Homogeneous Catalysis of Electrochemical Hydrogen Evolution by Iron(0) porphyrins

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Summary

• The catalyst
• General background
• Cyclic voltammetry studies
• Reaction pathway and mechanism
• Evolution
The catalyst

Introduced as TPPFe(III)Cl

Active form is TPPFe(0)^2-

An acid as proton source
General background

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Still an interesting goal (chemicals, energy)
General background

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1996: mainly heterogeneous catalysts
- Pt catalyst (works, but major drawbacks)
- Functionalization of electrodes, other metals
General background

**Homogeneous** Catalysis of Electrochemical Hydrogen Evolution by Iron(0) porphyrins

Less adsorption and diffusion limitation

1996: no hydrogenase mimics, mainly mechanistic studies
General background

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Catalytic activity of metal-porphyrin complexes still known

Porphyrrins absorb light (mechanistical studies)
Cyclic voltammetry studies

Excellent method for the field

Scan of potential, measure of the current

Thermodynamic and kinetic parameters accessible (mechanistic studies)

Mechanistic verification by simulation
Cyclic voltammetry studies

Overpotential: -1.60 vs SHE in DMF
Faradaic yield

Selective, stable catalyst

TON: 22 after 1h (good in 1996, very slow now)
Reaction pathways

• The reaction involves the coordination sphere of the Fe(0) => same complex with Cu (similar potential) ineffective

• Ability to explain the 3,3’ peak
  => Fe(II)H⁻ intermediate
Reaction pathways

- TPPFe(II)H-/TPPFe(I)H$_2^-$  -1.88 V vs SCE
- Same complex with Et and n-Bu replacing H  
  => -1.950 V vs SCE and -1.956 V vs SCE
Proposed mechanism

\[
\text{PFe(II)} + e^- \rightleftharpoons \text{PFe(I)}^- \quad (E^0 = -1.035 \text{ V vs SCE})
\]

\[
\text{PFe(I)}^- + e^- \rightleftharpoons \text{PFe(0)}^{2-} \quad (E^0 = -1.600 \text{ V vs SCE})
\]

\[
\text{PFe(0)}^{2-} + \text{AH}^+ \xrightleftharpoons{2 \times 10^8 \text{ M}^{-1} \text{s}^{-1}} \text{PFe(II)H}^- + \text{A}
\]

\[
\text{PFe(II)H}^- + \text{AH}^+ \xrightleftharpoons{4 \times 10^5 \text{ M}^{-1} \text{s}^{-1}} \text{H}_2 + \text{PFe(II)} + \text{A}
\]

\[
\text{PFe(II)H}^- + e^- \rightleftharpoons \text{PFe(I)H}^{2-} \quad (E^0 = -1.950 \text{ V vs SCE})
\]

\[
\text{PFe(I)H}^{2-} + \text{AH}^+ \rightarrow \text{H}_2 + \text{PFe(I)}^- + \text{A}
\]

\[
\text{PFe(II)} + \text{PFe(0)}^{2-} \rightarrow 2\text{PFe(I)}^- \quad (\Delta G^0 = -0.565 \text{ eV})
\]

\[
\text{PFe(II)} + \text{PFe(I)H}^{2-} \rightarrow \text{PFe(I)}^- + \text{PFe(II)H}^- \quad (\Delta G^0 = -0.915 \text{ eV})
\]

\[
\text{PFe(I)}^- + \text{PFe(I)H}^{2-} \rightarrow \text{PFe(0)}^{2-} + \text{PFe(II)H}^- \quad (\Delta G^0 = -0.280 \text{ eV})
\]
Proposed mechanism

Experimental

Simulated
Findings and more recent work

- Confirmation of the heterolytic way

Homolytic (bimettalic)  Heterolytic (monomettallic)
Findings and more recent work

- Few studies treating that particular catalyst further
- Biomimetic approach (hydrogenases)

- Cobalt based
Findings and more recent work

• High turnover frequencies and total turnover number

• Overpotentials too large
  => try to improve by varying the ligands, the metal ion…

• Try to do it in water
Was the paper good?

- Interesting findings, supported by data
- Not much ideas for further work or background
- Not much details on the technical part of the experiment
References


Professor Hu’s course