Investigating carbon dioxide sorption properties of two isostructural Co(II) and Zn(II) mixed-ligand metal-organic frameworks containing imide based ligands

E. Batisai[1], L. Mbonzhe[1]

University of Venda, P. Bag X5050, Thohoyandou, 0950, South Africa

Eustina.Batisai@univen.ac.za

Metal–organic frameworks (MOFs) are porous materials composed of metal ions or clusters coordinated to organic ligands.[1] Due to their tunable structures and porosity, MOFs have attracted attention for a variety of applications, including gas storage, separation, sequestration, drug delivery, and catalysis.[2–5] Flexible MOFs or soft porous crystals, can undergo dynamic structural transformations in response to external stimuli.[6] This structural flexibility can enhance their performance, particularly in selective gas adsorption and sensing applications.[6] In this study, we present the synthesis, characterization, and carbon dioxide sorption studies of two isostructural, flexible MOFs: $\{[Co(OBZ)(L1)_{0.5}]\cdot 2DMF\}_n$ (1) and $\{[Zn(OBZ)(L1)_{0.5}]\cdot 2DMF\}_n$ (2). Where L1 is 2,7-bis(pyridin-3-ylmethyl)benzo[lmn][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone and H_2OBZ is 4,4′-oxybis(benzoic acid). The two MOFs were synthesized using the solvothermal method and characterized using single-crystal X-ray diffraction (SCXRD), powder X-ray diffraction (PXRD), and thermogravimetric analysis (TGA). Carbon dioxide sorption experiments were conducted up to 20 bar at 298 K. SCXRD analysis revealed that both MOFs are three-dimensional structures with 12% potential solvent-accessible volume. PXRD shows a structural change upon activation, which indicates structural flexibility. The CO_2 sorption isotherms of the two MOFs differ significantly. MOF 1 displays a type IV isotherm with pronounced hysteresis upon desorption. The MOF adsorbs 0.6 mmol g^{-1} CO_2 up to 15 bar after which the structure opens and adsorbs and additional 1.3 mmol g^{-1}, resulting in a total of 1.9 mmol g^{-1} at 20 bar. In contrast, MOF 2 shows a typical type I isotherm, reaching a maximum CO_2 uptake of 1.2 mmol g^{-1} at 20 bar.

[1] James, S. L. (2003). *Chem. Soc. Rev.* **32**, 276–288.

[2] Horcajada, P., Gref, R., Baati, T., Allan, P. K., Maurin, G., Couvreur, P., Ferey, G., Morris, R. E. & Serre, C. (2012). *Chem. Rev.* **112**, 1232–1268.

[3] Li, H., Li, L., Lin, R.-B., Zhou, W., Zhang, Z., Xiang, S. & Chen, B. (2019). *EnergyChem* **1**, 100006.

[4] Mbonzhe, L. & Batisai, E. (2022). *Results Chem.* **4**, 100648.

[5] Zhao, X., Wang, Y., Li, D.-S., Bu, X. & Feng, P. (2018). *Adv. Mater.* **30**, 1705189.

[6] Chang, Z., Yang, D.-H., Xu, J., Hu, T.-L. & Bu, X.-H. (2015). *Adv. Mater.* **27**, 5432–5441.