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Adsorption behavior of tetraethylenepentamine-functionalized Si-MCM-41 for CO_2 adsorption

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ABSTRACT

Carbon dioxide (CO_2) mitigation is of prime importance due to its prodigious release into the atmosphere from power plants and other industrial sources which directly influence the climate change. Adsorption process is considered as an attractive process for CO_2 separation and purification due to low energy requirement, cost-effective and ease in applicability over wide range of operating conditions. In this work, mesoporous Si-MCM-41 was functionalized with different loadings of tetraethylenepentamine (TEPA) to study its performance for CO_2 adsorption using gravimetric technique. The adsorption data shows that incorporation of TEPA into Si-MCM-41 promotes CO_2 adsorption and the adsorption capacity increases with increasing loading of TEPA from 10 to 50 wt.%. The 50 wt.% TEPA-functionalized Si-MCM-41 shows the CO_2 adsorption capacity of 54.65 mg/g at 25 °C and 1 bar. Further studies shows that the adsorption capacity of 50 wt.% TEPA-Si-MCM-41 increases with increasing temperature from 25 to 75 °C with the highest CO_2 adsorption capacity of 70.41 mg/g at 75 °C and 1 bar. Infrared spectroscopy was used to study the interaction mechanism of CO_2 with amino groups using the 50 wt.% TEPA-Si-MCM-41. FTIR spectra of CO_2-saturated 50 wt.% TEPA-Si-MCM-41 samples showed peaks related to carbamates formation which is the evidence of chemisorption process.

1. Introduction

At present, fossil fuels are primary energy sources which provide 87% share in global energy consumption needs (Dudley, 2012) and will remain mainstay of energy utilization for the foreseeable future. This large consumption of fossil fuels is the cause of unfettered release of CO_2 into the atmosphere. CO_2 is the main greenhouse gas that contributes to global warming more than 60% due to its large emission (Chang et al., 2009). To cope with global warming requires substantial and sustainable mitigation of CO_2 emission. Post-combustion capture system has the greatest near-term potential for reducing CO_2 emission because it can be installed into the prevailing plants without much modification which produce two-third of the CO_2 emission in power sector (Lee et al., 2012; Figueroa et al., 2008). For CO_2 capture and separation from post-combustion process, various technologies have been proposed such as chemical absorption, membrane and cryogenic. However, these technologies shows various serious drawbacks which are well documented in the literature (Idem et al., 2006; MacDowell et al., 2010; Kargari and Ravanchi, 2017; Xu et al., 2012; Brunetti et al., 2010; Scholes et al., 2009). In order to overcome drawbacks related to these technologies, adsorption process has been proposed for CO_2 mitigation.

Adsorption is considered to be the competitive and feasible alternative process for CO_2 removal from post-combustion process due to low energy requirement, cost advantage and ease of applicability over relatively wide range of temperatures and pressures. The key component of the adsorption process is the adsorbent which must exhibits high CO_2 adsorption capacity and selectivity (Xu et al., 2002, 2005). Physical adsorbents such as zeolites (Cavenati et al., 2004; Siriwardane et al., 2005), activated carbons (ACs) (Van Der Vaart et al., 2000)

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and metal organic frameworks (MOFs) (Chowdhury et al., 2009) show high adsorption capacities at ambient temperature. However, moisture sensitiveness, low selectivity, rapid decline at higher adsorption temperatures and low adsorption at relatively lower CO_2 partial pressure limit their application of CO_2 separation from flue gas (Cavenati et al., 2004; Van Der Vaart et al., 2000; Brandani and Ruthven, 2004; Sircar et al., 1996; Bastin et al., 2008; Liang et al., 2009). On the other hand, hydrotalcites (Ding and Alpay, 2000) and metal oxides (Gupta and Fan, 2002; Yong et al., 2002) are chemical adsorbents and require high temperature for operation. These adsorbens show low CO_2 adsorption capacities, high regeneration energy and rapid degradation (Ding and Alpay, 2000; Yong et al., 2001; Abanades and Alvarez, 2003) as main drawbacks for practical application.

As a result, significant research has been focused on development of materials that could be used as adsorbents to capture CO_2 from large point emission sources (i.e. power plants). For such point sources, selective adsorbents with high adsorption capacity and operate relatively at higher temperature (above room temperature and up to ~150 °C) are desired (Xu et al., 2002). One of the solutions to improve the adsorption capacity of the adsorbent is to modify mesoporous siliceous materials with a substance exhibiting CO_2-affinity sites. Amine-modified mesoporous materials have recently emerged as a promising class of solid adsorbents that can effectively adsorb CO_2 and regenerated using variety of approaches (Bollini et al., 2011). Mesoporous material known as MCM-41 has extraordinary properties such as uniform hexagonal cylindrical pore system, tunable pore size (15–100 Å), high surface area (>700 m^2/g), large pore volume ($\geq$0.7 cm^3/g), large number of silanol groups (~40–60%), negligible pore blocking effect, high surface reactivity, easiness in modification of surface properties and excellent thermal, hydrothermal, chemical as well as mechanical stability (Beck et al., 1992; Selvam et al., 2001). Generally, CO_2 adsorption capacity of mesoporous Si-MCM-41 at low pressure is limited (Ramli et al., 2014a). Therefore, there is less practical interest in utilizing pristine Si-MCM-41 for CO_2 adsorption process. However, the functionalization of Si-MCM-41 with amines shows an attractive alternative option for its application in CO_2 adsorption process. Amine functional groups are useful for enhancing CO_2 adsorption capacity and selectivity. High porosity characteristic is promising for incorporation of amine.

Type of amine was found to play an important role in determining the performance of the functionalized adsorbent. Kamarudin and Alias (2013) functionalized mesoporous MCM-41 with primary amine (monoethanolamine) and secondary amine (diethanolamine), which showed maximum CO_2 adsorption performance at 25 °C. Conversely, Xu et al. (2002) functionalized MCM-41 with a polymer polyethylenimine (PEI) which contains primary, secondary and tertiary amino groups, that showed maximum CO_2 adsorption performance at 75 °C. Liu et al. (2013) functionalized MCM-41 with tetraethylenepentamine (TEPA) which contains primary and secondary amino groups and investigated CO_2 adsorption performance at 35 °C. Yue et al. (2008) on the other hand reported the maximum CO_2 adsorption on TEPA-functionalized MCM-41 at 75 °C.

This paper intends to to study in detail the CO_2 adsorption using TEPA-functionalized Si-MCM-41 and propose the interaction mechanism of CO_2 with amino groups of adsorbent.

2. Materials and methods

2.1. Materials

Sodium silicate ($NaSiO_3$; SiO_2 25.5–28.5%, Na_2O 7.5–8.5%; Merck) as a silica source, cetyltrimethylammonium bromide (CTABr; Purity ≥ 98%; Sigma–Aldrich) as structure directing agent, sulphuric acid (H_2SO_4 98%; J.T. Baker); deionized water as a solvent for synthesis of Si-MCM-41; tetraethylenepentamine (TEPA; Merck) as functionalizing agent and methanol (Purity 99.9%; Merck) as a solvent for impregnation of amine molecules.

2.2. Synthesis and functionalization of Si-MCM-41

The synthesis protocol adopted in this work is described elsewhere (Ramli et al., 2012). Si-MCM-41 was synthesized by hydrothermal process at 100 °C for 8 days, dried at 120 °C for 24 h and calcined at 550 °C for 6 h in N_2 flow. Functionalization of pristine Si-MCM-41 with 10–50 wt.% TEPA loading was achieved via wet impregnation method as reported elsewhere (Ahmed et al., 2012). In this method, the required amount of TEPA was dissolved in 10 g of methanol solvent and stirred for 15 min. Then, 2 g of pristine Si-MCM-41 were dispersed into the amine solution. The resultant slurry was vigorously stirred for about 30 min, and then dried at 70 °C for 16 h in vacuum oven at reduced pressure of 700 mmHg. The TEPA functionalized Si-MCM-41 samples were labeled as X TEPA-Si-MCM-41, where X symbolizes the loading weight percentage of TEPA.

2.3. Characterization

N_2 adsorption–desorption analysis of all samples was carried out using Micromerics ASAP 2020 volumetric adsorption analyzer (Micromeritics Instrument Corporation, USA). The analysis was performed at −196 °C and 0.01 to 1 bar relative pressure. Prior to analysis, pristine Si-MCM-41 sample was degassed for 2 h at 250 °C and TEPA-functionalized Si-MCM-41 samples were degassed for 4 h at 100 °C under vacuum (*ca.* 300 μm Hg) in the degas port of the apparatus. The specific surface area was determined using Burnauer–Emmett–Teller (BET) method (Brunauer et al., 1938) whereas both the average diameter and total pore volume were computed from adsorption branches of isotherms by Barrett–Joyner–Halenda (BJH) method (Barrett et al., 1951). High resolution transmission electron microscopy (HRTEM) images of all samples were recorded using a Zeiss LIBRA 200FE transmission electron microscope at 30,000 magnification. Field emission scanning electron microscopy (FESEM) micrographs of all samples were recorded on a Zeiss SUPRA 55VP microscope operated at acceleration voltage of 7.00 kV and at magnification of 30,000×. Fourier transform infrared spectroscopy (FTIR) analysis of CO_2-saturated samples was performed on a SHIMADZU 8400S spectrometer over the range of 400–4000 cm^{-1} using KBr pellet technique at ambient conditions.

2.4. CO_2 adsorption measurement

CO_2 adsorption capacity as a function of pressure was measured for all samples using Rubotherm gravimetric-densimetric gas sorption apparatus (Bochum, Germany). Pure CO_2 was used for the adsorption measurements. The entire system is controlled by a computer based-operating system using *MessPro* software for operations.

In a typical adsorption run, a blank test of the empty sample container was performed to determine the mass and volume of sample container (m_{SC} and V_{SC}) at 25 °C in N_2 stream with a flow rate of 100 ml/min. Afterwards, the sample is weighed and placed in the sample container. The chamber in which the sample container is placed, is then closed and high pressure is applied to check for any leakage in the system. Leak test was performed whenever the chamber is disassembled. The sample was then reactivated in a vacuum at 100 °C to remove all physiosorbed species until there is no more weight loss and therefrom mass of the sample (m_S) was obtained. After reactivation, the sample was cooled down to the analysis temperature and buoyancy test was carried out using He