Adsorption of benzene, cyclohexane and hexane on ordered mesoporous carbon

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ABSTRACT

Ordered mesoporous carbon (OMC) with high specific surface area and large pore volume was synthesized and tested for use as an adsorbent for volatile organic compound (VOC) disposal. Benzene, cyclohexane and hexane were selected as typical adsorbates due to their different molecular sizes and extensive utilization in industrial processes. In spite of their structural differences, high adsorption amounts were achieved for all three adsorbates, as the pore size of OMC is large enough for the access of these VOCs. In addition, the unusual bimodal-like pore size distribution gives the adsorbates a higher diffusion rate compared with conventional adsorbents such as activated carbon and carbon molecular sieve. Kinetic analysis suggests that the adsorption barriers mainly originated from the difficulty of VOC vapor molecules entering the pore channels of adsorbents. Therefore, its superior adsorption ability toward VOCs, together with a high diffusion rate, makes the ordered mesoporous carbon a promising potential adsorbent for VOC disposal.

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Introduction

Volatile organic compounds (VOCs) are a class of air pollutants in industrial processes and daily human consumption (Lin et al., 2011; Parmar and Rao, 2009; He et al., 2012; Hernandez et al., 2003; Ghoshal and Manjare, 2002; Reguer et al., 2011; Gonzalez-Miquel et al., 2013). Because of their high vapor pressure and low boiling point, they are prone to be emitted into the atmosphere, causing great environmental problems because of their intrinsically hazardous properties. Not only they are the main precursors of photochemical reaction in the atmosphere, inducing ozone destruction and photochemical smog, but they are also toxic toward human health, and may cause pathogenic, mutagenic and even fatal diseases (Wang et al., 2007; Parmar and Rao, 2009;

He et al., 2012; Hernandez et al., 2003). Unfortunately, with the continuous development of industrialization in recent years, the emissions of VOCs have gradually increased to a new high level (Ghoshal and Manjare, 2002; Wu et al., 2011). In order to reduce the harmful effect of VOCs on the environment and humans, stringent regulations have already been enforced to limit further VOC emission. Meanwhile, the abatement technologies for VOCs have aroused great attention and they are considered a major component in the elimination of pollution.

Various kinds of methods, such as catalytic oxidation, adsorption, absorption, photocatalytic processes, and biological methods are employed for the abatement of VOCs (Wang et al., 2007; Parmar and Rao, 2009; He et al., 2012; Hernandez et al., 2003; Ghoshal and Manjare, 2002; Reguer et al., 2011;

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Gonzalez-Miquel et al., 2013). Among them, adsorption technology seems to be the preferred choice due to its great advantages of convenience and high efficiency (Hernandez et al., 2003; Ghoshal and Manjare, 2002; Reguer et al., 2011). In addition, the adsorption process is an important intermediate step when considering the recovery of valuable VOCs (Ghoshal and Manjare, 2002; Ramirez et al., 2005). It is generally accepted that for adsorption technology, a proper adsorbent is important for the efficient removal of VOCs. Until now, activated carbon has been used as the most popular adsorbent due to its low cost and relatively good adsorption properties (Ramirez et al., 2005; Lillo-Rodenas et al., 2006; de Souza et al., 2012). However, some weaknesses have limited its further application. Activated carbon is a typical microporous adsorbent, with most pores in the micropore range (<2 nm), which may slow the transport velocity of VOC molecules. In addition, the irregularly shaped pores in activated carbon increase the diffusion resistance of adsorbate molecules during the adsorption process and a long time is needed to reach adsorption equilibrium (Nevskaia et al., 2004; Ji et al., 2010; Britt et al., 2008). Thus a new adsorbent with high specific surface area, large pore volume and relative larger pore size is urgently needed.

Ordered mesoporous carbon (OMC) is a kind of mesoporous material possessing high specific surface area, large pore volume and tunable pore size, which can be used as a catalyst support and adsorbent as well as in electric capacitors (Wang et al., 2013; Hartmann et al., 2005; Tanaka et al., 2013). Generally, OMC can be synthesized using low-molecular-weight resol as carbon source, silica as an additive and triblock copolymer Pluronic F127 as a structure-directing agent *via* the evaporation-induced self-assembly (EISA) method (Ma et al., 2013; Li and Zhao, 2013). Benefiting from its relatively large surface area and pore volume, OMC shows great potential advantages as an adsorbent in environmental remediation processes. Hartmann et al. (2005) investigated the adsorption properties of Vitamin E on mesoporous carbon molecular sieves, and the large adsorption amount indicated the superior adsorption properties of mesoporous carbon molecular sieves compared to microporous carbon adsorbents. In addition, they certified that the adsorption process takes place in the channels of the mesoporous carbon adsorbent, contrary to the conventional opinion that mesoporous channels only provide passage for adsorbate molecules rather than supplying efficient adsorption sites (Hartmann et al., 2005). Zhuang et al. (2009) used OMCs for the efficient disposal of wastewater containing bulky dye molecules for the first time. The results suggested that OMC can be used as an efficient adsorbent for removing bulky dye molecules from water. They proved that a mesoporous carbon with high surface area, large pore volume and bimodal pores showed the highest adsorption capacity among three selected OMCs with different pore structures. Recently, Yuan et al. (2013) adopted OMC as an adsorbent for the separation of CO_2 and N_2 from CH_4, and the results indicated that OMC is a useful adsorbent, displaying both high selectivity and large adsorption capacity. These relevant studies indicate the superior adsorption properties of OMC. However, as a typical class of pollutant, the adsorption properties of VOCs on OMC have been relatively less studied, to the best of our knowledge.

In this study, OMC was synthesized *via* the EISA route and the adsorption properties of three typical kinds of VOCs on OMC were studied to investigate the potential application of OMC in VOC adsorption. The selected VOCs were benzene, cyclohexane and hexane, which have different molecular structures based on six carbon atoms and are used in substantial amounts in industrial processes. The adsorption equilibrium and kinetics of the selected VOCs were studied and isosteric heats of adsorption were calculated. In addition, relationships between the adsorption properties and structures of the selected VOC molecule were discussed.

1. Materials and methods

1.1. Chemicals

Poly(propylene oxide)-b-poly(ethylene oxide)-b-poly(propylene oxide) triblock copolymer Pluronic F127 was purchased from Sigma-Aldrich Company. Ethyl silicate (SiO_2, 28.4%+), phenol (99.5%+), formaldehyde solution (37.0%–40.0% aqueous solution), sodium hydroxide (96.0%), hydrochloric acid (36.0%–38.0%), ethanol (99.7%+), and hydrofluoric acid (40.0%+) were purchased from Sinopharm Chemical Reagent Company. All chemicals were used as received without any purification process. Deionized water was used in all the experiments.

1.2. Synthesis of materials

Resol was first prepared from phenol and formaldehyde solution in a base-catalyzed process and refrigerated for the later procedure. Then the OMC was synthesized *via* the EISA process with some minor modifications by our group (Gao et al., 2011). Typically, 1.6 g F127 was dissolved in 6.0 g ethanol at 313 K, then 5.0 g resol solution was added to form mixture A. 2.08 g TEOS was added into the 1.0 g HCl solution (0.2 mol/L) and stirred for 30 min at 313 K to form mixture B. Then, mixture B was poured into A. After stirring for 30 min, the solution was transferred into dishes. The transparent thin film was scraped from dishes after the evaporation of ethanol and placed into a tubular furnace for a further carbonization process. The film was calcined at 623 K for 3 hr under nitrogen protection with a heating rate of 2 K/min and a nitrogen flow of 50 mL/min, respectively. Then the temperature was raised to 1173 K with the heating rate being 1 K/min and remained 2 hr for further carbonization. After that, the obtained composite was stirred in HF solution for 12 hr to remove the silica and finally synthesized OMC was obtained after drying at 378 K for 5 hr.

1.3. Material characterization

X-ray diffraction (XRD) patterns were recorded on a PANalytical X'Pert PRO MPD using Cu-Kα radiation (λ = 1.540598 Å). High-resolution transmission electron microscopy (HRTEM) analysis was conducted on a JEOL 2011 microscope at 200 kV. Textural properties were obtained using nitrogen sorption isotherms at liquid nitrogen temperature on a NOVA 1200 gas sorption analyzer. The BET surface area was calculated using experimental points at relative pressures of P/P_0 = 0.05–0.25. Total pore volume was obtained by the nitrogen amount adsorbed at P/P_0 = 0.99. Pore size distributions were calculated by analyzing the desorption branch of isotherms based on the