中国煤制烯烃技术进展

Coal-to-Olefin Technology in China

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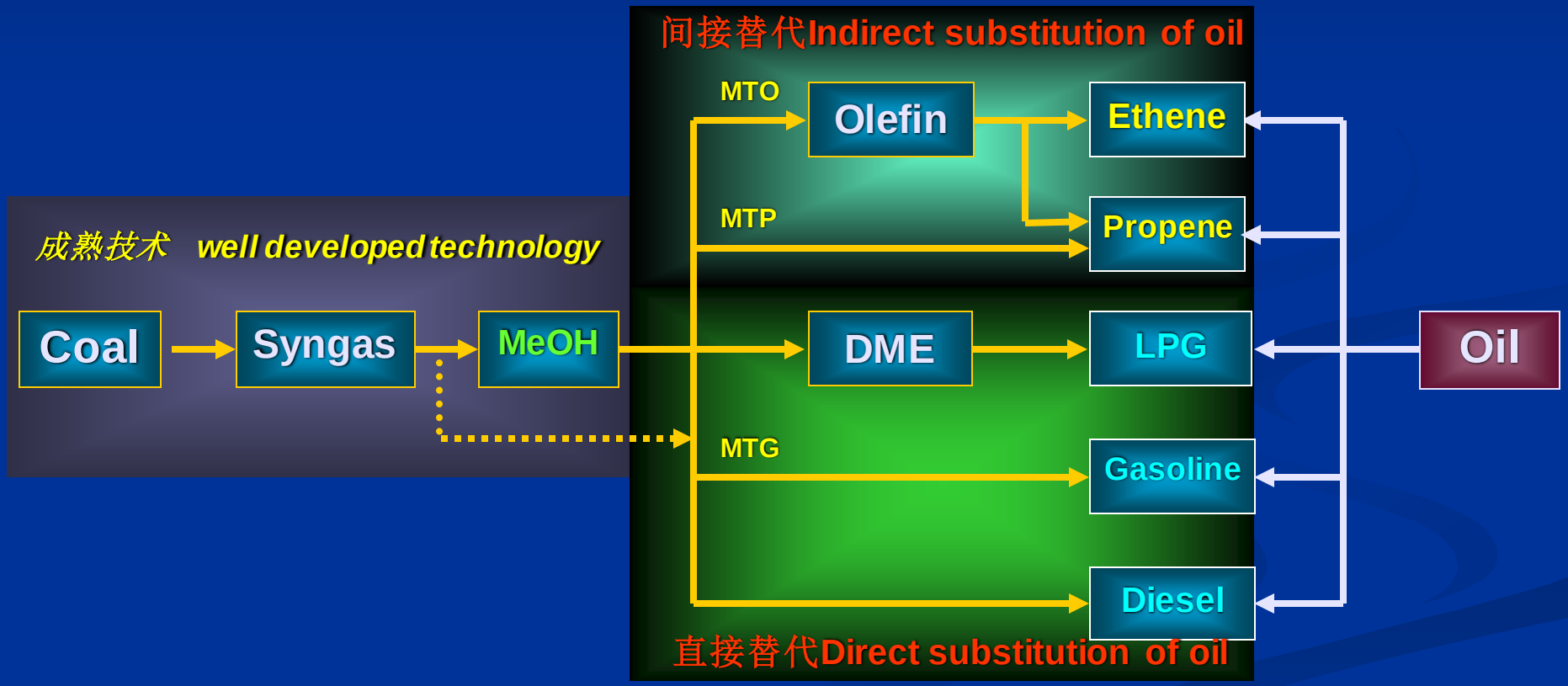
内容 Content

- 背景 Background
- 甲醇制乙烯和丙烯 Methanol to Ethylene and Propylene
  - DMTO技术 DMTO technology
  - 技术经济 Economics
  - 工业化 Commercialization
- 甲醇制丙烯 Methanol to Propylene
  - FMTP技术 FMTP technology

甲醇：联系煤化工与石油化工的桥梁
Methanol: an important product linking petrochemicals to coal chemical industry



烯烃生产技术路线和MTO
Technical Routes for Olefin Production & MTO

Naphtha Feedstock

China	US	Japan
67%	39%	93%

石脑油 Naphtha

>800°C, H_2O, $C_2^= + C_3^=$
Yield～45%

乙烷 Ethane

>800°C， $+H_2O$

乙烯
丙烯
C_2H_4
C_3H_6

煤、天然气 Coal, Natural Gas → 合成气 Syngas → 甲醇 Methanol → DMTO (MTO)

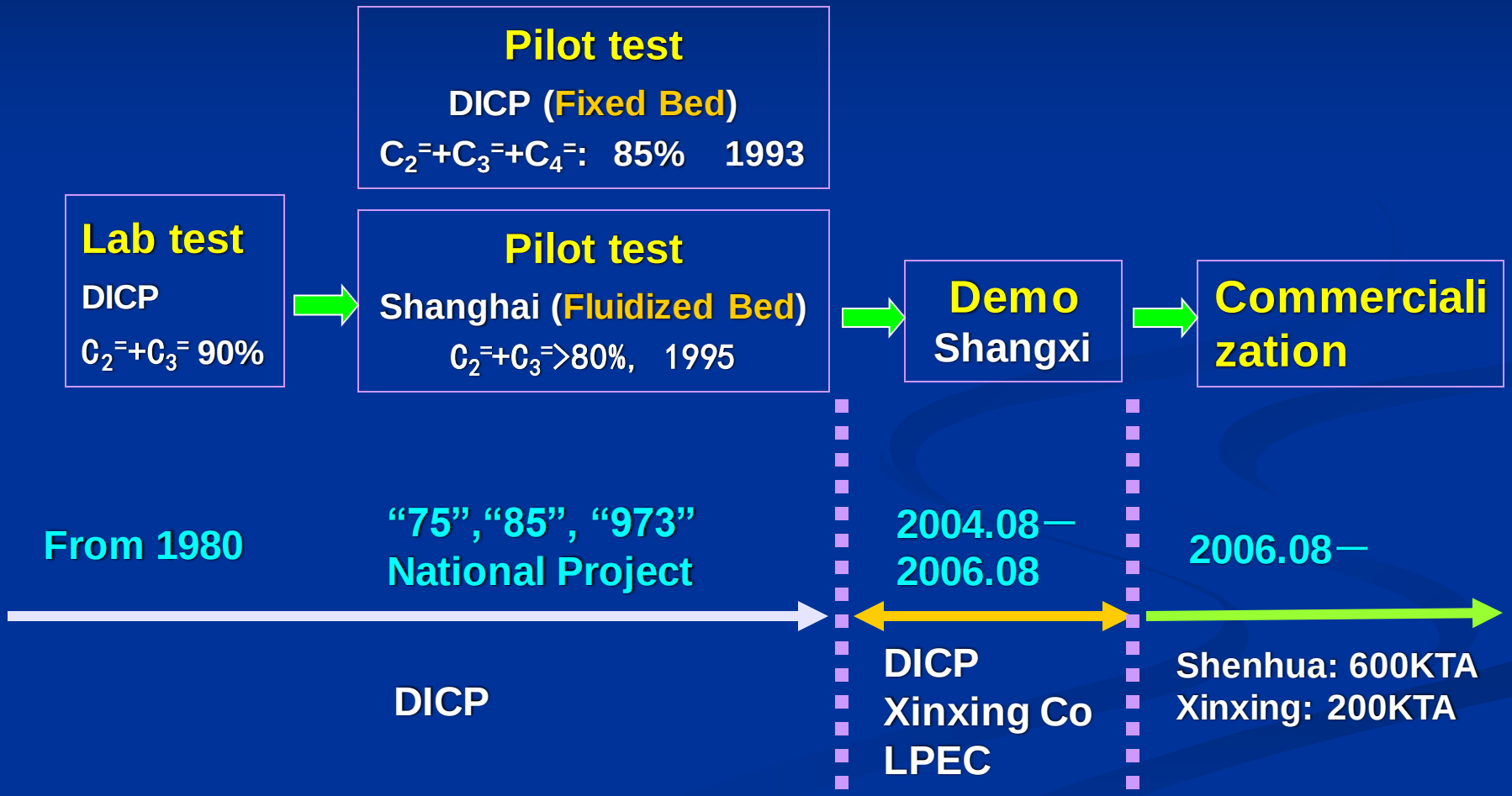
Well developed technology

MTO反应特点
Characteristic of Methanol to Olefin reaction

- 酸性催化特征 Acid catalyzed reaction
- 高转化率：100% High conversion
- 低压反应 Low pressure is favorable to light olefin selectivity
- 强放热 Exothermic reaction
  - 400-500°C，100% conversion
  - ΔH = -22.4～-22.1 KJ/mol methanol
- 快速反应 Fast reaction
  - 100% conversion at 0.04s contact time
- 分子筛催化的形状选择性效应：高选择性 Shape selective effect should be applied for high olefin selectivity
  - First generation of catalyst: Modified ZSM-5
  - Small pore SAPO molecular sieve could be good candidate for developing new catalyst

大连化物所DMTO研究历程

DMTO R&D in DICP



DMTO技术 DMTO technology

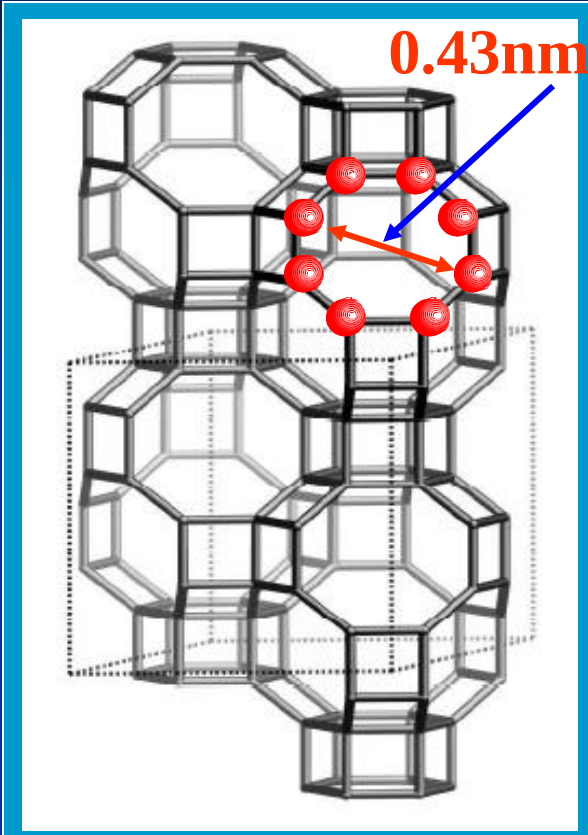
SAPO分子筛的研究 ***Research on Small pore SAPO molecular sieves***

- 早期专利 UCC patent in 1982 (USP4440871) on SAPOs
- DICP首次报道了SAPO-34对MTO的优异性能

  DICP first demonstrated good performance of SAPO-34 in MTO reaction
  - *Applied Catalysis，Vol.40, No1-2，p316，1988；Applied Catalysis, vol.64，p31-40, 1990*
- DICP对SAPO分子筛的合成及机理进行了系统深入的研究

  Synthesis and mechanism were well studied on small pore SAPO molecular sieves
  - 集中于SAPO-34 Focused on SAPO-34
  - 其他小孔SAPO分子筛 Other small pore SAPOs were also synthesized and tested

SAPO-34分子筛
SAPO-34 Molecular Sieve

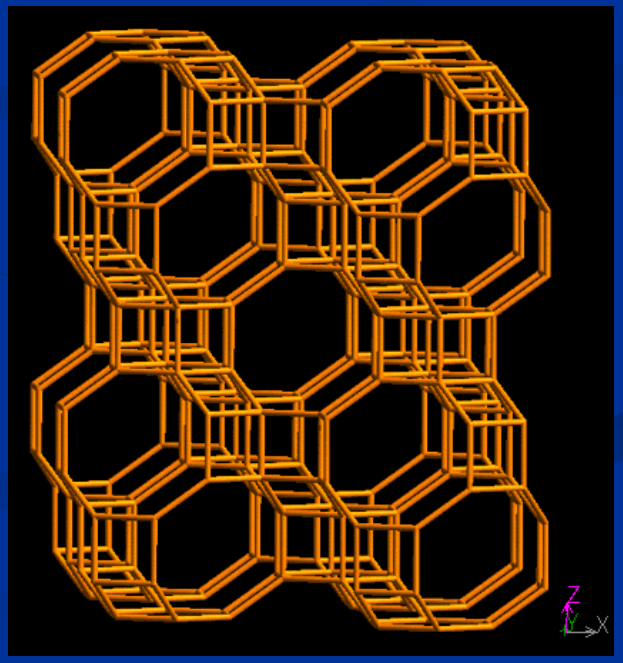


C_2H_4
0.39nm

C_3H_6
0.43nm

C_6H_6
0.58nm

SAPO-34 framework
CHA-type



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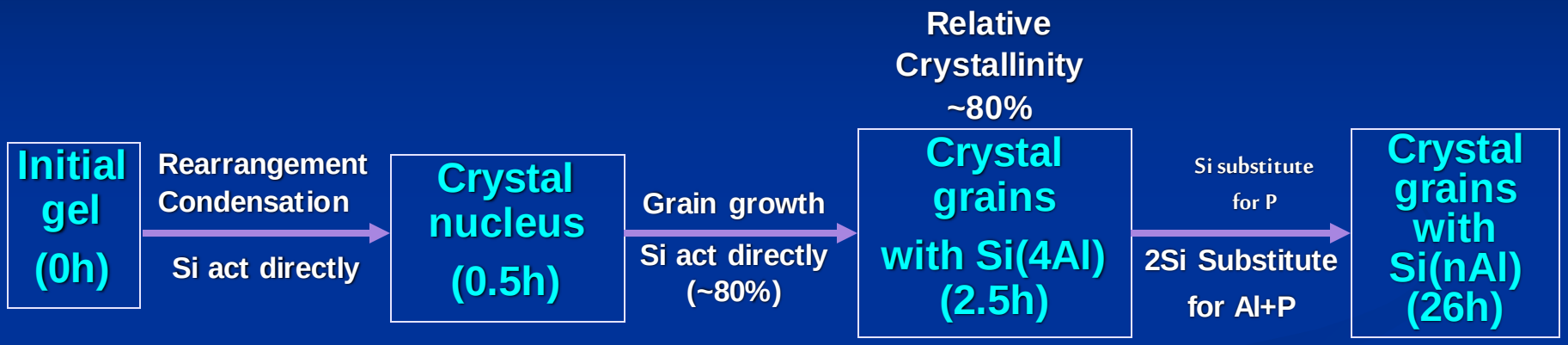
SAPO-34合成方法的创新
New methods for SAPO-34 synthesis

	Template 模板剂	
First patent	tetraethylammonium hydroxide	USA4440871
DICP	triethylamine (TEA), diethylamine (DEA), TEA+DEA	EP1142 833A1
Other Methods	dipropylamine, isopropylamine, piperidine, Morpholine	

SAPO-34的晶化机理
Crystallization mechanism of SAPO-34

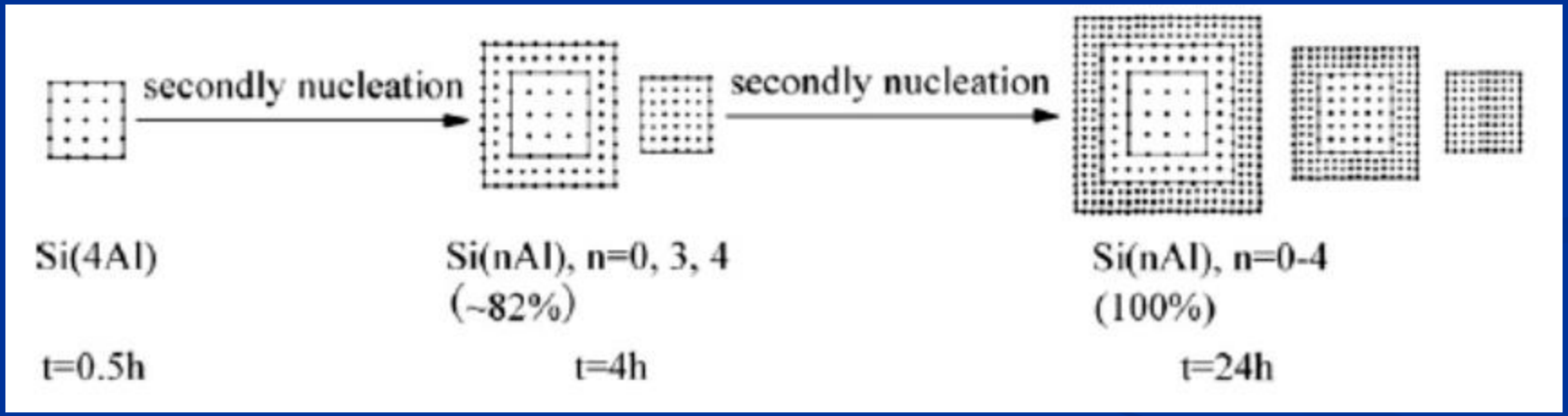


- *MICROPOROUS AND MESOPOROUS MATERIALS*, 115 (3): 332-337 NOV 1 2008, Synthesis of SAPO-34 with only Si(4Al) species: effect of Si contents on Si incorporation mechanism and Si coordination environment of SAPO-34
- PCT/CN2007/002375
- PCT/CN2007/002376, PCT/CN2007/002332, PCT/CN2007/002333

SAPO-34的晶化机理
Crystallization mechanism of SAPO-34

晶化过程中Si在晶粒中的非均匀分布模型

Schematic diagram of crystallization process with Si distribution in the crystals



Microporous and Mesoporous Materials, 114 (1-3): 416-423 SEP 1 2008

流化催化剂研制
Development of fluidized catalyst

喷雾干燥系统

Spring Dryer for Fluidized Catalyst Preparation

提升管反应系统

Fluidized Reaction System

(raiser reactor, continuous reaction-regeneration)

Catalyst loading amount: 10kg

密相循环流化床反应系统

Dense Phase Fluidized Reaction System with Catalyst Recycling and product separation

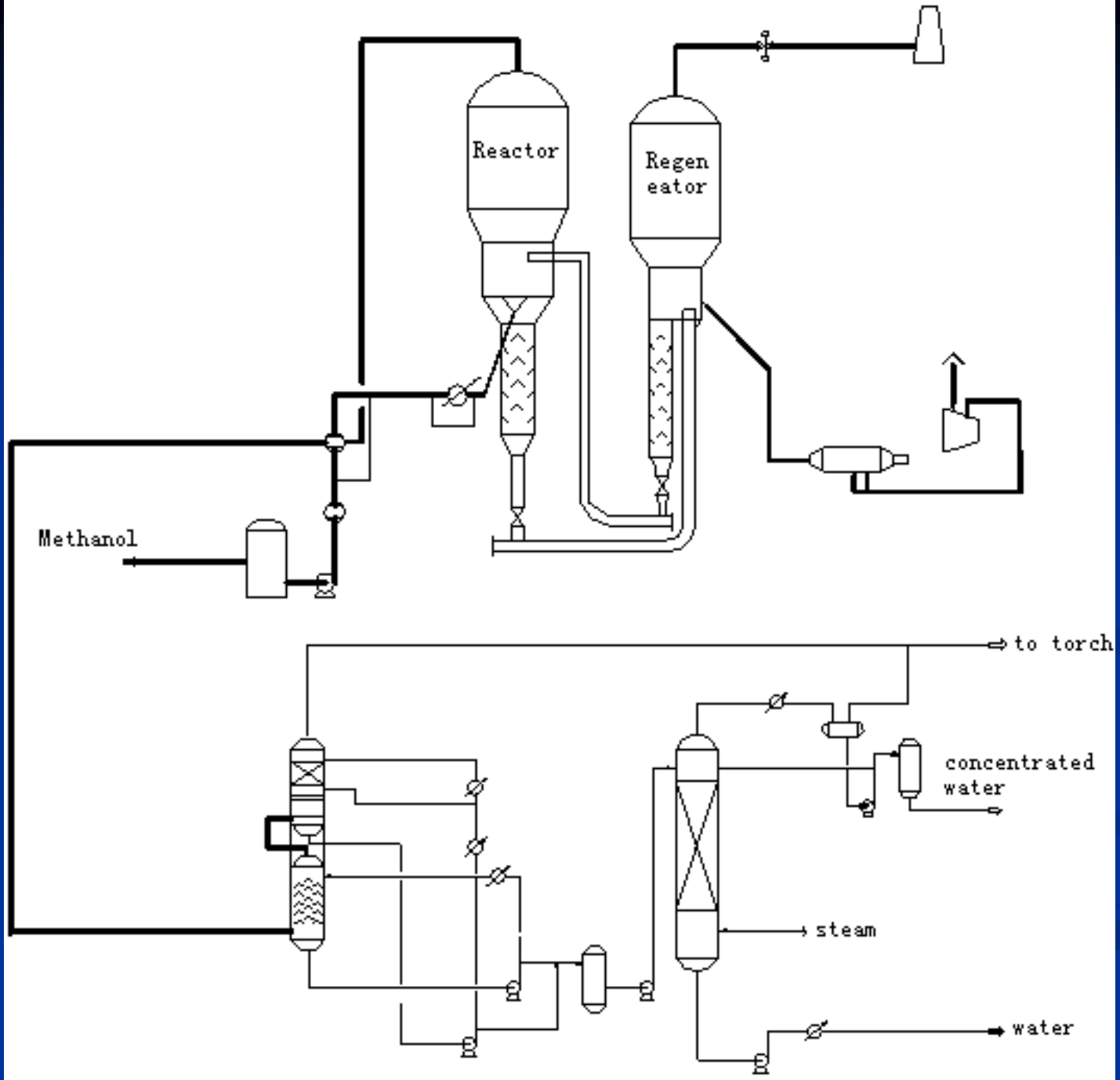
Catalyst loading amount: 20kg

DMTO Demonstration

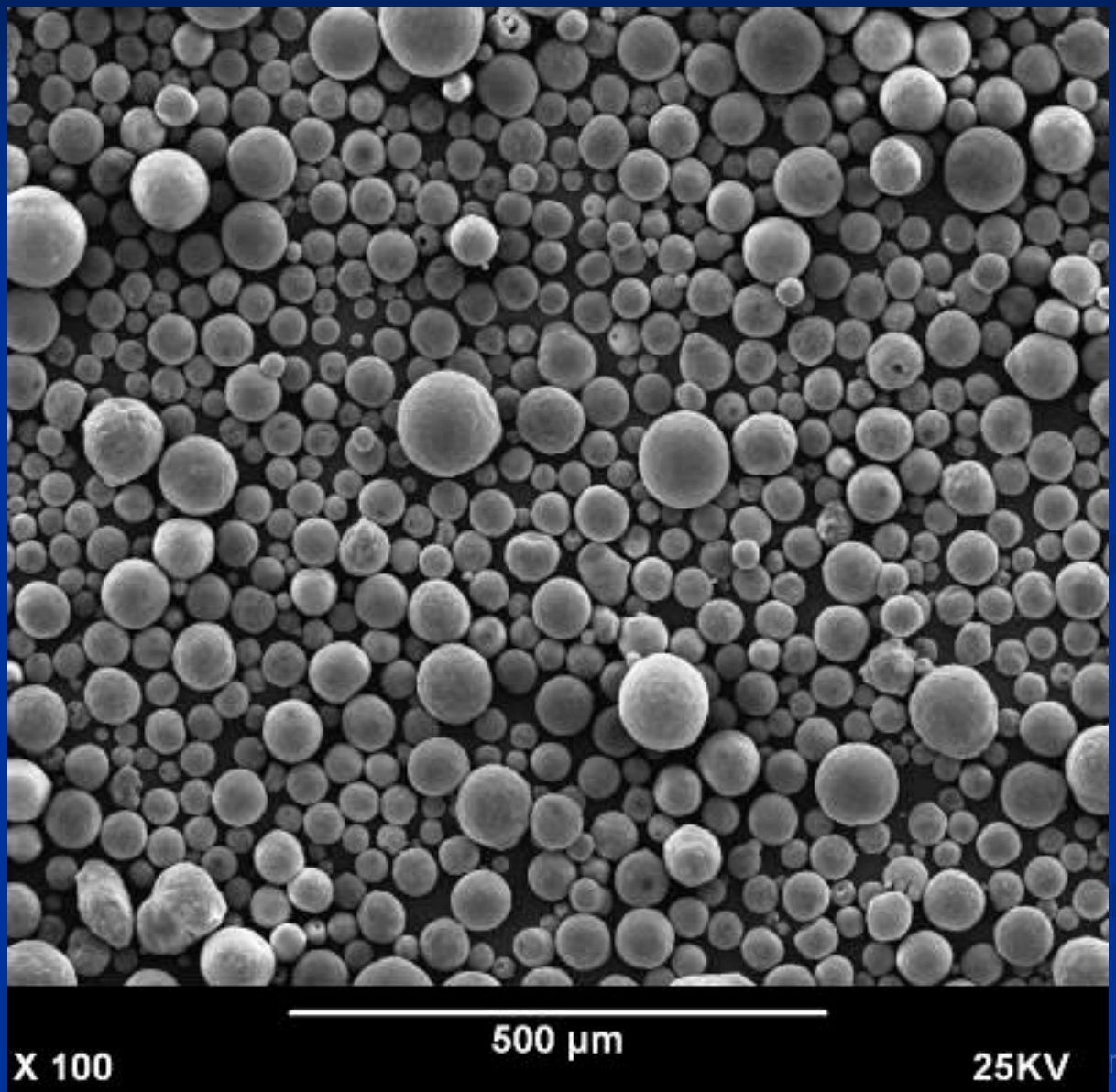
- 目标 Objective
  - 通过工业性试验，开发我国自有知识产权的DMTO 工业化成套技术，为建设以煤为原料生产低碳烯烃的工业化装置奠定技术基础
  - **To develop DMTO technology for the design of large scale commercial units**
- 合作三方 Partner
  - 中国科学院大连化学物理研究所 **Dalian Institute of Chemical Physics**
    - 提供中试工艺技术和催化剂 **Providing pilot technology for design and the catalyst**
  - 中国石化集团洛阳石油化工工程公司 **Luoyang Petrochemical Engineering Company, Sinopec**
    - 工程放大和试验装置设计 **Engineering design**
  - 陕西新兴煤化工科技发展有限责任公司 **Shanxi Xinxing Coal Chemical Technology Ltd**
    - 投资建设、管理运行试验装置 **Investment, construction, management, operation**
    - 股东：陕西省投资集团公司，正大煤化有限公司，陕西煤业集团公司 **Joint venture company: Shanxi Investment Group, Zhengda Coal Chemical Ltd, Shanxi Coal and Chemical Group**

工业化试验装置建设及试验
Design and Construction

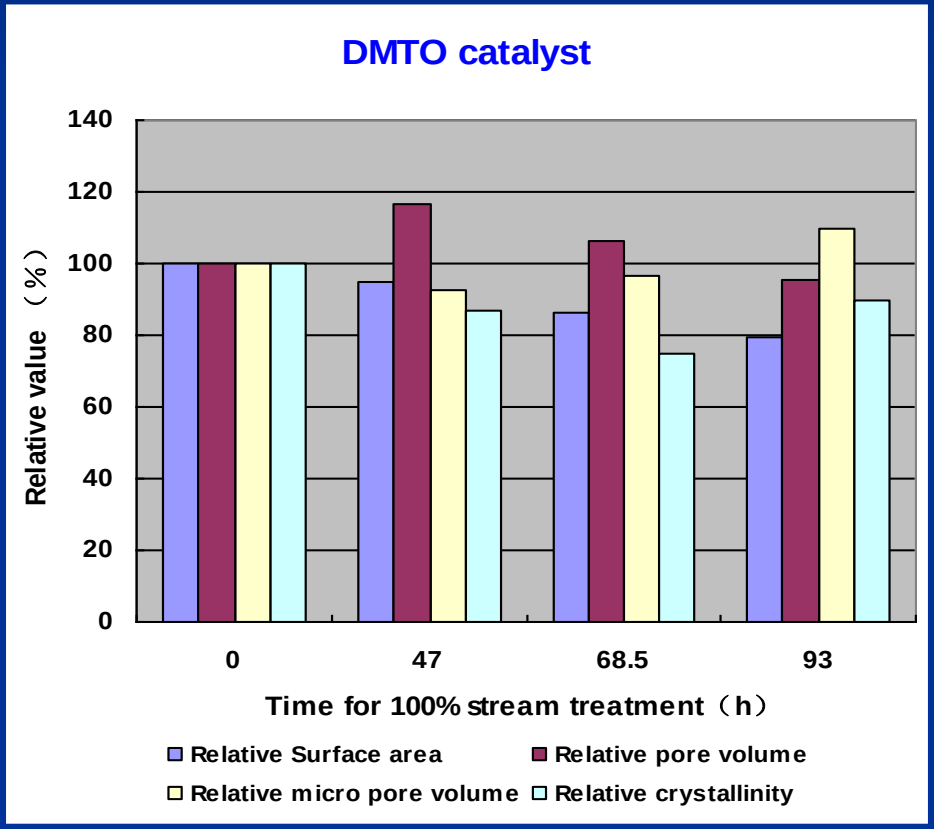
- 2004年8月项目正式启动 The project started on August 8 of 2004
- 2004年10月11日项目可行性研究报告通过审查 Feasibility study finished and passed on October 11 of 2004
- 2005年2月27日基础设计通过审查 Basic design finished and passed on February 27 of 2005
- 2005年12月份装置建设竣工 Construction finished in December of 2005
- 规模 Scale: 50t/d of MeOH
- 世界第一个同类规模装置 First unit at such scale for MTO demo in the world

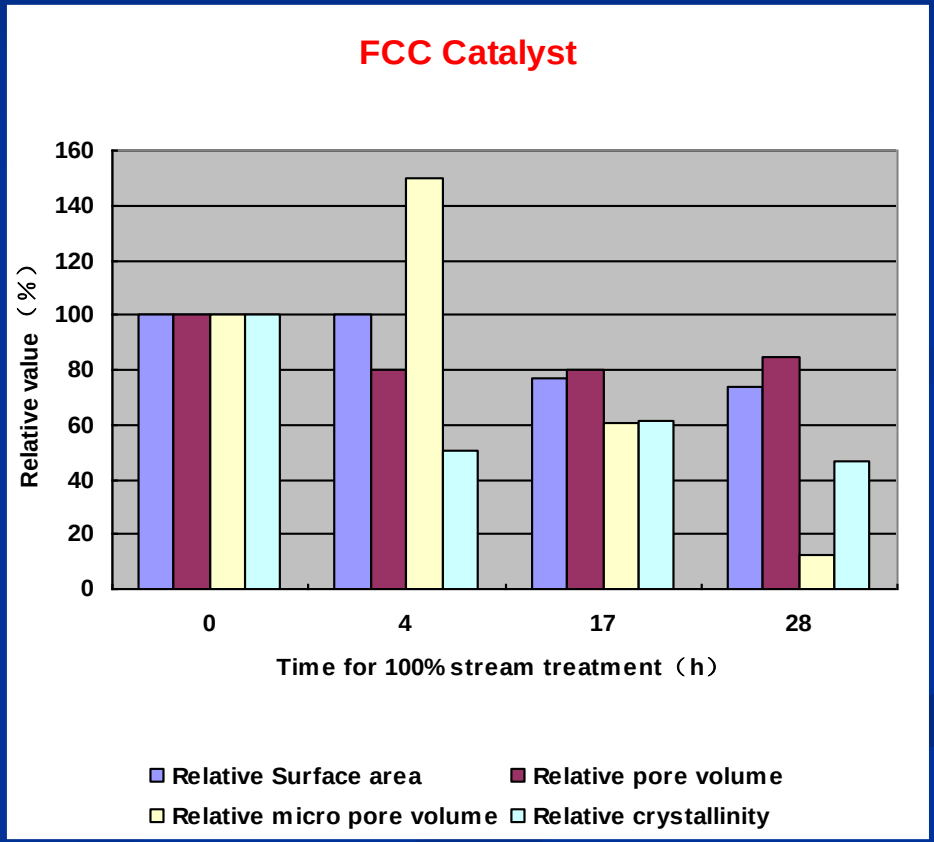

Reactor
Regen
eator
Methanol
to torch
concentrated
water
steam
water

催化剂 DMTO catalyst

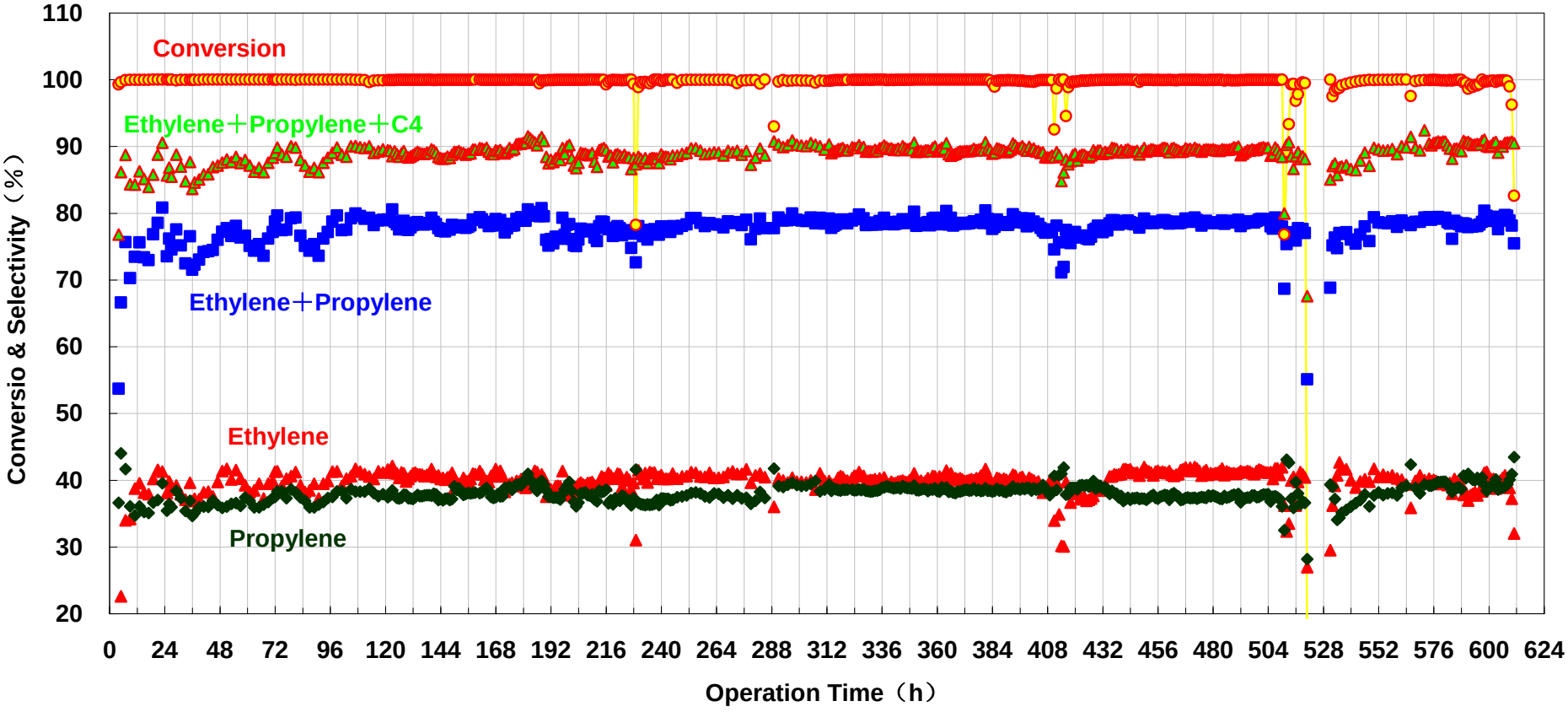


催化剂热稳定性和水热稳定性
Hydrothermal stability of the catalyst

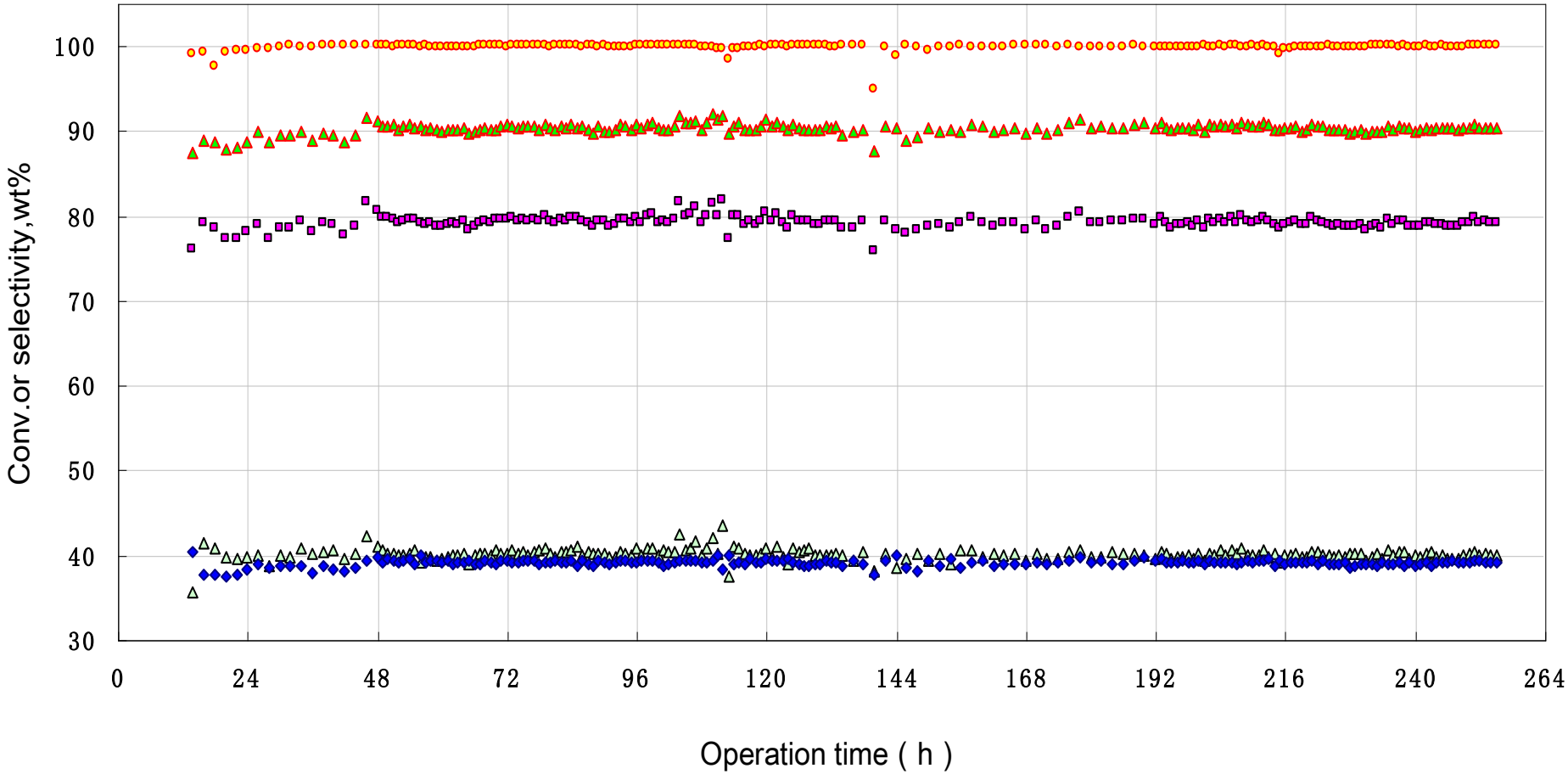




条件试验和优化
Variables test and optimization



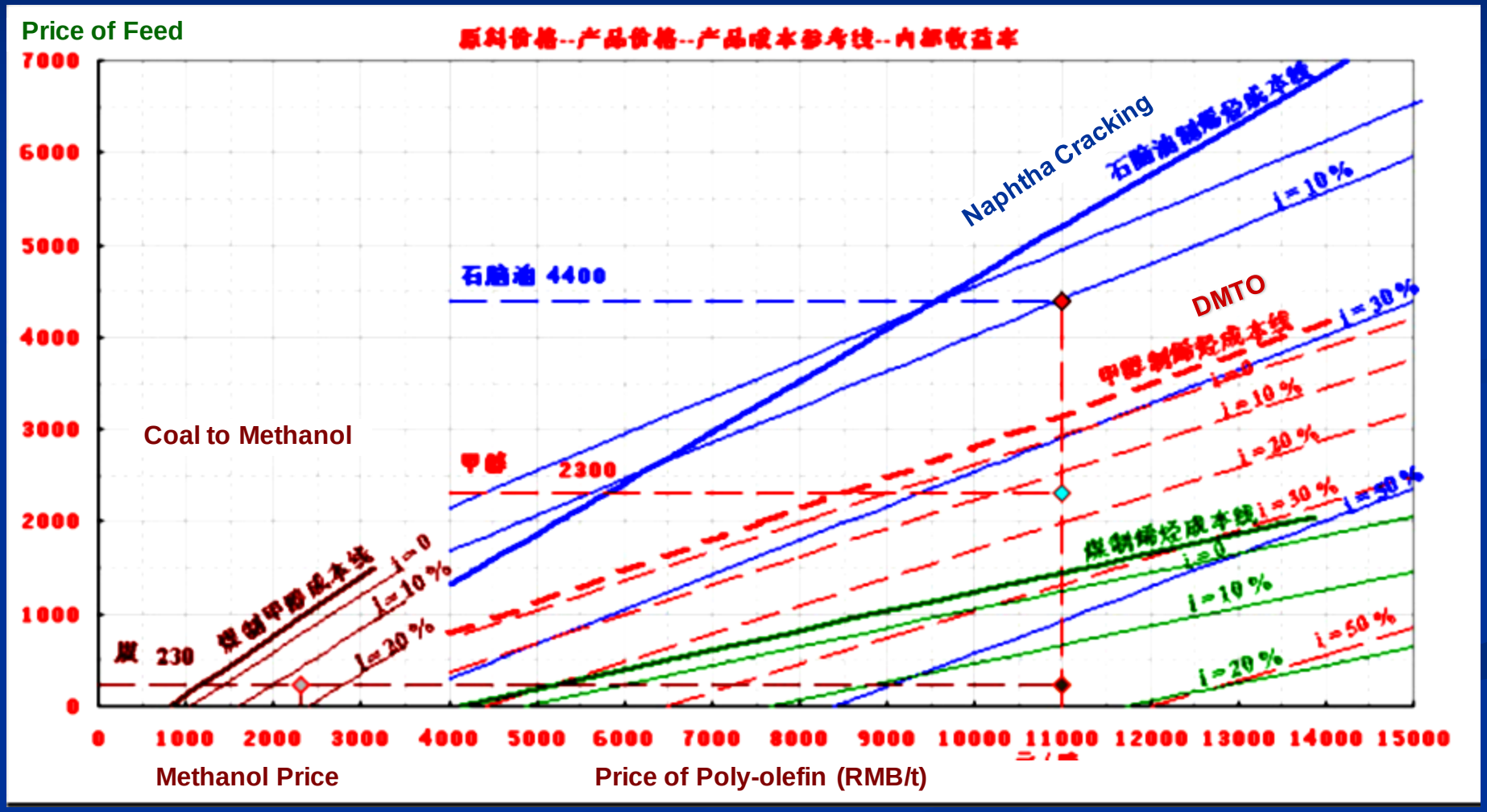
典型结果 Typical results



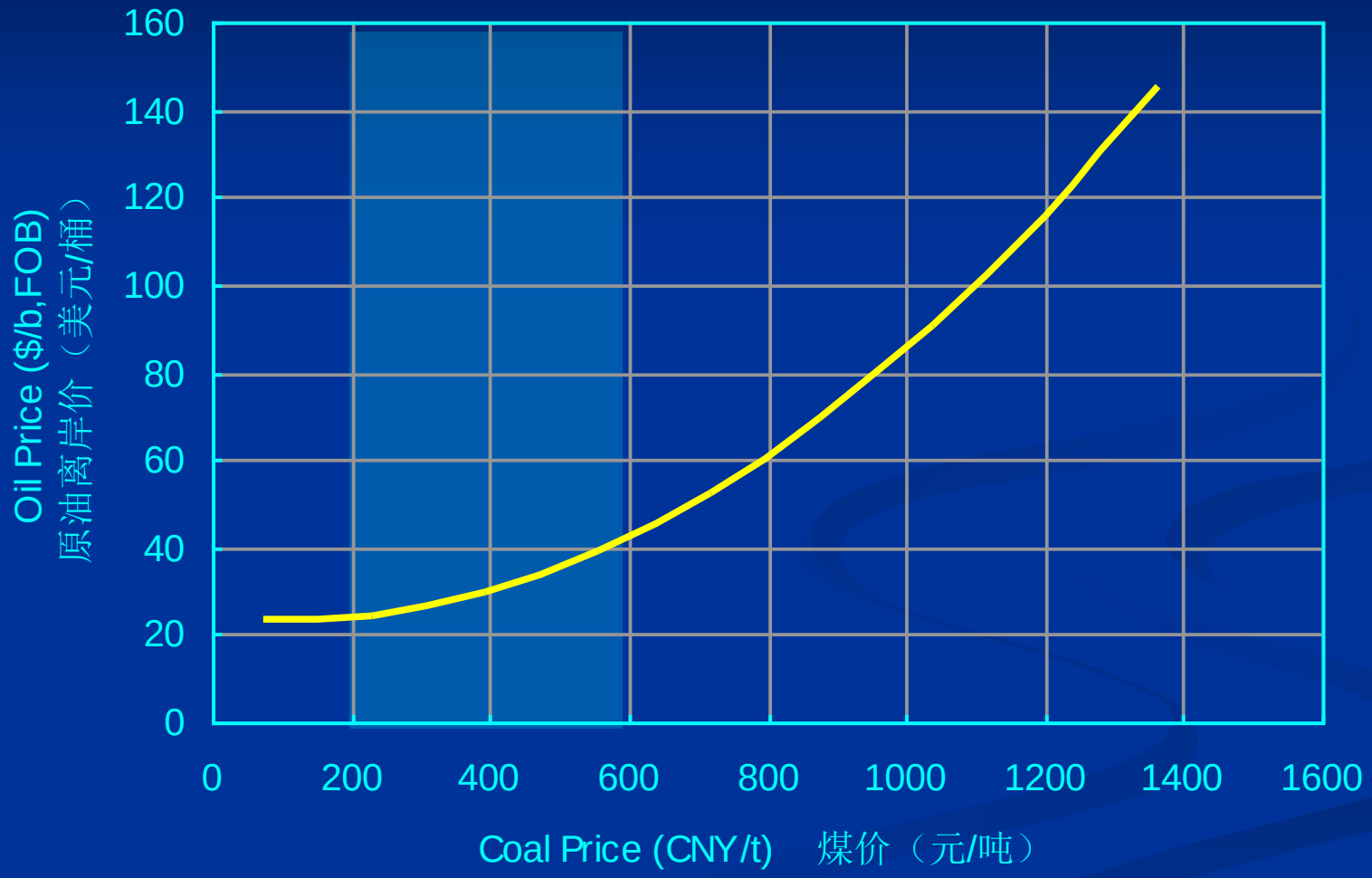
DMTO工业性试验结果
Results DMTO Demonstration test

项目	DMTO工业性试验	DMTO demonstration
原料	甲醇	MeOH
规模	50吨/天	50t/d
反应器类型	流化床	Fluidized bed
原料单程转化率	大于99%	>99%
乙烯+丙烯 产率wt%	33.73	
乙烯+丙烯 选择性wt%	79.1	
原料消耗/单位质量烯烃	2.96	
催化剂	D803C-II01	

DMTO和石脑油裂解经济性对比
Economics: DMTO & naphtha cracking



相同烯烃生产成本时煤炭价格与原油离岸价格的对应关系
Relationship between coal and oil prices at same olefin cost



DMTO技术工业化应用 Commercialization of DMTO

- 工业装置建设 Construction of commercial plant
  - 神华包头项目 Baotou Project of Shenhua Group
  - 规模 Scale： 600kta olefin
  - 国家发改委核准 （06.12）Approved by NDRC（Dec，06）
  - 2010年开车运行 Will be operated in 2010
  - 世界上第一套煤制烯烃工厂 First coal to olefin plant in the world
- 正在向海外技术许可 The construction of commercially unit will be licensed outside China
  - 许多国际烯烃公司寻求技术许可或合作 Many international olefin companies have contact us for the technology licensing
  - 与CBI-Lummus合作 Cooperating with CBI-Lummus

神华包头项目
Baotou Project of Shenhua Group

甲醇制丙烯
Methanol to Propylene (MTP)

- FMTP技术 FMTP Technology
- 合作各方
  - 中国化学工程集团公司 China National Chemical Engineering Group Co., Ltd
  - 清华大学 Tsinghua University
  - 淮南化工集团公司 Anhui Huainan Chemical Group Co., Ltd

开发历程
Developing Progression

- 1999～2007：催化剂合成及工艺技术研究

  Catalyst synthesis and technologic research

- 2008.12：流化催化剂成功放大生产

  Successful scale-up production of the catalyst used in a fluidized bed reactor

- 2009.10： FMTP工业试验成功

  Successful FMTP pilot plant test

  世界第一套流化MTP工业性试验装置 First demonstration unit in the world on Fluidized MTP

3万吨甲醇/年 FMTP工业试验装置
30KTA (Methanol) FMTP Demonstration Plant

Continuously running for 470hr 连续运转470小时

技术指标 Results

甲醇转化率 %	Methanol Conversion %	99.9
丙烯选择性（C基） %	Propylene Selectivity (Carbon Based) %	67.3
吨甲醇/吨丙烯	t Methanol/t Propylene	3.39

结束语

- 中国发展了DMTO技术和FMTP技术，完成了工业性试验

  DMTO and FMTP technologies have been developed, and demonstration tests were finished in China

- DMTO技术的工业应用，将使中国首先实现煤制烯烃过程工业化

  The application of DMTO technology will leads to a first commercial coal to olefin process in China

致谢
Acknowledgement

- 国家发改委 National Development and Reforming Committee (NDRC)
- 科技部 Ministry of Science and Technology
- 中国科学院 Chinese Academy of Sciences
- 陕西省政府 Government of Shanxi Province
- 石油和化工协会 Oil and Chemical Association
- 所有的合作伙伴 All partners for technology development
- 神华集团 Shenhua Group
- 从事DMTO和FMTP研究的同事们 Colleagues on DMTO and FMTP

Thanks !