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Catalytic wet air oxidation of phenol over carbon nanotubes: Synergistic effect of carboxyl groups and edge carbons

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ABSTRACT

It has been widely documented that the oxygen-containing functionalities, especially carboxyl groups, on carbon surfaces play crucial roles in the catalytic wet air oxidation (CWAO) reactions. Herein, the CWAO of phenol with molecular O_2 as terminal oxidant using cylindrical and herringbone carbon nanotubes (CNTs) underwent different treatments as catalysts were conducted in batch mode. It was uncovered that the catalytic function of carboxyl groups strongly depended on the structure of CNTs. Parallel CNTs (*p*-CNTs) with cylindrical graphitic walls displayed the highest catalytic activity after nitric acid oxidation, due to the carboxylated carbon debris (CDs) coating on surfaces. For herringbone CNTs (*h*-CNTs), carboxyl groups are mostly linked to its sidewalls, where abundant edge carbons were exposed, providing an enhanced CWAO activity. The positively synergistic effect of carboxyl groups and adjacent edge carbons was responsible for the activation of O_2, leading to the improved CWAO activity. This study provides a new insight into the structural effect of carbon materials on the CWAO of phenol.

1. Introduction

With the rapid industrialization, a large amount of waste water has been produced and discharged to the nature surface water. The bio-toxic organic contaminants, represented by phenol and its derivates, are highly hazardous to the aquatic life [1]. It is necessary to treat the phenol-contaminated waters before disposal. A lot of efforts were devoted to developing effective methods to remove these pollutants, such as adsorption and biological treatment. However, they are mostly impractical for the removal of phenolic waste water at a large scale [1,2]. Catalytic wet air oxidation (CWAO) was reported as an effective and environmentally benign technology to remove refractory organic pollutants, such as dyes, phenol, and other organic compounds [3–5]. In this process, at high pressures (5–200 MPa) and temperatures (150–325 °C), the organic pollutants could be totally oxidized into CO_2, H_2O and other less-toxic intermediates using suitable catalysts [4].

The transition metal-based catalysts, such as Pt, Ru, Pd, Ir, Rh, Rd, Fe, Mn, Zn, Cu etc. have been investigated as CWAO catalysts [6–9]. Arena et al. [7] have applied ceria-based noble metal (Pt/CeO_2) and transition metal-oxide ($MnCeO_x$) as catalysts for the CWAO of phenol. They found that $MnCeO_x$ ensured a fast and complete phenol conversion with a high total organic carbon (TOC) removal (>80%), while Pt/CeO_2 elongated the lifetime of catalyst and confer a higher resistance to deactivation. Fortuny et al. [8] utilized the bimetallic metal oxides (e.g., CoO, FeO, MnO or ZnO and CuO) supported on γ-Al_2O_3 as catalysts for the CWAO of phenol. The combination of ZnO-CuO/γ-Al_2O_3 was found to be superior for this reaction. Yang et al. [9] prepared CeO_2-TiO_2 catalysts for the CWAO of phenol in batch mode. These metal-based catalysts have displayed good performance in the CWAO of phenol. However, some disadvantages limited the practical applications: e.g. the high cost, easy deactivation by the deposition of carbonaceous materials, and leaching the active sites, which could cause the secondary pollution [6].

Recently, the nanocarbons as metal-free catalysts have attracted a lot of attentions, due to the high specific surface areas, corrosion resistance, environmental acceptability, thermal stability and readily surface modification [10–12]. The defects and surface chemistry of carbon materials were believed to play significant roles in the oxidative dehydrogenation of hydrocarbons [13–15], the activation of methane [16,17], hydrogenation of nitrobenzene [18], the hydroxylation of benzene to phenol [19], selective oxidation [20–24], the dehydration of alcohols [25,26] and environmental remediation [27–32]. So far, activated carbons

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(AC), carbon xerogels and carbon nanotubes have been proved to be excellent catalysts for the CWAO of phenol [1,33,34]. Nevertheless, the exploration of active sites over these carbon materials is rather complex than we expected and still a challenge for the CWAO. The carboxylic groups have been considered as the active sites for the CWAO of phenols [35]. Yang et al. and Wang et al. found that the carboxylic groups and weakly acidic nature of the surface of the functionalized carbons impacted the CWAO of phenol [35–38]. In contrast, Figueiredo and co-workers reported that HNO_3 treatment on CNTs displayed a negative effect on the CWAO activity, and they believed that the carbon materials with more basic character may be more active for CWAO. Furthermore, Yang et al. noticed that although the RGO and GO contained the similar amount of carboxylic acid groups, the RGO still showed the lower catalytic activity than the GO did in the CWAO of phenol [37]. Font et al. applied AC as catalyst for the CWAO of phenol in a fixed bed reactor and found that the decrease of surface area and mass consumption over AC resulted in the loss of activity in this reaction [39]. Overall, the intrinsic active sites for the CWAO of phenol catalyzed by carbon materials are still undefined and more detail investigations on the surface chemistry and structure of carbon materials are needed.

In this work, CNTs with parallel and herringbone-like walls were selected as catalysts for the CWAO of phenol. The surface chemistry of these two types of CNTs were investigated carefully. On both of the CNTs, the carboxylic groups acted as active sites. However, compared with parallel CNTs (*p*-CNTs), the herringbone CNTs (*h*-CNTs) displayed an intrinsic difference on the catalytic activity in the reaction. To our best knowledge, it is the first time to notice the positive effect of edge carbons in the CWAO of phenol. The high activity of the *h*-CNTs can be attributed to the synergistic effect of the edge carbons and carboxylic groups.

2. Experimental section

2.1. Catalyst preparation

The graphite and AC were purchased from Qingdao Taineng Graphite Co. Ltd. The *h*-CNTs were purchased from the Shenzhen Nanotech Port Co., Ltd. The *p*-CNTs were synthesized according to our previous works [21,22]. In brief, *p*-CNTs were produced by a chemical vapor deposition (CVD) method with liquefied petroleum gas as carbon source over a $FeMo/Al_2O_3$ catalyst in a horizontal tubular quartz furnace with 4 cm inner diameter (i.d.). The details of $FeMo/Al_2O_3$ catalyst can be found in Ref. [40]. Before the growth of CNTs, the catalyst was activated by a mixture of H_2 and N_2 (25 and 25 $Ncm^3\ min^{-1}$) for 30 min. The growth of CNTs was carried out at 700 °C for 130 min with 20 $Ncm^3\ min^{-1}$ liquefied petroleum gas, 10 $Ncm^3\ min^{-1}$ H_2, and 50 $Ncm^3\ min^{-1}$ N_2. Graphite oxide (GO) was prepared from graphite powders by the modified Hummers' method [41], and then reduced with hydrazine hydrate (N_2H_2) to produce reduced graphite oxide (r-GO) [42]. All the carbon catalysts were washed by 12 mol/L HCl solution to remove the metal impurities before usage.

The CNTs were functionalized as follows: the CNTs were refluxed in 9 mol/L HNO_3 solution at 110 °C for 2 h, and then washed by deionized water for several times, followed by drying at 110 °C overnight. The NaOH treatment for removing carbon debris (CDs) was conducted as follows: a certain amount of CNTs was dispersed into an 8 mol/L NaOH solution, and then the mixture was sealed into a 50 mL Teflon-lined autoclave, which was flushed by N_2 before heating. The autoclave was heated to 100 °C with a stirring speed of 1100 rpm for 48 h. Finally, the mixture was filtered and the obtained solid sample was dried at 110 °C overnight.

2.2. Catalyst characterizations

Brunauer–Emmett–Teller (BET) specific surface areas (SSA) were measured by N_2 adsorption at liquid N_2 temperature in an ASAP 2010 analyzer. Raman spectra were obtained in a LabRAM Aramis micro Raman spectrometer with an excitation wavelength at 633 nm with 2 μm spot size. Transmission electron microscope (TEM) images were obtained with a FEI Tecnai G2 12 microscope operated at 100 kV. The specimens for TEM were prepared by ultrasonically suspending the sample in acetone and depositing a drop of the suspension onto a grid. X-ray photoelectron spectroscopy (XPS) was performed in a Kratos Axis ultra (DLD) spectrometer equipped with an Al Ka X-ray source in ultrahigh vacuum (UHV) ($<10^{-10}$ Torr). Binding energies (±0.2 eV) were referenced to the C_{1s} peak at 284.6 eV as graphite.

2.3. The CWAO of phenol

The catalytic wet air oxidation of phenol was carried out in a magnetic stirred 50 mL Teflon-lined autoclave in batch mode. Typically, 30 mL 1000 mg/L phenol solution and 50 mg catalyst were charged into the autoclave. 1100 rpm stirring speed was used to minimize the effect of mass transfer and homogenize the mixture [23]. Before reaction, the reactor was flushed with N_2. Then, the reactor was heated to a stable operational temperature, and subsequently pure O_2 was fed into the reactor (defining $t = 0$). The residual concentration of phenol can be determined by High Performance Liquid Chromatography (Agilent Hypersil ODS, 5 μm × 250 mm × 4.6 mm) equipped with an ultraviolet (254 nm). A column temperature of 298 K and a flow of 1 $mL\ min^{-1}$ were applied. The mixture of methanol and 1% acetic acid solution (V/V = 50/50) were used as eluent.

2.4. Electrochemical measurements

The amount of edge carbons was determined by an electrochemical method developed by Hallam et al. and Yuan el al [43–45]. The electrochemical measurements were performed in a three-electrode cell connected to an electrochemical analyzer (CH Instruments 760D). Cyclic voltammogram (CV) was carried out on a GC electrode (4 mm in diameter) with 10 mL catalyst ink (catalyst loading 159.2 $mg\ cm^{-2}$) in O_2 saturated 0.1 M KOH and 0.005 M $K_3[Fe(CN)_6]$ solution with a certain scan rate.

The apparent overall electron transfer rate, k^0_{obs}, typically arises from two structural contributions, edge plane (k^0_{edge}) and basal plane (k^0_{basal}), as described in Eq. (1) [43,44]:

$$k^0_{obs} = k^0_{edge}\,(\theta_{edge}) + k^0_{basal}\,(1\text{-}\theta_{edge}) \quad (1)$$

For the CNTs, the electron transfer at the edge plane is much faster than that of basal plane, thus in current situation, $k^0_{edge} \gg k^0_{basal}$ [43]. According to the literature, the k^0_{edge} was 0.1 cm/s [46]. The global coverage of edge plane defects of CNTs could be quantified with k^0_{obs} determined from the Nicholson method [47], which was utilized to deduce the standard electron transfer rate by using the following Eq. (2) [43–45]:

$$\psi = k^0_{obs}\,[D_0 \pi \nu n F/(RT)]^{-1/2} \quad (2)$$

Where D_0 is the diffusion coefficient of ruthenium(III)hexamine (9.1×10^{-6}, 0.1 M KCl) [48], ν ($V\ s^{-1}$) is the scan rate, F is the Faraday constant, n is the number of electrons transferred in the electrochemical process. R and T the gas constant and absolute temperature (298 K), respectively. ψ is the kinetic parameter, which could be estimated under different scan rates using the empirical