CO₂ Conversion to Organic Compounds and Polymeric Precursors

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Outline

- Energy Supply in Brazil
- Presentation of the Lacqua’s projets
- Motivation for CO₂ conversion
- Industrial uses of CO₂
- Challenges for CO₂ conversion
- CO₂ Conversion by heterogeneous catalysis
- CO₂ Conversion by Homogenous catalysis
- CO₂ Capture using metal organic frameworks
- Future Goals
Energy Supply in Brazil

Energy Supply in Brazil, 2007
46.4% of Renewable Energy

- **Petroleum and derivatives** 36.7%
- **Ethanol - Sugar cane** 16%
- **Hydroelectricity** 14.7%
- **Biomass** 15.6%
- **Natural Gas** 6.3%
- **Coal** 6.2%
- **Nuclear** 1.4%
LACQUA – IQ/UFRJ
Laboratory of Catalysis and Environmental Chemistry

CO$_2$ Capture with MOFs
(Metal Organic Frameworks)

Conversion of CO$_2$ into Organic Products

METHANOL, FORMIC ACID, FORMALDEHYDE POLYMERS PRECURSORS
Motivation for CO$_2$ Conversion

A CO$_2$ based secondary energy cycle (Smith and Thambimuthu 1991)
### Main Sources of CO\(_2\)

**Table SPM.1.** Profile by process or industrial activity of worldwide large stationary CO\(_2\) sources with emissions of more than 0.1 million tonnes of CO\(_2\) (MtCO\(_2\)) per year.

<table>
<thead>
<tr>
<th>Process</th>
<th>Number of sources</th>
<th>Emissions (MtCO(_2) yr(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Fossil fuels</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Power</td>
<td>4,942</td>
<td>10,539</td>
</tr>
<tr>
<td>Cement production</td>
<td>1,175</td>
<td>932</td>
</tr>
<tr>
<td>Refineries</td>
<td>638</td>
<td>798</td>
</tr>
<tr>
<td>Iron and steel industry</td>
<td>269</td>
<td>646</td>
</tr>
<tr>
<td>Petrochemical industry</td>
<td>470</td>
<td>379</td>
</tr>
<tr>
<td>Oil and gas processing</td>
<td>Not available</td>
<td>50</td>
</tr>
<tr>
<td>Other sources</td>
<td>90</td>
<td>33</td>
</tr>
<tr>
<td><strong>Biomass</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bioethanol and bioenergy</td>
<td>303</td>
<td>91</td>
</tr>
</tbody>
</table>

IPCC - *Third Assessment Report (TAR)*
## Current Industrial Uses of CO₂

<table>
<thead>
<tr>
<th>Industrial Processes that use CO₂</th>
<th>Global Capacity /year</th>
<th>Quantity of CO₂ fixed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Urea</td>
<td>95 Mt</td>
<td>54 Mt</td>
</tr>
<tr>
<td>Salicylic Acid</td>
<td>70 Mt</td>
<td>25 Mt</td>
</tr>
<tr>
<td>Methanol</td>
<td>20 Mt</td>
<td>2 Mt</td>
</tr>
<tr>
<td>Cyclic Carbonates</td>
<td>80 Mt</td>
<td>~ 40 kt</td>
</tr>
<tr>
<td>Polypropilenocarbonate</td>
<td>70 Mt</td>
<td>~30 kt</td>
</tr>
</tbody>
</table>

Expected Benefits from $\text{CO}_2$ Conversion

Environmental
- Contribution to the reduction in $\text{CO}_2$ emissions

Economical
- $\text{CO}_2$ conversion into products of economical value

Social
- Contribution to a better human health & better climate conditions

Scientifical
- Synthesis of new designed catalysts and the study of C1 chemistry
Conversion of CO₂ into Organic Products

**Motivation**
- Non-fossil Energy
- Reuse CO₂ reduction

**Fuel Utilisations**

- Energy

**Energy**

- Fossil Fuel
- Biomass

CO₂
Challenges to CO$_2$ Conversion

- Use of CO$_2$ as the starting material for the synthesis of organic chemical products, carbohydrates and polymers

- Need of pure and concentrated CO$_2$ for conversion processes – implies the costs of capture and transportation

- Energy demand for CO$_2$ conversion – use of energetic reagents and good catalysts

- Global market context for the products that are synthesized from CO$_2$
Examples of Industrial Processes That Use CO$_2$

**Urea Production**

$$\text{CO}_2 + 2 \text{NH}_3 \rightarrow \text{H}_2\text{N-CO-NH}_2 + \text{H}_2\text{O}$$

T = 185-190°C, P=150-220 atm

It occurs in two steps

$$\text{CO}_2 + 2 \text{NH}_3 \rightarrow \text{H}_2\text{N-COO}^-\text{NH}_4^+$$

$$\text{H}_2\text{N-COO}^-\text{NH}_4^+ \rightarrow \text{H}_2\text{NCONH}_2 + \text{H}_2\text{O}$$

- It is the product that uses the greatest amount of CO$_2$
- Global production in 2002 – 100 millions of tons/year = 22 millions of tons CO$_2$
- More than 54 % of global capacity is in Southeast Asia
- Urea can be used as a fertilizer (46%) or raw material for carbonates
- It can be associated with CO$_2$ Capture
Production of Dimethyl Carbonate (DMC) without phosgene and chlorine

- The usual route for DMC synthesis

\[
\text{CO} + \text{Cl}_2 \rightarrow \text{COCl}_2
\]

\[
\text{COCl}_2 + 2 \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{OCOOCH}_3 + 2 \text{HCl}
\]

(1) Ethylene carbonate production process

(2) Dimethylcarbonate and ethylene glycol production process

Industrial Process from Asahi Chemical Industry:

- Polymers synthesis since 2002
- Production 50,000 ton/year
- Removal of CO₂ 1730 ton/10,000 ton PC

yield, selectivity: >99 %
Some Features of CO₂ Conversion In Research

Methanol

CO₂

Formic Acid, Formiates and amides

Petrochemicals

Dimethylcarbonate and polycarbonates

Metal catalysts: Ru, Rh, Ni, Pd, Pt

Homogenous and Heterogenous Catalysis.
Capture and Conversion of CO$_2$ into Organic Carbon Products and Polymeric Precursors

Synthesis of catalysts able to aid CO$_2$ conversion
Conversion of CO$_2$ into organic products

Fixation of CO$_2$ into Organic Products

METHANOL, FORMIC ACID, FORMALDEHYDE
PRECURSORS OF POLYMERS
EXPERIMENTAL

1- Heterogenous Catalysis- Hydrogenation of CO₂

Ni, Ru catalysts

CO₂ + H₂ → Organic products

2- Homogeneous Catalysis – CO₂ reaction with methanol

Sn catalysts

CO₂ + H₃C-OH → Organic products
Experimental Steps: Part I - Heterogenous Catalysis-Hydrogenation of CO$_2$ - Synthesis of Catalysts

- Synthesis of catalysts based on complexes of nickel and ruthenium – eleven catalysts were synthesized.

- Synthesis of the mesoporous (silicate)

- Intercalation of the cationic complexes of nickel and ruthenium into the mesoporous

- Characterization of the catalysts:
  - Elemental Analysis
  - Infrared Spectroscopy
  - X-ray diffraction
  - Nuclear Magnetic Resonance
  - Thermogravimetric Analysis
  - Electronic analysis
# Intercalation results

<table>
<thead>
<tr>
<th>Sample</th>
<th>Distance $d$ (Å)</th>
<th>$\Delta d$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium mesoporous</td>
<td>15.21</td>
<td>-</td>
</tr>
<tr>
<td>mesoporous+surfactant/ButOH</td>
<td>20.67</td>
<td>5.46</td>
</tr>
<tr>
<td>Ni$^{2+}$ intercalated</td>
<td>15.17</td>
<td>5.50</td>
</tr>
<tr>
<td>Ru$^{3+}$ intercalated</td>
<td>15.28</td>
<td>5.39</td>
</tr>
<tr>
<td>Cat Ni1 intercalated</td>
<td>18.21</td>
<td>2.46</td>
</tr>
<tr>
<td>Cat Ni2 intercalated</td>
<td>18.92</td>
<td>1.75</td>
</tr>
<tr>
<td>Cat Ru1 intercalated</td>
<td>18.21</td>
<td>2.46</td>
</tr>
</tbody>
</table>
Conversion Results of Heterogeneous Catalysis

11 Catalysts synthesized – 7 were active – 20 to 30 % of conversion, pressure = 1 atm

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Product</th>
<th>Temp (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cat 1</td>
<td>Formaldehyde</td>
<td>149</td>
</tr>
<tr>
<td>Cat 2</td>
<td>Formaldehyde</td>
<td>111-124</td>
</tr>
<tr>
<td>Cat 3</td>
<td>Methanol, Formic acid, formaldehyde</td>
<td>150-152</td>
</tr>
<tr>
<td>Cat 4</td>
<td>Methanol</td>
<td>152</td>
</tr>
<tr>
<td>Cat 5</td>
<td>Formic acid</td>
<td>152</td>
</tr>
<tr>
<td>Cat 6</td>
<td>Methanol</td>
<td>150-152</td>
</tr>
</tbody>
</table>
Conclusions from Conversion of CO$_2$ into Organic Products by Heterogeneous Catalysis

♦ 11 Catalysts were synthesized and characterized

♦ Seven catalysts were able to convert CO$_2$ $\rightarrow$ 30 % of total conversion

♦ The main products of the conversion were: methanol, formic ac. and formaldehyde

♦ Mild conditions for conversion: $P= 1$ atm and $\Delta T = 120$ to $150$ °C

♦ 1 Patent submitted.
2- CO$_2$ Conversion by Homogeneous Catalysis

CO$_2$ reaction with methanol

Sn modified alcoxide catalyst

CO$_2$ + H$_3$C-OH $\rightarrow$ Organic products

catalytic test in a Parr reactor

Sn alcoxide catalyst

Methanol

CO$_2$

2 h 423 K

Solid

Liquid

GCMS Analysis
The Sn catalyst before and after the Conversion Test

Data from near infrared spectrum and far infrared spectrum of the catalyst before and after the catalytic test showed that

The catalyst is stable
GCMS Spectrum of the obtained product

Scan 457 (2.695 min): 2,5-D

\[
\text{OMe} \\
\text{Me} - \text{C} - \text{Me} \\
\text{OMe}
\]
GCMS Spectrum of the obtained product

Scan 647 (3.780 min): 2-D

MeO\text{C}Pr-n
Conclusions from Homogeneous Catalysis Conversion of CO$_2$ into Organic Products

- CO$_2$ insertion into Sn-O bond of the catalyst
- Formation of Oxygenated organic products
Conversion of CO$_2$ into Organic Products

Petroleum Derivatives
Natural Gas
Biomass

CO$_2$

CO$_2$eq emissions

CURRENT INDUSTRIAL PROCESSES

REUSE CO$_2$ FIXATION

Industrial Processes + Carbon Capture & Reuse

CHEMICALS
Methanol, Formic Acid, Formaldehyde

JLMiranda
Projects on CO$_2$ Capture

- Synthesis of new metal organic frameworks: chromium, copper and zirconium

- Synthesis of MOFs with lower cost

- Collaboration with Professor Christian Serre-Institute Lavoisier, Université de Versailles Saint-Quentin-en-Yvelines.
Future Goals

- Study of the recycle of the catalysts
- Comparison between nickel and ruthenium catalysts
- Use of zinc catalysts in homogeneous catalysis
- Synthesis of new MOFs with lower cost and greater selectiveness
- Use of ethanol to react with CO$_2$
Acknowledgments

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Thank you for your attention

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