Discussion and analysis: Strength and weakness of molecular HER catalysts

General comments on molecular catalysts

Hydrogen evolution might be catalyzed by a discrete molecule. Normally such molecule is a metal complex, ML_n.

Strength of molecular catalyst:

(1)The structure of molecular catalysts and catalytic intermediates can be probed using readily available tools such as NMR and X-ray crystallography. The active site of catalyst is often obvious, e.g., the metal center or certain ligand sites. The catalytically active species are more uniform than those of heterogeneous catalysts which consist of multiple reaction sites. Molecular catalyst is more or less a "single-site" catalyst.

(2)Molecular catalyst is module and can be turned systematically to vary the catalytic property. For ML_n, the catalyst can be changed by varying M, L, or both. Since each complex can contain multiple and different ligands, molecular catalysts are more diverse than heterogeneous catalysis.

(3)The rational design and development of molecular catalysts are more advanced than heterogeneous catalysis. This is a result of the points (1) and (2).

(4)The reaction rate (TOF) of a molecular catalyst is often higher than a heterogeneous catalyst.

General comments on molecular catalysts

Hydrogen evolution might be catalyzed by a discrete molecule. Normally such molecule is a metal complex, ML_n.

Drawback of molecular catalyst for HER:
(1)Stability of molecular catalyst tends to be lower than heterogeneous catalyst. Ligands can be decomposed or substituted under the hush reaction conditions of HER (reductive; acidic).
(2)A molecular catalyst with sophisticated ligand tends to be expensive and hard to prepare.
(3)When dissolved in solution, molecular catalyst need to diffuse to the electrode to participate in catalysis. So not all catalysts are active at the same time. It was shown that as if only catalyst in a 2 μm thick layer near the electrode is active for homogeneous electrocatalysis.
(4)A molecular catalyst has a much larger footprint (area) than a single metal or a small heterogeneous cluster. As a result, less catalyst can be loaded in a fixed area.
(5)To have a molecular catalyst moving around in solution makes the design of an electrochemical device difficult. For example, in membrane electrolyzer, the membrane only allows the movement of proton. Such design is not suitable for molecular catalysis.