

Rhenium-bipyridyl-carbonyl molecular catalyst heterogenization in LSH layered hydroxides; characterization, redox properties and effect of the catalyst anchoring on CO₂ electroreduction activity

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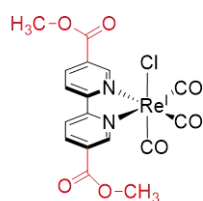
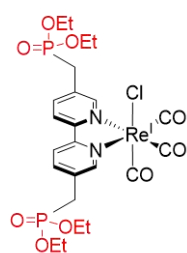
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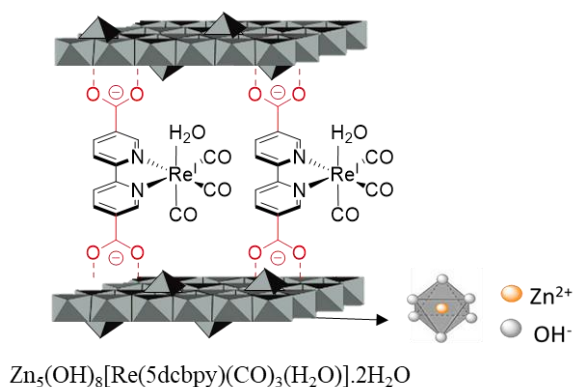
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Heterogenization of molecular catalysts on (photo)electrode surfaces is required to design devices enabling to store renewable energy in chemical bonds. Among the various strategies to immobilize molecular catalysts, direct chemical bonding presents some advantages due to the robustness of the linkage¹. When the catalyst is, as it is often the case, 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 properties and on the catalytic properties of the complex. Although the role of substituents present on ligands of molecular catalysts has been studied in many cases², the question of the effect of anchoring groups has not been specifically reported. Herein we will illustrate this issue through the detailed investigation of rhenium tris-carbonyl bipyridine (bpy) complexes. We will show that the presence of methoxycarbonyl groups on bpy (cf. scheme), used as a mimic for covalent attachment of the Re complex on a material, such as LSH, dramatically decrease the potential of the formation of the catalytic active species for CO₂ electroreduction. A detailed study combining cyclic voltammetry and spectroscopies reveals the underlying reasons for such a drastic effect. Then, we will show that using different anchoring groups, such as diethylmethyl phosphonate ester not conjugated with the bpy ligand (cf. Scheme), allows preserving the catalytic activity toward CO₂ electroreduction at reasonable applied potential.

EXAMPLES OF STUDIED COMPLEXES



HYBRID CATALYST



Scheme

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¹ Whipple, D. T.; Kenis, P. J. A. Prospects of CO₂ Utilization via Direct Heterogeneous Electrochemical Reduction. *J. Phys. Chem. Lett.* **2010**, *1*, 3451–3458

² Boraghi, M.; White, T. A.; Pordel, S.; Payne, H. Substituents and Cocatalyst Effect on the Catalytic Response and Overpotential of Re(I) Catalysts for CO₂ Reduction. *ACS Appl. Energy Mater.* **2021**, *4*, 13725–13734.