

XAS Study of Thermal and Hydrothermal Stability of Two Iron Containing Molecular Sieves

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Hybrid inorganic-organic coordination polymers or metal-organic framework (MOF) materials represent an extensive group of materials where inorganic building units are interconnected through rigid organic molecules (typically polycarboxylates) forming crystalline structure [1,2]. Currently they are attracting a tremendous amount of interest because of their unique chemical and structural characteristics, which enable a variety of applications [3] such as heterogeneous catalysis, ion exchange, gas separation and storage, heat storage and drug delivery.

We have studied hydrothermal and thermal stability of the two iron benzene-1,3,5-tricarboxylates (Fe)-MIL-45 [4] and (Fe)-MIL-100 [5]. XANES and EXAFS analysis was used to study the structural changes in the samples upon hydrothermal and thermal treatment. Fe K-edge XANES and EXAFS spectra of (Fe)-MIL-45 and (Fe)-MIL-100 samples were measured at the A1 and C stations of HASYLAB in the transmission detection mode. In both cases a Si(111) double-crystal monochromator was used with 1.5 eV resolution at 7 keV. Harmonics were effectively eliminated by detuning the monochromator crystal using a stabilization feedback control. The intensity of the monochromatic X-ray beam was measured by three consecutive ionization chambers. The first was filled with 900 mbar N₂, the second with 380 mbar Ar and the third with 700 mbar Ar at the A1 station and 960 mbar N₂, the second with 315 mbar Ar and the third with 700 mbar Ar at beamline C. The absorption spectra were measured within the interval from -250 eV to 1000 eV relative to the Fe K-edge. In the XANES region equidistant energy steps of 0.3 eV were used for a precise determination of the edge shape and position, while for the EXAFS region equidistant k-steps ($\Delta k \approx 0.03 \text{ \AA}^{-1}$) were adopted with total integration time of 1 s/step. The exact energy calibration was established with simultaneous absorption measurements on the Fe metal foil placed between the second and the third ionization chamber. The spectra were analyzed with the IFEFFIT code ATHENA [6].

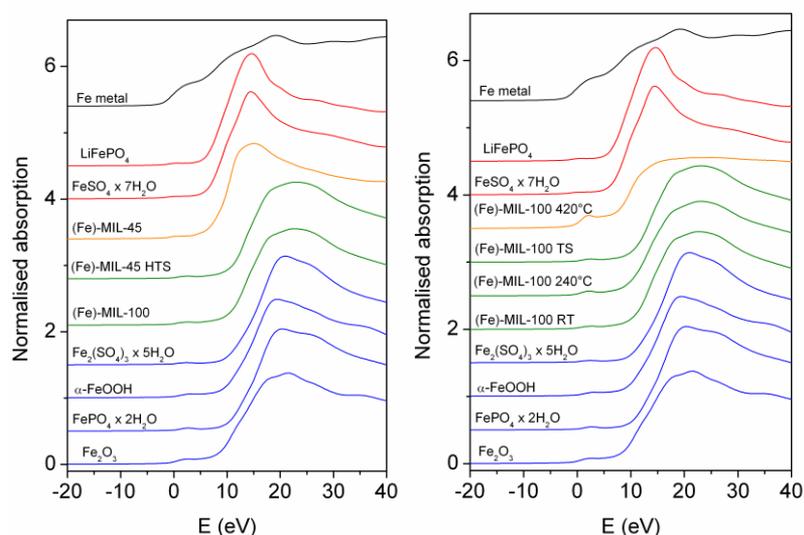


Figure 1: Fe K-edge XANES spectra of (Fe)-MIL-45, (Fe)-MIL-45 HTS boiled in water, (Fe)-MIL-100 in the left image; (Fe)-MIL-100 RT as-synthesised, (Fe)-MIL-100 at 240 °C, thermally treated (Fe)-MIL-100

TS measured at room temperature and (Fe)-MIL-100 at 420 °C in the right hand side image along with the Fe reference compounds: Fe₂O₃, FePO₄·2H₂O, α-FeOOH, Fe₂(SO₄)₃·5H₂O, FeSO₄·7H₂O, LiFePO₄ and Fe metal. Energy scale is relative to Fe K-edge in Fe metal (7112.0 eV)

XANES study of as-synthesized samples revealed, that iron was in trivalent form in (Fe)-MIL-100 and in divalent in (Fe)-MIL-45, which confirmed the reduction of Fe³⁺ to Fe²⁺ during the synthesis of (Fe)-MIL-45, since Fe³⁺ was used as the starting iron source in the synthesis of both materials (Fig. 1 left).

Hydrothermal stability was studied by boiling the samples in water. (Fe)-MIL-100 retained its structure in boiling water for at least 16 hours, whereas (Fe)-MIL-45, which is thermally stable up to 400 °C, is converted to (Fe)-MIL-100 already after 10 minutes of boiling (Fig. 1 left, Fig. 2 left). The irreversible transformation was also confirmed by XRD.

Thermal stability of (Fe)-MIL-100 was studied by heating the sample in situ in the oven positioned between the first and the second ionisation cell. The sample was heated to a predetermined temperature and when the temperature stabilized, XAS spectra were measured. After heating the sample to 240 °C no significant difference to the as-synthesised (Fe)-MIL-100 can be seen in the XANES spectra (Fig. 1 right). This clearly demonstrates that no significant difference in the valence state occurs after heating the sample to 240 °C. EXAFS spectra, however, indicate some structural changes (Fig. 2 right) which can be partially contributed to larger Debye-Waller factors of the sample heated to 240 °C. Whereas, some appear to originate from structural differences since after cooling the sample to room temperature ((Fe)-MIL-100 TS) the differences to the as-synthesised are still evident. However, after heating (Fe)-MIL-100 sample to 420 °C, Fe-O bonds between iron and carboxylic oxygens split and individual atoms of iron remain. The transformation is evident from the XANES spectrum of the sample (Fig. 1 right). Fe K-edge position is shifted to lower energies, close to the edge position of Fe metal. The assumption of individual atoms of iron in the carboxylate matrix is supported by the absence of any notable EXAFS signal. Detailed quantitative analysis based on the FEFF model is expected to confirm or disprove any structural changes upon thermal treatment.

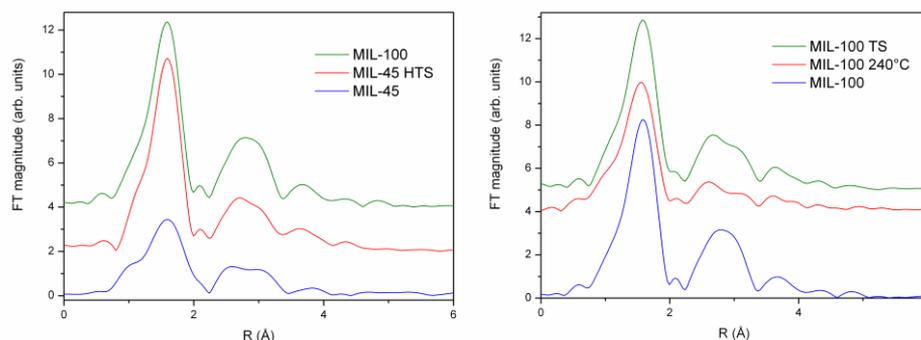


Figure 2: The k^3 weighted Fourier transform spectra of (Fe)-MIL-100, (Fe)-MIL-45 boiled in water and (Fe)-MIL-100 in the left image; (Fe)-MIL-100, (Fe)-MIL-100 at 200 °C and thermally treated (Fe)-MIL-100 measured at room temperature in the right hand side image, all calculated in the k range of 3 ... 13 Å⁻¹.

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References

- [1] G. Férey, *Chem. Soc. Rev.*, **37**, 191 (2008).
- [2] S. Kitagawa, R. Kitaura and N. Shin-ichiro, *Angew. Chem., Int. Ed.* **48**, 2334 (2004).
- [3] A. K. Cheetham, C. N. R. Rao and R. K. Feller, *Chem. Comm.* 4780 (2006).
- [4] M. Riou-Cavellec, et al., *Solid State Sci.* **4**, 267 (2002).
- [5] P. Horcajada, et al., *Chem. Comm.* **27**, 2820 (2007).
- [6] B. Ravel, M. Newville, *J. Synchrotron Rad.* **12**, 537 (2005).