Electrification and Decarbonization of Chemical Synthesis

Prof. Karthish Manthiram

Department of Chemical Engineering
Massachusetts Institute of Technology

Email: karthish@mit.edu
Website: manthiram.mit.edu
Carbon footprint of chemical manufacturing

Chemical industry emits 7% of global GHG emissions

Note: GHG emissions for olefins in this figure represent that of the steam cracking process. Ammonia is presented on a different axis on the right.

Source: DEHEMA
Defining Paradigms in Chemical Synthesis

**Biosynthesis**
Nature’s route for synthesizing a molecule

**Semi-synthesis**
Synthesis of a molecule using a starting material isolated from a natural source

**Total Synthesis**
The preparation of a complex molecule beginning with simple, commercially available precursors

**Cross-cutting themes:** thermodynamics, energy balances, and mass balances
Replacing pressure with voltage

\[ \frac{1}{2} \text{N}_2 + \frac{3}{2} \text{H}_2 \rightarrow \text{NH}_3 \]

**Thermochemical**

- Higher pressures to achieve reasonable conversions
- \( X < 20\% \)

**Electrochemical**

- At ambient pressure (1 atm):
  - Voltage also improves kinetics, so can operate at lower temperature
  - \( X > 99\% \)

What happens if we replace hydrogen gas with water?

Can we react water and nitrogen to produce ammonia?

$$\text{N}_2 + 3\text{H}_2\text{O} \rightarrow 2\text{NH}_3 + \frac{3}{2}\text{O}_2$$

**Thermochemical**

No conversion at reasonable temperatures

**Electrochemical**

Can achieve reactivity at room temperature, with reduced voltage requirements at higher temperatures

Continuous electrically-driven ammonia synthesis

Our system achieves the highest rates for a continuous electrochemical process (quantitative $^{15}$N confirmation)

Understanding of coupled transport-kinetics is essential for a sparingly soluble reagent

Ammonia is a nexus molecule for chemical synthesis.

- **NH₃** (ammonia)
  - Hydrogenation of **CH₄**, O₂
  - Oxidation of **HCN**
  - Reaction with **CO₂**
  - Reaction with **H₂O**

- **NH₄Cl** (ammonium chloride)
  - Reaction with **NaOCl**

- **NH₂Cl** (dichloroamine)
  - Reaction with **HCl**

- **NH₂OH** (hydroxylamine)
  - Reaction with **SO₂**, H₂O

- **(NH₄)₂CO₃** (ammonium carbonate)
  - Reaction with **CO₂**, H₂O
  - Reaction with **NaNO₂**

- **NH₄NO₂** (ammonium nitrite)
  - Reaction with acid

- **HNO₂** (nitrous acid)
  - Reaction with NaOH

- **HNO₃** (nitric acid)
  - Reaction with O₂, H₂O

- **(NH₂)₂CO** (urea)
  - Reaction with **CO₂**

- **H₂NCONH₂** (hydrazine)
  - Reaction with 533 K

- **Nylon 6**

**Other molecules**
- **Amino acids**
- **Hydrazine**
- **HCN** (cyanide)
- **NO** (nitric oxide)
- **Explosives, Fertilizers**

**Reactions**
- 1200°C, Pt
- 7 atm, 850°C, Pt
- 1 atm, 300°C, excess NH₃
**Outline**

**Total Synthesis**

- **Semi-synthesis**
- **Biosynthesis**
  - Nature's route for synthesizing a molecule
  - Synthesis of a molecule using a starting material isolated from a natural source
  - The preparation of a complex molecule beginning with simple, commercially available precursors

---

**Air, water, and renewable electrons are distributed, sustainable resources**

**Electrical potential enables mild conditions of operation, replacing temperature and pressure**

---

**N₂ as N-atom source**

**CO₂ as C-atom source**

- \( R^1 \) Br
- \( R^1 \) NMe₃
- \( (+) \) Pt
- \( (-) \)
- Constant voltage
- 30 examples up to 87% yield

**H₂O as O-atom source**

- \( R_1 \) \( (l) \) + \( H_2O \) \( (l) \) → \( R_1 \) \( (l) \) + \( H_2 \) \( (g) \)
Direct use of CO$_2$ in chemical synthesis

Forming diverse C-C bonds using CO$_2$ directly remains underdeveloped for industrial use at large-scales

**Forming C-O bonds (industry)**

- **Terephthalic acid**
  - $\text{O}_2$ $\xrightarrow{\text{CO}_2}$ $\text{O}_2$
  - 15 bar, 140 - 160 °C

- **Phenylalanine**
  - Require reactive and unstable organometallics

**Forming C-N bonds (industry)**

- **2NH$_3$** $\xrightarrow{\text{CO}_2}$ $\text{NH}_4^+$
  - 110 atm, 160 °C

- **O$_2$** $\xrightarrow{\text{NH}_4^+}$ $\text{H}_2\text{O}$
  - 160 - 180 °C

- **H$_2$$\text{C}_2$$\text{O}_2^-$** $\xrightarrow{\text{NH}_4^+}$ $\text{H}_2\text{NCOOH}$ + H$_2$O
  - 160 - 180 °C

**Forming C-C bonds (laboratory)**

- **R-M** $\xrightarrow{\text{Ni (Cat.), CO}_2}$ **R-COOH**
  - **R**
  - **X = Cl, Br**
  - **Zn and MgCl$_2$, rt**

- **Ar $\text{X}^-$** $\xrightarrow{\text{Ni (Cat.), CO}_2}$ **Ar-COOH**
  - **Ar**
  - **X = Cl, Br**
  - **Mn, 90 °C**

- **Ar $\text{X}^-$** $\xrightarrow{\text{CO}_2}$ **Ar-COOH**
  - **Ar**
  - **X = F, Cl, Br**
  - **(+)** and **(-)**

**Stoichiometric metal reductant**

**Sacrificial anode (Mg, Al)**

**Limited scope of substrates**
Electro-carboxylations without sacrificial anodes

**Electrocarboxylation to form C-C bonds**

High functional group tolerance

\[
\begin{align*}
\text{R}^1 \text{Br}^- + \text{NMe}_3 & \xrightarrow{(+\text{Pt})} \text{R}^1 \text{COOH} \\
\end{align*}
\]

DMF (0.1M), rt CO\(_2\), Bu\(_4\)PBF\(_4\)

Constant voltage

No column chromatography

No sacrificial anodes and metal reductant (need to consider counter electrode chemistry for commodity chemicals)

**Wide substrate scope**

Starting with smaller-scale, fine chemical examples, and expanding to the more difficult commodity chemicals

Outline

**Total Synthesis**

Semi-synthesis

Biosynthesis: Nature’s route for synthesizing a molecule

- Synthesis of a molecule using a starting material isolated from a natural source
- The preparation of a complex molecule beginning with simple, commercially available precursors

- Air, water, and renewable electrons are distributed, sustainable resources
- Electrical potential enables mild conditions of operation, replacing temperature and pressure

**PARADIGM**

Complete synthesis of a molecule from carbon dioxide, dinitrogen, and water

- N2
- NH3
- CO
- C2H4
- H2O

**N2 as N-atom source**

- Nitrogen Transport
- Lithium Plating
- Nitride Evolution
- Ammonia Evolution
- Copper Electrode

**CO2 as C-atom source**

- R1 Br
- R1 NMMe3
- DMF (0.1 M), rt
- CO2, Bu4PBF4
- (+) Pt
- Constant voltage

- 30 examples up to 87% yield

**H2O as O-atom source**

- (l) + H2O (l)
- R1
- R2
- (l)
- H2 (g)
Direct use of oxygen

\[ \text{O}_2 \text{ activation w/ Ag} \]

\[ \text{H}_2\text{C} = \text{CH}_2 + \frac{1}{2} \text{O}_2 \xrightarrow{270-290^\circ \text{C}} \text{O} \]

\[ \text{H}_2\text{C} = \text{CH}_2 + 3\text{O}_2 \xrightarrow{[\text{Ag/Al}_2\text{O}_3]} \text{2H}_2\text{O} + 2\text{CO}_2 \]

**Complete combustion of ethylene**

Epoxide synthesis routes

High temperature
High pressure
Overoxidation to \( \text{CO}_2 \)

Epoxidation agents

**Chlorohydrin process**

\[ 2\text{ }\text{CH}_2 = \text{CH}_2 + 2\text{HOCl} \xrightarrow{30-50^\circ \text{C}} \text{OHCl} + \text{Cl} \text{OH} \]

\[ \text{OHCl} + \text{Cl} \text{OH} + \text{Ca(OH)}_2 \xrightarrow{2-3 \text{ bar}} 2\text{O} + \text{Ca(Cl)}_2 + 2\text{H}_2\text{O} \]

Hazardous reagents
Stoichiometric byproducts
Poor atom economy

**Peroxide-based process**

Olefin substrate m-CPBA

Epoxide
Stoichiometric byproduct

Need to develop carbon-neutral, safe, and efficient epoxidation pathway
**Sustainable O-atom transfer reactions**

$$ \text{R}_1 \text{R}_2 (l) + \text{H}_2\text{O} (l) \rightarrow \text{R}_1 \text{R}_2 (l) + \text{H}_2 (g) $$

Energy landscape for O-atom transfer reactions

\[
\text{Reaction: } R_1 R_2 (l) + H_2O (l) \rightarrow \text{O} (l) + H_2 (g)
\]

Thermodynamic cell voltage for epoxidation using water is 0.8 V, as compared to 1.2 V for water splitting – can lower the energy footprint of water splitting

Mechanism is much like water splitting, without formation of oxygen-oxygen bond

Conversion

Outline

**Total Synthesis**

**Biosynthesis**
Nature’s route for synthesizing a molecule

**Semi-synthesis**
Synthesis of a molecule using a starting material isolated from a natural source

**PARADIGM**

- **N₂** as N-atom source
  - Air, water, and renewable electrons are distributed, sustainable resources

- **CO₂** as C-atom source
  - Electrical potential enables mild conditions of operation, replacing temperature and pressure

- **H₂O** as O-atom source

Complete synthesis of a molecule from carbon dioxide, dinitrogen, and water

**Copper Electrode**

**30 examples up to 87% yield**

**CO₃** + Br⁻ \[ \rightarrow \] **R** \[ , R¹ = \text{alkyl, aryl} \]

**DMF(0.1M), rt**

**Bu₄PF₄**

**(+)** Pt

**Constant voltage**

**R¹** \[ \rightarrow \] **RCOOH**
Chemical synthesis needs methane-parity

We often hear about grid-parity, but commodity chemical synthesis methane-parity is important

Electricity is 3x-5x more expensive than natural gas
Ratio of electricity price to natural gas price for industrial users per MJ of energy

Source: EIA, Eurostat, IAEE, CEIC, IFPEN, JPMAM. 2018. The 7 US states shown are the largest industrial users of US primary energy.

Dramatic drop in levelized cost of electricity

Source: IRENA

Reaching methane-parity may be on the horizon
Electrochemical unit operations

**Raw materials**
- Petroleum
- Natural gas
- Chlorine
- Oxygen
- Nitrogen

**Commodity chemicals**
- Ethylene
- Propylene
- Butylenes
- Benzene
- Cyclohexane
- Ethylbenzene
- Adipic Acid
- Styrene
- Caprolactam
- Cumene
- Phenol
- Acetone
- Butadiene
- Isobutylene

**Secondary commodity chemicals**
- Terpenic Acid
- Xylene
- p-Xylene
- Toluene
- Ethylene Oxide
- Ethylene Glycol
- Propylene Oxide
- Acrylonitrile
- Vinyl Chloride
- Methanol
- Formaldehyde

**Intermediates**
- Polyethylene
- Polypropylene
- Butadiene
- Acrylic acid
- Polyvinyl chloride
- Ammonium nitrate
- Adipic acid
- Nitric acid

**Finished Products and Consumer Goods**
- Textiles
  - Fabrics
  - Upholstery
  - Fabrics
  - Home furnishings
- Safe food supply
  - Food packaging
  - Preservatives
  - Beverages
  - Beverages
- Transportation
  - Tires
  - Anti-freeze
  - Beverage containers
- Housing
  - Plywood
  - Varnishes
  - Paints
- Recreation
  - Athletic equipment
  - Protective equipment
  - Sports equipment
- Communications
  - Molded electronics
  - Computer accessories
  - Optical fiber coatings
- Health and hygiene
  - Plastic
  - Cosmetics
  - Medical products
- Pharmaceuticals

(EERE 2004)
Acknowledgements

Aditya Limaye
Joy Zeng
Sierra Brooks
Nikifar Lazouski
Dengtao Yang
Kindle Williams
Nathan Corbin
Minju Chung
Joseph Maalouf
Zachary Schiffer
Michal Gala

Funding

manthiram.mit.edu
@ManthiramLab
@KManthiram
Haber Bosch process leads to large carbon dioxide emissions

\[ \frac{1}{2} \text{N}_2 + \frac{3}{2} \text{H}_2 \rightarrow \text{NH}_3 \]

Need sustainable, modular production methods for ammonia
Distribution can contribute significantly to fertilizer prices

Cereal and coarse-grain production potential in Africa (millions of tons)

- Yield improvement
- Land expansion potential
- Land expansion with improved yield
- Postharvest-loss reduction

Urea and DAP fertilizer prices by country

Source: FAO; Global Yield Gap Atlas; McKinsey analysis

McKinsey & Company
Ammonia is a nexus molecule: food, health, plastics, and energy

<table>
<thead>
<tr>
<th>Hydrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy density</td>
</tr>
<tr>
<td>0.03 kWh/L at 1 bar</td>
</tr>
<tr>
<td>1.3 kWh/L at 700 bar</td>
</tr>
<tr>
<td>Compression losses</td>
</tr>
<tr>
<td>7-19%</td>
</tr>
<tr>
<td>Transport and storage</td>
</tr>
<tr>
<td>$0.1/kWh</td>
</tr>
</tbody>
</table>

H$_2$O $\xrightarrow{\text{O}_2}$ H$_2$ $\xrightarrow{\text{N}_2}$ NH$_3$ $\xrightarrow{\text{N}_2}$ H$_2$ $\xrightarrow{\text{O}_2}$ H$_2$O

Energy input

Transport (low cost)

Energy output

Ammonia functions as hydrogen carrier
Lithium mediated ammonia synthesis

Cycle involving electrochemical and thermochemical steps

Proof of concept studies are promising but limited


Tsuneto, A. J. Electroanal. Chem. 1994

8.4% FE
0.55 nmol cm⁻² s⁻¹