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Influence of the different oxidation treatment on the performance of multi-walled carbon nanotubes in the catalytic wet air oxidation of phenol

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HIGHLIGHTS

- Carbon nanotubes were used as catalysts in the catalytic wet air oxidation of phenol.
- Four chemical oxidants (HNO_3/H_2SO_4, H_2O_2, O_3 and air) were used to modify the CNTs.
- The O_3-functionalized CNTs exhibit the highest activity and the perfect stability.

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ABSTRACT

Multi-walled carbon nanotubes (MWCNTs) functionalized by different oxidants (HNO_3/H_2SO_4, H_2O_2, O_3 and air) have been used as catalysts for the wet air oxidation of phenol. To investigate the effect of the oxidation conditions on the structure of the functionalized MWCNTs, various characterization techniques, e.g., scanning electron microscopy (SEM), transmission electron microscopy (TEM), Raman spectroscopy, Fourier-transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS) have been used. The MWCNTs treated with O_3 and H_2O_2 show higher amounts of oxygen-containing functional groups and carboxylic acid groups, and a weaker acidic nature, in comparison with those treated with other oxidizing agents. All the functionalized MWCNTs exhibit good activity in the catalytic wet air oxidation (CWAO) of phenol. However, the MWCNTs treated with O_3 show the highest activity with desirable stability in comparison with other functionalized MWCNTs, indicating that the functionalization of carbon nanotubes with O_3 is a very promising strategy in synthesizing efficient catalysts for CWAO.

1. Introduction

Wet air oxidation (WAO) is well proved to be one of the effective technologies for eliminating hazardous, toxic and highly concentrated organic compounds in the industrial wastewaters coming from chemical, petrochemical, pharmaceutical, agricultural and textile plants [1,2]. The WAO shows good performance under high temperature (125–320 °C) and pressure (0.5–20 MPa) using oxygen or air as an oxidant, while its practical application has been limited due to severe operating conditions and high investment costs [3,4]. Various catalysts used in the WAO reaction, the catalytic wet air oxidation (CWAO), can significantly decrease reaction temperature, enhance decomposition efficiency of organic compounds and shorten reaction time [5]. In comparison with homogenous catalysts, heterogeneous catalysts are more promising because they are not necessary to remove metal ions of the effluents after the reaction. In the last decades, heterogeneous noble metal catalysts (Ru, Pt, Pd, Ag, etc.) and metal oxide catalysts (CuO, Fe_2O_3, CoO, MnO_2, etc.) have been developed and show good activities in the CWAO of organic compounds [6–12], while the catalyst deactivation has also been observed due to the leaching of active phase and/or the adsorption of carbonaceous compounds on the surface of the catalysts [13–16]. Therefore, a great deal of attention has paid to the development of active and stable heterogeneous catalysts for use in the CWAO.

Recently, various carbon materials, including activated carbon (AC), graphite, carbon nanotubes (CNTs), carbon fibers, etc., with good chemical stability under acidic and basic reaction conditions have been used as supports. Especially, it is interesting that carbon materials in the absence of any active phase have been applied as catalysts in some catalytic fields [17–21]. In the CWAO of organic compounds, carbon materials have been directly used as catalysts [18,22–28]. For example, AC after treatment with strong oxidants has been firstly used as a catalyst in the CWAO of phenols and *p*-coumaric acid, and very desirable catalytic behavior has been observed. Moreover, carbon nanofibers (CNFs), multi-walled

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carbon nanotubes (MWCNTs), graphite with high surface area, as well as carbon xerogel modified by oxidation treatments, have shown good activity in the CWAO of phenol, organic acids (*p*-coumaric acid and oxalic acid) and aniline [25–28]. During the reaction, functional groups introduced on the surface of carbon materials via chemical modification have played an important role in the performance of carbon materials. Among various modification methods, wet chemical techniques using different oxidizing acids (HNO_3, HNO_3/H_2SO_4, etc.) and strong oxidants ($KMnO_4/H_2SO_4$, O_3, H_2O_2, air, etc.) are the most prevalent ones due to easy implementation in laboratorial and industrial settings [29].

Among those carbon materials, the CNTs, due to their excellent chemical stability and desirable catalytic performance, have been appointed as the promising materials for the CWAO of organic compounds at high temperature in the presence of oxygen/air. Different oxidation reagents (HNO_3, HNO_3/H_2SO_4, O_3, air, etc.) have been used to chemically modify the MWCNTs, which have significantly affected the surface properties (functional groups, pH_{pzc}, specific surface area, etc.) and catalytic performance of the MWCNTs [25,27,28]. For instance, strong oxidizing acids (HNO_3 and HNO_3/H_2SO_4) have generated a lot of oxygen-containing functional groups on the surface of the MWCNTs, and the functionalized MWCNTs have exhibited good activity in the CWAO of phenol [25,27]. In the literature [28], the MWCNTs were, respectively, treated with urea, N_2 and HNO_3, the functional groups have been introduced on the surface of the MWCNTs. It is found in the CWAO of oxalic acid that the MWCNTs with N-containing functional groups and the basic nature markedly have shown higher activity than that of the ones treated with HNO_3. These results indicate that the oxidizing conditions (oxidants and reaction conditions) exert an important effect on the structure and catalytic performance of the MWCNT in the CWAO of organic compounds, while the effect is not investigated in detail in the CWAO.

Herein the commercial MWCNTs as raw materials and phenol as a model pollutant have been investigated in the CWAO. Different oxidizing conditions have used for functionalizing the MWCNTs in the paper, to get a better insight into the relationship between the surface characteristic and catalytic performance of the MWCNTs and achieve efficient oxidation method of the MWCNTs in the CWAO of phenol. Moreover, the stability of the functionalized MWCNTs has been evaluated in the CWAO of phenol.

2. Materials and methods

2.1. Materials

Raw MWCNTs used in all experiments (ID: 3–10 nm, OD: 6–20 nm, purity > 99.5%) were supplied by Beijing Cnano Technology Limited in China. The chemical reagents were purchased from Chemical Reagent Beijing Company without further purification. Methanol, H_3PO_4 and acetic acid used in HPLC analysis were purchased from Sigma–Aldrich. O_3 was produced by EXT-120T ozone generator (Longevity Resources Inc., Canada) using pure oxygen as feed.

2.2. Catalyst preparation

Raw MWCNTs were immersed in a 37% HCl solution with sonicating for 30 min at room temperate (RT), washed with deionized water to remove metal catalysts in the MWCNTs, dried at 80 °C overnight, and then crushed for further oxidation treatment. The pre-treated MWCNTs were modified under different oxidizing conditions. (1) HNO_3/H_2SO_4. The pre-treated MWCNTs were immersed in the 67% HNO_3–98% H_2SO_4 solution with sonicating for 30 min, and then refluxed at 50 °C for 4 h. Two volume ratios of HNO_3/H_2SO_4 were used, namely 1:3 and 1:1. The resulting solids were washed with deionized water, dried at 80 °C overnight, crushed to obtain the acid-treated MWCNTs, and named as MWCNTs-NS-1/3 and MWCNTs-NS-1/1. (2) H_2O_2. The pre-treated MWCNTs were added into 30% H_2O_2 solution at RT for 12 h under continuously stirring. The resulting solids were filtered, washed with deionized water, dried at 80 °C overnight and crushed to obtain the H_2O_2-treated MWCNTs (MWCNTs-H). (3) O_3. The pre-treated MWCNTs were oxidized by gas O_3 of ca. 30 mg min^{-1} for 150 min at RT to obtain the O_3-treated MWCNTs (MWCNTs-O). (4) Air. The pre-treated MWCNTs were heated at 500 °C for 2 h in a tubular furnace under air to obtain the air-treated MWCNTs (MWCNTs-A). (5) The pre-treated MWCNTs were oxidized in deionized water at 155 °C under oxygen pressure of ca. 1.5 MPa for 2 h with stirring. The received solids were separated with 0.45 μm filter, dried at 80 °C overnight and crushed to obtain the functionalized MWCNTs (MWCNTs-W).

2.3. Catalyst characterization

Surface areas of the MWCNTs were measured by N_2 physisorption at 77 K in a TriStar II 3000 gas adsorption analyzer. Before each measurement, samples were outgassed at 200 °C for 4 h. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to obtain the information about the morphology of the MWCNTs. SEM analysis was carried out on the HITACHI S-4500 at an accelerating voltage of 15 kV. TEM analysis was measured with a JEOL 2010 HRTEM operated at an accelerating voltage of 120 kV. Raman spectroscopy was used to study the surface structure of the MWCNTs with a Spex 1403 Raman spectrometer at an excitation laser wavelength of 633 nm in the range of 800–2000 cm^{-1}. Fourier-transform infrared spectroscopy (FT-IR) was applied to identify surface functional groups on the MWCNTs with a Bruker Fourier-transform spectrophotometer Magna-IR 750. X-ray photoelectron spectroscopy (XPS) was used to investigate surface elements of the MWCNTs before and after oxidation treatments. XPS measurement was carried out on the PHI ESCA 5700 instrument, with an Al Kα X-ray source (1486.6 eV) and pass energy of 29.35 eV operating at a pressure of 7×10^{-10} Torr. The C1s band at 284.60 eV was taken as an internal standard to correct possible deviations caused by electric charge of samples. The pH at the point of zero charge (pH_{PZC}) of the MWCNTs was measured according to the literature [30].

2.4. CWAO procedure

The CWAO reaction was performed in a 1 L reactor equipped with a magnetically driven stirrer. The reactor was described in previous study [10]. Firstly, a catalyst and 500 mL phenol solution were loaded into the reactor. N_2 was purged into the reactor to remove air, and then the reactor was heated to the desirable temperature. Pure oxygen was introduced into the reactor, and the reaction started under stirring. The time was as the reaction “zero”. Samples were periodically taken from the reactor, and filtered with 0.45 μm filter for analysis. The used MWCNTs were recovered at the end of each experiment, washed by deionized water, and dried at 80 °C for 24 h for reutilization in cyclic experiments.

2.5. Analytic methods

Phenol concentration was analyzed by HPLC (LC-10AD, PE) using an Eclipse XDB-C18 column, and the mobile phase was the mixture of methanol and 0.2% acetic acid aqueous solution (60/40, v/v) with the flow rate of 1.0 mL min^{-1}, and UV detective wavelength was set at 254 nm. The intermediates were measured with the mobile phase of 0.01 M H_3PO_4 aqueous solution and methanol (90:10, v/v) at 210 nm wavelength. Total organic carbon (TOC) of