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Computational simulation study of the influence of faujasite Si/Al ratio on CO_2 capture by temperature swing adsorption

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ABSTRACT

Grand Canonical Monte-Carlo simulations are used to assess ten faujasite structures, the well-known family of zeolites with different Al content in post-combustion CO_2 capture via Temperature Swing Adsorption (TSA) processes, at 313–473 K and 100 kPa. Selectivity, regenerability, purity, isosteric heat and working capacity values, for each structure, have been calculated from simulations, providing a rather complete evaluation of adsorbents' performance. Additionally, for all the structures the temperature dependence of the heat capacity has been modeled to estimate the thermal regeneration energy. Calculated heat capacities range from 0.78–0.86 kJ/kg K at 313 K to 0.98–1.15 kJ/kg K at 473 K, values considerably lower than those corresponding to aqueous amine solutions. Comparison of TSA results with previous Vacuum and Pressure Swing Adsorption (VSA and PSA) ones shows that there is no structure that works well for all three processes. Instead, each process reaches optimum conditions for certain range of Al content. Results indicate that high Al content faujasites, 64-to-96-FAU, are the most effective for TSA with working capacities above 1.7 mol/kg, doubling PSA/VSA values. Intermediate Al content 48-,64-FAU perform better at VSA conditions and low Al content 12-,24-FAU structures are more suitable for PSA processes. At moderate operative conditions (i.e., regeneration temperature of 413 K), TSA shows the highest purities (above 99% for one-stage process), followed by VSA and PSA. Finally, TSA is more effective in cleaning faujasites with 48 or more Al, compared to PSA/VSA, leading to a higher regenerability (energetic cost index range between 2.3 and 2.4 GJ/tCO_2).

1. Introduction

Economic growth and industrial development have resulted in an increased burning of fossil fuels, leading to growing emissions of atmospheric CO_2 [1]. These emissions may be reduced by a variety of measures, such as improving energy efficiency, and/or developing alternative energy sources, e.g. wind and solar power. However, the necessary transition into a sustainable energy mix, and the phasing out of fossil fuel combustion, is unlikely to occur at a sufficiently fast pace, unless additional, negative emission methods are considered.

Reduction of energy-related CO_2 emissions might be undertaken by means of Carbon Capture and Sequestration/Utilization (CCS/U) techniques. In CCS/U, carbon dioxide is separated from the flue gas of a power plant, compressed to supercritical conditions to transport it, and either stored or reused as a raw material in industry[2–6].

Separation technologies with proven adequacy for post-combustion processes are absorption, membrane use, and adsorption [7]. Whereas the membrane technology is currently waiting its application to mass production, absorption is more mature, but it results in high-energy consumption during the absorbent regeneration step [8] (*i.e.*, about 30% of the output of the power plant) [9]. Alternatively, CO_2 can be captured through adsorption in the pores of solid materials [10,11]. Adsorption technology is based on the preferential affinity of CO_2 to the adsorbent pores, compared to other flue gas components. After the adsorption step, molecules are desorbed from the solid by lowering the pressure (Pressure Swing Adsorption, PSA) or heating the solid material (Temperature Swing Adsorption, TSA) inside the column. The PSA process in which the desorption is performed below atmospheric pressure is called Vacuum Swing Adsorption (VSA). After this operation, the adsorbent is ready for a further cycle. All these methods have been used successfully for air fractionation, hydrogen production, carbon dioxide capture (CCS/U) and removal of volatile organic compounds (VOC) [12–18]. Among these methods, TSA is particularly promising, owing to difficulties with compressing or applying a vacuum to such large volumes of gas stream, as well as to the potential availability of low-grade heat in a power plant as a source of energy for regeneration [19].

Zeolites, activated carbons and metal-organic frameworks (MOFs) are promising adsorption materials, presenting high CO_2 working

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Nomenclature

BTC	Benzene-1,3,5-tricarboxylate
C	Ideal gas concentration at the feeding-gas conditions (kmol m^{-3})
C_p^i	Heat capacity of i component (kJ kg^{-1} K^{-1})
CCS/U	Carbon capture and sequestration/utilization
dobpdc	4,4′-Dioxidobiphenyl-3,3′-dicarboxylate
en	Ethylenediamine
EOS	Equation of state
FAU	Faujasite
GC	Grand canonical
GCMC	Grand canonical Monte Carlo
IAST	Ideal adsorbed solution theory
L	Length of packed bed (m)
LJ	Lennard-Jones
LSX	Low silica X
LTA	Linde type A
MC	Monte Carlo
MEA	Monoethanolamine
mmen	*N,N′*-dimethylethylenediamine
MOF	Metal organic framework
N	Amount adsorbed per mass of adsorbent (mol kg^{-1})
NIST	National Institute of Standards and Technology
$N_{k,sat}$	Maximum loading (saturation) of component A (kmol m^{-3})
P_{TOT}	Total initial pressure (kPa)
PSA	Pressure swing adsorption
q_i	Partial charge of atom i (e^-)
q_{ST}	Isosteric heat of adsorption at infinite dilution (kJ mol^{-1})
R	Gas constant (8.314 kPa m^3 $kmol^{-1}$ K^{-1})
r_{ij}	Distance between a pair of atoms i and j (m)
$S_{A/B}$	Selectivity
t	Time (s)
T	Temperature (K)
TSA	Temperature swing adsorption
u	Superficial gas velocity (m s^{-1})
U_{ij}	Potential energy between a pair of atoms i and j (kJ mol^{-1})
U_g	Total potential energy of an isolated guest molecule (kJ mol^{-1})
V	Total volume of packed bed (m^3)
VOC	Volatile organic compounds
VPSA	Volume pressure swing adsorption
VSA	Volume swing adsorption
W	Adiabatic energy requirement for compression/vacuum (kJ)
WC	Working capacity of the targeted component in the mixture (mol kg^{-1})
x_A	Mole fraction of component A in the adsorbed phase
y_A	Mole fraction of component A in the gas (bulk) phase
z	Distance along the adsorber (m)

Greek symbols

ϵ	Voidage of bed
ε_{ij}	Lennard-Jones potential well depth (kJ mol^{-1})
ε_0	Vacuum permittivity (F m^{-1})
κ	Polytropic parameter of gases
η	Feeding/vacuum blower efficiency
ϕ	Adsorbed composition factor [adim.]
ρ_S	Framework density (kg·m^{-3})
σ_{ij}	Lennard-Jones potential diameter (m)
τ	Time necessary per saturation in a cycle [adim.]
μ	Chemical potential (kJ mol^{-1})
ν	Intersticial gas velocity (m s^{-1})

Subscripts

ads/feed	Adsorption or feeding conditions
des/regen	Desorption or regeneration conditions
k	Species in the gas mixture ($k = A, B, C, \ldots$)
out	Mixture exiting the adsorber

capacity and selectivity for CO_2 over N_2, together with low regeneration energy [10,20–25]. In particular, zeolites are inexpensive porous materials that are already produced on a large scale for many commercial applications. Thus, they have been used successfully in PSA and TSA processes for CCS/U [26–28]. Furthermore, they present higher thermal and mechanical stability than other common adsorbents such as MOFs, although the latest often possess higher surface areas [29,30].

Zeolites are molecular sieves with a 3D framework structure possessing orderly distributed micropores with diameters up to 2 nm. The different ways in which TO_4 tetrahedrals (T = Si or Al atom) can be connected lead to a rich variety of zeolite structures [31–33]. Faujasites are a zeolite family built from Si, Al and O atoms, with a crystal composition that vary with the Si/Al ratio (*i.e.*, $(Na_2O)_{n/2}(Al_2O_3)_{n/2}(SiO_2)_{192-n}$, $0 \le n \le 96$) [34], and consist of sodalite cages which are connected through hexagonal prisms. The properties of the faujasites depend on the nature, number and distribution of the framework cations. As the Si/Al ratio decreases, the cation content increases, the thermal stability diminishes, the surface becomes more hydrophilic and the zeolite increases its catalytic properties. These changes are of great importance in the energetic cost of the CO_2 capture and in the regenerability of the adsorbent material [35]. Thus, the open three-dimensional pore system of FAU-type zeolites allows exceptional properties for using it in adsorptive separations compared to other zeolite families [36].

Computational methods have been employed in a complementary fashion to experimental investigations. Grand-canonical Monte Carlo (GCMC) simulations allow the prediction of adsorption isotherms, adsorption selectivities and preferred adsorption sites at a very moderate computational expense, making an important contribution to the microscopic understanding of gas adsorption and separation in porous materials [37]. In a previous work [38], we have employed GCMC simulations to study the separation of post-combustion $CO_2/N_2/O_2$ mixtures via PSA and VSA processes in FAU-type zeolites with different Si/Al ratio. An analysis of the influence of the Si/Al ratio on the CO_2 capture performance revealed that faujasites having intermediate Al content are the most effective for P/VSA processes. In the present work, we have performed new GCMC simulations for all faujasite structures considered in Ref. [38] to study the separation of post-combustion $CO_2/N_2/O_2$ mixtures via TSA processes. Thus, we have calculated selectivities, working capacities and purities at TSA conditions and then, compared the results obtained with those for PSA and VSA processes. Moreover, we have calculated the thermal regeneration energy (*i.e.,* the energy required for heating and desorb) and compare it with the adiabatic work for expansion/compression required in VSA/PSA processes.

This document is structured as follows: Section 2 describes the methodology, the computational details and the evaluation criteria used to rank all the faujasite structures simulated. Section 3 reports the