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Adsorption equilibrium and kinetics of CO_2, CH_4, N_2O, and NH_3 on ordered mesoporous carbon

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ABSTRACT

Ordered mesoporous carbon was synthesized by a self-assembly technique and characterized with TEM, Raman spectroscopy, and nitrogen adsorption/desorption for its physical and pore textural properties. The high BET specific surface area (798 m^2/g), uniform mesopore-size distribution with a median pore size of 62.6 Å, and large pore volume (0.87 cm^3/g) make the ordered mesoporous carbon an ideal adsorbent for gas separation and purification applications. Adsorption equilibrium and kinetics of carbon dioxide, methane, nitrous oxide, and ammonia on the ordered mesoporous carbon were measured at 298 K and gas pressures up to 800 Torr. The adsorption equilibrium capacities on the ordered mesoporous carbon at 298 K and 800 Torr for ammonia, carbon dioxide, nitrous oxide, and methane were found to be 6.39, 2.39, 1.5, and 0.53 mmol/g, respectively. Higher adsorption uptakes of methane (3.26 mmol/g at 100 bar) and carbon dioxide (2.21 mmol/g at 13 bar) were also observed at 298 K and elevated pressures. Langmuir, Freundlich, and Toth adsorption equilibrium models were used to correlate all the adsorption isotherms, and a simplified gas diffusion model was applied to analyze the adsorption kinetics data collected at 298 K and four different gas pressures up to 800 Torr.

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1. Introduction

Porous and nano-structured carbon materials are considered to be very promising in numerous applications as adsorbents, catalyst supports, and double-layer capacitors [1–4] because of their unique pore structures, low cost, light weight, and natural abundance of ingredients to synthesize them [5]. Ordered mesoporous carbon (OMC) is a unique porous carbon that was initially synthesized with a hard-template method by Ryoo et al. [6]. In the hard-template method, a mesoporous silica template such as SBA-15 or MCM-48 is first prepared, followed by doping a suitable carbon precursor on the silica template, then carbonizing carbon precursor to pure carbon at a high temperature, removing the silica template by dissolving it in a strong acid, and finally generating the ordered mesoporous carbon samples. On the other hand, synthesis of ordered mesoporous carbon by the soft-template method or self-assembly, originally developed by Dai and co-workers [7], is a relatively new and better technique as compared with the hard-template method. The drawbacks of the hard-template method include the instability during the graphitization step, difficulties in getting monolithic structures, involvement of toxic chemicals, and tediousness of the entire process [8,9]. These issues can be properly addressed or minimized in the soft-template process. In the self-assembly process, a single polymer or the carbon precursor is prepared, part of which is used as the templating agent and the remaining portion acts as the carbonization agent, thereby not requiring any separate template removal stage as required in the hard-template method.

Methane (CH_4), carbon dioxide (CO_2), nitrous oxide (N_2O), and ammonia (NH_3) are the common gases that have been extensively studied for adsorption for numerous purposes. CH_4, CO_2, and N_2O are greenhouse gases and believed to be directly responsible for the greenhouse effect giving rise to uncontrolled increase in mean global temperature. Methane adsorption is also a very popular research area for establishing adsorbed natural gas (ANG) technology for future energy systems. Ammonia is industrially important but a major pollutant that needs to be removed from many industrial gas streams.

Several types of adsorbents investigated for their CO_2 adsorption capacities include the CWZ-35 type of activated carbon [10], amine-treated mesoporous silica [11], and chemically activated urea–formaldehyde and melamine–formaldehyde resins [12]. Fauth et al. [13], Essaki et al. [14], and Kato et al. [15] made use of certain lithium-based adsorbents like lithium zirconate and lithium silicate to adsorb CO_2 in the temperature swing approach. Xu et al. [16,17] prepared a MCM-41 type of adsorbent impregnated with polyethylamine (PEI) to adsorb CO_2 up to 246 mg/g. The highest CO_2 adsorption of 35 mmol/g was reported by Millward and Yaghi [18] using MOF-177 at 45 bar and room temperature.

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Methane sorption was performed in various kinds of carbonaceous adsorbents. Lee et al. [19] used phenol-based activated carbons to adsorb CH_4 up to 8.055 mmol/g at 35.64 bar and 193.15 K. Himeno et al. [20] performed CH_4 adsorption on different kinds of commercially available activated carbons and the maximum adsorption uptake was found to be 10 mol/kg at 3000 kPa and 273 K. Zhou et al. [21] loaded the multiwall carbon nanotube with water and reported CH_4 uptake of 8 wt.% at 10 MPa and 275 K. A much higher methane adsorption capacity of 30 wt.% on an activated carbon preloaded with water was also obtained by the same research group at 10 MPa and 277 K [22].

Adsorption of nitrous oxide on carbonaceous materials and other adsorbents is hardly reported. The most common technique for removing N_2O is to decompose or reduce it over a suitable catalyst. The catalysts that were commonly used are zirconia [23], platinum [24,25], α-manganese sesquioxide [26], and the MFI-type of zeolite, such as Fe–ZSM-5 at 773 K and in the presence of a small amount of NO_x as the promoter [27–34]. Recently, it was experimentally confirmed that bimetallic FER catalyst containing iron and ruthenium increases the catalytic activity [35,36]. A N_2O adsorption uptake of 2.5 mol/kg on the silicalite-1 at 273 K and 120 kPa was reported by Groen et al. [37]. Adsorption of N_2O was also investigated in a certain type of pseudomorphs by Lamb and West [38]. Unlike nitrous oxide, carbonaceous materials were commonly used in adsorption of ammonia. Ellison et al. [39] performed NH_3 adsorption in single-wall carbon nanotubes. Park and Jin [40] used an ozone-treated activated carbon to adsorb NH_3. Ab initio calculation by Widjaja et al. [41] predicted Si(1 0 0) as a suitable adsorbent for NH_3.

The main objective of this study is to measure and compare the adsorption properties of carbon dioxide, methane, nitrous oxide, and ammonia on the ordered mesoporous carbon synthesized by the soft-template approach. The ordered mesoporous carbon was first prepared using the soft-template approach, and then characterized with transmission electron microscopy (TEM) for its ordered graphitic structure, Raman spectroscopy for its characteristic functional groups, and nitrogen adsorption and desorption at 77 K for its pore textural properties. Adsorption equilibrium and kinetics on these four adsorbate gases were measured at ambient temperatures (298 K) and gas pressures up to 800 Torr, which allow us to compare adsorption properties of these gases on the ordered mesoporous carbon under identical conditions. High-pressure adsorption experiments were performed for carbon oxide and methane at 13 bar and 100 bar, respectively, and at room temperature (298 K) to measure the adsorption capacities of these gases at elevated pressures. Adsorption equilibrium and kinetics models were also used to analyze the adsorption isotherms and kinetics data obtained in this work.

2. Experiments

2.1. Synthesis of ordered mesoporous carbon

The ordered mesoporous carbon samples were synthesized by the soft-template approach following the procedures developed by Dai's group [7]. The amounts of 1.25 g of phloroglucinol (99.99%, Across Chemicals) and 1.25 g of F127 (BASF) were dissolved in 4.26 g of deionized water and 4.76 g of 99.9% ethanol (Fisher). Then five drops of 37% hydrochloric acid (Across Chemicals) were added to the solution as a catalyst; the resulting solution was stirred for 30 min until light pink color appeared in the solution. The amount of 1.3 g of 37% formaldehyde was then added and the solution became cloudy after 30 min of stirring. After stirring for an hour the mixture was allowed to settle for 15 min. The bottom layer of the mixture contained the polymer solution and upper layer was basically composed of ethanol–water mixture. The bottom layer was separated from the mixture and put in a tube furnace for carbonization. The carbonization was carried out under a nitrogen gas flow at temperatures from 100 to 400 °C with a ramp rate of 1 °C/min, and from 400 to 850 °C with a ramp rate of 5 °C/min. The carbon product was finally maintained in the tube furnace under nitrogen flow at 850 °C for 2 h followed by cooling under a nitrogen flow.

2.2. Characterizations of ordered mesoporous carbon

To determine the inner matrix and pore structure of OMC, the carbon sample was examined with a transmission electron microscope (Hitachi H7650). The graphitic structure was determined by a Renishaw invia Raman spectrophotometer using a He–Ne laser source with a wavelength of 633 nm. The carbon sample was also characterized for its pore textural properties using a Micromeritics ASAP 2020 surface area and porosity analyzer. The pore textural properties including Langmuir and BET specific surface area, pore volume, and pore size were calculated by analyzing the nitrogen adsorption and desorption isotherms with the help of Micromeritics ASAP 2020 built-in software. Before starting the adsorption experiments, the sample was degassed in situ at 300 °C for 4 h to remove any guest molecule from the pores of OMC.

2.2.1. Gas adsorption measurements at ambient pressure and temperature

CH_4, CO_2, N_2O, and NH_3 adsorption equilibrium and kinetics on OMC samples were measured volumetrically in a Micromeritics ASAP 2020 adsorption apparatus at ambient temperature (298 K) and gas pressures up to 800 Torr. Ultrahigh-purity gases were introduced to the adsorption unit for adsorption measurements. The change of gas pressure in the sample chamber with time was monitored and converted by the instrument's software into the transient adsorption amount, which provided the adsorption kinetic data. The final adsorption amount at the terminal pressure gave the adsorption equilibrium amount at a given pressure. Fractional adsorption uptake curves were collected at different pressures at the time of generating kinetic data.

2.2.2. High-pressure adsorption data for CO_2 and CH_4

The high-pressure adsorption was performed gravimetrically in a Rubotherm magnetic suspension balance at room temperature (298 K) and pressure up to 15 and 100 bar for carbon dioxide and methane, respectively. The process flow diagram for the Rubotherm balance is shown in Fig. 1. Like all other gravimetric devices, this balance was also pre-examined with a blank run of empty balance and volume run sample loaded balance in order to measure the weight and volume of empty sample holder and sample itself before introducing the particular gas of interest, in this case, methane and carbon dioxide. The detailed operation procedures were described in our previous publications [42,43].

3. Results and discussion

3.1. Physical properties

3.1.1. TEM images

Fig. 2a shows a high-resolution TEM image of the ordered mesoporous carbon synthesized by the soft-template approach. The structural arrangement of our ordered mesoporous carbon sample is similar to that of synthesized by hard-template method reported by other researchers [44,45]. It can be seen from the image shown in Fig. 2a that this OMC has the same highly ordered graphitic structure with parallel channels (graphite ribbons) as shown in