Novel Catalytic Process Technology for Utilization of CO$_2$ for Ethylene Oxide and Propylene Oxide Production

DE-FE0030678

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Materials Background

Previous Work (NETL, DE-FE00004329)

• Mixed metal oxide (MMO) developed
• \((\text{Fe}_2\text{O}_3)(\text{SnO}_2)_{1.41}(\text{Al}_2\text{O}_3)_{1.82}\)
• Utilization of \(\text{CO}_2\) for char gasification


- Required high temperature for removal of oxygen from \(\text{CO}_2\) (~800° C)
- High temperature difficult for selective oxidations
- Needed to develop new material
New Materials Working at Lower Temperature

- Screened and discovered new compositions
- Have comparable overall capacity for oxygen from CO$_2$
- Remove oxygen at lower temperatures compared to the earlier materials
- Work funded in 2015 by CCEMC, Alberta, CAN K130115

Market Potential: Carbon Monoxide

- CO produced has numerous applications
- More than 59 Mt of CO are used annually
- Large and growing market for CO globally ($23 billion, 5.7% expected annual growth)

- Industrial CO source could drive new economic activity
- Significant CO stream
Evaluation of Material for EtO Selectivity

- Evaluated new materials in automated fixed-bed micro-reactor
- MKS FTIR multi-gas analyzer
- GC-MS
- Probed optimal reaction conditions using DOE
- Identified relatively low temperature region for operation
- Higher temperature than conventional EtO process
  - 300° C
  - 20 bar total pressure
  - 1 C₂H₄: 2 CO₂

- FTIR Multi-gas analyzer results for EtO
- Result shown for many cycles
Comparison to Conventional EtO Production

- Ethylene epoxidation has been practiced for many years with single pass conversions and overall yield being low.
- FTIR showed similar yield as \( \text{O}_2 \)-based catalysts but uses \( \text{CO}_2 \).

Conventional epoxidation catalyst used with air or oxygen:

\[
\text{Ag} \quad \text{Ag} \quad \text{Ag} \quad \text{Ag} \\
\text{Al} \quad \text{Al} \quad \text{Al} \quad \text{Al} \\
\text{O} \quad \text{O} \quad \text{O} \quad \text{O} \\
\text{silver particles on } \alpha\text{-alumina} + \text{Cl}^-, \text{NO}_3^-, \text{Cs}^+, \text{Na}^+, \text{Li}^+
\]

**Many promoters investigated to promote selectivity and activity.**

**EtO Producers**

<table>
<thead>
<tr>
<th>EtO Producers</th>
<th>Current Production Processes</th>
</tr>
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<tbody>
<tr>
<td>Dow Chemical</td>
<td>METEOR™ EtO/glycol process technology, polyethylene (1,300 kt), ethylene dichloride/vinyl chloride monomer (730 kt)</td>
</tr>
<tr>
<td>Shell Global</td>
<td>Shell MASTER Process, Shell OMEGA Process, mono-ethylene glycol (450 kt), styrene monomer (450 kt)</td>
</tr>
<tr>
<td>Scientific Design</td>
<td>Couples EO/EG technology with its SynDox® catalysts. Catalysts used at more than 100 EO/EG plants worldwide</td>
</tr>
</tbody>
</table>

Market Potential: Ethylene Oxide

- Large and growing market for EtO in North America and globally
- Ethylene oxide demand is over 24 Mt globally (~$40 billion USD)
  - 14th most produced organic chemical
  - Global demand expected to grow 6% per annum
  - 4th largest industrial emitter of CO₂ (6.3 Mt per annum globally)
RTI’s technology enables CO$_2$ from other sources to be utilized to produce ethylene oxide
- Reduces CO$_2$ emissions from conventional ethylene oxide process (direct CO$_2$ emissions of average plant are 150-200 kt-CO$_2$/yr)
- Consumes CO$_2$ as a process feed gas
- Reduces footprint of CO production (0.67 kg-CO$_2$/kg-CO)
A 350 kt production plant could reduce CO$_2$ emissions by 1 Mt per annum
## Improving the Material

- Addition of promoters to the mixed-metal oxide for increased activity for EtO production
- Optimization of the metal-oxide phases and support for synergistic adsorption and mechanical properties for better EtO selectivity
- Improve metal oxide–support interaction by selection of:
  - support materials
  - particle size
  - porosity
  - ratio of metal-oxide phases on the surface or subsurface of the catalyst
- Changing the fabrication process conditions
  - e.g., calcination temperature

<table>
<thead>
<tr>
<th>Success Metric</th>
<th>Ideal Target</th>
<th>Minimum Requirement</th>
</tr>
</thead>
<tbody>
<tr>
<td>EtO selectivity</td>
<td>56%</td>
<td>37%</td>
</tr>
<tr>
<td>EtO yield</td>
<td>11.5%</td>
<td>5%</td>
</tr>
<tr>
<td>CO:EtO mass ratio</td>
<td>4</td>
<td>7</td>
</tr>
<tr>
<td>Metal oxide replacement cycle</td>
<td>10 years</td>
<td>3 years</td>
</tr>
<tr>
<td>Demonstrated operational time</td>
<td>200 hr</td>
<td>100 hr</td>
</tr>
</tbody>
</table>
Framework for Project

“Novel Catalytic Process Technology for Utilization of CO₂ for Ethylene Oxide and Propylene Oxide Production” (DE-FE0030678)

Key Focus Areas

Characterizing and Refining Metal Oxide Formulation (Tasks 2, 3)

Extension to PO (Task 5)

Bench-Scale Evaluation (Task 4, 7)

Process Modeling and Technology Assessments (Task 6, 8, 9)

**Timeframe:** BP1: 10/1/17 to 09/30/18, BP2: 10/1/18 to 09/30/19

**Budget:**
- BP1 $461,651 (DOE) + $100,000 (cost share)
- BP2 $338,349 + $100,000 (cost share)

**Total Budget =** $1,000,000

RTI International - Dr. S. Jim Zhao, Principle Investigator
US DOE/ NETL – Steve Mascaro, Project Manager
Identifying MMO Phases by XRD

- XRF confirmed quantities of metals anticipated in the MMO's
- Mole ratio of $M_1/M_2$ varied to elucidate importance in CO$_2$ reduction
- Mole ratio to support varied to elucidate metal-support interactions
- XRD confirmed common metal oxide phases
- Small nanoparticle size of metal oxides
- Low crystallinity of support phase in primary samples
Characterizing the MMO using pulsed CO$_2$- Chemisorption

Experimental demonstration of CO$_2$ reduction
Catalytic CO$_2$-to-CO conversion $< 600$ °C

Test conditions:
- 400-600° C
- 1 atm CO$_2$
- 5% H$_2$ at 400° C

Reduction step
- Confirms CO$_2$ reduction
- 400° C low level of activity
- 500 -600° C higher activity
- ~2 wt% CO$_2$ reduction capacity shown in these experiments
Summary of CO₂ Reduction Findings

- A metal/support interaction is conducive to oxygen abstraction from CO
- The optimum metal oxide mole ratio for CO₂ reduction is approximately 0.25
- Increasing the crystal size from ~30 to ~50 nm does not appear to have a significant impact on CO₂ reduction
- Chloride is neither a poison nor a promoter to CO₂ reduction
- For this type of MMO, CO₂ reduction can be achieved at temperatures 500-600°C
Testing MMO’s for Ethylene Epoxidation

- Used a microreactor
- Fixed bed
- Micro-GC and FTIR gas analysis
- Carbon trap on product stream to further verify products
- Started with a baseline material to reproduce earlier results

<table>
<thead>
<tr>
<th>Pretreatment</th>
<th>Reaction</th>
<th>Oxidation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas Composition (vol%)</td>
<td>Reduction - CO: 5</td>
<td>CO$_2$: 17.5 - 32.5</td>
</tr>
<tr>
<td></td>
<td>Oxidation - CO$_2$: 5</td>
<td>C$_2$H$_2$: 5 - 12.5</td>
</tr>
<tr>
<td></td>
<td>N$_2$: balance</td>
<td>N$_2$: balance</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>500-600</td>
<td>325-350</td>
</tr>
<tr>
<td>Pressure (bar)</td>
<td>20</td>
<td>20</td>
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</table>
• Observed CO and ethylene oxide by FTIR
Task 3 Results with micro-GC detection

(1) pretreated with 5% CO to reduce, (2) 5% CO₂ to oxidize, at 500°C, 20 bar. (3) Reaction with 25% CO₂, 5% ethylene at 350°C at 20 bar. (4) Oxidation with 5% O₂ at 500°C, 20 bar.

- Observed CO, but very little ethylene oxide
Task 3 Results Repeated with FTIR detection

1. Pretreatment with 5% H₂ to reduce 5% CO₂ to oxidize, at 500° C, 20 bar
2. CO₂, 5% ethylene at 350° C at 20 bar

FTIR signals

- Confirmed ethylene oxide not being produced
Simulating the leak of oxygen into the reactor produces ethylene oxide.
Thermodynamics of CO$_2$ Reduction/ Ethylene Epoxidation

- Thermodynamically favorable reactions can be postulated for both redox steps
- The cycle is not closed, probably why ethylene oxidation is not being observed
Conclusions and Future Directions

- Characterized mixed metal oxides for thermochemical CO\(_2\) reduction
- Identified formulation for CO\(_2\) reduction between 500-600\(^\circ\) C
- Confirmed the production of CO in microreactor testing under process conditions
- Met BP1 milestones for characterization

- Baseline catalyst testing shows inconsistencies in transfer of oxygen derived from CO\(_2\) to ethylene to form ethylene oxide
- Have not yet met BP1 milestone for refinement of MMO to show higher EtO yield
- Could apply existing CO\(_2\) reducing formulation to other MT market chemicals as alternative to epoxides

- Need to refine phase selection to meet thermodynamic requirements
Acknowledgements

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