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Title:

Intentional creation of defects within UiO-66 type metal-organic frameworks: a theoretical rationalization

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Abstract: (Your abstract must use **Normal style** and must fit in this box. Your abstract should be no longer than 300 words. The box will 'expand' over 2 pages as you add text/diagrams into it.)

The catalytic activity of metal-organic frameworks (MOFs) can be tuned by using different organic linkers [1], post-synthesis metal substitution, etc. These techniques change the behaviour of the active site, which appearance is not always known on beforehand. Within the family of Zr-benzenedicarboxylate (Zr-BDC or UiO-66) type MOFs, missing linkers were found to be responsible for the catalytic activity [1]. Therefore, experimental procedures were developed to create more of such active Zr-sites by adding an excess of modulator (MDL) to the synthesis mixture [2]. Subsequently, the incorporated modulators can be removed by a post-synthesis treatment at elevated temperature, thereby creating new active Zr-sites. In this contribution, we aim at explaining experimental observations with computational insights, focusing on the modulating species trifluoroacetic acid (TFA), HCl and H_2O [3]. At synthesis conditions, the coordination strength of these species predicts the stability (from high to low): BDC > TFA > HCl > H_2O. High MDL:BDC ratios are thus required to achieve incorporation. Post-synthesis removal of the defect-coordinating species follows, as expected, the opposite trend: H_2O > HCl > TFA > BDC. Thermal activation also promotes dehydroxylation or water removal from inorganic $[Zr_6O_4(OH)_4]^{12+}$ bricks and for a $[Zr_6O_5(OH)_2]^{12+}$ brick this process is competitive with removal of a coordinating TFA. Finally, we discuss a mechanistic study of the dehydroxylation process to unravel the exact nature the Zr-sites of various inorganic bricks.

References

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