Mesoporous carbon adsorbents from melamine–formaldehyde resin using nanocasting technique for CO_2 adsorption

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ARTICLE INFO

ABSTRACT

Mesoporous carbon adsorbents, having high nitrogen content, were synthesized *via* nanocasting technique with melamine–formaldehyde resin as precursor and mesoporous silica as template. A series of adsorbents were prepared by varying the carbonization temperature from 400 to 700°C. Adsorbents were characterized thoroughly by nitrogen sorption, X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), thermogravimetric analysis (TGA), elemental (CHN) analysis, Fourier transform infrared (FTIR) spectroscopy and Boehm titration. Carbonization temperature controlled the properties of the synthesized adsorbents ranging from surface area to their nitrogen content, which play major role in their application as adsorbents for CO_2 capture. The nanostructure of these materials was confirmed by XRD and TEM. Their nitrogen content decreased with an increase in carbonization temperature while other properties like surface area, pore volume, thermal stability and surface basicity increased with the carbonization temperature. These materials were evaluated for CO_2 adsorption by fixed-bed column adsorption experiments. Adsorbent synthesized at 700°C was found to have the highest surface area and surface basicity along with maximum CO_2 adsorption capacity among the synthesized adsorbents. Breakthrough time and CO_2 equilibrium adsorption capacity were investigated from the breakthrough curves and were found to decrease with increase in adsorption temperature. Adsorption process for carbon adsorbent–CO_2 system was found to be reversible with stable adsorption capacity over four consecutive adsorption–desorption cycles. From three isotherm models used to analyze the equilibrium data, Temkin isotherm model presented a nearly perfect fit implying the heterogeneous adsorbent surface.
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Introduction

Increasing concentration of carbon dioxide (CO_2), a major anthropogenic greenhouse gas, needs to be addressed because of its detrimental effect on the global climate. Its major source is the combustion of fossil fuels like coal, oil and gas, to deal with the world's energy requirements, which contribute to around 40% CO_2 emissions (Figueroa et al., 2008; Yang et al.,

2008). Global atmospheric CO_2 concentration has reached a value of ~395 ppmv at present from a preindustrial value of ~280 ppmv and is expected to reach a level of ~570 ppmv by 2100 (Samanta et al., 2012). Various approaches available for reducing CO_2 emissions include reducing energy demand by energy efficiency improvement, increasing renewable and nuclear energy usage, and carbon capture and sequestration (CCS) (Spigarelli and Kawatra, 2013; Steeneveldt et al., 2006;

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Yang et al., 2012). CCS is the only means of drastically reducing CO_2 emissions in the near term besides the consumption of fossil fuels for energy demands (Spigarelli and Kawatra, 2013; Yang et al., 2008). It could act as a bridging strategy in providing time for the advancement of fossil fuel alternatives. State-of-the-art available CCS technologies include chemical absorption, cryogenic separation, membrane separation and adsorption (Thiruvenkatachari et al., 2009). Mature technologies like absorption with amines suffer from high energy penalty for regeneration, amine degradation, and corrosion problems (Aaron and Tsouris, 2005). Less energy intensive processes like adsorption propounds huge potential in capture of CO_2 as they can produce high purity streams with low energy consumption and ease of operation. Hence a wide variety of adsorbents are studied to separate CO_2 from fossil fuelled power plants including zeolites (Cavenati et al., 2004; Siriwardane et al., 2001), carbon based adsorbents (Drage et al., 2007; Lu et al., 2008), metal organic frameworks (Li et al., 2012) and amine-supported materials (Gray et al., 2008; Harlick and Sayari, 2007). Carbon based adsorbents present numerous advantages like high adsorption capacity, fast adsorption kinetics and low regeneration energy. Moreover, they can be obtained from large variety of low cost sources, have high specific surface area and their porous structure can be tailored in addition to high chemical and mechanical stability and hence are deemed to be one of the promising CO_2 adsorbents (Sevilla et al., 2011; Stein et al., 2009).

According to IUPAC, the pores of a carbon material can be classified into three categories, namely micropore (<2 nm), mesopore (2–50 nm) and macropore (>50 nm) (Lee et al., 2006). Mesopores in the carbon material not only act as main transport arteries for the adsorbate but also contribute significantly to adsorption (Hu et al., 2000). Many methods have been employed to synthesize mesoporous carbon materials including carbonization of carbon-containing precursor, sol–gel process and nanocasting (Karandikar et al., 2007; Ryoo et al., 1999; Zhao et al., 2010). But due to the complexity of the carbon structure evolution, it is very difficult to generate carbon materials with controlled pore structures from the conventional activation techniques (Karandikar et al., 2007). Nanocasting is a powerful method for fabrication of mesoporous and hierarchical porous carbon materials that are more difficult to synthesize by conventional processes. It includes the infiltration of a carbon precursor in the template pores followed by heat treatment under controlled atmosphere and finally template removal to leave behind a porous carbon (Lee et al., 2004; Valdés-Solís and Fuertes, 2006; Zhao et al., 2006). The space once occupied by the template is thus transferred into the pores in the resulting carbon materials, and the carbon in the pores of the template becomes the continuous carbon framework (Liang et al., 2008; Lu and Schüth, 2006). Moreover, incorporation of nitrogen groups in the carbon framework provides the basic character thereby increasing the specific interactions between the carbon surface and CO_2 molecules. This can be achieved either by incorporating basic amine groups on the porous support or by using carbon precursors with high nitrogen content. Incorporation of basic amine groups by impregnation or grafting facilitates CO_2 binding but also leads to a loss of reusability after few adsorption cycles and also needs high regeneration energy in

certain cases (Hao et al., 2010; Sevilla et al., 2011; Thote et al., 2010). Alternatively, nitrogen containing carbon adsorbents can be prepared directly from nitrogen containing polymers such as acetonitrile, aniline, melamine *etc.* with templates like zeolite Y, MCM-41, and SBA-15 (Drage et al., 2007; Lu et al., 2004; Vinu et al., 2008; Wang et al., 2012). Pevida et al. (2008) prepared nitrogen enriched carbon adsorbents from melamine–formaldehyde resin by nanocasting and reported CO_2 adsorption capacity of 2.25 mmol/g at 25°C under pure CO_2 atmosphere by TGA method. Hao et al. (2010) prepared nitrogen-doped porous carbon monolith by direct pyrolysis of copolymer of resorcinol, formaldehyde, and lysine that exhibited CO_2 adsorption capacity of 3.13 mmol/g for 100% CO_2 at 25°C and 1 atm.

In this work, a series of mesoporous carbon adsorbents were synthesized *via* nanocasting technique by varying the carbonization temperature. They were characterized for their textural, elemental and surface properties. The effectiveness of these synthesized materials as CO_2 adsorbents was evaluated by fixed-bed column adsorption experiments using simulated flue gas. The effect of temperature and CO_2 feed concentration was investigated on the equilibrium adsorption capacity and breakthrough time. Suitability of these adsorbents in cyclic process application was also studied by temperature swing adsorption with nitrogen as the purge gas. Equilibrium adsorption data was illustrated by suitable adsorption isotherm models.

1. Experimental

All the reagents and solvents were procured from M/s S. D. Fine Chemicals India Ltd. Mesoporous silica (MCM-41 type) as template was procured from M/s Tianjin Chemist Scientific Ltd., Tianjin, China. It has a specific surface area of 450 m^2/g and an average pore diameter of 3.5 nm. Grade-1 (99.999% pure) dry helium, dry nitrogen and dry carbon dioxide gases were purchased from M/s Sigma Gases and Services, India.

1.1. Adsorbent synthesis

Synthesis of mesoporous carbon adsorbent involved three steps: (a) templated resin synthesis, (b) carbonization of the templated resin and (c) template removal. Melamine–formaldehyde resin was used as the precursor and mesoporous silica was used as the template.

Melamine 46.6 g and 200 mL of 5 wt.% methanol solution were mixed and heated to 70°C. To this mixture, 200 mL of 37% (W/V) formaldehyde solution was slowly added over the duration of 3 hr to form hexamethylolmelamine and the pH was adjusted to 8–9 by adding K_2CO_3. Reaction temperature was raised to 75°C to carry out advanced polymerization. Solution pH was adjusted to 7–8 by adding 0.1 mol/L NaOH solution and 0.4 g of di-sodium tetra borate (borax). The reaction mixture was stirred for further 2 hr. After this, the reaction mixture was cooled to room temperature followed by addition of 6 mL of 48% H_2SO_4 solution. To this reaction mixture, 15.0 g of template (mesoporous silica) was added and thoroughly mixed into the solution. This templated resin was cured at 60°C for 2 hr and then left at room temperature