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Catalytic wet air oxidation of phenol with functionalized carbon materials as catalysts: Reaction mechanism and pathway

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ABSTRACT

The development of highly active carbon material catalysts in catalytic wet air oxidation (CWAO) has attracted a great deal of attention. In this study different carbon material catalysts (multi-walled carbon nanotubes, carbon fibers and graphite) were developed to enhance the CWAO of phenol in aqueous solution. The functionalized carbon materials exhibited excellent catalytic activity in the CWAO of phenol. After 60 min reaction, the removal of phenol was nearly 100% over the functionalized multi-walled carbon, while it was only 14% over the purified multi-walled carbon under the same reaction conditions. Carboxylic acid groups introduced on the surface of the functionalized carbon materials play an important role in the catalytic activity in CWAO. They can promote the production of free radicals, which act as strong oxidants in CWAO. Based on the analysis of the intermediates produced in the CWAO reactions, a new reaction pathway for the CWAO of phenol was proposed in this study. There are some differences between the proposed reaction pathway and that reported in the literature. First, maleic acid is transformed directly into malonic acid. Second, acetic acid is oxidized into an unknown intermediate, which is then oxidized into CO₂ and H₂O. Finally, formic acid and oxalic acid can mutually interconvert when conditions are favorable.

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Introduction

Wet air oxidation (WAO) is one of the most effective technologies for degrading hazardous, toxic and highly concentrated organic contaminants in aqueous solutions. In WAO, organic compounds can be ultimately oxidized to CO₂ and H₂O and some other innocuous end products without the emission of HCl, NO_x, and SO_x, dioxins and fly ash (Luck, 1999; Yang et al., 2005).

Although WAO is a promising technology, its application in industrial wastewater treatment is limited because it is usually performed at high temperature (125–320°C) and pressure (0.5–20 MPa). Catalytic wet air oxidation (CWAO) is more promising than WAO because it can be performed under much milder

conditions. In recent years many noble metal catalysts and transition metal oxide catalysts have been proposed for CWAO (Yang et al., 2007a, 2010; Li et al., 2007; Fortuny et al., 1999; Liu et al., 2006). Although these catalysts have presented high activity in CWAO, the deactivation of catalytic activity usually occurs during the reaction. The catalytic activity deactivation mainly results from the leaching of active components from the catalysts under the severe operating conditions (Fortuny et al., 1999; Kim et al., 2007). Therefore, we sought to develop effective catalytic systems using readily available and stable materials.

Since carbon materials including graphite, activated carbon (AC), multi-walled carbon nanotubes (MWCNTs) and nanofibers are stable under both acidic and basic reaction conditions, the use

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of them as catalyst supports arouses great interest (Serp et al., 2003; Liu et al., 2008; Gallezot et al., 1997; Huang et al., 2009). Carbon materials can be also used as catalysts directly (Serp et al., 2003; Liu et al., 2011, 2013; Pyun, 2011). AC with high surface area was investigated first as a catalyst in CWAO and there have been many studies on its activity and stability (Stuber et al., 2005; Suarez-Ojeda et al., 2005, 2007; Santiago et al., 2005; Morales-Torres et al., 2010). Later the use of MWCNTs and commercial nanofibers (CNFs) as catalysts was also studied in CWAO (Serp et al., 2003; Yang et al., 2007b, 2008; Soria-Sánchez et al., 2011). Soria-Sánchez et al. (2011) studied the CWAO of phenol over CNFs, CNTs and graphite. They thought that the surface functional groups on the materials might be favorable for the activity of the catalysts. In our previous work, we also found that the surface functional groups on MWCNTs have a great effect on catalyst activity (Yang et al., 2007b, 2008). However, the mechanism whereby the surface functional groups influence catalytic activity remains unclear (Barbier et al., 1998; Rivas et al., 1998). Moreover, which types of surface functional groups play a main role in catalyst activity is also unknown. Finally, the reported reaction pathway for the CWAO of phenol over carbon materials includes many assumptions, and deserves more study.

In this study, we developed carbon material catalysts, including MWCNTs, carbon fibers (CFs) and graphite, with different chemical treatment methods. The catalysts were characterized by scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FT-IR). In addition, we studied the effect of surface functional groups on the catalyst activity of the carbon materials in the CWAO of phenol, detected the free radicals produced in the reaction with electron paramagnetic spin resonance (ESR), and analyzed the intermediates produced in the oxidation of various compounds. Based on the results from these experiments we investigated the mechanism through which surface functional groups influence the catalyst activity of carbon materials and explored the reaction pathway for the CWAO of phenols over the carbon materials.

1. Materials and methods

1.1. Reagents and materials

5,5-Dimethyl-1-pyrroline-*N*-oxide (DMPO) was purchased from Sigma-Aldrich Chemical Company (St. Louis, MO, USA). A stock solution of DMPO (100 mmol/L) was prepared and stored in the dark at -20°C . Commercial graphite and CFs were obtained from Tianjing Chemical Reagent Company in China (Tianjing, China). MWCNTs from Tsinghua Nafine Nano-powder Commercialization Engineering Centre (Beijing, China) were prepared by a chemical vapor deposition (CVD) method (Yang et al., 2007b). The other reagents were purchased from Beijing Chemical Company in China (Beijing, China) and used without further purification.

1.2. Catalyst preparation

Before use, the graphite and CFs were immersed in a HNO_3 solution (5%) for 24 hr while the MWCNTs were immersed in an HCl solution (37%) for 30 min. Then each sample was divided into two parts. One part was washed several times with deionized water, dried at 80°C in air overnight and then crushed. The resulting samples were referred to as purified carbon materials. The other part was functionalized by wet-chemical treatment with strong acids ($\text{HNO}_3\text{-H}_2\text{SO}_4$) to introduce surface functional groups onto the surface of the carbon materials as follows: (1) The graphite was impregnated

in a mixture of 67% HNO_3 and 98% H_2SO_4 (1:3, in volume), sonicated for 20 min and kept overnight at room temperature; (2) The CFs were refluxed at 85°C for 2 hr in a mixture of 67% HNO_3 and 98% H_2SO_4 (1:3, in volume); and (3) The MWCNTs were sonicated for 20 min in a mixed solution of 67% HNO_3 and 98% H_2SO_4 (1:3, in volume), and then refluxed at 50°C for 4 hr (Yang et al., 2007b).

1.3. Characterization

The surface areas and pore structure of the carbon materials were determined by N_2 adsorption at 77 K in an automated gas sorption system (Autosorb, Quantachrome, Boynton Beach, FL, USA). Before each measurement, the samples were outgassed at 573 K for 3 hr. SEM measurement was carried out on a scanning electron microscope (HITACHI S-4500, Tokyo, Japan) at an accelerating voltage of 15 kV. The FT-IR analysis was carried out on a spectrophotometer (Magna-IR 750, Bruker, Karlsruhe, Baden-Württemberg, Germany). A spectrum was recorded in the range of $500\text{--}4000\text{ cm}^{-1}$ (100 scans) at a resolution of 4 cm^{-1} . Boehm titration was conducted to determine the number of oxygen-containing functional groups on the surface of carbon materials according to the procedures described by Boehm (2002). One gram of carbon sample was added into 50 mL of NaHCO_3 solution (0.05 mol/L) and stirred at room temperature for 24 hr. The resultant slurry was then filtered and titrated with HCl to determine the number of carboxylic acid groups.

1.4. Catalytic test and analysis

CWAO of phenol was carried out in a 1-L autoclave reactor, which was specifically described in our previous study (Zhu et al., 2002). First 500 mL of 2000 mg/L phenol solution and 0.4 g of carbon materials (if necessary) were introduced to the reactor. The reactor was then sealed. After purging with nitrogen gas for 10 min, the reactor was heated to the reaction temperature of 160°C . As soon as the temperature was reached, pure oxygen was introduced into the reactor until the total pressure was equal to 2.5 MPa. This time was set as “zero” reaction time. Afterwards, the reaction was performed for 120 min. During the reaction, water samples were periodically taken from the reactor. The used carbon materials were washed with deionized water, dried about 80°C overnight, and then analyzed to characterize their structure.

In order to determine the adsorption capacity of the carbon materials for phenol, adsorption experiments were conducted with the carbon materials at room temperature for 24 hr. The dosage of the carbon materials and initial phenol concentration were the same as in the experiments for the CWAO of phenol.

The experiments for the CWAO of carboxylic acids were conducted according to the procedures mentioned above. The tested carboxylic acids included maleic acid, acrylic acid, malonic acid, oxalic acid, acetic acid and formic acid. The used catalyst was the functionalized MWCNTs.

The catalytic activity of the carbon materials in CWAO was assessed by the removal of phenol. The concentration of phenol was determined using an HPLC method with an ODS-3 column and a UV detector (LC-10AD, Shimadzu, Kyoto, Japan). The mobile phase was a mixture of methanol/water (0.1% acetic

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