseous volatile organic compounds (VOCs) has not been reported yet, and the corresponding fundamental mechanisms of VOCs adsorption and the subsequent VOCs degradation remain controversial. In this work, theoretical chemistry calculations were carried out to explore the VOCs removal mechanism by the persulfate-based advanced oxidation processes (P-AOPs) for VOCs removal over single walled carbon nanotubes (SWCNT). This study provided detailed theoretical insights into the SWCNT/P-AOPs for VOCs treatment in terms of adsorption, activation, mineralization, and diffusion of VOCs or peroxymonosulfate (PMS). Various VOCs were found to be preferentially adsorbed onto SWCNT, and the adsorption strength of VOCs was found to be significantly dependent on their polarizability. On the other side, PMS adsorbed on SWCNT could be efficiently activated through accepting π electron in the sp² carbon matrix of SWCNT rather than the electrons at dangling bonds to generate •OH radicals attributed to the strong interaction between PMS and SWCNT. Formaldehyde was then taken as an example to evaluate the catalytic degradation pathways via SWCNT/P-AOPs. Under the attack of •OH radicals, the ultrafast degradation pathway of formaldehyde with no byproduct CO was identified with ultralow reaction energy barrier and large energy release. In addition, factors affecting the adsorption of organic compounds were identified and the detailed PMS activation pathway was present directly in this work. Above all, this work extended the carbons/P-AOPs system to VOCs abatement and presented systematic evidences for the essential mechanisms associated with VOCs adsorption and PMS activation by SWCNT, and the corresponding removal pathway and mechanism were also understood.

1. Introduction

In the past several decades, a large number of volatile organic compounds (VOCs) released into atmosphere have imposed serious threats to human health and environment (Carlo et al., 2004; Zhang et al., 2018; Dai et al., 2017; Gentner et al., 2017). Therefore, practical, low-cost, and efficient technologies for VOCs elimination are urgently needed (He et al., 2019). Owing to the strong oxidation capacity and high efficiency, persulfate-based advanced oxidation processes (P-AOPs) have been widely reported for organic pollutants remediation in waterbody (Miklos et al., 2019; Cheng et al., 2019; Zhang et al., 2015). In recent years, several research efforts of utilizing P-AOPs as an alternative technology for gaseous VOCs treatment have also been

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In P-AOPs, persulfate such as peroxymonosulfate (PMS) and peroxydisulfate (PDS) can be activated by catalysts (e.g., Co, Fe, Mn cations and their oxides, as well as carbon-based materials) to generate reactive oxygen species (ROSs), such as •OH (standard redox potential SRP = 2.8 V) and \bullet SO₄ (SRP = 2.5–3.1 V) radicals, to destroy resistant organic pollutants (Chen et al., 2008; Jiang et al., 2013; Liang et al., 2012). For example, by employing citric acid chelated Fe^{2+} as a homogeneous activator for persulfate to generate radicals and destroy BTEX (benzene, toluene, ethylbenzene, and xylenes) exhaust gases, a degradation efficiency of approximate 50% was achieved (Liang et al., 2009). Among the core activators for ROSs generation, carbonaceous materials (e.g., carbon nanotubes (CNTs), graphene, carbon

nanodiamonds) have aroused extensive interest in P-AOPs and were successfully applied in the removal of aqueous organic pollutants since it can overcome the inherent drawbacks of secondary pollution such as metal leaching and undesirable metal sludge, which is commonly encountered in traditional metal-containing catalyst (Duan et al., 2016a, 2018a, 2018b; Sun et al., 2012). On the other hand, the carbocatalyst with large specific surface area and high porosity can act as an excellent adsorbent for organic pollutants including VOCs, enhancing the contact of pollutants with ROSs. Unfortunately, the investigation of carbocatalyst/P-AOPs for VOCs abatement was not reported yet. The theoretical merits of carbocatalysts on VOCs adsorption and persulfate activation motivate us to utilize carbocatalyst/P-AOPs in treating VOCs exhaust gases.

Referring to recent progress of carbocatalyst/P-AOPs, the adsorption of organic pollutants and persulfate along with the catalyzed pathways for the possible ROSs generation are two critical factors responsible for the removal performance of organic pollutants (Chen et al., 2018a). Adsorption itself is an efficient non-destructive method for VOCs removal (Liu et al., 2009). On the other hand, a satisfying adsorption capacity of carbocatalysts enables organic molecules and persulfates to approach the active sites on carbocatalysts more easily, facilitating the fast mineralization of organic molecules (Wang et al., 2015). The surface chemistry of carbocatalysts and the structure properties of both organics and persulfates have been investigated to understand the adsorption of organics on carbon materials (Duan et al., 2018b). The effects of diverse functional groups in organics and carbons (Franz et al., 2000), the electrostatic interaction (Coughlin and Ezra, 1968), electron donor-acceptor interaction (Rong et al., 2002), the hydrogen bond (Zhu et al., 2017) and the π - π interaction (Lillo-Ródenas et al., 2005) between organic compounds and carbon adsorbents have also been considered in the discussion of organic pollutants adsorption on carbon materials. However, there are limited studies on systematic evaluation for the influence factors of organic pollutants adsorption on carbon materials, and the role of various factors remains controversial. For carbon-catalyzed persulfate activation, the free radical and non-radical pathways with different oxidative capacity dominate the research highlights, and both the pathways were discovered in CNTs/P-AOPs. The transferred electrons, such as the delocalized π electrons from the defects of carbocatalysts (e.g., vacancies and zigzag/armchair edges) (Oh et al., 2016) were believed to be attributed to the dissociation of O-O bond in persulfate for radicals generation. However, the edge defects of carbocatalysts were reported to be associated with non-radical pathway (e.g., electron transfer shuttle, surface active species, singlet oxygen) in other works (Zhou et al., 2015; Duan et al., 2016b; Choi et al., 2012). In fact, the direct evidence for the intrinsic nature that how those carbons exactly activate the persulfate are scarcely present in previous studies. The possible ROSs generation mechanism and the role of carbon in persulfate activation are still ambiguous, which are directly decisive to the removal capability of P-AOPs for VOCs.

For a systematic and reliable evaluation of the potential application of carbocatalyst/P-AOPs for VOCs treatment, enriching VOCs and activating persulfate to generate ROSs on carbocatalyst are two key steps. Density functional theory (DFT) was employed as a powerful tool in uncovering the origin of adsorption behavior, electron transfer, electron configuration evolution of compounds, thermodynamics and kinetics of chemical reaction (Zhang et al., 2019; Patterson et al., 2001; Li et al., 2014) to address the issues above. Herein, we proposed a facile strategy for VOCs removal through P-AOPs over single-walled carbon nanotubes (SWCNT) via traditional spraying method based on DFT calculations as illustrated in Fig. 1. PMS solution droplets were sprayed onto SWCNT, where PMS can be activated. At the same time, the exhaust gases flow through SWCNT and VOCs molecules can be adsorbed onto SWCNT or absorbed into the PMS solution droplets, and further interacted with the generated ROSs. During the process, the adsorption of PMS, water, and VOCs, the activation of PMS in solution in the presence of VOCs, and the migration of VOCs on SWCNT surface are the essential aspects to



Fig. 1. Simplified reaction flow diagram for P-AOPs over SWCNT for VOCs removal.

evaluate the performance of catalytic removal of VOCs. As shown in Fig. 2, adsorption energies of PMS, H₂O, and VOCs molecules on SWCNT were calculated firstly to understand their stability in the catalytic system. Then the electrostatic potential distribution and molecular properties of dipole and average polarizability were calculated to investigate the adsorption mechanism of PMS and VOCs, and the adsorption of VOCs on different carbon supports (multiple walled carbon nanotubes (MWCNT), graphene, active carbon (AC), porous SWCNT) were studied to understand the effects of carbons structures on VOCs adsorption. Furthermore, the reaction thermodynamics was investigated by calculating energy barrier (E_{bar}) and reaction energy (E_{R}) of PMS activation for ROSs generation, and the partial density of states (PDOS) and Hirshfeld analysis were conducted to discover the mechanism of electron transfer. Finally, to further understand the feasibility of SWCNT/P-AOPs for practical VOCs removal, formaldehyde, which has been recognized as one of the most concerned VOCs due to its hazard and extensive use in various industries and household products (Chen et al., 2018b; Salthammer et al., 2010), was selected as a model molecule for degradation investigation by P-AOPs. The diffusion of VOCs on SWCNT surface and then degradation by ROSs were investigated by calculating corresponding diffusion barrier (Ediff-bar), diffusion heat (E_{diff}), E_{bar} , and E_R .

2. Calculation details

All DFT calculations were carried out using the DMol3 module (Delley, 2000) in Materials Studio. As shown in Fig. 2, the Generalized Gradient Approximate (GGA) (Perdew and Yue, 1986) was employed as exchange-correlation functional with the correction by the Peidew–Burke–Ernzerhof (PBE) method (Perdew et al., 1996). Double numerical plus polarization (DNP⁺) (Delley, 2006) was applied as the basic set with the orbital cut off of 4.0 Å in all calculations. The core electrons were treated by all electron method in which all the electrons in the system were considered for calculation. The convergence tolerance of energy was set to 10^{-5} Hartree (1 Hartree = 27.21 eV), and the maximal allowed force and displacement were 0.002 Hartree/Å and 0.005 Å, respectively. The DFT+D method within the Tkatchenko-Scheffler (TS) scheme (Tkatchenko and Scheffler, 2009) was used to take the van der Waals disperse correction into account.

Three-dimensional periodic boundary conditions of SWCNT, graphene and porous SWCNT were applied in the simulation while nonboundary conditions for active carbon (amorphous carbon) and



Fig. 2. Methodology of DFT calculations for this study. The sequence of steps is indicated numerically.

MWCNT owing to the affordable calculation expense, and their sizes were showed in Fig. 3. The simulation model of SWCNT consists of a $1 \times 1 \times 6$ (5, 5) SWCNT supercell and after losing four carbon atoms the model turns to porous SWCNT. Vacuum thickness of 20 Å was applied in boundary conditions to minimize the error resulted from mirror molecules and the separation of k-point grid was set 0.01 Å⁻¹. Linear synchronous transit/quadratic synchronous transit (LST/QST) (Thomas et al., 1977) approaches were implemented for searching the minimum energy reaction pathway, which was further confirmed by the Nudged elastic band (NEB) method (Henkelman and Jonsson, 2000).

In the case of the adsorption of PMS, the solvation effects were taken into consideration using the Conductor-like Screening Model segment activity coefficient (COSMO-SAC) model (Lin and Sandler, 2002). During PMS activation, a H_2O molecule was introduced in the calculation system to consider the possibility that water might participate in the PMS activation for ROSs generation, and similar models have been reported reliable and successfully applied in predicting the accurate binding energy and reaction energy according to previous studies (Rimarčík et al., 2010; Marković et al., 2016; Zhan and Dixon, 2001). To comprehensively understand the effect of structure properties of VOCs molecules, different sorts of industrially emitted VOCs were taken into consideration as listed in Table 1, which covers most types of common VOCs. Corresponding critical physicochemical indexes, including static average polarizability ($\overline{\alpha}$) and hydrophobicity parameter log K_{ow} , are available from US Environmental Protection Agency's EPISuiteTM and summarized in Table 1. In this work, the adsorption energy (E_{ads}) of PMS on SWCNT was defined as follows:

$$E_{ads} = E_{adsorbent/PMS} - (E_{PMS} + E_{adsorbent})$$
(1)

where $E_{adsorbent/PMS}$, E_{PMS} and $E_{adsorbent}$ are the energies of adsorbent/PMS complex, isolate PMS molecule and adsorbent, respectively. For the adsorption of VOCs molecules (E_{ad}) and co-adsorption with PMS (E_{co-ad}), the adsorption energy was identified as following:



Fig. 3. Optimized atomic structures of (a) SWCNT, (b) porous SWCNT, (c) graphene, (d) AC and (e) MWCNT. The green curve in (b) represents the boundary of vacancy defect. The black and white balls are carbon and hydrogen atoms, respectively (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

Table 1

Different common VOCs and corresponding critical physicochemical properties, the dipole (p), average polarizability ($\overline{\alpha}$), and the hydrophobicity parameter (log K_{ow}).

| VOCs types | VOCs | p (D. 1) | $\overline{\alpha}$ | log | | |
|---------------------------------|---------------------|-------------|---|---|-----------------|--|
| | | (Debye) | DFT $(10^{-24}$ cm ³) | Experiment (10 ⁻²⁴ cm ³) | K _{ow} | |
| Alkane | Methane | 0.001 | 2.65 | / | 1.09 | |
| | Ethane | 0.001 | 4.39 | 4.5 | 1.81 | |
| | Propane | 0.090 | 6.26 | / | 2.36 | |
| | Hexane | 0.001 | / | 11.8 | 3.90 | |
| Cycloalkane | Cyclohexane | 0.000 | / | 10.8 | 3.44 | |
| Alkene | Ethylene | 0.011 | 4.15 | 4.2 | 1.13 | |
| Alkyne | Acetylene | 0 | 3.30 | 3.4 | 0.5 | |
| Nitrogen- containing VOCs | Ethylenediamine | 0.024 | 7.21 | 7.3/9.15 | -2.04 | |
| | Ethylamine | 1.22 | 5.84 | / | -0.18 | |
| | Acrylonitrile | 3.915 | 6.36 | 6.4 | 0.25 | |
| Chlorinated VOCs | Chloromethane | 1.841 | 4.34 | 4.5 | 1.09 | |
| | Chloroethylene | 1.329 | 6.05 | 6.2 | 1.62 | |
| Oxygen- containing VOCs | Formaldehyde | 2.247 | 2.73 | 2.8 | 0.35 | |
| | Acetaldehyde | 2.775 | 4.68 | 4.6 | 0.63 | |
| | Acetone | 2.989 | 6.51 | 6.6 | -0.24 | |
| | Methanol | 1.668 | 3.38 | 3.4 | -0.77 | |
| Sulfur- containing VOCs | Methyl mercaptan | 1.413 | 5.30 | 5.5 | 0.78 | |
| Aromatic VOCs | Benzene | 0.000 | / | 10.7 | 2.13 | |
| | Toluene | 0.406 | / | 12.3 | 2.73 | |
| | Benzaldehyde | 3.487 | / | 13.1 | 1.48 | |

$$E_{\rm ad} = E_{\rm VOCs/adsorbent} - (E_{\rm VOCs} + E_{\rm adsorbent})$$
⁽²⁾

$$E_{\text{co-ads}} = E_{\text{VOCs-adsorbent/H}_2\text{O}@PMS} - (E_{\text{VOCs}} + E_{\text{adsorbent/H}_2\text{O}@PMS})$$
(3)

where $E_{VOCs/adsorbent}$, E_{VOCs} , $E_{adsorbent/H_2O@PMS}$, $E_{VOCs-adsorbent/H_2O@PMS}$ represent the energies of VOCs/adsorbent, isolate VOCs molecules, H₂O@PMS complexes on the carbon adsorbents, and VOCs-adsorbent/ H₂O@PMS, respectively.

3. Results and discussion

3.1. Adsorption of PMS on SWCNT

The adsorption of PMS on pristine SWCNT was investigated first, and the most energetically stable atomic structure of PMS/SWCNT is shown in Fig. 4(a), with corresponding calculation data listed in Table S1. The results show that the PMS lies on the outer surface of the SWCNT at a distance of 3.128 Å with E_{ads} being -15.91 Kcal/mol and negligible electron transfer Q of 0.02 e between PMS and SWCNT. The lengths of O-O bond (l_{0-0}) and S-O bond (l_{s-0}) in the PMS are almost the same as those in free PMS, and there is no chemical bonding between PMS and SWCNT. We then compared the adsorption behavior of individual H₂O, PMS molecule and H₂O@PMS complex on SWCNT (Fig. 4 (a)-(c)), and found that PMS had preferential adsorption onto the SWCNT with much higher Ead than that of H₂O (-15.91 Kcal/mol for PMS vs -3.66 Kcal/ mol for H₂O as shown in Table S1). Moreover, the adsorption of H₂O on SWCNT was enhanced remarkably to -6.10 Kcal/mol with the addition of PMS, which can be ascribed to the hydrogen bond between H₂O and PMS as demonstrated in the electrostatic potential profile in Fig. S1(a). This enhanced adsorption can improve the hydrophilicity of SWCNT and the contact of the PMS solution droplets with SWCNT, which is helpful to stabilize the solution droplet on the outer surface of SWCNT and further improve the catalytic oxidation performance. Note that the binding between water and PMS had negligible effects on the adsorption structure of H₂O and PMS.



Fig. 4. Adsorption configurations of (a) single H_2O molecule, (b) free PMS, (c) PMS@ H_2O complex on pristine SWCNT and counterparts (d), (e) and (f) on porous SWCNT. The black, red, white, and yellow balls are carbon, oxygen, hydrogen, and sulfur atoms, respectively. The green cycle represents the vacancy boundary (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

3.2. Adsorption of different VOCs on SWCNT

The adsorption behavior of VOCs with varying structure properties on SWCNT were investigated. The adsorption configurations are shown in Figs. S2 and S3, while the corresponding E_{ad} of VOCs and the electron transfer (Q) from the VOCs to SWCNT are listed in Tables 2 and S2 respectively. The results show that the E_{ad} of all VOCs studied in this work are stronger than E_{ads} of water (3.66 Kcal/mol, Table S1), from which we can deduce that VOCs preferentially adsorb on SWCNT compared with water vapor in VOCs exhaust. In addition, there is no chemical bond formation between VOCs and SWCNT with negligible Q, indicating noncovalent weak interaction between VOCs and SWCNT. The dipole moment (*p*) and static average polarizability ($\overline{\alpha}$) of chemicals are two of crucial descriptors for evaluating the noncovalent weak interaction and more specifically the electrostatic interaction. The *p* is the permanent dipole moment of chemicals, while $\overline{\alpha}$ is a critical index reflecting the susceptibility of chemicals' instantaneous dipole moment (μ) to external electric field (E) (Text S3). Therefore, the effects of p and $\overline{\alpha}$ of the VOCs on E_{ad} were investigated to understand the mechanism of this noncovalent weak interaction for an in-depth insight into the selective adsorption of VOCs onto SWCNT. The experimental $\overline{\alpha}$ values of some VOCs molecules considered in this work are absent in the database of US Environmental Protection Agency's EPISuite™. On the other hand, the calculation for $\overline{\alpha}$ of the VOCs with relatively heavy molecular mass (e.g., aromatic derivatives) by DFT method is impressively expensive. Therefore, DFT calculated $\overline{\alpha}$ values were applied to estimate the desired $\overline{\alpha}$ values for this study. As shown in Table 1, the calculated $\overline{\alpha}$ values are in good accordance with experimental data, which is indicative of the good reliability of our computational methodology. The linear relationship between E_{ad} and $\overline{\alpha}$ is shown in Fig. 5(a). The E_{ad} shows strongly linear dependence on $\overline{\alpha}$: $E_{ad} = -0.972\overline{\alpha}$ -1.578 with the coefficient of determination $R^2 = 0.964$. As for the polar molecules, there is no explicit relationship between E_{ad} and p as shown in Fig. 5(a). The results manifest that the surface electrostatic field of the SWCNT has very limited influence on VOCs adsorption energies through *p* of VOCs in this system. Instead, $\overline{\alpha}$ of VOCs predominates the interaction between VOCs and SWCNT.

For further insights into the enrichment behavior of VOCs on SWCNT, the effect of hydrophobic interactions between VOCs and SWCNT on VOCS adsorption was investigated by performing the correlation analysis between E_{ad} and K_{ow} of VOCs. In general, $K_{ow} < 10$ represents hydrophilic molecules, and a higher K_{ow} represents more hydrophobic ones (Schwarzenbach et al., 2003). As clearly illustrated in

Fig. 5(a) that there is no explicit relationship between E_{ad} and log K_{ow} . The poor correlation between the adsorption coefficient and K_{ow} of organic compounds on carbon materials (SWCNT, MWCNT, etc.) has been previously reported (Chen et al., 2007), where focused on the organic contaminant in water body and only the aromatic derivatives of log $K_{ow} > 1$ attracted their attention. Actually, our results for VOCs of log $K_{ow} > 1$ show a similar tendency between adsorption and log K_{ow} to their experimental ones. However, in this work a clear volcano-like tendency can be found at log $K_{ow} = 1$, implying the different effects of hydrophobicity interaction on the E_{ad} of hydrophilic and hydrophobic VOCs.

The findings inspired us to investigate the role of the specific structure of SWCNT in the adsorption behavior of VOCs. Therefore, other carbon materials including multiple walled carbon nanotubes (MWCNT), activated carbon (AC), graphene and porous SWCNT with distinct structure properties were employed for VOCs adsorption as references. The atomic structures of VOCs adsorption on MWCNT, graphene, AC and porous SWCNT were shown in Figs. S3-S6, corresponding E_{ad} and electrons transfer were summarized in Tables 2 and S2 respectively. There was no obvious chemical bond formation observed between VOCs and these carbon supports in Figs. S3-S6 with neglective Q, implying all the adsorption of VOCs on carbon supports are physically noncovalent interaction. Then the relationship between E_{ad} of VOCs on MWCNT, graphene, AC and porous SWCNT and their $\overline{\alpha}$, p and log K_{ow} of VOCs were shown in Fig. 5(b)-(e) respectively. Surprisingly, all the carbon supports shown the same results of VOCs adsorption behaviors that $\overline{\alpha}$ is the predominate factors in VOCs adsorption. The SWCNT, MWCNT and graphene shown comparable R² for the correlation between E_{ad} and $\overline{\alpha}$, varying from 0.964 to 0.970, while R² was slightly dropped to 0.946 for AC and more obviously to 0.856 for porous SWCNT, indicating the porous properties or the defects might influence the role of $\overline{\alpha}$ in VOCs adsorption. To shed light on the origin of the decline of R² for porous SWCNT adsorbent, the surface electrostatic field of porous SWCNT was investigated and the average electrostatic potential curve perpendicular to pristine SWCNT and porous SWCNT surface and corresponding electrostatic potential contour were shown in Fig. 6(a) and (b) respectively. A locally negative weak electrostatic potential can be clearly observed on the surface of porous SWCNT in Fig. 6 (b) with comparation to pristine SWCNT in Fig. 6(a). The negative electrostatic field on the surface of porous SWCNT directly changed the interaction between VOCs and carbon atoms and affected their E_{ad} . To reveal the formation mechanism of this negative electrostatic filed on porous SWCNT, the electrons deformation was studied and shown in

| Table | 2 |
|-------|---|
|-------|---|

The adsorption energy E_{ad} or co-adsorption energy E_{co-ad} . The units of E_{ad} or E_{co-ad} are Kcal/mol.

| VOCs | SWCNT | SWCNT | | Graphene | AC | AC | |
|------------------|-------------------|-----------------|-------------------|-------------|--------------|--------|-------------------|
| | E_{ad} | $E_{\rm co-ad}$ | E_{ad} | $E_{ m ad}$ | $E_{\rm ad}$ | | E_{ad} |
| Methane | -3.61 | -2.11 | -3.59 | -4.83 | -4.34 | -3.27 | |
| Ethane | -5.53 | -3.93 | -4.99 | -7.11 | -5.89 | -4.26 | |
| Propane | -7.03 | -5.52 | -7.99 | -10.08 | -10.27 | -6.57 | |
| Ethylene | -5.98 | -4.28 | -5.07 | -6.87 | -5.78 | -4.98 | |
| Acetylene | -5.23 | -5.02 | -4.34 | -5.81 | -4.22 | -3.90 | |
| Ethylenediamine | -9.25 | -13.87 | -9.55 | -12.52 | -11.10 | -7.51 | |
| Ethylamine | -7.18 | -10.41 | -7.31 | -9.81 | -10.80 | -5.77 | |
| Chloromethane | -6.08 | -4.96 | -5.91 | -7.36 | -7.18 | -5.82 | |
| Chloroethylene | -7.45 | -6.59 | -7.24 | -9.53 | -8.52 | -5.18 | |
| Formaldehyde | -4.49 | -5.62 | -4.83 | -5.67 | -6.24 | -4.82 | |
| Acetaldehyde | -5.95 | -6.51 | -6.93 | -8.73 | -8.07 | -6.15 | |
| Acetone | -8.16 | -9.95 | -9.34 | -12.05 | -9.22 | -7.42 | |
| Methanol | -6.14 | -6.86 | -5.78 | -8.05 | -3.88 | -5.99 | |
| Methyl mercaptan | -6.46 | -6.19 | -6.67 | -8.09 | -8.78 | -6.79 | |
| Acrylonitrile | -7.46 | -7.68 | -8.10 | -10.19 | -8.87 | -7.02 | |
| Benzene | -11.90 | -10.58 | -12.77 | -17.00 | -14.43 | -8.39 | |
| Toluene | -14.51 | -12.77 | -15.13 | -20.41 | -17.56 | -10.37 | |
| Hexane | -13.41 | -12.82 | -14.32 | -18.06 | -15.38 | -11.54 | |
| Cyclohexane | -8.96 | -8.63 | -11.86 | -15.19 | -14.12 | -8.37 | |
| Benzaldehyde | -13.41 | -14.60 | -14.81 | -20.71 | -17.26 | -10.70 | |



Fig. 5. Correlations between the $\bar{\alpha}$, dipole *p*, and log K_{ow} of different VOCs and their adsorption energy E_{ad} or co-adsorption energy E_{co-ad} with PMS on (a) SWCNT, (b) MWCNT, (c) graphene, (d) AC, (e) porous SWCNT.

Fig. 6(d). Obvious electrons accumulation can be observed at the center of the vacancy defect, which can be ascribed to the electrons of dangling bond on the edge carbon atoms. The locally negative electrostatic field resulted from the electrons of dangling bond affect the interaction between VOCs and SWCNT and weaken the influence of $\overline{\alpha}$ on E_{ad} . Therefore, the $\overline{\alpha}$ dominated adsorption mechanism is the result of the electrostatic interaction between VOCs and the positive electrostatic potential on the surface of carbon supports, once the surface electrostatic field changes, the adsorption mechanism might be disturbed.

Based on above discussion, we were motivated to study the effects of PMS and water on VOCs adsorption as the oxygen-rich PMS anion and

water is supposed to also introduce a negative electrostatic field on SWCNT after their adsorption. Thus, the investigation for the coadsorption of VOCs with PMS on SWCNT was conducted, the coadsorption configuration of VOCs and PMS were shown in Fig. S7, corresponding adsorption energy of VOCs $E_{\text{co-ad}}$ and Q were collected in Tables 2 and S2 respectively. The nonvalent interaction was identified with no chemical bond formation and neglective Q during the coadsorption of VOCs and PMS. The correlations between $E_{\text{co-ad}}$ and $\bar{\alpha}$, pand log K_{ow} of VOCs were shown in Fig. 5(a). The results shown the comparable mechanism of VOCs adsorption with those discussed above although the R² was obviously decreased to 0.745, the $\bar{\alpha}$ is still the major



Fig. 6. Electrostatic potential evolution along z axis and the global electrostatic potential of (a) pristine SWCNT, (b) porous SWCNT and (c) PMS@H2O complex on pristine SWCNT, the red and blue colors represent positive and negative potential, respectively, (d) electrons deformation of porous SWCNT, the red color represents electrons accumulation while blue for electrons loss (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

factor that decides the adsorption behavior of VOCs with the existent of PMS and water. The average electrostatic potential curve perpendicular to SWCNT surface and the electrostatic potential contour of PMS@H2O/ SWCNT system were shown in Fig. 6(c), which clearly illustrated that the electrostatic potential above SWCNT had been transformed to negative after PMS adsorption. Thus, the remarkable decline in R² was ascribed to the much stronger negativity induced by the PMS anions and H₂O on SWCNT surface with comparation to that by dangling bond on porous SWCNT.

It is known that $\overline{\alpha}$ is closely related to the molecular weight of VOCs, and the heavier molecules normally possess a larger $\overline{\alpha}$ value. This is the reason that Grimme argued that the molecular size of organic chemicals dominated the intermolecular interaction in some organics' dimers (Grimme, 2008). In general, organic chemicals with the same functional groups can improve their $\overline{\alpha}$ value by prolonging the hydrophobic carbon

chain, resulting in higher hydrophobicity of the organics and larger log $K_{\rm ow}$. Taking the saturated straight-chain paraffin for example, the $\overline{\alpha}$ values of methane, ethane, propane and hexane increase by around $1.8\times 10^{-24}\,\text{cm}^3$ with every additional –CH_2– group in the order of CH_4 $(2.7) < C_2 H_6 \ (4.5) < C_3 H_8 \ (6.4) < C_6 H_{14} \ (11.8) \ (unit \ is \ 10^{-24} \ cm^3,$ Table 1). Meanwhile, $\log K_{ow}$ increases due to the incremental hydrophobic -CH₂- chain: CH₄ (1.09) < C₂H₆ (1.81) < C₃H₈ (2.36) < C₆H₁₄ (3.90) (Table 1). This explains the enhanced adsorption of VOCs of log $K_{\rm ow} > 1$ with the rising $K_{\rm ow}$ in Fig. 5 due to the elevated $\overline{\alpha}$ value. In contrary, the hydrophilic VOCs with relatively less alkyl group components can also improve their $\overline{\alpha}$ values by possessing more hydrophilic functional groups (e.g., oxygen, nitrogen-containing groups) which reduce their K_{ow} values at the same time, resulting in stronger adsorption of VOCs with log K_{ow} decreasing when log $K_{ow} < 1$. For instance, obtaining another $-NH_2$ group, the $\overline{\alpha}$ value of ethylenediamine (7.3) is

improved compared with that of ethylamine (5.9). At the same time, the log $K_{\rm ow}$ of ethylenediamine declines to -2.04 from -0.18 of ethylamine, and the corresponding adsorption energies are enhanced. Therefore, the origin of this volcano tendency is actually the consequence of $\overline{\alpha}$ affecting the adsorption of VOCs on SWCNT.

Another interesting phenomenon is that benzene and cyclohexane have the similar molecular configuration and comparable $\overline{\alpha}$, while both the E_{ad} and E_{co-ad} of benzene are stronger than those of cyclohexane. This can be ascribed to the special π - π interaction between the electron-rich benzene ring and the bulk sp² hybridized carbon on SWCNT surface, which has been reported in previous studies (Rapacioli et al., 2005), although such an effect was found not the dominant factor in the intermolecular noncovalent interaction between organic dimers according to Grimme. In this work, the special π - π interaction was also found in the adsorption of the unsaturated straight-chain paraffin on SWCNT. $\overline{\alpha}$ of ethane (4.5) was a little higher than that of ethylene (4.2), while E_{ad} of ethylene was -5.98 Kcal/mol with comparison to that of -5.53 Kcal/mol for ethane. In this way, the acetylene with a higher degree of unsaturation can provide more delocalized π electrons for the π - π interaction and accordingly should present a stronger π - π interaction with SWCNT. However, E_{ad} of acetylene declined to -5.23 Kcal/mol. The lower $\overline{\alpha}$ value of acetylene (3.4) is responsible for the decline of E_{ad} . Therefore, the influence of the π - π interaction on the adsorption energy of VOCs on SWCNT was inferior to that of $\overline{\alpha}$. From the above discussion, we can deduce that among the multiple influence factors, the static polarizability predominates the adsorption of VOCs on SWCNT, and the hydrophilicity interaction would further improve the adsorption energy when water or PMS exists. As for the structure properties of carbon materials, the morphology properties of carbons can barely affect the adsorption of VOCs but the porous properties or defects could influence the role of $\overline{\alpha}$ in VOCs adsorption due to the evolution of surface electrostatic potential. Therefore, VOCs with larger $\overline{\alpha}$ value, higher ratio of hydrophilic groups to carbon, and that contain unsaturated carbon atom or aromatic benzene ring (for larger molecular size) are expected to be preferentially adsorbed onto SWCNT with the existence of PMS and water.

3.3. Identification of ROSs generation mechanism in the SWCNT/P-AOPs system

Due to the failure of determining the feasibility of PMS activation for the generation of radicals based on the electron transfer from the activator to PMS and the prolonged O-O bond (l_{O-O}) (Table S1), which are desirable for activating PMS into radicals in previous reports (Li et al., 2016; Zhou et al., 2019; Zhao et al., 2019), in this work it was evaluated by investigating the barrier for the cleavage of the O-O bond in PMS and the energy potential profile is shown in Fig. 7(a). Normally it is believed that reactions will proceed readily at room temperature when the reaction energy barrier is lower than 21 Kcal/mol (Zhou et al., 2019; Zhao et al., 2019; Maryasin and Maulide, 2019). The calculated Ebar and EB of PMS decomposition on SWCNT are respectively 16.76 Kcal/mol and -8.02 Kcal/mol, which demonstrate thermodynamically feasible reaction. Interestingly, the spin density population of the final state (FS) by Hirshfeld method in Fig. 8(a) shows the spin density of 0.42 e/Å³ on the oxygen atom of OH species but zero on others, implying the unpaired electrons on OH species, thus producing •OH radical and sulfate anion. In this work, the primary motivation focuses on the predictive possibility for SWCNT@PMS application in VOCs removal. As •OH radical is the final ROSs instead of sulfate radicals in this system, multiple factors should be taken into account, such as the unique electron configuration induced by defects, the role of functional groups, the electronic configuration of organic compounds and so on, which will be investigated in detail in our future work.

To better understand the low energy barrier of PMS activation reaction, we calculated the atomic charge and electron transfer (Q) from SWCNT to PMS for the initial state (IS), transition state (TS) and final



Fig. 7. (a) Energy potential profile of PMS decomposition on SWCNTs and corresponding deformation density in this system. The green color represents electron accumulation while the yellow color represents electron deficiency (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

state (FS) during PMS activation (Table S3). SWCNT charged +1.020 e and the OH and SO₄ species charged -1.69 e totally after the decomposition of PMS. Especially, those carbon atoms near the PMS adsorption site were positively charged, and the most positively charged carbon atoms (C1 and C3) were those close to the oxygen atom from SO₄ group in PMS, implying the SO₄ group was at the frontier of electron transfer between the carbon matrix and PMS. In addition, the partial density of states (PDOS) was calculated to trace the valence electrons of C1 which was the nearest to the O-O bond of PMS. Fig. 9(a)-(c) show that C2p orbit dominates the contribution to the total DOS (TDOS) near Fermi level. As seen in Fig. 9(d), the first peak in the valent band determines the energy level of the highest occupied states of the electrons. The major peaks of C2p orbit in IS, TS, and FS are located at different energy levels in an order of FS (-0.23 eV) > TS (-1.38 eV) > IS (-1.81 eV), which demonstrates the possibility of moving electrons of C2p orbit towards the high energy level in the process of PMS activation. It is known that DOS (i.e., density of states) represents the number of electron states in the energy range *E* to $(E + \Delta E)$: $N(E) \times \Delta E = N_e$, where *N* (E) and N_e are the values of DOS and the number of electrons respectively (Hoffmann, 1988). Based on this definition, the integral of N(E) with respect to energy from the specified level to the Fermi level gives the total number of electrons in this energy range:

$$N_e = \int_E^{Fermilevel} N(E) dE \tag{4}$$

Thus, the larger area of color shadow in Fig. 9(d) represents more electrons. The results show that FS of SWCNT has the most electrons



Fig. 8. (a) Spin density distribution for the energetically favorable configuration of decomposition product by PMS activation on (a) SWCNT and (b) porous SWCNT. C1, C2, C3, C4 and C5 represent carbon atoms at different positions. The boundary of vacancy defect is labeled in green color (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).



Fig. 9. PDOS of C1 from: (a) the initial state (IS), (b) transient state (TS), and (c) final state (FS) during the PMS activation reaction. (d) PDOS of the C2p orbits from (a), (b), (c) are separated and collected in (d). The fermi level is located at 0 eV.

near the Fermi level, followed by TS and finally IS, and the accumulated electrons near Fermi level can hop out from the C2p orbital to activate PMS. Noted that from -3.75 eV to Fermi level in Fig. 9, the component of s orbital in sum of PDOS (TDOS) is 0, implying that the electrons in this energy range are p_z-p_z (the 2p orbital perpendicular to SWCNT surface) π electrons instead of p_x-p_y (the 2p orbital parallel to SWCNT surface) σ electrons. Therefore, the contribution of each angular momentum of C2p orbit to atomic charge on C1 was calculated and summarized in Table S4. There is negligible change in the charge of C2p_x and C2p_v orbits in the activation reaction, while the charge of C2p_z decreases from 0.922 e in IS to 0.914 e in TS and finally to 0.907 e in FS. It is reasonable that the absolute value of the change in charge is small, because only one carbon atom is taken into account in the above discussion, and the tendency is enough to demonstrate the loss of π electrons on carbon atoms of SWCNT during PMS activation. Therefore, the mechanism of PMS activation by pristine SWCNT for radicals generation in the present system can be summarized as follows: firstly, the free PMS in droplet is preferentially captured by SWCNT because of the hydrophobicity of the pristine SWCNT, and then the delocalized π electron in the sp² carbon matrix of SWCNT is excited and shuttled to PMS. The electron-gaining PMS tends to prolong the O-O bond and finally cleave to produce \bullet OH radicals and SO₄²⁻ anions. Particularly, in geometry optimization, the isolate PMS decomposes spontaneously through O-O cleavage after obtaining one electron (Fig. S4).

When the existence of dangling bond in the vacancy defects of SWCNT, the effect of porosity properties of SWCNT on PMS activation was studied. The energy stable atomic configuration of H₂O, PMS, and PMS@H₂O adsorption on porous SWCNT were shown in Fig. 4(d)-(f) respectively with corresponding E_{ads} , Q and structure parameters listed in Table S1. No newly formed bond was found during PMS and water adsorption as illustrated in Fig. 4(d)–(f), while Table S1 shows the E_{ads} of PMS and Q were obviously enhanced to -23.00 Kcal/mol and 0.19 e, the distance between PMS and porous SWCNT was decreased from 3.285 to 1.715 Å with comparison to those in pristine SWCNT system, indicating an improved interaction between PMS and SWCNT. Moreover, the O-O was slightly prolonged to 1.470 while S-O shortened to 1.718 Å, implying the tendency of broking O-O bond. Then the activation of PMS on porous SWCNT was investigated and the energy potential profile was shown in Fig. 7(b). As clearly seen in Fig. 7(b), the E_{bar} was significantly decreased to 4.57 Kcal/mol with an explosive $E_{\rm R}$ of -142.96 Kcal/mol, suggesting an impressively promoted catalyzation of O-O cleavage in PMS. However, the electrons deformation analysis of FS in Fig. 7(b) manifests that the catalysis product OH and SO₄ species were bonded to the edge carbon atoms of vacancy defect. The spin density analysis in Fig. 8(b) shows that there are not any unpaired electrons on the surface bonded OH and SO₄ species, implying the deactivation of the generated ROSs. This is to say PMS catalyzation by vacancy defect of SWCNT should exactly be a consuming process rather than an effective activation for radical's generation which has been emphasized in previous studies (Oh et al., 2016). This finding suggests that the role of dangling bond of edge carbon atoms in PMS activation should be reconsidered in future.

3.4. Mineralization of formaldehyde in the SWCNT/P-AOPs system

Formaldehyde was selected as a model molecule for subsequent degradation investigation to further understand the feasibility of SWCNT/P-AOPs for practical VOCs removal. Herein, possible degradation pathways of formaldehyde were investigated in detail to provide direct evidences for clearly clarifying the mechanism of formaldehyde decomposition in our catalytic system. The energy potential profile of the possible degradation pathways for CH₂O is shown in Fig. 10, and the corresponding thermodynamic properties E_{bar} , E_{R} are listed in Table S5. Despite that the initial step is barrier-free for all the three pathways, energy barriers are present for the •OH addition reaction at the subsequent steps. Fig. 10 clearly shows that Pathway II is favorable with the



Fig. 10. Energy potential profile for possible degradation pathways of formaldehyde by •OH radicals. The star represents the rate-determining step of corresponding pathways.

lowest energy barrier for the rate-determining step, i.e., dehydrogenation of formic acid by \bullet OH and \bullet COOH generation. The E_{bar} and E_{R} for this step are respectively 2.16 Kcal/mol and -28.15 Kcal/mol, much lower than those in Pathways I and III at the corresponding ratedetermining steps. The Ebar and ER in Pathways I are respectively 15.75 Kcal/mol and 10.19 Kcal/mol, and they are 65.81 Kcal/mol and 19.25 Kcal/mol in Pathways III, respectively. The ultralow E_{bar} in Pathways II is in good agreement with the experimentally reported value of 1.96 Kcal/mol in the hydrogen abstraction reaction from aquatic formic acid under the attack of •OH (Chin et al., 1994). Thus, from the thermodynamic perspective with relatively low energy barriers, Pathways I and II are available for formaldehyde degradation in our system, and Pathway II is the dominative pathway for its negligible energy barrier and more negative values of $E_{\rm R}$ for the entire reaction process, which is indicative of the ultrafast degradation of CH₂O. For the degradation of formic acid to CO along Pathway III, the ultrahigh barrier of 65.81 Kcal/mol and the positive $E_{\rm R}$ manifest that it is thermodynamically infeasible, indicating the low possibility to produce the byproduct of toxic CO.

3.5. Migration of formaldehyde on the SWCNT in P-AOPs system

As discussed above, VOCs gases are mainly degraded at the adsorption sites of the PMS solution droplets. For those directly adsorbed at the hydrophobic sites on SWCNT surface, the diffusion behavior of VOCs molecules over the SWCNT surface was investigated for the feasibility of VOCs moving to the reaction sites. Fig. 11 (a) and (b) show the mimic diffusion pathways of formaldehyde to the water droplet over SWCNT. The $E_{\text{diff-bar}}$ and E_{diff} are respectively 1.60 and -3.76 Kcal/mol in the axis direction, and they are 2.69 and -3.98 Kcal/mol respectively in the peripheral direction. The effect of porous properties of SWCNT on formaldehyde diffusion was also taken into consideration. As Fig. 11(c) and (d) illustrated that when the formaldehyde migrates beyond the vacancy defect, the *E*_{diff-bar} and *E*_{diff} in the axis direction and peripheral direction fallen by almost a half to 0.93 and 1.32 Kcal/mol respectively, implying the porosity can facilitate the formaldehyde migration. The ultra-low diffusion barrier and exothermic process demonstrate that the diffusion of formaldehyde from hydrophobic site to water droplet site on the SWCNT is thermodynamically feasible. Thus, SWCNT with synergistic adsorption and catalysis functionality can provide the platform for VOCs and PMS solution residing, the ultrafast degradation of dissolved VOCs molecules in PMS solution droplets make it possible to continuously release more active sites for re-adsorbing residual VOCs molecules, and the fast diffusivity further makes the residual VOCs adsorbed on SWCNT surface feasible to move toward PMS solution droplets for degradation. Note that corresponding experiments are currently going at



Fig. 11. Schematic diffusion pathways for formaldehyde towards water droplet along (a) axis direction and (b) peripheral direction of SWCNT, and the counterparts on porous SWCNT (c) and (d). The boundary of vacancy is labeled in green color in panel (c) (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

our research group, and preliminary results demonstrated validation of this SWCNT/P-AOPs catalytic oxidation system for VOCs treatment, which will be reported in our future works.

4. Conclusions

In this work, the SWCNT/P-AOPs catalytic oxidation system, was firstly extended to remove VOCs in industrial waste gases through spraying PMS solution over SWCNT. The crucial factors involving the VOCs adsorption and PMS activation by SWCNT were comprehensively investigated. The adsorption energies of VOCs on carbons are significantly dependent on the polarizability $\overline{\alpha}$ of VOCs, which is of paramount significance for understanding the adsorption mechanism of VOCs on SWCNT. The electron transfer mechanism for PMS activation of radical pathway by SWCNT was identified by multiple evidences including PDOS, Hirshfeld charge and thermodynamics analysis. The π electrons of bulk carbon atoms in SWCNT were found to be responsible for O-O dissociation in PMS, and •OH as the generated ROSs was identified, improving the understanding of PMS activation mechanism by SWCNT or other carbocatalysts. Formaldehyde was taken as a model pollutant to evaluate the catalytic degradation pathways via SWCNT/P-AOPs. The ultrafast degradation and diffusivity of formaldehyde with no CO byproduct was demonstrated via SWCNT/P-AOPs. Therefore, this work provided an in-depth understanding of the intrinsic nature of SWCNT for VOCs adsorption and PMS activation for ROSs generation with promising application of SWCNT/P-AOPs for satisfying VOCs abatement.

CRediT authorship contribution statement

Zhenhua Dai: Investigation, Data curation, Formal analysis, Writing - original draft. Didi Li: Data curation, Writing - review & editing. Zhimin Ao: Conceptualization, Supervision, Funding acquisition, Validation, Writing - Review & editing. Shaobin Wang: Supervision, Writing - review & editing. Taicheng An: Writing - review & editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jhazmat.2020.124684.

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