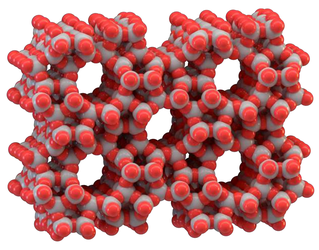
Selective capture and separation of industrial post-combustion gases with FAU-type zeolites: a computational study

Hèctor Prats, Daniel Bahamón, Pablo Gamallo, Gerard Alonso, Xavier Giménez and Ramón Sayós

Departament de Ciència dels Materials i Química Física & Institut de Química Teòrica i Computacional, Universitat de Barcelona, C. Martí i Franquès, 1, 08028 Barcelona, SPAIN.



INTRODUCTION

Carbon dioxide (CO_2) is the primary greenhouse gas emitted through human activities, mainly generated from the combustion of fossil fuels (*i.e.*, oil, coal and natural gas) for energy and transportation [1-3]. Economic growth and industrial development has led to a growing increase in the amount of atmospheric CO_2, and the undesirable global warming and climate change have attracted increasing attention. Solid adsorbent based systems have demonstrated potential toward reducing cost and improving performance compared to existing systems that rely on aqueous amine solutions.

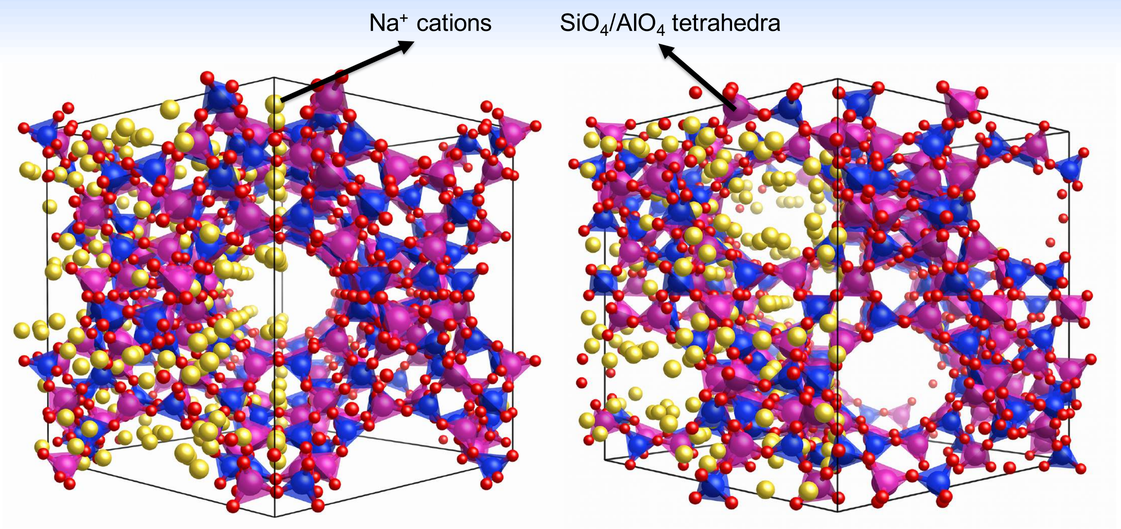
In particular, zeolites are inexpensive porous materials that are already produced on a large scale for many commercial applications, showing exceptionally high adsorption selectivity for CO_2 over N_2 [4-6] This separation is usually done by means of the Pressure Swing Adsorption (PSA) process, that rely on the fact that under high pressure, gases tend to be attached to solid surfaces, and when the pressure is reduced, the gas is desorbed.

In this work, a series of NaFAU-type zeolite adsorbents has been evaluated for potential application in post-combustion CO_2 capture using Grand Canonical Monte Carlo (GCMC) simulations, varying the Al-content in the structure. Simulations for adsorption of pure components and typical post-combustion mixtures were performed for ten different FAU-type structures.

METHODS AND COMPUTATIONAL DETAILS

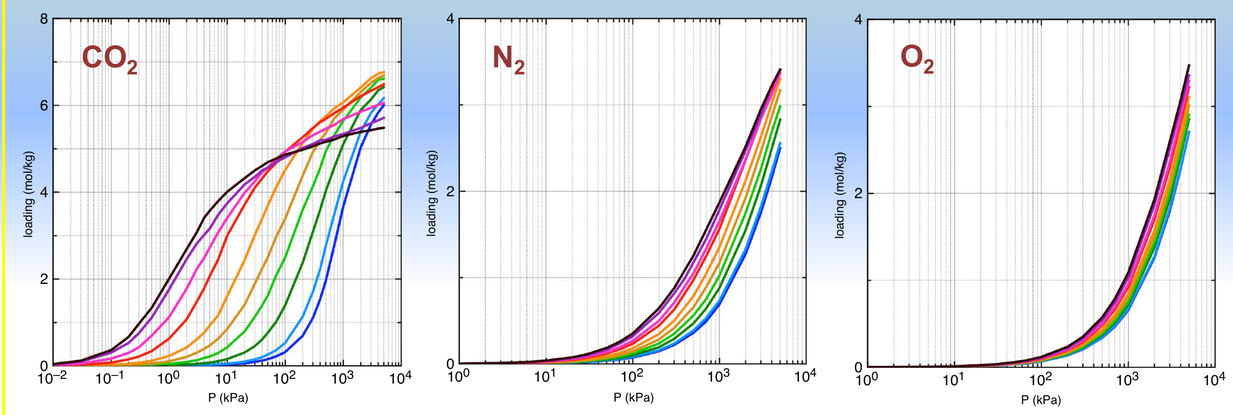
Grand Canonical Monte Carlo simulations exchanges atoms or molecules with an imaginary gas reservoir at constant temperature, volume and chemical potential. Then, the amount of molecules adsorbed is calculated using a statistically averaged approach after the equilibrium stage.

All simulations were performed at 313K, using $2x10^6$ and $5x10^6$ MC steps for system equilibration and production, respectively. The zeolite structures were assumed to be rigid during the sorption process, except for the Na^+ cations, which can move freely along the framework, adjusting their positions depending on their interactions with the framework atoms.



PURE ADSORPTION ISOTHERMS

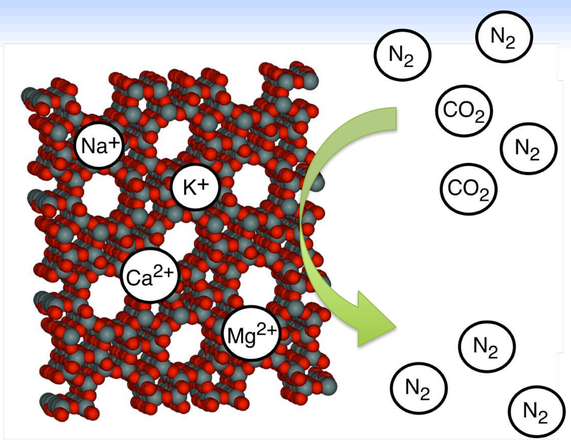
The ten different structures considered in the present work have been labelled as n-FAU, where n is the number of aluminium or sodium atoms per unit cell (*i.e.*, n= 0, 6, 12, 24, 32, 48, 64, 77, 88 and 96).



- In all cases, the amount of CO_2 adsorbed is significantly higher than that of N_2 and O_2, indicating good selectivity towards carbon dioxide.
- As the Al and Na^+ content of the zeolite framework increases, the amount of gas molecules adsorbed is higher, specially for CO_2 at low pressures, where the loading corresponding to the 96-FAU structure (*i.e.*, 96 Na^+ cations per unit cell) at 1 bar is 15 greater than that of the 0-FAU structure.
- However, zeolites with high Al content reach saturation faster than the other structures, and the amount of CO_2 molecules adsorbed at saturation conditions is lower, due to the volume occupied by the sodium cations.
- As the Al and Na^+ content of the zeolite framework increases, the selectivity for CO_2 relative to N_2 becomes higher (*i.e.,* from around 10^1 to 10^3 for 0-FAU and 96-FAU, respectively).
- The isosteric heat of adsorption is also higher in the zeolites presenting high Al/Na^+ content.
- The selectivity for CO_2 relative to N_2 decreases as the pressure is increased for zeolites having 64 or more Na^+ atoms per unit cell, remains constant for zeolites having between 12-48 Na^+ atoms per unit cell, and is slightly increased for zeolites having less than 12 Na^+ atoms per unit cell.

$CO_2/N_2/O_2$ MIXTURE RESULTS

Despite the large number of adsorbents that have been reported in the context of CO_2 capture, the majority of studies have relied exclusively on pure CO_2 and N_2 isotherms, which has made it challenging to identify the best materials for capturing CO_2 from a flue gas mixture. In addition, mixed gas adsorption measurements are often time-consuming, requiring carefully designed custom equipment and complex data analysis. According to the typical post-combustion gas composition, we considered a **ternary mixture of CO_2 (15%), N_2 (80%) and O_2 (5%).**

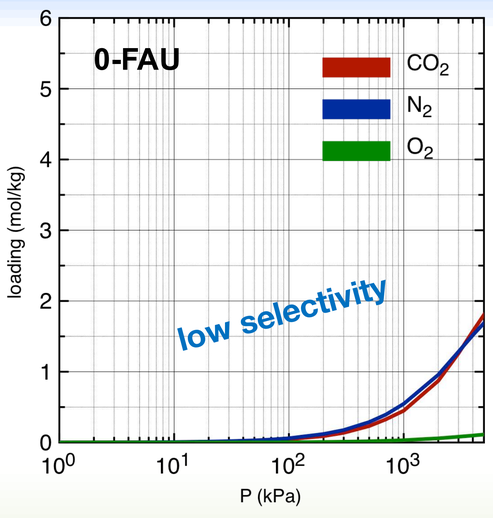


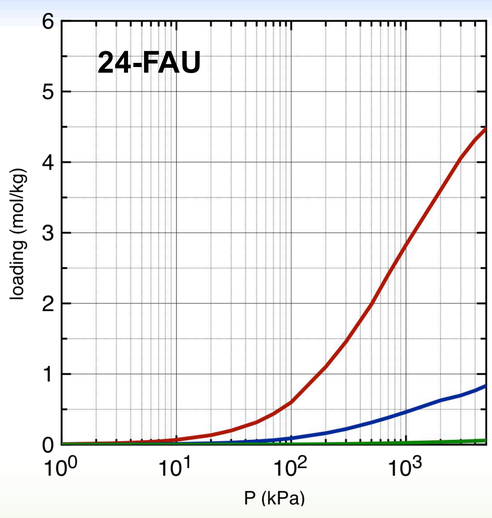
INDICATORS FOR SEPARATION PROCESSES

- **Isosteric heat of adsorption (q_{CO2}):** provides information about the energy released during the adsorption process, and is a key parameter for evaluating the cost of desorption/regeneration. It can be calculated from energy/particle fluctuations in the grand canonical ensemble.
- **Selectivity:** good indicator for mixtures, the selectivity for CO_2 relative to N_2 is calculated by

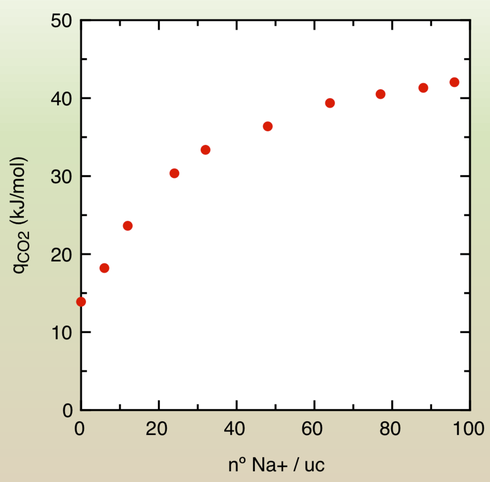
$$S_{CO2/N2} = \left(\frac{X_{CO2}}{X_{N2}}\right)\left(\frac{Y_{N2}}{Y_{CO2}}\right)$$

were X and Y are the mole fractions in the adsorbed phase and in the bulk phase, respectively.

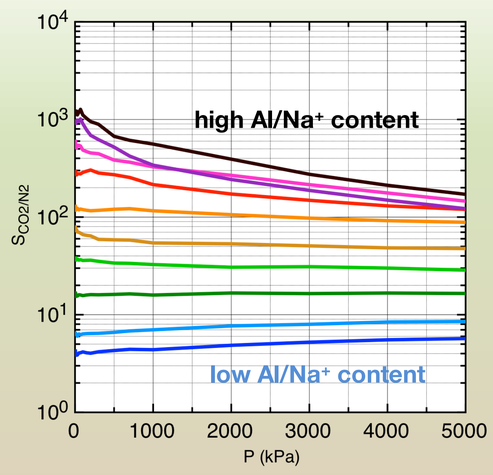


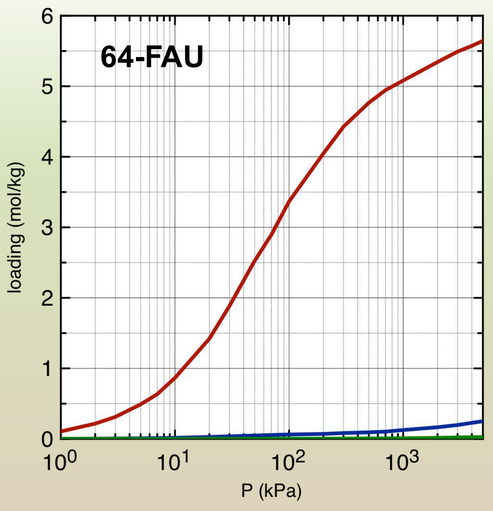


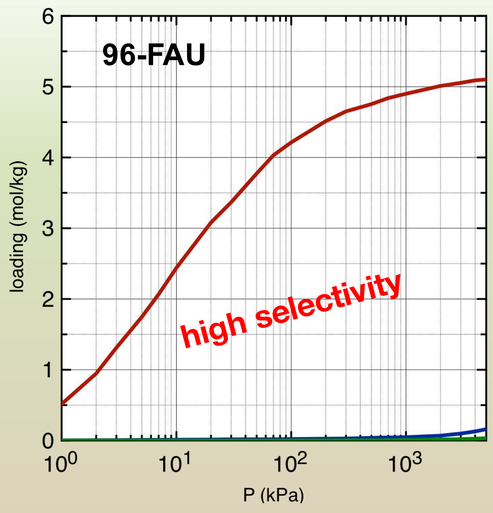
Isosteric heat of adsorption



CO_2/N_2 selectivity







ACKNOWLEDGEMENTS

Financial support to this research has been provided by the Spanish MINECO CTQ2014-53987-R grant and, in part, from the Generalitat de Catalunya grant 2014SGR1582. HPG thanks Generalitat de Catalunya for a predoctoral FI-DGR-2015 grant.

REFERENCES

[1] J. R. Li, J. Sculley, H. C. Zhou, *Chem. Rev.*, **2012**, 112, 869
[2] D.M. D'Alessandro, B. Smit, J. R. Long, *Angew. Chem., Int. Ed.*, **2010**, 49, 6058
[3] M. Z. Jacobson, *Energy Environ. Sci.*, **2009**, 2, 148
[4] Y. He, W. Zhou, R. Krishna, B. Chen, *Chem. Commun.*, **2012**, 48, 11813
[5] Y. Q. Lan, H. L. Jiang, S. L. Li, Q. Xu, *Adv. Mater.*, **2011**, 23, 5015
[6] H.-L. Jiang, D. Feng, K. Wang, Z.-Y. Gu, Z. Wei, Y.-P. Chen, H.-C. Zhou, *J. Am. Chem. Soc.,* **2013**, 135, 13934

CONCLUSIONS

The results presented in this poster show the adsorption of post-combustion mixtures in different zeolite structures, and confirm that zeolites can effectively separate CO_2 from a mixture with N_2 and O_2. Moreover, the effectiveness of this separation is highly dependent on the Al/Na^+ content and on the working conditions.

Zeolites with high Al/Na^+ content would adsorb more CO_2 molecules under adsorption conditions (i.e., high pressure), but at the desorption step (*i.e.,* low pressure) the number of desorbed molecules will be lower, due to the high isosteric heat of adsorption. In the other hand, as we lower the Al/Na^+ content, the purity of the desorbed CO_2 becomes lower, and an additional separation step would be required.

One must evaluate the difference between the number of CO_2 molecules adsorbed at adsorption conditions (*i.e.*, 1-20 bar) minus the number of molecules adsorbed at desorption conditions (*i.e.,* 0.05-1 bar). This value depend on the pressure range used industrially, but for every pressure range one can select the most suitable zeolite structure that maximizes this value, according to the results obtained from ternary mixtures in the present study.