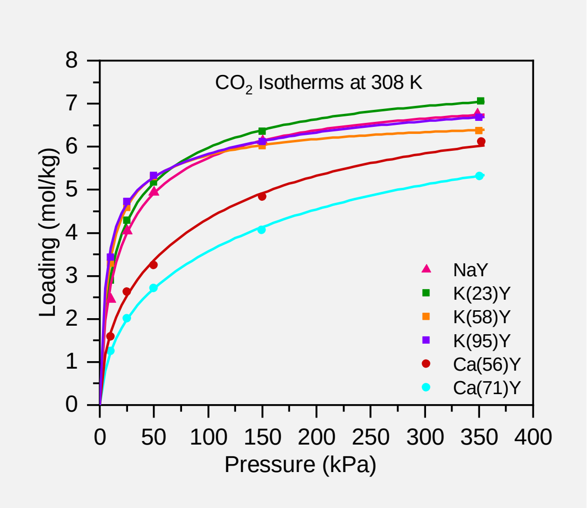
ORAL

(TOPIC- Reaction and Separation Processes)

Single- and multi-component fixed-bed adsorption of CO_2, CH_4, and N_2 on ion-exchanged binder-free NaY zeolites.

E. Aly[1,2,*], *Lucas .F.A.S. Zafanelli*[1], *A. Henrique*[1], *Francisco A. Da Silva*[2], *Alírio E. Rodrigues*[3], *José A.C. Silva*[1]
[1]*Instituto Politécnico de Bragança, Campus Santa Apolónia, 5300-253, Bragança, Portugal;* [2]*University of Aveiro, Portugal Campus Universitario de Santiago, 3810-168, Aveiro, Portugal;* [3] *University of Porto, Rua Dr. Roberto Frias, S/N, 4099-002, Porto, Portugal; *ezzeldin@ipb.pt*



Ion-exchange was performed on bare commercial binder-free NaY zeolite with alkali (K^+) and alkaline earth (Ca^{2+}) metal cations in the range 23, 58, and 95% exchange for K^+, and 56 and 71% for Ca^{2+}, to be used as candidates regarding CO_2 post-combustion capture (PCC) and biogas upgrading by adsorption processes. Adsorption equilibrium isotherms of CO_2, CH_4 and N_2 were measured on all these cation-exchanged samples using a chromatographic technique between 308 and 348 K and pressures up to 350 kPa and modelled by the dual-site Langmuir isotherm. The CO_2 adsorption capacity increases as Na^+ is exchanged further by K^+ and the reverse for the Ca^{2+} exchange. The single- and binary-component breakthrough curves were numerically simulated and accurately predicted using the Aspen Adsorption package. This work discloses the importance of ion-exchange on binder-free beads of NaY zeolite to improve its performance in PCC and biogas upgrading applications.

Introduction

The generation of carbon dioxide is inherent in the combustion of fossil fuels, and the efficient capture of CO_2 from industrial operations is regarded as an important strategy to achieve a significant reduction in atmospheric CO_2 levels. Post-combustion capture (PPC) is referred to as the capture of CO_2 from sectors relying on fossil-fuel combustion such as power generation, steel making, and cement industries. It is a technically and economically viable solution to reduce carbon emissions as it can be implemented with ease into new and existing facilities without affecting the process upstream. Processes for removing CO_2 from methane (CH_4) are also important for upgrading both renewable and non-renewable energy sources such as landfill gas, biogas, and natural gas. These gases contain a large amount of CH_4 along with CO_2, nitrogen (N_2), and some traces of impurities, that need to be removed to meet pipeline grade specifications. Adsorption processes are promising capture technologies as they can use solid adsorbent to separate the CO_2 from other gas constituents, by using their cage-like structure to act in the limit as molecular sieves.

Zeolites Y and X belong to the family of aluminosilicate molecular sieves with a faujasite-type structure (FAU), being different only by the Si/Al atomic ratio (1.5 – 3.0 for NaY compared to 1.0 – 1.5 for NaX).[1] The FAU structure demonstrates extreme versatility in gas separations through ion exchange and metal impregnation. The type of cation influences the electric field inside the pores, the available pore volume, and the adsorption of polar and non-polar molecules due to the induced electrostatic interactions of the ionic surface. Therefore, ion-exchange can be used as a tool for tailoring the structure to obtain specific performances. [2]

Objectives

This work aims to investigate by a series of fixed-bed breakthrough experiments the adsorption of single, binary and ternary mixtures of $CO_2/CH_4/N_2$ in binder-free beads of K(23)Y, K(58)Y, K(95)Y, Ca(56)Y, and Ca(71)Y exchanged from the bare NaY zeolite, between 308 and 348 K and total pressures up to 350 kPa (under compositions typical of post-combustion and biogas upgrading processes).

Methods

The faujasite type-Y zeolites studied in this work were synthesized in the binder-free form in the labs of Chemiewerk Bas Köstritz GmbH (Germany). The beads particle diameter ranges between 1.6-2.5 mm. The exchange started from a commercial type of binder-free Y sodium zeolite form (Köstrolith NaYBFK) with a Si/Al ratio of 2.5 to achieve 23, 58, and 95% potassium- and 56 and 71% calcium-exchange degree value.

A single and multi-component breakthrough apparatus has been used to study the fixed bed adsorption of CO_2 and N_2 and their binary mixture. The apparatus is shown in previous works [3].

In chromatographic breakthrough experiments, the dynamic equilibrium loading is calculated by integrating the molar flow profiles of the breakthrough curves by using the following equation [4]:

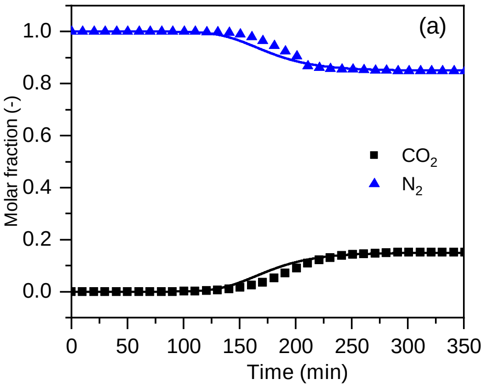
$$q_{exp,i} = \frac{1}{m_{ads}}\left(F_{f,i}t_n - \int_0^{t_\infty} F_i\,dt - \varepsilon_b V_c C_{i0}\right) \qquad (1)$$

where m_{ads} = adsorbent mass in the column; $F_{f,i}$= feed molar flowrate of component i at the inlet of the fixed bed; F_i = molar flow rate of component i at the outlet of the fixed bed; t_∞= saturation time; ε_b= bed porosity; V_c= column volume; and C_{0i} = feed concentration of component i at the inlet of the fixed bed.

Results

The Graphical Abstract shows a comparison of the CO_2 isotherms between NaY, K(23)Y, K(58)Y, K(95)Y, Ca(56)Y, and Ca(71)Y, collected at 308 K. The sorption hierarchy order at low pressure (in the range until 50 kPa) observed is: Ca(71)Y < Ca(56)Y < NaY < K(23)Y < K(58) < K(95)Y. As the level of ion-exchange rate from Na^+ to K^+ increases, the CO_2 adsorption loading increases, where the opposite is observed when the ion-exchange changes from Na^+ to Ca^{2+}. At 25 kPa, the loading of binder-free NaY is equal to 4.05 mol/kg, compared to 4.29 for K(23)Y, 4.59 for K(58)Y, 4.72 for K(95)Y, 2.63 for Ca(56)Y and only 2.01 mol/kg for Ca(71)Y at 308 K. These results indicate a good response between the acidic CO_2 to the basic properties of the zeolites containing larger monovalent cations at low pressure. Larger cations such as K^+ accept less charge transfer from the neighboring lattice oxygen atoms, these oxygen atoms therefore remain more negatively charged and hence more basic, increasing the binding energy to guest CO_2 molecule. Moreover, the CO_2 loading of Ca(71)Y is significantly lower than in all the rest (e.g. around a half of that on bare NaY), which is due to the decrease of the amount of exchangeable cations between the divalent Ca^{2+} cations and the adsorbate molecules.

The studied binary experiments consist of 15% CO_2 / 85% N_2 (vol.%) mixture, representing a typical post-combustion stream. Figure 1a shows the adsorption breakthrough curves in binder-free K(95)Y for the binary mixture at 313 K. Figure 1b displays the breakthrough curves for ternary mixtures feeds of CO_2/CH_4/N_2 (20/20/20 vol.% balanced with He) on binder-free zeolite KY. As can be seen in Figure 1c, the binary experiment show a selectivity of CO_2 over N_2 around 105 at 10 kPa and 313 K; the ternary system resulted in a selectivity of CO_2 over CH_4 and over N_2 of around 19 and 45 at 313 K, respectively, under the same conditions. These results indicate that binder-free K(95)Y works well in the low-pressure region and therefore, is a promising adsorbent for the recovery of CO_2 from post-combustion streams. Numerical simulations were performed with a model implemented in Aspen Adsorption simulator, allowing to predict accurate breakthrough curves for dynamic experiments carried out in a fixed bed adsorption system, as shown in Figure 1.



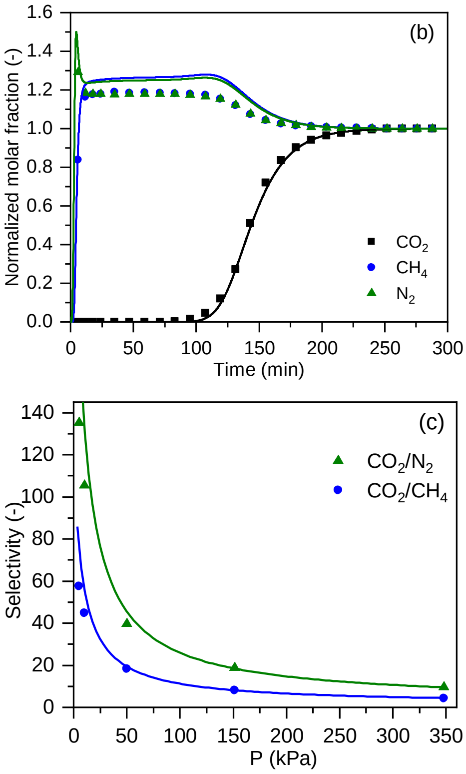


Figure 1. Breakthrough curves of (a) binary and (b) ternary fixed bed experiments, and (c) selectivity of CO_2/N_2 and CO_2/CH_4; at 313 K in binder-free K(95)Y zeolite.

Conclusion

Adsorption equilibrium measurements of CO_2, CH_4 and N_2 were performed on a series of ion-exchanged binder-free FAU type-Y zeolites using a chromatographic technique through a set of fixed bed breakthrough experiments. It was demonstrated that the CO_2 adsorption capacities at low pressure increases as follows: Ca(71)Y < Ca(56)Y < NaY < K(23)Y < K(58) < K(95)Y. The binary-component experiments of CO_2/N_2 mixture indicate that binder-free K(95)Y is a promising adsorbent for the recovery of CO_2 from post-combustion streams with a loading of 4.14 mol/kg, and a selectivity of around 105 over N_2 at 313 K. Aspen Adsorption v.10 was used to predict the single- and binary-component breakthrough curves. The mathematical model on the software was validated experimentally and the fitting of the numerical data through the transport and model parameters proves the capability of the model to describe the dynamics of adsorption in a fixed bed column.

Acknowledgements

The authors are grateful to the Foundation for Science and Technology (FCT, Portugal) for financial support through national funds FCT/MCTES (PIDDAC) to CIMO (UIDB/00690/2020 and UIDP/00690/2020) and SusTEC (LA/P/0007/2021). National funding by FCT, Foundation for Science and Technology, through the individual research grant under project PDTC/EQU-EPQ/0467/2020.

CICECO – Aveiro Institute of Materials, UIDB/50011/2020 & UIDP/50011/2020 & LA/P/0006/2020, financed by national funds through the FCT/MCTES (PIDDAC).

Kristin Gleichmann and Chemiewerk Bad Koestritz GmbH for kindly providing the binder-free beads of zeolites studied in this work.

References

[1] D. M. Ruthven, *Principles of Adsorption and Adsorption Processes*, 1st ed. New York: John Wiley & Sons, 1984.

[2] O. Talu, S. Y. Zhang, and D. T. Hayhurst, “Effect of cations on methane adsorption by NaY, MgY, CaY, SrY, and BaY zeolites,” *J. Phys. Chem.*, vol. 97, no. 49, pp. 12894–12898, Dec. 1993, doi: 10.1021/j100151a043.

[3] E. Aly *et al.*, “Fixed Bed Adsorption of CO2, CH4, and N2 and Their Mixtures in Potassium-Exchanged Binder-Free Beads of Y Zeolite,” *Ind. Eng. Chem. Res.*, vol. 60, no. 42, pp. 15236–15247, Oct. 2021, doi: 10.1021/acs.iecr.1c02261.

[4] D. D. Do, *Adsorption Analysis: Equilibria and Kinetics*, vol. 2. World Scientific, 1998. doi: 10.1142/9781860943829.

[5] D. Bonenfant, M. Kharoune, P. Niquette, M. Mimeault, and R. Hausler, “Advances in principal factors influencing carbon dioxide adsorption on zeolites,” *Sci. Technol. Adv. Mater.*, vol. 9, no. 1, 2008, doi: 10.1088/1468-6996/9/1/013007.