Mixed-valance Ce:Zr MOFs: controlling the oxidation state of cerium in one pot synthesis approach.

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The redox properties of Zr based MOFs (UiO or MOF-808) are quite limited. The Zr tetravalent cataions are very stable and the generation of a redox pair in the frameworks is not easy. For such reasons, Stock's group[1] and others have proposed the preparation of Ce or Ce/Zr MOFs with the same topology to introduce a Ce(IV)/Ce(III) pair that would work as redox functionality. Actually, they have already reported both structures, UiO and MOF-808, made out of pure Ce and Ce/Zr.

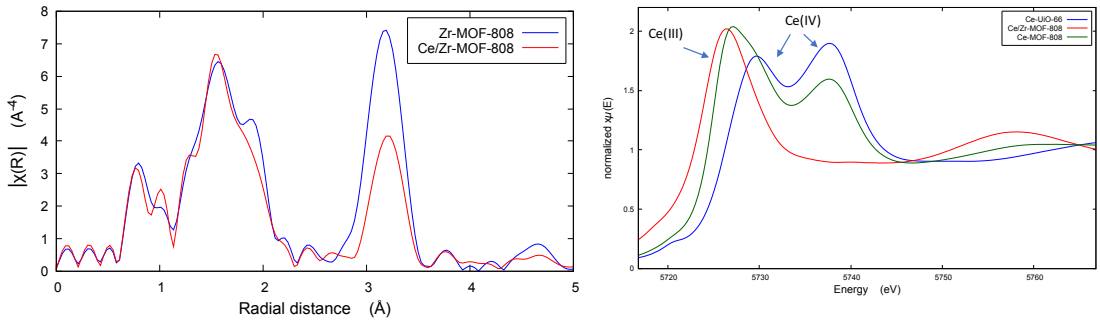
The preparation and characterization of these mixed metal MOFs is far for being trivial, since we can be in different situations such as: the formation of segregated phases of Ce-MOF and Zr-MOF, cluster having only Ce or Zr in the same crystal and finally the desired one, clusters where both metals are present (true mixed-metal MOF).

Apart from the true mixed-metal nature of the MOF, it is also crucial to control the oxidation state of Ce. Ce(III) and Ce(IV) are both stable at ambient conditions and both have the same coordination, so both can be used for producing MOF of the same topology. The tailoring of the Ce oxidation state would lead to a fine control of the redox properties.

In this work we have developed a method in which we can prepare Ce/Zr-MOFs (UiO and MOF-808) having only Ce(III), mixed-valence Ce(IV)/Ce(III), or only Ce(IV) as desired. In order to check the success of the synthesis, we have used a large number of characterization techniques such as: UV-vis, XRD, N_2 adsorption isotherms, TGA, Raman spectroscopy, XRF, XPS and EXAFS.

If we look up the Zr K-edge EXAFS spectra, more concretely the fourier transform (left graph), we see that the first shell (due to Zr-O_a 1.6 Å and Zr-O_b 1.9 Å) is modified and some oxygen vacancies are created when Ce is added to the framework, proving already that the Zr hexanuclear cluster are altered with Ce atoms. This effect is even more accentuated when we look at the second shell (due to Zr-Zr 3.2 Å), where we do see that the Zr coordination drastically decreases, indicating the success incorporation of Ce in the Zr_6 clusters.

If we look at the Ce L3 edge, XANES region (right graph), we see that we could prepare MOF having only Ce(III) or only Ce(IV) as well as mixed-valance Ce(III)/Ce(IV). The same findings have been encountered with the other characterization techniques.



Summarizing, we have designed a method to prepare mixed-metal-valance MOFs. Not only a second metal can be incorporated in a MOF structure, but we also can choose the oxidation state of this metal.

1. M. Lammert, Gli and N. Stock, *Dalton Transactions*, 2017, 46, 2425-2429.