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Research article

Development of polyethylenimine-functionalized mesoporous Si-MCM-41 for CO_2 adsorption

Sohail Ahmed[a], Anita Ramli[b,*], Suzana Yusup[a]

[a] *Department of Chemical Engineering, Universiti Teknologi PETRONAS, 32610 Bandar Seri Iskandar, Perak, Malaysia*
[b] *Department of Fundamental and Applied Sciences, Universiti Teknologi PETRONAS, 32610 Bandar Seri Iskandar, Perak, Malaysia*

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ABSTRACT

This work describes the functionalization of mesoporous Si-MCM-41 with different loadings of polyethylenimine (PEI), their characterization and detailed study of their CO_2 adsorption performance. A series of Si-MCM-41 samples functionalized with 10–50 wt% PEI was synthesized by wet impregnation method. The physicochemical properties such as pore structural ordering and textural properties of the samples were characterized by X-ray diffraction and N_2 adsorption/desorption analysis, respectively. The XRD analysis of pristine Si-MCM-41 showed well-defined four diffraction peaks of (100), (110), (200) and (210) planes. Upon loading of 10–50 wt% PEI, intensity of these diffraction peaks reduced gradually due to decrease in scattering contrast. Also, N_2 adsorption/desorption analysis showed change in textural properties from porous to non-porous material as the loading of PEI increased from 10 to 50 wt%. To optimize the loading of PEI for maximum CO_2 adsorption, samples were screened at 25 °C and 0–1 bar using a gravimetric method. The sample containing 50 wt% PEI showed the highest CO_2 uptake of 47.93 mg/g due to high content of CO_2–affinity sites and was further used to investigate the effect of temperature ranging from 25 to 125 °C on CO_2 adsorption performance. The best CO_2 adsorption (99.44 mg/g) was obtained at 100 °C and 1 bar due to flexible behavior of PEI. At this optimized temperature, the Si-MCM-41 containing 50 wt% PEI was used to evaluate the effect of pressure ranging from 0 to 20 bar where it showed increase in CO_2 adsorption uptake of 156 mg/g. Si-MCM-41 containing 50 wt% PEI showed strong affinity for CO_2 compared to N_2 and H_2. In a regeneration study, a gradual decline in CO_2 uptake was observed as the number of adsorption/desorption cycles increased. Infrared spectroscopy revealed carbamates formation confirming the interaction of CO_2 with the amino groups of PEI incorporated into Si-MCM-41 containing 50 wt% PEI *via* chemisorption.

1. Introduction

Globally, the unabated use of fossil fuels for energy production is the main cause of unfettered release of CO_2 into the atmosphere. This anthropogenic CO_2 is the principal driver of global climate change known as global warming [1,2]. At present, fossil fuels provide $>$ 85% of the energy required globally because of their low cost, availability, reliable technology for energy production, and energy density [1]. According to Intergovernmental Panel on Climate Change (IPCC), CO_2 emissions resulting from burning of fossil fuels and industrial processes produced approximately 78% of all greenhouse gas emission [3] and the resultant high level of CO_2 in the atmosphere contributes to 60% of the effects of global warming [4]. The emission of CO_2 is anticipated to increase as long as fossil fuels continue to be the main energy source for humankind [5].

Several strategies are available to reduce CO_2 emissions to the atmosphere including increasing energy efficiency, using non-carbon or renewable energy sources (e.g. solar and wind energy), and CO_2 capture and storage (CCS). However, the development of environmentally benign sources is slow, primarily because of high costs, the need to update existing infrastructure, and the abundance of fossil fuels [6]. At present, fossil fuels are the major source of energy and will remain the main source of energy for the foreseeable future. As a result, CCS is widely considered as a promising technology to decrease CO_2 emissions from major energy sources such as power plants and other large industrial facilities [7]. The separation of CO_2 is the most energy intensive step in CCS accounting for 70% or more of the costs [8]. CCS is considered a main technological strategy for mitigating CO2 emissions because it allows the retension of the prevailing carbon-based setup, while decreasing the effects of CO_2 on the earth's climate system [6].

Various pathways has been proposed for CO_2 capture, including post-combustion, pre-combustion, and oxy-fuel combustion processes.

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[*] Corresponding author.
E-mail address: anita_ramli@utp.edu.my (A. Ramli).

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Among these, post-combustion has the greatest potential to be retrofitted to existing plants. In post-combustion, CO_2 gas is captured from the flue gases produced after the combustion of fossil fuels or other carbonaceous materials [5,9]. In the post-combustion process, various technologies can be used for CO_2 capture, including chemical absorption [10,11], cryogenic separation [12,13], membrane-based separation [13,14], and adsorption separation process [15,16]. Adsorption is considered a promising method of CO_2 capture because of its various advantages such as low energy requirement, low cost, and ease of applicability under various conditions [17,18]. Adsorption involves the selective removal of CO_2 from a gas stream by an adsorbent, followed by the regeneration of the adsorbent [4]. The key issue in adsorption is development of an effective adsorbent with high adsorption capacity, selectivity and, regenerability.

In 1992, Mobil Corporation scientists developed M41S, a new family of mesoporous molecular sieves [19]. MCM-41, a member of this family, has emerged as a unique material for various applications. MCM-41 exhibits remarkable, structural and textural features including a highly ordered uniform hexagonal pore structure arrangement tunable pore size, large pore volume, high surface area, large number of silanol groups, and ease of modifying of surface properties [19,20]. These properties make MCM-41 a candidate for CO_2 adsorption; however, pristine MCM-41 shows low CO_2 adsorption capacity [21]. Fortunately, the properties of MCM-41 allow the modification of its properties by introducing new functional groups. As amines are basic in nature, the functionalization of MCM-41 with amines would provide amino groups, which could serve as CO_2 affinity sites and enhance the adsorption capacity and selectivity of MCM-41.

Amine-based adsorbents have been developed since 1974 [22]. A breakthrough in the development of amine-based adsorbents was achieved in 2001, when Sunita Satyapal synthesized a polyethylenimine (PEI)–modified high surface area solid polymethyl methacrylate known as HSC^+, which has since been used for CO_2 removal in space shuttle applications [23]. This work laid the foundation for the use of amine-functionalized adsorbents for CO_2 capture in various applications. Xu and coworkers proposed the novel “molecular basket” concept by modifying mesoporous MCM-41 with low molecular weight polyethylenimine (PEI) by impregnation and obtained the best CO_2 adsorption capacity at 75 °C [24]. Franchi and coworkers impregnated pore-expanded MCM-41 with diethanolamine and investigated its application in CO_2 capture at 25 °C [25]. Yue and coworkers modified as-synthesized MCM-41 with tetraethylenepentamine and investigated its CO_2 adsorption capacity at 75 °C [26]. Kamarudin and Alias modified Si-MCM-41 with monoethanolamine and diethanolamine and studied the CO_2 adsorption behaviour at 25 °C [27].

In this work, we have described in detail the functionalization of Si-MCM-41 with 10–50 wt% of branched polyethylenimine (PEI), characterization and effect of amine loading on CO_2 adsorption capacity. Furthermore, the effects of temperature and pressure on the CO_2 adsorption capacity of the sample with the optimal PEI content were investigated. Finally, selectivity and regeneration studies were conducted to evaluate the performance of the adsorbent.

2. Experimental

2.1. Materials

The experimental materials were as follows: sodium silicate (Na_2SiO_3, Merck) as a silica source; cetyltrimethylammonium bromide (CTAB, Sigma Aldrich) as a structure directing agent; sulfuric acid (H_2SO_4 98%, J. T. Baker) as a pH regulating agent; deionized water as a solvent for the synthesis of Si-MCM-41; branched polyethylenimine (PEI, 50 wt% solution in water; Mn ~1800; Sigma Aldrich) as a functionalizing agent; and methanol as a solvent for impregnation.

2.2. Synthesis and functionalization of Si-MCM-41

Si-MCM-41 was fabricated according to a method reported elsewhere [28]. Briefly, Si-MCM-41 was synthesized via a hydrothermal process at 100 °C for eight days in a Teflon-lined stainless steel autoclave. The solid product was then recovered by filtration, washed several times with copious amount of deionized water and dried at 120 °C in an oven for 24 h. The as-synthesized Si-MCM-41 was then calcined in flowing N_2 gas at 550 °C with ramping of 5 °C/min for 6 h to remove the structure directing agent.

The calcined Si-MCM-41 was functionalized with amine using the method reported in the literature [29]. Calcined Si-MCM-41 was functionalized with 10–50 wt% branched polyethylenimine (PEI) via wet impregnation. According to the procedure, required amount of PEI was added to 10 g of methanol and stirred for 15 min to completely dissolve the amine. Subsequently, 2 g of calcined Si-MCM-41 was dispersed into the amine solution. The obtained slurry was stirred vigorously for 30 min to uniformly disperse the amine molecules into Si-MCM-41 framework. The product was then dried at 70 °C for 16 h in a vacuum oven at a reduced pressure of 700 mm Hg. The PEI functionalized samples were labeled as X PEI-Si-MCM-41, where X denotes the weight percentage of loaded PEI.

2.3. Characterization

All samples were analysed by X-ray powder diffraction (XRD) using a Bruker D8 Advance diffractometer (Germany) with monchromated Cu Kα radiation with a wave length of 1.54 Å generated at a current of 40 mA and a potential of 40 kV. The XRD patterns were obtained on the 2-Theta scale in the angular range of 1.5°–10°. The step size and step time were 0.010° and 4 s, respectively.

N_2 adsorption/desorption analysis of all samples was performed using a Micromeritics ASAP 2020 volumetric adsorption analyzer (Micromeritcs Instrument Corporation, Norcross, GA, USA). Measurements were conducted using N_2 gas as an adsorbate at -196 °C (liquid N_2 temperature) in the relative pressure range of 0.01–1 bar. Prior to analysis, the calcined Si-MCM-41 sample was degassed for 2 h at 250 °C and the PEI-functionalized

Si-MCM-41 samples were degassed for 2 h at 100 °C with ramping of 10 °C/min under vacuum (ca. 300 μm Hg) to remove all physisorbed species from the adsorbent surface in the degas port of the apparatus. The surface area of each sample was measured using the Brunauer-Emmett-Teller (BET) method [30] at a relative pressure of 0.06–0.25. The pore volumes and average pore diameters were calculated from the adsorption branches of the isotherms using Barrett–Joyner–Halenda (BJH) method [31].

The optimized sample was analysed by Fourier transformed infrared spectroscopy (FTIR) analysis before and after CO_2 adsorption at different temperatures. FTIR analysis was performed at ambient conditions using a SHIMADZU 8400S spectrometer in the 400–4000 cm^{-1} region using the KBr pellet technique.

2.4. Gas adsorption study

Pure gas adsorption on the samples was studied using a gas sorption unit (i.e. Rubotherm gravimetric-densimetric apparatus; Bochum, Germany) operated by *MessPro* software. Prior to measuring sample adsorption, the system was evacuated for 30 min. Gas was flowed into the system at a rate of 100 mL/min to saturate the sample. To obtain the adsorption isotherm, the pressure of the gas in the system was increased stepwise to the required pressure level after equilibrium was achieved at every step at constant temperature. The data recorded during the adsorption measurement werre the balance reading (m_{BAL}; i.e. mass of the adsorbed substance and the container), temperature (T) and pressure (P). The density of the gas in the measuring cell was calculated from the temperature and pressure of the gas using