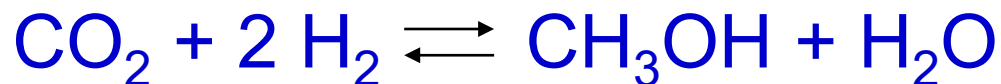
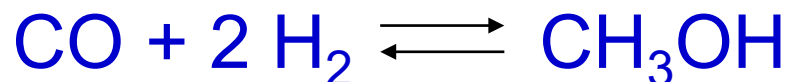


The reactions

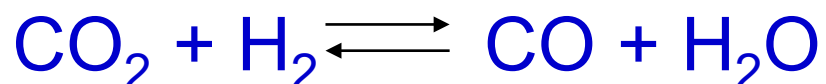
■ Methanol: (metal catalyst)



$$\Delta H^0_{298 \text{ K}} = -40.9 \text{ kJ/mol}$$

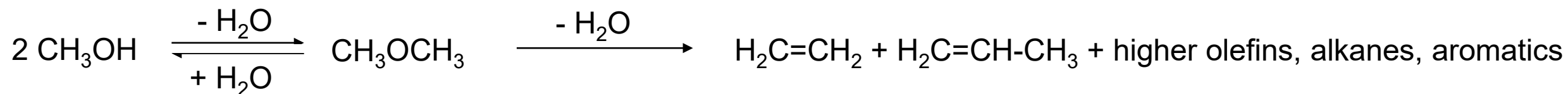


$$\Delta H^0_{298 \text{ K}} = -90.7 \text{ kJ/mol}$$



$$\Delta H^0_{298 \text{ K}} = 49.8 \text{ kJ/mol}$$

■ MTO: (zeolite catalyst)



Extremely exotherm: 56 kJ/mol per CH₃OH (45 kJ/mol per DME)

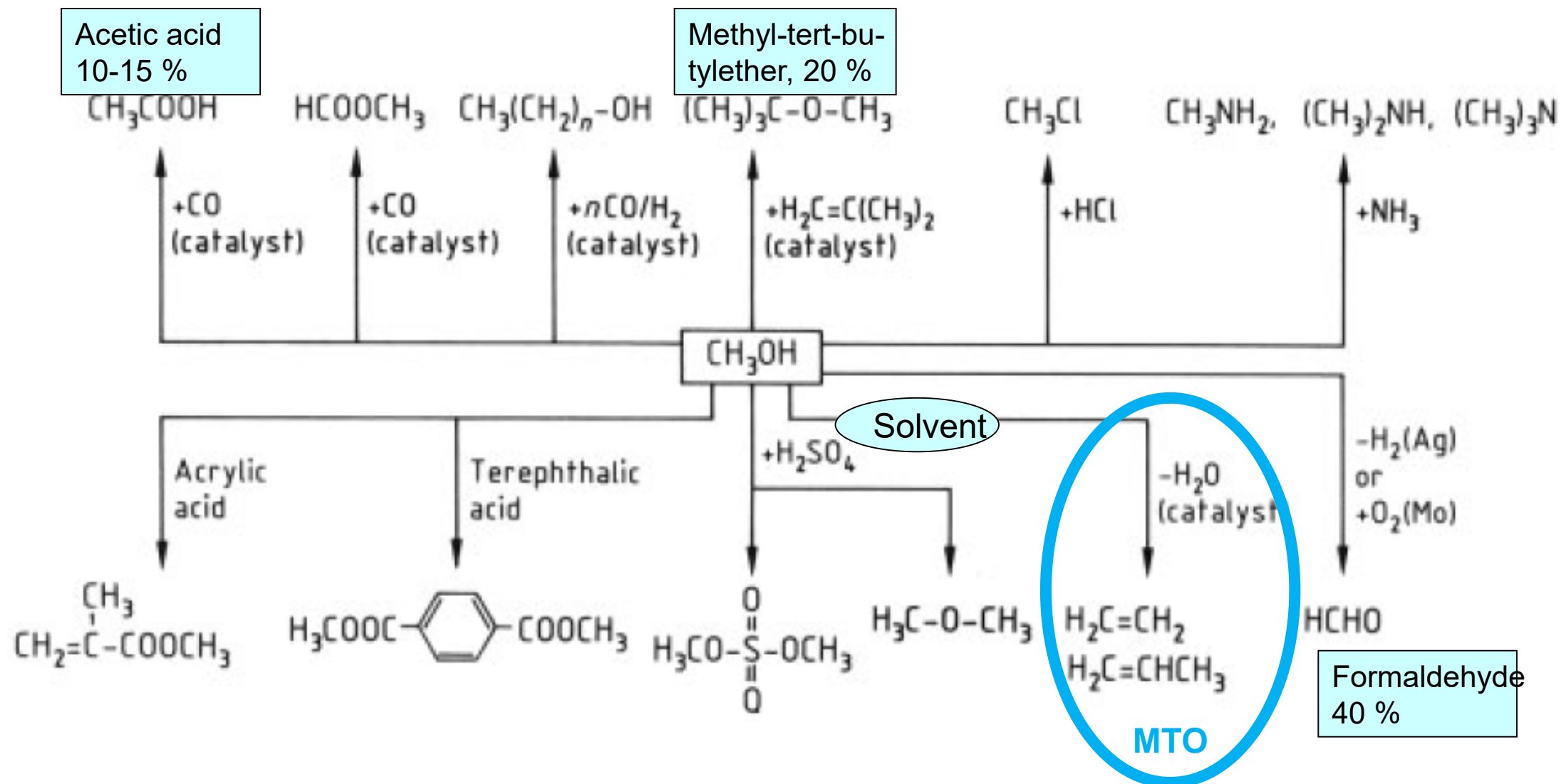
Autocatalytic in nature (both olefins and aromatic cycle)

Deactivation by coking.

Challenges: heat transport and regeneration



Methanol as base chemical



MTO over zeolites

- Key aspects
 - Selectivity to Light Olefins
 - Stability
- Selectable / Tunable Properties of Zeolites
 - Pore opening and Cage size
 - Acidity
 - Mesostructure
- Best catalyst to date: SAPO-34

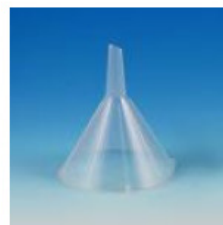


METHANOL-TO-OLEFINS (MTO)



Polyethylene and Polypropylene

- Thousands of uses of polyethylene and polypropylene.

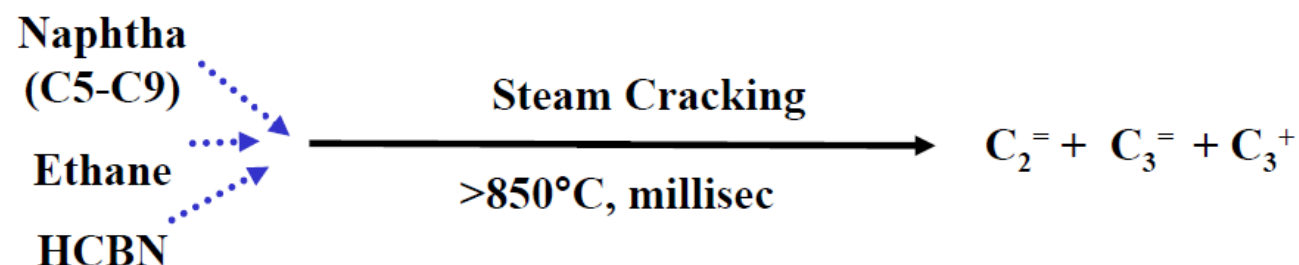


Courtesy: Simon R. Bare



Polyethylene and Polypropylene

- Main source of the ethylene and propylene (monomer feedstock for polyethylene and polypropylene) is steam cracking of naphtha or other hydrocarbon.

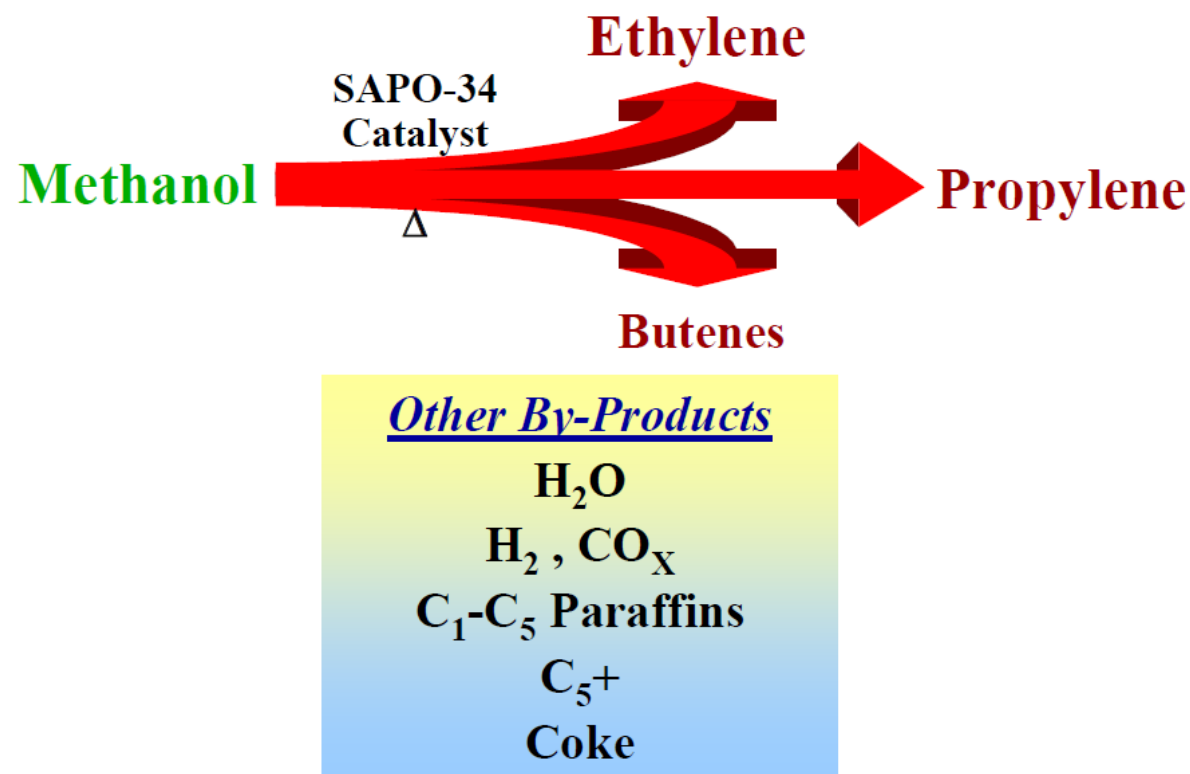


Courtesy: Simon R. Bare



Methanol-to-Olefins (MTO) reaction

- Methanol is an alternate source of light olefins.
- Dehydration with shape selective transformation to low molecular weight alkenes.

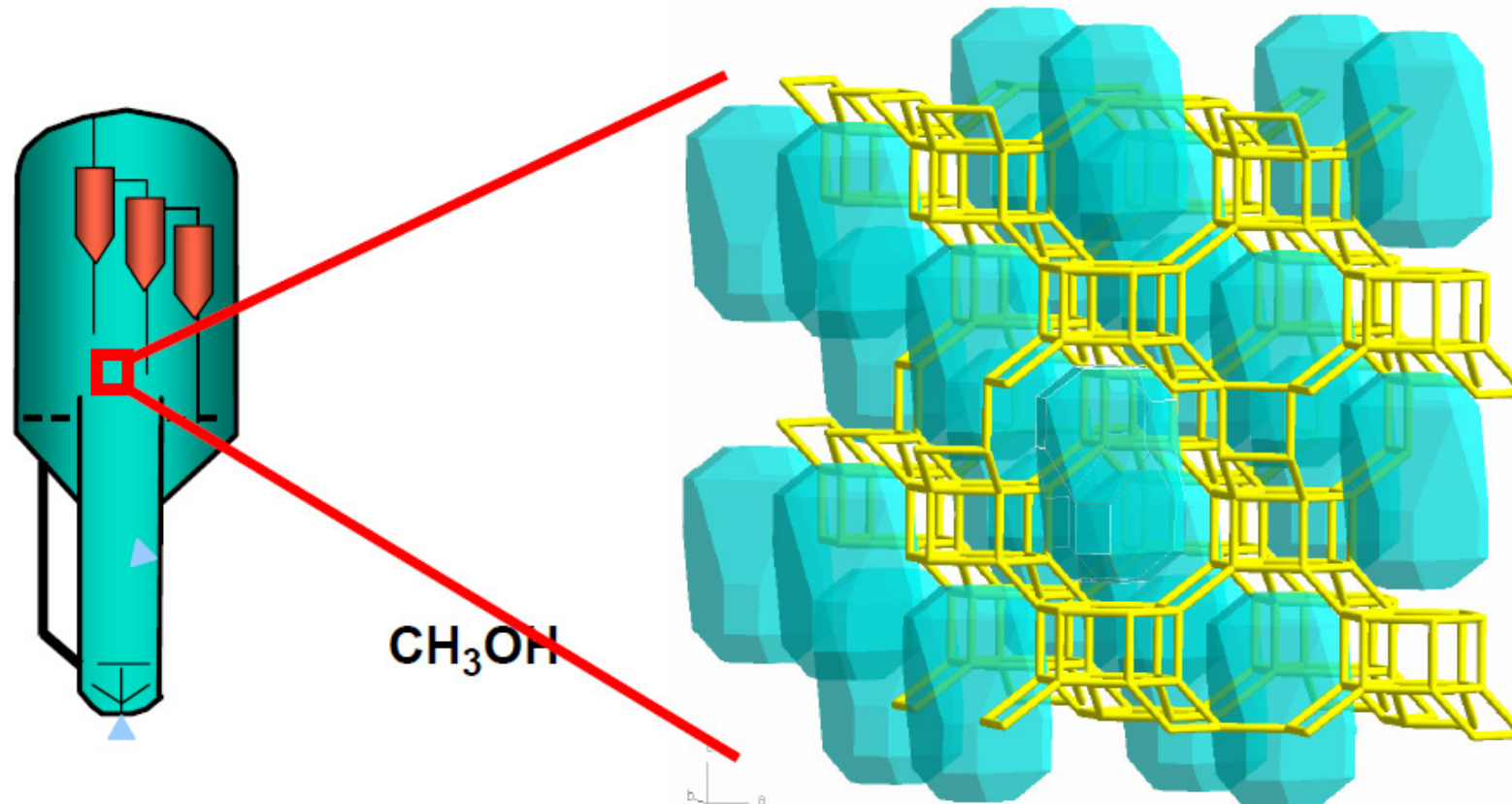


Courtesy: Simon R. Bare



UOP/Hydro MTO Process

SAPO-34 Catalyst



Courtesy: Simon R. Bare, Unni Olsbye



SAPO-34 for MTO Process

- High selectivity and yield to light olefins.

Material	SAPO-34
T atom %	10% Si (gel)
Selectivities (2 hr)	
C ₂ -C ₄ olefins	96
CH ₄	1.4
C ₂ H ₆	0.3
C ₃ H ₈	0.9
Stability	
hr at >50% conversion	>40
Coking	
carbon on used catalyst	19% after 54 HOS

- Many acid catalysts are active for the methanol dehydration – what makes SAPO-34 the preferred catalyst?

Courtesy: Simon R. Bare

Yuen, et al., Microporous Materials, 2 (1994) 105



What is a Zeolite?

Zeolite

From Wikipedia, the free encyclopedia

Zeolites (Greek, *zein*, "to boil"; *lithos*, "a stone") are minerals that have a micro-porous structure. The term was originally coined in the 18th century by a Swedish mineralogist named Axel Fredrik Cronstedt who observed, upon rapidly heating a natural mineral, that the stones began to dance about as the water evaporated. Using the Greek words which mean "stone that boils," he called this material zeolite.

- **Zeolites occur in nature.**



Mordenite



Chabazite



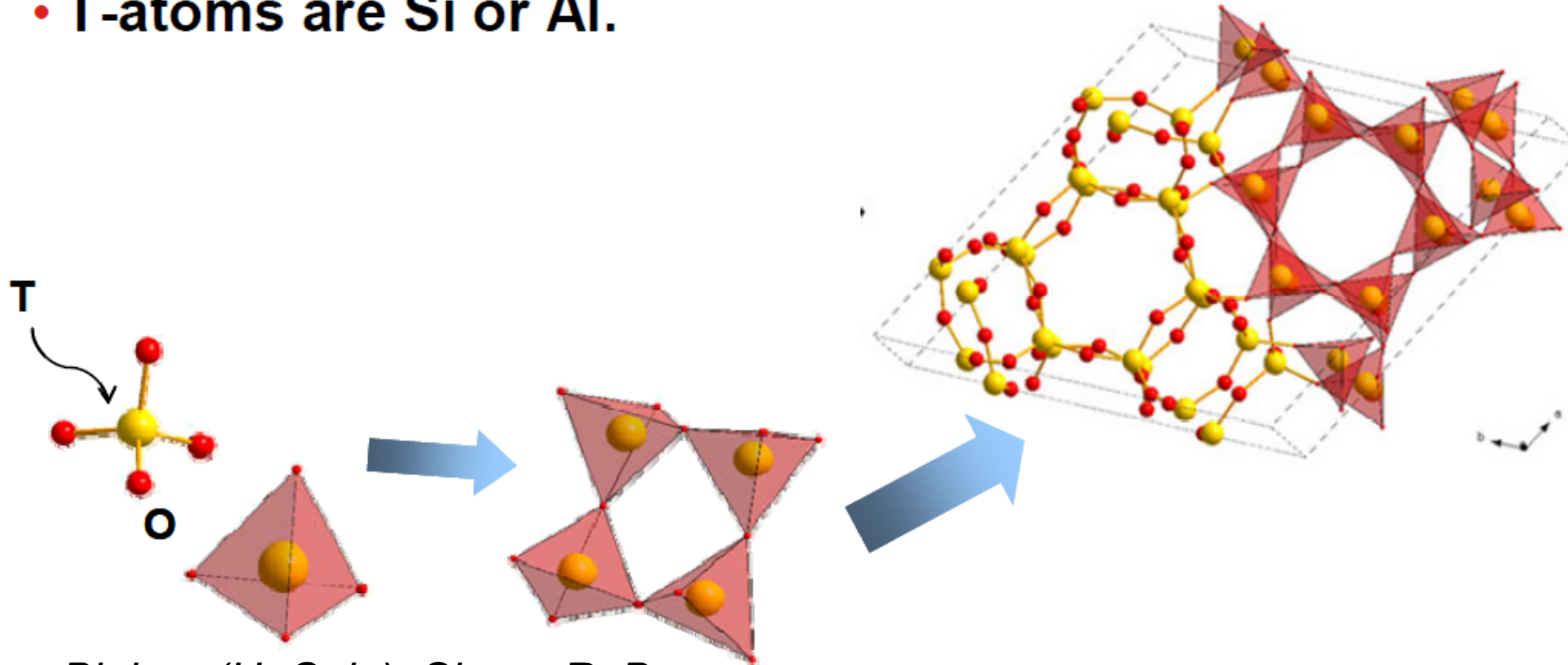
Natrolite

Courtesy: Simon R. Bare



Zeolites

- Zeolites consist of a framework built of tetrahedra.
- Each tetrahedron comprises a T-atom bound to four O atoms.
- Oxygen bridges connect the tetrahedra.
- T-atoms are Si or Al.

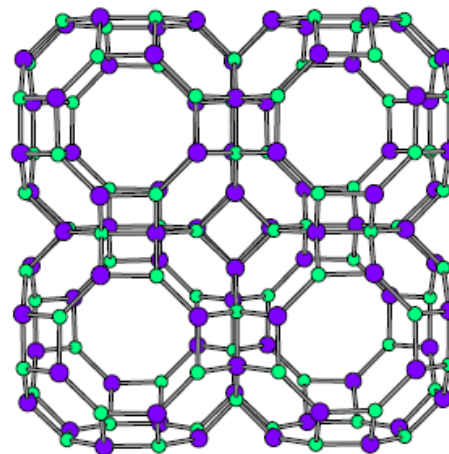
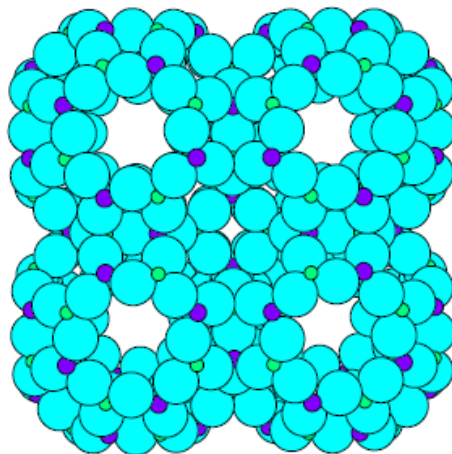
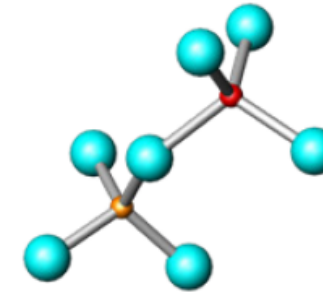


Courtesy: Francesca Bleken (U. Oslo), Simon R. Bare

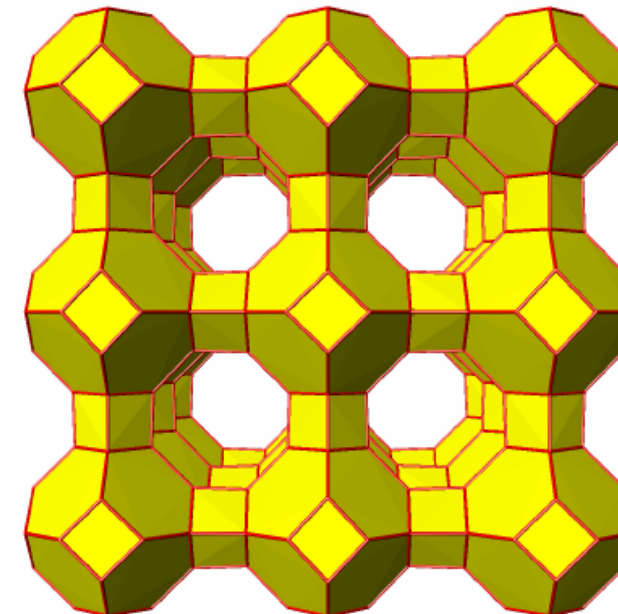


Zeolites

- Alumino-silicate framework
- Crystalline, microporous (pore diameter 3-14Å)
- Framework density < 20 T-atoms/ $1000\text{\AA}^3$



LTA = Zeolite A

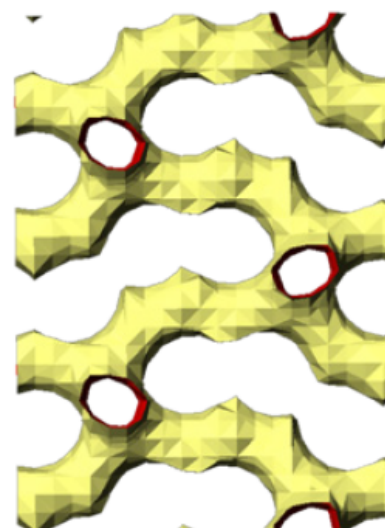
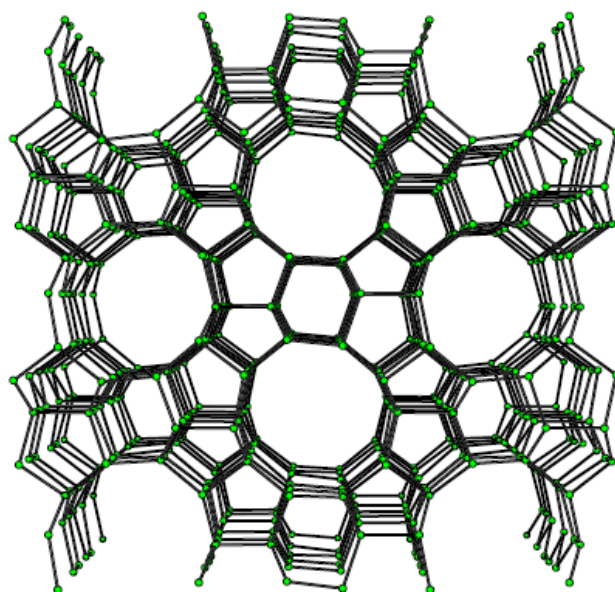
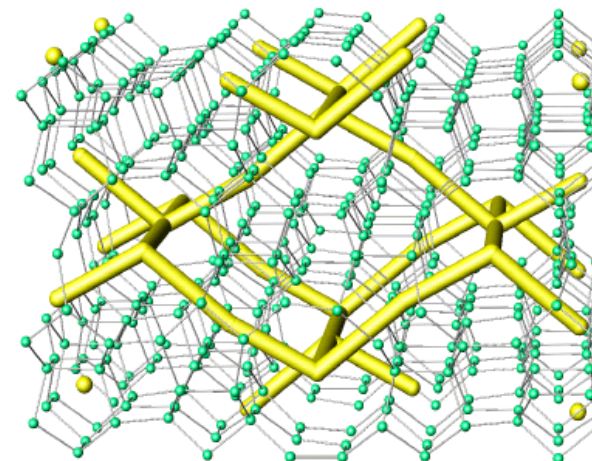


Courtesy: Simon R. Bare



Ways to Visualize a Zeolite: ZSM-5 (MFI)

- Medium pore size 5.1 x 5.5Å
 - Wire frame structure showing only T-atoms
 - Pore structure – critical for thinking about a molecule diffusing through the structure.



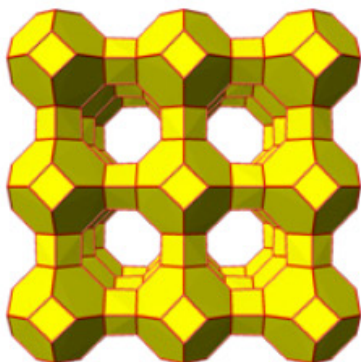
Courtesy: Simon R. Bare



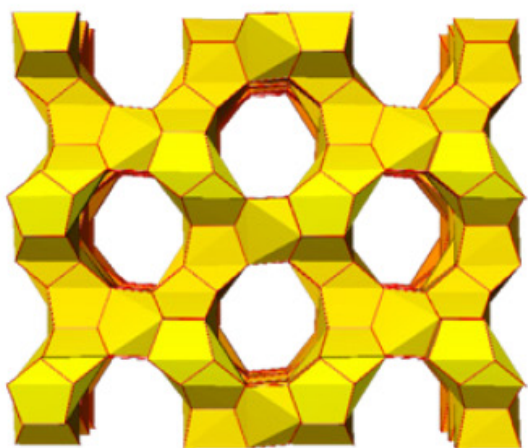
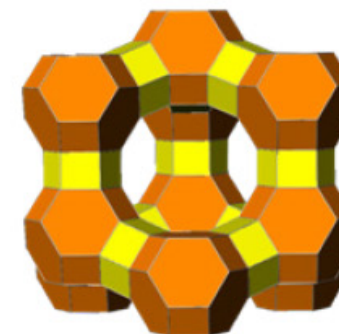
Ranges of Pore Sizes

- Zeolites exhibit a range of pore sizes of molecular dimensions (molecular sieves).

Small
8-ring
~ 4Å

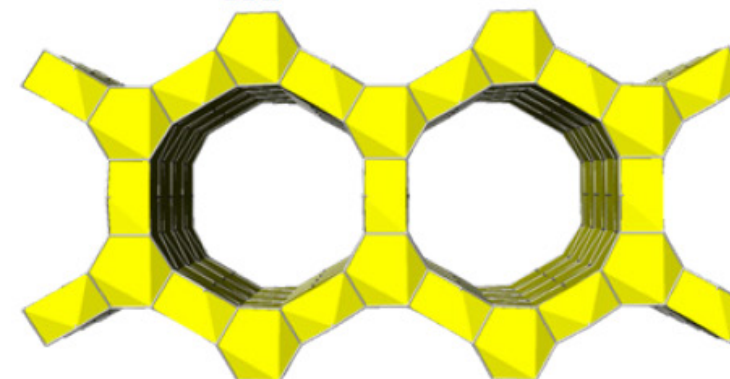


Large
12-ring
~ 6-8Å



Medium
10-ring
~ 5-6Å

Very Large
>12-ring
>8Å

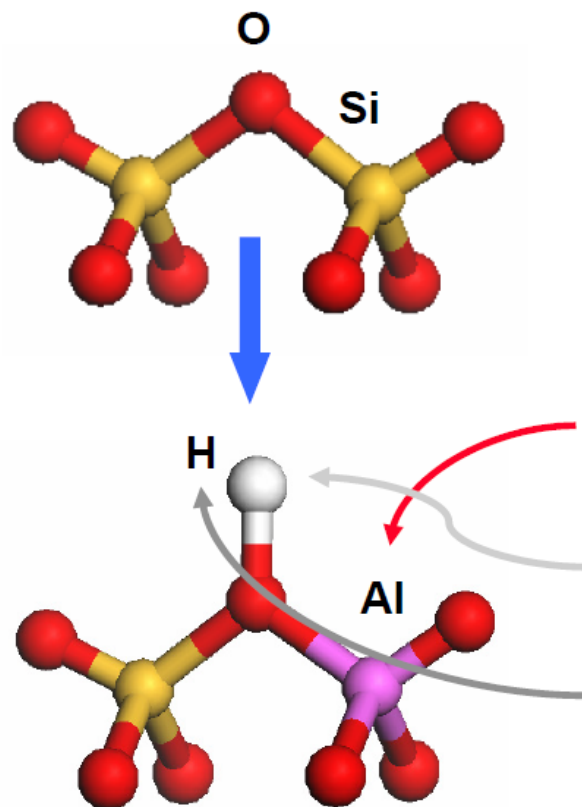


Courtesy: Simon R. Bare



Acid Sites in Zeolites

- Substitute Al^{3+} for Si^{4+} : charge imbalance – need additional cation to compensate.



- No total charge.
- One extra charge per Al atom introduced into the lattice.
- Cations compensate for total charge.
- Protons as cations give Brønsted acid properties.

Courtesy to Francesca Bleken,

Courtesy: Francesca Bleken (U. Oslo), Simon R. Bare



Commercial Catalytic Uses of Zeolites (Refinery and Petrochemicals)

<u>Process</u>	<u>FAU</u>	<u>LTL</u>	<u>MOR</u>	<u>BEA</u>	<u>MWW</u>	<u>MFI</u>	<u>AEI</u>	<u>FER</u>	<u>RHO</u>	<u>CHA</u>	<u>???</u>
Ethylbenzene					x	x					x
Cumene	x		x	x	x	x					
Other aromatics						x					
Xylene isom						x					x
C4 isom			x								
C4 ⁺ isom						x		x			x
C5 ⁺ isom						x					x
Iso-dewaxing							x				
Amination			x			x			x	x	
C3,C4 arom						x					
Naphtha arom		x									
FCC	x					x					
Dewaxing						x					
Hydrocracking	x					x					
MTG						x					
MTO						x				x	
Toluene trans-alkylation						x					x
SCR (automotive)				x		x				x	

FAU = Y, USY

MWW = MCM-22

RHO = zeolite RHO

LTL = Linde L, K-L

MFI = ZSM-5

CHA = chabazite, SAPO-34

MOR = mordenite

AEI = SAPO-11, SM-3

BEA = beta

FER = ferrierite

Courtesy: Simon R. Bare

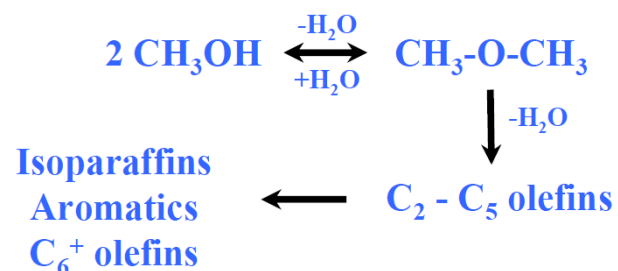
K. Tanabe and W. Holderich, Appl. Catal. A, 399 (1999) 181



MTO milestones (1)

Time of Initial Discovery	Composition
Late 40's to Early 50's	Low Si/Al Ratio Zeolites
Mid 50's to late 60's	High Si/Al Ratio Zeolites
Early 70's	Pure SiO ₂ Molecular Sieves
Late 70's	AlPO ₄ Molecular Sieves
Late 70's to Early 80's	SAPO and MeAPO Molecular Sieves
Late 70's	Metallo-silicates, -aluminosilicates
Early to Mid 90's	Mesoporous Molecular Sieves Octahedral-tetrahedral Frameworks

- 1975 – Mobil Oil discloses ZSM-5 catalyst for conversion of methanol to gasoline (MTG)



Discovery of ALPO and SAPO Materials

- In late 70's Edith Flanigen's group at Union Carbide given the challenge:

“Discover the next generation of molecular sieve materials”

- Words of Edith Flanigen

• MTO Demo Unit

- Started-up in 1995 at Norsk Hydro facilities in Norway
- Used commercial methanol feedstock

- UOP and Total Petrochemicals announced in Dec 2005 an integrated demonstration unit consisting of both a UOP/HYDRO Methanol-to-Olefins unit and a Total Petrochemicals/UOP Olefin Cracking unit.

- Construction started at Total's petrochemical complex in Feluy, Belgium. Start-up in 2008.



Courtesy: Simon R. Bare

Chang, Silvestri, and Smith, US 3894103 and 3928483



MTO Milestones (2)

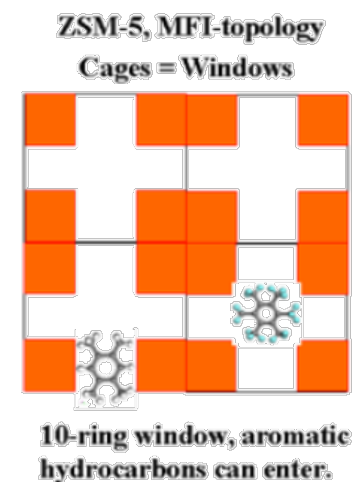
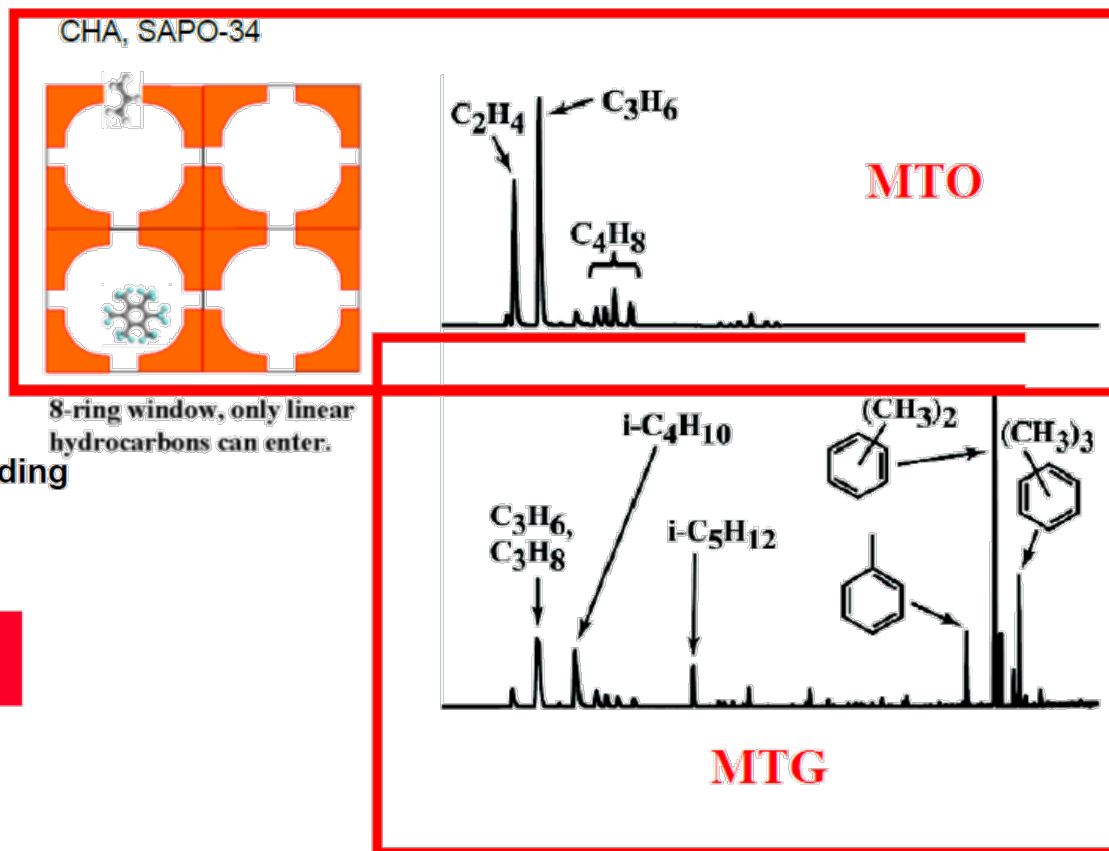
- DMT0 technology 2010 – world's first commercial MTO unit (Baotou, China) – 0.6 Mt/a $C_2^= + C_3^=$.
- DMT0-II: Coupled with FCC to crack higher olefins and aromatics to light olefins. Common regenerator and catalyst!
- 2018: 18 DMT0 units – 7.16 Mt/a



Methanol to Hydrocarbons

- **Medium-pore zeolites (ZSM-5)**
 - Major olefin product is Propylene
 - Significant C_{5+} /aromatics by-products
 - Slow deactivation
- **Small-pore molecular sieves (SAPO-34)**
 - Major olefin products are Ethylene and Propylene
 - Fast deactivation by aromatic coke
 - SAPO molecular sieves more stable than corresponding zeolite structure

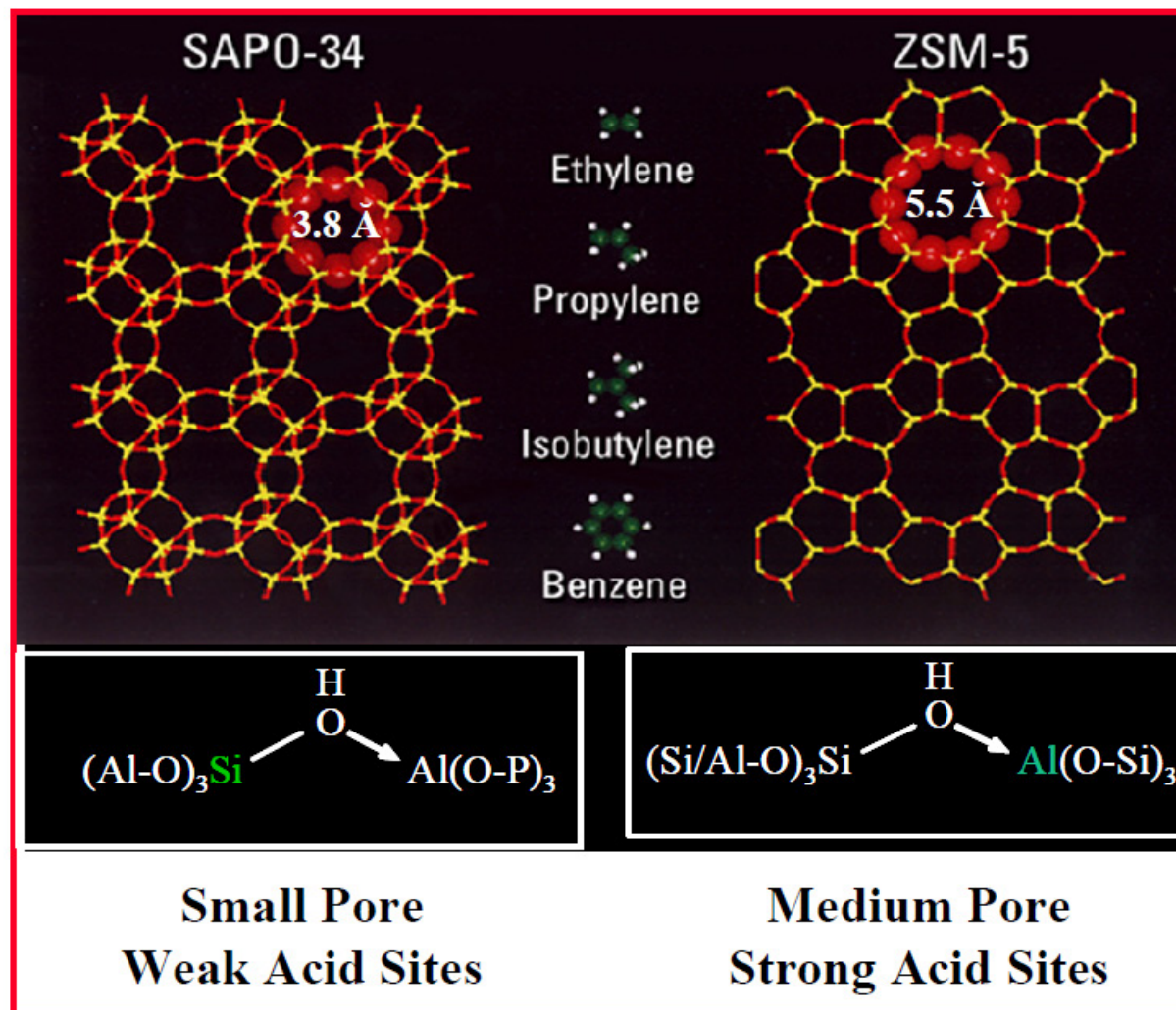
Shape Selectivity



Courtesy: Simon R. Bare

Methanol to Hydrocarbon Catalysis, J. F. Haw, et al., Acc. Chem. Res. 2003, 36, 317

Structural Comparison

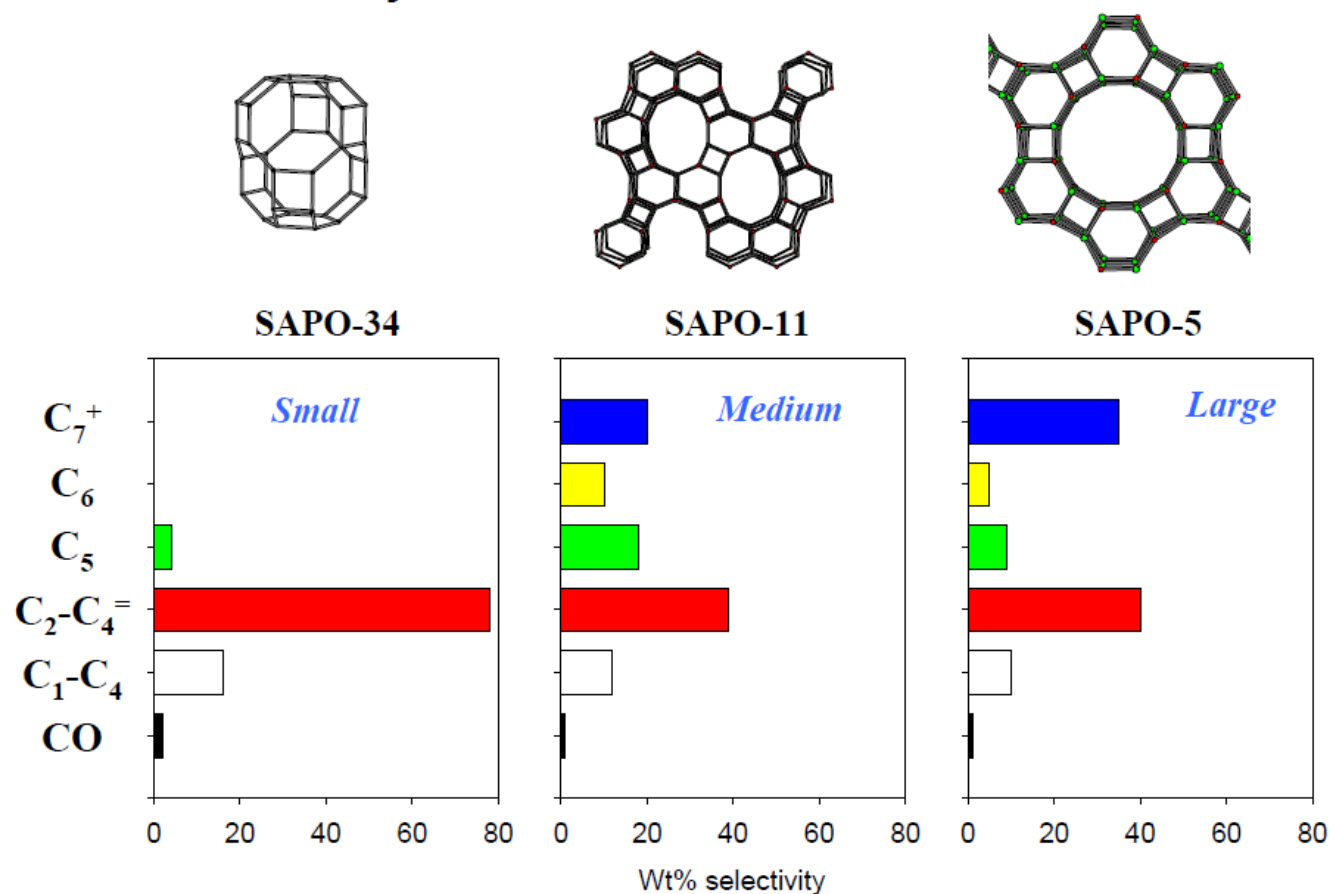


Courtesy: Simon R. Bare



Small, Medium and Large Pore

- Small, medium and large pore SAPO's show MTO activity – but distinct selectivity differences.



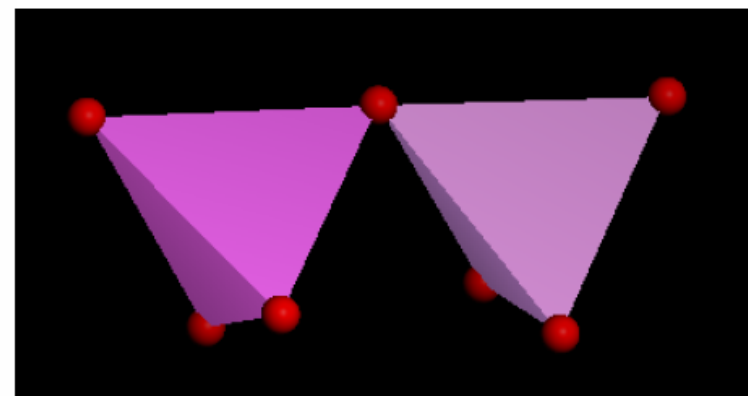
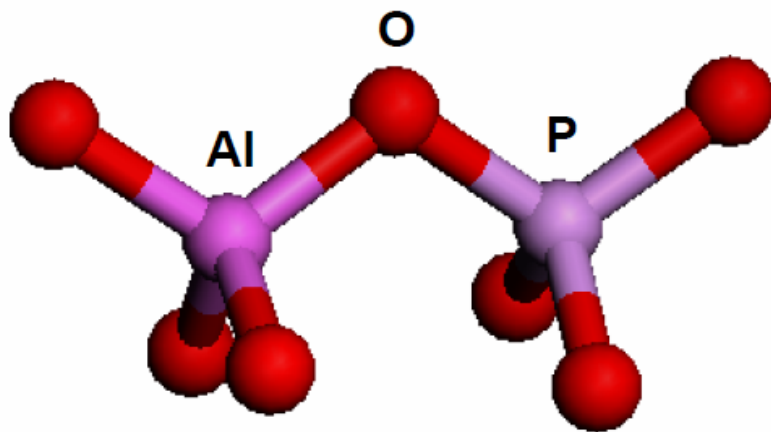
350C, WHSV = 0.3 hr⁻¹,
MeOH = 0.02 bar, N₂ = 0.98 bar

S.M. Yang et al, Stud. Surf. Sci. Catal., 61, 429 (1991)

Courtesy: Simon R. Bare

Alumino-Phosphate (AlPO_4) Molecular Sieves

- Microporous solids similar to silico-aluminate zeolites – but composed of interlinked tetrahedra of AlO_4 and PO_4 vs. AlO_4 and SiO_4 .
- Alternating Al-O-P bonds
- Almost never Al-O-Al, and never P-O-P (due to charge and lack of hydrothermal stability).

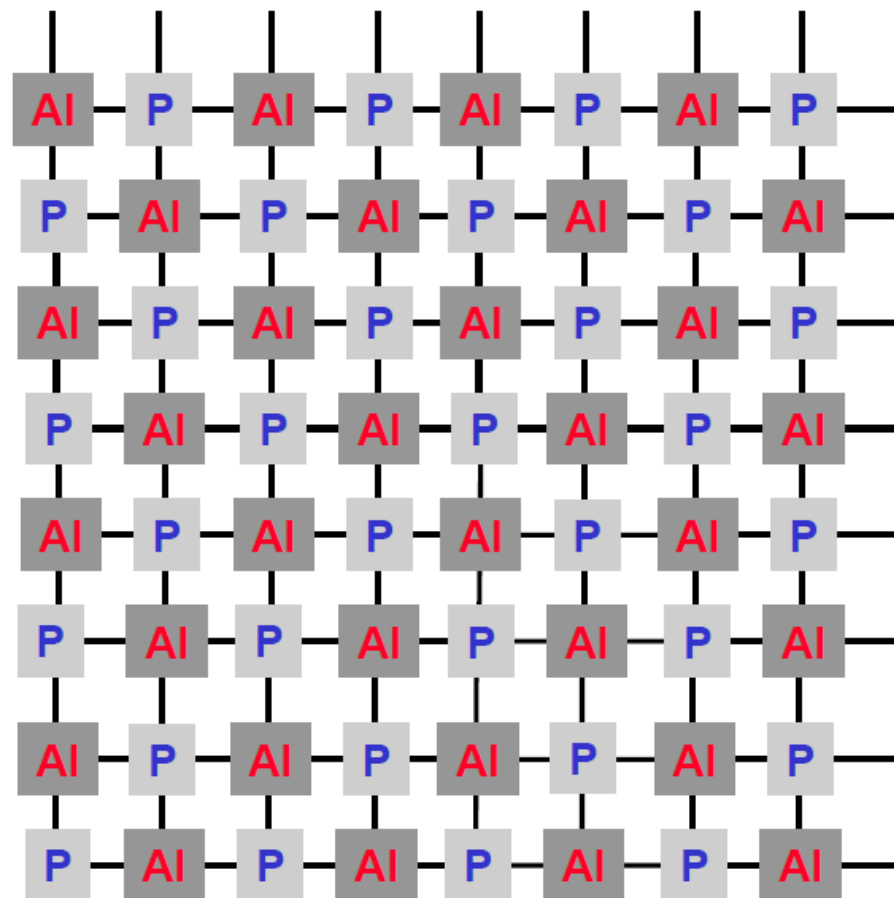


Courtesy: Simon R. Bare



Idealized 2D-Connectivity of Tetrahedral AlPO_4 Framework

- Al and P strictly alternating.
- Neutral framework.



Courtesy: Simon R. Bare



Si Substitution for P in AlPO_4 to give SAPO

- Si substitution for P in AlPO_4 yields negative framework charge and Brønsted acid sites.

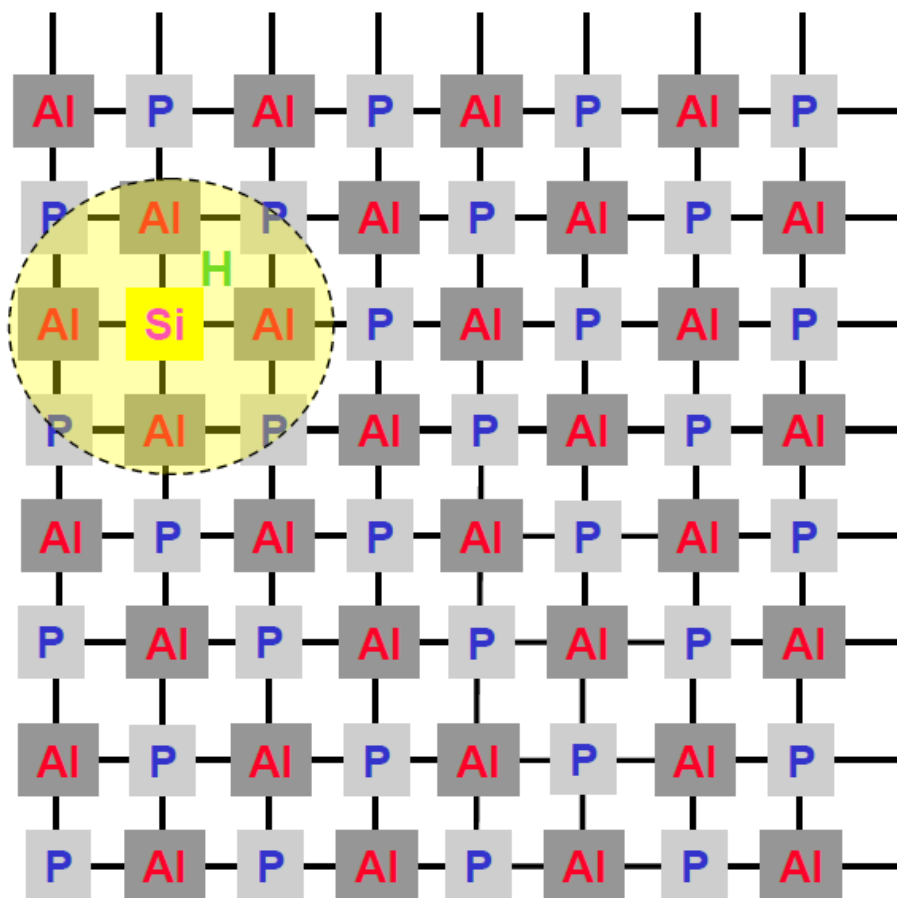
Isolated Si: $\text{Si}^{+4} \rightarrow \text{P}^{+5}$

Negative framework charge

Template decomposition $\rightarrow \text{H}^+$

No Si-O-P

No P-O-P



Courtesy: Simon R. Bare



Si Substitution Produces Brønsted Acid Sites

Isolated Si

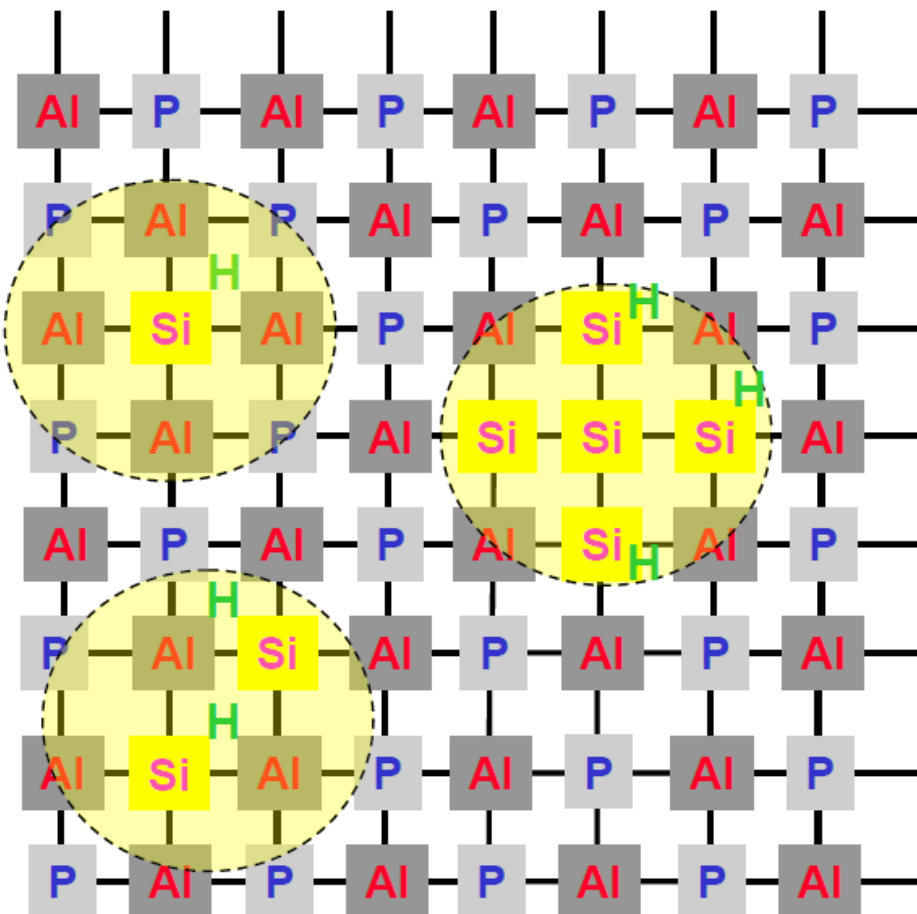
1 Si = 1 P

1 Si = 1 H⁺

Adjacent
isolated Si

2 Si = 2 P

2 Si = 2 H⁺



Si island

5 Si = 4 P + 1 Al

5 Si = 3 H⁺

Yes

Al-O-P

Si-O-Al

Si-O-Si

No

Al-O-Al

P-O-P

Si-O-P

Courtesy: Simon R. Bare



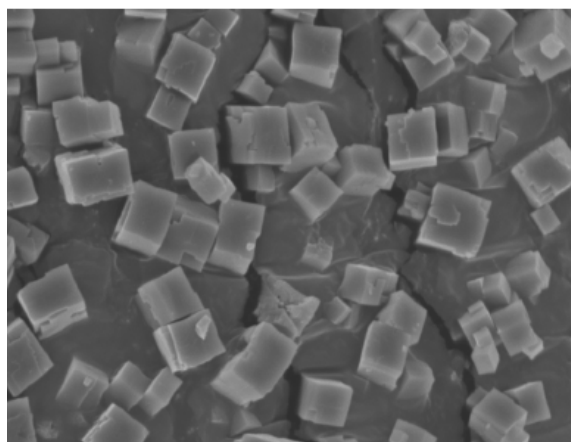
Desired structure and Templates

SYNTHESIS OF SAPO-34

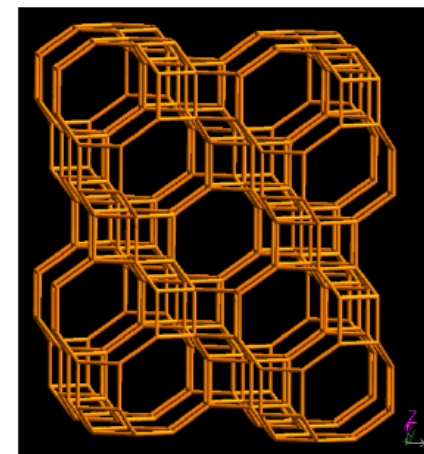
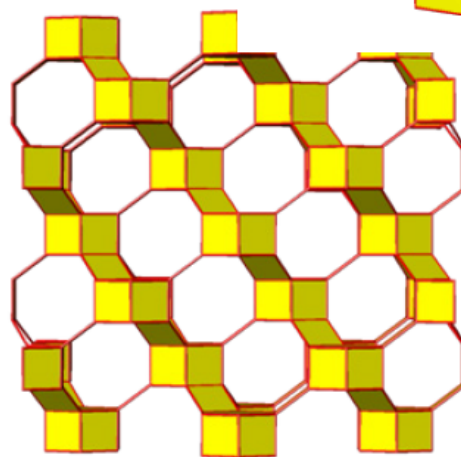
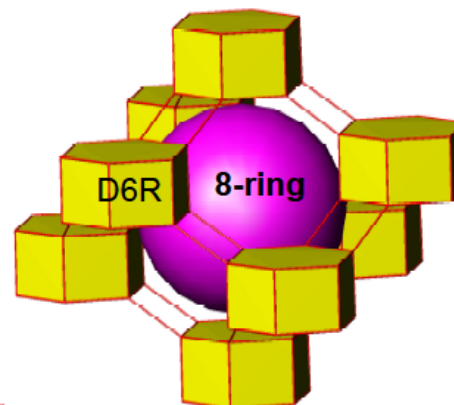


SAPO-34 (CHA) Structure

- Three-dimensional pore system consisting of large cavities (about 9.4Å in diameter) separated by small windows (3.8 x 3.8Å)
- Periodic building unit is the double 6-ring layer – connected through 4-rings.



*SEM of SAPO-34 crystals
~1 μm*



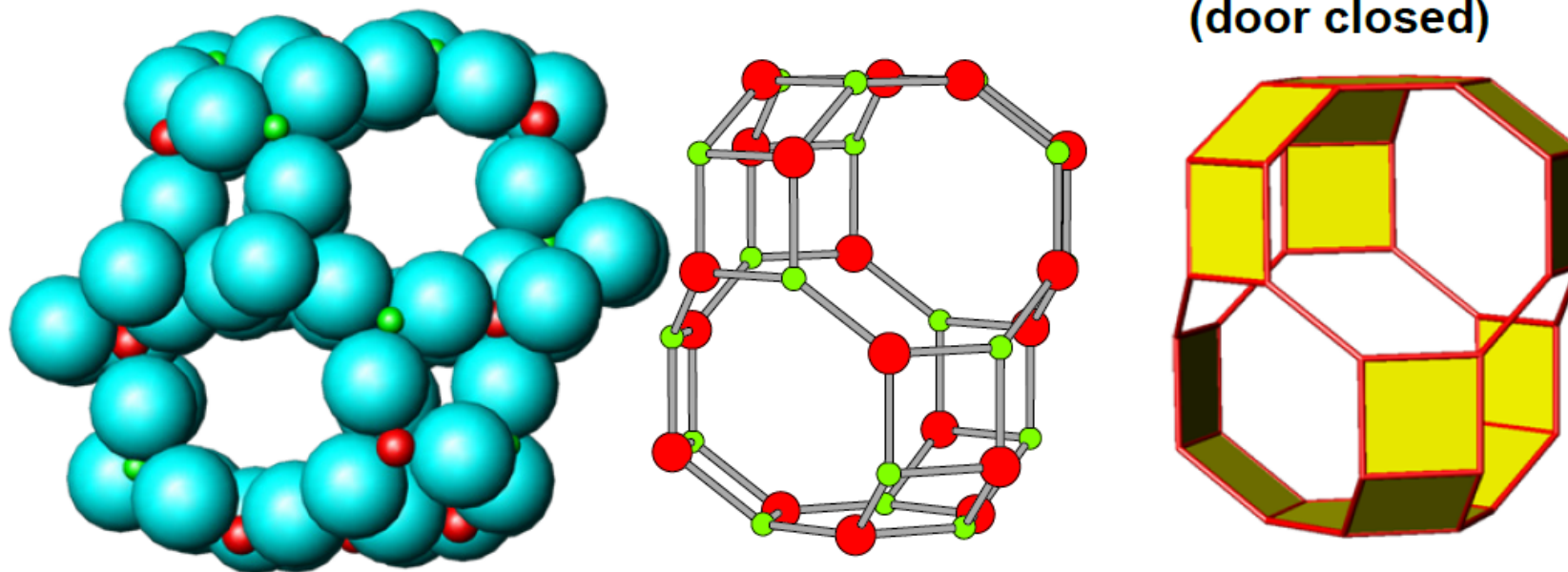
Courtesy: Simon R. Bare



CHA Framework: Structural Characteristics

- The CHA cage.

4-rings inaccessible
to most molecules
(door closed)



Cage bounded by 36 TO_2
Dimensions: 7.5 x 8.2 Å
Pore opening: 4.4 x 3.6 Å
Every TO_2 shared by 3 cages

Courtesy: Simon R. Bare



SAPO-34 vs. SSZ-13

- SSZ-13 has same structure (CHA) as SAPO-34 but is an aluminosilicate zeolite.
- Selectivity to olefins substantially less in SSZ-13.

Material	SAPO-34	SSZ-13 (Chabazite)	SSZ-13 (Chabazite)	SSZ-13 (Chabazite)
T atom %	10% Si (gel)	18% Al	10% Al	3.3% Al
Selectivities (2 hr)				
C ₂ -C ₄ olefins	96	69	75	87
CH ₄	1.4	3.9		
C ₂ H ₆	0.3	5.4		
C ₃ H ₈	0.9	18.9		
Stability				
hr at >50% conversion	>40	6	13	7
Coking				
carbon on used catalyst	19% after 54 HOS	16.6% after 18 HOS	19.3% after 18 HOS	15.0% after 18 HOS

Courtesy: Simon R. Bare

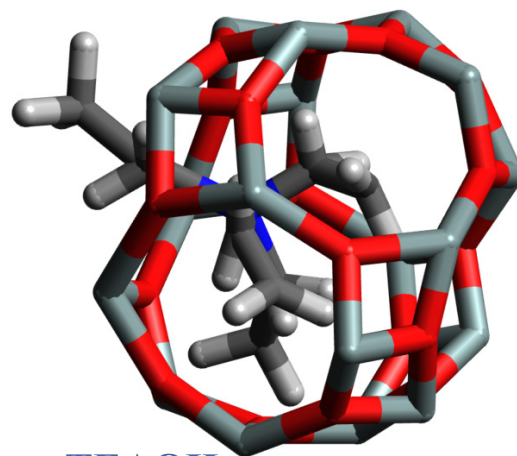
Yuen, et al., *Microporous Materials*, 2 (1994) 105



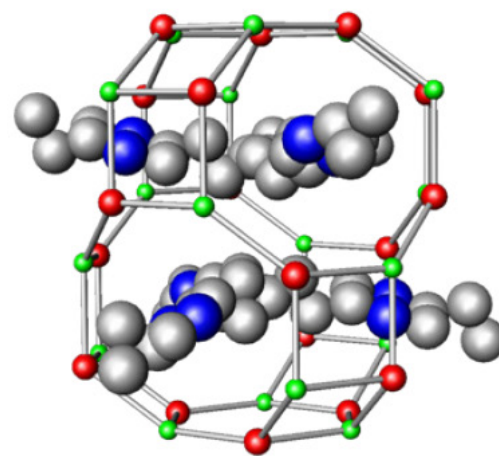
Synthesis of SAPO-34: Templates

>30 templates make SAPO CHA framework type.

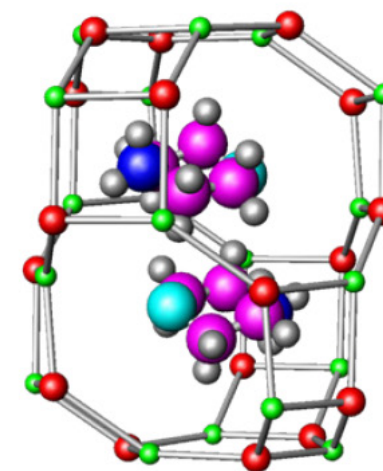
- Most not well studied



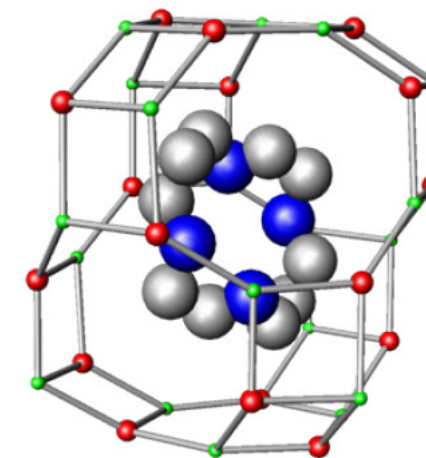
TEAOH
(most common)



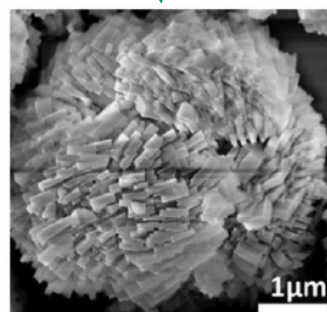
N-Mebutylamine



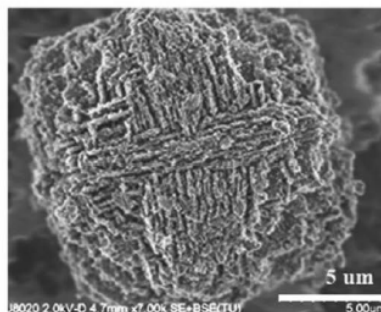
Morpholine



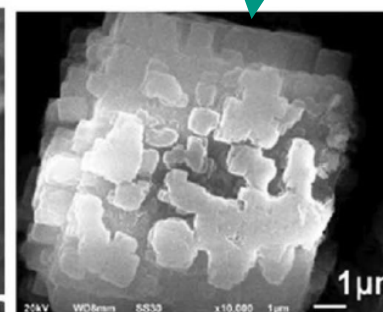
Cyclam



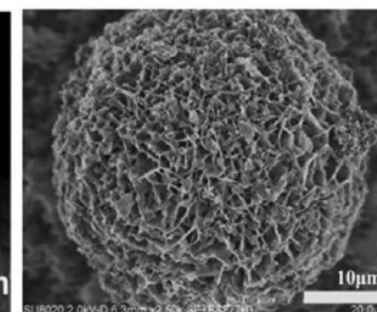
TEAOH



TEA



MOR



DEA

Adv. Mater. 2019, 31, 1902181

Courtesy: Simon R. Bare

Characterization of Zeolites

- Acidic sites
 - NH_3 -TPD
 - Pyridine-FTIR
 - Low-temperature CO-FTIR
- Framework
 - Hydroxyl-FTIR
 - Solid-State NMR
- Meso- / micro-structure
 - SEM
 - TEM



Acidic Sites: Use of Base for Characterization

- Acidic catalyst surface may expose both protic (Brønsted) and aprotic (Lewis) sites.
- Protic sites in a zeolite are surface hydroxyl groups OH.
- Aprotic sites in zeolite are typically extraframework Al surface cations.
- Basic probe molecule will interact with OH via hydrogen bonding:



- If OH is sufficiently acidic then proton transfer:



- For aprotic sites the base will form a Lewis acid-base adduct:

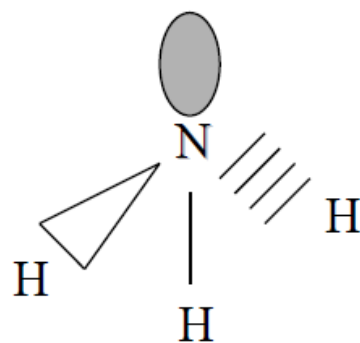


Courtesy: Simon R. Bare

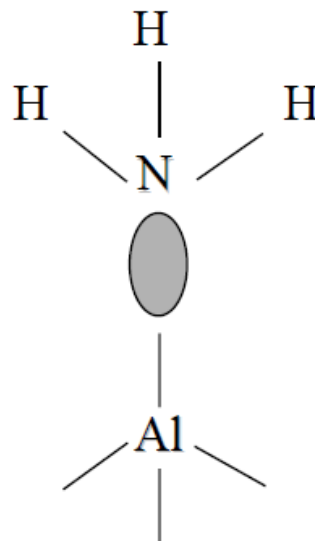


Ammonia Temperature-Programmed Desorption (NH₃-TPD)

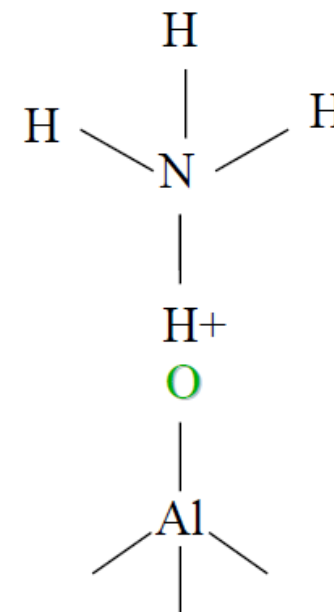
- NH₃ TPD is used to measure the amount and relative strength of the acid sites.
- NH₃ small molecule but not very specific.



Ammonia



Lewis acid (electron acceptor)



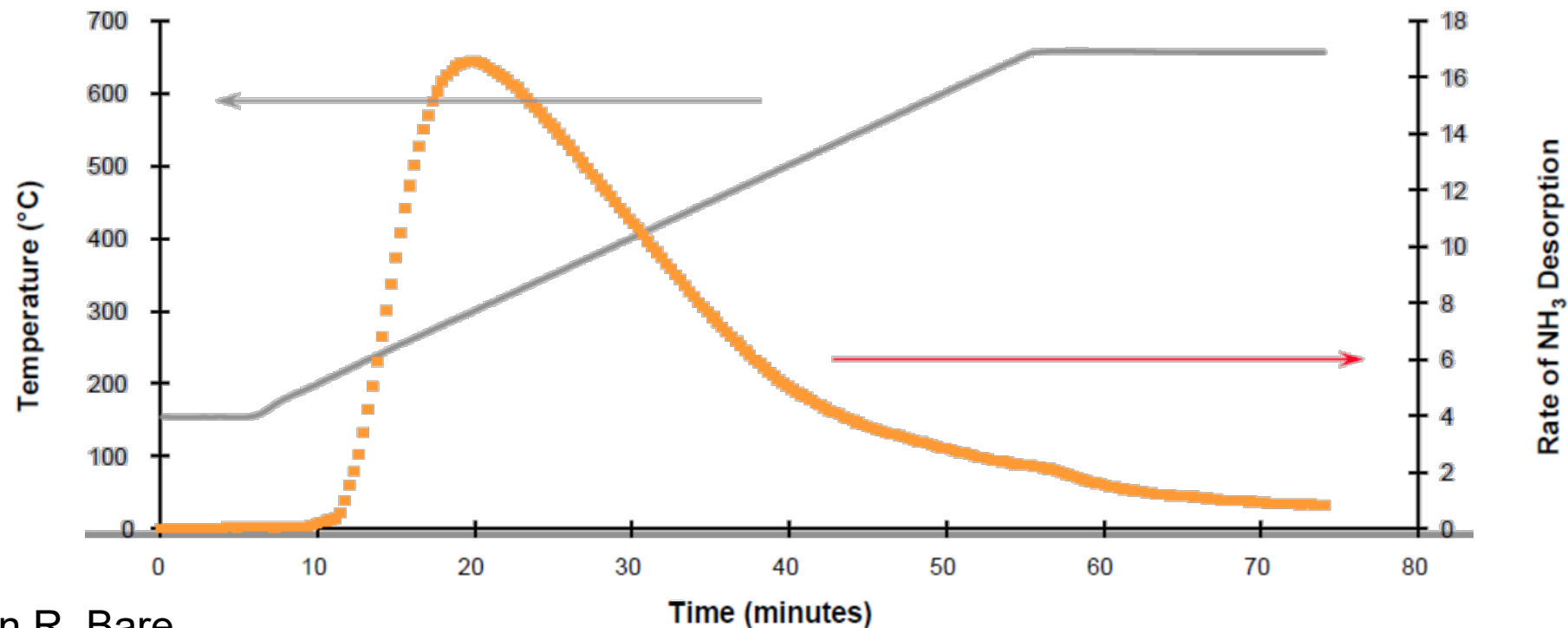
Brønsted acid (proton donor)

Courtesy: Simon R. Bare



Ammonia Temperature-Programmed Desorption (NH₃-TPD)

Linear temperature ramp. Amount of ammonia desorbed as a function of temperature recorded and quantified.

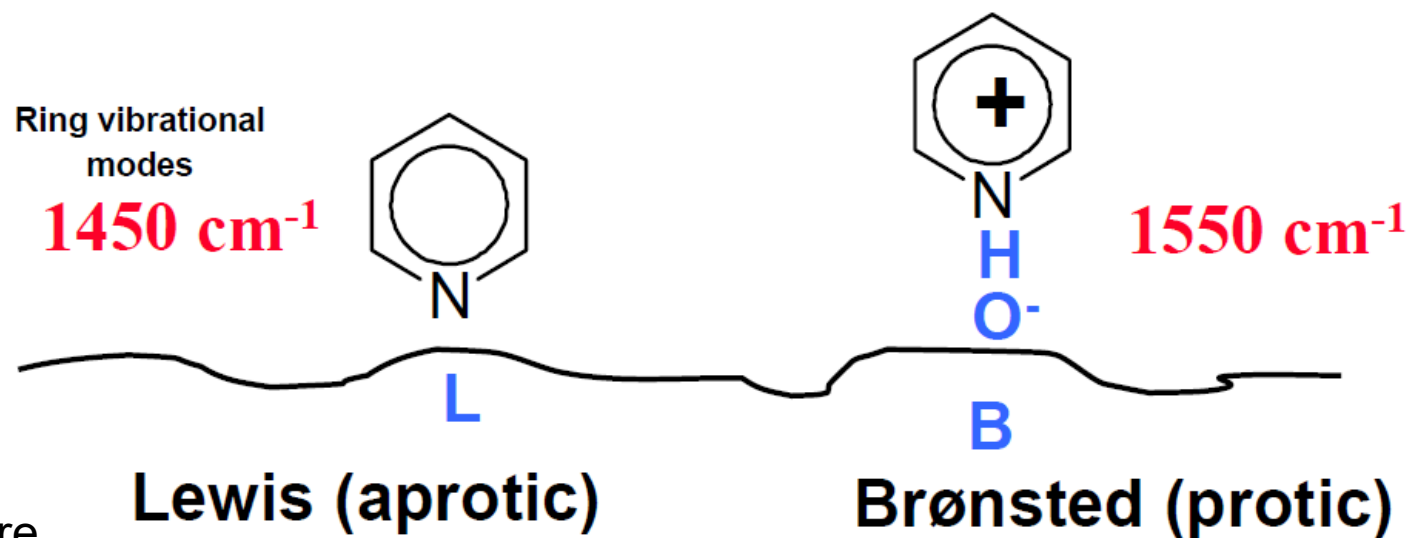


Courtesy: Simon R. Bare



Pyridine-FTIR

- Pyridine is a weak base which coordinates with both Brønsted and Lewis acid sites.
- Distinct FTIR-active bands are observed for each type of acid site.
- The integrated intensity provides a relative measure of the number of each site.
- The desorption temperature provides a relative measure of the acid site strength.
- Most useful when comparing a series of samples.

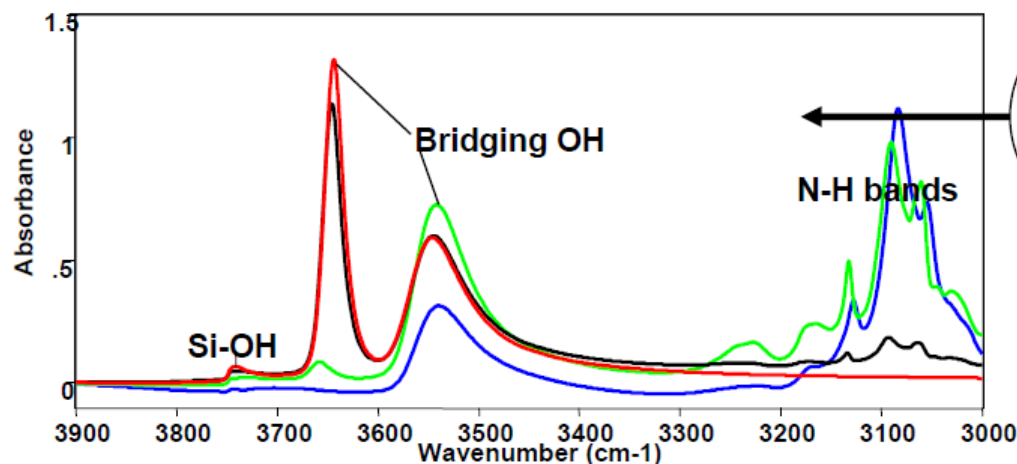


Courtesy: Simon R. Bare



Pyridine-FTIR

Hydroxyl Region Pyridine Adsorption



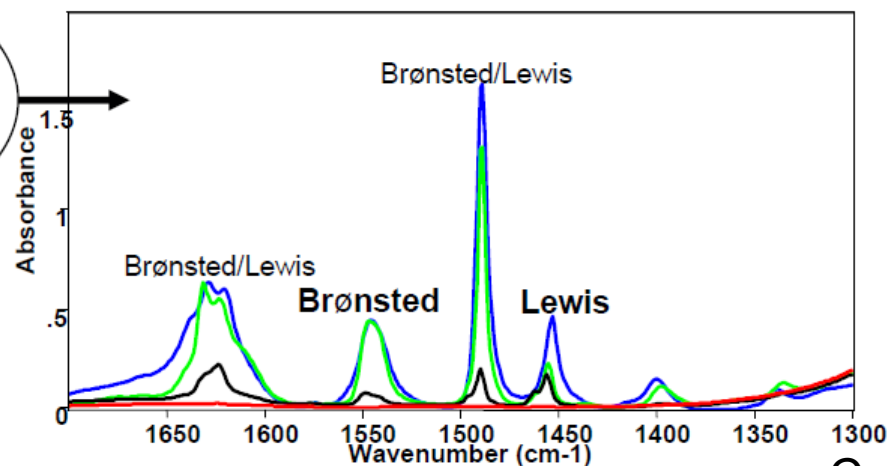
Pyridine adsorption attenuates bridging OH groups; bands are restored upon pyridine desorption

File # 1 : Y-64PRTC

Pyridine adsorption yields distinct Brønsted and Lewis acid site absorbance bands in this region

Key: Pretreated
After 150C
After 300C
After 450C

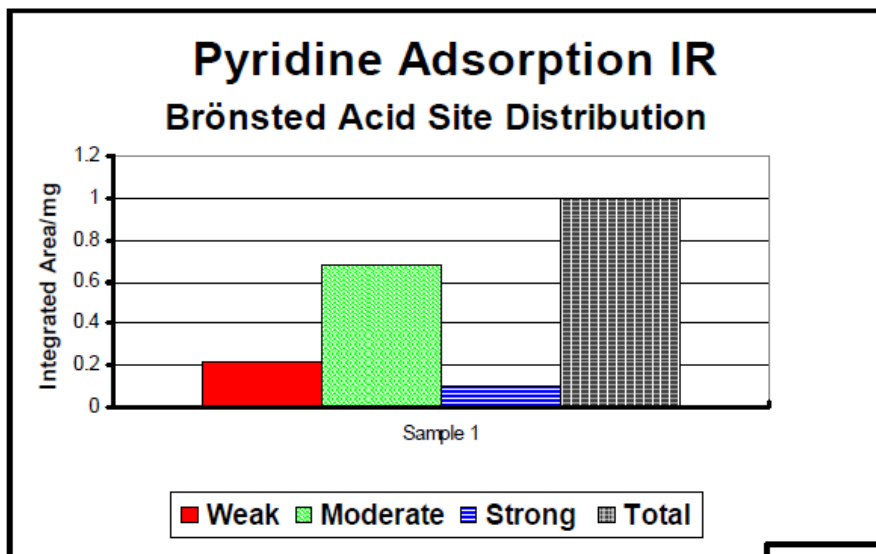
Pyridine Adsorption Spectral Region



File # 1 : Y-64PRTC

Courtesy: Simon R. Bare

Pyridine-FTIR: Acidic Site Distribution



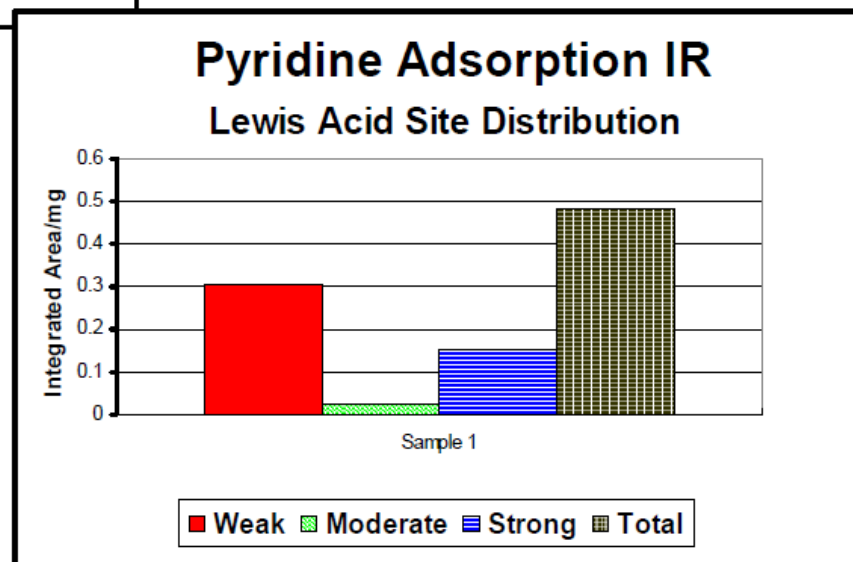
Integrated area of pyridine adsorbed on Brønsted acid site; $\sim 1550 \text{ cm}^{-1}$

Integrated area of pyridine adsorbed on Lewis acid site; $\sim 1450 \text{ cm}^{-1}$.

Weak Site: pyridine desorbed between 150°C and 300°C

Moderate site: pyridine desorbed between 300°C and 450°C

Strong site: pyridine remaining after 450°C desorption



Courtesy: Simon R. Bare



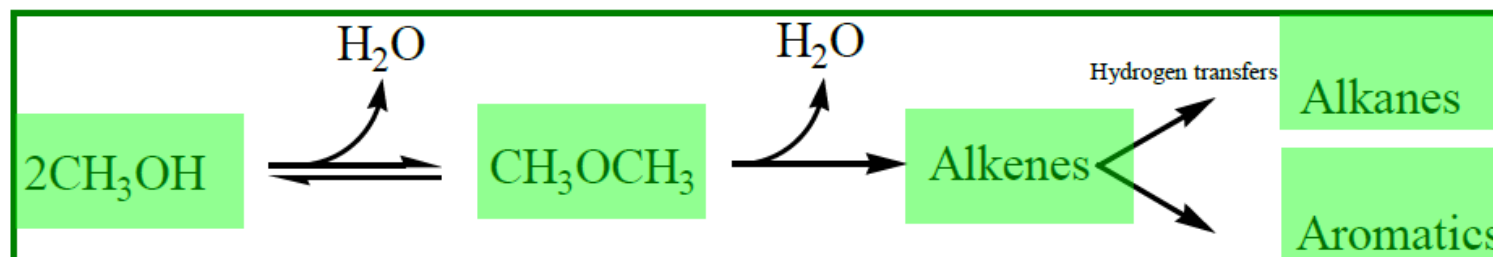
Reaction, Deactivation, Regeneration

MECHANISM OF MTO



Mechanism of MTO

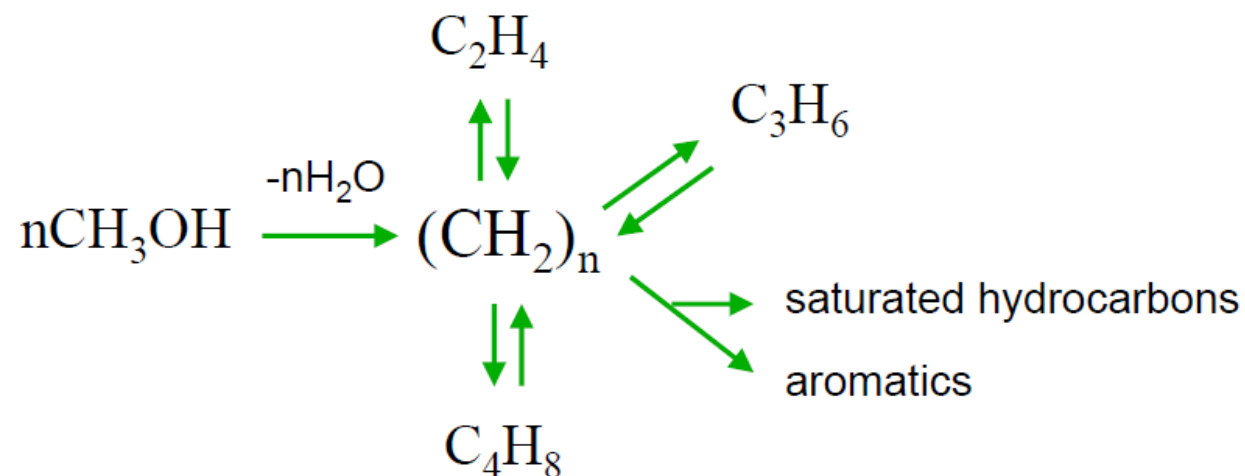
- More than 20 proposed mechanisms during the past 30 years (Involving intermediates such as radicals, carbenes, oxonium ions, carbocations)



- How can two or more C_1 -entities react so that C-C bonds are formed?
- No simple β -hydride elimination so no straightforward mechanism to olefins from methanol.
- Don't have time to go into great detail on some of the elegant mechanistic work performed.

Courtesy: Simon R. Bare

Hydrocarbon Pool (HCP) Mechanism



- What is the identity of the hydrocarbon pool?
- How does it operate?

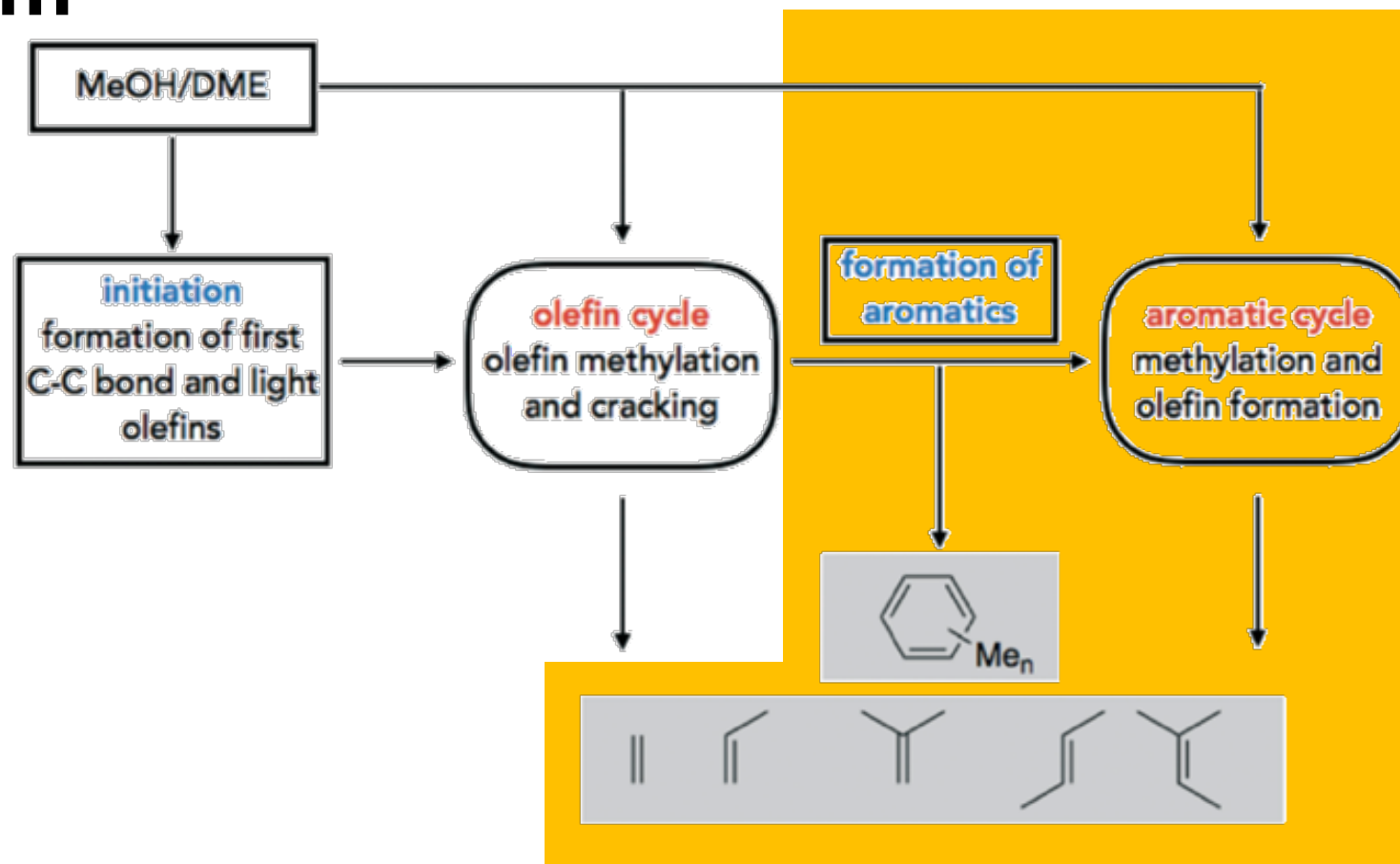
I.M. Dahl and S. Kolboe, J. Catal. 149 (1994) 329,

I.M. Dahl and S. Kolboe, J. Catal. 161 (1996) 304.

Courtesy: Simon R. Bare



Mechanism



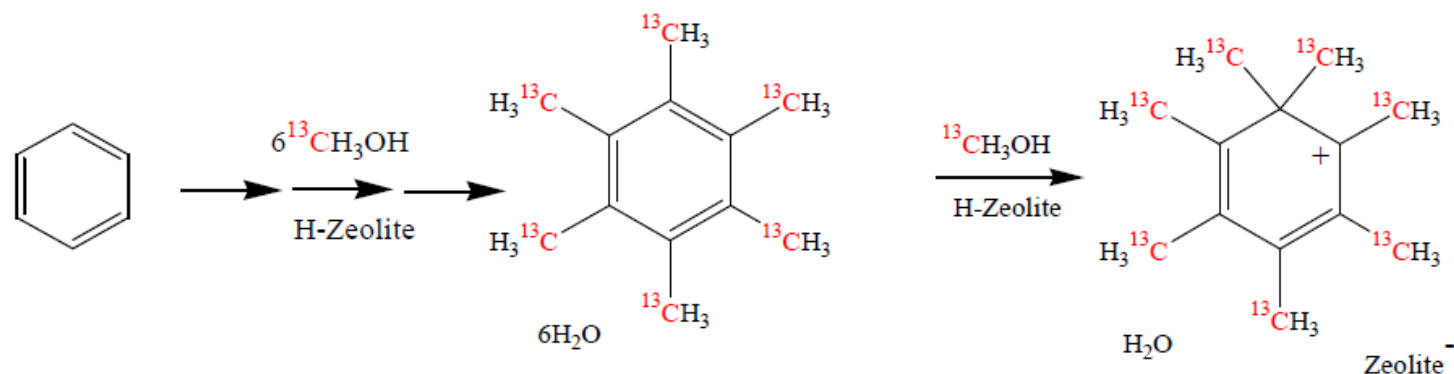
HCP

Olsybe et al. *Angew. Chem. Int. Ed.* **2012**, 51, 5810 – 5831

Plessow & Studt, *Catal. Sci. Technol.* **2018**, 8, 4420.



HCP: Initial Formation of HMB and heptaMP⁺



Hexamethylbenzene:
Six labelled atoms

Heptamethylbenzenium:
Seven labelled atoms

Hexamethylbenzene in zeolite pore can take up another CH₃ to form heptamethylbenzenium ion

Courtesy: Simon R. Bare

M. Bjørgen, U. Olsbye, D. Petersen and S. Kolboe, *J. Catal.* (2004), 221, 1-10.



HCP: Paring and Exocyclic (Side-Chain) routes

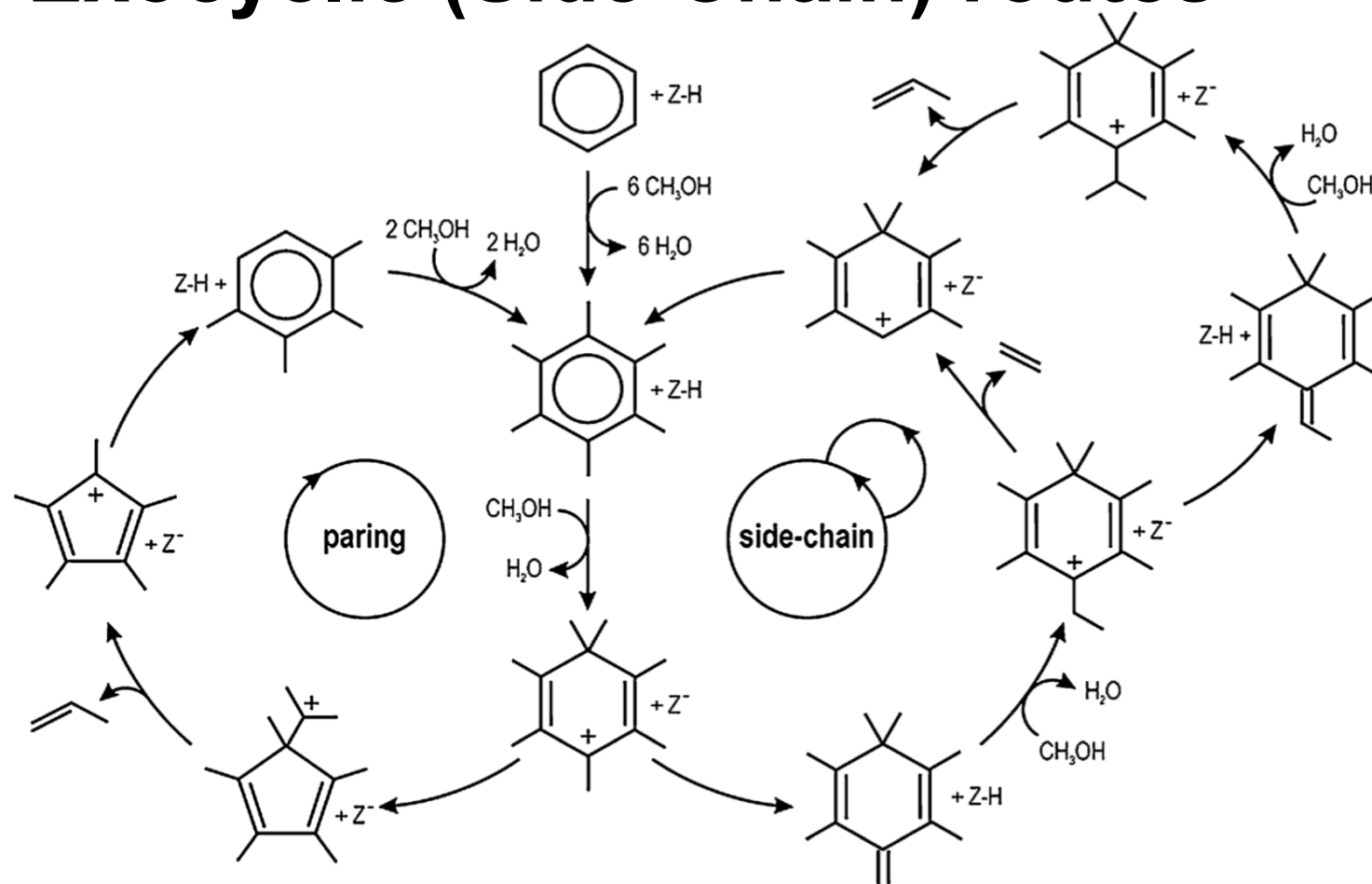


Figure 10. Representation of the paring and side-chain reaction concepts in MTH catalysis. From Ref. [120].

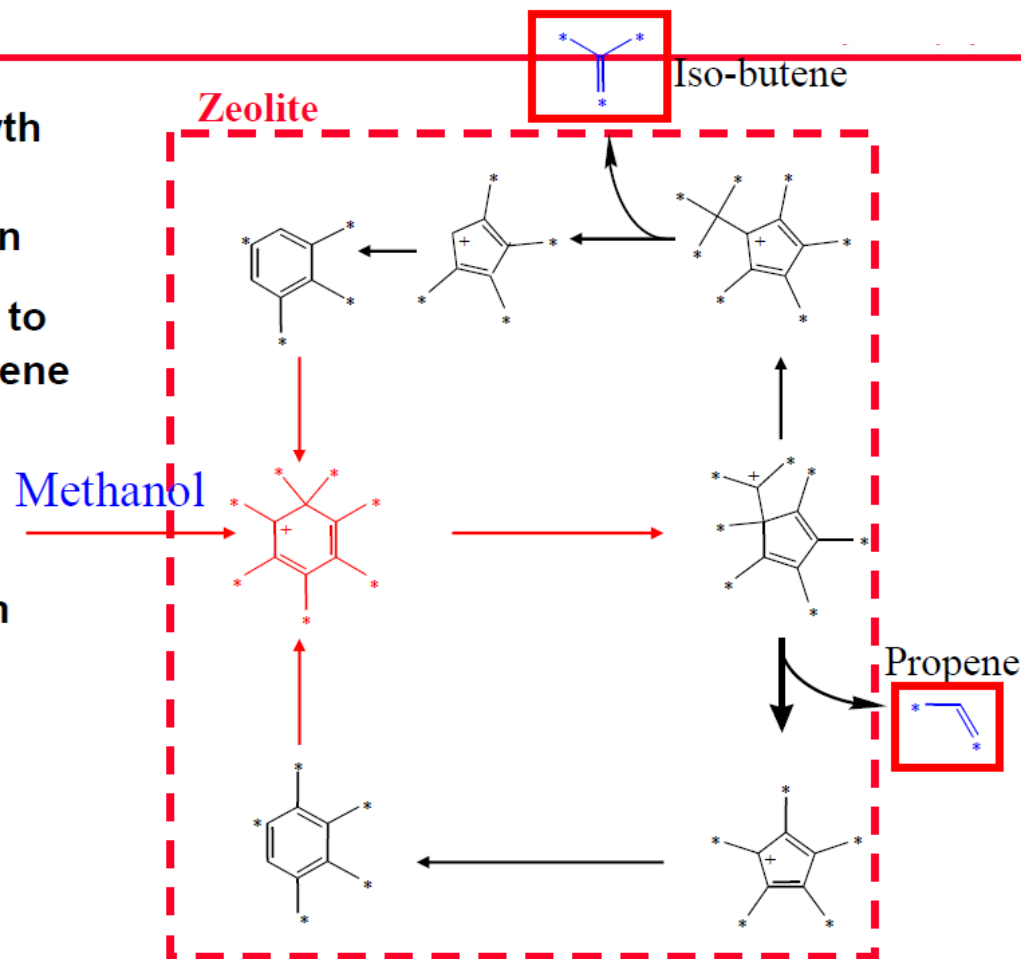
Olsybe et al. *Angew. Chem. Int. Ed.* **2012**, 51, 5810 – 5831



HCP Paring Route

Alkyl side chain growth
by ring
contraction/expansion
Leads predominantly to
propylene and isobutene

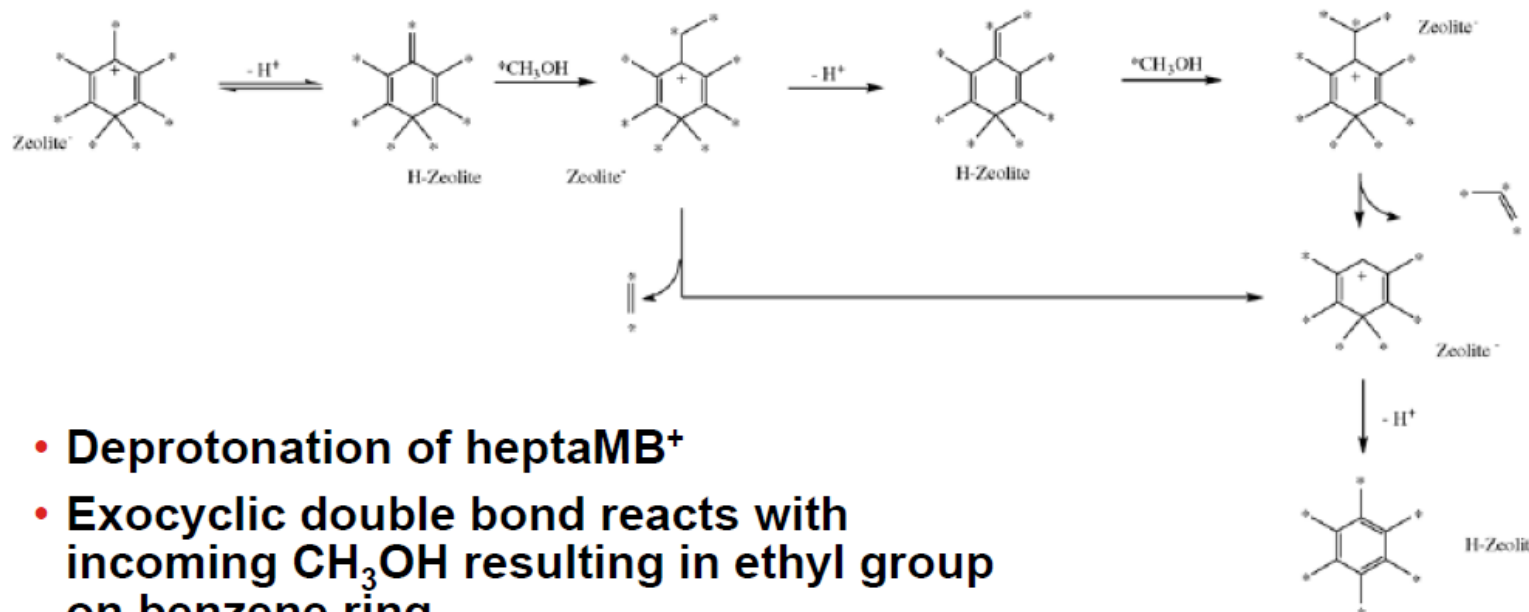
Leads to carbon atom
interchange between
ring and substituents



M. Bjørgen, U. Olsbye, D. Petersen and S. Kolboe, *J. Catal.* (2004), 221, 1-10.

Courtesy: Simon R. Bare

HCP Exocyclic Route

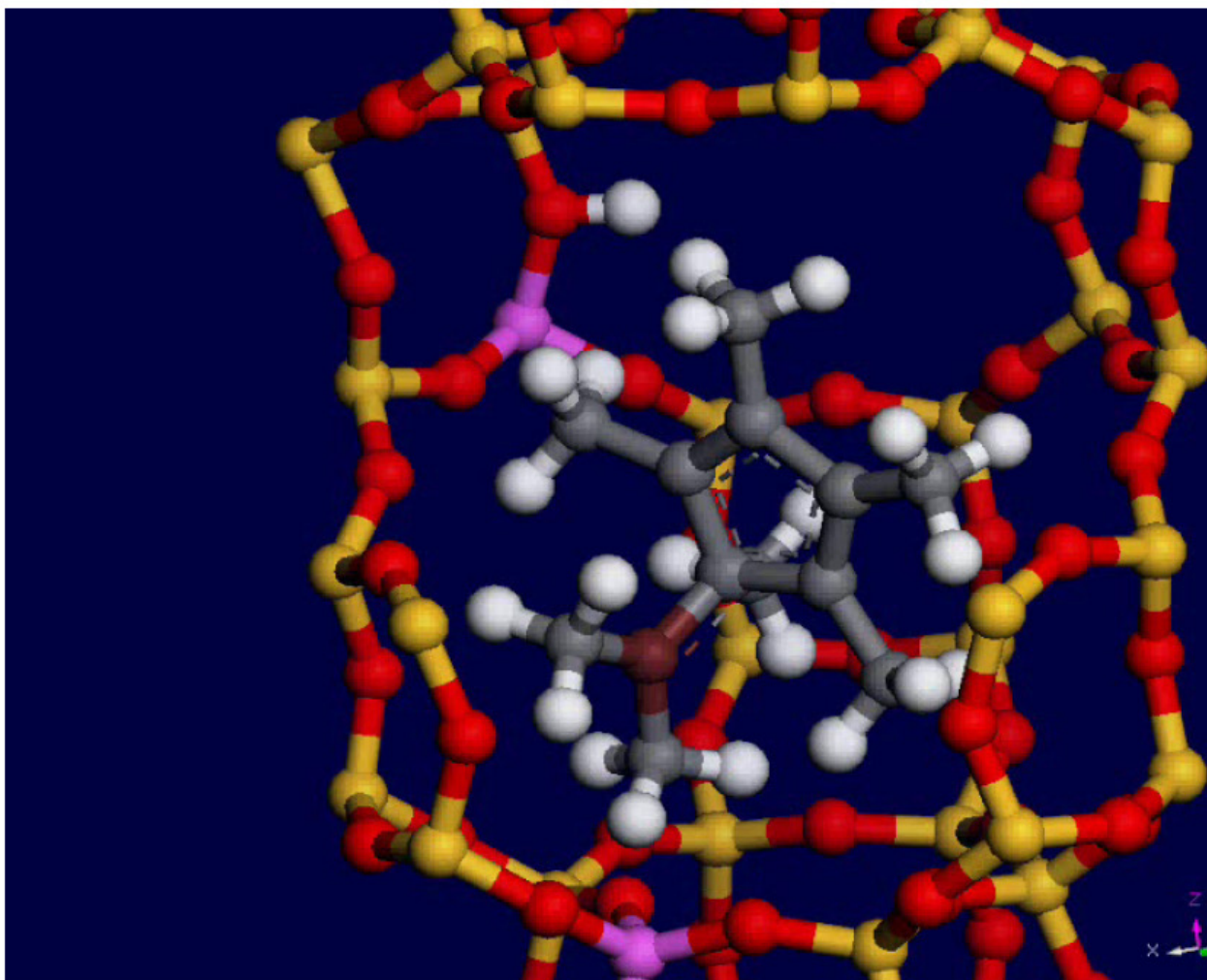


- Deprotonation of heptaMB⁺
- Exocyclic double bond reacts with incoming CH₃OH resulting in ethyl group on benzene ring
- Subsequent dealkylation to ethylene
- Essential intermediate in cycle is formation of two gem-methyl groups attached to benzene ring.

Courtesy: Simon R. Bare

M. Bjørgen, U. Olsbye, D. Petersen and S. Kolboe, *J. Catal.* (2004), 221, 1-10.

MTO Site: Organic-Inorganic Hybrid

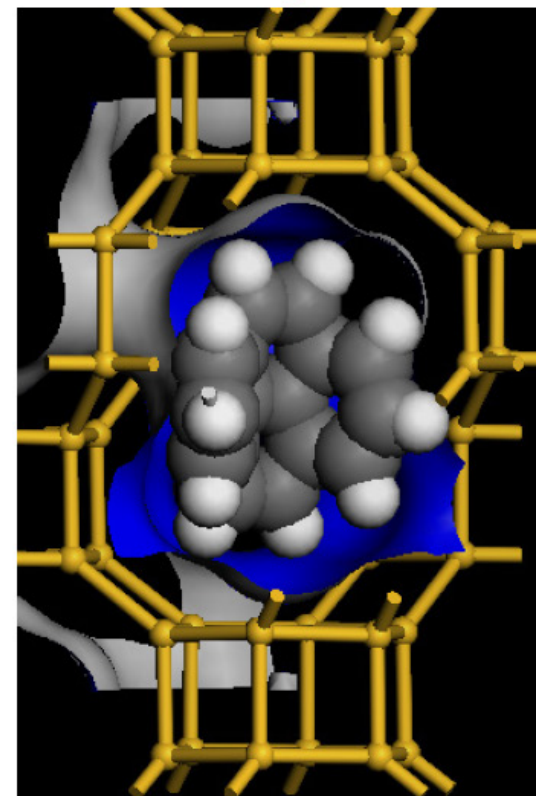
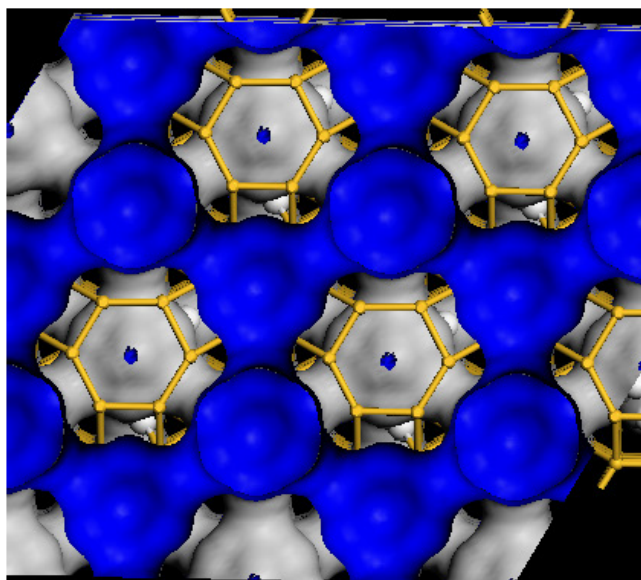


Courtesy: Unni Olsbye, Simon R. Bare



SAPO-34 active catalyst

- SAPO-34 (CHA) has large cages connected with small windows.
- Large aromatics are accumulated in these cages during the reaction.
- An array of nanoreactors!



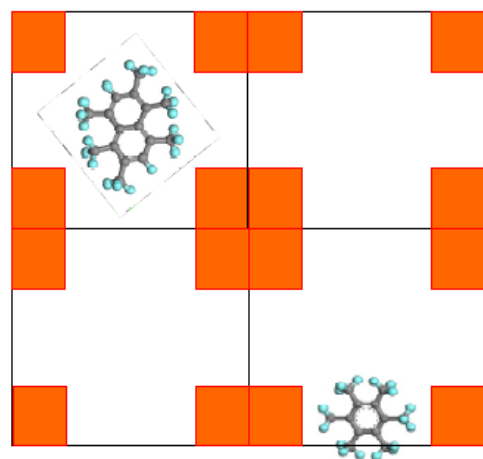
Courtesy: Unni Olsbye, Simon R. Bare (001) projection



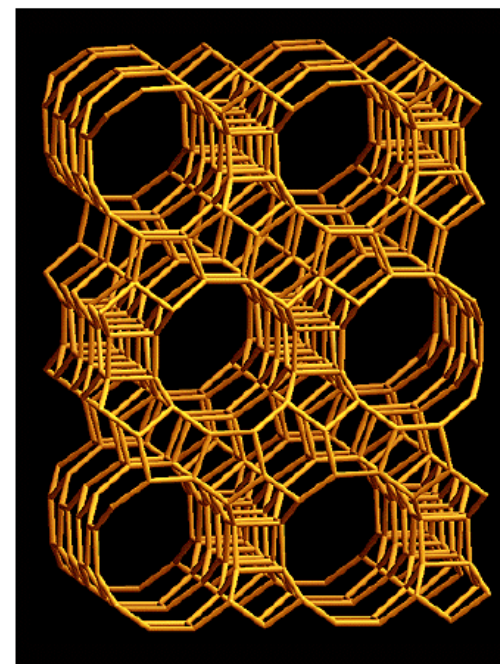
Proof of HCP: Intermediates on BEA zeolite

- The beta zeolite is a wide pore zeolite allowing direct introduction of rather large molecules.
- It is not interesting as a commercial catalyst for MTO/MTH chemistry.

Model: Beta, BEA-topology
Cages = Windows



12-ring window, substituted aromatic hydrocarbons can enter.

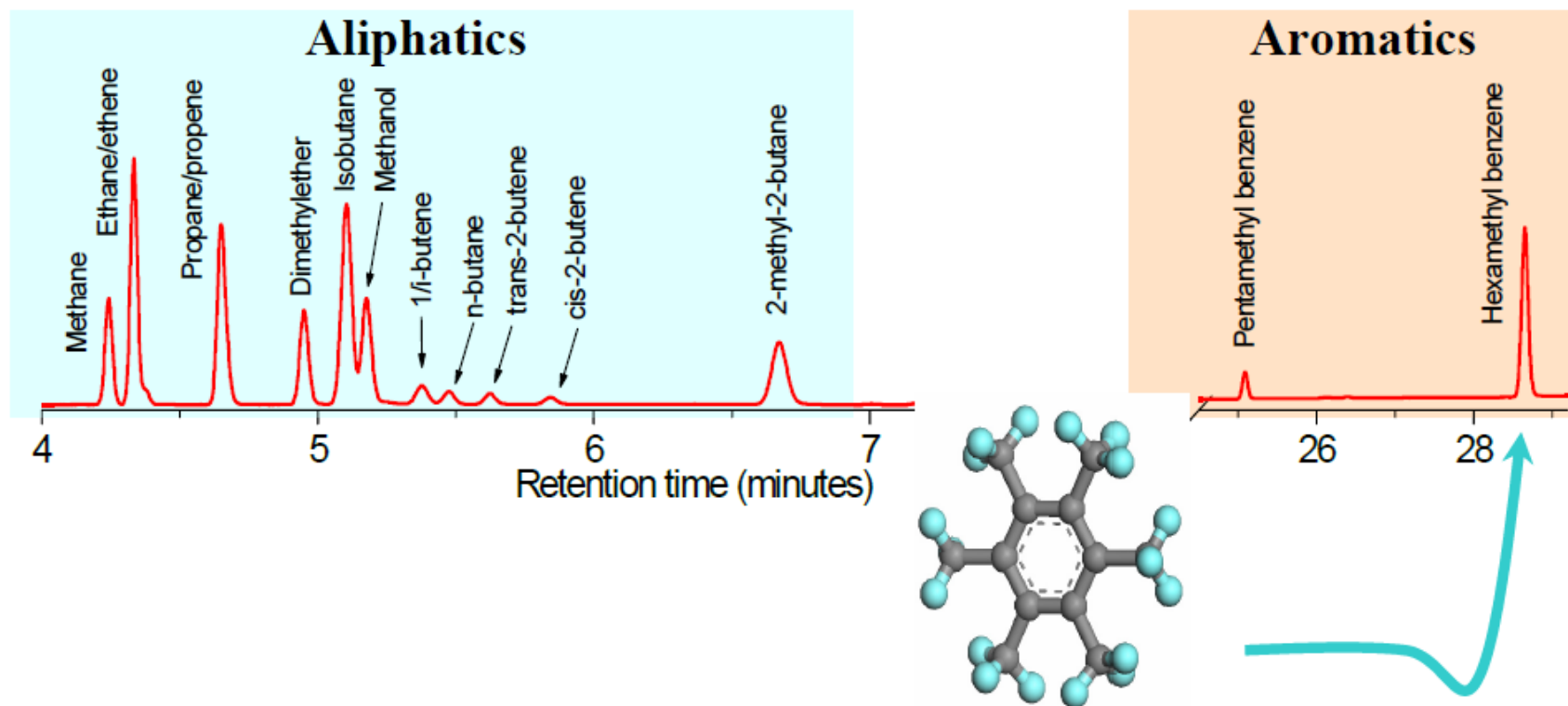


7.7 x 6.6 Å

Courtesy: Simon R. Bare



Proof of HCP: Intermediates on BEA zeolite



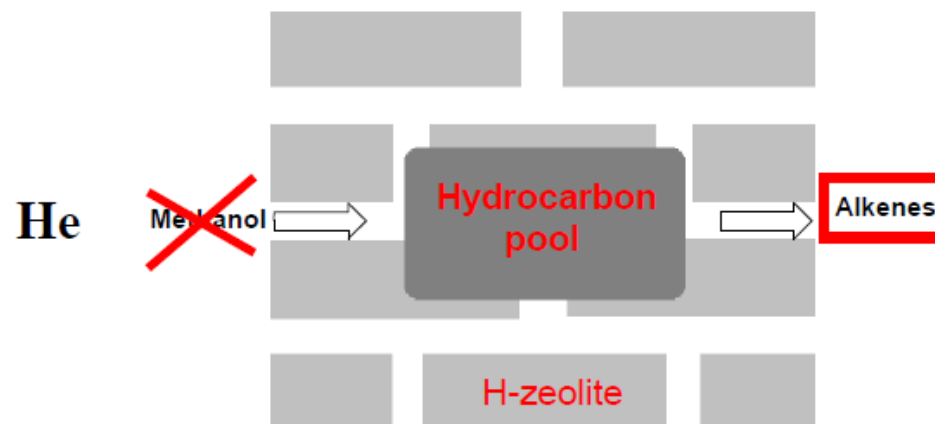
Hexamethylbenzene is a dominant gas phase product

Bjorgen, M. and Kolboe, S. *Appl. Catal. A* 2002, 225, 285-290.

Courtesy: Unni Olsbye, Simon R. Bare



Proof of HCP: direct analysis of trapped intermediates



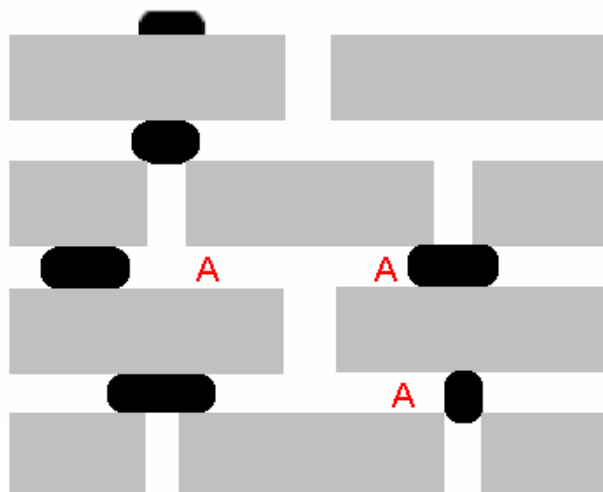
The olefin production goes on for several minutes after the methanol feeding has been terminated

What is the active pool contained inside the zeolite?

Courtesy: Unni Olsbye, Simon R. Bare



Proof of HCP: Hydrocarbons retained in Zeolite Pores



Analysis (GC-MS,
HRMS, NMR)

- ✓ **Analyzed *ex-situ* by:**
 - ✓ Quenching the reaction (after a set time, few mins)
 - ✓ Dissolving the zeolite (15% HF)
 - ✓ Extracting the organic material from the water phase
- ✓ **Trapped organic species are liberated and can be analyzed**

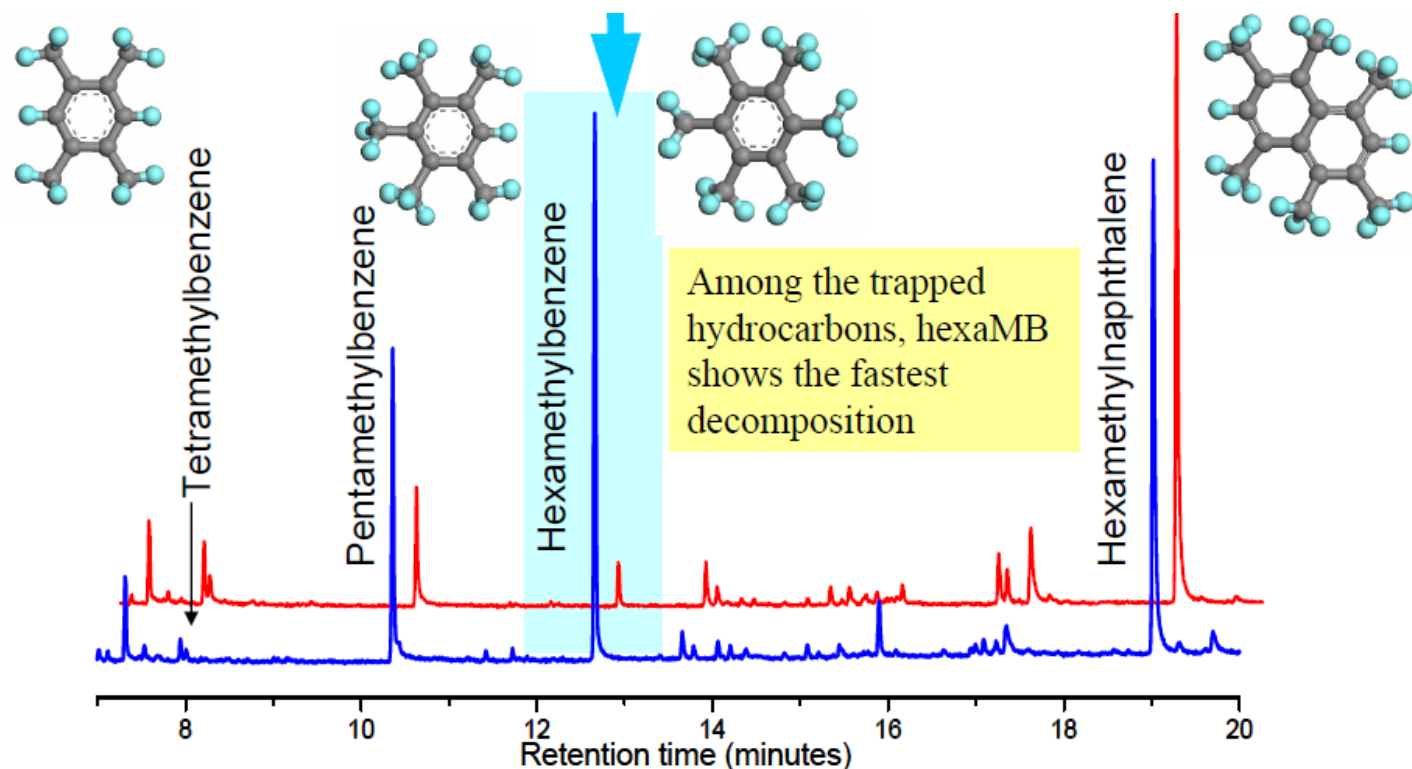
Courtesy: Unni Olsbye, Simon R. Bare



Trapped Hydrocarbons

- Methanol reacted over the H-beta zeolite (GC-MS)

Almost exclusively polymethylbenzenes

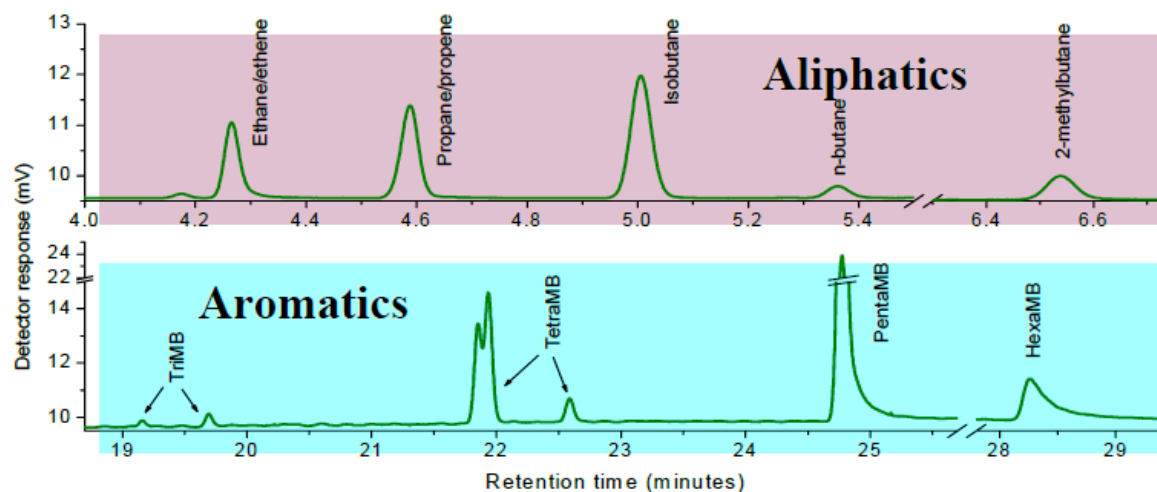


Courtesy: Unni Olsbye, Simon R. Bare



Trapped intermediates in SAPO-34 are same as Products in H-BEA

- The same gas phase products as observed when methanol was reacted
- The retained compounds were the same as those obtained from methanol



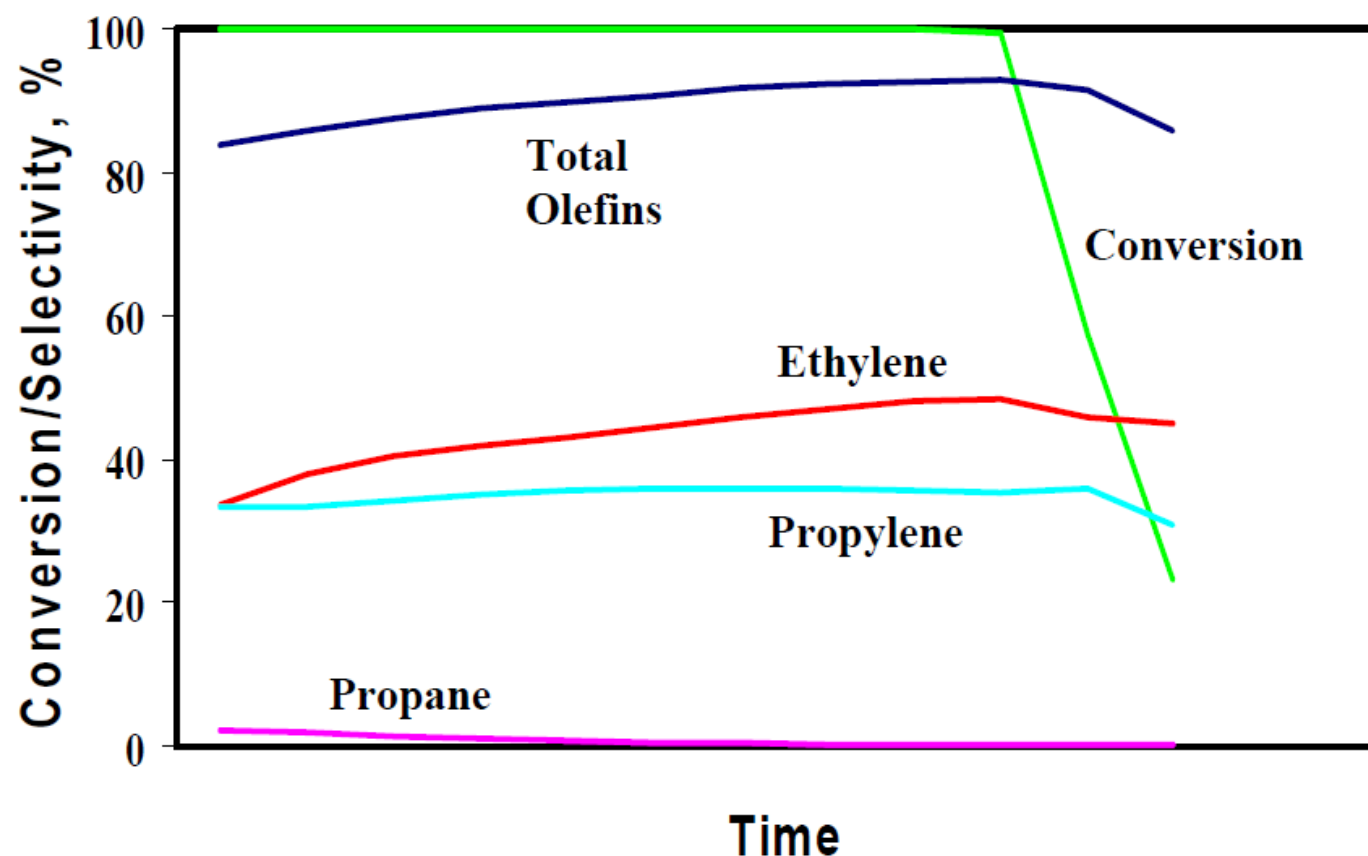
Bjorgen, M.; Olsbye, U.; Kolboe, S. *J. Catal.* 2003, 215, 30-44.

Courtesy: Unni Olsbye, Simon R. Bare



Deactivation in Fixed-Bed Reactor

- SAPO-34 catalyst highly active with good selectivity then conversion drops rapidly.

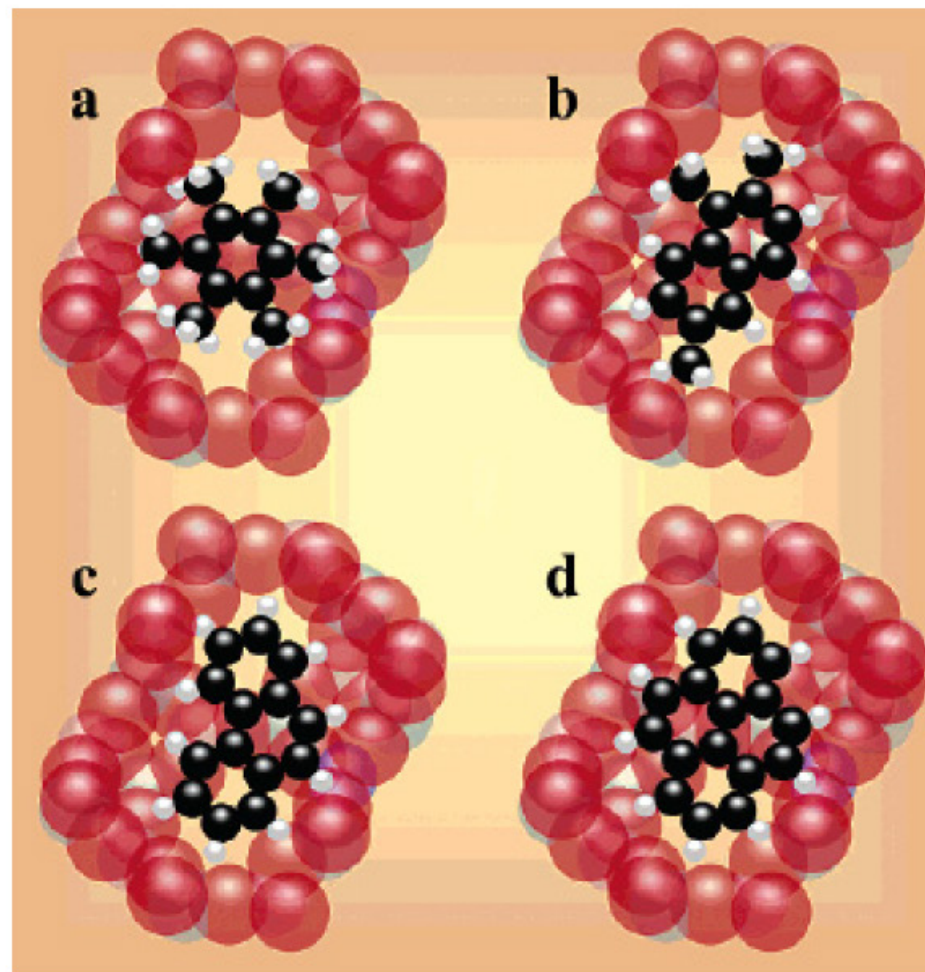


Courtesy: Simon R. Bare



Molecular View on Initial Deactivation

- Hexamethylbenzene in CHA cage
- With increasing TOS some methylbenzenes age into methylnaphthalenes.
- Further aging to phenanthrene causes loss of activity
- Largest ring system to form in SAPO-34 is pyrene.



Haw, Accts. Chem. Res. 36 (2003) 317

Courtesy: Simon R. Bare



MTO Reactor Design

- **Fixed Bed Reactor**

- rapid deactivation due to coke formation
- reactor would have to swing between process & regeneration
- product composition varies with time
- expensive high-temperature valves required

- **Fluidized-Bed Reactor**

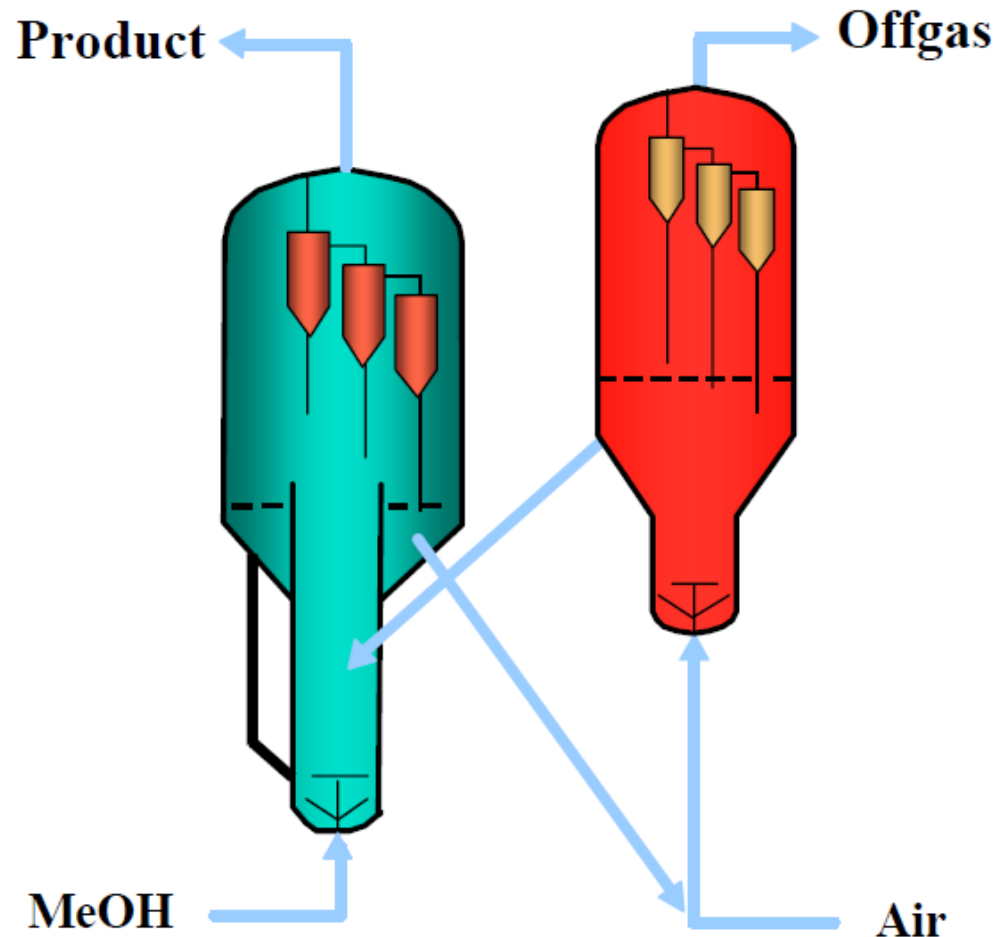
- transport reactor, internal catalyst circulation
- continuous movement of portion of used catalyst to separate regenerator
- reduced catalyst inventory, increased capacity
- uniform product distribution with time

Courtesy: Simon R. Bare

Fluidized-Bed Reactor

Fast Fluidized-Bed

Regenerator

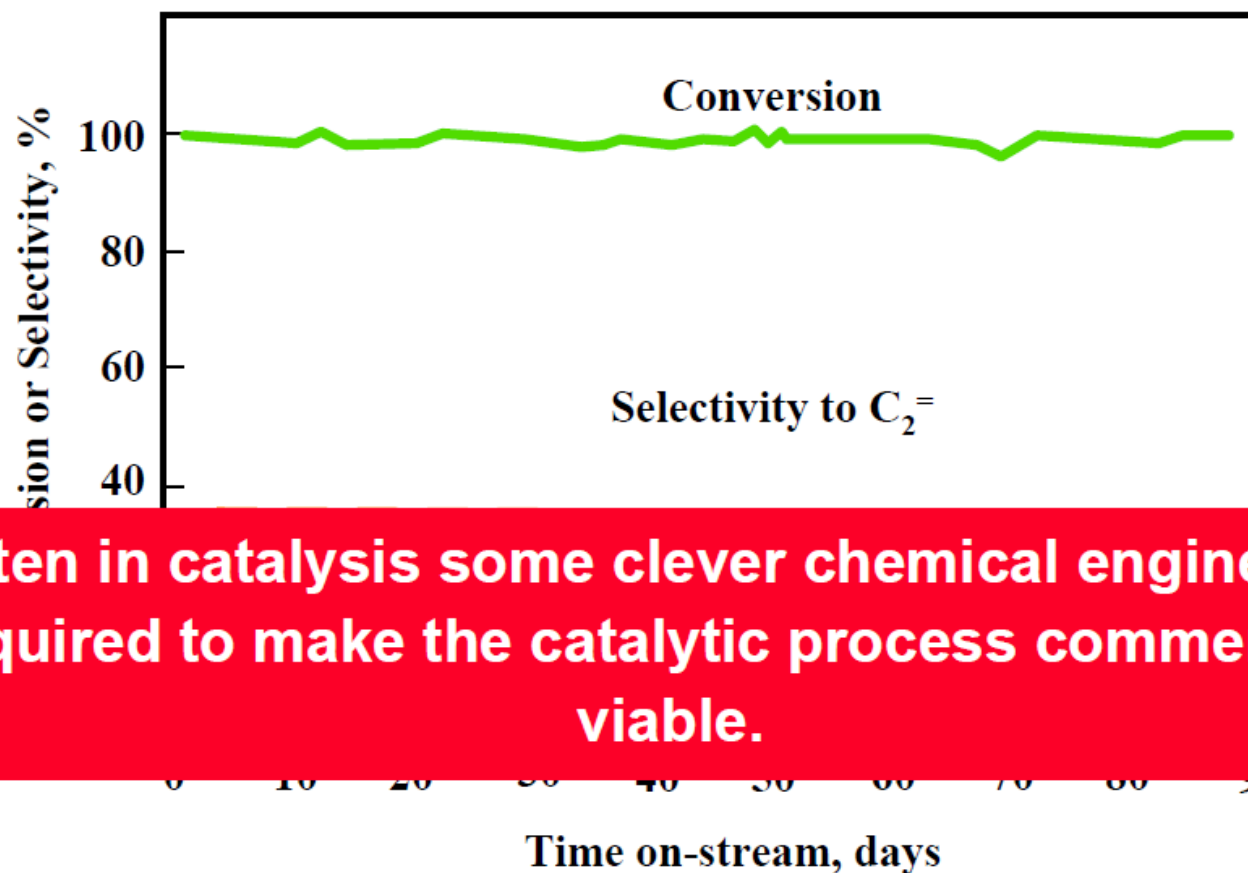


Courtesy: Simon R. Bare



Fluidized-Bed Reactor Results

- Conversion and selectivity remain high over months of operation.

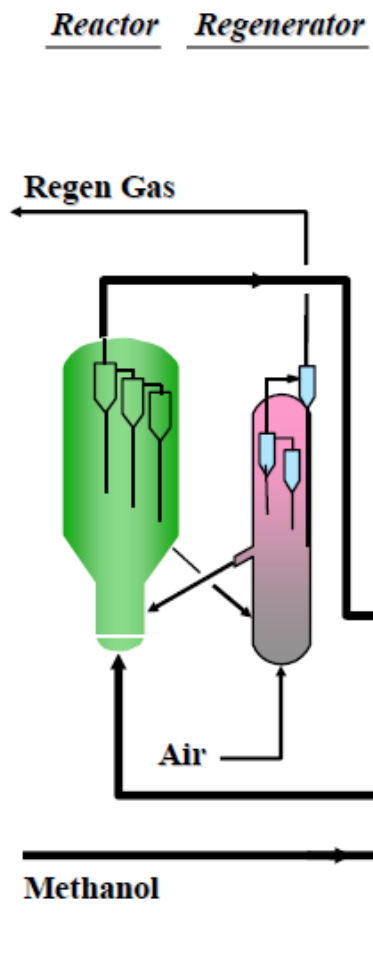


Often in catalysis some clever chemical engineering required to make the catalytic process commercially viable.

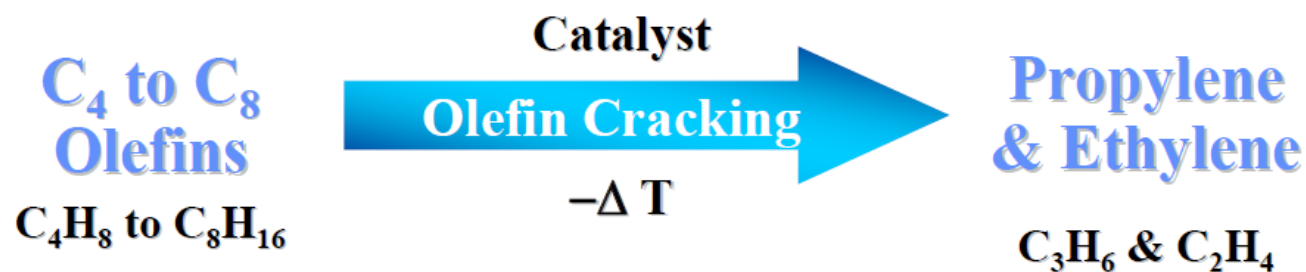
Courtesy: Simon R. Bare



Combined with Olefin Cracking



- Another piece of the process.....
- Production of propylene and ethylene from C₄ to C₈ olefins.



TOTAL PETROCHEMICALS

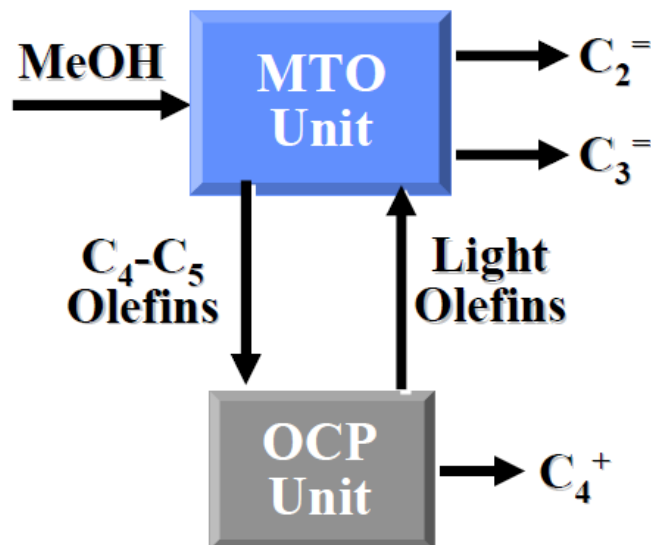


Courtesy: Simon R. Bare



Olefin Cracking Integration with MTO

- Upgrade C_4+ MTO product to $C_2=$ and $C_3=$.



- 20% increase in light olefin yields
- Nearly 80% reduction in C_4+ by-products
- Can achieve 2:1 propylene/ethylene product ratio

TOTAL PETROCHEMICALS



HYDRO

Courtesy: Simon R. Bare



Olefin Cracking Integration with MTO



Other By-Products

H_2O
 H_2 , CO_X
 C_1 - C_5 Paraffins
 C_5+
Coke

Courtesy: Simon R. Bare



MTO Summary

- Olefins needs for catalysts: high selectivity and catalyst stability
 - Zeolite – molecular sieve – control of entering and exiting molecules)
 - 8-member rings
 - Light olefins C_2H_4 and C_3H_6
 - Higher olefins (C_{4+}) and aromatics
 - Acidity moderate
- Best catalyst SAPO-34
 - Methanol → methylated Benzene in SAPO-34 cages
ACTIVE SITE
 - Deactivation by polyaromats → Combustion to regenerate
 - Combination with higher HC cracking

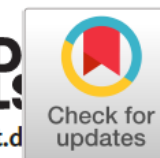


Literature with primary references

PROGRESS REPORT

MTO Catalysts

ADVANCED
MATERIALS
www.advmat.d



Recent Progress in Methanol-to-Olefins (MTO) Catalysts

Miao Yang, Dong Fan, Yingxu Wei, Peng Tian, and Zhongmin Liu**

Dedicated to Dalian Institute of Chemical Physics, Chinese Academy of Sciences on its 70th anniversary

Methanol conversion to olefins, as an important reaction in C1 chemistry, provides an alternative platform for producing basic chemicals from non-petroleum resources such as natural gas and coal. Methanol-to-olefin

Among the 8-MR molecular sieves, silicoaluminophosphate SAPO-34 with 3D channels and moderate acid strength represents the most interesting one, the light olefins selectivity of which could reach up to 90%.

Adv. Mater. 31 (2019) 1902181, DOI: 10.1002/adma.201902181

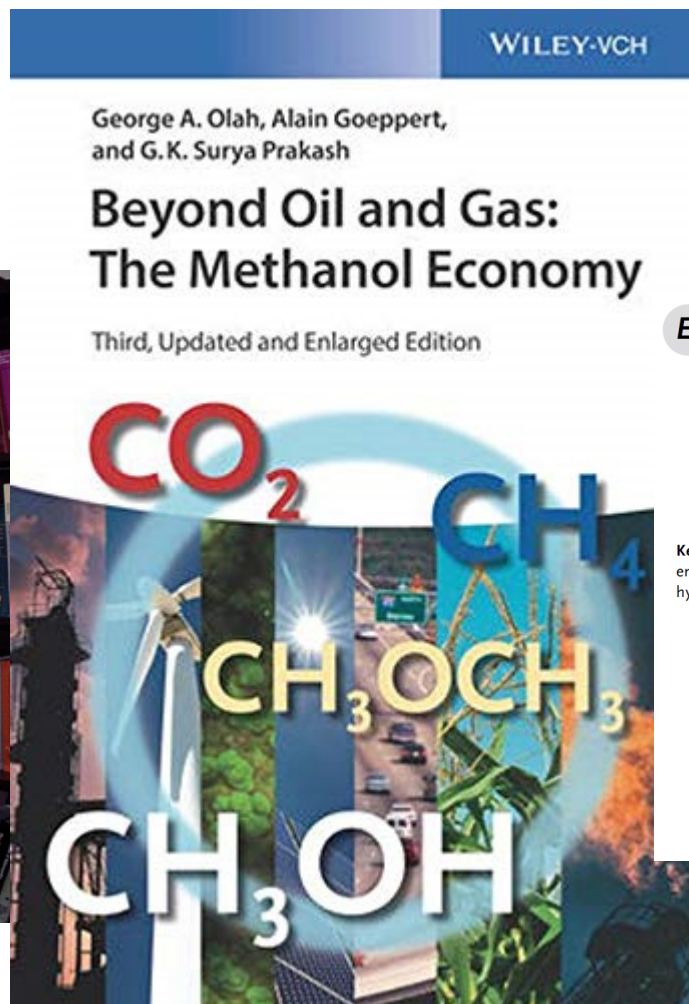
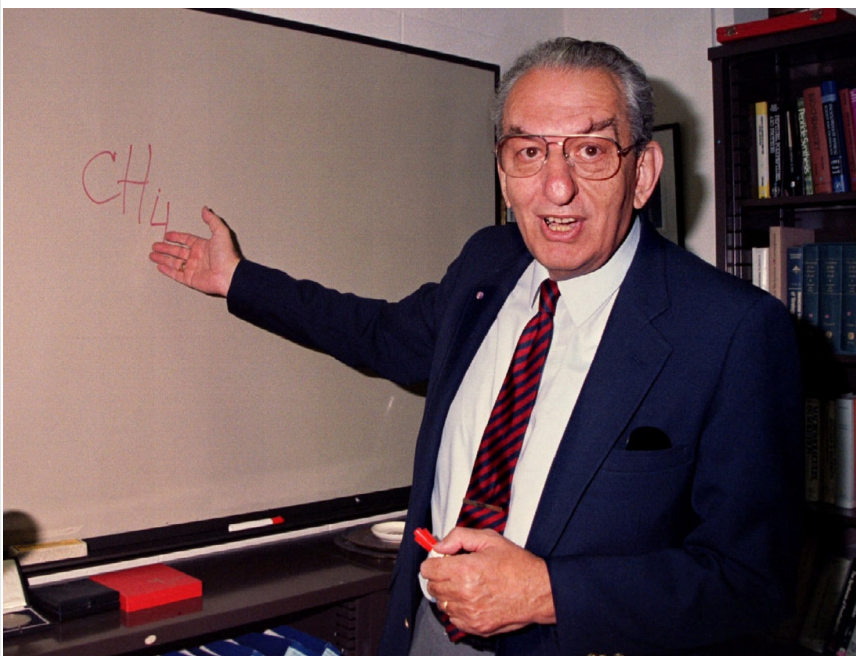


Literature: The Methanol Economy

George A. Olah

1927-2017

Nobel Prize in Chemistry 1994



Angew. Chem. Int. Ed. 2005, 44, 2636 –2639

Essays

Alternative Energy Sources

Beyond Oil and Gas: The Methanol Economy**

George A. Olah*

Keywords:

environmental chemistry · hydrocarbons ·
hydrogen · methanol

Oil and natural gas together with coal, the main fossil fuels, not only remain our major energy sources but they are also the feedstocks for a great variety of manmade materials and products that range from gasoline and diesel oil to varied petrochemical and chemical products, including synthetic materials, plastics, and pharmaceuticals. What nature gave us as a gift, formed over the

purposes began slowly and became more widespread in the 16th and 17th centuries mainly in England as a replacement for wood, which was becoming scarcer. Coal became dominant in the 18th century with the invention of the steam engine and the industrial revolution, which was also fueled by coal, that followed. In the 19th and 20th centuries, coal continued to satisfy the

significant, but will not fundamentally change the long-range outlook.

Besides petroleum oil and natural gas (and also coal), we have additional sources of "heavy" hydrocarbons, such as heavy-oil deposits in Venezuela, oil shales in various geological formations including the US Rocky Mountains, and vast tar sand deposits in the Canadian province Alberta. The relatively stable

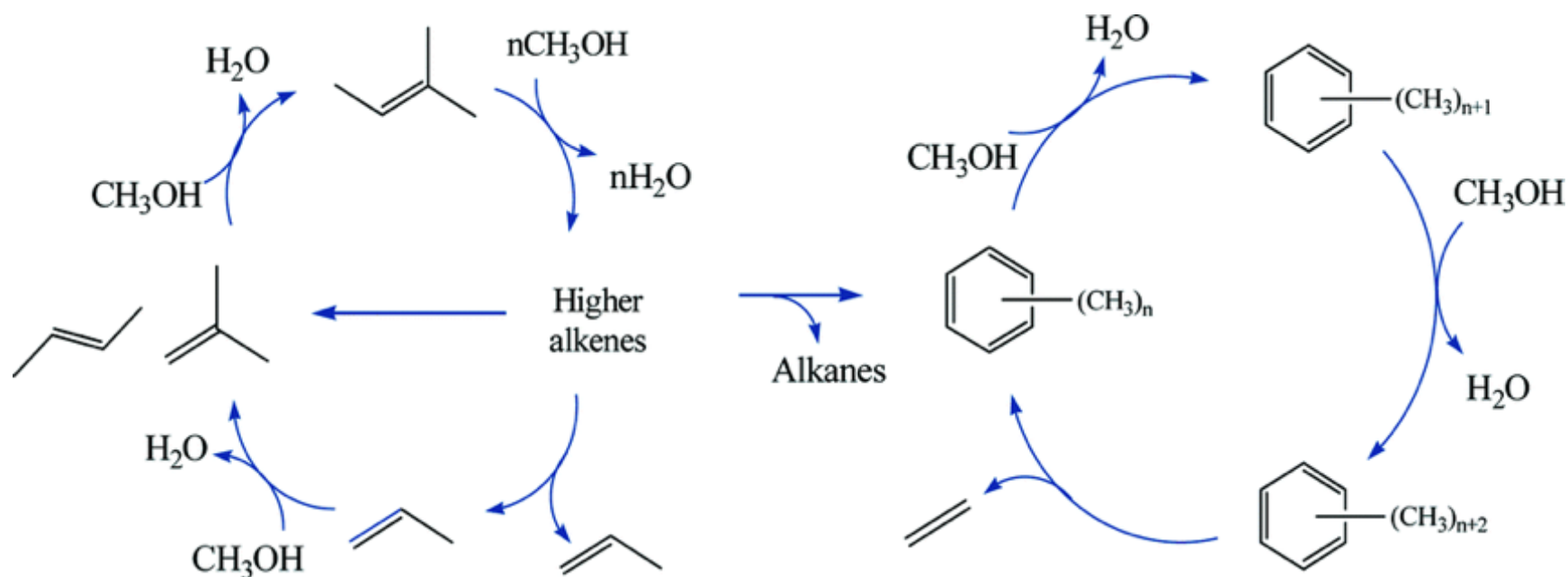




EXTRA SLIDES

Mechanism

Proposed dual cycle mechanism

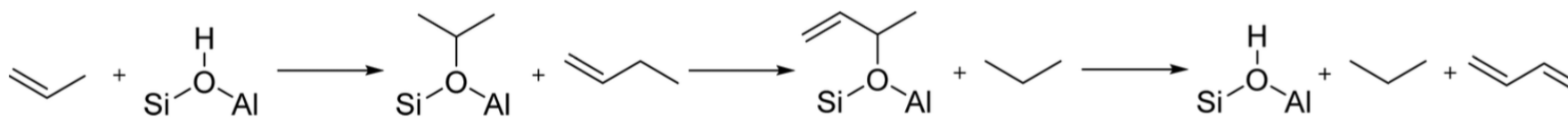
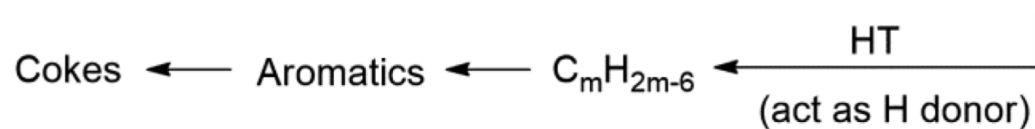
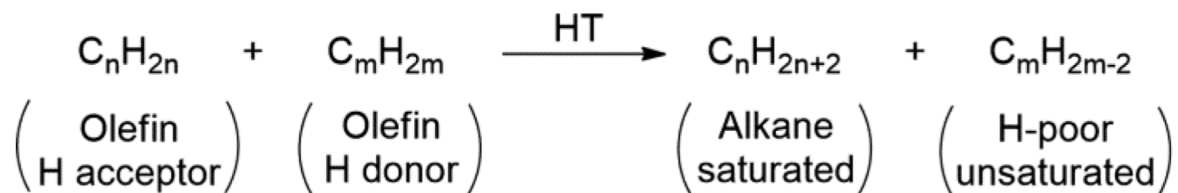


Olsbye et al. *Angew. Chem. Int. Ed.* **2012**, 51, 5810 – 5831

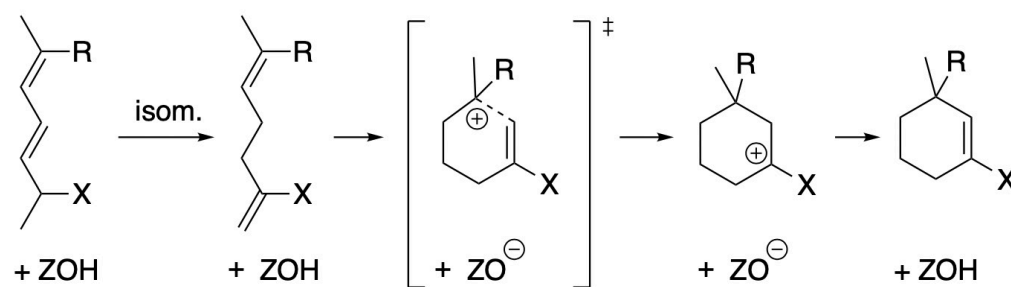


Mechanism

Formation of aromatics

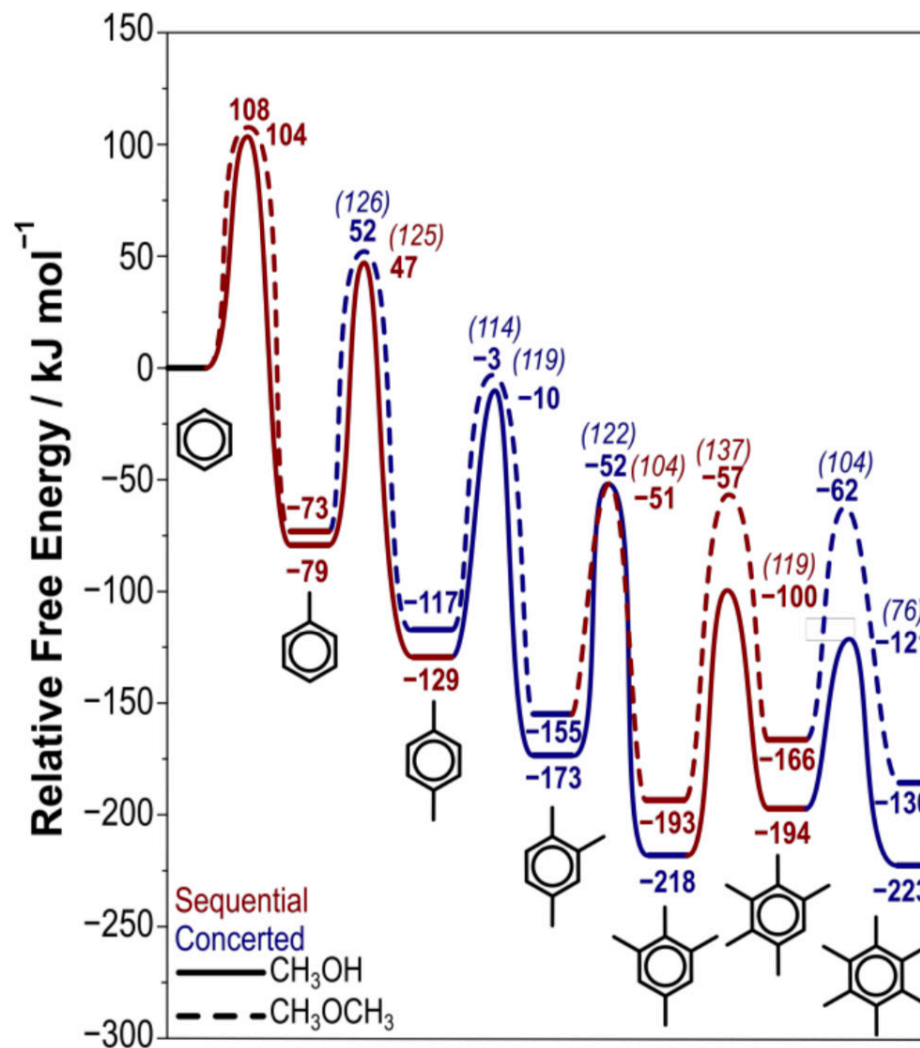


a) Cyclization via carbenium ion



Müller et al, *JACS* **2016**, 138, 15994.

Mechanism

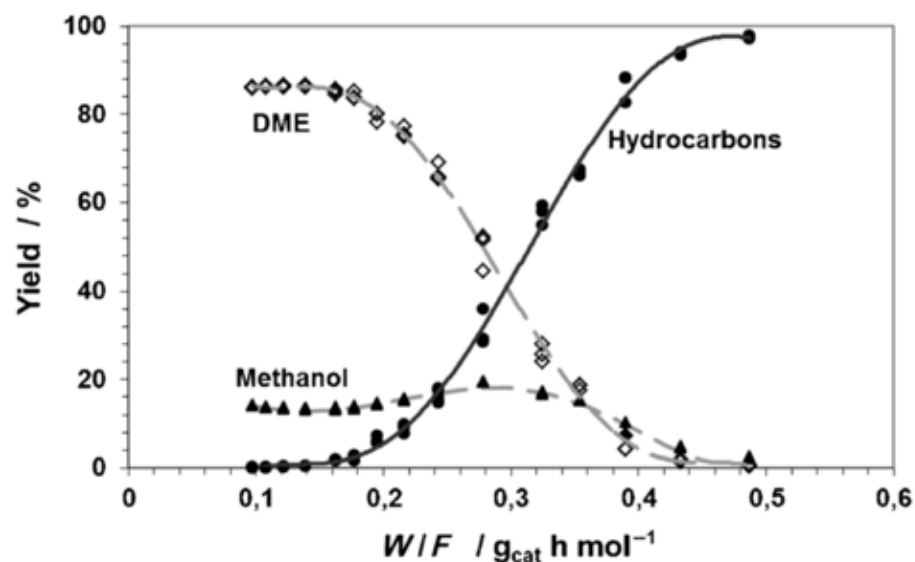


Methylation results in heavily methylated aromats

DeLuca et al, <https://doi.org/10.26434/chemrxiv.8016017.v1>

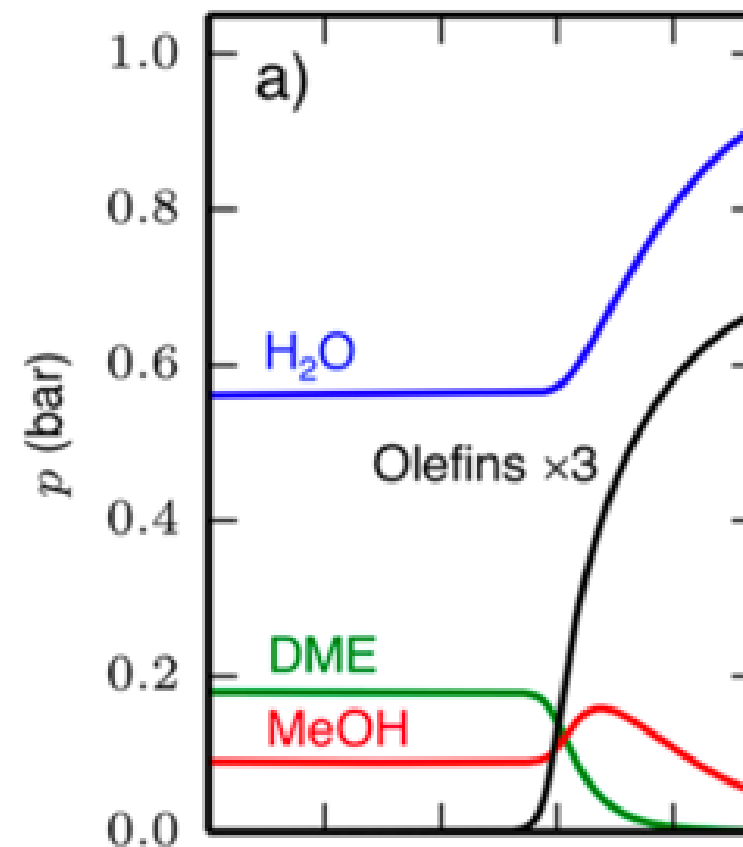
Mechanism

experiments



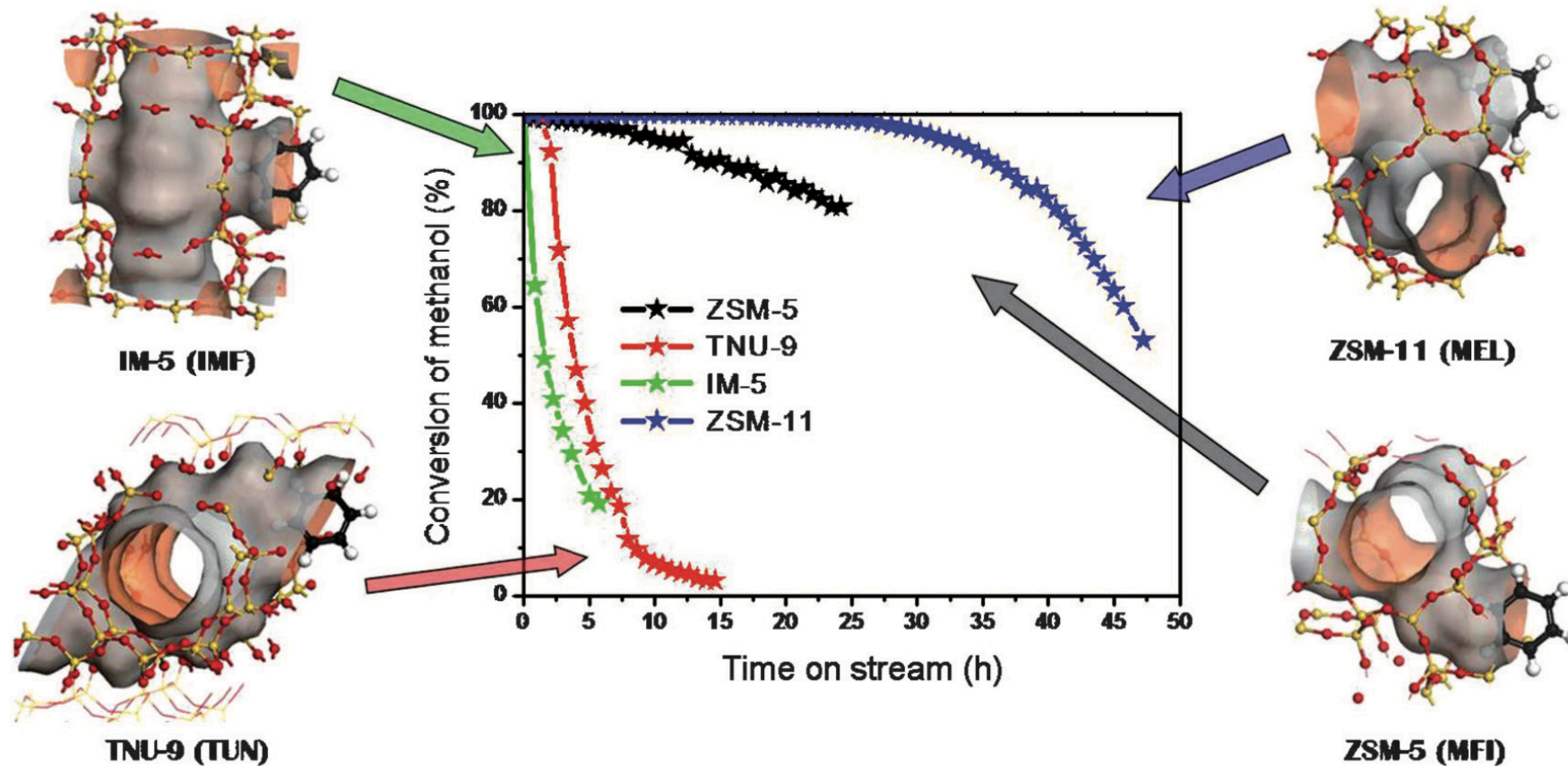
Olsbye et al. *Angew. Chem. Int. Ed.* **2012**, 51, 5810 – 5831

theory



Plessow et al. *JACS* **2019**, 141, 5908

Deactivation



Rapid deactivation after hours of operation

Olsbye et al. *Angew. Chem. Int. Ed.* **2012**, 51, 5810 – 5831

Deactivation

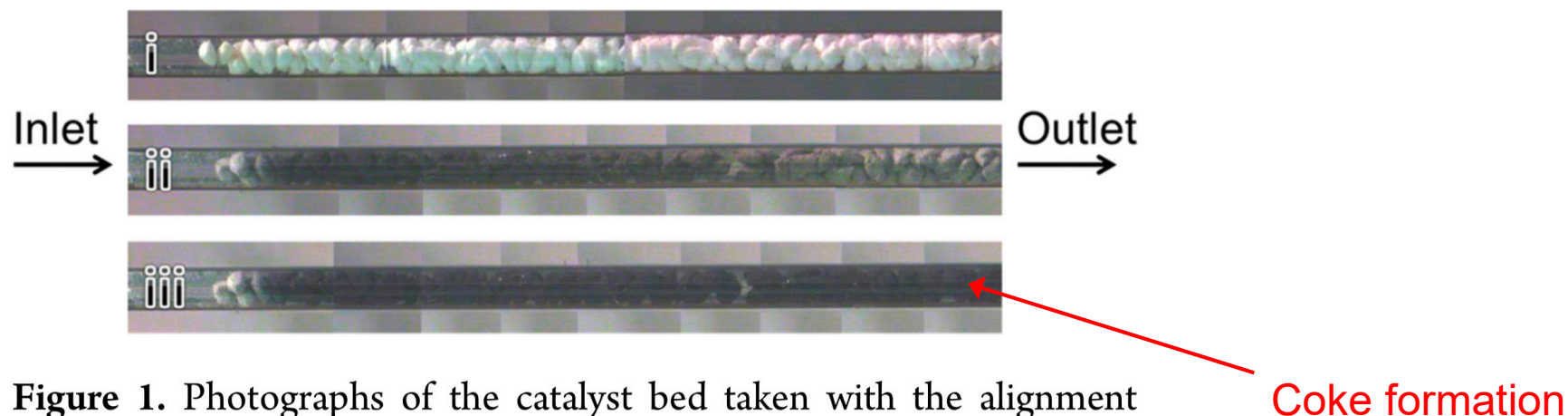


Figure 1. Photographs of the catalyst bed taken with the alignment camera for (i) the activated, fresh catalyst sample; (ii) after 75 min on stream; and (iii) for the completely deactivated catalyst. Reaction at $\text{WHSV} = 20 \text{ g}_{\text{MeOH}} \text{ g}_{\text{catalyst}}^{-1} \text{ h}^{-1}$, P_{atm} and $400 \text{ }^{\circ}\text{C}$.

Royo-Gama et al. *J. Phys. Chem. Lett.* **2018**, 9, 1324.

Deactivation

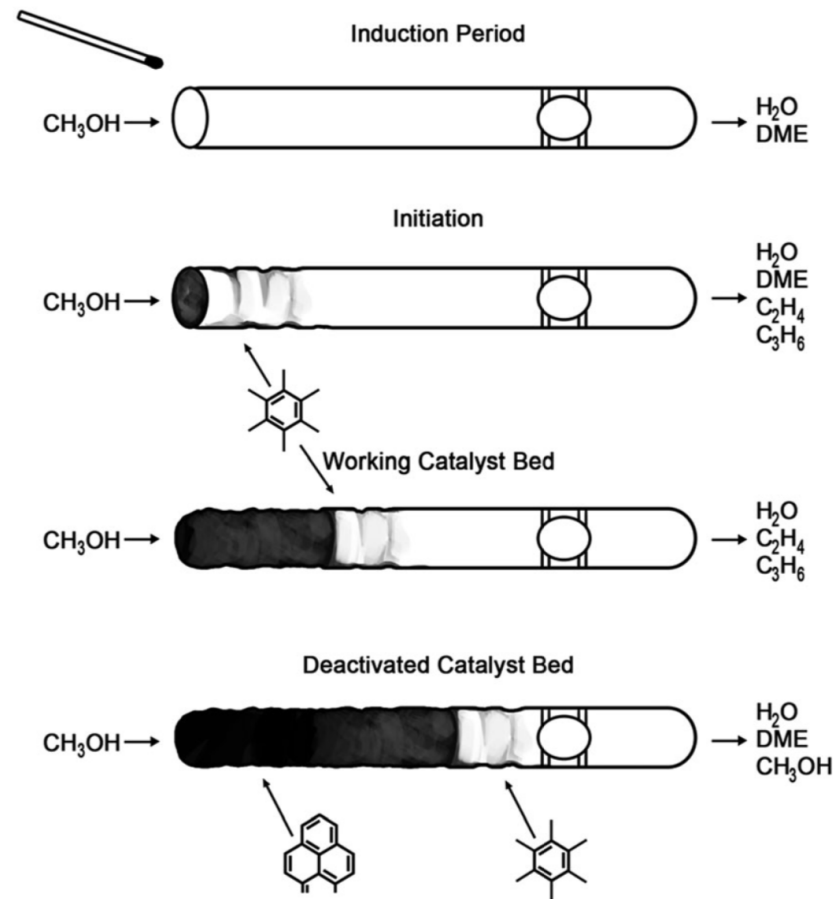
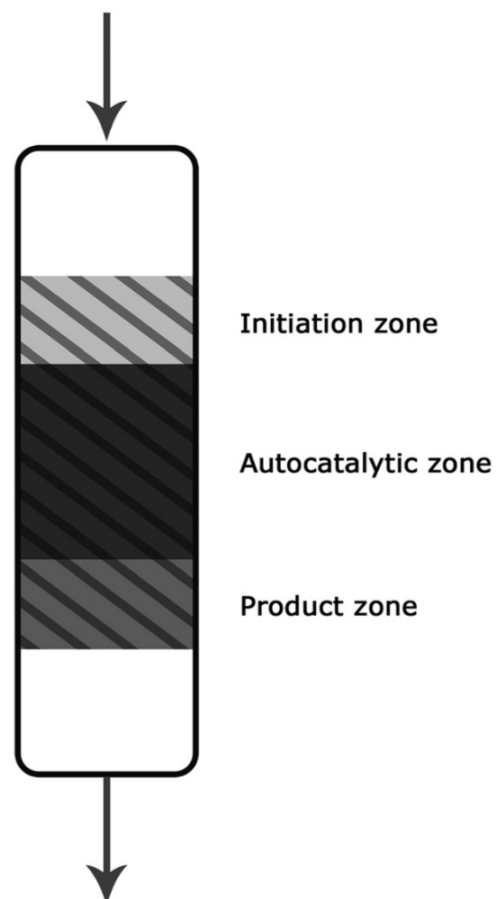
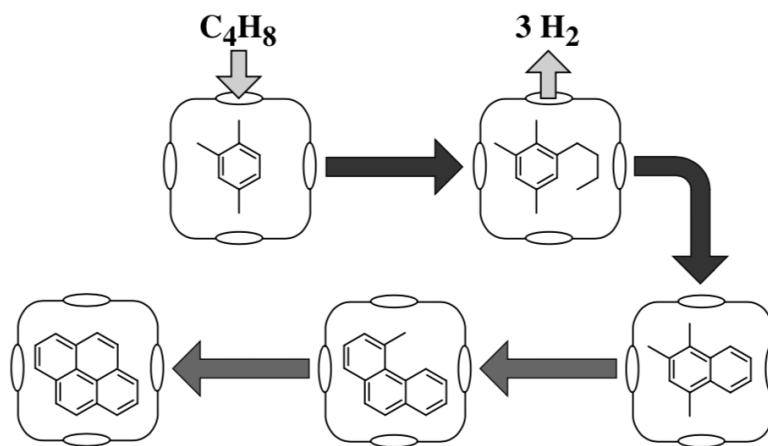
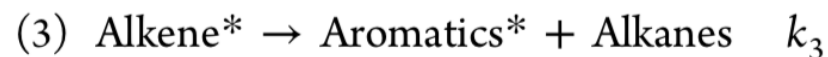
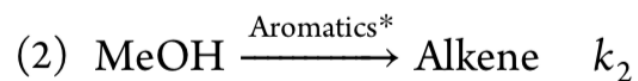
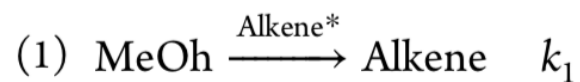


Fig. 24 James Haw's pictorial representation of a deactivating MTH catalyst (SAPO-34) as a burning cigar. Adapted from ref. 144.

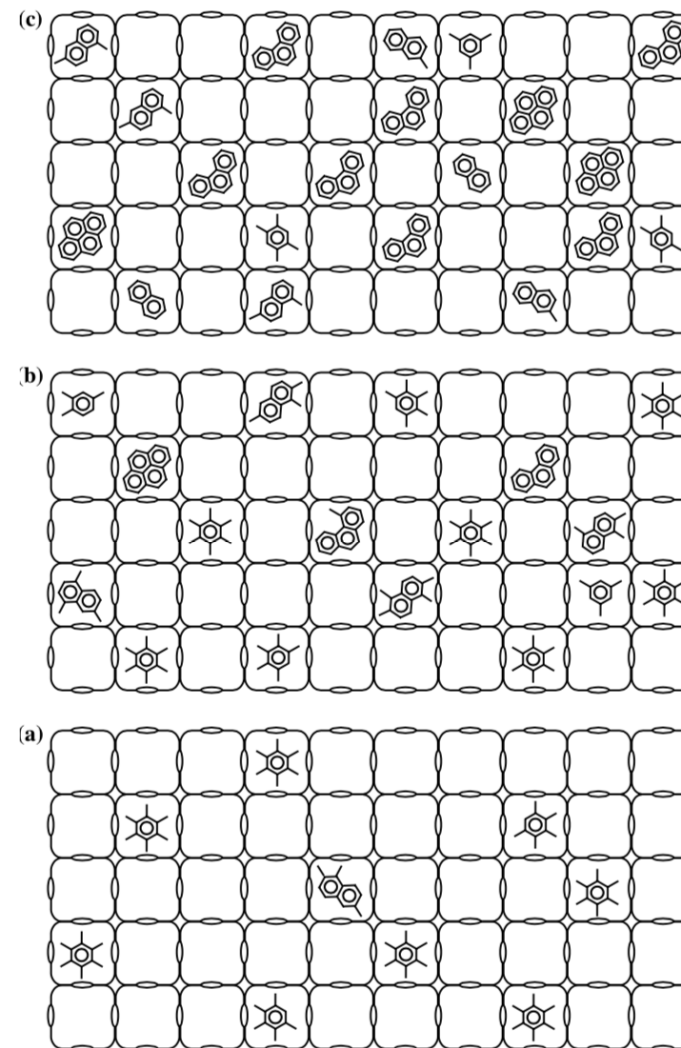
Olsybe et al. *Angew. Chem. Int. Ed.* **2012**, 51, 5810 – 5831

Haw & Marcus, *Top. Catal.* **2005**, 34, 41.

Deactivation



Royo-Gama et al. *J. Phys. Chem. Lett.* **2018**, 9, 1324.



Haw & Marcus, *Top. Catal.* **2005**, 34, 41.