WASTES IV

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Editors:
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WASTES: SOLUTIONS, TREATMENTS AND OPPORTUNITIES IV

WASTES: Solutions, Treatments and Opportunities IV contains selected papers presented at the 6th edition of the International Conference Wastes: Solutions, Treatments and Opportunities, that took place on 6-8 September 2023, in Coimbra, Portugal. The Wastes conference, which takes place biennially, is a prime forum for sharing innovations, technological developments and sustainable solutions for waste management and recycling sectors worldwide, with the participation of experts from academia and industry. The papers included in this book cover a wide range of topics, including:

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WASTES: Solutions, Treatments and Opportunities IV is aimed at academics and professionals involved in waste management and recycling sectors globally.

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The Wastes Selected Papers Series presents the latest theoretical research and innovative technologies and techniques in the waste field, as well as tools and strategies to improve corporate environmental performance

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Post-combustion CO_2 capture using ion-exchanged binder-free NaY zeolites

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ABSTACT: 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) by adsorption processes. Adsorption equilibrium isotherms of CO_2 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 related applications.

1 INTRODUCTION

1.1 *Post-combustion capture*

Climate change mitigation is a topic that keeps attracting attention and is currently more relevant than ever. Carbon dioxide (CO_2) emissions from fossil fuel combustion and industrial processes contributes to around 78% of total GHG emissions and is thereby one of the most serious global problems (Freund 2015). 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. Solid sorbents such as zeolites are very attractive in post-combustion applications due to their nonvolatile and nontoxic properties, their ability to be produced commercially with low costs, and their high selectivity and adsorption capacity for CO_2. One of the biggest challenges in PCC is separating the relatively low concentration of CO_2 (around 12 to 15% in fuel-fired power plants) from the large amounts of nitrogen (N_2) in the flue gas. This is achievable since CO_2 always adsorbs stronger than N_2 due to its larger polarizability and greater quadrupole moment.

1.2 *Binder-free zeolites*

Zeolites are normally synthesized in the powder form and must be refined using a binder to join all particles together to form mechanically stable macroscopic particles like beads (spheres) or pellets. Such binder usually does not contribute to the adsorption, taking unnecessary space, and consequently, reducing the adsorption capacity at about the percentage of the added binder (up to 20%). Moreover, other factors such as undesired chemical reactions and unfavorable pore size distribution may decrease the adsorption uptake even further. To avoid such problems, a new technology was found where the zeolite impurity (binder) is converted to zeolite matter

during a hydrothermal conversion after the manufacturing procedure. In this way, the new material will be purely composed of zeolite (100% zeolite content), creating a much better secondary pore system, while being mechanically stable. This allows binder-free zeolites to possess larger amount of macropores as well as better pore size distribution and generally demonstrating better dynamic adsorption properties in comparison to the conventional material (Gleichmann, Unger, and Brandt 2016).

1.3 *Ion-exchange in faujasite framework*

Zeolite Y belong to the family of aluminosilicate molecular sieves with a faujasite-type structure (FAU). 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 (Talu, Zhang, and Hayhurst 1993). Therefore, ion-exchange can be used as a tool for tailoring the structure of the framework to obtain enhanced separation performance regarding PCC applications.

2 MATERIALS AND METHODS

2.1 *Adsorbent and adsorbate*

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 from 1.6 to 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.

Air Liquide supplied the adsorbate and inert gases with the following specifications: He ALPHAGAZ 2 (99.9998 %), CO_2 N48 (99.998%), CH_4 N35 (99.95%), and N_2 N50 (99.999%).

2.2 *Experimental procedure*

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 (Aly et al. 2021). Table 1 shows the main adsorbents and column properties used in the experiments throughout this work.

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 (Do 1998):

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

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= adsorption column volume; and C_{0i} = feed gas-phase concentration of component i at the inlet of the fixed bed.

3 RESULTS AND DISCUSSION

3.1 *Adsorption Equilibrium of CO_2 and N_2 on the series of ion-exchanged binder-free zeolite*

Figure 1a 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 (a) 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. Generally, basic zeolites that possess strong electropositivity usually show a strong adsorption capacity with acidic molecules that have a great permanent quadrupole moment such as CO_2 (Bonenfant et al. 2008). 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. In the case of exchange with Ca^{2+} cations, two monovalent Na^+ cations are exchanged by one divalent Ca^{2+}, leading to a significant reduction of the number of exchangeable cations, and therefore there is less absorbent-adsorbate interactions and consequently decreasing the binding energy of the guest CO_2 molecule.

The N_2 isotherms presented in Figure 1b show a similar trend of sorption hierarchy as that of CO_2 (at low pressure), with K(95)Y being the stand-out performer under all sets of temperatures. At 50 kPa and 308 K, the N_2 loading of binder-free K(95)Y is equal to 0.19 mol/kg, compared to 0.13-NaY, 0.12-K(23)Y, 0.15-K(58)Y, 0.13-Ca(56)Y and 0.11-Ca(71)Y mol/kg. Zeolites with smaller pores size such as binder-free K(23)Y and NaY show a relatively low N_2 uptake when compared to other the K^+ exchanged adsorbents. This could indicate that both zeolites show less affinity towards molecules with higher kinetic diameter such as N_2, which can lead to higher CO_2/N_2 selectivity and thereby improving the CO_2 separation performance from flue gas.

Figure 1c shows the experimental and predicted (DSL model) pure-component selectivities of CO_2 over N_2 as function of pressure at 308 K. Overall, the selectivities are high; with binder-free K(23)Y and K(58)Y showing the highest values: 42 and 41, respectively, compared to 34 for NaY, 32 for K(95)Y, 27 for Ca(56)Y, and 24 for Ca(71)Y at 308 K and 50 kPa.

Table 1. Adsorbent and column properties.

Binder-free zeolite	NaY	K(23)Y	K(58)Y	K(95)Y	Ca(56)Y	Ca(71)Y
Weight (g)	24.80	25.58	25.03	26.20	24.90	25.59
Diameter (mm)	1.60 − 2.50	1.60 − 2.50	1.60 − 2.50	1.60 − 2.50	1.60 − 2.50	1.60 − 2.50
Bed density (g/cm^3)	0.615	0.634	0.621	0.649	0.618	0.635
Bed porosity = 0.4						
Particle porosity = 0.254						
Column Length = 0.0646 m						
Column Internal Diameter = 0.0282 m						
Cross-Sectional Area = $6.24 \times 10^{-4}\ m^2$						
Volume = $4.03 \times 10^{-5}\ m^3$						

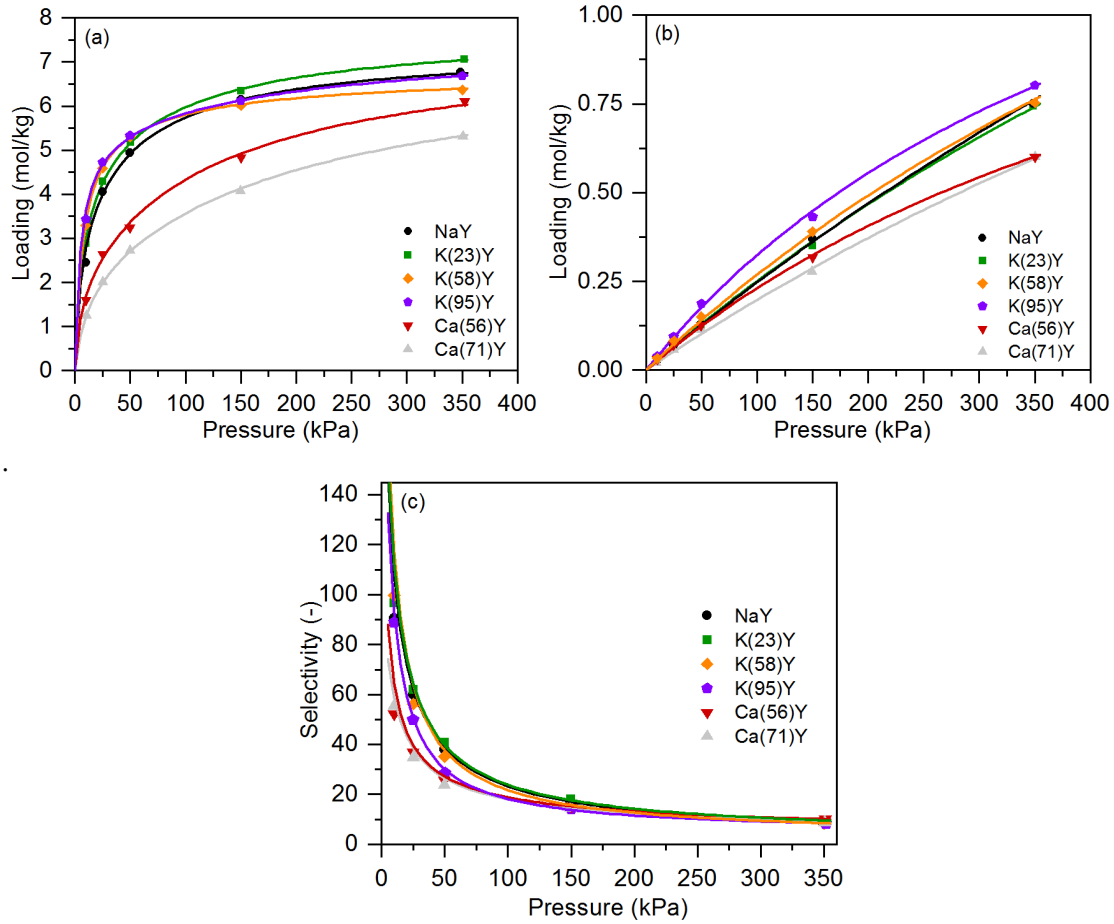

Figure 1. Comparison of (a) CO_2 and (b) N_2 adsorption isotherms and (c) selectivity of CO_2/N_2 in different ion-exchanged zeolites at 308 K.

3.2 *Binary adsorption experiments for CO_2/N_2 mixtures under typical PCC operating conditions*

A series of binary breakthrough experiments in the ion-exchanged zeolites were performed under typical PCC operating conditions: 15% CO_2 and 85% N_2 vol.% at 101.3 kPa and 308 K. To evaluate the CO_2 separation performance of the materials studied in this work, adsorbent metrics (e.g. CO_2 loadings, selectivities, and working capacities) were measured according to a procedure described elsewhere (Yang 1997) and compared with other adsorbents studied an reported in literature, such as benchmark zeolite 13X in binder form beads, Mg-MOF-74, UTSA-16, and CS-AC (Rajagopalan, Avila, and Rajendran 2016).

The working capacity values for CO_2 reported were calculated between the regeneration pressure of 3, 10, and 15 kPa and the feed pressure of 101.3 kPa, representing a range of Vacuum Swing Adsorption (VSA) PCC processes, as studied elsewhere (Li et al. 2008). Figure 2 shows a comparison of CO_2 working capacities for all the materials under the above-mentioned conditions. The results indicate that all of the studied binder-free zeolites have better working capacities when compared to the benchmark zeolite 13X and to the carbonaceous material CS-AC. Between 10 and 101.3 kPa, binder-free K(23)Y possesses the highest CO_2 working capacity of 2.98 mol/kg, compared to 2.94 for the bare NaY, 2.38 for K(58)Y, 2.19 for K(95)Y, 2.64 for Ca(56)Y, 2.33 for Ca(71)Y. In the reported literature values, we read 1.83 for zeolite 13X, 2.08 for MOF Mg-MOF-74, 2.61 for MOF UTSA-16, and 2.72 mol/kg for CS-AC.

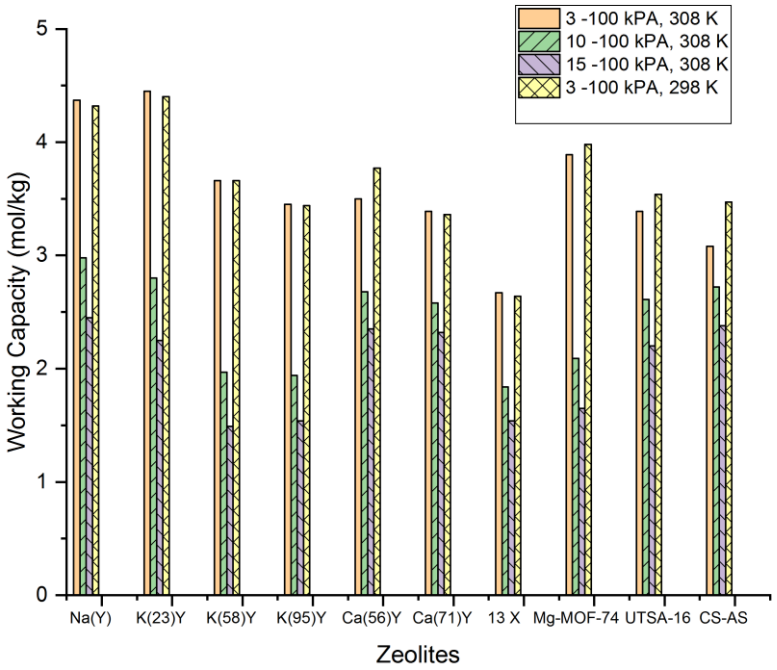

Figure 2. Comparison of CO_2 working capacities under various PCC operating conditions

3.3 *Modeling of binary-component breakthrough experiments for CO_2/N_2 mixture*

The development of a mathematical model that can describe the dynamics of adsorption is essential to obtain a better understanding of the adsorption behavior in a fixed bed. By considering all transport phenomena, the model may provide means of estimating the breakthrough curves and the column dynamic capacity without extensive experimentation. Moreover, the model can be used to evaluate the effects of various process parameters and for the design and optimization of a more advanced cyclic process. In this work, Aspen Adsorption v.10 was used to generate a mathematical model through the established adsorption equilibrium and kinetics of sorption of CO_2 and N_2 to simulate the binary-component breakthrough experiments on the cation-exchanged binder-free zeolites. Figure 3 shows the adsorption breakthrough curves along with the simulations for the binary CO_2/N_2 in binder-free K(23)Y at 308, 328, and 348 K. The effect of changing the temperature is observed as the breakthrough time decreases with increasing temperature (308 to 348 K). The simulations results fit well with the experimental breakthrough curves, indicating that the mathematical model provides accurate numerical predictions.

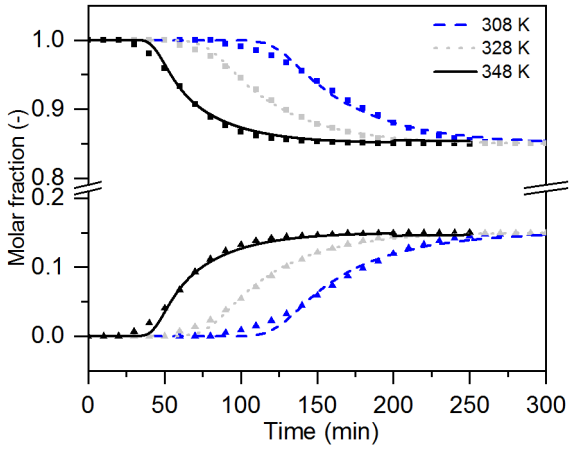

Figure 3. Breakthrough curves for binder-free K(23)Y zeolite in binary CO_2 (▲) and N_2 (■) fixed bed experiments at 308, 328, and 348 K.

4 CONCLUSIONS

Adsorption equilibrium measurements of CO_2 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 shown that binder-free K(23)Y and K(58)Y generally possess the highest pure-component CO_2/N_2 selectivities: 42 and 41 compared to 34 for NaY, 32 for K(95)Y, 27 for Ca(56)Y, and 24 for Ca(71)Y at 308 K and 50 kPa. The binary-component experiments of CO_2/N_2 mixture indicate that binder-free K(23)Y is a promising adsorbent for the recovery of CO_2 from post-combustion streams with a loading of 4.19 mol/kg, and a selectivity of around 118 over N_2. It also demonstrated a high working capacity under different conditions in the range of VSA PCC processes: 4.45, 2.80 and 2.25 mol/kg respectively between the regeneration pressure of 3, 10, 15 kPa and atmospheric feed pressure.

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