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Amine modified and pelletized mesoporous materials: Synthesis, textural–mechanical characterization and application in adsorptive separation of carbondioxide

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ABSTRACT

Adsorption-mediated CO_2 separation can reduce the cost of carbon capture and storage. Amine modified sorbents are promising candidates for carbon capture. To investigate the details of CO_2 adsorption, three types of mesoporous materials, MCM-41, MCM-48 and SBA-15 were synthesized, pelletized and further pellets were impregnated with 50 wt.% of polyethyleneimine (PEI) in methanol to evaluate the performances of the materials in terms of CO_2 adsorption. The powdered mesoporous materials were also impregnated with 50 wt.% of PEI. The materials were characterized by XRD, TGA, FT-IR, SEM, TEM, N_2-physisorption and BET techniques. The mechanical strength of pellets was examined by vertical crushing method. The surface area, pore volume and pore diameter of pellets were lower than powdered materials. This decrease may be due to partial blocking of pore entry and surface coverage of additives during shaping of pellets. A detailed TGA study is carried out of pellets by varying the composition to optimized the wt.% composition of the different ingredients to attain the maximum mechanical strength and high adsorption of CO_2. All the PEI-loaded pelletized materials exhibited substantially higher reversible CO_2 adsorption–desorption behaviors with $>$99% recovery. The results indicate pellets containing methyl cellulose and activated carbon show better mechanical strength and CO_2 adsorption. The above study also proved that MCM-48 is a better material as compared to MCM-41 and SBA-15 for pelletization and loading of PEI. The material with 50 wt.% loading of PEI on MCM-48, showed maximum adsorption of 1.094 W/W_0 at 80 °C with an impressive mechanical strength of 6.1 MPa.

1. Introduction

In the 20th century, environmental issues due to emissions of pollutants from combustion of fossil fuels as a source of energy have become global problems, including air toxics and greenhouse gases (GHG). CO_2 has been identified as greenhouse gas, which contributes to the global climate change and global warming. According to the third assessment report of Intergovernmental Panel on Climate Change (IPCC), there has been global increment of the atmospheric concentration of CO_2 by about 100 ppm (36%) over the last 250 years, from a range of 275–285 ppm in the pre-industrial era (1000–1750) to 379 ppm in 2005 [1]. The highest average growth rate of atmospheric CO_2 concentration was recorded from 1995 to 2005 (19 ppm increment) for any decade since direct atmospheric CO_2 measurement began in the 1950s [2]. The main source of emission of CO_2 is burning of fuel, such as natural gas, coal and petroleum for the production of electricity and transportation [3].

Capture and sequestration of CO_2 has been considered as one of the options to reduce CO_2 emission. Various processes, such as liquid solvent absorptions [4], membrane separation [5], and pressure (and/or temperature) swing adsorption P(T)SA [4,6], have been proposed for the separation of CO_2 emitted by power plants. However, the costs of CO_2 separation from flue gases account for approximately 70–80% of the total energy cost for CO_2 sequestration. The high cost of Carbon Capture and Storage (CCS) currently prohibits the economical separation of CO_2 from flue gases under current technologies. Therefore, it is important to develop new energy-efficient techniques for CO_2 separation.

The conventional PSA or PTSA process using zeolite requires a dehumidification step which consumes about 30% of the total energy, because water vapor is adsorbed more strongly than CO_2 on a zeolite surface. Therefore, a new adsorbent [7–16] that preferably adsorbs CO_2 in the presence of water vapor is desirable for the development

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of a simple and energy-efficient CO_2 removal process that will eliminate the dehumidification step.

Recently, organically functionalized mesoporous silica (mesoporous materials have pores with sizes between 2 and 50 nm, according to IUPAC) has attracted considerable attention because of the wide range applications as adsorbents and catalysts [11–24]. Since mesoporous silica has uniform and large pores as well as high surface area, a large number of active sites or adsorption sites can be introduced uniformly on pore walls of mesoporous silica by its surface modification with organosilane molecules. Owing to the high cost of regeneration process, regenerable solid adsorbents appear to be alternative for CO_2 adsorption over the conventional methods. Physical adsorbents based on carbons and zeolites are able to reversibly adsorb large quantity of CO_2 at room temperature.

The amine modified mesoporous materials adsorb CO_2 over N_2 selectively. This is due to the difference in sublimation and boiling points of duo gases. There are several methods like, the physical adsorptions, pore filling and chemical bonding of amines, the surface of silica can be modified. These materials are successively to achieve the preferential uptake of CO_2 [25–31]. There are many reports available as evidence which show that some solid materials adsorb CO_2 chemically [32–34]. The well known mechanism of amine and CO_2 is reported for aqueous solution of amine or blended amine for gas–liquids system [35,36]. It is expected that when amine group is well tethered on solid surface, they can react with CO_2 and chemisorptions can dominate the adsorption process. The chemical reaction of CO_2 and amine leads to the formation of ammonium carbamate salt which is thermally unstable and thereafter, releases CO_2 at high temperature. Battjes and coworkers [37] showed that alkyl ammonium carbamates are the principal product of reactions between primary or secondary amines and CO_2. Some other research groups have reported that reaction of primary amines with CO_2 under non aqueous conditions give rise to formation of ammonium–carbamate ion pairs at room temperature. At lower temperatures, the dimeric form of carbamic acid has been reported [38,39]. However, these details are clarified in the liquid phase. The chemistry of CO_2 adsorption by amine tethered solid silica adsorbents will be certainly different. The chemisorptions of CO_2 on amine modified porous silica materials have been extensively studied [25,34,40–44] however, the identity of some chemisorbed species and the role of surface modification it yet to be determined.

A very interesting chemistry has been noticed when amine modified solid adsorbents is used for CO_2 capture in presence of water. It is observed that the carbamate which is formed during reaction of primary or secondary amine with CO_2 undergoes further reaction with CO_2 and water and leads the formation of bicarbamate. Several researchers [29,34,45–48] have reported that in the presence of water, one mole of amines can theoretically chemisorb one mole of CO_2. But in the absence of water, this ratio is shifted to two moles of amine to one mole of CO_2. This increased CO_2 capacity of amine modified solid adsorbents in presence of water was a unique property observed.

However, the attachment of various types of amino groups to the surface of mesoporous materials and their CO_2 adsorption properties have been systematically investigated by several research groups [13,26,34,42,47–56]. But the application of pelletized materials or amine modified pelletized materials are not observed for adsorptive separation of CO_2. The application of pelletized adsorbents for separation of CO_2 can be excellent candidates to replace old traditional amines and mesoporous powdered materials. The pelletized adsorbents are advanced and industrially acceptable than their powdered counterpart and have several advantages when they are used in fixed bed chemical reactor.

Literature survey reveals that Niklas Hedin et al. studied in detail, the molecular aspects of the temperature-dependent uptake of dry CO_2 in situ by using techniques FTIR and SEM [57]. They proposed the first molecular evidence for the physisorption in mesoporous silica adsorbents modified with propyl amines. Both chemisorbed and physisorbed CO_2 were detected. They concluded that both extracted and post synthetic samples interacted differently with CO_2. Most CO_2 adsorption proceeded by physisorption in the extracted samples whereas the post synthetic samples showed significantly smaller fractions of physisorbed CO_2. The post synthetic adsorbents took more CO_2 at high temperatures than at low temperatures. This trend was not typical for equilibrium adsorption and suggested the presence of a kinetic barrier at low temperatures. From mid IR and near IR, it was clear that in both the samples, extracted and post synthetic ones, carbamate is formed upon CO_2 adsorption. But it was deduced that fewer carbamates formed on the extracted samples ($2.8–3.1/nm^2$) than on the post synthetically modified samples ($1–1.6/nm^2$). Therefore, they finally concluded that the average loading is not the crucial parameter in the formation of carbamate–ammonium ion pairs. But a certain degree of heterogeneity (i.e., a local high density of tethered groups) in the surface modification is needed to form carbamate–ammonium ion pair. These ion pairs enhanced the selectivity of CO_2 over N_2 adsorption.

The present work included the synthesis of mesoporous materials, MCM-41, MCM-48 and SBA-15 which possess well ordered hexagonal, cubic and hexagonal structures, respectively. The powdered mesoporous materials were impregnated with 50 wt.% polyethyleneimine (PEI). Further, mesoporous materials were pelletized by using different types of binder ingredients (bentonite, methyl cellulose, activated carbon, polyvinyl alcohol, calcium sulfite and calcium titanate) to improve the mechanical properties of pelletized adsorbent. The pelletized adsorbents were impregnated with 50 wt.% of PEI to synthesize an advanced and modified adsorbent. The textural and physico-chemical properties of powdered and impregnated pelletized materials were characterized by X-ray diffraction (XRD), thermogravimetric analysis (TGA), Fourier Transform-Infra Red (FT-IR), scanning electron microscopy (SEM), transmission electron microscopy (TEM), N_2-adsorption–desorption isotherm and Brunauer–Emmet–Teller (BET) techniques. The mechanical strength of the pellets was examined by vertical crushing method. In this report, we investigate the pore structures and CO_2 adsorption properties of MCM-41, MCM-48, SBA-15, 50 wt.% PEI impregnated powdered adsorbents and 50 wt.% PEI impregnated pelletized adsorbents. Since mechanical strength is an important characteristic of a material to ensure reliable performance of the material in a fix bed chemical reactor. A detailed and careful TGA study is carried out of pellets by varying the composition to optimize the wt.% composition of the different ingredients to get the maximum mechanical strength and high adsorption of CO_2. The CO_2 adsorption capacity was significantly increased after loading 50 wt.% PEI on the mesoporous materials. The fundamental insights obtained in this study are expected to assist in the rational design of novel functionalized mesoporous adsorbent materials for CO_2 separation from dilute sources.

2. Materials and method

2.1. Materials

Hexadecyltrimethylammonium bromide (CTABr), Ludox AS-40 colloidal silica, sodium hydroxide (NaOH), hydrochloric acid (HCl), Polyoxyethylene (23) lauryl ether (LE 4), Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (P123), Tetraethyl orthosilicate (TEOS), ammonium hydroxide (NH_4OH), methyl cellulose, bentonite, calcium sulfite ($CaSO_3$), calcium titanate ($CaTiO_3$), activated carbon, and polyvinyl alcohol, were purchased from Sigma-Aldrich and used without further purification.

2.2. Synthesis of MCM-41

MCM-41 was synthesized following published procedures with molar gel compositions of 1.0 SiO2:0.2 NaOH:0.27 TMAOH:0.27 CTABr:60 H_2O [58]. A typical synthetic procedure is as follows: first