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High pressure adsorption of CO_2 on MCM-41 grafted with quaternary ammonium ionic liquids

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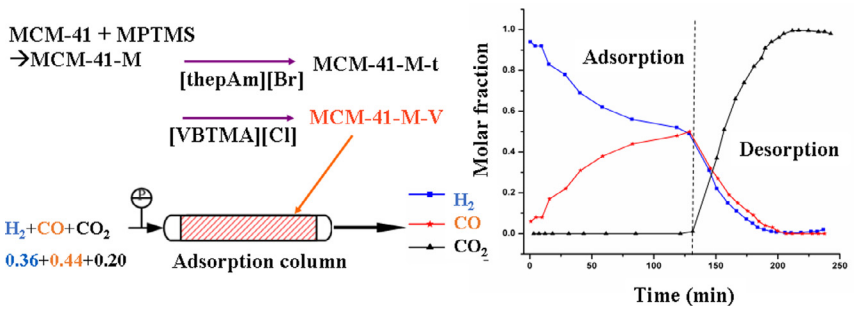
HIGHLIGHTS

- [thepAm][Br] and [VBTMA][Cl] were successfully bonded to MCM-41.
- The grafted MCM-41 showed high CO_2 adsorption at high pressure.
- The grafted MCM-41 acted as a selective separation agent to CO_2 over CO.
- The adsorption-desorption indicated stability of the hybrid adsorbent.
- The high pressure adsorption showed complete separation of CO_2 from a mixture.

GRAPHICAL ABSTRACT



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ABSTRACT

In order to improve CO_2 absorption capacity and selectivity in ionic liquids (ILs), grafting two quaternary ammonium ILs, (vinyl benzyl) trimethylammonium chloride ([VBTMA][Cl]) and tetra-n-heptyl ammonium bromide ([thepAm][Br]), on mesoporous MCM-41 was studied in this work. Results from the characterization of FT-IR, TGA, BET, TEM and elemental analysis showed that the ILs were successfully grafted on MCM-41. Gas excess loading (from 0.1 MPa to 8.0 MPa) was studied by using the high-pressure quartz spring method. Grafting the ILs on the supports caused loss in mesoporosity, resulting in slight decrease in CO_2 adsorption capacity, but enhanced the CO_2/CO selectivity. Meanwhile, the adsorbents grafted with [VBTMA][Cl] performed better in terms of excess CO_2 loading (3.90 mmol/g) and CO_2/CO selectivity (95) than those grafted with [thepAm][Br] corresponding to 3.65 mmol/g for CO_2 loading and 21 for CO_2/CO at 30.0 °C and 5.0 MPa. An adsorption–desorption (9.0 MPa) procedure at 30.0 °C was implemented to examine the selective CO_2 capture from the H_2, CO and CO_2 mixture by using the [VBTMA][Cl] grafted adsorbent and showed almost complete separation of CO_2 from the mixture.

1. Introduction

Industrialization and accelerated population growth during the past century have created tremendous pollutants for the environment. Air pollution poses the biggest challenge in the debate on environment safety [1]. Carbon dioxide (CO_2) from the exhausts of factories, industries and automobiles is one of the main air pollutants (waste gases). The major concern for this gas is its greenhouse effect; it increases atmospheric temperature contributing to more than 60% of global warming [2]. Hence, reduction of CO_2 is vital for human and for all life on earth. Several approaches have been adopted to decrease the levels of CO_2 in the atmosphere. For instance, non-carbon energy resources (wind, solar and biomass) have been suggested to replace fossil fuels. Furthermore, improving energy efficiency of fossil fuels by reducing greenhouse gas

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emissions per unit energy consumption has been proposed. The carbon capture and storage (CCS) approach emphasizes the development of CO_2 capture methods as well as sequestration technologies [3]. In fact, CO_2 removal consists of pre-combustion and post-combustion [4] procedures. The separation phase is energy intensive and thus, determines the cost (75–80% of the total cost) and choice of the CCS process. This is another justification for improving CO_2 capture processes through the search for innovative materials. Meanwhile, CO_2 adsorption/absorption capacity, selectivity, mechanical strength, chemical stability, regeneration possibility and cost are the most important criteria for selecting innovative CO_2 absorbent materials [5].

Ionic liquids (ILs) have also become industrially popular because of their unique properties such as lower volatility, better thermal stability, less degradation, low corrosive nature, high CO_2 selectivity (for N_2, CH_4 and H_2), and excellent physical absorption capacity [6] when compared to common physically absorbing solvents at comparable conditions. In spite of these wonderful properties, ILs have some disadvantages; low desorption rate, relatively high cost and potential toxicity to the environment are concerns for large scale industrial application [7,8]. Solid porous inorganic or organic polymer materials such as silica gel offer another paradigm for CO_2 capture with high energy-efficiency, fast adsorption/desorption rate and low cost. Even so, some existing problems relating to adsorption capacities at low pressures as well as low selectivity against competing components from flue gas are of grave concern [9]. Supported ionic liquid membranes (SILM) have been found to be ideal for the capture of CO_2 [8]. Similarly, this separation technique has some inherent limitations: facile disarrangement, non-uniformity and poor reusability. Therefore, strategy utilizing covalent bonds to link ILs and adsorbents in an effort to mitigate some of these limitations is of potential importance [10,11]. For instance, Zhu et al. [7] grafted phosphorus-based ILs onto silica support and reported improvement in retention of the IL as well as stability of grafted adsorbents. Their coated IL layers also acted as selecting film and allowed CO_2 to permeate to the adsorption sites on the solid materials but impeded undesirable components such as N_2. Cheng, et al. [11] synthesized polymerized ILs with (vinylbenzyl) trimethylammonium cation ($[VBTMA]^+$) and grafted the same onto mesoporous silica (mesosilica) support. The grafted ILs could adsorb CO_2 rapidly with good adsorption (0.4025 mmol/g), selectivity and repeatability capabilities. In another study and with a thiol functional group, (3-mercaptopropyl) trimethoxysilane (MPTMS), a saline coupling agent was grafted onto silica, the grafted adsorbent was found to be an efficient and recyclable solid acid catalyst that could be reused without noticeable loss of reactivity [12].

Besides $[VBTMA]^+$, another quaternary ammonium IL, tetra-n-heptyl ammonium bromide ([thepAm][Br]), has been proposed as an alternative candidate for trapping CO_2 [13,14]. On the other hand, MCM-41 is reported to have higher volumetric CO_2 uptake capacity per unit of surface area compared to other physical CO_2 adsorbents at high pressure [15]. Although there are many studies on the grafting of ILs, they are mainly centered on procedures at relatively low pressures. However, an IL-grafted porous material obtained CO_2 adsorption of 1.55 mmol/g with a corresponding CO_2/CO selectivity of 280 at 2.0 MPa and 0.0 °C [16]. Therefore, in this work we synthesized two new CO_2 adsorbents by grafting two quaternary ammonium ILs ([VBTMA][Cl] and [thepAm][Br]) on MCM-41, and the performance for separation of CO_2 from the H_2, CO and CO_2 mixture was examined with an adsorption process with the background of high pressure syngas separation. The aim was to combine the advantages (unique properties) of the ILs and MCM-41 at high pressure in order to overcome the low CO_2 selectivity of MCM-41 as well as the relatively low CO_2 absorption capacity of the ILs.

2. Experimental

2.1. Materials

MCM-41 with a surfactant template was purchased from Qingdao Silica Gel Factory. (3-mercaptopropyl) trimethoxysilane, MPTMS, with 97% purity was provided by TCI Shanghai. Tetra-n-heptyl ammonium bromide ([thepAm][Br]) and (vinylbenzyl) trimethylammonium chloride ([VBTMA][Cl]) were purchased from Meryer (Shanghai) Chemical Technology Co., Ltd. Analytical grade toluene, acetone, trichloromethane, methanol and ethanol were purchased from chemical reagent Co., Ltd, Shanghai, China. Carbon dioxide (purity 99.9%), hydrogen (purity 99.9%) and carbon monoxide (purity 99.9%) were purchased from Linde Gas, Xiamen, China.

2.2. Synthesis and characterization

Calcination in air at 550.0 °C for 5 h in ambient atmosphere was used to remove the surfactant template from the MCM-41 [17]. The calcined MCM-41 was immersed in a 16 mL piranha solution (30:70(v/v) H_2O_2 and H_2SO_4) at 60.0 °C for 30 min. The mixture was then washed with distilled water until pH ≈ 7.0 to remove the excess of acid and dried subsequently at 100.0 °C then the dried sample was activated under vacuum at 150.0 °C for 1 h [18].

Grafting of MCM-41 with MPTMS was achieved as previously reported [12] with producing an intermediate material labeled as MCM-41-M (Fig. 1A). MCM-41-M was oxidized with H_2O_2 and H_2SO_4 at room temperature (Fig. 1B) to obtain MCM-41-M-SO_3H which was subsequently reacted with [thepAm][Br] to obtain the first adsorbent MCM-41-M-t (Fig. 1C). The second adsorbent MCM-41-M-V was obtained by reaction/grafting of [VBTMA][Cl] with MCM-41-M and polymerization with a similar procedure reported for other ILs [19] (Fig. 1D). The procedures for preparing MCM-41-M and then the two adsorbents were described in detail in Supplementary Section S1.

2.3. Characterization

The synthesized adsorbents were characterized by a Fourier Transform Infrared Spectroscopy (FT-IR, Nicolet 380, Thermo Electron Corporation, USA). Elemental analysis was carried out using a Vario EL III elemental analyzer. The pore volume, Brunner-Emmet-Teller (BET) specific surface area and Barrett-Joyner-Halenda (BJH) pore size were analyzed by the N_2 adsorption and desorption measurement (ASAP 2020 Micrometrics, USA). Microstructure was examined by using a transmission electron microscope (JEM-1400Plus) at 120 kV. Thermogravimetric analysis (TGA) was performed on an SDTQ 600 instrument from room temperature to 1000 °C under nitrogen atmosphere at a 10.0 °C/min heating rate.

2.4. Gas excess loading and CO_2 capture

The gas (CO_2, CO and H_2) excess loading experiments and CO_2 capture from H_2, CO and CO_2 mixture were measured by the high-pressure quartz spring method [20] (see Supplementary Section S2). The same apparatus was used for the adsorption (5.0 MPa)–desorption (0.1 MPa) process to evaluate cyclic stability of MCM-41-M-V to capture pure CO_2 at 40.0 °C. This process was designed for pre-combustion applications such as in syngas from coal where CO_2 capture occurs at high partial pressures [21]. Accordingly, an adsorption-desorption process was designed as shown in Fig. 2. The process consists mainly of three units: the mixture gas reservoir, the adsorption column (I.D. 10 mm; length 25 cm), and the exit gas detector and collection. The CO_2, CO and H_2 gases were separately loaded into the mixture gas reservoir at