Catalytic activity, stability and structure of multi-walled carbon nanotubes in the wet air oxidation of phenol

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ABSTRACT

Multi-walled carbon nanotubes (MWCNTs), with no supported metal, were used as catalysts in the wet air oxidation of phenol. The MWCNTs were chemically modified using HCl or HNO_3–H_2SO_4. They were characterized by BET, SEM, TEM, FT-IR and Raman spectroscopy. The functionalized MWCNTs exhibited both high activity and good stability in the wet air oxidation of phenol. At 160 °C and 2.0 MPa with an initial phenol concentration of 1000 mg/L, 100% phenol conversion and 76% total organic carbon abatement could be achieved after 120 min reaction. Upon reaction, the short chain carboxylic acids mainly maleic/fumaric, malonic, oxalic, formic and acetic acid were produced. Surface functional groups (–COOH) were shown to play a key role in the high activity of the functionalized MWCNTs. A mechanism for the CWAO of phenol was proposed.

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1. Introduction

Wastewater originating from chemical, petrochemical, pharmaceutical, agricultural and textile production plants very frequently contains toxic, hazardous and highly concentrated organic compounds. If directly discharged into the environment, the wastewater may cause severe damage and threat to the ecosystem in water bodies and human health. Consequently, the development of effective technologies to treat the industrial wastewater is crucial. Biological technologies are the most common methods treating the wastewater. However, the toxicity of organic compounds present in the effluent might destroy the microorganisms. The wet air oxidation (WAO) is one of the chemical oxidation methods, which could effectively convert hazardous, toxic and highly concentrated organic pollutants to CO_2, H_2O and innocuous end products with any toxic emissions at high temperature (120–350 °C) and high pressure (0.5–20 MPa) using oxygen as the oxidant [1,2]. However, severe reaction conditions and high operating costs hinder its application for treating the industrial wastewater. Using a catalyst in the WAO may allow to reduce the operating conditions, to shorten the reaction time, to enhance the oxidation efficiency and to decrease the operating cost. Heterogeneous catalysts appear to be more promising for treatment of the industrial wastewater without an additional separation step to remove metal ions in the effluent. In the last decades, various heterogeneous catalysts including noble metals deposited on the supports and transition metal oxides have been developed. They showed good catalytic activity in the catalytic wet air

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oxidation (CWAO) of organic pollutants [3–7]. The loss of the activity affects the economy of the process and limits the commercialization of the oxidation technology. Therefore, we focused our efforts on the development of the effective oxidation system in which easily available catalysts are used to treat the industrial wastewater at lower costs.

Since the first report concerning carbon nanotubes (CNTs), a lot of attention has been paid to their synthesis, characterization and application due to the unique structural, mechanical and electronic properties of the materials [8,9]. Recently, researchers have used CNTs as an ideal candidate for catalytic materials, since they represent a novel class of advanced materials. The detailed reasons are listed as below [10]: (1) the high surface area is helpful to adsorb reactants/products, and the specific mesoporous structure decreases the mass-transfer limitations of the reactants/products; (2) the good thermal stability and the resistance to acidic/basic medium are suitable for severe reaction conditions. CNTs were studied either as supports or catalysts. As a support, CNTs showed more advantages in some catalytic reactions than the conventional supports (such as active carbon, graphite and Al_2O_3) [11,12]. A few reports showed that CNTs could directly be used as catalysts, for instance, the methane decomposition [13], the electrochemical oxidation of aniline [14], the oxidative dehydrogenation of ethylbenzene [15,16], the oxidation of p-toluidine and aniline [17,18], and the hydroxylation of aromatic hydrocarbon [19]. Furthermore, the mechanism of CNTs as catalytic materials is gaining more attention.

Multi-walled carbon nanotubes (MWCNTs)-supported Pt, Ru, and Cu catalysts displayed good activities in the CWAO of aniline [20–23], however no report was found regarding the application of the MWCNTs as catalysts in the CWAO of organic compounds. On the other hand, activated carbon (AC) possessing the same chemical compound and the different textural properties with the MWCNTs, was preformed to treat phenols, 2-chlorphenol, sodium dodecylbenzene sulfonate, o-cresol and aniline in the continuous reactor under 140 °C and 2 bar of oxygen pressure. The commercial AC has displayed good degradation for organic compounds and bifunctional effects as adsorbent and catalyst [24–26]. These results lead us to explore the potential of CNTs directly used as catalysts in the oxidation reaction.

In this study, MWCNTs were used as raw materials. They were further modified using the most common method, the nitric acid treatment. The MWCNTs were characterized by BET, scanning electron microscopy (SEM) and transmission electron microscopy (TEM), infrared (FT-IR) and Raman to investigate their surface areas, morphologies and surface functional groups. Phenol was selected as the model pollutant, and the activity and stability of the MWCNTs were evaluated in the CWAO of phenol in a batch reactor. The reaction intermediates were identified, and a mechanism was proposed.

2. Experimental

2.1. Materials

The MWNCTs, prepared by chemical vapor deposition (CVD) using a Fe/Al_2O_3 catalyst, were obtained from Tsinghua _

Nafine nano-powder Commercialization Engineering Center [27]. The inside diameter was 3–10 nm, the outside diameter was 6–20 nm, and the length/diameter ratio was in the range of 100–1000. Raw MWCNTs contained some amorphous carbon and some catalyst particles. The purity was higher than 99.5%.

Raw MWCNTs were immersed in a 37% HCl solution and sonicated for 20 min, and then the mixture was continued overnight to remove metal catalyst particles. The HCl-treated MWCNTs were divided into two parts. One part was washed several times with deionised water, dried overnight in air at 80 °C, and then crushed leading to a powder referenced as A-MWCNTs. The other part was immersed and dispersed in a 67%HNO_3–98%H_2SO_4 (1:3, volume) solution and sonicated for 20 min. The suspension was further refluxed at 50 °C for 4, 12 and 16 h. The materials were washed several times with deionised water, dried at 80 °C overnight, and crushed. The corresponding materials were referenced as B-MWCNTs. The B-MWCNTs refluxed for different times were labeled as B-MWCNTs/4 h, B-MWCNTs/12 h and B-MWCNTs/16 h.

2.2. Catalytic wet air oxidation procedure

The CWAO of phenol was carried out in an autoclave equipped with a magnetically driven stirrer. The reactor was previously described in our study [3]. First, 0.8 g catalyst and 500 mL phenol solution (1000 mg/L) were loaded into the autoclave purged under Ar to remove air in the reactor. After heating to 160 °C, pure oxygen was added. The oxygen pressure was 2 MPa. The oxidation reaction was performed for 120 min. Samples were withdrawn periodically from the reactor to analyze the reaction mixture by HPLC (Shimadzu, LC-10AD) using an Inertsil ODS-3 column and measure the total organic carbon (TOC) by a TOC 5000A analyzer. To analyze phenol, the mobile phase consisted in a mixture of methanol and 1% acetic acid aqueous solution (50/50, volume). The flow rate was fixed at 1 mL/min, and UV detector wavelength was set at 254 nm. To analyze intermediates, the mobile phase consisted in a mixture of methanol and 0.1% H_3PO_4 aqueous solution (10/90, volume). The flow rate was 1 mL/min, and UV detector wavelength was 210 nm. TOC was measured to evaluate the mineralization degree of organic compounds.

The initial phenol concentration used for the calculation of the transformation of phenol reaction rate was the concentration measured just before the introduction of O_2. With the MWCNTs as catalysts, less than 4% phenol removal was observed before O_2 admission, indicating that the adsorption of phenol in the MWCNTs is very low at the reaction conditions.

2.3. Characterization of the MWCNTs

The surface areas of the MWCNTs were determined by N_2 adsorption at 77 K in a Quantachrome Autosorb Automated Gas Sorption System. Before each measurement, samples were outgassed at 573 K for 3 h. SEM and TEM were used to study the morphology of the MWCNTs. SEM measurement was carried out on the HITACHI S-4500 at an accelerating voltage of 15 kV. The remaining catalyst particles in the MWCNTs were analyzed by SEM using a JEOL JXA-840 equipped with Oxford ISIS300 energy-dispersion microanalysis system.

TEM measurement was conducted on a JEOL 2010 HRTEM operated at an accelerating voltage of 120 kV. Samples were dispersed in ethanol solution under ultrasonic vibration, and deposited on C film. Raman measurement was carried out with a Spex 1403 Raman spectrometer at an excitation laser wavelength of 633 nm to investigate the MWCNTs structure. FT-IR was used to identify the surface functional groups on the MWCNTs using a Bruker Fourier-transform spectrophotometer Magna-IR 750. Bohem titration was carried out to determine the number and type of the surface oxygen groups [26]. One gram of the samples was placed in 50 ml of the solution (0.05 N of NaOH and NaHCO₃) for a period of 24 h and the acidic surface oxides were determined by back titration with HCl solution after reaching the equilibrium.

3. Results and discussion

3.1. Characterization of the MWCNTs

3.1.1. SEM, TEM and BET
Fig. 1 shows SEM images of the MWCNTs. For the acidic-treated MWCNTs (in Fig. 1a and Fig. 1b), the morphologies seem to not change, and the length of nanotubes is several microns long. The morphology of the used B-MWCNTs/4 h is shown in Fig. 1c, and remains the same as that of the fresh B-MWCNTs/4 h. Moreover, EDX analysis indicates that the metal catalyst attached to the B-MWCNTs is totally removed.

To identify in more detail the structure of the MWCNTs, TEM was used to investigate their morphologies. Fig. 2 displays TEM images of the MWCNTs. Raw materials contain some impurities [27]. In Fig. 2, it is observed that: (1) the impurities in the acidic-treated MWCNTs are obviously decreased, a few were seen in the A-MWCNTs, and they were not observed in the B-MWCNTs/4 h; (2) the tip of the nanotubes is open in the acidic-treated MWCNTs; (3) for the fresh B-MWCNTs/4 h (in Fig. 2b), the outer diameter of the nanotubes is about 20 nm, and the distance of the inner graphite layers is about 0.34 nm; (4) for the used B-MWCNTs/4 h (in Fig. 2c), the wall shape preserves the good structure, and the length and diameter do not change during the CWAO of phenol. In the SEM and TEM images (in Figs. 1 and 2), it is obtained that the morphologies of the MWCNTs keep the perfect structure during the acidic treatment and the oxidation reaction, indi-

cating that they could be used as catalytic materials in the CWAO.

Table 1 shows the BET surface areas of the samples. Raw MWCNTs display high surface area of 148.9 m²/g, and it is found that the acidic treatment affects the surface areas of the MWCNTs. The change of the surface areas is related to the open tips of the MWCNTs. This is helpful for N₂ to enter and adsorb on the internal tubes of nanotubes, and leads to the surface areas increase. However, there are residual impurities in the A-MWCNTs, they could block the tubes and make the surface area lower than that of the B-MWCNTs. In Table 1, it is noticed that the surface areas of the B-MWCNTs slightly decrease with increasing the reflux time. The change could be due to the oxidation of the walls with increasing the reflux time for the B-MWCNTs.

3.1.2. Raman
Raman technique was used to investigate the structure properties of the MWCNTs. Two characteristic bands for the MWCNTs at 1584 and 1323 cm⁻¹ are detected in Fig. 3. G-band at ∼1584 cm⁻¹ is attributed to the vibration of sp²-hybridized carbon atoms in a two-dimensional hexagonal lattice, and reflects the structural integrity to the sp²-hybridized carbon atoms of the nanotubes [28]. D-band at ∼1323 cm⁻¹ is related to local defects originating from structural imperfection and amorphous carbon in the nanotubes. The ratio between D-band (I_D) and G-band (I_G) is sensitive to the chemical processing, and is an index of the defects of the MWCNTs [28]. For raw MWCNTs, the ratio is 1.40. The open tips of the nanotubes increase the surface defects, so it is found that the ratio (1.44) slightly increases in the A-MWCNTs. For the B-MWCNTs/4 h, the ratio of I_D/I_G (1.57) is clearly higher than that of the A-MWCNTs, indicating that the surface functional groups are generated on the MWCNTs after the treatment of HNO₃–H₂SO₄. The result is in agreement with that of [29]. In the used B-MWCNTs/4 h (in Fig. 3e), it is observed that G-bandwidth and the ratio of I_D/I_G do not change, indicating that the structure keeps the good integrity in the CWAO of phenol. The result is in agreement with that of SEM and TEM. In Fig. 3, it is proven that the B-MWCNTs keep the integrity of the nanotubes structure in the CWAO of phenol and the functional groups are created on the surface of the B-MWCNTs after the treatment of HNO₃-H₂SO₄.
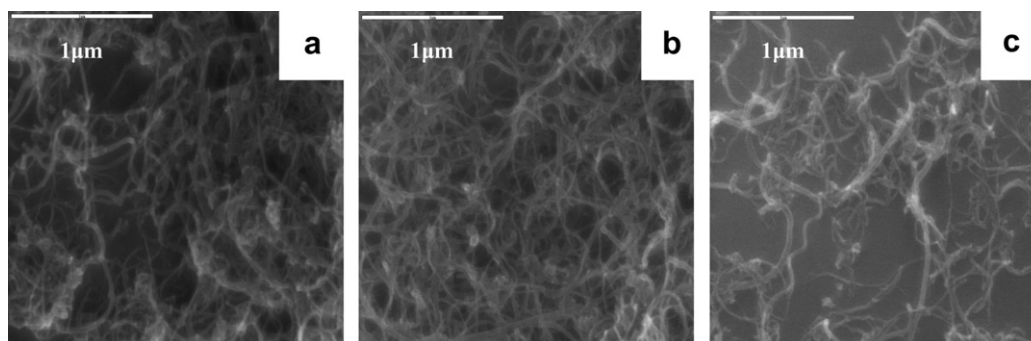

Fig. 1 – SEM images of the MWCNTs. (a) A-MWCNTs; (b) B-MWCNTs/4 h and (c) the used B-MWCNTs/4 h for 3rd cycle.

Fig. 3 – Raman spectra of the MWCNTs. (a) raw MWCNTs; (b) A-MWCNTs; (c) B-MWCNTs/4 h; (d) the used B-MWCNTs/4 h for 1st cycle and (e) the used B-MWCNTs/4 h for 3rd cycle.

Fig. 4 – FT-IR spectra of the MWCNTs. (a) raw MWCNTs; (b) A-MWCNTs; (c) B-MWCNTs/4 h and (d) the used B-MWCNTs/4 h for 1st cycle.
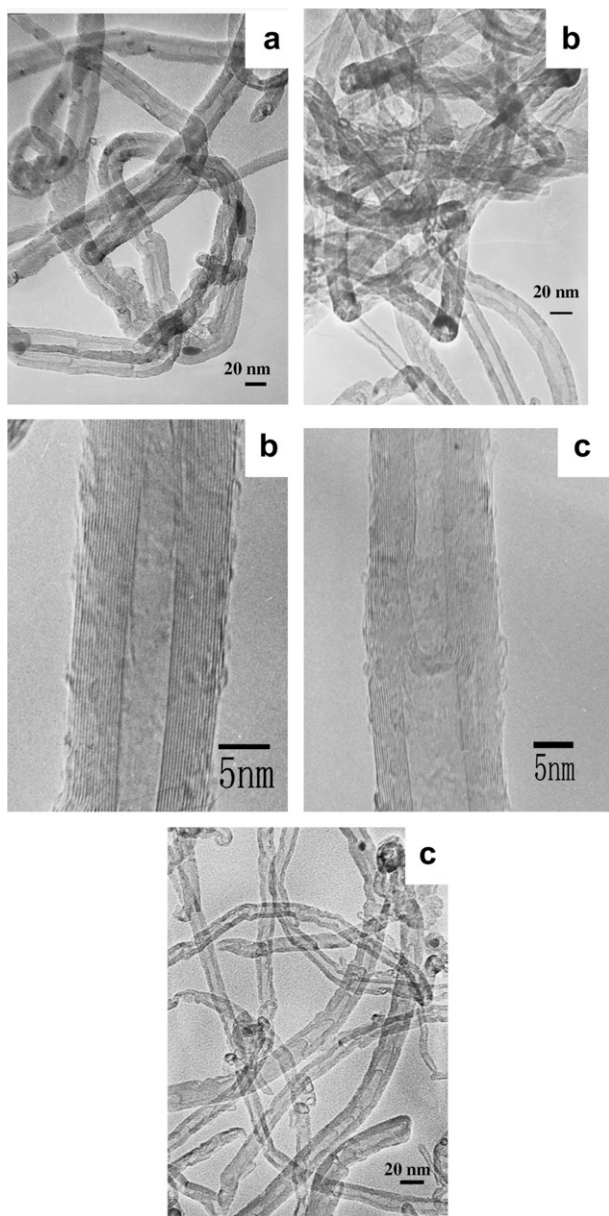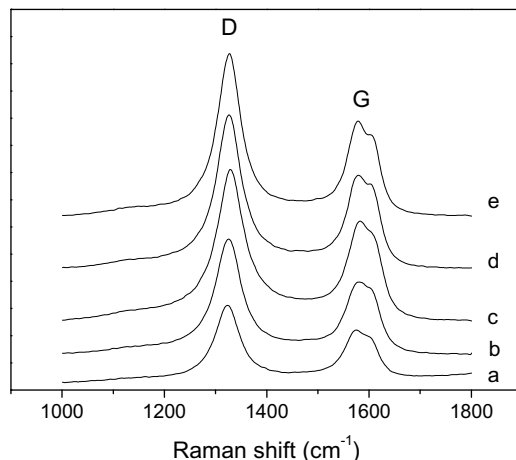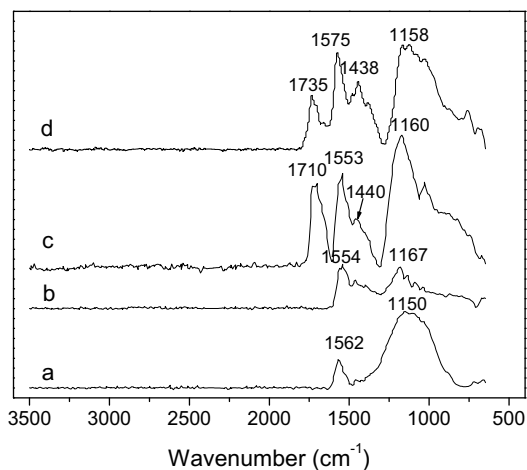
Fig. 2 – TEM images of the MWCNTs. (a) A-MWCNTs; (b) B-MWCNTs/4 h and (c) the used B-MWCNTs/4 h for 3rd cycle.

Table 1 – The surface areas of the MWCNTs	
Samples	Surface area (m^2/g)
Raw MWCNTs	148.9
A-MWCNTs	160.9
B-MWCNTs/4 h	194.7
B-MWCNTs/12 h	190.2
B-MWCNTs/16 h	172.6

3.1.3. FT-IR

The surface functional groups could influence the chemical and physical properties of carbon materials [29]. FT-IR was used to characterize the MWCNTs to get more insight on the surface functional groups. Fig. 4 shows FT-IR spectra of the MWCNTs in the range 700–3500 cm^{-1}. Two bands are detected at 1150 and 1562 cm^{-1} for raw MWCNTs and A-MWCNTs (in Fig. 4a and Fig. 4b), and the band ~1562 cm^{-1} is attributed to the graphitic structure of the sp^2-hybridized carbon in CNTs [30,31], while the band at ~1150 cm^{-1} is assigned to sp^3 carbon [32]. No other bands are observed, indicating the absence of the surface functional groups in raw MWCNTs and A-MWCNTs. For the B-MWCNTs/4 h (in Fig. 4c), three bands are detected at 1160, 1553, 1710 cm^{-1}, and one appears as a shoulder at 1440 cm^{-1}. Two bands at 1710 and 1440 cm^{-1} are attributed to C=O stretching mode in the carboxylic acid group and quinone group, respectively [31]. This indicates that the surface functional groups are created in the B-MWCNTs/4 h. For the used B-MWCNTs/4 h (in Fig. 4-d), the bands at 1158, 1438 and 1575 cm^{-1} are detected, and do no have any change, while the band at 1710 cm^{-1} moves to 1735 cm^{-1} after the oxidation reaction.

It is attributed to C=O stretching mode in ester groups [29,33]. The shift of the band might form esters between the carboxylic groups and phenol/intermediates in the CWAO of phenol.

It is noticed that a band around 3500 cm^{-1} assigned to –OH functional groups is not observed in all spectra (in Fig. 4). The result is not in agreement with the results previously [34,35]. For CNTs, raw materials, synthesis methods and treatment procedures to modify the functional groups could affect the nature of the functional groups in CNTs. Zhang et al found that the MWCNTs supplied from Tsinghua_Nafine nano-powder Commercialization Engineering Center were modified with the solution of H_2SO_4–H_2O_2 and OH– functional groups were also not observed in the MWCNTs [36]. His result is consistent with ours. It is indicated that the nature of CNTs might effectively affect the kind of the surface functional group.

3.1.4. *Effect of the reflux time*

In order to investigate the effect of the reflux time on the nature and concentration of the surface functional groups in the B-MWCNTs, they were refluxed in the solution of HNO_3–H_2SO_4 at 50 °C for 4, 12 and 16 h. Figs. 5 and 6 display SEM and TEM images for the B-MWCNTs refluxed at the different times. When the reflux time increases to 16 h, the length is obviously shortened, and the wall is oxidized. It means that the concentration of the surface functional groups for B-MWCNTs could be affected with increasing the reflux time. In Fig. 7, the bands are detected at 1165, 1445, 1565 and 1718 cm^{-1}, and are consistent with that of the B-MWCNTs/4 h. C=O stretching mode in the carboxylic acid groups and quinone groups are generated on the surface of the B-MWCNTs/12 h and B-MWCNTs/16 h. In the Raman spectra, the bands at ~1584 and 1323 cm^{-1} are observed. The ratio of I_D/I_G for the B-MWCNTs/16 h obviously increases to over 1.66 during the reflux time of 16 h, indicating that the higher concentration of the functional groups increases with increasing the reflux time. To obtain information about the number of surface oxygen groups on the B-MWCNTs, Boehm titration was used and the result was shown in Table 2. It is found that the content of acidic sites and the carboxylic acid groups increases with increasing the reflux time from 4 to 16 h. It is clearly proven that the higher concentration of the surface oxygen groups effectively increases with the increase of the reflux time.
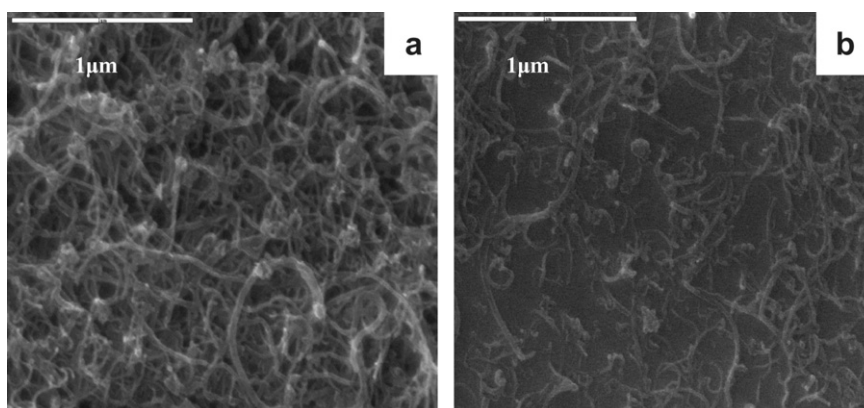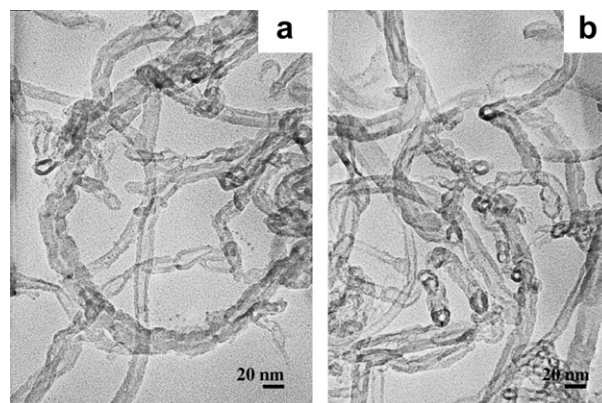

Fig. 6 – TEM images of B-MWCNTs. (a) B-MWCNTs/12 h and (b) B-MWCNTs/16 h.
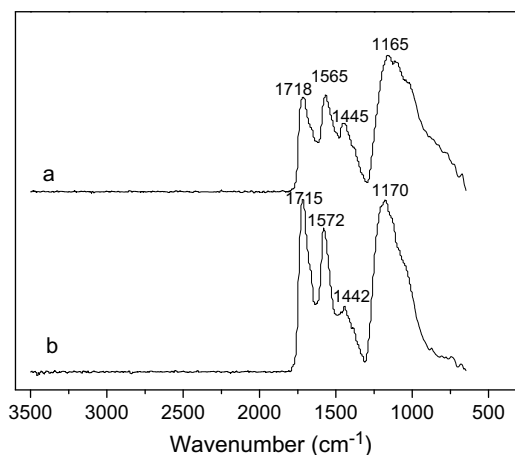

Fig. 7 – FT-IR spectra of B-MWCNTs. (a) B-MWCNTs/12 h and (b) B-MWCNTs/16 h.

3.2. *CWAO of phenol over the MWCNTs*

CWAO of phenol was tested in a batch reactor at the reaction temperature of 160 °C, oxygen pressure of 2 MPa and an initial phenol concentration of 1000 mg/L, and the results were

Fig. 5 – SEM images of B-MWCNTs. (a) B-MWCNTs/12 h and (b) B-MWCNTs/16 h.

Table 2 – The surface oxygen groups for B-MWCNTs		
Samples	Surface groups density (mmol/g)	
	Acidic sites	Carboxylic
B-MWCNTs/4 h	1.52	1.45
B-MWCNTs/12 h	2.11	1.95
B-MWCNTs/16 h	2.44	2.23

Table 3 – Catalytic activities of B-MWCNTs/4 h for the recycling use in the CWAO of phenol (160 °C and 2 MPa)		
Cycle times	Phenol removal (%)	TOC removal (%)
1st	97.2	77
2nd	99	75
3rd	98.5	72
After 120 min reaction.		

shown in Fig. 8. Without any catalysts, only 11.6% phenol removal is obtained after 120 min reaction. With the A-MWCNTs as the catalyst, 22% phenol and 10% TOC removal are obtained after 120 min reaction. It is noticed that the B-MWCNTs/4 h as catalysts display the highest activity in the CWAO of phenol, 100% phenol and 76% TOC are removed in 120 min. Due to the strong adsorption capacity of carbon materials with the high surface areas, it is necessary to evaluate the adsorption of phenol in the B-MWCNTs/4 h. By using N_2 instead of O_2, it is obtained that about 4% phenol is removed in the oxidation reaction with B-MWCNTs/4 h after 120 min reaction. This indicates that the adsorption of phenol is very low, and the B-MWCNTs/4 h have the excellent activity in the oxidation of phenol.

Recycling experiments for the CWAO of phenol were also performed to investigate the stability of the B-MWCNTs/4 h. After a first run, they were filtered off, washed with deionzed water, and then dried at 80 °C overnight to reuse in another reaction with a fresh solution of phenol at the same operating condition as the fresh B-MWCNTs/4 h for the oxidation reaction. Upon recycling, the B-MWCNTs/4 h keep the good activity and display good reproducibility of results for 3 time cycles in the reaction (in Table 3). For example, over 98% removal of phenol preserves no change in the recycling reactions. TOC removals are over 70% and slightly decrease, and keep over 91% of the initial activity in 120 min reaction during 3 time cycles. The results of the activity and stability of the B-MWCNTs/4 h demonstrate that they are the excellent catalyst and have the sufficient stability in the oxidation reaction. Compared with CeO_2 and CeO_2/γ–Al_2O_3 catalysts, the B-MWCNTs/4 h show the higher catalytic activity in the

CWAO of phenol at the same operating conditions [4], indicating that the MWCNTs are the promising materials not only as supports but also as catalysts in the environmental protection.

B-MWCNTs refluxed at the different times were further tested in the CWAO of phenol to investigate the effect of the concentration of the surface functional groups on the activity of the B-MWCNTs. As shown in Fig. 9, it is observed that: (1) the B-MWCNTs show high activities in the oxidation reaction, and the activities increase with increasing the reflux time; (2) the B-MWCNTs/16 h show the highest activity, 100% phenol and 80% TOC are removed after 45 min reaction. The result indicates that the higher concentration of the functional groups could effectively enhance the activity of the B-MWCNTs in the CWAO of phenol, and the surface functional groups play an important role in degradation of phenol.

In Table 3, it is observed that total mineralization of phenol was not achieved after 120 min reaction when phenol is totally removed in the CWAO over B-MWCNTs/4 h, indicating that some intermediates are formed and not converted to CO_2 and H_2O during the reaction. Intermediates were identified with HPLC, mainly hydroquinone and short chain acids as maleic/fumaric, malonic, oxalic, acetic and formic acid. Fig. 10 shows the concentration profiles of phenol and intermediates in the presence of the B-MWCNTs/4 h as a catalyst. Some intermediates as catechol and benzoquinone are not detected at the beginning of the reaction. It can be supposed that the intermediates show a high oxidation rate. Furthermore, the short chain carboxylic acids are continuously formed and accumulated in the oxidation reaction. After
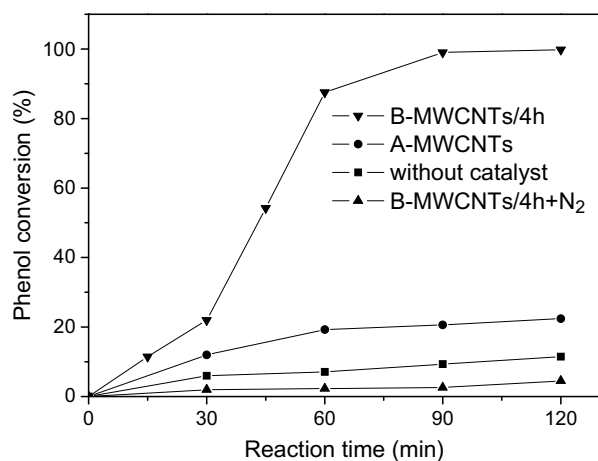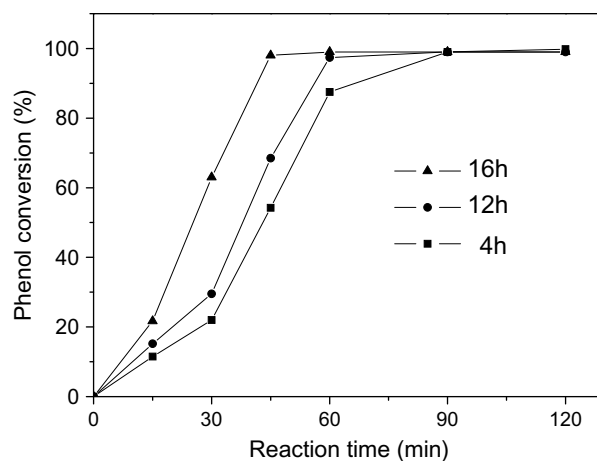

Fig. 8 – Phenol conversion in the CWAO over the MWCNTs at reaction temperature of 160 °C, oxygen pressure of 2 MPa and catalyst loading of 0.8 g.

Fig. 9 – Phenol conversion in the CWAO over B-MWCNTs at reaction temperature of 160 °C, oxygen pressure of 2 MPa and catalyst loading of 0.8 g.
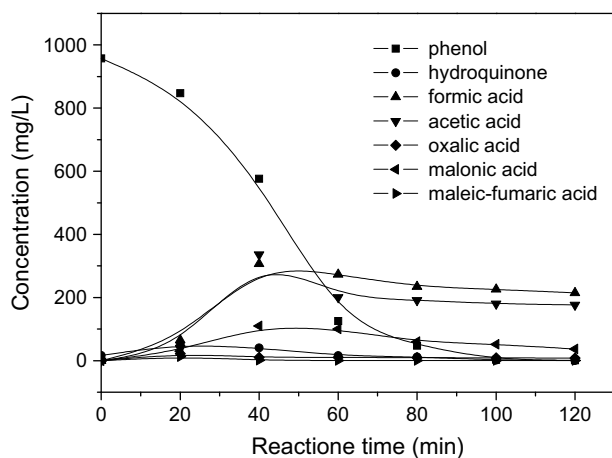
Fig. 10 – Concentration of intermediates in the CWAO of phenol over B-MWCNTs/4 h at reaction temperature of 160 °C, oxygen pressure of 2 MPa and catalyst loading of 0.8 g.

40 min reaction, the concentration of these acids gradually decreases, while it changes slowly for acetic and formic acid, indicating that the oxidation rate of them is the key step for the total mineralization of phenol to CO_2 and H_2O.

CWAO of organic compounds involves a free radical chain reaction according to some reports [37]. Hydroperoxyl radical (HO_2), the strong oxidation species, is formed with oxygen gas as the oxidant, and its formation is an important step in the CWAO of organic compounds. The radical could rapidly oxidize the organic compounds to CO_2, H_2O and intermediates. Analyzing the structure and activity of the MWCNTs, it is found that the surface functional groups play an important role in high activity of the B-MWCNTs. Only C=O stretching modes in the carboxylic acid groups and quinone groups are created on the surface of the B-MWCNTs. However, C=O double band in the quinone groups is more stable and is not easier to be broken than that of C–O in the carboxylic acid groups. Therefore, we suppose that –COOH functional group affects the activity of the B-MWCNTs in the CWAO of phenol. A possible reaction mechanism to produce the radical (HO_2) using the B-MWCNTs is proposed and shown in Fig. 11. Firstly, O_2 in the liquid adsorbs on the surface of the B-MWCNTs, and then is dissociated on the graphite layers to produce the dissociated oxygen atoms [15]. The carboxylic groups (–COOH)
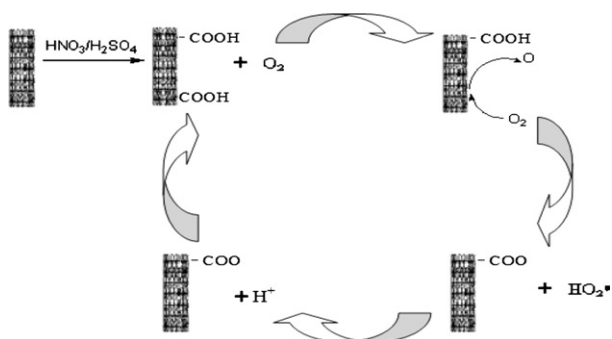
on the B-MWCNTs and the dissociated oxygen atoms could produce HO_2 by the hydrogen band. The radical can arouse some radical chain reactions, lead to molecular breakdown, and then decompose phenol to CO_2, H_2O and some intermediates in the CWAO of phenol. Therefore, the B-MWCNTs could effectively improve the formation of the radicals, and make organic compounds decomposed in the oxidation reaction. This leads to that the B-MWCNTs/4 h as catalysts exhibit good activity in the CWAO of phenol. Moreover, the higher concentration of the surface functional group (–COOH) in the B-MWCNTs is helpful to form the radical of HO_2. It is obtained that the B-MWCNTs/16 h with high concentration of the functional groups display the highest activity. During the oxidation reaction, the intermediates are produced and detected, such as maleic/fumaric, malonic, oxalic, acetic and formic acid. They could adsorb and react with the functional groups on the surface of the B-MWCNT, and produce esters. This could make the band of C=O stretching vibration move, and the carbonyl groups of ester are observed on FT-IR spectra of the used B-MWCNTs/4 h. On the other hand, –COOH functional group could be reformed through the hydrolysis reaction at high reaction temperature, so the B-MWCNTs/4 h display good reproducibility in the CWAO of phenol.

4. Conclusion

The effective oxidation reaction system using the MWCNTs as catalysts for the CWAO of phenol is reported in this paper. It is observed in the SEM, TEM and Raman spectra that the MWCNTs preserve the good structure in the oxidation reaction. Moreover, the B-MWCNTs exhibit both high activity and good stability in the CWAO of phenol. 100% phenol and 76% TOC are removed at 120 min reaction at reaction temperature of 160 °C, oxygen pressure of 2 MPa and the initial phenol concentration of 1000 mg/L. The good stability of the B-MWCNTs is obtained in several running cycles. Increasing the reflux time for the B-MWCNTs could lead to produce the higher concentration of the functional groups and obtain the higher activity. Our research confirms the potentialities of CNTs not only as supports but also as catalysts at the environmental protection. More studies with the MWCNTs as the new materials to evaluate the application of CWAO of the refractory organic compounds will be carried out.

Acknowledgements

Fig. 11 – A mechanism producing HO_2 in the CWAO of phenol over B-MWCNTs.

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