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The effect of surface oxygenated groups of carbon nanotubes on liquid phase catalytic oxidation of cumene

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It is of particular interest to reveal the influence of surface oxygenated groups and surface defects of carbon catalyst on liquid phase oxidation reactions. Herein, the surface oxygenated groups and defects were introduced on the surface of carbon nanotubes (CNTs) using the gas-phase oxidation method with O_2 and the liquid-phase oxidation method with concentrated HNO_3. The result strongly confirms that the surface oxygenated groups on CNTs have a negative effect on catalytic activity for cumene oxidation. To the best of our knowledge, for the first time, we have distinguished experimentally the effect factor that the oxidized CNTs decreased the catalytic activity of liquid phase aerobic oxidation reaction is surface oxygenated groups instead of surface defects. Meanwhile, the mechanism that the oxidized CNTs decrease catalytic activity has also been revealed. It has been proven that the oxidized CNTs serve as free radical quenchers, capturing the free radical intermediate of reaction and inhibiting the free radical chain transfer, thereby reduces the catalytic activity of free radical reaction in liquid phase. This study gains a new insight into the effect of surface structures on carbon-catalyzed liquid phase oxidation, and further pushes forward the research on carbon catalysis.

1 Introduction

Since the landmark report made by Iijima,[1] the carbon nanotubes (CNTs) with a diameter at the nanoscale and a variable length, have attracted intense attention because of their superior physical and chemical properties. Recently, carbon nanomaterials have been developed as an important type of metal-free catalysts. They exhibit superior catalytic performance compared to the traditional metal catalysts in many fields, such as hydrocarbon conversion, fine chemicals production, fuel cells and solar energy.[2,3]

Surface structure of the catalyst has a huge impact on the activity for catalytic reaction. The oxygen-containing functional groups are easily introduced onto the surface of carbon materials, which has intrigued us to investigate the effect of surface oxygenated groups on carbon catalysis. Recently, numerous studies have proven that the oxidized CNTs can catalyze the oxidative dehydrogenation (ODH) of ethylbenzene[4,5] and light alkane[6,7] due to the contribution of surface oxygenated groups. And a widely accepted reaction mechanism proposes that rich-in-electron diketone-like carbonyl groups on the surface of carbon materials are the active sites in gas phase dehydrogenation reactions.[6,8,9] However, the nature of the active sites of carbon catalytic materials is still unclear in many liquid phase oxidation processes because of the much more complicated process than that in the gas phase oxidative dehydrogenation. Besson *et al* [10] found that the selectivity of adipic acid in the liquid phase oxidation of cyclohexanone could be as high as 33% by actively treating carbon material with phenolic resin. But, there was no obvious linear correlation between the amount of oxygenated groups and catalytic activity of cyclohexanone oxidation. Yang *et al* [11,12] suggested that carboxyl groups on carbon nanotubes acting as the active sites were contributed to phenol oxidation reaction, while Aguilar *et al*[13] proposed that the catalytic activity for the catalytic wet air oxidation of ammonia was not affected by the surface acidic groups on carbon materials, but alkaline ketones/benzoquinone groups played the role of active sites. Peng's group[14] found that in the liquid aerobic oxidation of cyclohexane to adipic acid, the surface oxygenated groups on CNTs had a negative effect on catalytic activity. This reason was probably the introduction of functional groups and defects resulting in a localization of electrons, while CNTs with longer range order and electron delocalization are preferred for the reaction. Besides the aerobic oxidation of cyclohexane, a similar reaction mechanism has also been proposed for other aerobic oxidation process, such as ethylbenzene to acetophenone,[15] cyclohexene to cyclohexanone,[16] cumene to hydroperoxide cumene.[17,18] In general, the oxidized CNTs have a negative effect on the liquid phase oxidation of radical-based carbocatalysis. But so far it is very difficult to distinguish experimentally their roles of surface oxygenated groups and defects due to their concurrence on the oxidized CNTs.[15-18] Moreover, it is still unclear how the surface oxygenated groups on CNTs reduce catalytic activity of the liquid phase aerobic oxidation reactions.

To this end, it is of particular interest to reveal the influence of surface oxygenated groups and surface defects on carbon

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on liquid phase oxidation reactions. It is well known that the selective liquid-phase aerobic oxidation of cumene to cumene hydroperoxide (CHP) is extremely important in chemical industry.[17] Herein, the aerobic oxidation of cumene catalyzed by CNTs has been used as an example to explore the role of surface oxygenated groups and defects on carbon nanotubes. The surface of CNTs was modified to introduce surface oxygenated groups and defects using the gas-phase oxidation method with O_2 and the liquid-phase oxidation method with concentrated HNO_3. For the first time, we have distinguished the effect of surface oxygenated groups and surface defects on the liquid phase oxidation reaction. Meanwhile, the mechanism that the oxidized CNTs decreased catalytic activity has been revealed. It has been proven that the oxidized CNTs could serve as free radical quenchers, capturing the free radical intermediate of reaction and inhibiting the free radical chain transfer, thereby reduces the catalytic activity of free radical reaction in liquid phase.

2 Experimental

2.1 Preparation of catalysts

Pristine commercial carbon nanotubes (denoted as CNTs, S_{BET} =79.8 m^2g^{-1}, d= 30-50 nm, Shenzhen Nanotech Port Co. Ltd, China) were stirred in concentrated HCl (12 mol/L) for 2h to remove the residual iron metal. The surface of CNTs was modified to introduce oxygen-containing functional groups and defects with two kinds of methods.

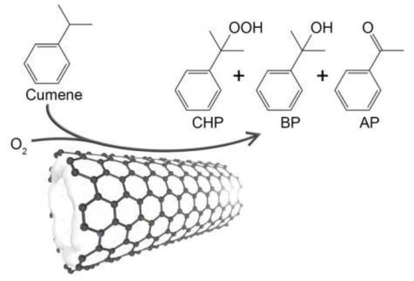
For the gas-phase oxidation method, the acid-washed CNTs were subjected to the oxidation treatment in a horizontal tubular quartz furnace under 5% O_2/He at 300℃, 400℃, 500℃ for 2h and then cooled to room temperature. The as-prepared samples were denoted as CNTs-300, CNTs-400, CNTs-500, respectively. For the liquid-phase oxidation method, the acid-washed CNTs were heated in 9 mol/L HNO_3 and refluxed for 4h and then washed with deionized water until the pH=6~7, finally dried in air at 110℃ for 12h. The obtained samples were denoted as O-CNTs. In addition, O-CNTs were annealed in a horizontal tubular quartz furnace under argon atmosphere at 300℃, 500℃, 600℃, 700℃, 800℃, 900℃ for 2h and cooled to room temperature. These samples were denoted as O-CNTs-300, O-CNTs-500, O-CNTs-600, O-CNTs-700, O-CNTs-800, O-CNTs-900, respectively.

2.2 Characterizations

Brunauer-Emmett-Teller (BET) specific surface areas were measured by N_2 adsorption at 77 K in an ASAP 2010 analyzer. The Raman spectra were obtained in a LabRAM Aramis micro Raman spectrometer with an excitation wavelength at 532 nm with 2 mm spot size. The surface oxygenated groups were analyzed by Boehm titration.[19] X-ray photoelectron spectroscopy(XPS) analysis was performed in a Kratos Axis ultra (DLD) spectrometer equipped with an Al Kα X-ray source in ultrahigh vacuum (UHV) ($<10^{-10}$ Torr). The surfaces of samples were cleaned by heat treatment at 373K in UHV prior to the measurements. The binding energies (±0.2 eV) were referenced to the C1s peak at 284.6 eV. Transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) images were obtained with a FEI Tecnai G2 12 microscope operated at 100 kV and a JEOL JEM-2010 microscope operated at 200kV, respectively.

2.3 Catalytic reaction

The oxidation reactions of cumene were carried out in a three-necked flask (25 mL), supplied with a magnetic stirrer, oil bath and reflux condenser. Cumene (10 mL) and catalysts (100 mg) were added into the flask and sonicated for 1 min, then heated to the preset temperature followed by the bubbling of oxygen at a constant flow rate 10 ml/min. The main product of reaction is cumyl hydroperoxide (CHP), and the by-products are acetophenone (AP) and 2-benzyl-2-propanol (BP), as shown in Scheme 1. The iodometric method was used to determine the concentration of CHP. After the reduction of generated CHP to BP via triphenylphosphine reaction, the other products in the liquid phase were detected by gas chromatography (Agilent GC-6820) equipped with a 30m×0.25mm×0.25μm HP-5 capillary column and a flame ionization detector (detector temperature 493K, injector temperature 473K, and oven temperature 413K) using toluene as external standard.



Scheme 1. The schematic pathway of cumene oxidation on CNTs.

3 Results and discussion

3.1 The effect of surface oxygenated groups on catalytic activity

To explore the effect of surface oxygenated groups on cumene oxidation catalyzed by CNTs, a series of oxidized CNTs were prepared by gas-phase or liquid-phase oxidation, and typical TEM images are shown in Figure 1A. The structure of graphite layers was destroyed by oxidation treatment, forming the oxidized CNTs with holes (Figure 1A-a) or asparagus type (Figure 1A-b) or the collapsed opening (Figure 1A-c). These defects on CNTs could accommodate surface oxygenated groups. The surface composition and defects were investigated by XPS and Raman spectra, and the results are illustrated in Figure 1B and 1C. As shown in Figure 1B, all the samples exhibit two distinct peaks at binding energy of 284 and 532 eV for carbon (C1s) and oxygen (O1s), respectively. The peak area at 532 eV increased with the degree of oxidation increasing. Obviously, the total oxygen content on CNTs increased with the gas-phase oxidation temperature increasing. Meanwhile, CNTs treated by nitric acid could introduce the maximum content of oxygen functional groups, and the oxygen content on surface of CNTs reached to 5.73 at.%. Boehm titration was used to determine the distribution of surface oxygenated groups.[20] Table 1 indicates that the content of hydroxyl on the surface of the CNTs slightly decreases with the temperature increasing in gas phase oxidation,

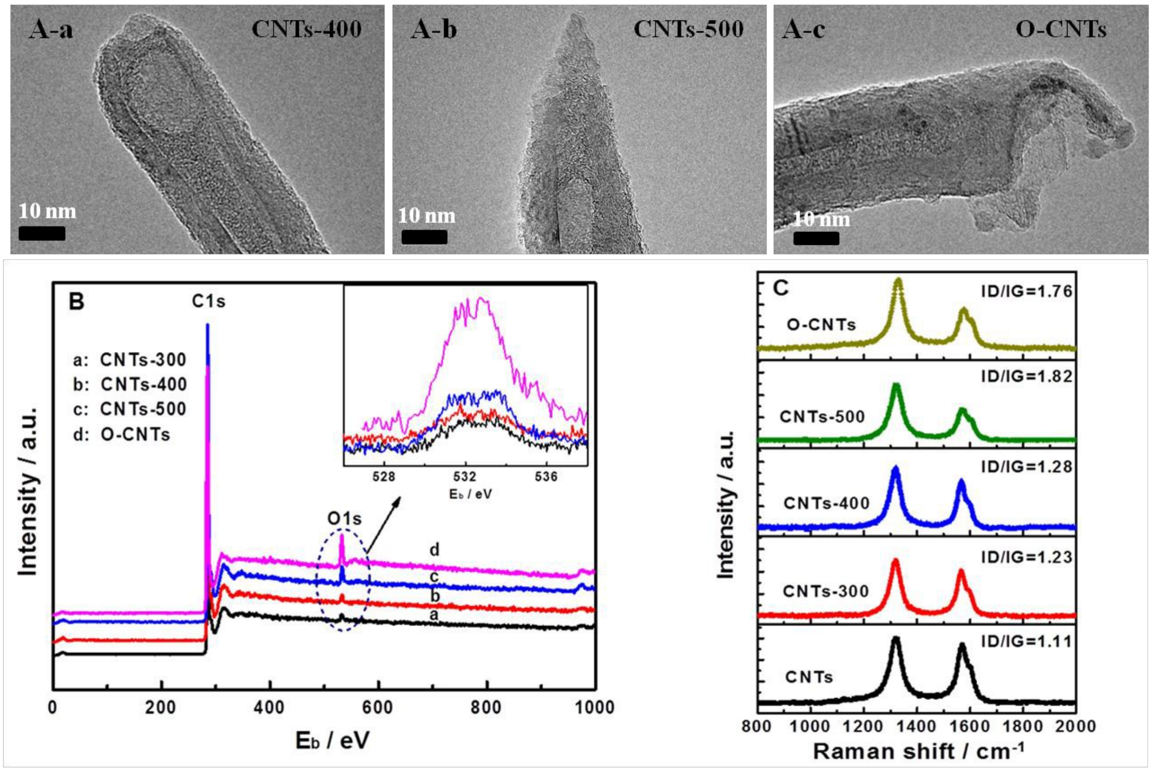


Figure 1. TEM images (A), XPS (B) and Raman spectra (C) of samples

while the amount of carboxyl increases obviously. The total percentage of oxygenated groups increases with enhancing the oxidation degree. Moreover, O-CNTs from liquid-phase oxidation gained the maximum amount of oxygen species and the surface oxygenated groups are mainly composed of carboxyl. These results are agreement with the XPS analysis.

From Figure 1C, it can be seen two characteristic peaks at approximately 1580 cm^{-1} (G-band) and 1320 cm^{-1} (D-band). The G-band corresponds to the optical phonon modes of E2 g symmetry in graphite indicating the presence of crystalline graphite carbon, whereas the D-band is attributed to disorders and structural defects in the graphite structure.[20,21] The intensity ratio of D-band to G-band, namely, I_D/I_G is used to evaluate the defects of carbon-based nanostructures.[22] The higher I_D/I_G is, the more defects in the carbon-based nanostructures have. The result shows that the value of I_D/I_G increased with the gas-phase oxidation temperature increasing. In addition, O-CNTs had a high I_D/I_G, which is similar to that of CNTs-500. Combining with the TEM, Raman and XPS results, it can be concluded that both oxygen oxidation and nitric acid oxidation could introduce the oxygenous groups and defects on the surface of the CNTs.

Table 1. Characterization results and catalytic activity of CNTs treated by different methods

Catalysts	Boehm titration, mmol/g			O content [a] at%	I_D/I_G [b]	Conversion [c] %
	-OH	-C=O	-COOH			
CNTs	0.26	0.19	0.4	1.32	1.11	24.06
CNTs-300	0.27	0.21	0.97	2.25	1.23	23.12
CNTs-400	0.26	0.17	1.35	2.39	1.28	17.78
CNTs-500	0.18	0.22	1.60	4.91	1.82	7.09
O-CNTs	0.31	0.08	1.91	5.73	1.76	0.60
CNTs-400-T	0.21	0.14	0.26	1.29	1.20	29.57
CNTs-500-T	0.26	0.08	0.19	1.89	1.80	28.96

[a] From XPS results; [b] From Raman spectra; [c] Reaction conditions: catalyst (10 mg), cumene (10 ml), O_2 (10 ml/min), 353 K and 8 hrs.

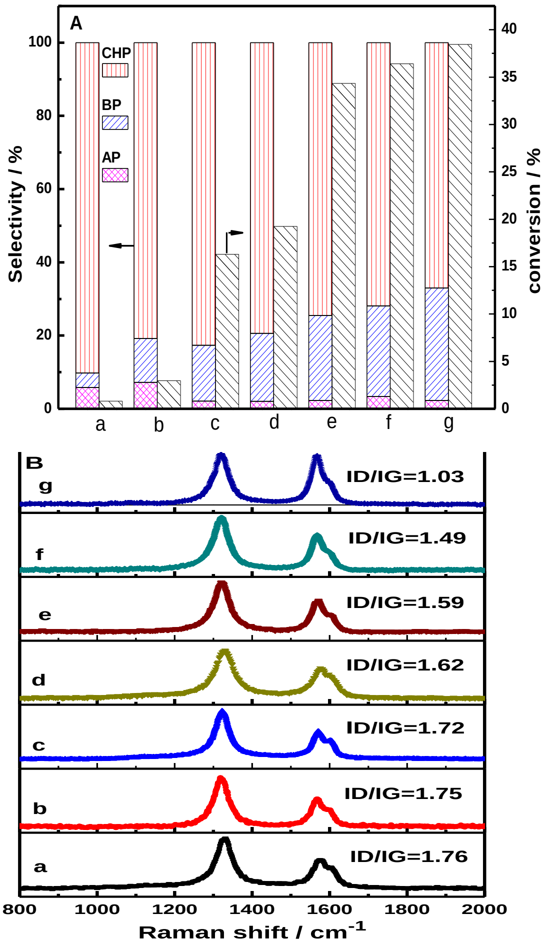


Figure 2. The catalytic performance for cumene oxidation (A) and Raman spectra (B) of the annealed CNTs. a: O-CNTs, b: O-CNTs-300, c: O-CNTs-500, d: O-CNTs-600, e: O-CNTs-700, f: O-CNTs-800 and g: O-CNTs-900.

The catalytic performance of the oxidized CNTs for the liquid-phase oxidation of cumene is shown in Table 1. The original CNTs afforded 24.06% cumene conversion with 88.4% selectivity to CHP. For the oxidized CNTs treated by the gas-phase oxidation, the catalytic activity obviously decreased with the oxidation degree increasing. Notably, O-CNTs exhibited the worst catalytic activity, only gained 0.6% conversion after 8h of reaction, which was even lower than that of blank experiment (2.7%). This result strongly implies that the catalytic activity for cumene aerobic oxidation in the liquid phase is closely related to the surface structure of the CNTs, and the amount of surface oxygenated groups and defects on CNTs have a negative effect on catalytic activity whatever the CNTs are oxidized by nitric acid or by oxygen.

To further verify the effect of surface structure on carbocatalysis, the recovery of catalytic activity of oxidized CNTs was considered after removing the oxygenated groups. It was reported that annealing treatment under inert atmosphere could selectively decompose surface oxygenated groups on carbon materials.[23-25] The decomposition temperatures, which were proven by temperature-programmed desorption and XPS analysis, were circa 400-450 °C for carboxyls, 550-600 °C for anhydrides, 650-700 °C for lactones and phenol (-OH) and 800 °C for carbonyls/quinones.[23] The O-CNTs were evaluated as the most common oxidized CNTs. Figure 2A shows the effect of the annealing temperature on the catalytic performance of cumene oxidation. According to the widely accepted decomposition process, the role of surface oxygenated groups on CNTs has been revealed as below. The activity just recovered a little when carboxyl began to remove at 300 °C, then improved rapidly when carboxyl was removed at 500 °C. A further increase in activity was observed when anhydride was eliminated at 600 °C, revealing that anhydride also played an adverse role, as the anhydride may be hydrolyzed to a carboxylic group in the reaction. In this situation, the cumene conversion reached to 19.2%, which is close to that of the commercial CNTs (24.8%). The lactone, phenol and hydroxyl groups were decomposed when the treating temperature increased to 700 °C, and there was a notable phenomenon that the activity with 34.3% conversion was even higher than that of pristine CNTs. When the treating temperature further increased to 900 °C, the cumene conversion reached to 38.5% as most of the oxidized functional groups were eliminated. The residual surface oxygenated groups on O-CNTs-900 (oxygen content of about 1 at%) was lower than that on the original CNTs (oxygen content of 1.32 at%). These results demonstrate that the catalytic activity of the annealed O-CNTs could be recovered successfully or even higher than that of the original CNTs. It indicates that all of the oxygenated groups on the surface of the CNTs were adverse for cumene aerobic oxidation. Based on the analysis of the oxygenated groups (Table 1), we deduced carboxylic group may be main factor playing a negative role in liquid oxidation.

It is well known that the surface defects of the oxidized CNTs by acid can be partially repaired with the increasing annealing temperature.[26,27] As shown in Figure 2B, the I_D/I_G ratio decreased with the increasing annealing temperature due to the defects repaired. Therefore, it is very difficult to distinguish experimentally their effects of surface oxygenated groups and defects on catalytic activity due to the concurrence of them on the HNO_3 oxidized CNTs.

Herein, the oxidized CNTs by oxygen were designed to further study the role of oxygenated groups and surface defects of the CNTs on cumene oxidation reaction. CNTs-500 was calcined at 800 °C for 2 h under argon atmosphere and denoted as CNTs-500-T. Figure 3A displays that the surface of the CNTs-500 was seriously corroded and lots of defects could be observed on the surface. After the annealing, many defects could still be observed on the surface of the CNTs-500-T as shown in Figure 3B, especially the holes on tube wall were hardly repaired by the annealing treatment. This result was further confirmed by Raman characterization as shown in Figure 3C. The I_D/I_G ratio slightly decreased from 1.82 to 1.80 after annealing treatment, implying that defects still exist on the surface of the CNTs-500-T. From Table 1, it can be seen that the cumene conversion catalyzed by the CNTs-500-T reached to 28.96%, which is 4 times that by CNTs-500. The similar result was also observed on CNTs-400 and CNTs-400-T. These results demonstrate that the oxidized CNTs by oxygen could be recovered successfully after removing the surface oxygenated groups, even if most of defects still remained on the surface of the CNTs, as shown in Scheme 2. To the best of our knowledge, for the first time, we have confirmed the effect factor that the oxidized CNTs decreased the catalytic activity of liquid phase aerobic oxidation reaction was surface oxygenated groups instead of surface defects.

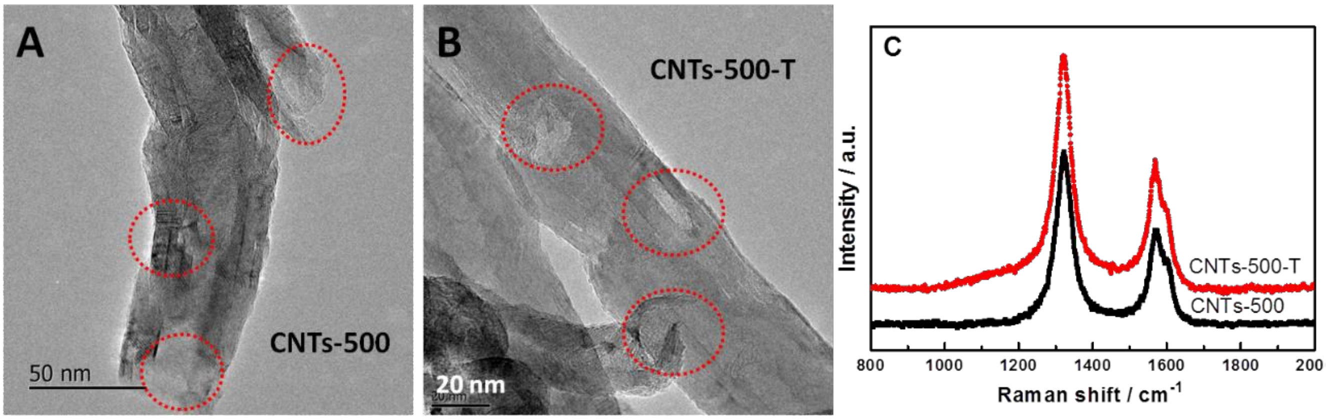
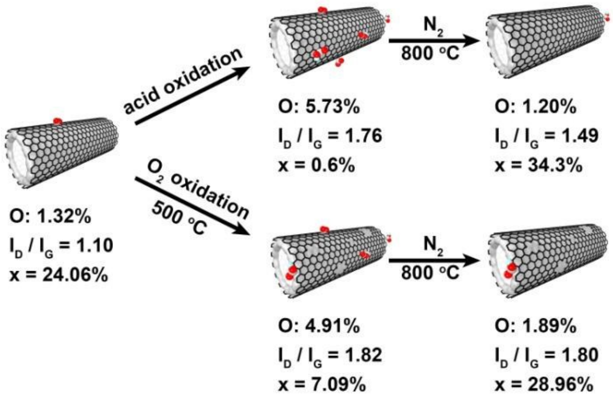


Figure 3. TEM images (A and B) and Raman spectra (C) for CNTs-500 and CNTs-500-T. The red circles denote the defects.



Scheme 2. The effect of surface oxygenated groups and defects on cumene conversion on CNTs.

3.2 The mechanism of catalytic activity decreasing by surface oxygenated groups

Based on the above discussion, the surface oxygenated groups on the oxidized CNTs have been proven to decrease the catalytic activity of cumene oxidation reaction. However, it remains unclear how the surface oxygenated groups on CNTs decrease catalytic activity. According to the effect of surface structure on heterogeneous catalysis, popularly, this peculiar phenomenon was attributed to following several probable reasons. The surface carboxyl groups could change the wettability of CNT surfaces, making CNTs more hydrophilic and polar and unsuitable for the adsorption of nonpolar compounds.[28,29] The surface carboxylic groups might increase diffusional resistance[30] and reduce the accessibility and affinity of CNTs surfaces for organic chemicals.[29,31] However, based on the experimental fact that O-CNTs as catalyst exhibited lower activity (0.6%) than that of blank experiment (2.7%), we have speculated that the above reasons are not main influencing factors of decreasing catalytic activity for cumene oxidation. Thus, a probable reason is that the oxidized CNTs with surface oxygenated groups affect the oxidation reaction process.

It is widely accepted that the cumene oxidation is a typical free radical reaction, including chain initiation, chain propagation and chain termination. And the chain initiation is very important in this process. Main free radical intermediates are cumenyl radical (R•) cumenyl oxygen radical (RO•) and cumenyl peroxy radicals (ROO•).[17,18] In order to further clarify the effect of surface oxygenated groups on cumene oxidation process, we have proposed one probable conjecture: the oxidized CNTs act as a radical quencher, capturing the radicals in the process of reaction, and leading to the termination of reaction.

In order to confirm our conjecture, the followed experiments were designed. O-CNTs were added to the pristine CNTs to study the catalytic performance in cumene reaction. We found that the cumene conversion was 11.79% with 100 mg CNTs and 20 mg O-CNTs as catalyst (Table 2, entry 3). Further increasing the O-CNTs to 50 mg, the cumene conversion dramatically decreased to 3.47% (Table 1, entry 4), just a little higher than the blank conversion (Table 2, entry 1). When the amount of the added O-CNTs reached to 70 mg, the cumene conversion was only 2.07%, even lower than the blank conversion. The result shows that the conversion of cumene decreased rapidly with the adding amount of O-CNTs even if CNTs with high activity remained in the reaction system. This phenomenon supports strongly our conjecture that the oxidized CNTs act as a radical quencher to capture the radicals and quench the reaction. In order to verify further this conclusion, we added O-CNTs to the metal oxide catalyst CuO system, which was reported to have a good catalytic activity in the oxidation reaction of cumene.[32] As expected, the conversion of cumene also decreased from 27.03% to 6.71% when adding 50 mg O-CNTs to 100 mg CuO catalyst (Table 2, entry 7 and 8).

In fact, many researchers have also reported that the CNTs could act as radical trappers. Watts et al.[33] firstly observed the multi-wall CNTs (MWCNT) serving as the weak antioxidants to stabilize the polymer in the process of heating. Delayed oxidative degradation of MWCNT/polyethylene composites was also investigated by Bocchini et al.[34] The possible antioxidant mechanism is that the CNTs behave as radical scavengers in chain reactions[33,35] owing to their high electron affinities similar to that of C60.[36] In order to scavenge free radicals, the CNTs can either donate or accept electrons based on an electron transfer mechanism.[37] Furthermore, researchers found that the surface oxygenated groups on CNTs have a significant impact on the behavior of trapping radicals. Galano et al.[38]

Table 2. The effect of amount of adding O-CNTs on catalytic performance for cumene oxidation

Entry	Catalyst	Conversion (%)	S_{AP} (%)	S_{BP} (%)	S_{CHP} (%)	Y_{CHP} (%)
1	Blank	2.69	0.41	0.40	99.19	2.67
2	CNTs	24.06	1.58	10.00	88.42	21.27
3	CNTs+20 mg O-CNTs	11.79	4.90	6.26	88.84	10.47
4	CNTs+50 mg O-CNTs	3.47	3.85	7.65	88.50	3.07
5	CNTs+70 mg O-CNTs	2.07	2.38	4.01	93.61	1.94
6	100 mg O-CNTs	0.60	-[a]	-[a]	97.80	0.59
7	CuO	27.03	2.90	16.14	80.96	21.88
8	CuO+ 50 mg O-CNTs	6.71	8.38	2.17	89.45	6.00

Reaction time of 2 hrs, other conditions as shown in Table 1. [a] Hard to quantitative analysis due to the lower concentration.

reported that carboxylated single-walled carbon nanotubes (SWCNT) have a better ability to capture free radicals than non-functionalized SWCNT by density functional theory calculations. That is to say, the oxidized CNTs with high electron affinities can adsorb and stabilize the free radical intermediates on CNTs, inhibiting the free radical chain transfer. Once a first radical is attached to the nanotube, further additions are increasingly feasible, suggesting that CNTs can act as free-radical sponges.[39] These results can well explain why the annealed O-CNTs-900 has higher catalytic activity (38.5%) than that of the original CNTs (24.06%) due to the lower content of surface oxygenated groups on O-CNTs-900.

Thus it can be known that the oxidized CNTs can serve as a free radical quencher, capturing the free radical intermediate of reaction and inhibiting the free radical chain transfer, resulting in a decreased activity of free radical reaction in liquid phase. This result can explain the effect of the oxidized CNTs on a series of free radical oxidation reactions catalyzed by carbon materials,[14-18] which was different from the gas phase oxidative dehydrogenation reactions catalyzed by carbon.[6-8] Similarly, for the liquid phase oxidation of non-radical carbocatalysis, if surface oxygenated groups involved in reaction, they have a positive effect, such as oxidation of benzyl alcohol on GO;[40] if surface oxygenated groups did not involve in reaction, they have little effect, such as oxidation of benzyl alcohol in HNO_3 assisted carbon-catalyzed oxidation system.[41]

4 Conclusions

In this work, the surface of CNTs has been introduced surface oxygenated groups and defects by the gas-phase oxidation with O_2 and the liquid-phase oxidation with concentrated HNO_3. We proved that the oxidized CNTs are adverse for liquid phase catalytic oxidation of cumene. The catalytic activity decreases with the increasing oxidation degree. Further studies indicated that the defect has little effect on the activity of cumene oxidation, and the oxygenated surface functional groups on CNTs is the main factor for the decrease of catalytic activity. To the best of our knowledge, we have distinguished the effect of surface oxygenated groups and surface defects on liquid phase oxidation reaction of cumene for the first time. Meanwhile, the mechanism that the oxidized CNTs decrease catalytic activity has been revealed. It has been proven that the oxidized CNTs could serve as free radical quenchers, capturing the free radical intermediate of reaction and inhibiting the free radical chain transfer, thereby reduces the catalytic activity of free radical reaction in liquid phase. This study gains a new insight into the effect of surface structures on carbon-catalyzed liquid phase oxidation, and further pushes forward the research on carbon catalysis.

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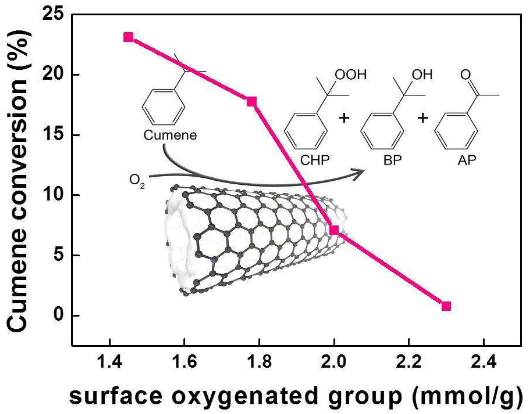
Graphical abstract



Surface oxygenated groups, instead of surface defects, play a negative role in the liquid phase radical oxidation reaction catalyzed by carbons.