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Zeolite monoliths with hierarchical designed pore network structure: Synthesis and performance

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HIGHLIGHTS

- Self standing zeolite monoliths with hierarchical pore network structure synthesized.
- Pore network consists of mutually interconnected macro, meso and microscale channels.
- The performance of prepared monoliths on CO_2 separation from CO_2/N_2 mixture was superior to commercial beads.
- Increase the density and connectivity of the channels increased diffusivity and decreased the pressure drop.

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ABSTRACT

Structured adsorbents with attractive characteristics have been developed for use in CO_2 capture applications. 5A zeolite monolithic structures with a hierarchical designed channel/pore system and high zeolite content approaching 92 wt% were prepared. The body of the monoliths contained three different sizes of channels and pores; macro, meso and micro. The developed monoliths showed outstanding performance on CO_2 separation from CO_2/N_2 gas mixtures compared to commercial 5A beads. The equilibrium isotherms of pure gas adsorption were collected, CO_2/N_2 binary gas breakthrough experiments were conducted, and pressure drop along beds packed with the monoliths or 5A beads was measured. The experimental data were simulated and the results showed that effective diffusivity was six times higher and pressure drop was 1.3 times lower for 5A monolith bed compared to 5A beads bed. The high effective diffusivity, low pressure drop and comparable adsorption capacity of the prepared 5A monoliths indicate that they are ideal candidates for rapid pressure swing adsorption applications.

1. Introduction

Over the past decade, there has been a considerable interest in the development of novel materials and new techniques for CO_2 capture and storage. The main strategies for CO_2 capture are post-combustion separation, pre-combustion separation and oxy-fuel combustion. For post-combustion CO_2 capture, a range of techniques such as absorption, membrane separation, and adsorption have been used to separate CO_2 mainly from N_2 in the flue gas [1].

Zeolites like NaX and NaY have been used widely as adsorbents for post-combustion CO_2 capture. They showed high adsorption capacity and selectivity compared to other adsorbents when they were used for CO_2 capture from flue gas streams or removal of trace CO_2 and water vapor [2–4].

Conventional adsorption separation relies on random packing of zeolite pellets/beads of a few millimeters in vertical vessels columns. The gas mixture is directed through the packed bed and the molecules of interest diffuse into the adsorbent pores while the weakly adsorbed components elute from the column through the outlet stream. High throughputs require high gas velocities leading to high pressure drop and heat and mass transfer limitation which results in high energy consumption and high capital cost [2,5–9]. To overcome this problem, enormous efforts have been devoted over the past decade to developing and optimizing different configurations of structured adsorbents with improved separation performance such as monoliths, laminates and foams [2,5–7,9]. Monoliths are structured materials with parallel gas flow channels. The shape and the diameter of the parallel channels and their density per cross sectional area of the monolith are controllable. Zeolite monoliths can either be zeolite-substrate monoliths or self standing zeolite monoliths. The former are prepared by depositing (e.g. wash coating) or growing a layer/film of zeolite or zeolite plus binder on non-removable monolithic substrates. The latter

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can be prepared by molding a paste of zeolite or zeolite plus binder into monolithic structures. These structures have been prepared with desirable pressure drop and diffusion characteristics, however at the cost of sacrificing adsorption capacity.

Our group has investigated a large variety of options for creating zeolite monoliths such as zeolite coated monoliths [6,7]. To date, these structures have suffered from low zeolite loading (usually less than 50%). Mosca et al. prepared 13X zeolite-substrate monoliths by growing a thin film of 13X zeolite on porous cordierite monoliths with 400 cpsi [2]. The performance of this film on CO_2 adsorption was examined and the results showed 100 times less pressure drop and 67 times lower CO_2 adsorption capacity compared to commercial 13X beads. The low adsorption capacity was attributed to low zeolite loading per unit mass of the monolith. Rezaei et al. investigated the influence of increasing the cell density of the substrate on the performance of zeolite-substrate monoliths [9]. Accordingly, 13X zeolite films with 1.6 μm thickness were grown on cordierite substrates with 900 and 400 cpsi. The CO_2 isotherms of 13X zeolite-substrate monoliths with 900 cpsi showed higher adsorption capacity than the 400 cpsi monolith due to higher zeolite loading per unit mass. However, the CO_2 breakthrough curve of the former was broader compared to the latter indicating higher mass transfer resistance [9].

The structure of interest in this work is a monolith made predominantly from zeolite so as to maximize zeolite loading and to avoid the single-sided mass transport characteristic of zeolite-substrate monoliths [10]. In addition we wanted to overcome the possible separation of the zeolite film from the substrate upon frequent heating for activation [9].

Self standing SOD zeolite monolith with hierarchical porosity and good stability was obtained by pseudomorphic transformation of meso–macroporous silica monolith [11]. In another study, a silica monolith was transformed into micro–meso–macroporous type beta zeolite monolith by using carbon as a transitional template to support the pore channels of a silica monolith from collapsing during the conversion of silica into zeolite [12]. Monolith of type P zeolite with micro–macropores was synthesized starting with gel casting the aged zeolite gel and silica followed by vapor phase transport synthesis [13]. All the above studies, however, required an autoclave for the phase transport step which reduces their efficiency for large scale applications.

Alternatively, different shapes and sizes of zeolite monoliths consisting of a desired number of parallel channels (cell density) can be prepared by extruding a paste of zeolite powder and a binder using a die extruder. A square channel 5A zeolite monolith consisting of 25 wt% Na-bentonite as a binder was fabricated for air separation using a constant volume method [14]. The authors suggested that the monoliths might produce less pressure drop compared to beads; however the work does not show pressure drop measurements. In another study, 4A honeycomb monolith with 424 cpsi was prepared and their behavior in term of adsorbing propane and propylene gases was measured and compared to commercial extrudates [15]. The adsorption equilibrium of pure gases was in agreement with commercial extrudates; however, the values of diffusivity coefficients were three orders of magnitude smaller due to the blockage of the micropores by the binders.

To date, self standing zeolite monoliths prepared by using die extruder technique are bundle of parallel channels with walls made of microporous zeolite and binder. Thus, they offer limited diffusion paths for guest molecules; namely, parallel channels, micropores associated to zeolite framework and interstitial voids between zeolite crystal and binder.

This study presents, for the first time, the preparation of 5A zeolite monoliths with hierarchical designed channel/pore system and high zeolite loading (92 wt%) that show high effective diffusivity and low pressure drop. The hierarchical channels/pores system engineered throughout the body of the monoliths consisted of large parallel channels, macro-scale channels, mesopores and micropores. The mesopores and micropores are associated to the structure of the primary building units of the monoliths which are micro–mesoporous 5A zeolite particles [16,17]. It is known that 5A zeolite is one of the most efficient types of zeolites for CO_2 recovery [18]. The performance of the monoliths on CO_2 capture from 15% CO_2/85% N_2 gas mixture was tested and compared to commercial beads. Monoliths with zeolite: binder ratio close to and less than commercial beads were prepared. The influences of the channels concentration and the binder ratio on the monolith performance were examined. The experimental data were simulated and the effective diffusivities were calculated to examine the potential of these novel monoliths for PSA processes.

2. Materials and methods

2.1. Preparation of hierarchical 5A zeolite monoliths

The parent micro–mesoporous 4A zeolite was synthesized following the procedure reported in our previous work, the produced sample is named ZANa [16,17]. The resultant powder was ion exchanged to form micro–mesoporous 5A zeolite which is named ZACa. More details about the synthesis method are included in the Supporting information, Sections 1.1 and 1.2.

Self standing ZACa zeolite monoliths were prepared from a mixture of powders including the pre-synthesized ZACa zeolite powder, silicon resin (233 Flake, 52 wt% silica, Dow Corning), methyl cellulose (Sigma–Aldrich) as plasticizing organic binder, and Poly (vinyl alcohol) (Sigma–Aldrich) as a co-binder [19–21]. Thereafter, a desired amount (Table 1) of plastic fibers (0.16 mm Dia., 15 mm L; normally used for paper machine forming fabric, Huyck) was added to the dry mixture. Finally, a sufficient amount of water to prepare a plasticized and readily formable mixture was added. After calcination, 52% of the added amount of silicon resin will remain in the form of silica and act as a permanent binder in the fired monolith. Therefore, the amount of silicon resin used in our experiments was calculated based on the concentration of the permanent binder required in the final monolith (Table 1).

For example, to prepare the monolith denoted M8 with final weight (fired monolith) of 2.75 g consisting of 77.3% zeolite A (ZACa) and 22.3% silica (Table 1); 2.13 g ZACa powder was blended together with 1.20 g of pre-ground silicon resin, 0.15 g methyl cellulose (5.45 wt% of fired monolith) and 0.04 g PVA (1.45 wt% of fired monolith). Then, 0.25 g (9.0 wt% of fired monolith) plastic fibers were mixed with the powder mixture followed by adding 1.5–2 ml of deionised water (43–50 wt% of total powders). In the next stage, the plasticized mixture was deposited into the feedhole (15 mm ID) of a custom made die (Fig. 1A). In order to obtain a strong monolith, a pressure up to 20 bar was applied to the mixture by using a press pelletizer (Pressmate XRF Scientific). To opti-

Table 1
Characteristics of the prepared monoliths.

Sample	ZACa[a] (wt.%)	SiO_2[a] (wt.%)	Plastic fiber[b] (wt.%)	Parallel channels	Wall thickness[c] (mm)
M6	77.3	22.7	2.5	21	2.3
M7	77.3	22.7	9.0	21	2.3
M8	77.3	22.7	9.0	50	0.9
M9	92.0	8.0	9.0	50	0.9

[a] Weight percentage of zeolite and silica in the final fired monoliths.
[b] Weight percentage of plastic fiber calculated based on the weight of the final fired monoliths.
[c] Approximate values obtained by simple mathematic calculation.