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BOOK OF ABSTRACTS

separation performance between ZIF-11 and ZIF-8. RHO topology performs much better than SOD topology in separating H_2 from CO_2 and CH_4, presumably ascribed to the *d8r*-cage with a smaller pore diameter than the *sod*-cage of ZIF-8. A quaternary mixture, consisting of hydrogen, carbon monoxide, nitrogen, and oxygen, is simulated to highlight the effect of the narrow-pore topology on separating H_2 from CO. ZIF-7 topology, with the smallest pore cage, shows the highest potential, considering the adsorption selectivity of CO/H2 up to 33 (**Figure 29**). While the selectivity for ZIF-11 is limited to 7. Although large-pore topologies (*i.e.,* 11.07 Å *sod*, 14.17 Å *lta*) contribute to a high adsorption of CO_2 and CH_4 due to their high surface area, the *d8r*-cage can facilitate a stronger binding interaction to enhance the separation performance of ZIF-11. As for the narrow-pore topology (ZIF-7), the *sod*-cage with the pore diameter of 4.31 Å results in a higher adsorption heat but hinders the structure from achieving higher capacity for CO_2 and CH_4. It appears that the adsorption of CO, O_2, and N_2 is not sensitive to the surface area of the topology, but strongly depend on the pore size. ZIFs can also be served as fillers for mixed matrix membranes because of their molecular sieving effect, this work can be beneficial to a selection of topological structures of ZIFs with high performance for the sieving-based purification of hydrogen-rich fuel gas.

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O08.10. EFFECT OF CATION EXCHANGE IN THE SORPTION OF CO_2, CH_4 AND N_2 AND THEIR MIXTURES ON BINDER-FREE FAUJASITE ZEOLITE Y

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Ion-exchange was performed on commercial binder-free NaY zeolite with alkali metal and alkaline earth metal cations to produce binder-free beads containing 23, 58 and 95% of potassium, as well as 56 and 71% of calcium exchanged from the bare samples. These cation-exchanged faujasites were studied by adsorption of carbon dioxide (CO_2), methane (CH_4), and nitrogen (N_2) through single, binary, and ternary fixed bed breakthrough experiments, covering the temperature range between 308 and 348 K and pressure up to 350 kPa. The single and multi-component breakthrough apparatus that was used to study the fixed bed adsorption of CO_2, CH_4, and N_2 and their binary/ternary mixture, is illustrated in Figure 1. The dynamic equilibrium loading is calculated by integrating the molar flow profiles of the breakthrough curves, as explained in previous works [1]. The adsorption equilibrium data was then modelled by the extended dual-site Langmuir model, and the breakthrough curves were numerically simulated using ASPEN ADSORPTION.

Adsorption equilibrium measurements of CO_2 on each of the restructured materials can reveal different behaviours and trends based on the modification of the intracrystalline environment through ion-exchange. Factors such as cation size, surface basicity, number and location of exchangeable cations, and strength of electric field can all have a great impact on the performance of the adsorbent. Figure 2 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. A trend in the order of adsorption at low pressure (between 0 and 50 kPa) is observed: Ca(71)Y < Ca(56)Y < NaY < K(23)Y < K(58) < K(95)Y. As the exchange rate from Na^+ to K^+ increases, the CO_2 adsorption capacity increases at low pressure. At 25 kPa, the loading of binder-free NaY is equal to 4.05 mol/kg, compared to 4.29 for K(23)Y, 4.57 for K(58)Y, 4.97 for K(95)Y, 2.63 for Ca(56)Y and only 2.02 mol/kg for Ca(71)Y. This indicates a good response between the acidic CO_2 to the basic properties of the zeolites containing larger monovalent cations at low pressure.[2] Bigger cations such as K^+ exhibit strong interaction with CO_2, since they are both preferentially exchanged in the supercages; while smaller cations such as Na^+ have less molecular interaction with the adsorbate molecules, since they are spread around the zeolite framework accessing narrow locations such as the sodalite cages, where CO_2 cannot reach due to its size.[3] Moreover, the CO_2 loading of Ca(71)Y is significantly lower than all the rest (around half of that of NaY), which is due to the decrease of the amount of exchangeable cations between the divalent Ca^{2+} cations and the adsorbate molecules. For partial pressures above 200 kPa, K(23)Y and NaY are characterized with the highest adsorption capacity followed by K(95)Y and K(58)Y, then Ca(56) and finally Ca(71)Y, as shown in Figure 2. These trends are explained by the reduction of the basic strength and the electropositivity of exchangeable cations in larger ions, since they accept less charge transfer from the neighboring lattice oxygen atoms when compared to smaller cations. This leads to the weakening of the electric field induced by the exchangeable cations and so the adsorption capacity is reduced. [4] It is also explained by the volume occupied by the large cations, which reduces the space available for adsorption of CO_2 when the pores are reaching saturation.

The studied binary experiments consists of 15% CO_2 and 85% N_2, representing a typical post-combustion stream. Figure 3a shows the adsorption breakthrough curves in binder-free K(95)Y for the binary mixture at 313 K. Figure 3b 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, under conditions in the range used for biogas upgrading regarding the removal of CO_2. As can be seen in Figure 3c, the binary experiment show a selectivity of CO_2 over N_2 around 105 at 313 K; the ternary system resulted in a selectivity of CO_2 over CH_4 and over N_2 of around 14 and 32 at 313 K, respectively. These results indicate that binder-free K(95)Y works best in the low-pressure region and therefore, is a promising adsorbent for the recovery of CO_2 from post-combustion streams. Overall the numerical simulations performed on ASPEN ASDSORPTION provided results with decent accuracy and the model can predict the systematic behaviour of the breakthrough experiments as well as the dynamics of the fixed bed adsorption system, as shown Figure 3.

Briefly, most of the studied ion-exchanged materials show a lot of potential for the capture of CO_2 from CO_2/N_2 and CO_2/CH_4/N_2 mixtures. Nevertheless, each adsorbent differs from one another and can only reach its full potential under specific conditions. Therefore, it is possible to tune the adsorptive properties of zeolites by ion exchange, to optimize the most suitable material that enriches substantially the CO_2 adsorption for a specific process.

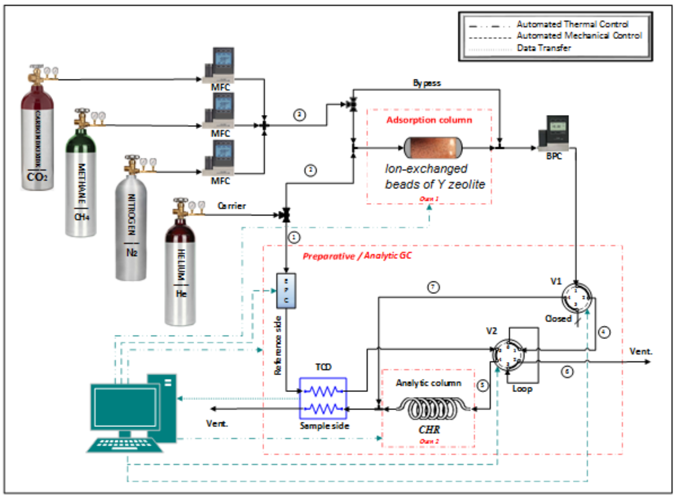

Figure 1- Schematic drawing of the experimental apparatus used to perform single- and multicomponent breakthrough experiments.

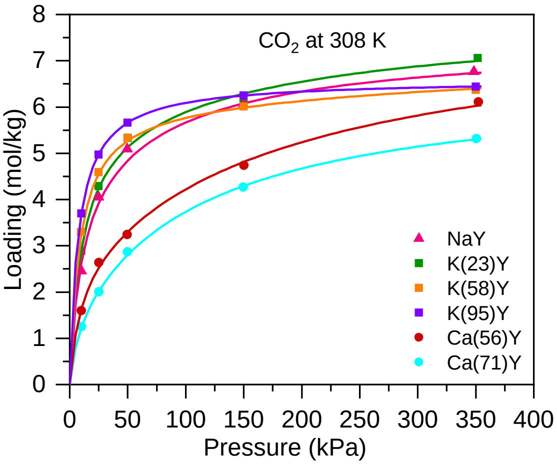

Figure 2- Comparison of CO_2 adsorption isotherms in different ion-exchanged zeolites

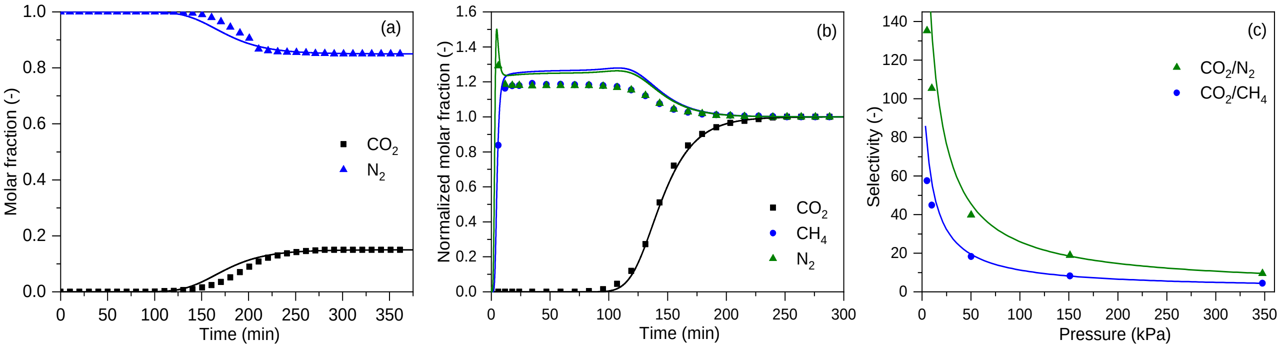

Figure 3 - Breakthrough curves for binder-free K(95)Y in (a) binary and (b) ternary fixed bed experiments at 313 K. (c) Selectivity of CO_2/N_2 and CO_2/CH_4 at 313 K in binder-free K(95)Y zeolite. Experimental = symbols; Numerical = lines.

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O08.11. FINE-TUNING THE MOLECULAR SIEVING PROPERTY OF ZEOLITES BY POST-SYNTHETIC FUNCTIONALIZATION FOR LIGHT OLEFIN/PARAFFIN SEPARATION

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