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Investigation of CO₂ adsorption on a selection of zeolites by combining in-situ high-resolution powder X-ray diffraction, isotherm modeling, and simulation

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The adsorption of carbon dioxide (CO₂) by porous materials such as zeolites is of great importance to address current environmental issues, and many zeolites have been used as CO₂ capture agents [1]. Combustion gases, important contributors to the greenhouse effect, are generally composed of a mixture of gases (N₂, CO₂, H₂O, CH₄ ...), leading to competition for the most favorable adsorption sites and consequently a decrease in the zeolite's selectivity toward CO₂ adsorption. Determination of the preferred sorption sites for each gas of the mixture is then necessary to gain insights into the host-guest and guest-guest interactions that govern the adsorption capacity of the adsorbent. We propose an approach where high-resolution powder X-ray diffraction, isotherm modeling, and simulations are combined to determine the preferred sorption sites for pure CO₂ and CO₂ in a mixture to unravel the adsorption process of CO₂ in a set of different zeolites.

Selected zeolites were chosen according to their affinity towards each of the constituents of the gas mixtures. We were especially interested in the silica-alumina ratio, to influence the hydrophobicity of the material, and also in the pore size to favor certain types of gas molecules, in order to increase the adsorption capacity towards CO₂. Monte-Carlo sorption simulations were conducted on each of the promising zeolites, in the presence of CO₂ alone and CO₂ in a gas mixture. Si-STT zeolite is an interesting hydrophobic zeolite because it possesses a high adsorption capacity (2.8 mmol.g⁻¹ at 1bar) and an advantageous selectivity towards CO₂ in the presence of other gases such as CH₄ (Fig. 1A).

The evolution of the crystallographic structure of each zeolite with applied CO₂ pressure, from 0 to 25 bar, was monitored *in situ* using high-resolution powder X-ray diffraction (ID22, ESRF). The specific positions of the CO₂ molecules were extracted through Rietveld refinement and experimental adsorption isotherms have been retrieved. Furthermore, local information, specific to each adsorption site, was also obtained from parametric Rietveld refinement [2], where structural evolution and adsorption modeling are intrinsically part of the crystallographic model. Using this approach on CO₂@Si-STT, we showed that, over the four sites where CO₂ molecules locate in the Si-STT zeolite (Fig. 1B), the most-favored site (mol4), at the center of the 9 member-ring, follows a Langmuir adsorption model, with the homogeneous adsorption of isolated molecules (Fig. 1C). On the other hand, the less-favored sites (mol2), display a Toth adsorption behavior, under the influence of molecule-molecule interactions.

These experimental results, combined with Monte Carlo simulations, provide a deeper comprehension of the CO₂ adsorption mechanisms, and allow these zeolites to be probed through the host-guest and guest-guest interaction specific to each of them.

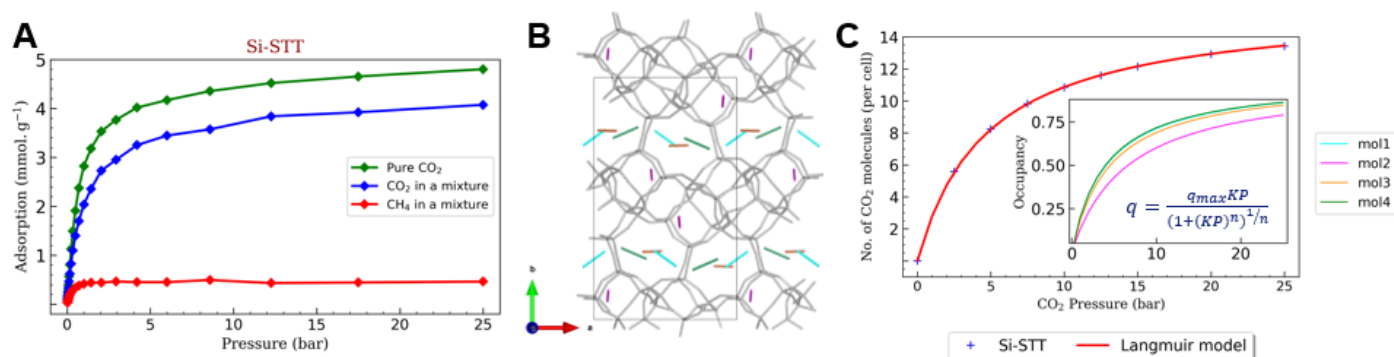


Figure 1. A - Simulated adsorption isotherm of pure CO₂ and a binary mixture of CO₂/CH₄ for Si-STT at 298K. B – Crystallographic model for CO₂@STT at 25 bar. C- Global adsorption isotherm of CO₂ and site-specific isotherms extracted from parametric Rietveld refinement of Si-STT

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[2] Lill, J., Dejoie, C., Giacobbe, C., Fitch, A.N. (2022). *J. Phys. Chem. C*, **126**, 2214-2225.