Coordination chemistry approach for selective CO₂ electroreduction reaction in layered hydroxide materials

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The production of reduced carbon-based chemicals and energetic compounds from carbon dioxide remain as a major endeavor for scientists in chemistry and catalysis. In this matter, carbon monoxide and formic acid emerge as suitable products from CO₂ electroreduction for hydrogen storage under ambient conditions.¹ Many catalysts have been developed, among them, metallic-organic complexes, metals,² metal alloys,³ metal oxides⁴ and porous materials.⁵ In order to overcome some drawbacks faced by these catalysts (i.e. chemical and physical stability) we have employed layered simple hydroxides (LSH) as host matrices for iron/cobalt porphyrins, pyrroles and bipyridines (Figure 1) as potential ligands for an intralayer coordination chemistry approach.

In the present work, matrix functionalization with the mentioned molecules has been achieved thru two experimental approaches. The first one being the direct coprecipitation of the layered hydroxide from an aqueous solution of the metal source (typically $Zn(NO_3)_2$) and the molecule of interest by a slow addition of sodium hydroxide. This procedure has proven efficient for intercalation of porphyrins and pyrroles but unsuitable for bipyridines, therefore, a pre-functionalization of the host matrix with another labile molecule has to be performed, being the most common dodecylsulfate (DS) and dodecylbenzenesulfonate (DBS0). In this manner an anion exchange reaction can take place, in which the DS or DBS0 can be substituted by bipyridines as in the present study.

Preliminary tests for coordination of Ru(II) and Co(II) have been done without conclusive evidence about coordination/formation of the desired complexes. Instead, it has been observed a lability of the zinc hydroxide layers towards incorporation of cobalt into its structure.

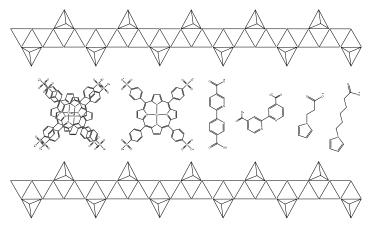


Figure 1 Schematic representation of the functionalized layered hydroxides

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