Novel Catalytic Process Technology for Utilization of CO₂ for Acrylonitrile Production

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**Objective:** Develop and optimize novel catalytic process for utilization of CO₂ as a feedstock and oxidant for the production of valuable chemicals

**Key Metrics**
- Demonstration of CO₂-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

**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 CO₂ for Acrylonitrile Production

- Carbon monoxide (C=O)
- Carbon dioxide (CO₂)
- Propylene (C₃H₆)
- Ammonia (NH₃)
- Acrylonitrile (CH₂C≡NO)
- Water (H₂O)

Downstream products

Megatons market
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.

**Acrylonitrile**

Thermodynamics of CO\(_2\) utilization for acrylonitrile

\[
\Delta G_{700} = -2.731
\]

\[3 \text{CO}_2 + \text{NH}_3 + \text{H}_2\text{C} = \text{CH}_3 \rightarrow \text{H}_2\text{C} = \text{N} + 3 \text{H}_2\text{O} + 3 \text{CO}\]
Favorable Gibb’s energy calculations for utilization of CO₂ 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
• Demonstration of CO₂-ACN catalyst reactivity in fixed-bed microreactor using initial catalyst formulations.
• Initial data gathering for process model.
• Data from lab-scale testing of CO₂-ACN.
• Modifying catalyst formulations for improved performance
• Study of individual mechanistic steps
Experimental Set Up

Reaction Conditions
Feed Composition: Stoichiometric
Reaction T: 500-800° C
Reaction P: 1 atm
Catalyst Loading: 0.5 grams
Renewable ammoxidation of propylene with CO$_2$ as sole oxidant

**Propylene ammoxidation (SOHIO process)**

C$_3$H$_6$ + 3/2 O$_2$ + NH$_3$ → C$_3$H$_3$N + 3H$_2$O

55% ~83% molar yield  \(\text{(12)}\)

**RTI proposed CL-Ammoxidation process using CO$_2$ as sole oxidant**

**Ammoxidation step:**

C$_3$H$_6$ + NH$_3$ + 3MeO$_x$$_{700-800 \degree C}$ → C$_3$H$_3$N + 3MeO$_{x-1}$ + 3H$_2$O  \(\text{(13)}\)

**CO$_2$ reduction (catalyst oxidation) step:**

3MeO$_{x-1}$ + 3CO$_{700-800 \degree C}$ → 3MeO$_x$ + 3CO  \(\text{(14)}\)
Chemical looping-ammonoxidation with CO\textsubscript{2} (CO\textsubscript{2}-CL-Ammox)

**Ammoxidation step**
- % conversion NH\textsubscript{3}
- % conversion C\textsubscript{3}H\textsubscript{6}

**CO\textsubscript{2} Reduction step**
- CO\textsubscript{2} is the only oxygen source during the redox cycles
  - \( X(\text{CO}_2) = \frac{\text{Total molar amount of O in the product}}{\text{Total molar amount of O in the CO}_2 \text{ feed}} \times 100 \)
Chemical looping-ammoxidation with CO$_2$ (CO$_2$-CL-Amox)

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

$a_i, a_0$: C atom amount in product $i$ and feed respectively; $n_i, n_0$: Molar flow rate of product $i$ and feed, mol/min.
Chemical looping-ammoxidation with CO₂ (CO₂-CL-Ammox)

Acrylonitrile
- Target product

Acetonitrile
- Known byproduct
- Minimization will improve acrylonitrile yield

Propanitrile
- H₂ produced with current catalyst formulations

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

\(a_i, a_0\): N atom amount in product \(i\) and feed respectively;
\(n_i, n_0\): Molar flow rate of product \(i\) and feed, mol/min.
NH₃ oxidation- CO₂ reduction cycle test in AutoChem reactor

3 redox cycles, in each cycle:

**Step 1**: Reduction of metal (oxide) species with NH₃ (10% NH₃ in He) at 500 °C.

\[
\text{NH}_3(g) \rightarrow 1.5\text{H}_2(g) + 0.5\text{N}_2(g) \quad \Delta H_{298}^0 = 45.9 \text{ kJ mol}^{-1}
\]

\[
\text{NH}_3(g) + 0.5\text{M}_x\text{O}_y \rightarrow \text{H}_2(g) + 0.5\text{N}_2(g) + 0.5\text{H}_2\text{O}(g) + 0.5\text{M}_x\text{O}_{y-1}
\]

**Step 2**: TPO of metal oxides with CO₂ (20% CO₂ in He) from 200 °C to 700 °C at 10 °C/min.

\[
\text{M}_x\text{O}_{y-1} + \text{CO}_2 \rightarrow \text{M}_x\text{O}_y + \text{CO}
\]

- 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 NH₃.
- Step 2 in analysis mode and its TCD signals were recorded.
NH₃ oxidation - CO₂ reduction cycle test in AutoChem reactor

(a) Blank reactor

(b) 12111-20_3% Mo/gamma Al₂O₃

MₓOᵧ⁻¹ + CO₂ → MₓOᵧ + 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
• 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!

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