



Robust and selective MOF for CO₂ conversion



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Introduction

High levels of CO₂ in the atmosphere have contributed negatively to climate change, global warming and ocean acidification. Therefore, here we provide a possible solution to help reduce these levels together with the production of CH₄, a high-value chemical intended for energy purposes. The approach we utilize was invented by our group, making use of a metastable intermediate HMOF to synthesize stable and functional phosphonate MOFs (*fig. 1*), known for having challenging synthesis but enabling an exceptional variety of coordination modes. This promotes high tunable pores which can be designed for specific applications such as the catalytic reaction of CO₂ molecules to produce CH₄ (Sabatier reaction).

Experimental Design

The aqueous solutions of Ni²⁺ and the chosen ligand are mixed dropwise whose precipitate is the Ni-hydrogen-bonded MOF (Ni-HMOF). After 24h at room temperature, the aqueous solution of Cr³⁺ is also added. 24h later, the precipitate Ni-Cr-HMOF is filtrated and washed. Then, it is heated up to 130°C to dehydrate it into the final Ni-Cr-MOF. Finally, it is placed in the vacuum oven at 110°C to remove any solvent molecules.

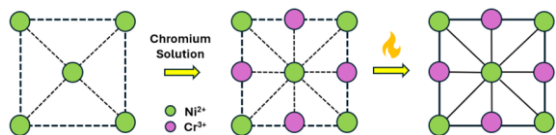


Figure 1. Scheme of the synthesis process.

Results

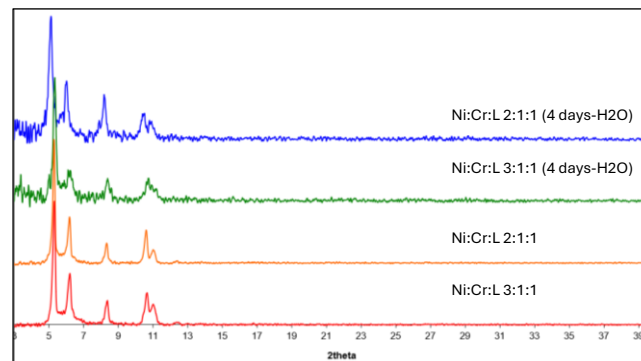


Figure 2. XRD spectra of the MOFs in water for 4 days.

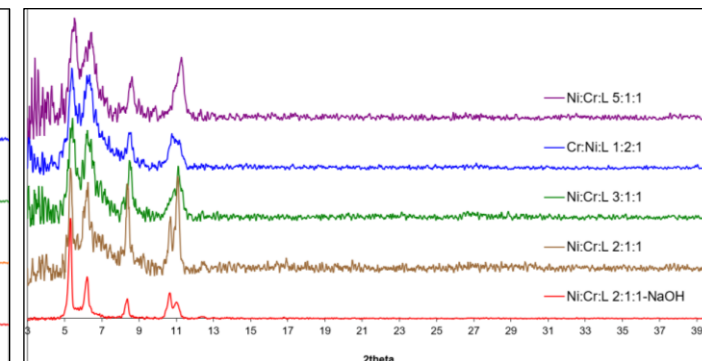


Figure 3. XRD spectra of the synthesized MOFs.

Final MOFs maintained their structure after being in water for 5 days thanks to Cr³⁺ which gives stability to the framework (*fig. 2*). Different ratios of Ni²⁺ (*fig. 3*) gave similar structures but with a higher metal dispersion which provides the catalytic properties for the CO₂ methanation. The addition of particular solvents to the synthesis yielded more crystalline MOFs with higher metal-ligand ratio as well as a higher thermal stability. The MOFs are stable up to 450°C. The preparation of this MOF is reproducible giving a yield up to 89%. The method of developing hydrogen-bonded MOFs first to be dehydrated finally into MOFs allows to introduce both Ni²⁺ and Cr³⁺ into a framework as if done directly to MOF only Cr³⁺ would be present due to its high enthalpy driving force.

Conclusions & Future Work

Thanks to this HMOF-to-MOF method, we are able to introduce two distinct metals in phosphonate MOFs with two purposes: giving stability and adding catalytic properties to the structure. The weak hydrogen bonds between the metals and the phosphonic acid linkers allow re-organization during the growth. Catalytic tests are currently under study.

Acknowledgements: Special thanks to the Department of Chemistry (UofC) and the support of the Alberta Innovates scholarship.