

On the nature of adsorption sites for CO₂ in MOF Zn₂(bdc)₂dabco

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Zn₂(bdc)₂(dabco) is a zinc-based paddle-wheel type MOF (synthesis described in [1]). The structure of this MOF can be represented as a set of parallel rectangular channels. In order to investigate dynamic behavior of adsorbed CO₂ we used two different NMR techniques – spectroscopy and diffusometry complemented with simulation of molecular dynamics.

The ¹³C NMR spectra of adsorbed CO₂ display anisotropic “powder” pattern. The linewidth decreases with increasing temperature. The rotational motion of CO₂ remains highly restricted even at room temperature. The PFG NMR diffusometry provided CO₂ translational diffusion coefficients as large as $7.4 \times 10^{-9} \text{ m}^2\text{s}^{-1}$. Such a behavior cannot be explained by a simple “freezing in pores”.

The MD simulation reveals that the Zn₂(bdc)₂(dabco) MOF structure provides several CO₂ absorption sites at the Zn-paddle wheels. CO₂ molecules jump rapidly between the available adsorption sites. Analysis of MD trajectory shows a strong orientational preference of the CO₂ molecules along the axis of the paddle wheel connected with translational diffusion anisotropy with diffusion tensor having its largest component in direction of the MOF channels.

The specific lineshapes in the ¹³C NMR spectra are finally explained by combination of intrinsic ¹³C chemical shift anisotropy and CO₂ orientational anisotropy due to structural anisotropy of the channel system in Zn₂(bdc)₂(dabco) MOF crystallites.

References

- [1] D. Dytsev, H. Chun, K. Kim: *Rigid and flexible: A highly porous metal–organic framework with unusual guest-dependent dynamic behavior*. *Angew. Chem. Int. Ed.* **43**, 5033–5036 (2004)