Recent R&D Activities on Clean Coal Technology in DICP

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Content

• Brief Introduction of DICP

• Recent R&D Activities on Clean Coal Technology in DICP
History - An Institute of Chinese Firsts

- Established: 1949
- Zeolite Catalyst: 1956
- Gas Analysis for Nuclear Bomb Test: 1958
- Jet Fuel and Diesel: 1964
- Fuel Cells: 1978
- Catalyst for Spacecraft: 1980
- Chemical Lasers: 1982

Liquid Fuel from Syngas

History - An Institute of Chinese Firsts

1993: Catalytic Ethylbenzene Technology

2010: The World's First MTO Commercial Unit (DMTO)

2013: The World Largest Scale System of All Vanadium Flow Storage Battery

2017: The World's First Coal-to-Ethanol Demonstration

The World's Brightest FEL light in the VUV region - Dalian Coherent Light Source
Human Resources

- Member of CAS and CAE: 13
- Professor: 199
- Associate Professor: 444
- Staffs: 359
- Visiting Scholar: 58
- Postdoc: 135
- PhD Students: 573
- MS Students: 396
- Joint-Supervised Students: 181

~2300 working and studying in DICP
18 distinguished scientists have been elected from DICP as members of CAS and CAE. 13 of them are now working in DICP.
General Information of DICP (2012-2016)

- 1200 Employees
- 1100 Graduate Students
- 18 Research Laboratories
- 29 Spin-off Companies
- 10 International Research Centers
- ¥5000 Million Research Funds
- 50 Major Awards
- 4000 Publications
- 4000 Filed Patents
- 50 Industrial Applications
Content

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• Recent R&D Activities on Clean Coal Technology in DICP
DICP Major Activities in Clean Coal Researches

Coal → Syngas → CH₄ (Natural Gas) → Aromatics → Cyclohexane → Cyclohexanone → Caprolactam → Nylon

PTA

Aldehyde → Pyridine → Pesticide
Ethylene oxide → Cholamine → Ethylenediamine

Ethylene → Ethylbenzene → Styrene → Polystyrene

Propylene

Isopropanol
Acrylic acid
Epoxypropane → Epichlorohydrin

Dimethyl ether → Ethanol

PX → PTA

CO₂ → CO/Formic Acid

Integrated Use of CBM

Liquid Fuels

α-Alcohol / Naphtha

Ethanol / Acetic Acid / Ethyl Acetate

Methanol
DICP Major Activities in Clean Coal Researches

Coal → Syngas → CH₄ (Natural Gas) → Aromatics (PTA) → Cyclohexane → Cyclohexanone → Caprolactam → Nylon

- Methanol
- Ethanol / Acetic Acid / Ethyl Acetate
- α-Alcohol / Naphtha
- Liquid Fuels

CO₂ → CO/Formic Acid

Integrated Use of CBM

Syngas conversion

- Syngas methanation
- Syngas to fuel, wax and mixed α-alcohols
- Syngas to olefins
- Syngas to ethanol
Coal to SNG process can get higher energy efficiency with less water consumption and lower investment cost.

SNG can not only alleviate the contradiction between supply and demand of natural gas market, but also provide a preferred way of highly efficient and clean utilization of coal.
Breakthrough of Key Technologies

- **DICP Methanation Catalyst (13 Pieces of Chinese Patent Application)**

  The high temperature methanation catalyst was developed based on the novel synthesis technic and the materials with good hydrothermal stability which effectively prevented sintering of the nickel crystal. Catalyst had been tested with a total of 7,500 operating hours in the temperature range of 600-700 °C.

  The low temperature methanation catalyst has good activity and stability which ensure maximum conversion of CO and CO2. The catalyst had been tested with a total of 1,500 operating hours in the temperature range of 250-450 °C.


  The multi stage methanation process based on DICP’s novel methanation catalyst and its methanation reaction kinetics, addressed the essential question of reaction heat recovery and was also economic competitiveness for investment and operating costs.
**Providing A Total Solution**

- **Demonstration Project**
  - DICP’s proprietary methanation catalyst as well as process had been validated and demonstrated in two pilot scale plants under realistic industrial conditions.
  - The total running time had been up to more than 4,400 hours and SNG product meet with the requirements of the national pipeline natural gas.
  - Based on the results, 1 billion Nm³/a SNG process design package had been compiled and a preliminary review had been completed.

- **Catalyst Production**
  - A catalyst manufacture plant with the annual output of 50 tons was built in Dalian and thus DICP has the ability to supply commercial methanation catalyst.
  - Provide a package of solutions including licence, PDP, catalyst supply, onsite assistance and technical support.

  - **Technology**: Highly effective catalyst & reliable, flexible methanation process
  - **Economy**: Domestic technologies reduce the overall capital & operating expense
  - **Competitiveness**: Competitive advantages in technology, economy and after-sales technical service

Demonstrate device in Yima, Henan Province, with a capacity of 200 Nm³/h syngas

Demonstrate device in Guanghui Ltd., Xinjiang Region, with a capacity of 6000 Nm³/d SNG
Multi-techniques for Ethanol Production from Coal

1 kt/a pilot plant test of ethanol synthesis from syngas have conducted in 2016

300 kt/a ethanol and iso-propanol production from acetic acid/propene as feed-stocks have done in 2015

30 kt/a demon for hydrogenation of acetic acid to ethanol have done in 2016

Pilot plant test for hetero-oxo-synthesis of methanol and syngas and its hydrogenation to ethanol
Syngas to Fuel, Wax and Mixed α-alcohols

3kt/a Demon test have been done using a Co/SiO₂ catalyst and a fixed bed reactor in 2007.

200kt/a 3 industrial facilities are being built in China using Co/SiO₂ catalyst and fixed-bed reactor.

150 kt/a demonstration have been succeed to produce selectively naphtha and diesel using Co/AC catalyst and slurry reactor in 2015-2017.

DICP process

α-alcohols direct synthesis from syngas

Sasol process

Syngas → F-T → Sep. → α-Oli-fin → hydroformylation → Aldehydes → Hydrogenation → Mixed Alcohols (C₂–C₁₈)

HTFT catalyst

Fuel

Industrial Demon. will be tested in 2018
Heterogeneous Hydroformylation of Olefins to High Alcohols

- DICP process
- Heterogeneous catalysis
  Trickle or slurry reactor

Traditional Process for hydroformylation

- olefin
  - CO
  - H₂

The cost of octanol will cut down ca. 300 RMB in DICP process, the market is ca. 1.5 m ton/year

Simultaneous solve of separation and high performance

- Fundamental understanding at molecular level to setup and develop theory for single sites catalysis.
- Novel catalysts with high performance will be developed, the pilot tests for C3=/C4= hydroformylation reactions will be conducted.
Two different types of active sites for CO activation and C-C coupling. Leading to selectivity beyond ASF distribution limit.

Remove oxygen with CO, possibly circumventing energy-intensive water-gas-shift process.

The role of oxides and zeolites, activation of CO, and possible reaction intermediate were studied by in situ-XPS, synchrotron-based vacuum ultraviolet photoionization mass spectrometry (SVUV-PIMS), etc.
DICP Major Activities in Clean Coal Researches

**Coal** → Syngas → CH₄ (Natural Gas) → CO₂ (CO/Formic Acid) → CO₂ conversion

- **CO₂ conversion**
  - CO₂ Electroreduction to methanol and formic acid
  - Direct converting CO₂ to gasoline

Coal → Methanol → Ethanol / Acetic Acid / Ethyl / α-Alcohol / Naphtha → Liquid Fuels

Liquid Fuels → CO₂ → CO/Formic Acid

Integrated Use of CBM

- Ethylene oxide
- Choline
- Ethylenediamine
- Aldehyde
- Pyridine
- Pesticide
- Propylene
- Epoxypropane
- Acrylic acid
- Isopropanol

PX → Ethanol → Epichlorohydrin

PTA → Dimethyl ether → Epoxypropane
CO$_2$ Electroreduction to Formic Acid and CO

- Liquid Fuels and chemicals production from CO$_2$ and H$_2$O with electricity from renewable energy or abundant nuclear energy
- Simplified process, without H$_2$, reaction temp: r.t. to 800 °C
- Electricity storage and carbon recycling simultaneously

Direct hydrogenation of CO₂ into liquid fuels can mitigate CO₂ emissions and reduce the rapid depletion of fossil fuels. Here we show a multifunctional catalyst that converts CO₂ to gasoline with high selectivity due to synergistic catalysis of active sites.

“This work can be considered as a breakthrough in CO₂ catalysis” (referee)

J. Wei, Q. Ge,* R. Yao, Z. Wen, C. Fang, L. Guo, H. Xu, J. Sun*
Selected as a Research Highlight in Nature 2017, 545, 7653
Direct Converting CO$_2$ to Gasoline

- **Product:** Conformed to China V-5 Gasoline standard
- **Catalyst:** Well stability after 1000 h running
Direct Converting CO₂ to Gasoline

- Confirmation of active sites: Na-Fe₃O₄/Fe₅C₂/zeolite
- Gasoline sel. reaches the highest value among reports
DICP Major Activities in Clean Coal Researches

**Methanol conversion**

- Methanol to olefins (DMTO technologies)
- Methanol to propylene (DMTP)
- Co-production of p-X and olefin by methanol and toluene
- Ethanol from DME carbonation and hydrogenation
- Methanol-coupled-naphtha to light olefins

Coal → Syngas → CH₄ (Natural Gas) → Aromatics → Cyclohexane → Cyclohexanone → Caprolactam → Nylon

Coal → Methanol → Ethylene → Ethylbenzene → Styrene → Polystyrene

Coal → Methanol → Aldehyde → Pyridine → Pesticide

Coal → Methanol → Ethylene oxide → Cholamine → Ethylenediamine

Coal → Methanol → Ethanol / Acetic Acid / Ethyl Acetate

Coal → Methanol → Propylene → Isopropanol

Coal → Methanol → Acrylic acid

Coal → Methanol → Epoxypropane → Epichlorohydrin

Coal → Methanol → Dimethyl ether → Ethanol

Coal → Methanol → PX → PTA
Roadmap for DMTO Process Development

- **Lab test**
  - DICP
  - ZSM-5
  - SAPO

- **Pilot test**
  - DICP (Fixed Bed)
  - C_2^+ + C_3^+ + C_4^+ : 85% 1993

- **Pilot test**
  - Shanghai (Fluidized Bed)
  - C_2^+ + C_3^+ > 80%, 1995

- **Demo**
  - Shaanxi
  - 2004.08 - 2006.08

- **Commercialization**
  - Shenhua: 600 KT/a
  - Yanchang: 600 KT/a
  - 2006.08 -

- **DMTO-II Demo**
  - C_2^+ + C_3^+ : ~86% 2010.06

- **From early 1980s**
  - “75”, “85”, “973” National Project

- **National Development and Reforming Committee of China (NDRC)**

**DME/Methanol to olefins = DMTO (DICP’s MTO)**
Progress on Reaction Mechanism

Carbenium ions in different cages and channels have been observed

<table>
<thead>
<tr>
<th>Type</th>
<th>8-ring with cage</th>
<th>10-ring channel</th>
<th>12-ring channels</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cages or Channels</strong></td>
<td>RHO</td>
<td>CHA</td>
<td>AEI</td>
</tr>
<tr>
<td><strong>Size (nm²)</strong></td>
<td>1.14 x 1.14</td>
<td>0.67 x 1.00</td>
<td>1.16 x 1.27</td>
</tr>
<tr>
<td><strong>SAPOs</strong></td>
<td>DNL-6</td>
<td>SAPO-34</td>
<td>SAPO-18</td>
</tr>
<tr>
<td><strong>Si-Al Zeolites</strong></td>
<td>H-SSZ-13</td>
<td>H-RUB-50</td>
<td>H-ZSM-22</td>
</tr>
<tr>
<td><strong>AIPO₄</strong></td>
<td>AIPO-18</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Summary on Mechanism

The mechanism picture of the reaction

- Methylation reaction could not be avoid
- Cavity (size and environment) controls the selectivity
- Acidity changes the balance between the mechanisms
Scale-up of DMTO Reactor

<table>
<thead>
<tr>
<th>Scale-up Level</th>
<th>MeOH Feed</th>
<th>Cat Inventory</th>
<th>Ugas</th>
<th>Fluidization</th>
</tr>
</thead>
<tbody>
<tr>
<td>Micro Scale</td>
<td>~1.2 kg/d</td>
<td>0.01 kg</td>
<td>~2-- 25 cm/s</td>
<td>Bubbling bed</td>
</tr>
<tr>
<td>Pilot Scale</td>
<td>~120 kg/d</td>
<td>1 kg</td>
<td>~5-- 25 cm/s</td>
<td>Bubbling bed</td>
</tr>
<tr>
<td>Demo Scale</td>
<td>50,000 kg/d</td>
<td>300 kg</td>
<td>~1-2 m/s</td>
<td>Turbulent bed</td>
</tr>
<tr>
<td>Commercial Scale</td>
<td>5500,000 kg/d</td>
<td>45,000 kg</td>
<td>~1-2 m/s</td>
<td>Turbulent bed</td>
</tr>
</tbody>
</table>
# DMTO Demonstration Results: 72 Hours Calibration

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Feedstock</strong></td>
<td>CH$_3$OH</td>
</tr>
<tr>
<td><strong>Scale</strong></td>
<td>50t/d</td>
</tr>
<tr>
<td><strong>Reactor type</strong></td>
<td>Fluid bed</td>
</tr>
<tr>
<td><strong>Single pass conversion %</strong></td>
<td>&gt;99%</td>
</tr>
<tr>
<td><strong>Yield of ethylene and propylene, wt %</strong></td>
<td>33.73</td>
</tr>
<tr>
<td><strong>Selectivity of ethylene and propylene, wt %</strong></td>
<td>&gt;79.1</td>
</tr>
<tr>
<td><strong>Feedstock consumption for each ton of ethylene and propylene, t/t</strong></td>
<td>2.96</td>
</tr>
<tr>
<td><strong>Catalyst</strong></td>
<td>D803C-II-01</td>
</tr>
</tbody>
</table>
New Generation of DMTO Technology (DMTO-II)

Technical Principle

DMTO

2.96 tons MeOH → 1 ton Olefin

MeOH → Fluidized Reaction → Olefin Mixtures → Separation → C₄⁺ + C₂⁺ + C₃⁺ (Semifinished product ~80%)

DMTO-II

2.6-2.7 tons MeOH → 1 ton Olefin

MeOH → Fluidized Reaction → Olefin Mixtures → Separation → C₄⁺ + C₂⁺ + C₃⁺ (Semifinished product 85-90%)
Commercialization of DMTO

Baotou Coal-to-Olefin Project of China Shenhua Group

- 1,800 KTA Methanol → 600 KTA polyolefin
- Approved by NDRC (Dec, 2006)
- Construction was finished on May 31, 2010
- First coal to olefin plant in the world
World First Coal to Olefin Plant in Baotou of China Shenhua Group
DMTO Unit of Coal to Olefin Project in Baotou of China Shenhua Group
Typical Products in DMTO Plant (1.8 Million Tons MeOH)

- Methanol consumption for 1 ton olefin is 2.96 ton
- Ethylene and propylene selectivity ~80%

Diagram showing the process flow with various components and product outputs.

- Methanol: 1800 kt/a
- CO, CO₂
- Reactor
- Regenerator
- Compressor
- Quenching and water scrubbing tower
- Water
- Recovery section
- Fuel gas: 46.1 kt/a
- Ethylene: 305.7 kt/a
- Propylene: 298.1 kt/a
- C₄: 83.0 kt/a
- C₅⁺: 32.4 kt/a
So far, DMTO technology has been licensed in 24 commercial units (14 MMt/a) in the domestic market. 12 commercial installations (7MMt/a) have commissioned in just five years.
DMTO-III Technology

Technical features

- New generation of DMTO catalyst
- Higher operation pressure
- One unit: 3 Mt/a → 1.15 Mt/a light olefin
- Ethylene + Propylene Selectivity: ~90%

DMTO-III

100% MeOH → Fluidized Reaction → Olefin mixtures → Separation → C_4+ + C_2= + C_3=

~2.6 tons MeOH → 1 ton Olefin
DMTP technology

- **Multi-functional catalyst**
  - methanol conversion;
  - ethylene conversion;
  - and C$_4$+ cracking

- **High efficient fluidized bed reactors**
  - methanol and ethylene conversion in one reactor
  - adjustable propylene yield
Simulation results based on pilot tests (1t/d)

(MeOH Conversion=100%)

<table>
<thead>
<tr>
<th>Case</th>
<th>Ethylene (wt%)</th>
<th>Propylene (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>74.16</td>
<td>10.37</td>
</tr>
<tr>
<td>2</td>
<td>77.08</td>
<td>8.82</td>
</tr>
<tr>
<td>3</td>
<td>80.23</td>
<td>4.44</td>
</tr>
</tbody>
</table>
Co-production of p-X and Olefin by Methanol and Toluene

Why co-production?

Fluidized bed reactors
Typical Results

M/T = 10 (mol), MeOH WHSV = 1.6 h⁻¹

- PX
- Methanol conv.
- Ethylene + propylene + PX
- Toluene conv.
Ethanol from DME Carbonation and Hydrogenation

Hydrocarbons

\[
\text{H}_3\text{C-O-CH}_3 + \text{CO} \xrightarrow{\text{zeolite}} \text{H}_3\text{C-C-O-CH}_3
\]

\[
\text{CH}_3\text{OH} + \text{H}_3\text{C-CH}_2\text{OH}
\]

2\text{H}_2

2\text{CH}_3\text{OH} = \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O}

Total: \quad \text{CH}_3\text{OCH}_3 + 2\text{CO} + 4\text{H}_2 = 2\text{CH}_3\text{CH}_2\text{OH} + \text{H}_2\text{O}

Total from syngas: \quad 2\text{CO} + 4\text{H}_2 = \text{CH}_3\text{CH}_2\text{OH} + \text{H}_2\text{O}
Improvement of Catalyst Life

- 2010: 300hs
- 2011: 300hs
- 2012: 1150hs
- 2013: 6400hs
- 2015

Graph showing DME Concentration (% vs. Time-on-Stream / h)
The world’s first Coal-to-Ethanol (methanol to ethanol) Demonstration with 100,000 metric tons of pure ethanol per year in January 2017
Summary

• Systematic research and development have been processed on clean coal utilization in DICP, providing technical support to harmonious development of coal chemical industry and petrochemical industry.

• Several technologies have been utilized in industrial implementation, such as DMTO, ethanol technology, etc.

• The industrialized projects stood the tests of fluctuations in oil prices and develop rapidly, which show excellent market competitiveness.

• Although great achievements have been obtained in Coal Chemical Industry in China, there still has tremendous development space in the future.

• Technical innovation is always the most important for the world’s green growth and sustainable development.
Welcome you to Visit DICP

Thank you!