

Towards the heterogenization of molecular catalysts for the (photo)electrocatalytic reduction of CO₂. Effect of anchorage functions on catalytic activity. The example of rhenium carbonyl molecular catalysts

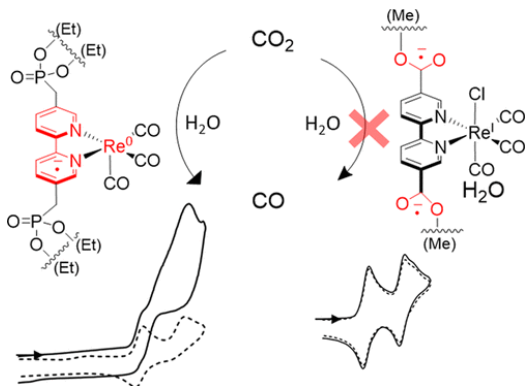
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The reduction of CO₂ is a domain of intense activity with the aim to use CO₂ as a source of carbon for fuels or, more broadly, for commodity molecules. Efforts are thus made to develop selective catalysts for CO₂ (photo)electroreduction. In that endeavour, molecular catalysts have advantages which is the fine control of their structure and properties. Molecular catalysts are usually first studied as homogeneous catalysts to evaluate their activity however, to move forward applications, it is often better to design devices in which the molecular catalyst is heterogenized on electrode (or photoelectrode) surface to perform processes enabling to store renewable energy in chemical bonds. Among the various strategies to immobilize molecular catalysts, direct chemical bonding to conductive surfaces presents some advantages because of the robustness of the linkage. When the catalyst is a transition metal complex, the anchoring group has to be connected to the complex through the ligands, and an important question is thus raised on the influence of this function on the redox and on the catalytic properties of the complex.

In this communication, we illustrate this issue through the detailed investigation and we show the effect of conjugated and non-conjugated substituents, structurally close to anchoring functions previously used to immobilize rhenium carbonyl bipyridyl molecular catalysts for supported CO₂ (photo)electroreduction. We show that carboxylic ester groups, mimicking anchoring the catalyst via carboxylate binding to the surface, have a drastic effect on the catalytic activity of the complex toward CO₂ electroreduction. The reasons for such an effect are revealed via a combined spectro-electrochemical analysis showing that the reducing equivalents are mainly accumulated on the electron-withdrawing ester on the bipyridine ligand preventing the formation of the rhenium(0) center and its interaction with CO₂. Alternatively, alkyl-phosphonic ester substituents, not conjugated with the bpy ligand, mimicking anchoring the catalyst via phosphonate binding to the surface, allow preserving the catalytic activity of the complex (Figure).^[1]



References

[1] M. Guyot, M.-N. Lalloz, J. S. Aguirre-Araque, G. Rogez, C. Costentin, S. Chardon-Noblat, *Inorg. Chem.* **2022**, published online doi.org/10.1021/acs.inorgchem.2c02473.

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