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天然气化学
Natural Gas Chemistry

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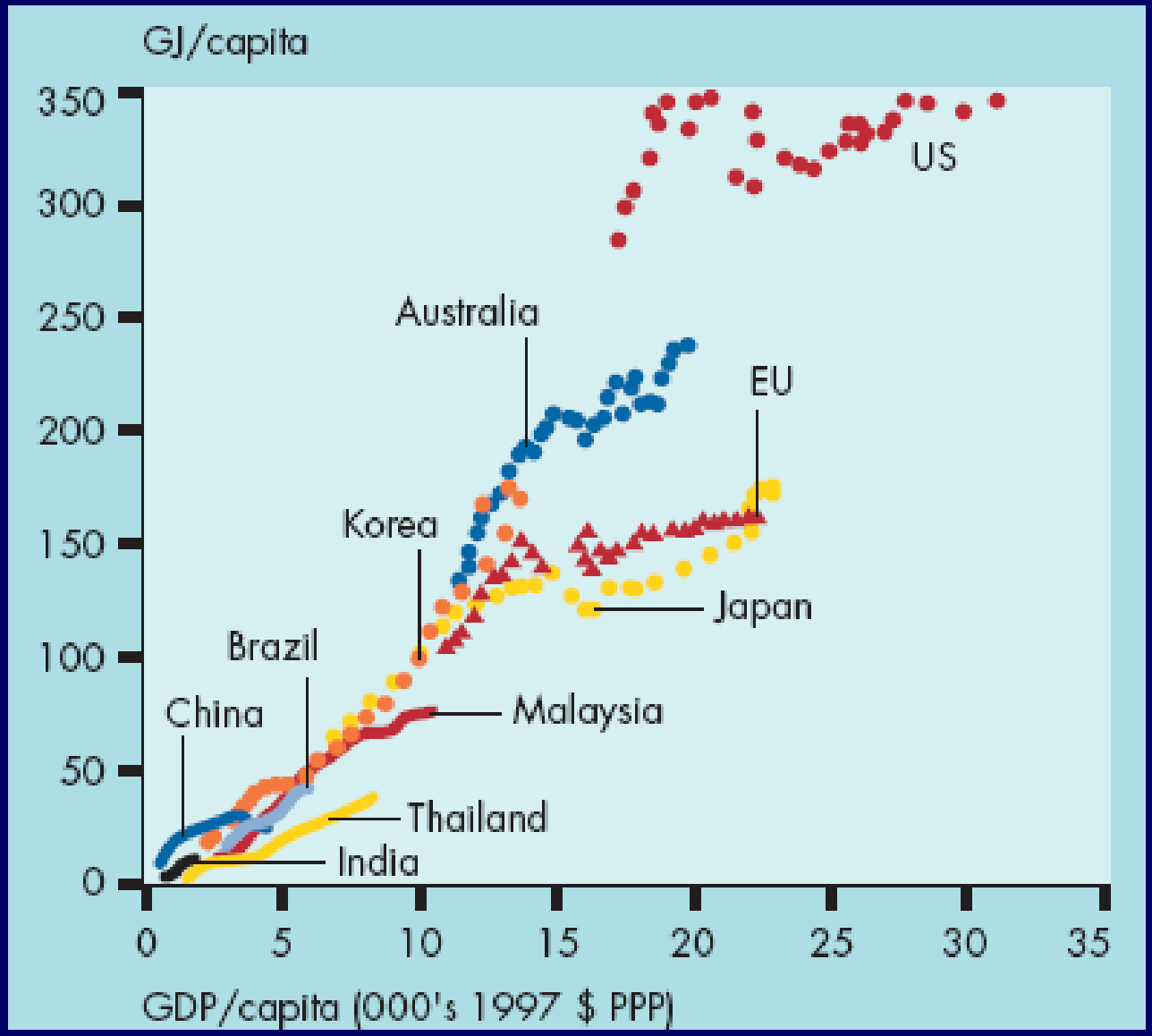
Outlines

1. General introduction to energy map
2. General about Natural Gas
3. Conversion and utilization of Natural Gas
   - 3.1 Direct Conversion
   - 3.2 Indirect conversion via syngas

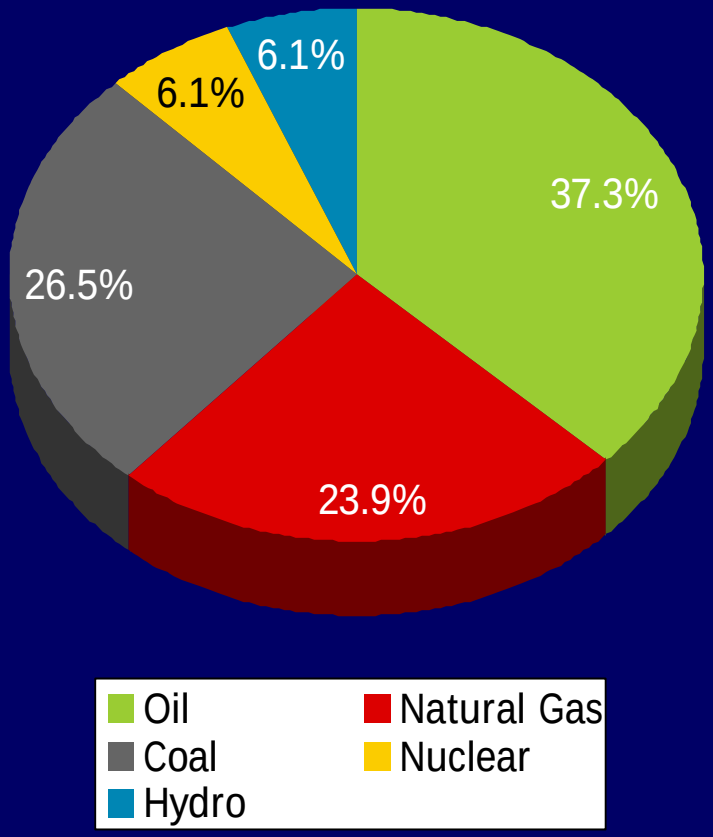
简单历史

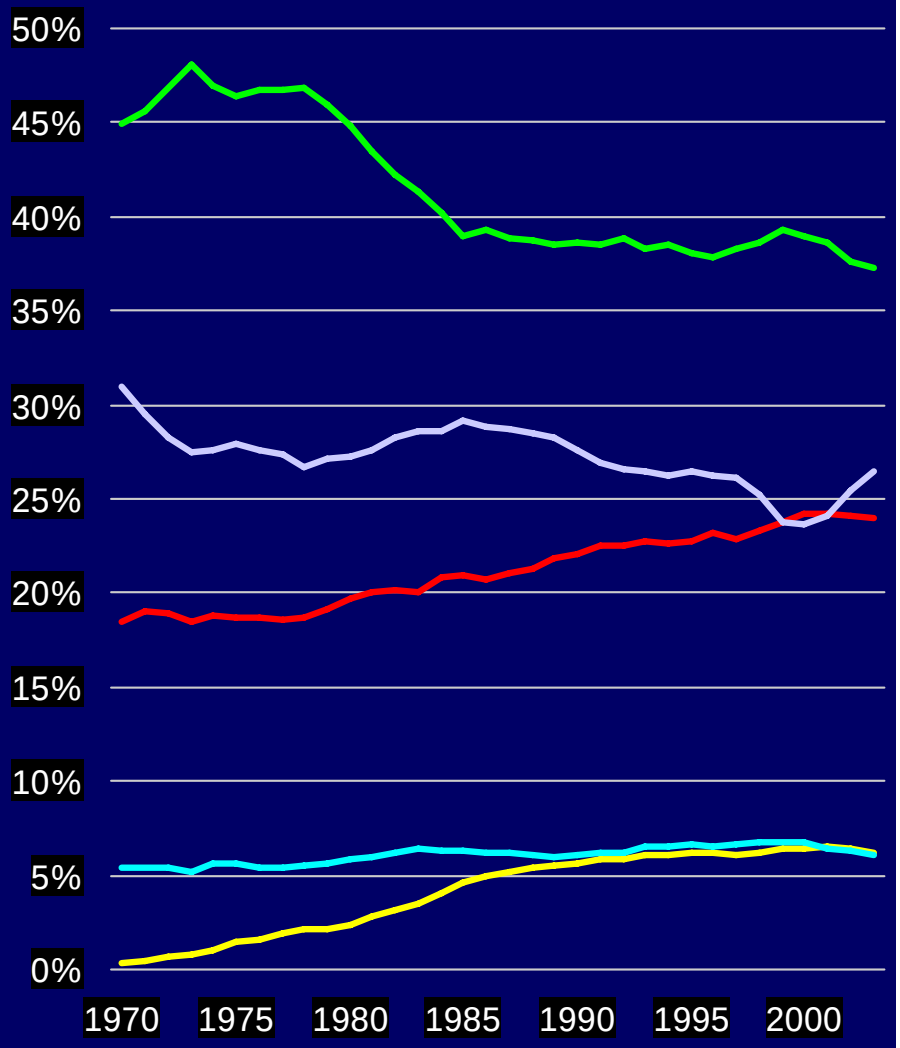
- 19世纪前，以木材、粮食、农副产品为基本原料的化工；
- 19世纪末，煤化工：焦化、干馏、气化等；
- 20世纪初，煤化工进一步发展；
- 20世纪50年代，石油的年消耗量增大，炼油、石油加工业；
- 20世纪末，化工80％以上的基础原料来自石油化工；
- 20世纪80年代，石油资源日趋枯竭，OPEC禁运措施，价格猛涨，以及环境影响，研究和开发替代石油的新能源；

Energy use grows with economic development



Current and historical global energy mix



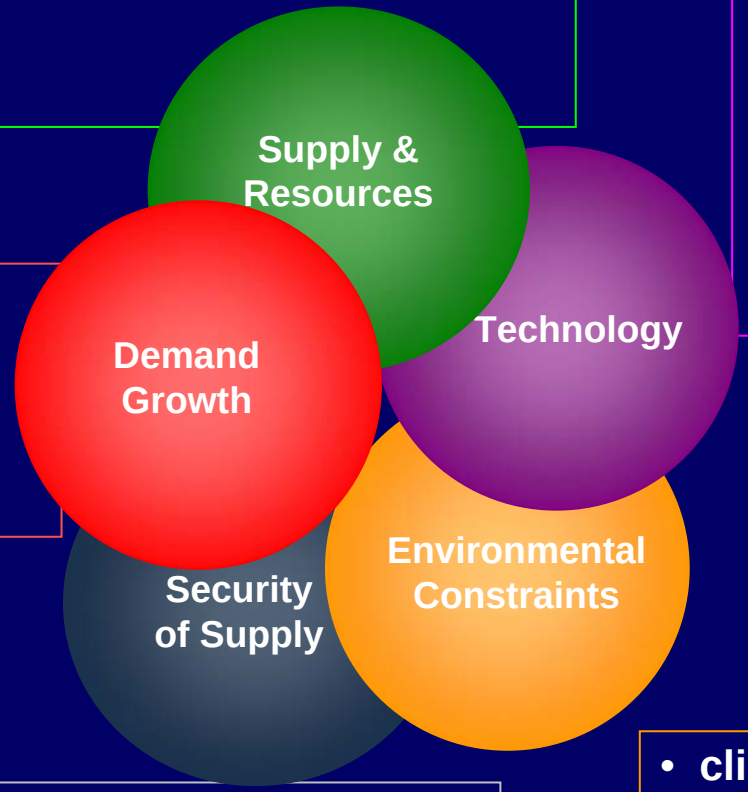


预计**2025**年天然气的比重将高于**40**%，超过石油的能源结构中的比重。

Source: BP Statistical Review

Five key drivers of the energy future

- significant hydrocarbon resource potential
- **misalignment between resource location and demand**
- growing supply challenges
- growth of renewables



- advances in all technologies especially info-tech, biotech and nanotech
- potential for breakthroughs in energy production, conversion or storage

- **rapid GDP growth** esp. in developing countries
- growth of megacities
- changing customer preferences

- significant rise in import dependence
- new policy initiatives to enhance **energy security**
- growing competition for energy resources

- **climate change and potential for carbon constraints**
- regulation relating to local pollution

Source: BP Statistical Review

Renewed interest in N Gas:

- Environmental restriction and Relatively clean N Gas
- More domestic gas than once thought
- Energy imbalance and security
- Expanded uses

Outlines

1. General introduction to energy map
2. General about natural gas
3. Conversion and utilization of natural gas

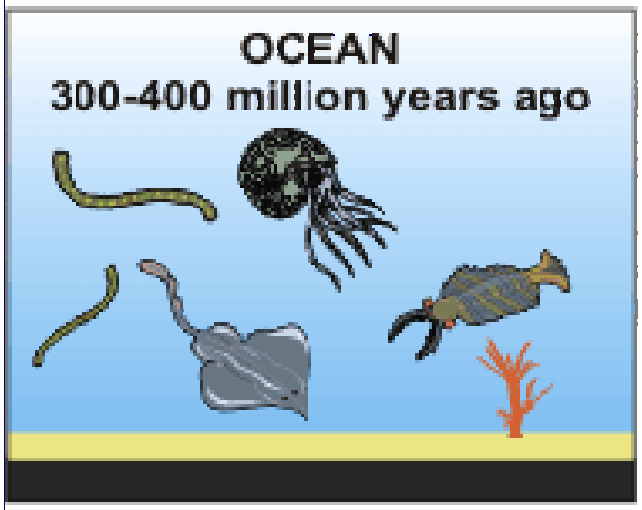
What is NG?

Colorless, shapeless, and odorless in its pure form, a mixture of hydrocarbon gases.

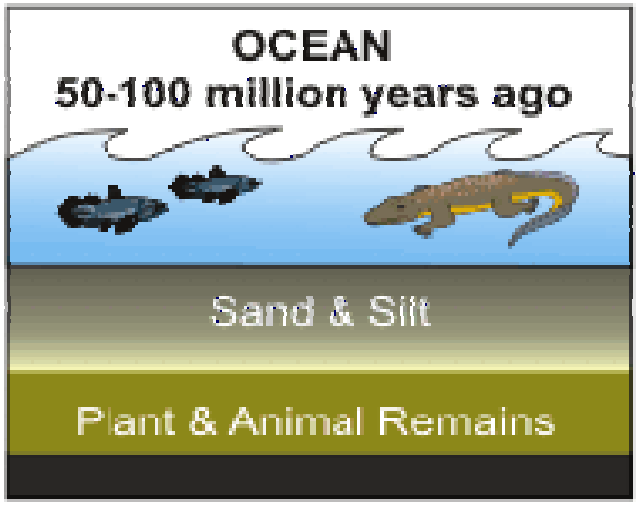
Typical Composition of Natural Gas

Methane	CH_4	70-90%
Ethane	C_2H_6	
Propane	C_3H_8	0-20%
Butane	C_4H_{10}	
Carbon Dioxide	CO_2	0-8%
Oxygen	O_2	0-0.2%
Nitrogen	N_2	0-5%
Hydrogen sulphide	H_2S	0-5%
Rare gases	A, He, Ne, Xe	trace

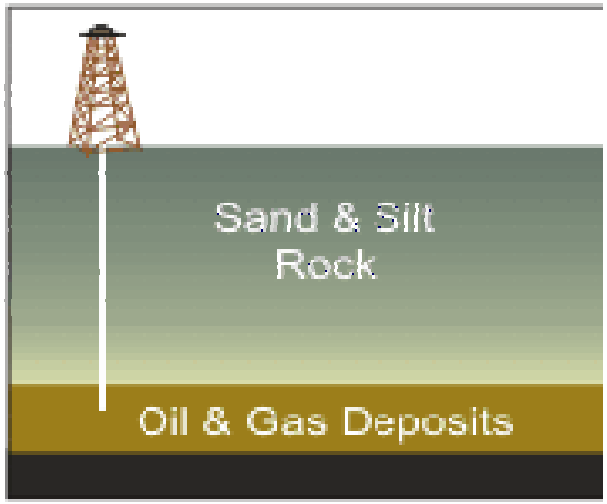
PETROLEUM & NATURAL GAS FORMATION



Tiny sea plants and animals died and were buried on the ocean floor. Over time, they were covered by layers of silt and sand.



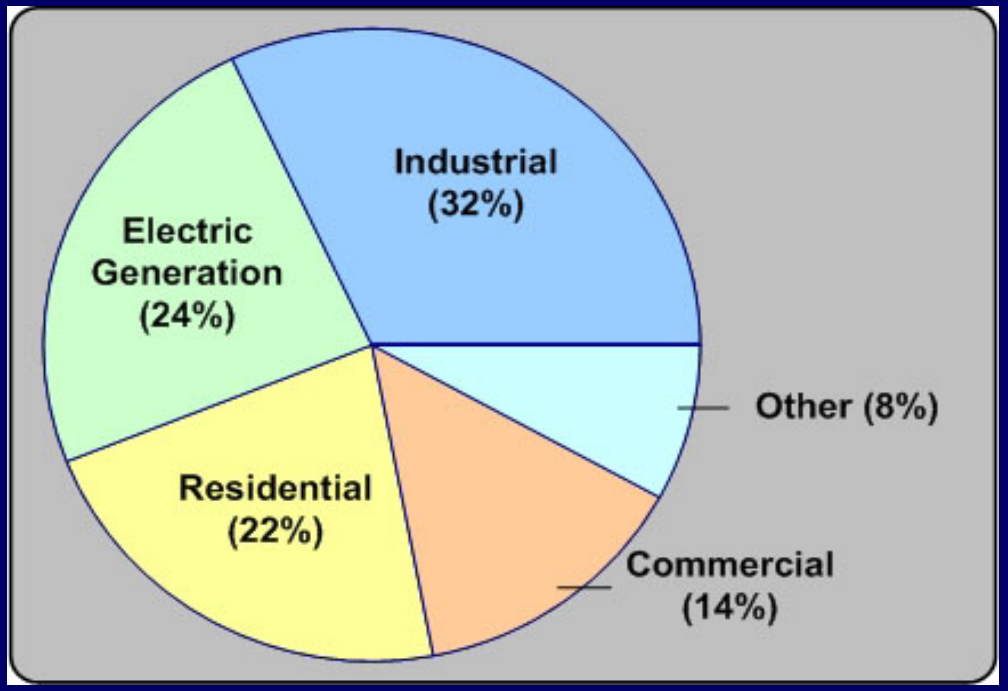
Over millions of years, the remains were buried deeper and deeper. The enormous heat and pressure turned them into oil and gas.



Today, we drill down through laye of sand, silt, and rock to reach the rock formations that contain oil and gas deposits.

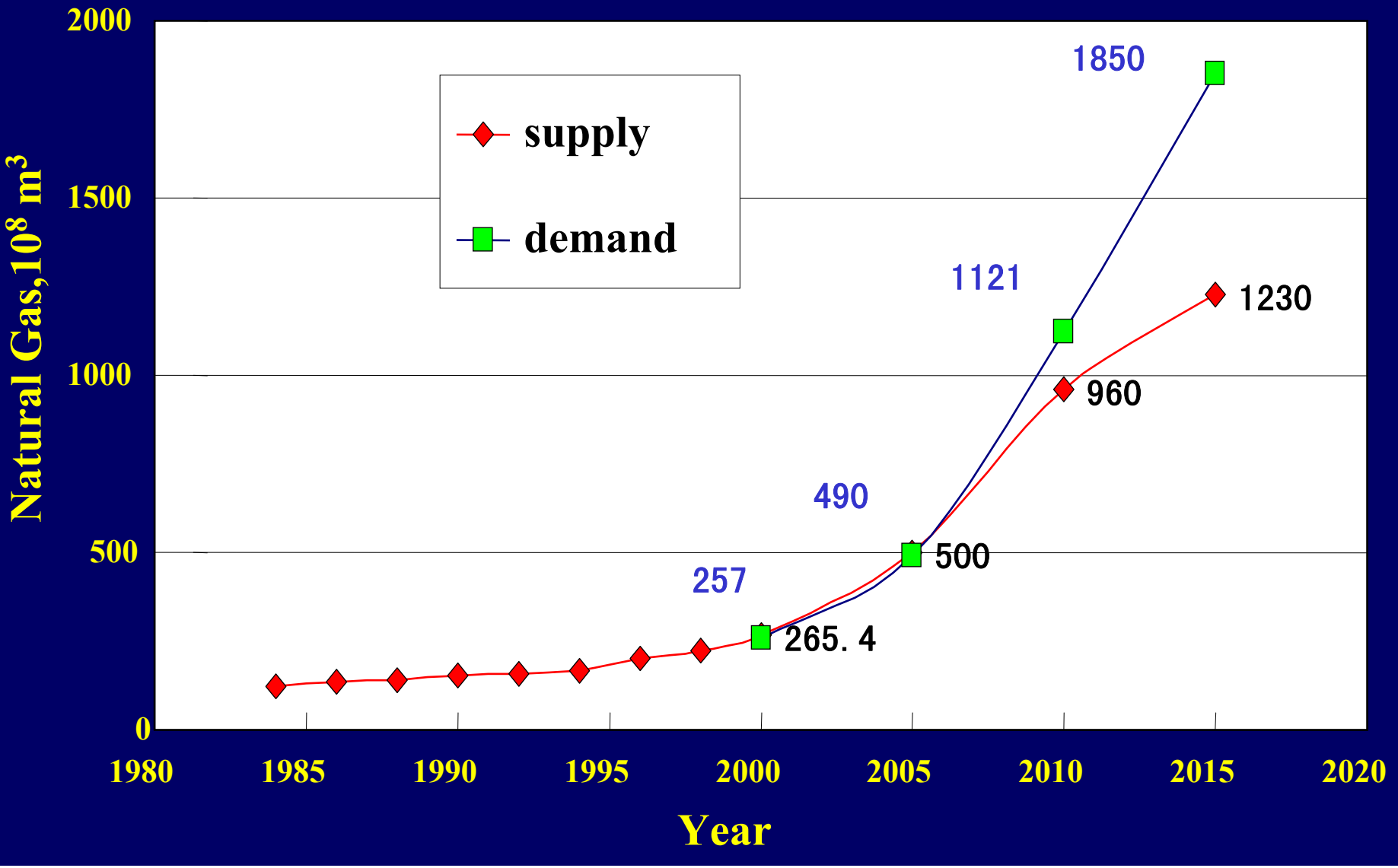
Usa of Natural Gas

1. Clean fuel commercial and residential use;
2. Raw material for chemical industry (ammonia synthesis, methanol, ethylene, propene, hydrogen, syngas, acetylene, carbon black...)



Note: 76% ammonia, 80% methanol, 42% ethylene comes from Natural Gas.

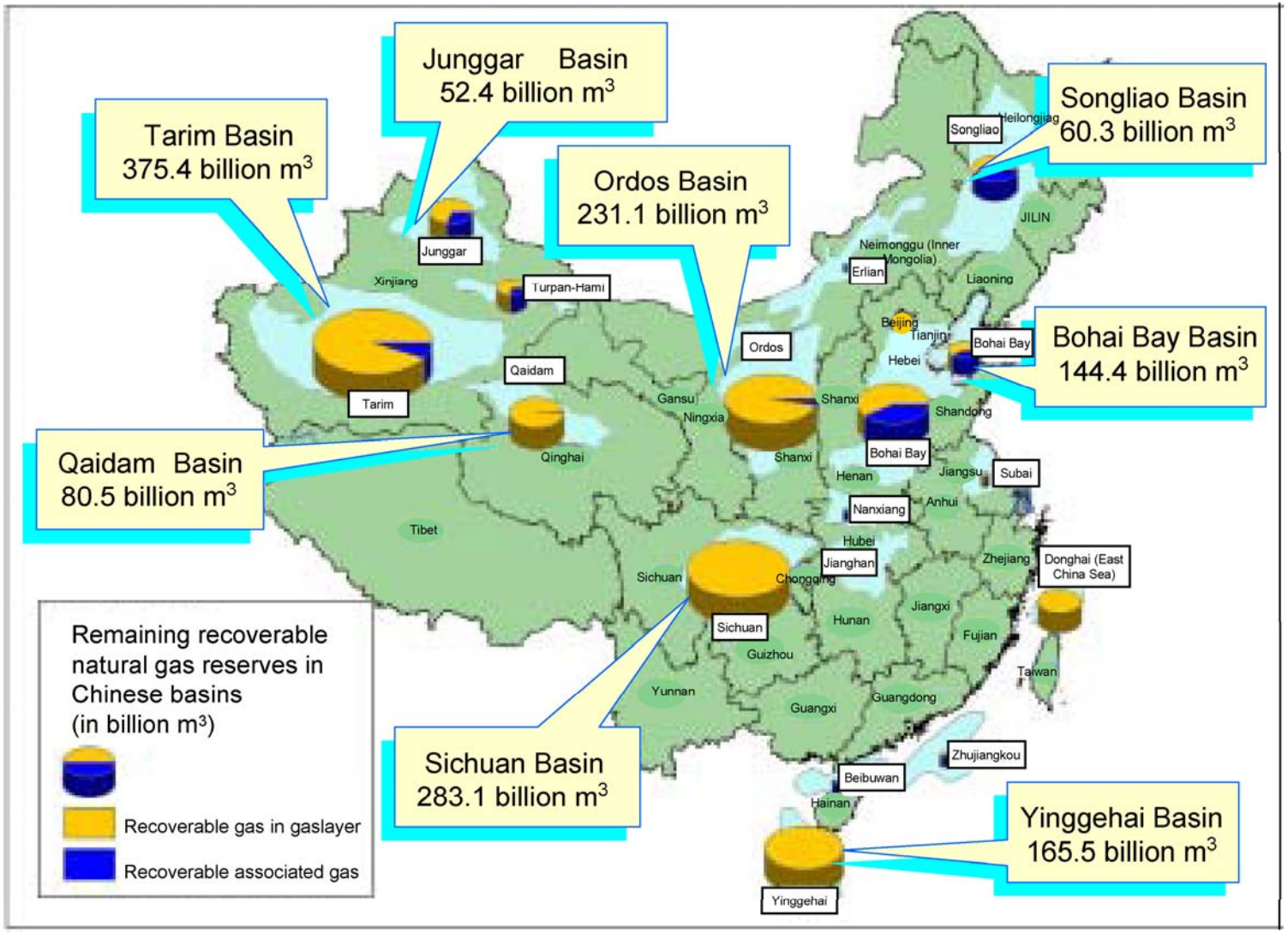
The supply and demand of NG in China



NGas Utilization in China

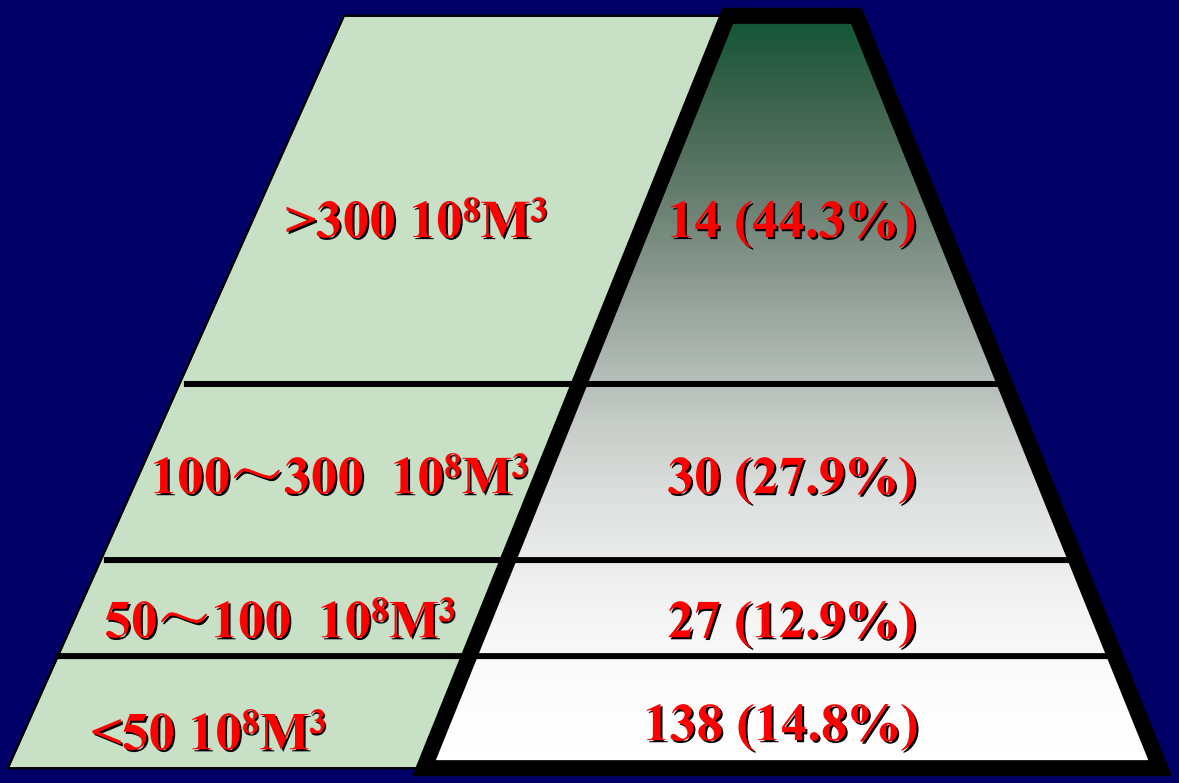
	2000	2010	2020
Domestic （10^8M^3）	**200**	**740**	**1030**
Natural Gas	200	710	950
Coal-based		30	80
Import （10^8M^3）		**260**	**600**
pipe line		200	400
LNG		60	200
Total	**200**	**1000**	**1630**

NGas Resource Distribution in China



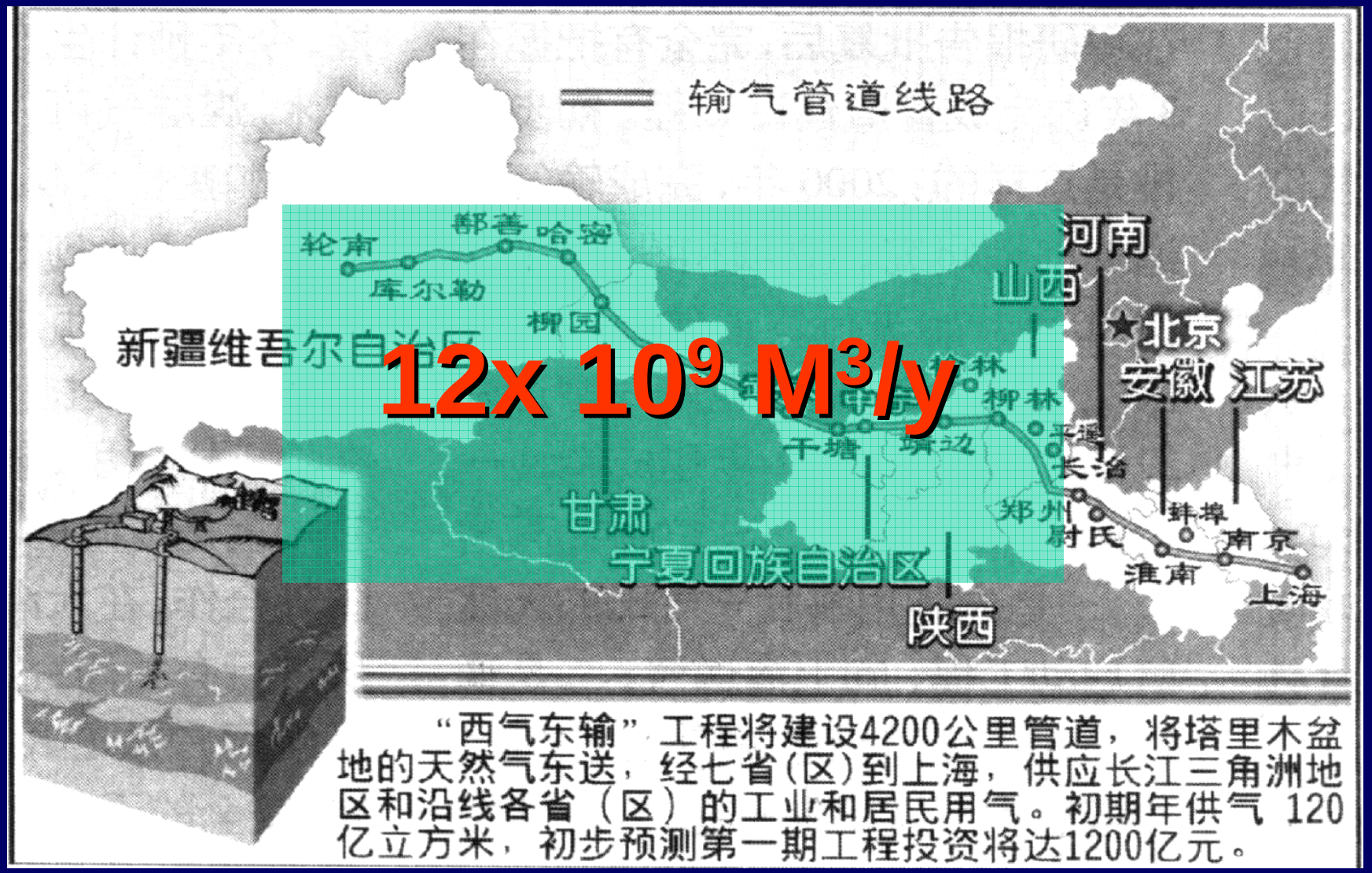
Source: Institute of Energy Economics, Japan (based on 1994 official figures)

Size Distribution of Gas Fields in China



204 Gas Fields in Total

Pipeline Project in China



Outlines of this lecture

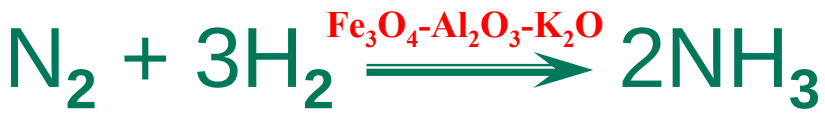
1. General introduction to energy map
2. General about Natural Gas
3. Conversion and utilization of Natural Gas

What and how? Why important?

天然气转化和利用的核心是催化

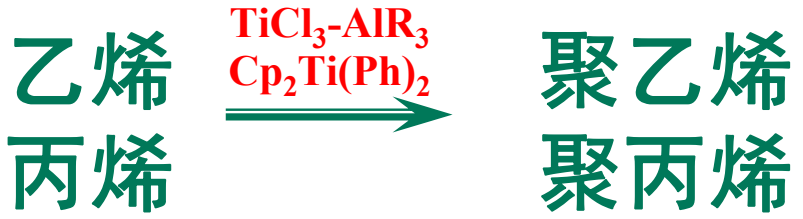
优化能源结构、保护生态、缓解石油供应不足

催化对社会进步的贡献



合成氨熔铁催化剂

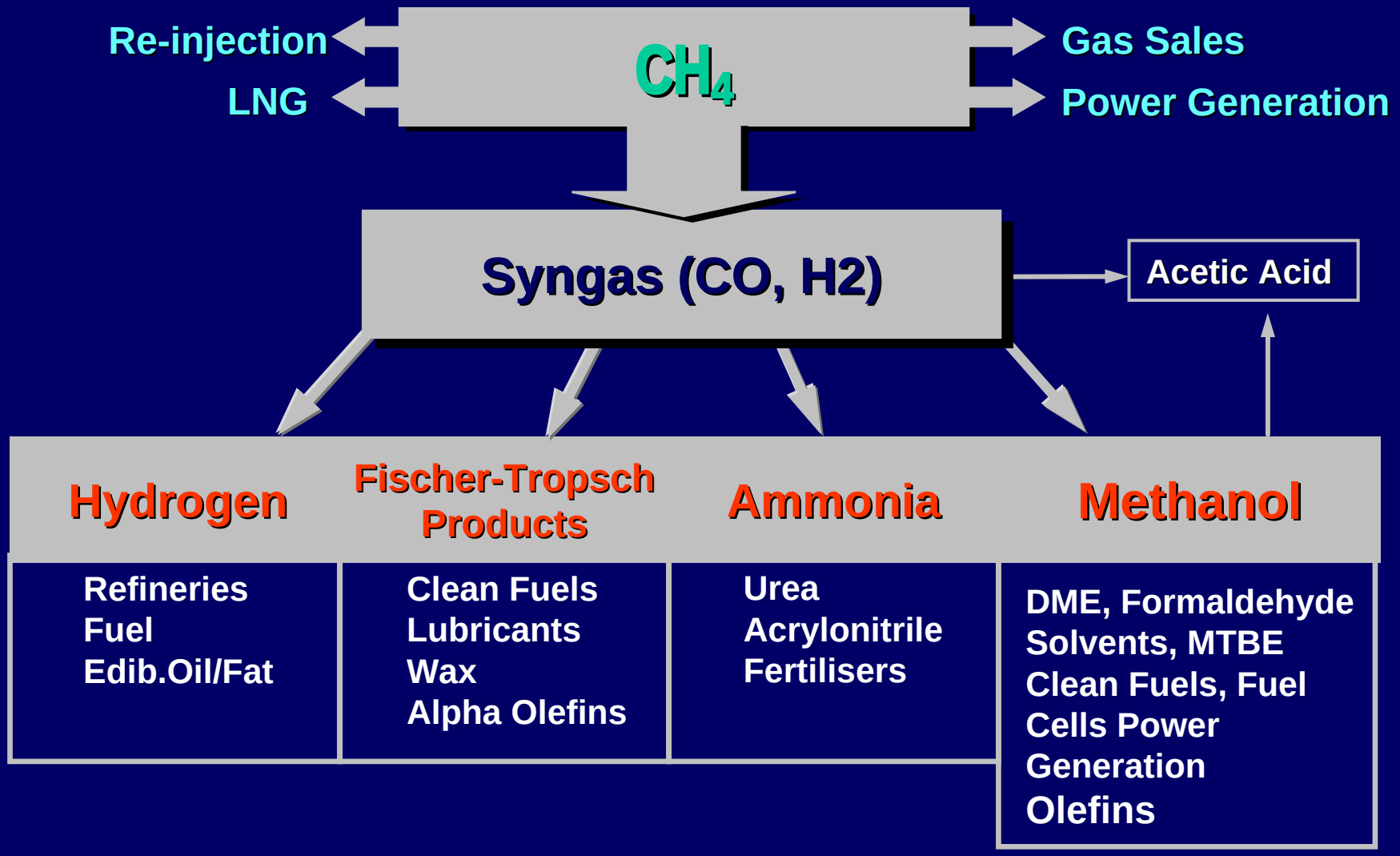
- 使化肥工业迅速发展
- 迎来了现代农业
- 1918年诺贝尔化学奖



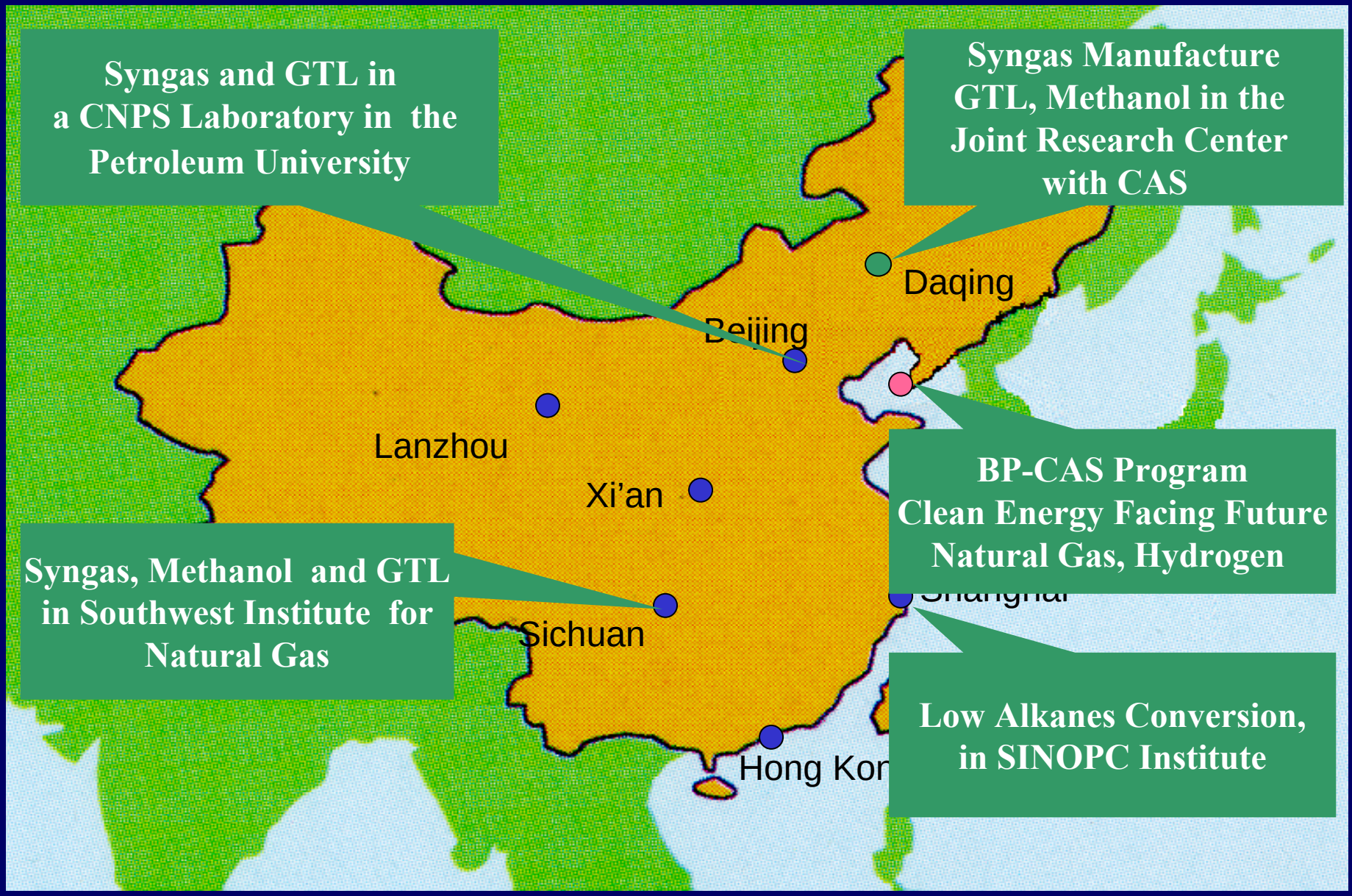
Ziegler-Natta催化剂

- 塑料产量增加了100倍
- 奠定了石化工业的基础
- 1963年诺贝尔化学奖

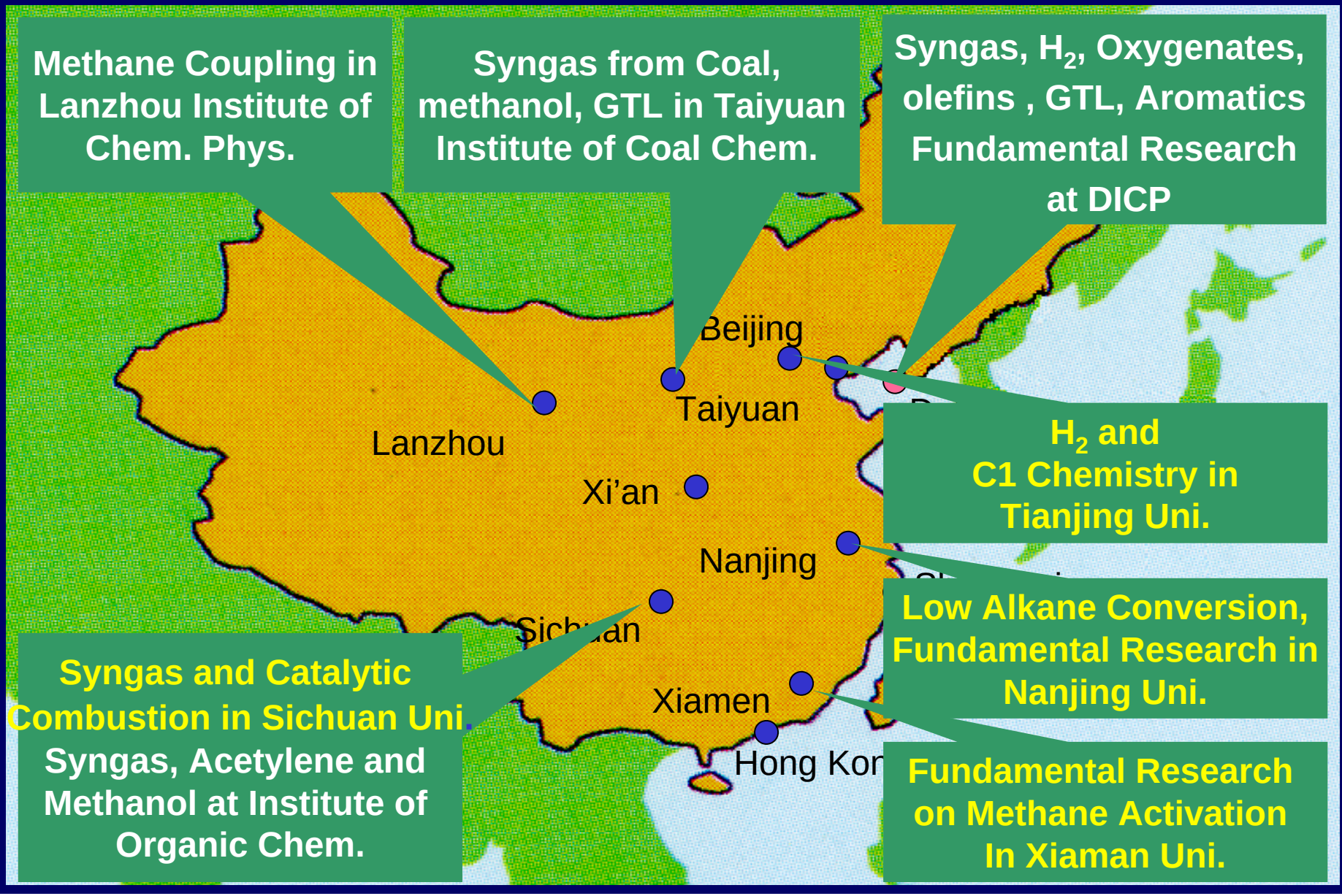
国际天然气利用研究情势



Research in Industrial Companies



Research in Academia



National Major Basic Research Program (MOST, 973)

天然气、煤层气优化利用的催化基础

99年10月 – 2004年9月；

设计2个大学，3个研究所，共32位教授和35位研究人员；

总体目标：发展一系列以催化为核心的科学和技术…转化为高洁净度液体燃料和具更高经济价值且便于运输的甲醇、烯烃、芳烃和含氧化物等基本化工原料。

基础研究：以C-H选择活化和定向转化为目标，创新催化过程和催化剂，建立和发展动态催化理论，从本质上认识“控制活化、选择转化”的核心问题。

National Major Basic Research Program (MOST, 973)

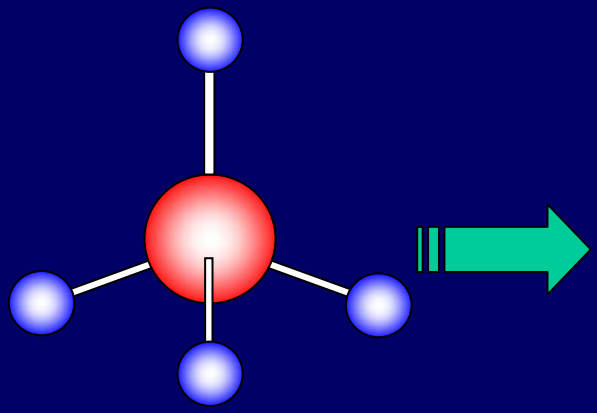
天然气及合成气高效催化转化的基础研究

2005年1月 – 2009年12月；

涉及8个大学，2个研究所，60多位研究人员；

子课题：天然气制合成气及规模制氢和CO_2处理；
合成气制取高品质液体燃料；
合成气制含氧化物；
基于合成气和天然气的高温燃料电池；
天然气直接催化转化；
天然气高效转化的非常规过程；
催化剂和催化体系的构效关系和动态表征；
催化过程的微观机制和反应中间体的鉴定。

Features of CH_4



C-H 键能:	438.8kJ•mol^{-1}
电离势:	12.5eV
质子亲和势:	4.4eV
酸性 (pKa):	48

自然界中最稳定的有机分

最具挑战性和机遇

Property of CH_4

Molecular weight	16.04
Volume (standard)(L/mol)	22.38
Density (101.32kPa, 0°C)(kg/m3)	0.7167
Boiling point/K	111.75
Thermal conductivity (101.32kPa, 0°C)(W/m.K)	0.03
Explosion limit in air (20°C)%	5.3-14.0
Autogenous ignition T/K	811
Combustion heat/(kJ/m3)	35877

一些简单反应的标准自由能变化

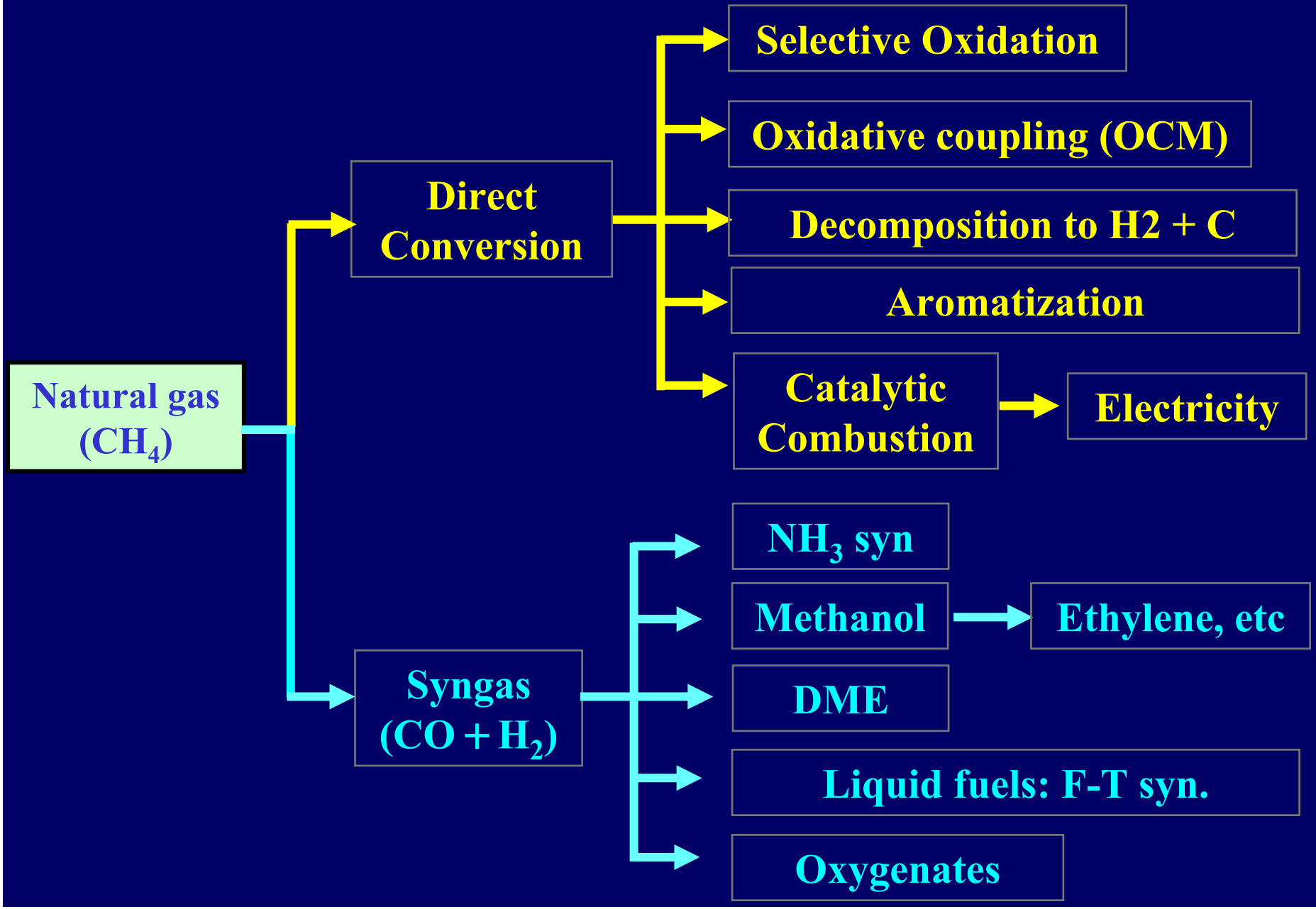
Reaction	ΔG^{Θ}/ (kcal/mol)	
	400 K	1000 K
$2\ CH_4 \rightarrow C_2H_4 + 2\ H_2$	18.9	9.5
$2\ CH_4 \rightarrow C_2H_6 + H_2$	8.6	8.5
$2\ CH_4 + O_2 \rightarrow C_2H_4 + 2\ H_2O$	-34.6	-36.4
$2\ CH_4 + ½\ O_2 \rightarrow C_2H_6 + H_2O$	-18.4	-14.5
$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$	-26.0	-27.8
$CH_4 + ½\ O_2 \rightarrow CH_3OH$	-25.4	-18.0
$CH_4 + CO \rightarrow CH_3CHO$	16.0	33.6
$CH_4 + CO_2 \rightarrow CH_3COOH$	19.2	35.5
$CH_4 + H_2O \rightarrow CO + H_2$	28.6	-6.5
$CH_4 + CO + ½\ O_2 \rightarrow CH_3COOH$	-40.0	-10.0

甲烷的转化和利用，化学工业出版社，2005

甲烷的催化转化

- **C-H** 键的活化是催化循环的一部分，而不是计量反应；
- 催化体系有足够的选择性，即产物中**C-H**键比甲烷稳定；
- 体系的活性应该足够高使反应在温和条件下进行。

Conversion of methane



Selective Oxidation

气相均相氧化

反应条件 4 MPa，450－500°C，影响因素很多。

气固多相催化氧化

反应条件 450－700°C，多采用 SiO_2 或 Al_2O_3 负载的 MoO_3, V_2O_5 等催化剂；甲醇产率<5％。

注：问题难以控制选择性氧化。从工业化角度，转化率 >10%，选择性 >80%。

液相催化氧化

常以过渡金属配合物为催化剂，以强酸、超强酸、超临界流体为溶剂，以 O_2、H_2O_2、$K_2S_2O_8$、SO_3 为氧化剂。

Difficulty of direct methanol synthesis:

C-H bonding of

CH_4	434.7 kJ/mol
CH_3OH	388.7 kJ/mol

Some transition metal complexes could selectively activate the more stable C-H bond?

Oxidative addition; σ bond displacement; ***free radical; electrophilic activation.***

Advantage of low T synth:

Protection of product in acid medium (ester)

Examples for low T…

Direct Conv

G. Olah *Electrophiles and superacids,*

$$CH_4 + HF + SbF_5 \rightarrow [CH_5][SbF_6]$$

$$[CH_5][SbF_6] \xrightarrow{-H_2} [CH_3][SbF_6] \xrightarrow{CH_4} [C_2H_7][SbF_6]$$

$$H_2 + SbF_5 \rightarrow 2HF + SbF_3$$

Periana et al. *Science, 1993, 340; Science 1998, 560.*

Net reaction: $CH_4 + 1/2O_2 \xrightarrow[180\ ℃]{HgSO_4/H_2SO_4} CH_3OH$

Con.$_{CH4}$ 50%, yield 43%

More examples…

Fujiwara et al. *Angew. Chem. Int. Ed. 2000, 2475*

$CaCl_2$, $Pd(OAc)_2/Cu(OAc)_2$

$$CH_4 + CO \xrightarrow[K_2S_2O_8,\ 85\ ^{o}C]{CF_3CO_2H/(CF_3CO_2)_2O} CH_3COOH$$

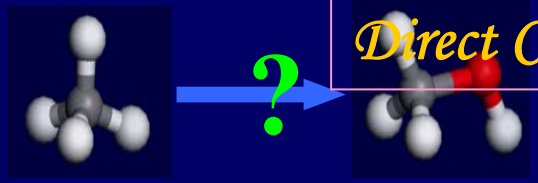
20 atm CH4; 0.5 mmol CaCl2, 15 h reaction time, 1.05 mmol product.

Bell et al. *JACS 2003, 125, 4406*

$$CH_4 + SO_2 + K_2S_2O_8 \xrightarrow[65\ ^{\circ}C]{CF_3SO_3H,\ CaCl_2} CH_3SO_3H$$

69 atm CH_4; triflic acid; 10 h, 1.44 mmol product.

Work of Sen et al.



$$H_2O_2 + CH_4 \xrightarrow[PdCl2,\ 90\ ^\circ C]{(CF_3CO)_2O} CF_3COOCH_3$$

80 °C

$$CF_3COOH + CH_4 + Pd^{2+} \longrightarrow CF_3COOCH_3 + Pd^{0} + 2H^{+}$$

$$CF_3COOH + CH_3OH$$

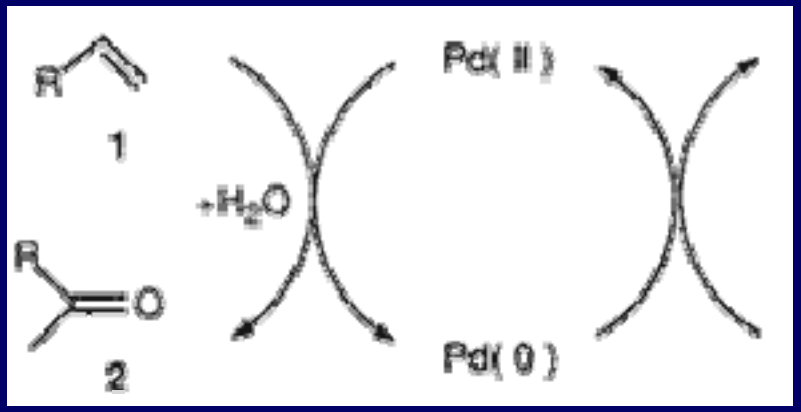
?

Stoichiometri

E. Gretz, et al. J. Am. Chem. Soc. 109 (1987) 8109;
L. Kao, et al. J Am Chem Soc 113 (1991) 700

$Pd^0 \rightarrow Pd^{2+}$?

- Wacker process: $CuCl_2/CuCl/O_2$



- Others?

The Wacker Process

Developed simultaneously by Wacker-Chemie and by the group of Moiseev.

It involves the reaction of ethylene with $PdCl_2$ in HCl (reaction 1). Pd(II) is reduced to Pd black. To make the reaction catalytic, Pd(0) is reoxidized by $CuCl_2$ and O_2 (reactions 2 and 3).

$$C_2H_4 + PdCl_4^{2-} + 3H_2O \longrightarrow CH_3CHO + Pd^0 + 2H_3O^+ + 4Cl^- \quad (1)$$

$$Pd^0 + 2CuCl_2 + 2Cl^- \longrightarrow PdCl_4^{2-} + 2CuCl \quad (2)$$

$$CuCl + 4H_3O^+ + 4Cl^- + O_2 \longrightarrow 4CuCl_2 + 6H_2O \quad (3)$$

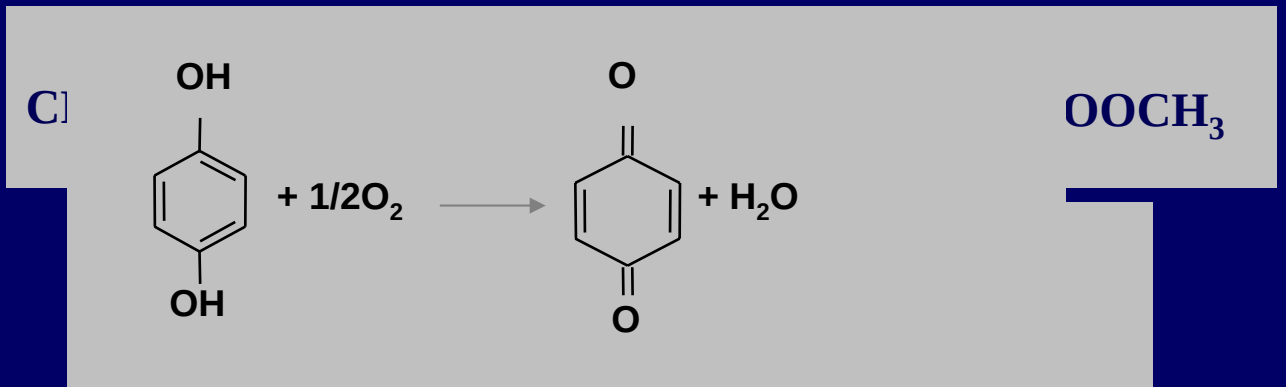
Better to explore…

- To make a catalytic process;
- To avoid HCl, H_2SO_4, SO_3, SO_2;
- To use O_2 as oxidant.

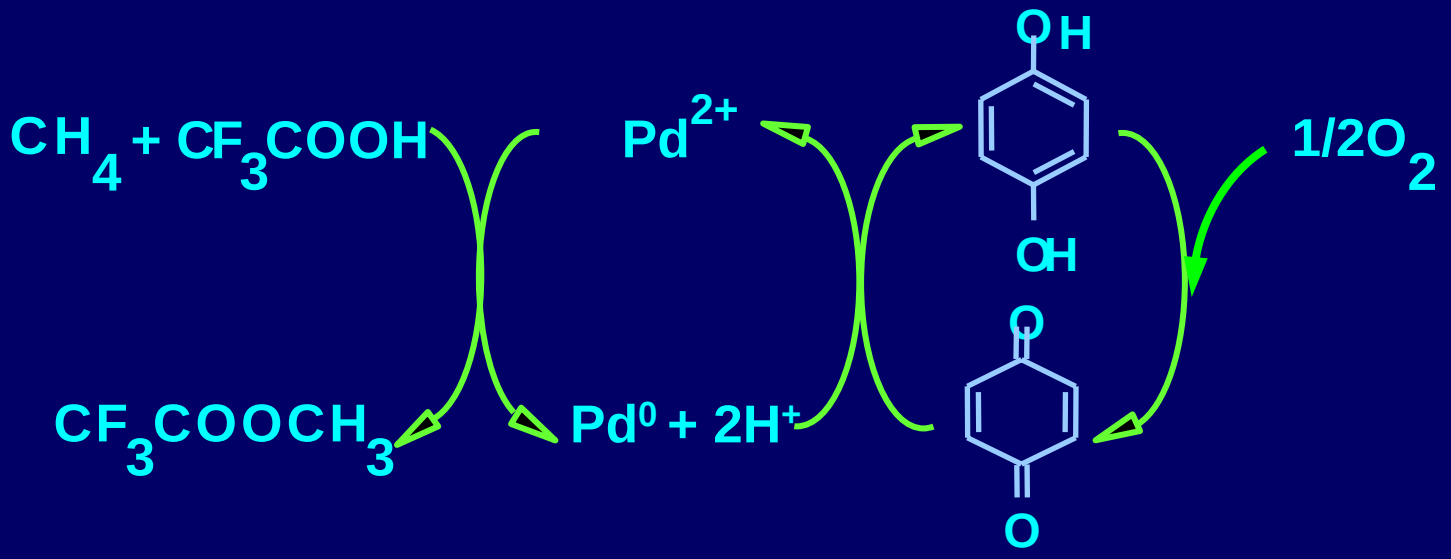
Combination of Pd^{2+} and Q

Run	Pd^{2+} (μmol)	Q (μmol)	O_2 (atm)	CF_3COOCH_3 (μmol)	Pd^{2+a} (%)
1	10	0	0	9.5	--
2	10	20	0	30	--
3	10	50	0	55	--
4	10	100	0	60	92
5	10	20	1	34	15
6	10	50	1	67	27

Conditions: CF_3COOH: 3 ml (39 mmol), CH_4: 54 atm (114 mmol),
O_2: 1 atm (2 mmol), 80 °C, 10 h; a: Remaining Pd^{2+} after the reaction.

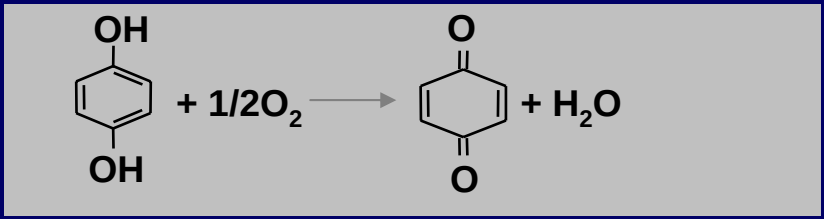


Scheme of methane oxidation



Search for active oxidants to speed up:

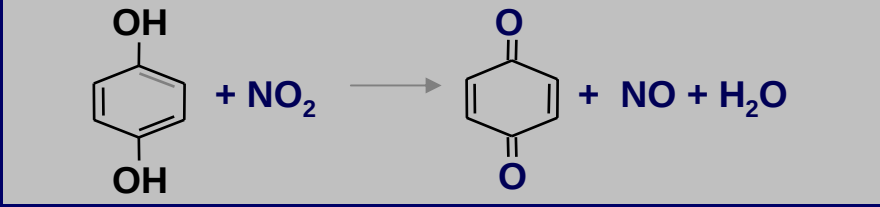
Direct Conv



- **nitrogen oxide** /CH_2Cl_2

Bosch, et al. *J. Org. Chem.* **1994**, *59*, 2529.

Feasibility test in CF_3COOH

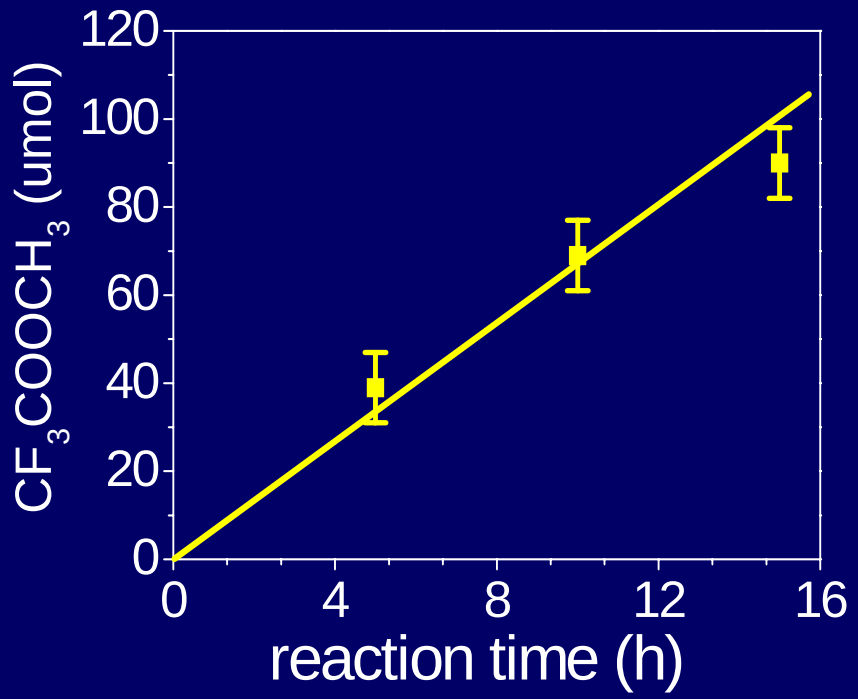


Combination of Pd^{2+} & Q:

Direct Conv

Run	Pd^{2+} (μmol)	Q (μmol)	$NaNO_2$ (μmol)	O_2 (atm)	CF_3COOCH_3 (μmol)	Pd^{2+a} (%)
1	10	0	0	0	9.5	--
2	10	20	0	0	30	--
3	10	50	0	0	55	--
4	10	100	0	0	60	92
5	10	20	0	1	34	15
6	10	50	0	1	67	27
7	10	20	20	1	69	98
8	5	20	20	1	32	95
9	20	20	20	1	106	54
10	10	50	100	1	70	95
11	10	100	100	1	67	98

CF_3COOH: 3 ml (39 mmol), CH_4: 54 atm (114 mmol), O_2: 1 atm (2 mmol), 80 °C, 10 h;
a: Remaining Pd^{2+} after the reaction.



The yield to CF_3COOCH_3 versus the reaction time.

- A catalytic process
- Q and NaNO2 key to prevent the precipitation of Pd
- Pd key, determining the TON
- TON: 0.7 h^{-1}

Further confirmation

Run	Pd^{2+} (μmol)	Q (μmol)	$NaNO_2$ (μmol)	O_2 (atm)	CF_3COOCH_3 (μmol)	Pd^{2+a} (%)
1	0	20	0	1	0	--
2	0	0	20	0	0	--
3	0	0	20	1	0	--

isotope experiments *GC-MS*

14 atm $^{13}CH_4$
40 atm $^{12}CH_4$

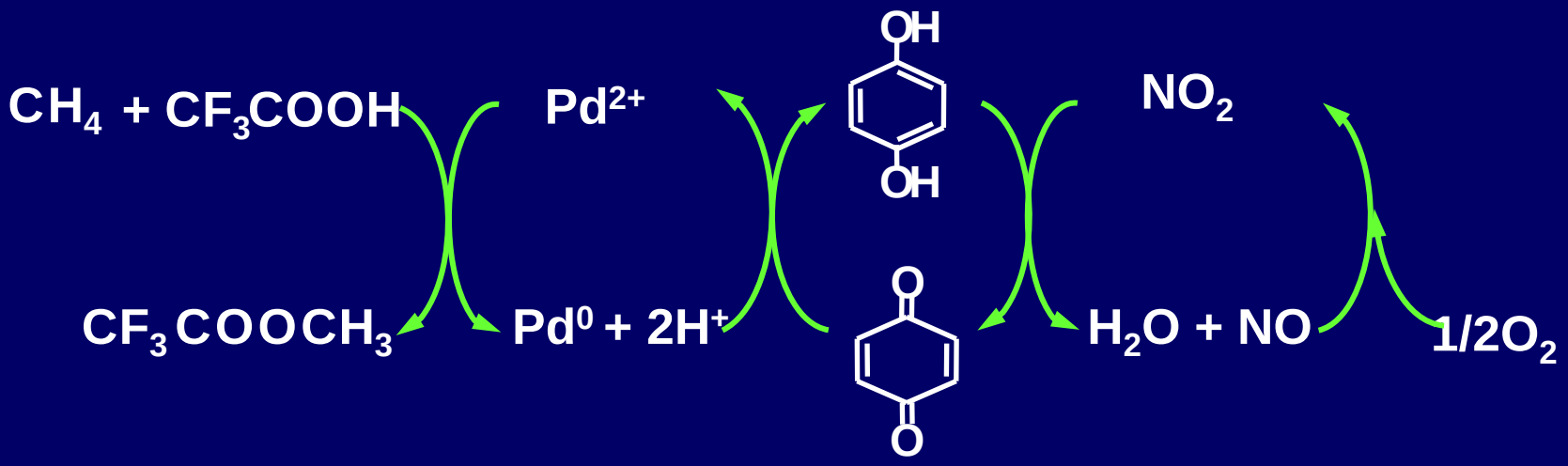
O_2

CF_3COOH

$-COO^{13}CH_3$ (m/e = 60)
$-COO^{12}CH_3$ (m/e = 59)

1 / 3

Low T selective oxidation of CH_4



$CH_4 + 1/2O_2 \rightarrow CH_3OH$

Catalytic process in one pot at 80 °C

O_2 as oxidant

TON = 0.7 h^{-1}

An, Pan, Bao et al. JACS 128 (2006) 16028.

直接法制甲醇的状况

直接法的优点：

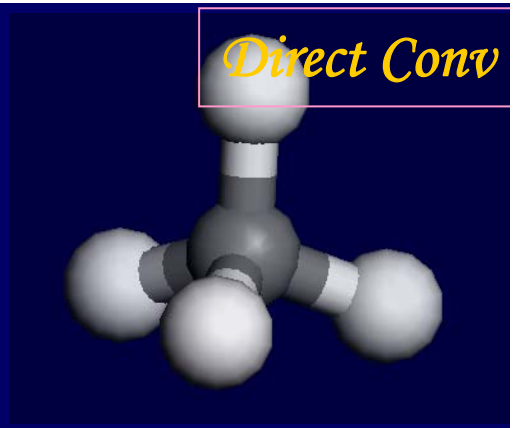
反应放热，从能耗上有利；工艺和设备简单。

工业化的要求：

单程转化率10～15%, 选择性 80 ～ 90%

目前水平：

转化率2 ～ 4%，选择性 40 ～ 70%



High Temperature Conversion of Methane to Aromatics

Typical HT Direct Conversion Process

- **Selective Oxidation**

$$CH_4 + O_2 \rightarrow CH_3OH + CO_2 + H_2O$$

- **Oxidative Coupling**

$$CH_4 + O_2 \rightarrow C_2H_x + CO_2 + H_2O$$

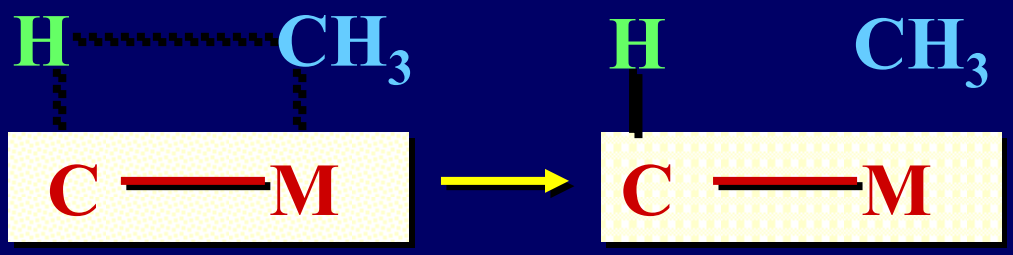
A New Route…

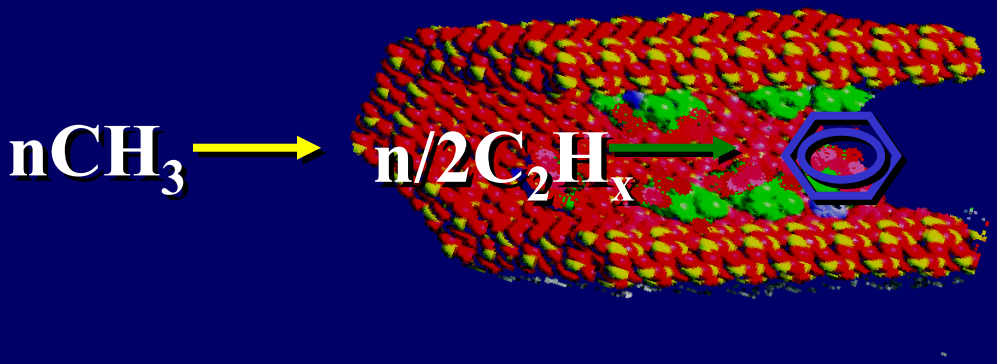
To higher hydrocarbons, without forming CO_2 ?

$$6CH_4 \xrightarrow{\text{Mo/HZSM-5}} C_6H_6 + 9H_2$$

Y. Xu, et al.,Catal. Lett. 21 (1993) 35-41

Conversion of methane to aromatics



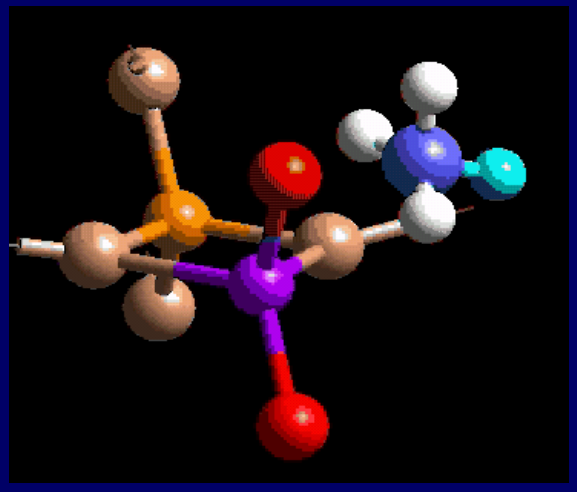


Catalysts Mo, W, Re…

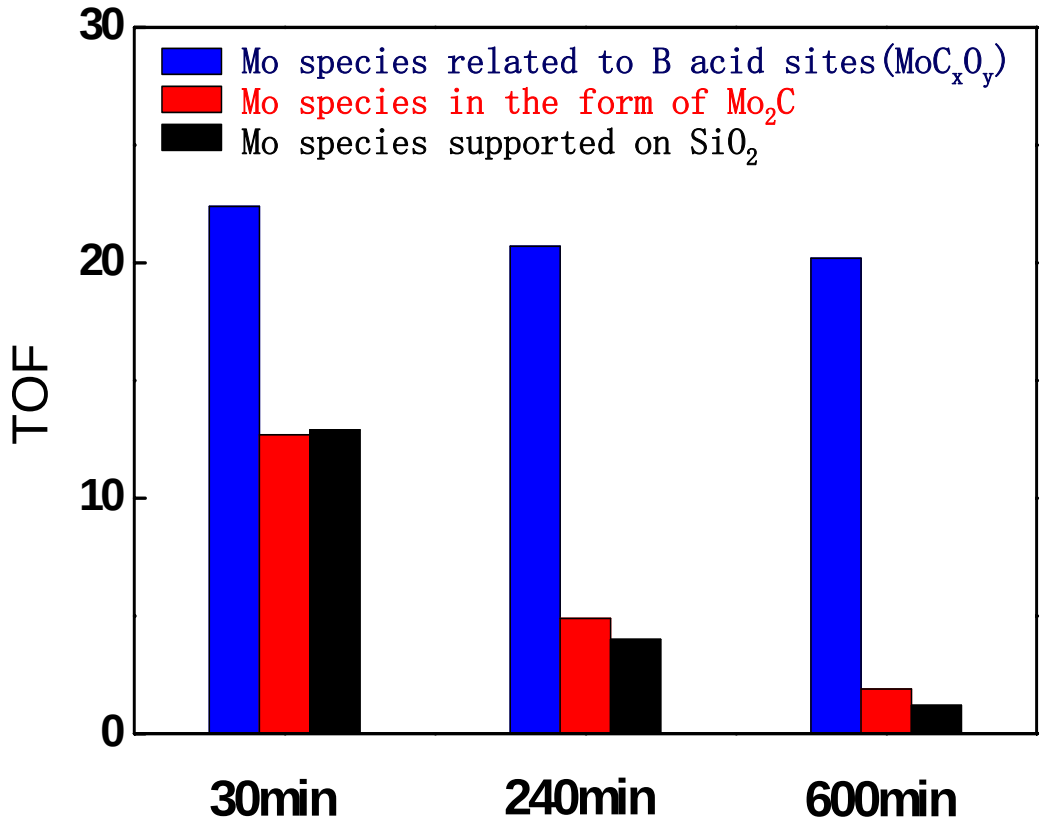
HZSM-5, MCM-22…

Bifunctionality of Mo/HZSM-5

Acidity and catalytically active sites



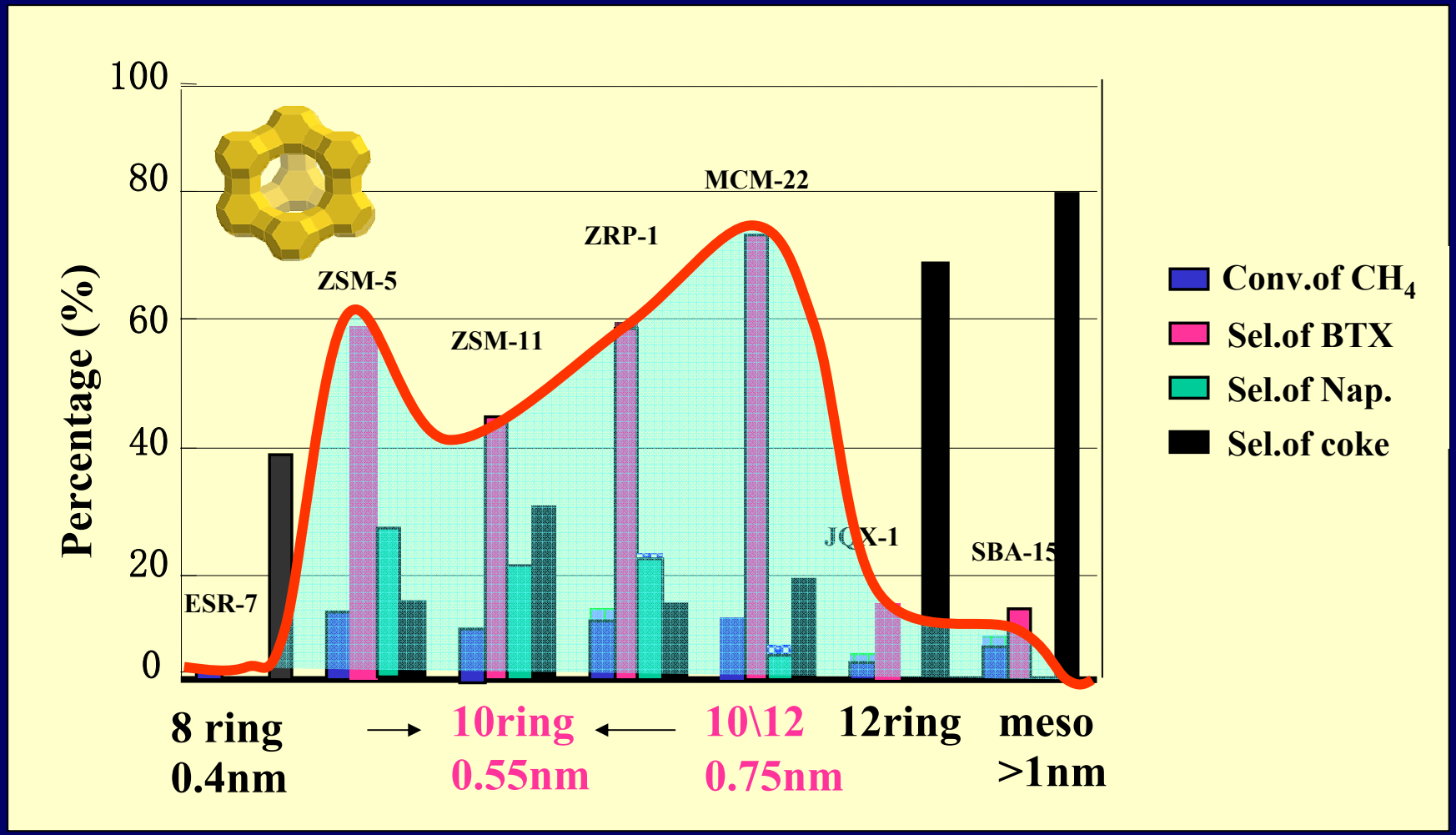
Aromatization over different Mo species



- **Highly active and stable MoC_xO_y;**
- **Low activity and stability of Mo_2C;**
- **0.5 acidic sites per unit cell required for aromatization.**

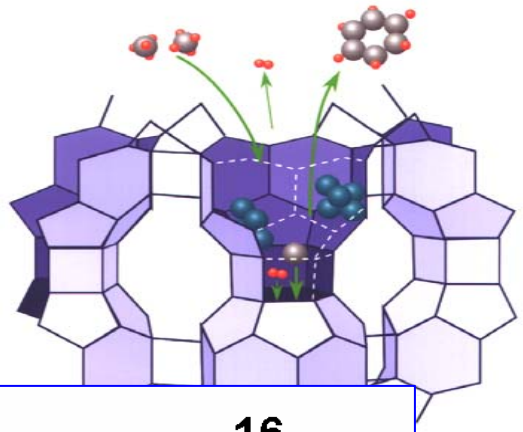
D. Ma, X. Bao et al., Chem. Eur. J. 8 (2002), Y. Xu, X. Bao, et al., J. Catal. 216 (2003)

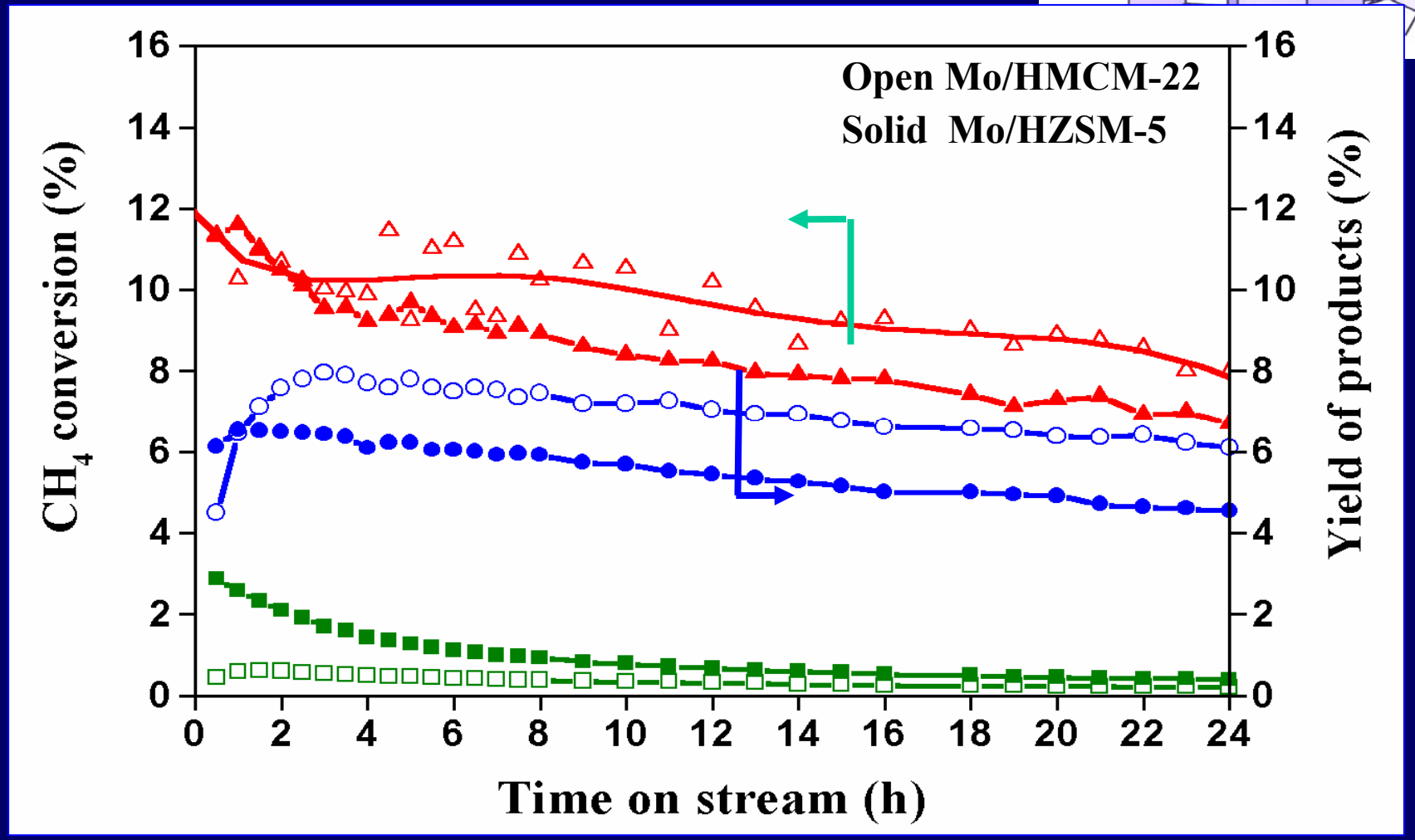
Effect of pore morphology



Applied Catalysis A-general 188 (1-2)，J. Catal. 216 (2003)

Comparison between Mo/ZSM-5 and Mo/MCM-22





Y. Shu, X. Bao et al., Catal. Lett. 70 (2000) 67.

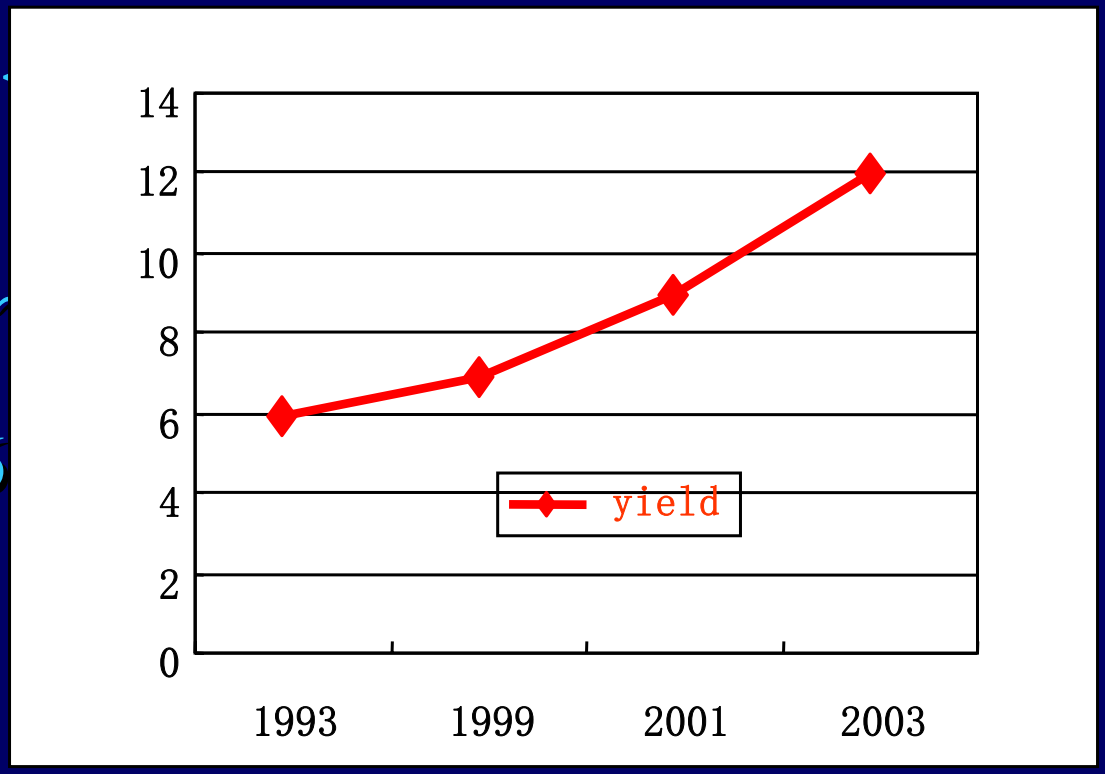
Pore morphology of carriers

Shape selectivity

- **size (**dynamic diameter of benzene (0.59 nm)
- **crossing with two-dimensional structure**
- **micro-mesoporous composite**

Achievements over the years

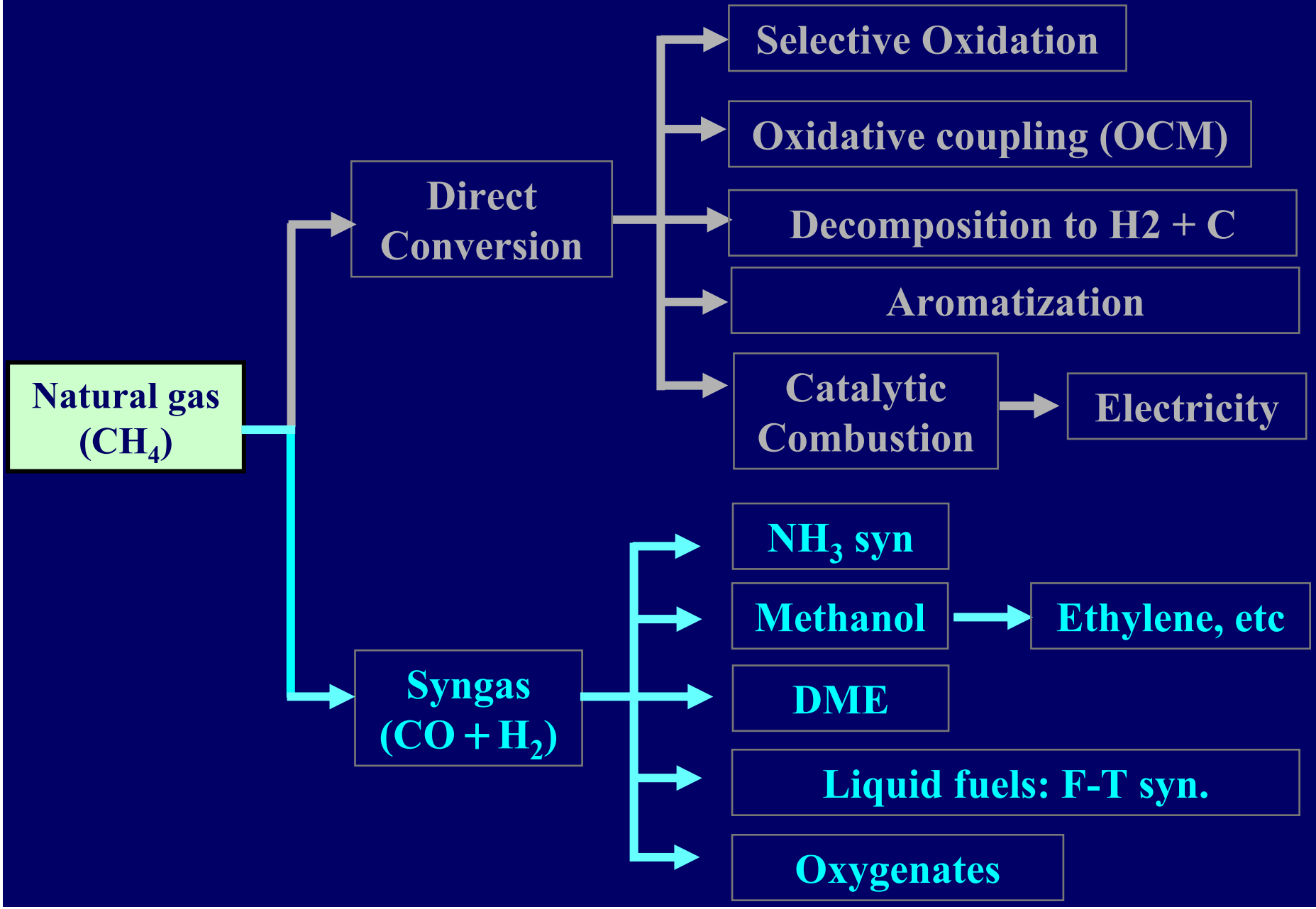
	before 99	2003
Convers		
Yield to Benzene		
Life time	6	



700°C , 1atm with a flow rate of 1500mL/gcat. h

Conversion of methane

Indirect Conv



Methane to syngas

$CH_4 + ½\ O_2 \rightleftharpoons CO + 2\ H_2$ $\quad \Delta H_{298K} = -35.5$ kJ/mol

$CH_4 + H_2O \rightleftharpoons CO + 3\ H_2$ $\quad \Delta H_{298K} = 206.29$ kJ/mol

$CH_4 + CO_2 \rightleftharpoons 2CO + 2\ H_2$ $\quad \Delta H_{298K} = 247$ kJ/mol

一般采用镍催化剂，反应温度700 °C以上，通过调节改变原料气比例和反应可以调节合成气的组成。

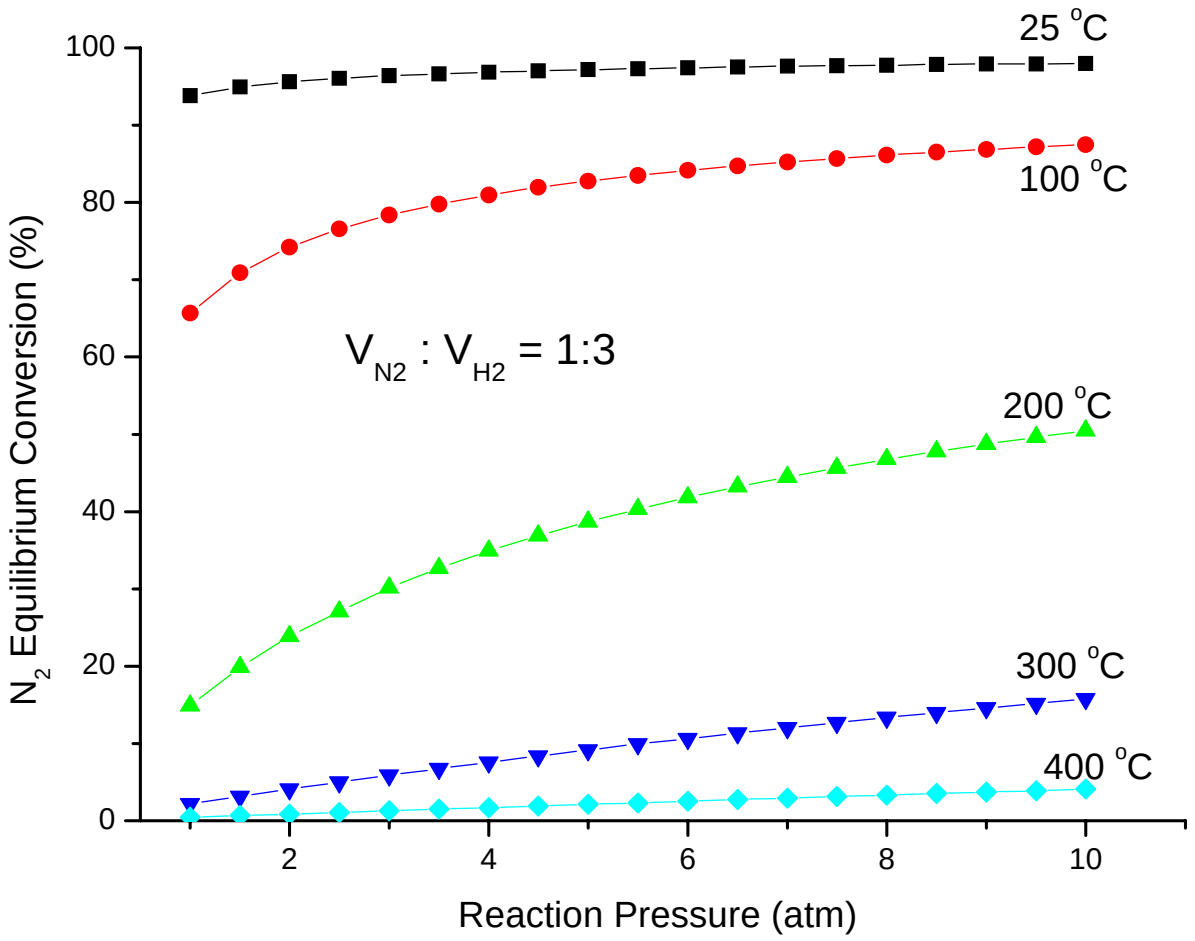
Syngas to ammonia

国际上合成氨的原料构成 / %

原料	1929	1939	1953	1965	1975	1980	1985	1990
焦炭、煤	65.2	53.6	37.0	5.8	9.0	5.5	6.5	13.5
焦炉气	15.8	27.1	22.0	20.0				
天然气	—	1.3	26.0	44.2	62.0	71.5	71.0	77.0
石脑油	—	—	—	4.8	19.0	15.0	13.0	6.0
重油	—	—	—	9.2	5.0	7.5	8.5	3.0
其他	19.0	18.0	15.0	16.0	5.0	0.5	1.0	0.5
合计	100	100	100	100	100	100	100	100

我国合成氨的原料构成 / %

原料	1983	1991	1994
焦炭、煤	65.4	67.0	64.0
焦炉气	0.8	1.3	1.2
天然气	19.2	17.5	18.9
石脑油	7.9	4.3	6.6
重油	5.9	9.4	8.7
其他	0.8	0.5	0.6
合计	100	100	100


25 °C
100 °C
200 °C
300 °C
400 °C
V_{N2} : V_{H2} = 1:3
N_2 Equilibrium Conversion (%)
Reaction Pressure (atm)
0
20
40
60
80
100
2
4
6
8
10

热力学平衡转化率

$$N2 + * \rightleftharpoons N_2* \quad (2)$$

$$N_2* + * \rightleftharpoons 2N* \quad (3)$$

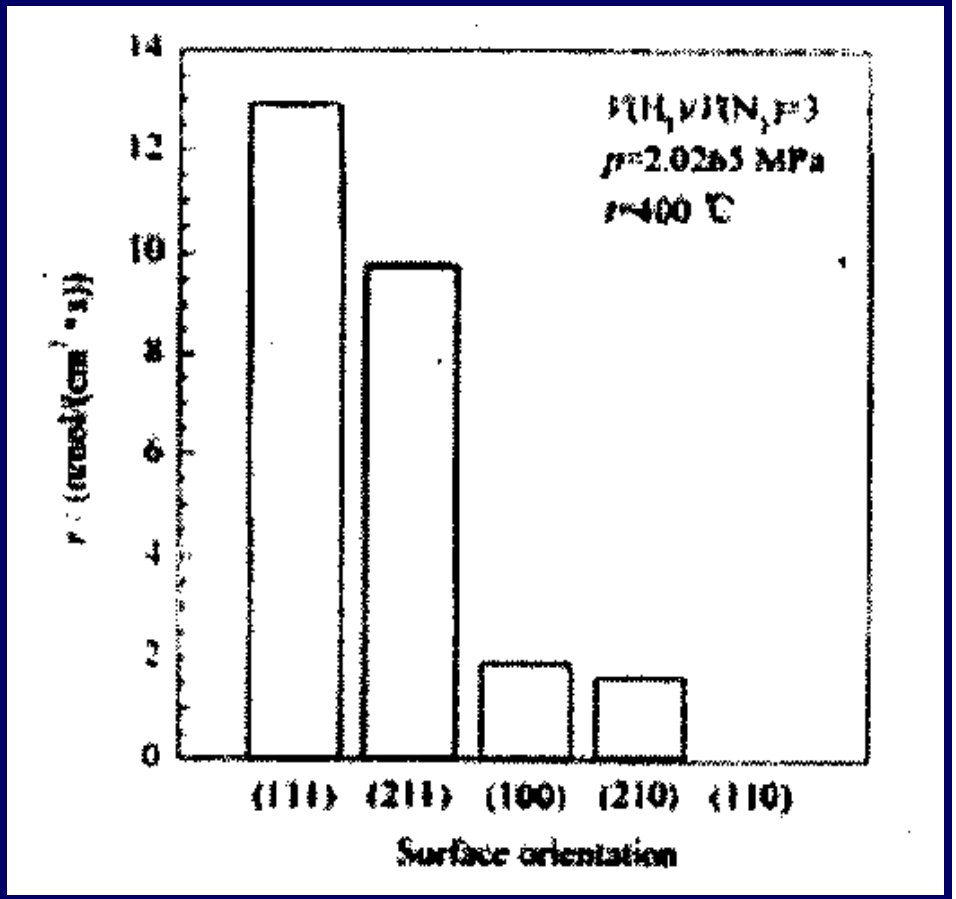
$$N* + H* \rightleftharpoons NH* + * \quad (4)$$

$$NH* + H* \rightleftharpoons NH_2* + * \quad (5)$$

$$NH_2* + H* \rightleftharpoons NH_3* + * \quad (6)$$

$$NH_3* \rightleftharpoons NH_3 + * \quad (7)$$

$$H2 + 2* \rightleftharpoons 2H* \quad (8)$$

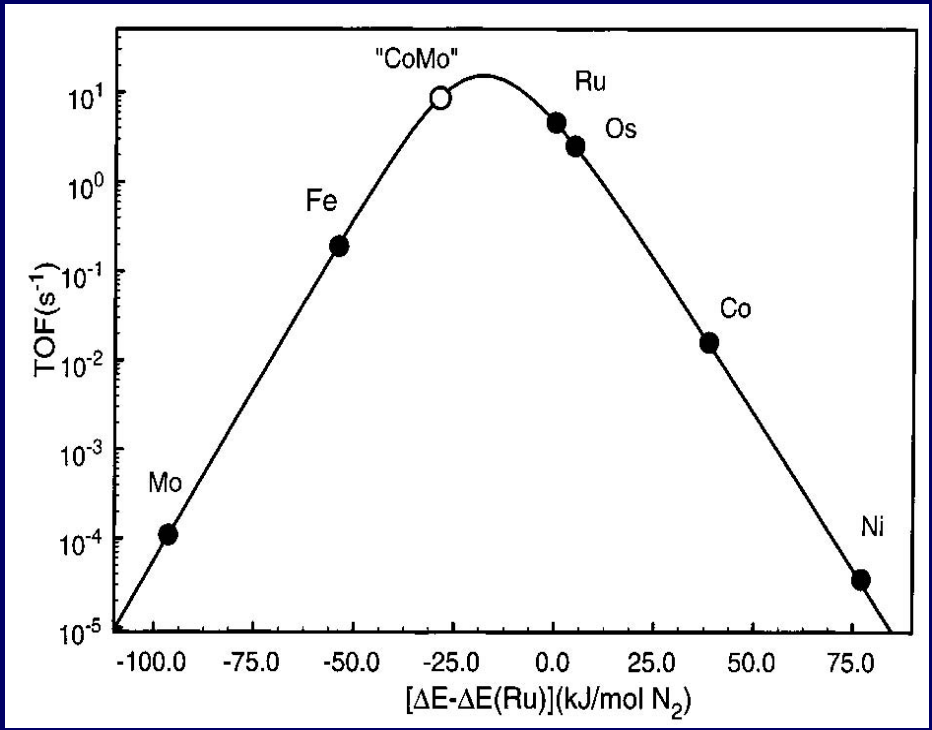


Fe (111) is 430 times more active than Fe (110) and Fe (100) is 30 times higher.

Al_2O_3 and K_2O are additives.

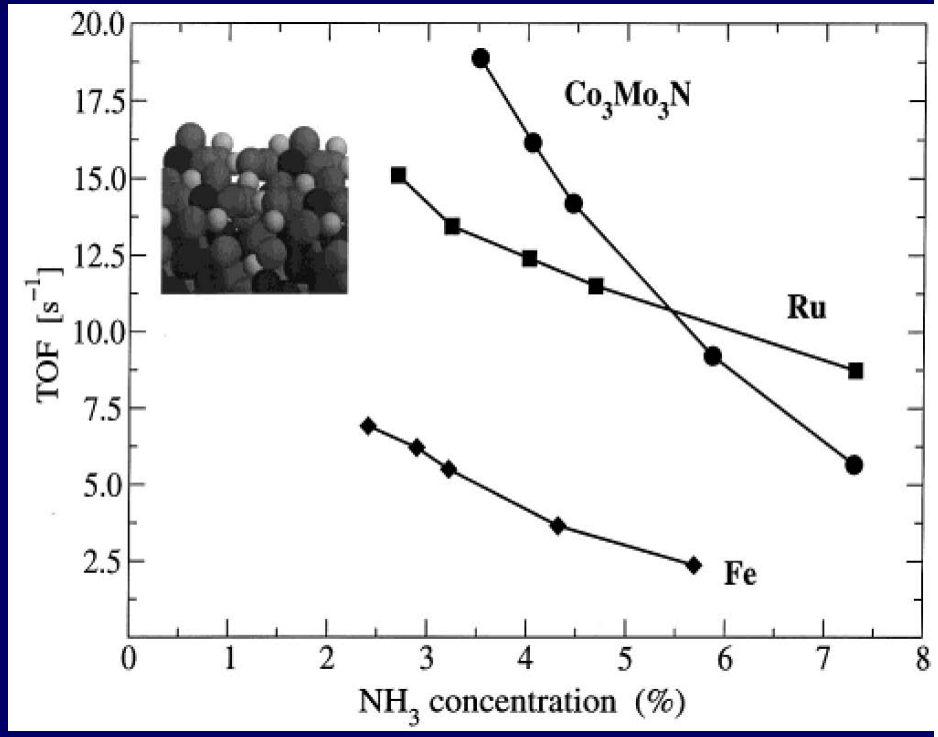
$A1_20_3$ 首先在表面生成与 Fe_30_4同晶的 $FeA1_20_4$,然后以这种新的表面为模板，使 α -Fe 晶体生长向(111)或(211)面定向暴露在反应混合物中

Recent progress in NH_3 synthesis



N_2在不同物质上的吸附热及其与氨合成活性的关系

Norskov, JACS 2001



Co_3Mo_3N, Ru, Fe催化剂的氨合成活性

Ba is a significantly better promoter for metals at the right-hand side of the volcano curve than for metals at the left side, whereas the opposite is true for the alkali metal promoters. JC 2003.

Effect of catalyst supports

Effect of various carbon-based supports on ammonia synthesis activity (ml NH_3/h g-cat)

Carbon supports	Reaction temperature (K)				
	573	623	633	653	673
C_{60-70}[a]			9.831	4.420	3.686
C_{60-70}[b]	3.37	13.3			9.66
Graphite[a]			5.161	7.578	11.057
MWNT[a]			18.597	38.434	45.873

K/Ru/C = 2/10/100, atmospheric pressure, $N_2/3H_2$ 30 ml/min, GHSV 637 h^{-1}.

Activity of K-promoted Ru catalysts supported on:

SiO_2< zeolite (NaX) < AC<γ-Al_2O_3 < CeO_2 < C_{60-70} < MWNT

Liao DW, Appl. Surf. Sci. 2001.

Syngas to methanol

methanol

Methanol (CH_3OH) is an alcohol fuel.

lower emissions, higher performance, and lower risk of flammability than gasoline.

Methanol is a fundamental raw material for chemicals.

The third most demanded raw materials for organics following olefins and aromatics, to HCHO, CH3COOH, MTBE, 醋酸酐，甲酸甲酯，二甲醚，乙二醇，乙醛，乙醇等。

Syngas to methanol

合成氨和甲醇是天然气化工中具有优势的大宗化学品领域，工艺成熟，但对新型高效催化剂和反应器的研究一直没有间断。

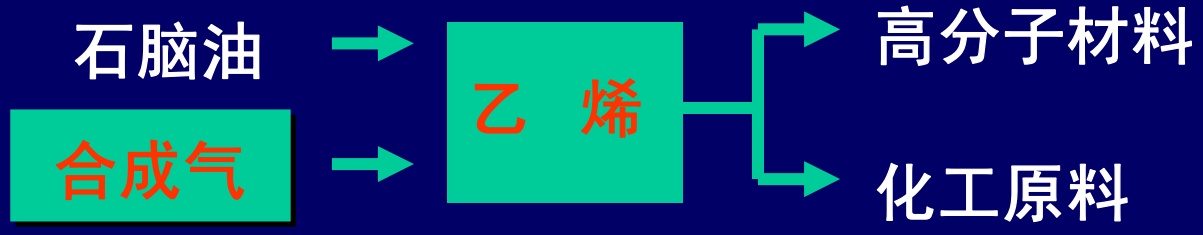
$$CO + 2H_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CH_3OH$$

第一套装置BASF在20世纪20年代建立。采用ZnO-Cr2O3为催化剂，反应温度350－450°C，反应压力为25－75MPa。

1966年英国ICI推出了低压合成甲醇，采用高活性的Cu基催化剂，压力5－10MPa。

MTO

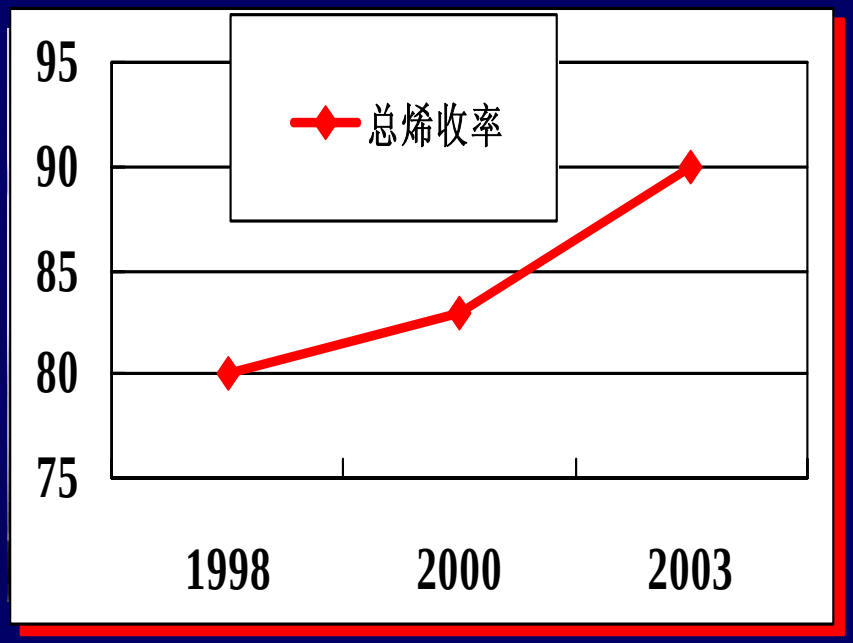
Syngas to olefin via methanol

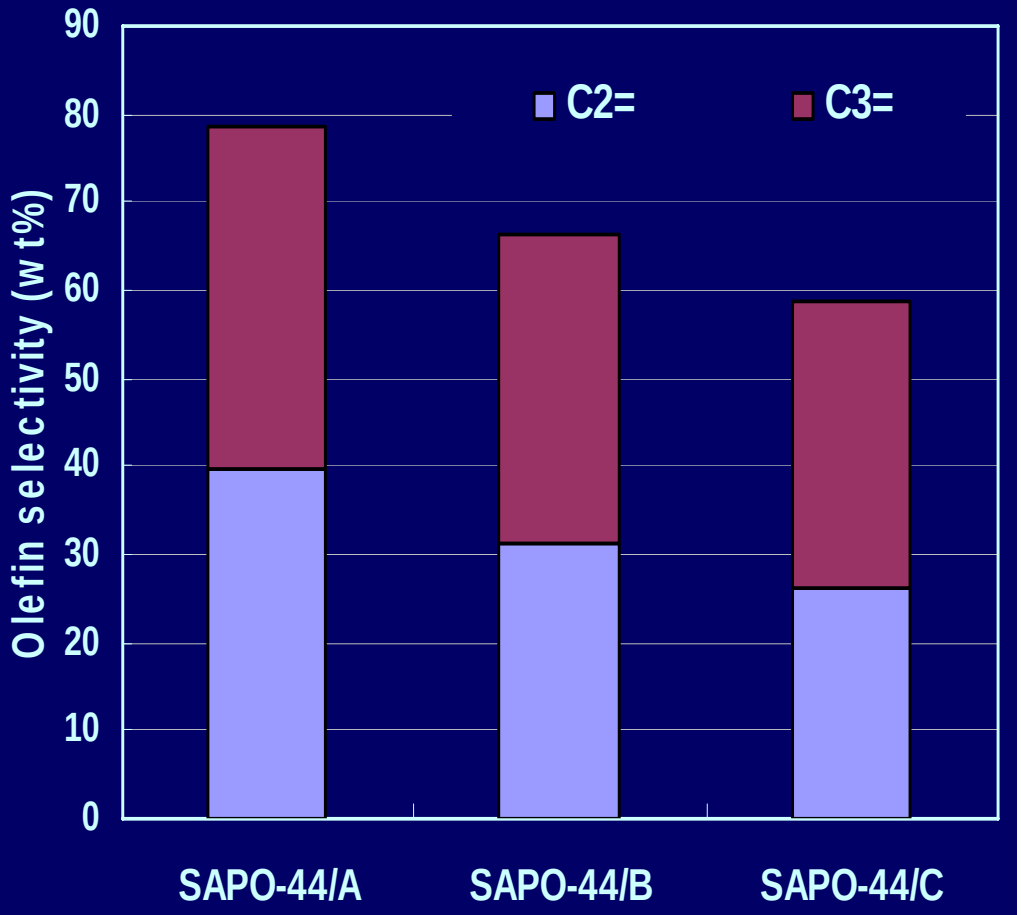


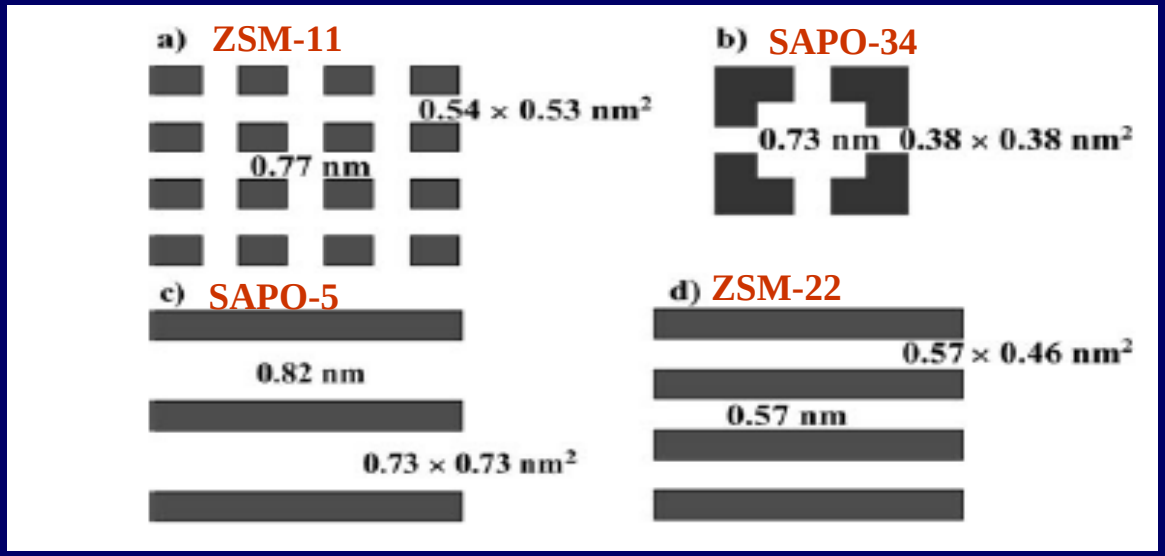
Demand of Ethylene

Year	Ethylene demand/Mton
1995	2. 39
1997	2. 70
2000	3. 50
2010	8. 00

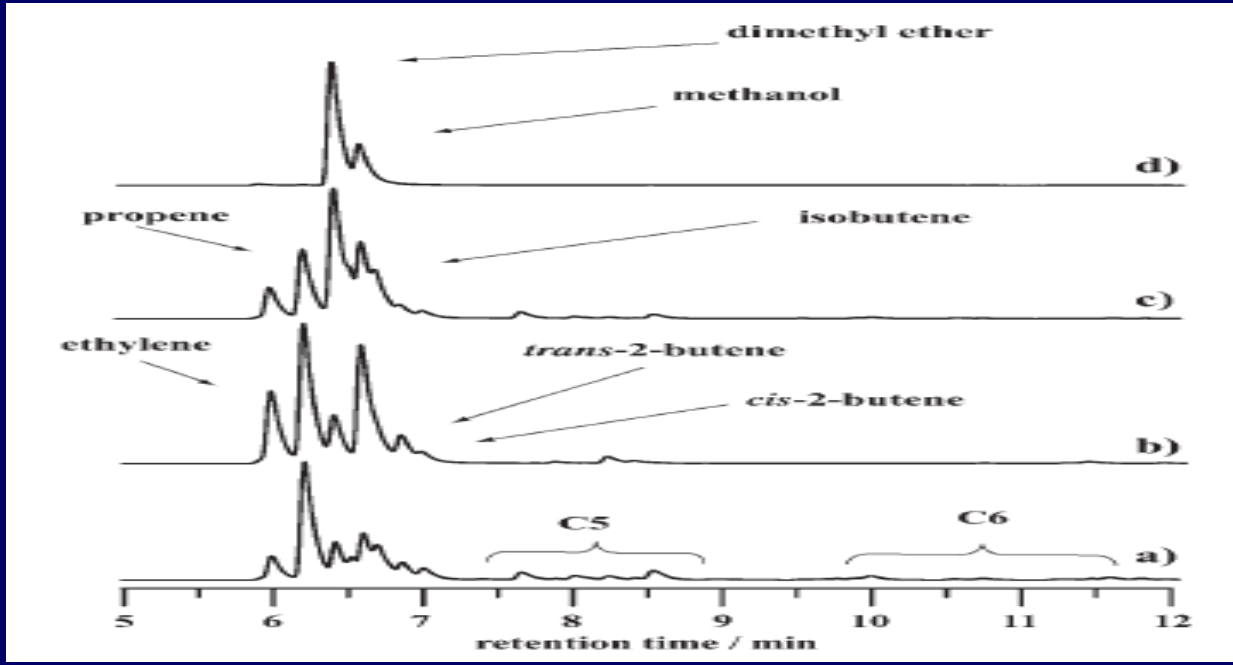
分子筛催化性能随结构的变化







Pulsed methanol reaction at 400 °C, GC analysis results



low

70%

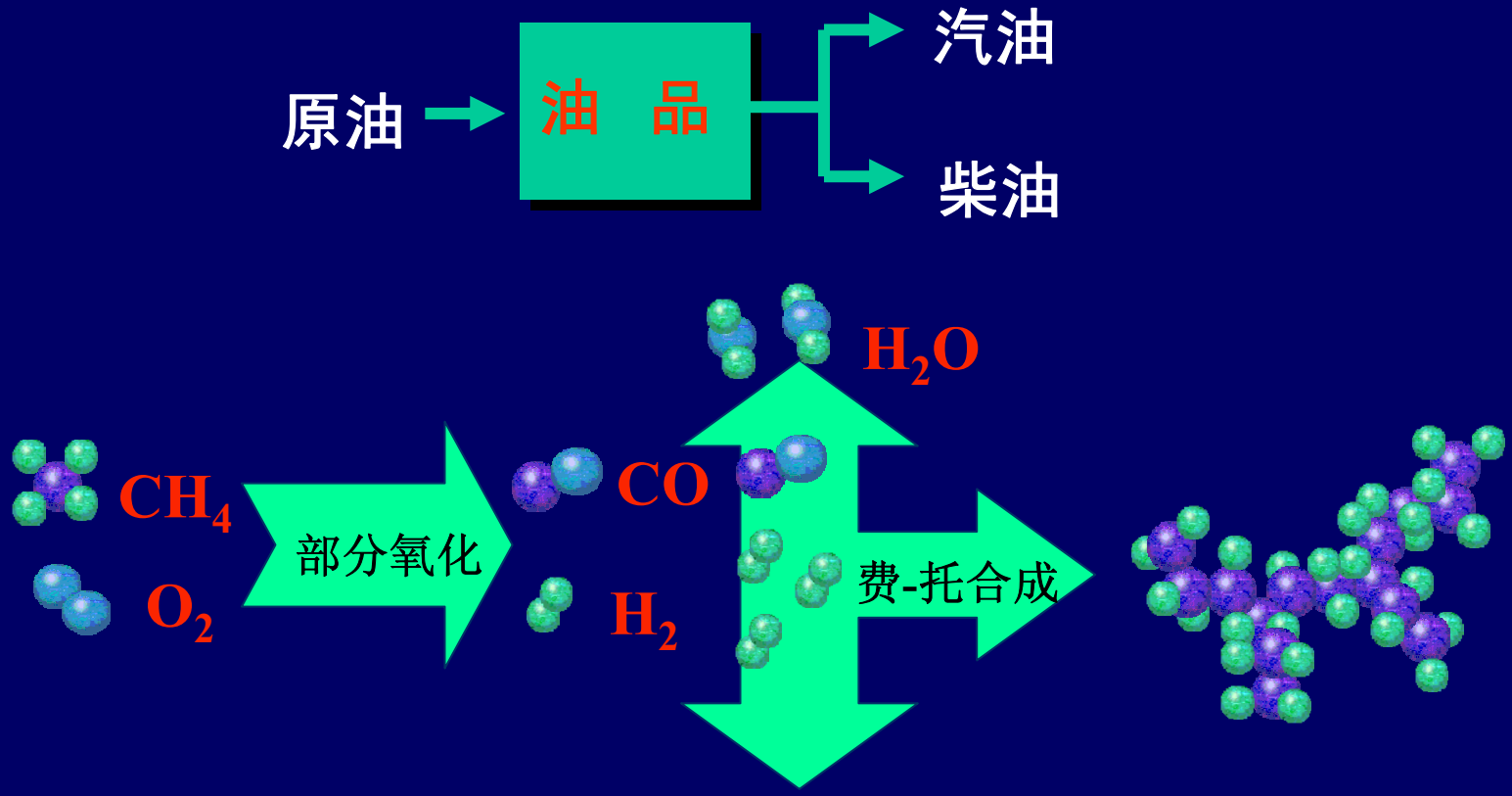
80%

90%

Angew. Chem. Int. Ed. 2006, 45, 6512 –6515

F-T

Fischer-Tropsch过程制备液体燃料



复杂的F-T反应：

$$nCO + (2n+1)H_2 \rightarrow C_nH_{2n+2} + nH_2O$$

$$nCO + 2nH_2 \rightarrow C_nH_{2n} + nH_2O$$

$$nCO + 2nH_2 \rightarrow C_nH_{2n+2}O + (n-1)H_2O$$

$$CO + H_2O \rightarrow CO_2 + H_2$$

还有：水煤气变换、醇脱水、烯烃加氢、异构化、析炭反应等

产物：低碳烃 ($C_1 \sim C_4$)、汽油 ($C_5 \sim C_{11}$)、柴油 ($C_{12} \sim C_{18}$)、蜡 (C_{19+}) 及醇、醛、酸、酯等。

F-T 合成油的历史和主要国际公司

- **1925, Fischer & Tropsch**
- **30年代中压合成，先后在德、美、法、前苏联、南非等建立合成油厂；**
- **60年代，石油开采，F－T失去活力**
- **70年代，石油资源紧张，F－T开发继续。**

Sasol（南非）;Shell （荷兰）； Exxon(美国);
Syntroleum （美国)； BP（英国）； Rentech （美国).

合成气制液体燃料

钴基催化剂－500小时稳定性试验结果：

甲烷选择性<6%

C_5^+选择性>90％

链增长几率>0.90

蜡油比在3.8左右

形成低甲烷重质烃固定床工艺与Shell 公司水平相当，高于其他国际公司

热力学…

$CO + H_2 \rightarrow CH_4 + H_2O$	$\Delta H_{298K} = -206 kJ/mol$
$CO + 5H_2 \rightarrow C_2H_6 + 2H_2O$	$\Delta H298K = -347 kJ/mol$
$2CO + 2H_2 \rightarrow CH_3COOH$	$\Delta H298K = -215 kJ/mol$
$2CO + 3H_2 \rightarrow CH_3CHO + H_2O$	$\Delta H298K = -457 kJ/mol$
$2CO + 4H_2 \rightarrow CH_3CH_2OH + H_2O$	$\Delta H298K = -256 kJ/mol$

强放热反应，在50－350 °C内，产物生成的概率是

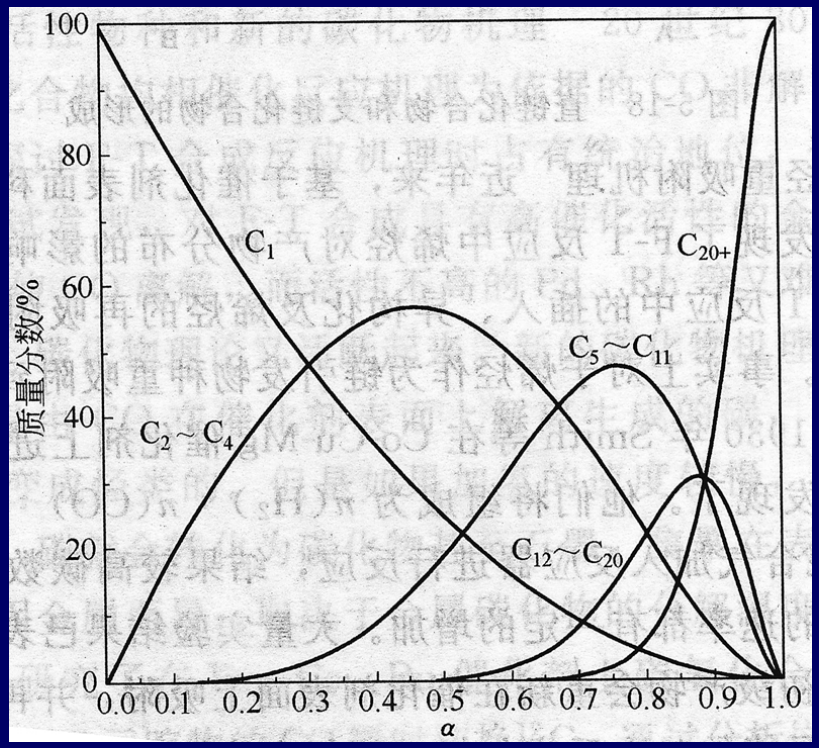
CH_4>饱和烃>烯烃>含氧化物。

实际产物分布与催化剂、反应条件等相关。

Anderson-Schulz-Flory 分布

F-T

$$m_n = (1-a)a^{n-1}$$

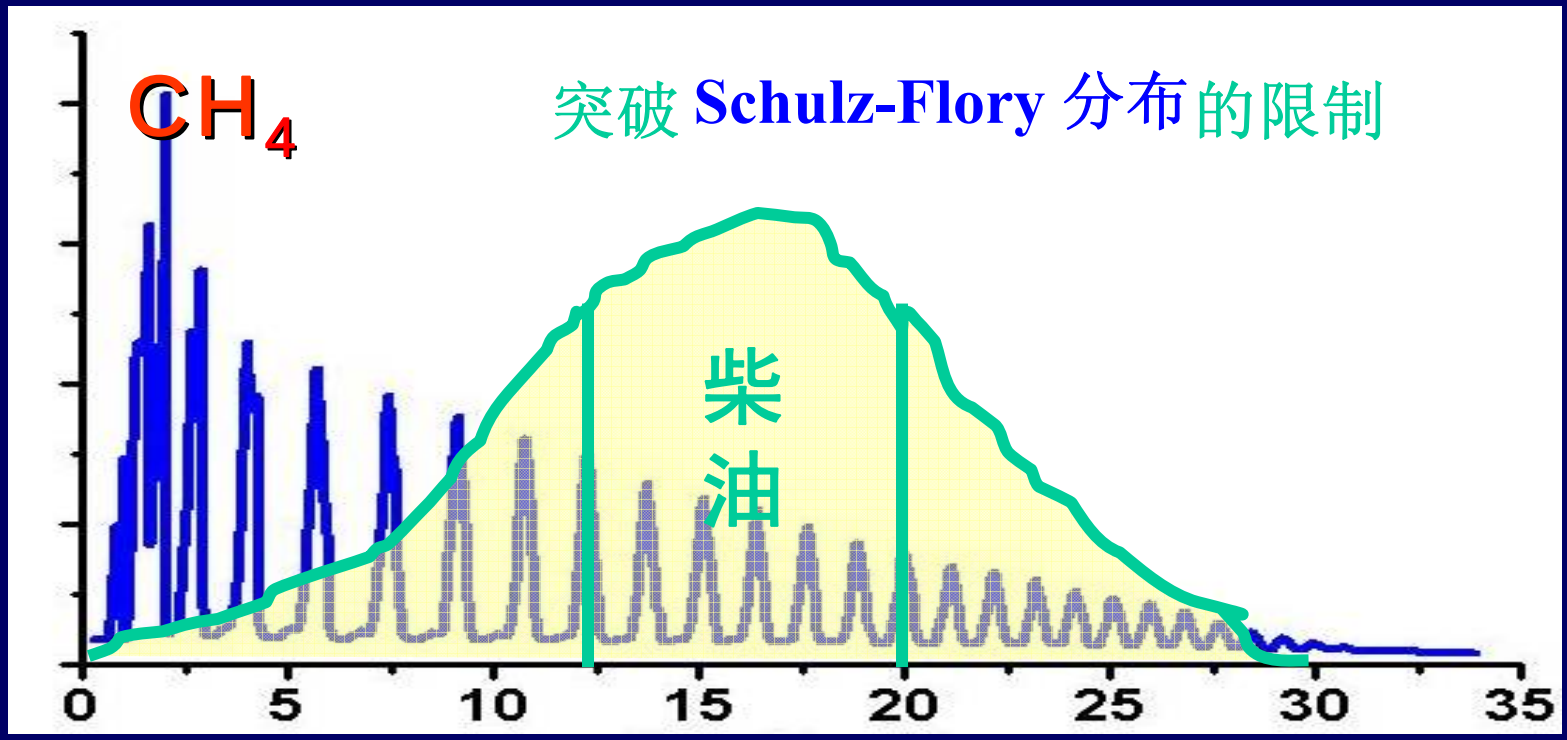


m： 具有n个碳原子的烃类产物的mol分数；

a： 碳链增长概率，取决于催化剂和反应条件，随温度升高而降低，随H_2/CO ratio而降。

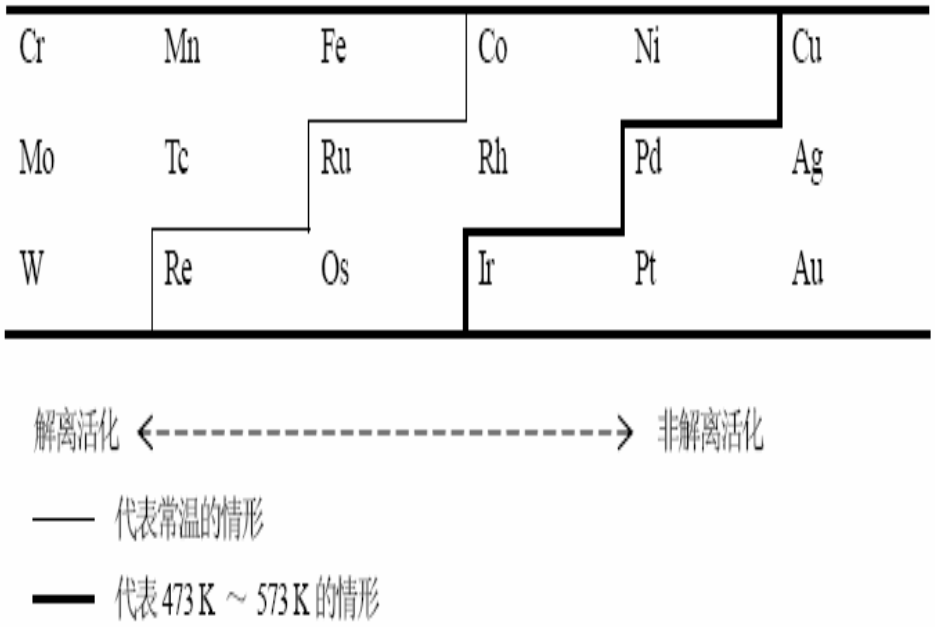
Ru-based cats	0.85 ~ 0.95
Co-based cats	0.70 ~ 0.80
Fe-based cats	0.50 ~ 0.70

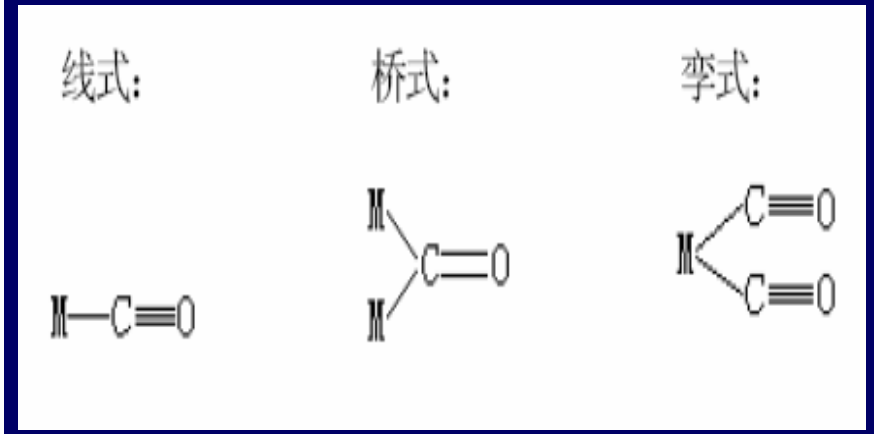
F–T过程中的产物控制



Product distribution

F-T





H_2 dissociative adsorption on most transition metal.

Cu (molecular adsorption) → methanol

Ni (dissociative adsorption) → CH_4

Co, Fe (strong bonding of Metal-C) → C_{2+}

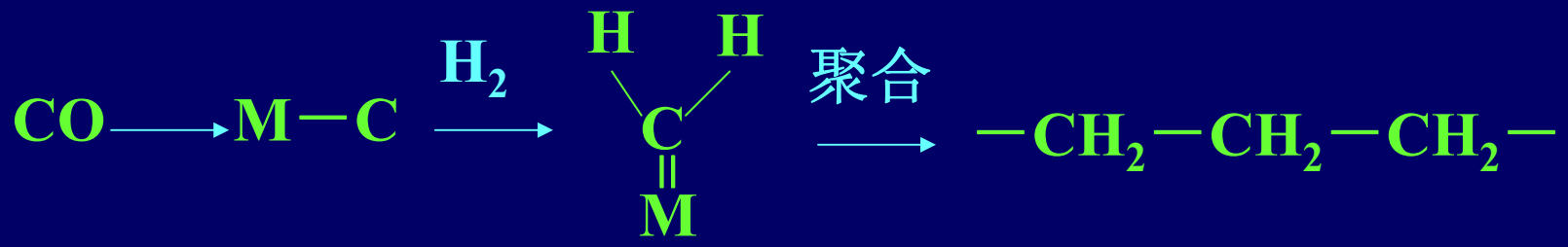
Reaction mechanisms under debate:

碳化物机理
含氧中间体机理
CO插入机理
双中间体机理
C2活性物种理论
烯烃重吸附理论

涉及：链引发（即反应开始时活泼的表面物种的形成）
链增长（碳链的形成）
链终止（最终产物的生成）

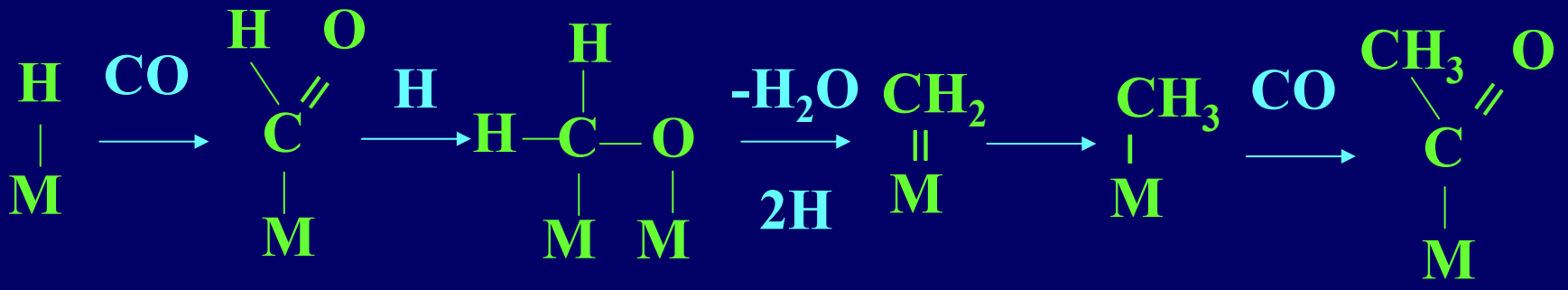
F-T

➢ 碳化物机理：



金属碳化物　　亚甲基

➢ CO插入机理：



➢ 烯烃重吸附机理：

烯烃重新在催化剂表面吸附，加氢生成烷烃、异构化、裂解反应、插入反应等。

Possibility of syngas to olefins?

Fe基催化剂特点:

常用的载体： Al_2O_3, SiO_2, zeolite, Activated carbon

助剂： K, Cu, Mn

优点： 低碳烯烃高选择性， 高辛烷值的汽油；

缺点： 对水煤气变换高活性， 高温时易积炭， 链增长能力差。

其它： 在反应中复杂的相组成变化。

注：燃烧的抗震程度以辛烷值表示， 辛烷值越高表示抗震能力愈高

Possibility of syngas to olefins?

Progress

Degussa,

Fe-ZnO-K_2O-V (or Mn, Ti) (100:10:4~8)

H_2/CO = 1/:1, 75% sel. $C_2^=$~$C_4^=$

Shell,

Fe-K-Cu-Zn/SiO_2 (25:5:10:20), mainly 58% C_{5+}

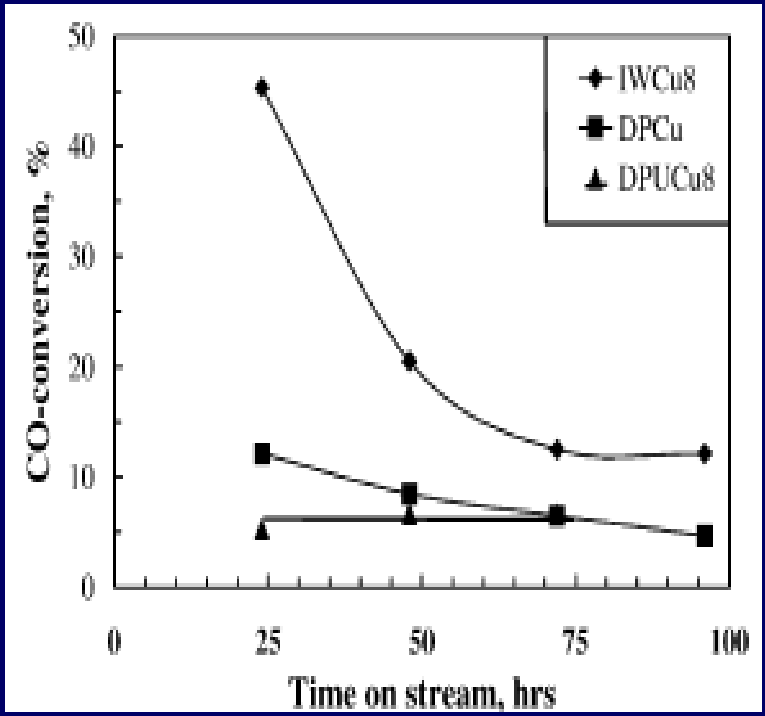
cracking in the following step

DICP

Yield of $C_2^=-C_4^=$ olefin at different operation conditions by direct conversion method ($H_2/CO = 2$)

Operation condition		$C_2^=-C_4^=$ yield (g/m^3)	
CO conversion (%)	$C_2^=-C_4^=$ selectivity (wt.%)	Single pass	Recycle
78.6	71.6	68.1	86.6
92.1	69.5	77.5	84.1
45.3	76.2	41.8	92.2

Use Carbon as support…



Catalysts	IW	DPU
CO rate[a]	−2.25E−0(	−1.71E−06
CO_2 rate (WGS)	6.97E−07	5.96E−07
FTS rate	1.55E−06	1.11E−06
Activity (μmol/s gFe	45.06	56.81
Alpha (α)	0.65	0.65
Selectivity (%)		
C_1	14.59	15.43
C_2–C_4	42.11	39.86
C_5–C_{11}	41.62	42.16
C_{12+}	1.69	2.55
$C_2{=}/(C_2 + C_2{=})$[b]	0.11	0.09
CO_2	6.83	9.81

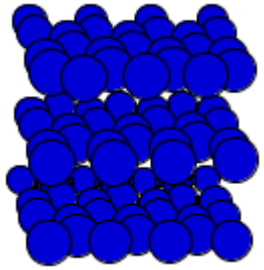
Steen, catal.today 2002

Coville, appl.catal. 2005

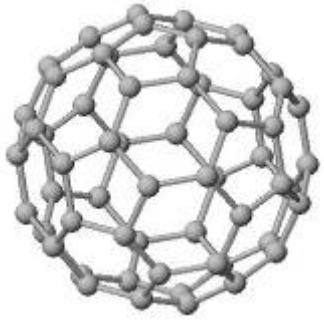
General finding: Lower CH_4 and higher olefin selectivity compared to other Fe/C cats. **Reasons** are not known yet.

碳材料家族

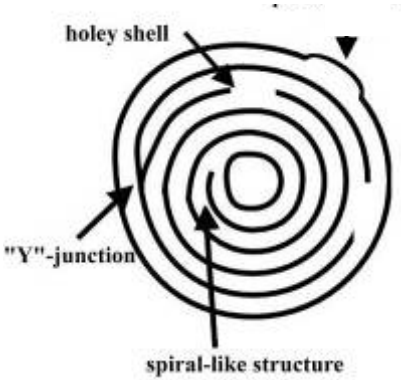
sp^2 bonding carbon



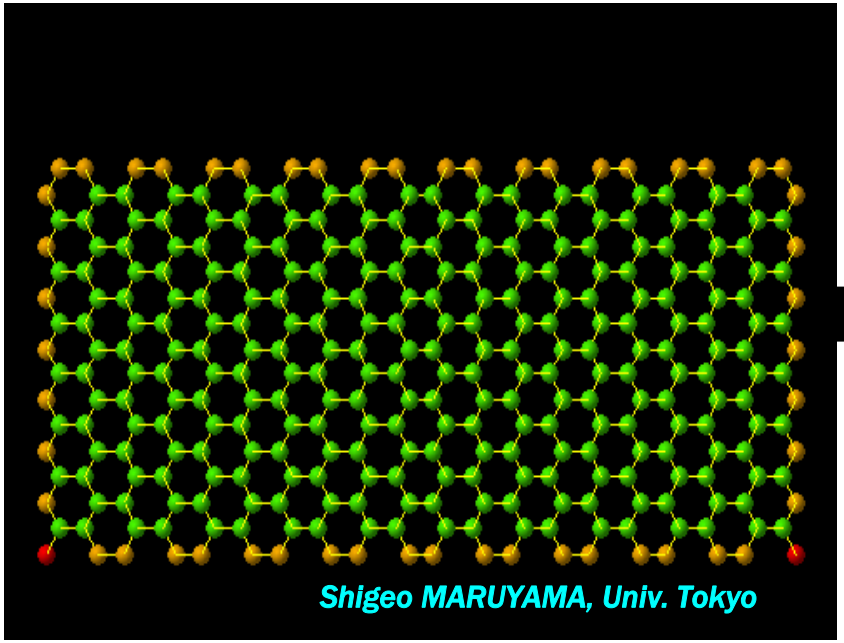
graphite

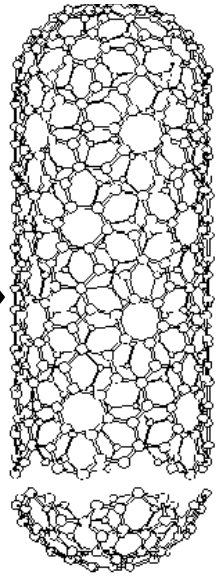


fullerene

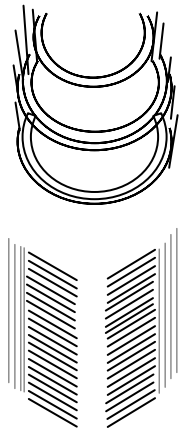


onion-like carbon (OLC)





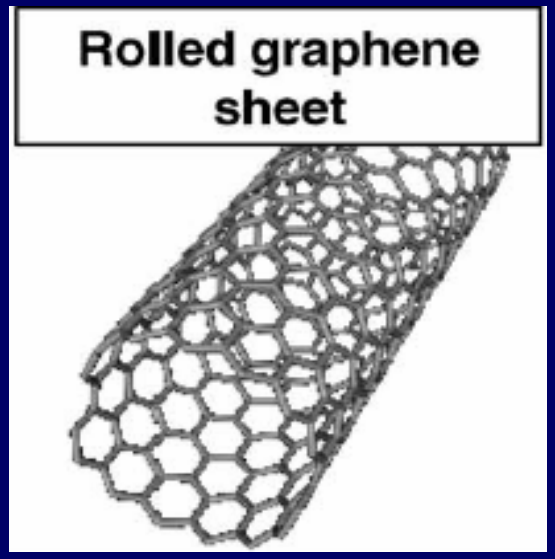
nanotube

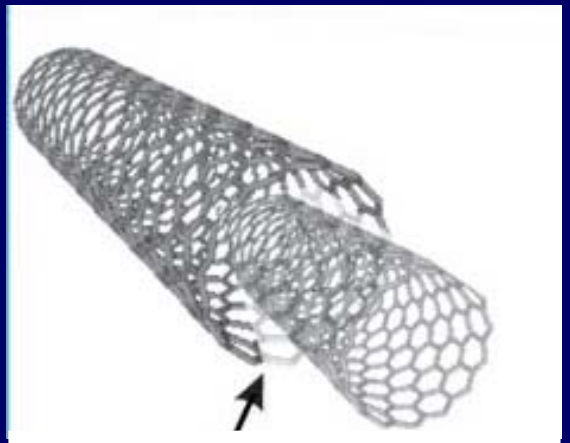


filaments

Carbon Nanotubes

F-T





Multiwalled CNTs

- Higher purity compared to AC
- Well defined morphology of nanochannels
  - Geometrical confinement;
- Graphitic layers
  - Thermal stability, electron conductivity;
- Unique H_2 adsorption and activation capability.

More examples

F-T

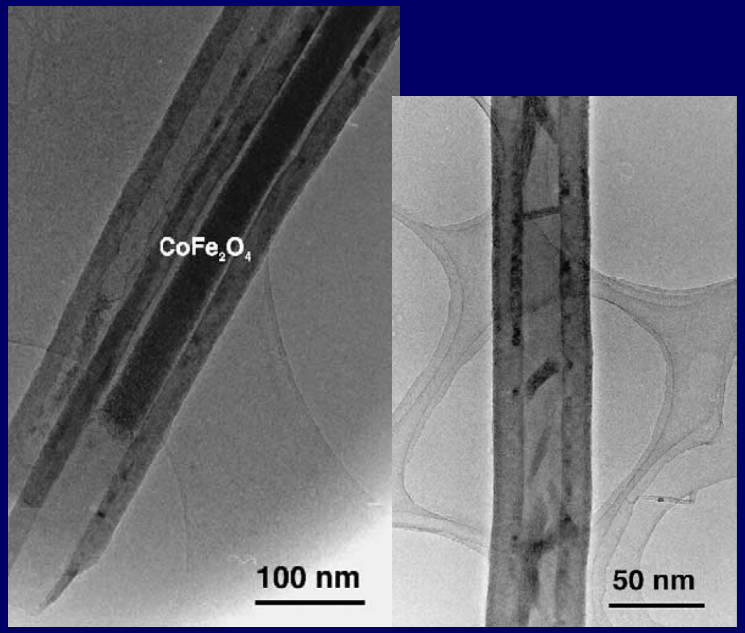
Cat.	Reaction	Comments	Ref.
Rh/MWNT	NO decomposition	Higher conversion than with a Rh/Al2O3	Luo et al., Catal Lett 2000
Co/MWNT	Cyclohexanol dehydrog.	Act. & sel. to cyclohexanone	Liu et al., Catal Lett 2001
Pt/CNT	Cathod catalyst	higher power density	Sun et al, Carbon 2002
Co/MWNT	F-T synthesis		Steen et al, Catal Today 2002; Bezemer et al., JACS 2006
Rh/MWNT	Cinnamaldehyde hydrog.	Act. 3 times higher than Rh/C catalyst	Giordano et al., Eur J Inorg Chem 2003
Pt/CNT	Nitrobenzen hydro.	High act. compared AC	Li et al., J Mol Cat 2005

F-T

Why encapsulates?

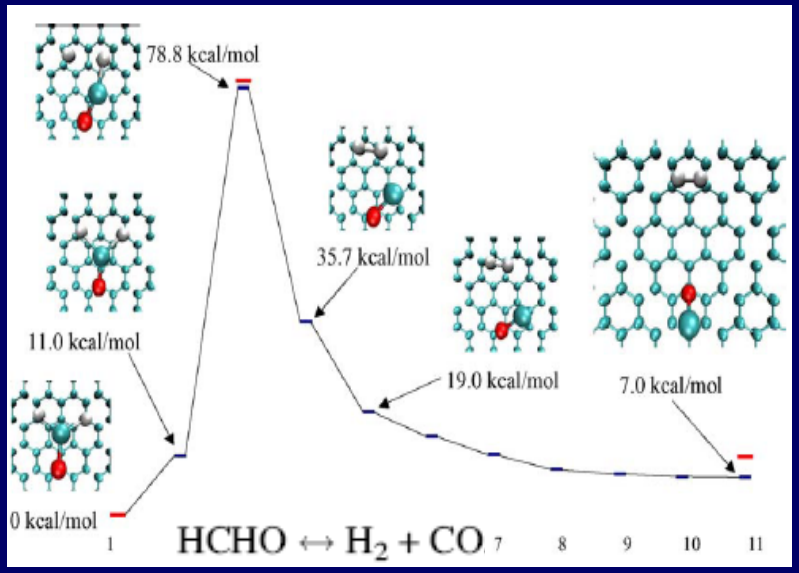
Geometrical confinement

Curvature causes binding energy: Interior > groove sites > external. [Yates, Chem Phys Lett 383 (2004) 314]



Template for Beta-zeolite synthesis and $CoFe_2O_4$

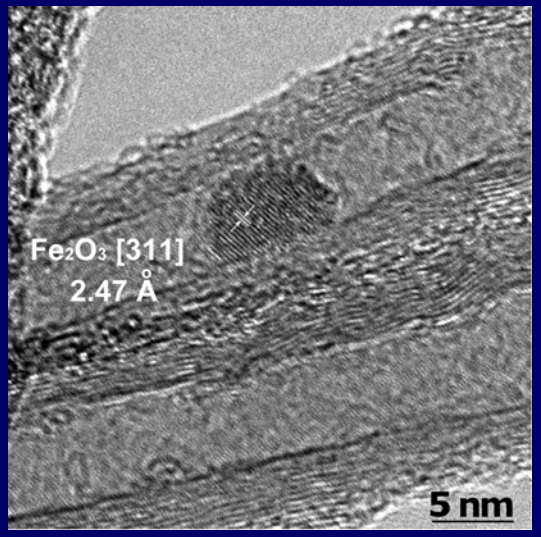
Nhut et al., Appl. Catal. 2003, 254, 345

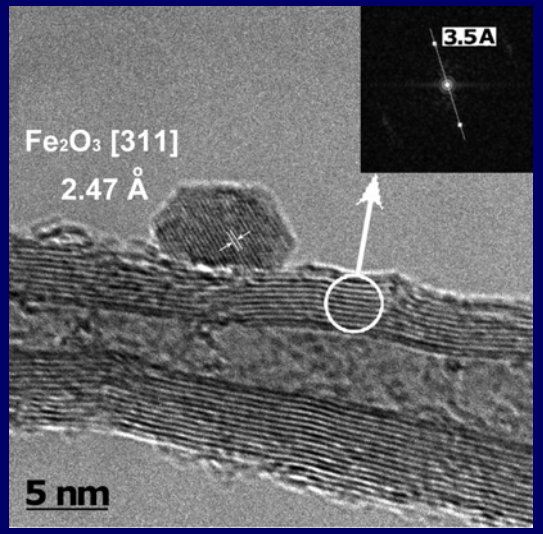


Theoretical calculation: Reaction in CNT channels

Santiso et al. Appl.Surf.Sci.2005, 252, 766

F-T





Introduction of Fe_2O_3 nanoparticles into carbon nanotube channels

(a) Fe_2O_3 nanoparticles inside nanotubes; (b) Fe_2O_3 nanoparticles dispersed on its outer wall

Chen, Pan, Bao et. al., JACS, 2006, 128, 3136.

Syngas directly to olefin

F-T

物理化学性质的表征并与反应活性关联

- **TEM, SEM等**

  → 形貌，如粒子大小，分散情况等；

- **XRD, Mossobauer谱，XPS**

  →制备过程和反应前后催化剂组成、晶相和价态的变化；

- **TPR等技术**

  →表面铁氧化物中在载体表面还原的难易程度，金属－载体的相互作用，吸附脱附行为等；

- **FT-IR，Raman**

  →表面活性物种；

- **XAFS**

  →晶体周围环境的信息，如金属原子的配位数等…

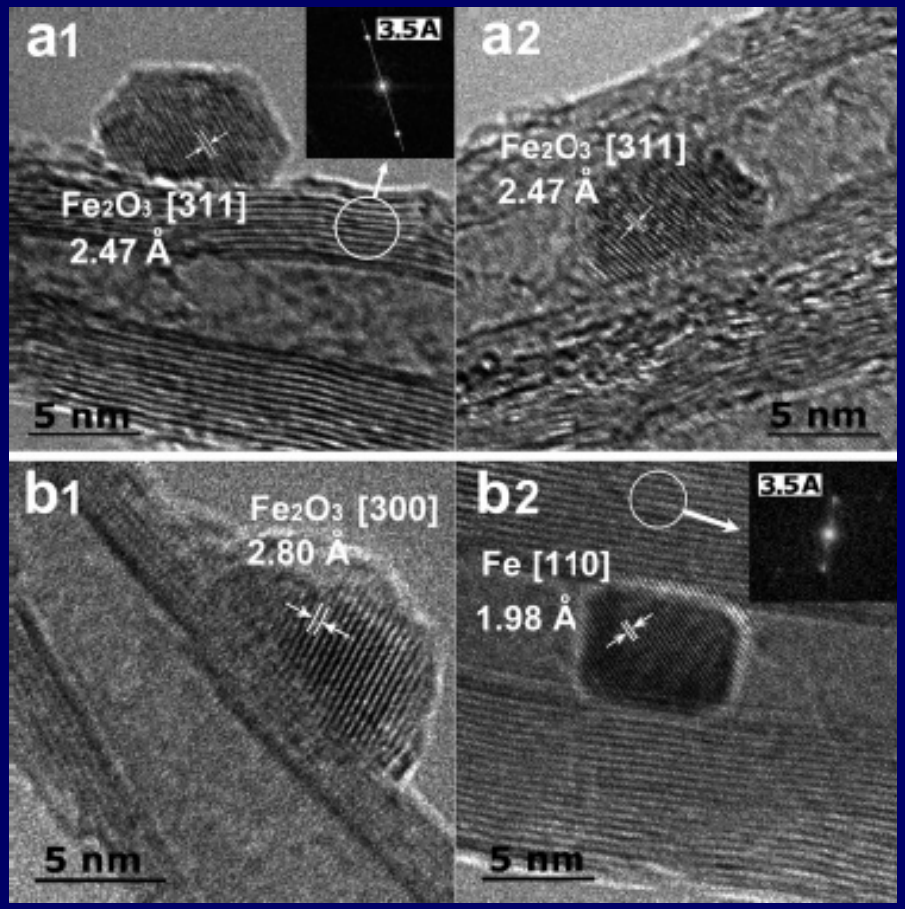
Fe_2O_3@CNTs encapsulates

F-T

TEM Images

RT

600℃



Chen, Pan, Bao et. al., JACS, 2006, 128, 3136.

Autoreduction of Fe_2O_3@CNTs with varying diameters

F-T

$$Fe_2O_3@CNTs \xrightarrow{T} Fe@CNTs + CO$$

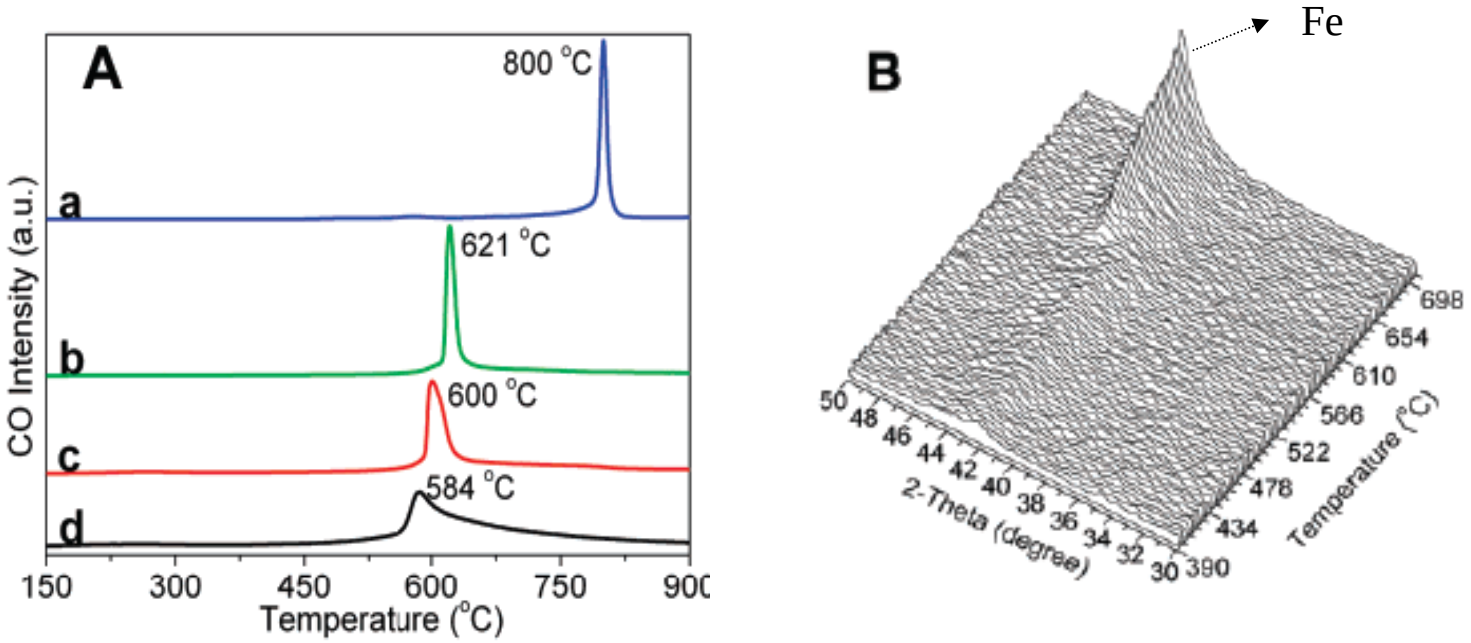


Figure 3. (A) CO evolution during TPR of the Fe_2O_3/CNT composites. (a) Fe_2O_3-*out*-CNT(4); (b) Fe_2O_3-*in*-CNT(8); (c) Fe_2O_3-*in*-CNT(4); (d) Fe_2O_3-*in*-CNT(2). (B) the chemical transformation of Fe_2O_3-*in*-CNT(2) monitored by in situ XRD.

Chen, Pan, Bao JACS, article, 2007, 129, 7421

Fe_2O_3@CNTs encapsulates

F-T

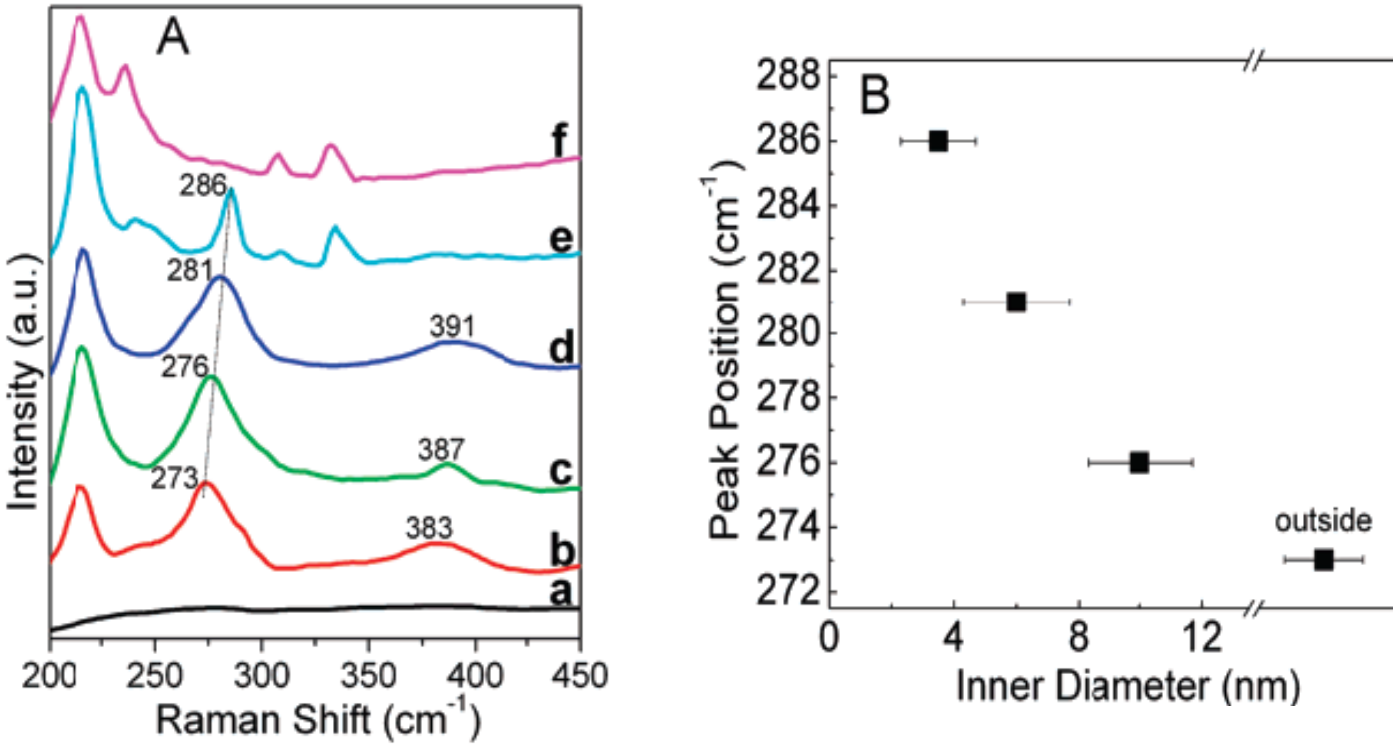


Figure 2. (A) Room-temperature Raman spectra of the Fe_2O_3 particles encapsulated within various CNT channels. (a) Blank CNT(4); (b) Fe_2O_3-*out*-CNT(4); (c) Fe_2O_3-*in*-CNT(8); (d) Fe_2O_3-*in*-CNT(4); (e) Fe_2O_3-*in*-CNT-(2); (f) blank CNT(2). (B) Raman shift versus the inner diameter of CNTs.

Fe-O mode: Bulk Fe_2O_3 at 283 cm^{-1}

F-T

Fe_2O_3@CNTs encapsulates

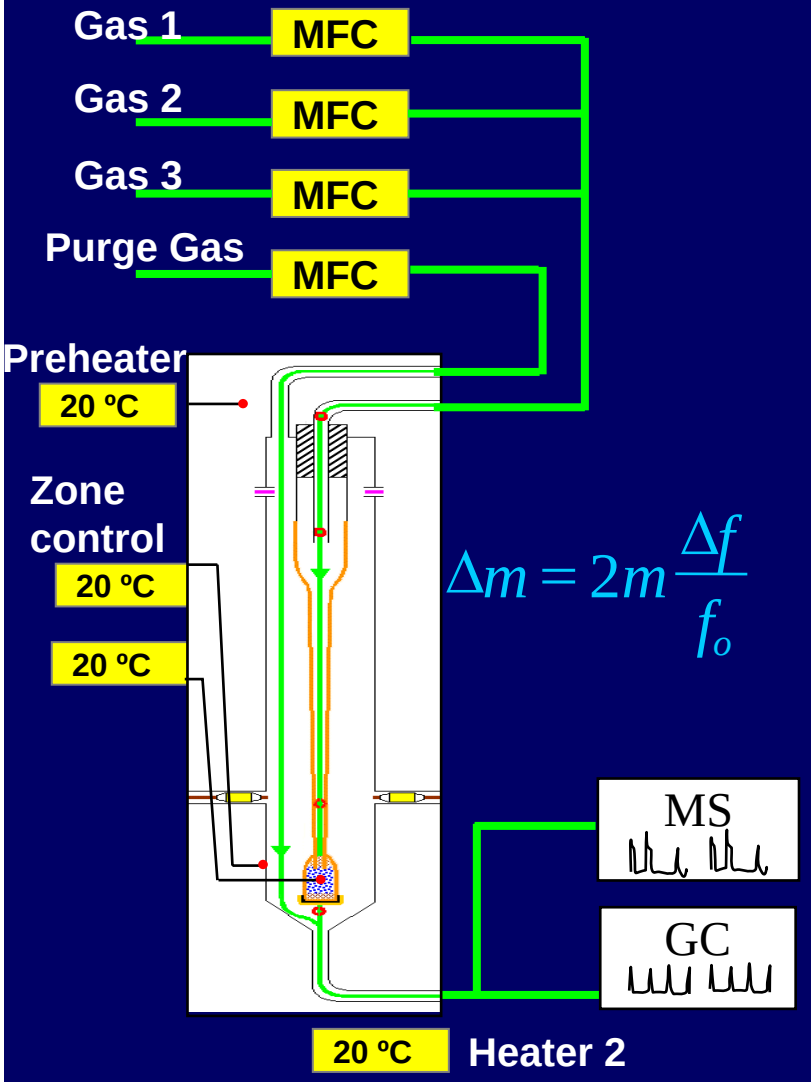
Table 1. Autoreduction Temperatures (*T*) of the Encapsulated Fe_2O_3 within Various CNTs Detected by TPR, in situ XRD, and Raman Spectroscopy

sample	*T* by TPR (°C)	*T* by XRD (°C)	*T* by Raman (°C)
Fe_2O_3-*in*-CNT(8)	621	~ 615	~ 620
Fe_2O_3-*in*-CNT(4)	600	~ 600	~ 610
Fe_2O_3-*in*-CNT(2)	584	~ 590	~ 590

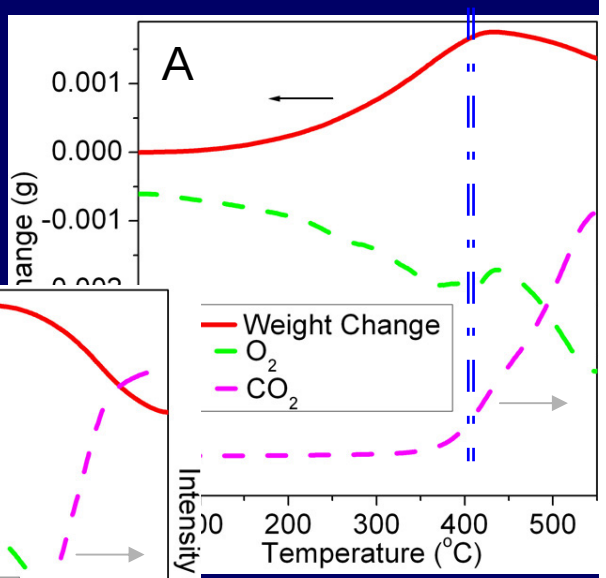
Chen, Pan, Bao JACS, article, 2007, 129, 7421

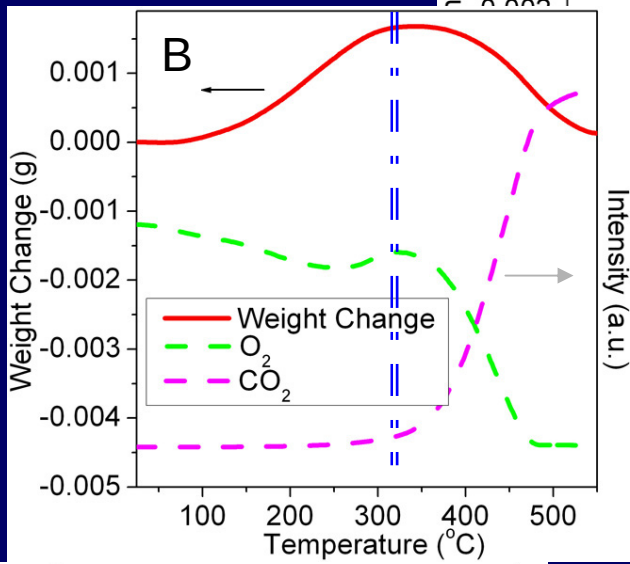
Oxidation of Fe@CNT encapsulates

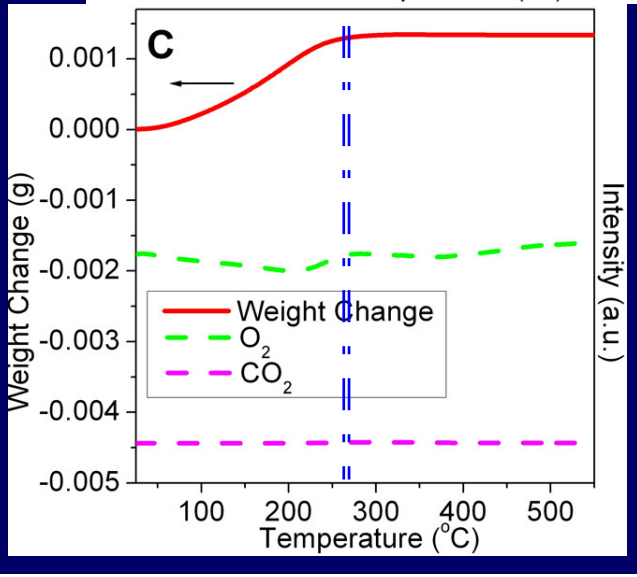
$$Fe@CNTs + O_2 \rightarrow Fe_2O_3@CNTs$$



$$\Delta m = 2m\frac{\Delta f}{f_o}$$







A: Fe-*in*-CNTs;

B: Fe-*out*-CNTs;

C: Fe-*in*-SBA-15

Transformation monitored in situ by XRD

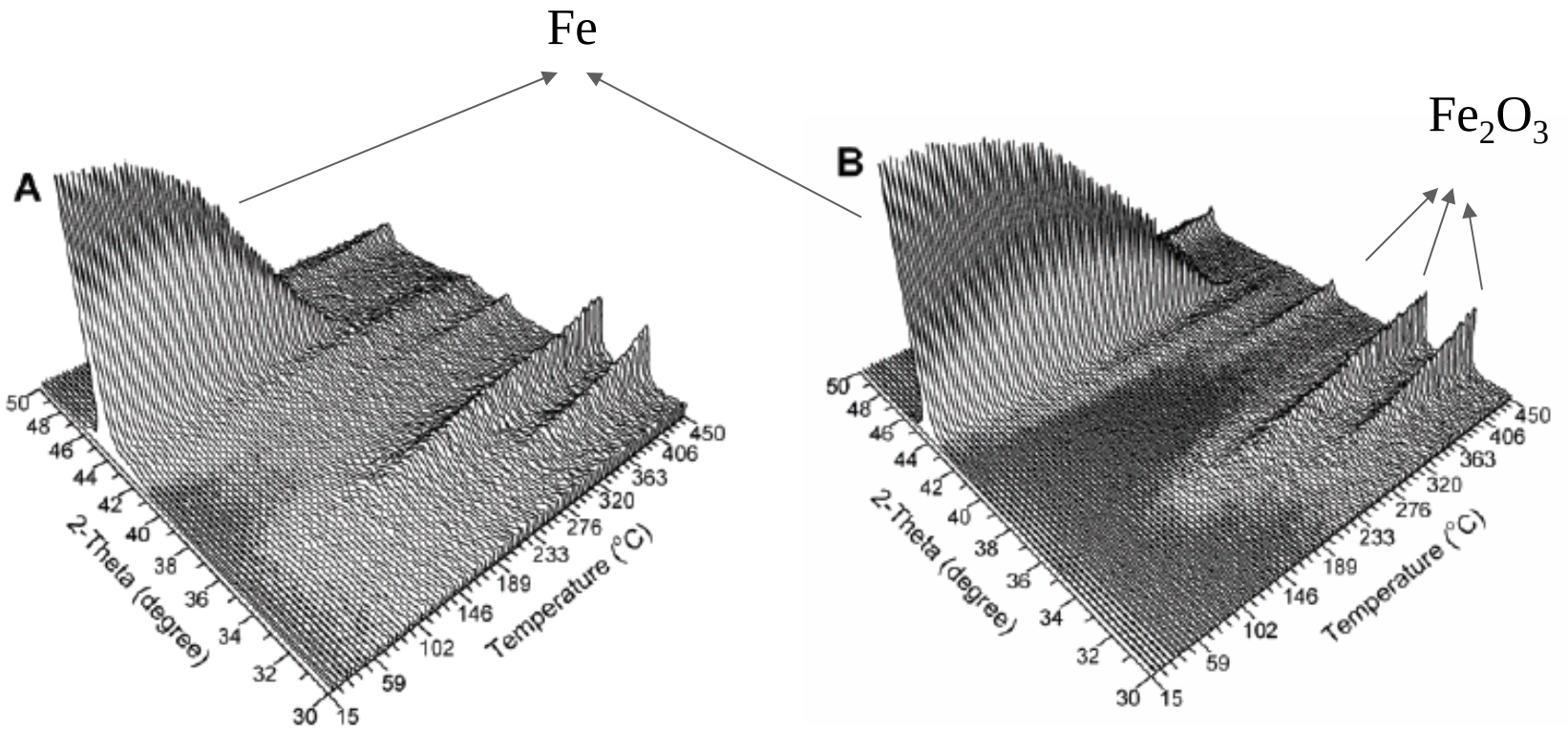


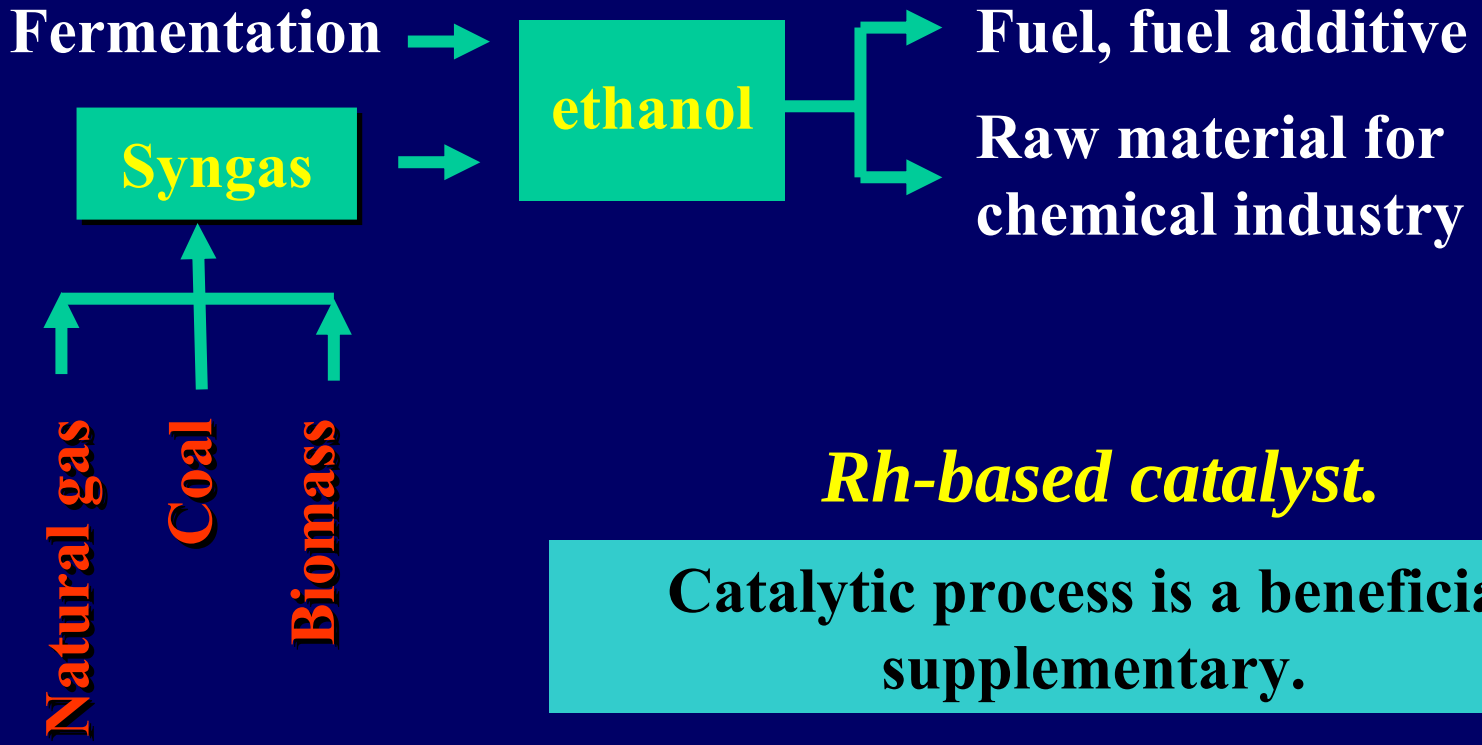
Figure 4. In situ XRD patterns of (A) Fe-*out*-CNT(4); (B) Fe-*in*-CNT(4); (C) the intensity change of the Fe diffraction peaks during temperature programmed oxidation. The dotted line in (C) denotes Fe-*out*-CNT(4), and the solid line, Fe-*in*-CNT(4).

Chen, JACS, article, 2007, 129, 7421

Stabilization of metallic Fe inside carbon nanotube channels.

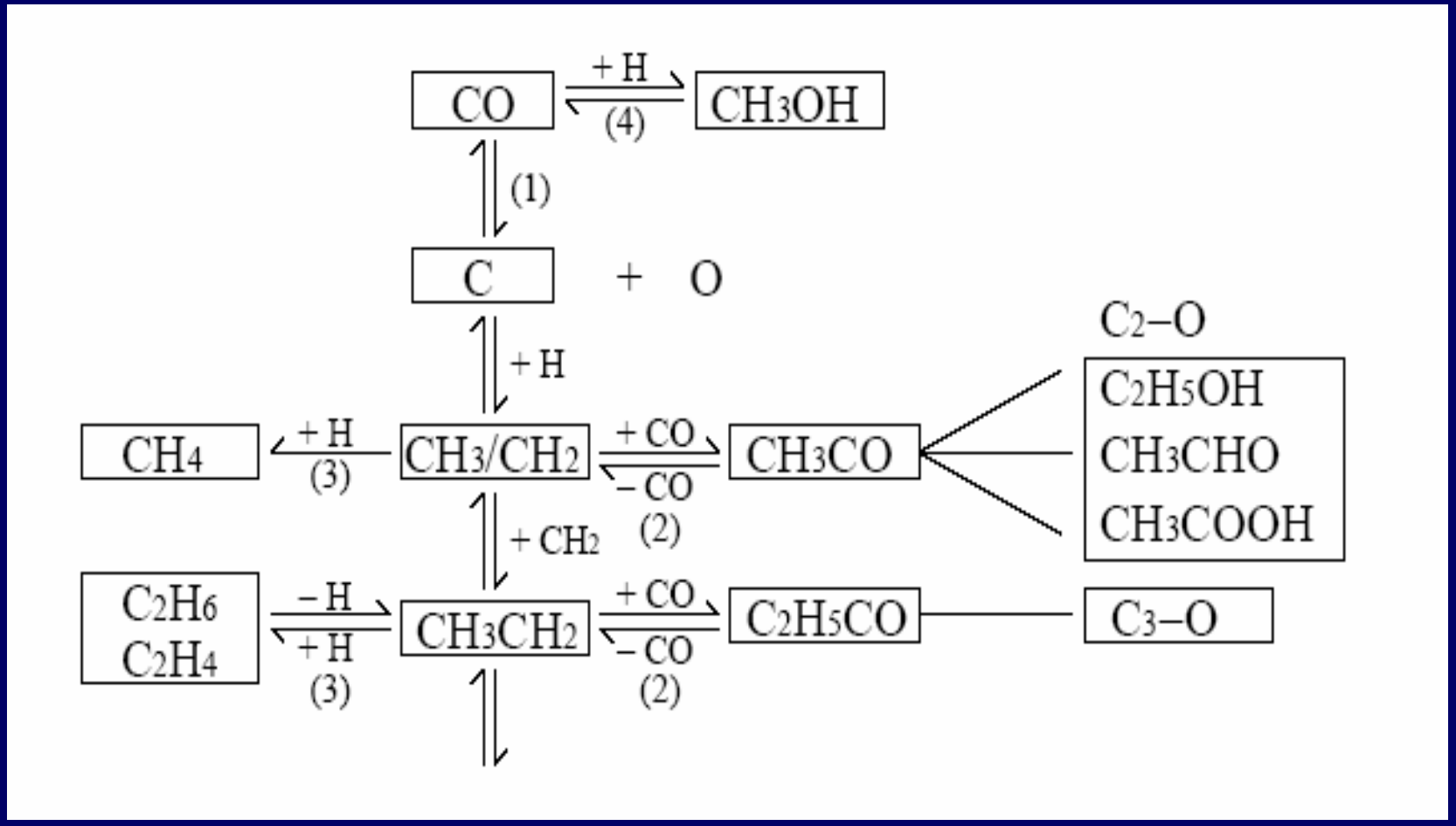
Corelation between the structure and catalytic activity & selectivity?

C2 oxygenates synthesis (mainly ethanol)



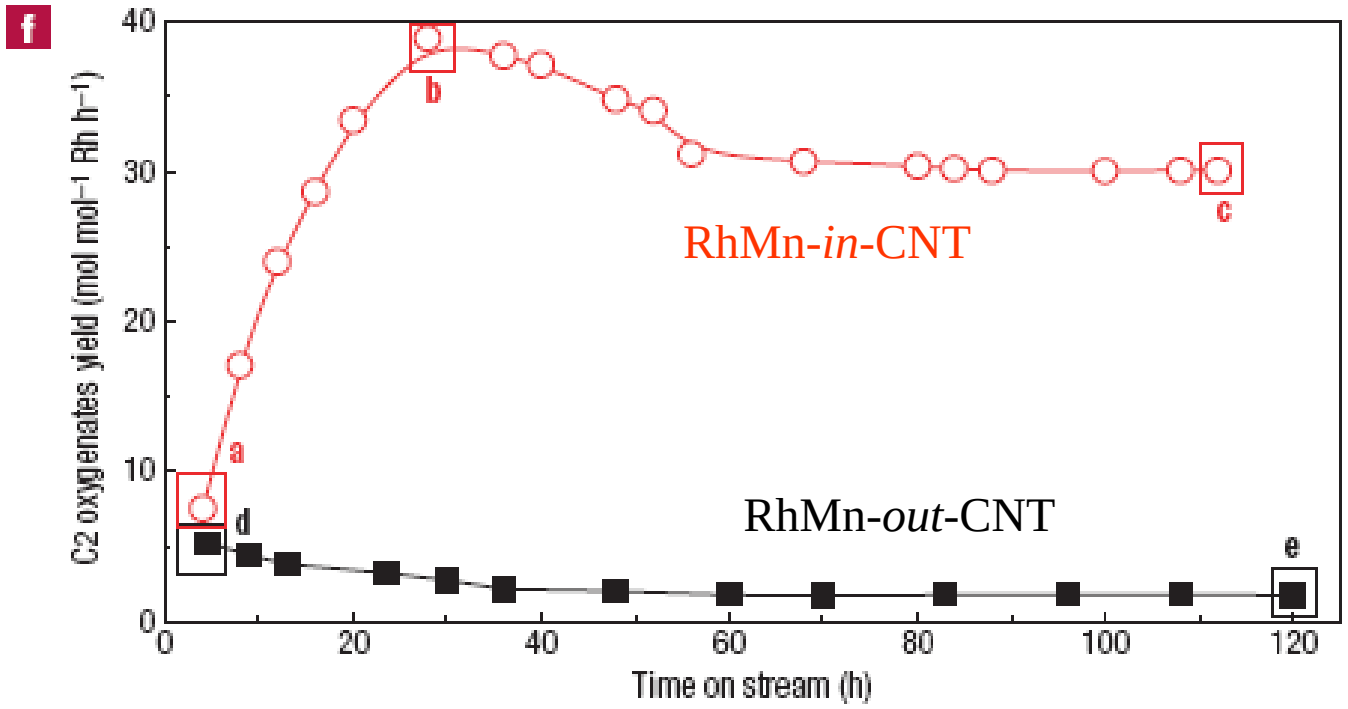
Rh-based catalyst.

Catalytic process is a beneficial supplementary.



Scheme of oxygenate synthesis from syngas

Beyond the effect of particle size…



C_2 oxygenates yield as a function of time on stream

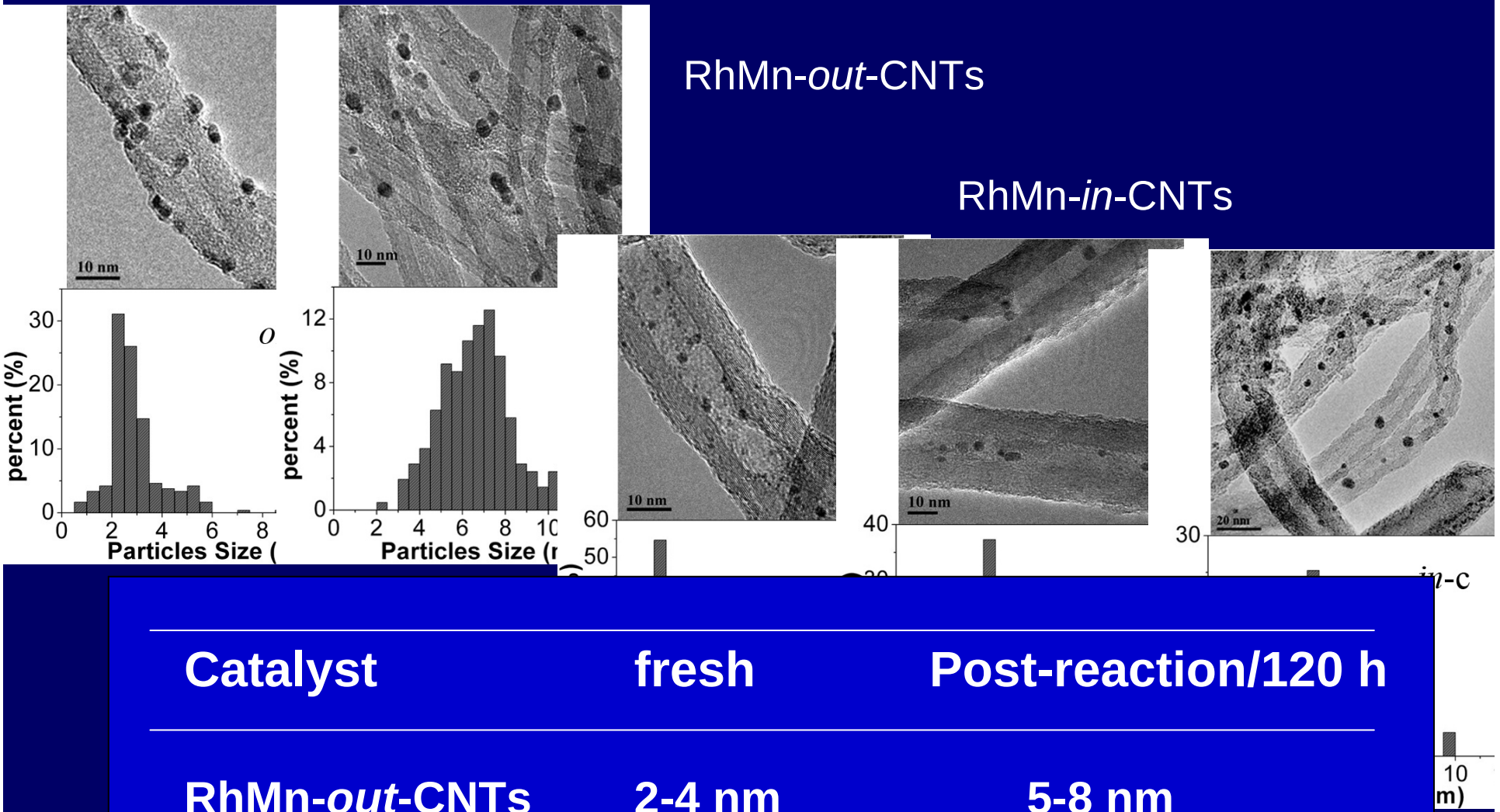
Pam, Fan, Chen, Bao et al, Nature Materials 2007, 6, 507

The effect of particle size

C2-Oxy

RhMn-*out*-CNTs

RhMn-*in*-CNTs



Catalyst	fresh	Post-reaction/120 h
RhMn-*out*-CNTs	2-4 nm	5-8 nm
RhMn-*in*-CNTs	1-2 nm	4-5 nm

Syngas to higher alcohols

Definition: a mixture of alcohols of $C_1 \sim C_6$.

Usage: Clean transportation fuel or fuel additives, high octane number; raw material of chemicals.

Cats in research: Modified F-T cats (Cu-Co, Mo-based); Modified methanol cats (Cu-Zn, Zn-Cr-based).

Difficulties: Low activity, selectivity, stability, and economically unfavorable

CNT-promoted methanol cats

CNTs+Cu-ZnO-Al_2O_3 in the syngas conversion to methanol

	$CuZnOAl_2O_3$	12.5%CNTs-$CuZnOAl_2O_3$
CO conversion	**29.5%**	**42.4%**
MeOH formation rate /μmol MeOH s^{-1} $(m^2surf\ Cu)^{-1}$	**0.095**	**0.118**

493K, 2.0MPa, feed gas $H_2/CO/CO_2/N_2$ = 62/30/5/3(v/v), GHSV = 3000 h^{-1}

The promotion effect :

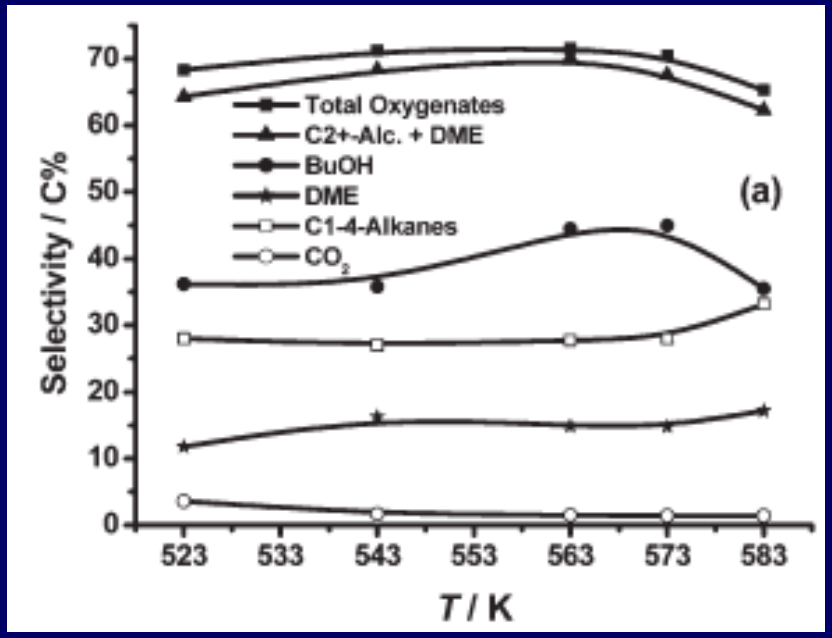
(1) an excellent dispersant of catalyst components;

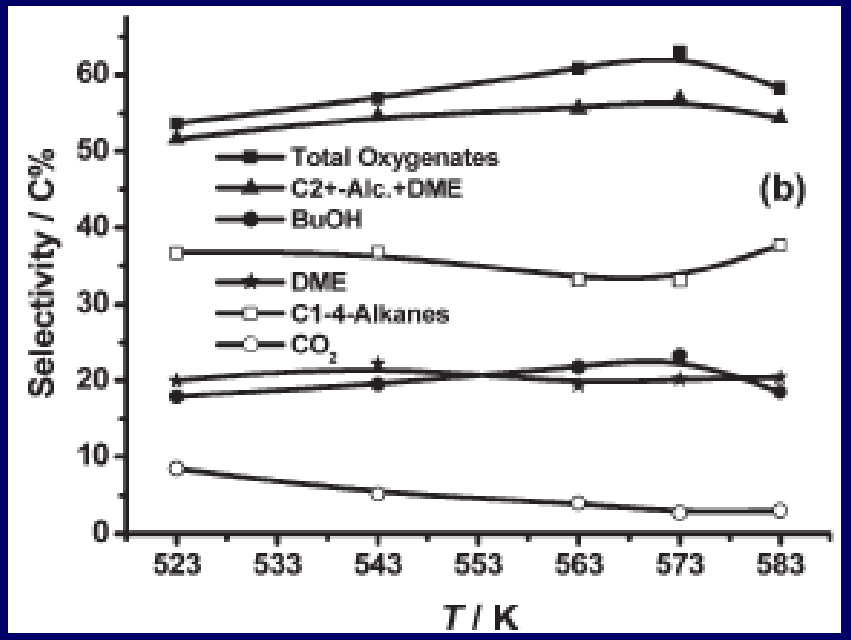
(2) an excellent adsorbent, activator and reservoir of H_2.

HB Zhang's group, Chem. Commun., 2005, 5094;
Catal. Lett. 85, 2003, 237

CNT-promoted cats

alcohols

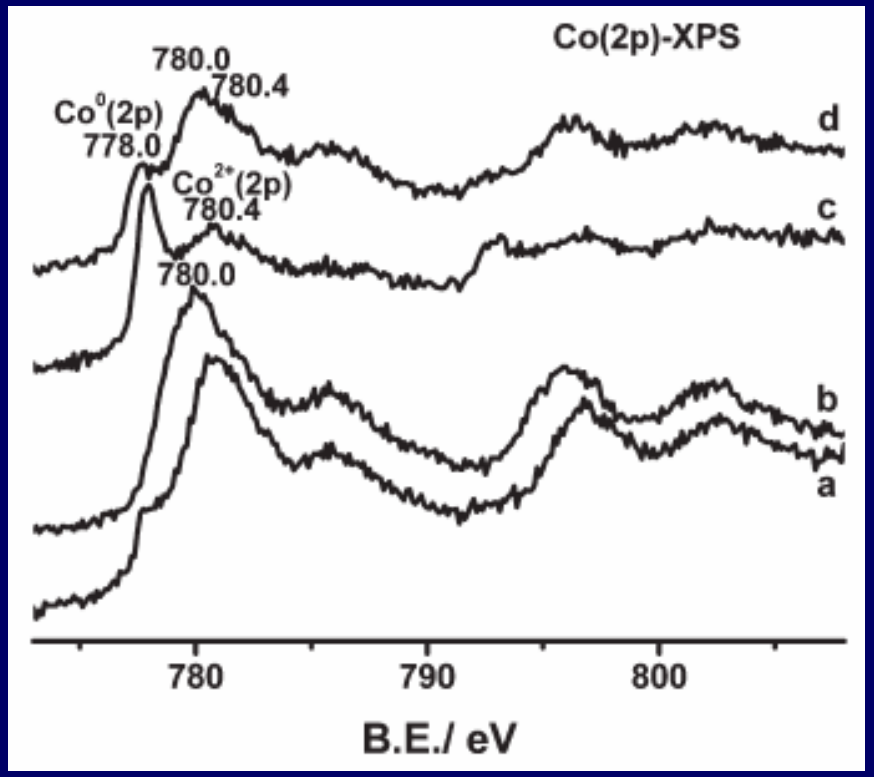




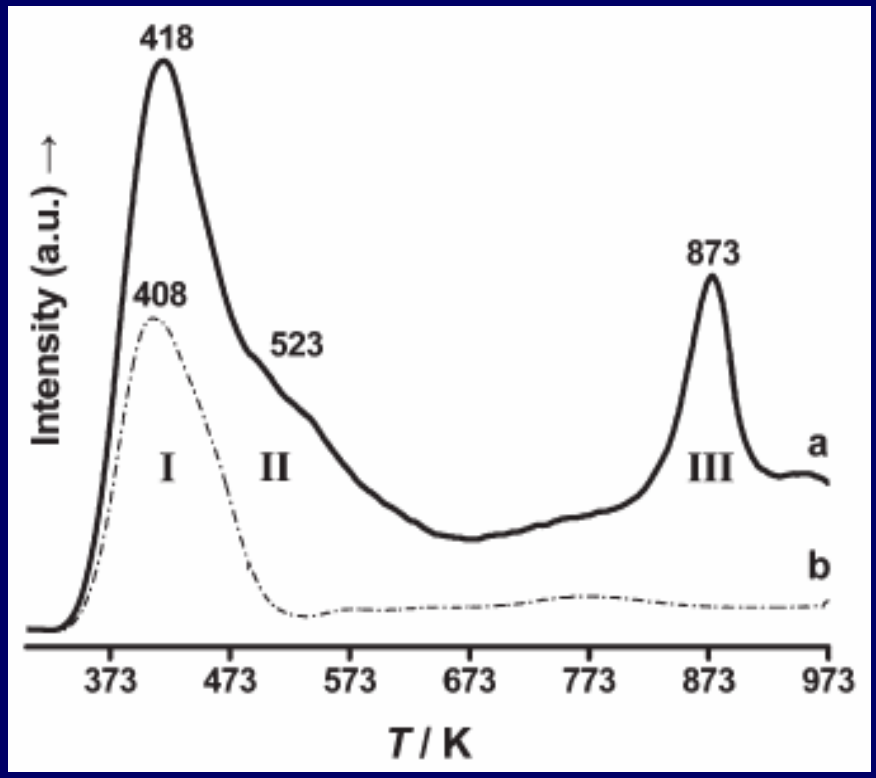
Co_3Cu_1-11%CNTs Co_3Cu_1

At 50 bar, $H_2/CO/CO_2/N_2$ = 46/46/5/3, GHSV 10^4 ml $h^{-1}gcat^{-1}$.

TPR indicated a lowered reduction temperature, increasing the Co_xCu_y species reducible to lower valence-state.



(a)Co_3Cu_1 and (b) Co_3Cu_1-11%CNT fed with CO_2 containing syngas; (c)Co_3Cu_1 and (d) Co_3Cu_1-11%CNT fed with CO_2 free syngas.



H_2-TPD (a) Co_3Cu_1-11%CNT; (b) Co_3Cu_1

Indicate: (1) presence of surface Co^{n+} species ($CoOOH/Co_3O_4$) may be closely related to the highly selective formation of HAS.

(2) Presence of reversible active H species.

主要科学问题

- 选择氧化过程中的氧物种及选择性控制
- 合成气转化中的产物分布的控制调节，尤其 CH_4 形成机理和抑制
- 甲烷的高效直接转化，包括酶催化转化
- 以甲醇为原料的新化学过程
- 贵金属替代的可能性

主要科学问题

- 催化过程的原位、动态表征
- 高温稳定催化剂的控制合成
- 基于纳米概念的催化理论

部分阅读文献：

1. G.A. Somorjai, Chemistry in Two Dimensions: Surfaces. Cornell University Perss, Ithaca, NY 1981 和中译本。
2. G.A. Somorjai, Introduction to Surface Chemistry and Catalysis, John Wiley & Sons, Inc. 1993.
3. A. Sen, Catalytic functionalization of carbon-hydrogen and carbon-carbon bonds in protic media, Acc. Chem. Res. 31 (1998) 550.
4. R.H. Crabtree, Aspects of Methane Chemistry, Chem. Rev. 95 (1995) 987.
5. Z. Liu et al., New Progress in R & D of lower olefin synthesis, Fuel Processing Technology 62 (2000) 161.
6. H. Dai, Carbon Nanotubes: Synthesis, Integration, and Properties, Accounts Chemical Research 35 (2002) 1035.
7. R.A. Sheldon, Chemicals from synthesis gas, D. Reidel Publishing Company, 1983.
8. 贺黎明，沈召军，甲烷的转化和利用，化学工业出版社，2005.
9. 汪寿建等，天然气综合利用技术，化学工业出版社，2003.
10. 周怀阳等，天然气水合物，海洋出版社，2000.