Novel Catalytic Process Technology for Utilization of CO_2 for Acrylonitrile Production

DE-FE0030678

Angela Zheng, Aravind V. Rayer, Jian-Ping Shen, Zach Davis-Gilbert, Tim Bellamy, and Marty Lail

Andrew Jones and Jose Figueroa

Acknowledgement and Disclaimer

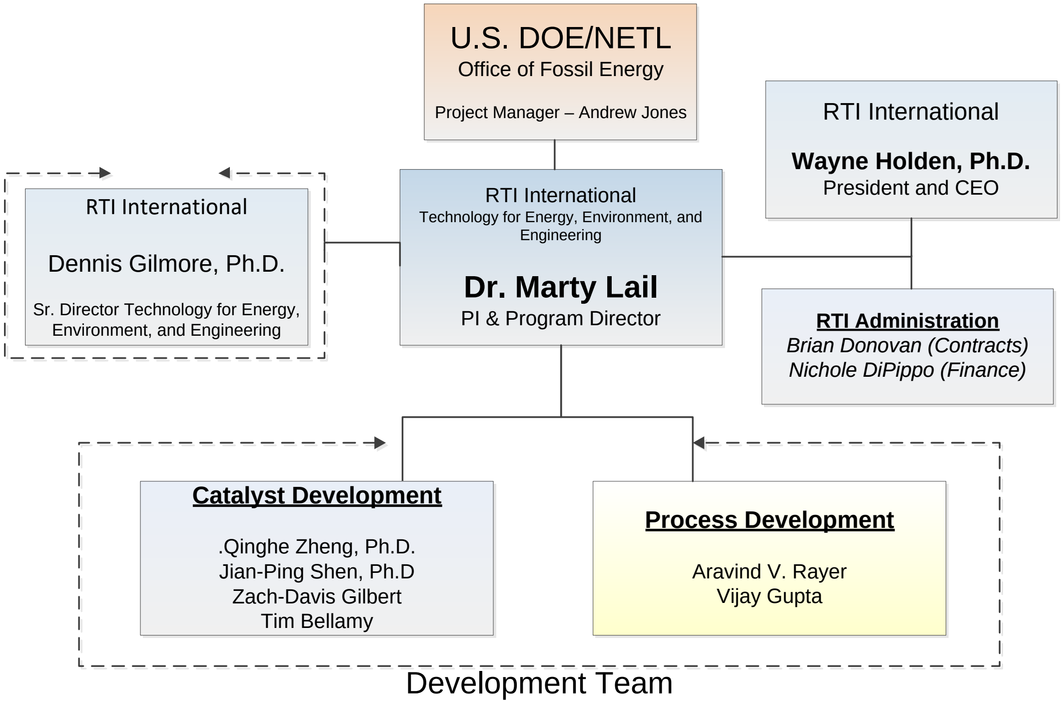
Acknowledgement: This presentation is based on work supported by the Department of Energy under Award Number DE-FE0030678.

Project Summary

Objective: Develop and optimize novel catalytic process for utilization of CO_2 as a feedstock and oxidant for the production of valuable chemicals

Key Metrics

- Demonstration of CO_2-ACN catalyst reactivity showing percent-level production ACN
- Data from lab-scale testing showing 50% yield CO



Specific Challenges

- Development of catalyst with required selectivity
- Cost competitiveness with commercial ACN

Timeframe: 10/01/2017 to 06/30/2020

Total Funding: $1,000,000

BP2 Tasks

BP2 Tasks

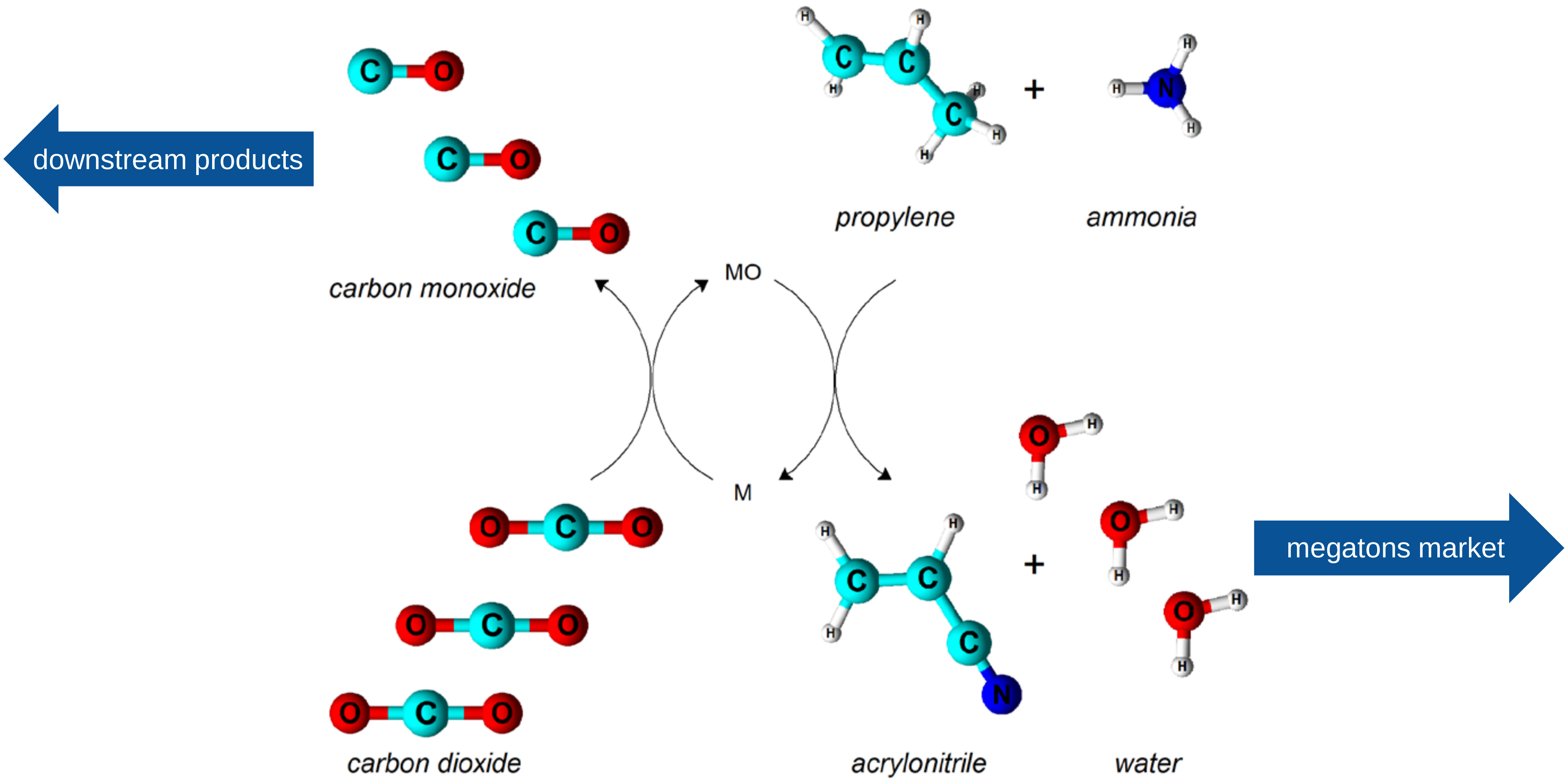
Task 6.0 Evaluation and Optimization of the CO_2-Reducing Catalysts for Propylene Ammoxidation

Task 7.0 Build Aspen Process Model for ACN Process

Task 8.0 ACN Process TEA and LCA

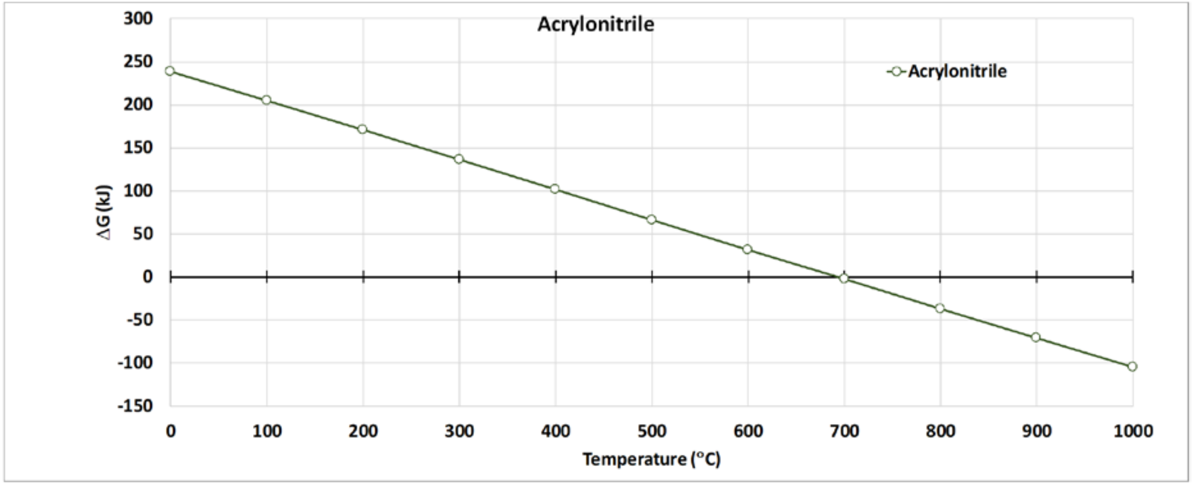
Task 9.0 Technology gap analysis

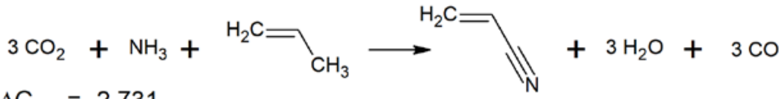
Novel Catalytic Process Technology for Utilization of CO_2 for Acrylonitrile Production



Acrylonitrile

Thermodynamics of CO_2 utilization for acrylonitrile





$\Delta G_{700} = -2.731$

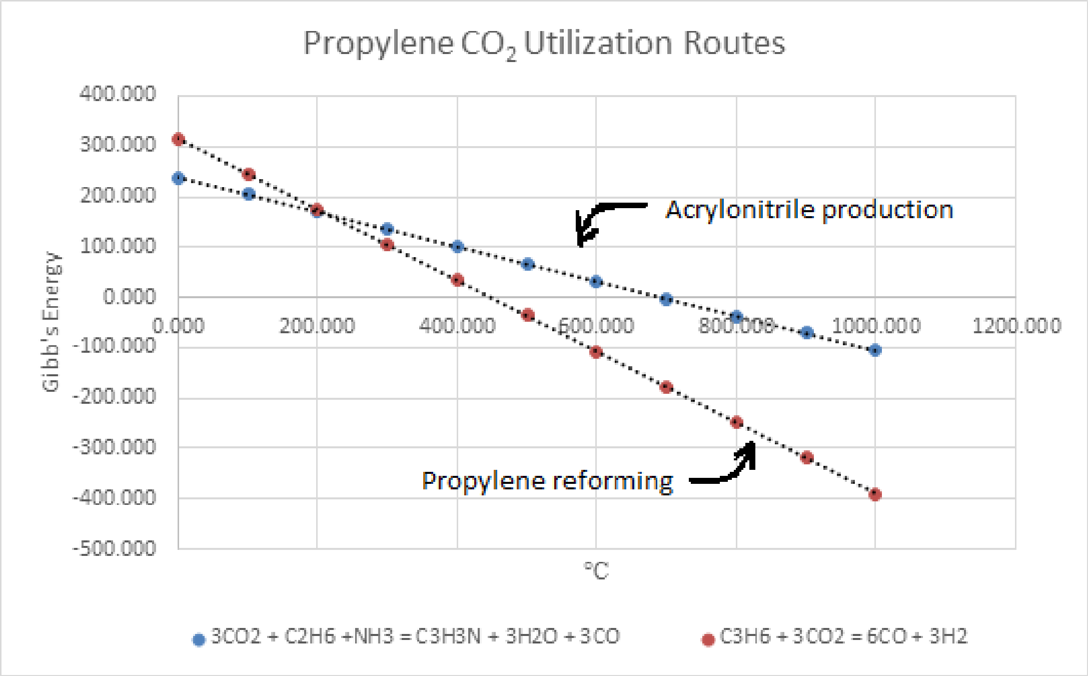
Opportunity

- $1500-$1700/ton
- ~10MT/year demand
- ~3.5% anticipated growth
  - PAN
  - ABS
  - SAN
  - Nylon 6,6

Long history of production starting with the SOHIO process using a fluidizable catalyst, propylene, ammonia, and oxygen.

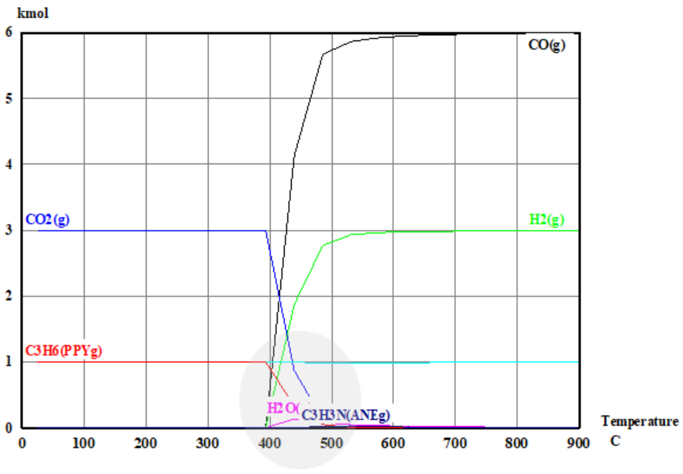
CO_2 utilizing route would consume CO_2 as a feedstock and produce CO as a second product

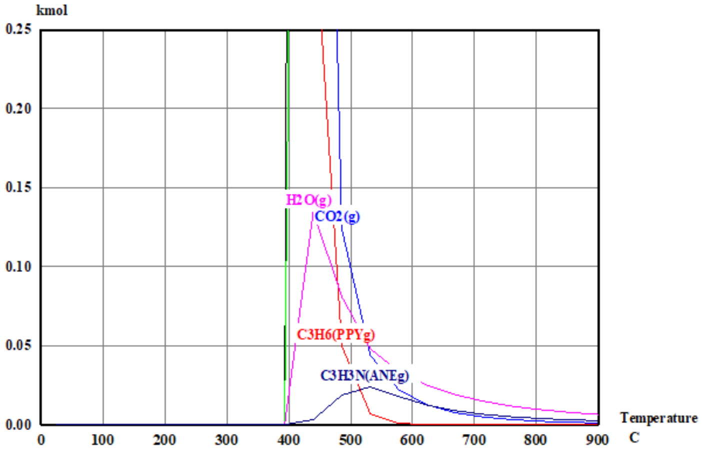
Competitive Reaction of Propylene Reforming

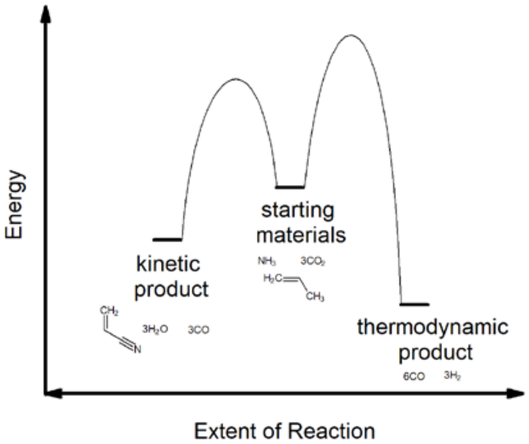


Favorable Gibb's energy calculations for utilization of CO_2 with propylene to make acrylonitrile (blue circles) or syn gas (red circles)

Equilibrium Composition and Kinetic Control







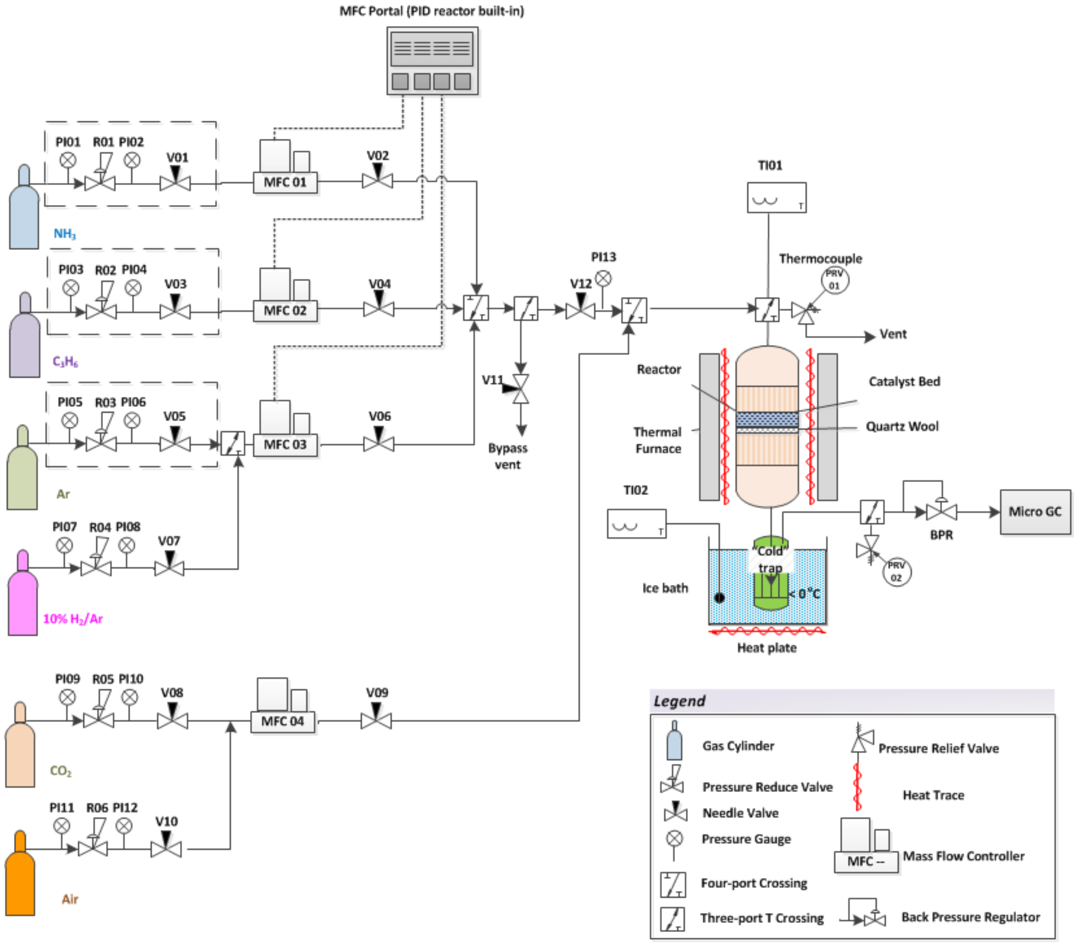
Equilibrium composition calculations for carbon dioxide, ammonia, and propene over the temperature range 0-1000°C. Left shows full scale, right is magnification of grey circle in left

Thermodynamic control of reaction products compared to kinetic control

CO_2-AN Path Underway (present status)

- Demonstration of CO_2-ACN catalyst reactivity in fixed-bed microreactor using initial catalyst formulations.
- Initial data gathering for process model.
- Data from lab-scale testing of CO_2-ACN.
- Modifying catalyst formulations for improved performance
- Study of individual mechanistic steps

Experimental Set Up



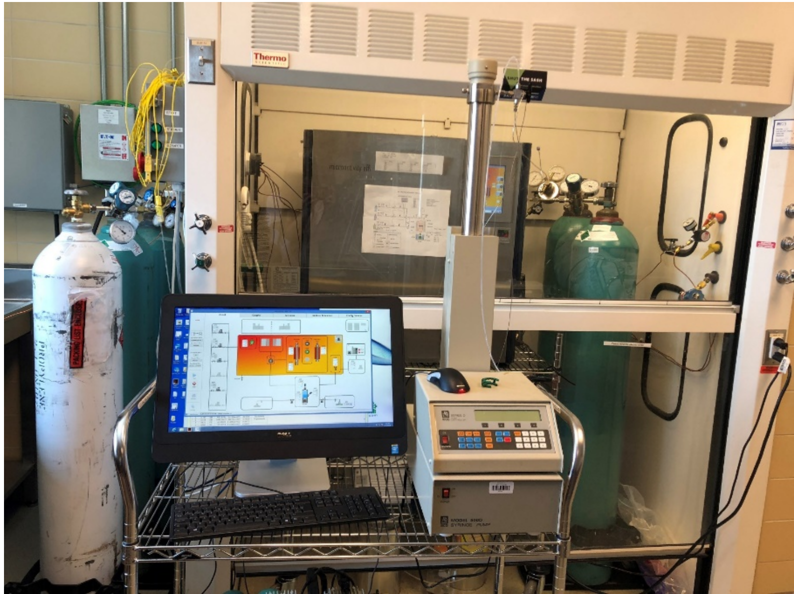
Reaction Conditions

Feed Composition: Stoichiometric

Reaction T: $500-800^\circ$ C

Reaction P: 1 atm

Catalyst Loading: 0.5 grams



Chemical Looping Mode Operation

Renewable ammoxidation of propylene with CO_2 as sole oxidant

Propylene ammoxidation (SOHIO process)

$$C_3H_6 + 3/2\ O_2 + NH_3 \rightarrow C_3H_3N + 3H_2O \qquad (12)$$

55% ~83%
molar yield

RTI proposed CL-Ammoxidation process using CO_2 as sole oxidant

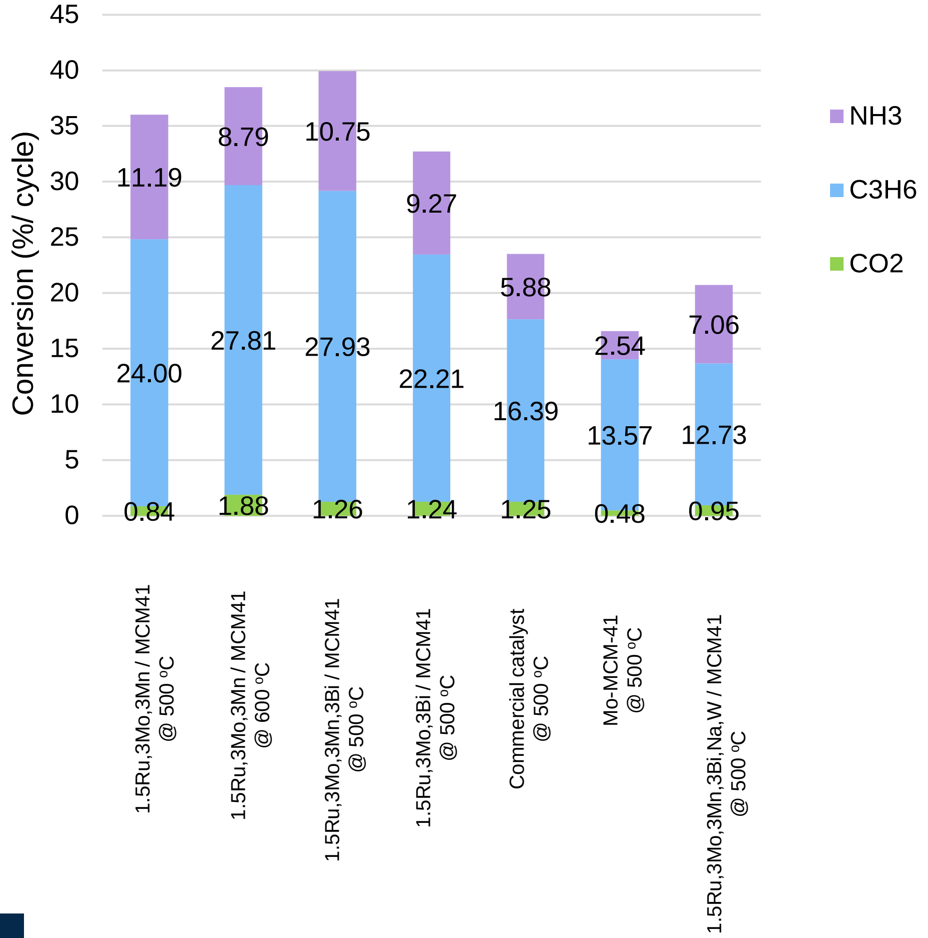
Ammoxidation step:

$$C_3H_6 + NH_3 + 3MeO_x \xrightarrow{700-800\ ^{\circ}C} C_3H_3N + 3MeO_{x-1} + 3H_2O \qquad (13)$$

CO_2 reduction (catalyst oxidation) step:

$$3MeO_{x-1} + 3CO_2 \xrightarrow{700-800\ ^{\circ}C} 3MeO_x + 3CO \qquad (14)$$

Chemical looping-ammoxidation with CO_2 (CO_2-CL-Ammox)



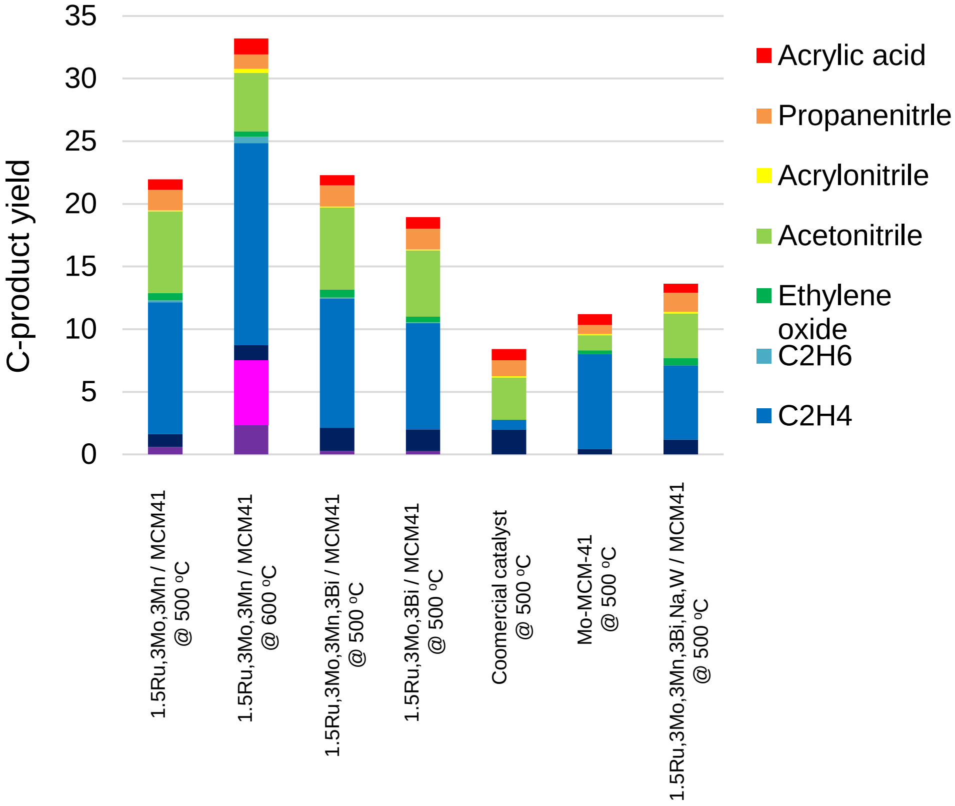
Ammoxidation step

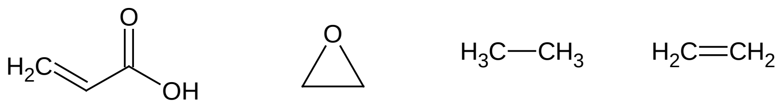
- % conversion NH_3
- % conversion C_3H_6

CO_2 Reduction step

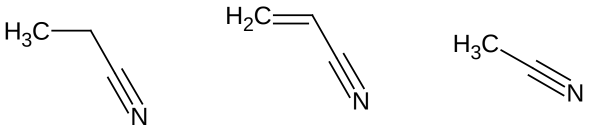
- CO_2 is the only oxygen source during the redox cycles
- $X(CO_2)=\frac{\text{Total molar amount of O in the product}}{\text{Total molar amount of O in the } CO_2 \text{ feed}} \cdot 100$

Chemical looping-ammoxidation with CO_2 (CO_2-CL-Ammox)





acrylic acid | ethylene oxide | ethane | ethylene

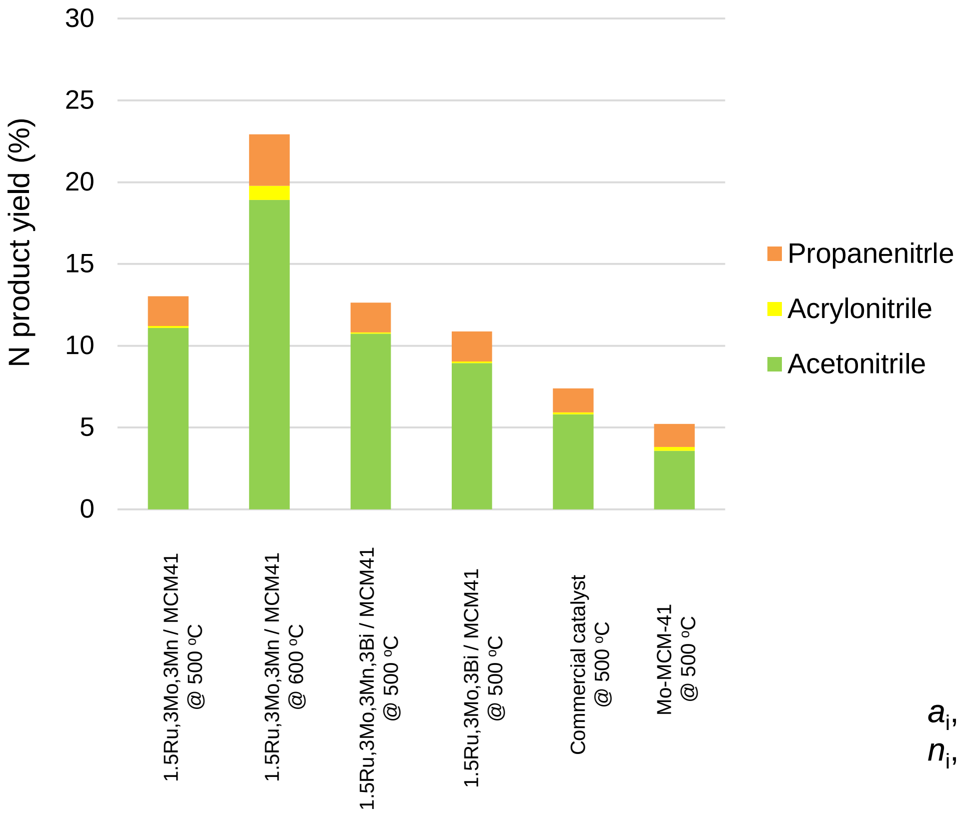


propane nitrile | acrylonitrile | acetonitrile

a_i, a_0: C atom amount in product *i* and feed respectively;
n_i, n_0: Molar flow rate of product *i* and feed, mol/min.

$$\text{C yield} = \frac{a_i n_i}{\sum a_0 n_0} \times 100\ \%$$

Chemical looping-ammoxidation with CO_2 (CO_2-CL-Ammox)



Acrylonitrile
- Target product

Acetonitrile
- Known byproduct
- Minimization will improve acrylonitrile yield

Propanitrile
- H_2 produced with current catalyst formulations

a_i, a_0: N atom amount in product *i* and feed respectively;
n_i, n_0: Molar flow rate of product *i* and feed, mol/min.

$$\text{N yield} = \frac{a_i n_i}{\sum a_0 n_0} \times 100$$

NH_3 oxidation- CO_2 reduction cycle test in AutoChem reactor

3 redox cycles, in each cycle:

Step 1: Reduction of metal (oxide) species with NH_3 (10% NH_3 in He) at 500 ^{o}C.

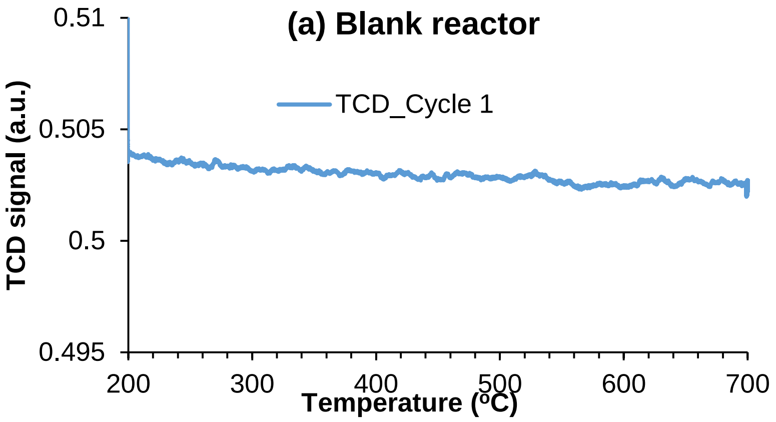
$$NH_3(g) \rightarrow 1.5H_2(g) + 0.5N_2(g) \qquad \Delta H^0_{298} = 45.9 \text{ kJ mol}^{-1}$$
$$NH_3(g) + 0.5M_xO_y \rightarrow H_2(g) + 0.5N_2(g) + 0.5H_2O(g) + 0.5M_xO_{y-1}$$

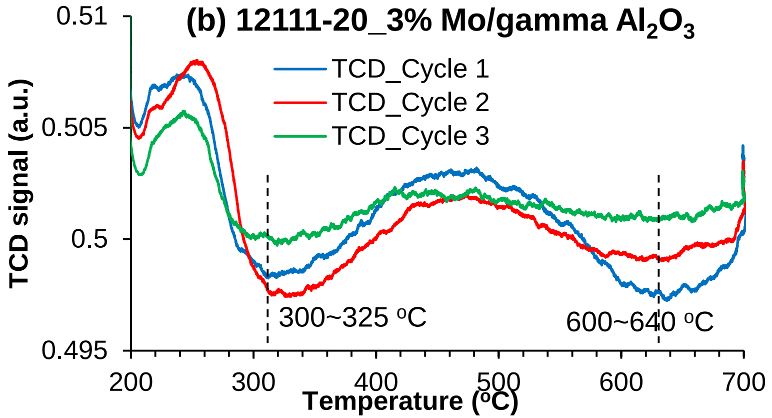
Step 2: TPO of metal oxides with CO_2 (20% CO_2 in He) from 200 ^{o}C to 700 ^{o}C at 10 ^{o}C/min.

$$M_xO_{y-1} + CO_2 \rightarrow M_xO_y + CO$$

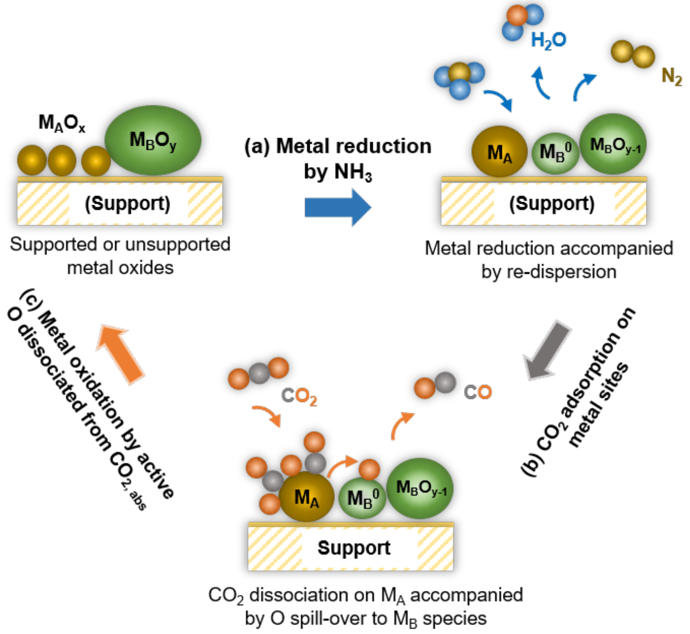
- He purge in between Step 1 and 2 and during temperature ramp.
- Step 1 in prep mode (to avoid potential corrosion of TCD detector with moist NH_3.
- Step 2 in analysis mode and its TCD signals were recorded.

NH_3 oxidation- CO_2 reduction cycle test in AutoChem reactor





$$M_xO_{y-1} + CO_2 \rightarrow M_xO_y + CO$$



Future Work

- Optimization of the CO_2-Reducing Catalysts for acrylonitrile and minimization of propylene reforming
- Build Aspen Process Model for ACN Process
- ACN Process TEA and LCA
- Technology gap analysis

Summary

- Conversion of CO_2 to acrylonitrile underway
- Initial test results show production of acrylonitrile
- Several other nitriles produced
- Catalyst can be improved for selectivity for acrylonitrile to achieve project goals
- Autochem results consistent with mechanism

Thanks for your attention!

Marty Lail, Ph.D.
Senior Director, Carbon Capture and Conversion
Technology for Energy, Environment, and Engineering
RTI International
3040 Cornwallis Rd.
Research Triangle Park, NC 27709
919-485-5703 (o)
919-809-2204 (l)