Microporous and Mesoporous Materials 197 (2014) 278–287

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

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

# Polyallylamine and NaOH as a novel binder to pelletize amine-functionalized mesoporous silicas for $CO_2$ capture

Worasaung Klinthong, Chih-Hung Huang, Chung-Sung Tan *

*Department of Chemical Engineering, National Tsing Hua University, Hsinchu 30013, Taiwan, ROC*

ARTICLE INFO

*Article history:*
Received 17 February 2014
Received in revised form 3 June 2014
Accepted 26 June 2014
Available online 5 July 2014

*Keywords:*
Pellet
Binder
Polyallylamine
Amine-functionalized mesoporous silicas
$CO_2$ capture

ABSTRACT

A binder solution containing polyallylamine (PAA) and NaOH is proposed to construct pellets from powdered amine-functionalized mesoporous silica, thereby providing active sites for $CO_2$ capture. Various powdered amine-functionalized adsorbents were prepared and pelletized, including 3-aminopropyltriethoxysilane-functionalized MCM-41 obtained through post-modification and direct synthesis, and polyethylenimine-loaded MCM-41 obtained through impregnation. The effects of the concentrations of PAA and NaOH on the strength, durability, and $CO_2$ adsorption capacity of the pellets were evaluated, as the anhydrous and humid $CO_2$ adsorption behavior and cyclic thermal stability. The pellets prepared after mixing the powdered adsorbents with an aqueous solution of 3 wt% PAA and 2 wt% NaOH exhibited the $CO_2$ adsorption capacity slightly lower than the powdered adsorbent, a recovery of greater than 90% of the powdered adsorbents was observed, while their mechanical strength was over 0.4 MPa and the weight could be retained over 90% in durability tests. Moreover, the pelletized adsorbents possessed the high thermal stability in cyclic adsorption/desorption. As a result, the proposed binder formula can be used to provide pelletized amine-functionalized adsorbents for $CO_2$ capture from power plants.

## 1. Introduction

Carbon dioxide is a key global warming gas and its capture and sequestration is an important issue that has drawn global attention. Although the use of alkanolamines as chemical absorbents is currently one of the most viable means of capturing $CO_2$, this technology has several drawbacks, including high degrees of corrosion and expensive regeneration of the absorbents [1,2]. The application of mesoporous silicas might possibly overcome these drawbacks, because their adsorption capacities toward $CO_2$ can be enhanced by loading alkaline groups, such as amines, onto their internal surfaces [3]. In general, the $CO_2$ adsorption performances of amine-based silica adsorbents are influenced by several factors, including the loading method, the nature of the amine, the surface silanol content, the loading conditions, etc. [4–12].

Although alkanolamines impregnated onto mesoporous silicas can exhibit extremely high $CO_2$ adsorption capacities, they often lack thermal stability during desorption and encounter a large resistance to diffusion [9,12,13]. Several approaches have been proposed to overcome these thermal limitations, including the covalent grafting of aminosilanes, especially 3-aminopropyltriethoxysilane (APS), onto porous silicas through post-modification [4,5,8,14] or direct synthesis [15–17], ring-opening polymerization of amine monomers onto oxide support (hyperbranched aminosilica materials) [18,19], and the impregnation of polyamine onto porous supports. Silylation of aminosilane-grafted adsorbents onto the intrachannel surfaces of a template-removed mesoporous silica provided a material that exhibited a comparatively higher adsorption rate and higher stability in cyclic runs relative to those of alkanolamine-impregnated adsorbents [11]. Polyethylenimine (PEI), a sterically bulky branched polymer having a repeating unit featuring amino groups and a low heat of adsorption, has generally been loaded into porous silicas through impregnation [20–25]. It has been reported that high PEI-loaded adsorbents significantly enhance the $CO_2$ adsorption capacity while decreasing of pore characteristics; thus, a balance exists between the adsorption event supplying additional active sites on one hand, yet blocking up the channels on the other. Moreover, PEI-loaded adsorbents can exhibit high thermal stability over numerous regeneration cycles at moderate temperatures (110–145 °C) [20]. Although these amine-functionalized powdered materials are proven to be effective adsorbents for $CO_2$ capture, they cannot be used directly in large-scale applications because their small particle sizes have several practical drawbacks, especially a large pressure drop in gas–solid systems [26]. With a view toward industrial applications, pelletized adsorbents are preferred over powdered forms, especially they used in a fixed bed adsorber.

---

* Corresponding author. Tel.: +886 3572 1189; fax: +886 3572 1684.
*E-mail address:* cstan@mx.nthu.edu.tw (C.-S. Tan).

http://dx.doi.org/10.1016/j.micromeso.2014.06.030
1387-1811/© 2014 Elsevier Inc. All rights reserved.

Pelleting can not only improve the strength of a material but also decrease the cost of its transportation, operation, and storage [27]. A pellet possessing high mechanical strength and durability can avoid damage and the formation of fines or fragments and, thereby, prevent increased pressure drop in a fixed bed adsorber. Binders play important roles in pelleting systems; they are applied to increase the mechanical strength of the pellets. The binders can be either inorganic or organic materials, including bentonite, various polymeric materials, etc. [28]. Polymers are organic binders that can be adsorbed onto pore surface and functional groups on surface. A network is generated by the addition of a polymeric binder, which functions as a bridge linking the particles together. The polymer chains adsorbed on the particles become entangled, thereby tightening the structure and bringing the particles even closer together [29]. Polyallylamine (PAA) is a representative polyamine featuring a long allyl chain and a large mass-fraction of basic primary amino groups. PAA can link particles through the cohesive forces among themselves and adhesive forces between PAA and particles, making it a particularly good candidate for use as a binder material. In particular, the basic primary amino groups also allow the adsorption of $CO_2$ while minimizing thermal mass and providing good oxidative stability [30].

With the goal of practical $CO_2$ capture, mesoporous supports modified with various amines as well as their $CO_2$ adsorption performance have been studied systematically; although the pelleting of powders has also been investigated extensively, the application of amine-functionalized pelletized materials has been reported rarely. Sharma et al. [31] prepared powdered and pelletized mesoporous silicas that were further impregnated with PEI; the pore characteristics and $CO_2$ adsorption performance were then investigated. The pore characteristics of mesoporous silicas decreased dramatically after pelleting, making them less effective for PEI impregnation. As a result, loading amines onto supports prior to pelletizing is proposed herein as a means to more thoroughly apply the pore structures of mesoporous silica. Moreover, the use of amine-containing polymers as binders can make up for the loss of $CO_2$ adsorption capacity after pelleting. Therefore, the objective of this study was to pelletize amine-functionalized mesoporous silicas using a binder solution containing PAA and NaOH. Various powdered amine-functionalized adsorbents were used as modeled samples in this study, including APS-functionalized MCM-41 prepared through post-modification and direct synthesis [16], and PEI-loaded MCM-41 prepared through impregnation. A high recovery of the $CO_2$ adsorption capacity and high mechanical strength were observed after pelleting. To verify the applicability of pelletized amine-functionalized adsorbents, the $CO_2$ adsorption under anhydrous and humid conditions and the cyclic $CO_2$ adsorption/desorption stability were also examined in this study.

## 2. Experimental

### 2.1. Synthesis of powdered adsorbents

Four types of powdered adsorbents were prepared: APS-grafted calcined MCM-41 prepared in refluxing toluene and in supercritical (SC) propane; as-synthesized APS-functionalized MCM-41 prepared through direct synthesis; and PEI-loaded MCM-41 prepared through impregnation.

#### 2.1.1. APS-grafted calcined MCM-41 prepared in refluxing toluene

The APS-grafted calcined MCM-41 material was prepared in refluxing toluene following the procedures reported by Chang et al. [5]. Commercial calcined MCM-41 (MCM-41, Sigma–Aldrich; 1 g) was dispersed in anhydrous toluene (50 mL) and stirred for 30 min at room temperature. APS (10 mL, Sigma–Aldrich) was added and the resulting mixture was heated under reflux at 100 °C for 16 h. The suspended solid product was filtered off, washed with anhydrous ethanol (EtOH, 500 mL), and then dried at 70 °C overnight in the open air to give APS-MCM(R).

#### 2.1.2. APS-grafted calcined MCM-41 prepared in SC propane

The APS-grafted calcined MCM-41 material was prepared in SC propane following the procedures reported by Huang et al. [14]. MCM-41 (0.88 g) was dried under vacuum at 150 °C for 12 h and then placed into a 50-mL reactor along with APS (8.80 mL). Pressurized propane was fed into the reactor until a desired pressure of 11.0 MPa was reached. The temperature was increased to 100 °C and the grafting was performed for 16 h. The solid product was washed with anhydrous EtOH (500 mL), and then dried at 70 °C overnight in the open air to give APS-MCM(S).

#### 2.1.3. As-synthesized APS-functionalized MCM-41 prepared through direct synthesis

The as-synthesized APS-functionalized MCM-41 material was prepared through direct synthesis following the procedures reported by Klinthong et al. [16]. The pH of a solution of cetyltrimethylammonium bromide (CTAB, Sigma–Aldrich; 3.79 g) in deionized water (200 g) was increased to 13 through the addition of tetramethylammonium hydroxide (TMAOH, Alfa Aesar; 5.65 g). The silica sources, tetraethyl orthosilicate (TEOS, Acros) and APS, were then added such that the molar composition of the mixture was 0.5 TEOS:0.5 APS:0.12 CTAB:0.36 TMAOH:130 $H_2O$. The solution was stirred vigorously for 2 h at ambient temperature and then kept statically in a Teflon autoclave at 100 °C for 4 days. The solids were filtered off, washed with deionized water (3 L) and EtOH (500 mL), and then dried at 70 °C to give APS/MCM.

#### 2.1.4. PEI-loaded MCM-41 through impregnation

MCM-41 (4 g) was added into a stirred solution of PEI (4 g) in methanol (80 g). After stirring and heating the mixture under reflux for 8 h, the liquid part of the mixture was evaporated off at 80 °C and then the solid part was dried at 100 °C for 1 h, giving PEI/MCM.

### 2.2. Synthesis of pelletized adsorbents

#### 2.2.1. Formula of binder solution for pellet production

Initially, the formula of the binder solution, containing PAA (molecular weight: 17,000; Sigma–Aldrich) and NaOH (Acros), was investigated using APS-MCM(R) as the powdered adsorbent. The binder solutions were prepared by diluting 20% PAA solution with deionized water to give 2.0–5.0% PAA solutions. NaOH was added to obtain 0.5–3.0% NaOH in the PAA solutions. An aliquot of the binder solution (1.0 g) was added to APS-MCM(R) (1.0 g) and stirred for 5 min. The mixture was poured into a mold and dried at 80 °C for 2 h. The resulting white cylindrical pellets of APS-MCM(R), herein named APS-MCM(R)-P, where P denotes the pelletized product, were obtained with a diameter of 5.0 mm and a height of 2.0 mm (Fig. 1).

#### 2.2.2. Pellet production of powdered adsorbents

A powdered adsorbent (APS-MCM(S), APS/MCM, or PEI/MCM; 1.0 g) was pelletized using a binder solution (1.0 g) having a selected formula. The mixture was poured into the mold and dried at 80 °C for 2 h. The resulting pelletized products are named herein as APS-MCM(S)-P, APS/MCM-P, and PEI/MCM-P.

### 2.3. Characterization

The $N_2$ physical adsorption/desorption isotherms of the samples were measured at −196 °C using a Micromeritics Tristar 3000