

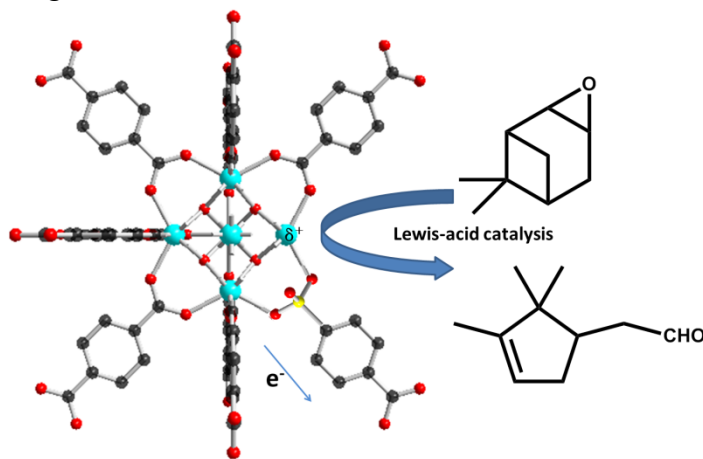
## Defect engineering of UiO-66 using 4-sulfobenzoic acid

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UiO-66[1], a highly stable Zr-based MOF, is widely studied and regarded as one of the most promising MOF materials for practical applications.[2] Recent studies on defect engineering in UiO-66 observed a large increase in sorption and catalytic activity due to an increasing number of defects.[3] In this work, we use 4-sulfobenzoic acid as an agent to increase the number of defects per unit cell and hence the catalytic activity of the material. We discuss the role of the agent as ‘modulator’ or as ‘co-ligand’ in the structure. Moreover and more importantly, by an extended post-synthesis treatment, we were able to obtain for the first time 3 defects per unit cell as determined from NMR and TGA measurements. The materials are evaluated in the catalytic isomerization of  $\alpha$ -pinene oxide. This reaction allows to differentiate Lewis and Brønsted acid catalysis thanks to differences in product selectivity. Our materials exhibit a high catalytic activity (100% conversion in 1h) and selectivity ( $\geq 67\%$ ) towards campholenic aldehyde in comparison to pure UiO-66, showing the increased Lewis acid character of the defected materials.



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[2] Y. Bai, Y. Dou, L. H. Xie, W. Rutledge, J. R. Li, H. C. Zhou, *Chem. Soc. Rev.* (2016), 45, 2327-2367.

[3] Z. Fang, B. Bueken, D. E. De Vos, R. A. Fischer, *Angew. Chem. Int. Ed. Engl.* (2015), 54, 7234-7254.

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