

IMPROVEMENT OF CO₂ ADSORPTION VIA LIGAND VARIATION IN ALUMINIUM-BASED METAL ORGANIC FRAMEWORK MATERIALS (AL-MOFS)

Tomaz Kos¹, Emanuela Žunkovič¹, Venčeslav Kaučič^{1,2}, Nataša Zabukovec Logar^{1,2}

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

²Center of Excellence Low-Carbon Technologies, Hajdrihova 19, 1000 Ljubljana

e-mail: tomaz.kos@ki.si

ABSTRACT

Metal–organic frameworks (MOFs) have emerged as a new class of crystalline porous materials and attracted tremendous attention from the scientific community in recent years¹. MOFs are constructed from inorganic vertices (metal ions or metal ion clusters) and bridging organic linkers connected to each other by coordination bonds. They have tuneable pores and functionalities, and usually exhibit very high surface areas. The potential applications of porous MOFs cover a broad range of fields like sorption, separation and catalysis. Physical and chemical properties of the linkers usually play a decisive role in the properties of these materials. In order to achieve functionality for specific application (like CO₂ sorption) the MOF's structure can be functionalized by targeted pre-synthetic ligand design or post-synthetic ligand modification^{2,3,4}.

We have studied the effect of ligand functionality on the CO₂ sorption in a selected Al-based MOF system (DUT-5)⁵. Biphenyl dicarboxylate was systematically replaced by bipyridine dicarboxylate in the reaction mixture, while all the other synthetic parameters were kept constant. The prepared samples were analyzed for their crystallinity, phase purity, elemental composition and porosity by using XRD, EDX, SEM and nitrogen physisorption.

The CO₂ sorption isotherms of selected products, which will be presented together with structure characterization data, show that the presence of bipyridine in the structure improved the final CO₂ uptake significantly in comparison with the pure biphenyl analogue.

Keywords: metal organic framework, MOF, CO₂ adsorption, DUT-5

INTRODUCTION

Metal–organic frameworks (MOFs) have emerged as a new class of crystalline porous materials and attracted tremendous attention from the scientific community in recent years¹. MOFs have infinite crystalline lattices which generally involve two main components of inorganic vertices (metal ions or clusters) and bridging organic linkers/struts a network connected to each other by coordination bonds (Figure 1).

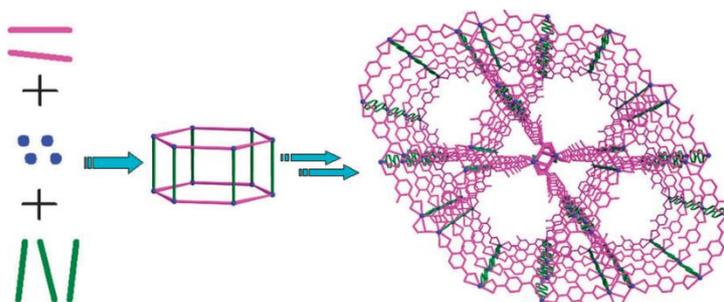


Figure 1. A general scheme of MOF synthesis (sticks represent organic linker and circle metal ions or clusters)
[1]

MOF have tuneable pores and functionalities, and usually exhibit very high surface areas. Physical and chemical properties of the organic linkers usually play a decisive role in the final properties of porous MOF materials and determinate their potential applications in fields like sorption, separation and catalysis. In case of application of MOF for CO₂ sorption its structure can be functionalized by targeted pre-synthetic ligand design or post-synthetic ligand modification. In order to achieve the desired functionality^{2,3,4}.

Aim of our work was to study the effect of ligand functionality on the CO₂ sorption in a selected Al-based MOF system (DUT-5)⁵ in order to improve sorption. In the reaction mixture ligand biphenyl dicarboxylate was systematically replaced by bipyridine dicarboxylate in the reaction mixture, while keeping other synthetic parameters constant (Figure 2).

EXPERIMENTAL

Synthesis of three Al-MOF samples proceeded according to the procedure described in the literature⁵ (Figure 2), with the exception that the ligand biphenyl-4,4'-dicarboxylic acid (BPDC) was systematically replaced by 0%, 8% or 15% of 2,2'-Bipyridine-5,5'-dicarboxylic acid (BipyDC) in samples A, B and C respectively (Table 1).

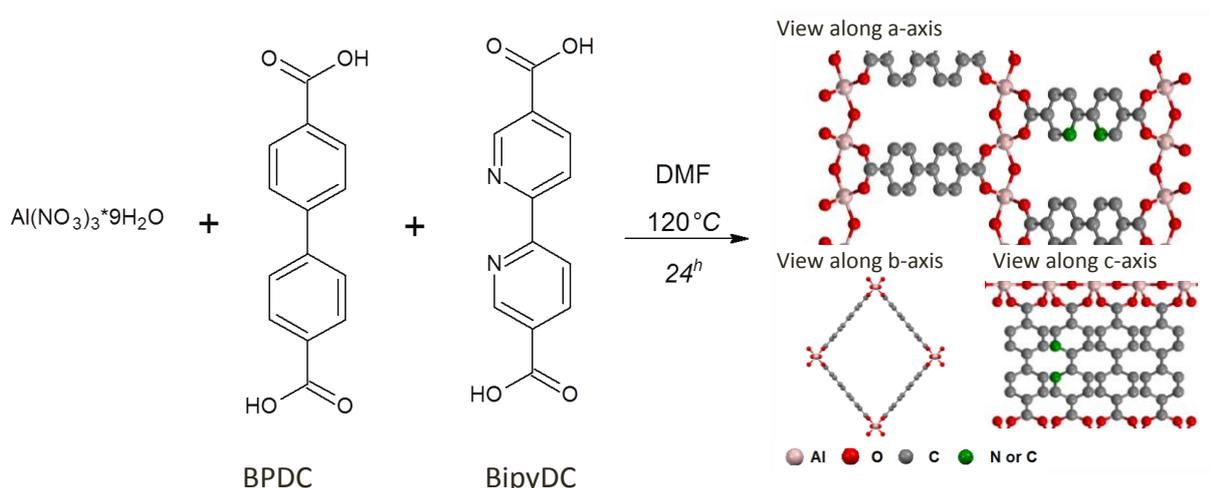


Figure 2. Schematic presentation of syntheses procedure and obtained structures (structures are isostructural with DUT-5).

Table 1: Synthesis details and sorption data for three samples with different content of bipyridile ligand in the synthesis; i.e. A=0%, B=8%, C=15%.

Sample	A	B	C
m(BPDC) : m(BipyDC)	100:0	92:8	85:15
BET surface ($p/p_0=0.3$) in m^2/g	1159	1404	1150
Excess CO ₂ adsorption at RT (295 K) and 40 bar in % (wt/wt)	57	72	64

RESULTS AND DISCUSSION

The prepared samples A, B, and C were analyzed for their crystallinity, phase purity, elemental composition and porosity by using XRD, EDX, SEM and nitrogen physisorption.

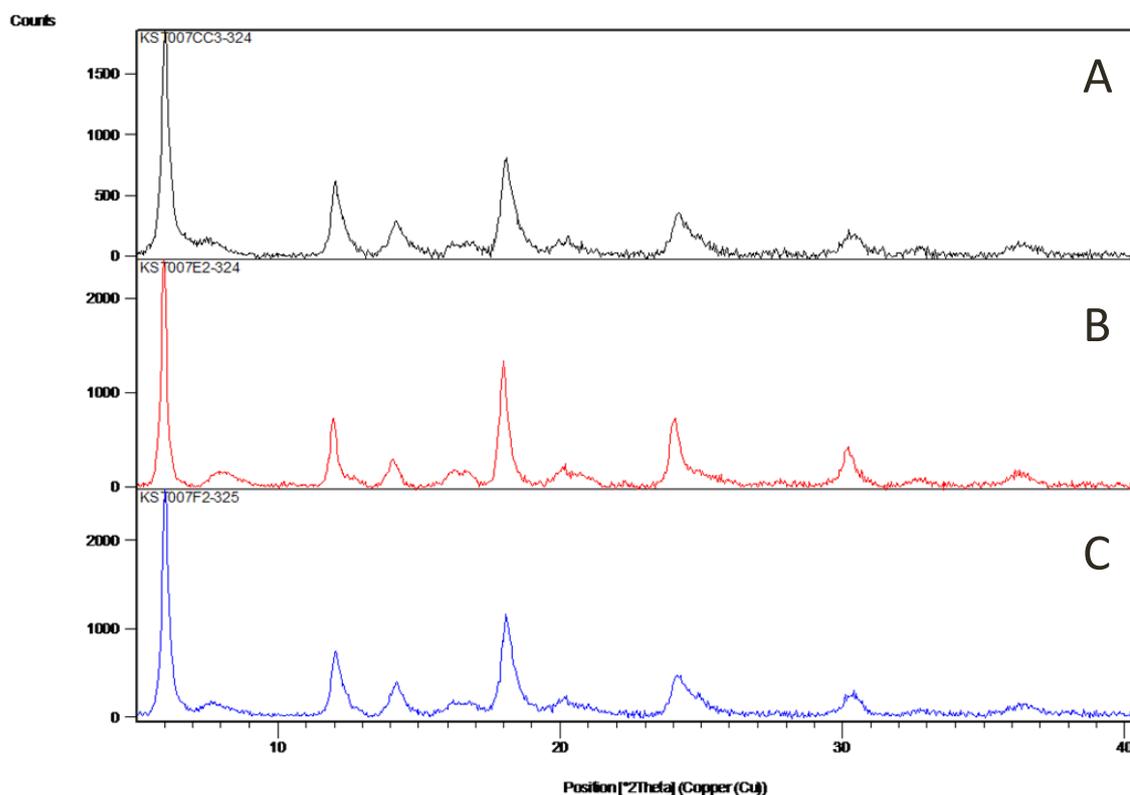


Figure 3. Powder X-ray diffraction data of the three samples A, B and C (see Table 1)

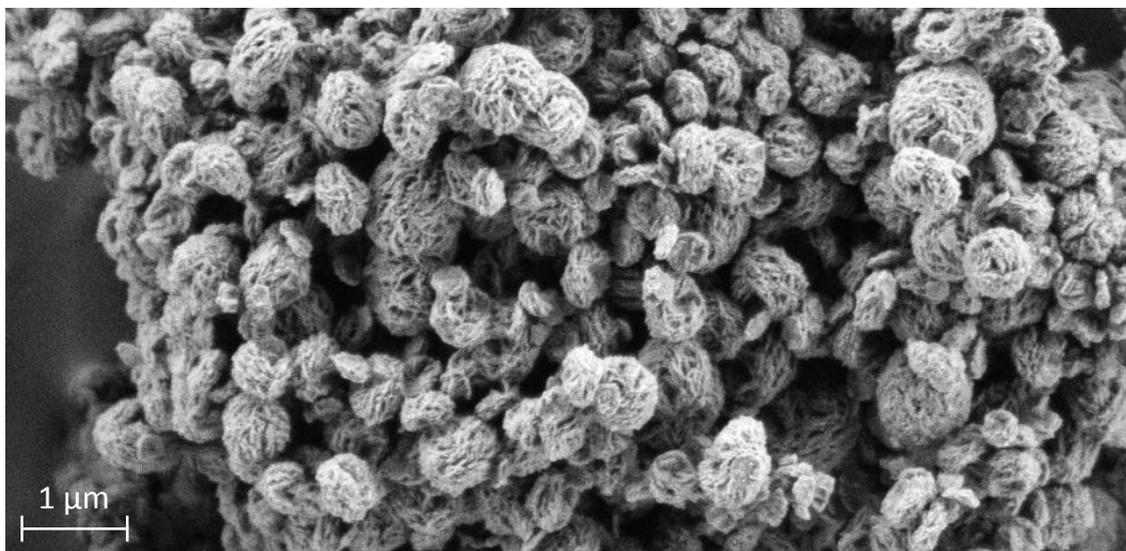


Figure 4. SEM micrograph of the sample B (morphology is similar in all three samples).

XRD and SEM results confirmed that structures of samples A, B and C are isostructural with the structure reported for DUT-5⁵. SEM picture shows the round shaped particles with evident porous structure and size around 500 nm.

CO₂ sorption data for samples A, B and C at room temperature is presented at Figure 5. The positive effect is most pronounced in sample B with 8% bipyridile ligand where a 25% improvement in CO₂ uptake was measured.

Sample C with higher amount of bipyridile ligand shows smaller improvement probably due to the presence of the excess bipyridile ligand in the MOF structure.

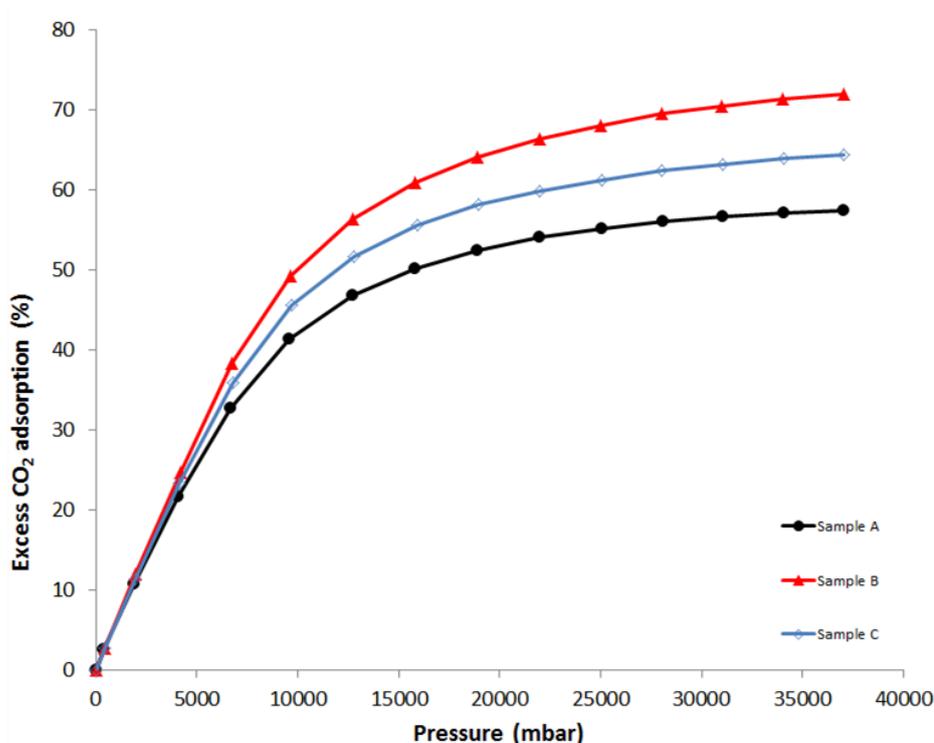


Figure 5. High-pressure carbon dioxide adsorption isotherms measured at 295 K for samples A, B and C

CONCLUSION

Compared to the pure biphenyl analogue, systematic introduction of the bipyridine ligand resulted in significant improvement in CO₂ uptake. The positive effect is most pronounced in sample B with 8% bipyridile ligand where a 25% improvement in CO₂ uptake was measured. The future activities will focus on the activation of the MOF structures in order to clarify the mechanism of improvement.

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