# NICS–24: A NEW MICROPOROUS MOF FOR SELECTIVE $CO_2$ CAPTURE

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## ABSTRACT

Metal-organic frameworks (MOFs) are porous coordination polymers comprised of metal nodes and ligands. Their significant attributes include a large surface area, inherent porosity, and customizable shapes and sizes of pores and cavities. This unique combination of features positions MOFs as promising materials for the efficient separation and storage of gases. It is well known that amine groups within MOFs positively impact $CO_2$ adsorption due to the specific interactions. In this research, we demonstrate that incorporating linkers with an increased number of $NH_2$ groups enhances $CO_2$ adsorption efficiency.

**Key words:** metal-organic framework, $CO_2$ capture, PXRD.

## INTRODUCTION

The increase of carbon dioxide ($CO_2$) concentration in the Earth's atmosphere, one of the greenhouse gases, has a great impact on the environment and climate change. In order to reduce $CO_2$ emissions, it is necessary to use energy more efficiently (and more conservative), adopt circular economy habits, use more renewable energy sources, commit to sustainable mobility, etc. One of the pathways for removal $CO_2$ from the atmosphere is its capture, utilization and storage (CCUS) – a process in which carbon dioxide is selectively separated, compressed and transported for a long-term storage or conversion [1]. The $CO_2$ level is also important in the closed spaces like offices, airplanes, submarines, spaceships, *etc.* as its increased concentration reduces air quality and can have harmful effect on human health [2]. Metal-organic frameworks (MOFs) are porous coordination polymers composed of metal nodes and ligands. Due to their large surface area and porosity, tailorable shape and size of pores and cavities, they have great potential to find use as adsorbents, catalysts, molecular sieves, functional materials etc. [3]. In last 20 years, MOFs have been systematically explored for separation and storage of many gasses and it has been found that they are well-suited materials for $CO_2$ adsorption [4]. In recent research, it was shown that a MOF composed from Zn(II), oxalate and 1,2,4-triazolate ions, $[Zn_2(C_2O_4)Tz_2]$ (CALF–20), is selective towards $CO_2$ in wet conditions, has good thermal stability, can be relatively easily regenerated and prepared from cheap starting materials [5]. Moreover, due to such properties it is being used as an active component in composite material for $CO_2$ capture in a cement plant [6].

Herein, we report the synthesis of a new MOF, NICS–24, composed of Zn(II), oxalate and 3,5-diamino-1,2,4-triazolate ions. The thermal and textural properties, along with $CO_2$ adsorption, were investigated and compared with those of compositionally similar frameworks, CALF–20 and CALF–15 ($Zn_2(C_2O_4)Atz_2$; Atz = 3-amino-1,2,4-triazole).

## EXPERIMENTAL

NICS–24 was synthesized *via* three routes: 1) by hydrothermal reaction of 1.9 eq (eq = molar equivalent) ZnO, 1 eq of $H_2C_2O_4$ and 3 eq of 3,5-diamino-1,2,4-triazole (Datz) for 3 days at 120 °C; 2) via the hydrothermal reaction of zinc oxalate dihydrate and 3 eq of Datz for 2 days at 180 °C; and 3) using the of solvent-assisted linker exchange (SALE) method from CALF–20 for 3 days at 120 °C, in methanol/water solvent mixture. In all procedures, reactants were stirred for 5–10 minutes before transferred to the oven. In the SALE method, an excess of

of 3,5-diamino-1,2,4-triazole (3 molar equivalents), with respect to CALF–20, was used. The white, polycrystalline product was separated from the reaction mixture either by filtration or centrifugation and dried at 60 °C overnight.

CALF–20 was synthesized using a known procedure [5]. CALF–15 was synthesized by a new method: 2 eq of ZnO, 1 eq of oxalic acid and 5 eq of Atz were suspended in water, stirred for 10–15 min and then heated for 3 days at 90 °C. White, polycrystalline product was centrifuged, washed with water and dried at 60 °C overnight.

PXRD data were collected on a PANalytical X'Pert PRO diffractometer using CuK$\alpha$ radiation ($\lambda$ = 1.5418 Å) at room temperature. Thermogravimetric measurements were done on a TA Instruments Q5000 instrument in an airflow of 10 cm$^3$ min$^{-1}$ with a heating rate of 5 °C min$^{-1}$, with final temperature of 750 °C. Sorption data for $CO_2$ and $N_2$ were collected on IQ3 Anton Paar instrument. Specific surface area was determined by BET method based on $CO_2$ isothermal data collected at 273 K in the relative pressure region between 0.024 – 0.009. Pore size distribution was determined by NLDFT using model with $CO_2$ as an adsorbate and carbon as an adsorbent at 273 K. Prior to the sorption measurements, samples were degassed at 60 °C for 2h and 100 °C for 10 h.

## RESULTS AND DISCUSSION

NICS–24 was repeatedly obtained as a microcrystalline product and therefore the structure had to be determined from PXRD data. Unit cell was indexed with TOPAS 4.2 [7], starting structure model determined by direct methods using EXPO2014 [8] and the structure was solved and refined using Topas Academic 6 [9]. Plot of Rietveld refinement, and crystallographic data are presented in Figure 1 and Table 1, respectively.



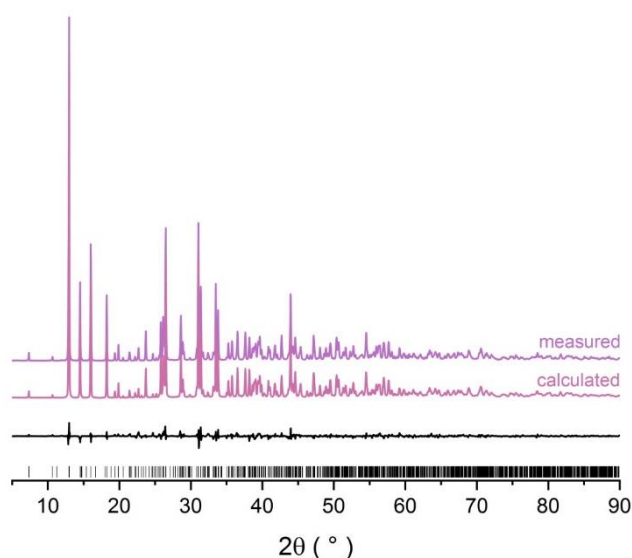|  | NICS–24 |
|---|---|
| Formula | $C_6H_8N_{10}O_4Zn_2$ |
| $M_w$ | 415.0 |
| Crystal system | Monoclinic |
| Space group | $P2_1/c$ |
| $a$ (Å) | 8.5703(3) |
| $b$ (Å) | 23.9768(9) |
| $c$ (Å) | 7.3145(3) |
| $\beta$ (°) | 104.892(2) |
| $V$ (Å$^3$) | 1452.6(1) |
| $Z$ | 2 |
| R$_{wp}$(all data) | 10.2 |
| R$_p$ | 7.6 |
| GOF | 3.2 |

Figure 1. Rietveld plot for NICS-24 structure. The difference plot is indicated by a black line and the positions of calculated Bragg reflections are shown as a vertical black markers.

Table 1. Crystal data and structure refinement parameters for NICS-24

In the structure of NICS–24, two crystallographically different Zn(II) centers are present. Zn1 is bound to four O atoms from two oxalate and two nitrogen atoms from two Datz ligands, creating distorted octahedral geometry around Zn1. On the other hand, Zn2 is tetrahedrally coordinated exclusively to Datz ligands [Figure 2, left]. Framework expands/propagates through three dimensions generating two square-shaped channels along [001] direction

[Figure 2, right], with the larger channel occupied by two molecules of water. Structure of NICS–24 differs from CALF–20 and CALF–15 frameworks whose structures have two-dimensional channels along [100] and [011] directions [5, 10].
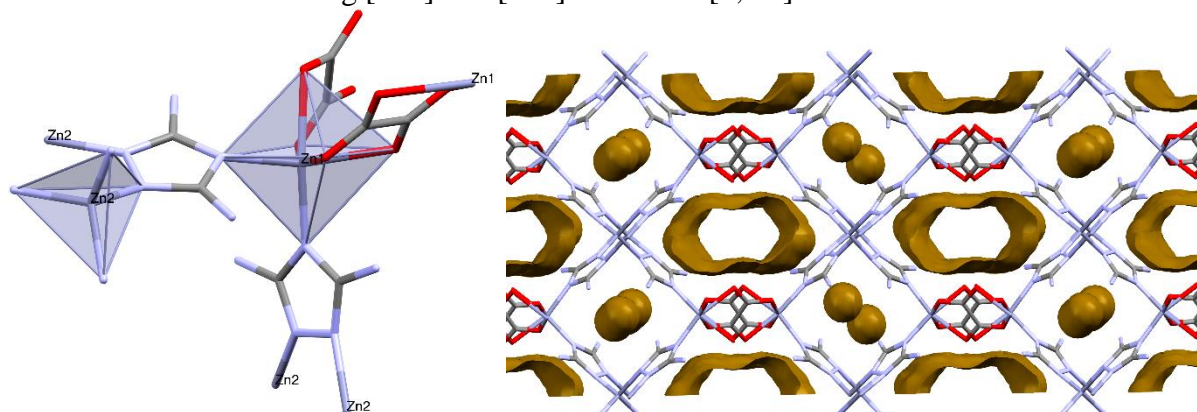


Figure 2, left: coordination environment around Zn ions in NICS–24. Right: the packing of NICS–24 framework with visualized voids/channels. Hydrogen atoms and water molecules are omitted for clarity. Atom color code: carbon – grey, oxygen – red, nitrogen – light purple, zinc (labelled) – dark purple.

Thermogravimetric analysis shows that thermal stability of all investigated materials is relatively similar, in the range 300 – 400 °C (Figure 3). The stability of the frameworks decreases in following order: CALF–20 > NICS–24 > CALF–15. The relative mass loss of NICS–24 up to 200 °C is 8.4% (theoretical mass = 8.7 %), corroborating the presence of two water molecules in the channels of the framework as observed in the crystal structure.
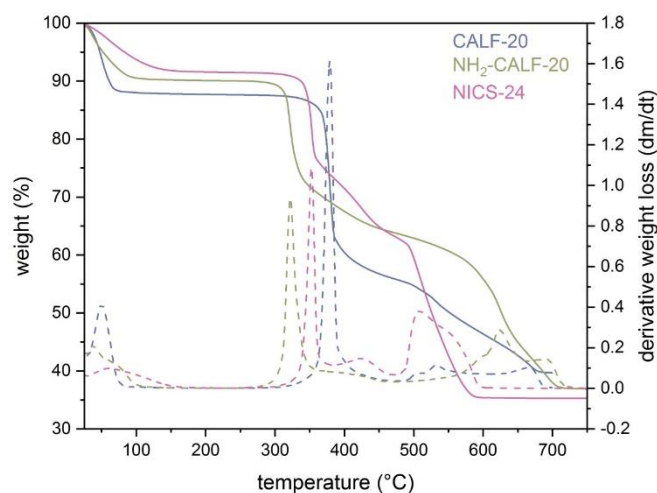


Figure 3. TG and DTG curves of investigated MOFs.

Textural properties (porosity) were determined by $CO_2$ sorption isotherms measured at 273 K for all samples (Figure 4, left) due to the inability of CALF–15 and NICS–24 to adsorb $N_2$ at 77 K. CALF–20 exhibits Langmuir-type isotherm which is in accordance with previously published data [5], steadily approaching the saturation with the final $CO_2$ uptake of 112 cm$^3$ g$^{-1}$ STP with BET surface area of 402 m$^2$ g$^{-1}$. CALF–15 shows Type I isotherm with gradual gate opening effect, reflected in significant increase of $CO_2$ adsorption in the $p/p_0$ pressure range between 0.01 – 0.015. After that pressure region, the isotherm curve follows the trend observed for the CALF–20. BET surface area of CALF–15 is somewhat lower (314 m$^2$ g$^{-1}$) compared to CALF–20 due to the narrower pores. NICS–24 exhibits similar Type I isotherm as with CALF–15, although with slightly lower equilibrium uptake at saturation, resulting in BET surface area of 274 m$^2$ g$^{-1}$. Pore size distribution, obtained by NLDFT, gives maxima at 3.6 Å and 4.9 Å confirming the presence of two types of channels in the structure of NICS–24.
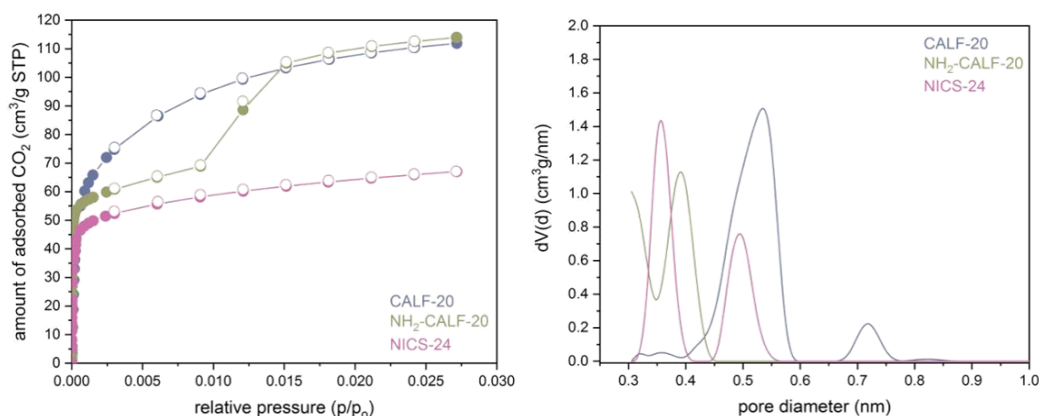
Figure 4. $CO_2$ isotherms at 273 K (left) and corresponding pore size distributions (right) of investigated MOFs.

## CONCLUSION

We synthesized a new metal-organic framework, NICS–24 ($Zn_2(C_2O_4)$(3,5-diamino-1,2,4-triazolate)$_2\times2H_2O$), through a hydrothermal reaction involving zinc oxide or zinc oxalate, oxalic acid and 3,5-diamino-1,2,4-triazolate. Additionally, this material can be synthesized by solvent-assisted ligand exchange from CALF–20, serving as a parent MOF. NICS–24 is a microporous compound, featuring two channels along the crystallographic *c*-axis that are suitable for selective adsorption of $CO_2$ over $N_2$ and $H_2O$. Its thermal and water stability, along with $CO_2$ selectivity makes this material a viable candidate for indoor $CO_2$ capture. Ongoing investigations aim to comprehensively characterize the properties of this material.

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