



MICROWAVE ASSISTED SYNTHESIS OF MOF-5 AT ATMOSPHERIC PRESSURE

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MOF-5 was efficiently and quickly synthesized by a new method: microwave-assisted synthesis under atmospheric pressure, affording a microporous material with large surface areas. Its physicochemical and textural properties are similar to those synthesized by convective solvothermal synthesis.

INTRODUCTION

Metal-organic frameworks (MOFs) are zeolite analogue materials with high surface areas, permanent porosity and adsorption capacity. This new class of porous materials shows high promises in gas storage and separation applications as well as in catalysis, gas-sensing and photovoltaics.^{1,2}

Among metal-organic frameworks, MOF-5, $Zn_4O(1,4\text{-benzenedicarboxylate})_3$, originally described in 1999, is the most studied metal-organic framework and was intensively investigated due to its high surface area as well as the cheap raws.³ In 2003, the first investigation of hydrogen storage in MOFs was reported for MOF-5.⁴ Palladium loaded MOF-5 exhibits an increased hydrogen adsorption capacity and a high catalytic activity.⁵ Different synthetic methods were developed with the aim of obtaining high surface area and large pore volume. Typically, MOF-5 can be synthesized by mass transfer techniques (e.g. diffusion of amine into reaction mixture),⁶ solvothermal methods⁷⁻⁹ or atmospheric pressure synthesis.¹⁰⁻¹² Due to the

need of synthesis time reduction and increase of energy efficiency, new solvothermal techniques using microwave irradiation¹³⁻¹⁶ and ultrasounds were developed.¹⁷ The MOF-5 syntheses at ambient pressure presented in literature were activated by convective heating.^{10,11}

This work presents a new synthetic method of MOF-5: the microwave assisted synthesis at atmospheric pressure. This method combines microwave heating advantages such as: reproducibility, faster kinetics, selectivity of phase, rapid heating and shorter reaction time, with the advantage of atmospheric pressure synthesis that doesn't imply the heating of a closed bottle containing nitrates and volatile solvents. A comparison between a MOF-5 sample prepared by our method and a MOF-5 sample prepared by convective solvothermal method was also made.

RESULTS AND DISCUSSION

MOF-5, further on named MOF-5(μ w), was produced for the first time by applying microwave

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technique for synthesis at ambient pressure. The activation of the reaction was performed with a large-band of microwave frequencies pulse and a pulsatory regim of power. The patented device¹⁸ for microwave treatment, conceived and built-up at National Institute for Research and Development of Isotopic and Molecular Technologies (INCDTIM, Cluj-Napoca), is equipped with a temperature controller and an adjustable power output (maximum 900 W at 2450 MHz). The processing device generator emits repetitive pulses power in each second of treatment time, with controllable filling factor and large-band of microwave frequencies of each microwave pulse. Both the total pre-settled treatment time and/or reaction mixture temperature control the power of microwave in probe. The reaction temperature is controlled by a specific microwave temperature sensor who works in a temperature range of (-55)-(+125) °C with 0.1 °C sensibility. The treatment precinct is a mono-modal microwave cavity with coaxial geometry. The cavity was projected to present the maximum volume for a mono-modal distribution at 2.45 GHz frequency. The mono-modal distribution of microwave power density allows a rapid treatment with maximum energy transfer. For MOF-5(μ w) synthesis the filling factor of the microwave pulse was set at 40%, the

temperature at 80°C and the total length of the process at 210 seconds.

For comparison, MOF-5 hereafter denoted MOF-5(s), was also prepared under solvothermal conditions, by convection heating in an oven.¹⁹

A total time of 7 h at 100°C is needed to obtain MOF-5 under solvothermal synthesis, while MOF-5(μ w) required only 84 seconds effective microwave exposure at 80°C to make crystals with consistent properties.

Both MOF-5 products were characterized by powder X-ray diffraction, infrared vibrational spectroscopy, thermogravimetric analysis and nitrogen adsorption/desorption at 77K.

XRD patterns for MOF-5 samples, synthesized under microwave irradiation and by solvothermal method, are shown in Fig. 1, and are compared with pattern simulation from the crystal structure.¹⁷ Both sample patterns show good overall agreement with the simulated one, confirming that samples, MOF-5(μ w) and MOF-5(s), are pure MOF-5 materials. The XRD pattern of MOF-5(μ w) exhibits broader Bragg reflections than MOF-5(s) pattern, indicating the presence of smaller crystallites. Although we tried to minimize exposure of samples at atmospheric moisture, a peak appears at $2\theta = 8.8^\circ$ in the patterns of MOF-5(μ w) and MOF-5(s), which is associated with water effect on MOF-5 structure.^{20, 21}

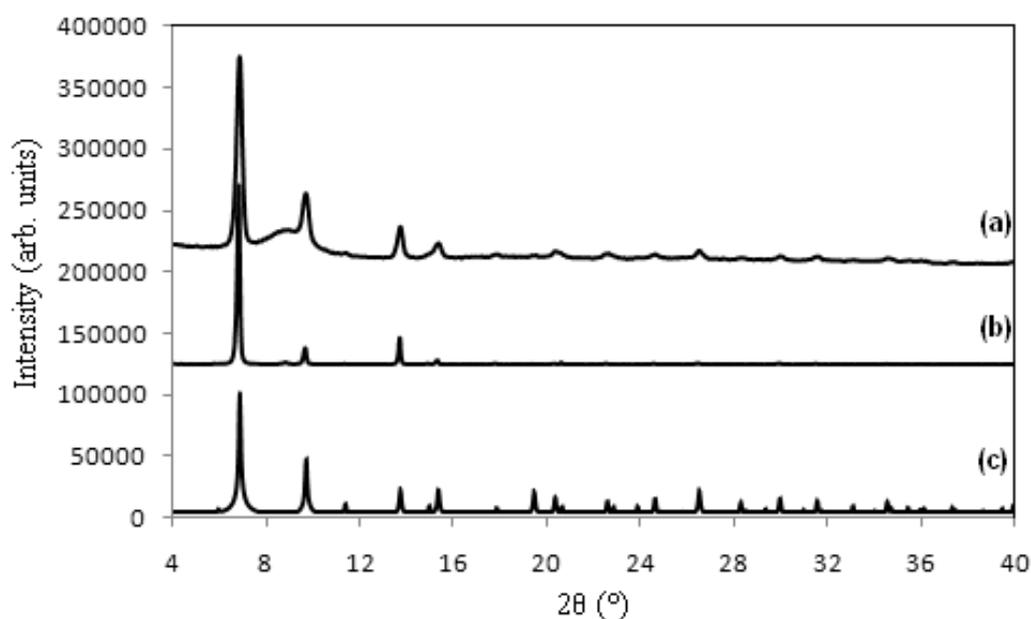


Fig. 1 – MOF-5 XRD patterns: (a) microwave synthesized, (b) solvothermal synthesized and (c) simulated from single crystal X-ray data.²⁰

MOF-5(μ w) is also characterized by IR spectroscopy. Its IR spectrum shows the expected strong absorptions for symmetric and anti-symmetric stretching vibrations of COO from carboxylates at 1595 and 1393 cm^{-1} , respectively, confirming the presence of the dicarboxylate groups within MOF-5(μ w).

The thermal stability was studied using thermogravimetric analysis (Fig. 2), which also shows that both solvothermal and microwave MOF-5 probes are similar. It must be mentioned that MOF-5(s) specimen was degassed at 120°C for 24 h. Therefore, it showed negligible weight loss until a dramatic weight loss occurring in the

temperature range of 425-500°C, due to decomposition of the MOF-5 crystals. For the MOF-5 (μ w) probe degassed at 100°C for 5 h, the thermogram shows two additional slopes of weight loss. The first weight loss (1.6 %) occurred between 50 and 120°C is attributed to a theoretical loss of 1.8% for one water molecule, while the second weight loss (19.2%) situated between 120 and 175°C corresponds to a theoretical loss of 19.9% for 0.5 water and 2.5 DMF molecules. The major weight loss (49.5%) starting at $\sim 350^\circ\text{C}$ corresponds to the decomposition of MOF-5 framework.

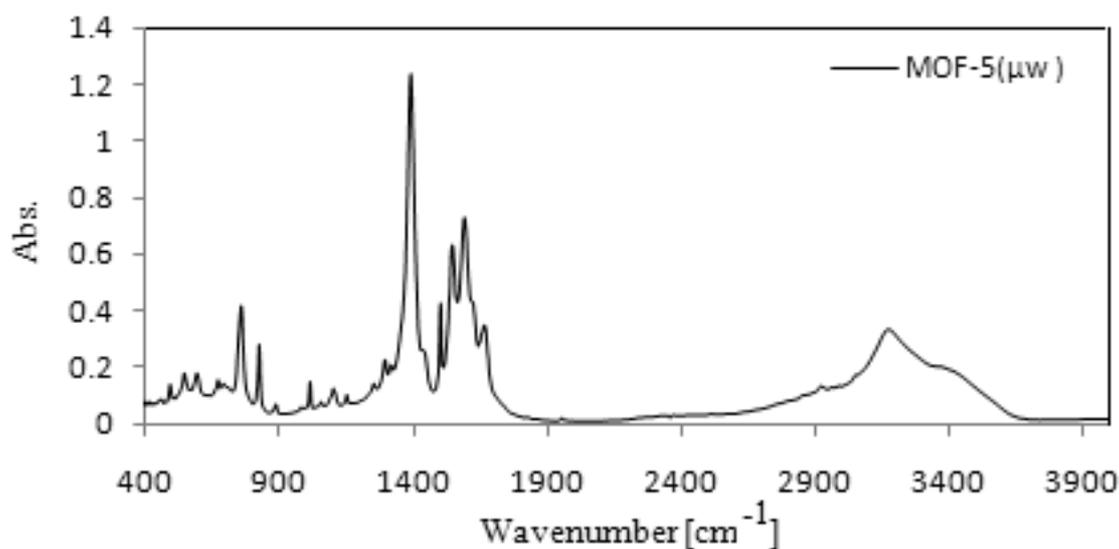


Fig. 2 – IR spectrum of MOF-5(μ w).

To verify the porosity of MOF-5(μ w) and MOF-5(s) samples, nitrogen gas sorption isotherms were measured at 77K. Prior to gas sorption measurements both MOF-5 samples were degassed at 220°C under vacuum for 3 h. Nitrogen adsorption/desorption isotherms of the activated samples are presented in Fig. 3; both samples exhibited type I isotherms with no significant hysteresis. BET and Langmuir surface areas of MOF-5(μ w) were 2489 and 2880 m^2/g , respectively, with 1.06 cm^3/g pore specific volume, whilst the corresponding values for MOF-5(s) were 2680 and 3153 m^2/g ,

respectively, with 1.14 cm^3/g pore specific volume. The values of surface area (BET and Langmuir) for MOF-5(s) were slightly larger than those for MOF-5(μ w), but both of them are in the range of the reported values.

The quantitative evaluations of both MOF-5 sample microstructures were made by Horvath–Kawazoe method and they indicate that the pore diameter of MOF-5(μ w) is ca. 8.4 Å which is consistent with MOF-5(s) diameter of ca. 8.34 Å. The pore size distributions for MOF-5(μ w) and MOF-5(s) are displayed in Fig. 4.

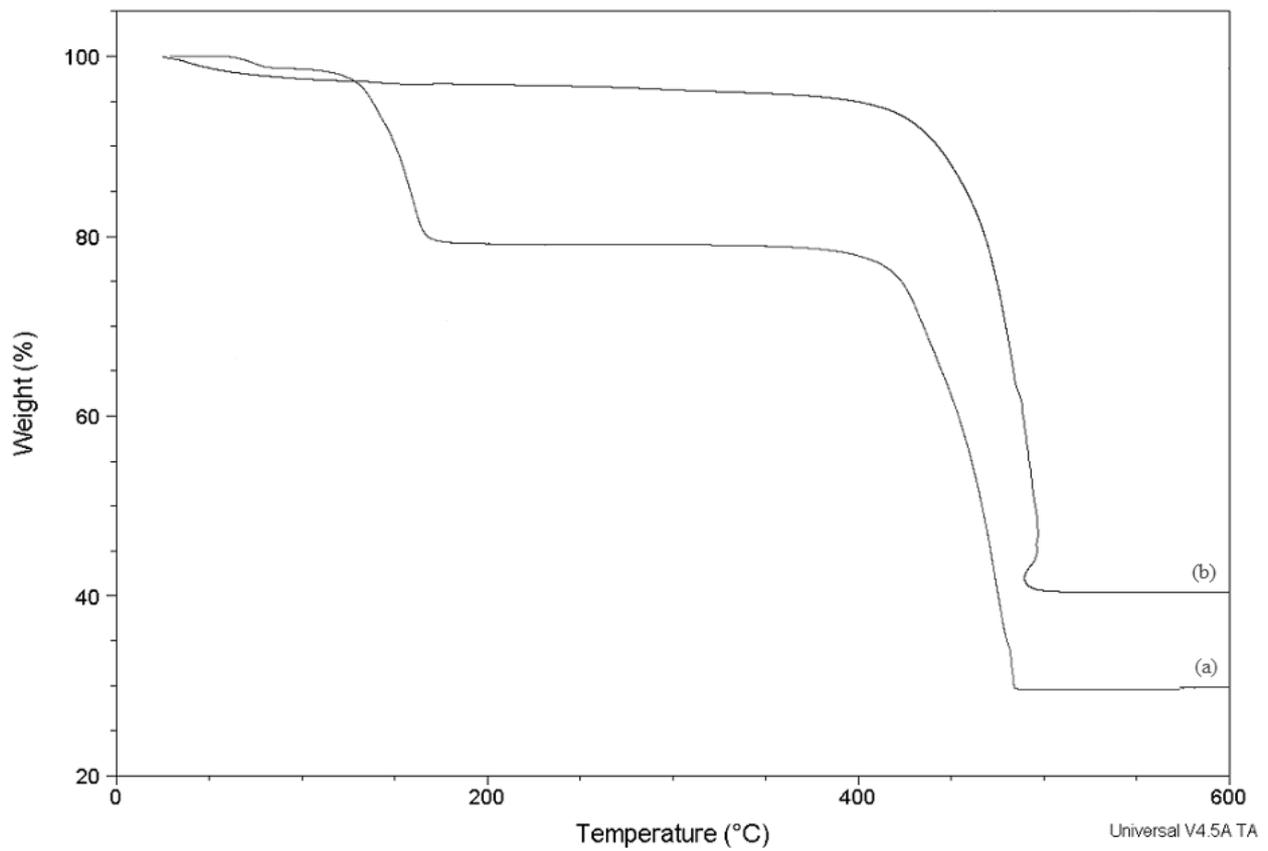


Fig. 3 – TGA curves for (a) MOF-5(μw) and (b) MOF-5(s).

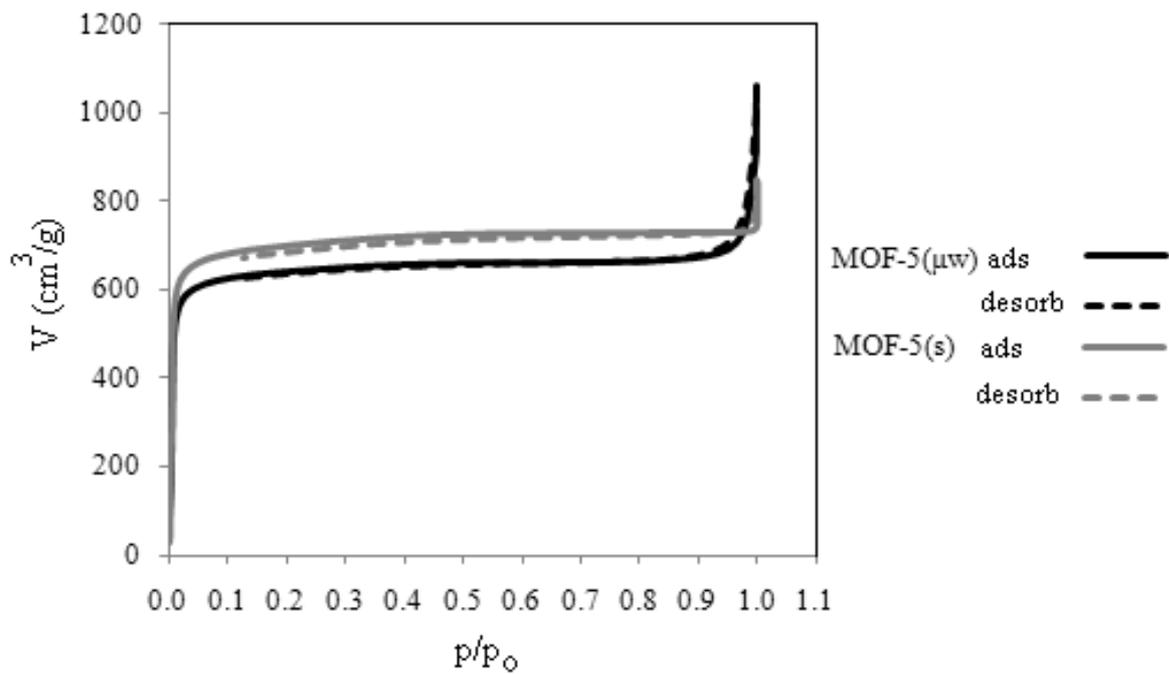


Fig. 4 – Nitrogen adsorption/desorption isotherms of MOF-5(μw) (black) and MOF-5(s) (grey) measured at 77K.

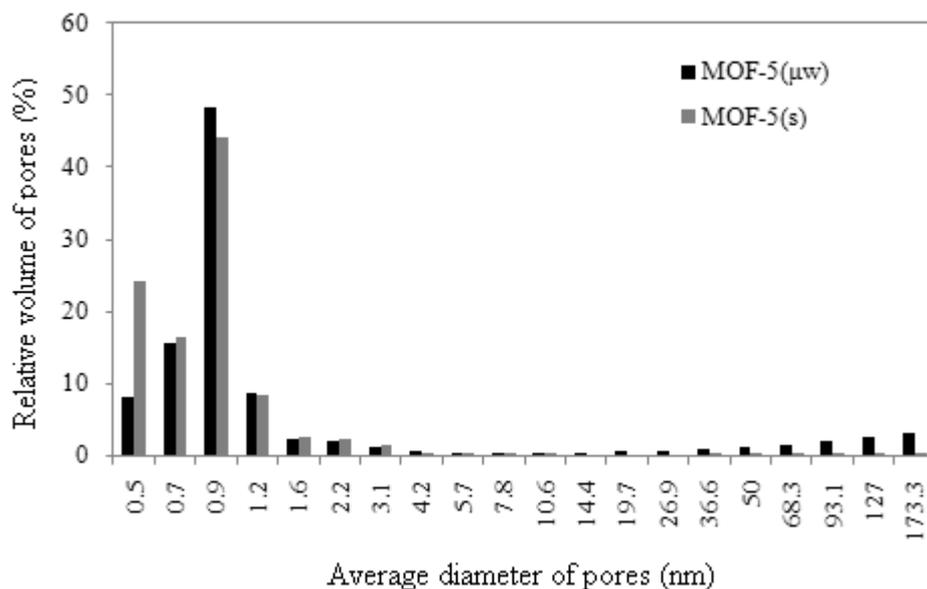


Fig. 5 – The pore size distribution of MOF-5 materials.

EXPERIMENTAL

The XRD patterns of the dried samples were recorded on Bruker D8 Advance powder X-ray diffraction apparatus using Cu K α radiation. The simulated PXRD pattern was based on the supplemental crystal data for IRMOF-1 in reference 20. IR spectra were recorded as KBr pellets on a Jasco FT/IR-610 spectrophotometer. The BET and Langmuir analyses were performed by N₂ adsorption/desorption, at liquid nitrogen temperature, after sample degassing, under vacuum, at 493 K, for 3h, using a Sorptomatic 1990 instrument (Thermo Electron). The estimated specific surface areas of the samples were calculated using the Brunauer-Emmett-Teller and Langmuir methods in the p/p₀ range of 0.02-0.1, 0.02-0.35, respectively. Thermogravimetric analyses were carried out in air with a heating rate of 10°C/min, using a thermogravimetric analyzer SDT Q600.

MOF-5 materials were synthesized by a modified method given in literature,¹⁹ as follows:

Microwave synthesis of MOF-5, Zn₄O[C₆H₄(CO₂)₂]₃

The reaction mixture, obtained by mixing a solution of Zn(NO₃)₂·6H₂O (0.9 g, 3 mmol) in dimethylformamide (DMF) (50 ml) with a solution of terephthalic acid 98% (0.169 g, 0.1 mmol) in DMF (48 ml) and H₂O (2 ml), was loaded in a Teflon pot, adapted to coaxial geometry of unimodal treatment precincts of device for microwaves power treatment. The filling factor of the microwave pulse was set at 40%, the temperature at 80°C and the total length of the process at 210 seconds. Then, microwave irradiation was started. After the completion of the process, the mixture was allowed to cool to room temperature and transferred in an argon-filled flask. All subsequent manipulations were performed under inert atmosphere using anhydrous solvents. The solvent was siphoned off and the remaining solid washed six times with anhydrous DMF, each time letting the solid soak in DMF for

12 h. Then the DMF was siphoned off and the solid washed with anhydrous CH₂Cl₂ using the same procedure as with DMF. After the final CH₂Cl₂ wash, the solvent was siphoned off and the included solvents were removed under dynamic vacuum as follows: 3h at 50°C and 3h at 100°C. Yield: 0.123g (47%). The powder X-ray diffraction pattern of the sample matched with the pattern simulated from the single crystal structure of Zn₄O[C₆H₄(CO₂)₂]₃.²⁰

Solvothermal synthesis of MOF-5, Zn₄O[C₆H₄(CO₂)₂]₃

The solvothermal MOF-5 was prepared using a similar reaction mixture as indicated for microwave MOF-5 compound. The reaction mixture was loaded in a 220 ml Teflon autoclave, sealed and placed in an oven. The autoclave was heated at 100°C for 7 h. The product was purified and activated using the procedure described above for the microwave assisted reaction. The included solvents were removed under dynamic vacuum as follows: 24h at 120°C. Yield: 0.143g (55%). The powder X-ray diffraction pattern of the sample matched with the pattern simulated from the single crystal structure of Zn₄O[C₆H₄(CO₂)₂]₃.²⁰

CONCLUSIONS

We have shown that MOF-5 is efficiently and quickly synthesized by microwave-assisted synthesis under atmospheric pressure, affording a microporous material with large surface areas. Its physicochemical and textural properties are similar to those synthesized by convective solvothermal synthesis.

This method proved to be a viable alternative to the conventional heating or microwave irradiation

solvothermal synthesis. This new microwave technique is greener, faster and with lower power consumption than convective heating solvothermal method. In contrast to the microwave-assisted solvothermal synthesis, our method is safer because it does not imply the heating of a closed bottle containing nitrates and volatile solvents.

The authors have applied for a patent for this method.

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