Investigation of Iron(III) Schiff-Based Complexes for Carbon Dioxide Reduction

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Carbon dioxide (CO_2) reduction is attracting great consideration due to environmental challenges[1] and the interest in its transformation into high-value-added chemicals,[2] such as urea, polycarbonate, salicylic acid and methanol. An attractive perspective for a carbon neutrality economy with a potential impact on the United Nations Sustainable Development Goals.[3] To achieve this ambitious aim, research primarily focuses on designing stable and robust catalysts that can efficiently perform the CO_2 reduction reaction (CO_2RR). Like other redox reactions involved in energy-related schemes,[4] a catalyst is required for the process to proceed at sustainable rates. Recent works on CO_2RR catalysts based on noble metals[5] have pushed active research on more attractive and cheap alternatives: earth-abundant transition metals like manganese, iron, cobalt, and copper. Iron stands out as a fascinating active site to catalyse CO_2RR[6] thanks to its rich chemistry, broad application in several redox processes, low cost and environmental compatibility. However, despite the high activity of molecular catalysts, they often suffer from deactivation mechanisms, resulting in metal nanoparticle formation.

Synthesis and characterization of metal complexes for their catalytic use in electrochemical CO_2 reduction are discussed here. A family of Salen-like tetradentate Schiff-base iron(III) complexes, $Fe(L_{N2O2})Cl$, were explored. These catalysts exhibit peculiar stability due to ligand-to-metal electronic polarization and the participation of iron in the π-bond systems. These complexes show the possibility of electrochemically generating iron(I) species: the key intermediate capable of reacting with CO_2, forming carbon monoxide (CO) and formic acid (HCOOH) while competing with dihydrogen evolution reaction (HER). As a result, the reaction selectivity is guided by the complexes reactivity and by the co-catalyst effect, which way the role of the proton-donors is so important.

These $Fe(L_{N2O2})Cl$ complexes mediate the two-electron two-proton CO_2 reduction to CO by means of an iron(I) intermediate, upon the addition of a suitable proton source. This was proven with gas chromatography and spectroscopy techniques and further evidenced by cyclic voltammetry (CV) through increased catalytic current density. Moreover, target CVs studies and chronoamperometry analysis allow the evaluation of different key parameters, such as the overpotential, the rate constant, faradaic yield, selectivity and the turnover frequency; these are useful tools to characterize the catalytic behaviour of these compounds. Then, based on the analysis of the supernatant composition, and morphological and electrochemical investigation of the electrode after the electrolysis, the complexes were shown to undergo competitive degradation, limiting their activity and lifetime.

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