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Aluminophosphate monoliths with high CO₂-over-N₂ selectivity and CO₂ capture capacity

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Monoliths of microporous aluminophosphates (AlPO₄-17 and AlPO₄-53) were structured by binder-free pulsed current processing. Such monoliths could be important for carbon capture from flue gas. The AlPO₄-17 and AlPO₄-53 monoliths exhibited a tensile strength of 1.0 MPa and a CO₂ adsorption capacity of 2.5 mmol g⁻¹ and 1.6 mmol g⁻¹, respectively at 101 kPa and 0 °C. Analyses of single component CO₂ and N₂ adsorption data indicated that the AlPO₄-53 monoliths had an extraordinarily high CO₂-over-N₂ selectivity from a binary gas mixture of 15 mol% CO₂ and 85 mol% N₂. The estimated CO₂ capture capacity of AlPO₄-17 and AlPO₄-53 monoliths in a typical pressure swing adsorption (PSA) process at 20 °C was higher than that of the commonly used zeolite 13X granules. Under cyclic sorption conditions, AlPO₄-17 and AlPO₄-53 monoliths were regenerated by lowering the pressure of CO₂. Regeneration was done without application of heat, which would regenerate them to their full capacity for CO₂ adsorption.

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Introduction

Porous aluminophosphates (AlPO₄-*n*) are attractive materials for gas separation,^{1–3} adsorption,⁴ catalysis⁵ and host-guest chemistry.⁶ The 8-ring aluminophosphates exhibit crystalline micropores with pore windows that are similar to the kinetic diameter of light gas molecules. These aluminophosphates are therefore, of interest for CO₂, CH₄ and N₂ separation.^{2,3,7} Liu *et al.*³ have shown that the 8-ring aluminophosphates AlPO₄-17 and AlPO₄-53 offer high CO₂ capture capacities, high CO₂-over-N₂ selectivities and ease of regeneration. Deroche *et al.*⁷ reported that AlPO₄-18 has a lower heat of CO₂ sorption than most zeolites. A low heat of CO₂ sorption would decrease the energy penalty associated with regeneration of the adsorbent to its full CO₂ adsorption capacity in a cyclic adsorption process.

Microporous powders are usually structured into granules and beads because beds of micron-sized powders exhibit very large pressure drops. A large pressure drop can result in clogs or blockages in some gas separation processes.^{8,9} Typically, structured adsorbents are produced by shaping a mixture of the porous powder with an inorganic and organic binder into a body of the desired geometry.^{10–12} The powder body is thermally treated to increase the mechanical strength. While aluminophosphates, silicoaluminophosphates and other ortho and pyro-phosphates powders have been processed to produce hierarchically porous catalytic supports with catalytic

components, (*e.g.* Pt, Ag on zeolite Y, and zeolite ZK-5),^{13–17} reports on structuring of AlPO₄-*n* powders to produce structured adsorbents are sparse.¹⁸

The efficiency of an adsorbent is decreased when the active component – the microporous powder – is diluted by a large proportion of an inert binder. Moreover, the inert binder is selectively removed in a chemically corrosive environment.¹⁹ The selective removal of the binder can result in lowered mechanical stability of the structured adsorbent. The presence of the inert binder may also alter the adsorptive properties of the structured adsorbent.⁸ Hence, there is a great interest in developing binder-less processing routes that can produce mechanically strong structured adsorbents with maximized volume efficiency. Previously, it was demonstrated in an elaborate, multi-step process, that clay and silica binders can be converted into active porous materials by hydrothermal treatment.^{20–24} We developed a versatile pulsed current processing (PCP) route to directly produce mechanically strong, yet binder-free, hierarchically porous monoliths from *e.g.* microporous zeolite, mesoporous silica and macroporous diatomite powders.^{25–29}

In this work, we demonstrate that mechanically stable and binder-less structured adsorbents of AlPO₄-17 and AlPO₄-53 can be produced by PCP. With the optimized PCP temperature and pressure, the PCP-produced monoliths displayed a high CO₂ capture capacity and outstanding CO₂-over-N₂ selectivity. The CO₂ working capacity in a typical PSA process was evaluated and compared with commercial granules of zeolite 13X. Cyclic adsorption capacity and regeneration conditions to a full CO₂ adsorption capacity were determined for the AlPO₄-17 and AlPO₄-53 monoliths as well.

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Experimental

Materials

The materials used were: aluminum iso-propoxide (98 wt%, Aldrich), ortho-phosphoric acid (85.0 wt% aqueous H_3PO_4 , Aldrich), methylamine (Aldrich), N,N,N',N' tetramethyl-1,6-hexanediamine (TMHD, Aldrich) double deionized water (DDW), commercial 13X (Pingxiang Xintao Chemical Packaging Co. Ltd., China) beads of 1.5–2.5 mm in diameter.

Synthesis of AlPO_4 powders

AlPO_4 -17 synthesis. AlPO_4 -17 was synthesized *via* hydrothermal synthesis. 3.42 g of aluminum iso-propoxide (98 wt%, Aldrich) was mixed in 9 cm^3 of deionized water for 10 minutes. Thereafter 2.30 g of phosphoric acid (85 wt%, Aldrich) was added and the mixture was further agitated for 20 minutes. Then, 3.44 g of N,N,N',N' tetramethyl-1,6-hexanediamine (TMHD, Aldrich) was added to the mixture. The resulting gel was stirred for an additional 2 hours before it was transferred to Teflon lined stainless steel autoclave and heated to 200 °C for 9 h under static conditions.

AlPO_4 -53 synthesis. AlPO_4 -53 was synthesized using similar steps as AlPO_4 -17. 3.13 g of aluminum iso-propoxide (98 wt%, Aldrich) was mixed in 21 cm^3 of deionized water for 10 minutes. Thereafter 3.46 g of phosphoric acid (85 wt%, Aldrich) was added and the mixture was further agitated for 20 minutes. Then, 3.40 g of methylamine (Aldrich) was added to the mixture. The resulting gel was stirred for an additional 2 hours before it was transferred to Teflon lined stainless steel autoclave and heated to 150 °C for 168 h under static conditions. After hydrothermal synthesis, the AlPO_4 products were separated from the reaction gel, washed with deionized water, and dried overnight at 100 °C. The organic structure direction agent (SDA) was removed by calcination. AlPO_4 -17 was calcined at 600 °C (heating rate 10 °C min^{-1}) for 6 hours under a slow flow of air. AlPO_4 -53 was calcined at 400 °C (heating rate 10 °C min^{-1}) for 48 hours under a slow flow of air.

Processing. Calcined AlPO_4 -17 and AlPO_4 -53 powders were consolidated into cylindrical monoliths in a graphite die of 12 mm in diameter by pulsed current processing (PCP) in a so-called spark plasma sintering equipment (Dr Sinter 2050, Sumitomo Coal Mining Co., Ltd., Japan). Such consolidation was driven by electric heating in combination with compressive pressure. The powder assemblies were heated at a heating rate of 100 °C min^{-1} up to the target temperature, where the temperature was held for 3 minutes. A pressure of 20 MPa and 50 MPa was applied during heating and holding cycles. The temperature was measured using a K-type thermocouple. After the heating cycle, the die assemblies were cooled down to 100 °C before the ejection of consolidated monoliths from graphite dies.

Characterization. The microstructure of cylindrical monoliths was characterised with a field emission gun scanning electron microscope (FEG-SEM), JSM-7000F (JEOL, Tokyo, Japan) operating at an acceleration voltage of 5 kV. A small amount of each powder and a part of cleaved monolith

were put on a double-sided carbon adhesive tape with the aluminum stub as the base for SEM. The crystal structure of as-synthesized powders and PCP consolidated monoliths were characterized by X-ray diffraction (XRD) on a PANalytical X'Pert PRO powder diffractometer (PANalytical, Almelo, Netherlands) ($\text{CuK}\alpha 1$ radiation $\lambda = 1.540598$ Å) operating at 45 kV and 40 mA settings. XRD data was collected between $2\theta = 5.0$ – 60.0° . The strength of the PCP consolidated monoliths of 12 mm in diameter and 8 mm in height was determined by diametral compression test by applying a displacement rate of 0.5 mm min^{-1} on a Zwick Z050 (Zwick GmbH Co & KG, Ulm, Germany) instrument. Mercury intrusion porosimetry was used to determine macropore volumes and pore size distributions for pores with diameters of 3 nm to 125 μm in PCP consolidated monoliths using an Auto Pore III 9410 (Micromeritics, Norcross GA, USA).

Nitrogen adsorption-desorption experiments were performed at -196 °C on a Micrometrics ASAP2020 surface area analyzer (Micromeritics, Norcross GA, USA). The specimens were degassed at high vacuum (1×10^{-4} Pa) at 300 °C for 6 hours. The Brunauer-Emmet-Teller (BET) surface area was calculated using the nitrogen uptake of the specimen in the relative pressure range of 0.05–0.15 p/p_0 . The CO_2 and N_2 adsorption measurements were performed on a Micrometrics Gemini V 2390 apparatus (Micromeritics, Norcross GA, USA) equipped with the room temperature add-on. CO_2 and N_2 adsorption measurements were recorded at 0 °C and 20 °C within a pressure range from 0 to 101 kPa. Isothermal conditions (± 0.1 °C) were maintained by a circulating bath (Huber Ministat 230) which contains a low molecular weight siloxane polymer. The temperature in the Dewar flask was measured by an external thermocouple and cross-calibrated to that of the circulating bath. Prior to adsorption measurements, the calcined AlPO_4 - n powders and the consolidated monoliths were pre-treated under a flow of dry N_2 gas at a temperature of 300 °C for 8–10 h. The cyclic performance of the monoliths was tested by recording the CO_2 uptake of the samples after regeneration by only vacuum at room temperature.

The traditional Langmuir isotherm model with two parameters was used to describe the adsorption isotherms of CO_2 and N_2 . The traditional Langmuir isotherm model can be written as:³

$$q = \frac{q_m b P}{1 + b P} \quad (1)$$

where q and q_m are the uptake and the maximum uptake, respectively, b is equation constant and P is the equilibrium pressure. Langmuir model parameters were used as an input to the ideal adsorbed solution (IAS) theory to predict binary adsorption selectivity ($\alpha_{\text{CO}_2/\text{N}_2}$) from the single-component adsorption isotherms of CO_2 and N_2 .

Results and discussion

We previously studied binder-less consolidation of zeolites,^{26–28} mesoporous silica,²⁹ and diatomite²⁵ by pulsed current

processing (PCP) and showed that the porous particles could be consolidated into hierarchically porous monoliths without the addition of binders. In this study, monoliths of AlPO_4 -17 and AlPO_4 -53 have been successfully consolidated using the same technique. We have found that a temperature of 650 °C and a compressive pressure of 20 MPa and 400 °C and 50 MPa is suitable for PCP of AlPO_4 -17 powder (AlPO_4 -17(p)) and for AlPO_4 -53 powder (AlPO_4 -53(p)), respectively, for producing mechanically stable monoliths with a high surface area. These consolidated AlPO_4 -17 (AlPO_4 -17mPCP650) and AlPO_4 -53 (AlPO_4 -53mPCP400) monoliths are relatively strong and display gas adsorption properties similar to the starting powders. Diametral compression tests of AlPO_4 -17mPCP650 and AlPO_4 -53mPCP400 have shown that the monoliths exhibit a tensile strength of 1.0 MPa (Table 1), comparable to zeolite monoliths prepared by PCP and colloidal processing.^{26,30,31}

The SEM micrographs of the monoliths (Fig. 1) show that the rod-like AlPO_4 -17 and polyhedral AlPO_4 -53 crystals have retained their well-defined and faceted morphologies after PCP. Fig. 1 display pores in-between the crystals in the PCP AlPO_4 s. The median diameters of these macropores have been quantified by mercury intrusion porosimetry (Table 1), which show that the macropores are significantly larger in the AlPO_4 -17 monolith when compared to the AlPO_4 -53 monolith. Large macropores are advantageous as they limit the pressure drop over an adsorption column and enhance the mass transport of gas molecules.^{30,32–34}

An optimum balance between adsorption activity, mass transfer and mechanical stability is required for gas separation by swing adsorption processes.^{8,33,35} The combination of an optimized temperature and pressure during PCP has resulted in structured monoliths of AlPO_4 -17 and AlPO_4 -53 with a high CO_2 capture capacity and a relatively high mechanical strength (Table 1). The CO_2 and N_2 uptake on these monoliths of AlPO_4 -17 and AlPO_4 -53 (Fig. 2) show that the PCP temperature has significantly influenced the capacity for adsorption of CO_2 . The AlPO_4 -17 monoliths that have been treated by PCP at 650 °C have only a 12% reduced capacity as compared to the powder, Fig. 2a and b. We ascribe this minor reduction in the CO_2 uptake to the bonding of AlPO_4 -17 crystals at contact points. These contact points can alter the local microporous

Fig. 1 Scanning electron micrographs from fractured surfaces of: (a) AlPO_4 -17mPCP650; (b) AlPO_4 -53mPCP400. The insets show photographs of the monoliths.

structure^{27,28} during the PCP treatment by local amorphization or phase transformation to a non-adsorbing phase. If the temperature during the PCP is higher than 650 °C, the capacities of the AlPO_4 -17 monoliths are further reduced. AlPO_4 -17 based monoliths that have been consolidated at 750 °C can only adsorb 1.2 mmol g^{−1} of CO_2 . Similarly, the AlPO_4 -53 monoliths that have been subjected to PCP at 400 °C and 50 MPa pressure also have only a slight decrease in the capacities to adsorb CO_2 and N_2 , Fig. 2c and d. The N_2 uptake on AlPO_4 -17 and AlPO_4 -53

Fig. 2 Adsorption isotherms of CO_2 and N_2 at 0 °C on powders and monoliths of AlPO_4 -17 and AlPO_4 -53 PCP consolidated at compressive pressure of 20 and 50 MPa, respectively; (a) CO_2 uptake on AlPO_4 -17: powder ($\square$), monoliths prepared at 650 °C ($\circ$), 750 °C (∇), and 950 °C (Δ); (b) N_2 uptake on AlPO_4 -17: powder ($\square$), monoliths prepared at 650 °C ($\circ$), 750 °C (∇), and 950 °C (Δ); (c) CO_2 uptake on AlPO_4 -53: powder ($\blacksquare$), monoliths prepared at 400 °C ($\bullet$), 500 °C ($\blacktriangledown$), and 950 °C ($\blacktriangle$); (d) N_2 uptake on AlPO_4 -53: powder ($\blacksquare$), monoliths prepared at 400 °C ($\bullet$), 500 °C ($\blacktriangledown$), and 950 °C ($\blacktriangle$); (e) CO_2 uptake at 20 °C on monoliths: AlPO_4 -17-based prepared at 650 °C ($\circ$) and AlPO_4 -53-based prepared at 400 °C ($\bullet$); (f) N_2 uptake at 20 °C on monoliths: AlPO_4 -17-based prepared at 650 °C ($\circ$) and AlPO_4 -53-based prepared at 400 °C ($\bullet$).

Table 1 BET surface area, Langmuir surface area, macropore volume, macroporosity, median pore diameter and mechanical strength of monoliths prepared by pulsed current processing

Monoliths	AlPO_4 -17mPCP650	AlPO_4 -53mPCP400
^a S_{BET} (m ² g ^{−1})	464	223
^b S_{Langmuir} (m ² g ^{−1})	548	256
^c $V_{\text{Macropore}}$ (cm ³ g ^{−1})	0.26	0.32
^c Macro-porosity (vol.%)	31.0	41.0
^c Median pore diameter (μm)	3.50	0.70
Mechanical strength (MPa)	1.05 ± 0.10	0.85 ± 0.10

^a BET surface area is calculated from N_2 adsorption data recorded at −196 °C. ^b Langmuir surface area is calculated from CO_2 adsorption data at 0 °C. ^c Macropore volume, macroporosity, and median pore diameter are determined by mercury intrusion porosimetry.

powders and monoliths is small, as expected from the low electric quadrupole moment of N₂ (-4.6×10^{-40} C m⁻²) compared to CO₂ (-14×10^{-40} C m⁻²).³⁶

When the AlPO₄-17(p) and AlPO₄-53(p) have been processed above the optimal temperature for PCP, the microporous powders transformed into a new dense AlPO₄ phase and a crystalline AlPO₄ phase, respectively (Fig. 3). These monoliths then have negligible capacities to adsorb CO₂ and N₂ (Fig. 2). Analyses of the XRD data (Fig. 3) show that AlPO₄-17 transforms into a sodalite AlPO₄ phase and that AlPO₄-53 transforms into tridymite AlPO₄ phase at 950 °C. It should be mentioned that although the sodalite structure is porous, the pore windows are too small for diffusion of CO₂ and N₂ molecules.

The CO₂ adsorption capacity at 0 °C of the AlPO₄-17mPCP650 is 2.5 mmol g⁻¹ and 1.65 mmol g⁻¹ for the AlPO₄-53mPCP400 at a partial pressure of 100 kPa (see Fig. 2). The N₂ adsorption is low on both monoliths, but is significantly lower on the AlPO₄-53mPCP400, 0.05 mmol g⁻¹ (100 kPa) than that of the AlPO₄-17mPCP650, 0.24 mmol g⁻¹ (100 kPa). The difference in CO₂ and N₂ adsorption capacity of AlPO₄-17mPCP650 and AlPO₄-53mPCP400 suggest that AlPO₄-17mPCP650 have high capacity for CO₂ adsorption and AlPO₄-53mPCP400 display an extraordinary high CO₂-over-N₂ selectivity.

CO₂ selectivity is an important requirement for separation of CO₂ from flue gas. We can obtain a simple estimate of the CO₂-over-N₂ selectivity, $S_{\text{CO}_2/\text{N}_2}$, for a typical flue gas mixture that contains 15 mol% CO₂ and 85 mol% N₂ as the ratio of equilibrium mole fraction of CO₂ adsorbed at 15 kPa ($x_{\text{CO}_2}^{15}$) over the equilibrium mole fraction of N₂ adsorbed at 85 kPa ($y_{\text{N}_2}^{85}$), as follows.

$$S_{\text{CO}_2/\text{N}_2} = \frac{x_{\text{CO}_2}^{15}}{y_{\text{N}_2}^{85}} \frac{85}{15} \quad (2)$$

The $S_{\text{CO}_2/\text{N}_2}$ at 20 °C is 17 for AlPO₄-17mPCP650 and 102 for AlPO₄-53mPCP400. The high CO₂-over-N₂ selectivity of AlPO₄ has been ascribed to kinetic or molecular sieving effects.^{3,37} Molecular sieving or kinetic effects are related to the kinetic diameter of CO₂ (3.3 Å) and N₂ (3.64 Å) and the size of the 8 ring window of AlPO₄-17 and AlPO₄-53. AlPO₄-17 is a 8-ring aluminophosphate with a window size of 3.6×5.1 Å².³⁸ AlPO₄-53 is also a 8-ring aluminophosphate with a window size of 4.3×3.1 Å² along [100] direction,³⁸ which is close to the kinetic diameter of CO₂ molecule. More physically correct estimates of the thermodynamic selectivity make use of ideal adsorbed solution (IAS) theory developed by Myers and Prausnitz.^{39–41} It allows estimation of the co-adsorption equilibria for CO₂ and N₂ mixtures from the single component isotherms of CO₂ and N₂. In IAST, Myers and Prausnitz³⁹ defined selectivity within a two phase model as the ratio of mole fraction of CO₂ in the adsorbed state (x_{CO_2}) over the mole fraction of CO₂ (y_{CO_2}) in the gas phase divided by the same relative fractions for N₂ ($x_{\text{N}_2}, y_{\text{N}_2}$).

$$\alpha_{\text{CO}_2/\text{N}_2} = \frac{x_{\text{CO}_2} y_{\text{N}_2}}{x_{\text{N}_2} y_{\text{CO}_2}} \quad (3)$$

Table 2 shows that the binary CO₂-over-N₂ selectivity is very high for AlPO₄-53mPCP400. Hence, the favourable pore window dimensions of AlPO₄-53 are preserved after PCP and the monolith could selectively retard the diffusivity of N₂ and reduce its uptake kinetically or by molecular sieving.^{3,26,40,42} The AlPO₄-17mPCP650 has high CO₂ uptake but the CO₂-over-N₂ selectivity is significantly smaller compared to AlPO₄-53mPCP400. CO₂ separation in industrial practice, e.g. flue gas scrubbing and natural or biogas upgrading, is considered economically feasible by adopting pressure swing adsorption (PSA) or vacuum swing adsorption process (VSA) at moderate temperatures, providing that the adsorbent has a low pressure drop, high working capacity and also small sensitivity to water adsorption.^{43–46} In the interest of potentially using AlPO₄ monoliths in swing adsorption carbon capture processes (PSA or VSA), the amount of CO₂ that can be removed per kilogram of structured AlPO₄ monoliths needs to be determined. We have estimated the CO₂ capturing capacities in an idealized PSA process using

Fig. 3 X-ray diffractograms of powders and monoliths of AlPO₄-17 (a) and AlPO₄-53 (b). The temperatures given in the figure represent the maximum temperature employed during pulsed current processing.

Table 2 CO₂ and N₂ Henry's law constant and calculated CO₂-over-N₂ selectivity of monoliths prepared by pulsed current processing. The AlPO₄-17-based monolith was treated at 650 °C and the AlPO₄-53-based one at 400 °C

Monoliths	Adsorbate	q_m^a (mmol g ⁻¹)	b^b (1 kPa ⁻¹)	K_H ($q_m \times b$) CO ₂	K_H ($q_m \times b$) N ₂	K_H CO ₂ /K _H N ₂	Binary selectivity ($\alpha_{\text{CO}_2/\text{N}_2}$) ^c
AlPO ₄ -17mPCP650	CO ₂	4.389	0.0067	0.029	—	12.78	15
AlPO ₄ -17mPCP650	N ₂	1.095	0.0021	—	0.0023	—	—
AlPO ₄ -53mPCP400	CO ₂	1.878	0.0157	0.0295	—	99.33	2800
AlPO ₄ -53mPCP400	N ₂	0.0799	0.0039	—	0.0003	—	—

^a Obtained from fitting adsorption isotherm at 293 K by Langmuir model. ^b Obtained from fitting adsorption isotherm at 293 K by Langmuir model.

^c Calculated by ideal adsorption solution theory at 100 kPa in CO₂ and N₂ binary mixture of composition 15 mol% CO₂ and 85 mol% N₂.

the CO₂ adsorption isotherms in Fig. 2. The estimates in Fig. 4 assume that the flue gas from a small scale combustion plant contains 15 mol% CO₂ and 85 mol% N₂. The total pressure of

the process is assumed to swing from 1 bar to 6 bar in a simple and hypothetical PSA process. The temperature of the flue gas is assumed to be 20 °C, this is mainly because CO₂ adsorption data are quite commonly reported at this temperature. We consider a small scale combustion plant only, as we doubt that it will be economic or technically possible to compress the full flue gas stack. In this gas mixture, the partial pressure of CO₂ at 1 bar and 6 bar in the flue gas corresponds to 0.15 bar and 0.90 bar, respectively. For these conditions, the CO₂ capture capacity can be defined as the difference between CO₂ uptake at 0.9 bar and 0.15 bar and represent the moles of CO₂ gas that can be removed in a PSA cycle per kilogram of the adsorbent.

Fig. 4a and b show the CO₂ capture capacity of AlPO₄-17mPCP650 and AlPO₄-53mPCP400 in the highlighted region that corresponds to these PSA conditions, *i.e.* varying pressure from 1 bar to 6 bar. The CO₂ capture capacity of monoliths of AlPO₄-17mPCP650 is 1.4 mmol g⁻¹. The CO₂ capture capacity is comparable to that of several MOFs with large uptakes of CO₂, *e.g.* MOF 5,⁴⁶ Mg-MOF-74,⁴⁶ MOF-508⁴⁷ and higher compared to zeolite adsorbents^{48,49} (Table 3).

The CO₂ capture capacity of monoliths of AlPO₄-53mPCP400 at 20 °C is 0.8 mmol g⁻¹. The CO₂ capture capacity is lower than AlPO₄-17mPCP650, however the CO₂ selectivity is higher on AlPO₄-53mPCP400. When compared with the CO₂ capture capacity of commercial granules of zeolite 13X, AlPO₄-17mPCP650 and AlPO₄-53mPCP400 display higher CO₂ capacities. Zeolite 13X is widely researched and accepted as a standard material with a potential use in CO₂ capture.^{30,31,50,51} The CO₂ capture capacity of 13X granules is 0.7 mmol g⁻¹ and 0.67 mmol g⁻¹ in the first and second adsorption cycle, respectively. The total CO₂ adsorption capacity of 13X granules is reduced irreversibly after the first cycle from 2.9 to 2.5 mmol g⁻¹ (Fig. 4c). This irreversible reduction is probably related to chemisorption of CO₂ on 13X granules as the reduced CO₂ capacity between the two cycles cannot be overcome without high temperature regeneration.^{50,51} It should be noted that the flue gas contains water vapors which could reduce the CO₂ capture capacity of AlPO₄ monoliths and 13X granules further. However, it has been reported that aluminophosphates are less hydrophilic at lower partial pressure of water vapors.^{2,52} Liu *et al.*³ reported that the water adsorption capacity of AlPO₄-17, AlPO₄-53 and 13X powders was 0.17, 0.15 and 0.37 g g⁻¹, respectively. Zeolite 13X has a so-called type-1 water adsorption isotherm⁵³ and the AlPO₄-ns have so-called type-V water adsorption isotherms.⁵²

Fig. 4 Determination of ideal working capacity of AlPO₄-17mPCP650, AlPO₄-53mPCP400, and commercial 13X granules in a hypothetical pressure swing adsorption (PSA) cycle. The working capacity in a PSA process is the difference in uptake between the high (6 bar) and low (1 bar) pressure extremes which correspond to 0.90 and 0.15 bar CO₂ pressure in flue gas containing 15 mol% CO₂ and 85 mol% N₂. (a) CO₂ adsorption isotherm of AlPO₄-17mPCP650 (○) and AlPO₄-53mPCP400 (●) at 0 °C; (b) CO₂ adsorption isotherm of AlPO₄-17mPCP650 (○) and AlPO₄-53mPCP400 (●) at 20 °C; (c) CO₂ adsorption isotherm of 13X granules, first CO₂ adsorption cycle (○) and second CO₂ adsorption cycle (13X granules were regenerated by lowering the pressure (near vacuum conditions) without application of heat after first CO₂ adsorption cycle) (●). The shaded areas (in a–c) show the pressure swing cycle between 0.15 to 0.9 bar (corresponding to 1 bar and 6 bar pressure of flue gas containing 15 mol% CO₂ and 85 mol% N₂) and the parallel horizontal lines (in a–c) show the CO₂ working capacity of AlPO₄-17mPCP650, AlPO₄-53mPCP400 in (a) and (b) and 13X beads in (c).

Table 3 CO₂ capture capacity in a hypothetical pressure swing adsorption process at room temperature for MOFs and zeolite adsorbents in comparison with AlPO₄-17mPCP650 (current work)

Adsorbent (monoliths/powder)	CO ₂ capture capacity (mmol g ⁻¹)
AlPO ₄ -17mPCP650	1.4
MOF-5	0.7
Mg-MOF-74	2.1
MOF-508	1.6
Silicalite	0.6
HZSM-5	1.0

Fig. 5 The cyclic CO₂ adsorption capacity of monoliths prepared by pulsed current processing at two temperatures 0 °C (○) and 20 °C (●). (a) AlPO₄-17mPCP650, (b) AlPO₄-53mPCP400. After each cycle, monoliths were regeneration only by lowering the pressure without application of heat.

These shape differences implied that AlPO₄-17 and AlPO₄-53 not only adsorbed less water in the low pressure region compared to 13X zeolite, but that they are significantly less hydrophilic. Therefore, there will be no or only a slight reduction in the CO₂ capture capacity from (wet) flue gas. 13X granules show limited CO₂ capture capacity under PSA conditions (Fig. 4c) however they may be more useful materials in a VSA process where the pressure varies between 0.01 to 0.3 bar (ref. 48) for CO₂ capture from dry flue gas.

The cyclic adsorption performance of an adsorbent is an important property for its long term usage. Fig. 5 shows that the CO₂ capture capacity of AlPO₄-17mPCP650 (Fig. 5a) and AlPO₄-53mPCP400 (Fig. 5b) monoliths do not show any significant changes over five adsorption cycles. The monoliths have been regenerated by lowering the pressure (near-vacuum conditions) and without applying heat. The unchanged CO₂ capture capacities are attributed to the absence of chemisorption on the less hydrophilic framework of AlPO₄-17 and AlPO₄-53 materials.^{3,52} The cyclic adsorption performance of AlPO₄ monoliths is superior to zeolite 13X, which loses a fraction of its CO₂ adsorption capacity after first adsorption cycle (Fig. 4c). Typically, zeolites require heating to a high temperature for regeneration to their full CO₂ adsorption capacity.^{26,42,51} Overall, the AlPO₄-17mPCP650 and AlPO₄-53mPCP400 show high mechanical stability, high CO₂ capture capacity in PSA, low hydrophilicity, cyclic performance and easy regeneration. These render them as potential materials with good CO₂ capture capacities, long life time and low cost for CO₂ capture from flue gas. They are in particular interesting for CO₂ removal processes that can tolerate a pressurization step.

Conclusions

Hierarchically porous and mechanically stable monoliths of AlPO₄-17 and AlPO₄-53 have been produced by pulse current processing (PCP) without adding any inorganic binders. The monoliths based on AlPO₄-17 show high CO₂ capture capacities and those based on AlPO₄-53 show very high CO₂-over-N₂ selectivities for a hypothetical flue gas mixture consisting of CO₂ and N₂. The estimated CO₂ capture capacities of the AlPO₄-17 and AlPO₄-53 monoliths are superior to those of the standard zeolite 13X granules in a hypothetical PSA process. These monoliths display excellent cyclic performance and are also

expected to be less affected by water than zeolite based monoliths. The low water sensitivity will reduce the cost for drying of the flue gas in an actual implementation of an adsorption driven capture of CO₂. Over all, the adsorptive properties, mechanical strength, CO₂ capture capacity and low energy cost for regeneration of aluminophosphate monoliths render them candidate structured adsorbents for CO₂ capture from pressurized flue gas mixtures.

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