

# Active Cu species during CO oxidation on Cu metallated Zr-based UiO-66: *Operando* XAFS-DRIFTS spectroscopy and HAADF-STEM

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Metal-organic frameworks (MOFs) emerged recently as highly promising microporous materials with intriguing properties for various applications, including heterogeneous catalysis.<sup>1</sup> Since they allow to precisely tailor and control the electronic properties and local environment of the active sites, their reactivity can be sensitively tuned for a variety of reactions.<sup>2</sup> Using CO oxidation as model reaction,<sup>3</sup> we investigated the catalytic performance of Cu metallated UiO-66, a Zr-based MOF ( $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{BDC})_6$  (BDC = 1,4-benzene-dicarboxylate)) with high chemical and thermal stability.<sup>4,5</sup> Employing a combination of kinetic and *operando* XAFS and FTIR spectroscopy as well as HAADF-STEM measurements, we aim at identifying the chemical nature and structure of the active Cu species during reaction.

Kinetic measurements on the Cu@UiO-66 catalyst, performed after reductive (10%  $\text{H}_2/\text{N}_2$ ; 1 h, 250°C) pretreatment in a  $\text{CO}/\text{O}_2$  (1:1) gas mixture, showed that the activity increases slowly from 4.0 to 6.5  $\mu\text{molCO}_2 \text{ gCu}^{-1} \text{ s}^{-1}$  between 80°C and 120°C, while from 150°C to 250°C the increase was much more pronounced, from 7.0 to 144  $\mu\text{molCO}_2 \text{ gCu}^{-1} \text{ s}^{-1}$ . Time-dependent measurements at 250°C revealed a stable activity, with no measurable deactivation over 1500 min. Time-resolved diffuse reflectance FTIR (DRIFTS) measurements at temperatures between 80°C and 250°C indicated that CO adsorbs as mono and/or multiple-carbonyls on  $\text{Cu}^{1+}$  (2138, 2120, 2109  $\text{cm}^{-1}$ ).<sup>6</sup> On the other hand, XANES measurements at the Cu K-edge showed that after pretreatment Cu exists mainly as  $\text{Cu}^{1+}$ , while during CO oxidation a gradual transformation of  $\text{Cu}^{1+}$  to  $\text{Cu}^{2+}$  occurs, reaching a composition of 30±5 %  $\text{Cu}^{1+}$  and 70±5%  $\text{Cu}^{2+}$  under steady-state conditions. The dominance of  $\text{Cu}^{2+}$  during reaction was confirmed by XPS measurements after reaction, which revealed a strong Cu 2p satellite peak characteristic for  $\text{Cu}^{2+}$  interacting with surface ligands, e.g., OH groups or carboxylate.<sup>6</sup> Based on EXAFS measurements, Cu is predominantly bound to oxygen, with an average coordination of 2.0±0.5 at a Cu-O bond distance of 1.90±0.02 Å under steady-state conditions.<sup>7</sup> In agreement with those findings, HAADF-STEM measurements indicated that Cu exists as highly dispersed atomic species, both in fresh Cu@UiO-66 and after subsequent reaction. Finally, results of detailed structural characterization and from DFT computations of the Cu@UiO-66 will be presented.

Consequences of these findings for the mechanistic understanding of the CO oxidation reaction on these catalysts will be discussed.

## References

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