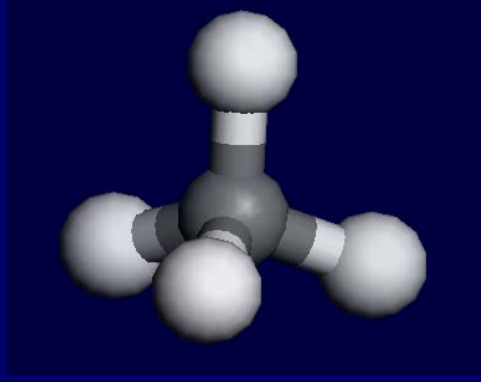
Direct Catalytic Conversion of Methane

Xiulian Pan, Zengjian An, Ding Ma, Yide Xu, Xinhe Bao

State Key Laboratory of Catlaysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences

www.fruit.dicp.ac.cn



Methane is a highly symmetrical molecule and is very difficult to activate

C-H bond strength:	438.8kJ•mol^{-1}
Ionization potential:	12.5eV
Proton affinity:	4.4eV
Acidity (pKa):	48

Introduction

Methane

- **C_{2+} Hydrocarbons**
  - By OCM
  - By high temperature coupling of methane
  - By two step methane homologation
- **Syngas ($CO + H_2$)**
  - By steam reforming of methane
  - By partial oxidation of methane
  - By oxy-steam and/or CO_2 reforming of methane
- **Syngas → Methanol → Hydrocarbons**
  - → Hydrocarbons or Oxygenates (by FT-synthesis)
- **Methanol/formaldehyde, carbon disulfide, methyl chloride, etc.**
  - ↓ Hydrocarbons
- **Carbon and Hydrogen**

Catal. Rev.-Sci. Eng., 2003,45, 151

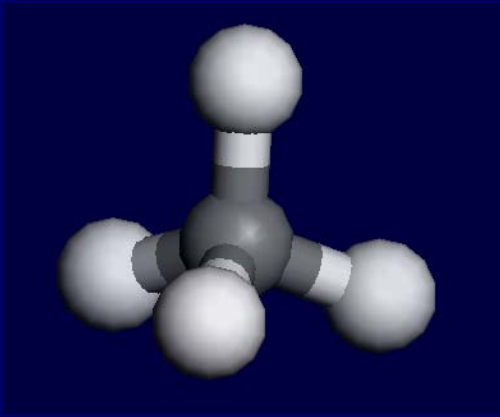
Example 1

$$CH_4 + 1/2O_2 \rightarrow CH_3OH$$

Example 2

$$6CH_4 \rightarrow C_6H_6 + 9H_2$$

Example 1



Low Temperature Catalytic Oxidation of Methane

Examples…

Electrophiles and superacids,

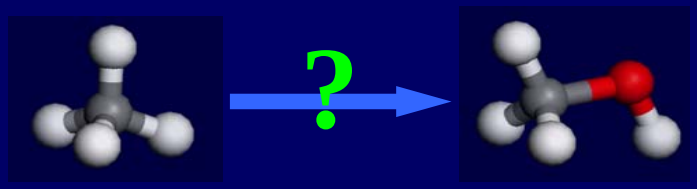
$$CH_4 + HF + SbF_5 \rightarrow [CH_5][SbF_6]$$

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

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

G. Olah, ACC. Chem. Res. 1987, 20, 422.

Work of Periana et al.



$$CH_4 + H_2SO_4 + SO_3 \xrightarrow[180\ ^\circ C]{HgSO4} CH_3OSO_3H + H_2O + SO_2$$

$$CH_3OSO_3H + H_2O \longrightarrow CH_3OH + H_2SO_4$$

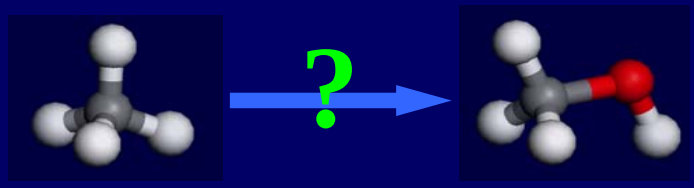
$$SO_2 + 1/2O_2 \longrightarrow SO_3$$

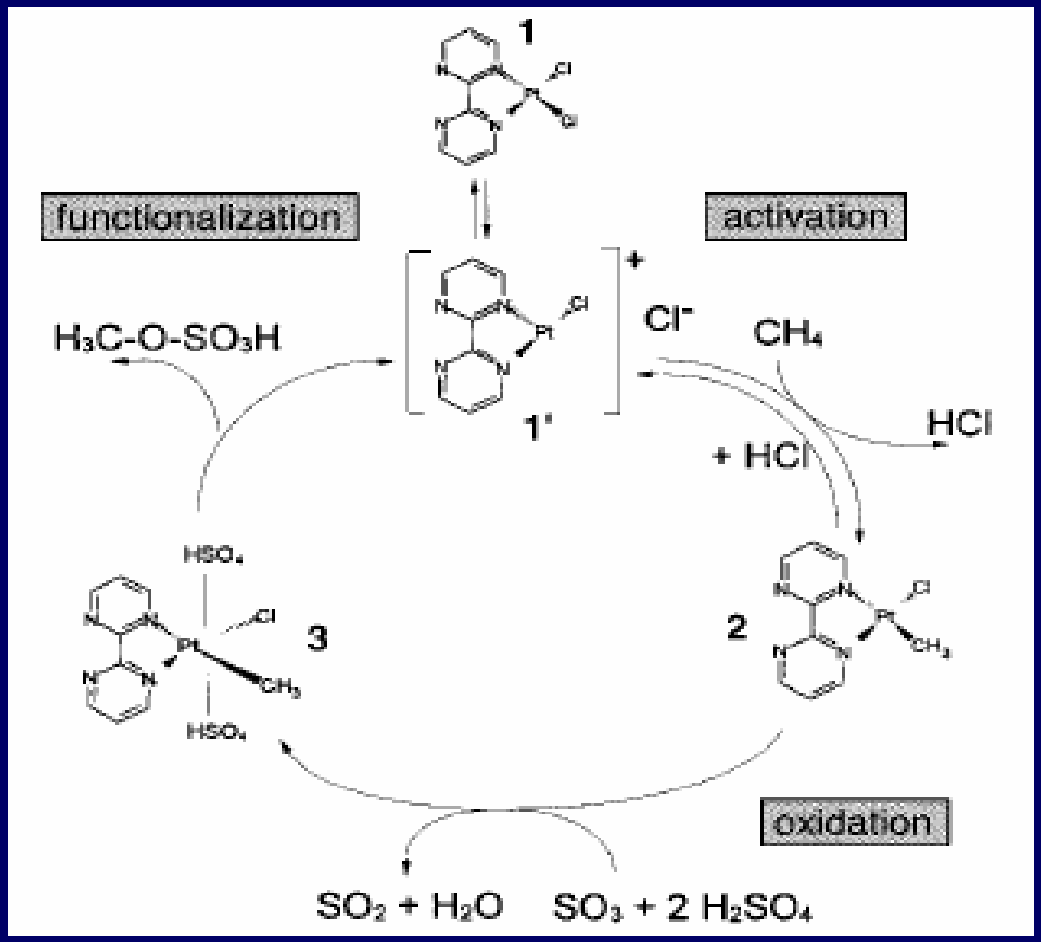
Net reaction: $CH_4 + 1/2O_2 \xrightarrow[180\ ^\circ C]{HgSO4} CH_3OH$

CH_4 conversion 50%, yield 43%

Periana et al. Science, 1993, 340

Work of Periana et al.





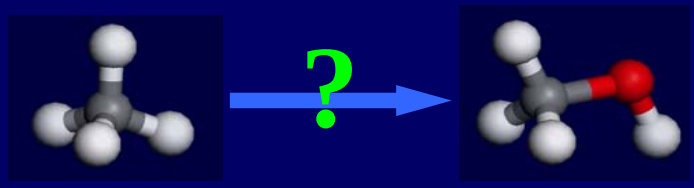
A more effective catalyst---- Pt-complex was developed, methane conversion was 72%.

Conv. 90%,
Sel. 81%
220 °C, 35 bar CH4

Methyl bisulfate on the Pt-complex catalyst in fuming sulfuric acid.

Periana et al. 1998, Science, 280, 560.

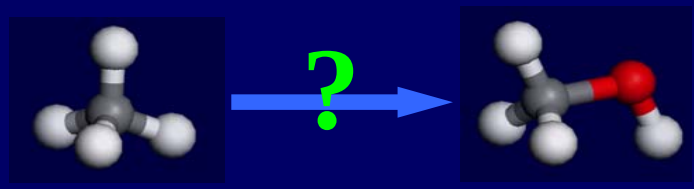
Work of Fujiwara et al.



Catal.	Solvent	Oxidant	Reagent	T (℃)	TON (h^{-1})
$CaCl_2$	CF_3CO_2H / $(CF_3CO_2)_2O$	$K_2S_2O_8$	CO	85	0.2
Angew. Chem. Int.					
Pd $(OAc)_2$ /$Cu(OAc)_2$				80	< 1
J. Organometal. Chem. 1994, 473: 329					
Mg	CF_3CO_2H	$K_2S_2O_8$	CO	80	< 0.1
Appl. Organometal. Chem. 1999, 13: 539					

Carboxylation to acetic acid

Work of Bell et al.

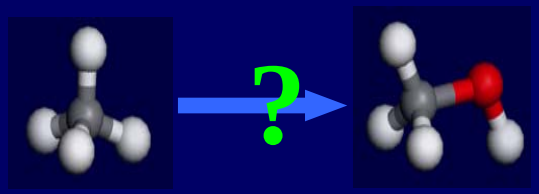


$$CH_4 + SO_2 + K_2S_2O_8 \xrightarrow[65\ ^\circ C]{CF_3SO_3H,\ CaCl_2} CH_3SO_3H$$

69 atm CH4 (268 mmol); 2.4 atm SO2 (13.14 mmol); 5 mmol K2S2O8; 5 mL triflic acid; 10 h.

J. AM. CHEM. SOC. 2003, 125, 4406-4407

Work of Sen et al.



$$CF_3COOH + CH_4 + Pd^{2+} \xrightarrow{80\ °C} CF_3COOCH_3 + Pd^{0} + 2H^{+}$$

$$CF_3COOCH_3 \rightarrow CF_3COOH + CH_3OH$$

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

- adamantane
- ethane
- arene
- methane

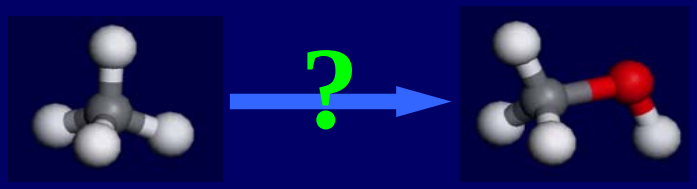
E. Gretz, et al. J. Am. Chem. Soc. 109 (1987) 8109;
L. Kao, et al. J Am Chem Soc 113 (1991) 700

We want…

To make a catalytic process ;

To avoid HCl, H_2SO_4, SO_3, SO_2, H_2O_2;

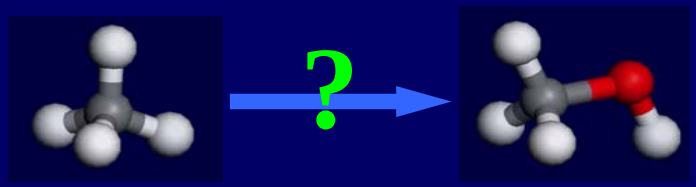
To use O_2 as oxidant.



Redox couples forming electron transfer chain in biological oxidation processes

High efficiency

O_2 as oxidant



Redox couples forming electron transfer chain in nature

Gretz, E.; et al. *J. Am. Chem. Soc.* 1987, *109*, 8109-8111.

$$CF_3COOH + CH_4 + Pd^{2+} \xrightarrow{\textbf{80 °C}} CF_3COOCH_3 + Pd^{0} + 2H^{+} \quad (1)$$

$$\downarrow$$

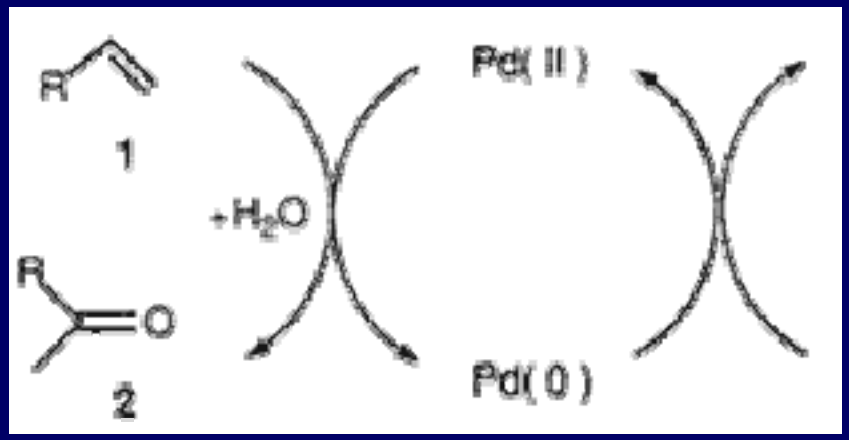
$$CF_3COOH + CH_3OH$$

Stoichiometric

?

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

- **Wacker process: $CuCl_2/CuCl/O_2$**



The Wacker Process

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

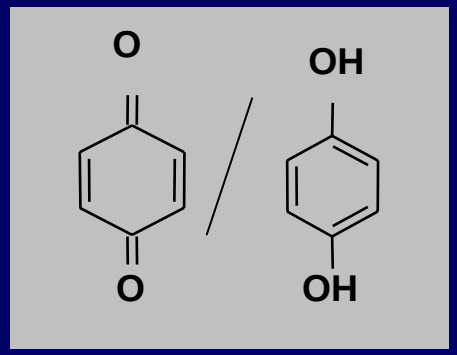
It involves the reaction of ethylene with $PdCl_2$ in HCl (reaction 1). Pd(II) is reduced to Pd black. To make the reaction catalytic, Pd(0) is reoxidized by $CuCl_2$ and O_2 (reactions 2 and 3).

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

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

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

➢ Quinone / Hydroquinone



Backvall *et al. J. Am. Chem. Soc. 1990, 112, 5160*

Search for active oxidants for regeneration of $Pd^0 \rightarrow Pd^{2+}$

Run	oxidant	CF_3COOCH_3 (μmol)	TON[a]
1[b]	-----	0.07	0.7
2	$Cu(oAc)_2$	0.04	0.8
3	$FeCl_3$	0.03	0.6
4	$K_2S_2O_8$	0.06	1.2
5	**Q**	**0.12**	**2.4**
6	$LiNO_3$	0.07	1.4
7	H_2O_2[c]	0.09	1.8

Conditions:

50 μmol $Pd(oAc)_2$, 500 μmol oxidant, 3 ml (39 mmol) CF_3COOH, 80 ℃, 10 h, CH_4: 55 atm.

a: molar ratio of CF_3COOCH_3/ $Pd(oAc)_2$.

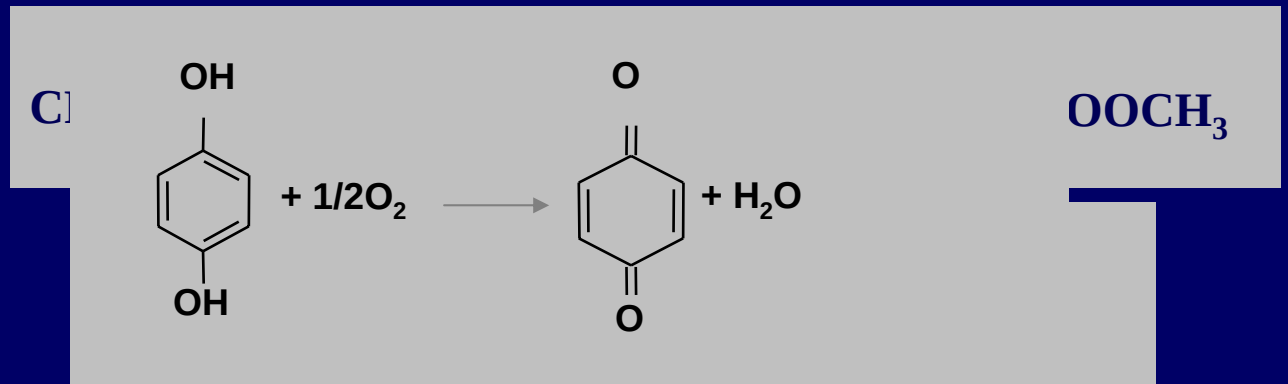
b: $Pd(oAc)_2$: 100 μmol.

c: 880 μmol.

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 ºC, 10 h; a: Remaining Pd^{2+} after the reaction.



Determination of remaining Pd^{2+} in the solution by Gravimetric method

Evaporation of solvent

Addition of water

$H_2Q + Pd^0 + Pd(CFCOOH)_2$

Addition of dimethylglyoxime/ethanol solution

$H_2Q + Pd^0 + Pd(dmg)_2$

washed with anhydrous alcohol

Addition of HNO_3 acid

$H_2Q \rightarrow Q$ (water soluble)

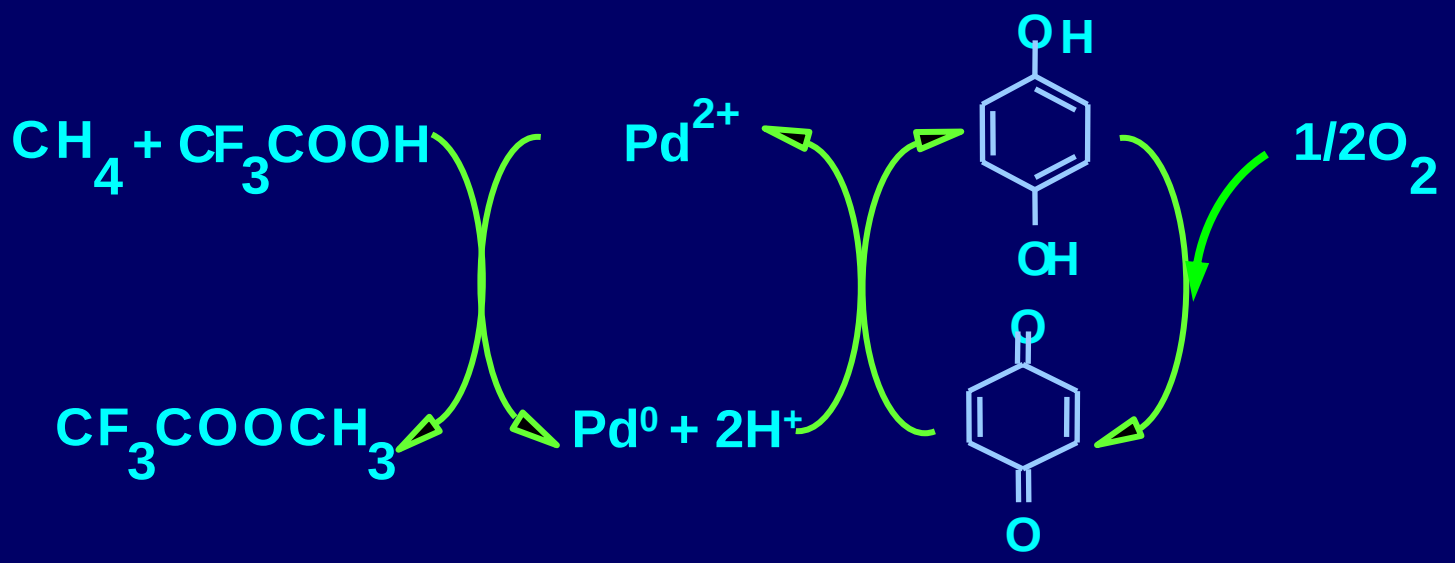
$Pd^0 \rightarrow Pd^{2+}$

Centrifugal separation

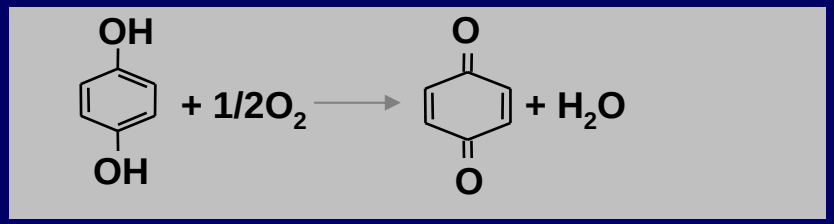
$Pd(dmg)_2$

Weight

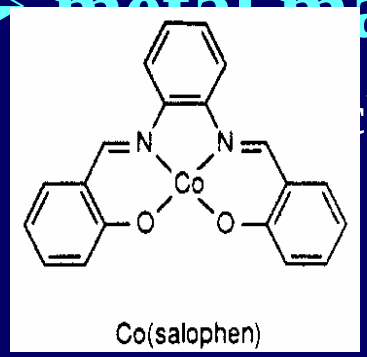
Scheme of methane oxidation

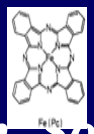


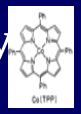
Search for active oxidants to speed up:



- **metal macrocycles:**







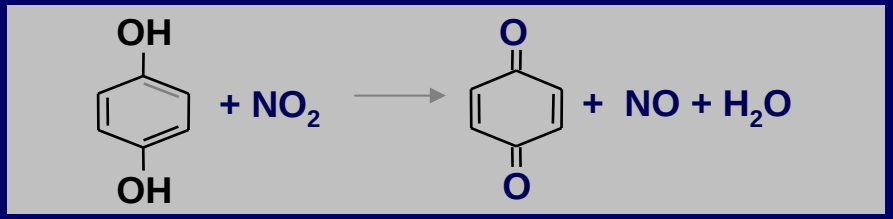
kv et al. J. Am. Chem. Soc. 1990, 112, 5160

Co(salophen), Co(TPP), iron phthalocyanine (Fe

Unstability

- **nitrogen oxide** /CH_2Cl_2

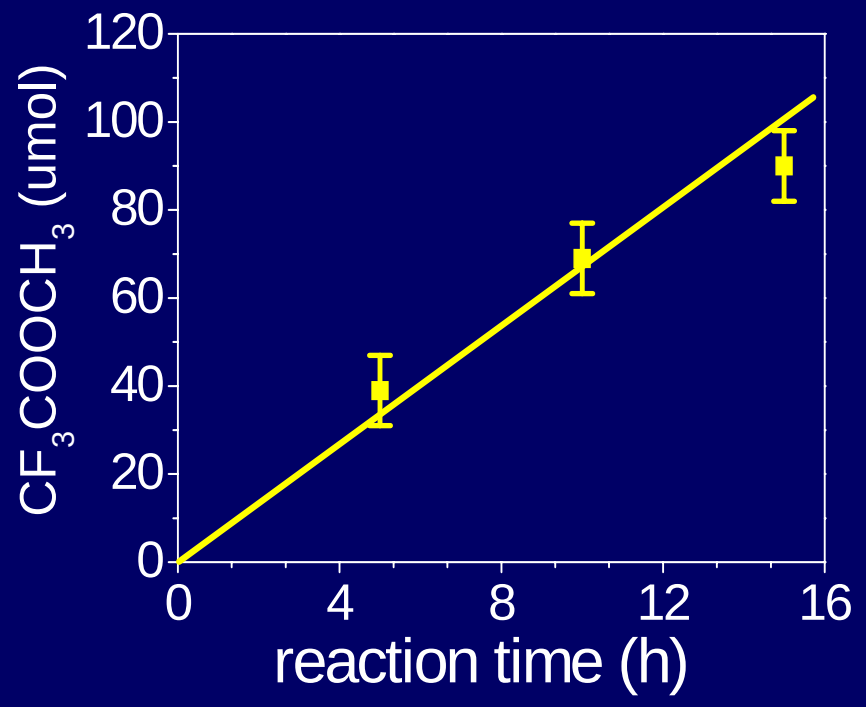
Feasibility test in CF_3COOH



Combination of Pd^{2+} and Q for aerobic oxidation of CH_4

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 ºC, 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}

Additional experiments for 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	--

Conditions: CF3COOH: 3 ml (39 mmol), CH4: 54 atm (114 mmol),
O2: 1 atm (2 mmol), 80 ºC, 10 h;
a: Remaining Pd^{2+} after the reaction.

Additional experiments for further confirmation

isotope experiments

GC-MS

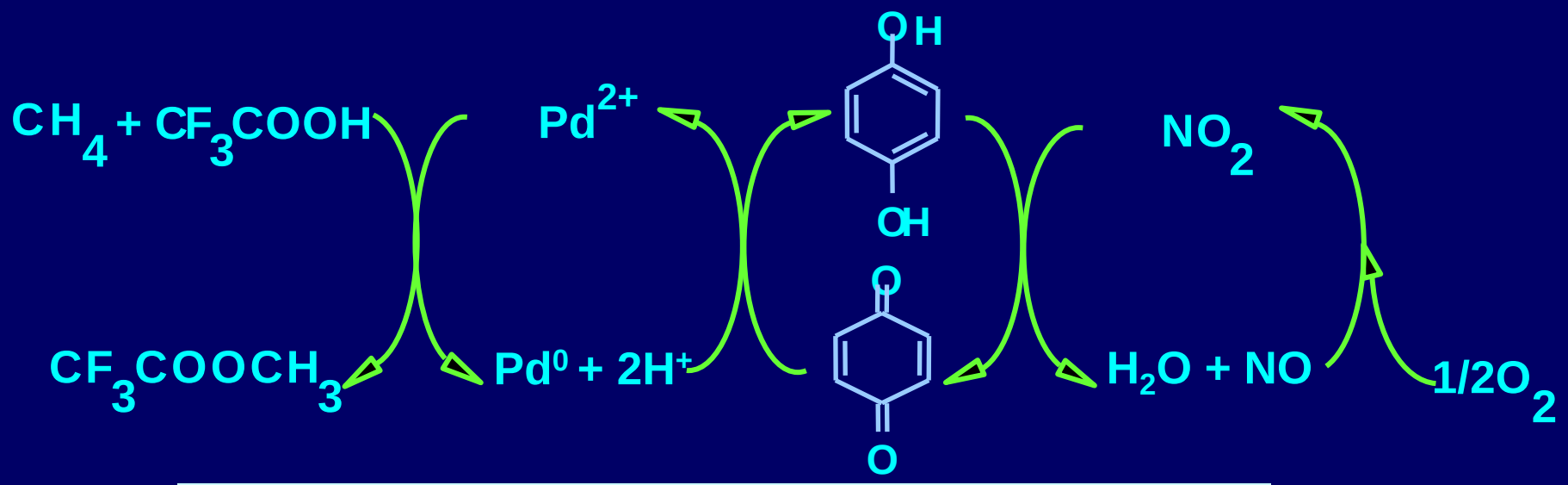
14 atm $^{13}CH_4$
40 atm $^{12}CH_4$

$$\xrightarrow[CF_3COOH]{O_2}$$

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

$$\frac{1}{3}$$

Features



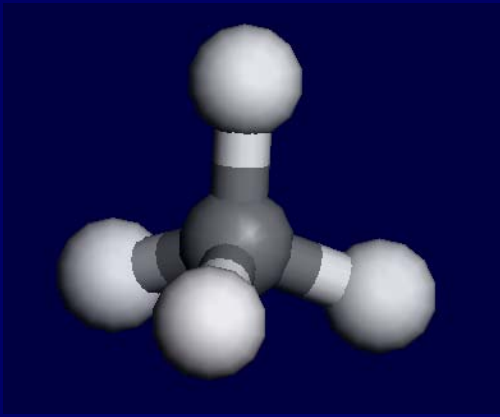
$$CF_3COOH + CH_4 + 1/2O_2 \rightarrow CF_3COOCH_3 + H_2O$$

$$CH_4 + 1/2O_2 \rightarrow CH_3OH$$

$$CF_3COOCH_3 + H_2O \rightarrow CF_3COOH + CH_3OH$$

- ✓ **Catalytic process in one pot at 80 °C**
- ✓ **HCl, H_2SO_4 avoided**
- ✓ **O_2 as oxidant**

Example 2



High Temperature Conversion of Methane to Aromatics

Typical HT Direct Conversion Process

- **Selective Oxidation**

$$CH_4 + \boxed{O_2} \rightarrow CH_3OH + \boxed{CO_2} + H_2O$$

- **Oxidative Coupling**

$$CH_4 + \boxed{O_2} \rightarrow C_2H_x + \boxed{CO_2} + H_2O$$

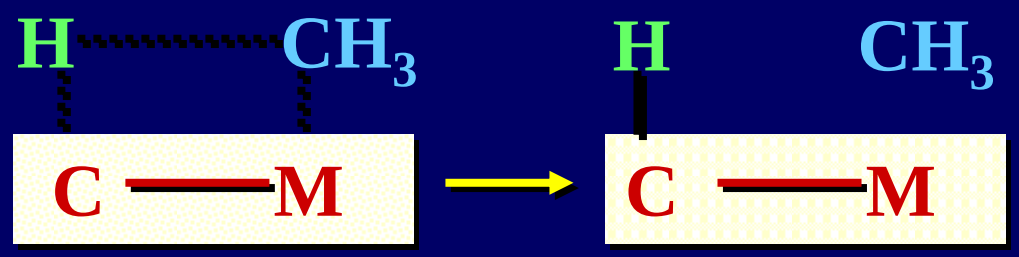
A New Route…

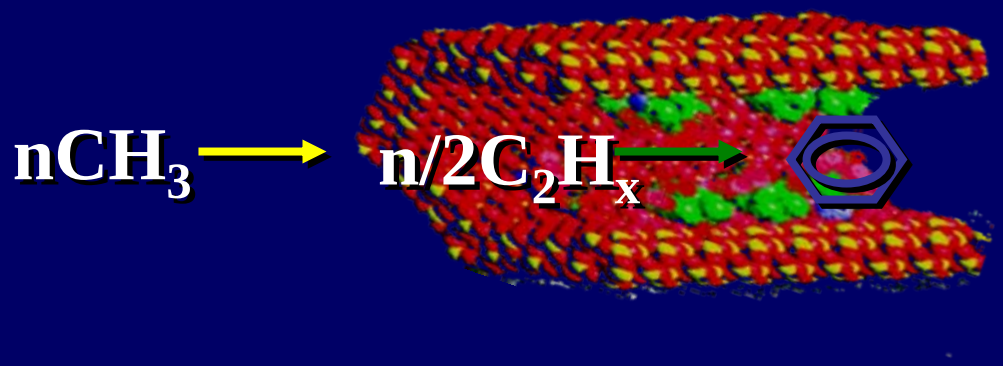
To higher hydrocarbons, without forming CO_2 ?

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

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

Conversion of methane to aromatics





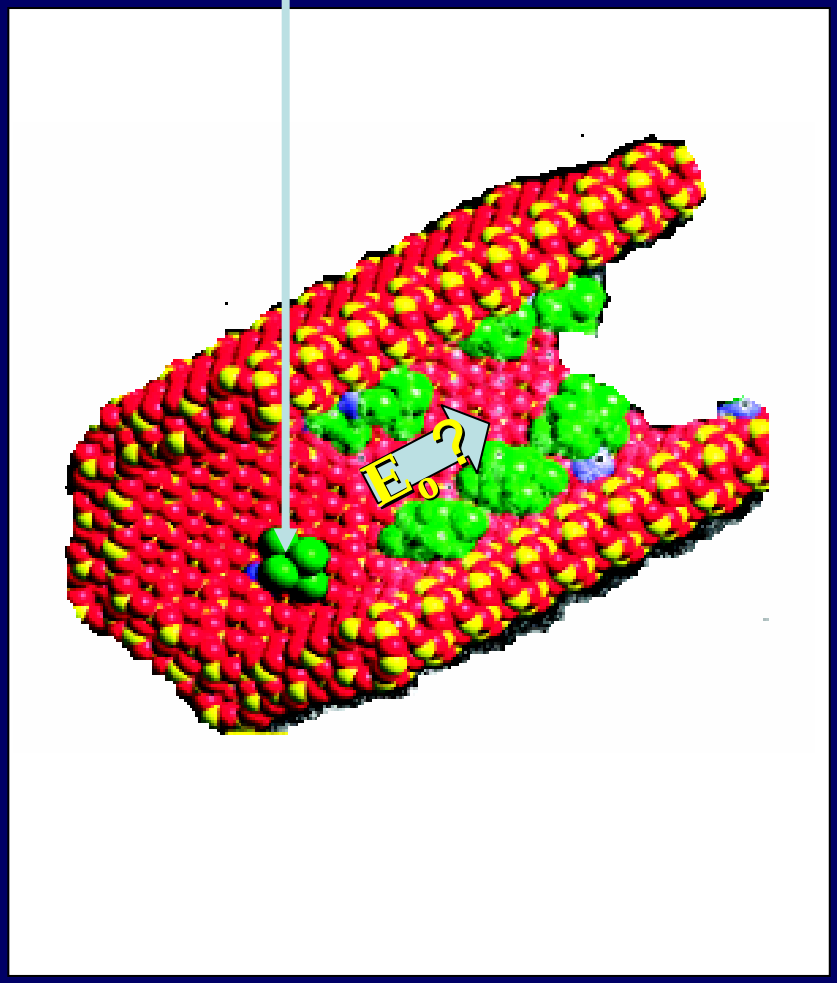
Catalysts Mo, W, Re…

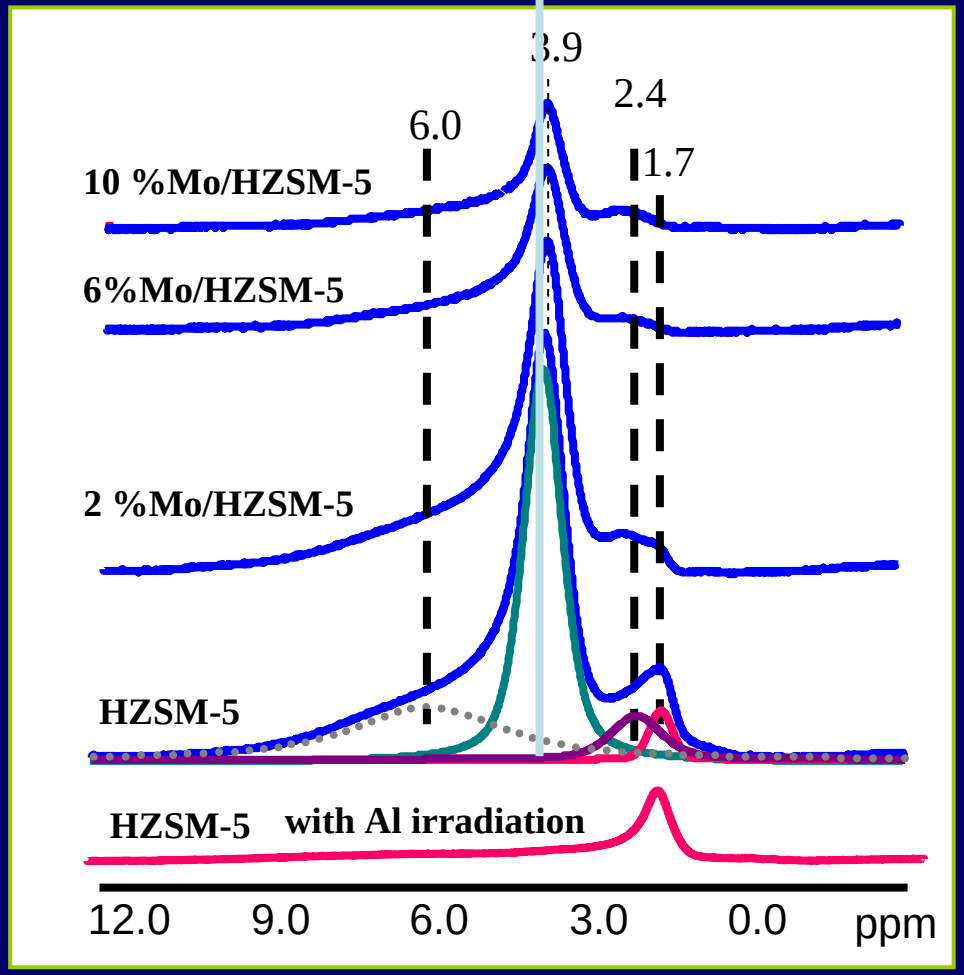
HZSM-5, MCM-22…

Bifunctionality of Mo/HZSM-5

Acidity and catalytically active sites

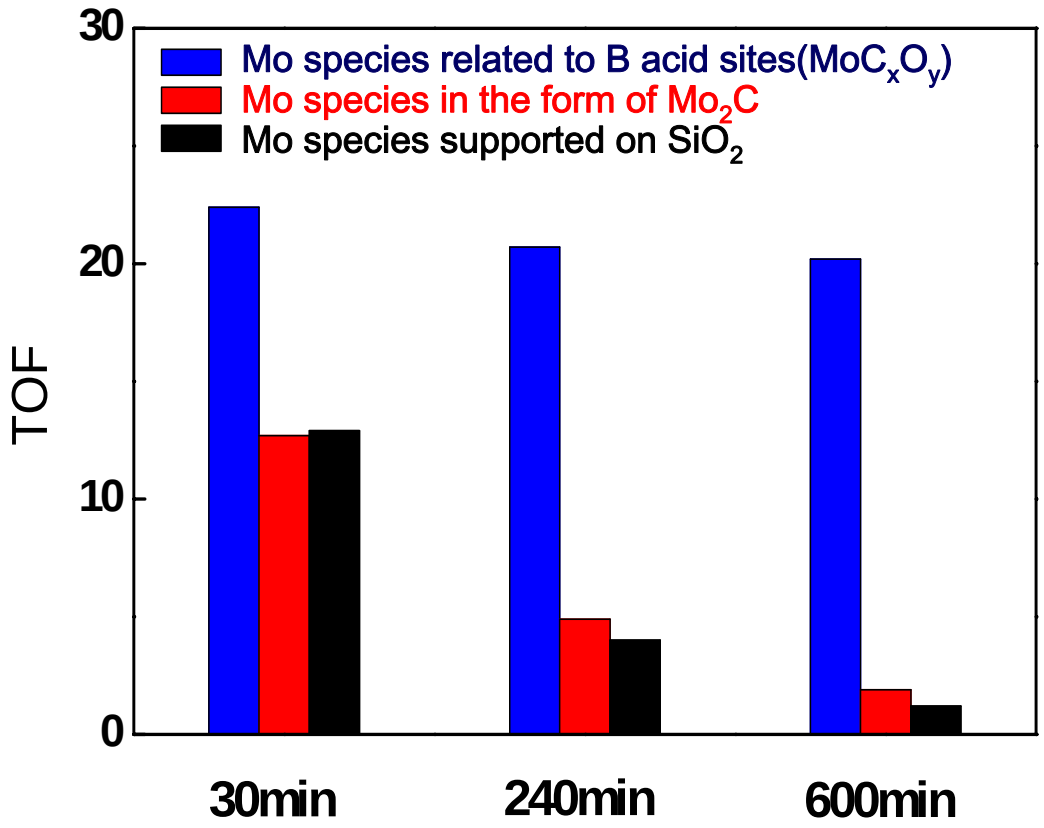
Loadings of Mo in Mo/HZSM-5





D. Ma, X. Bao et al., Angew. Chem-Inter Edit. 39 (2000); Chem. Eur. J., 8 (2002) .

Aromatization over different Mo species

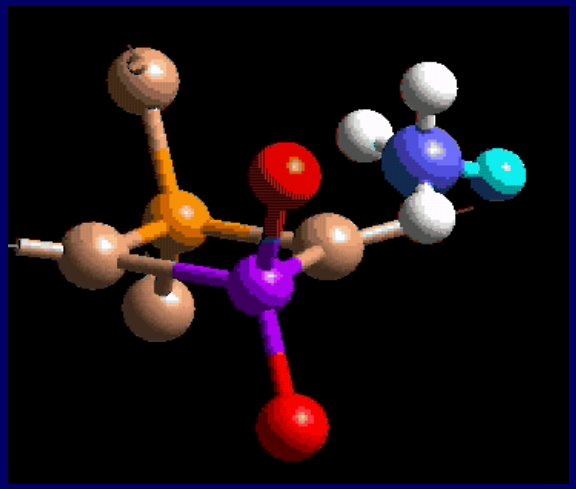


- **Highly active and stable MoC_xO_y;**
- **Low activity and stability of Mo_2C;**
- **0.5 acidic sites per unit cell required for aromatization.**

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

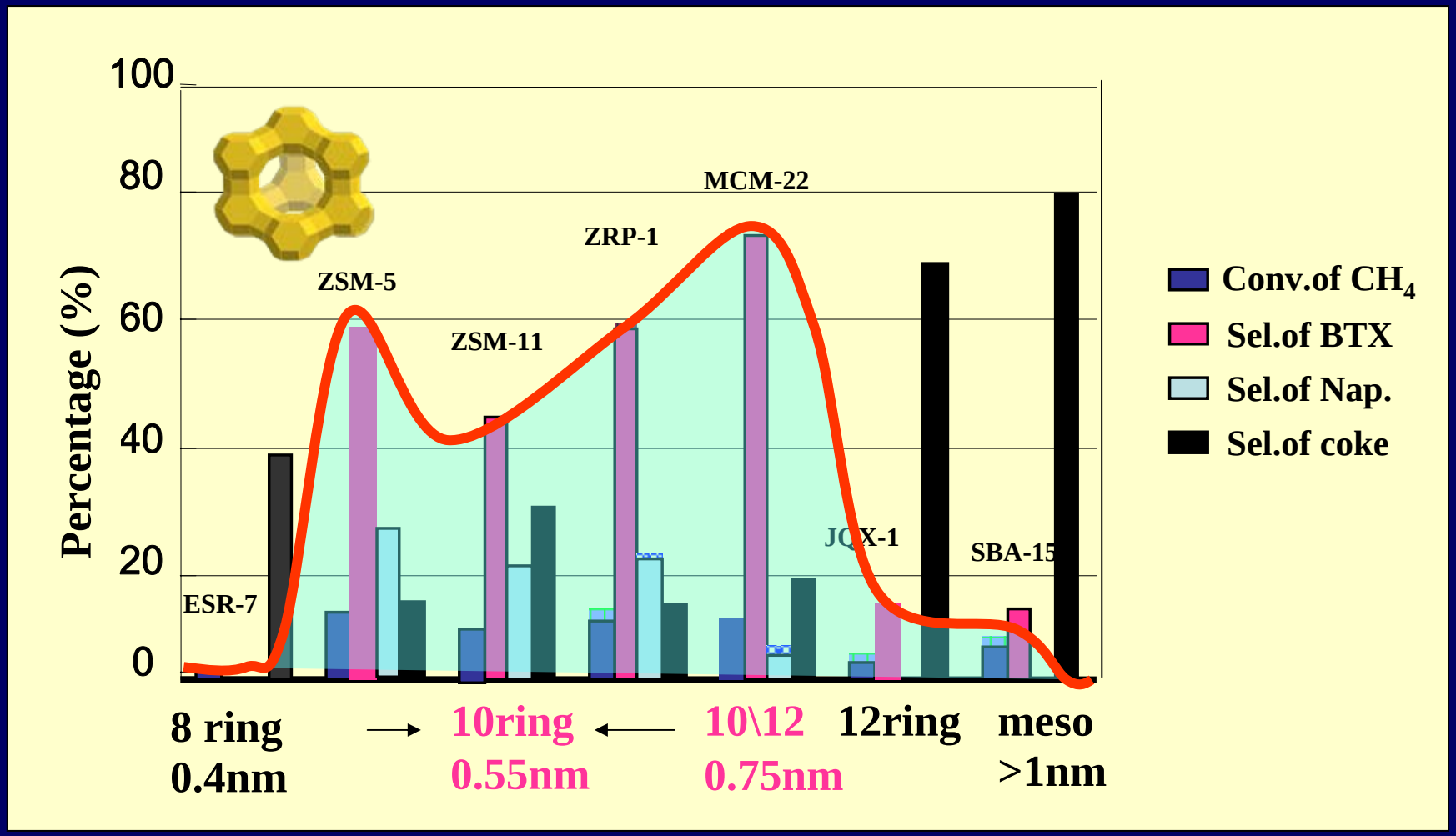
Bifunctionality of Mo/HZSM-5

- Acidic sites
- MoC_xO_y active species



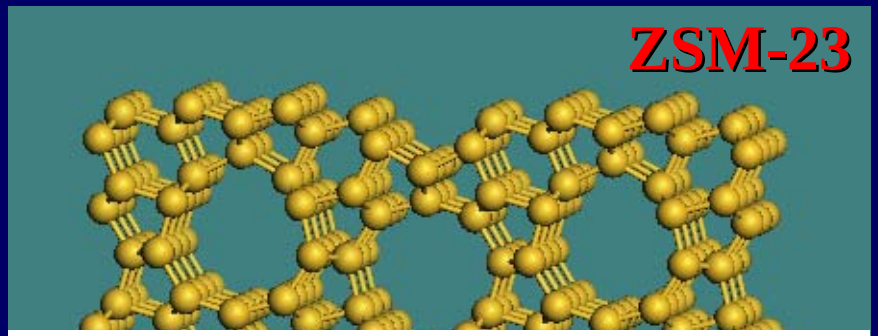
Pore Morphology of Catalyst Carriers

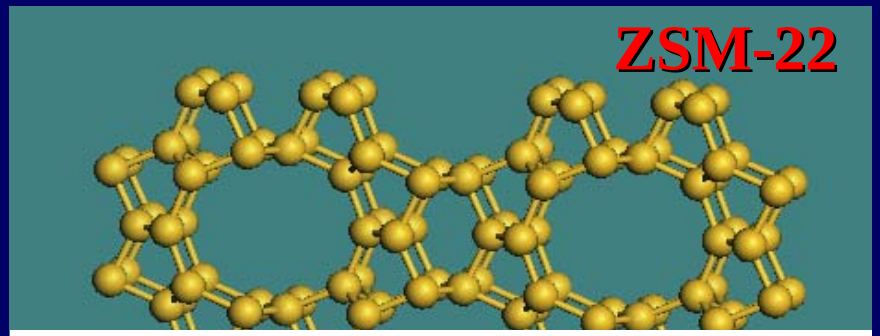
Pore morphology of zeolite supports

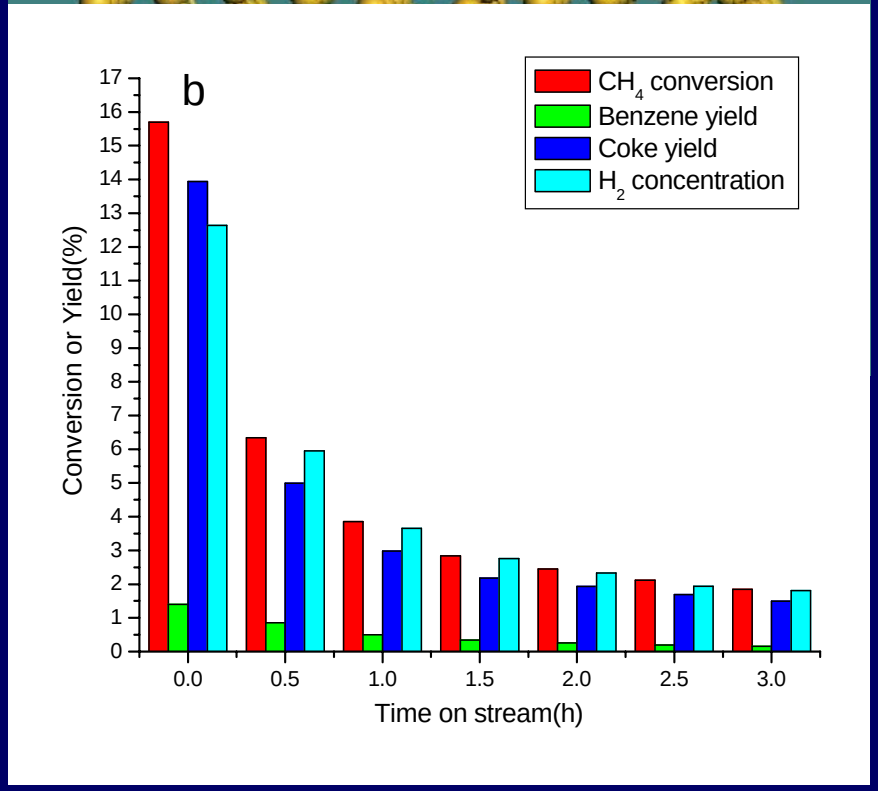


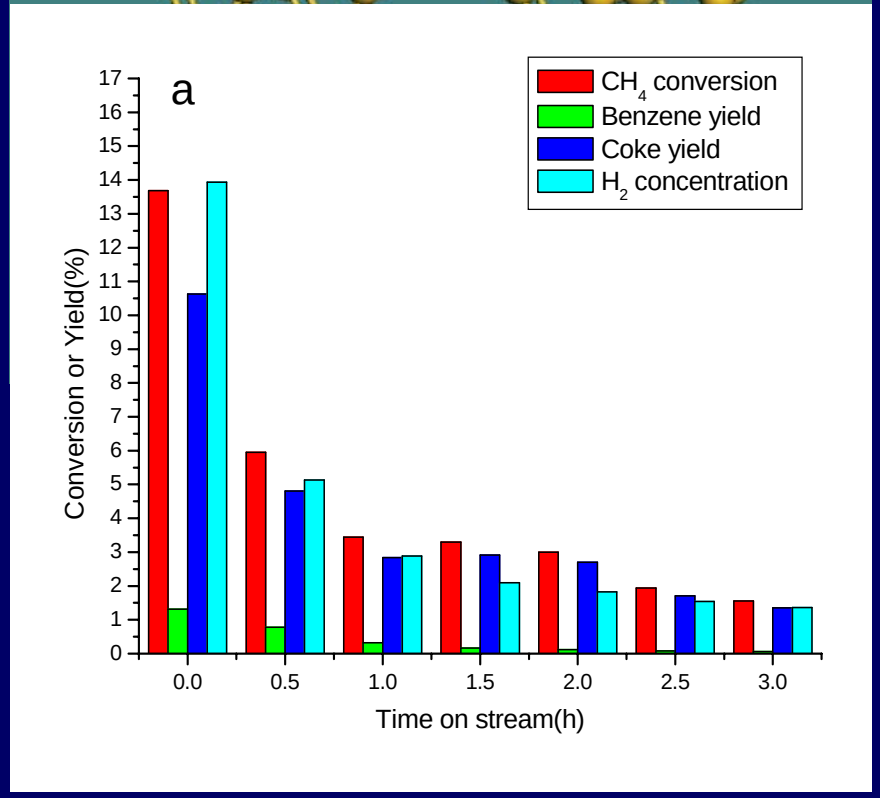
Applied Catalysis A-general 188 (1-2) , J. Catal. 216 (2003)

Morphology of Zeolites

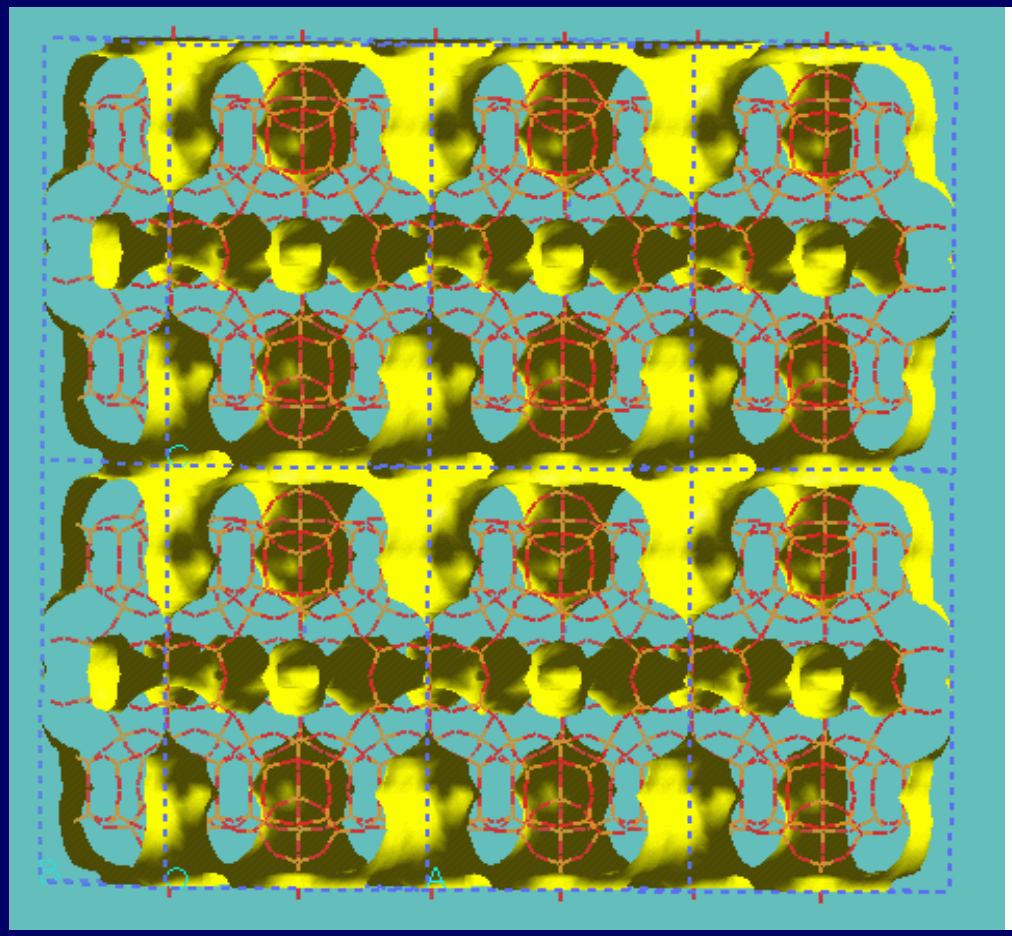


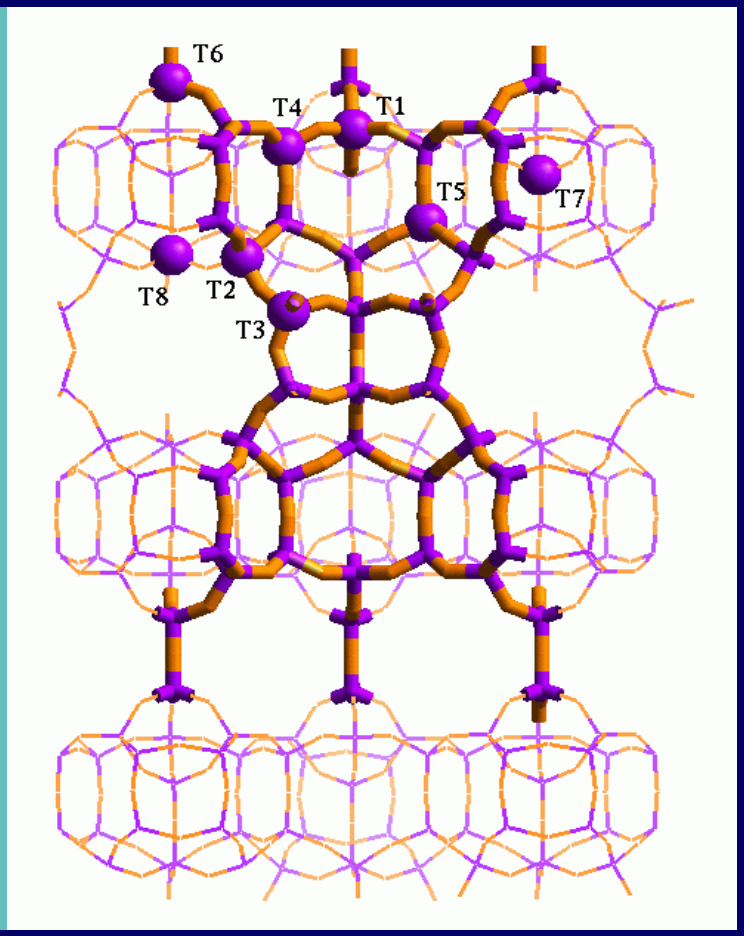






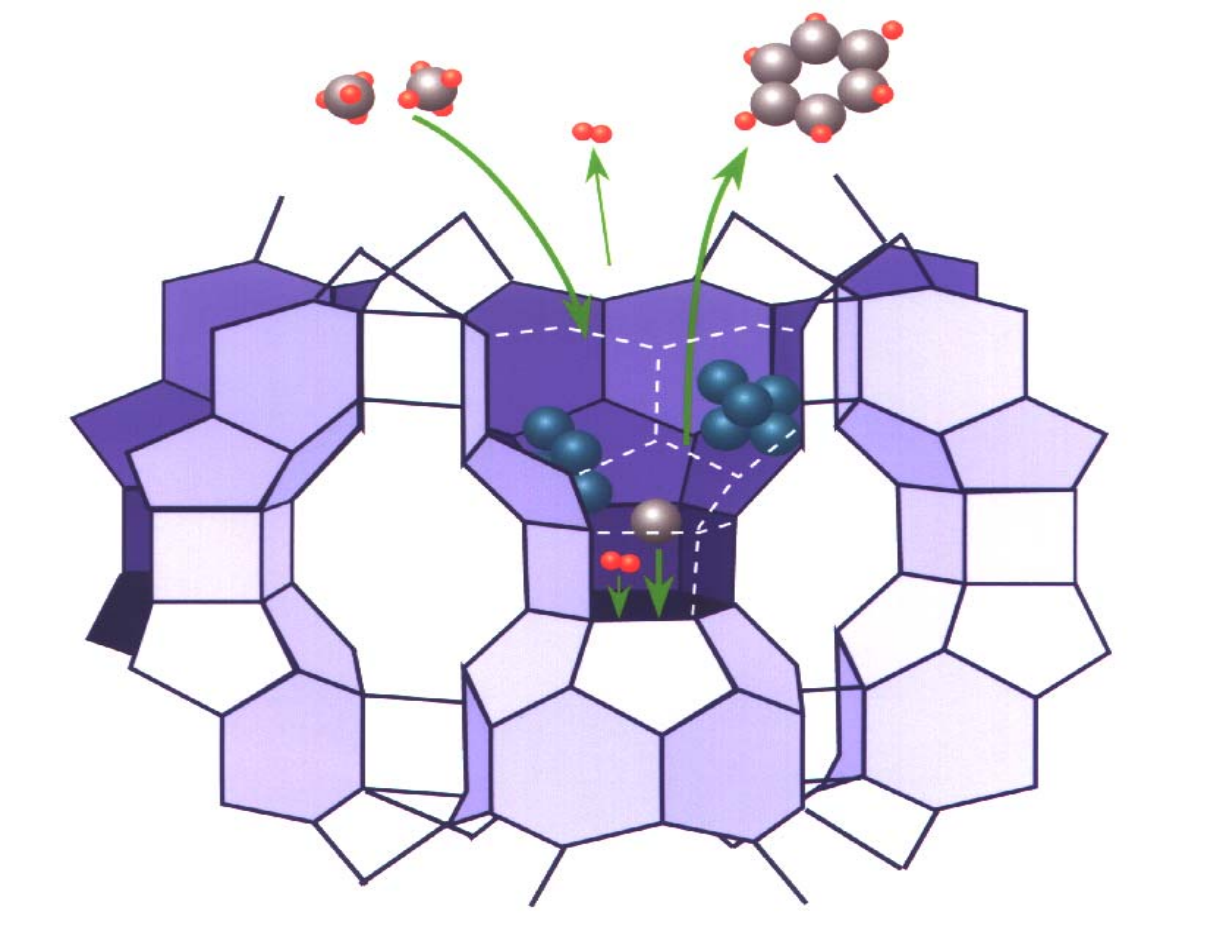
Morphology of zeolites



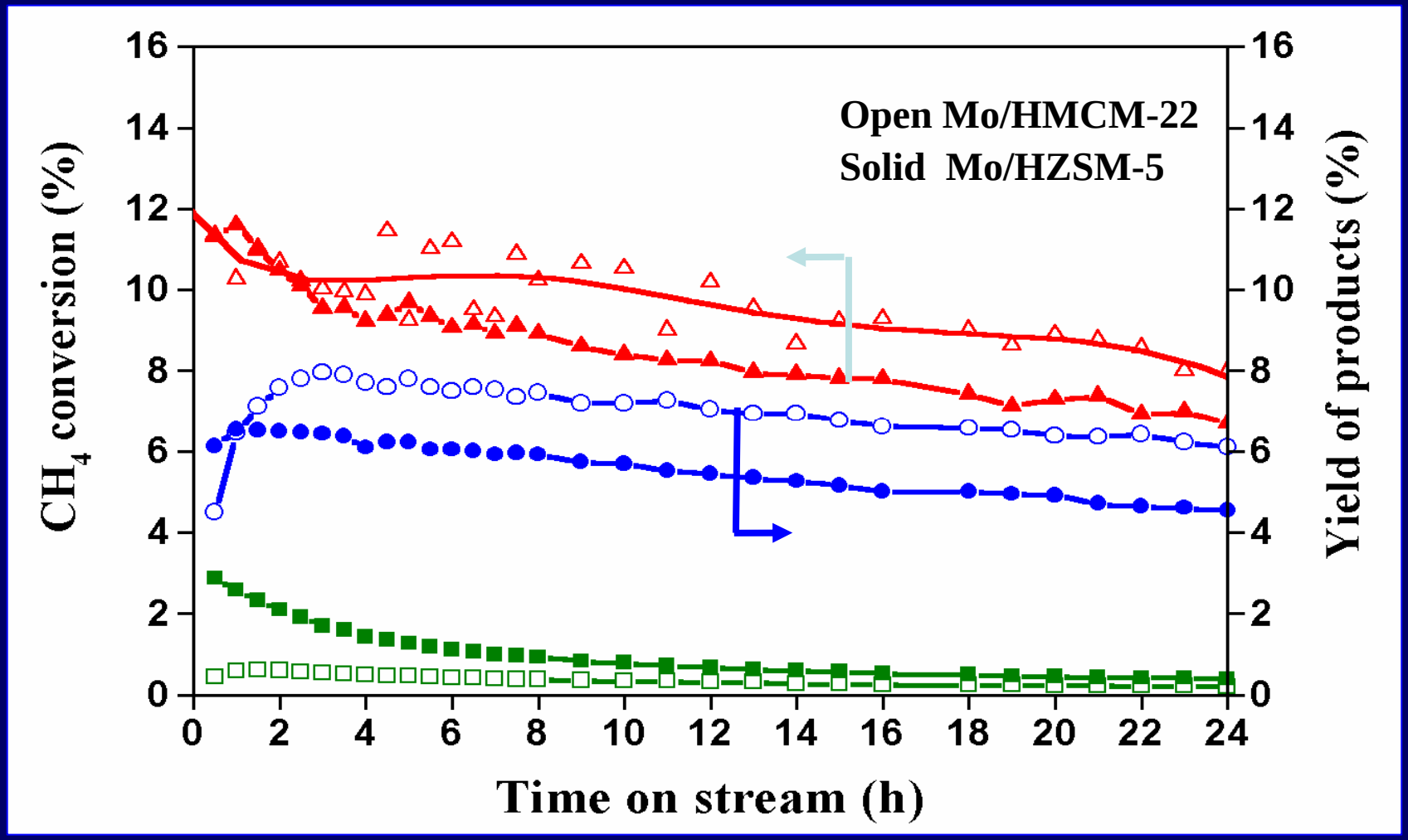


MCM-22

Mo/MCM-22

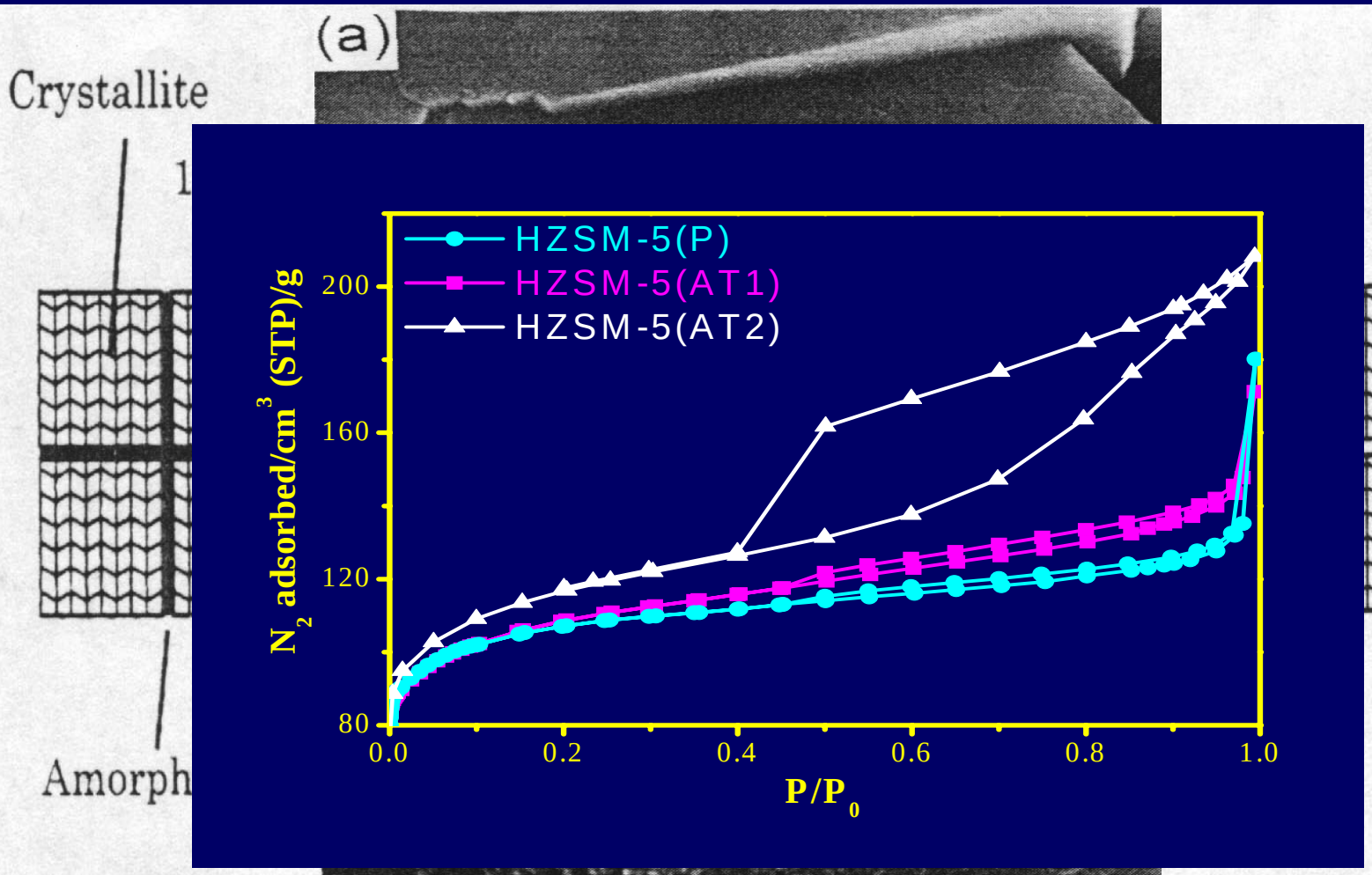


Comparison between Mo/ZSM-5 and Mo/MCM-22

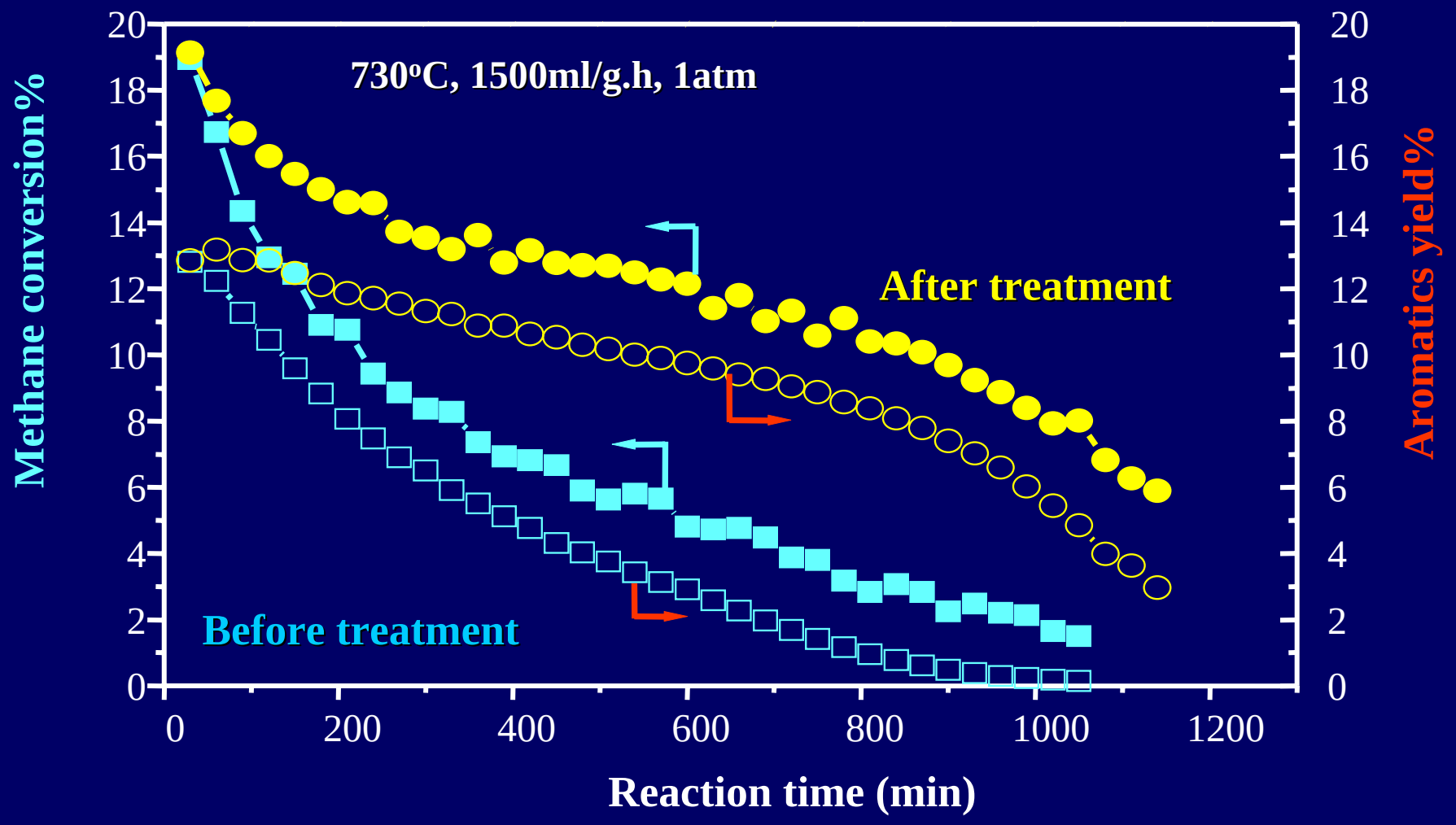


Y. Shu, X. Bao et al., Catal. Lett. 70 (2000) 67.

Modification of HZSM-5 with alkali treatment



Modification of zeolite carrier



Catal. Lett. 91 (2003) 155-167

Pore morphology of carriers

Shape selectivity

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

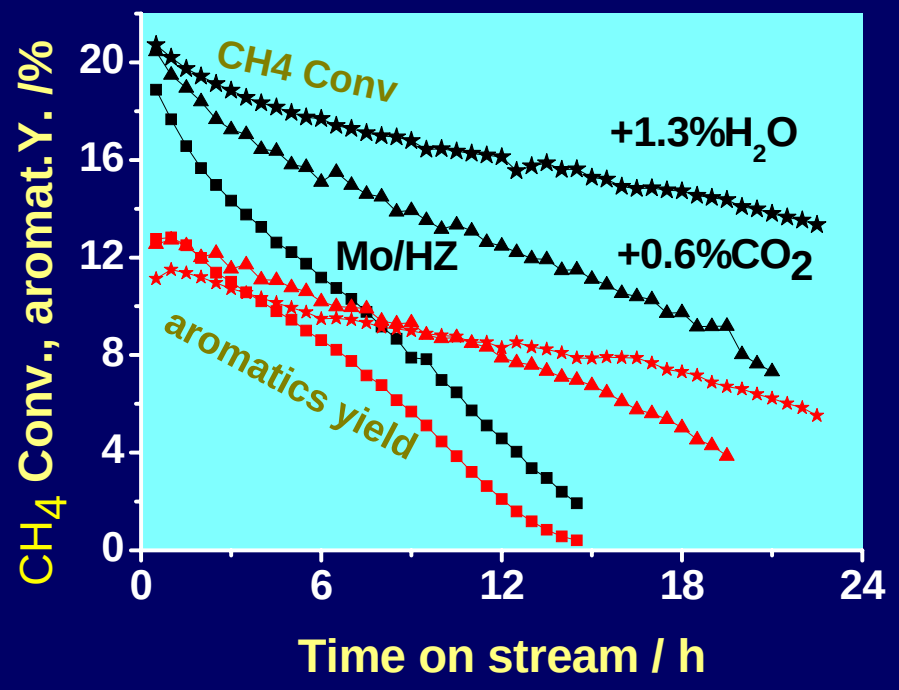
A Coupled Process

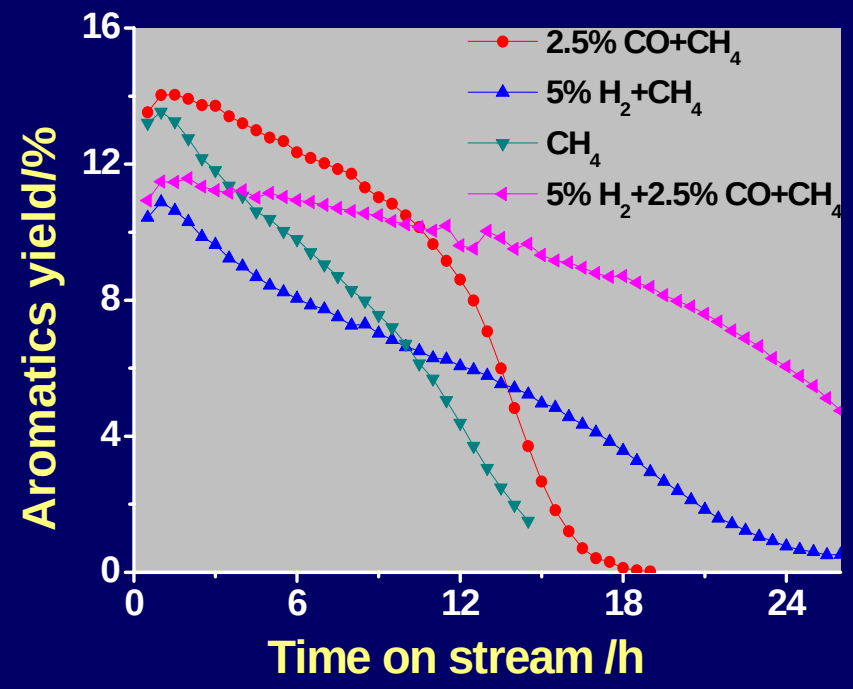
Aromatization + Oxidative Coupling

Why to couple?

Aromatization : $CH_4 \rightarrow$  $+ H_2 +$ Coke

Effect of co-feeding CO, CO_2, H_2, CO/H_2, H_2O





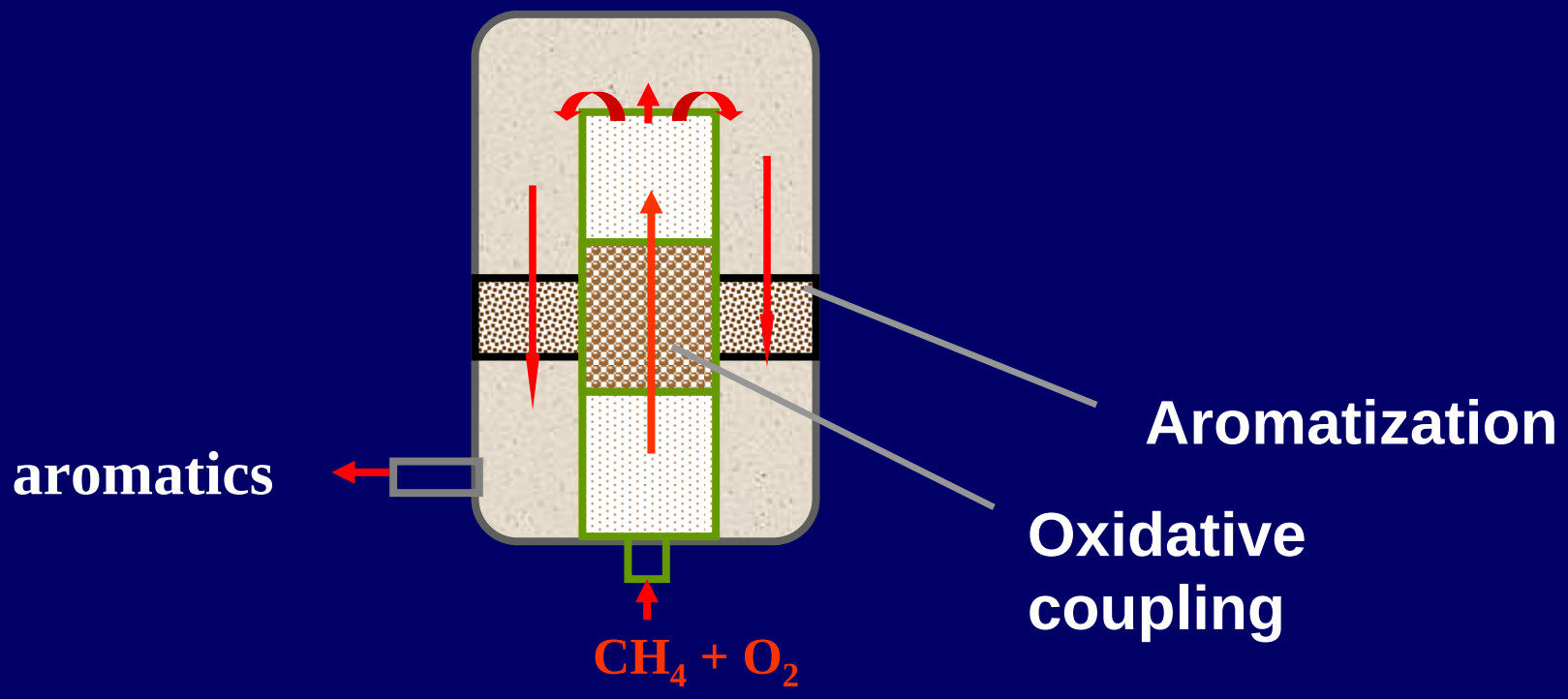
→ **Improved yield and stability**

Why to couple?

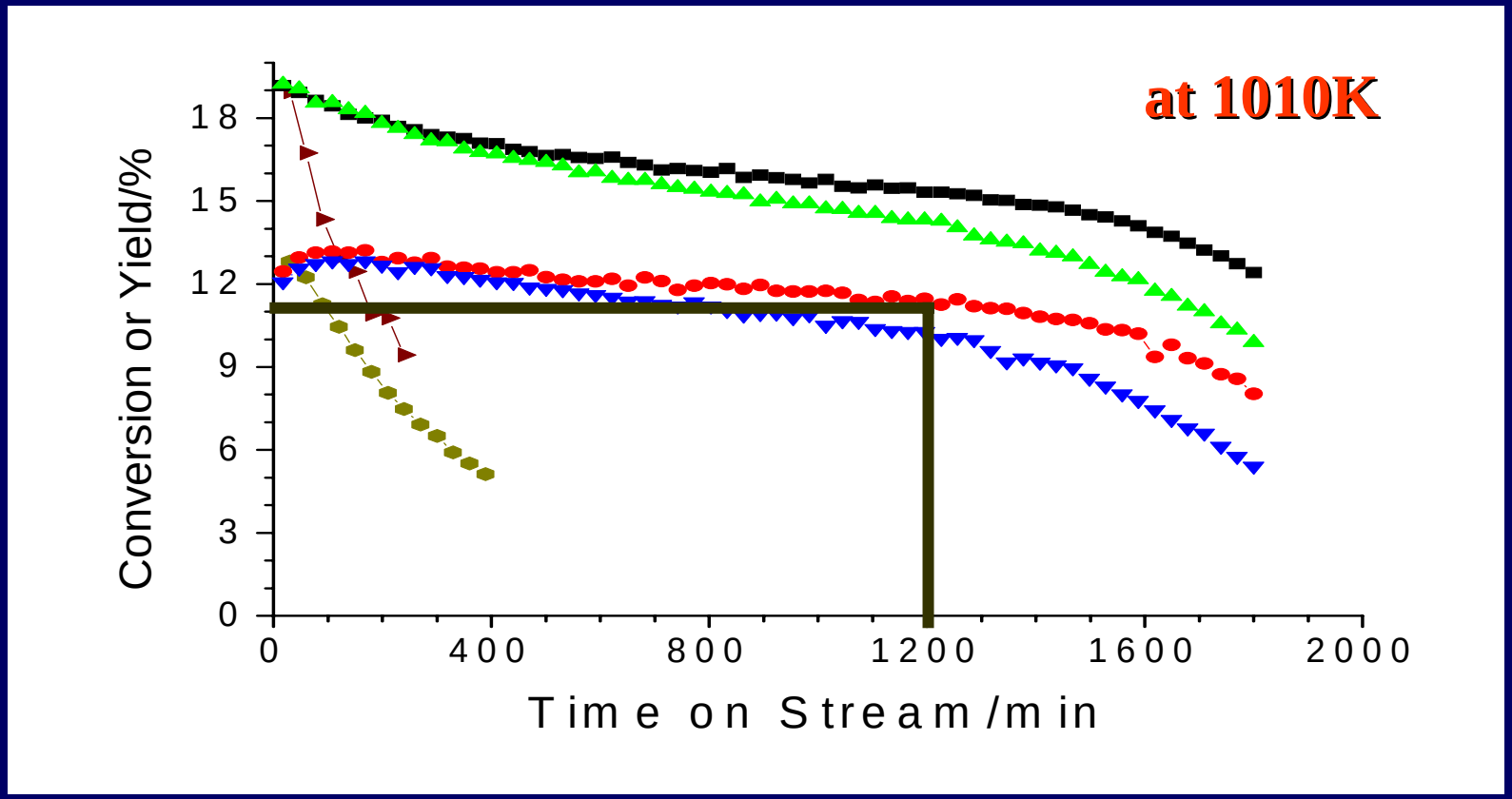
OCM : $CH_4 + O_2 \rightarrow C_2H_4 + CO_2$

Aromatization : $CH_4 \rightarrow$  $+ H_2 +$ Coke $\rightarrow 2CO$

Aromatization of methane by coupling oxidative coupling



Aromatization + Oxidative Coupling



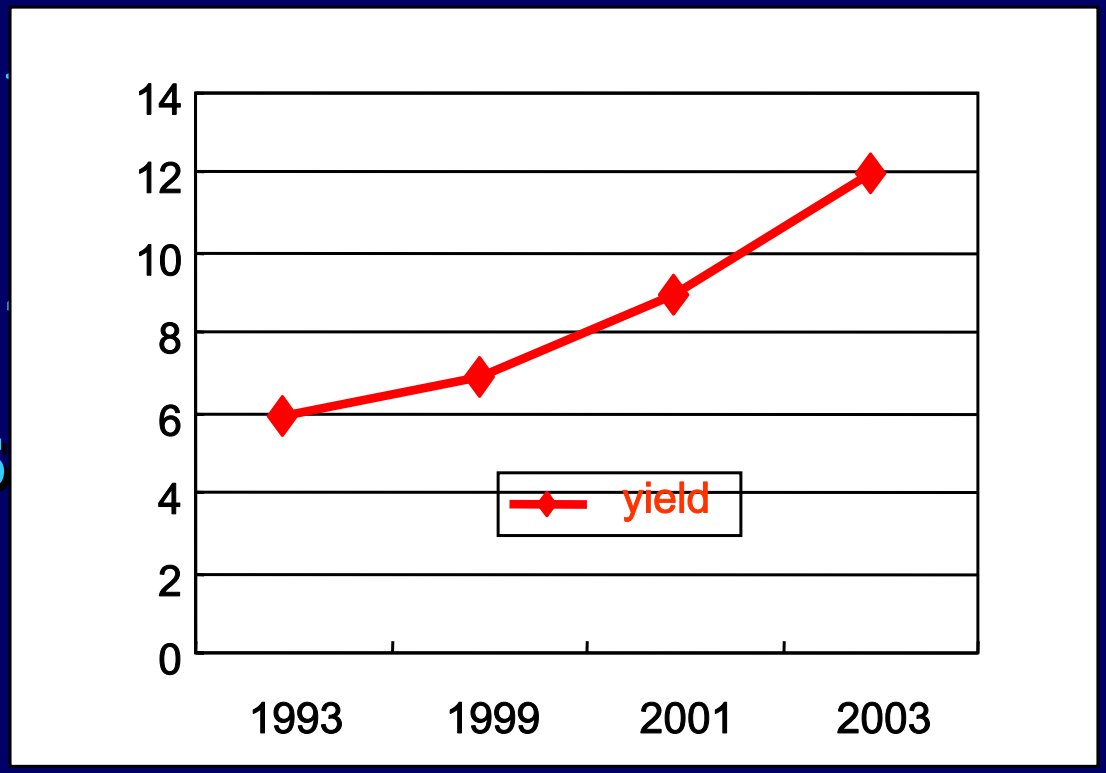
CH_4 conversion (■) on SLC-6Mo/HZ[a], (▲) on SLC-6Mo/HZ[b],

Yield to aromatics (●) on SLC-6Mo/HZ[a], (▼) on SLC-6Mo/HZ[b],

J. Catal. 216 (2003), Catal. Lett. 89 (2003) 275-279 .

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

谢 谢

Thank you