Chapter IV: Molecular Catalysis for CO_2 Reduction

Table of contents

- Scale of CO_2 chemistry
- Fundamental chemistry of CO_2
- Molecular catalysis for electrochemical reduction of CO_2

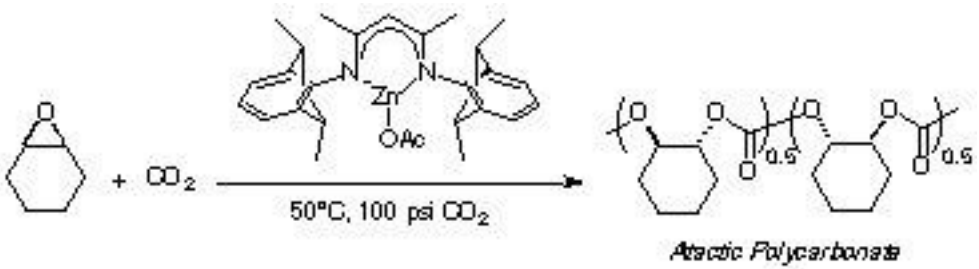
I. Scale of CO_2 chemistry

Chemical methods of removing (utilizing) CO_2

1. plant more trees (capacity, respiration balance)
2. make coca-cola etc.
3. make urea, carbonate, etc.

$$2\ NH_3 + CO_2 \rightarrow H_2N\text{-}COONH_4$$
$$H_2N\text{-}COONH_4 \rightarrow (NH_2)_2CO + H_2O$$

4. make bio-degradable polymer



Nice, useful, and sometimes profitable chemistry
All small scale compared to the 20 billions of tons of CO_2 released every year...

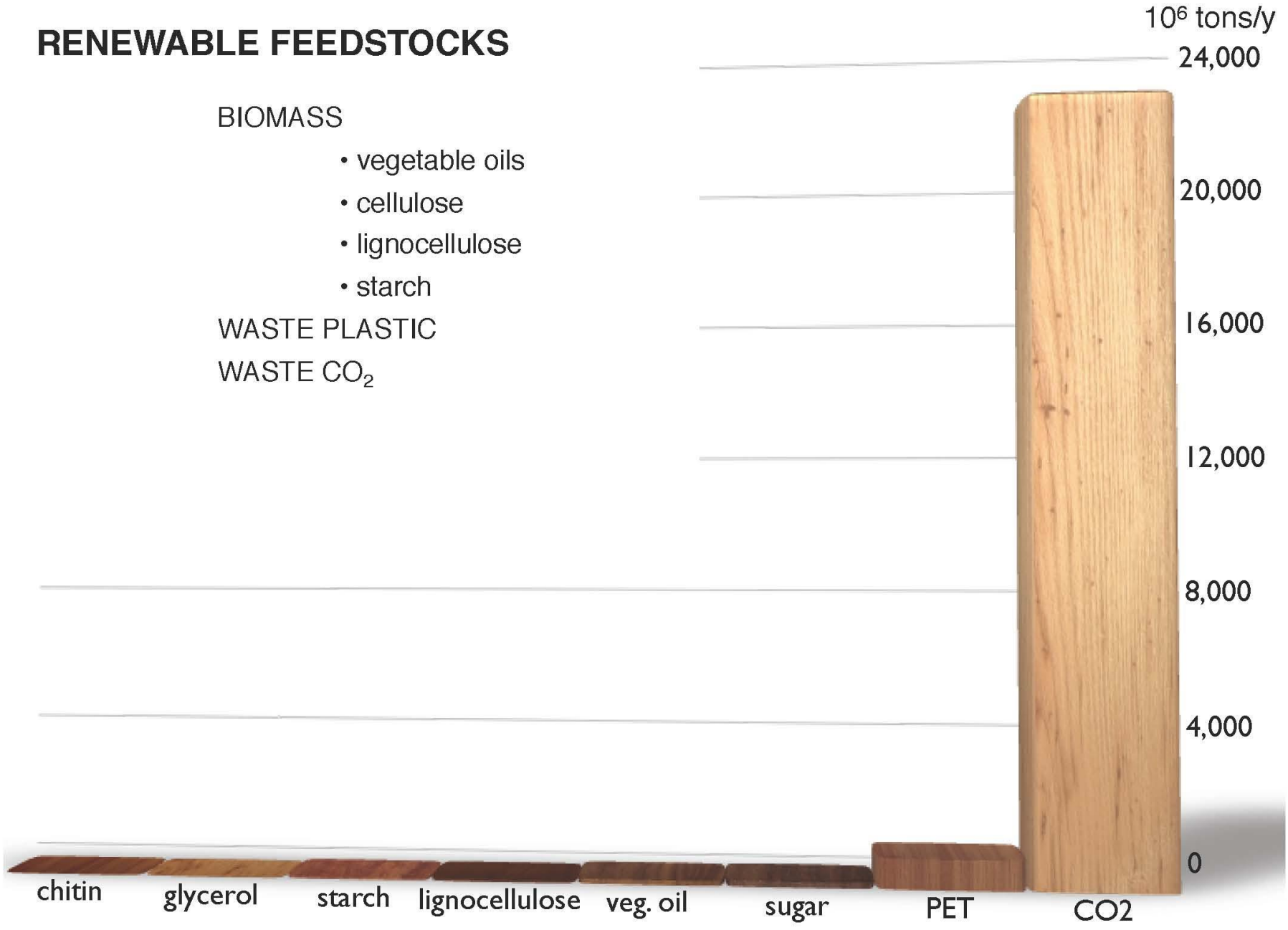
RENEWABLE FEEDSTOCKS

BIOMASS

- vegetable oils
- cellulose
- lignocellulose
- starch

WASTE PLASTIC

WASTE CO_2



Some CO_2 chemistry that are scalable

1. With hydrogen – consider CO_2 as a storage media for H_2
   Hydrogen need to be produced from renewable energies via water splitting

Option A:

$CO_2 + H_2 \rightarrow HCOOH$

Use:

(1) Formic acid can be used as energy source for formic acid fuel cell

(2) Formic acid is a liquid, and it is easy to carry. Formic acid can decompose to CO_2 and H_2 easily, with the help of a catalyst. So formic acid can be considered as a hydrogen storage materials. 4.3 wt%.

Option B:

$CO_2 + 3\ H_2 \rightarrow CH_3OH + H_2O$

Use:

(1) Methanol can be used as energy source for methanol fuel cell

(2) Methanol can be used for direct combustion, to replace petro

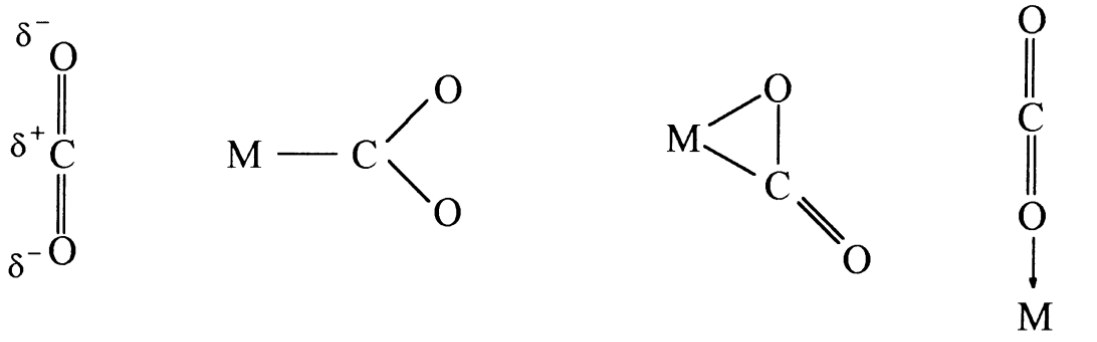
(3) Methanol is the starting materials to make nearly all chemical products that are produced from fossil resources

II. Fundamental chemistry of CO_2

Interactions of CO_2 and transition metals

A metal is often used to activate CO_2

Typical binding modes of CO_2



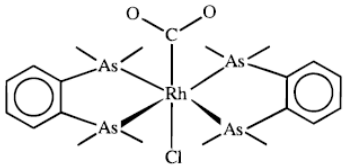
$\eta^1(C)$ $\eta^2(C, O)$ $\eta^1(O)$

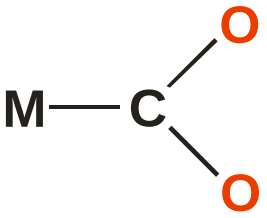
The first two coordination modes are commonly observed; the last one is rarely observed, but it might be invloved as unstable catalytic intermediates.

Yin et al. Coord. Chem. Rev. **1999**, 181, 27.

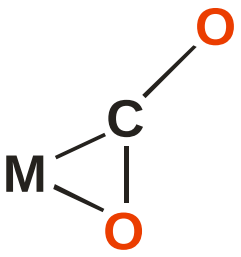
Common coordination modes of CO_2

Herskowitz (1977)
$[(diars)_2M(CO_2)(Cl)]$
M = Ir, Rh



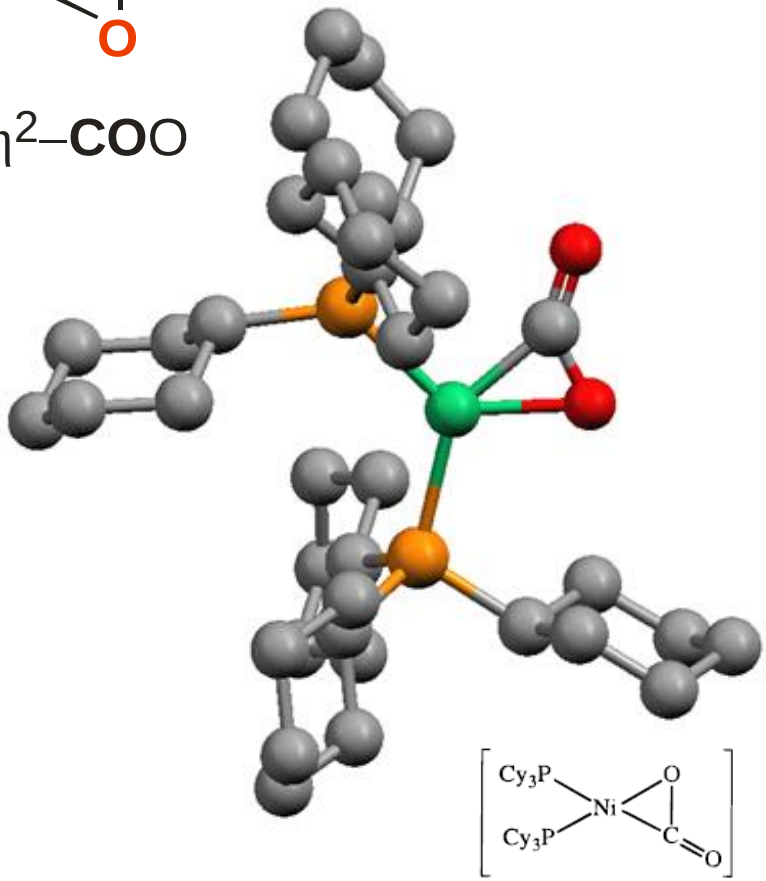


η^1–**C**O_2



η^2–**CO**O

Aresta (1975)
$[(Cy_3P)_2Ni(CO_2)]$



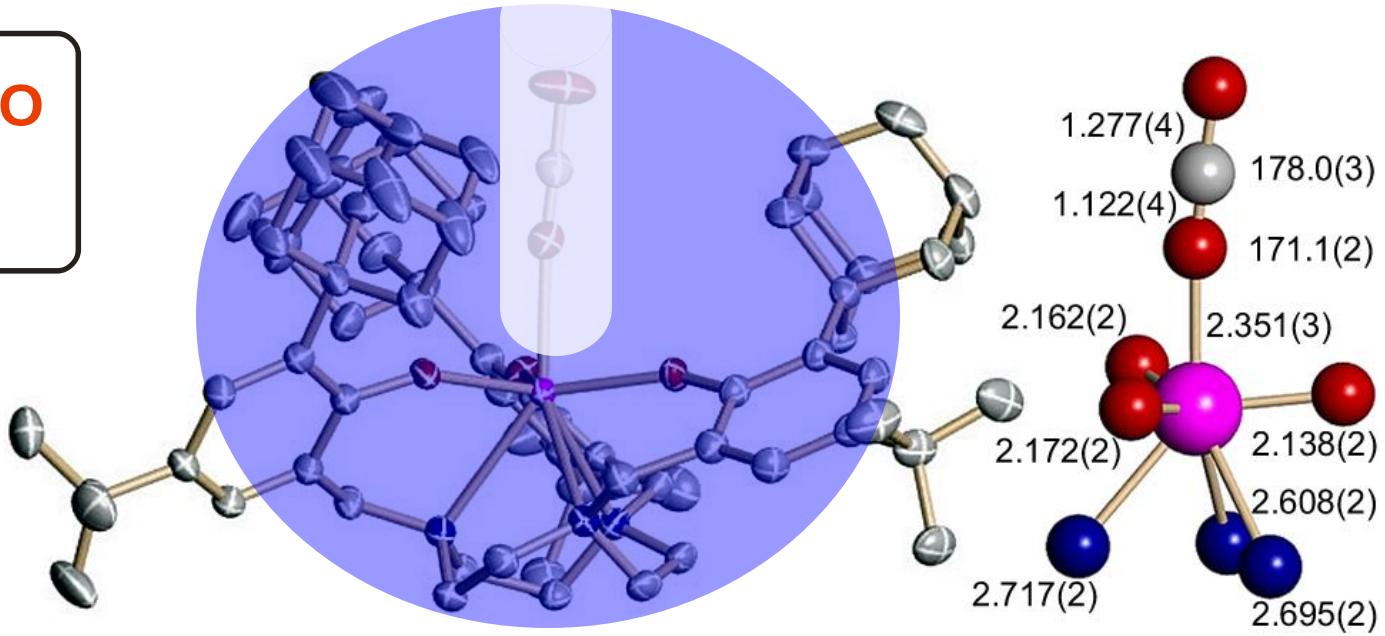
H. Tanaka *et al.*
***Organometallics* (1992) *11*, 1450**

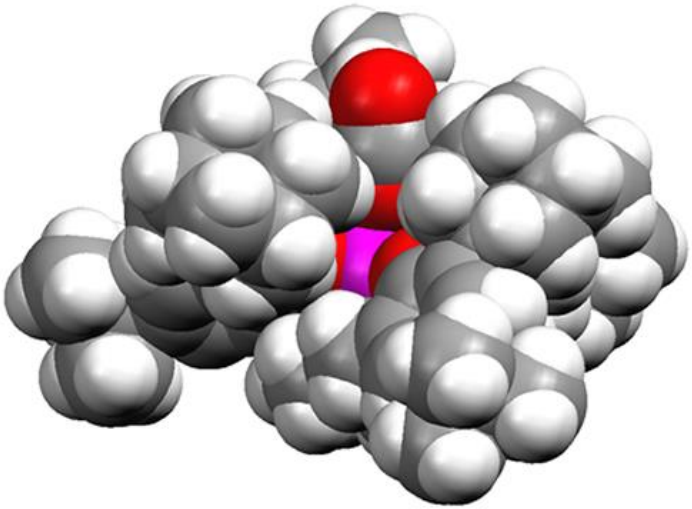
A. Dohring *et al.*
***Z. Naturforsch.* (1985) *40*, 484**

A rare coordination mode of CO_2

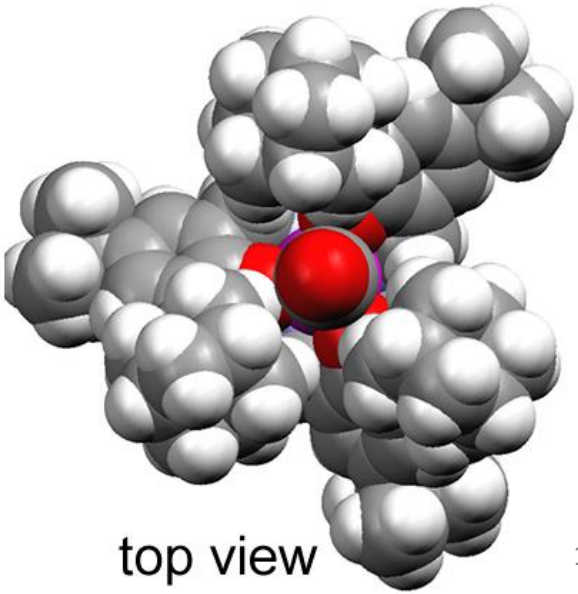
M—O—C—O

η^1–**O**CO





side view

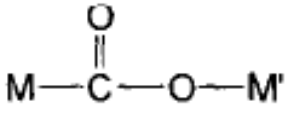


top view

I. Castro-Rodriguez & K. Meyer
in *Science* **2004**, *305*, 1757—17579.

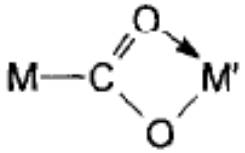
CO_2 as a bridging ligand

The coordination of M to the central C atom results in a relatively high negative charge on the terminal O atoms and increase in their nucleophilicity, thus promoting its coordination to another metal (M' and M'').

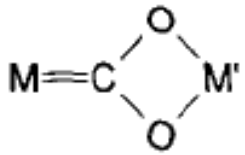


I

μ_2–η^2



IIa



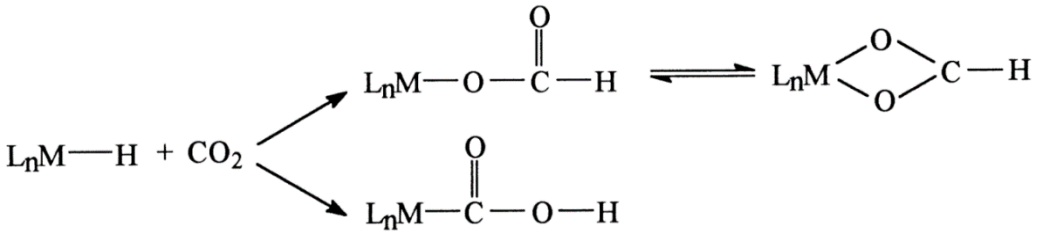
IIb

μ_2–η^3

Leitner, W. Coord. Chem. Rev. **1996**, 153, 257-284

A fundamental step in metal-catalyzed CO_2 reduction

CO_2 insert into M-H bond



formate, more common

carboxylic acid

In this reaction, CO_2 may or may not first coordinate to the metal

Summary of fundamental chemistry of CO_2

- CO_2 is an inert molecule. The reactivity of CO_2 can be enhanced by interaction with a catalyst.
- Several basic coordination modes of CO_2 to metal(s) are known.
- Insertion of CO2 to a metal-H bond is an imporant step in chemical reduction of CO_2.

III. Molecular catalysis for electrochemical reduction of CO_2

Why electrochemical reduction CO_2?

Electrochemical CO_2 reduction is an alternative to water splitting

Energy stored:

Water splitting: $2\,H_2O \xrightarrow{\text{energy}} 2\,H_2 + O_2$ E = 1.23 V

CO_2 reduction:

$2CO_2 \xrightarrow{\text{energy}} 2\,CO + O_2$ E = 1.34 V

$2CO_2 + 2H_2O \xrightarrow{\text{energy}} 2\,HCOOH + O_2$ E = 1.43 V

$CO_2 + H_2O \xrightarrow{\text{energy}} HCOH + O_2$ E = 1.30 V

$2CO_2 + 4\,H_2O \xrightarrow{\text{energy}} 2\,H_3COH + 3\,O_2$ E = 1.20 V

$CO_2 + 2\,H_2O \xrightarrow{\text{energy}} H_4C + 2\,O_2$ E = 1.06 V

All these C-based fuels have higher density than H_2, so they are easier to store and transport.

An overall CO_2 reduction reaction consistes of two half reactions:
(1)Oxygen evolution reaction (OER)

$$2H_2O \rightarrow \ O_2 + 4\ H^+ + 4\ e^-$$

(2) Electrochemical CO_2 reduction

$$CO_2 + 2H^+ + 2e^- \longrightarrow CO + H_2O$$
$$CO_2 + 2H^+ + 2e^- \longrightarrow HCOOH$$
$$CO_2 + 4H^+ + 4e^- \longrightarrow HCOH + H_2O$$
$$CO_2 + 6H^+ + 6e^- \longrightarrow CH_3OH + H_2O$$
$$CO_2 + 8H^+ + 8e^- \longrightarrow CH_4 + 2\ H_2O$$

Thermodynamic aspects of electrochemical CO_2 reduction

1 e reduction of CO_2 is difficult, because CO_2^- radical is very unstable

$$CO_2 + e^- \longrightarrow \cdot CO_2 \qquad E^o < -1.5 \text{ V vs. RHE}$$

Multi-e reduction of CO_2 have lower thermodynamic potentials (vs. RHE)

$$CO_2 + 2H^+ + 2e^- \rightleftharpoons CO + H_2O \qquad E^o = -0.11 \text{ V}$$

$$CO_2 + 2H^+ + 2e^- \rightleftharpoons HCOOH \qquad E^o = -0.20 \text{ V}$$

$$CO_2 + 4H^+ + 4e^- \rightleftharpoons HCOH + H_2O \qquad E^o = -0.07 \text{ V}$$

$$CO_2 + 6H^+ + 6e^- \rightleftharpoons CH_3OH + H_2O \qquad E^o = 0.03 \text{ V}$$

$$CO_2 + 8H^+ + 8e^- \rightleftharpoons CH_4 + 2\,H_2O \qquad E^o = 0.17 \text{ V}$$

Compare to hydrogen evolution:

$$2H^+ + 2e^- \rightleftharpoons H_2 \qquad E^o = 0 \text{ V}$$

Challenge in electrochemical CO_2 reduction

Challenge for catalysis

1. The thermodynamic potentials of CO_2 reduction are close to hydrogen evolution. Proton is more reactive than CO_2. Therefore, hydrogen evolution is a common side reaction. To alleviate hydrogen evolution, CO2 reduction is commonly done in neutral to basic water, or in organic solvents.
2. Many carbon-based products are produced at similar potentials. The selectivity of CO_2 reduction is a problem.
3. Known catalysts have generally a low efficiency: small current density at high overpotentials.
4. The common problems for all electrocatalysts – cost and stability of catalysts

$$CO_2 + 2H^+ + 2e^- \longrightarrow CO + H_2O$$
$$CO_2 + 2H^+ + 2e^- \longrightarrow HCOOH$$
$$CO_2 + 4H^+ + 4e^- \longrightarrow HCOH + H_2O$$
$$CO_2 + 6H^+ + 6e^- \longrightarrow CH_3OH + H_2O$$
$$CO_2 + 8H^+ + 8e^- \longrightarrow CH_4 + 2\,H_2O$$

Among various CO_2 reduction reactions, we will only focus on the 2e reduction to form either CO or HCOOH as products. There are two reasons for this:
(1) The energy content of CO or HCOOH is even higher than CH_3OH or CH_4.
(2) 2e reduction is generally easier to control than 6e or 8e reduction.

$$2CO_2 \xrightarrow{\text{energy}} 2\,CO + O_2 \qquad E = 1.34\ V$$
$$2CO_2 + 2H_2O \xrightarrow{\text{energy}} 2\,HCOOH + O_2 \qquad E = 1.43\ V$$
$$CO_2 + H_2O \xrightarrow{\text{energy}} HCOH + O_2 \qquad E = 1.30\ V$$
$$2CO_2 + 4\,H_2O \xrightarrow{\text{energy}} 2\,H_3COH + 3\,O_2 \qquad E = 1.20\ V$$
$$CO_2 + 2\,H_2O \xrightarrow{\text{energy}} H_4C + 2\,O_2 \qquad E = 1.06\ V$$

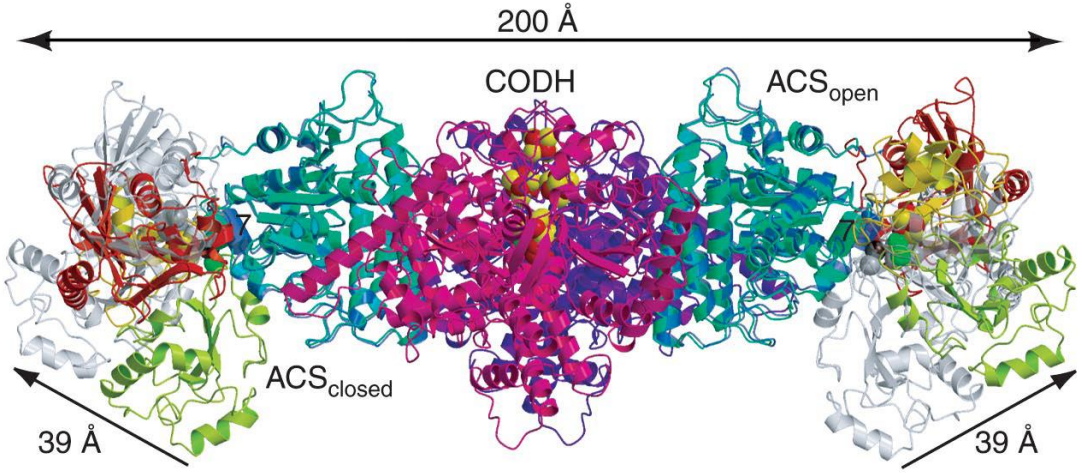
III-1. A biological catalyst

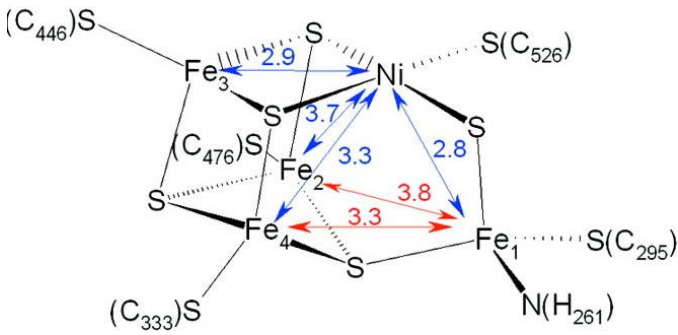
Enzymatic CO_2 Reduction: FeNi-CODH

Carbon monoxide dehydrogenases (CODH) are enzymes that catalyze the electrochemical interconversion of CO_2 and CO.

$$CO_2 + 2H^+ + 2e^- \rightleftharpoons CO + H_2O$$

The anaerobic form of enzyme contains FeNi in the active site.

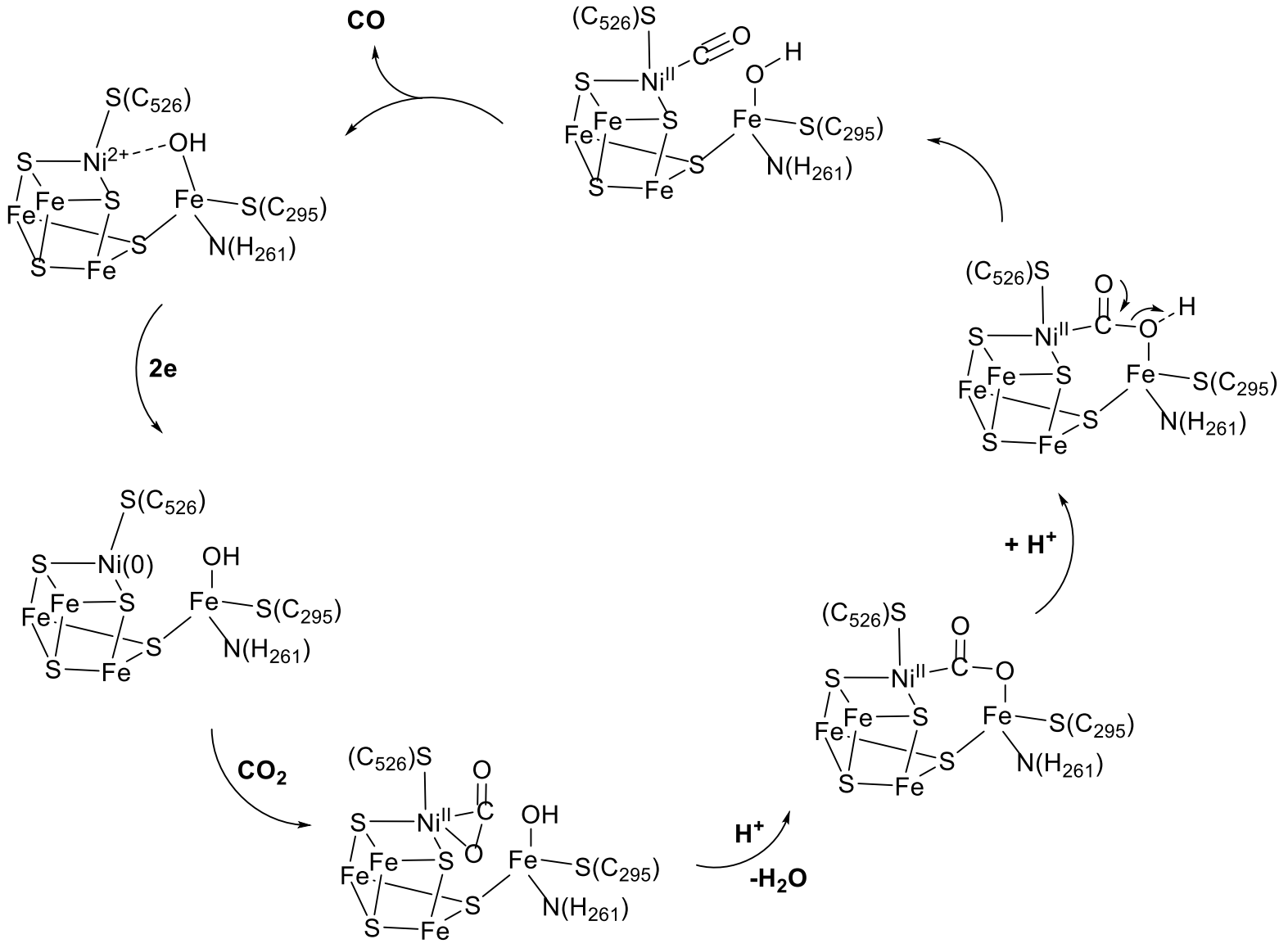




Active site

Crystal structure of FeNi-CODH (in a protein assembly).

Proposed mechanism of CO_2 reduction by FeNi-CODH



Kubiak et al. Chem. Soc. Rev. 2009, 38, 89.

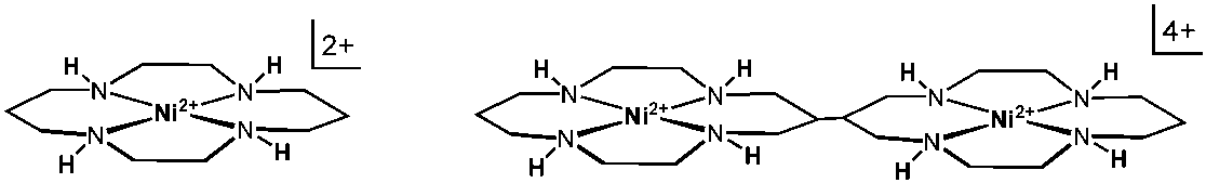
III-2. Molecular catalysts

Electrocatalytic 2 electron CO_2 reduction

$CO_2 + 2H^+ + 2e^- \rightleftharpoons CO + H_2O$ E = -0.11 V vs. RHE

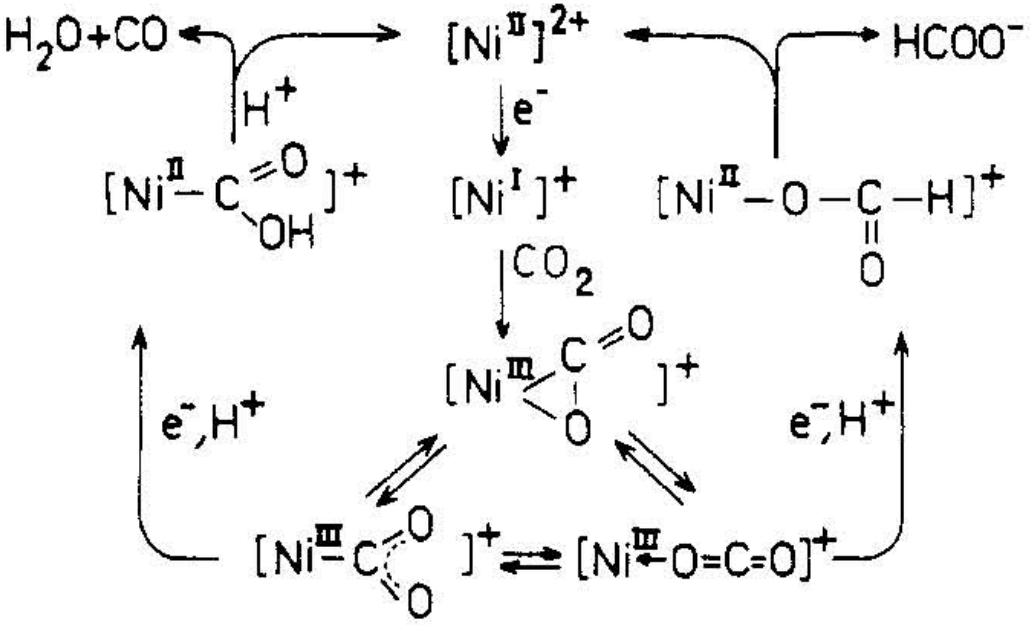
$CO_2 + 2H^+ + 2e^- \rightleftharpoons HCOOH$ E = -0.20 V vs. RHE

$2H^+ + 2e^- \rightleftharpoons H_2$ E = 0 V vs. RHE



These nickel complexes were found to catalyze CO_2 reuction in DMF
At -1.6 V vs. SCE; the product is a mixture of CO and HCOOH

Origin of the different products

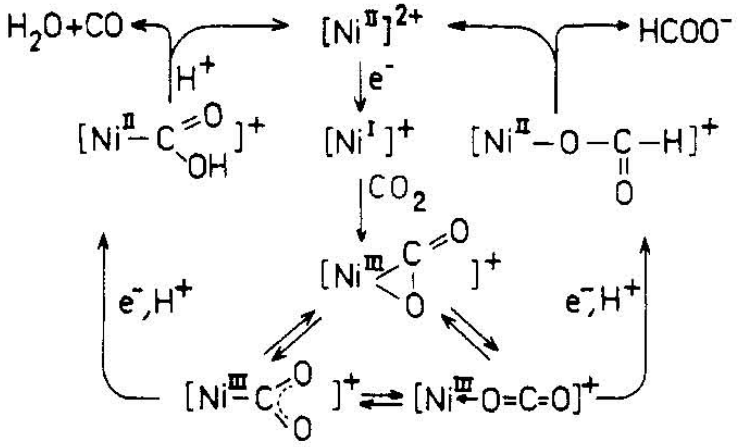


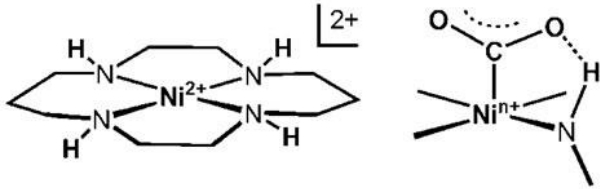
Whether CO or HCOOH is produced depending on the intermediates of Ni-CO_2 complex; A C-bound CO_2 leads to CO; a O-bound CO_2 leads to HCOOH

Collin, Sauvage et al. Inorg. Chem. 1988, 27, 1986.

Selective 2 electron CO_2 Reduction: to CO

at pH>4 in water, however, only CO is produced with these complexes. At E = ~ -1 V vs. RHE. No HCOOH nor H_2 is produced. So the reaction is selective for CO formation.



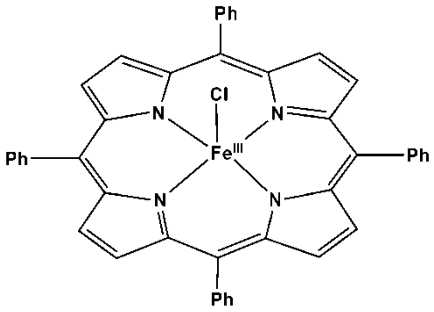


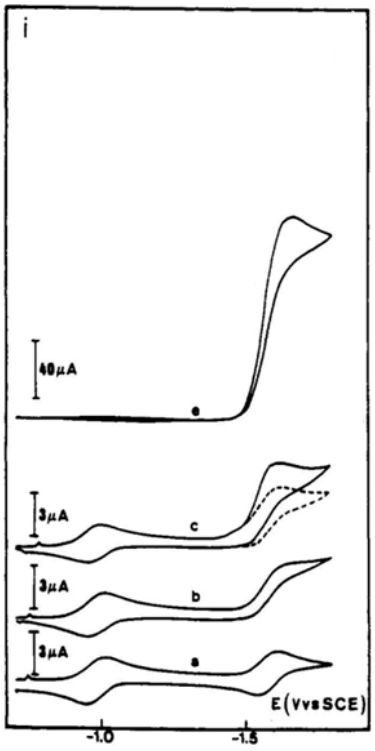
Hydrogen Bonding

It is proposed that hydrogen bonding interaction between the NH ligand and the terminal O of coordinated CO_2 stablized the C-bound Ni-CO_2 intermedaite, so CO formation is selective.

Sauvage et al. JACS **1986**, *108*, 7461.

Selective 2 electron CO_2 Reduction: to CO





Cat + CF_3CH_2OH +CO_2
Big catalytic current for CO_2 reduction
Only CO is produced

Cat + CF_3CH_2OH Small catalytic current for HER

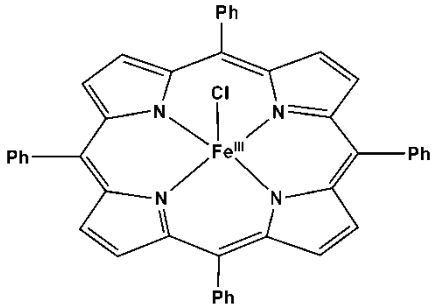
Cat + CO_2 Small catalytic current for CO_2 reduction

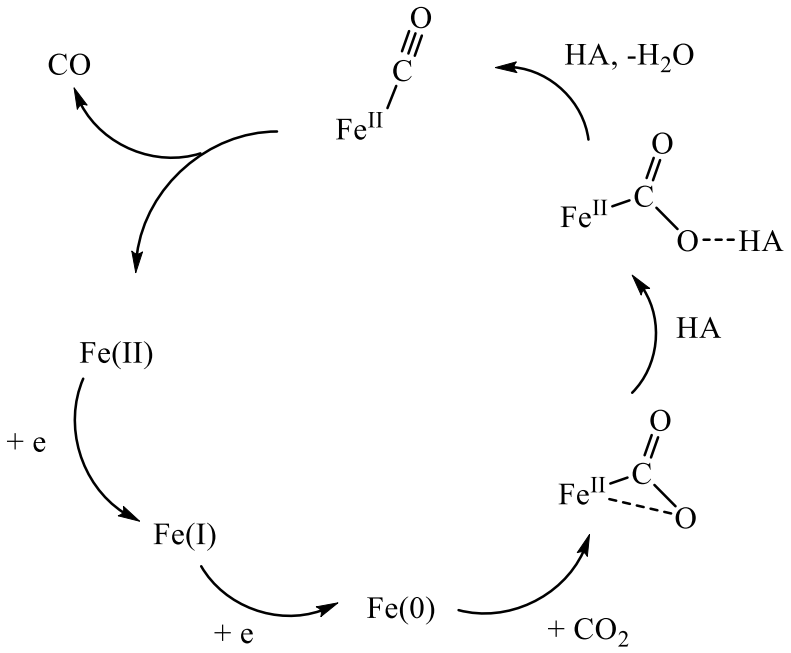
Cat (Fe(I) to Fe(0) at -1.6 V)

Saveant et al. JACS **1994**, *116*, 5015; JACS **1996**, *118*, 1769.

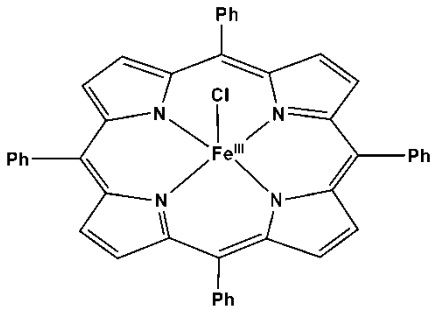
Selective 2 electron CO_2 Reduction: to CO

Proposed mechanism:



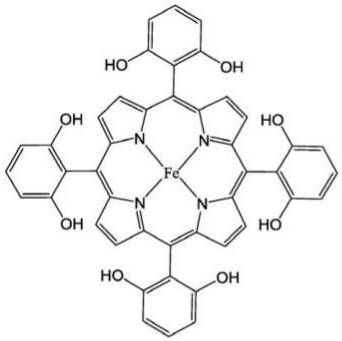


How about putting hydrogen bonding units on the Fe-porphyrin complex?

from 

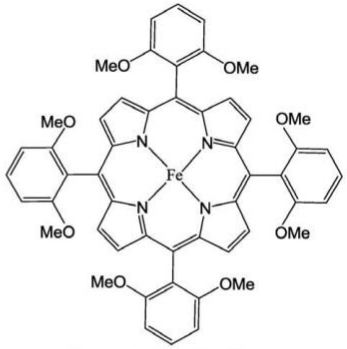
to

FeTDHPP



Iron 5,10,15,20-tetrakis(2',6'-dihydroxylphenyl)-porphyrin

FeTDMPP



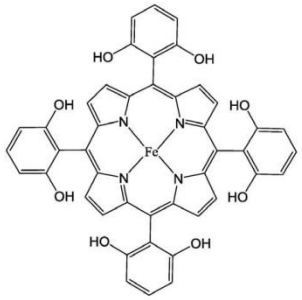
Iron 5,10,15,20-tetrakis(2',6'-dimethoxyphenyl)-porphyrin

FeTDHPP has a similar electronic property to FeTDMPP
FeTDHPP can engage in hydrogen bonding, while FeTDMPP cannot.

Saveant et al. Science 2012, 338, 90.

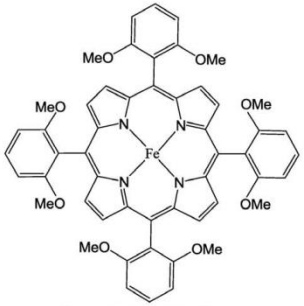
How about putting hydrogen bonding units on the Fe-porphyrin complex?

FeTDHPP

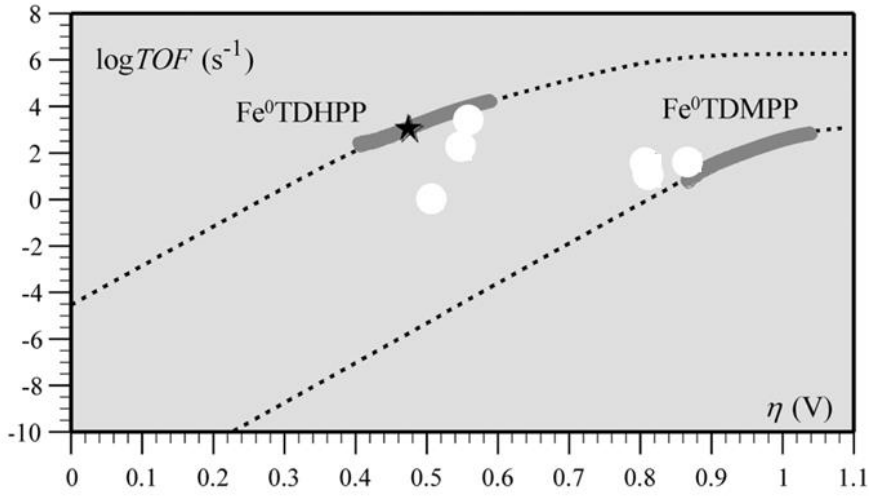


Iron 5,10,15,20-tetrakis(2',6'-dihydroxylphenyl)-porphyrin

FeTDMPP



Iron 5,10,15,20-tetrakis(2',6'-dimethoxyphenyl)-porphyrin

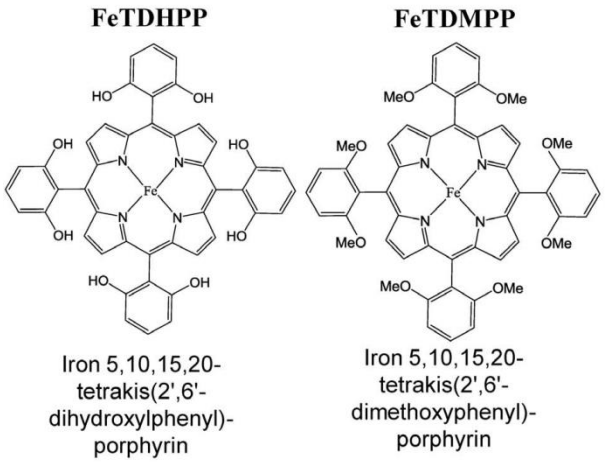


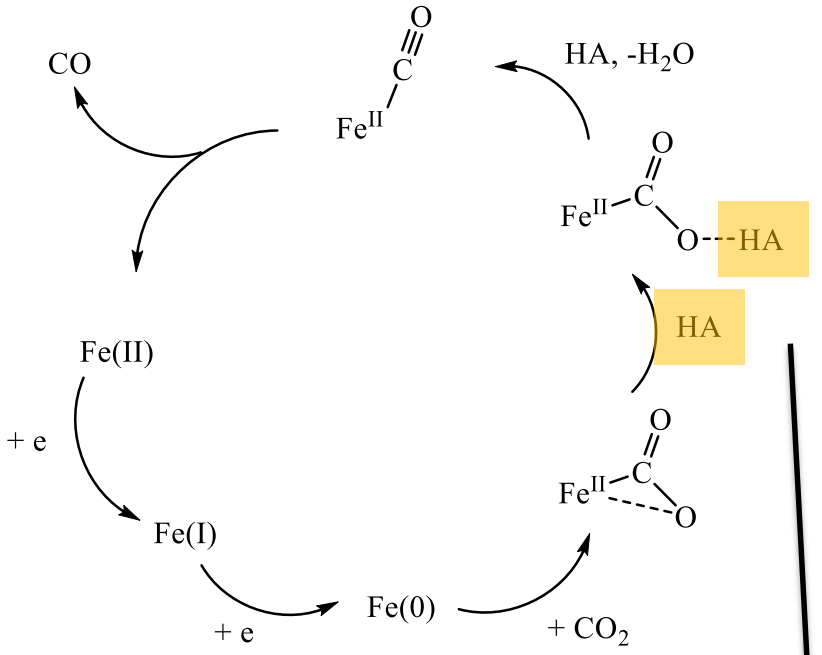
Having a hydrogen bonding unit in the molecule shifts the overpotential towards smaller values while maintaining similar turnover frequencies.

Saveant et al. Science 2012, 338, 90.

Selective 2 electron CO_2 Reduction: to CO

Proposed mechanism:





Intra-molecular proton donor speeds up the reaction

Conclusion

- The CO_2 emission is at a massive scale; only chemistry that uses a huge amount of CO_2 might have an impact in decreasing the global CO_2 emission.

- CO_2 is a relatively inert molecule that can be activated by a metal catalyst.

- Molecular complexes can serve as catalysts for electrocatalytic CO_2 reduction. The most abundant examples concern 2-electron reduction of CO_2 to form formate or CO. The selectivity might be controlled by tuning the ligand environment of the metal catalysts.