A molecular approach for rational catalyst design and understanding CO_2 electrochemical reduction

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The increasing levels of CO_2 in the atmosphere and the growing effects of global warming lead to the urgent need for sustainable strategies for CO_2 utilization and conversion. In this perspective, the electrochemical reduction of CO_2 triggered by renewable sources and catalyzed by transition metals represents a promising strategy to contrast massive utilization of fossil resources for the production of fuels and commodity chemicals.[1] A rational catalyst design is key to improve the efficiency of the overall catalytic process by controlling crucial aspects, such as overpotential, selectivity and stability. From this viewpoint, molecular catalysts, characterized by well-defined organometallic platforms, offer unique opportunities to provide a fundamental understanding of the CO_2 reduction reaction at a molecular level.[2]

In this contribution, the electrocatalytic CO_2 reduction performances of some representative families of homogeneous molecular catalysts based on earth-abundant transition metal will be discussed.[3-4] Complementary electrochemical, spectroscopic and *in situ* spectroelectrochemical studies allowed a detailed mechanistic investigation of the catalytic pathway based on the experimental detection of key intermediates involved in the process. The results highlight the critical role of intrinsic catalyst properties as well as the external reaction conditions, on the reactivity and selectivity of molecular catalysts. Furthermore, the confinement of molecular catalysts into reticular framework will be discussed as a strategy to perform CO_2 electroreduction in aqueous media, focusing on how basic principles of molecular catalysis and reticular chemistry may be used to alter the reaction mechanism and catalyst performances.[5]

References

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Federico Franco obtained a PhD in Chemistry and Material Sciences at the Università degli Studi di Torino (2016) under the supervision of Prof. Roberto Gobetto with a thesis on the development of homogeneous molecular catalysts for the electro- and photocatalytic CO_2 reduction. In 2016, he joined as a postdoctoral researcher the group of Prof. Julio Lloret-Fillol at the Institute of Chemical Research of Catalonia (ICIQ) in Tarragona (Spain), where he focused on the mechanistic understanding of molecular catalysts for the electro- and photochemical activation of small molecules, including hydrogen evolution reaction, CO_2 reduction and organic transformations, by using *in situ* spectroelectrochemical techniques. He also worked on molecularly-defined reticular heterogeneous systems (COFs) for the electrochemical CO_2 activation and conversion. In 2019, he moved to the Department of Interface Science at the Fritz-Haber Institute of the Max Planck Society (group of Prof. Beatriz Roldan Cuenya, Berlin, Germany), where he studied *in situ*/*operando* spectroscopy applied to nanostructured electrocatalysts, especially focusing on nitrogen, nitrate and nitrite reduction reactions to ammonia. In 2021, he incorporated as a *Juan de la Cierva* Researcher in the group of Prof. Emilio Palomares-Gil at the ICIQ of Tarragona, where he is currently working on the design and development of metal or metal oxide-based hybrid nanomaterials for electrocatalytic applications.