



CO₂ adsorption on oxygen enriched porous carbon monoliths: Kinetics, isotherm and thermodynamic studies



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ARTICLE INFO

Article history:

Received 21 July 2017

Received in revised form 29 August 2017

Accepted 15 November 2017

Available online 22 November 2017

Keywords:

Nanocasting
Carbon monoliths
CO₂ capture
Kinetics
Thermodynamics

ABSTRACT

The present study reports the use of nanocasted carbon monoliths (CMs) as adsorbents synthesized by using furfuryl alcohol as carbon precursor and silica monoliths (SM) as a template for CO₂ capture. The oxygen content decreases from 18.92 to 14.38% with increase of carbonization temperature from 550 to 950 °C. BET surface area and total pore volume of CM carbonized at 950 °C was found to be maximum i.e. 1225 m² g⁻¹ and 1.26 cm³ g⁻¹, respectively with the presence of a large number of micropores and mesopores. Performance evolution of the CMs was done thermogravimetrically at different adsorption temperatures and CO₂ concentrations and found that, CM-950 shows the highest CO₂ capacity (1.6 mmol g⁻¹) which is approximately three times higher than SM (0.52 mmol g⁻¹). The CMs exhibit stable CO₂ uptake capacities (≥1 mmol g⁻¹) with easy regenerability over multiple adsorption-desorption cycles. Furthermore, fractional order kinetic model provided the best description over all adsorption temperatures and CO₂ concentrations. Heterogeneous nature of the carbon surface was confirmed from the Temkin isotherm fit and isosteric heat of adsorption (Q_{st}) values.

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Introduction

Global warming is the challenging environmental problem due to increase in the concentration of greenhouse gases such as carbon dioxide (CO₂), methane (CH₄), chlorofluorocarbons (CFCs) and nitrous oxide (N₂O), and among these CO₂ concentration in the atmosphere has increased by 40% in comparison to the levels of preindustrial era [1] and its contribution as a product of combustion of coal (fossil fuels) is around 60% to enhance the greenhouse effect [2]. The present CO₂ concentration is 408.84 ppm [3] which may be reached to 570 ppm by 2100 [4]. Higher concentration of CO₂ at this rate will create problem like climate changes, serious health issues for the living-beings, increase in the acidity of sea level and the rise of global surface temperature [5,6]. Therefore, viable and imperative methods to reduce the concentration of CO₂ emission into the atmosphere are really necessary [7]. Fossil fuel power plants are the major source of anthropogenic CO₂ emission, therefore efficient capture of CO₂ from these power plants is very essential to reduce the level of

atmospheric CO₂. The three basic technological routes used to capture CO₂ are pre-combustion, oxy-fuel combustion and post-combustion capture [8,9]. In the pre-combustion capture, CO₂ is captured prior to the combustion and in oxy-fuel combustion, the capture of CO₂ from flue gases created during fuel combustion with oxygen whereas, in post-combustion, the removal of CO₂ from flue gas occurs after combustion. Both, oxy-fuel and post-combustion system applied to conventional gas or coal fired based power plants [8,9]. Post-combustion capture is the one of the main technology to scale down the emission of CO₂ because this can be easier to retrofit into the existing plants like coal-fired power station as well as it is more applicable for gas plants than the pre-combustion or oxy-fuel combustion [10]. Up to date, various technologies have been proposed for the post-combustion capture such as adsorption, cryogenic separation, membrane separation, and absorption of CO₂ into amine solutions [11–14]. Adsorption with the porous solid adsorbents seems to be viable due to high CO₂ uptake, less energy requirements, and inexpensive as compared to other technologies. However, choice of the adsorbent plays an important role to make it successful technology [4,15].

In recent years, a number of porous solid adsorbents for CO₂ capture have been developed [16,17], including porous carbons [18], zeolites [19], amine-modified silicas [20], MOFs [21], etc. Among them, porous carbons have advantages of low cost, wide

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availability, adjustable porosity and fast adsorption kinetics which are most suitable for CO₂ capture in a wide range of operating conditions [22,23]. They can be synthesized by various techniques like nanocasting, direct carbonization, chemical activation of carbon precursor, and sol–gel process [24,25]. Among these methods, adsorbents prepared by nanocasting technique are very effective and simple which involves the impregnation of the precursor in the template, followed by carbonization of the impregnated template and then removal of the template. Also, porosity development and tuning/increasing surface area of the adsorbents can be possible by using this technology [18]. Hao et al. [26] synthesized nitrogen containing monoliths from the copolymer of formaldehyde, resorcinol, and lysine by direct pyrolysis process. They examined CO₂ adsorption capacity of 3.13 mmol g⁻¹ and 0.62 mmol g⁻¹ under static conditions (1 bar pressure) at 25 °C and 120 °C, respectively. Hosseini et al. [27] prepared carbon coated monoliths from furfuryl alcohol as a carbon precursor and polyethylene glycol (PEG) as pore former. They found that the adsorption capacity of 0.52 mmol g⁻¹ at 30 °C under 15% CO₂ concentration flow. Furthermore, monoliths modified with NH₃ and KOH which acquired 0.58 mmol g⁻¹ and 0.66 mmol g⁻¹ of adsorption capacity under same conditions.

From the literature, it can be seen that the monoliths were prepared and modified by physical and chemical activation process, but not so much attention given by researchers on the nanocasting technique for CO₂ capture which is very important to control the textural properties of the adsorbents. Also, most of the performance evolution of the adsorbents carried out under static conditions which are not giving the real picture for separation of CO₂ from the flue gas point application [28]. Therefore, the goal of this study is to fulfill the gaps of the literature by using nanocasting technique for the preparation of carbon monoliths for CO₂ capture under dynamic conditions. The cyclic adsorption–desorption studies were performed to examine their stability and found that these monoliths show easy and stability over multiple cycles. Regeneration, kinetics, adsorption isotherm and thermodynamic studies were also performed in details. The present study also shows the dominance character of carbon monoliths on CO₂ uptake over silica monoliths and other adsorbents.

Experimental section

Materials

Tetraethylorthosilicate (TEOS) was purchased from Alfa Aesar, US. Polyethylene glycol (PEG) (MW 35,000 g mol⁻¹), octadecyltrimethylammonium bromide (CTAB), were purchased from Sigma–Aldrich, US. Trimethyl benzene (TMB), oxalic acid, furfuryl alcohol (FA) (98%), hydrofluoric acid (40%), were purchased from Loba Chemie, India. Nitric acid (69%) and ammonia (28–30%) were purchased from Merck, India. All reagents were used without further purification. Nitrogen (99.99%), high purity CO₂ gas (99.99%), and a standard mixture of CO₂ and N₂ (6%, 20%, 50% v/v) were supplied by M/S. Sigma Gases Services, India.

Synthesis of silica monolith template

The sol–gel method was used for the preparation of silica monoliths [29]. Initially, PEG was dissolved in water with a nitric acid solution (30% v/v). After the dissolution, TEOS was added and stirred at room temperature for 10–15 min until the solution becomes translucent. Then, CTAB surfactant was added into the solution as well as stirred continuously till the surfactant dissolved to the end. The molar ratio of the composition H₂O:HNO₃:TEOS:PEG:CTAB was taken 16.5:0.53:2.2: 9.5 × 10⁻⁴:0.2 for the synthesis of all the monoliths [30]. The sol was casted into the mold of the

desired shape and kept at 40 °C for at least 72 h for the transition of gel form and aging process respectively. Then, the monoliths were treated in 1 M NH₄OH solution (10X volume) at 90 °C for 9 h for the hardening mechanism followed by the neutralization with 0.1 M nitric acid solution. After that, monoliths were washed by using deionized water (5–7 times) and then, dried at 40 °C for 3–4 days. Finally, the calcination of the monoliths was done at 550 °C for 5 h with the heating rate of 1 °C/min. The resulting silica monolith was named as SM.

Synthesis of carbon monolith adsorbent

Silica monolith (treated as a hard template) was degassed using a vacuum pump and then FA solution was impregnated with the presence of oxalic acid as a catalyst (molar ratio of FA/oxalic acid = 250) and TMB as a solvent. Polymerization of FA was carried out at 50 °C for 24 h followed by 90 °C for another 24 h. The impregnated monoliths were carbonized under N₂ atmosphere using the following segments: heating for 3 h at 150 °C followed by heating at different carbonization temperatures (550, 650, 750, 850 and 950 °C) for 4 h (2 °C/min heating rate) to develop porosity. The carbon monolith was attained by removing the silica template with the etching of aqueous hydrofluoric acid solution (10%, by volume) for 24 h. The monoliths were washed by 5–6 times with water and then dried at 90 °C for 15 h. The resulting carbon monolith was named as CM-Y, where Y is the carbonization temperature (550, 650, 750, 850 and 950 °C) (Fig. 1).

Characterization methods

Nitrogen sorption isotherms were measured using a Microtrac Belsorp Mini-II (Bel, Japan, Inc.). The surface area was achieved by Brunner–Emmet–Teller (BET) method using nitrogen adsorption system. Prior to the measurement, the samples were outgassed under vacuum at 200 °C for 2 h. The total pore volume was calculated at a relative pressure of 0.99 with the amount of nitrogen adsorbed and the pore size distribution curves were obtained from Barrett–Joyner–Halenda (BJH) method. The micropore size distribution analysis attained by MP plot. SEM images of the samples were collected using scanning electron microscope (JEOL JSM – 6510 LV) at an accelerating voltage of 20 KV. The porous structure of the carbons was analyzed by high-resolution transmission electron microscopy (HRTEM) using FEI TECNAI G2 F20, Netherlands (at 200 kV). The thermal stability of the monoliths was analyzed with a TA Q500, USA thermal analyzer under continuous N₂ flow (50 ml min⁻¹). The weight of each crushed monolith was taken 20 mg in a platinum pan and heated from room temperature to 900 °C with the heating rate of 10 °C min⁻¹. Elemental analysis of the monoliths was analyzed by the organic elemental analyzer (Thermo Scientific Flash 2000). Raman spectra were recorded with a Raman spectrometer (Features STR 500 Airix) with an excitation wavelength of 532 nm. X-ray photoelectron microscopy (XPS, Omicron ESCA +) was performed with monochromated aluminium source (Al Kα radiation, hv = 1486.7 eV). Data processing was performed using the XPS peak 4.1 software.

CO₂ adsorption measurements

CO₂ adsorption–desorption studies of the synthesized monoliths were examined by a thermogravimetric analyzer (TA Q500 TA Instrument, USA). About 20 mg of adsorbent was placed in the platinum pan followed by elevated the temperature to 200 °C with the heating rate of 10 °C min⁻¹ under the N₂ flow (50 ml min⁻¹) and kept isothermal for 2 h to remove pre-adsorbed gases and moisture. Afterwards, the temperature was decreased to the

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