中國科學院大連化學物理研究所
DALIAN INSTITUTE OF CHEMICAL PHYSICS , CHINESE ACADEMY OF SCIENCES

Recent R&D Activities on Clean Coal Technology in DICP

Rui CAI

Nov. 30th, 2017

Content

- Brief Introduction of DICP
- Recent R&D Activities on Clean Coal Technology in DICP

History - An Institute of Chinese Firsts

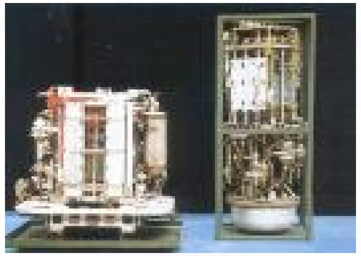
1949 – Estabilished

1956 – Liquid Fuel from Syngas

1958 – Zeolite Catalyst

1964 – Gas Analysis for Nuclear Bomb Test

1964 – Jet Fuel and Diesel



1978 – Fuel Cells

1980 – Catalyst for Spacecraft

1982 – Chemical Lasers

History - An Institute of Chinese Firsts

1993 — Catalytic Ethylbenzene Technology

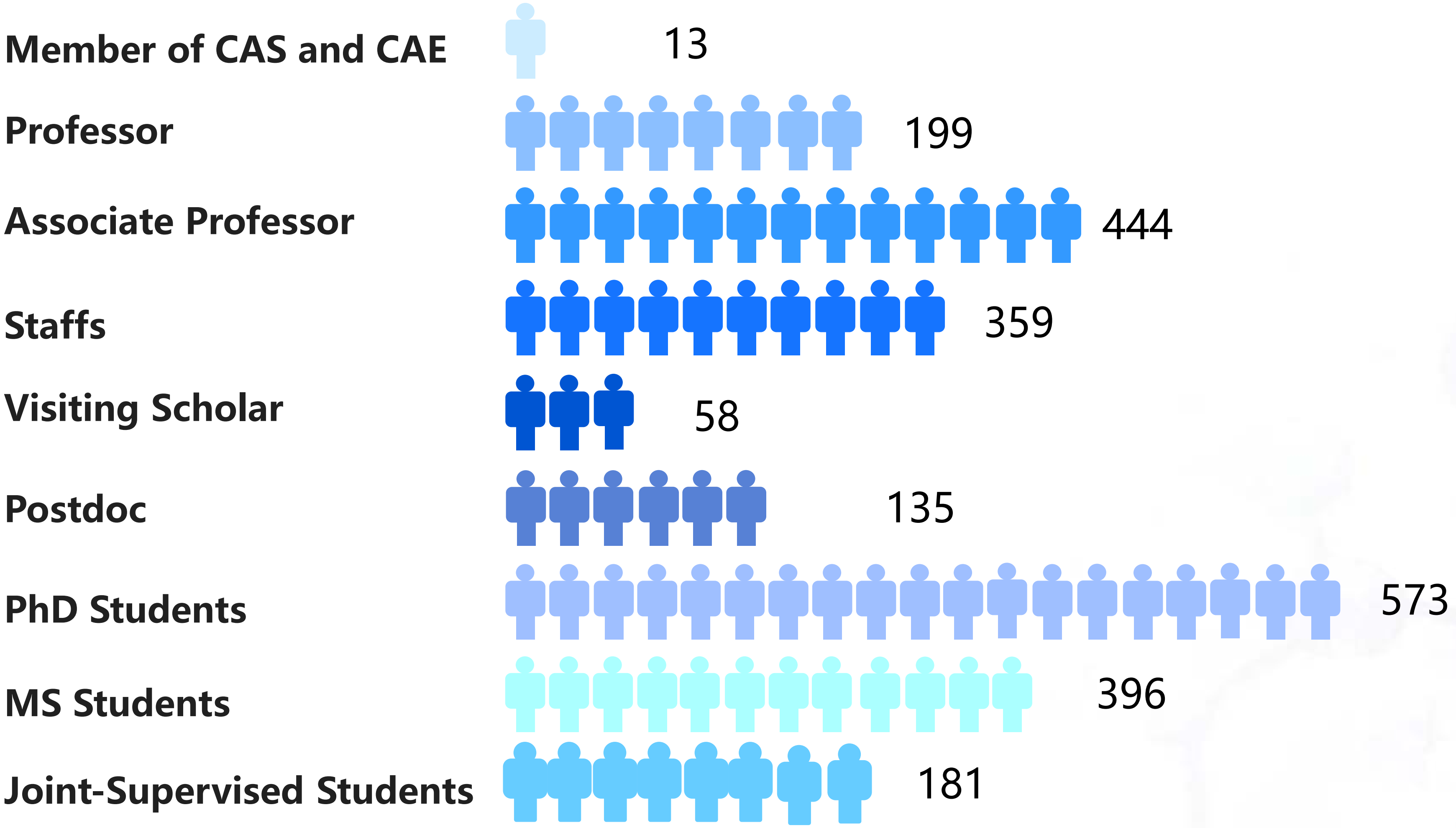
2010 — The World's First MTO Commercial Unit (DMTO)

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

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

2017 — The World's Brightest FEL light in the VUV region
-Dalian Coherent Light Source

Human Resources



~2300 working and studying in DICP

Members of CAS and CAE


Dayu ZHANG
(1906-1989)


Xiexian GUO
(1925-1998)


Peizhang LU
(1925-2017)


Cunhan ZHANG
(1928-)


Guozhong HE
(1933-)


Quan YUAN
(1934-)


Nanquan LOU
(1922-2008)


Qingshi ZHU
(1946-)


Liwu LIN
(1929-2014)


Guohe SHA
(1934-)


Shengli YANG
(1941-)


Baolian YI
(1938-)


Fengting SANG
(1942-)


Yukui ZHANG
(1942-)


Can LI
(1960-)


Xinhe BAO
(1959-)


Xueming YANG
(1962-)


Tao ZHANG
(1963-)


Zhongmin LIU
(1964-)

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

10 International Research Centers

4000 Publications

1100 Graduate Students

5000 Million Research Funds

4000 Filed Patents

18 Research Laboratories

50 Major Awards

50 Industrial Applications

29 Spin-off Companies

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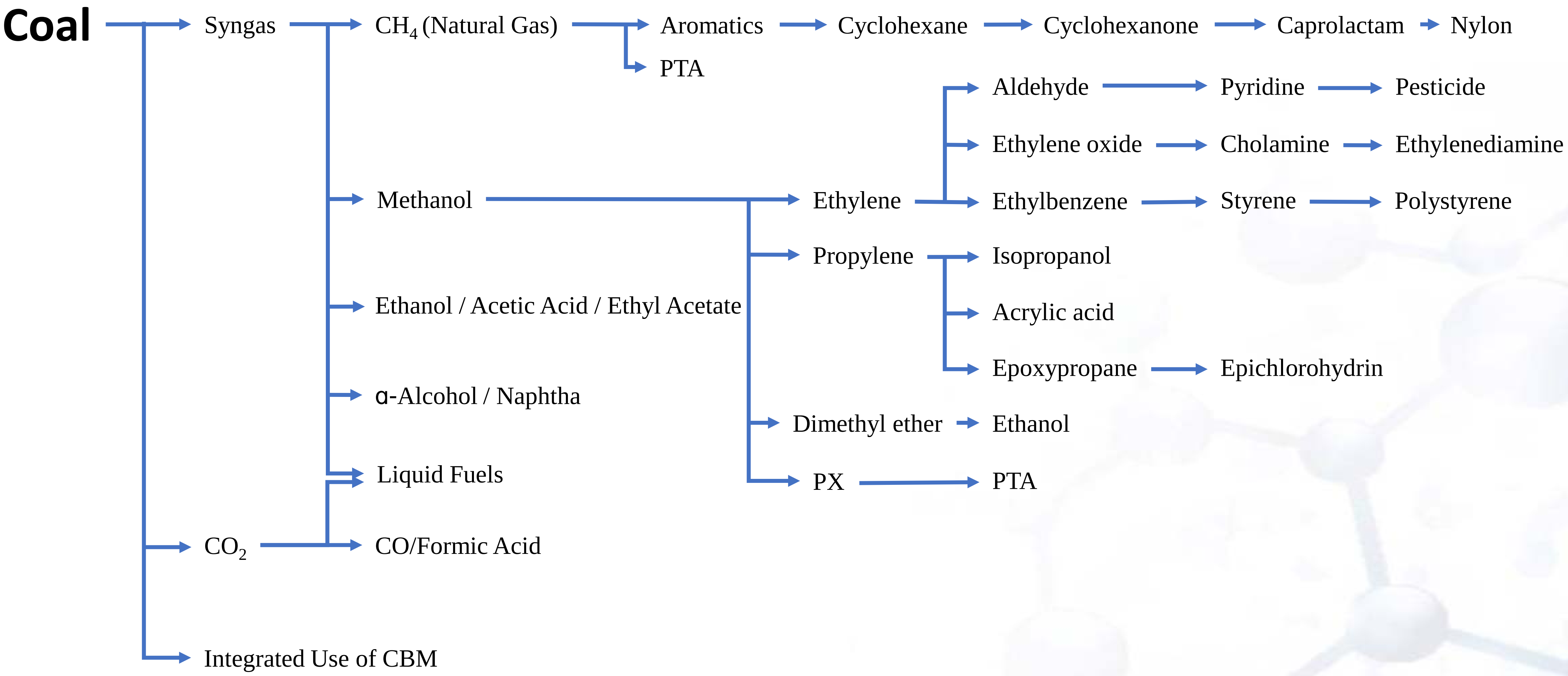
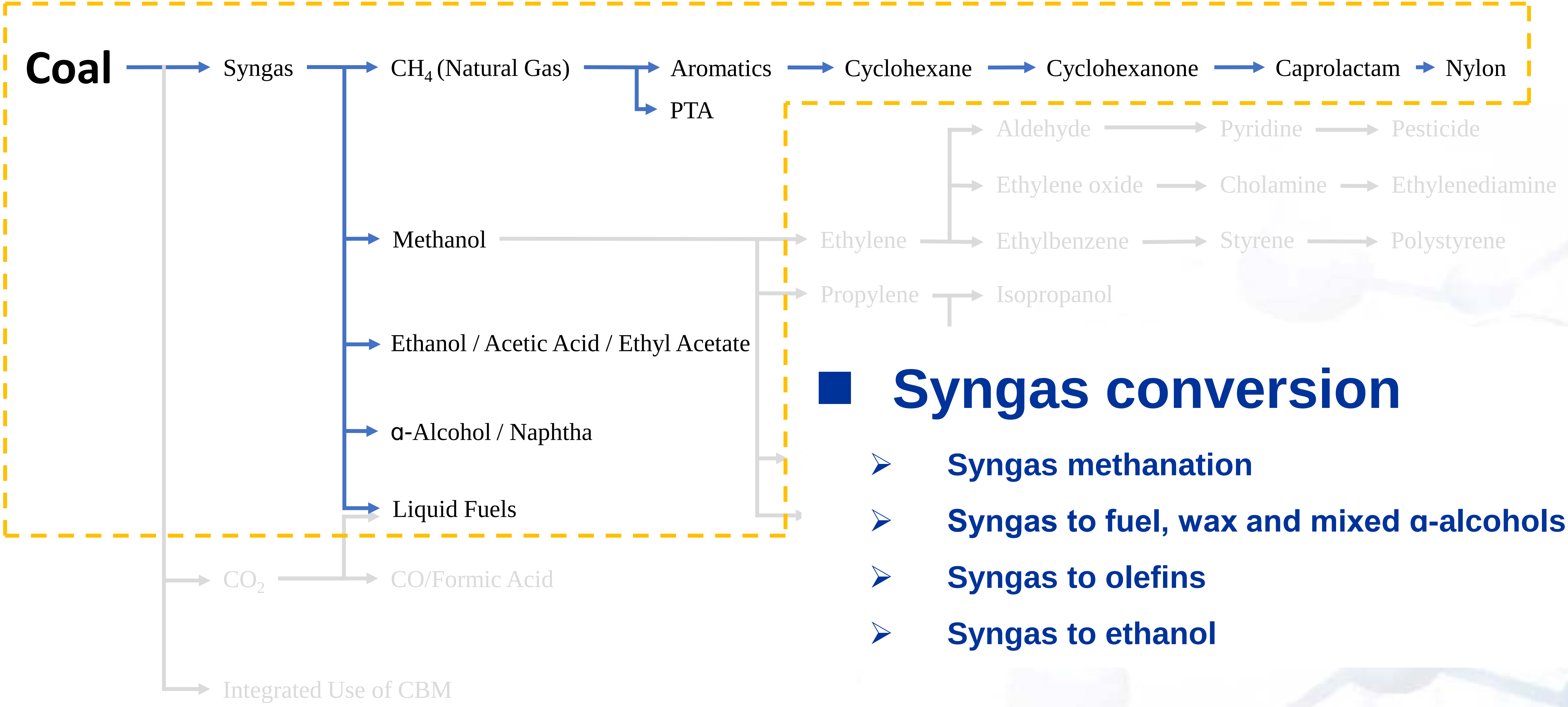
DICP Major Activities in Clean Coal Researches



DICP

DICP Major Activities in Clean Coal Researches



■ Syngas conversion

- ➢ **Syngas methanation**
- ➢ **Syngas to fuel, wax and mixed ɑ-alcohols**
- ➢ **Syngas to olefins**
- ➢ **Syngas to ethanol**

DICP

SNG Production from Syngas Methanation

rich coal

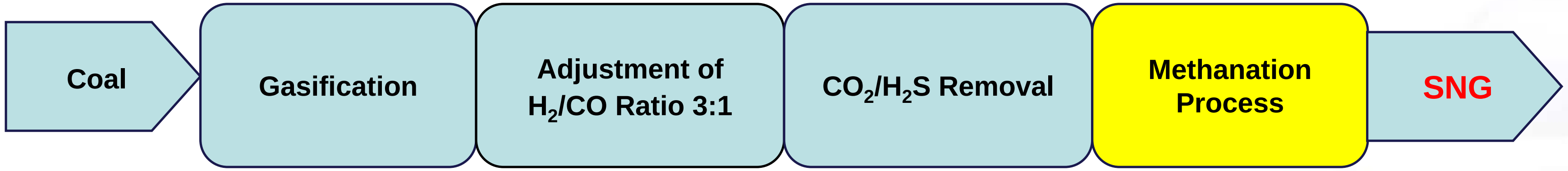
less natural gas

$CO + 3H_2 = CH_4 + H_2O \quad + 206kJ/mol$

$CO_2 + 4H_2 = CH_4 + 2H_2O \quad + 165kJ/mol$

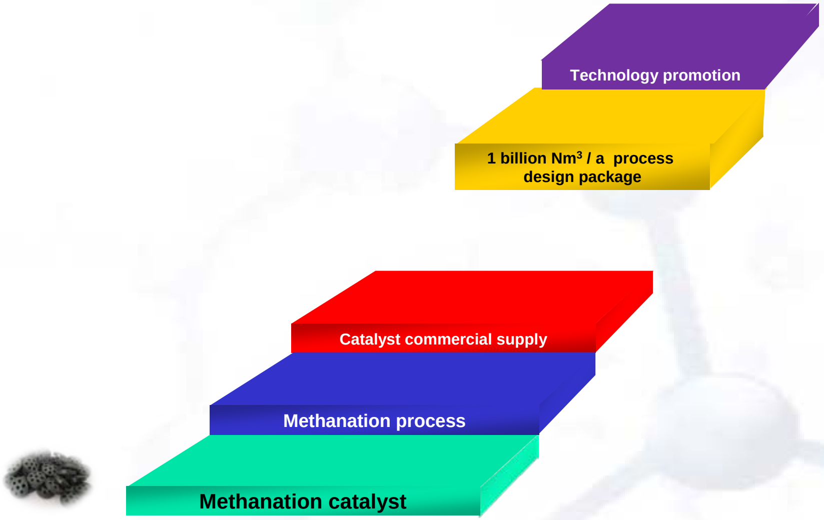
Syngas ⟺ SNG + Heat

Energy 100% ⟺ 80% + 20%



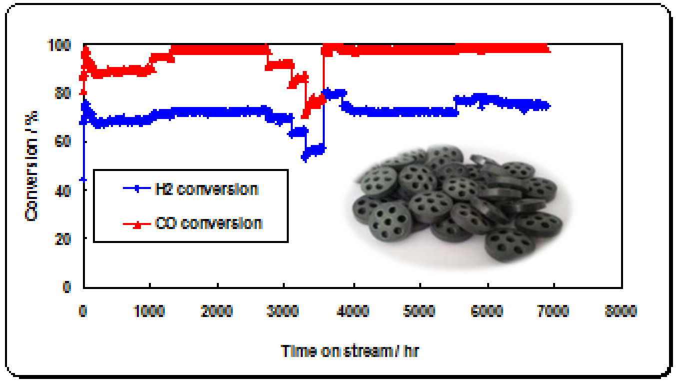
- Coal to SNG process can get higher energy efficiency with less water consumption and lower investment cost

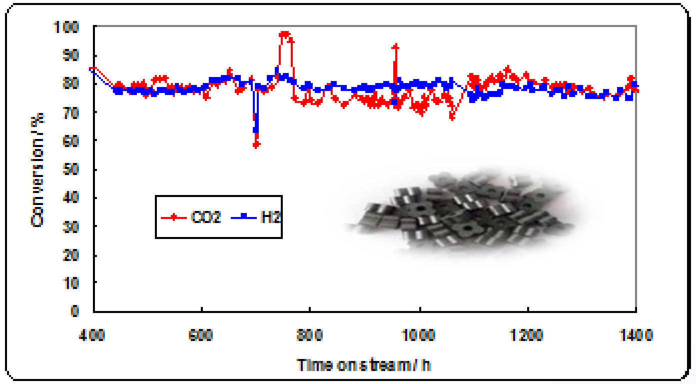
- SNG can not only alleviate the contradiction between supply and demand of natural gas market, but also provide a preferred way of highly efficient and clean utilization of coal



Breakthrough of Key Technologies

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

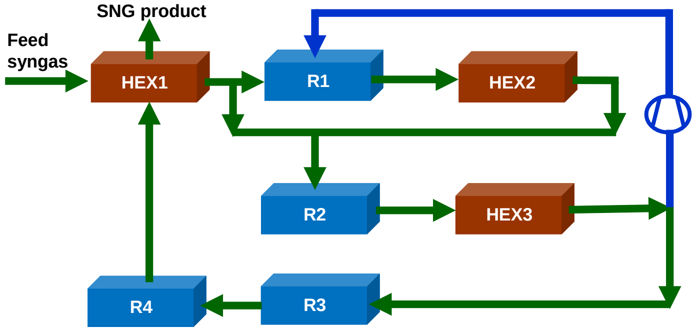


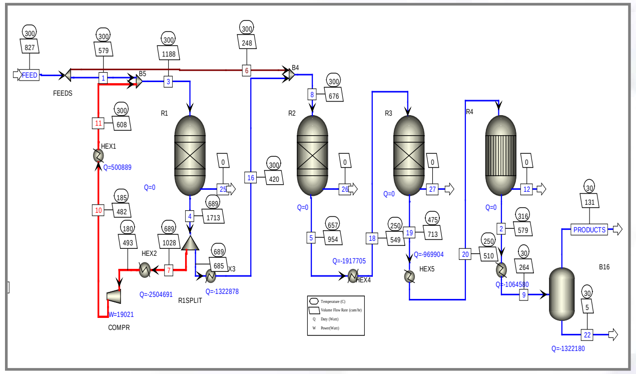


The high temperature methanation catalyst was developed based on the novel synthesis technic and the materials with good hydrothermal stability which effectively prevented sintering of the nickel crystal. Catalyst had been tested with a total of 7,500 operating hours in the temperature range of 600-700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

The low temperature methanation catalyst has good activity and stability which ensure maximum conversion of CO and CO_2 . The catalyst had been tested with a total of 1,500 operating hours in the temperature range of 250-450 ºC .

- **DICP Methanation Process (4 Pieces of Chinese Patent Application)**





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.

DICP

Providing A Total Solution

- **Demonstration Project**

Demonstrate device in Yima, Henan Province, with a capacity of 200 Nm^3/h syngas

Demonstrate device in Guanghui Ltd., Xinjiang Region, with a capacity of 6000 Nm^3/d SNG

- 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 Nm^3/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.

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

Provide a package of solutions including licence, PDP, catalyst supply, onsite assistance and technical support

DICP

Multi-techniques for Ethanol Production from Coal

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

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

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

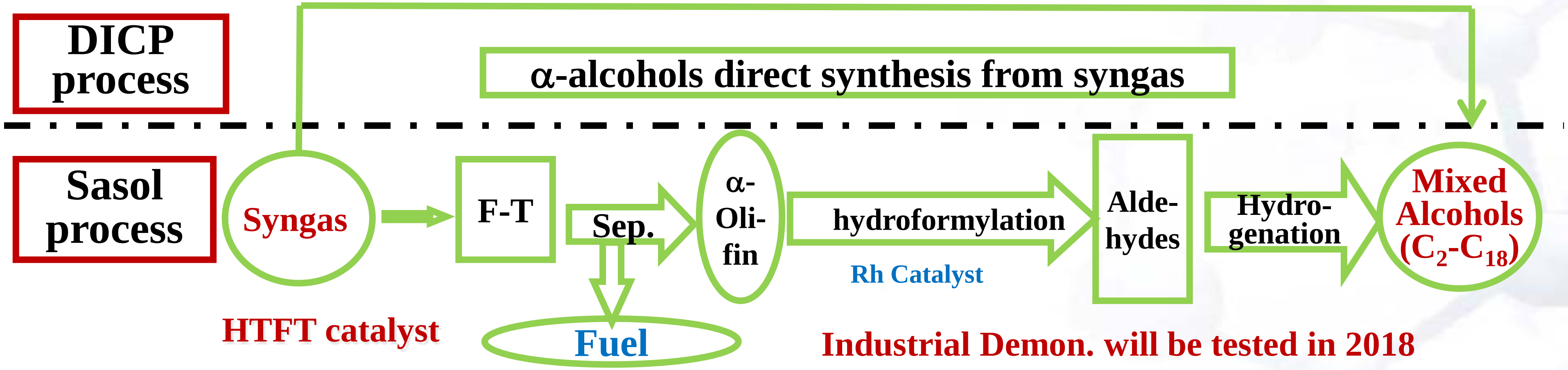
Pilot plant test for hetero-oxo-synthesis of methanol and syngas and its hydrogenation to ethanol

Syngas to Fuel, Wax and Mixed α-alcohols

3kt/a Demon test have done using a Co/SiO_2 catalyst and a fixed bed reactor in 2007

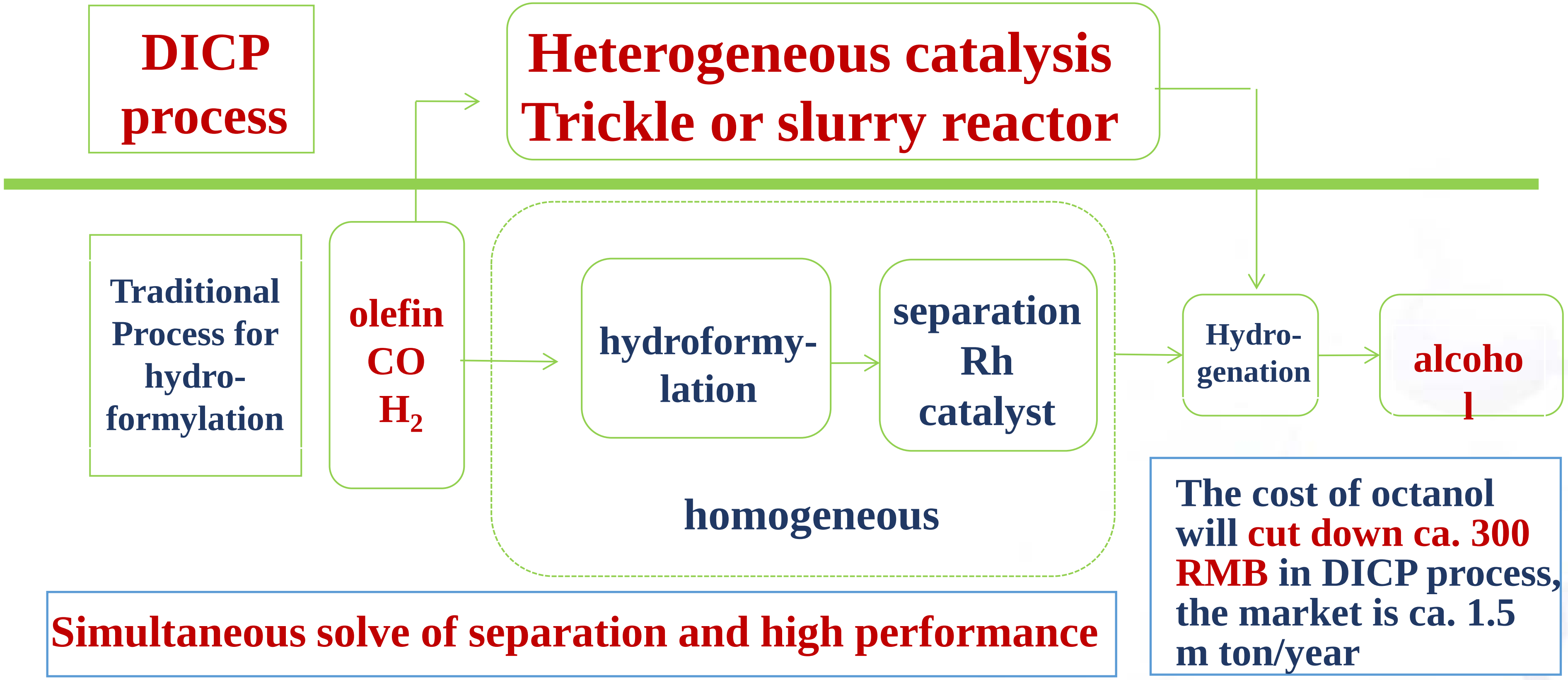
200kt/a 3 industrial facilities are being built in China using Co/SiO_2 catalyst and fixed-bed reactor

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



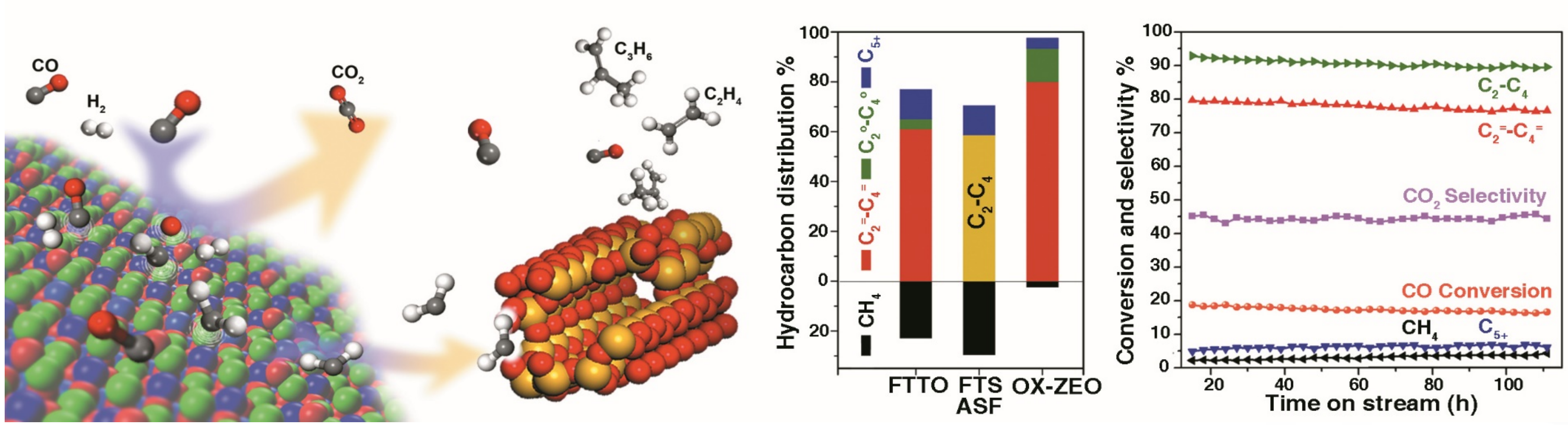
Industrial Demon. will be tested in 2018

Heterogeneous Hydroformylation of Olefins to High Alcohols



- 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.

Converting Syngas Directly to Light Olefins



- 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.

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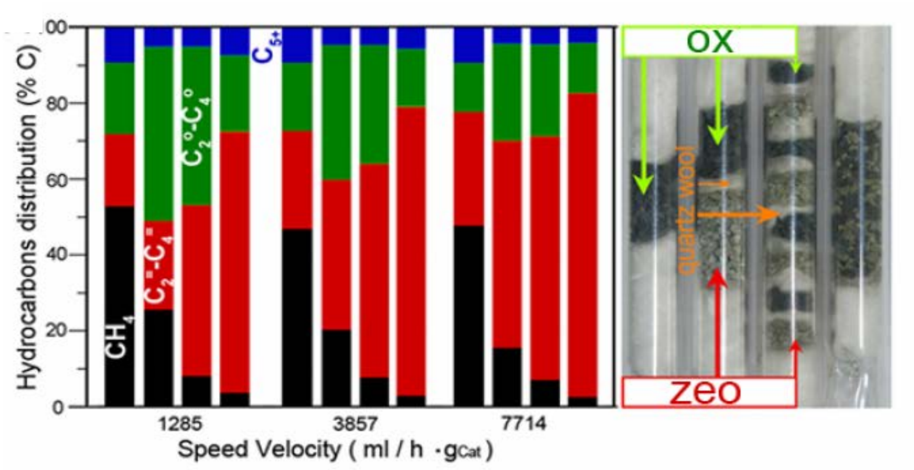
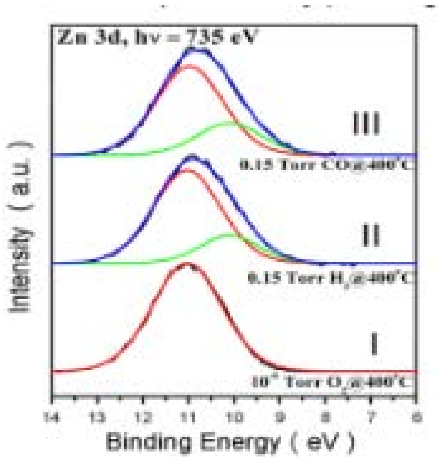
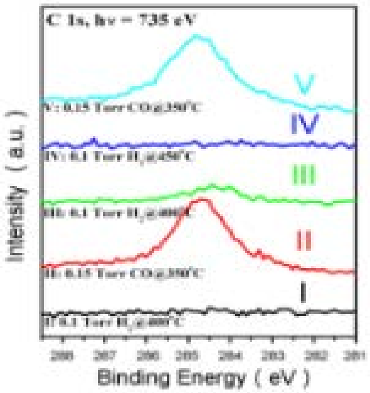
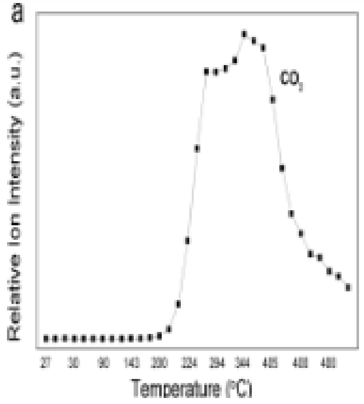
*Jiao, Li, Pan, Bao et al., **Science** 351(2016)1065.*
***Perspective,** De Jong, **Science** 351 (2016) 1030.*

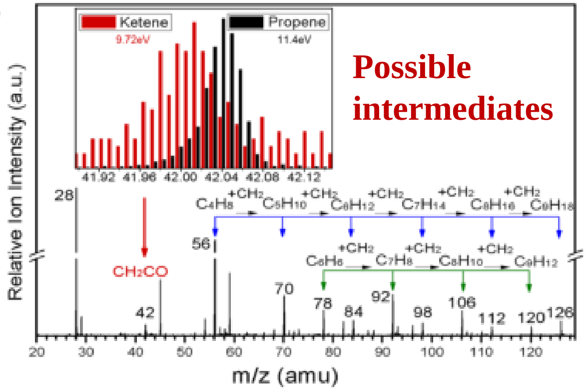
Reaction Mechanism





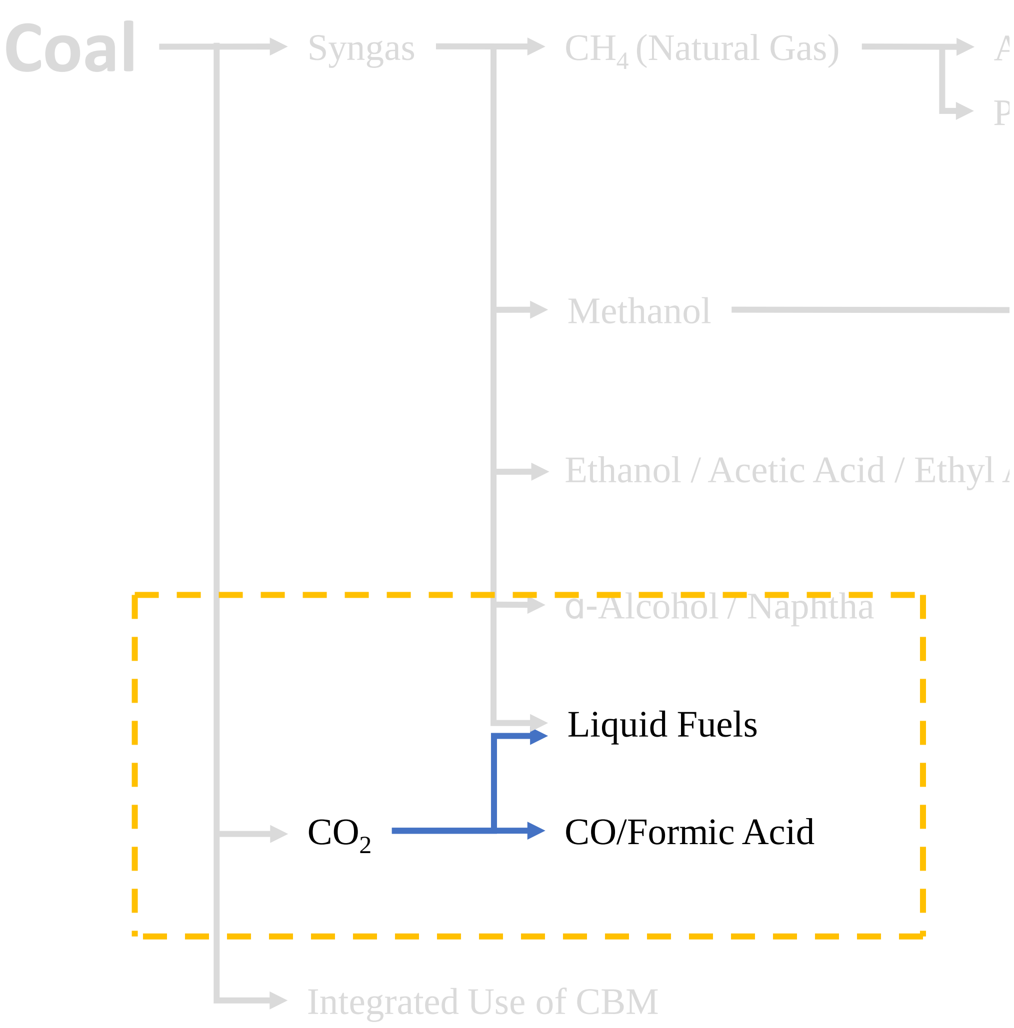






■ The role of oxides and zeolites, activation of CO, and possible reaction intermediate were studied by in situ-XPS, synchrotron-based vacuum ultraviolet photoionization mass spectrometry (SVUV-PIMS), etc.

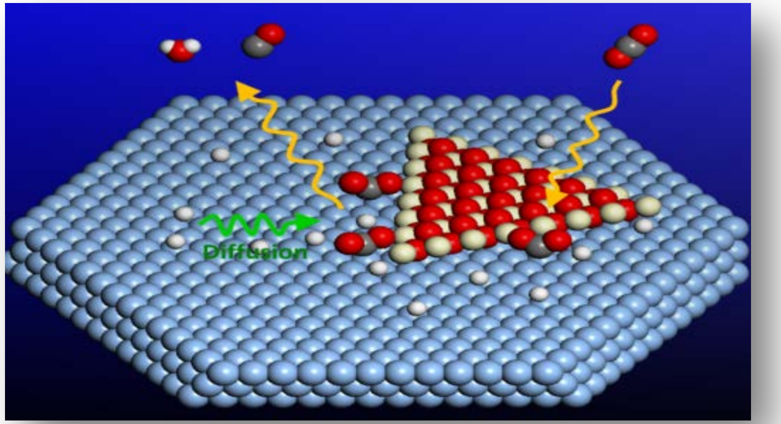
DICP Major Activities in Clean Coal Researches



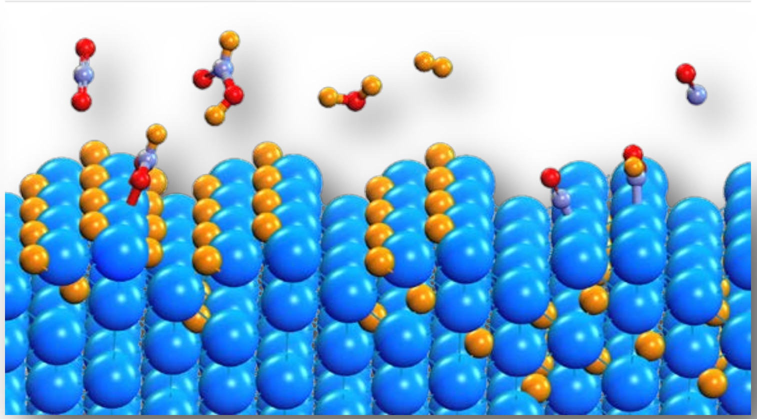
■ CO_2 conversion

- ➢ CO_2 Electroreduction to methanol and formic acid
- ➢ Direct converting CO_2 to gasoline

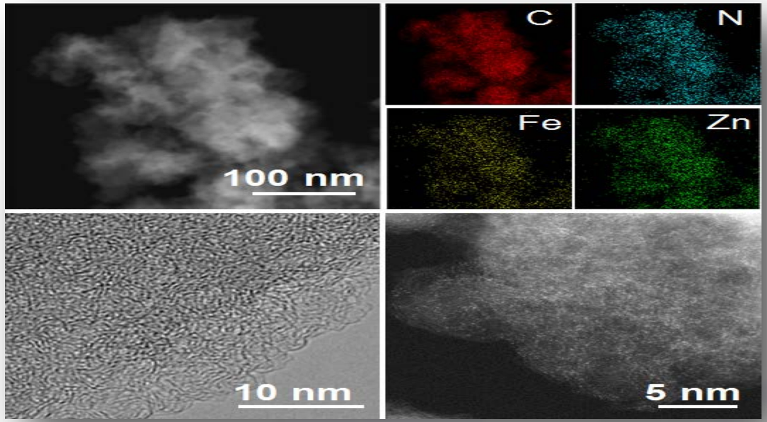
CO_2 Electroreduction to Formic Acid and CO



Metal-CeO_2 interface confinement



Active phase of Pd nanoparticles

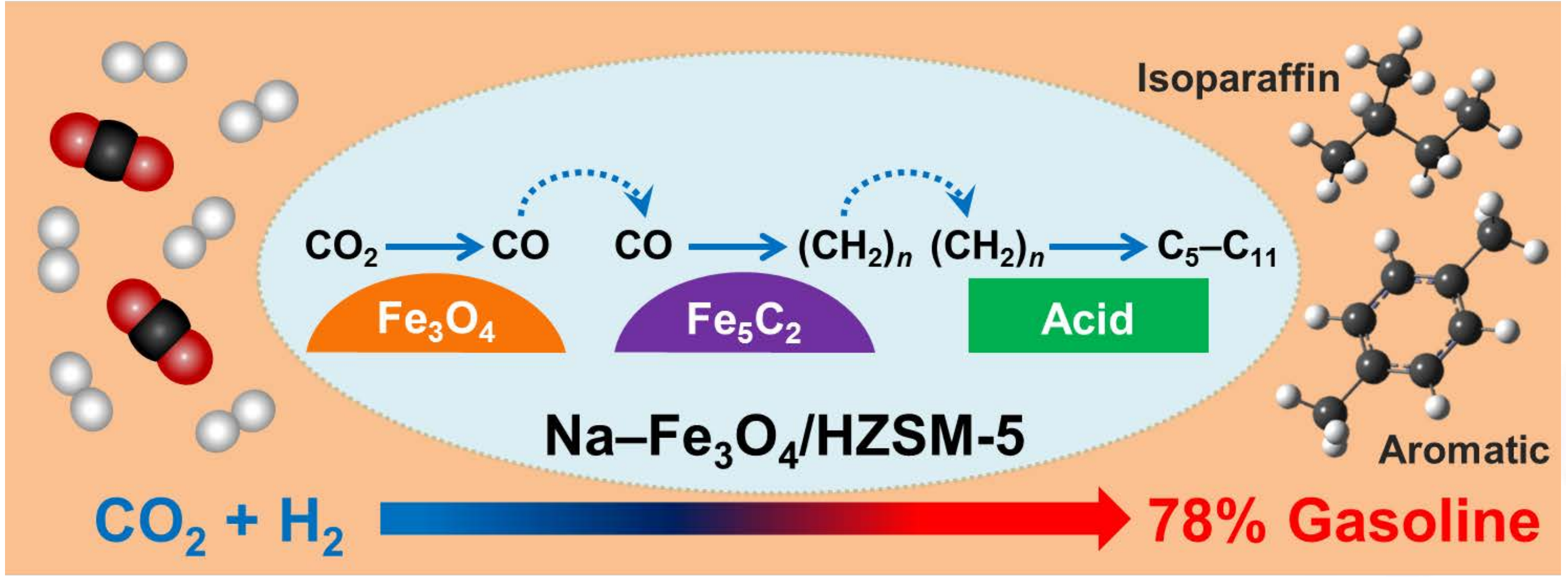


Transitional Metal-N-C electrocatalyst

- **Liquid Fuels and chemicals production from CO_2 and H_2O with electricity from renewable energy or abundant nuclear energy**
- **Simplified process, without H_2, reaction temp: r.t. to 800 ^oC**
- **Electricity storage and carbon recycling simultaneously**

J. Am. Chem. Soc., 2015, 137, 4288; ***Nano Energy***, 2016, 27, 35; ***Nano Research***, 2017, 10, 2181;
J. Am. Chem. Soc., 2017, 139, 5652; ***Nano Energy***, 2017, 38, 281; ***Chemical Science***, 2017, 8, 2569.

Direct Converting CO_2 to Gasoline



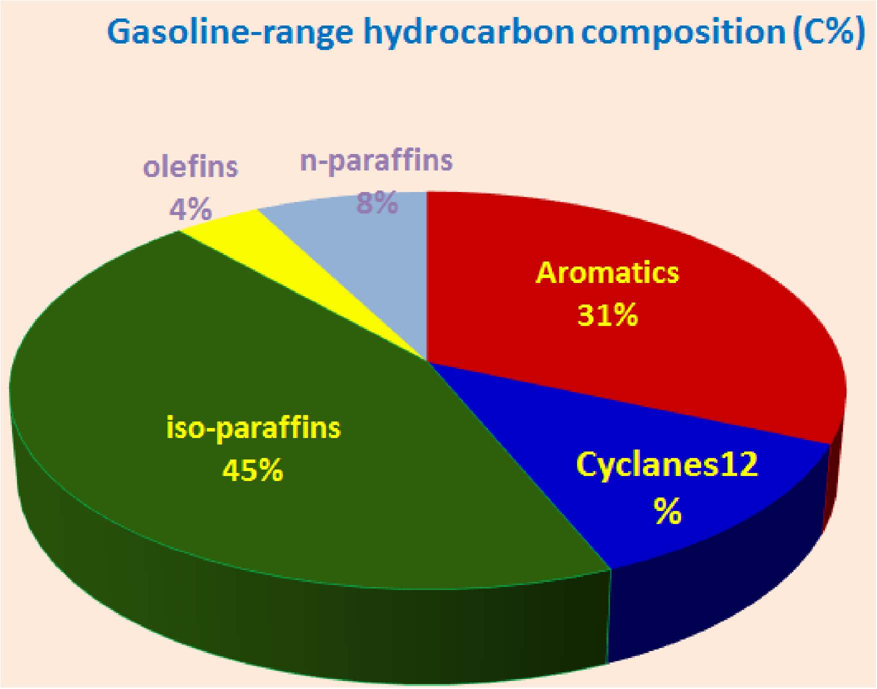
Direct hydrogenation of CO_2 into liquid fuels can mitigate CO_2 emissions and reduce the rapid depletion of fossil fuels. Here we show a multifunctional catalyst that converts CO_2 to gasoline with high selectivity due to synergistic catalysis of active sites.

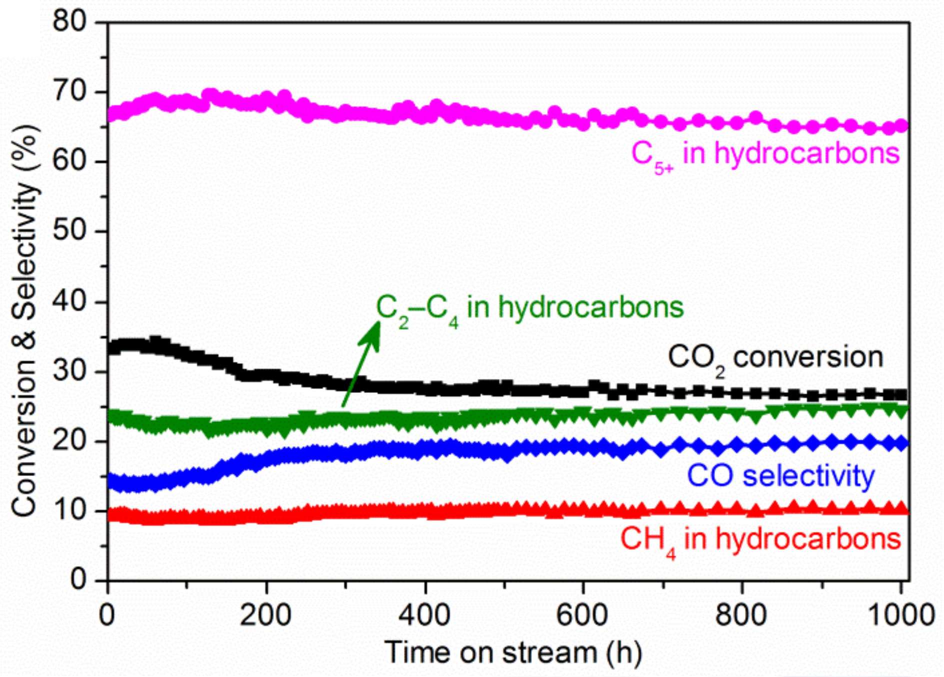
"This work can be considered as a breakthrough in CO_2 catalysis" (referee)

J. Wei, Q. Ge,* R. Yao, Z. Wen, C. Fang, L. Guo, H. Xu, J. Sun*
Directly Converting CO_2 into a Gasoline Fuel. ***Nat. Commun.*** 2017, 8, 15174
Selected as a ***Research Highlight*** *in* ***Nature*** 2017, 545, 7653

DICP

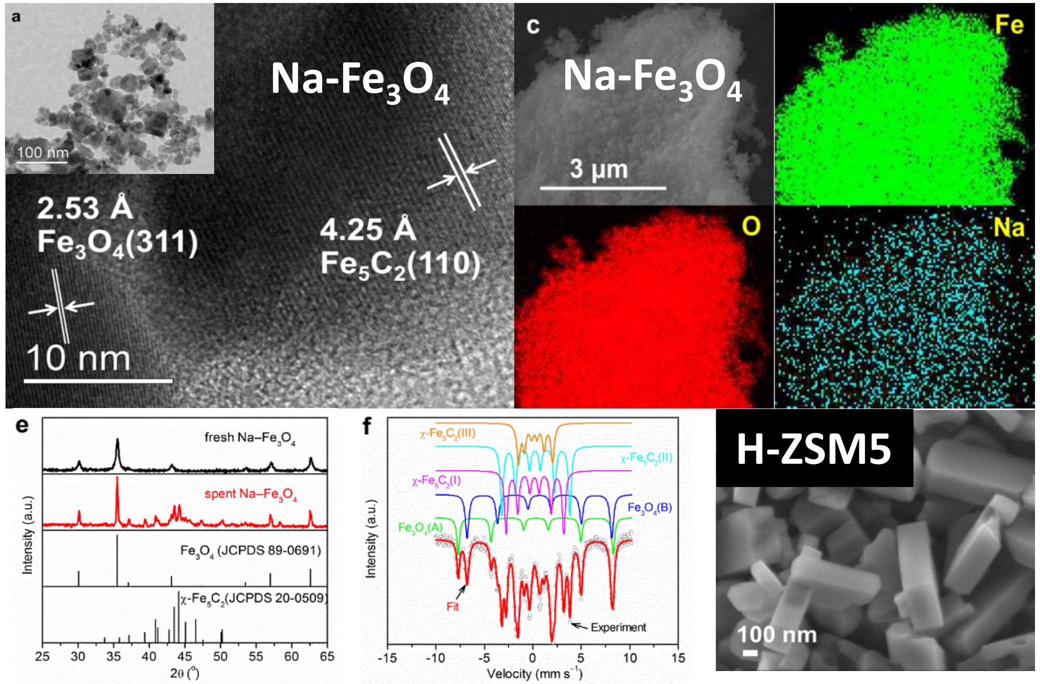
Direct Converting CO_2 to Gasoline





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

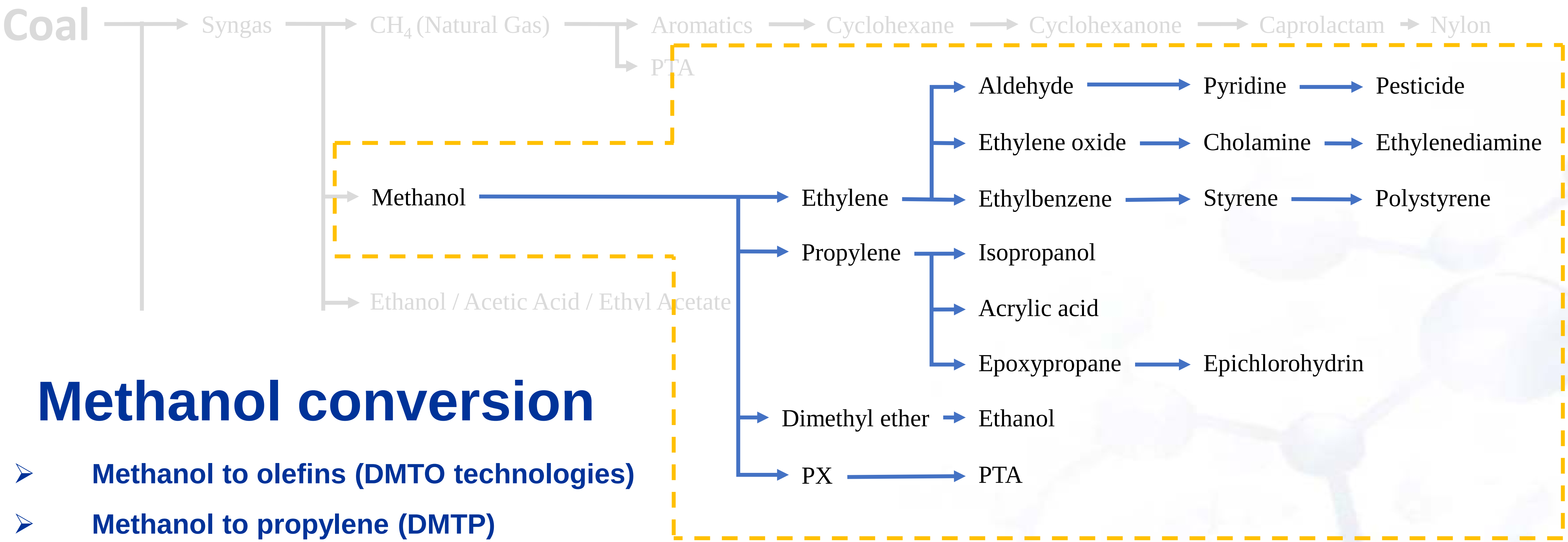
Direct Converting CO_2 to Gasoline



Catalyst	T /°C	P /MPa	X_{CO2} /%	CO /%	Hydrocarbon /%		
					CH_4	C_{2-4}	C_{5+}
FeZnZr/HZSM-5	360	5	19	57	2	46	52
FeZnZr@HZSM-5	340	5	14	41	2	64	34
Fe-Ce/KY	300	1	20	35	9	41	49
Fe/RbY	300	1	17	32	9	36	54
Our work	320	3	22	20	4	16	80
FeCuNa/HZSM-5	250	2	12	20	29	42	29
CuZnAl/HB	300	1	27	53	2	93	5
FeZnZr/HY	340	5	22	50	2	84	14
CuZnZr-Al/Pdβ	260	2	25	47	1	77	21

- Confirmation of active sites: Na-Fe_3O_4/Fe_5C_2/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**

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

DMTO-II Demo
$C_2^{=}+C_3^{=}$:~86%
2010.06

Commercialization
Shenhua: 600 KT/a
Yanchang: 600 KT/a

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From early 1980s

“75”,“85”, “973”
National Project

DICP

2004.08 -
2006.08

DICP
Xinxing Co
LPEC

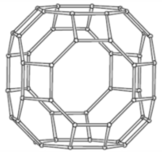
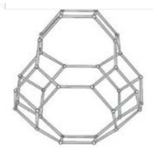
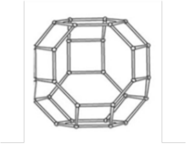
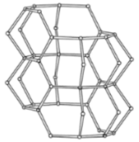
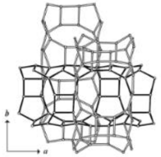
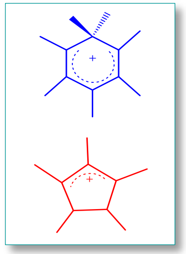
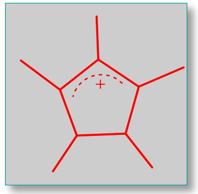
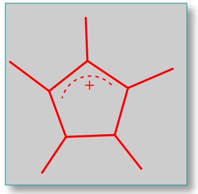
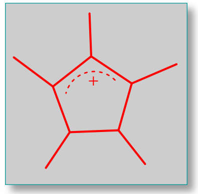
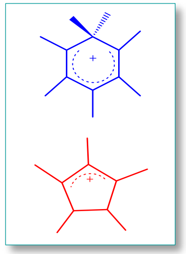
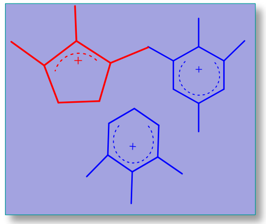
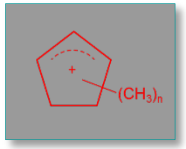
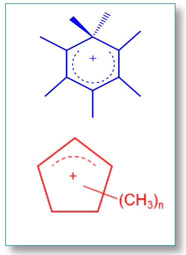
2006.08 -

National Development and Reforming Committee of China (NDRC)

DME/Methanol to olefins = DMTO (DICP’s MTO)

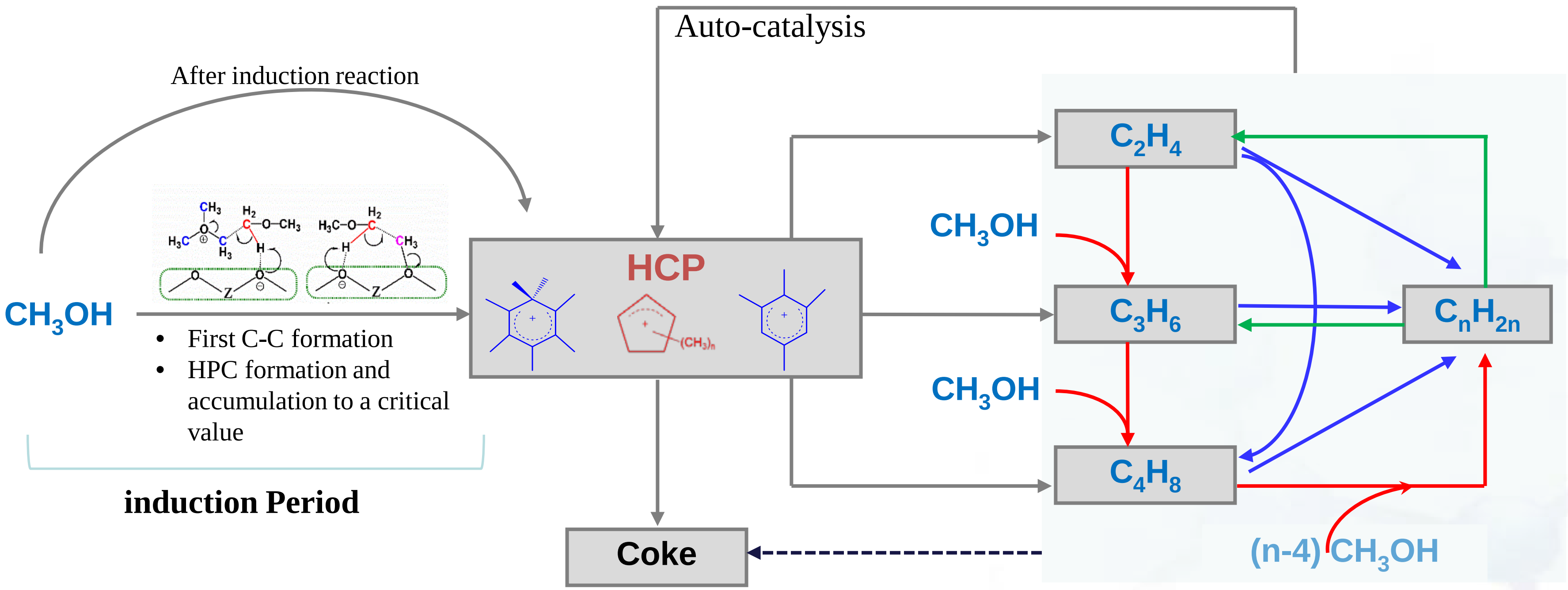
Progress on Reaction Mechanism

Carbenium ions in different cages and channels have been observed

	8-ring with cage				10-ring channel	12-ring channels
Type	RHO	CHA	AEI	LEV	TON	*BEA
Cages or Channels						
Size (nm^2)	1.14x 1.14	0.67 x 1.00	1.16 x 1.27	0.63 x 0.73	1-dimensional	3-dimensional
SAPOs	DNL-6 	SAPO-34 	SAPO-18 	SAPO-35 		
Si-Al Zeolites		H-SSZ-13 		H-RUB-50 	H-ZSM-22 	Beta 
$AlPO_4$			AlPO-18			

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

DICP

Scale-up of DMTO Reactor

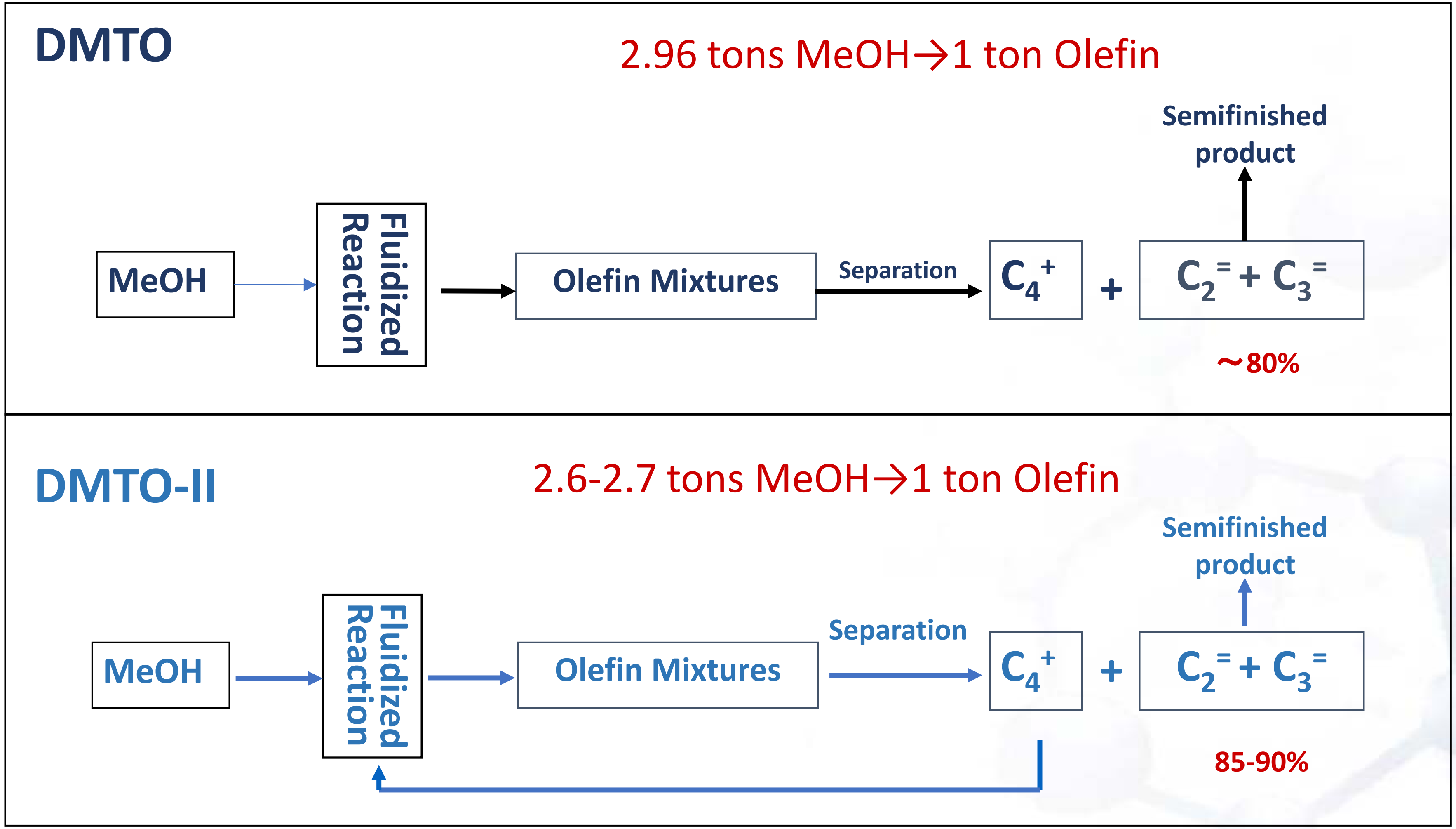
	Micro Scale	Pilot Scale	Demo Scale	Commercial Scale
MeOH Feed	~1.2 kg/d	~120 kg/d	50,000 kg/d	5500,000 kg/d
Cat Inventory	0.01 kg	1 kg	300 kg	45,000 kg
Ugas	~2-- 25 cm/s	~5-- 25 cm/s	~ 1-2 m/s	~1-2 m/s
Fluidization	Bubbling bed	Bubbling bed	Turbulent bed	Turbulent bed

DMTO Demonstration Results: 72 Hours Calibration

Feedstock	CH_3OH
Scale	50t/d
Reactor type	Fluid bed
Single pass conversion %	>99%
Yield of ethylene and propylene, wt%	33.73
Selectivity of ethylene and propylene, wt%	>79.1
Feedstock consumption for each ton of ethylene and propylene, t/t	2.96
Catalyst	D803C-II-01

New Generation of DMTO Technology (DMTO-II)

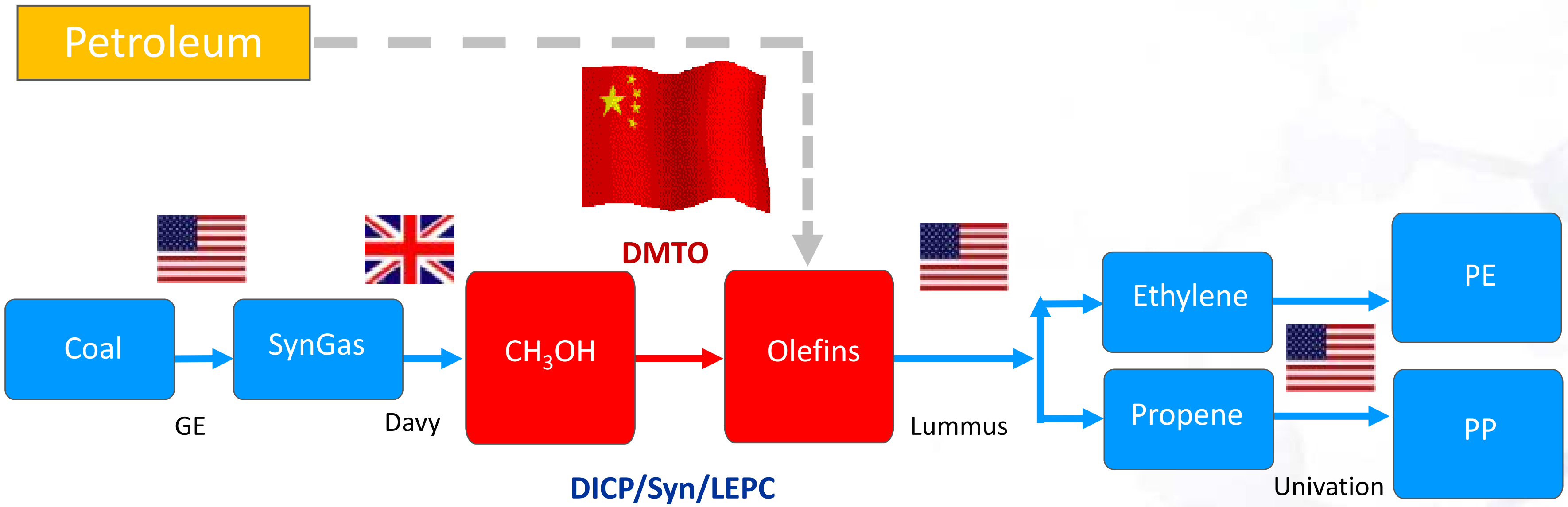
Technical Principle



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

Polymerization units

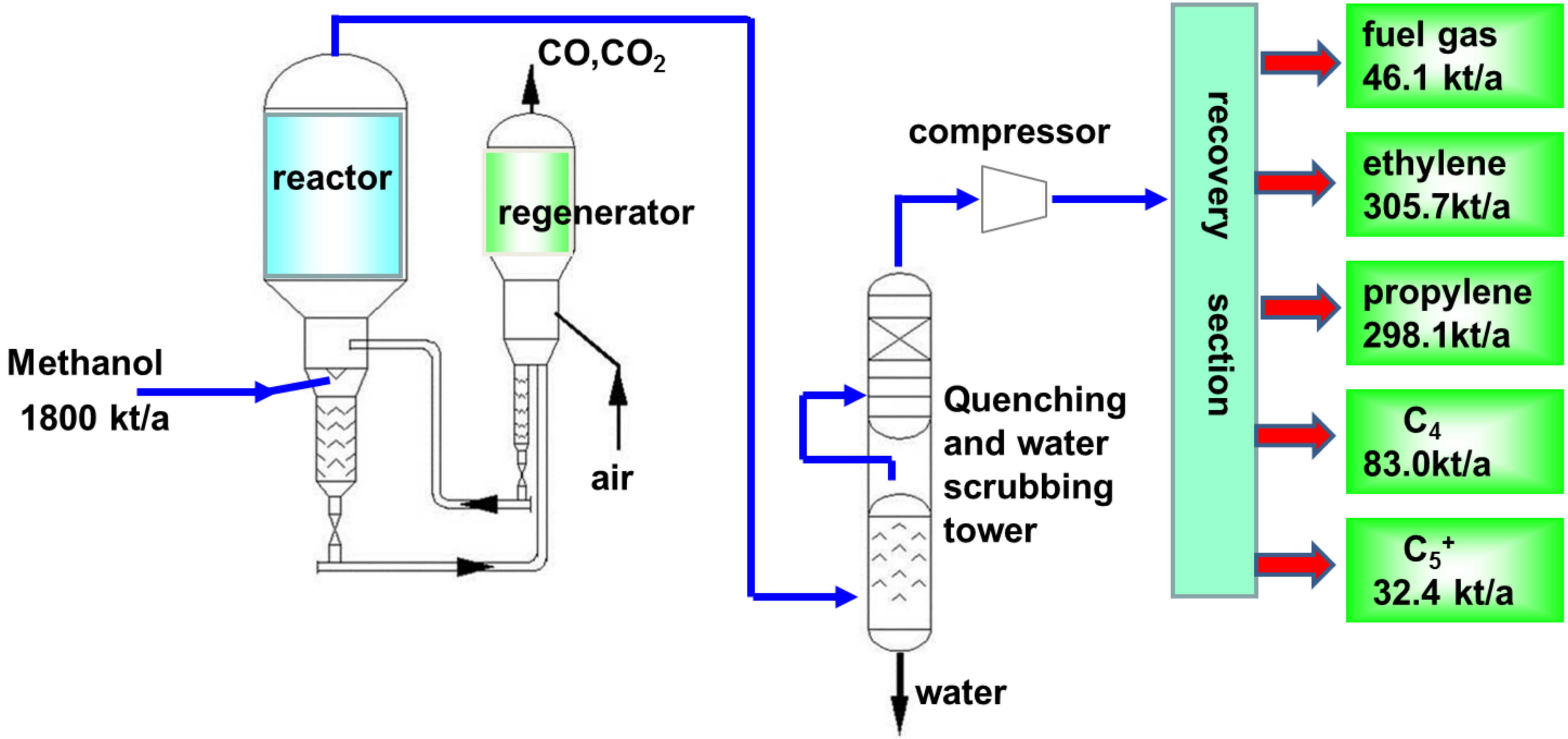
DMTO unit

Methanol synthesis unit

Coal supply

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%

DMTO Plants in China

1 t ethylene ~ 10 t crude oil
2016,
Domestic Production:
Ethylene 17.8 MMt (178 MMt crude oil)
Crude oil 200 MMt
Imported:
Crude oil 378 MMt

On Operation

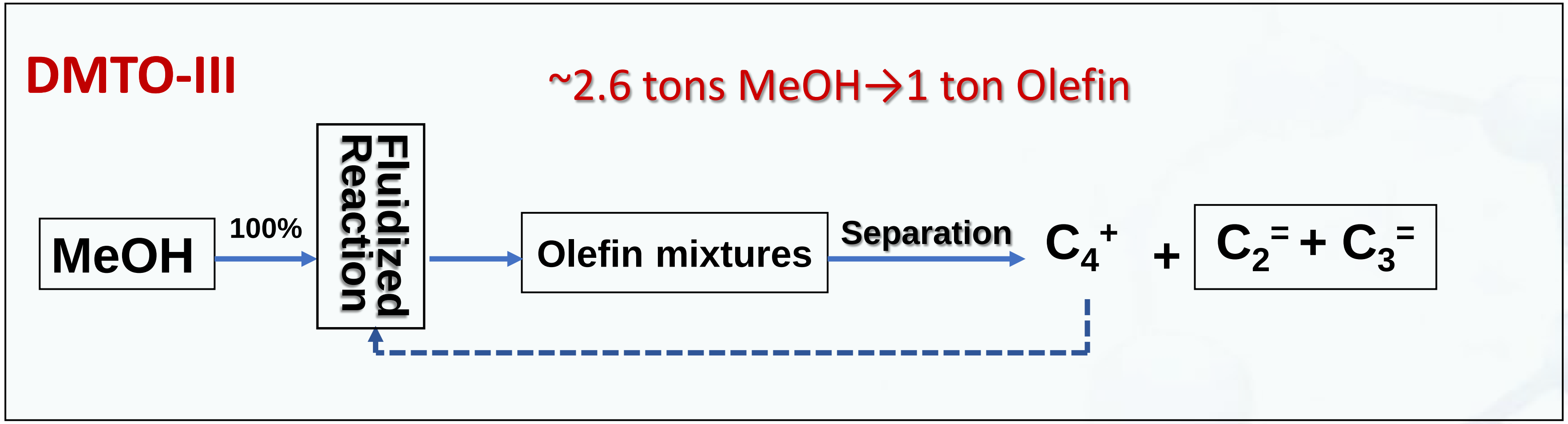
Licensee

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

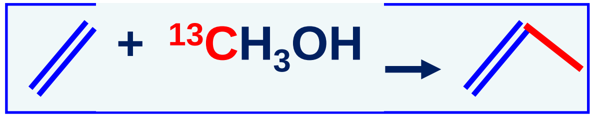
DMTO-III Technology

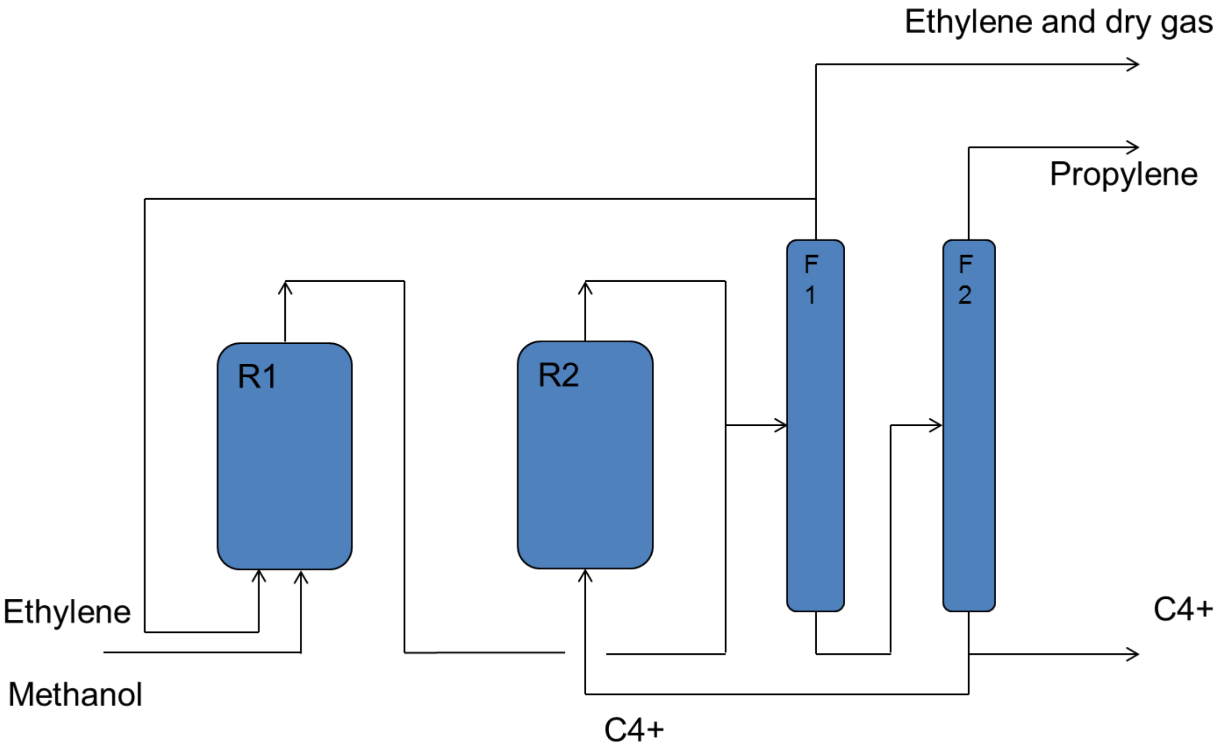
Technical features

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



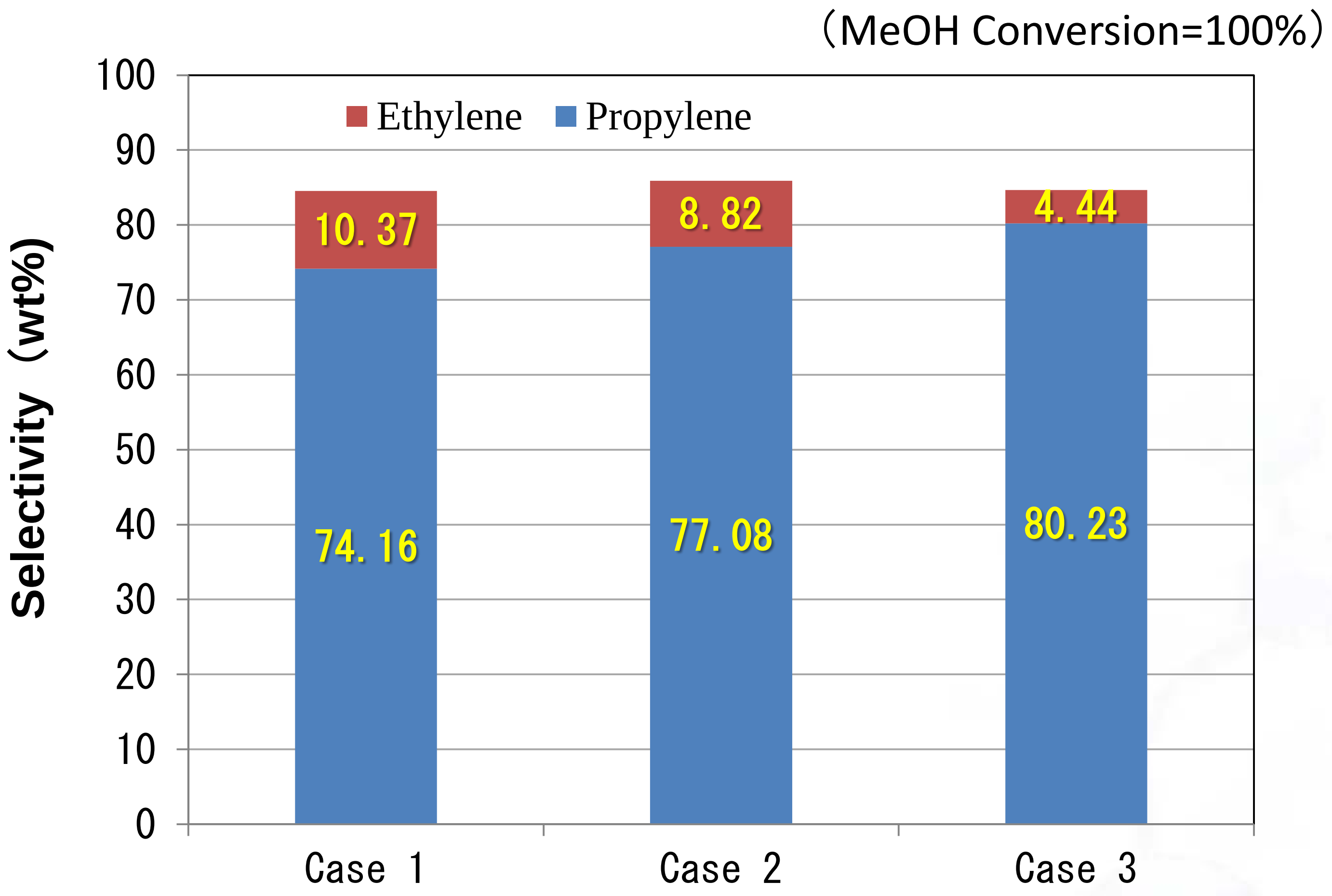
DMTP technology





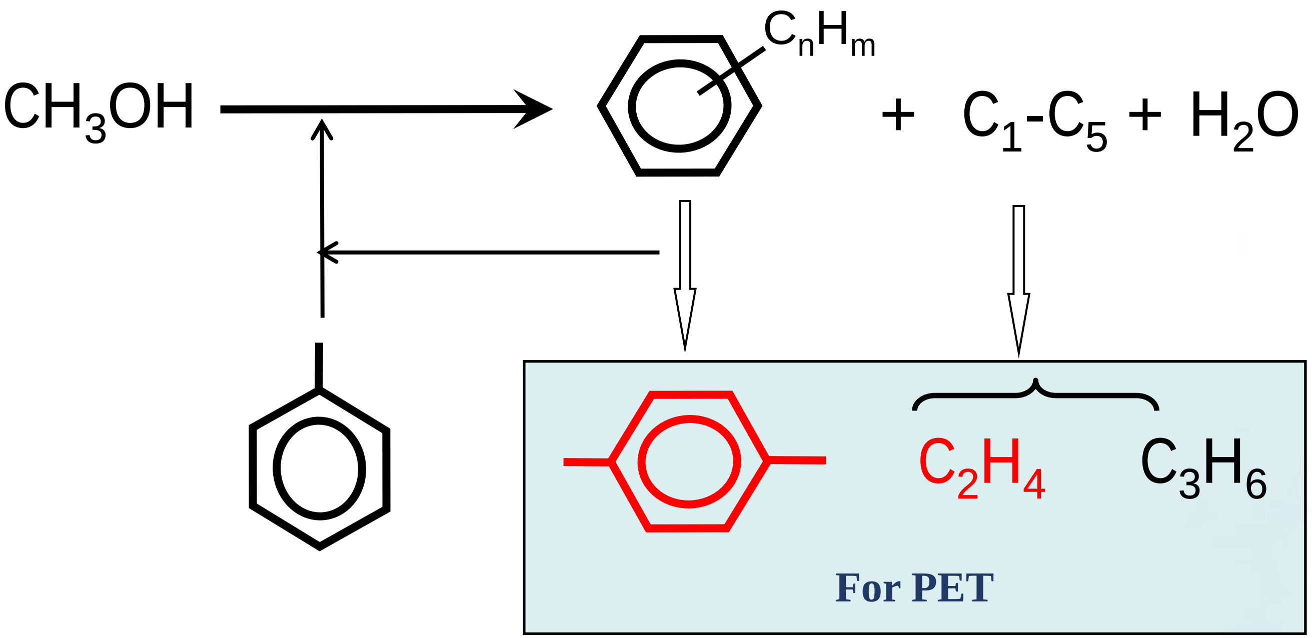
- **Multi-functional catalyst**
  - methanol conversion;
  - ethylene conversion;
  - and C_{4+} cracking
- **High efficient fluidized bed reactors**
  - methanol and ethylene conversion in one reactor
  - adjustable propylene yield

Simulation results based on pilot tests (1t/d)



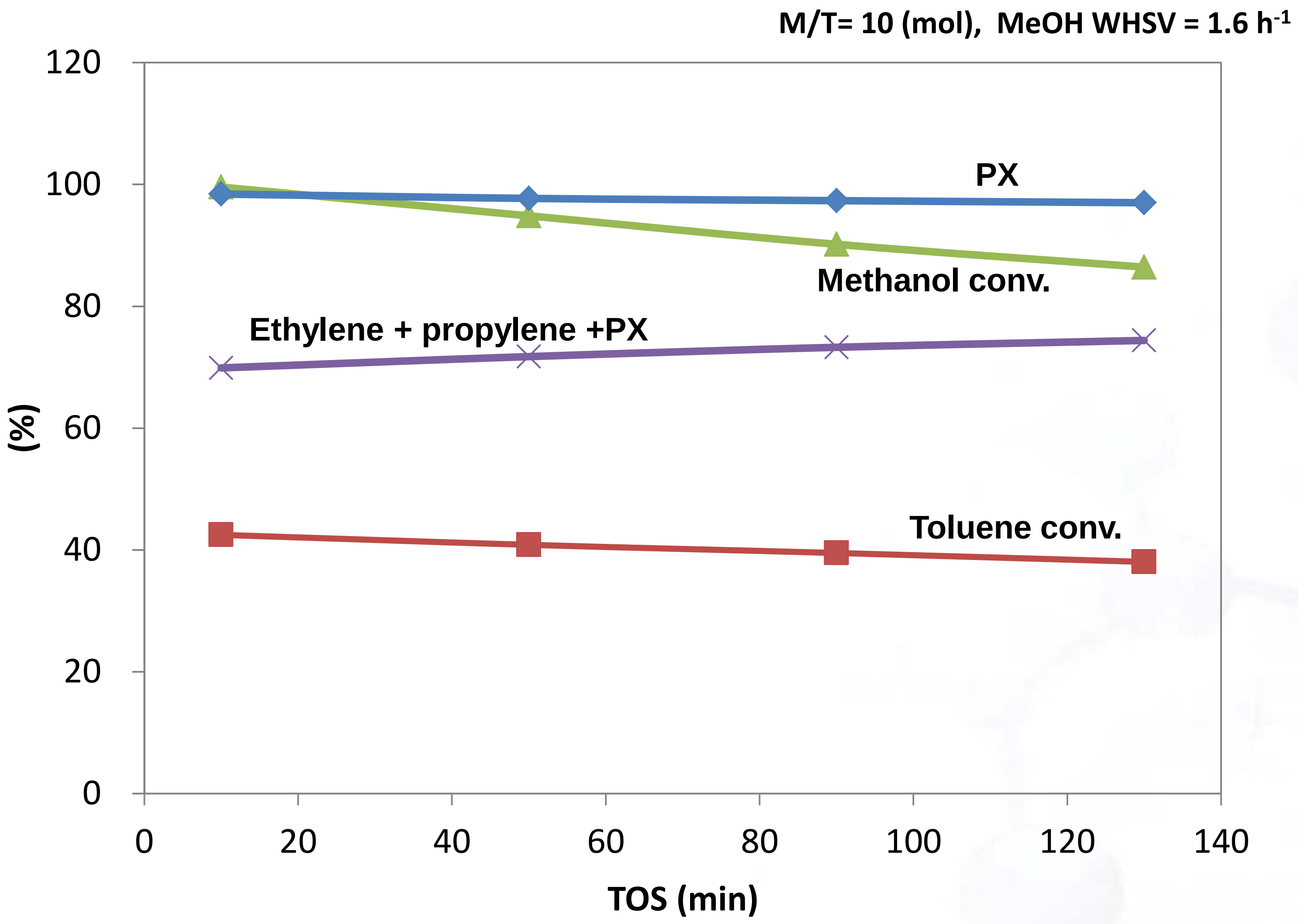
DICP

Co-production of p-X and Olefin by Methanol and Toluene

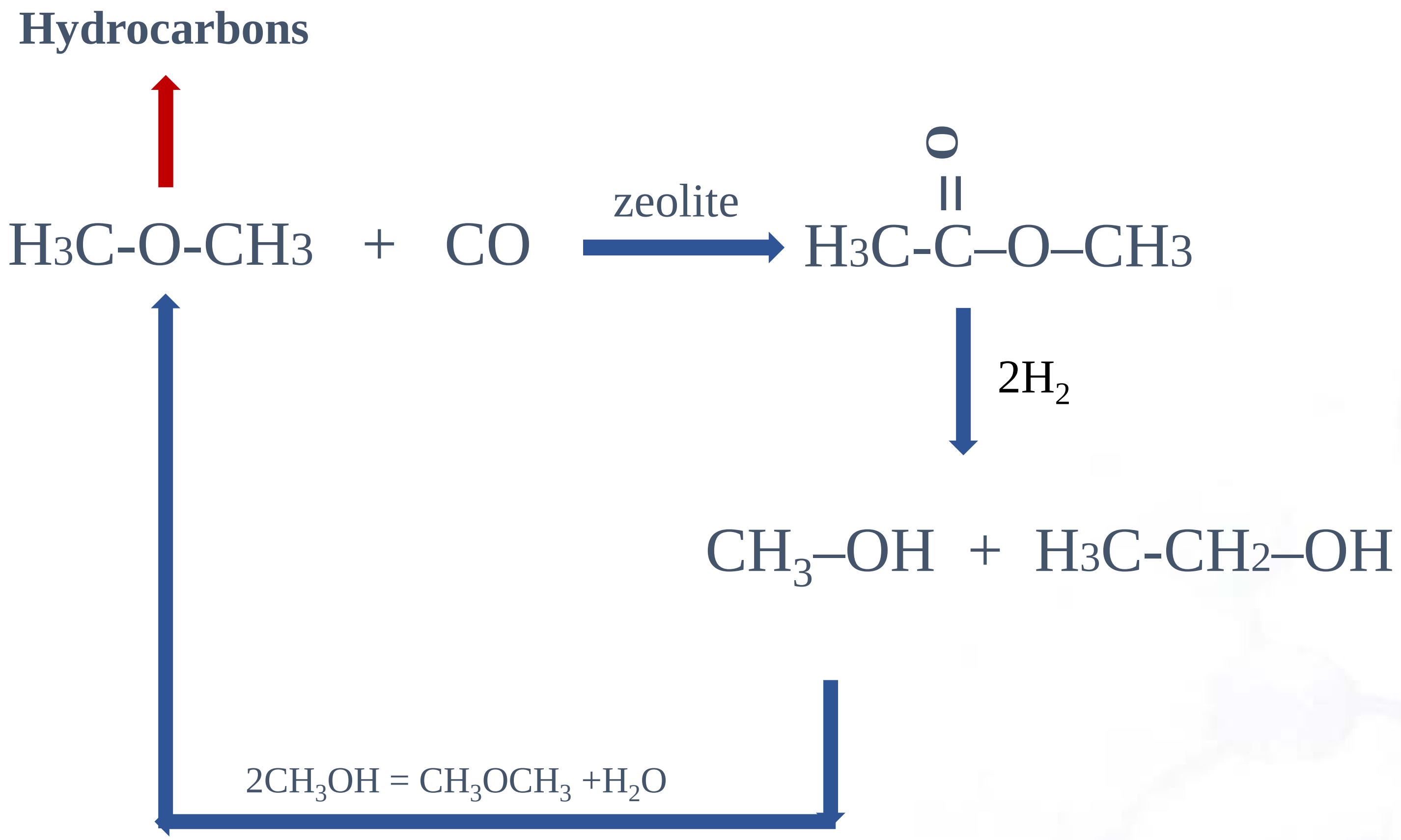


- *Why co-production?*
- *Fluidized bed reactors*

Typical Results



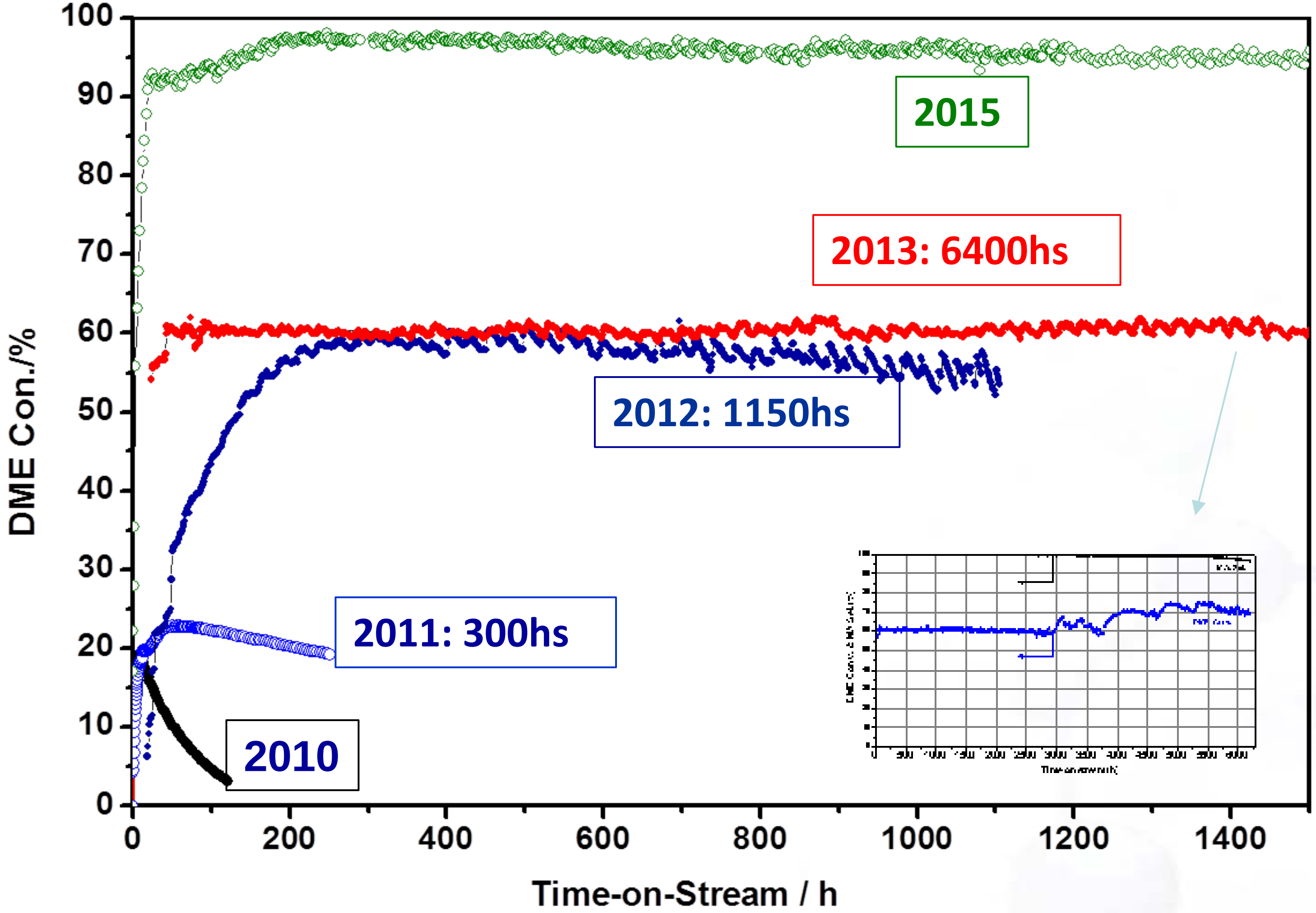
Ethanol from DME Carbonation and Hydrogenation



Total:	$CH_3OCH_3 + 2CO + 4H_2 = 2CH_3CH_2OH + H_2O$

Total from syngas :	$2CO + 4H_2 = CH_3CH_2OH + H_2O$

Improvement of Catalyst Life

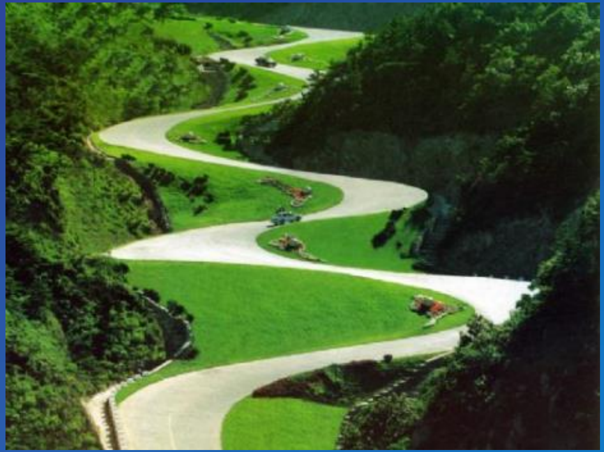


Ethanol from DME Carbonation and Hydrogenation

- 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.



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Thank you!
Welcome you to Visit DICP