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Reversible formation of defects in HKUST-1: a surface perspective by Soft X-ray Absorption Spectroscopy

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Metal–organic frameworks (MOFs) are widely studied nanoporous materials obtained from the coordination of metal ions or clusters (nodes) to polydentate organic molecules (linkers). This interaction yields three-dimensional structures featuring pores with ultrahigh internal surface areas (up to 10 000 m² g⁻¹) and highly reactive metal sites, to be exploited in a vast plethora of applications [1]. HKUST-1, a MOF containing Cu(II) and BTC (benzene-1,3,5-tricarboxilate), has been extensively characterized both for the reactivity of its open copper sites and the reversible formation of structural, "engineered" defective sites exhibiting Cu(I)/Cu(II) dimers [2]. However, despite the significant scientific effort, a full consensus on the formation, structure, and reactivity of the defects is yet to be reached. Such an understanding is crucial for the efficient application of HKUST-1 in CO2-related applications such as its separation from other gases and its storage. The defective metal sites play an important role in these implementations due to redox processes taking place.
Here, we would like to show new insights into the formation of Cu(I) defective metal sites on the surface of HKUST-1 and their interaction with CO₂ obtained with a newly developed setup for operando Ambient Pressure Near Edge X-ray Absorption Fine Structure (AP-NEXAFS) measurements [3]. Our proposed mechanism consists in a Cu(II)-catalyzed oxidative decarboxylation of the BTC ligand at 160 ℃, leading to Cu(I)/Cu(II) dimers where both copper atoms are coordinated by only three oxygen atoms [4]. Further, we prove that this process can be fully reversed by exposing the defective MOF to a CO₂ flux at ambient pressure and we quantify the surface ratio of the defective dimers formed upon thermal treatment (ca. 45%, much higher than the bulk ratio). Our findings also suggest that the CO₂ flux can also completitively inhibit the H₂-induced reduction of the metal sites. We believe that these studies will lead to an increased understanding of the surface properties of HKUST-1 and pave the way for its rational use in CO₂ separation and uptake processes.

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Primary author: Mr TOFONI, Alessandro (Sapienza Università di Roma)

Co-authors: Mr TAVANI, Francesco (Università di Roma "La Sapienza"); Dr BRAGLIA, Luca (CNR-Istituto Officina dei Materiali); Mrs MAURI, Silvia (CNR-Istituto Officina dei Materiali); Prof. COLOMBO, Valentina (Università degli Studi di Milano); Dr TORELLI, Piero (CNR-Istituto Officina dei Materiali); Prof. D'ANGELO, Paola (Università di Roma "La Sapienza")

Presenter: Mr TOFONI, Alessandro (Sapienza Università di Roma)

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