Sustainable Metal Catalysis
The Paradigm of Iron Metal

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CHEMICAL TRANSFORMATION

Substrate → Thermodynamics of Reaction like Temperature, pressure, pH etc. → Reaction Medium → Catalyst → Product → Hazards
Catalysis: It´s Everywhere in 21st Century

- Homogeneous catalysis
- Photo catalysis
- Electro catalysis
- Heterogeneous catalysis
- Bio catalysis
Why catalysis is Important???

✓ a key technology,

✓ Almost 80% of all chemical and pharmaceutical products on an industrial scale are synthesized via catalysis.
Catalyst

- Organic
- Organo metallic
- Bio
- Transition metal
  - Sustainable Metal
    - Iron
  - Nobel metal
    - Copper
During the last decades, manifold transition-metal catalysts especially based on precious metals such as Pd, Rh, Ir, and Pt have been proven to be efficient for a large number of applications.
Challenges....
It’s all about Money, Honey…..

the limited availability of these metals leads to their high price
Toxicity

➢ Air

➢ Water
California always had highest no of cars resulting in highest air pollution
Air Toxicity

This large number of cars had Catalytic converter with Pt/Pd metal as Catalyst resulting in High concentration of these Suspended particles in air.

This lead to air quality infusing various diseases particularly Cancer.
Air Toxicity

That is the reason California has highest number of Cancer patients and Latest prey to Cancer in California
Bioaccumulation refers to the accumulation of substances, such as pesticides, or other organic chemicals in an organism.

Bioaccumulation occurs when an organism absorbs a toxic substance at a rate greater than that at which the substance is lost. Thus, the longer the biological half-life of the substance the greater the risk of chronic poisoning, even if environmental levels of the toxin are not very high.

Bioconcentration is a related but more specific term, referring to uptake and accumulation of a substance from water.
Water Toxicity

Bioaccumulation of Metals in Food Chain

11,000 X Bald Eagle 110 ppt
5,000 X Fish Eating Birds 50 ppt
Effluent 0.01 ppt
Sculpin < 20 ppt
Plankton < 1.0 ppt

Bioaccumulation of TCDD in Food Chain
Life Cycle Analysis

- Materials Resources and Extraction
- End-of-Life Issues (recycling, etc.)
- Processing impact on Environment
- Materials for Green Energy
- Design for sustainability
- Use of Sustainable Materials
- Economic, Social, and Legislative Issues
LCA for Precious Metals
Precious Metal catalyst are unsustainable !!!
The increased use of catalysts based on first row transition metals, such as

- iron,
- copper, and
- manganese.
Iron: An Ideal Metal for Catalysts

biomimetic catalyses many oxidation reactions in nature

Fe

less toxic

beside Al almost frequent metal in earth mantle

cheap
Why Iron?

- The second most abundant metal in the earth crust (4.7 wt%).
- Various iron salts and iron complexes are commercially accessible on a large scale or easy to synthesize.
- Iron compounds are relatively nontoxic.
- Iron takes part in various biological systems as essential key element.
- The facile change of oxidation state and the distinct Lewis acid character.
- Iron catalysts allow in principle a broad range of synthetic transformations.
- One of cheapest Metal available.
It would appear that the current discussion about sustainability energy resources, non-toxic reagents, catalysts and green solvents, etc. has led to resurrection of iron catalysis in organic synthesis as a way to generate sustainable metal catalysis.
Iron will be a new star in the catalysis tool box?
Various forms of Catalytic Iron

- Iron
  - Heterogeneous
    - Nano Iron
    - Mesoporous
  - Homogeneous
    - Salts
    - Complexes
Iron salts as Catalysts

In the early 1950’s iron was used as a catalyst for cross-coupling Grignard reagents with acid chlorides.

In the ensuing years, iron was set aside due to the control and predictability that came with such metals as palladium or ruthenium.

Not until recently has iron begun to receive much attention again, due in the most part to its advantages of low cost and low toxicity.
Fe(0) is cost-effective, environmentally friendly alternative to Cr(II) for the olefination of carbonyls by activated polyhalides. Fe(0) proved compatible with a wide range of functionality, such as unprotected phenol, aryl nitro, carboxylic acid, and alkyl nitrile.

Fe(0)-Mediated Synthesis of Tri- and Tetra-Substituted Olefins from Carbonyls: An Environmentally Friendly Alternative to Cr(II)
J. R. Falck,* Romain Bejot, Deb K. Barma, Anish Bandyopadhyay, Suju Joseph and Charles Mioskowski
Iron complexes as Catalysts

Heme group of hemoglobin. This is one of the most commonly known iron complex in nature.

An iron (Fe) atom in the middle is shown in red, complexed to four interior nitrogen atoms shown in blue.
Qi-Lin Zhou and colleagues from Nankai University in Tianjin have developed an iron complex that converts diazoesters into chiral ethers and alcohols. Using iron rather than precious metals such as palladium and platinum is an important goal in synthetic chemistry to increase sustainability, since iron is cheap and environmentally benign.
Mesoporous Iron as catalyst

The **Fischer–Tropsch process** (or Fischer–Tropsch Synthesis) is a set of chemical reactions that convert a mixture of carbon monoxide and hydrogen into liquid hydrocarbons.

The process, a key component of **gas to liquids** technology, produces a petroleum substitute, typically from coal, natural gas, or biomass for use as synthetic lubrication oil and as synthetic fuel.

The F-T process has received intermittent attention as a source of low-sulfur diesel fuel and to address the supply or cost of petroleum-derived hydrocarbons.

A variety of catalysts can be used for the Fischer–Tropsch process, but the most common are the transition metals cobalt, iron, and ruthenium.
Iron catalyst in Fischer-Tropsch Synthesis
NanoIron as Catalyst

- The **Haber process**, also called the **Haber–Bosch process**, is the **nitrogen fixation** reaction of **nitrogen gas** and **hydrogen gas**, over an enriched iron or ruthenium **catalyst**, which is used to produce **ammonia**.

- The Haber process is important because previous to its discovery, ammonia had been difficult to produce on an industrial scale, and fertilizer generated from ammonia today is responsible for sustaining one-third of the Earth's population.
Nano Iron as Catalyst
Popularity of Iron as catalyst in recent past

- “Iron Catalysis in organic Chemistry” edited by Bernd Plietker
- ACS-GCI funding on developing Fe and Cu based catalyst at Yale University
- Innovations by Rhodia in Oxidation chemistry using Iron as Catalyst
- Siemens exploring Iron to use in Electronics
- 15th GC&E conference at Washington DC this time has Iron and Copper Sponsorship
Cross-Coupling Reactions

General Scheme of Cross-Coupling Reactions

R'-X + R-MX' $\xrightarrow{\text{Catalyst}}$ R-R' + MXX'

Substrate (Organic Electrophile)  Coupling Partner (Organometallic Nucleophile)  Coupling Product  Metal Halide

R = Alkyl, aryl, vinyl, allyl, alkynyl, benzyl
R' = Alkyl, aryl, vinyl, allyl, alkynyl, benzyl, acyl
X = I, Br, Cl, OTf, OTs
M = Mg, Zn, Cu, Sn, Si, B
## Summary of Cross-Coupling Reactions

- **Kumada et. al. and Corriu et. al. in 1972** independently described the first Ni-catalyzed cross-coupling of the Grignard reagents with alkenyl and aryl halides.

\[
R' - X + R - MX' \xrightarrow{\text{Catalyst}} R - R' + MXX'
\]

<table>
<thead>
<tr>
<th>Cross-Coupling Reactions</th>
<th>Catalyst</th>
<th>M</th>
<th>R</th>
<th>R'</th>
<th>X</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Kumada-Corriu</strong> (1972)</td>
<td>Ni or Pd</td>
<td>Mg</td>
<td>Aryl, alkyl, vinyl</td>
<td>Aryl, alkyl, vinyl</td>
<td>Cl, Br, I, OTs</td>
</tr>
<tr>
<td><strong>Sonogashira</strong> (1975)</td>
<td>Pd/Cul</td>
<td>Cu</td>
<td>Aryl, alkyl</td>
<td>Aryl, alkyl, vinyl</td>
<td>Br, I</td>
</tr>
<tr>
<td><strong>Negishi (1977)</strong></td>
<td>Ni or Pd</td>
<td>Zn</td>
<td>Aryl, allyl, benzyl, propargyl</td>
<td>Aryl, alkyl, vinyl, alkynyl, benzyl, allyl</td>
<td>Cl, Br, I, OTs</td>
</tr>
<tr>
<td><strong>Stille (1978)</strong></td>
<td>Pd</td>
<td>Sn</td>
<td>Aryl, vinyl, benzyl, alkynyl</td>
<td>Aryl, alkyl, vinyl, benzyl, allyl, acyl</td>
<td>Cl, Br, I, OTs</td>
</tr>
<tr>
<td><strong>Suzuki (1979)</strong></td>
<td>Pd</td>
<td>B</td>
<td>Aryl, alkyl</td>
<td>Aryl, alkyl, alkynyl</td>
<td>Cl, Br, I, OTs</td>
</tr>
<tr>
<td><strong>Hiyama (1988)</strong></td>
<td>Ni or Pd</td>
<td>Si</td>
<td>Aryl</td>
<td>Aryl, alkyl, vinyl</td>
<td>Br, I, OTs</td>
</tr>
</tbody>
</table>
Cross-coupling reactions are catalytic. Typically 1-10 mol% catalyst.

Cross-coupling reactions use readily available starting materials.

Cross-coupling reactions tolerate a wide range of functional groups.

Cross-coupling reactions give high yields of products.

Cross-coupling reactions are chemo-, regio- and stereo-selective.
Call for New Catalysts

- Pd catalysts are expensive: Pd(II) ~$160-260 per 5 g.
- Pd and Ni catalysts are toxic and not environmentally friendly.
- Pd- and Ni-catalyzed reactions need extended reaction times.
  Typically 2-40 h.
- Pd- and Ni-catalyzed reactions proceed at elevated temperatures.
  Typically 40 °C to 90 °C.
- Pd- and Ni-catalyzed reactions need ancillary ligands to render the catalysts sufficiently reactive.
Is Iron a Good Candidate?

- Fe catalysts are inexpensive and readily available.
  
  **Costs per gram**
  
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Cost per gram</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd(OAc)$_2$</td>
<td>$33$</td>
</tr>
<tr>
<td>Pd(acac)$_2$</td>
<td>$38$</td>
</tr>
<tr>
<td>Fe(OAc)$_3$</td>
<td>$4$</td>
</tr>
<tr>
<td>Fe(acac)$_3$</td>
<td>$0.4$</td>
</tr>
</tbody>
</table>

(Fe catalysts are ~ 10-100 times cheaper than Pd-catalysts)

- Fe catalysts are non-toxic and environmentally friendly.

- Fe catalysts are air and moisture stable and easy to store for long periods under normal laboratory conditions.

- Iron can exist in very low and very high oxidation states: Fe(-II), Fe(0), Fe(I), Fe(II), Fe(III), Fe(IV), Fe(V) and Fe(VI).
Kochi’s Pioneering Work

Cross-coupling of alkenyl halides with Grignard reagents

\[
R\text{MgBr} + R'\text{Br} \xrightarrow{\text{Fe(dbm)}_3 (0.3 \text{ mol\%})} \text{THF, 25 }^\circ\text{C, 45 min}} \xrightarrow{} RR'
\]

<table>
<thead>
<tr>
<th>R</th>
<th>R'</th>
<th>RR' (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl</td>
<td>CH₃CH=CH</td>
<td>99</td>
</tr>
<tr>
<td>Ethyl</td>
<td>CH₃CH=CH</td>
<td>58</td>
</tr>
<tr>
<td>Phenyl</td>
<td>PhCH=CH</td>
<td>32</td>
</tr>
<tr>
<td>Cyclohexyl</td>
<td>CH₃CH=CH</td>
<td>54</td>
</tr>
<tr>
<td>tert-Butyl</td>
<td>CH₃CH=CH</td>
<td>27</td>
</tr>
</tbody>
</table>

i. Proposed Catalytic Cycle I: Iron(I) as a catalytic species
Fenton's Reagent:

\[ \text{H}_2\text{O}_2 + \text{Fe}^{+2} \rightarrow \text{Fe}^{+3} + \text{OH} \square + \text{OH}^- \]
There are a complex series of chain reactions proceeding simultaneously which can regenerate Fe$^{+2}$

\[
\begin{align*}
\text{Fe}^{3+} + \text{H}_2\text{O}_2 & \rightarrow \text{FeOOH}^{2+} + \text{H}^+ \\
\text{FeOOH}^{2+} & \rightarrow \text{HO}_2^\cdot + \text{Fe}^{2+} \\
\text{HO}_2^\cdot + \text{Fe}^{3+} & \rightarrow \text{Fe}^{2+} + \text{O}_2 + \text{H}^+
\end{align*}
\]
The combination of the above reactions results in a redox cycle where ferrous iron (Fe\textsuperscript{2+}) is converted to ferric iron (Fe\textsuperscript{3+}) and ferric iron is reduced back to ferrous iron.

The rate of Fe\textsuperscript{2+}-H\textsubscript{2}O\textsubscript{2} oxidation is significantly greater than Fe\textsuperscript{3+}-H\textsubscript{2}O\textsubscript{2} reduction.

Therefore, the generation rate of hydroxyl radical in solution is often rate limited by the regeneration of ferrous ion.
Typical Fe:H$_2$O$_2$ ratios are 1:5-10 wt/wt, though iron levels < 25-50 mg/L can require excessive reaction times (10-24 hours). This is particularly true where the oxidation products (organic acids) sequester the iron and remove it from the catalytic cycle. Fenton’s Reagent is most effective as a pretreatment tool, where COD’s are > 500 mg/L.
Typical pH Profile of Fenton Reactions

![Graph showing pH profile over reaction time with notable pH changes at specific times for iron and hydrogen peroxide addition.](image-url)
Newreka’s Business focus

Driving innovations with focus on Iron as Sustainable metal catalyst

- Superacids
- Nano Iron Oxides
GOT QUESTIONS?

...WE HEAR YOU
Thank you for your kind attention!!!

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