



MODULATED SYNTHESIS OF ZR(IV) METAL-ORGANIC FRAMEWORK BASED ON A DICARBOXYLIC ACID (H₂BDC)

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Metal-organic frameworks (MOFs) are an emerging class of crystalline porous materials constructed from metal nodes or clusters coordinated by organic linkers into extended periodic network structures with interest in various applications [1, 2, 3]. In this paper it is presented a fast modulated synthesis of micro/meso-sized ZrMOF, porous materials known as UIO-66, containing terephthalic acid (H₂BDC) as organic linker and an excess of ZrOCl₂·8H₂O salt precursor. Different amount of acetic acid were added in order to control the crystallite and particle sizes of the product [4]. An improvement of the surface area and a modification of diameter pore structure were observed by increasing of the modulator concentration.

Experimental part

Reagents

- Zirconium oxychloride octahydrate (ZrOCl₂·8H₂O);
- terephthalic acid (H₂BDC);
- N,N-dimethylformamide (DMF);
- Acetic acid (CH₃COOH);
- Methanol (MeOH)

- The synthesis of Zr-dicarboxylate MOFs (ZrMOF-eq of Aac) was based on a previously reported procedure (Chen et al., 2018);
- ZrMOFs were synthesized in a closed bottom flask by heating solutions containing Zr salts (ZrOCl₂·8H₂O) as precursor, terephthalic acid (H₂BDC) and acetic acid (Aac) as organic modulator.

Characterization methods

- FT-IR
- TGA
- N₂ adsorption-desorption isotherms (textural parameters, pore size distribution, microporosity percent)

Table 1. Amounts of reactants for each sample with different eq. of AAc

ZrMOF_eq samples	ZrMOF_0eq	ZrMOF_13eq	ZrMOF_26eq	ZrMOF_52eq	ZrMOF_104eq
ZrOCl ₂ ·8H ₂ O (g)	1.15	1.15	1.15	1.15	1.15
Terephthalic acid (H ₂ BDC) (g)	0.4	0.4	0.4	0.4	0.4
Acetic acid (Aac) [mL]	-	2.5	5.3	10.6	21.2
Dimethylformamide (DMF) [mL]	18	18	18	18	18

Results

FT-IR

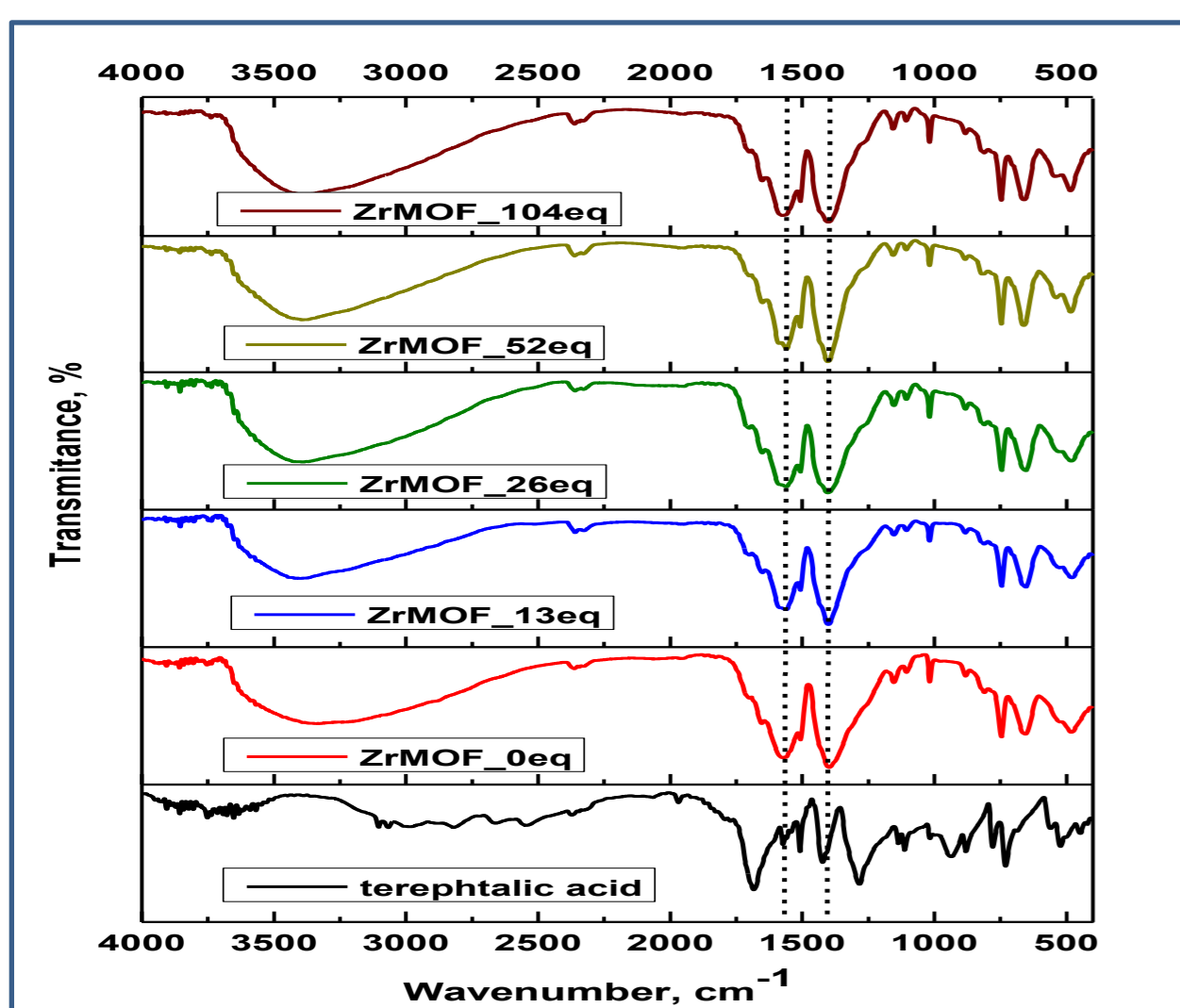


Figure 1. FT-IR of ZrMOF with different eq. of AAc

- 1580 cm⁻¹ reveal the presence of coordinated carboxylate groups by the asymmetric stretching vibrations;
- 1400 cm⁻¹ reveal the presence of coordinated carboxylate groups by the symmetric stretching vibrations;
- 1680 cm⁻¹ this band correspond to free ligand (H₂BDC);
- 1660 cm⁻¹ this band is attributed to the stretching modes of the carbonyl group (C=O) of the DMF residues entrapped inside the pores;
- 1156-1100 cm⁻¹ bands assigned to the C-H in-plan ring bending;
- 781-482 cm⁻¹ bands assigned to the C-H out of plane ring bending;
- 661-653 cm⁻¹ bands attributed to asymmetric vibration of the Zr-(μ₃-O) bridges in the framework building blocks;
- 500 cm⁻¹ stretching vibration of Zr-(OC) bonds.

TGA

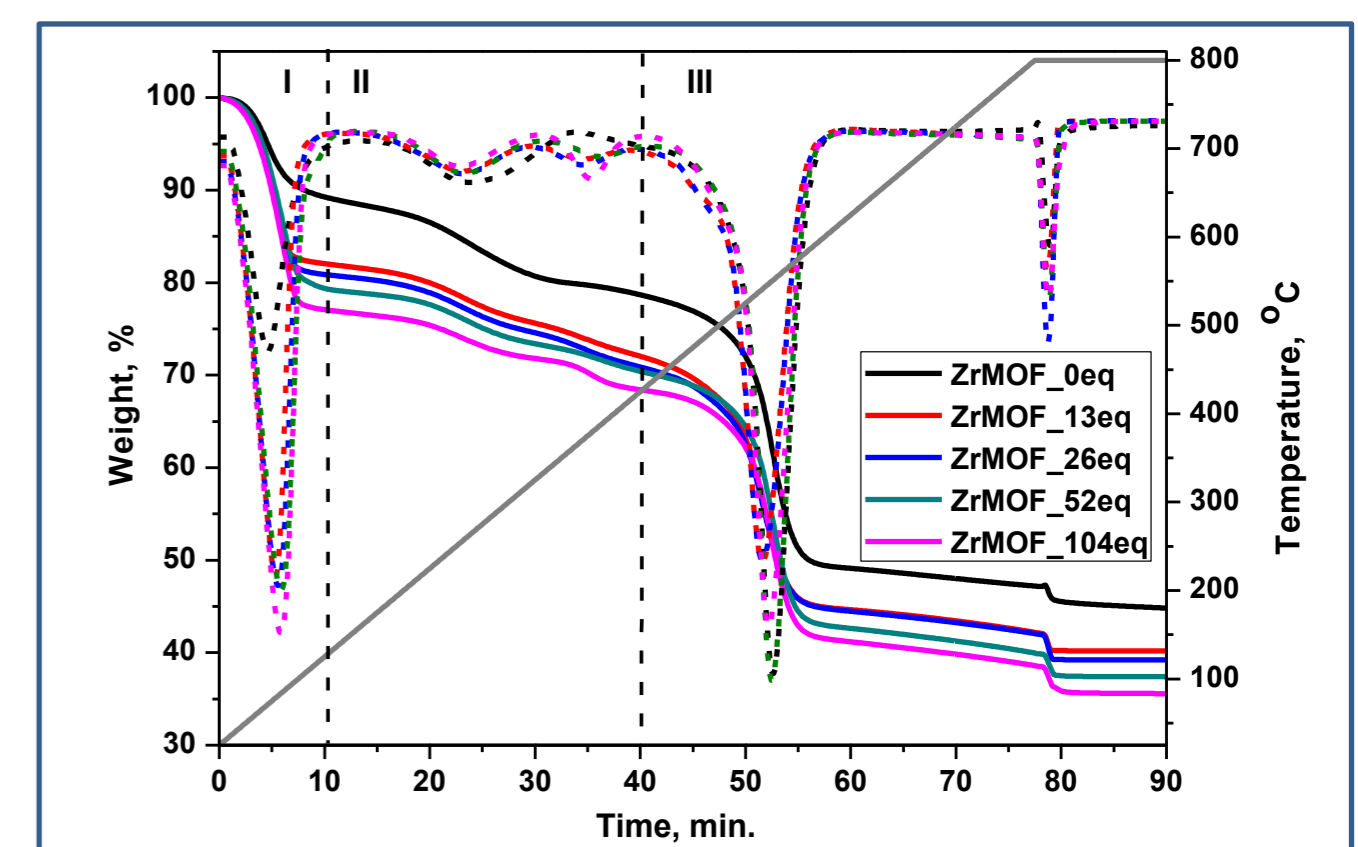


Figure 2. Normalized TGA (solid line) and DTA (short dash line) curves of the activated ZrMOFs after vacuum dried at 160°C

- 25-150 °C – this range of temperature is attributed to the loss weight of the physisorbed water;
- 150 °C – 330 °C - on this temperature interval range, the weight losses is associated with the dehydroxilation of the metal node;
- 330 °C – 420 °C – removal of AAc;
- 420 °C – decomposition of the terephthalic acid linker (H₂BDC) followed by the obtaining of ZrO₂ residue, after complete degradation of the organic moiety at 800°C.

- ZrMOF_0eq - type IVa isotherm, H4 type of hysteresis;
- ZrMOF_13eq – type IVa isotherm with H2b hysteresis;
- ZrMOF_26eq – type IVa isotherm with H1 hysteresis;
- ZrMOF_52eq – type Ib isotherm;
- ZrMOF_104eq – type Ib isotherm.

N₂ adsorption-desorption isotherms

Table 1. Textural parameters

ZrMOF_eq	DFT Pore diameter [nm]	BET surface area [m ² /g]	V-t method Micropore area[m ² /g]	Total pore volume [cm ³ /g]	Micropore volume [cc/g] Alpha -S
ZrMOF_0eq	4.57	373	261	0.20	0.11
ZrMOF_13eq	18.55	741	484	0.96	0.21
ZrMOF_26eq	28.36	703	382	1.16	0.17
ZrMOF_52eq	27.37	607	417	0.57	0.18
ZrMOF_104eq	3.77	692	486	0.46	0.22

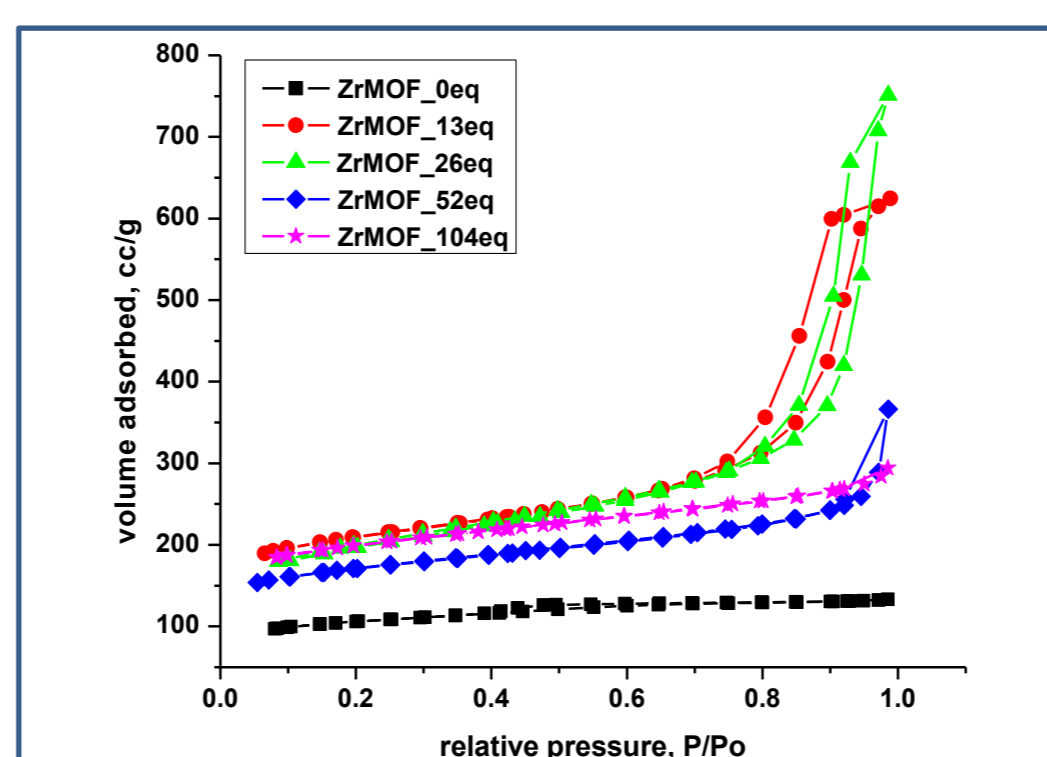


Figure 3. N₂ adsorption-desorption isotherms of ZrMOF samples

- The samples ZrMOF_0eq, ZrMOF_52eq and ZrMOF_104eq AAc exhibit unimodal pore size distribution in the micropore and mesopore region;
- Pore diameter ~4nm for ZrMOF_0eq and ZrMOF_104eq AAc;
- Sample ZrMOF_52eq AAc shows pore diameter of 27 nm;
- The sample ZrMOF_13eq AAc presents a bimodal pore size distribution with larger pores of 18 nm;
- The sample ZrMOF_26eq AAc exhibit multimodal pore size distribution with pore diameter of 28 nm.
- The highest mesoporosity percent was obtained for sample ZrMOF_26eq;
- The highest content of microporosity was observed for sample ZrMOF_0eq and sample ZrMOF_104eq AAc with a microporosity percent of ~70%.

Conclusions

- In excess of Zr(IV) precursor salt, we synthesized ZrMOFs by varying the amount of AAc (calculated by eq) from 0 to 104 eq, using as linker a dicarboxylic acid (terephthalic acid);
- The amount of modulator should be carefully chosen to control the surface area, pore volume and type of porosity;
- Thermogravimetric studies (TG) showed that by increasing the AAc concentration, the materials became more hygroscopic with some missing linker defects;
- N₂ adsorption-desorption isotherms exhibited that by increasing the amount of AAc, the surface area and pore diameter were improved;
- Concentration of AAc up to a certain value also, leads to an improvement of pore structure by producing mesopores at the expense of micropores.

Microporosity, %

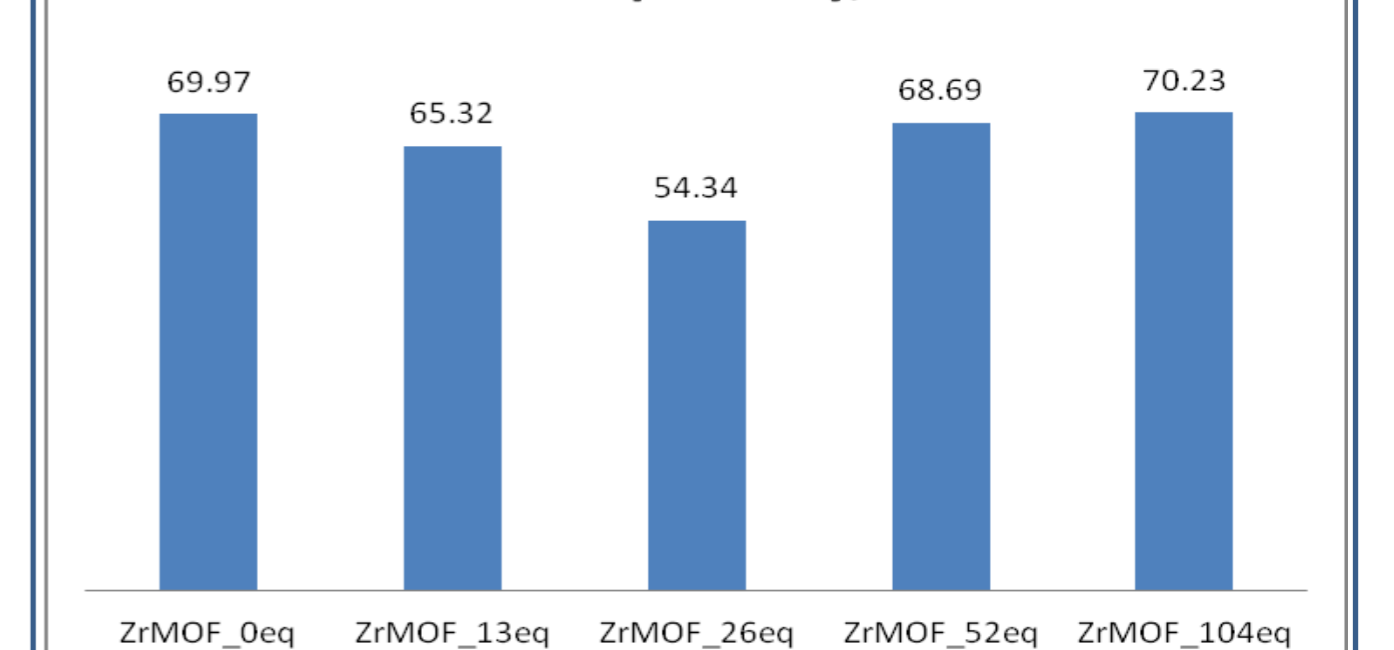


Figure 5. Microporosity percent calculated with Alpha-S method

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