Resource-Efficient Catalytic Technologies for Shale Gas Upgrading

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Shale Gas Monetization Workshop
Montgomery, TX

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Outline

- The global chemical industry
- Emerging feedstocks for making chemicals
- The need for resource-efficient technologies
- Examples with LCA analyses
- Concluding remarks
Growth of Global Chemical Industry

Figure 1. Chemical Industry Output: Developed Regions*

Figure 2. Chemical Industry Output: Developing Regions* & Countries with Economies in Transition

[Global Chemical Outlook, UN Environment Programme, 2012]
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Chemical intermediates (building blocks)

- <10% of crude oil used to make chemicals
- Chemicals more profitable than fuels
Natural Gas and Biomass as Alternate Feedstocks

- US natural gas production up ~28% since 2006, thanks to increased shale gas production [EIA, 2013]
- Biomass abundant for making chemical intermediates
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Natural Gas Production by Source

Typical Shale Gas Composition

[Energy Information Administration, 0383-2013]
<table>
<thead>
<tr>
<th>Company</th>
<th>Location</th>
<th>Proposed capacity, MMTY</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chevron Phillips</td>
<td>Baytown, TX</td>
<td>1.5</td>
</tr>
<tr>
<td>Exxon Mobil</td>
<td>Baytown, TX</td>
<td>1.5</td>
</tr>
<tr>
<td>Sasol</td>
<td>Lake Charles, LA</td>
<td>1.4</td>
</tr>
<tr>
<td>Dow</td>
<td>Freeport, TX</td>
<td>1.4</td>
</tr>
<tr>
<td>Shell</td>
<td>Beaver Co, PA</td>
<td>1.3</td>
</tr>
<tr>
<td>Formosa</td>
<td>Point Comfort, TX</td>
<td>0.8</td>
</tr>
<tr>
<td>Occidental/ Mexichem</td>
<td>Ingleside, TX</td>
<td>0.5</td>
</tr>
<tr>
<td>Dow</td>
<td>St. Charles, LA</td>
<td>0.4</td>
</tr>
<tr>
<td>LyondellBasell</td>
<td>Laporte, TX</td>
<td>0.4</td>
</tr>
<tr>
<td>Aither Chemicals</td>
<td>Kanawha, WV</td>
<td>0.3</td>
</tr>
<tr>
<td>Williams/Sabic JV</td>
<td>Geismar, LA</td>
<td>0.2</td>
</tr>
<tr>
<td>Ineos</td>
<td>Alvin, TX</td>
<td>0.2</td>
</tr>
<tr>
<td>Westlake</td>
<td>Lake Charles, LA</td>
<td>0.2</td>
</tr>
<tr>
<td>Williams/Sabic JV</td>
<td>Geismar, LA</td>
<td>0.1</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td><strong>10.2</strong></td>
</tr>
</tbody>
</table>

[Energy Information Administration 0383-2013]
Traditional C\textsubscript{2} and C\textsubscript{3} Utilization Schemes

- **ethylene**
  - polyethylenes
  - ethanol
  - ethylene oxide
  - vinyl acetate
  - 1,2-dichloroethane

- **propylene**
  - isopropyl alcohol
  - acrylonitrile
  - polypropylene
  - propylene oxide
  - acrylic acid
  - allyl chloride

- **ethylene glycol**
- glycol ethers
- ethoxylates
- tetrachloroethylene
- trichloroethylene
- vinyl chloride

- **engine coolant**
- polyesters
- polyvinyl chloride
- polyol
- propylene glycol
- acrylic polymers
- epichlorohydrin
- epoxy resins

[Adapted from Siirola, AIChE J. 2014 60 810]
NGLs as “Emerging Feedstocks”? 

- Low price of ethane favor increased use of ethane as cracking feedstock

So where are the R&D opportunities?

- Many commercial routes to chemicals from ethylene, propylene already in use

*Source: ICIS Consulting*
NGLs as “Emerging Feedstocks”?

New technologies targeted:

• New more efficient catalysts/processes with lower carbon footprint
  – Ethylene oxide, propylene oxide
  – Hydroformylation
  – Higher olefins
  – Dimethyl carbonate

• New, selective catalysts/processes for direct conversion of propane
  – Acrylic acid, acrylonitrile
  – Alkane metathesis
Comparing environmental impact of chemicals from shale gas vs. petroleum feedstock

• Recent LCA studies: GHG impacts of shale gas compare to conventional for power generation [Weber, Env. Sci. Tech. 2012 46 5688]

• Issues not captured in published LCAs:
  – Groundwater contamination issues [Jackson, PNAS 2013 110 11250; Warner, PNAS 2012 109 11961]
  – Regulatory, social, political considerations

• Policy issues likely driven by power/fuels considerations, not chemicals
Energy Intensity of Chemical Industry Provides Opportunity for Process Improvements

[Graph showing energy consumption and energy intensity for various industries with data points for refining, bulk chemicals, paper products, iron and steel mills, aluminum, cement manufacturing, and other industries.]

Global demand, inexpensive natural gas are increasing domestic plastic production
Ethylene Oxide

Product Distribution of Ethylene Oxide

- Ethylene Glycol 61%
- Miscellaneous 13%
- Surface Active Agents 16%
- Ethanolamines 4%
- Glycol Ethers 6%

Ethylene Oxide Market Size

- 3-4% annual growth
- EO Manufacturers’ Market Share
  - Dow 38%
  - SABIC 25%
  - BASF 13%
  - Shell 13%
  - Mitsubishi 8%
  - Eastman 2%
Conventional EO Production

\[
\frac{1}{2} \text{O}_2 + \text{C}_2\text{H}_4 \xrightarrow{\text{Cs/Rb, Ag/Al}_2\text{O}_3, 10-30 \text{ Bar, 200-260 } ^\circ\text{C}} \text{O}_3\text{C}_2\text{H}_4
\]

Up to 15% loss to burning
($2$ Billion Loss)

3.4 Million MT/year of CO\(_2\) produced as byproduct, equivalent to the pollution caused by 900,000 cars

Current EO technology has large carbon footprint!
Alternative Process with Total EO Selectivity

- 99+% EO selectivity
- No CO₂ as byproduct
- No O₂ in gas phase

Developed at the KU Center for Environmentally Beneficial Catalysis (CEBC)

ACS Kenneth Hancock Award for Green Chemistry to Madhav Ghanta

## Conventional vs. CEBC Process

<table>
<thead>
<tr>
<th>Metric</th>
<th>Conventional Process*</th>
<th>CEBC Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure, bar</td>
<td>10 to 20</td>
<td>50</td>
</tr>
<tr>
<td>Temperature, °C</td>
<td>200-300</td>
<td>20-40</td>
</tr>
<tr>
<td>Metal /price $/lb</td>
<td>Ag: $461/lb</td>
<td>Re: $3,000/lb</td>
</tr>
<tr>
<td>Ethylene Conversion¹</td>
<td>&lt;10% per pass</td>
<td>No such limitations</td>
</tr>
<tr>
<td>EO Selectivity²</td>
<td>80-90%</td>
<td>99+%</td>
</tr>
<tr>
<td>CO₂ byproduct</td>
<td>10-20%</td>
<td>No CO₂ detected</td>
</tr>
<tr>
<td>Productivity [g EO/h/(g Ag or Re)]</td>
<td>2.2 - 4.1</td>
<td>1.61 - 4.97</td>
</tr>
</tbody>
</table>

- H₂O₂ fully utilized toward EO formation on MTO catalyst
- Costs on par with conventional process³

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CEBC EO Process Conditions Similar to Propylene Oxide Technology

<table>
<thead>
<tr>
<th>Process Attribute</th>
<th>Dow/BASF PO Technology</th>
<th>CEBC EO Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent</td>
<td>Methanol</td>
<td>Methanol</td>
</tr>
<tr>
<td>Oxidant</td>
<td>H$_2$O$_2$</td>
<td>H$_2$O$_2$</td>
</tr>
<tr>
<td>Catalyst</td>
<td>Heterogeneous (TS-1)</td>
<td>Homogeneous (MTO)</td>
</tr>
<tr>
<td>Pressure</td>
<td>30-50 bars</td>
<td>50 bars</td>
</tr>
<tr>
<td>Temperature</td>
<td>25-40°C</td>
<td>25-40°C</td>
</tr>
</tbody>
</table>

- But, TS-1 is not active for ethylene epoxidation
- Opportunity to develop heterogeneous catalysts
  - W, Nb, Ce are cheaper (< $100/lb) compared to Re (~$3,000/lb)
# H₂O₂-Based Epoxidation with W- and Nb-based Catalysts: Previous Work

<table>
<thead>
<tr>
<th>Substrate Epoxidized</th>
<th>Temperature (°C)</th>
<th>Time (h)</th>
<th>Epoxide Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-Cyclooctene</td>
<td>50</td>
<td>12</td>
<td>66.5</td>
</tr>
<tr>
<td>Cyclohexene</td>
<td>45</td>
<td>12</td>
<td>58</td>
</tr>
<tr>
<td>Cyclooctene</td>
<td>90</td>
<td>24</td>
<td>65</td>
</tr>
<tr>
<td>Cyclohexene</td>
<td>40</td>
<td>40</td>
<td>32.5</td>
</tr>
</tbody>
</table>

- Are W and Nb-based catalysts applicable for selective ethylene epoxidation?
- What is the reaction mechanism? What is the extent of metal leaching?
- Is the H₂O₂ utilized selectively for forming EO? Does H₂O₂ decompose?

Metal-Loaded Catalysts

- KIT-6\textsuperscript{1} silicates used to incorporate W and Nb
  - W\textsuperscript{2} and Zr\textsuperscript{3} successfully incorporated
- TUD-1\textsuperscript{4} used to incorporate Ce

## Textural Properties Confirm Mesoporosity

<table>
<thead>
<tr>
<th>Sample</th>
<th>W-KIT-6(^1)</th>
<th>Nb-KIT-6</th>
<th>Ce-TUD-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal wt%</td>
<td>2.6-15.2</td>
<td>1.5-10.9</td>
<td>2-24.9</td>
</tr>
<tr>
<td>(S_{\text{BET}}) (m(^2)/g)</td>
<td>927-625</td>
<td>997-804</td>
<td>749-173</td>
</tr>
<tr>
<td>(V_{p,\text{BJH}}) (cm(^3)/g)</td>
<td>1.44-1.09</td>
<td>1.46-1.12</td>
<td>0.65-0.91</td>
</tr>
<tr>
<td>(d_{p,\text{BJH}}) (nm)</td>
<td>6.3-6.9</td>
<td>9.3</td>
<td>3.9-16.7</td>
</tr>
<tr>
<td>Total acidity (\text{NH}_3) mmol/g</td>
<td>0.26-0.48</td>
<td>0.27-0.75</td>
<td>--</td>
</tr>
</tbody>
</table>

TEM Confirms Ordered Mesoporous Structure

W-KIT-6, Pore size: 6.3-6.9 nm

Disordered Worm-hole Morphology of Nb-TUD-1 and Uniform Distribution of Nb-species

SEM of ~12wt% Nb-TUD-1

Electron Image 2

Si Kα1

O Kα1

Nb Lα1
DR-UV-Vis Spectra Reveal Different Types of Metal Incorporation

**W-KIT-6**

- O → WO$_4$
- Nanoparticulate, Oligomeric WO$_3$
- Bulk WO$_3$
- 15.2 wt.% W
- 11.3 %
- 5.9 %
- 2.6 %

**Nb-KIT-6**

- O → NbO$_4$
- (a) 1.5 wt % Nb
- (b) 3.7 %
- (c) 7.2 %
- (d) 13.4 %
- (e) Nb$_2$O$_5$

Cerium Coordination: DR-UV-Vis

- 265 nm: O^{2-} \rightarrow Ce^{3+} charge transfer transition

- 285 and 353 nm: nano-CeO_{2}
Catalyst Evaluation with Pressure-tuned Ethylene Solubility

- $P = 50$ bar; $T = 35 \, ^\circ\text{C}$; Stirrer speed = 1400 rpm;
- 50 wt% $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ (oxidant) = 8 g;
- Methanol (solvent) = 20 g; Batch time = 5 h.
- Catalyst amount = 300 - 500 mg (metal + support).

**Graph**

- $T_c = 9.4 \, ^\circ\text{C}$, $P_c = 50.76$ bar
- Ethylene mole fraction at 50 bar: **0.163**

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**Observed Reactions**

- Ethylene oxide

\[ \text{H}_2\text{C}==\text{CH}_2 + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{C}==\text{CH}_2 + \text{H}_2\text{O} \]

- Ethylene glycol

\[ \text{H}_2\text{C}==\text{CH}_2 + \text{H}_2\text{O} \rightarrow \text{HO}-\text{CH}_2\text{OH} \]

- 2-Methoxyethanol

\[ \text{H}_2\text{C}==\text{CH}_2 + \text{CH}_3\text{OH} \rightarrow \text{HO}-\text{CH}_2\text{OCH}_3 \]

- 2 H\text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2 \text{H}_2\text{O} 

**H\text{H}_2\text{O}_2 analysis:**
Ceric Sulfate Titration

**Metal content:**
ICP-OES

**Diagram:**
- Acetonitrile (Internal Standard)
- Ethylene
- Methanol
- EO
- 2-Methoxyethanol
- Ethylene glycol

**Table:**

<table>
<thead>
<tr>
<th>Time, Minutes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
</tr>
<tr>
<td>Ethylene</td>
</tr>
<tr>
<td>EO</td>
</tr>
<tr>
<td>2-Methoxyethanol</td>
</tr>
<tr>
<td>Ethylene glycol</td>
</tr>
</tbody>
</table>
Metal-exchanged Mesoporous EO Catalysts

![Graph showing EO productivity and yield over time for different catalysts.](image)

- **Pretreated Nb-TUD-1**
- **Nb-TUD-1 + NaHCO3**
- **Fresh Nb-TUD-1**

**Time, h**

**EO yield, mmol**

**EO Productivity, mg EO/h/g Metal**

- **W-KIT-5**
- **W-KIT-6**
- **Ce-TUD-1**
- **Nb-KIT-6**
- **Nb-KIT-5**
- **Nb-TUD-1**
- **Nb-TUD-1 + NaHCO3**

**Ag** catalyst for commercial process
**Re** catalyst for CEBC process

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Nb-TUD-1 and Nb-KIT-6 Active for *Propylene* Epoxidation as Well
Dimethyl Carbonate Production

• EO can be further carboxylated and transesterified to dimethyl carbonate
  – Non-phosgene route using CO₂ and methanol

• Potential for “one-pot” synthesis
Epoxidation Summary

• Homogeneous ethylene epoxidation with MTO catalyst and H$_2$O$_2$ as oxidant demonstrated.
  – Mild conditions: (20-40)°C, ~50 bar; Benign solvents.
  – Virtually total epoxide selectivity ~ 99+%; No CO$_2$ byproduct.
  – EO productivity comparable with Ag-catalyzed process
  – Lower environmental footprint
Epoxidation Summary

- W, Nb-KIT-6 and Ce-, Nb-TUD-1 catalysts are shown to be active for ethylene epoxidation with H$_2$O$_2$ as oxidant. No CO$_2$ formation.
- EO productivity on Nb-TUD-1 (~4,500 mg EO/h-g metal) superior to those observed on Re-based and conventional Ag catalysts.

Ongoing Work

- Strategies to further reduce metal leaching and H$_2$O$_2$ decomposition
- Computational studies of reaction pathways and metal leaching
- Continuous epoxidation with Nb-TUD-1 catalysts
- Potential applications to mixed ethane/ethylene feeds
Industrial Relevance of Hydroformylation

$$\text{alkene isomerization}$$

$$\text{alkene hydrogenation}$$

$$\text{side reactions}$$

$$\text{Rh or Co}$$

$$\text{linear (normal)}$$

$$\text{branched (iso)}$$

Hydroformylation Product
($>15\text{ billion pounds/year}$)

Chemical Intermediates

Plasticizers

Detergents

Surfactants


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A Rh-based hydroformylation process for higher olefin with high TOF, \( n/i \) and catalyst recovery is desirable.

**Substrate:** 1-Octene  
**Desired Product:** \( n \)-nonanal

[P. van Leeuwen, Homogeneous Catalysis, 2004]
CO$_2$-Expanded Liquids (CXLs) Provide Unique Properties

CO$_2$ dissolves, forming CXLs

CO$_2$-expanded Liquids (CXLs) Enhance Hydroformylation Rate and Regio-Selectivity!

<table>
<thead>
<tr>
<th>Total P</th>
<th>System</th>
<th>TOF, hr$^{-1}$</th>
<th>n/i</th>
</tr>
</thead>
<tbody>
<tr>
<td>64 bar</td>
<td>Syngas Only</td>
<td>195</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>6 bar Syngas + CO$_2$</td>
<td>290</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>6 bar Syngas + N$_2$</td>
<td>180</td>
<td>5</td>
</tr>
</tbody>
</table>

T = 60 °C, 1-octene/Rh/P = 2136/1/200

Catalyst:

# Syngas Solubility in Neat Solvent and in CXLs

<table>
<thead>
<tr>
<th>P, bar</th>
<th>x, H₂</th>
<th>x, CO</th>
<th>H₂/CO</th>
<th>x, H₂</th>
<th>x, CO</th>
<th>H₂/CO</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>0.0011</td>
<td>0.0019</td>
<td>0.60</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>25</td>
<td>0.0048</td>
<td>0.0079</td>
<td>0.60</td>
<td>0.0012</td>
<td>0.0019</td>
<td>0.62</td>
</tr>
<tr>
<td>38</td>
<td>0.0073</td>
<td>0.0124</td>
<td>0.59</td>
<td>0.0013</td>
<td>0.0021</td>
<td>0.65</td>
</tr>
<tr>
<td>56</td>
<td>0.0105</td>
<td>0.0177</td>
<td>0.59</td>
<td>0.0016</td>
<td>0.0022</td>
<td>0.72</td>
</tr>
</tbody>
</table>

- H₂ and CO solubility increased with syngas pressure
- H₂/CO ratio had little change
- H₂ and CO solubility increased a little with CO₂ pressure
- H₂/CO ratio increased in CXL

T = 50 °C. In 1-octene reaction mixture. H₂/CO ratio in syngas feed = 1. Standard deviations less than 5% for all data points.

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CXLs Enhance TOF and n/i

1-octene/Rh/P = 988/1/205; Solvent: toluene
Continuous Hydroformylation Using Nanofiltration Membranes

1-Octene → Syngas

Soluble “bulky” polymer catalyst

Nano-filtration membrane
(max T = 50 °C, 280 Dalton molecular weight cut-off)

Product stream
(Rh, P contents analyzed by ICP-AES)

(Polymer ligand: JanaPhos)

P loading: 0.65 mmol/g
MW: ~ 12,190 g/mol
PDI: ~ 1.3

[Desired filtration pressure: > 30 bar]

[R. Jana et al., Org. Lett. 2009 11 971]
Continuous CXL Reactor with Level Control
Continuous Hydroformylation in CXL Successfully Demonstrated

T = 50 °C; 6 bar syngas, 30 bar CO₂

TON after 52 hours: 17,351
Total lost in 52 h: Rh ~ 5%; P ~ 4.6%

<table>
<thead>
<tr>
<th></th>
<th>Syngas Only</th>
<th>CXL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time, h</td>
<td>22</td>
<td>52</td>
</tr>
<tr>
<td>Pressure</td>
<td>30 bar</td>
<td>6 bar syngas + 30 bar CO₂</td>
</tr>
<tr>
<td>LHSV, g 1-octene/g Rh/h</td>
<td>272</td>
<td>472</td>
</tr>
<tr>
<td>Conversion</td>
<td>~ 50%</td>
<td>~ 72%</td>
</tr>
<tr>
<td>n/i</td>
<td>~ 3.5</td>
<td>~ 8</td>
</tr>
<tr>
<td>TOF, h⁻¹</td>
<td>~ 125</td>
<td>~ 340</td>
</tr>
</tbody>
</table>
Conventional Octene Hydroformylation Process (Co-Catalyzed)

Reactors (165 °C, 208 bar)

1-Octene

Syngas

Catalyst Recycle and Regeneration (98 % Co recovery)

Acid makeup

Evaporator

Demetaling column

Preformer

Flash/mixer

Stripper Column

Decanter

Wash Column

Gas Purge

Crude product

150 kton/year

Aqueous purge

Water makeup

Crude product

Gas Purge

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Conceptual CEBC CXL Hydroformylation Process

1-Octene
Toluene
makeup
Syngas

Membrane reactor
(50 °C, 38 bar, 99.8% Rh Retention)

(4.5 wt% CO₂, 72 wt% toluene)

CO₂ make up
Purge

CO₂ recycle
(90% recovery)

CO₂ Separator

Toluene and unreacted 1-octene recycle (95% recovery)
150 kton/year

Gas purge
Distillation Column
Crude product for further processing

*Minimum toluene for catalyst dissolution: 33 wt%
Capital Investment Comparison

<table>
<thead>
<tr>
<th>Process</th>
<th>Reactor</th>
<th>Heat Exchangers</th>
<th>Distillation Columns</th>
<th>Separators</th>
<th>Compressors</th>
<th>Pumps and Filters</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional</td>
<td>11.3</td>
<td>7.6</td>
<td>8.2</td>
<td>3.5</td>
<td>0.6</td>
<td>0.9</td>
<td>32</td>
</tr>
<tr>
<td>CXL</td>
<td>4.2</td>
<td>2.7</td>
<td>5.4</td>
<td>0.8</td>
<td>6.3</td>
<td>0.9</td>
<td>20.3</td>
</tr>
</tbody>
</table>

* Price in million $ per year
## Operating Cost Comparison

<table>
<thead>
<tr>
<th>Process</th>
<th>Catalyst Make-up</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional</td>
<td>2%</td>
</tr>
<tr>
<td>CXL</td>
<td>0.2%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Process</th>
<th>Raw Materials</th>
<th>Utilities</th>
<th>Catalysts Make-up</th>
<th>Solvents</th>
<th>Other Variable Production Costs</th>
<th>Fixed Charges</th>
<th>Plant Overhead Cost</th>
<th>General Expenses</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional</td>
<td>296.4</td>
<td>19.0</td>
<td>0.7</td>
<td>0.0</td>
<td>30.8</td>
<td>8.3</td>
<td>6.0</td>
<td>66.7</td>
<td>427.8</td>
</tr>
<tr>
<td>CXL</td>
<td>298.6</td>
<td>16.4</td>
<td>3.8</td>
<td>0.3</td>
<td>23.5</td>
<td>2.2</td>
<td>3.0</td>
<td>62.9</td>
<td>410.7</td>
</tr>
</tbody>
</table>

* Price in million $ per year
Hydroformylation Summary

- CXLs provide benefits of enhancing TOF and regioselectivity toward linear aldehydes with simple Rh/TPP catalyst complexes
  - Higher $\text{H}_2$/CO ratio in the liquid phase at fixed syngas feed composition
  - Low syngas partial pressure (i.e. avoiding syngas inhibition)
- Continuous hydroformylation in CXL media demonstrated using nanofiltration membranes with JanaPhos ligand
  - Steady TOF ($\sim 340 \text{ h}^{-1}$), TON after 52 hours: 17,351; $S_{\text{aldehydes}} \sim 95\%$; $n/i \sim 8$
- Quantitative economic and environmental assessment shows excellent potential of continuous CXL-based process concept with in situ nanofiltration to be commercially viable and environmentally beneficial
Other Opportunities: Higher Olefins

- Linear $\alpha$-olefins
  - Ethyl Process (INEOS)
  - Gulf Process (CP Chem)
  - Shell Higher Olefins Process
- Selective ethylene oligomerization:
  - Trimerization (CP Chem)
  - Tetramerization (Sasol)
- Selective heterogeneous catalysts?
  - Control of branching, carbon # distribution
Other Opportunities: Direct Routes From Propane?

- Direct oxidation of propane to acrylic acid
  - Mixed-metal oxides (e.g. $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.12}\text{O}_n$) provide yields up to ~50% [e.g. Ushikubo US 5,380,933A 1995], sensitive to morphology
- Ammoxidation of propane to acrylonitrile
  - Mixed metal oxides (e.g. $\text{Mo}_{0.6}\text{V}_{0.187}\text{Nb}_{0.085}\text{Te}_{0.14}\text{O}_x$) have achieved yields in excess of 60% [Grasselli, Nanostructured Catalysts: Selective Oxidations, Ch.5, 2011]
- Improved understanding of catalyst phases needed for improved design
Other Opportunities: Metathesis of Light Alkanes?

- One-pot metathesis of propane or \( n \)-butane
- Three-step reaction scheme requires tandem or multi-functional catalysts
- Need for improved dehydrogenation catalysts and more robust metathesis

Concluding Remarks

• *Emerging feedstocks* (biomass, shale gas) provide exciting challenges for developing novel technologies with reduced environmental footprints
  – Potential game changers for the US chemicals industry
• Multi-scale approach that benefits from expertise of chemists and engineers to concurrently address all process elements (catalyst, reaction mechanisms, reactors, etc.) expedites discovery of *resource-efficient* technologies
• Quantitative *sustainability assessments* (economic, LCA) are powerful tools in guiding R&D toward practically viable processes
• *University/Industry/Government partnerships* that engage stakeholders across the entire value chain key for timely technology commercialization with emerging feedstocks
“Chemicals from Emerging Feedstocks” Initiative in Kansas

**Mission:** To develop economical technologies for chemicals/fuels that prevent waste, conserve resources.

- **Chemicals from Biomass:** USDA/ADM Grant ~$7 M/4 years; Awarded in 2011
- **Chemicals from Natural Gas:** NSF Grant ~$4.4 M/4 yrs; Awarded in 2013.
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