Adsorption (2008) 14: 687–693
DOI 10.1007/s10450-008-9126-9

Optimization of synthesis procedures for structured PSA adsorbents

Alessandra Mosca · Jonas Hedlund · Firas N. Ridha · Paul Webley

Received: 30 April 2007 / Revised: 22 January 2008 / Accepted: 18 April 2008 / Published online: 30 April 2008

Abstract Structured adsorbents in the form of supported thin zeolite films may represent a competitive alternative to traditional zeolite adsorbents in form of beads or pellets used in PSA processes, due to the reduction of mass- and heat-transfer limitations typical of packed beds. Thin NaX films were grown by hydrothermal treatment using a clear solution on cordierite monoliths. Films grown by a multiple synthesis procedure were dense and uniform with a very small amount of sediments adjacent to the film, which may be an advantage in PSA applications. The CO_2 adsorption capacity and the pressure drop for the supported films were compared to those of a packed NaX bed. Although the adsorption capacity of the column filled with the structured adsorbents was 67 times lower than when the column was filled with zeolite beads, the pressure drop was 100 times lower for the structured adsorbent. The adsorption capacity can be increased by increasing the film thickness or the cell density of the monoliths without increasing the pressure drop significantly, indicating the potential advantage of structured adsorbents in PSA processes. Further investigations are needed in order to prove this hypothesis.

Keywords Zeolite NaX · Traditional adsorbents · Structured adsorbents · PSA · Adsorption · Pressure drop

1 Introduction

Zeolites represent a broad class of crystalline aluminosilicate materials used in adsorption processes, catalysis, membrane, and sensor technology. Gas separation via adsorption can occur in the porous framework because of the interactions between the dipole moments of the gas molecules with the electrical field inside the pores of the adsorbent (equilibrium separation), size or steric exclusion of certain components (molecular sieving), or because of the ability of some components to enter the pores faster than others (kinetic selectivity). The vast majority of industrial gas separation processes by zeolite occurs via equilibrium. NaX zeolite is a widely used adsorbent for CO_2 recovery due to its high working capacity, equilibrium selectivity and low purge requirement (Chue et al. 1995; Chou and Chen 2004). High purity carbon dioxide can be obtained on zeolite X, where it adsorbs for equilibrium affinity between the quadrupole moment of the carbon dioxide molecules and the electrical field generated by the cations inside the zeolite pores.

Pressure swing adsorption is a widely used technique for carbon dioxide capture from flue gas (Gomes and Yee 2002; Chou and Chen 2004; Reynolds et al. 2006) or oxygen enrichment from air (Li et al. 1998a, 1998b). Adsorption columns with randomly packed zeolite beads, pellets and extrudates are generally used in PSA processes for oxygen production and carbon dioxide separation because of the high productivity and low cost of the adsorbent material. However, PSA processes which use adsorbing materials in this form have high pressure drop and heat—and mass—transfer limitations as main drawbacks.

A high pressure drop in the packed bed might generate high capital and operating costs for the pressurization/depressurization steps in a PSA process (Jain et al.

A. Mosca (✉) · J. Hedlund
Div. of Chemical Technology, Luleå University of Technology,
Luleå 971 87, Sweden
e-mail: Alessandra.Mosca@ltu.se

F.N. Ridha · P. Webley
Dept. of Chemical Engineering, Monash University, Clayton,
VIC 3800, Australia

2001; Li et al. 1998b). The long diffusion paths through meso- and macropores in the zeolite beads may induce heat—and mass—transfer limitations due to temperature and concentration gradients, thus decreasing the overall performance of the PSA process (Li et al. 1998b).

Recently, parallel flow monolith structures have received considerable attention for their use in adsorption processes. These materials have parallel channels with controllable shape and wall thickness (Cybulski and Moulijn 1998; Williams 2001). In addition, zeolite monoliths, consisting solely of zeolite and binder material (Lee et al. 2000; Li et al. 2001), have been prepared and tested in an air separation application.

Monoliths have been widely used in catalytic converters since the 1960s (Cybulski and Moulijn 1998; Williams 2001) rather than in PSA processes. Ceramic cordierite monoliths are mainly used as catalysts substrates in the automotive industry for oxidation of CO and CH_x, reduction of NOx, and as diesel particulate filters (DPF). The main advantage offered by monoliths compared to packed beds is the low pressure drop. Lower pressure drop is very important in PSA processes (Todd 2003) in terms of reduced power consumption, high product recovery, purity and productivity. In another study, the CO_2 adsorption and diffusion on a carbon monolith adsorbent were studied using the Zero Length Column (ZLC) method (Brandani et al. 2004). The ZLC curves show that at low purge rates the adsorption mechanism is equilibrium controlled, and at high flow rate kinetic-controlled. Further, the combined effect of axial mixing and resistance to mass transfer in the carbon monolith walls result in spreading of the CO_2/N_2 breakthrough curve.

The adsorption performance of 5A zeolite monoliths (made from zeolite with a binder rather than by coating a substrate) with square lattice channels and a wall thickness of 0.98 mm was compared to that of 5A zeolite pellets in the separation of oxygen from air (Li et al. 1998a, 1998b, 2001). The adsorption capacity and pressure drop in the zeolite monolith were slightly lower than in the pellets. The authors assign the poorer oxygen separation performance of the 5A monolith to the reduced ability to transfer the molecules from the gas phase to the adsorbent surface, as a result of the increased diffusion path in the thick walls of the zeolite monolith. However, the use of monoliths in adsorption processes may represent a competitive alternative to packed beds, leading to a more effective and lower cost processes by reducing the power demand and cycle time. Possible ways of improving the separation performance of the zeolite monoliths might be to reduce wall thickness, to increase cell density, or to use hexagonal rather than square cell shape (Patton et al. 2004).

Due to the high mass transport resistance in traditional zeolite adsorbents (beads, powder and extrudates) or in thick walls of whole zeolite monoliths, structured adsorbents in the form of monoliths coated with NaX *films* having a controllable thickness were developed in this work. CO_2 adsorption capacity and pressure drop were evaluated for the structured adsorbent and compared with NaX zeolite beads.

2 Experimental section

Porous cordierite monoliths (400 cpsi, Corning) were used as structured substrates for the zeolite film growth. The substrates were first rinsed in toluene, acetone and several times in a 0.1 M NH_3 solution. Prior to hydrothermal treatment, the monoliths were dried in a ventilated furnace at 110 °C, cooled thereafter in a desiccator and then the weight was recorded.

Growth of adsorbed 80 nm faujasite (FAU) seeds on the walls of the substrates was performed in a clear solution with molar composition of $80Na_2O:1Al_2O_3:9SiO_2:500H_2O$, as described by Öhrman et al. (2004a) about the growth of thin ZSM-5 film on cordierite monoliths. To prepare the clear solution, sodium metasilicate ($Na_2SiO_3 \times 9H_2O$, Sigma-Aldrich) was mixed with pelletized sodium hydroxide (99.9% NaOH, Merck) and distilled water. An aqueous solution of aluminium sulphate ($Al_2(SO_4)_3 \times 18H_2O$, Riedel-de-Häen) was added under vigorous stirring. The synthesis of the NaX film was performed in 1 step of 6 h and 40 min or in 5 steps of 1 h and 20 min in the clear solution, which was heated in an oil bath at 100 °C and atmospheric pressure under reflux. NaX crystals were also prepared in the clear synthesis solution for 1 h and 20 min, and used as a reference for the determination of the zeolite loading. Prior to characterization the samples were dried at room temperature and in a ventilated furnace at 100 °C over night, and cooled thereafter in a desiccator. The zeolite loading ($g_{zeolite}/g_{sample}$) of the structured adsorbents was determined by the weight gain, as the weight increase of the cordierite supports after hydrothermal treatment.

NaX (13X) molecular sieve zeolite beads (Qingdao JIT Corporation, Qingdao, China) with a diameter of 0.7 mm were used for comparison with the NaX film coated cordierite monoliths. The zeolite loading of the beads was determined by liquid N_2 adsorption on a Micromeritrics ASAP 2010 instrument, as the ratio between the BET surface area of the beads and the reference NaX crystals, as described by Öhrman et al. (2004b) for thin ZSM-5 film coated alumina beads. A Philips XL 30 scanning electron microscope (SEM) equipped with a LaB_6 emission source was used for studies of surface morphology and to measure film thickness. The monoliths were cut in the channel direction in order to characterize the films. The NaX beads were mounted in a phenolic resin (Phenolic Resin Black, Buehler LTD) and polished in order to obtain cross-sectional images. SEM

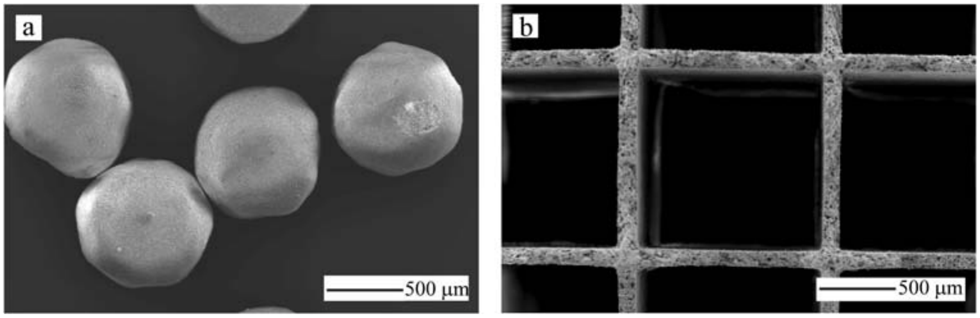

Fig. 1 Low magnification SEM images of (**a**) of the 13X beads and (**b**) of the cross-section of a 400 cpsi cordierite monolith

images were recorded on samples covered with a thin layer of gold (few nm) previously deposited by sputtering. X-ray diffraction data (XRD) were recorded with a Siemens D 5000 powder diffractometer equipped with a Cu-target in the Bragg–Brentano geometry. The specific carbon dioxide adsorption capacity (mmol/g_{sample}) of the structured adsorbents and NaX beads was measured at 0 °C by using a Micromeritrics ASAP 2010 instrument and was used to determine the adsorption capacity of a PSA column (2 cm in diameter and 30 cm long) loaded with NaX beads or three coated cordierite monoliths (2 cm in diameter and 10 cm long) connected in series. Liquid nitrogen sorption at liquid N_2 temperature was performed on the structured and traditional adsorbents by using a Micromeritrics ASAP 2010 instrument. The samples were outgassed at 300 °C under vacuum prior to analysis. The pore size distribution was determined by the Barret-Joyner-Halenda (BJH) method applied to the desorption branch. CO_2 breakthrough curves were determined by performing step experiments on a single PSA column loaded with three structured samples (0.99 $g_{zeolite}$ in total) or NaX beads (33.7 $g_{zeolite}$). The samples were activated in-situ and heated at a heating rate of 2 °C/min to 200 °C for 2 hours under a N_2 flow and cooled thereafter to room temperature at a cooling rate of 2 °C/min. The feed consisted of 10% CO_2 in N_2 and was injected at a volumetric flow-rate of 0.2 L/min. The data were collected by a CO_2 analyzer (Briage analyzers INC) using Advantech GeniDaq data acquisition software. The pressure drop was measured as a function of air flow rates for the zeolite beads and the structured adsorbents in a single PSA column (each 2 cm diameter and 30 cm long).

3 Results and discussion

3.1 Characterization by SEM, weight gain and XRD

Figure 1 shows low magnification SEM images (a) of the NaX beads and (b) of the cross-section of a 400 cpsi porous cordierite monolith. The beads are quasi-spherical with a diameter of about 700 µm (Fig. 1a). The thickness of the cordierite monolith wall is about 100 µm and the channel width is about 1.1 mm (Fig. 1b). Macropores with a size up to several µm are observed inside the walls of the ceramic cordierite support.

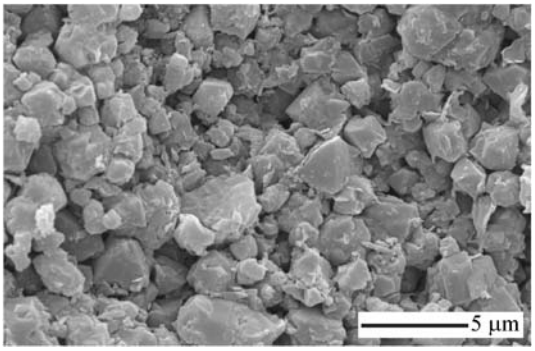

Fig. 2 SEM top-view image of the NaX molecular sieve zeolite beads

Figure 2 shows the cross-sectional image of the NaX beads. It is possible to identify the typical octahedral shape of the zeolite X crystals.

A zeolite film was grown in a longer hydrothermal treatment of 6 h and 40 min (not shown). The film was not continuous, and the presence of pin-holes and etched crystals may be due to the decreased hydrothermal stability of the zeolite crystals. Large sediments on top of the film and hydroxysodalite (HS) crystals were also detected by SEM. Hydroxysodalite probably formed because of the combined effect of the Al-leaching from the support and the thermodynamics of the system (HS is a more stable zeolite than NaX). As observed in a previous work by Lassinantti et al. (2000) on the growth of zeolite Y films on α-Al_2O_3 wafers, the film thickness as a function of time had a maximum and decreased upon long hydrothermal treatments, due to dissolution of the crystals in the film and formation of zeolite P. Sediments and zeolite crystals other than NaX may be a disadvantage in PSA applications in terms of reduced separation performance.

In order to minimize the detrimental effects of Al-leaching and sedimentation, a multiple step synthesis procedure was performed. The synthesis duration of 6 h and 40 min was divided in 5 steps of 1 h and 20 min. Top-view and cross-section images of the NaX film grown in the clear solution on the 400 cpsi cordierite supports in 5 steps of 1 h

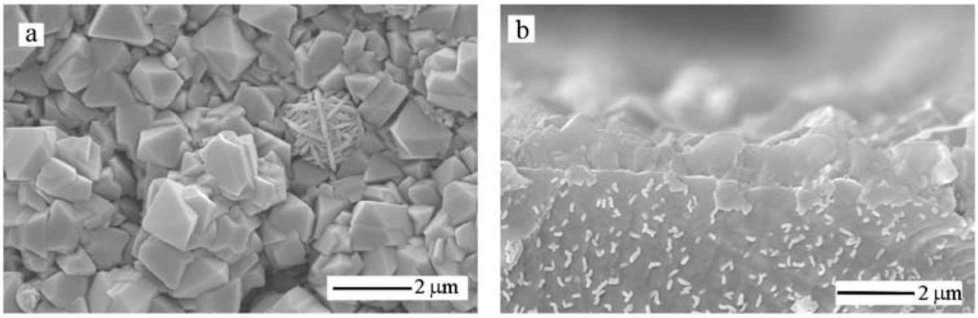

Fig. 3 Top-view (**a**) and cross-section (**b**) images of the NaX film sample grown in the clear solution in 5 steps of 1 h and 20 min on the 400 cpsi ceramic substrate

and 20 min (from now denoted as "structured sample") are shown in Fig. 3a, b. The film is dense and uniform and has a thickness of 1.5 μm. The amount of sediments on top of the NaX films, as well as the number and size of the HS crystals embedded in the zeolite coatings, lowered compared to the one grown in one longer hydrothermal treatment.

The weight gain for the NaX films grown in the clear solution on the porous support in one long hydrothermal treatment and in five steps is 0.030 and 0.036 $g_{zeolite}/g_{sample}$, respectively. The NaX film thickness recorded for the samples grown in one step is lower (0.7 μm) than the one of the structured adsorbent grown in 5 steps (1.5 μm), although the weight gain of the two samples is of the same order of magnitude. This indicates that more sediments are deposited on the monolith after 6 h and 40 min, according to SEM observations.

It could be inferred from these results therefore that suitable conditions for growth of structured adsorbents in the form of supported thin and dense zeolite films with limited amount of sediments for PSA applications is represented by the use of a multiple step synthesis.

Figure 4 shows the XRD patterns for the NaX beads and structured sample grown with the multiple step synthesis procedure. The XRD patterns are typical for randomly oriented NaX crystals, and no hydroxysodalite crystals are detected. The patterns are similar except for the presence of amorphous background, zeolite A and other unspecified reflections (probably due to the binder) in the beads, and cordierite reflections in the structured sample.

3.2 Comparison of the structured sample grown in 5 steps with traditional NaX zeolite beads

The zeolite loading of the beads (0.83 $g_{zeolite}/g_{sample}$) was 23 times higher than for the structured sample (0.036 $g_{zeolite}/g_{sample}$). This shows that the adsorption capacity of the structured sample should be about 23 times lower than the beads for any adsorption measurement, due to the lower amount of zeolite per g sample of the former one.

The carbon dioxide isotherms at 0 °C of the structured adsorbent and of the beads are shown in Fig. 5a, b.

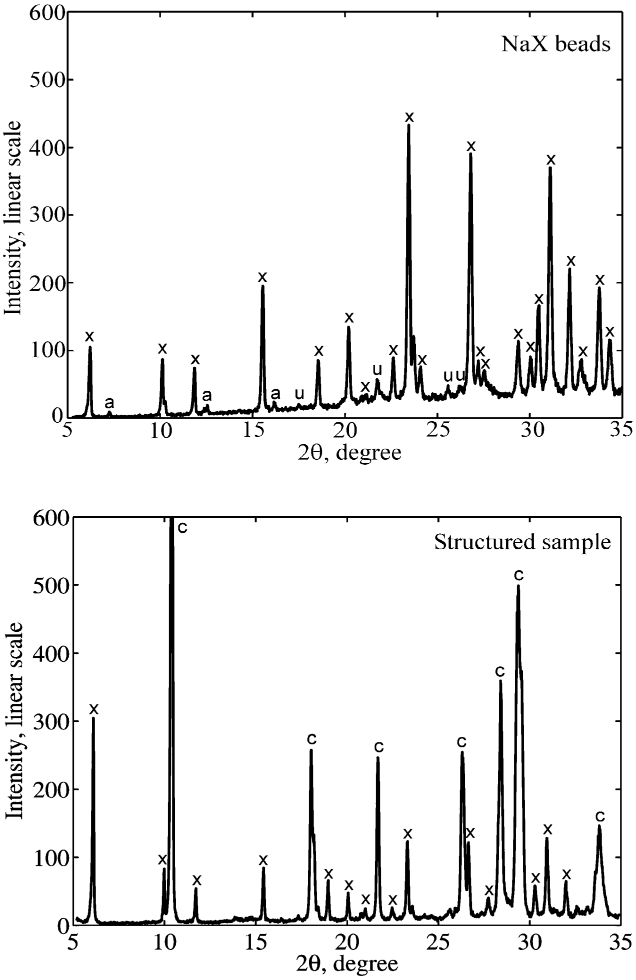

Fig. 4 XRD diffractograms of the NaX beads and structured adsorbent. 'x', 'a', 'u', and 'c' indicating NaX, zeolite A, unspecified reflection, and cordierite peaks, respectively

The CO_2 adsorption capacity per gram sample of the structured adsorbent is 25 times lower than the one measured for the NaX beads, thus in agreement with the zeolite loading measurements from liquid nitrogen sorption. The CO_2 adsorption capacity per unit volume of the adsorption column loaded with the structured adsorbents (0.06 mmol CO_2/cm^3) is about 67 times lower than for the packed bed (4.02 mmol CO_2/cm^3). This result indicates that, by in-

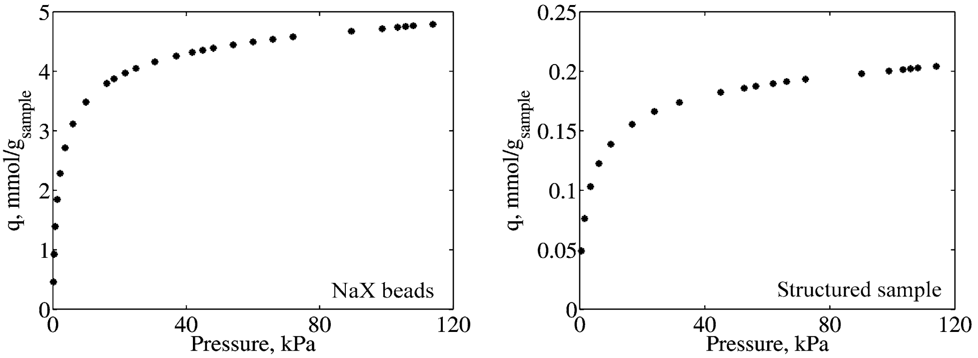

Fig. 5 CO_2 equilibrium isotherm measured at 0 °C on the NaX beads and structured adsorbent

creasing the film thickness 67 times to 100 µm, the adsorption capacity per unit volume of the structured adsorbent may equal that of the NaX beads. It is known from literature (Ruthven 1984) that the resistance to mass transfer in zeolite beads occurs in the meso- and macropores. The linear driving force approximation (Glueckauf and Coates 1947) is often used to describe the rate of uptake into an adsorbent:

$$\frac{d\overline{q}}{dt} = kD_e(q^* - \overline{q}) \tag{1}$$

In this expression, k (m^{-2}) is a factor related to the geometry of the material and D_e is the effective diffusivity ($m^2\,s^{-1}$). The factor k is $15/R^2$ or $3/l^2$ for beads or thin films, respectively (Patton et al. 2004). Since the cumulative mesopore volume determined by nitrogen adsorption of the beads ($0.08\ cm^3/g_{zeolite}$) and structured adsorbents ($0.03\ cm^3/g_{zeolite}$) is of the same magnitude, the effective diffusivity should be comparable in films and beads. If we assume that the effective diffusivity is the same in beads and films, the thickness l of a film with corresponding mass transfer resistance to beads with radius R can be estimated and it follows from above that:

$$l = \frac{R}{\sqrt{5}} \tag{2}$$

The radius of the beads used for comparison in the present work is 350 µm and the corresponding film thickness is thus 157 µm. A 67 times ticker film (100.5 µm) would thus have equal adsorption capacity per unit volume adsorption column and at the same time, lower resistance to mass transfer than the 700 µm beads used in this work (under the assumption that the effective diffusivity is the same in films and beads). Another option to increase the adsorption capacity per unit volume would be to use a support with higher cell density in combination with thicker film. However, a 67 times thicker film was not grown in the clear solution with the multiple step synthesis procedure used in the present work, since it would be unpractical to perform 335 growth steps. In future work, we plan to grow thicker films on supports with higher cell density in a flow reactor instead of using multiple growth steps.

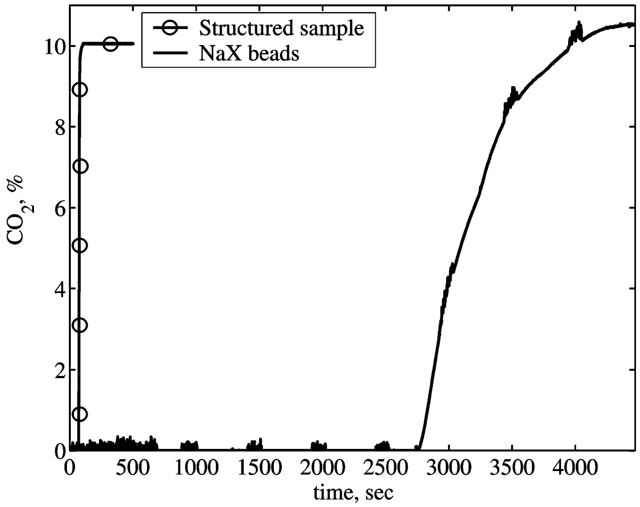

Fig. 6 CO_2 breakthrough curves measured with 10% CO_2 in N_2 with a flow of 0.2 L/min for the structured adsorbent and NaX beads

Figure 6 shows CO_2 breakthrough curves of the structured sample and packed bed. The breakthrough time is about 72 or 2800 s for the structured adsorbents or beads, respectively. The breakthrough time is thus 39 times longer for the beads than for the structured sample. The column was loaded with 0.99 or 33.7 g zeolite of the structured sample or the beads, respectively. The zeolite loading was thus 34 times larger for the beads than the structured sample. The breakthrough time is thus almost proportional to the zeolite loading, as expected. Thus, instead of increasing the film thickness, the cycle time could be about 39 times shorter for the structured adsorbent, which would result in similar productivity for a column loaded with structured sample compared to a column loaded with beads.

The pressure drop for the column loaded with the structured adsorbent (0.99 g zeolite) or the beads (69.6 g zeolite) as a function of flow rate of air is shown in Fig. 7. For volumetric flow rates between 1 and 7 L/min, the Re number varies between 3.52 to 24.74 and 0.27 to 1.94 for the packed bed and the structured adsorbents, respectively. The pressure drop measured in the packed bed (Fig. 7a) is 100 times higher than for the structured adsorbent (Fig. 7b), al-

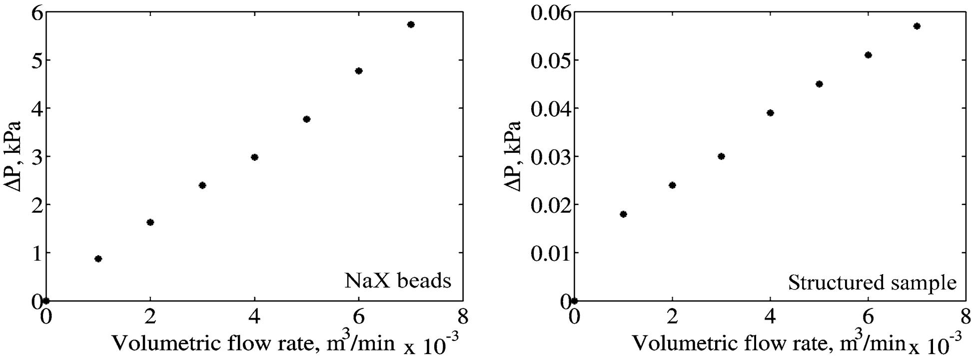

Fig. 7 Pressure drop measurements on the NaX beads and the structured adsorbent

though the volume of the packed bed and the monolith is the same. By increasing the film thickness 67 times to 100 µm to reach the same adsorption capacity for the structured adsorbent as for the beads, the channel width would reduce from 1100 to 900 µm. Since the pressure drop is inversely proportional to the channel width to the power of four (Patton et al. 2004), the pressure drop should only increase about 2.2 times for a structured adsorbent with a 100 µm film. Thus, a structured adsorbent with the same adsorption capacity as traditional beads will still have 45 times lower pressure drop than beads.

These results suggests that structured adsorbents have a great potential compared to traditionally used beads and that there is considerable scope to increase the film thickness and/or monolith cell density to increase the zeolite loading while still maintaining a lower pressure drop than that of a packed bed. In addition, shorter cycle times can be employed for the structured samples with thin films.

However, in order to verify that the structured adsorbents are better than the beads in a PSA process, a complete mathematical model and/or PSA experiments are needed, but this is beyond the scope of the present paper and will be presented in future work.

4 Conclusions

Dense, uniform structured adsorbents with limited amount of sediments were grown in 5 steps on porous ceramic cordierite supports. The CO_2 adsorption capacity and the pressure drop of the NaX film grown with the multiple-step synthesis on the porous support were compared with the ones of NaX beads. Due to the low zeolite loading, the adsorption capacity per unit volume adsorption column of the thin NaX films grown in 5 steps was about 67 times lower than the NaX beads. However, the pressure drop in the column loaded with the structured adsorbent was 100 times lower than for the NaX packed bed, thus representing an advantage for PSA applications. By increasing the film thickness 67 times it may be possible to equal the adsorption capacity of the beads, while the pressure drop of a PSA column loaded with the structured adsorbents still would be 45 times lower than when the column is loaded with beads. These results suggest the potential of structured adsorbents as competitive alternative to traditionally used packed beds in PSA processes. The adsorption capacity of the structured adsorbents may be increased by growing thicker NaX films on the cordierite monoliths or by using substrates with a higher cell density. In addition, heat—and mass—transport phenomena in the films should be investigated and PSA cycles evaluated to explore the possibilities of these novel adsorbents.

Nomenclature

$\overline{q}$: adsorbate loading on adsorbent, kg/kg
k: geometric factor in mass transfer coefficient expression in LDF equation, m^{-2}
D_e: effective diffusivity, m^2/s
q^*: adsorbate loading in equilibrium with fluid phase, kg/kg
l: zeolite film thickness, m
R: radius of a zeolite bead, m

Acknowledgements Qingdao JIT Corporation (Qingdao, China) is kindly acknowledged for providing the 13X molecular sieve zeolite beads.

References

Brandani, F., et al.: Adsorption kinetics and dynamic behaviour of a carbon monolith. Adsorption **10**, 99–109 (2004)

Chou, C.T., Chen, C.Y.: Carbon dioxide recovery by vacuum swing adsorption. Sep. Purif. Technol. **39**, 51–65 (2004)

Chue, K.T., et al.: Comparison of activated carbon and zeolite 13X for CO_2 recovery from flue gas by pressure swing adsorption. Ind. Eng. Chem. Res. **34**, 591–598 (1995)

Cybulski, A., Moulijn, J.A.: In: Cybulski, A., Moulijn, J.A. (eds.) Structured Catalysts and Reactors. Dekker, New York (1998). Chap. 2

Glueckauf, E., Coates, J.I.: Theory of chromatography. Part IV: the influence of incomplete equilibrium on the front boundary of chromatograms and on the effectiveness of separation. J. Chem. Soc. 1315–1321 (1947)

Gomes, V.G., Yee, K.W.K.: Pressure swing adsorption for carbon dioxide sequestration from exhaust gases. Sep. Purif. Technol. **28**, 161–171 (2002)

Jain, R., et al.: Air separation using monolith adsorbent bed. US Patent 6,231,644 (2001)

Lassinantti, M., et al.: Faujasite-type films synthesized by seeding. Microporous Mesoporous Mater. **38**, 25–34 (2000)

Lee, L.Y., et al.: Manufacture and characterization of silicalite monoliths. Adsorpt. Sci. Technol. **18**, 147–170 (2000)

Li, Y.Y., et al.: Zeolite monoliths for air separation. Part I: Manufacture and characterization. Trans. Inst. Chem. Eng. Part A **76**, 921–930 (1998a)

Li, Y.Y., et al.: Zeolite monoliths for air separation. Part II: Oxygen enrichment, pressure drop and pressurization. Trans. Inst. Chem. Eng. Part A **76**, 931–941 (1998b)

Li, Y.Y., et al.: The effect of the binder on the manufacture of a 5A monolith. J. Powder Technol. **116**, 85–96 (2001)

Öhrman, O., et al.: Synthesis and evaluation of ZSM-5 films on cordierite monoliths. Appl. Catal. A Gen. **270**, 193–199 (2004a)

Öhrman, O., et al.: ZSM-5 structured catalysts coated with silicalite-1. In: Proceedings of the 14th International Zeolite Conference, Cape Town (2004b)

Patton, A., et al.: Use of the linear driving force approximation to guide the design of monolithic adsorbents. Chem. Eng. Res. Design A8 **82**, 999–1009 (2004)

Reynolds, S.P., et al.: Stripping PSA cycles for CO_2 recovery from flue gas at high temperature using a hydrotalcite-like adsorbent. Ind. Eng. Chem. Res. **12**, 4278–4294 (2006)

Ruthven, D.M.: Principles of Adsorption and Adsorption Processes. Wiley, New York (1984). Chap. 1

Todd, R.S.: A theoretical and experimental study of a rapid pressure swing adsorption system for air separation. PhD thesis, Monash University, Australia (2003)

Williams, J.L.: Monolith structures, materials, properties and uses. Catal. Today **69**, 3–9 (2001)