An Ultramicroporous Metal–Organic Framework for CO_2 uptake and conversion

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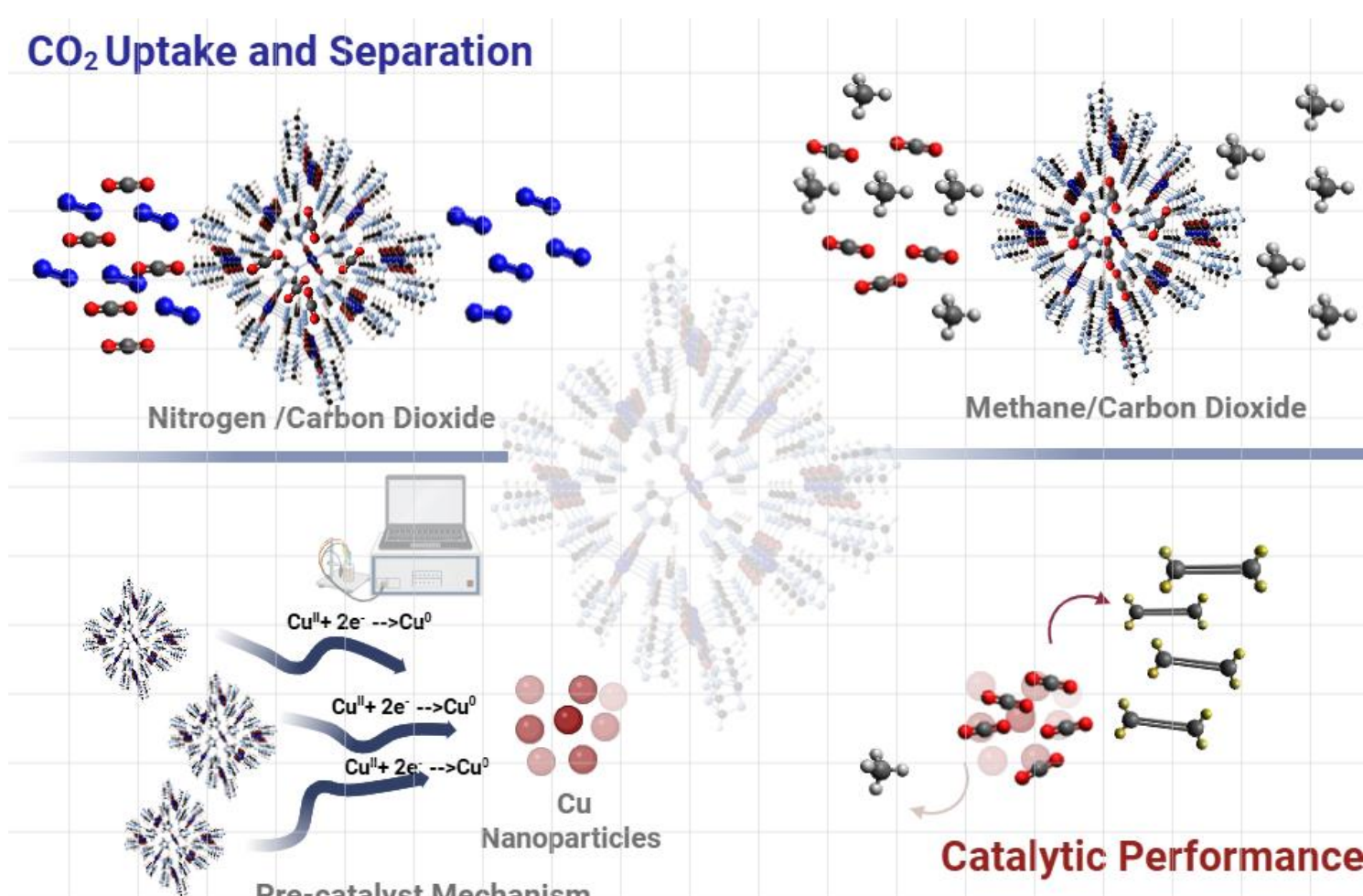[4]Institute of Chemical Research of Catalonia,Avinguda Països Catalans 16, Tarragona 43007, Spain
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INTRODUCTION & AIM

Capturing CO_2 from the atmosphere is a key challenge to mitigate global warming. Metal-Organic Frameworks (MOFs), thanks to their high porosity, tunable pores, and large surface area, are promising materials for CO_2 capture and separation. In particular, the ultramicroporosity (pore size < 0,7 nm) and the presence of nitrogen atoms are crucial requirements in the design of MOFs for CO2 separation. In 2021, some of us synthesized a new microporous MOF, formulated as $[Co(trz_2An)]n \cdot 3H_2O$ (CoMOF) [1], by combining 3,6-N-ditriazolyl-2,5-dihydroxy-1,4-benzoquinone, as organic linker, with Co^{II} metal nodes in a 1:1 stoichiometric ratio. This MOF showed a high capability to separate CO_2 from natural gas. On this basis, since cobalt is classified as a critical raw material, by using Cu^{II} metal ion, a new isomorphous MOFs able to separate and electrochemically convert CO_2

METHOD

Synthesis of CuMOF

$[Cu(trz_2An)] \cdot nH_2O$ has been synthesized optimizing the synthetic procedure reported In literature for $[Co(trz_2An)] \cdot 3H_2O$. $CuCl_2 \cdot 2H_2O$ (1.6mg, 0.05mmol) has been slowly added to a mixture of trz_2Anilate ligand (27.4mg, 0.05mmol), NaOH (8 mg, 0.10 mmol) and water (10 mL), and heated in a 20 mL autoclave under hydrothermal conditions at 140°C for 48 hours.
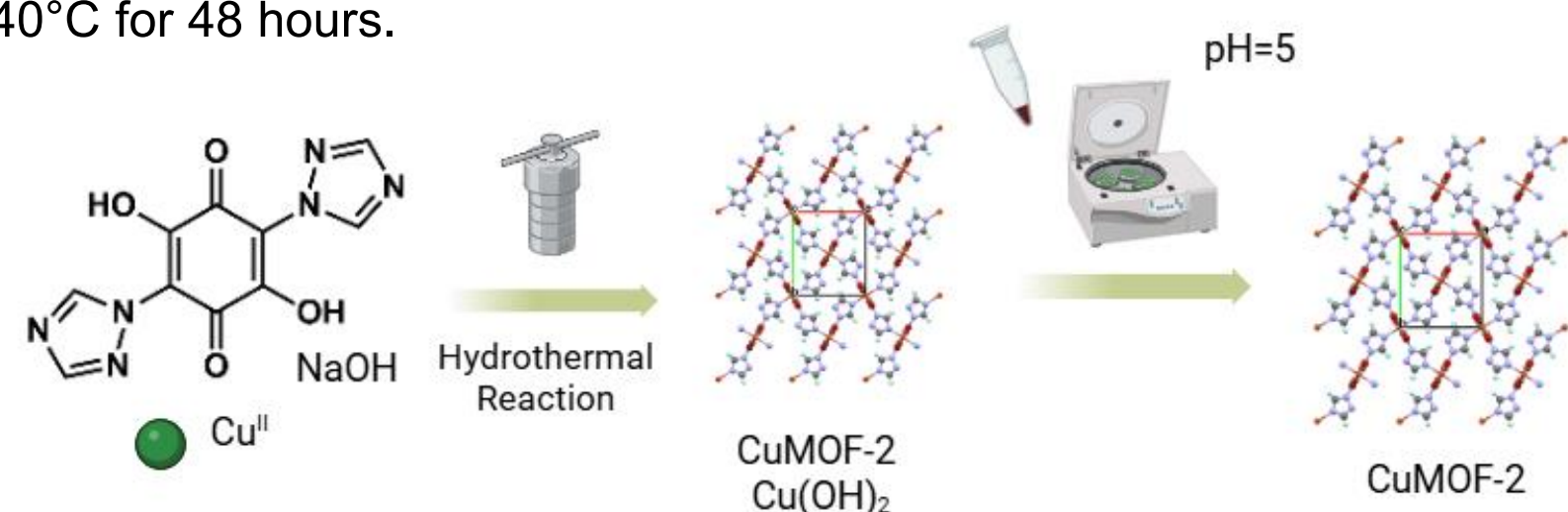
Dynamic CO_2 breakthrough measurements

These measurements were conducted in a homemade set-up using a fixed bed column with 1/2-inch tube (9.5 mm inner diameter) packed with approximately 0.98 g of CuMOF powder (0.87 g, once dehydrated), secured by glass wool at both ends to ensure complete column filling. Gas cylinders of CO_2 (Air Liquide, 99.998 %), CO_2/CH_4 mixture with composition of 50.3/49.7 % (Messer), N_2 (Praxair, 99.999 %), and He (Linde, 99.999 %) were used.

Chronoamperometry (CA) and chronopotentiometry (CP).

The same cell and potentiostat were employed for the CA and CP characterization. Both catholyte and anolyte compartments were connected to a peristaltic pump which forces the continuous flow of the KOH 1M electrolyte at a 1 mL min^{-1} rate. Gas-phase products were analyzed on-line by micro gas chromatography (μGC, Fusion, Inficon) with two distinct channels, containing a 10 m Rt-Msieve 5A column and an 8 m Rt-Q-Bond column, respectively.
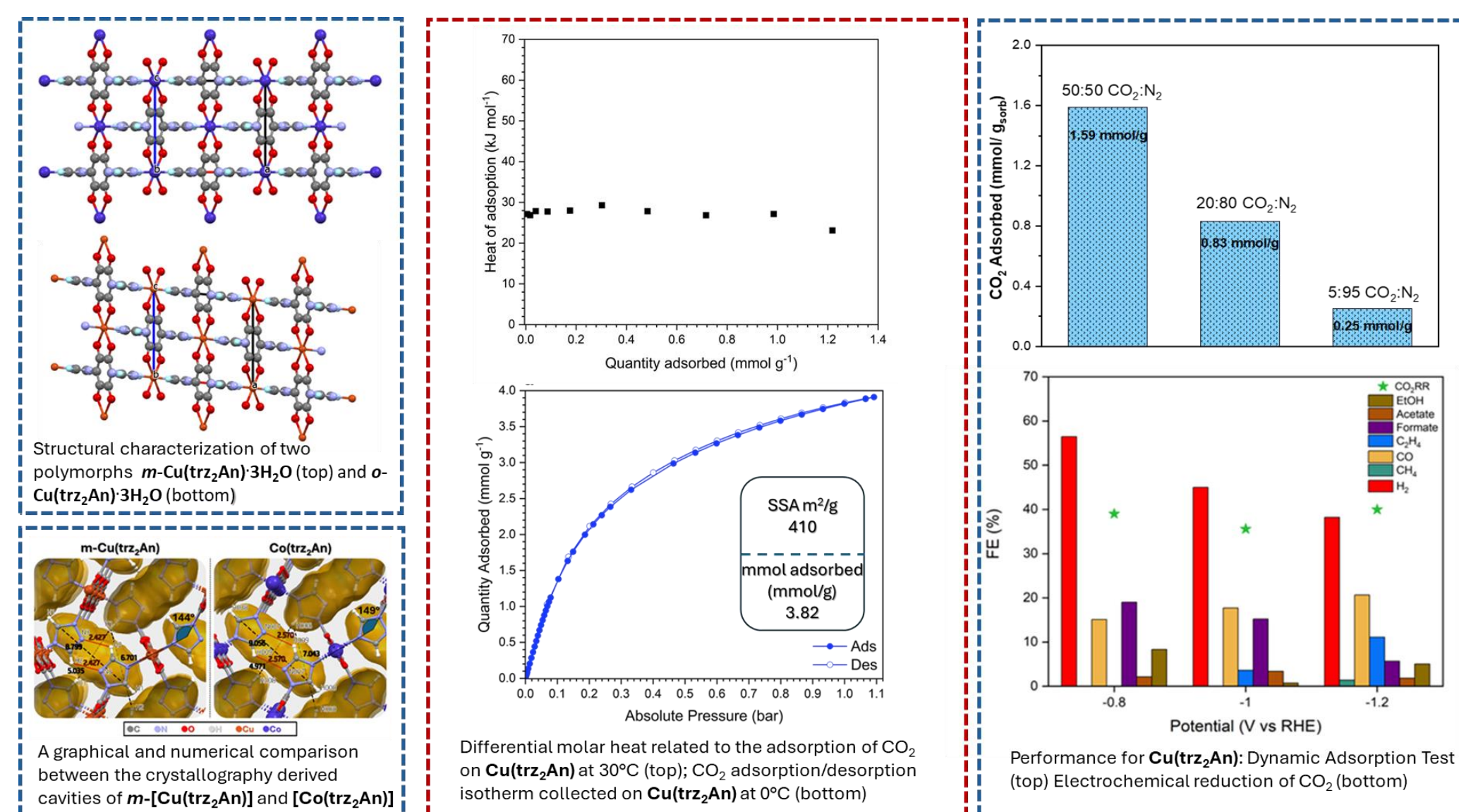
RESULTS & DISCUSSION

The optimized synthetic protocol, the structural characterization, the sorption and catalytic performances of the new Cu-based MOF. With the caveats, both $Cu(trz_2An)].nH_2O$ and $Co(trz_2An)].nH_2O$ exhibit similar accessible void space and pore sizes comparable with the kinetic diameter of CO_2. $Cu(trz_2An)]$ exhibits pore characteristics analogue to those of $[Co(trz_2An)]$, such as peanut-shaped cavities and a maximum pore diameter of approximately 3.4 Å, suggesting that both MOFs may act as sieves for N_2 and CH_4 (kinetic diameters: 3.3 Å for CO_2; 3.6 Å for N_2 and 3.8 Å for CH_4). The single component CO 2 adsorption isotherm at 0°C is indicative of a moderate adsorption capacity, reaching 3.82 mmolg -1 at 1 bar. The direct evaluation of the differential molar heat of CO_2 adsorption confirms a unique physisorption mechanism occurring, with an average value of 27.2 kJ mol -1. This analysis further confirms that the high selectivity with respect to N_2 towards CO 2 is related to a "size-based selectivity" due to the ultramicroporous channels of Cu(trz 2 An) rather than an "adsorptiveselectivity" based onf the chemical nature of the target gas. Dynamic Adsorption Measurements revealed i) a remarkable carbon dioxide uptake, ii) a high selectivity in CO_2 separation in CO_2:N_2 gas mixtures , iii) easy regeneration in mild conditions. The replacement of the CoII cation with CuII inherently opens new avenues in the field of CO_2 valorization through electrocatalysis. Recent studies involving in operando characterization techniques suggest that these compounds may more accurately be described as pre-catalysts, capable of generating ultra-small metallic copper nanoparticles, the true catalytic species, under applied reductive potential. [2] This change in the oxidation state should not be interpreted as catalyst instability, but rather as a deliberate strategy to create specific copper active sites that can selectively produce the most desirable reaction products.

Structural characterization of two polymorphs m-$Cu(trz_2An) \cdot 3H_2O$ (top) and o-$Cu(trz_2An) \cdot 3H_2O$ (bottom)

A graphical and numerical comparison between the crystallography derived cavities of m-$[Cu(trz_2An)]$ and $[Co(trz_2An)]$

Differential molar heat related to the adsorption of CO_2 on $Cu(trz_2An)$ at 30°C (top); CO_2 adsorption/desorption isotherm collected on $Cu(trz_2An)$ at 0°C (bottom)

Performance for $Cu(trz_2An)$: Dynamic Adsorption Test (top) Electrochemical reduction of CO_2 (bottom)

CONCLUSION

$[Cu(trz_2An)] \cdot nH_2O$ demonstrates: i) high selectivity and excellent separation efficiency for CO_2 in N_2/CO_2 and CH_4/CO_2 gas mixtures, with remarkable cyclability, and ii) promising catalytic activity for the electrochemical reduction of CO_2 (CO_2RR), selectively producing ethylene.Work can be anticipated in the direction of substituting copper with cheaper transition metal ions.

FUTURE WORK / REFERENCES

[1] M. Oggianu, M. L. Mercuri et al., *J. Mater. Chem. A*, 2021, **9**, 25189–25195.

[2] Z. Weng, H. Wang et al. *Nat. Commun.*, 2018, **9**, 41