Cerca del contingut de cations òptim en faujasites per a la captura de CO_2 de post-combustió amb processos d'adsorció tipus swing.

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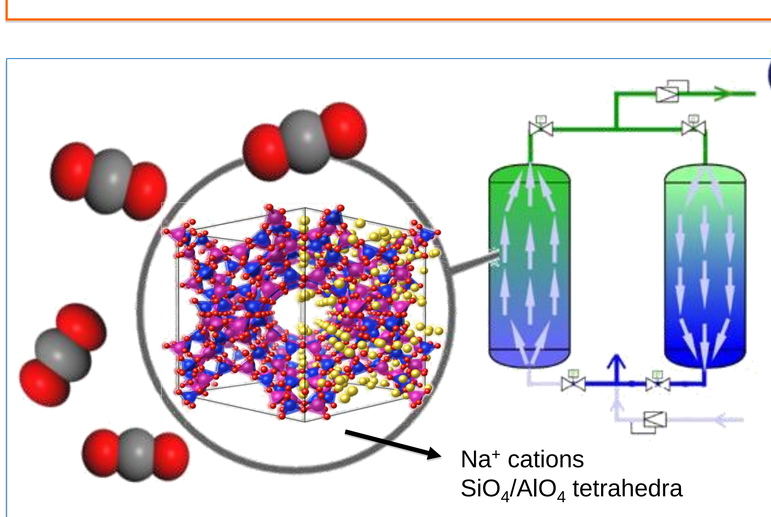
INTRODUCTION

Although absorption by amines is the industrial reference process for **CO_2 capture and separation**, the high energy requirements in regeneration [1] has driven the development of cost-effective systems that attenuate these disadvantages [2]. Swing Adsorption Cycles are an alternative technology to amines, allowing **high CO_2 capacities and high selectivities**, also demonstrating the **potential for greater versatility and energy efficiency** for specialized applications [3]. According to the adsorbent material employed **Pressure/Vacuum Swing Adsorption** (PSA/VSA) or **Temperate Swing Adsorption** (TSA) processes is preferred during the regeneration step.

Zeolites deserve special attention because they are **economical** porous materials already produced on a **large scale** for many commercial applications.

The different ways in which they can be connected lead to a rich variety of structures, allowing **controlling their adsorption properties** in a very direct way **by modifying the cation content** in the crystal [4,5]. In this sense, **computational methods** can be used in a complementary way to experimental investigations, allowing finding the most suitable structure.

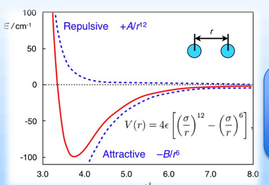
Here we present a molecular simulations evaluation of a series of FAU zeolites (faujasites) with different number of sodium cations, for their potential application in post-combustion CO_2 capture [6]. The analysis is performed from the zeolite topology to the mixed adsorption properties in PSA, VSA and TSA processes.



Methods and computational details

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

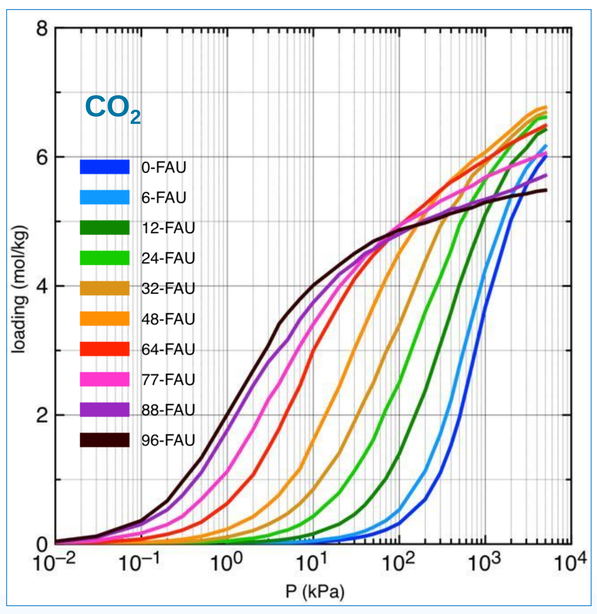
- The zeolite **structures** were assumed to be **rigid** during the sorption process, except for **the Na^+ cations**, which can move freely along the framework, adjusting their positions depending on their interactions with the framework atoms.
- Ten different structures considered: **n-FAU**, where **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**).



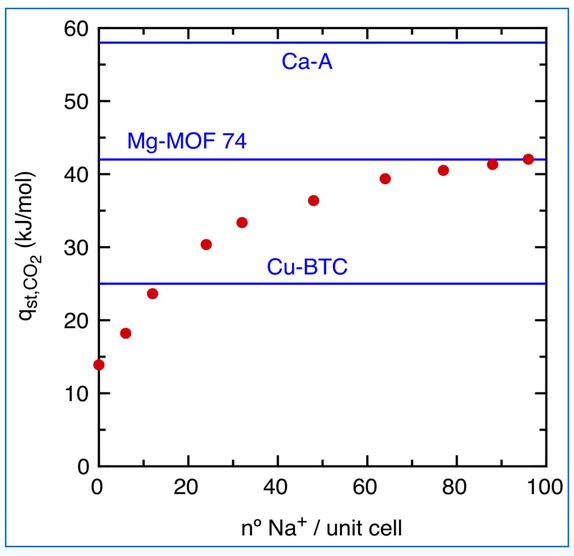
Force field fitting * → GCMC simulations → Adsorption isotherm, surface properties. → Lab and industrial process

* FF taken from previous work from Calero's group [7]

Pure adsorption isotherm



Isosteric heat of adsorption: energy released during the adsorption process, and it is a key parameter for evaluating the cost of desorption/regeneration.

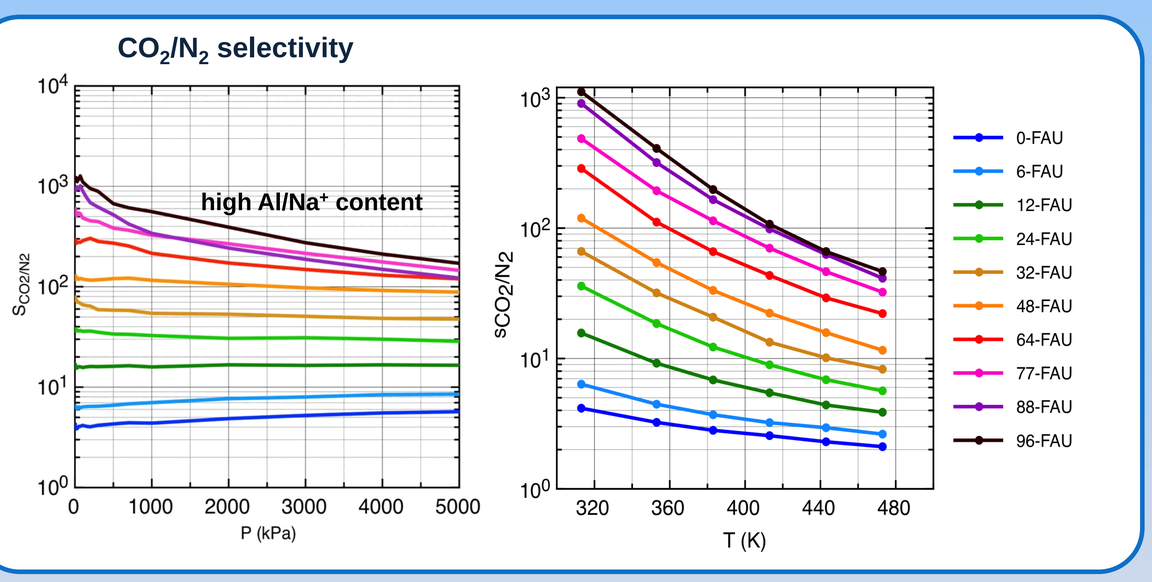


- As the Na^+ content in the zeolite framework increases, the amount of gas molecules adsorbed is higher, specially at low pressures. The **isosteric heat** of adsorption is also **higher** in the zeolites presenting **high Na^+ content**.
- However, zeolites with high Na^+ content reach saturation faster and the amount of CO_2 adsorbed at saturation conditions is lower, due to the volume occupied by the cations.

$CO_2/N_2/O_2$ MIXTURE RESULTS

According to the typical post-combustion gas composition, we considered also **ternary mixtures of CO_2 (15%), N_2 (80%) and O_2 (5%).**

- As the Na^+ content of the zeolite framework increases, the selectivity for CO_2 relative to N_2 becomes higher.



- The **selectivity for CO_2 relative to N_2 decreases** as the **pressure** and **temperature** are increased for zeolites.

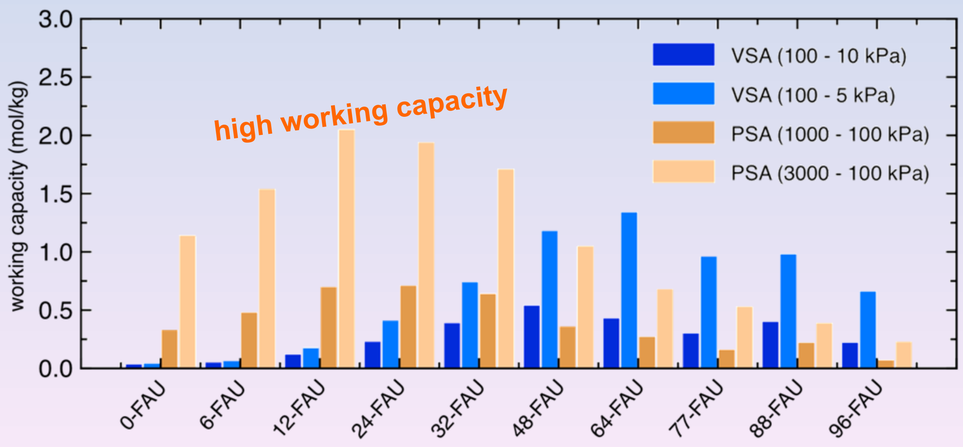
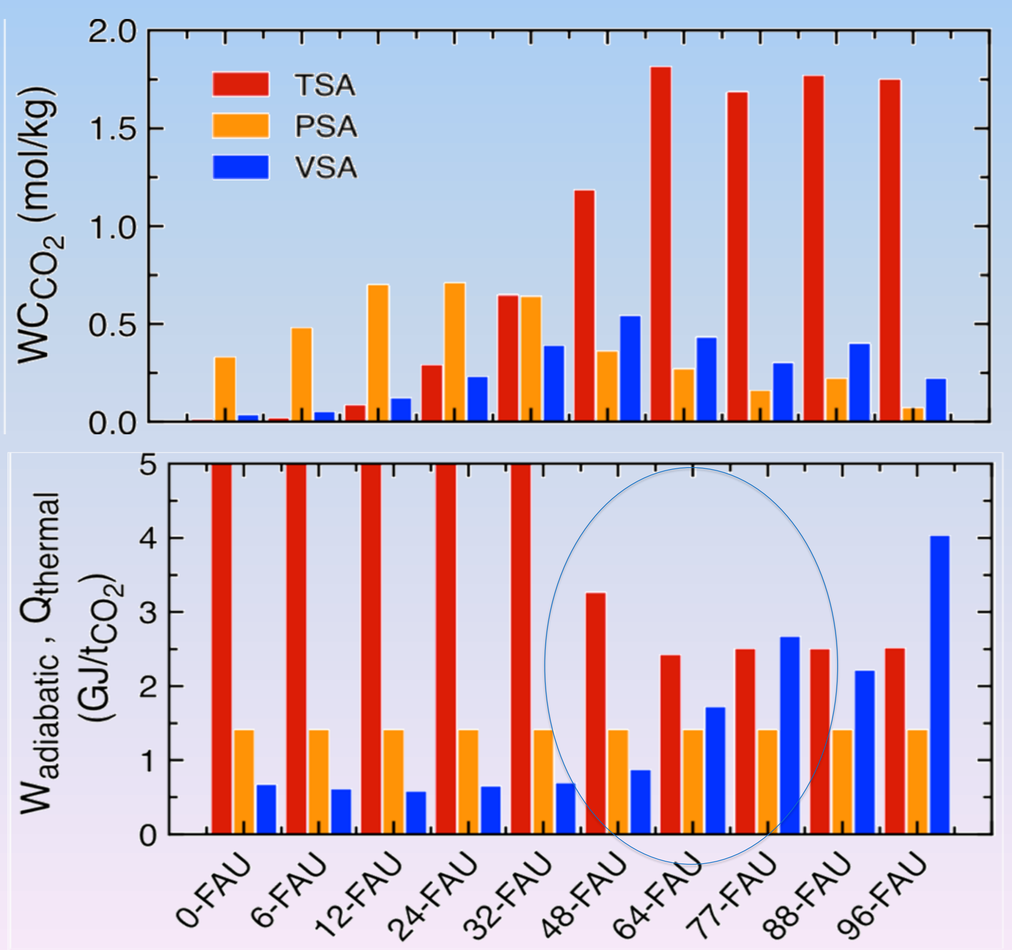


Figure. Working capacities at different operative conditions

Working capacity: represents the true amount of gas that can be separated and used for a specific application after capture; is obtained as the difference in amount between the adsorption and desorption conditions.

- **Heating (TSA)** or driving to **vacuum (VSA)** is useful for zeolites with **high cation content**.
- In general, structures **with higher amounts of cations allow higher purity due to higher selectivities**. However, the affinity of CO_2 is very high at low pressures in these structures, and therefore the **number of CO_2 molecules desorbed** under the regeneration conditions is small, making them much **less interesting for PSA and VSA**.
- Although **TSA results outweigh PSA and VSA in working capacities** for structures with high and medium cation content, the higher amount of CO_2 captured **demands a higher energy requirement.**



- In contrast, VSA processes are interesting for structures with intermediate cation content.

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CONCLUSIONS

- A systematic study was carried out by means of GCMC simulations to identify the optimum structural properties for the selective adsorption of CO_2 from a post-combustion stream in P(V)SA and TSA processes.
- The results 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 cation content and on the working conditions.
- The lower the Na^+ content, the lower the purity of the desorbed CO_2 stream, making an additional separation step to be required.
- One must evaluate the difference between the amount of CO_2 molecules adsorbed at adsorption conditions and remained at desorption conditions. These values depend on the pressure range used industrially, but for every pressure range one can select the most suitable zeolite structure that maximizes the working capacities.
- The analysis of the influence of cation content on CO_2 capture revealed that faujasites with intermediate sodium cation content are the most effective for these adsorption processes. Surprisingly, the best results of the current work clearly improve the performance of faujasite 13X (88-FAU) considered nowadays the reference in industry applications.