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COPPER(II) COMPLEXES WITH WATER-INSOLUBLE LIGANDS AS ELECTROCATALYSTS FOR CARBON DIOXIDE REDUCTION TOWARDS C1 AND C2 PRODUCTS

Resumo: The growing energy demand has led to excessive emissions of carbon dioxide (CO_2) into the atmosphere, resulting in several environmental problems. In this context, electrochemical reduction of CO_2 (CO_2R) emerges as a promising process that can both contribute to reduce net CO_2 emissions and be an alternative/sustainable method to produce valuable chemicals. However, there are some factors that limit the use of CO_2R in large scale, including high overpotentials and poor selectivity.^[1] Thus, efforts have been made towards the development of more active, selective and stable electrocatalysts. Copper was shown to be the only pure metal able to promote the electrochemical reduction of CO_2 to hydrocarbons.^[1] Due to this unique property, several copper-based electrocatalysts have been studied during the past few decades. Many copper complexes exhibited good activity towards CO_2R and it was shown that most of them experience restructuring processes under CO_2R conditions, affecting activity and selectivity. Additionally, there are some important evidences concerning the reversible restructuring,^[2] which can be an interesting approach to reach higher stability. In this study, the activity, selectivity and stability of different copper complexes for CO_2R were investigated. Both $[\text{Cu}(\text{bzimpy})\text{Cl}_2]$ and $[\text{Cu}(\text{pyrben})(\text{NO}_3)](\text{NO}_3)$ were considered, where *bzimpy* and *pyrben* stand for 2,6-bis(2- benzimidazolyl)pyridine and 2-(2-pyridyl)benzimidazole, respectively. The products distribution was monitored by on-line EC-MS (Electrochemistry Coupled to Mass Spectrometry) and the quantification was made by Gas Chromatography. Briefly, the results showed that both complexes were active for CO_2R and a faradaic efficiency of 31% towards ethylene was obtained with the $[\text{Cu}(\text{bzimpy})\text{Cl}_2]$ at -1.24 V vs. RHE. Besides, this material showed higher stability than $[\text{Cu}(\text{pyrben})(\text{NO}_3)](\text{NO}_3)$ after polarizations in high positive potentials (0.96 V vs. RHE).

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