

Experiment Report Form



Experiment title: Structure and redox properties of mixed Ce-Zr UiO-66 MOFs

Experiment number:
CH-4669

Beamline: BM31	Date of experiment: from: 15/02/2017 to: 21/02/2017	Date of report: 02/03/2018
Shifts: 18	Local contact(s): Michela Brunelli	

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Abstract

Bimetallic Ce/Zr-UiO-66 metal-organic frameworks are promising materials for various catalytic applications, representing, together with other bimetallic MOFs, a new generation of porous materials. However, no direct proof for the presence of both metals in a single cornerstone of UiO-66 MOF was reported so far. Employing element-selective XAS techniques herein we were able to shed light on this matter [1]. Besides, we were able to demonstrate the possibility to reduce a single Ce ion in the pure Ce-UiO-67 MOF upon the interaction with TEMPO [2].

Experimental

Ce and Zr K-edge EXAFS spectra were measured for the series of UiO-66 MOFs with BDC linkers and for Ce-UiO-67 before and after interaction with TEMPO. For Ce/Zr-UiO-66 several materials were prepared with different Ce/Zr ratio in the cornerstones. Optimized quantities of MOF powders were pressed in self-supporting pellets of 5 mm diameter using the pressure less than 500 kg/cm². The measurements were conducted in transmission mode using Si (111) double-crystal monochromator. Three gas-filled ionization chambers were used for photon detection. The data quality was good, which allowed the EXAFS data collection up to $k=20 \text{ \AA}^{-1}$ for most samples, but in order to compare all the data in the same range, the Fourier transform were performed in 3.65-16.8 \AA^{-1} range, limited by signal-to-noise ratio in the spectra of the samples with the lowest concentration of Ce and Zr.

Results and discussion

Ce/Zr-UiO-66

Fourier-transformed Zr and Ce K-edge EXAFS data for UiO-66-BDC MOFs are shown in Figure 1. The shape of the peaks in 1-2.5 Å range does not change much upon the increase of Ce content, which evidences rather small variations in the O-coordination of Zr and Ce atoms. However, very significant changes are observed in the position and intensity of the second peak, which appears due to the scattering from the heavy atoms (Ce or Zr) inside the hexanuclear cornerstones. That means that the average values of Zr-Zr, Zr-Ce, Ce-Zr and Ce-Ce interatomic distances, as well as the corresponding disorder, depend on Ce/Zr ratio.

Combined fitting of both Ce and Zr K-edge EXAFS data allowed to prove the existence of mixed Zr_xCe_{6-x} cornerstones in the bimetallic Ce/Zr-UiO-66 MOFs and to determine their stoichiometry at different Ce content. Resulting manuscript is currently under review [1].

Ce-UiO-67

X-ray absorption near edge structure (XANES) at the Ce L₃- and Ce K-edge was performed to assess the average oxidation state of Ce throughout the whole structure (Figure 2). This type of analysis is very reliable, since XANES features of both Ce L₃- and Ce K-edges are known to be mostly dependent on the average oxidation state of Ce ions, being much less affected by the variations of local geometry.

No measurable Ce³⁺ was present before reaction but after reduction by the TEMPO/benzyl alcohol mixture, the fraction of reduced Ce was calculated to be $19.4 \pm 0.2\%$ and $16.9 \pm 0.2\%$ at the Ce L₃ and the Ce K-edge respectively (Figure 2; the reported errors are of statistical origin; the intrinsic error associated to such XANES analyses is in the order of 5%). The best-fit curves are able to remarkably reproduce the experimental data, which is confirmed by the low R-factors (0.0013 at Ce L₃ and 0.0001 at Ce K-edge). The calculated Ce³⁺-fraction corresponds to an average of approximately one Ce³⁺ ion per hexanuclear cluster (16.7%). This clearly demonstrates that Ce⁴⁺-MOFs can accommodate valence changes in the hexanuclear cluster, and hence catalyze redox reactions through the reduction of Ce⁴⁺ cations.

Resulting manuscript was recently published [2].

References

- [1] K.A. Lomachenko, J. Jacobsen et al., **2018**, submitted.
- [2] S. Smolders, K.A. Lomachenko et al., *ChemPhysChem* **2018**, 19, 373-378.

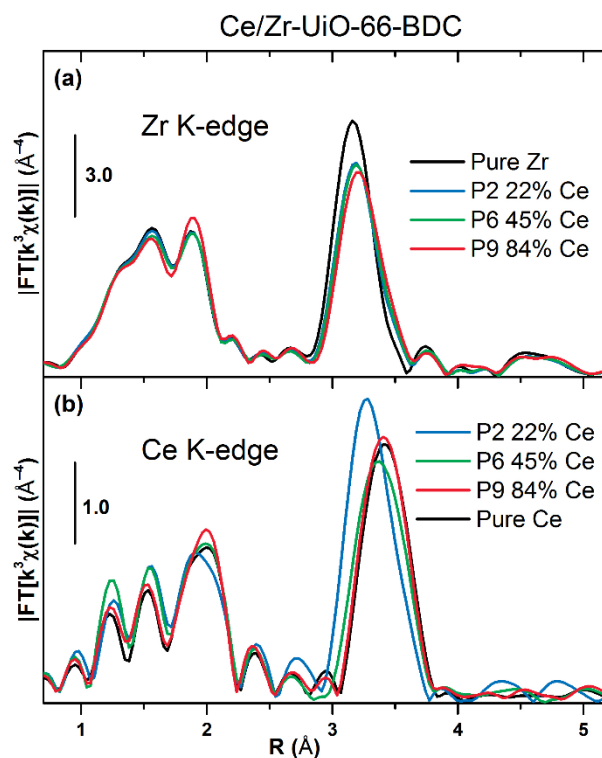


Figure 1 Moduli of the phase-uncorrected Fourier transforms of k^3 -weighted EXAFS data collected at Zr K-edge (a) and Ce K-edge (b) for UiO-66-BDC MOFs with different Ce/Zr ratio.

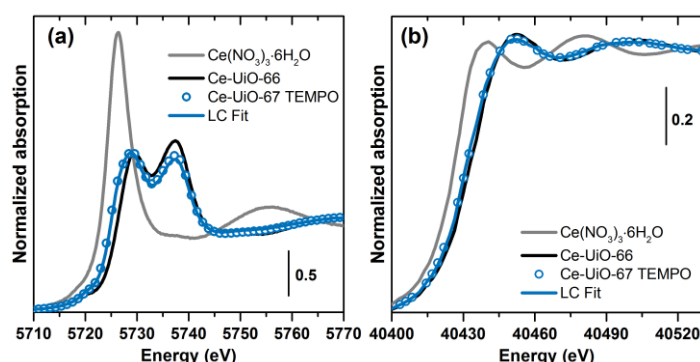


Figure 2. Experimental Ce L₃-edge (a) and Ce K-edge (b) XANES spectra of Ce-UiO-67-red; results of linear combination fitting performed using the spectra of Ce-UiO-66 and Ce(III) nitrate as standards.