

Summary

The thesis is based on the electrochemical activation of CO₂ towards several types of catalysts, having as common characteristic, the attempts and realization of single metal active sites. Different approaches were investigated, throughout the Lewis acids doping of organic polymers, taking the advantages of peculiar structures like the one of the Molecular Organic Framework (MOF) and finally more challenging approaches starting from metallorganic complexes building heterogeneous materials based on metalloporphyrin.

The complete physical and chemical characterization of those catalysts was performed by several techniques like the Attenuated Total Reflectance Fourier Transform Infrared spectroscopy (ATR-FT-IR), UV-Vis spectroscopy and Diffuse Reflectance Measurement, Powder X-Ray Diffraction (XRD), X-Ray Photoelectron Spectroscopy (XPS), Field-Emission Scanning Electron Microscopy (FE-SEM), Brunauer–Emmett–Teller surface analysis (BET) and Thermo-Gravimetric and Evolved Gas Analyses (TGA-EGA). Parallel to them, fundamental electrochemical analysis were performed in order to detect and quantify the possible selectivity towards the CO₂ conversion and to compare it to the competitive H₂ evolution reaction, such as: Cyclic Voltammetry (CV), Electrochemical Impedance Spectroscopy (EIS) and Chronoamperometry (CA).

The catalysts were able to produce variegated products of great interest for both the fuels and chemicals industrial sectors. Indeed, carbon monoxide, formate, ethylene and methane could be synthesized at different rate and selectivity based on the different type of catalysts. In order to optimize such conversion processes, also the experimental setting followed a continuous improvement all along the years, strictly following the upgrade obtained from the scientific community highly active in this research field. Indeed, starting from simpler apparatus based on H-cell, the electrochemical setup followed itself a great improvement passing through the batch cell till the most performing flow cell employment.

The interest to stabilize single metal centers, considered to be the active species for the CO₂ conversion through electrochemical process, hid in some way a more complex topic: the nature of the true active site under an electrochemical bias. Indeed, the work, following the updates coming from the most recent literature, highlights the real nature of the catalyst under potential that is often underestimated. Indeed, only performing specific physical and chemical characterization under potential, it is possible to analyze the active species all along an electrochemical process. In our specific case we were indeed able to identify metallic clusters formed during the catalysis that they were completely unpredicted in the previous literature for the last part of the thesis.