

The chemical nature of CO₂ adsorption on zeolites

Przemyslaw Rzepka

ETH Zurich, Institute for Chemical and Bioengineering, CH-8093, Zurich, Switzerland
przemyslaw.rzepka@chem.ethz.ch

Adsorption-driven CO₂ capture is one of the most promising carbon capture and storage (CCS) technologies, which aim to remove CO₂ from N₂ in post-combustion flue gas. Nano-porous zeolites are of particular interest to adsorption applications because of their CO₂ capacities and selectivities, robustness, and often low costs. The nature of CO₂ adsorption is various. The process may act as physical adsorption with intermolecular interactions of the van der Waals type or as chemisorption with a significantly perturbed electronic structure of CO₂ and the formation of CO₃²⁻ and HCO₃⁻ species.¹

Adsorption-driven processes can be implemented only if highly functional adsorbent materials have been developed. Zeolite A is one of the most successful adsorbents. Rzepka *et al.*² broadly discussed the potential enhancement of the selectivity of CO₂ over N₂ and CH₄ by replacing Na⁺ with larger monovalent cation e.g. K⁺ in the pore windows of zeolite A. Figure 1 shows the cations positioned at the 4- and 6-rings and the 8-ring apertures of the aluminosilicate framework of zeolite A. K⁺ ion was favored at the 8-ring sites, and also gradually substituted the 6-ring sites with increasing x in [Na_{12-x}K_x]-A.² Large cation did not fit the mirror plane of the 6-ring and was placed on its both sides.² Cations sitting in 8-rings and 6-rings appear to tailor the size of main pore windows.

The effective pore size was shown to depend on the K⁺ content and to separate small CO₂ molecules from large N₂ and CH₄ due to differences in their diffusivities. Various compositions of [Na_{12-x}K_x]-A demonstrated gradual decline of CO₂ uptake with x and a total exclusion of N₂ and CH₄ already for low x .² Most of already absorbed CO₂ molecules were revealed to bridge adjacent 8-ring sites (Figure 1). They are relatively weakly physisorbed, and therefore most of the working capacity of CO₂ adsorption is related to this site.¹ On the other hand some of CO₂ molecules coordinated to a cation in the 8-ring plane (the second most populated site of CO₂ adsorption) demonstrated perturbed electronic structure.¹ These chemisorbed carbonate species cannot be removed by simple evacuation.¹

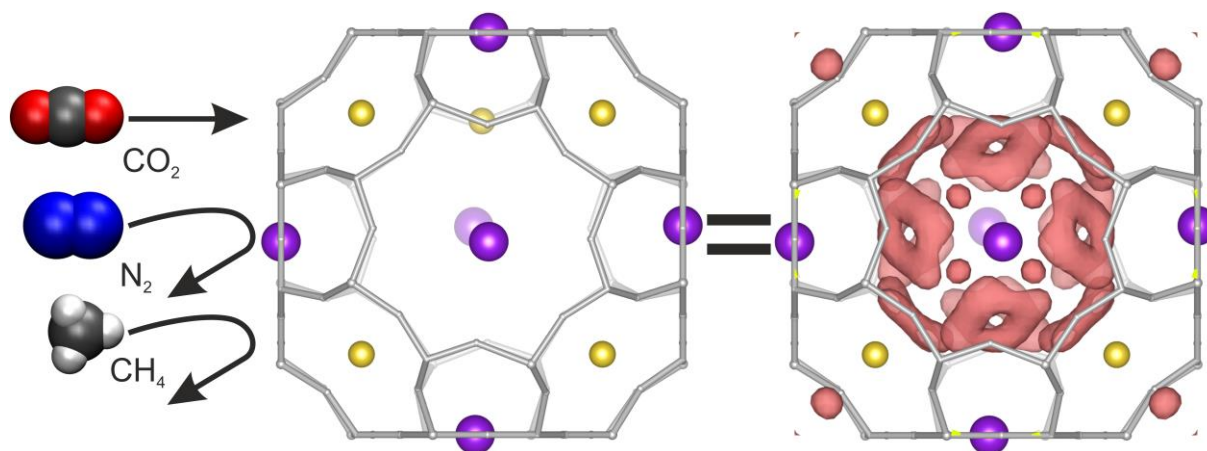


Figure 1. Selective adsorption of CO₂ on [Na₉K₃]-A (left). Na⁺ and K⁺ positions represented by yellow and magenta balls. Nuclear densities of adsorbed CO₂ molecules (right).

Rzepka *et al.*² also reported that adsorbed CO₂ molecules displaced the cations into the α -cages and resulted into a slight contraction of the overall distribution of extra-framework cations in zeolite structure upon the adsorption of CO₂.² 4- and 8-ring sites cations are attracted by CO₂ molecules and shifted towards the center of zeolite cavities.² The time-averaged repositioning stands in an agreement with the “trapdoor” mechanism reported also for zeolites Rho, X and chabazite.

References

1. Rzepka, P. et al. Site-Specific Adsorption of CO₂ in Zeolite NaK-A. J. Phys. Chem. C 122, 27005–27015 (2018).
2. Rzepka, P. et al. CO₂-Induced Displacement of Na⁺ and K⁺ in Zeolite [NaK]-A. J. Phys. Chem. C 122, 17211–17220 (2018).