

## Single Site Catalyst Supported in Mesoporous UiO-66 for Catalytic Conversion of Carbon Dioxide to Formate

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### Abstract

Carbon dioxide utilisation strategies are of paramount importance, yielding various products such as methanol and formate. Formate is an excellent hydrogen carrier in fuel cells, making it a highly exploitable chemical on the hydrogen energy storage front. Formate has an energy content that is at least five times greater than that of commercially available lithium-ion batteries. Herein, we have prepared mesoporous metal–organic frameworks (MOFs) (m-UiO-66 and m-UiO-66-NH<sub>2</sub>), using a Zr-based secondary building unit (SBU) and terephthalate linkers. The MOFs were used to support the half-sandwich (tetrazolylpyridyl)iridium(III) complex to make single-site catalyst (Ir(III)@m-UiO-66 and Ir(III)@m-UiO-66-NH<sub>2</sub>) for CO<sub>2</sub> conversion to formate. Both Ir(III)@m-UiO-66 and Ir(III)@m-UiO-66-NH<sub>2</sub> exhibited improved activity for CO<sub>2</sub> hydrogenation to formate in a heterogeneous system. Ir(III)@m-UiO-66-NH<sub>2</sub> and Ir(III)@m-UiO-66 had turnover numbers of 3313 and 3076 TON, respectively, under optimized conditions. X-ray photoelectron spectroscopy (XPS) showed possible interaction of the complex with the MOF as evidenced by a downfield shift in the binding energies of the Ir 4f electronic environment. The catalysts showed post-catalysis stability, as confirmed by PXRD, FTIR, and XPS. The Ir 4f binding energies of the materials after catalysis showed an up-field shift confirming the presence of Ir–H species which are the active species for catalysis.