



Adsorption of acetaldehyde onto carbide-derived carbon modified by oxidation



Hongyan Wang^a, Yifei Sun^a, Tianle Zhu^{a,*}, Wenzheng Wang^a, Hua Deng^b

^a School of Chemistry and Environment, Beijing Key Laboratory of Bio-Inspired Energy Materials and Devices, Beihang University, Beijing 100191, China

^b Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

HIGHLIGHTS

- The influence of oxidation modification on the properties of CDC was studied.
- The relationship between the properties and adsorption performance was studied.
- The acidic oxygen-containing groups in CDC increase the adsorption capacities.
- DFT predicts the role of acidic oxygen-containing groups for adsorption.

ARTICLE INFO

Article history:

Received 30 January 2015

Received in revised form 21 March 2015

Accepted 23 March 2015

Available online 28 March 2015

Keywords:

Adsorption

Acetaldehyde

Carbide-derived carbon

Oxidation

Density functional theory

ABSTRACT

The adsorption of acetaldehyde over carbide-derived carbon (CDC) modified with nitric acid, hydrogen peroxide, or air was investigated. The physicochemical properties of the original and modified CDCs were characterized by N₂ adsorption, Fourier transform infrared spectrometer, temperature programmed desorption and X-ray photoelectron spectroscopy. It was observed that the oxidation modification, especially the nitric acid treatment, could significantly enhance the adsorption performance of CDC for acetaldehyde. The increase of acidic oxygen-containing groups like carboxylic acids and anhydrides in the modified CDCs results in the increase of adsorption performance. The density functional theory calculations and in situ Diffuse Reflectance Infrared Fourier Transform Spectroscopy show that these acidic oxygen-containing groups display strong hydrogen bonding interactions with acetaldehyde molecule, leading to the enhanced adsorption performance.

© 2015 Published by Elsevier B.V.

1. Introduction

The air quality of cabins such as manned spacecraft and submarine has been a great concern since the cabins are in airtight states. A healthy and safe atmosphere is a fundamental requirement for the crew members' health, the quality of their work, and even the safety of airtight cabins. To meet this requirement, the development of highly reliable and efficient life-support system is required. A key function of the system is the removal of trace volatile organic compounds (VOCs), which are introduced through the offgassing of spacesuit materials, or through the metabolic production (e.g. breathing, sweating, etc.) of crew members. These VOCs can be hazardous to crew members' health with side effects ranging from headaches to heart damage, based on the exposure level and duration [1–4]. Therefore, the removal of VOCs is essential for improving cabin air quality.

Adsorption by activated carbon (AC) is a common approach for VOC removal in cabins and works well for macromolecule organic

compounds like aromatics [2,3]. However, those highly volatile, low molecular weight organic compounds such as acetaldehyde are typically poorly adsorbed onto the traditional AC. In our previous study, we found out that a new type of porous carbon material, carbide-derived carbon (CDC), could adsorb much more acetaldehyde than commercial activated carbons and appears as a promising adsorbent in cabins due to its unique pore properties [5]. However, it is well known that the adsorption performance of an adsorbent such as carbon material depends not only on its pore properties but also on its surface chemistry [6]. The surface chemistry of carbon is related to the presence of heteroatoms (e.g. hydrogen, oxygen, nitrogen, sulfur and phosphorus), which are bonded at the edges of the graphite-like layers and form organic functional groups such as carboxylic acids, anhydride, lactones, phenols, amines, nitro compounds, and phosphates [7]. These functional groups, especially oxygen functional groups, have significant influence on the performance of AC as adsorbent, because they can promote the polarity and wettability of carbon and consequently benefit the adsorption performance, especially for the polar organic compounds [8]. Considering the huge

* Corresponding author.

influence of oxygen functional groups on the performance of carbon materials, methods allowing the control of both the nature and concentration of oxygen functional groups for specific applications have been studied and the oxidation treatment is the most commonly used method. The oxidation process of carbon materials can be carried out in the gas phase (dry method) using oxygen, air, or ozone [9,10], or in the liquid phase (wet method) by means of H_2O_2 , HNO_3 , $(\text{NH}_4)_2\text{S}_2\text{O}_8$, etc. [9,11] to introduce surface oxygen complexes on the carbon surface. There are many factors that are responsible for the nature of surface groups created during oxidation treatment, such as the type of the oxidant, the oxidation temperature and time. Besides, the characteristics of carbon materials including origin and history of preparation also play an important part [12,13]. However, to the best of our knowledge, the influence of oxidation modification on the pore properties and surface chemistry of CDC, and the relationship between these properties and adsorption performance, have not been systematically studied. The unique structure of CDC may yield surface properties that are different from those of most other carbon materials, which may affect its adsorption performance significantly.

For these reasons, the main objective of this study was to investigate the effect of oxidation modification, by means of liquid phase oxidation (HNO_3 and H_2O_2) and gas phase oxidation (air), on the properties and adsorption performance of CDC for acetaldehyde. The pore structure and surface chemistry of CDCs were characterized by N_2 adsorption, fourier transform Infrared Spectrometer (FT-IR), temperature programmed desorption (TPD) and X-ray photoelectron spectroscopy (XPS). Meanwhile, the adsorption phenomena were simulated by the density functional theory (DFT) and compared with the experimental results.

2. Experimental

2.1. Preparation of original and modified CDCs

The original CDC was prepared by selective etching Ti from commercial TiC precursor (99.5% purity, 30–40 mesh, Zhuzhou GuangYuan Cemented Material Co., Ltd, PR China) by freshly prepared chlorine. The chlorination equipment and methodology is well described elsewhere [5]. The TiC precursor was placed in a horizontal quartz tube furnace. The tube was purged with argon (Ar) at room temperature for 30 min to remove air, and then heated to 700 °C at the heating rate of 10 °C min^{-1} . Once the desired temperature was reached, the Ar flow was stopped and chlorine gas was passed through the tube furnace at a flow rate of about 30 ml min^{-1} for 2 h, and then the furnace was cooled down to room temperature under Ar purge.

Subsequently, the CDC was oxidized in the liquid phase (HNO_3 , H_2O_2) and gas phase (air). In the first two cases, 1 g of CDC was mixed with 10 ml of HNO_3 (5 mol ml L^{-1}) or H_2O_2 (30%) solutions for 12 h at room temperature. The oxidized CDCs were washed with deionized water until neutral pH, and dried at 105 °C for 3 h. The samples were designated as CDC-N and CDC-H, respectively. For the gas phase oxidation, the CDC was heated in the tube furnace from room temperature to 300 °C under the constant flow of N_2 , and then, the reactor was kept at this temperature under a flow of air for 1 h. After that, the furnace was cooled down to room temperature in N_2 and the sample obtained was denoted as CDC-A. All samples prepared were kept in glove box under N_2 atmosphere, before subsequent experiments.

2.2. Evaluation of adsorption performance

The details of the adsorption test were well described in previous work [5] and only brief description was given here. The

acetaldehyde was prepared by bubbling air into liquid acetaldehyde that was kept at 10 °C with a thermostat water bath. Then, the acetaldehyde was mixed with diluent gas at a gas-mixing chamber to obtain the desired concentration ($23 \pm 0.5 \text{ mg m}^{-3}$), which was monitored by an online gas chromatograph (GC-17A, Shimadzu) with a flame ionization detector. The adsorption measurement of acetaldehyde was performed in a continuous flow fixed-bed quartz reactor (i.d. = 10 mm) containing 0.26 g adsorbent, operating under atmospheric pressure at 25 °C. Relative humidity of the reaction gas was $35 \pm 5\%$. It was noteworthy that prior to all measurements, samples were degassed at 120 °C in flow of N_2 for 1 h to clear the possible adsorbates.

2.3. Characterizations of adsorbents

The porosity of CDCs was characterized by N_2 adsorption at -196 °C using a QuadraSorb Station 1 instrument. Prior to the N_2 adsorption, the samples were first outgassed at 200 °C for more than 12 h. The specific surface area (SSA) was calculated by using the Langmuir method. The micropore volumes (V_{mic}) were determined by the t-method. The pore size distributions (PSDs) were determined by using the nonlocal density functional theory method for slit shaped pores provided by Quantachrome data reduction software.

The FT-IR measurements were performed on a FT-IR spectrometer (E55Xfra106, BRUKER, Germany) in the frequency range of 400–4000 cm^{-1} , using KBr disk method.

The TPD was performed with a custom built setup equipped with a mass spectrometer (Omnistar™ Baltazar). In a typical experiment, the sample (100 mg) was placed in an U-shaped quartz tube inside an electrical furnace and heated up to 900 °C at 10 °C min^{-1} in a constant Ar flow of 50 ml min^{-1} . The desorbed CO_2 ($m/z = 44$) and CO ($m/z = 28$) were monitored with the mass spectrometer during the heating process. Prior to desorption experiments, the samples were degassed for 1 h in Ar stream (50 ml min^{-1}) at 120 °C.

XPS were acquired on an ESCALAB 250 electron spectrometer equipped with a 150 W Al K α radiation as a primary excitation source. The binding energy scale was calibrated to 284.6 eV for the main C1s peak.

In situ Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) spectra were recorded in a Nicolet 6700 FTIR spectrometer equipped with a smart collector and a liquid N_2 cooled MCT detector. The DRIFTS cell (Harrick) with ZnSe windows is fitted a heating cartridge that allows sample to be heated under atmospheric pressure. Before each experiment, 0.05 g finely ground sample was pretreated at 120 °C for 1 h in a flow of N_2 and then cooled down to room temperature. The background was collected before switching N_2 with the reaction gas and the spectra were recorded with a resolution of 4 cm^{-1} and accumulating 32 scans after subtraction of the background.

2.4. DFT calculation

The molecular geometries of all compounds (acetaldehyde, CDC models and their adsorption complexes) were fully optimized using the DFT at the B3LYP/6-31G(d) computational level. All DFT calculations were performed with the Gaussian 09 program [14]. The original CDC model, graphene was composed of 4 benzene rings and hydrogen atoms that were used to saturate the carbon atoms with dangling bonds at the edge of graphene sheet, which is nearly the same size of model reported in previous work [15]. The oxygen functional groups considered in this work are carboxylic acid, anhydride and phenol groups. These functional groups were selected based on the characterization results that confirmed their presence and effects on adsorption. The acetaldehyde

Download English Version:

<https://daneshyari.com/en/article/6584939>

Download Persian Version:

<https://daneshyari.com/article/6584939>

[Daneshyari.com](https://daneshyari.com)