Understanding of the Oxidation Behavior of Benzyl Alcohol by Peroxymonosulfate via Carbon Nanotubes Activation

Jiaquan Li, Mengting Li, Hongqi Sun, Zhimin Ao,* Shaobin Wang,* and Shaomin Liu*

ABSTRACT: Selective oxidation of benzyl alcohol (BzOH) into benzaldehyde (BzH) is very important in synthetic chemistry. Peroxymonosulfate (PMS) is a cheap, stable, and soluble solid oxidant, holding promise for organic oxidation reactions. Herein, we report the catalytic PMS activation via carbon nanotubes (CNTs) for the selective oxidation of BzOH under mild conditions without other additives. A remarkable promotion of BzH yield with a selectivity over 80% was achieved on modified CNTs, i.e., O-CNTs via the radical oxidation process, and the oxygen functionalities for catalysis were comprehensively investigated by experimental study and theoretical exploration. To understand the different surface oxygen species on CNTs for the activation of PMS, density functional theory (DFT) calculations were performed to investigate the adsorption behavior of PMS on various CNTs. The electrophilic oxygen was identified as the electron captor to activate PMS by O–O bond cleavage to form $\text{SO}_5^{\ddagger}$ and $\text{SO}_4^{\ddagger}$ radicals. The nucleophilic carbonyl groups can also induce a redox cycle to generate *OH and $\text{SO}_4^{\ddagger}$ radicals, but phenolic hydroxyl groups impede the radical process with antioxidative functionality. The carbocatalysis-assisted PMS activation may provide a cheap process for the selective oxidation of alcohols into aldehydes or ketones. The insight achieved from this fundamental study may be further applied to other organic syntheses via selective oxidation.

KEYWORDS: carbon nanotubes, peroxymonosulfate, selective oxidation, radical process, oxygen functionalities

INTRODUCTION

Selective oxidation of alcohols into aldehydes or ketones is one of the most important reactions in the synthesis of organic compounds. Benzyl alcohol (BzOH) oxidation has attracted extensive attention because the produced benzaldehyde (BzH) can serve as a versatile intermediate in the manufacture of many fine chemicals. A variety of reaction routes have been developed based on different catalysts and oxidants. Stoichiometric metal oxides (chromates and permanganates) and peroxides (hydrogen peroxide and t-butylhydroperoxide) are frequently employed as oxidants, where the former oxidants cause pollution by the nature of heavy metals and the latter suffer from the poor stability in storage and transportation. In view of green chemistry, molecular oxygen as an oxidant has economical and environmental advantages over other oxidants. Noble metals such as Au and Pd can catalyze BzOH oxidation with high efficiency under moderate conditions, but large-scale applications are hampered by the scarcity and high cost of the catalysts. Transition-metal-based catalysts are developed as substitutes for noble metals, but high reaction temperatures or extra additives/co-catalysts are the major issues impeding the application of O$_2$ as an oxidant.

Peroxymonosulfate (PMS, $\text{HSO}_5^-$), as a chemically stable and inexpensive solid oxidant, has received continuous attention in the oxidation of alcohols and can afford high ketone/aldehyde yields. Nevertheless, PMS in these cases only serves as the precursor to generate the actual oxidizing agents through the reaction between PMS and some additives such as ketones, o-iodoxybenzoic acid, 2-iodoxybenzenesulfonic acid, and Cl$^-$/Br$^{\ddagger}$ instead of using as an oxidant in the alcohol oxidation. Recently, it has been reported that PMS can be activated by carbon catalysts and present superior activity in advanced oxidation processes (AOPs) for aqueous contaminant degradation. Metal-free carbon materials such as carbon nanotubes (CNTs), reduced graphene oxides, and nanodiamonds can afford high activity in phenol degradation under mild conditions, and the carbonyl groups would facilitate the electron transfer from an sp$^2$ carbon network to PMS to generate highly reactive radicals. However, there is still a lack of systematic investigation on the catalytic roles of other oxygenated functional groups in PMS activation with high activity in phenol degradation under mild conditions, and the carbonyl groups would facilitate the electron transfer from an sp$^2$ carbon network to PMS to generate highly reactive radicals.
solid experimental evidence. In addition, to the best of our knowledge, the feasibility and efficiency of carbocatalyst-activated PMS in the selective oxidation of BzOH have never been reported.

In this paper, we present a novel process of selective oxidation of BzOH with CNT-activated PMS as the terminal oxidant. PMS was activated by annealed O-CNTs under benign conditions without any additives for BzOH oxidation. Experimental and theoretical studies on the catalytic roles of different surface oxygen species on CNTs, including carbonyl, phenolic hydroxyl, and carboxylic acids and electrophilic peroxide/superoxide, were comprehensively conducted. The oxidizing species responsible for BzH formation were identified in detail.

**RESULTS AND DISCUSSION**

Commercial multiwalled carbon nanotubes (MWCNTs) were first sonicated in a mixture of nitric acid and sulfuric acid to remove metal residuals and introduce oxygen species onto the carbon surface to obtain O-CNT. Then, the O-CNT was annealed in N2 at different temperatures between 400 and 1000 °C for the removal and redistribution of surface oxygen groups. The samples obtained are noted as OCNT-400, OCNT-600, OCNT-800, and OCNT-1000. According to transmission electron microscopy (TEM) images (Figure S1), both O-CNT and OCNT-800 are rich in crooked tubular segments and amorphous carbon fragments on the outer layer of the tubes, contributing to the structural and topological defects. The ratio \( I_D/I_G \) from Raman spectra (Figure 1) reflects the defectiveness of CNT samples, and the \( I_D/I_G \) value increased from 0.97 to 1.57 after the oxidation of original MWCNT due to acid etching and tube shortening. The \( I_D/I_G \) value further increased as the annealing temperature increased, and \( I_D/I_G \) of OCNT-1000 can reach 1.91. The results indicate that the high-temperature annealing treatment introduces numerous defect sites from the decomposition of oxygen groups.

Catalyst performance tests were conducted in aqueous acetonitrile to afford adequate solubility for both aromatic compounds and PMS. Table 1 lists the catalytic performances of various catalysts in BzOH oxidation by PMS. The reaction temperature was controlled at 50 °C, much lower than the typical selective oxidation by \( \text{O}_2 \). Without catalyst addition, only 14.7% conversion of BzOH and a very minimal BzH yield (1%) were observed (entry 1) through the self-activation of PMS. After adding MWCNT, BzOH conversion and BzH yield were increased, but to a very limited degree. The presence of oxygen species on the carbon surface (O-CNT) immediately conferred the catalytic system a higher reaction efficiency up to 22.8% BzH yield, due to the generation of active oxygen species on the CNT surface. After annealing of O-CNT, the catalytic activity of the O-CNT was further enhanced and the BzH selectivity/yield was significantly increased with the highest values up to 80.1/46.2% for OCNT-800 (at an annealing temperature of 800 °C). To shed some light on the reaction pathway, an oxygen-free process was conducted by removing the dissolved oxygen from the solvent via flowing \( \text{N}_2 \) through the reaction solution (entry 7). There was no decline in BzH yield in \( \text{O}_2 \)-free solution, indicating that the activation of PMS and the selective oxidation process are independent of the dissolved \( \text{O}_2 \). In comparison to metal-free CNT catalysts, a noble-metal material (commercial Pt@Al2O3, 1 wt % of Pt, entry 9) and a transitional-metal oxide (commercial \( \text{Fe}_3\text{O}_4 \), entry 10) were tested under the similar reaction conditions, but their oxidation efficiencies were much lower than the annealed CNTs. Notably, neither benzoic acid nor other byproducts were found in the above cases according to gas chromatography–mass spectrometry (GC–MS) results, indicating that BzOH was either partially oxidized into BzH or fully oxidized into \( \text{CO}_2/\text{H}_2\text{O} \) in this reaction system.

Previous studies reveal that carbon-based catalysts can activate PMS to generate hydroxyl radicals (\( \cdot\text{OH} \)) and sulfate radicals (\( \text{SO}_4^{2-} \)) for the degradation of aqueous organics. A nonradical process also exists in AOPs through adsorption/chemical bonding between the organic substrates/\( \text{O}−\text{O} \) bond of PMS and sp²-hybridized carbon network after N heteroatom doping, where the carbon catalyst acts as a bridge to enable the electron transfer from the organic compounds to PMS. The radical generation routes of \( \cdot\text{OH}, \text{SO}_4^{2-} \), and \( \text{SO}_5^{2-} \) from PMS are presented in eqs 1–4. The \( \text{SO}_4^{2-} \) radicals are reported to have a higher oxidation potential (2.5–3.1 V) than \( \cdot\text{OH} \) (2.7 V) and \( \text{SO}_5^{2-} \) (1.1 V). In addition, \( \text{SO}_4^{2-} \) radicals can produce \( \text{SO}_3^{2-} \) radicals and singlet oxygen (\( \cdot\text{O}_2 \)) by self-decomposition (eq 5).

Table 1. Selective Oxidation of Benzyl Alcohol by Various Catalysts

<table>
<thead>
<tr>
<th>entry</th>
<th>catalyst</th>
<th>BzOH conversion (%)</th>
<th>BzH selectivity (%)</th>
<th>BzH yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MWCNT</td>
<td>14.7</td>
<td>6.8</td>
<td>1.0</td>
</tr>
<tr>
<td>2</td>
<td>O-CNT</td>
<td>22.2</td>
<td>62.6</td>
<td>13.9</td>
</tr>
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<td>3</td>
<td>OCNT-400</td>
<td>39.1</td>
<td>58.3</td>
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</tr>
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<td>4</td>
<td>OCNT-600</td>
<td>47.0</td>
<td>80.9</td>
<td>38.1</td>
</tr>
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<td>OCNT-800</td>
<td>57.9</td>
<td>72.2</td>
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</tr>
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<td>OCNT-1000</td>
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<td>46.2</td>
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<tr>
<td>7b</td>
<td>OCNT-800</td>
<td>59.2</td>
<td>79.1</td>
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</tr>
<tr>
<td>8</td>
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<td>75.3</td>
<td>45.4</td>
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<td>Pt@Al2O3</td>
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<td>71.2</td>
<td>12.8</td>
</tr>
<tr>
<td>10</td>
<td>Fe3O4</td>
<td>10.9</td>
<td>21.7</td>
<td>2.4</td>
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</tbody>
</table>

*Reaction conditions: 10 mg of catalyst, 0.2 mmol BzOH, 0.22 mmol PMS, 10 mL of acetonitrile/water (1:1, volume ratio), 50 °C, 5 h. The dissolved oxygen in the solvent was removed before reaction by continuous \( \text{N}_2 \) bubbling, and the reaction was carried out under \( \text{N}_2 \) protection.*
radicals (Figure 2a) and $^1$O$_2$ (Figure 2b) during the reactions was recorded by in situ electron paramagnetic resonance (EPR) using 5,5-dimethyl-1-pyrroline N-oxide (DMPO) and 2,2,6,6-tetramethyl-4-piperidinol (TMP) to trap the radicals and singlet oxygen, respectively. The peak intensities of the $^·$OH/SO$_4$$^{2−}$ radicals and singlet oxygen induced by CNTs followed the sequence of OCNT-800 > O-CNT > free PMS, demonstrating that the annealed O-CNT produced more radicals and $^1$O$_2$ species than the O-CNT without annealing.

$$\text{HSO}_3^- + e^- \rightarrow ^·\text{OH} + \text{SO}_4^{2−} \quad (1)$$
$$\text{HSO}_3^- + e^- \rightarrow \text{OH}^- + \text{SO}_4^{−}^- \quad (2)$$
$$^·\text{OH} + \text{SO}_4^{2−} \leftrightarrow \text{OH}^- + \text{SO}_4^{−}^- \quad (3)$$
$$\text{HSO}_3^- - e^- \rightarrow \text{H}^+ + \text{SO}_4^{−}^- \quad (4)$$
$$2\text{SO}_3^{2−} \rightarrow \text{SO}_4^{−}^-\text{O}_2\text{SO}_4^{−}^- \rightarrow ^1\text{O}_2 + 2\text{SO}_4^{−}^- \quad (5)$$

To identify the intrinsic oxidizing components that are responsible for the conversion of BzOH and the formation of BzH, we further conducted a series of quenching experiments. Ethanol and tert-butanol (TBA) were adopted as quenching agents owing to their different scavenging abilities. Ethanol is used to quench $^·$OH and SO$_4$$^{2−}$ radicals with high reaction rates. tert-Butanol (TBA) is an effective $^·$OH scavenger but less effective in scavenging SO$_4$$^{2−}$. The quenching reaction rate constants for the two scavengers are summarized in Table S1. A comparison of quenching effects in low (1 equiv of PMS) and high (100 times of PMS) dosages of the quenching agents on the oxidation efficiency with OCNT-800 is displayed in Figure 2c,d. The dosage of TBA did not cause a severe decrease of the oxidation efficiency, and there is only 10% loss of BzH yield with 100 times of TBA loading, indicating that the $^·$OH radicals play a minor role in the BzH formation. A substantial decrease in BzH yield was observed when ethanol was added, with only 2% BzH yield remained at 100 times of ethanol dosage. The quenching results reveal that SO$_4$$^{2−}$ radicals with a high oxidative potential significantly contribute to the selective oxidation of BzOH into BzH whereas the radical formation processes via eqs 1−4 suggest that the electron transfer between PMS and carbocatalysts plays a pivotal role in radical generation by either electron gain or loss. The oxygenated functional groups and defect sites on CNTs can break the inertness of the highly stable sp$^2$ graphitic structure and act as catalytic active sites. A wide range of oxygen species, including ketonic carbonyl (C═O), phenolic hydroxyl (C−OH), and carboxylic acid (COOH) groups, coexist on CNTs. In the view of electroafrica, there are electrophilic (peroxides and superoxides) and nucleophilic (e.g., C═O) oxygen species on carbocatalysts. The electrophilic peroxy ($O_2^{2−}$) and superoxide ($O_2$$^−$) species are electron-deficient and tend to attack electron-rich molecules. The electron-rich C═O groups can serve as an electron donor. In general, both nucleophilic C═O and electron-rich groups can activate PMS to generate reactive radicals through electron transfer between PMS and oxygen functional groups. Meanwhile, in the field of polymer materials, it is known that hindered phenolic antioxidants are able to prevent the degradation of polymers since the phenolic groups can give H atoms to stop the free-radical chain reaction. Therefore, phenolic hydroxyl groups on a carbocatalyst may possess similar functionality to capture the generated radicals and impede the selective oxidation of BzOH.

In this study, the iodometric titration method was used to quantitatively determine the amount of surface electrophilic oxygen species from the peroxides or superoxides on the CNT catalysts. The derived amount of I$_2$ by Na$_2$S$_2$O$_3$ titration can quantitatively reflect the presence of the electrophilic oxygen species (Supporting Information). Such an iodometric oxidation method can be specifically used to deactivate the electrophilic oxygen groups, which will be discussed in the future study.

Figure 2. EPR spectra of O-CNT- and OCNT-800-catalyzed PMS activation in the presence of (a) DMPO (DMPO-$^·$OH—●, DMPO-SO$_4$$^{−}^-$—⧫) and (b) TMP. (c, d) Quenching effects on the selective oxidation of benzyl alcohol. Reaction conditions: 10 mg of OCNT-800, 0.2 mmol BzOH, 0.22 mmol PMS, 10 mL of acetonitrile/water (1:1, volume ratio), 50 °C, 5 h.
reaction mechanism. The contents of the surface oxygen before and after the catalytic reaction and the amount of electrophilic oxygen derived from pristine MWCNT and O-CNTs annealed at different temperatures are presented in Table 2. After acid etching/oxidation, a remarkable increase of the total oxygen content and electrophilic oxygen was observed on MWCNT. As the annealing temperature increased, the total oxygen content reduced due to the decomposition of the oxygen species with different thermal stabilities. Meanwhile, the amount of electrophilic oxygen increased with rising annealing temperature because the desorption of oxygen groups (carboxyl, lactone, ether, etc.) in thermal treatment leads to the exposure of highly active defect sites, on which the oxygen groups (Scheme S1) can be formed in an oxygen-containing atmosphere. Notably, the content of the electrophilic oxygen (8.7 × 10⁻⁴ mol/g cat.) was observed to be the highest on OCNT-800 and at a lower amount on OCNT-1000. At the temperature exceeding 1000 °C, the phenolic hydroxyl and carbonyl groups started to decompose accompanied by the vanishing of some structural defects. The deconvolution of O 1s X-ray photoelectron spectroscopy (XPS) (Table 2 and Figure S2) of different annealed O-CNT shows the coexistence of C=O, O==C−O, and C−O groups on CNTs. OCNT-1000 contained less C=O groups but more O==C−O and C−O groups than OCNT-800, indicating that the defect sites on OCNT-1000 were more likely to generate O==C−O/C−O instead of C=O. As a result, the regeneration of C==O and electrophilic oxygen are impeded on OCNT-1000.

The electrophilic oxygen groups on MWCNT, O-CNT, and OCNT-800 were then selectively deactivated (MWCNT-KI, OCNT-KI, and OCNT-800-KI) by iodometric oxidation to unveil the catalytic role of the electrophilic oxygen in PMS activation. The catalytic performances of those samples before and after the titration are displayed in Figure 3. Though the activity of MWCNT, O-CNT, and OCNT-800 varied greatly in PMS activation, the samples showed consistent performances after the electrophilic oxygen groups were eliminated. The BzOH conversion and BzH yield dramatically decreased to approximately the same level after the titration treatment for the three samples. Notably, OCNT-800-KI gave even slightly lower activity than OCNT-KI, agreeing well with the peak intensity variation in EPR (Figure S3). We can infer that the enhanced catalytic performance after annealing of O-CNT mainly originates from the generation of electrophilic oxygen species, which contribute to the effective production of SO₅⁻² and SO₄⁻ radicals.

The catalytic behavior of the C==O, C−OH, and COOH groups in the oxidation of BzOH was further explored by selective deactivation and small-molecule mimics of each group. The three target oxygen groups (C==O, C−OH, and COOH) on O-CNT were deactivated by phenylhydrazine (PH), benzoic anhydride (BA), and 2-bromo-1-phenyl-ethanone (BrPE), respectively, to obtain the relevant derivatives through highly specific reactions between the titrants and oxygen groups (Scheme S1). The derived samples were referred to as OCNT-PH, OCNT-BA, and OCNT-BrPE. Meanwhile, p-benzoquinone, 1,2-dihydroxybenzene, and 1,4-dicarboxybenzene were used to mimic C==O, C−OH, and COOH in the absence of catalysts. The selective oxidation results are listed in Table 3. After the C==O groups on O-CNT were deactivated (entry 2), both the BzOH conversion and BzH yield decreased evidently. Meanwhile, adding p-benzoquinone as the mimic of C==O leads to a considerable increase in conversion/yield (entries 5 and 6), confirming that C==O played an essential role as the electron donor in PMS activation. The removal of C−OH on O-CNT slightly enhanced the conversion/yield (entry 3), while the additional C−OH mimics lead to a reduced BzH yield (entry 7). To further confirm the role of C−OH groups, a larger amount of C−OH was produced on O-CNT by wet chemical reduction using NaBH₄. The conversion of O==C−O into C−OH groups (XPS, Figure S4) leads to a significant decrease in the BzH yield from 22.8 to 6.9% on O-CNT (Figure S5). Thus, it can be inferred that the phenolic hydroxyl groups are impediments during the radical evolution. As for carboxyl groups, entries 4 and 8 showed a subtle but still beneficial effect of COOH on the reactions, which might be owing to the C==O in COOH groups. The EPR tests showed that the

![Figure 3. Selective oxidation of benzyl alcohol on CNT catalysts before and after the elimination of surface electrophilic oxygen species by KI. Reaction conditions: 10 mg of catalyst, 0.2 mmol BzOH, 0.22 mmol PMS, 10 mL of acetonitrile/water (1:1, volume ratio), 50 °C, 5 h.](https://dx.doi.org/10.1021/acscatal.9b05273)
Dihydroxybenzene (0.4 mmol) was used to mimic hydroxyl group. The proposed mechanism of PMS activation on CNTs are able to gain electrons from HSO$_5^-$ radicals. Thus, the selective oxidation of BzOH to BzH radicals. The electrophilic peroxide and superoxide −O groups on CNTs to generate *OH and SO$_4^{2-}$ radicals. The electrophilic peroxide and superoxide species on CNTs are able to gain electrons from HSO$_5^-$ and produce SO$_4^{2-}$ radicals, which can be further transformed into SO$_4^{2-}$ radicals. Thus, the selective oxidation of BzOH to BzH is significantly enabled by the radical process. The stability of OCNT-800 in successive tests was investigated, and both the BzOH conversion and BzH yield decreased after each run (Figure S7a). The BzH yield decreased from 47.4% in the first run to 28.1% in the second run and further reduced to 5.6% after the fourth run. Then, the catalyst after the fourth run was annealed at 800 °C (Recovered OCNT-800) and a full recovery was observed (47.6% BzH yield). The deactivation of the carbocatalyst was also found in aqueous contaminant degradation processes using PMS, and our catalyst showed better recovery ability. The XPS survey spectra and O 1s deconvolution demonstrate that the surface oxygen content on the catalyst increased after each run (Figure S7b). The oxidative environment during the reaction mainly induced the regeneration of C−O and O−C−O groups on the carbon surface, while the C=O groups showed some obvious change (Figure S8). The determination of electrophilic oxygen on the catalysts after each run by the iodometric titration (Figure S7b) reveals almost a total consumption of the electrophilic oxygen from the fresh catalyst (8.7 × 10$^{-4}$ mol/g cat.) to the fourth run (0.7 × 10$^{-4}$ mol/g cat.). After the annealing recovery treatment, the amount of electrophilic oxygen increased back to 5.2 × 10$^{-4}$ mol/g cat. It can be inferred that the electrophilic oxygen groups were consumed during the reaction, which is responsible for the fast deactivation of the catalyst. This consumption also confirms the occurrence of electron transfer from PMS to electrophilic oxygen. As a result, the electrophilic oxygen is reduced to enable the radical process for the BzOH oxidation instead of the nonradical process in which the carbon catalyst serves as an electron bridge. The C=O groups stay unchanged after the catalytic reaction because of a reversible conversion between C=O and C−O groups, thus forming a redox cycle.

To fully understand the roles of different oxygen-containing functional groups in promoting the PMS activation, all possible adsorption of PMS molecules (H$_2$SO$_5^-$) on various CNT sites with the lowest energy configuration is described in Figure 4.

<table>
<thead>
<tr>
<th>entry</th>
<th>catalyst</th>
<th>BzOH conversion (%)</th>
<th>BzH selectivity (%)</th>
<th>BzH yield (%)</th>
</tr>
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<tbody>
<tr>
<td>1$^a$</td>
<td>OCNT-c</td>
<td>42.6</td>
<td>52.3</td>
<td>22.3</td>
</tr>
<tr>
<td>2</td>
<td>OCNT-PH</td>
<td>22.2</td>
<td>25.4</td>
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</tr>
<tr>
<td>3</td>
<td>OCNT-BA</td>
<td>48.2</td>
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<td>26.8</td>
</tr>
<tr>
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<td>OCNT-BPE</td>
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<td>49.2</td>
<td>20.9</td>
</tr>
<tr>
<td>5$^a$</td>
<td>C=O</td>
<td>14.7</td>
<td>6.8</td>
<td>1.0</td>
</tr>
<tr>
<td>6$^a$</td>
<td>C−OH</td>
<td>24.6</td>
<td>50.6</td>
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</tr>
<tr>
<td>7$^a$</td>
<td>COOH</td>
<td>14.1</td>
<td>7.0</td>
<td>0.8</td>
</tr>
<tr>
<td>8$^b$</td>
<td></td>
<td>15.4</td>
<td>9.1</td>
<td>1.4</td>
</tr>
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</table>

$^a$Reaction conditions: 10 mg of catalyst, 0.2 mmol BzOH, 0.22 mmol PMS, 10 mL of acetonitrile/water (1:1, volume ratio), 50 °C, 5 h. OCNT-PH/PMS were remarkably weakened compared to O-CNT/PMS (Figure S6). The other two derivates showed no apparent difference in radical generation compared to O-CNT, which also agrees with the results in Table 3 that the catalytic activity of O-CNT was not profoundly altered after C− OH/COOH deactivation. The corresponding data of the adsorption energy and bond length (O−O, −OH, −C=O, −C−O, −C=O, −O−O) are listed in Table 4. For −OH, −COOH, and −C=O groups, their behavior in affecting the O−O bond in PMS (HO−SO$_3^-$) was investigated. For electrophilic −O−O/−O−O groups on CNTs, we focused on their abilities to stretch and cleave the O−H in PMS (H−OOSO$_3^-$) to echo the experimental results. As summarized in Table 4, the bond length l$_{O−O}$ of free PMS molecules is 1.326 Å whereas l$_{O−O}$ was remarkably stretched when PMS was adsorbed on pristine CNT and nucleophilic O-CNT, implying the potential to be transformed into HO and SO$_4^−$. The adsorption energies of PMS on CNTs ranged from

ACS Catal. 2020, 10, 3516–3525

https://dx.doi.org/10.1021/acscatal.9b05273

Research Article

ACS Catal. 2020, 10, 3516–3525

https://dx.doi.org/10.1021/acscatal.9b05273
Table 4. Adsorption Energy (E_{ads}) of PMS on CNT, the O\(–\)O Bond Length (l_{O–O}) of PMS (HO-OSO_3), and the O\(–\)H Bond Length (l_{O–H}) of PMS (H-OSO_3) in Different Density Functional Theory (DFT) Models Shown in Figure 4

<table>
<thead>
<tr>
<th>configuration</th>
<th>E_{ads} (eV)</th>
<th>l_{O–O} (Å)</th>
<th>l_{O–H} (Å)</th>
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<tr>
<td>free PMS</td>
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</tr>
<tr>
<td>(a)</td>
<td>-1.17</td>
<td>1.434</td>
<td>1.004</td>
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<td>(b)</td>
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<tr>
<td>(d)</td>
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<tr>
<td>(e)</td>
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<td>1.005</td>
</tr>
<tr>
<td>(f)</td>
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<tr>
<td>(g)</td>
<td>-1.25</td>
<td>1.438</td>
<td>0.998</td>
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</table>

-1.07 to -1.66 eV, among which the maximum E_{ads} of PMS on HO-CNT was -1.66 eV with the longest l_{O–O} of 1.466 Å. It should be noted that in the case of HO-CNT, the H atom in the -OH group was separated from the O atom and was bonded to the PMS molecule, while the -OH group on CNT was transferred to the C=O group, which helps to explain the highest E_{ads} and longest l_{O–O} in the HO-CNT system. This process implies that the PMS activation on -OH is not feasible from the thermodynamic perspective according to a previous report.\(^{12}\)

Particularly, there is no obvious change in l_{O–O} of PMS when adsorbed by -O–O/\(-/\-O=O\) on the CNTs with comparable adsorption energy to pristine CNT, implying a different activation mechanism for PMS activation in -O–O/\(-/\-O=O\) systems. Thus, based on the experimental results, the cleavage of O–O and O–H bonds of PMS on nucleophilic and electrophilic O-CNTs was investigated using transition-state searching method. The possible energy potential profiles of these reactions are shown in Figure 5. The reaction energy barriers E_b corresponding to different paths are displayed in Figure S9. For the pristine CNT, despite the O–O bond stretching, the E_b value of the O–O bond cleavage to produce SO_4^{2-} was 1.64 and 1.72 eV at bulk carbon and edge sites, respectively. As previously reported, the critical energy barrier of 0.9 eV would determine the possibility of a chemical reaction at room temperature.\(^{47,48}\) Thus, it is difficult to generate radicals through PMS activation by pristine CNT. For PMS activated by nucleophilic O-CNT, the O–O bond cleavage and the energy barrier E_b follow the order of OH > COOH > C=O. The highest E_b of 0.91 eV in the HO-CNT@PMS system demonstrates the ultralow degradation rate of PMS for radical formation. Meanwhile, it was found that in all of these three systems, the generated OH was directly bonded to the carbon atoms on the CNT, implying the possible quenching of *OH by CNT itself. The binding between *OH and CNT results in the decrease of the yield of free *OH radicals, which explains the ultrashort lifetime of *OH in comparison to SO_4^{2-}.\(^{49}\) Particularly, in the case of the HOOC-CNT@PMS system, we found that SO_4^{2-} can be feasibly bonded to the α-C (the C atom directly bonded to -COOH) of the COOH function to form C=SO_4 in geometry optimization. Thus, two pathways of PMS activation by COOH function should be taken into consideration: pathway 1, HSO_5^- + CNT → C=OH + C=SO_4; pathway 2, HSO_5^- + CNT → C=OH + SO_4^{2-}. The calculated E_b values for breaking the O–O bond are 0.35 and 0.40 eV in pathways 1 and 2, respectively. The energy barriers of the two pathways are slightly different, manifesting that they can occur simultaneously on the HOOC-CNT. In addition, the desorption of the SO_4 group from C=SO_4 generated in pathway 1 was investigated to evaluate the possibility of the regeneration of reactive SO_4 radicals (MS to FS for the case of -COOH in Figure 5). The extremely high E_b of 1.48 eV for this process implies that the SO_4^{2-} regeneration is impossible. Thus, the generated SO_4^{2-} radicals from PMS is easily inactivated by the α-C of the COOH function. Therefore, the COOH groups on CNT do not play a dominant role in activating PMS. The rather low E_b of 0.53 eV in O=O=C-CNT@PMS system manifests that the activation of PMS is efficient to break the O–O bond and to produce free radicals, in good consistency with the experimental observation. For electrophilic -O–O– and -C=O=O, it is shown that the H–O bond is broken to produce SO_4^{2-} and, and the energy barrier was calculated to be 0.39 and 0.11 eV respectively, implying that the nucleophilic C=O and electrophilic groups can promote the activation of PMS but in different mechanisms. The ultralow E_b value in electrophilic groups manifests the ultrafast formation rate of SO_4^{2-}, which can subsequently transfer into 1O_2. These simulation results fit perfectly with our experimental observation.

Finally, the effects of different reaction conditions (reaction time, temperature, PMS dosage, catalyst dosage, and solvent) on catalytic efficiency were studied using OCNT-800 as a representative catalyst (Table 5). At increased reaction time (entries 1, 2, 3), temperature (entries 2, 4, 5), and PMS loading (entries 2, 9, 10), both the BzOH conversion and BzH yield increased but the BzH selectivity decreased due to the overoxidation. Notably, the BzH yield reached 56.9% with 92.2% BzOH conversion when the PMS loading was doubled. On the other hand, doubling the catalyst dosage (entry 11) slightly increased the conversion, selectivity, and BzH yield. The reaction is also strongly influenced by the composition of the solvent. Acetonitrile/water turned out to be the best solvent (Table S2), and the catalytic efficiency was enhanced with a higher proportion of acetonitrile in the solvent (entries 2, 6, 7), which is possibly due to the limited aqueous solubility of BzOH and the hydrophobic nature of CNTs.\(^{50}\) A higher acetonitrile/water ratio facilitates the adsorption of BzOH and PMS on CNTs’ surface for further reactions, whereas the overhigh acetonitrile/water ratio (entry 8) leads to poor
H$_2$O$_2$ and PMS can a $\alpha$ quenched by the resulting in a nonsignificant e of electrophilic oxygen. The carbonyl groups treatment conferred highly active defect sites on CNTs for the generation of SO$_5$ and correlated to be the consumable active sites for the electrophilic oxygen species on CNTs were quantitatively determined by selective deactivation and small-molecule mimics. Electro-superoxide groups on CNTs were fundamentally investigated (DFT) calculations con that inhibits the radical process. Density functional theory optimized to further improve the BzH yield.

### EXPERIMENTAL SECTION

#### Preparation of Annealed CNT Samples.
Multiwalled carbon nanotubes (MWCNTs) were purchased from Timesnano, Chengdu, China. The length, inner diameter, and purity of the MWCNTs are 10–30 μm, 10–20 nm, and 95%, respectively. The other chemicals used in this study were supplied by Sigma-Aldrich. To prepare the annealed CNTs, first, 5 g of MWCNT was mixed with 250 mL of an acid mixture composed of 1:3 volume ratio of HNO$_3$ (65–88%) and H$_2$SO$_4$ (95–98%), which was sonicated at 50 °C for 5 h. Then, the acid mixture was diluted and cooled down to room temperature. The oxidized MWCNT was filtered and washed with ultrapure water until the pH of the filtrate reached 7. The precipitate was dried at 60 °C for 48 h and ground to obtain the oxidized carbon nanotubes (O-CNT). Then, O-CNT (0.5 g) was annealed in a N$_2$ atmosphere at 400, 600, 800, or 1000 °C for 1.5 h at a heating rate of 5 °C/min to obtain OCNT-400, OCNT-600, OCNT-800, and OCNT-1000, respectively.

#### Iodometric Titration of Electrophilic Oxygen on Carbons.
A CNT sample (50 mg) was added to a mixture containing 5 mL of KI (40 g/L), 5 mL of H$_2$SO$_4$ (0.05 mol/L), and two drops of (NH$_4$)$_2$Mo$_7$O$_24$ (30 g/L). The reactions between electrophilic oxygen on the CNT surface and KI are shown in eqs 6–7. For convenience, the amount of detected I$_2$ was designated as the total amount of electrophilic oxygen. After 5 min sonication followed by 1 h stirring at room temperature in the dark, I$_2$ was oxidized to I$_3^-$. Then, the precipitate was filtered out and washed with ultrapure water to remove the adsorbed ion and dried at 60 °C for 12 h. All of the filtrate was collected and then 0.3 g of the soluble starch indicator was added to the solution. The I$_2$ in the filtrate was titrated by Na$_2$S$_2$O$_3$ (2 × 10$^{-4}$ mol/L), as demonstrated in eq 8, until the blue color disappeared. The total concentration of the electrophilic oxygen (mol/g cat.) on the sample was calculated by eq 9, where c (mol/g), V (mL), and m (g) represent the electrophilic oxygen concentration, volume consumption of the Na$_2$S$_2$O$_3$ solution, and mass loading of the CNT sample, respectively.
O₂⁻² + 2KI + H₂SO₄ → O²⁻ + 2KHSO₄ + I₂ + H₂O  
(6)

2O₂⁻ + 6KI + 6H₂SO₄ 
→ O²⁻ + 6KHSO₄ + 3I₂ + 3H₂O  
(7)

I₂ + 2Na₂S₂O₃ → 2NaI + Na₂S₄O₆  
(8)

c (electrophilic oxygen) = 1 × 10⁻⁷ V/m  
(9)

Selective Deactivation of Oxynitrogen Groups on OCNT. In the preparation of OCNT-PH, 0.2 g of O-CNT and 0.5 g of phenylhydrazine (PH), and 100 μL of HCl (38%) were mixed in 10 mL of CHCl₃ solvent and stirred at 60 °C for 24 h with N₂ protection. The precipitate was filtered out, washed with CHCl₃ several times, and then dried at 60 °C for 24 h to obtain OCNT-PH.

For the synthesis of OCNT-BA, 0.2 g of O-CNT and 1 g of benzoic anhydride (BA) were mixed in 10 mL of CHCl₃ solvent and stirred at 60 °C for 24 h with N₂ protection. The precipitate was filtered out, washed with CHCl₃ several times, and then dried at 60 °C for 24 h to obtain OCNT-BA.

OCNT-BrPE was prepared as follows: 0.2 g of O-CNT and 0.5 g of 2-bromo-1-phenylethanone (BrPE) were mixed in 10 mL of CHCl₃ solvent and stirred at room temperature for 10 h in a N₂ atmosphere in the dark. The precipitate was filtered out, washed with CHCl₃ several times, and then dried at 60 °C for 24 h to obtain OCNT-BrPE.

The wet chemical reduction of O-CNT was conducted using NaBH₄ to transform the surface C=O into C–OH groups. For the reduction, 0.1 g of O-CNT and 1 g of NaBH₄ were dissolved in 10 mL of ethanol and stirred in a N₂ atmosphere at 50 °C for 12 h. The precipitate was filtered out, washed with HCl and water, and then dried at 60 °C for 24 h to obtain OCNT-NaBH₄.

Catalytic Selective Oxidation of BzOH. In a typical reaction process for the selective oxidation of benzyl alcohol, 10 mg of catalyst was added into 10 mL of the solvent mixture (acetonitrile/water = 1:1, volume ratio) in a 25 mL flask and sonicated for 5 min. Then, 0.2 mmol BrOH and 0.22 mmol PMS (oxone, KHSO₅·0.5KHSO₄·0.5K₂SO₄) were added to initiate the oxidation. The solution was stirred at 50 °C for 5 h. After the flask was cooled down, 0.2 mmol anisole was injected into the flask as an internal standard. A certain volume (1 mL) of the solution was withdrawn by a syringe, and the precipitate was filtered by a Millipore film. The organic compounds in the solution were extracted by 6 mL of toluene for three times, and the organic phase was collected. The composition of the products was analyzed by GC/MS using a 30 m × 0.25 mm × 0.25 μm HP-SMS capillary column and FID detector.

Characterization Measurements. Transmission electron microscopy (TEM) imaging was conducted on a JEOL 2100 microscope. Raman spectra were obtained under ambient conditions on a Renishaw Raman spectrometer with a 785 nm laser beam. X-ray photoelectron spectroscopy (XPS) data were obtained with a Kratos AXIS Ultra DLD system using Al Kα radiation. The base pressure was about 1 × 10⁻⁸ torr. The binding energy value was referenced to the C 1s line at 284.6 eV from defect-free graphite. Deconvolution of the O 1s spectra was performed using mixed Gaussian–Lorentzian component profiles after subtraction of a Shirley background using XPSPEAK41 software. The electron paramagnetic resonance (EPR) was conducted on a Bruker EMS-plus instrument to record the evolution of free radicals during the selective oxidation, and the data were analyzed by Xeon software. 5,5-Dimethyl-1-pyrroline N-oxide (DMPO) and 2,2,6,6-tetramethyl-4-piperidinol (TMP) were used as spin-trapping agents.

Computational Methods. To understand the role of different surface oxygen species on CNTs, including ketonic carbonyl (–C=O), phenolic hydroxyl (C–OH), carboxylic acid (–COOH), and electrophilic peroxide (O–O–)/superoxide (O=O=O), in the activation of PMS, density functional theory (DFT) calculations were performed to investigate the adsorption behavior of PMS on CNTs (including pristine CNT and O-CNTs). The spin-unrestricted DFT calculations were conducted in Dmol3 package using general gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional. An all-electron double numerical plus polarization (DNP) was employed as the basis set. The convergence tolerance of energy was assumed at 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 TS scheme was used in all calculations to take the van der Waals forces into account.

Transmission electron microscopy (TEM) imaging was conducted on a JEOL 2100 microscope. Raman spectra were obtained under ambient conditions on a Renishaw Raman spectrometer with a 785 nm laser beam. X-ray photoelectron spectroscopy (XPS) data were obtained with a Kratos AXIS Ultra DLD system using Al Kα radiation. The base pressure was about 1 × 10⁻⁸ torr. The binding energy value was referenced to the C 1s line at 284.6 eV from defect-free graphite. Deconvolution of the O 1s spectra was performed using mixed Gaussian–Lorentzian component profiles after subtraction of a Shirley background using XPSPEAK41 software. The electron paramagnetic resonance (EPR) was conducted on a Bruker EMS-plus instrument to record the evolution of free radicals during the selective oxidation, and the data were analyzed by Xeon software. 5,5-Dimethyl-1-pyrroline N-oxide (DMPO) and 2,2,6,6-tetramethyl-4-piperidinol (TMP) were used as spin-trapping agents.

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For the PMS molecule adsorbed on CNTs, the adsorption energy E_ads is defined as

E_ads = E_{PMS/CNT} − (E_{PMS} + E_{CNT})  
where E_{PMS/CNT}, E_{PMS}, and E_{CNT} are the total energies of the PMS/CNT system, the isolated PMS molecule, and CNT in the same slab, respectively. To further investigate the activation mechanism of PMS on different CNTs, linear synchronous transit/quadratic synchronous transit (LST/QST) tools in Dmol3 package were used, which have been well validated to determine the structure of the transition state and the minimum-energy reaction pathway.

ASSOCIATED CONTENT
Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.9b05273.

Experimental material, characterizations, and catalytic results; TEM images; reaction rate constants of di ff erent surface oxygen species on CNTs, including ketonic carbonyl (–C=O), phenolic hydroxyl (C–OH), carboxylic acid (–COOH), and electrophilic peroxide (O–O–)/superoxide (O=O=O); EPR spectra of OCNT-800 and OCNT-800-KI; and selective deactivation pathways (PDF)

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the Australian Research Council (ARC) discovery projects (DP170104264, DP190103548), National Natural Science Foundation of China (21607029 and 21777033), Science and Technology Program of Guangdong Province (2017B020216003), and the Innovation Team Project of Guangdong Provincial Department of Education (No. 2017KCXTD012). The authors acknowledge the instrumental support from John de Laeter Centre, Curtin University, for XPS analysis.

■ ABBREVIATIONS USED

BzOH, benzyl alcohol; BzH, benzaldehyde; CNTs, carbon nanotubes; PMS, peroxymonosulfate; AOPs, advanced oxidation processes; DMPO, 5,5-dimethyl-1-pyrroline N-oxide; TMP, 2,2,6,6-tetramethyl-4-piperidinol; TBA, tert-butanol; PH, phenylhydrazine; BA, benzoic anhydride; BrPE, 2-bromo-1-phenylethanone

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