The effect of solution/free volume ratio on the MOF-5 characteristics

G Blanita¹, D Lupu¹, M Lazar¹, A R Biris¹, V Pascualau², O Ardelean¹, I Coldea¹, I Misan¹, G Popeneciu¹ and M Vlassa²

¹National Institute for Research and Development of Isotopic and Molecular Technologies, 65-103 Donath, 400293 Cluj-Napoca, Romania
²Babes-Bolyai University, Faculty of Chemistry and Chemical Engineering, 11 Arany Janos, 400028 Cluj-Napoca, Romania

E-mail: gabriela.blanita@itim-cj.ro

Abstract. The influence of solution/free volume ratio on the specific surface area and pore volume of MOF-5 was investigated. MOF-5 was synthesized, by solvothermal reaction, using an identical starting mixture, at different solution/free volume ratio of 0.245, 0.807 and 3.429. The specific surface area decreased from 3018 m²/g to 2680 m²/g and 1099 m²/g respectively. The nitrogen adsorption capacity decrease in the same manner from 817.35 cm³/g to 740.75 cm³/g and 294.56 cm³/g respectively.

1. Introduction
Metal-organic frameworks are a well known class of porous materials due to their extremely high surface area and pore volume. Among them, MOF-5, Zn₄O(1,4-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 and raw materials [1]. In 2003, the first investigation of hydrogen storage in MOFs was reported for MOF-5 [2]. Since then, different synthetic and activation procedures were developed with the aim of obtaining maximum hydrogen storage capacity [3-6]. The specific surface area and pore volume are two factors that govern the hydrogen storage in MOF materials.

This work presents the influence of solution/free volume ratio on the specific surface area and pore volume of MOF-5 synthesized by solvothermal method.

2. Experimental

2.1. General
The studied materials were treated under argon atmosphere, using a vacuum line. The Zn(NO₃)₂·6H₂O was purchased from Acros, the terephthalic acid (98%) was purchased from Aldrich. CH₂Cl₂ and dimethylformamide (DMF) were purchased from Merck.

The prepared MOF-5 samples were characterized by X-ray powder diffraction (XRD), TG analysis, IR spectroscopy and N₂ adsorption/desorption. The XRD patterns of the dried samples were recorded on Bruker D8 Advance powder X-ray diffraction apparatus using Cu Kα radiation.
Nitrogen adsorption/desorption isotherms were obtained on a Sorptomatic sorptometer at liquid nitrogen temperature. The samples were degassed at 493°C for 3 h prior to adsorption. The specific surface areas of the samples were calculated by the Brunauer-Emmett-Teller method in the p/p₀ range of 0.02-0.1. IR spectra were recorded as KBr pellets on a Jasco FT/IR-610 spectrophotometer. TG analysis was carried out in argon with a heating rate of 10°C/min using a thermogravimetric analyzer SDT Q600.

2.2. Synthesis

MOF-5 materials were synthesized by modified method given in literature, at different solution/free volume ratio of 0.245, 0.807 and 3.429 [6]. In a typical synthesis, 1.8 g Zn(NO₃)₂·6H₂O and 0.34 g 1,4-benzenedicarboxylic acid were dissolved in 196 ml DMF and 4 ml H₂O. Then the reaction mixture was loaded into a 400 ml autoclave, sealed and placed in an oven. The autoclave was heated at 100°C for 7 h. After the completion of the reaction, the mixture was allowed to cool down to room temperature and transferred in an argon-filled flask. All subsequent manipulations were preformed under argon atmosphere. 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 CH₂Cl₂ was removed under vacuum (10⁻² mbar, 6 h) to give Zn₄O(1,4-benzenedicarboxylate)₃.

3. Results and discussion

Zn₄O(1,4-benzenedicarboxylate)₃ materials were synthesized, by solvothermal reaction, at 100°C for 7 h, using an identical starting mixture, at different solution/free volume ratio of 0.245 (MOF-5b), 0.807 (MOF-5a) and 3.429 (MOF-5c).

Table 1. Specific surface area and pore specific volume of MOF-5a, MOF-5b and MOF-5c based on nitrogen adsorption/desorption isotherms.

| Compound   | S_BET (m²/g) | Pore specific volume (cm³/g) |
|------------|--------------|------------------------------|
| MOF-5a     | 2680         | 1.14                         |
| MOF-5b     | 3018         | 1.36                         |
| MOF-5c     | 1099         | 0.42                         |

Figure 1. XRD patterns of MOF-5a, MOF-5b, MOF-5c and simulated XRD pattern for MOF-5 crystal.

Figure 2. Nitrogen gas sorption isotherm at 77K for MOF-5a, MOF-5b and MOF-5c.
XRD patterns of MOF-5a, MOF-5b and MOF-5c are shown in figure 1. Simulated XRD pattern for MOF-5 are also included [7]. Clearly MOF-5a and MOF-5b have the same XRD patterns as MOF-5. The powder XRD pattern of MOF-5c deviates significantly from the simulated pattern for MOF-5 crystal.

MOF-5a and MOF-5b are stable until 400°C, as TGA curves revealed, which are consistent with the reported value for MOF-5 [1]. The thermal decomposition of MOF-5c starts at 300°C.

The IR spectra of MOF-5a, MOF-5b and MOF-5c show the expected strong characteristic bands [8] for the $\nu_{\text{sym}}$(CO) (1391 cm$^{-1}$, 1389 cm$^{-1}$, 1389 cm$^{-1}$, respectively) and $\nu_{\text{as}}$(CO) (1573 cm$^{-1}$, 1579 cm$^{-1}$, 1579 cm$^{-1}$, respectively), adsorbed water (3400-3200 cm$^{-1}$) and $\nu_{\text{sym}}$(Zn4O) (533 cm$^{-1}$, 524 cm$^{-1}$ and 523 cm$^{-1}$, respectively) [9].

Nitrogen adsorption/desorption isotherms were measured by the standard volumetric method at 77K. The corresponding data for surface area and specific pore volume are shown in Table 1. MOF-5b synthesized at solution/free volume ratio of 0.245, has the highest specific surface area and pore volume. The surface area decrease from 3018 m$^2$/g (MOF-5b) to 1099 m$^2$/g (MOF-5c) with the increasing solution/free volume ratio from 0.245 (MOF-5b) to 3.42 (MOF-5c).

It is thus clear that the solution/free volume ratio influences gas adsorptive capacity of MOF-5. As shown in figure 2, MOF-5b adsorbs 817.35 cm$^3$/N$_2$/g, followed by MOF-5a with 740.75 cm$^3$/N$_2$/g and by MOF-5c with 294.56 cm$^3$/N$_2$/g.

All the data obtained from XRD pattern, TGA curve, IR spectra and N$_2$ adsorption isotherm reveal that MOF-5c is a “MOF-5 like” material.

Conclusions
This study demonstrates that solution/free volume ratio in solvothermal synthesis affects the structure, surface area, pore specific volume and gas adsorption capacity of MOF-5.

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