Unraveling the effects of pore size and diamine functionalization on CO₂ diffusion in metal-organic frameworks using machine-learnings interatomic potentials

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 M_2 (dobdc) (dobdc⁴⁻ = 2,5-dioxido-1,4-benzenedicarboxylate; M = Mg, Mn, Fe, Co, Ni, Cu, Zn), commonly referred to as M-MOF-74, and its variants have been extensively studied for their outstanding CO₂ capture performance. In particular, diaminefunctionalized $M_2(dobpdc)$ (dobpdc⁴⁻ = 4,4'-dioxidobiphenyl-3,3'-dicarboxylate), an extended analogue of M2(dobdc), has demonstrated exceptional CO₂ selectivity under humid conditions owing to its unique cooperative CO₂ capture mechanism. Despite these advantages, its CO₂ diffusion behavior—a critical parameter for practical applications-remains poorly understood. Here, we systematically investigate the effects of pore size and diamine functionalization on CO₂ diffusion in Mg₂(dobpdc). By employing machine-learning interatomic potentials (MLPs), we achieve quantum-level accuracy within classical molecular dynamics (MD) simulations, enabling the examination of large-scale systems comprising over 4,000 atoms on nanosecond timescales. To elucidate the CO₂ diffusion behavior, we compare Mg₂(dobpdc) with its smaller-pore counterpart Mg₂(dobdc) and larger-pore analogue Mg₂(dotpdc) (2,5dioxido-1,4-terephthalate). Four distinct diamines-m-2 (N-N'-methyle-thylenediamine), m-2-m (N,N'-dimethylethylenediamine), e-2 (N-ehylethylenediamine), and e-2-e (N,N'diethylethylenediamine)-are appended to Mg₂(dobpdc) and Mg₂(dotpdc) to evaluate their influence on CO₂ diffusion. The developed MLPs exhibit root mean square errors (RMSEs) of less than 5 meV/atom for energies and 0.3 eV/Å for forces, compared to density functional theory (DFT) calculations, with MLP-optimized lattice parameters deviating from DFT values by no more than $\pm 2\%$. For bare MOFs, our MLPs accurately predict CO₂ binding enthalpies and the localized CO₂ feature near open Mg sites, consistent with experimental observations. This results in low diffusion coefficients (2.0 x 10^{-11} m²/s - 3.1 x 10^{-10} m²/s) at low CO₂ uptake. For Mg₂(dobpdc) and Mg₂(dotpdc), which possess larger pore sizes than Mg₂(dobdc), the diffusion coefficients increase with increasing CO₂ uptake. This trend is attributed to the saturation of Mg sites, which reduces interactions between free CO₂ molecules and Mg ions. At one CO₂ per Mg, the diffusion coefficients are calculated as 2.1 x 10⁻⁹ m²/s and 3.7 x 10⁻⁹ m²/s for Mg₂(dobpdc) and Mg₂(dotpdc), respectively. Diamine functionalization further enhances CO₂ diffusion (0.8 x 10^{-9} m²/s ~ 13.2 x 10^{-9} m²/s) by reducing access to open Mg sites and introducing complex interactions between diamine units and CO₂ and between ammonium carbamate units and CO₂. However, at high CO₂ loadings, steric hindrance caused by functionalized diamines decreases the diffusion coefficients (1.6 x 10^{-9} m²/s ~ 6.1 x 10⁻⁹ m²/s), particularly in Mg₂(dobpdc) due to its smaller pore size relative to Mg₂(dotpdc). These findings provide valuable insights into the interplay between pore architecture, functionalization, and CO₂ diffusion in bare and diaminefunctionalized MOFs. Our results not only deepen the understanding of CO₂ capture mechanisms but also provide a framework for designing next-generation materials optimized for carbon capture applications.