

Development and Mechanistic Study of $\text{Mn}(\text{CO})_3$ Single Sites in 2D-Covalent Organic Frameworks for Electrocatalytic CO_2 Reduction

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Global warming, climate change and our over-dependence on non renewable fossil fuels demand long-term solutions to reduce CO_2 emissions and develop sustainable energy technologies. The electrochemical CO_2 reduction has the potential to accomplish a “carbon-neutral energy cycle”, which incorporates CO_2 as the unlimited carbon source for the production of high-density fuels. In this regard, this work entails a fundamental understanding of the CO_2 mechanisms using Mn Single Atom Catalyst (SAC) within Covalent Organic Frameworks (COFs). The catalytic activity of the materials was benchmarked against other molecular supported catalysts reported in the literature. Compared to equivalent Mn derivatives, COFs exhibited higher selectivity and activity towards CO_2 reduction. Additionally, mechanistic studies based on *in situ* / *in operando* spectroelectrochemical techniques together with DFT calculations were used to detect key catalytic intermediates and correlate the catalytic activity with the mechanical constraints imposed to the $\{\text{Mn}(\text{CO})_3\}$ active sites by reticular framework. Of particular note is the detection of a radical intermediate within a Mn based COFs avoiding the detrimental formation of a dimeric specie determined as a resting state in the catalytic cycle. In addition, a variation of the bipyridyl linker within the COF, by introducing larger phenanthroline ligand, tuned the structural and electronic properties of the catalyst, consequently influencing on the catalytic CO_2 reduction activity. The presence of both pyridyl and phenanthroline within the COFs was found to increase the activity respect the equivalent molecular catalysts. However, structural parameters like the crystallinity and porosity of the reticular frameworks proved to play an important role in the stability of the catalysts. Overall, $\{\text{Mn}(\text{CO})_3\}$ -COFs exhibited higher catalytic activity than the equivalent molecular complexes; thereby suggesting the directions for developing COFs as ligands for CO_2 reduction.

References

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Figures

