

NOVEL ZINC OXALATE-TRIAZOLATE FRAMEWORK FOR SELECTIVE LOW-CONCENTRATION CO₂ CAPTURE

Klara Klemenčič¹, Andreas Puškarić^{1,2}, Matjaž Mazaj¹

¹National Institute of Chemistry, Hajdrihova 19, 1000 Ljubljana, Slovenia

²Ruđer Bošković Institute, Bijenička 54, 10000 Zagreb, Croatia

E-mail: klara.klemencic@ki.si

ABSTRACT

Metal-organic frameworks (MOFs) are highly structured materials with tunable porosity, enabling the potential for CO₂ capture. Nevertheless, many MOFs exhibit limited adsorption at low CO₂ pressures. Numerous studies report on strategies to enhance CO₂ adsorption capacity and selectivity, including the development of MOFs with open metal sites, ultra-microporous MOFs, and amine-functionalized MOFs. Introducing functional groups into the framework's surface effectively enhances gas adsorption in the low-pressure range (<1 bar). Herein, we report a novel MOF, obtained with the incorporation of zinc (II) ions, oxalic acid, and 1*H*-1,2,4-triazole-3,5-diamine, exhibiting a potential for efficient CO₂ capture under low pressure conditions.

Keywords: metal-organic framework, CO₂ capture, amine-functionalization.

INTRODUCTION

Metal-organic frameworks (MOFs) are a versatile group of porous materials known for their high degree of crystallinity and well-organized structures formed through the coordination bonds of metal ions or metal oxide clusters and organic ligands. What sets MOFs apart from other materials is their precisely regulated structural arrangements, providing tunable porosity and surface areas on a molecular level [1].

MOFs exhibit significant promise as adsorbents for CO₂ capture and separation owing to their exceptionally large surface areas, adjustable porosity, moderate CO₂ affinity, and suitable adsorption kinetics. While certain MOFs showcase outstanding CO₂ adsorption performance at elevated CO₂ pressure (*i.e.* MOF-177), many of these materials exhibit suboptimal CO₂ adsorption capacities at low CO₂ pressure, limiting their practical applicability. Enhancing gas adsorption and separation in the low-pressure region (under 1 bar) is effectively achieved through the modification of the pore surface by introducing functional groups into the framework. At low CO₂ pressures and ambient temperatures, the adsorptive characteristics are primarily influenced by the chemical nature of the pore surface. Materials with highly functionalized surfaces tend to exhibit superior high-capacity adsorption. Several studies have suggested that incorporating *i.e.* -NO₂, -NH₂, or -CH₃ functional groups results in the enhancement of the affinity toward CO₂ in some MOFs [2, 3].

The Calgary Framework-20 (CALF-20) is a MOF that has recently received great attention. CALF-20 is composed of layers of 1,2,4-triazolate-bridged zinc (II) ions, pillared by oxalate ions to form a 3D lattice and pore structure. It was recently demonstrated to be an excellent candidate for carbon capture MOF materials due to its high water resistance and strong CO₂ affinity. This has led to its deployment in a large-scale CO₂ capture facility at a cement production plant, where it has effectively captured up to 1 ton of CO₂ per day since early 2021 [4]. This is considered to be a rare example of a MOF transitioning from a lab-scale to an industrial application, meeting all the practical sorbent requirements.

Literature [5] also discusses a material composed of zinc (II) ions, oxalic acid, and 3-amino-1*H*-1,2,4-triazole (NH₂-CALF-20), exhibiting promising CO₂ adsorption behavior at low partial pressure. To explore the potential enhancements in CO₂ adsorption performance,

we aimed to introduce an additional -NH₂ functional group. Herein, we introduce a newly designed MOF based on zinc (II) ions, oxalic acid, and guanazole (1*H*-1,2,4-triazole-3,5-diamine) specifically tailored for CO₂ capture under lower pressure conditions.

EXPERIMENTAL

Synthesis of CALF-20: 0.2 g of zinc oxide was dissolved in 10 mL water. Then 0.16 g of oxalic acid and 0.34 g of 1*H*-1,2,4-triazole were added to the solution, followed by stirring for 15 minutes at room temperature. The resulting mixture was then transferred to a 23 mL Teflon autoclave and heated in a convection oven at 180 °C for 72 hours.

Synthesis of NH₂-CALF-20: the synthesis used a solvent-assisted ligand exchange method. Initially, 0.14 g of prepared CALF-20 was added in a 23 mL Teflon autoclave and dispersed in 7 mL of a methanol/water mixture (ratio 1:1) by stirring at room temperature for 15 minutes. Then, 0.17 g of 3-amino-1*H*-1,2,4-triazole was added to the mixture. After an additional 15 minutes of stirring, the mixture was heated in a convection oven at 120 °C for 72 hours.

Synthesis of Zn-oxalate-3,5-diamino-1,2,4-triazolate (NICS-24): the synthesis used a solvent-assisted ligand exchange method. Initially, 0.16 g of prepared CALF-20 was added in a 23 mL Teflon autoclave and dispersed in 7 mL of a methanol/water mixture (ratio 1:1) by stirring at room temperature for 15 minutes. Then 0.13 g of guanazole was added to the mixture. After an additional 15 minutes of stirring, the mixture was heated in a convection oven at 150 °C for 48 hours.

Characterization: Powder XRD data were collected on a PANalytical X'Pert PRO diffractometer using CuK α radiation ($\lambda = 1.5418 \text{ \AA}$) at room temperature in an angular range of 5 – 50° 2 θ with a step size of 0.034° per 100 s using a fully-opened 100 channel X'Celerator detector. Thermogravimetric measurements were performed on a TA Instruments Q5000 apparatus in air flow of 10 mL/min with a 10 °C/min ramp by heating the samples from 25 to 700 °C. Sorption data for CO₂ were collected on IQ Anton Paar adsorber. Before the measurements, samples were outgassed at 60 °C for 2 h and 100 °C for 10 h for CALF-20 and NH₂-CALF-20, for NICS-24 the outgas was performed at 150 °C for 4 h. Specific surface area was determined by BET theory based on CO₂ isothermal data measured at 273 K, whereas pore size distribution was determined by NLDFT using model which included CO₂ as adsorbate and carbon as adsorbent at 273 K.

RESULTS AND DISCUSSION

All prepared products were verified with XRD analysis. The high-resolution XRD powder pattern was used to determine the crystal structure of NICS-24 (Figure 1).

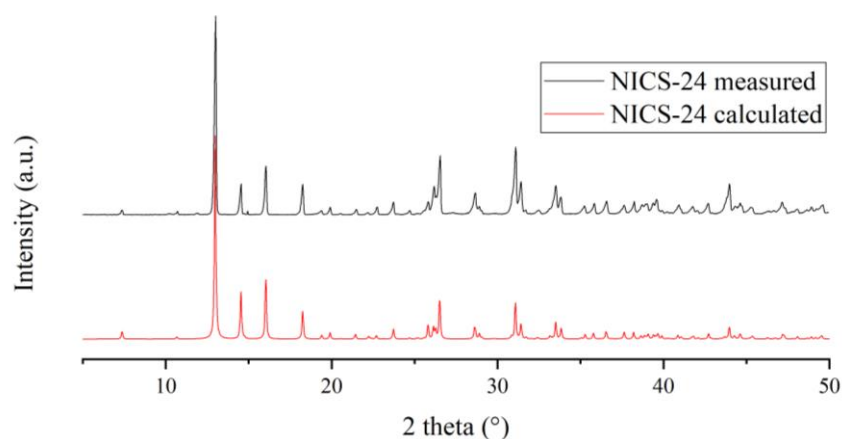


Figure 1. Comparison of X-ray diffraction patterns of NICS-24 as synthesized and calculated.

TGA analysis shows a gradual degradation of all synthesized frameworks around 450 °C resulting in the formation of a ZnO residue around 600 °C, respectively (Figure 2).

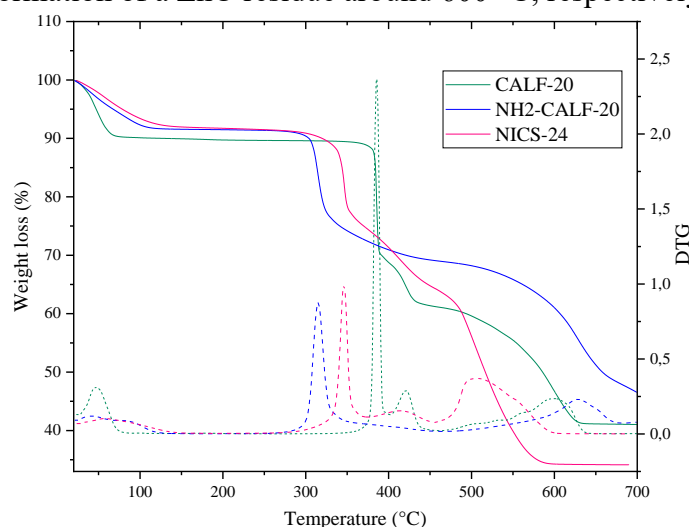


Figure 2. TG (full line) and DTG (dashed line) curves for CALF-20 (green), NH₂-CALF-20 (blue) and NICS-24 (pink).

The porosity properties of the prepared materials were investigated using CO₂ sorption isotherms measured from 273 K up to 313 K (Figure 3). CALF-20 displays a Langmuir-type isotherm consistent with previously published data [4]. In contrast, NH₂-CALF-20 exhibits a Type I isotherm, reaching saturation above 200 mbar, with a noticeable gate opening effect, leading to a significant increase in CO₂ adsorption between 300 - 500 mbar. Similarly, NICS-24 exhibits Type I isotherm as NH₂-CALF-20, with a slightly lower equilibrium uptake at saturation. The BET surface areas of the prepared materials and NLDFT profile peaks are depicted in Figure 4.

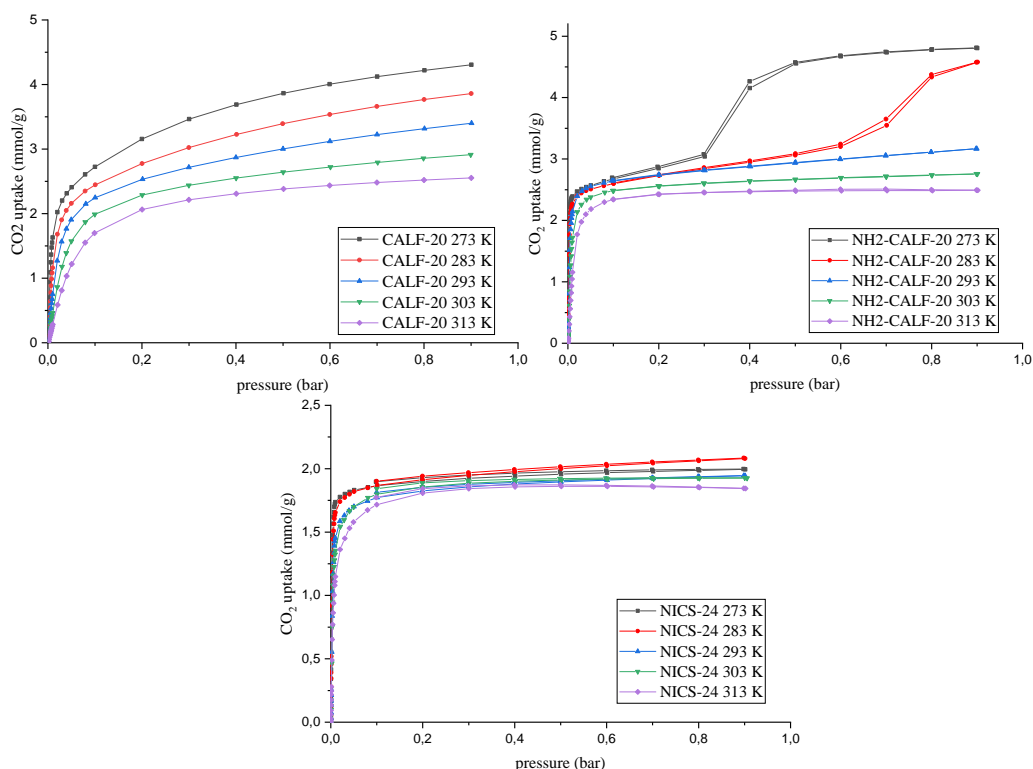


Figure 3. CO₂ isotherms of investigated materials measured at different temperatures (273 K-313 K).

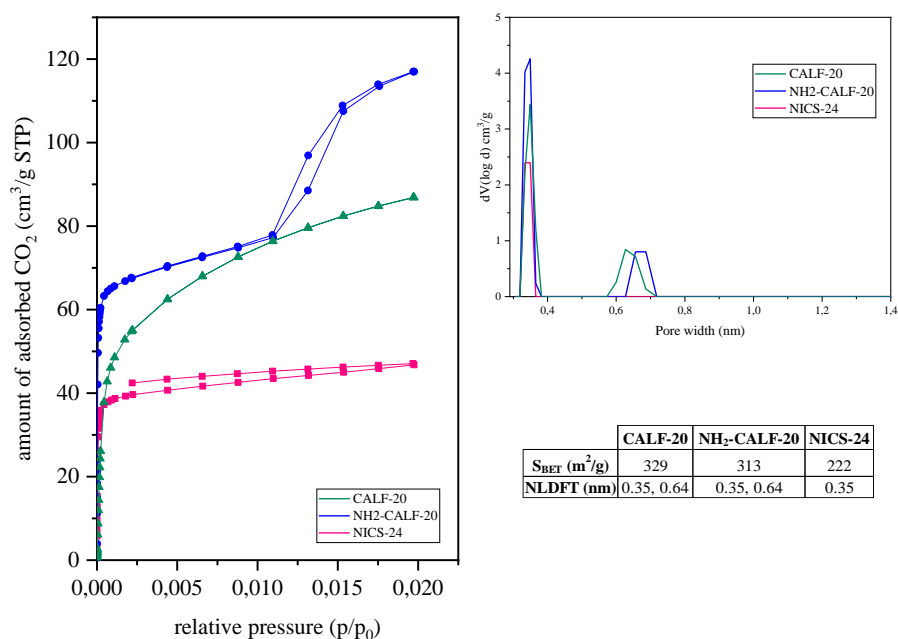


Figure 4. CO₂ isotherms measured at 273 K (left) with corresponding pore size distribution profiles and S_{BET} values (right).

CONCLUSION

MOFs represent a remarkable class of porous materials, distinguished by their precisely regulated structural arrangements, tunable porosity, and surface area. Their potential as CO₂ adsorbents, however, often faces limitations at low CO₂ pressures, prompting the exploration of novel strategies like functionalization for enhanced gas adsorption. The presented materials, CALF-20, NH₂-CALF-20, and NICS-24, exhibit distinct porosity properties and crystal structures, offering valuable insights for further optimization and application.

REFERENCES

- [1] Kenji Sumida, David L. Rogow, Jarad A. Mason, Thomas M. McDonald, Eric D. Bloch, Zoey R. Herm, Tae-Hyun Bae, and Jeffrey R. Long, *Chemical Reviews*, **2012**, 112(2), 724–781.
- [2] Stanislava Andonova, Elena Ivanova, Jie Yang, and Konstantin Hadjiivanov, *The Journal of Physical Chemistry C*, **2017**, 121(34), 18665–18673.
- [3] Jia Liu, Yajuan Wei, and Yanli Zhao, *ACS Sustainable Chemistry & Engineering*, **2019**, 7(1), 82–93.
- [4] Jian-Bin Lin, Tai T. T. Nguyen, Ramanathan Vaidhyanathan, Jake Burner, Jared M. Taylor, Hana Durekova, Farid Akhtar, Roger K. Mah, Omid Ghaffari-Nik, Stefan Marx, Nicholas Fylstra, Simon S. Iremonger, Karl W. Dawson, Partha Sarkar, Pierre Hovington, Arvind Rajendran, Tom K. Woo and George K. H. Shimizu, *Science*, **2021**, 374(6574), 1464–1469.
- [5] Ramanathan Vaidhyanathan, Simon S. Iremonger, Karl W. Dawson and George K. H. Shimizu, *Chem. Commun.*, **2009**, 5230–5232.