

Valorizing Carbon Dioxide into Commodity Chemicals (& Energy Carriers) using Catalysis

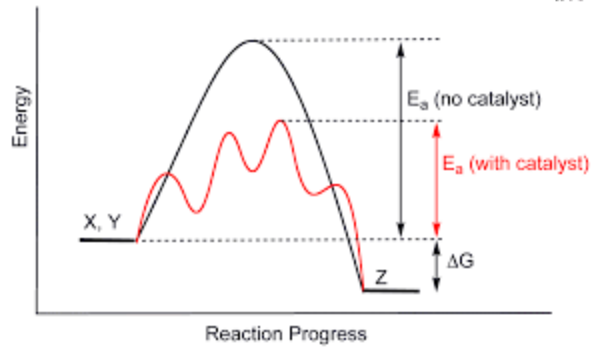
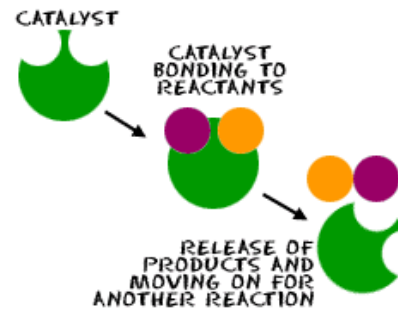
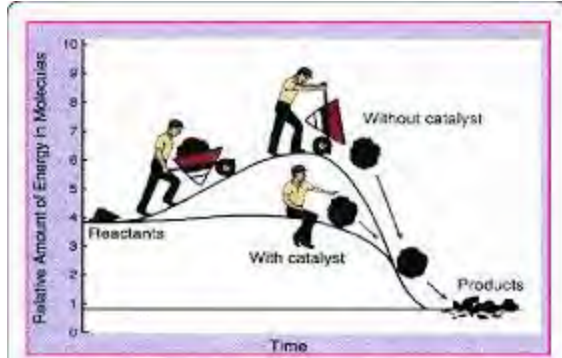


Wesley Bernskoetter
Department of Chemistry
Mizzou CEI: Oct 3, 2024

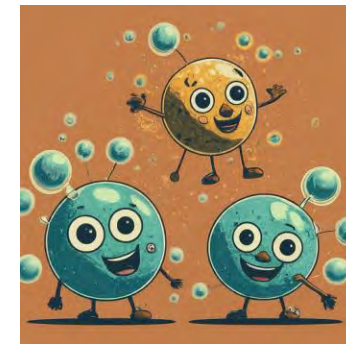
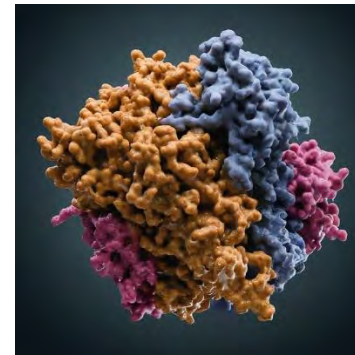


What are Catalysts?

high fidelity how ...



From web image search



From AI (Imagen 2)

What are Catalysts?

An alternate analogy

Catalysts are molecular machines...

...they assemble feedstock parts



After constructing product, they start the same process again

Motivations and Inspirations

CO₂-A Renewable C₁ Feedstock

- Highly abundant (10^{14} tons in atmosphere and oceans)
- Cheap availability
- Essentially non-toxic (compared to $\text{Cl}_2\text{C}=\text{O}$ & CO)
- It sticks to metals (the active part of most catalysts) reasonably well



Motivations and Inspirations

CO₂-A Renewable C₁ Feedstock

- Highly abundant (10^{14} tons in atmosphere and oceans)
- Cheap availability
- Essentially non-toxic (compared to $\text{Cl}_2\text{C}=\text{O}$ & CO)
- It sticks to metals (the active part of most catalysts) reasonably well



Motivations and Inspirations

CO₂-A Renewable C₁ Feedstock

- Highly abundant (10^{14} tons in atmosphere and oceans)
- Cheap availability
- Essentially non-toxic (compared to $\text{Cl}_2\text{C}=\text{O}$ & CO)
- It sticks to metals (the active part of most catalysts) reasonably well



Commodity Chemicals

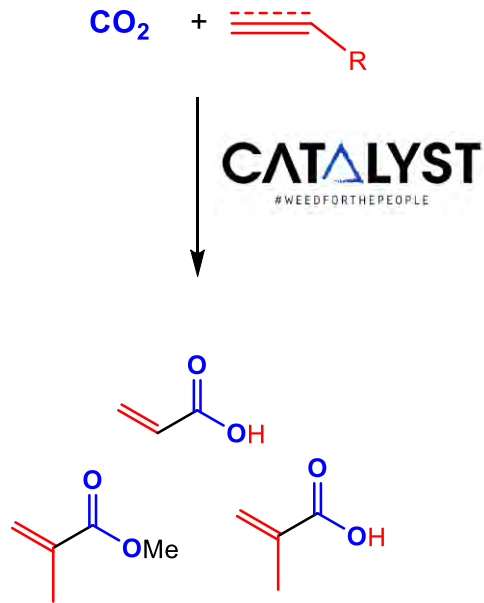
*chemicals we use to
make other stuff*

Molecular Energy Sources

*chemicals we use as
fuels or to store fuels*

Current & Recent CO₂ Catalysis Projects and \$

Sustainable Polymer Building Blocks

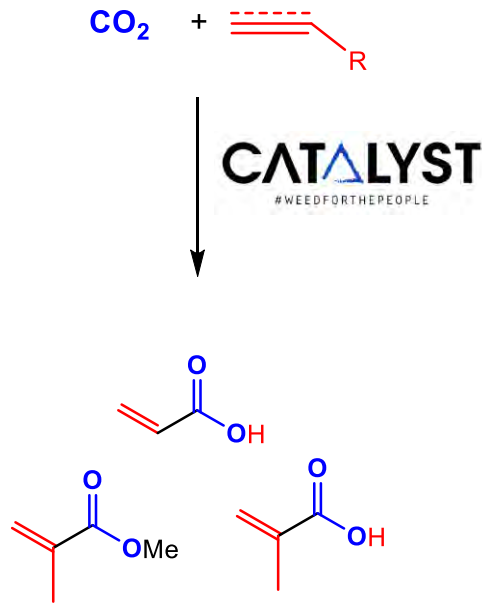


Acrylic polymers:
Diapers, Plexiglass



Current & Recent CO₂ Catalysis Projects and \$

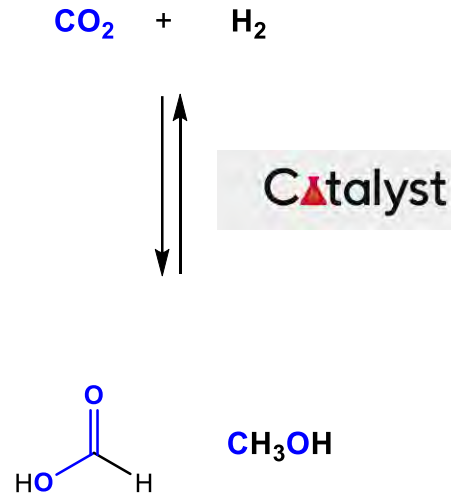
Sustainable Polymer Building Blocks



Acrylic polymers:
Diapers, Plexiglass



Methanol & Energy Storage

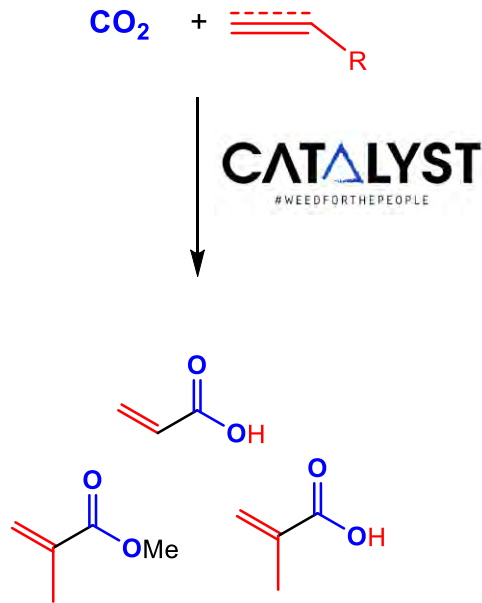


Input for Fuel Cells or
Storage for Hydrogen



Current & Recent CO₂ Catalysis Projects and \$

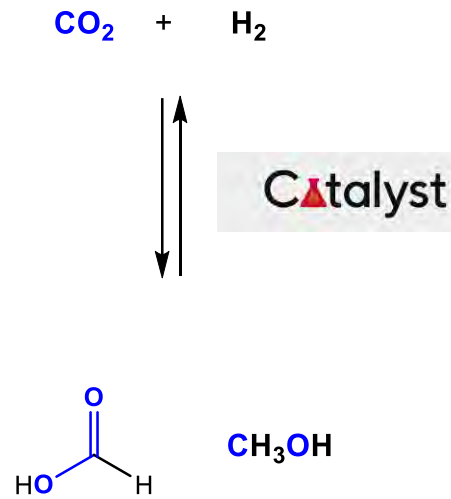
Sustainable Polymer Building Blocks



Acrylic polymers:
Diapers, Plexiglass



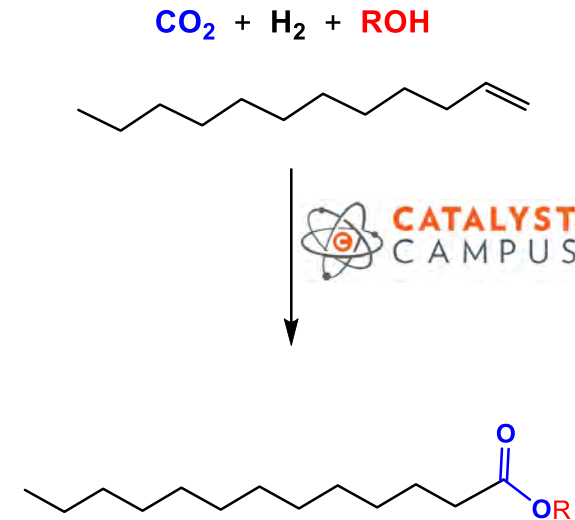
Methanol & Energy Storage



Input for Fuel Cells or
Storage for Hydrogen



Lower Carbon Intensity Diesel

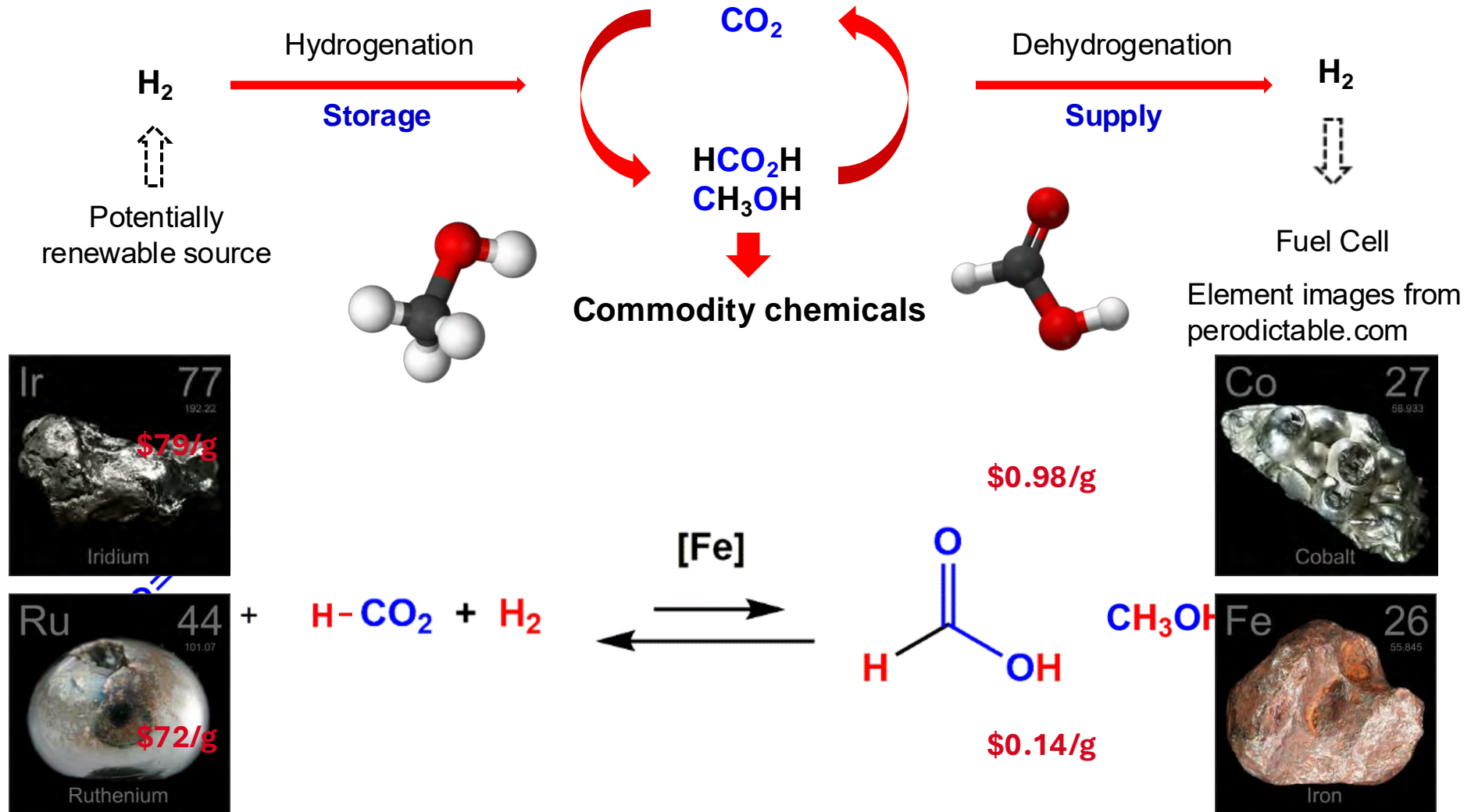


Diesel Fuel with Partial
Renewable Carbon Input



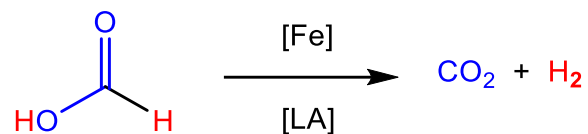
Reversible CO₂ Hydrogenation

For Chemicals & Energy



If At First You Fail...

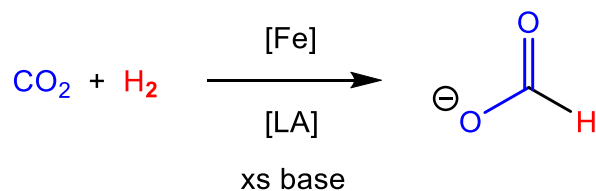
Formic acid dehydrogenation



2° PNP Fe(II) w/o LA: 200 TON

J. Am. Chem. Soc. **2014**,
136, 10234.

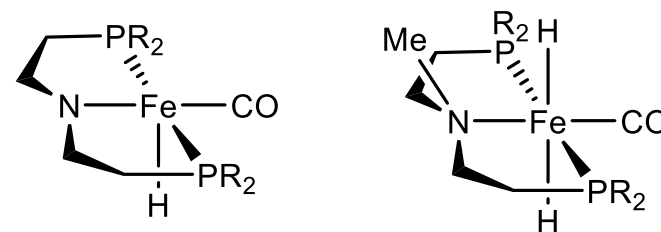
CO₂ hydrogenation to formate



2° PNP Fe(II) w/o LA: 900 TON

3° PNP Fe(II) w/o LA: 1100 TON

Chem. Sci. **2015**, 6, 4291.

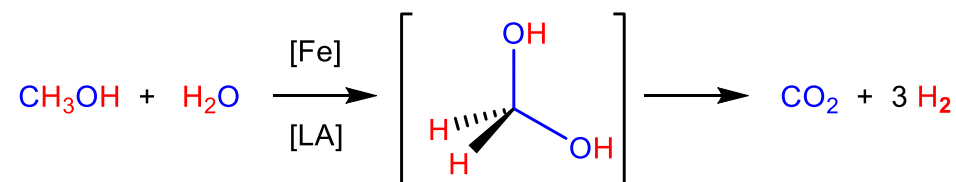


Catalysts Types

2° PNP Fe(II)

3° PNP Fe(II)

Methanol dehydrogenation



2° PNP Fe(II) w/o LA: 350 TON

ACS Catal. **2015**, 5, 2404.

...Add Lewis Acid

Formic acid dehydrogenation

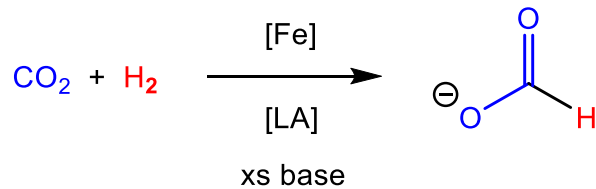


2° PNP Fe(II) w/o LA: 200 TON

2° PNP Fe(II) w/ LA: ~1 x 10⁶ TON

J. Am. Chem. Soc. **2014**,
136, 10234.

CO₂ hydrogenation to formate

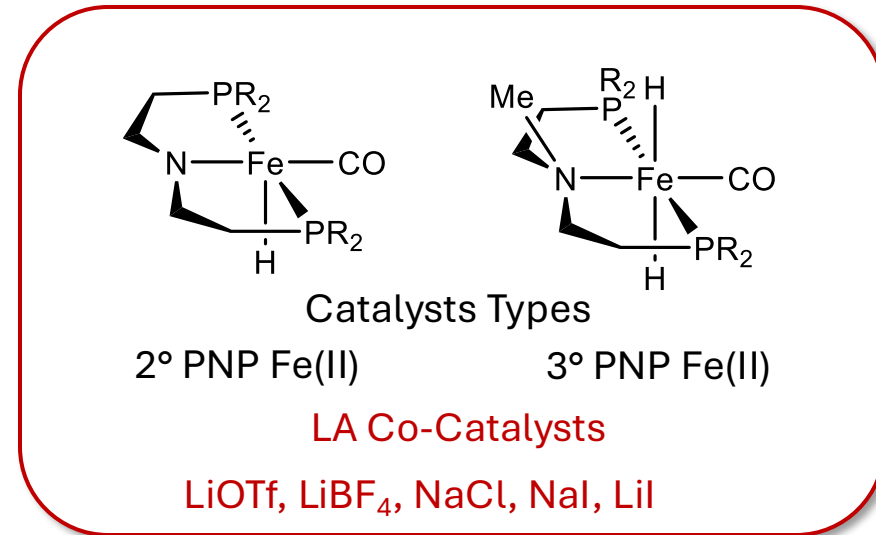


2° PNP Fe(II) w/o LA: 900 TON

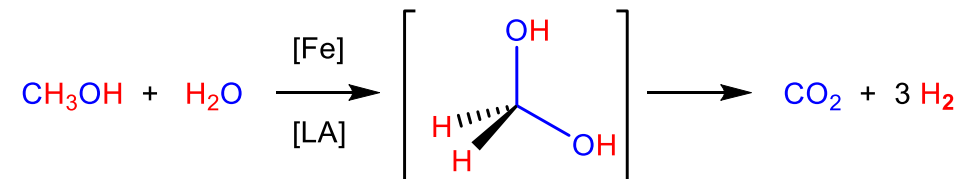
3° PNP Fe(II) w/o LA: 1100 TON

3° PNP Fe(II) w/ LA: 46,000 TON

Chem. Sci. **2015**, 6, 4291.



Methanol dehydrogenation



2° PNP Fe(II) w/o LA: 350 TON

2° PNP Fe(II) w/ LA: 51,000 TON

ACS Catal. **2015**, 5, 2404.

Lewis Acid Influence Is Widespread

1. Mn/Mn; R=CO
2. M=Fe, Ru; R=H
 X=PPr₂

Catalyst

Esterification

Resting state

Hydrogenation

MeOH

[H₂BC₆F₅]⁺[H₃A]⁻

"Hydrogenated" Frustrated Lewis pair

Co cat. LiOTf

30,000 turnovers

CO₂ + H₂

[DBU][HCOO]

TON > 30000 (R = H)

THF, DBU, LiOTf

10 bar, 80-100 °C, 24-72h

120H⁻

12 e⁻

Zn Cu

Carbon ● **Oxygen** ● **Hydrogen** ○

Faradaic efficiency (%)

Zn amount in Cu_xZn (%)

C₂H₅OH

29.1%

ORGANOMETALLICS

Molybdenum-Lithium Carbon Dioxide Hydrogenation

Ru cat. LiOTf

xs DBU

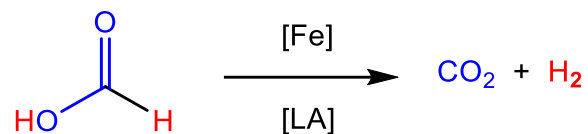
CO₂ + H₂

TON with LiOTf: 15,000

w/o LiOTf: 550

So What is the Lewis Acid Doing?

Formic acid dehydrogenation

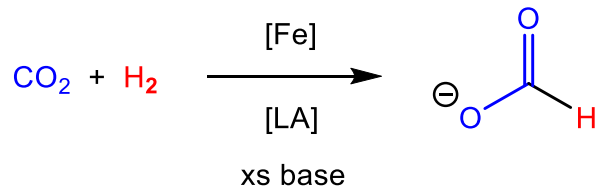


2° PNP Fe(II) w/o LA: 200 TON

2° PNP Fe(II) w/ LA: ~1 x 10⁶ TON

J. Am. Chem. Soc. **2014**,
136, 10234.

CO₂ hydrogenation to formate

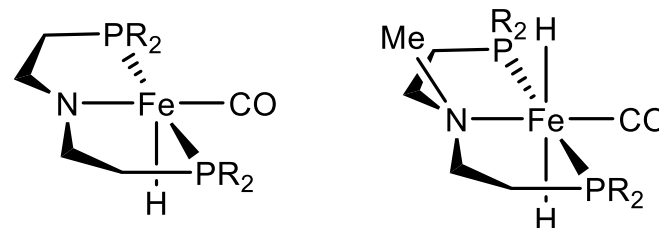


2° PNP Fe(II) w/o LA: 900 TON

3° PNP Fe(II) w/o LA: 1100 TON

3° PNP Fe(II) w/ LA: 46,000 TON

Chem. Sci. **2015**, 6, 4291.



Catalysts Types

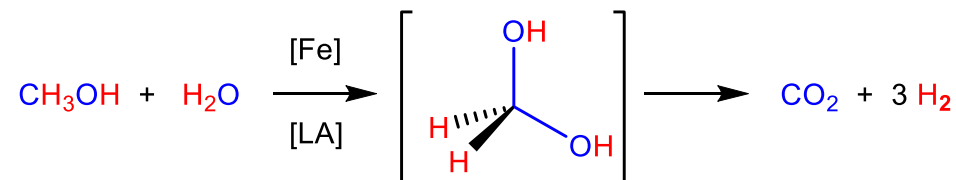
2° PNP Fe(II)

3° PNP Fe(II)

LA Co-Catalysts

LiOTf, LiBF₄, NaCl, NaI, LiI

Methanol dehydrogenation

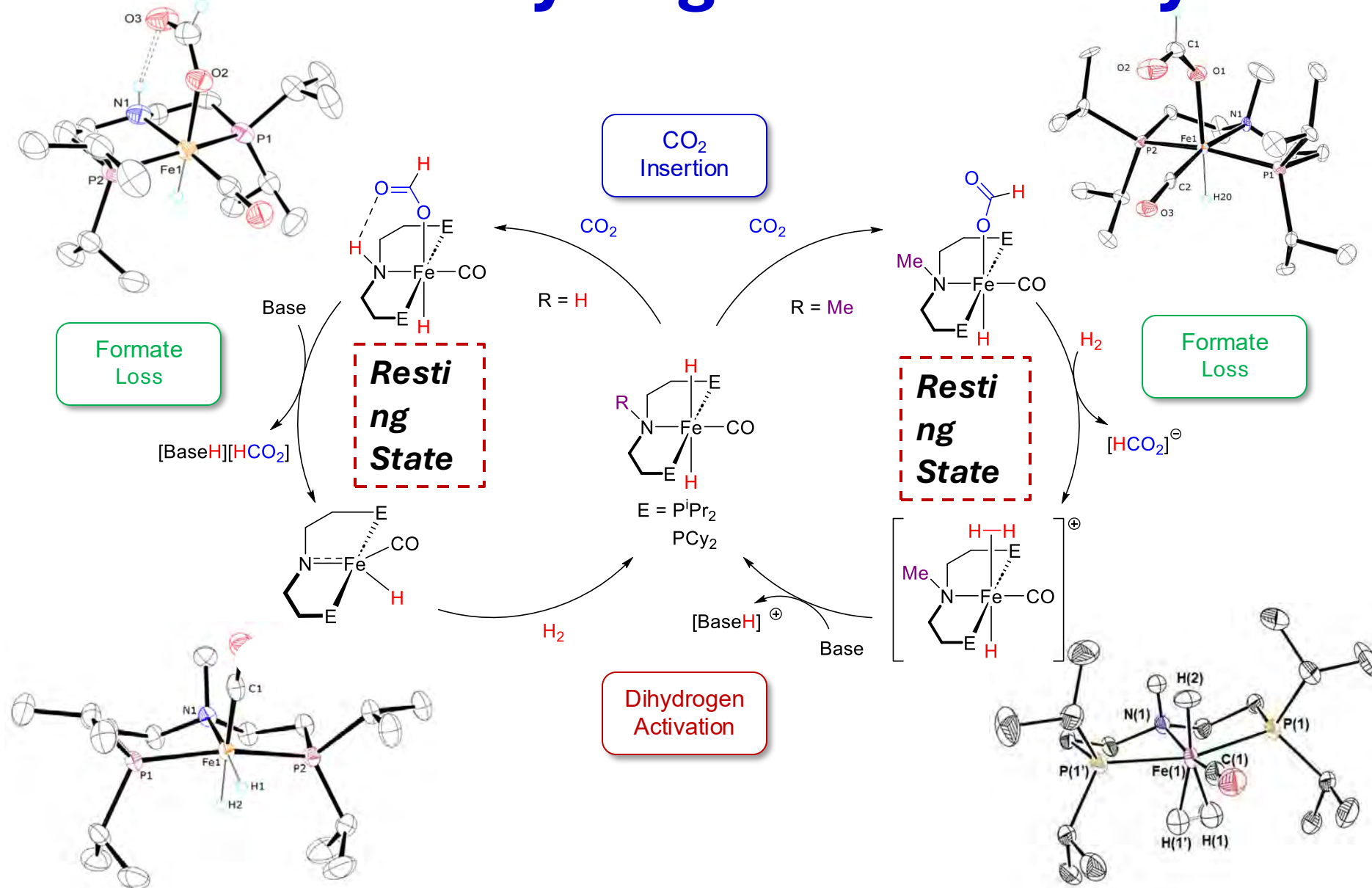


2° PNP Fe(II) w/o LA: 350 TON

2° PNP Fe(II) w/ LA: 51,000 TON

ACS Catal. **2015**, 5, 2404.

Mechanisms of Hydrogenation Catalysis



Chem. Commun. **2015**, 51, Am. Chem. Soc. **2021**,
16201. 143, 10631.

Chem. Sci. **2015**, 6, 4291.