

STUDY OF THE SOLVENT EFFECT ON THE SYNTHESIS OF TWO POROUS IRON CARBOXYLATES: MIL-100(Fe) AND MIL-45(Fe)

Tadeja Birsa Čelič¹, Nataša Zabukovec Logar¹, Mojca Rangus¹ and Venčeslav Kaučič^{1,2}

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

²Faculty of chemistry and chemical technology, University of Ljubljana, Aškerčeva 5, 1000 Ljubljana, Slovenia

E-mail: tadeja.birsa@ki.si

ABSTRACT

Here we report on the controlling role of acetone in the syntheses of two iron benzene-1,3,5-tricarboxylates MIL-45(Fe) and MIL-100(Fe) from the same reagents. Under hydrothermal conditions the formation of MIL-100(Fe) structure was observed, but with the addition of acetone to the reaction mixture MIL-45(Fe) structure was synthesised. Test of hydrothermal stability revealed that MIL-100(Fe) retained its structure in boiling water, whereas MIL-45(Fe) converted to MIL-100(Fe) already after a 15-minute treatment in water at 100 °C. Iron in the structure of MIL-45(Fe) is in divalent form, while in the structure of MIL-100(Fe) it is in Fe³⁺ oxidation state. The change in oxidation state from Fe²⁺ to Fe³⁺ for MIL-45(Fe) sample during hydrothermal treatment was determined by using XANES, thus corroborating the degradation of MIL-45(Fe) to MIL-100(Fe).

Keywords: metal organic framework, role of solvent, XAS.

INTRODUCTION

Metal-organic framework materials (MOFs) are currently attracting a tremendous amount of interest because of their unique chemical and structural characteristics, which enable a variety of applications [1]. Many researches have focused on the synthesis of new MOF materials and systematically investigated the role of pH, temperature, concentration, and time on their crystallisation [2]. Special emphasis has been recently put on the influence of the solvent properties, typically DMF, alcohols, ketones, alkanes, water and their mixtures, on the formation and structure transformations of MOFs [3]. Here we report on the controlling role of acetone in the syntheses of two iron benzene-1,3,5-tricarboxylates MIL-45(Fe) [4] and MIL-100(Fe) [5] from the same reagents.

EXPERIMENTAL

The syntheses were carried out from 3 to 7 days at 150 °C to 190 °C by using the constant FeCl₃·6H₂O/benzene-1,3,5-tricarboxylic acid ratio, while the molar ratio of H₂O/acetone varied from 1:1.07 to 1:0.13. NaOH was added to the reaction mixtures to deprotonate the tricarboxylic acid. No hydrofluoric acid or any other mineralizing agent was used in the syntheses. The size and morphology of crystals in the product were studied with a scanning electron microscope Zeiss Supra™ 3VP. The crystal structures of obtained materials were confirmed with powder or single-crystal X-ray diffraction. Hydrothermal stability of the products was evaluated by boiling in distilled water for different periods of time up to 16 hours under refluxing.

X-ray absorption (XAS) spectra of products and reference compounds were measured in the Fe K-edge energy region (7112 eV) in the transmission detection mode at XAFS beamline of the ELETTRA synchrotron facility in Basovizza, Italy in order to follow the changes in an average oxidation state and local structure of iron before and after hydrothermal treatment. A Si (111) double crystal monochromator was used with about 0.8 eV resolution at 7 keV. Higher harmonics were eliminated by a slight detuning of the monochromator crystals, keeping the intensity at 70 % of the rocking curve. The intensity of the monochromatic X-ray beam was measured by three consecutive ionization detectors, respectively filled with the

following three gas mixtures: (1) 580 mbar N₂ and 1420 mbar He; (2) 90 mbar Ar, 1000 mbar N₂ and 910 mbar He; (3) 350 mbar Ar, 1000 mbar N₂ and 650 mbar He. The absorption spectra were measured in the energy region from 250 eV before the Fe K-edge to 1000 eV above the Fe K-edge. In the XANES region equidistant energy steps of 0.25 eV were used, while in EXAFS region on equidistant step of 0.5 in k-range was used, with an integration time of 1 s per step. Exact energy calibration was established with the simultaneous absorption measurements on a Fe metal foil placed between the second and the third ionization chamber. The analysis of XANES spectra was performed with the IFEFIT program package [6] using FEFF6 code [7].

RESULTS AND DISCUSSION

The hydrothermal synthesis in the above mentioned time and temperature range always resulted in the formation of pure and highly crystalline large-pore MIL-100(Fe) structure. However, the addition of acetone into the same reaction mixture directed the crystallization to the formation of MIL-45(Fe) material with smaller pores in the whole range of studied H₂O/acetone ratios and with slight variations in the crystallinity and phase purity of the obtained materials (Figure 1).

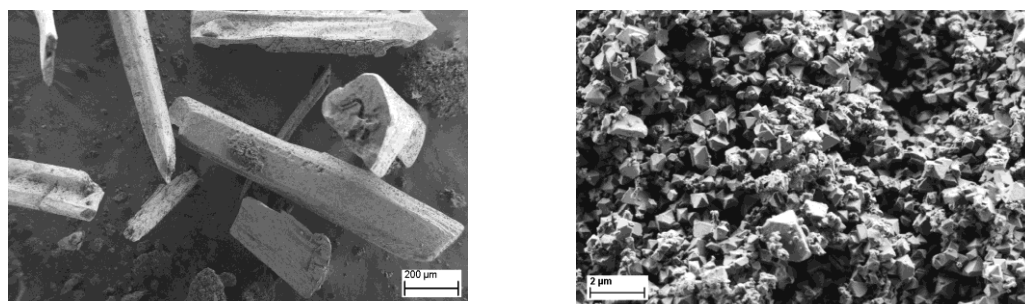


Figure 1. SEM images of MIL-45(Fe) obtained after 7 days at 190 °C with the molar ratio of H₂O/acetone 1:1.07 (left) and MIL-100(Fe) crystals obtained hydrothermally after 3 days at 150 °C (right).

MIL-100(Fe) is an iron(III) carboxylate built up from trimers of iron octahedra sharing common vertex μ_3 -O. The trimers are then linked by benzene-1,3,5-tricarboxylate linkers. Meanwhile MIL-45(Fe) exhibits an open-framework structure built up from chains of iron(II) octahedra that are linked through trimesate anions to form a three-dimensional framework. An investigation of the role of acetone on the synthesis of two porous iron carboxylates we started with XAS analyses of final powders and reaction gels of both materials. A detailed EXAFS data analysis demonstrated that local arrangement in the inorganic clusters in both materials is already formed in the reaction gels.

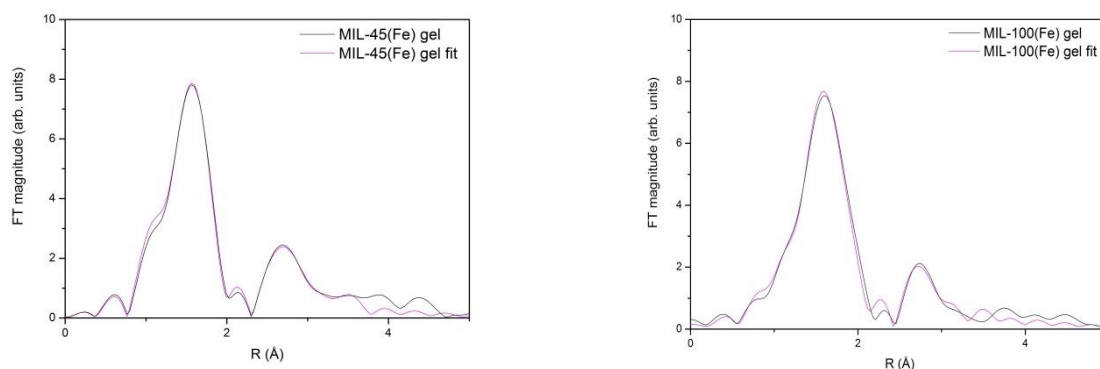


Figure 2. Summary of the EXAFS analysis performed on MIL-100(Fe) and MIL-45(Fe) gels in R-space. Both figures represent experimental curve (blue colour), superimposed with its best fit (magenta line).

Hydrothermal stability was studied by treating the samples in boiling distilled water. MIL-100(Fe) retained its structure in boiling water for at least 18 hours, whereas MIL-45(Fe), which is thermally stable up to 400 °C, is converted to MIL-100(Fe) already after 15 minutes of boiling. The irreversible transformation was confirmed by XRD.

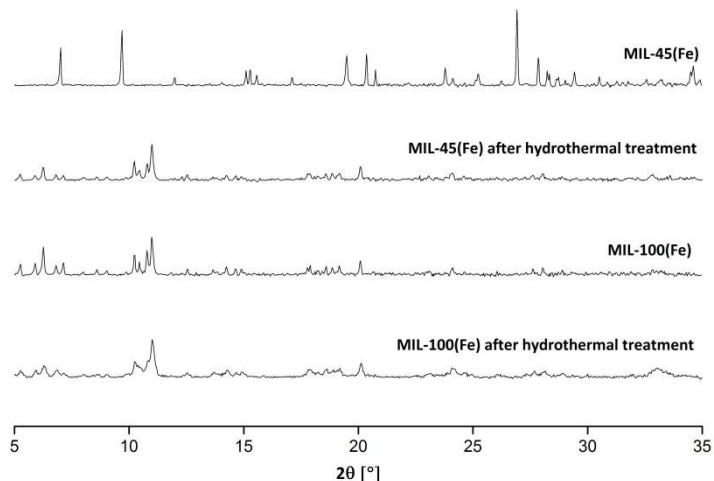


Figure 3. The test in boiling water revealed that material MIL-45(Fe) is not structurally resistant in hot water. Meanwhile, material MIL-100(Fe) does not change its crystalline structure during treatment for at least 18 hours.

XANES study of as-synthesized samples revealed, that iron was in trivalent form in MIL-100(Fe) and in divalent in MIL-45(Fe). This confirmed the reduction of Fe^{3+} to Fe^{2+} during the synthesis of MIL-45(Fe), since Fe^{3+} was used as the starting iron source in the synthesis of both materials. After the hydrothermal treatment the change in oxidation state from Fe^{2+} to Fe^{3+} was determined for MIL-45(Fe) sample, which is in accordance with its degradation to MIL-100(Fe).

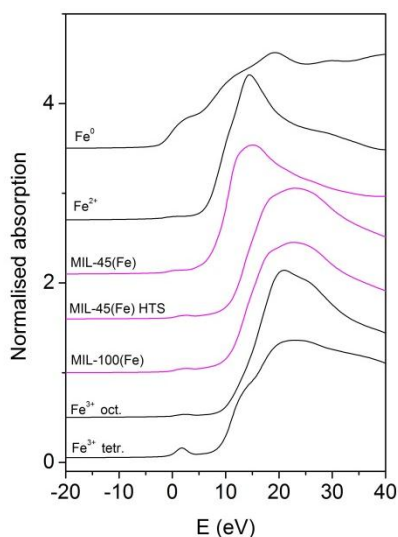


Figure 4. Fe K-edge XANES spectra of MIL-45(Fe), MIL-45(Fe)-hts, MIL-100(Fe) and standard Fe^{2+} , Fe^{3+} reference compounds. The spectra are displaced vertically for clarity.

CONCLUSION

The systematic investigation of the effect of variations in H_2O /acetone molar ratio on the reaction mixture revealed the controlling role of acetone in the formation of MIL-45(Fe)

and MIL-100(Fe) structures through oxidation-reduction and material-solvent interaction processes. The MIL-45(Fe) transformation to MIL-100(Fe) during hydrothermal treatment starts with a complete dissolution of the former structure in hot water.

ACKNOWLEDGEMENTS

This work was supported by the Slovenian Research Agency research programmes P1-0021. Access to SR facilities of ELETTRA (beamline XAFS, project 20085196) is acknowledged.

REFERENCES

- [1] G. Férey, *Chem. Soc. Rev.*, 2008, **37**, 191-214.
- [2] P. M. Forster, N. Stock, A. K. Cheetham, *Angew. Chem. Int. Ed.*, 2005, **44**, 7608-7611.
- [3] A.-Y. Fu, Y.-L. Jiang, Y.-Y. Wang, X.-N. Gao, G.-P. Yang, L. Hou, Q.-Z. Shi, *Inorg. Chem.*, 2010, **49**, 5495-5502.
- [4] M. Riou-Cavellec, C. Albinet, C. Livage, N. Guillou, A. Noguès, J.-M. Grenèche, G. Férey, *Solid State Sci.*, 2002, **4**, 267-270.
- [5] P. Horcajada, S. Surblé, C. Serre, D.-Y. Hong, Y.-K. Seo, J.-S. Chang, J.-M. Grenèche, I. Margiolaki, G. Férey, *Chem. Commun.*, 2007, **27**, 2820-2822.
- [6] J. J. Rehr, R. C. Albers, S. I. Zabinsky, *Phys. Rev. Lett.* 1992, **69**, 3397-3400.
- [7] B. Ravel, M. Newville, *J. Synchrotron Radiation*, 2005, **12**, 537-541.