Thin zeolite laminates for rapid and energy-efficient carbon capture

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Thin, binder-less zeolite NaX laminates, with thicknesses ranging between 310 to 750 μm and widths exceeding 50 mm and biaxial tensile strength in excess of 3 MPa, were produced by pulsed current processing. The NaX laminates displayed a high CO2 adsorption capacity and high binary CO2-over-N2 and CO2-over-CH4 selectivity, suitable for CO2 capture from flue gas and upgrading of raw biogas. The thin laminates displayed a rapid CO2 uptake; NaX laminates with a thickness of 310 μm were saturated to 40% of their CO2 capacity within 24 seconds. The structured laminates of 310 μm thickness and 50 mm thickness would offer low pressure drop and efficient carbon capture performance in a laminate-based swing adsorption technology.

Zeolites, aluminophosphates and carbon molecular sieves are commonly used adsorbents for gas separation, drying and gas purification1–4. Typically, the adsorbents are packed into vessels or columns and subjected to a pressure/vacuum swing adsorption process to selectively adsorb and desorb gas species5. Important requirements for adsorbents to be used in e.g. carbon capture from large power-plants, and low cost, small-scale solutions for biogas upgrading, include: low pressure drop, high uptake, high selectivity and short cycle time. Adsorbent beds consisting of packed granules or beads are simple to manufacture but suffer from large pressure drop, low volumetric efficiency and slow mass transfer coefficients. In addition, the pelletized or granulated adsorbents experience abrasion and surface wear during pressure cycling and disintegrate into fine dust particles which results in increased down times for swing adsorption equipment. Structured adsorbents in the form of monoliths, foams, honeycombs and laminates have the potential to overcome these problems4,6. Indeed, recent work has suggested that laminated adsorbents could significantly improve the efficiency through a combination of low pressure drop, rapid mass and heat transfer, high volumetric efficiency and extended durability that is needed for volume efficient and rapid swing adsorption technologies7–9.

Laminated adsorbents have been produced using a non-adsorbing support e.g. metal foil, woven wire mesh, woven glass fiber mesh etc10,11. Non-adsorbing binders, e.g. clays, are often added to improve the mechanical stability4,12,13. However, inert, non-adsorbing additives dilute the active components and thus result in a reduced volume efficiency. Hence, the development of new processes to produce self-standing laminated adsorbents with close dimensional tolerances and high mechanical stability without support material or addition of binders is of pivotal importance for cost- and volume-efficient gas separation processes with large flows, especially CO2 capture from power-plant flue-gas and biogas upgrading.

Binder-less processing routes of zeolites include hydrothermal transformation of inorganic binders, clay and silica, into zeolithic materials14–17 and pulsed current processing (PCP) to directly consolidate microporous powders4. We have previously shown that rapid heating of a powder body subjected to a compressive stress can generate binderless adsorbents18–20 with a significant mechanical strength from different types of porous powders, including zeolites and aluminophosphates.

In this study, we demonstrate that mechanically stable and thin self-standing laminates of NaX zeolite can be produced by a tailored pulsed current processing (PCP) method from NaX zeolite powder without addition of binders. We show that the laminate thickness can be easily controlled. Maximum PCP temperature and consolidation pressure were optimized to ensure a high mechanical strength and minimal loss of surface area. The PCP-produced laminates with thicknesses between 310 and 750 micrometers display hierarchical porous structure, rapid CO2 adsorption kinetics and a high mechanical stability. The thickness dependence of the CO2 adsorption kinetics of the laminates will be discussed.
Results and Discussions

Zeolite NaX laminates of thicknesses between 310 to 750 μm were produced by pulsed current processing (PCP). Thin laminates were obtained by spreading a specific amount of NaX powder homogeneously onto a graphite paper that was placed into the PCP mold. The uniform distribution and height of the powder on the graphite paper was assured by depositing the powder while the graphite paper was rotated and the loose powder layer was consolidated by prepressing at 50 MPa. The combination of pre-deposition of a thin and homogeneous powder layer and optimization of the PCP processing conditions produced self-standing binder-free NaX laminates with a dimensional variation of 15–20 μm (Table 1). The fabrication steps of the laminates are summarized in Fig. 1 together with a conceptual illustration on how structured laminates can be used in rapid swing adsorption processes where it is essential to minimize the pressure drop and heat accumulation4, 6, 7. Laminates with diameters up to 50 mm could be fabricated by PCP of pre-deposited the homogeneous powder layers (Fig. 2). The Scanning electron micrographs (SEM) of a representative zeolite NaX laminate illustrate uniform thickness of 310 μm (Fig. 2a). The high resolution electron micrograph of NaX laminate (Fig. 2b) shows that the NaX crystals stay intact during PCP thermal treatment (see Supplementary Information, section S1). The large and thin NaX laminates are suitable for constructing adsorption based devices consisting of stacks of laminates placed with a small gap that serves as flow channels for gas transport (Fig. 1). Keever et al. suggested that a laminate device with flow channel length of 100–200 mm and 50–75 μm channel width could operate at high cyclic frequencies21.

The biaxial tensile strength of PCP-consolidated binderless NaX laminates is over 3 MPa (Table 1). The biaxial tensile strength of the laminates is comparable to zeolite monoliths produced by PCP and by conventional processing methods incorporating significant amounts of inorganic binders16, 18, 19, 22. Biaxial strengths of 3 MPa are sufficient for low pressure swing adsorption processes where the pressure is altered between 1 bar and 6 bar23, 24. Moreover, in temperature swing based technologies, the binderless and homogeneous NaX laminates are expected to be superior to conventional laminates prepared with clay binders where the difference in thermal expansion between the clay and the zeolite could result in thermal cracking and degradation25, 26.

Mercury intrusion porosimetry data (Table 1) shows that the laminates display a hierarchical porosity with micropores defined by the structure and intrinsic porosity of the zeolite crystals, and macropores that are intraparticle voids between the NaX crystals. Previous work has shown that a hierarchical porous structure is essential for rapid gas adsorption and desorption5, 18. Optimization of the pressure and temperature during the PCP treatment retained the intraparticle voids in the PCP processed laminates due to small (local) densification at the particle contacts. The total porosity of 40% corresponds to the particle packing density of such non-spherical particles. The NaX laminates show a relatively small reduction of the BET surface area compared to the NaX powder, which suggests that the PCP-treatment only results in the formation of an amorphous phase locally at the contact points of adjacent NaX particles4, 18, 20. The NaX laminates of different thicknesses show comparable BET surface area suggesting that the pulsed current processing homogeneously consolidated the NaX powder into structured laminates of varying thicknesses.

| Specimen           | Laminate Thickness (μm) | BET surface area (m²/g) | t-Plot Micropore Area (m²/g) | External Surface Area (m²/g) | Average Macropore diameter (μm) | Porosity (%) | Biaxial Strength (MPa) |
|--------------------|-------------------------|-------------------------|------------------------------|-----------------------------|-------------------------------|--------------|------------------------|
| 13X Powder         | —                       | 742                     | 711                          | 31                          | —                             | —            | —                      |
| Laminate PCP at 510 °C | 310 ± 15               | 695 ± 15                | 669                          | 37                          | 0.55                          | 40           | 4.0 ± 0.4              |
| Laminate PCP at 510 °C | 600 ± 20               | 642                     | 40                           | 0.61                        | 39                            | 3.2 ± 0.2    |                        |
| Laminate PCP at 510 °C | 750 ± 20               | 651                     | 36                           | 0.56                        | 41                            | 4.5 ± 0.2    |                        |

Table 1. Textural properties, average micropore size, total macropore area, porosity and biaxial strength of 13X laminate. *Determined from N₂ adsorption at 77 K; *determined from mercury intrusion porosimetry.

Binary CO₂-over-N₂ selectivity and CO₂-over-CH₄ selectivity are important parameters for decarbonisation of flue gas and raw biogas. We estimate CO₂-over-N₂ and CO₂-over-CH₄ thermodynamic selectivities using ideal adsorbed solution (IAS) theory28 as follows

$$\alpha_{CO_2/N_2} = \frac{x_{CO_2} \cdot y_{N_2}}{x_{N_2} \cdot y_{CO_2}}$$

$$\alpha_{CO_2/CH4} = \frac{x_{CO_2} \cdot y_{CH4}}{x_{CH4} \cdot y_{CO_2}}$$

Where \( x_{CO_2}, x_{CH4} \) and \( x_N \) are mole fraction of CO₂, CH₄ and N₂ in the adsorbed state and \( y_{CO_2}, y_{CH4} \) and \( y_N \) are mole fraction of CO₂, CH₄ and N₂ in the gas phase. Table 2 shows that the binary CO₂-over-N₂ selectivity is 290 and CO₂-over-CH₄ is 96. These high binary selectivities meet the criteria of efficient CO₂ capture from power plant flue-gas and biogas upgrading27, 29.
Figure 4 shows the CO$_2$ uptake kinetics of NaX laminates of varying thicknesses. It is important to note that CO$_2$ adsorption kinetics on laminates are compared in the second adsorption cycle. The structured zeolite laminates to capture CO$_2$ are potentially suitable for pressure swing adsorption (PSA) and vacuum swing adsorption (VSA) processes, where the adsorbent is regenerated either by lowering the pressure or applying vacuum$^{5,30}$. Therefore, the contributions of chemisorbed CO$_2$ observed on zeolites in first adsorption cycle$^{31,32}$ are not...
relevant for estimates of the adsorption kinetics of a PSA/VSA process, where physisorption of CO₂ will dominate. The crystallinity, BET surface area and CO₂ adsorption capacity of the structured NaX laminates is similar to the NaX powder, which suggest that the durability of the laminates should be high and could sustain PSA/VSA cycles. The CO₂ adsorption kinetics on NaX laminates in Fig. 4 shows that laminates with thickness of 310 μm has faster CO₂ adsorption compared to the thicker laminates during the first 30–60 seconds. We find that the laminate of 310 μm thickness saturates to 40% of its maximum uptake capacity (q/q max = 0.4) in 24 seconds compared to 36 seconds for the laminate with a thickness of 600 μm and 52 seconds for the laminate with a thickness of 750 μm. The faster CO₂ uptake of thinner NaX laminate suggests that the CO₂ uptake of structured laminates is macroporous diffusion controlled. However, it can be seen in Fig. 4 that the CO₂ adsorption kinetics at longer times does not show significant difference on the thicknesses of the laminates suggesting that the diffusion mechanism becomes complex and other factors such as heat of adsorption, thermal conductivity, heat capacity of materials and heat transfer properties play role in controlling the long-time adsorption kinetics32, 33. The kinetic data suggests that it is of importance to design the structured laminate-based devices to effectively transfer the heat of adsorption from laminates for rapid CO₂ adsorption kinetics.

Conclusions
Pulsed current processing was used to produce binderless zeolite NaX laminates, 310 to 750 μm in thickness within 5% (15–20 μm) dimensional tolerances, for CO₂ capture. NaX laminates demonstrated biaxial tensile strength in excess of 2 MPa. The adsorption capacity of CO₂ was high 5.0 mmol/g, while the uptake of CH₄ and N₂ was relatively small; 0.4 mmol/g and 0.7 mmol/g, respectively. Ideal adsorption solution theory was used to estimate binary CO₂-over-N₂ selectivity (290 at 100 kPa at 25 °C) in 15 mol% CO₂–85 mol% N₂ gas mixture and CO₂-over-CH₄ selectivity (96 at 100 kPa at 25 °C) in 50 mol% CO₂–50 mol% CH₄ gas mixture. The uptake of CO₂ of the NaX laminates is fast and a laminate with a thickness of 310 μm reach 40% of maximum uptake in only 24 seconds. The adsorption kinetics slows down with increasing laminate thickness but laminates with a thickness of 750 μm reach 40% of maximum uptake in less than one minute. The results suggested that NaX laminates hold great potential for selective separation of CO₂ from N₂ and CH₄ in rapid swing adsorption processes.

Experimental
Materials. Zeolite NaX powder (Sigma-Aldrich GmbH, Germany) of 1–2 μm particle size was used as received.

Processing. Zeolite NaX laminates were produced in graphite dies of 52 mm in diameter by pulsed current processing (PCP). Spark plasma sintering (SPS) equipment (Dr. Sinter 2050, Sumitomo Coal Mining Co., Ltd.,
Japan) was used. The mass of NaX powder was used to optimize laminates thicknesses from 310μm to 750μm. The graphite dies containing NaX powder were prepressed at 50 MPa and then placed between SPS electrodes with a graphite spacer assembly. NaX powder assemblies were heated to target temperatures between 500 and 800°C and held for 3 minutes. The heating rate adopted was 100°C min⁻¹. 20 MPa compressive pressure was applied throughout the heating and holding time. The laminates were ejected from graphite dies after pressureless cooling in SPS machine down to 100°C.

**Characterization.** Field emission gun scanning electron microscope (FEG-SEM), JSM-7000 F (JEOL, Tokyo, Japan) was used to study the microstructure of NaX laminates. Low accelerating voltage of 5kV was used to avoid charging up of the surfaces under observation. A PANalytical X'Pert PRO powder diffractometer (PANalytical, Almelo, Netherlands) (CuKα, radiation λ = 1.540598 Å) was used to study the crystal structure of as-received powders and PCP processed laminates. The diffractometer was operated at 45 kV and 40 mA and X-ray diffraction data was collected between 20 = 5.0–60.0°. The biaxial tensile strength of the laminates was determined following ASTM F394 standard on a Zwick Z050 (Zwick GmBH Co & KG, Ulm, Germany). The biaxial tensile strength measurements were repeated for at least 5 laminates. Auto Pore III 9410 (Micromeritics, Norcross GA, USA) mercury intrusion porosimeter (MIP) was used to study the macropore volumes and pore size distributions in NaX laminates.

**BET surface area, CO₂ and N₂ adsorption and CO₂ adsorption kinetics.** ASAP2020 surface area analyzer (Micromeritics, Norcross GA, USA) was used to perform nitrogen adsorption–desorption measurements at –196°C. Prior to measurements, the NaX powder and laminates were outgassed at 300°C for 10 hours under near vacuum conditions. The nitrogen uptake at –196°C in 0.05–0.15 p/p₀ relative pressure range was used to determine the Brunauer-Emmett-Teller (BET) surface area of NaX powder and laminates. The same device, ASAP2020, was used for CO₂, CH₄, and N₂ adsorption measurements at 20 and 25°C from 0 to 101 kPa pressure. Prior to CO₂, CH₄, and N₂ adsorption measurements, the zeolite NaX powders and laminates were outgassed at 300°C for 10h under near vacuum conditions. A thermogravimetric analyzer (TGA) (Setaram Instruments, Caluire, France) was used to study the CO₂ adsorption kinetics on zeolite NaX laminates following the experimental conditions described elsewhere.

**Adsorption models and Ideal adsorbed solution theory (IAST).** Langmuir isotherm model with two parameters was used to extract the parameters from CO₂, CH₄, and N₂ adsorption isotherms. Three adsorption isotherms were used to extract parameters. These parameters were used as input for IAS theory estimation of binary adsorption selectivity (α₉/₀₂, α₉/₄₈) following our previous work.

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**Author Contributions**

All authors designed the work. S.O. defined the structure and property parameters. F.A. performed experiments and analyzed data and wrote the manuscript. S.O. and L.B. provided helpful suggestions for analysis, manuscript writing and revisions.

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