

Mechanism and Kinetics of Carbon Dioxide Adsorption in Metal Organic Frameworks

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Metal-organic frameworks (MOFs) are a class of porous material possessing high crystallinity, which may be specifically targeted to carbon dioxide (CO₂) capture and separation in order to meet global targets associated with the reduction of CO₂ emissions from industrial sources. The selectivity of MOFs for CO₂ uptake over other gases (e.g. N₂) may be improved through the introduction of functional groups known to interact with carbon dioxide, e.g. amines, which react with CO₂ in an acid-base mechanism. The specific mechanisms and kinetics of CO₂ adsorption in such materials are not widely understood, but may be elucidated using neutron diffraction techniques. We have previously employed neutron diffraction in preliminary experiments to investigate the in situ concentration-dependent behaviour of CO₂ adsorption in [Ni₂(dobdc)] (dobdc = 2,5-dioxido-1,4-benzenedicarboxylate) and our recently published piperazine-functionalised framework [Ni₂(dobdc)(pip)_{0.5}].[1] We are further expanding our repertoire of materials and types of functional groups investigated using this method; in particular, we are investigating the interaction of CO₂ molecules with pendant functional groups such as sulfones, primary amines and secondary amines. The nature of these interactions may be explored using X-ray diffraction, gas sorption, gravimetric analysis using mixed gas streams and infrared spectroscopy; however, neutron diffraction presents a powerful and unique in situ technique to probe the temperature- and concentration-dependent behaviour of CO₂ binding to identify intermediate binding species, fully explore the binding mode of CO₂ and investigate structural effects in the adsorbate material. Mixed gas (CO₂/N₂) experiments will be used to explore the specificity of the host-guest behaviour in these functionalised frameworks. Based upon this data, it will be possible to explore specific chemical factors contributing to selective CO₂ capture, and in doing so contribute to the design of new materials or improve upon existing ones for CO₂ uptake.

[1] Das, A., Southon, P., Zhou, M., Harris, A., Kepert, C., D'Alessandro, D., Dalton Trans., 2012, Accepted 5/8/2012. DOI:10.1039/C2DT31112G.