

# A new series of V<sup>IV</sup> based metal-organic frameworks having framework flexibility and high CO<sub>2</sub> adsorption capacity

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Flexible metal-organic frameworks (MOFs) form an interesting category of porous materials. The unique structural flexibility, so called *breathing* effect, is the key factor in the selective uptake of target gas molecules. Such structural transformation behavior may be applied in several domains such as gas separation, sensors, molecular recognition and drug delivery. The objective of this work was to synthesize new flexible MOFs and study the structural transformations upon gas, vapor and solvent sorption.

In this work, we report on new MOF structures bearing a V<sup>IV</sup>-carboxylate coordination unit and exhibiting flexibility under mild conditions. These new MOFs feature an extended MIL-47 structure, V<sup>IV</sup>O(NDC), denoted as COMOC-1<sup>1</sup>; and V<sup>IV</sup>O(BPDC), denoted as COMOC-2<sup>2</sup>, (NDC<sup>2-</sup> = 2,6-naphthalene dicarboxylate, BPDC<sup>2-</sup> = biphenyl-4,4'-dicarboxylate, COMOC = Center for Orded Materials, Organometallics and Catalysis, Ghent University). COMOC-2 shows a distinct breathing effect towards certain guest molecules. It shows a highly selective adsorption of CO<sub>2</sub> over CH<sub>4</sub> at workable temperatures (Fig.1). When the COMOC-2 structure contains mixed V<sup>III</sup>/V<sup>IV</sup> oxidation states, rather than solely V<sup>IV</sup> it becomes more difficult to trigger the flexibility in the framework. We have calculated the free energy profile as a function of the pore angle and found a tri-stable behavior of the material. Apart from a regular narrow pore form, also an overstretched narrow pore configuration was found theoretically.

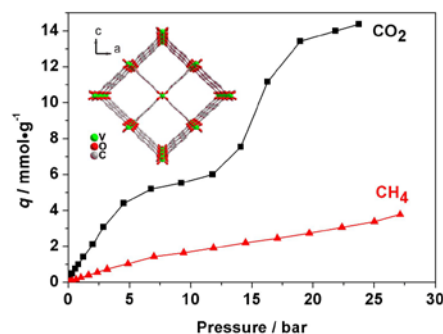


Figure 1. Adsorption isotherms of COMOC-2 for CO<sub>2</sub> and CH<sub>4</sub> at 265K.

## References

- (1) Y.Y. Liu et al., manuscript in preparation; (2) Y. Y. Liu et al., manuscript submitted to Angew. Chem. Int. Ed.

