Chemical Engineering Journal 306 (2016) 9–16

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Review

Improvement of adsorbent materials for CO_2 capture by amine functionalized mesoporous silica with worm-hole framework structure

Jian Jiao [*], Jing Cao, Yu Xia, Lizhen Zhao

Department of Applied Chemistry, School of Science, Northwestern Polytechnical University, Xi'an 710072, PR China

HIGHLIGHTS

- Amine functionalized MSU-J with 3-D connective channel is employed as a CO_2 absorbent.
- Amine-impregnated MSU-J exhibits higher CO_2 capture than amine-impregnated SBA-15.
- The pore diameter of MSU-J is up to 16 nm.
- The higher molecular weight of impregnant is benefit to thermostability and CO_2 capture.
- Hydrolyzation regenerates the Si—OH, which improves the efficiency of impregnation.

ARTICLE INFO

Article history:
Received 20 April 2016
Received in revised form 30 June 2016
Accepted 9 July 2016
Available online 11 July 2016

Keywords:
Mesoporous silica
Worm-hole framework structure
CO_2 capture
Organic amine
Adsorption condition

ABSTRACT

Amine functionalized mesoporous silica MSU-J with 3-D connective channel is employed as an effective absorbent for CO_2. CO_2 adsorption measurements were conducted by gravimetry to investigate the effects of (i) framework structure, (ii) mesoporous structure, (iii) the type of organic amine, (iV) hydrolyzation treatment, (V) cycle performance. Comparing with tetraethylenepentamine (TEPA) functionalized SBA-15, TEPA functionalized MSU-J has lower gas diffusion resistance. The CO_2 uptake of 25MSU-J is 139.6 $mg \cdot g^{-1}$, which is almost 2.5 times than that of SBA-15 of 58 $mg \cdot g^{-1}$ at 20 wt% TEPA loading. The different textured MSU-J is synthesized at 25 °C, 45 °C, 65 °C and impregnated with TEPA. 65MSU-J synthesized at 65 °C exhibits the larger pore size (16.2 nm) and CO_2 adsorption capacity due to pore size instead of larger specific surface area is more feasible for CO_2 diffusion. The MSU-J is impregnated with tetraethylenepentamine (TEPA), diethylenetriamine (DETA), triethylenetetramine (TETA). TEPA impregnated MSU-J possesses higher thermostability (200 °C) and CO_2 capture (164 $mg \cdot g^{-1}$) than counterparts, due to higher N content and the stronger combination between support and amine. The regeneration of Si—OH from Si—O—Si effectively improves the CO_2 adsorption capacity. Both MSU-J and hydrolyzing MSU-J exhibit good cycle performance of CO_2 capture after 6 times cycle.

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* Corresponding author.
E-mail address: jjiao@nwpu.edu.cn (J. Jiao).

http://dx.doi.org/10.1016/j.cej.2016.07.041
1385-8947/

1. Introduction

Up to now, the greenhouse effect has been becoming a serious threat to human living environment. So, the CO_2 controlling emission, capture and recycle attract worldwide attention, which reveals a profound prospect in field of solution of greenhouse and CO_2 recycling [1–5].

Many approaches such as physical adsorption, chemical adsorption and membrane separation process [6,7], attracted rapidly growing interest for CO_2 capture. Chemical adsorption based on the organic amine solution is currently one of the most effective approaches for the CO_2 capture and separation (CCS). Nevertheless, this method suffers a series of disadvantages. The increased solution viscosity arising from amine oxidative degradation impedes the transfer of gas as well as the high energy consumption and amine loss [8,9]. Being a less energy intensive alternative, membrane separation is also restricted for CO_2 capture due to the high cost and the obstacle in mass production [10]. Some porous materials (e.g., active carbon [11], zeolite [12], metal organic frameworks (MOF) [13]) exhibit the prospect for CO_2 capture. However, the drawbacks of these materials, such as diffusion resistance arising from limited pore volume and the poor CO_2 selectivity due to mere physical adsorption, restrict the efficience for CO_2 capture. It was found that porous material with large surface area and pore volume is a promise material for organic amine immobilization. The amine immobilized material exhibits the advantage of physical adsorption and chemical adsorption, and is also positive for CCS to overcome these deficiencies mentioned above [14].

Mesoporous silicas (e.g., SBA-15, MCM-41) are extensively used for amine immobilization by covalent bonds [18] or hydrogen bonds [19] and used for CCS due to the large pore volume, high specific surface area and high concentration of surface silicon hydroxyl [15–17]. Raúl Sanz et al. [18] used three methods (e.g., copolycondensation, amine-grafting and amine-impregnation) to functionalizing SBA-15 with aminopropyl, ethylene-diaminepropyl, diethylene-triaminepropyl, polyethyleneimine, and found that the physical impregnation was the most efficient method for CO_2 adsorption performance. Xu et al. [19] reported a polyethyleneimine (PEI) impregnating MCM-41 (MCM-41-PEI) for CO_2 adsorbent. When the loading of PEI was 50 wt%, the MCM-41-PEI exhibited a 215 mg-CO_2/g-PEI adsorption capacity at 75 °C, which was 24-fold or 1-fold increase in adsorption capacity in comparison with MCM-41 or pure PEI, respectively.

Son et al. [20] studied the relationship between CO_2 adsorption performance and the textural properties of MCM-41, MCM-48, SBA-16 ≈ SBA-15 and KIT-6 with pore diameter of 2.8 nm, 3.1 nm, 4.1 nm, 5.5 nm and 6.5 nm, respectively. The results manifested that the larger pore size, large pore volume and connected mesopore structure (e.g., MCM-48, HMS) were positive to enhance CO_2 adsorption capacity and to improve adsorption kinetics. Chen et al. [21] reported a PEI functionalized 3-D disordered wormhole framework structured mesoporous silica HMS with 2.8 nm pore diameter used as CO_2 capturer. When the loading of PEI was 60 wt%, the adsorption capacity of this absorbent is 184 $mg{\cdot}g^{-1}$ at 75 °C. This result also indicated that the framework structure of mesoporous silica play an additional role in the gas adsorption process besides intrinsic pore size and pore volume of mesoporous silica.

In this work, three-dimensional mesoporous silicas MSU-J with worm-hole framework structures and better pore connectivity was firstly used as adsorbent for CO_2. Comparing with MCM-41, SBA-15, HMS and other mesostructured silica, three dimensional worm-hole framework structured MSU-J synthesized by Park et al. [22] has large pore size (up to 10 nm), pore volume (up to 2.29 $cm^3{\cdot}g^{-1}$) and excellent connected mesopores, which is a promising organic amine support for improvement of gas transportation, and the CO_2 adsorption capacity and adsorption kinetics. SBA-15 is adopted as reference object of MSU-J to explain the relationship between the framework structure and the CO_2 adsorption efficiency. Three types of amine with different molecular weight were immobilized on the different MSU-J by impregnating to explain the effects of texture properties of MSU-J, structure and loading of amine on the CO_2 adsorption capacity. Furthermore, MSU-J was treated in boiling water to get more hydroxyl bonds by hydrolyzation. So, it was expected to immobilize more amine on the surface of MSU-J by the interaction between the hydroxyl bond and amino groups. The cycle performance of CO_2 adsorption for MSU-J with immobilizing amine was also studied.

2. Material and methods

2.1. Materials

The α, ω-polyoxypropylene diamine $H_2NCH(CH_3)CH_2[OCH_2CH(CH_3)]_{33}NH_2$ ($M_w \approx 2000$) with the commercial name Jeffamine D2000 (D2000) was obtained from Huntsman Corp. and used as template for synthesis of MSU-J. The triblock copolymer poly (ethylene oxide-*b*-propylene oxide-*b*-ethylene oxide) (Pluronic P123, $EO_{20}PO_{70}EO_{20}$) used as template for synthesis of SBA-15 was purchased from Aldrich Chemical Company. Tetraethyl orthosilicate (TEOS, ⩾98.0%) was purchased from Aladdin Industrial Corporation and used as the silica precursors to prepare mesoporous MSU-J and SBA-15 silicas. Diethylenetriamine (DETA, ⩾95.0%), triethylene tetramine (TETA, ⩾95.0%) and tetraethylenepentamine (TEPA, ⩾95.0%) were also purchased from Aladdin Industrial Corporation.

2.2. Preparation of mesoporous silica

The SBA-15 was synthesized at acid condition according to reference [23]. The P123 (4.02 g) surfactant was dissolved in the deionized water (30 g), and HCl (120 g, 2 mol/l), and was stirred at 45 °C for 1 h to get a homogenous mixture. Then the TEOS (8.71 g) was added to the surfactant solution under stirring for 20 h at 45 °C. The resulting mixture was allowed to age in oven at 80 °C for 48 h without stirring. Afterwards, the solid products were collected by filtration, washed and dried at 80 °C overnight. The surfactant was then removed by calcination at 600 °C for 4 h in air. In a typical synthesis of MSU-J silica from TEOS, the surfactant D2000 (25 g) was dissolved in ethanol (78.20 g) and then the desired amount of water (396 g) was added under stirring. TEOS (21.26 g) was added to the surfactant solution under vigorous