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Observation of Fe and Ni Sites in Metal-Organic Frameworks (MOFs)

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1. Background

Metal–organic frameworks (MOFs) are very attractive as catalysts for their highly ordered structures, large porosities, and diversified pore surfaces. Especially, their surfaces are mostly contributed from the highly ordered internal pores as observed in the crystal structures, which are not only beneficial for mechanism study but also can be easily functionalized by open metal sites (OMSs) with Lewis acidity and/or redox property. Some MOFs have been used as precursors to fabricate metal oxide/porous carbon nanocomposites as OER catalysts. However, it seems that MOFs themselves are unsuitable as OER catalysts, considering their poor stabilities (in water, especially basic conditions). Here, using an alkaline-stable Ni-MOFs featuring cooperative open metal-metal sites, Fe(III) doping experiments confirmed that the hydroxide adsorption capacities of the catalytic Ni(II) sites within the Ni-MOFs can be drastically enhanced with the assist of Fe(III) ions, giving improved electrocatalytic activities for the OER.

2. Experiments

X-ray absorption fine structure (XAFS) analyses of the MOFs with Fe and Ni atoms were performed at Aichi Synchrotron Radiation Center (BL5S1). Each powder sample pressed as pallets were analyzed.

3. Results and Discussion

Currently, element-selective XAFS, including X-ray absorption near-edge spectroscopy (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopy, has been considered as a necessary characterization for the MOF-derived single-atom catalysts, which can demonstrate the atomically dispersed metal atoms via verifying the absence of metal-metal bonds in the spectra.[1] So, XAFS analyses were performed to investigate the local environment of Fe and Ni atoms in MOFs. As shown in Figures 1 and 2, the obtained Fe/Ni K-edge XAFS spectra showed that our samples exhibited distinctly different profiles from those of corresponding known compounds. The coordination configurations were then determined by the Fourier transformed k^3-weighted $\chi(k)$-function of the corresponding EXAFS spectra in R space, which certified that Fe/Ni sites should be atomically dispersed in the samples. The on-going data analysis is about the structural fitting by virtue of DFT calculation.

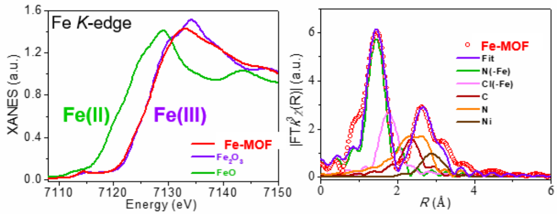

Figure 1. Fe K-edge XAFS spectra of Fe-MOF.

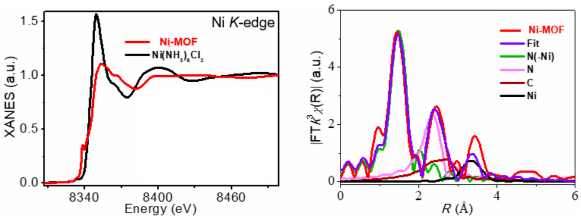

Figure 2. Ni K-edge XAFS spectra of Ni-MOF.

4. References

1. Xu, Q. et al. Puffing Up Energetic Metal-Organic Frameworks to Large Carbon Networks with Hierarchical Porosity and Atomically Dispersed Metal Sites. *Angew. Chem., Int. Ed.* (2019) 58, 1975-1979.