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. 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. Using CO oxidation as model reaction, we investigated the catalytic performance of Cu metallated UiO-66, a Zr-based MOF (Zr₆O₄(H)₆(BDC)₆ (BDC = 1,4-benzene-dicarboxylate)) with high chemical and thermal stability. 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% H₂/N₂; 1 h, 250°C) pretreatment in a CO/O₂ (1:1) gas mixture, showed that the activity increases slowly from 4.0 to 6.5 μmolCO₂ g⁻¹s⁻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 μmolCO₂ g⁻¹s⁻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 Cu¹⁺ (2138, 2120, 2109 cm⁻¹). On the other hand, XANES measurements at the Cu K-edge showed that after pretreatment Cu exists mainly as Cu¹⁺, while during CO oxidation a gradual transformation of Cu¹⁺ to Cu²⁺ occurs, reaching a composition of 30±5 % Cu¹⁺ and 70±5% Cu²⁺ under steady-state conditions. The dominance of Cu²⁺ during reaction was confirmed by XPS measurements after reaction, which revealed a strong Cu 2p satellite peak characteristic for Cu²⁺ interacting with surface ligands, e.g., OH groups or carboxylate. 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. 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

(1) H. Furukawa et al., *Science* 2013, 341, 1230444.