Catalytic Conversion of CO_2 into High Value Chemicals and Fuels

Daniel Haynes

Reaction Engineering Team

Energy Conversion Engineering Directorate

NETL

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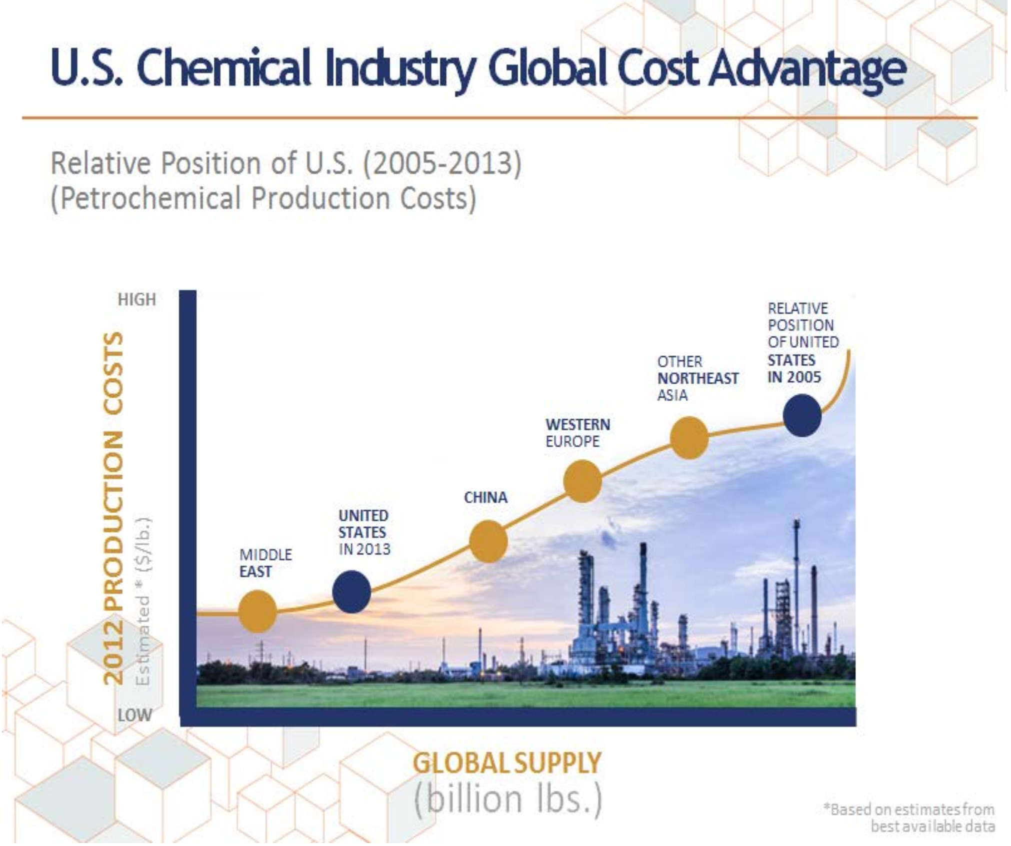
Solutions for Today | Options for Tomorrow

U.S. DEPARTMENT OF ENERGY

Problem/DEFICIENCY/Need

- **Recent fuel resource availability and regulatory actions provide unique opportunity for *Chemicals* production**
  - Shale gas revolution has led to cheap fossil fuel resources e.g. NG, coal, and biomass
    - Market for these fuels to be monetized into value added chemicals
  - **EPA Regulations on CO_2 emissions has created a market for CO_2 as a feedstock!**



"The shale gas revolution has enabled the US to move from a high-cost producer of key petrochemicals, to being the world's second lowest cost producer."

http://www.lngworldnews.com/eia-shale-gas-boosting-global-natural-gas-production-growth/
https://blog.americanchemistry.com/2014/10/u-s-manufacturing-exports-surging-due-to-shale-gas/

Ideal Solution

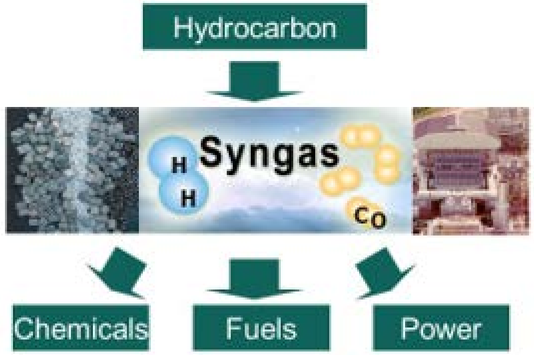
- **Improved catalyst technology is required to convert CO_2 or syngas into fuels**

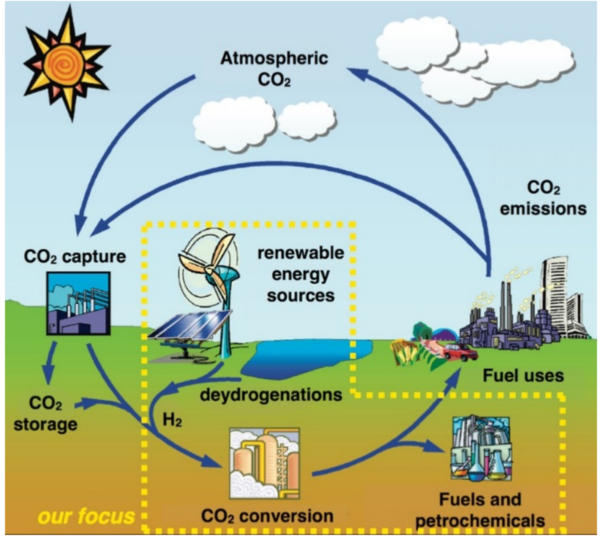
<u>Chemical Production requires</u>

- A catalyst to convert CO_2/CO with H_2 into value added chemicals
    - Thermally Stability
    - Flexible composition to tailor activity
    - Control carbon formation

<u>Electrochemical CO_2 Conversion requires</u>

- Small and positive applied voltage
- Resistant to undesirable side reactions
- Material stability during electrochemical operations in the solution phase

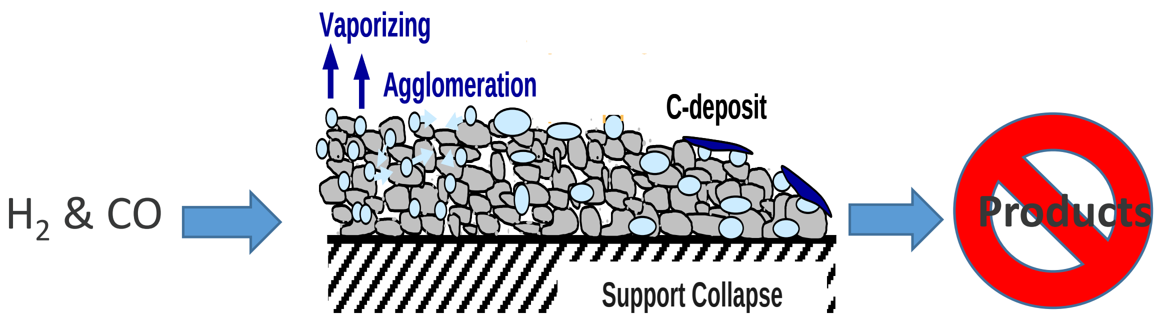




Current/Conventional Approaches

- **Traditional hydrogenation catalysts are the problem!**
- **Consist of metal deposited on high surface area support (Rh/Al_2O_3)**
  - High dispersion of the metal
  - ***Readily sinters when exposed to high temperatures***
    - **Leads to loss in active surface area**
    - **Decoupling of active phase and promoters**
    - **Sintering/activity loss is irreversible**
  - Carbon formation covers active sites

Catalyst Deactivation



Current/Conventional Approaches

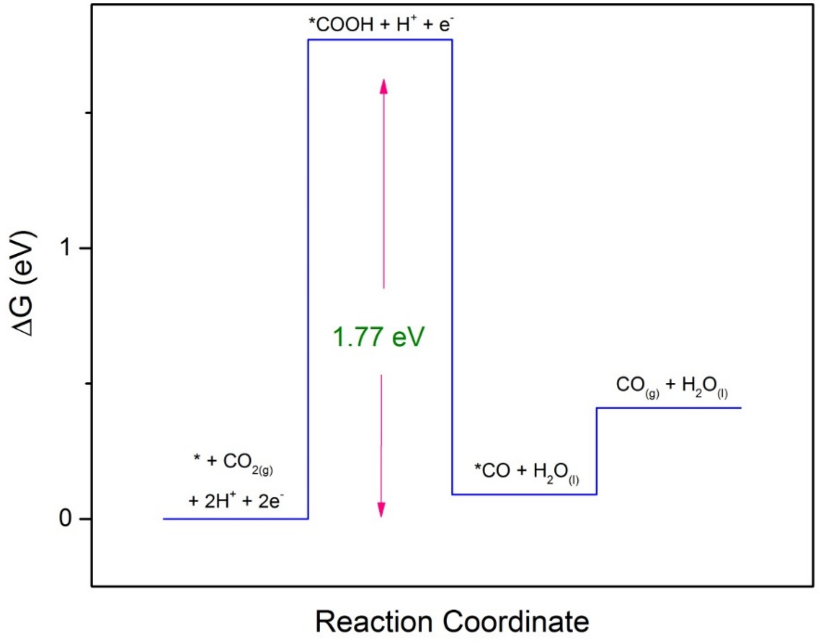
- **Issues with current CO_2 electrocatalysts**

Known catalysts are inefficient

* Large amounts of energy required to convert CO_2 to high value products

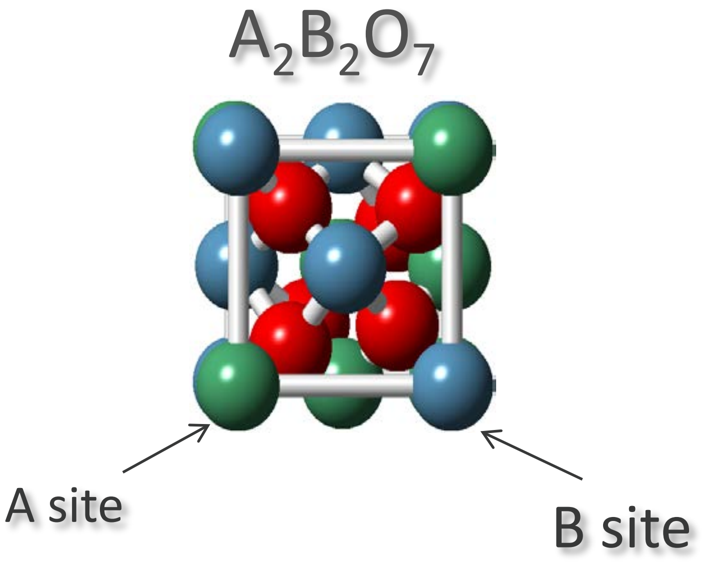
* CO_2 conversion rate needs improvement

* Poor selectivity – broad product distribution

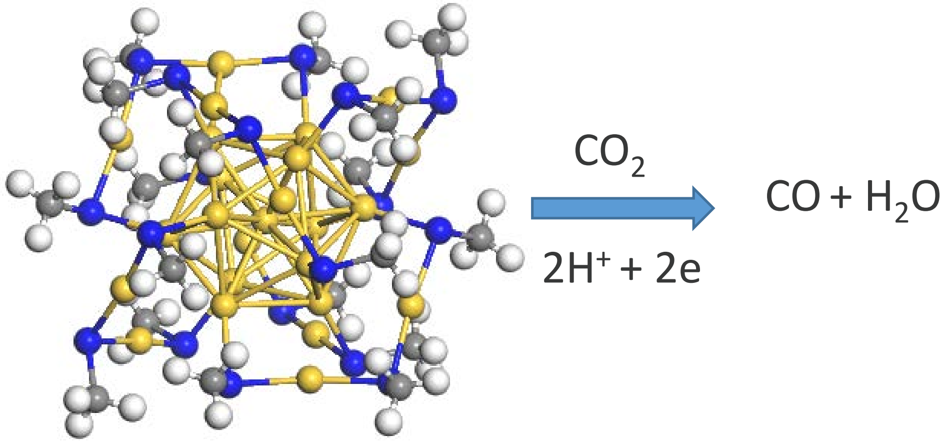


NETL Approach

- **Mixed metal oxide catalysts for hydrogenation** (e.g. pyrochlore, perovskite)
  - Crystalline materials with at least two different cations dispersed in an oxide framework
  - Thermally stable
  - Easily tailored composition to achieve a desired selectivity

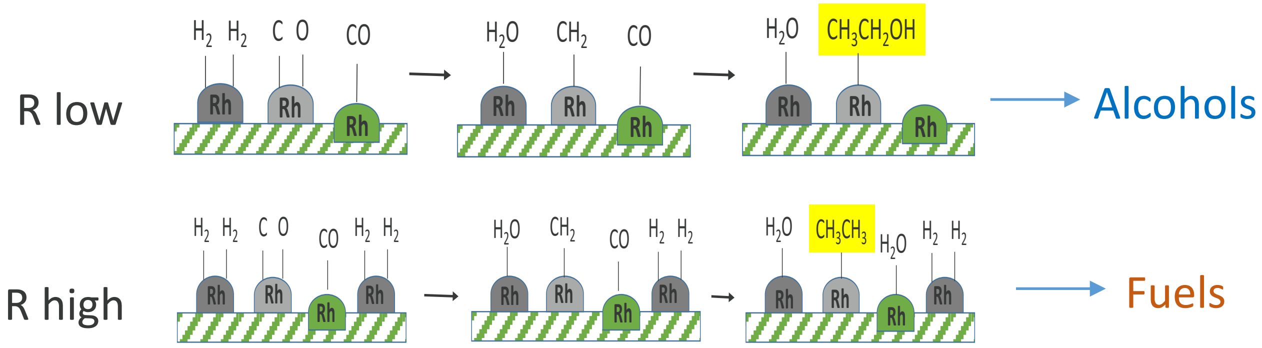


- **Organometallic Cluster Catalyst for CO_2 conversion**
  - Small (nanometer size) metal cluster
  - Stable at reaction conditions
  - Contains reaction sites that facilitate the conversion process

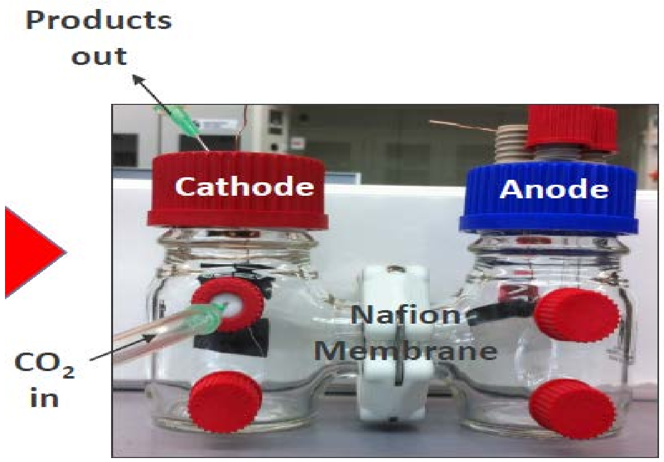


How it Works

- **Advantages of mixed metal oxides:**
  - **Active metal can be substituted *<u>into</u>* structure to stabilize small particles**
  - **Ratio (R) of supported to substituted active metal to control the selectivity**
    - Low ratio produces alcohols
    - High ratio produces hydrocarbons



- **Nanoparticle catalyst: Unprecedented catalytic performance**
  - 100 % selective and efficient
  - Most effective CO_2 catalyst ever reported



Kaufmann et al, J. Am. Chem. Soc 134, 10237 (2012)

Applications

- Target markets for the Mixed-Oxide catalysts and electrocatalysts are large chemical companies

<u>Major players are:</u>

- BASF SE
- Air Liquide SA
- Sasol Ltd
- The Linde Group
- <u>Their competition defines the competitive landscape of the global syngas and derivatives market</u>

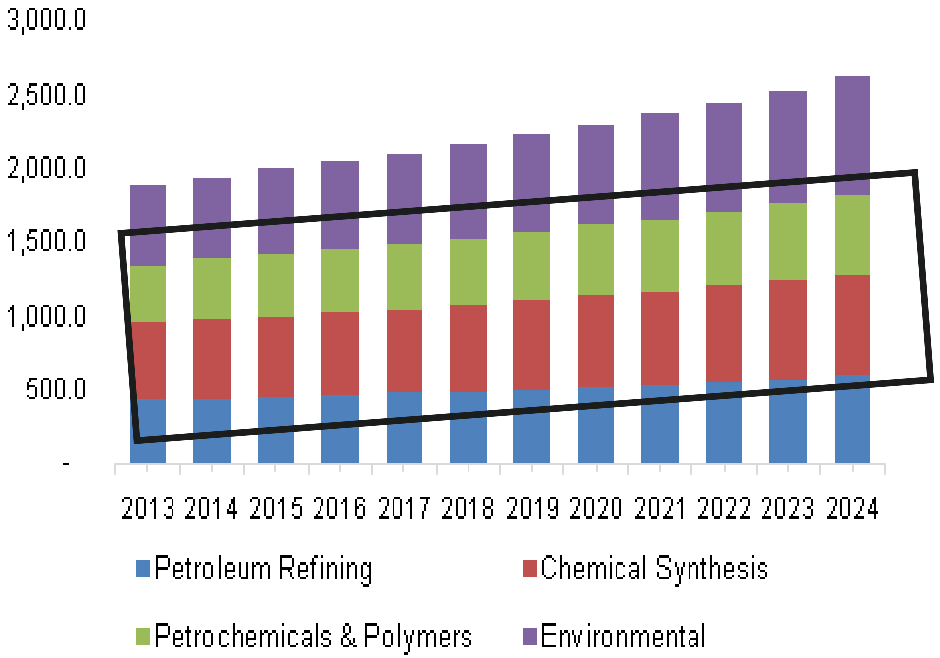
https://www.transparencymarketresearch.com/pressrelease/syngas-derivatives-market.htm

Market Opportunity

- **Adoption of technology by large chemical company could lead to significant sales!!**
  - North American catalyst market for chemicals production was ~3 billion USD in 2013!
  - Demand for fossil fuel derivatives is promoting future demand of catalysts

Consumption of syngas and derivatives expected to grow from 115,000 MWth in 2015 to 256,600 MWth in 2024- 9.4% CAGR

North America Catalyst Market Volume, By Application, 2013 - 2024 (Kilo Tons)

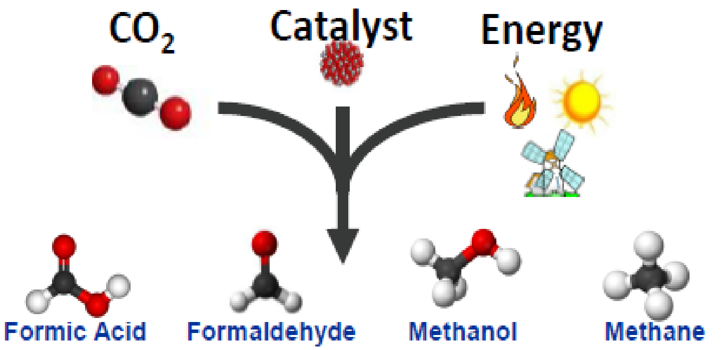


Value Proposition

- **Successful implementation leads to monetizing CO_2, NG, coal and biomass through value added chemicals**

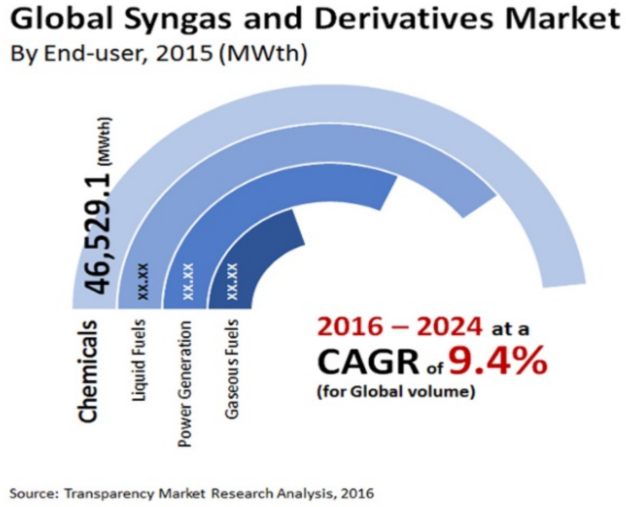
Benefits Include

- Less imported fuels and chemicals
- Decrease in CO_2 emissions through utilization
- Large potential market for catalysts- **$3 billion**
  - **Significant Sales!!**
- **Projected market growth rate of 9.4% CAGR to 2024**



	Formic Acid	Formaldehyde	Methanol	Methane
Approx Yearly Market	25 K Ton[1] ($25 M)	3 M ton ($720 M)	3.6 M ton ($1440 M)	484 M ton ($210,000 M)
Uses	Leather, Pulp	Urea Resins Phenol Resins	Fuel/MTG Formaldehyde	Fuel Acetic Acid

[1] Global Formic Acid Market: 0.5 M Ton ($750 M)

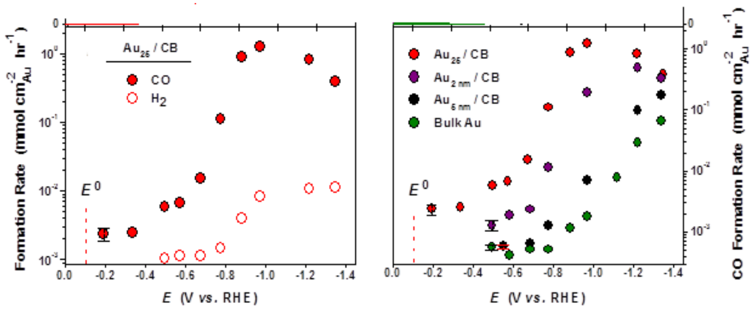


Current Status/Accomplishments

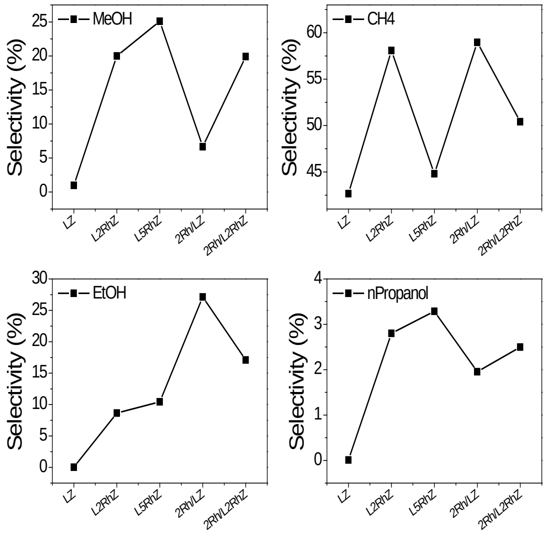
- **Both Technologies have generated IP and related publications**
  - Berry *et al.* US 9150476 for alcohol synthesis
  - Berry *et al.* US 9586449 for hydrocarbon synthesis
  - Kauffman, *et al*. US 9139920
  - Kauffman, Alfonso *et al. J. Am Chem. Soc.* 134, 10237 (2012)
  - Alfonso, Kauffman and Matranga, *J. Chem. Phys*. 144, 184705 (2016) – 2016 Editors Choice Award
  - Abdelsayeed et al. Catal. Today 207 (2013) 65 (alcohol synthesis using pyrochlores)

- **Both technologies have shown feasibility in proof of concept studies**
  - Level of commercial development- **Lab Scale**
    - Mixed metal oxide proven for alcohol synthesis
      - Evaluated a Rh- based pyrochlore oxide for lab-scale testing
      - Proved to be selective to EtOH and PrOH
    - Electrocatalyst-Catalyst, reactor and electrode scaled over 100 times
      - Able to produce CO yields ~ 15,000 L/g-h
      - Exhibited stable on/off cycling under ambient and general lab-based testing

Test Results



Electrocatalytic conversion of CO_2



Higher alcohol synthesis using pyrochlores

Next Steps

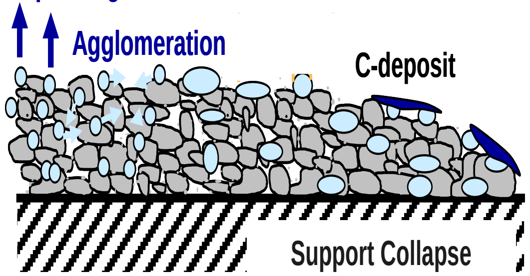
- **Technology currently only demonstrated on lab scales**
  - **Next steps for mixed oxide catalysts:**
    - Further formulate, characterize, and test mixed oxides to develop catalyst for specific value added products
    - Test in a scaled-up reactor system
  - **Next steps for the electrocatalyst**
    - Need to evaluate a larger prototype electrode system
  - Each technology is looking for a CRADA or License partner!

Summary - Technology Recap

Revisit:

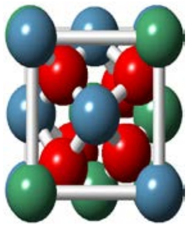
Problem: Deactivation and selectivity issues with current catalyst technology

- **NETL proposes:**
  - Mixed oxides as catalyst for chemical synthesis from syngas
  - Organometallic electrocatalyst for the conversion of CO_2 into CO.
- **Improved activity and selectivity compared to traditional materials**
- **Value proposition- Catalyst market for chemicals production is large $3 billion**
  - Has a 9.4% projected CAGR up to 2024
- **Next steps are to develop CRADA or Licensing agreement with partner**

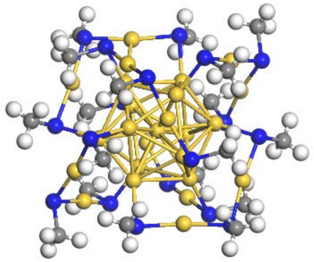


Catalyst Stability is an issue!

$A_2B_2O_7$



Mixed Metal Oxide



Organometallic Electrocatalyst

List of what the Technology Offers:

- Improved stability
- Tunability (mixed oxides)
- High efficiency (electrocatalyst)

Value Proposition or Competitive Advantages:

- Improved selectivity & stability
- Industrial catalyst market is large- $3 billion
- 9.4% CAGR

Envisioned Required Next Steps:

- Formulation development, characterization, testing for mixed metal oxides
- Further scale-up for electrocatalyst
- Develop CRADA or licensing agreement

Thank You

NATIONAL ENERGY TECHNOLOGY LABORATORY

<u>Mixed Metal Oxide development Team at NETL</u>

- Dushyant Shekhwat, Team Leader
- Dan Haynes, Research Engineer
- Mark Smith, Research Engineer
- Victor Abdelsayeed, Contractor Research Engineer
- David Berry, Associate Director

- NETL Partnership Options
  - Licenses
  - Cooperative Research and Development Agreements
  - Contributed Funds Agreements
- Technology Transfer Office contact information
  - Jessica Lamp, Tech Transfer Program Manager
- Jessica.Lamp@NETL.DOE.GOV

412-386-7417