Methanol to Olefins (MTO): Development of a Commercial Catalytic Process

Simon R. Bare

Advanced Characterization, UOP LLC

Modern Methods in Heterogeneous Catalysis Research

FHI Lecture November 30, 2007

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Polyethylene and Polypropylene

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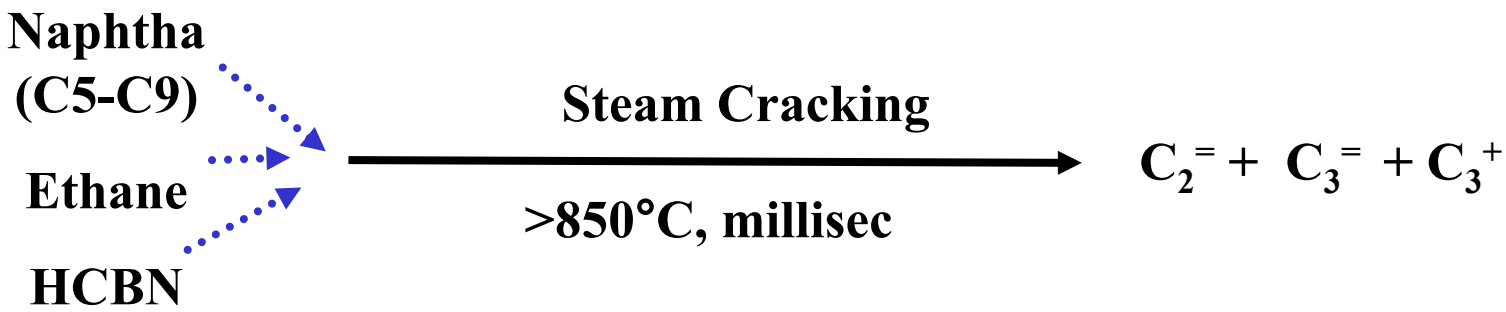
- **Thousands of uses of polyethylene and polypropylene.**

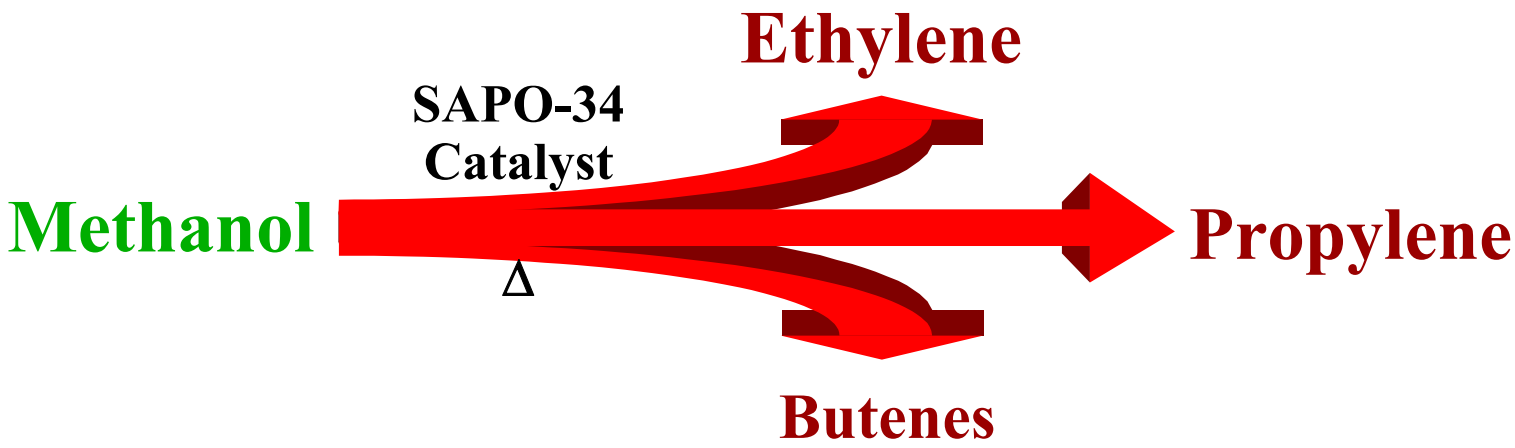
Polyethylene and Polypropylene

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



Methanol To Olefins (MTO) Reaction

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



Other By-Products

H_2O

H_2 , CO_X

C_1-C_5 Paraffins

C_5+

Coke

UOP/Hydro MTO Process

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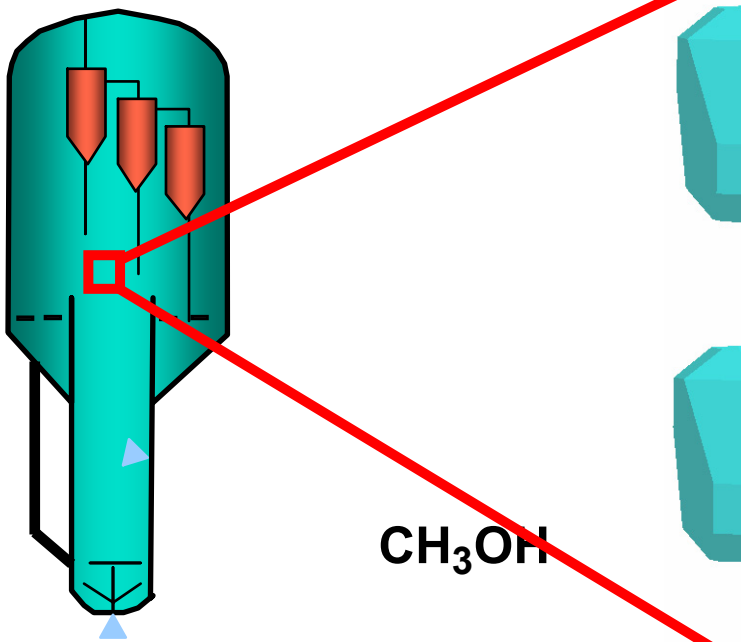
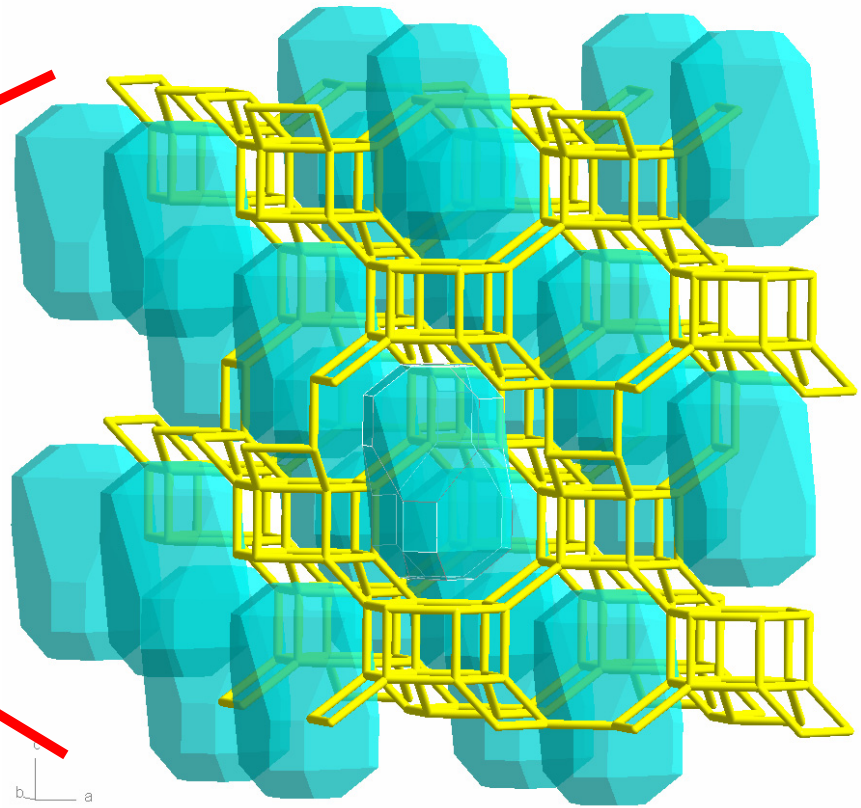
SAPO-34 Catalyst



CH_3OH



Courtesy to Unni Olsbye,
University of Oslo

MTO Reaction

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- **High selectivity and yield to light olefins.**

Material T atom %	**SAPO-34** **10% Si (gel)**
Selectivities (2 hr) C_2-C_4 olefins CH_4 C_2H_6 C_3H_8	 96 1.4 0.3 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?**

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

Outline

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- Zeolites
- Zeolites as industrial catalysts
- Acid sites in molecular sieves
- Aluminum phosphate ($AlPO_4$) molecular sieves
- Characterization methods for molecular sieves
- SAPO-34
- Methanol conversion using zeolites
- Zeolites vs. SAPO's in methanol conversion
- CHA and AEI
- MTO mechanism
- MTO reactor design
- Putting it all together: methanol & natural gas
- Discovery to commercialization

What is a Zeolite?

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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.**

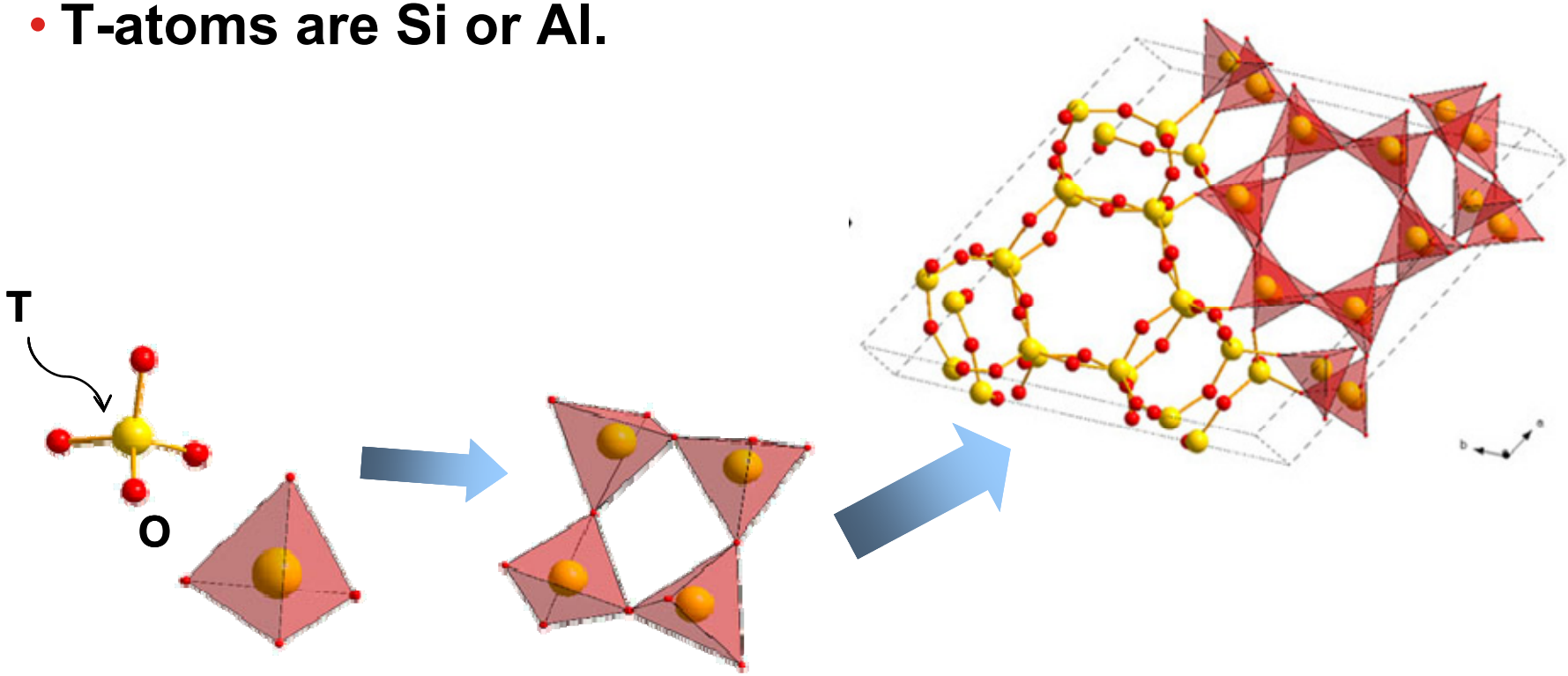
Mordenite

Chabazite

Natrolite

Zeolites

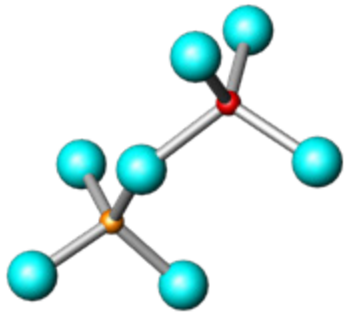
- Zeolites consist of a framework built of tetrahedra.
- Each tetrahedron comprises a T-atom bound to four O atoms.
- Oxygen bridges connect the tetrahedra.
- T-atoms are Si or Al.

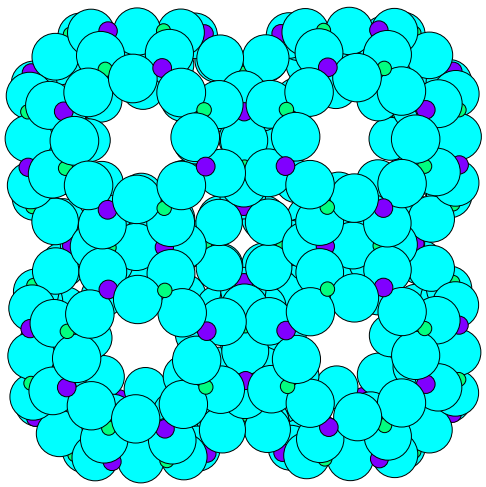


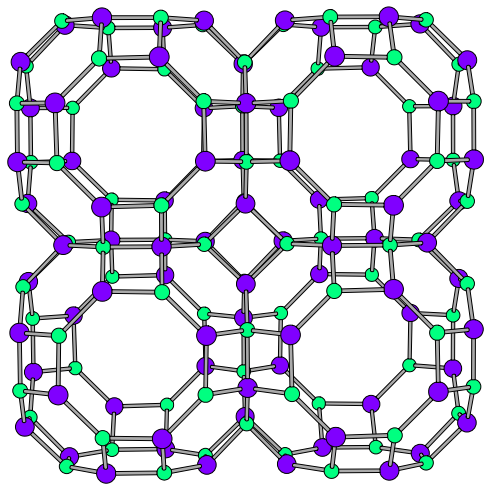
Courtesy to Francesca Bleken, University of Oslo

Zeolites

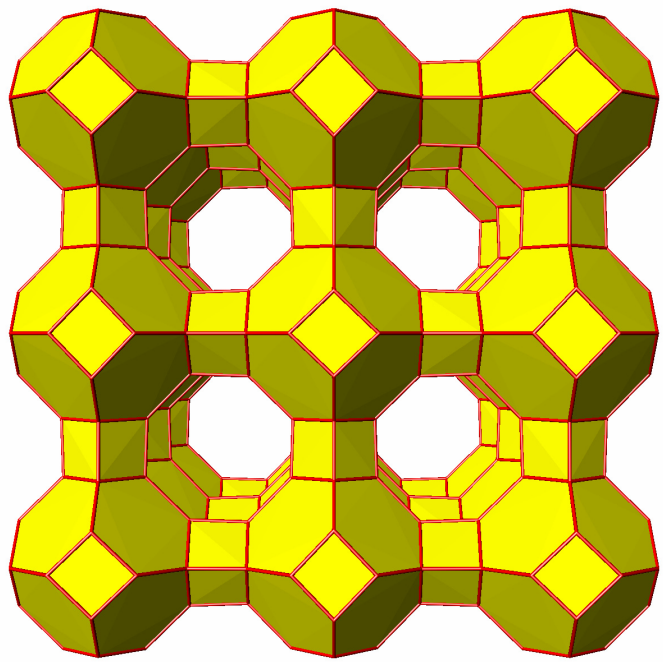
- Alumino-silicate framework
- Crystalline, microporous (pore diameter 3-14Å)
- Framework density <20 T-atoms/1000Å^3







LTA = Zeolite A



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

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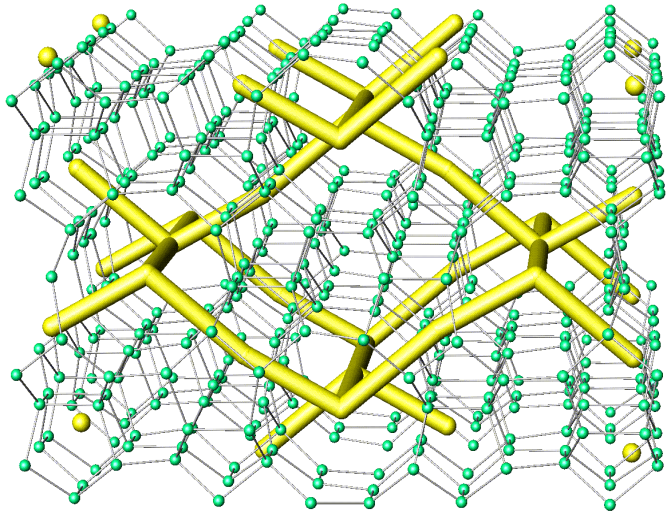
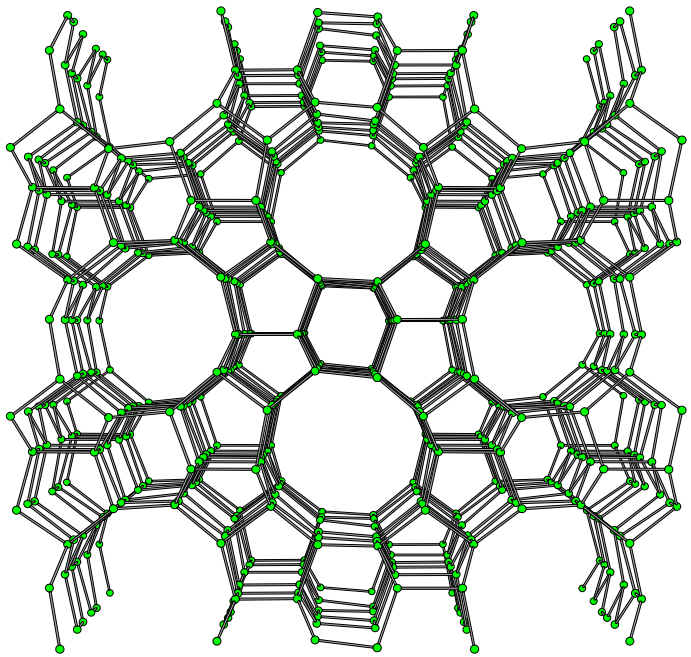
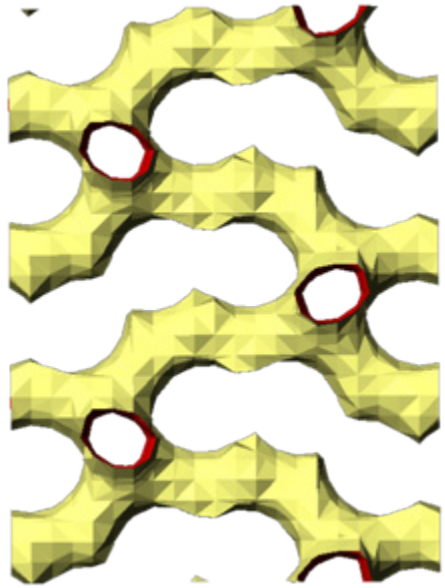
- **Medium pore size 5.1 x 5.5Å**
  - **Wire frame structure showing only T-atoms**
  - **Pore structure – critical for thinking about a molecule diffusing through the structure.**







Range of Pore Sizes

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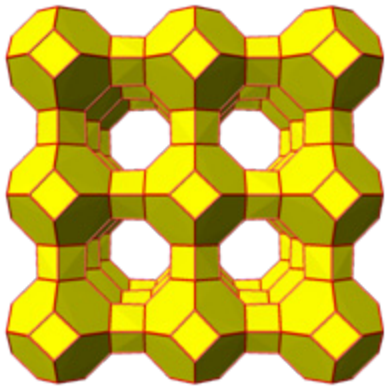
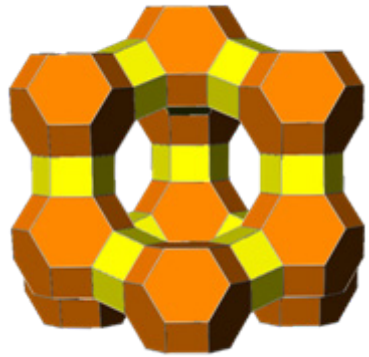
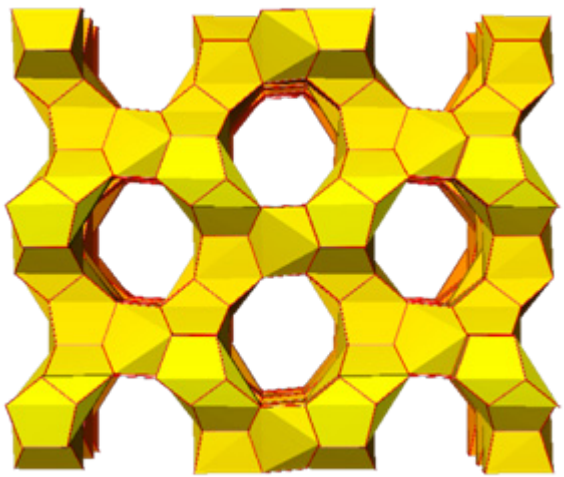
- **Zeolites exhibit a range of pore sizes of molecular dimensions (molecular sieves).**

Small
8-ring
~ 4A



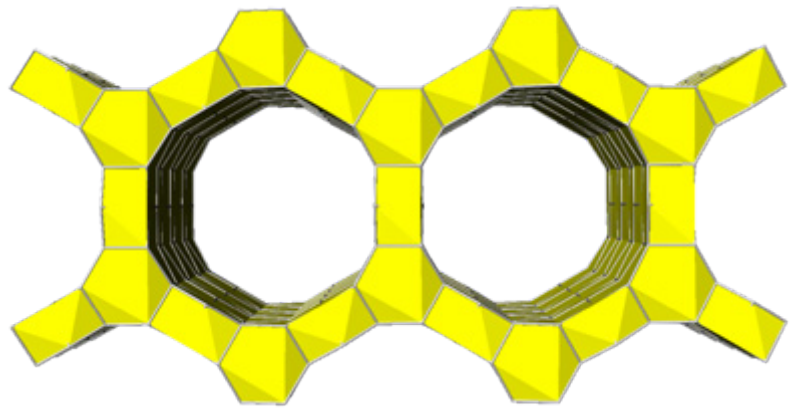
Large
12-ring
~ 6-8A





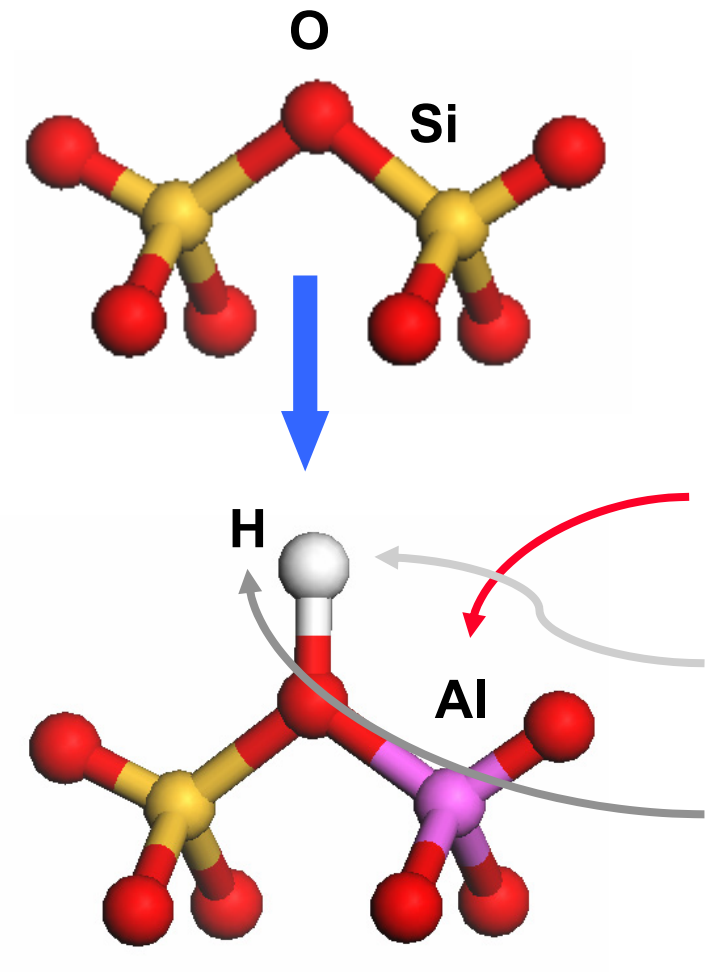
Medium
10-ring
~ 5-6A

Very Large
>12-ring
>8A



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, University of Oslo

Evolution of Molecular Sieve Compositions

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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

Framework Types

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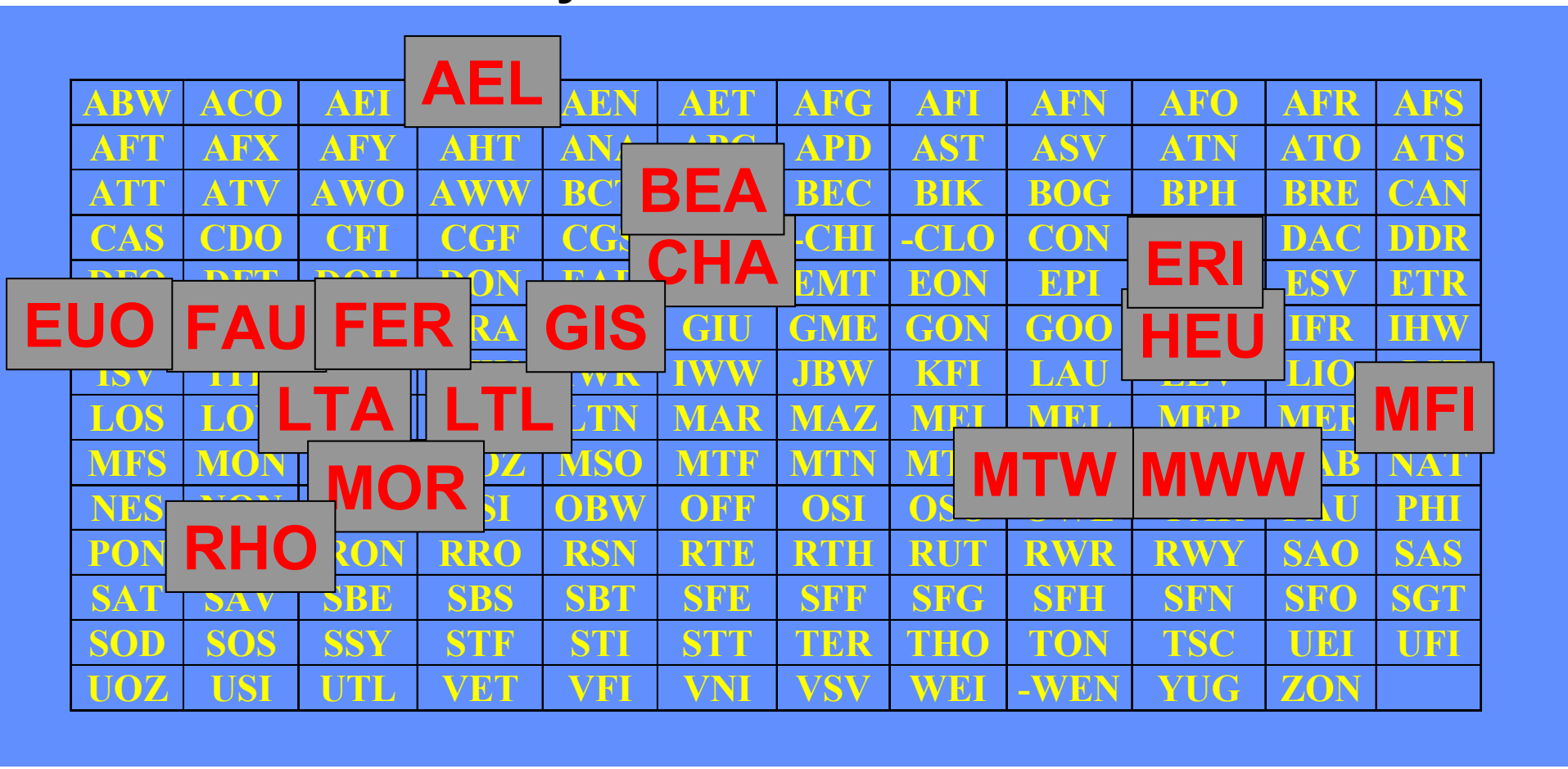
- 176 framework types recognized by the International Zeolite Association (IZA) (http://www.iza-online.org/).
- IZA Structure Commission assigns framework type codes to all unique and confirmed framework topologies.

ABW	ACO	AEI	AEL	AEN	AET	AFG	AFI	AFN	AFO	AFR	AFS
AFT	AFX	AFY	AHT	ANA	APC	APD	AST	ASV	ATN	ATO	ATS
ATT	ATV	AWO	AWW	BCT	*BEA	BEC	BIK	BOG	BPH	BRE	CAN
CAS	CDO	CFI	CGF	CGS	CHA	-CHI	-CLO	CON	CZP	DAC	DDR
DFO	DFT	DOH	DON	EAB	EDI	EMT	EON	EPI	ERI	ESV	ETR
EUO	FAU	FER	FRA	GIS	GIU	GME	GON	GOO	HEU	IFR	IHW
ISV	ITE	ITH	ITW	IWR	IWW	JBW	KFI	LAU	LEV	LIO	-LIT
LOS	LOV	LTA	LTL	LTN	MAR	MAZ	MEI	MEL	MEP	MER	MFI
MFS	MON	MOR	MOZ	MSO	MTF	MTN	MTT	MTW	MWW	NAB	NAT
NES	NON	NPO	NSI	OBW	OFF	OSI	OSO	OWE	-PAR	PAU	PHI
PON	RHO	-RON	RRO	RSN	RTE	RTH	RUT	RWR	RWY	SAO	SAS
SAT	SAV	SBE	SBS	SBT	SFE	SFF	SFG	SFH	SFN	SFO	SGT
SOD	SOS	SSY	STF	STI	STT	TER	THO	TON	TSC	UEI	UFI
UOZ	USI	UTL	VET	VFI	VNI	VSV	WEI	-WEN	YUG	ZON	

Zeolites as Industrial Catalysts

- But only ~18 framework types have seen commercial utility.



ABW	ACO	AEI	AEL	AEN	AET	AFG	AFI	AFN	AFO	AFR	AFS
AFT	AFX	AFY	AHT	ANA	APC	APD	AST	ASV	ATN	ATO	ATS
ATT	ATV	AWO	AWW	BCT	BEA	BEC	BIK	BOG	BPH	BRE	CAN
CAS	CDO	CFI	CGF	CGS	CHA	-CHI	-CLO	CON	ERI	DAC	DDR
DFO	DFT	DOH	DON	EAB	EMT	EON	EPI	ESV	ETR		
EUO	FAU	FER	GIS	GIU	GME	GON	GOO	HEU	IFR	IHW	
ISV	ITE	ITH	ITW	IWR	IWW	JBW	KFI	LAU	LIO		
LOS	LOV	LTA	LTL	LTN	MAR	MAZ	MEI	MEL	MEP	MER	MFI
MFS	MON	MOR	MOZ	MSO	MTF	MTN	MTT	MTW	MWW	NAB	NAT
NES	NON	NPO	NSI	OBW	OFF	OSI	OSO			NAU	PHI
PON	RHO	RON	RRO	RSN	RTE	RTH	RUT	RWR	RWY	SAO	SAS
SAT	SAV	SBE	SBS	SBT	SFE	SFF	SFG	SFH	SFN	SFO	SGT
SOD	SOS	SSY	STF	STI	STT	TER	THO	TON	TSC	UEI	UFI
UOZ	USI	UTL	VET	VFI	VNI	VSV	WEI	-WEN	YUG	ZON	

Commercial Catalytic Uses of Zeolites (Refining & Petrochemicals)

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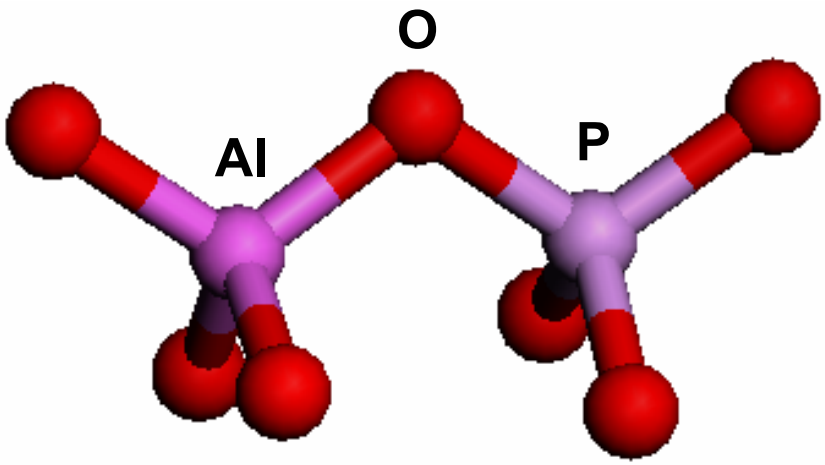
Process	*FAU*	*LTL*	*MOR*	*BEA*	*MWW*	*MFI*	*AEL*	*FER*	*RHO*	*CHA*	*???*
Ethylbenzene					x	x					x
Cumene	x		x	x	x	x					
Other aromatics						x					
Xylene isom						x					x
C4 isom			x								
$C4^{=}$ isom						x		x			x
$C5^{=}$ isom						x					x
Iso-dewaxing							x				
Amination			x			x			x	x	
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

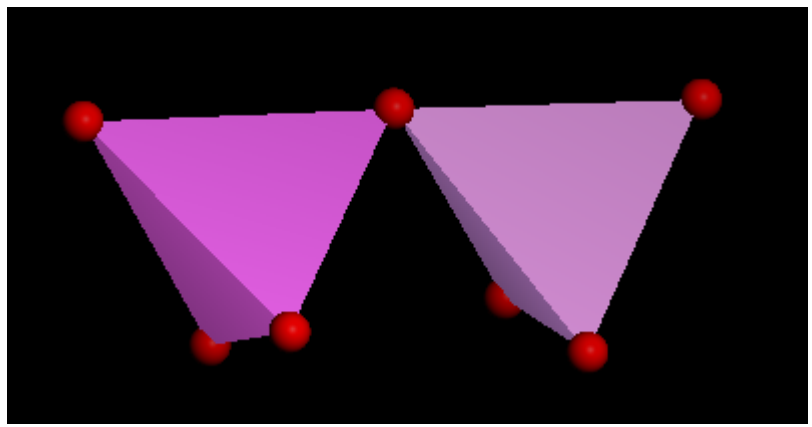
FAU = Y, USY LTL = Linde L, K-L MOR = mordenite BEA = beta
MWW = MCM-22 MFI = ZSM-5 AEL = SAPO-11, SM-3 FER = ferrierite
RHO = zeolite RHO CHA = chabazite, SAPO-34

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

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).





Idealized 2D Connectivity of tetrahedral $AlPO_4$ framework

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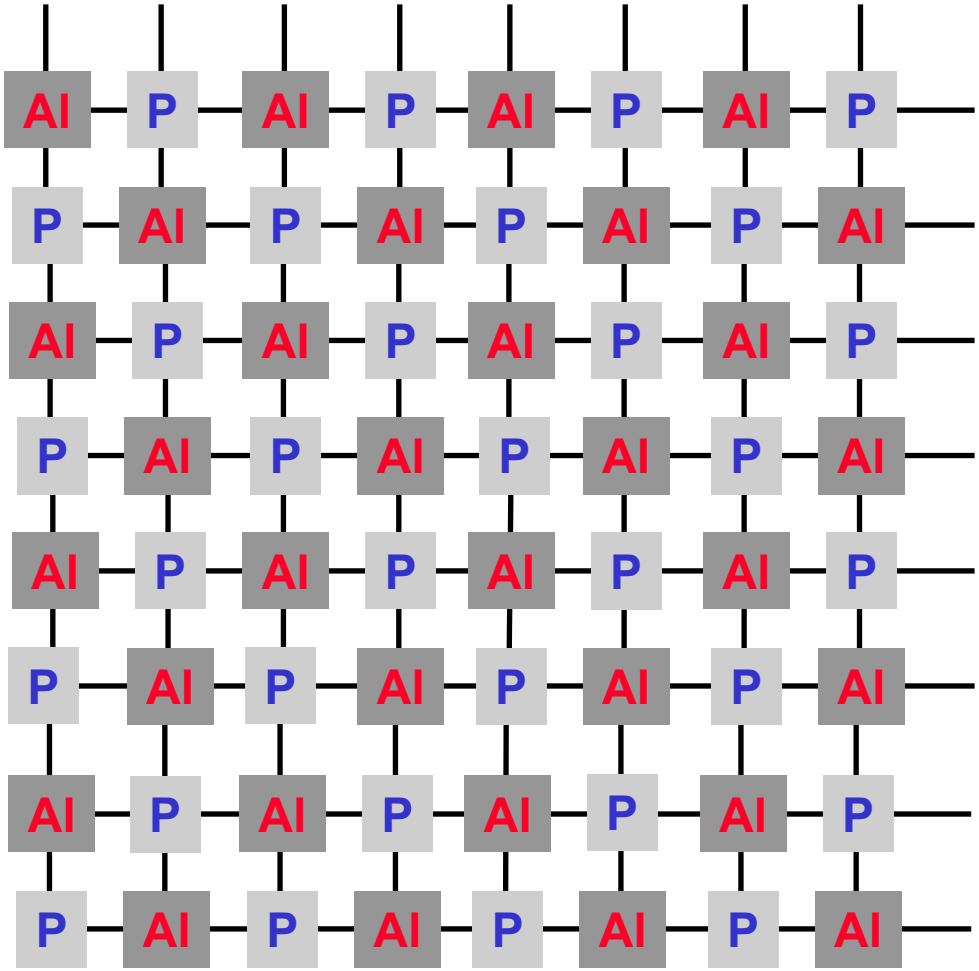
- Al and P strictly alternating.
- Neutral framework.



Si Substitution for P in $AlPO_4$ to give SAPO

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

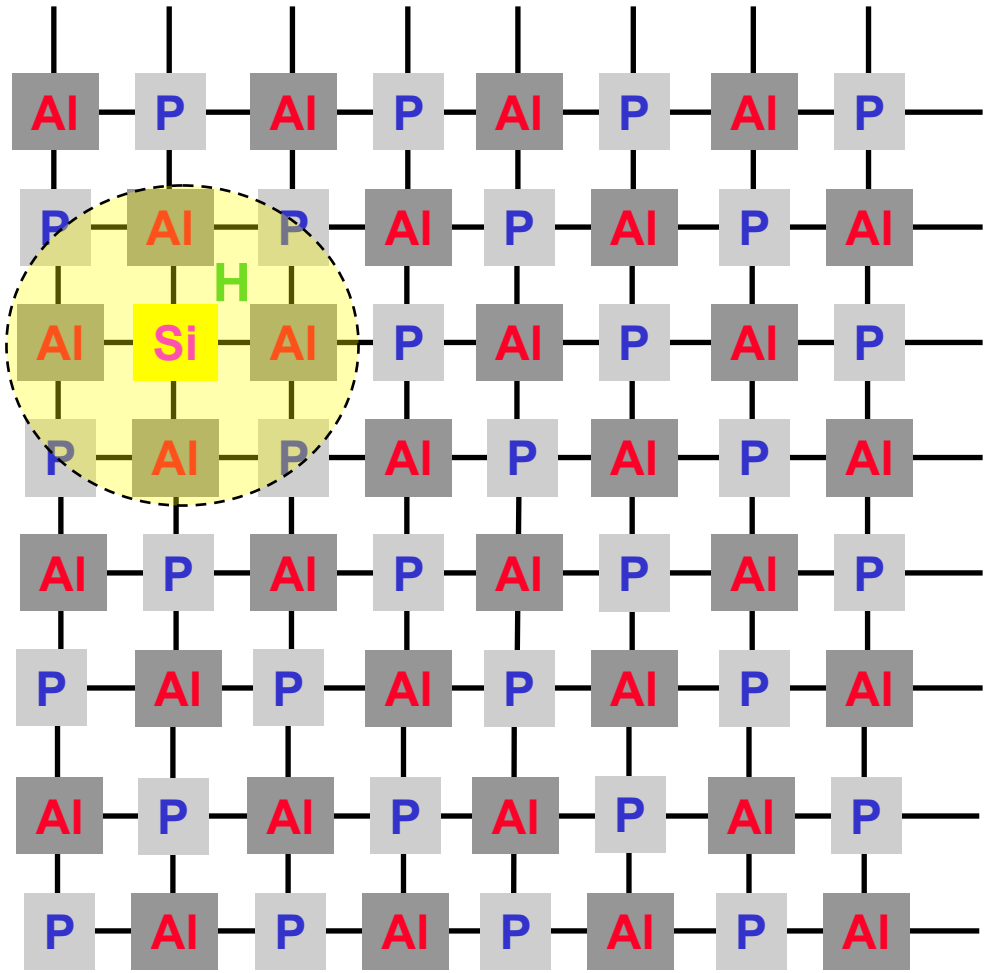
Isolated Si: $Si^{+4} \rightarrow P^{+5}$

Negative framework charge

Template decomposition $\rightarrow H^{+}$

No Si-O-P

No P-O-P



Si Substitution Produces Brønsted Acid Sties

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Isolated Si

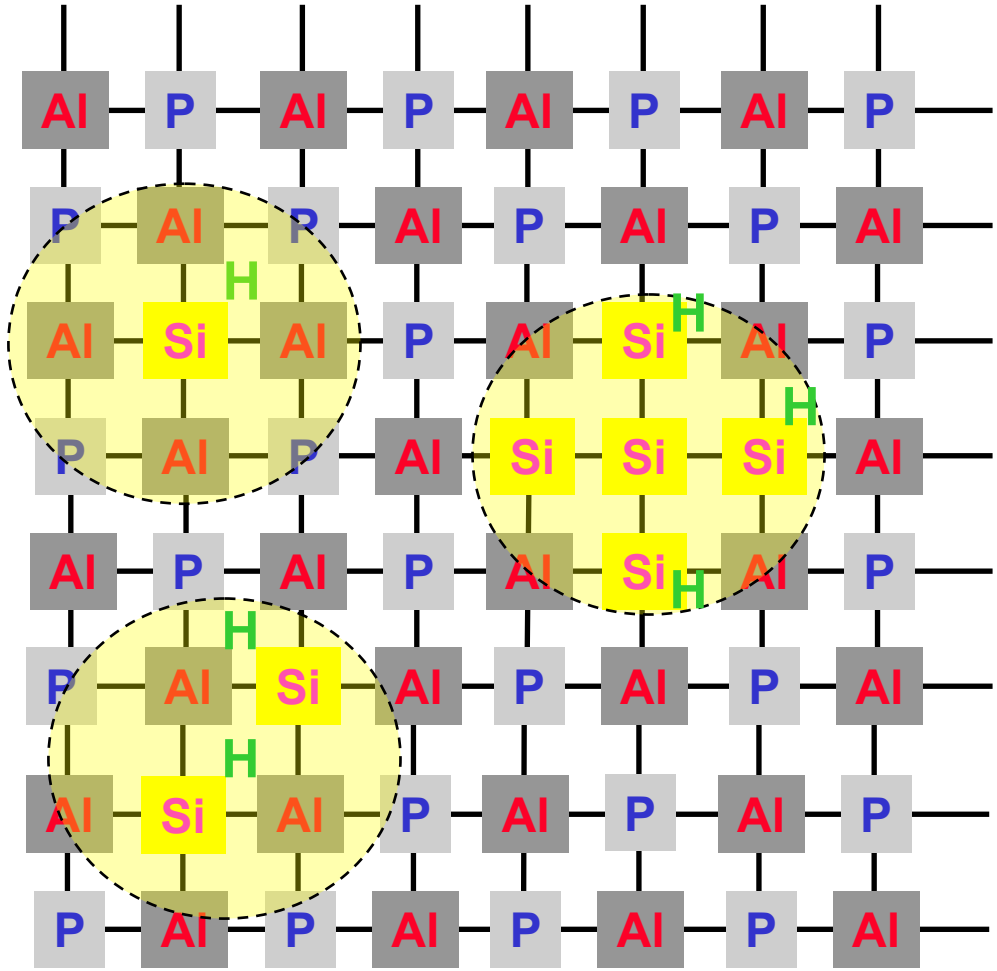
1 Si = 1P

1 Si = 1 H^+

Adjacent isolated Si

2 Si = 2P

2 Si = 2 H^+



Si island

5 Si = 4P + 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

Outline

- Zeolites
- Zeolites as industrial catalysts
- Acid sites in molecular sieves
- Aluminum phosphate ($AlPO_4$) molecular sieves
- **Characterization methods for molecular sieves**
- SAPO-34
- Methanol conversion using zeolites
- Zeolites vs. SAPO's in methanol conversion
- CHA and AEI
- MTO mechanism
- MTO reactor design
- Putting it all together: methanol & natural gas
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Characterization Methods for Zeolites

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- NH_3 TPD
- Hydroxyl FTIR
- Pyridine FTIR
- Framework FTIR
- Low temperature CO FTIR
- Solid State NMR
- Electron microscopy: SEM/TEM

- XPS
- XRD
- EXAFS
- Many others…..

Acidic Sites: Use of Base for Characterization

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- 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:

$$OH_s + B \Leftrightarrow OH_s \cdots B$$

- If OH is sufficiently acidic then proton transfer:

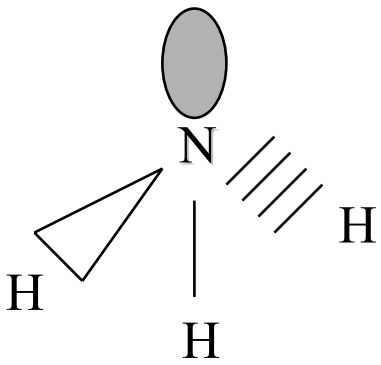
$$OH_s \cdots B \Leftrightarrow O_s^- \cdots H^+B$$

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

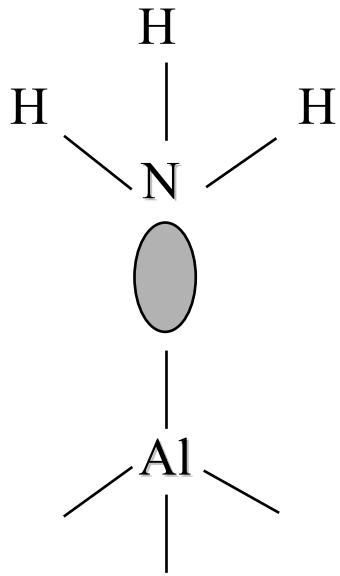
$$L + B \Leftrightarrow L \leftarrow B$$

Ammonia Temperature Programmed Desorption

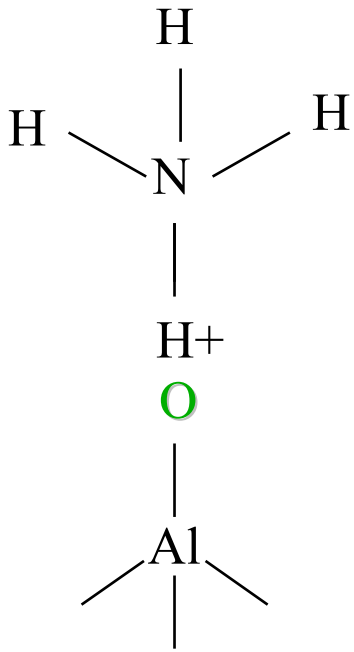
- NH_3 TPD is used to measure the amount and relative strength of the acid sites.
- NH_3 small molecule but not very specific.



Ammonia

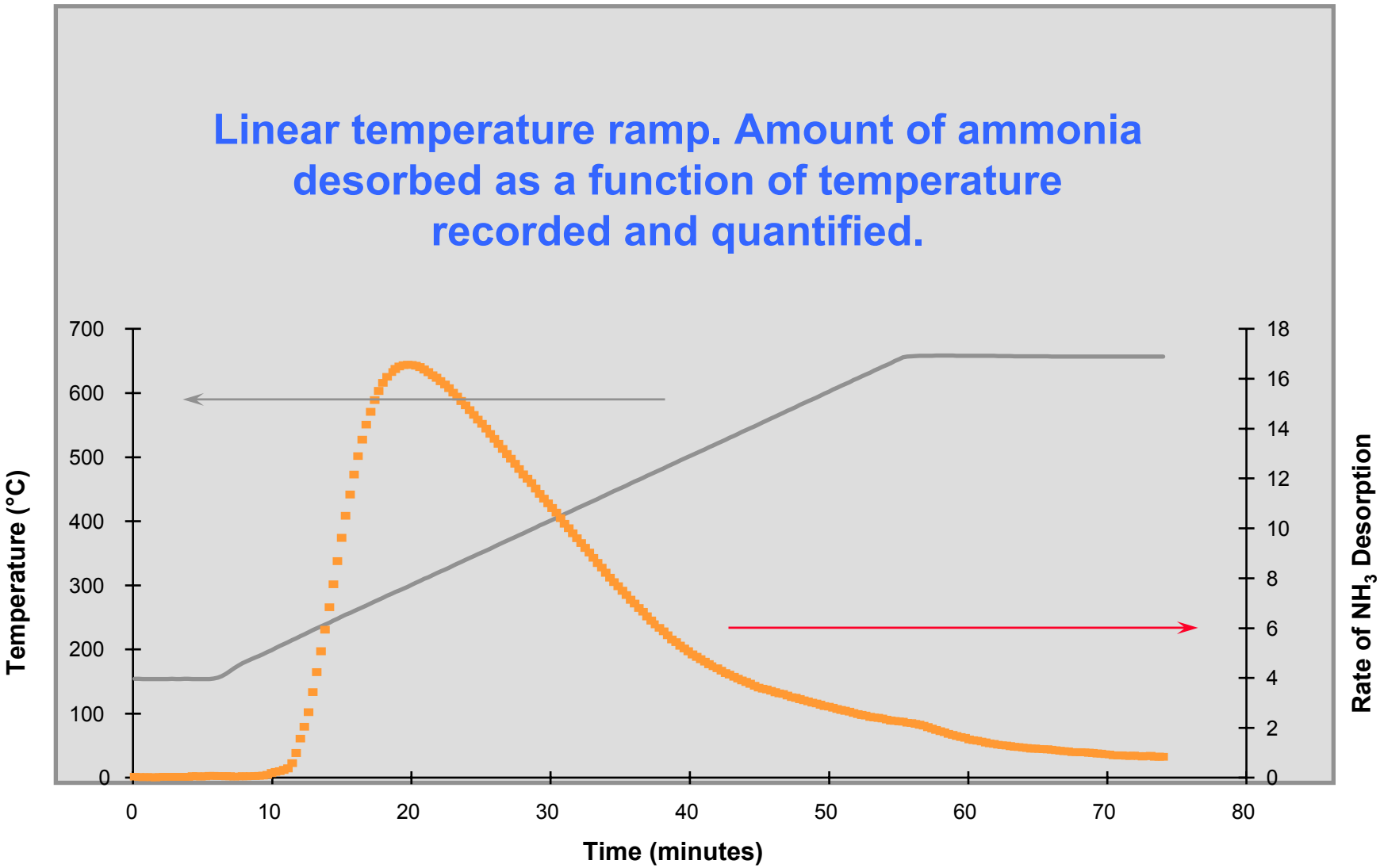


Lewis acid (electron acceptor)



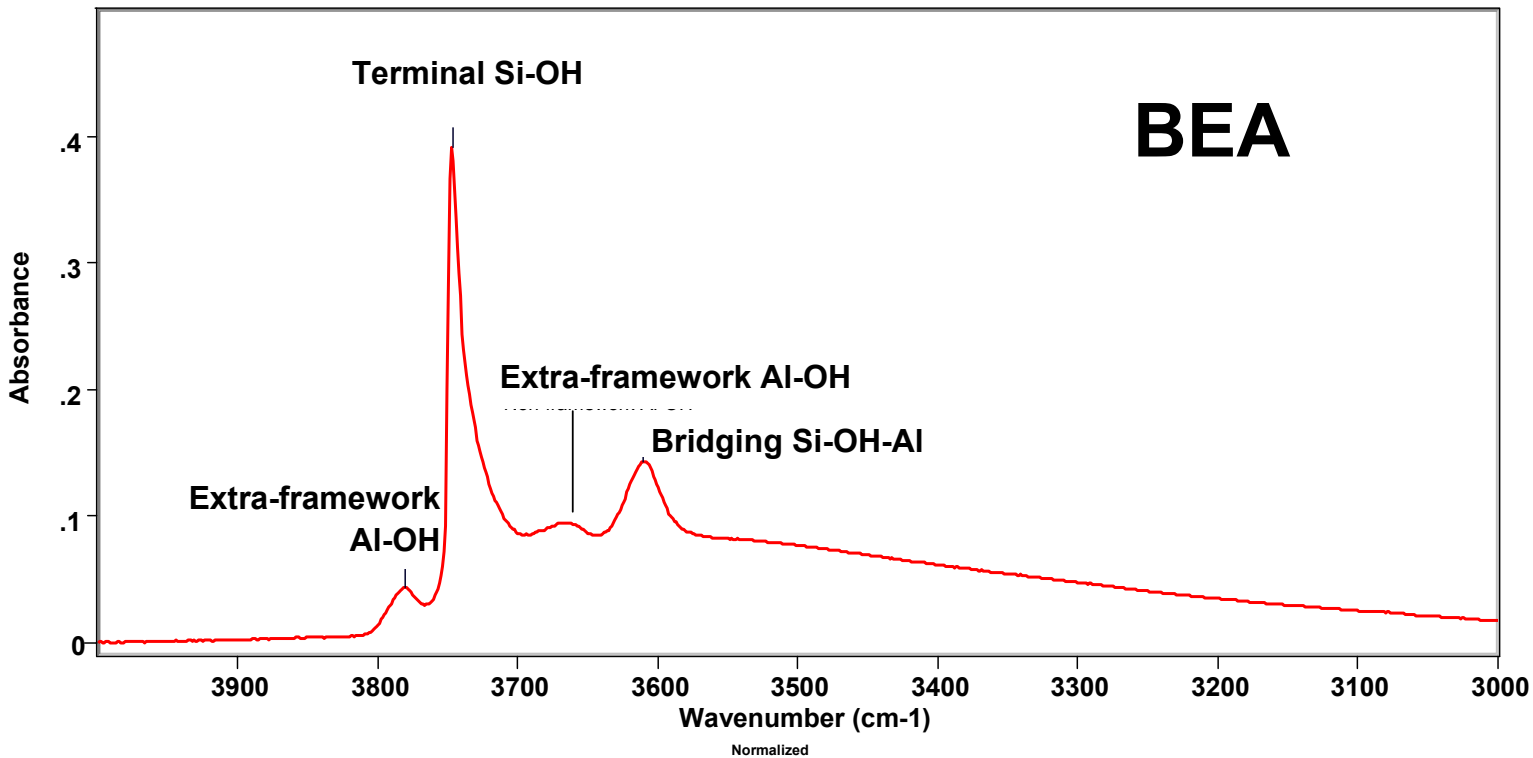
Brønsted acid (proton donor)

Ammonia Temperature Programmed Desorption



Hydroxyl FTIR

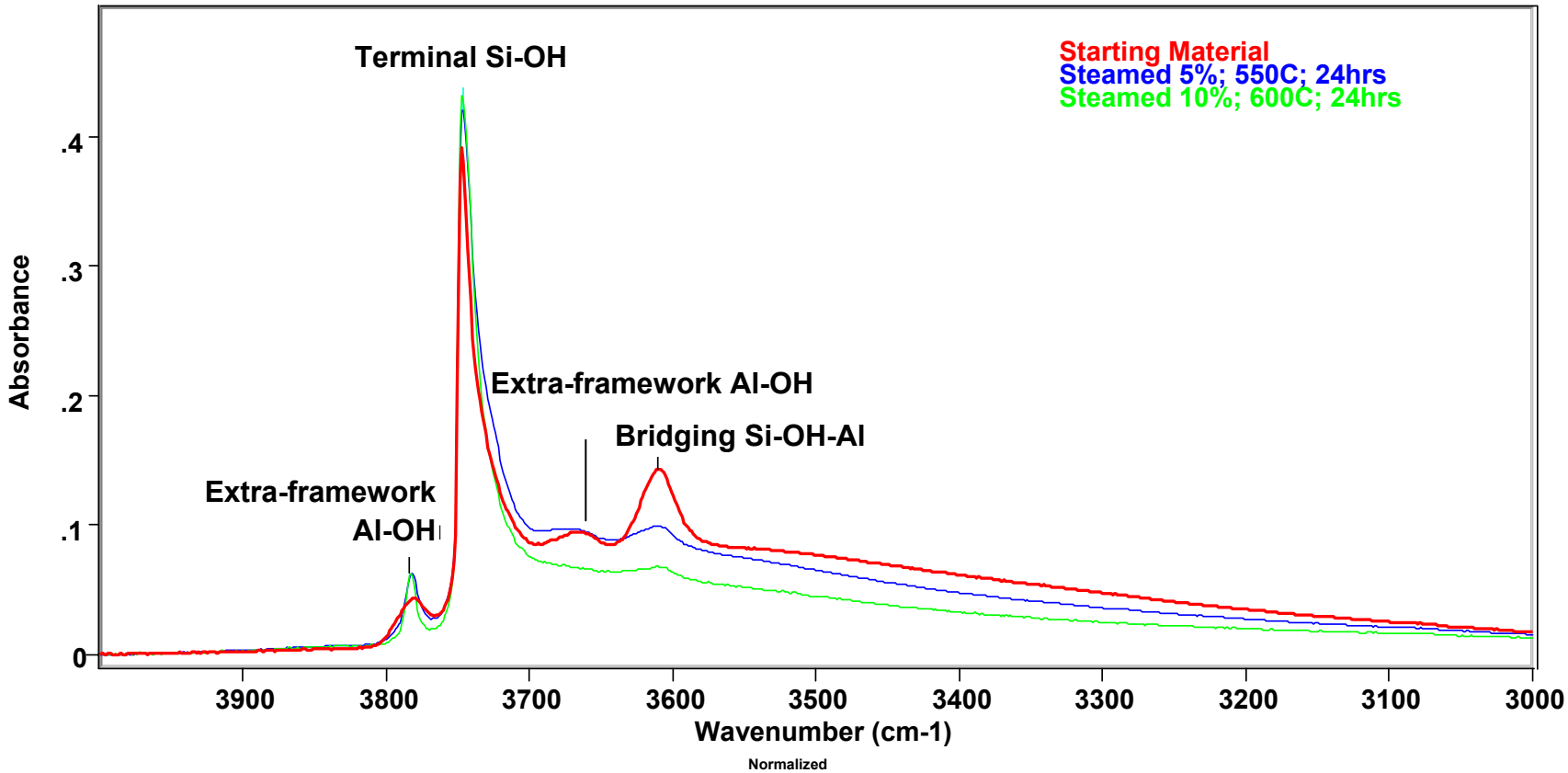
- Use FTIR to measure the infra red spectrum of the zeolite.
- The vibrational frequency of the hydroxyl species in the sample is dependent on the type of hydroxyl species present.
- Can differentiate between framework and extraframework species.



H. Knözinger in Handbook of Heterogeneous Catalysis, Vol 2, p. 707

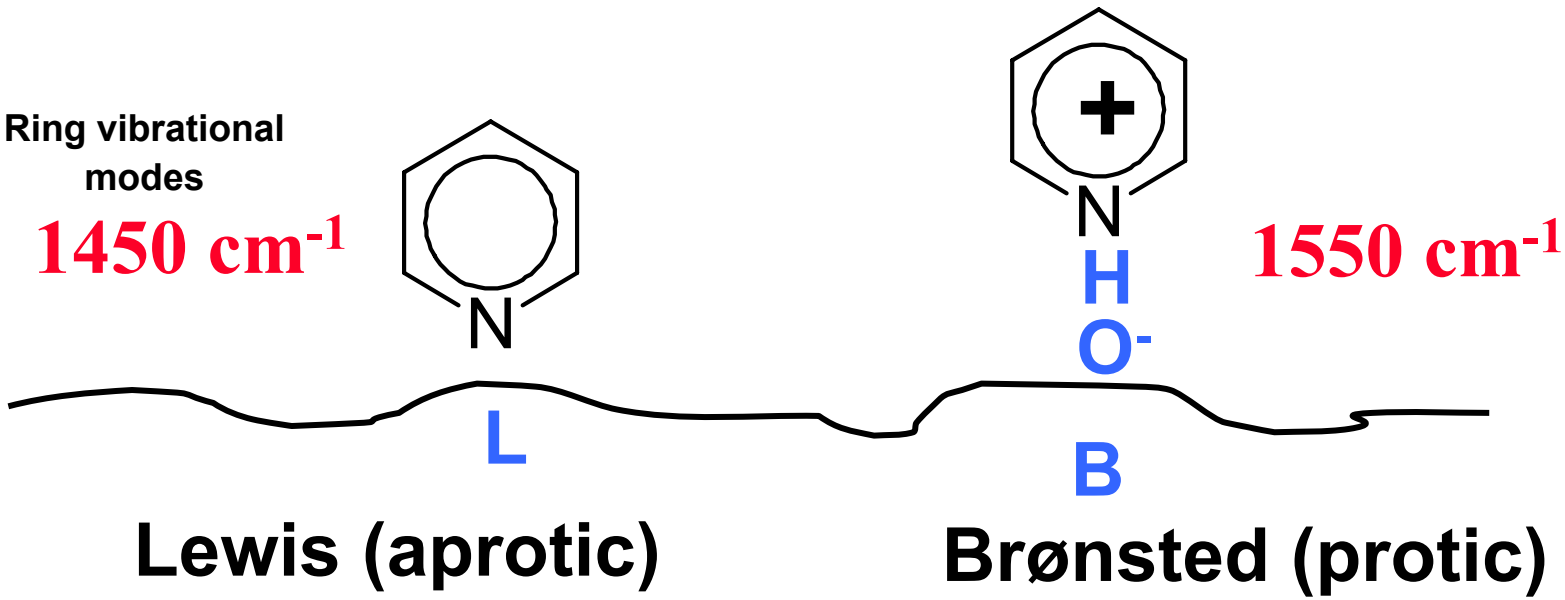
Hydroxyl FTIR

- Transformation of IR spectrum on steaming of zeolite BEA.
- Dealumination of framework Al species.



Pyridine FTIR: Basics

- 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.



Pyridine FTIR: Spectrum

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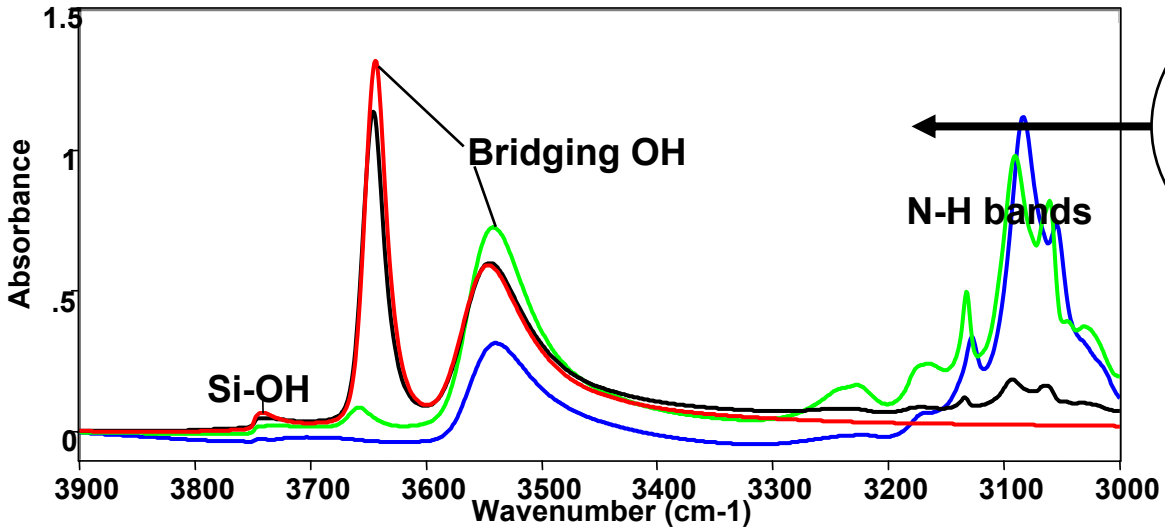
Hydroxyl Region Pyridine Adsorption

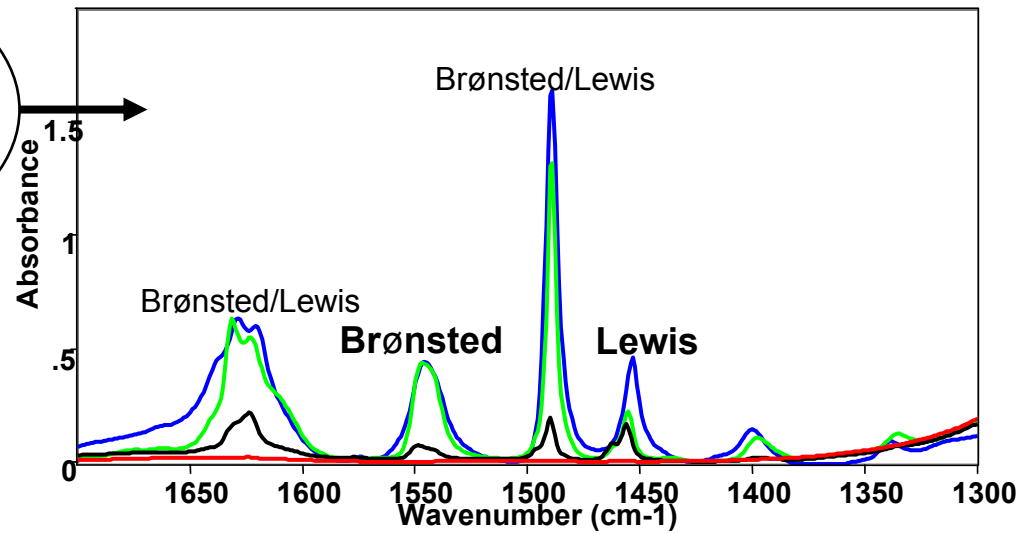


File # 1 : Y-64PRTC

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

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

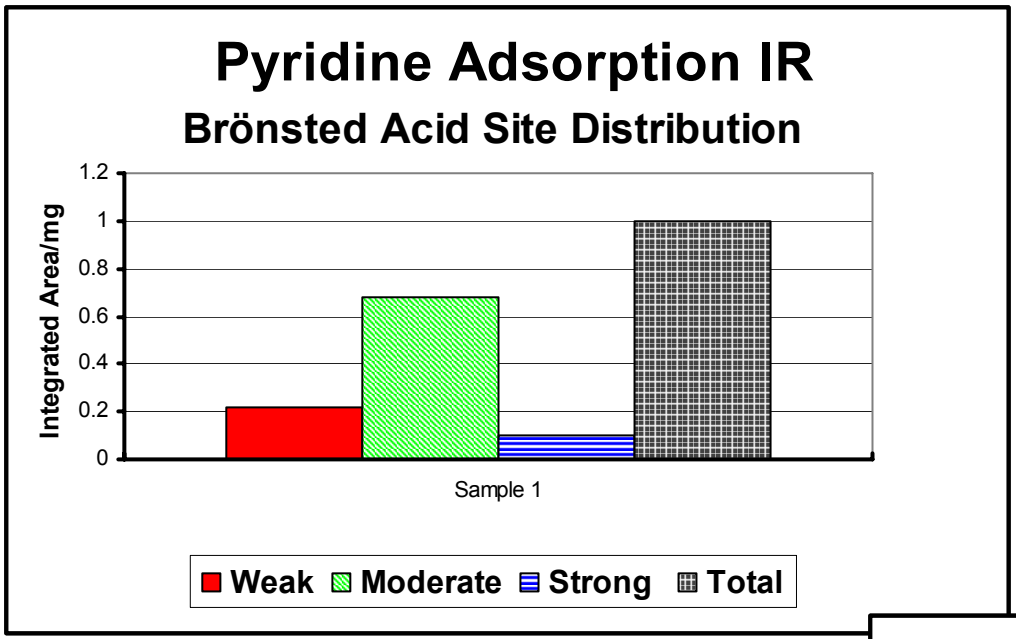
Pyridine Adsorption Spectral Region



File # 1 : Y-64PRTC

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

Pyridine FTIR: Acid Site Distribution



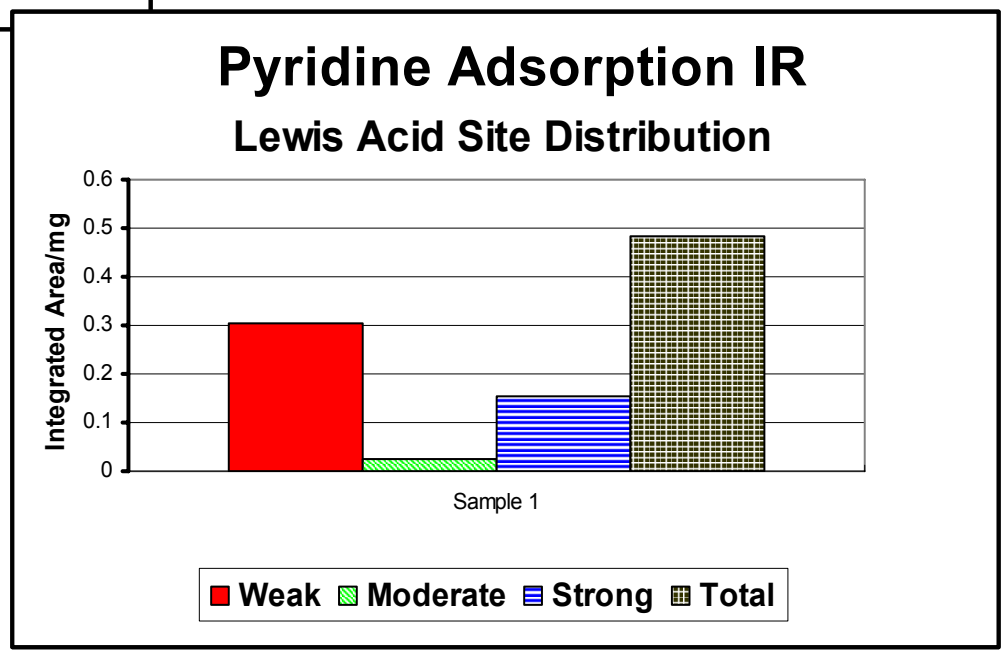
Integrated area of pyridine adsorbed on Brønsted acid site; ~ 1550 cm^{-1}

Integrated area of pyridine adsorbed on Lewis acid site; ~1450 cm^{-1}.

Weak Site: pyridine desorbed between 150ºC and 300ºC

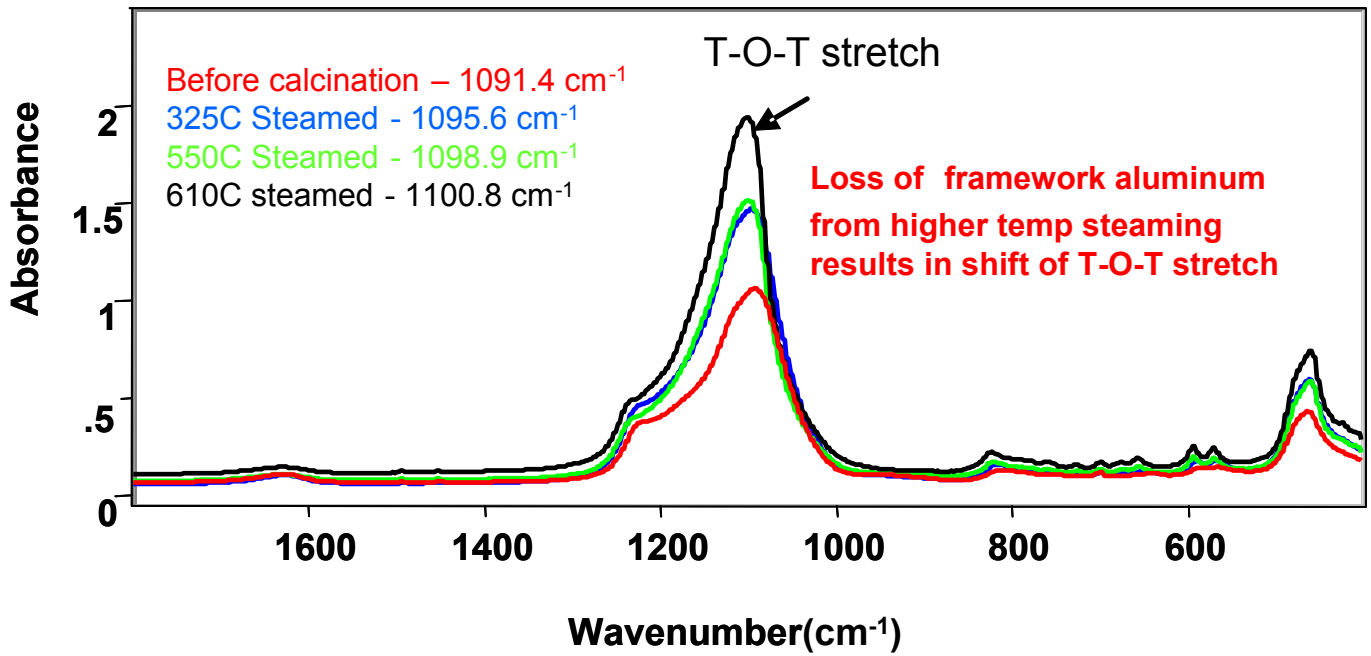
Moderate site: pyridine desorbed between 300ºC and 450ºC

Strong site: pyridine remaining after 450 ºC desorption



Framework FTIR

- **Framework region (1400 - 400 cm^{-1}) contains information on T-O-T modes, ring modes of zeolites**
- **T-O-$T_{(asym)}$ frequency shifts with Si/Al_2 ratio.**



Low Temperature CO FTIR

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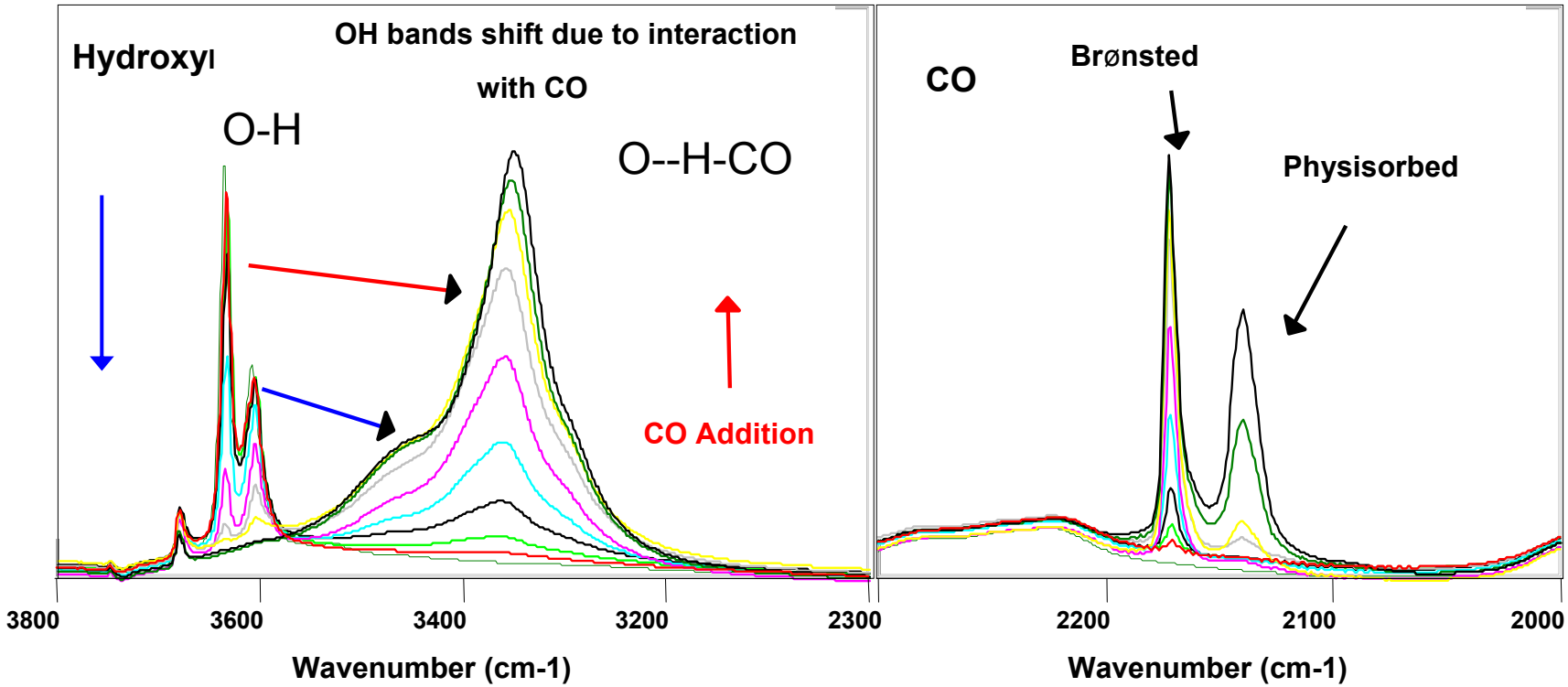
- CO is a small, very weak, soft base
  - Accessible to small pores
- Reversible adsorption at <150K
- Number/strength distributions without high temperature desorption
- Can detect very low levels of Brønsted acidity
- Complimentary, more detailed information
  - ν(CO) 2160-2190 cm^{-1}(B)
  - ν(CO) 2160-2240 cm^{-1}(L)
  - $\Delta\nu$(OH) 0-350 cm^{-1}(B)
- Shift in OH band gives measure of acid site strength

Low Temperature CO Adsorption



- All acid sites accessible to CO
- Interaction of CO with acid hydroxyl results in frequency shift → strength of sites
- Integrated CO band area → number of sites
- Difference spectra clarify OH band shifts

Low Temp CO Adsorption on Different Materials

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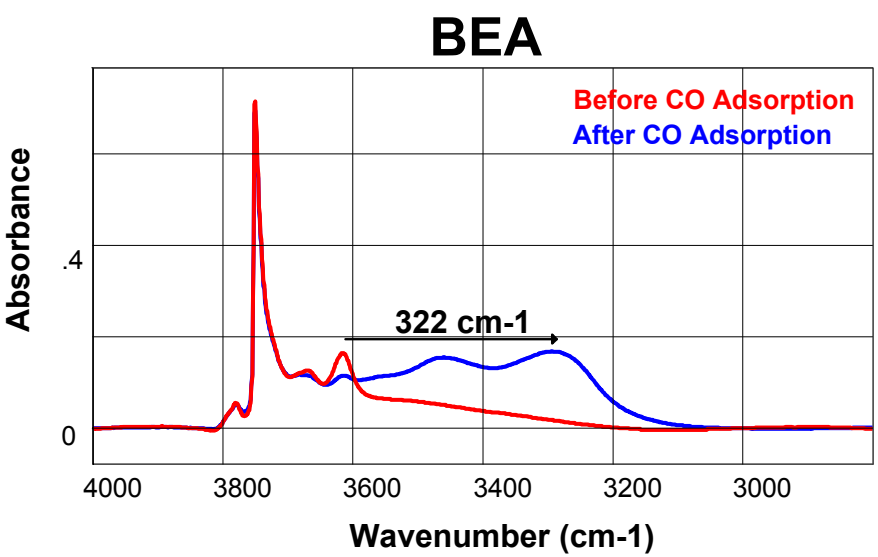
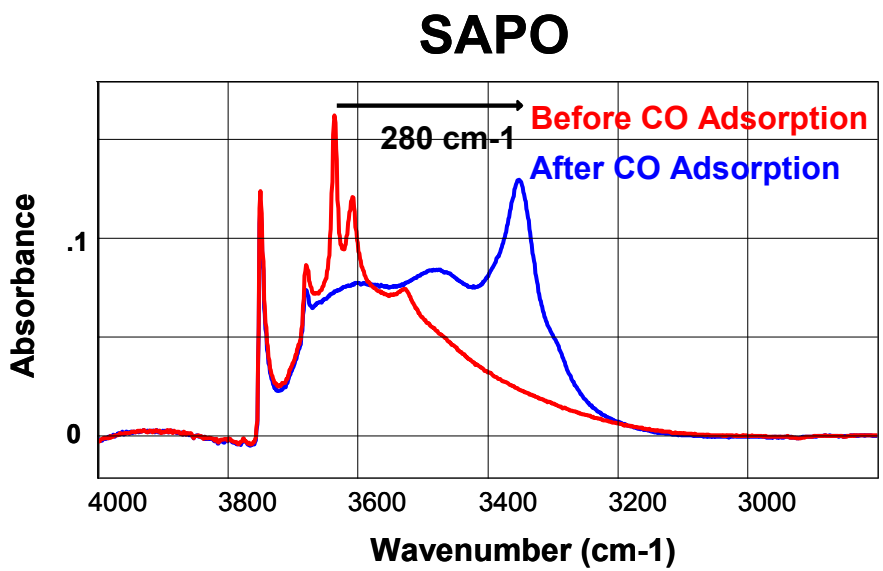
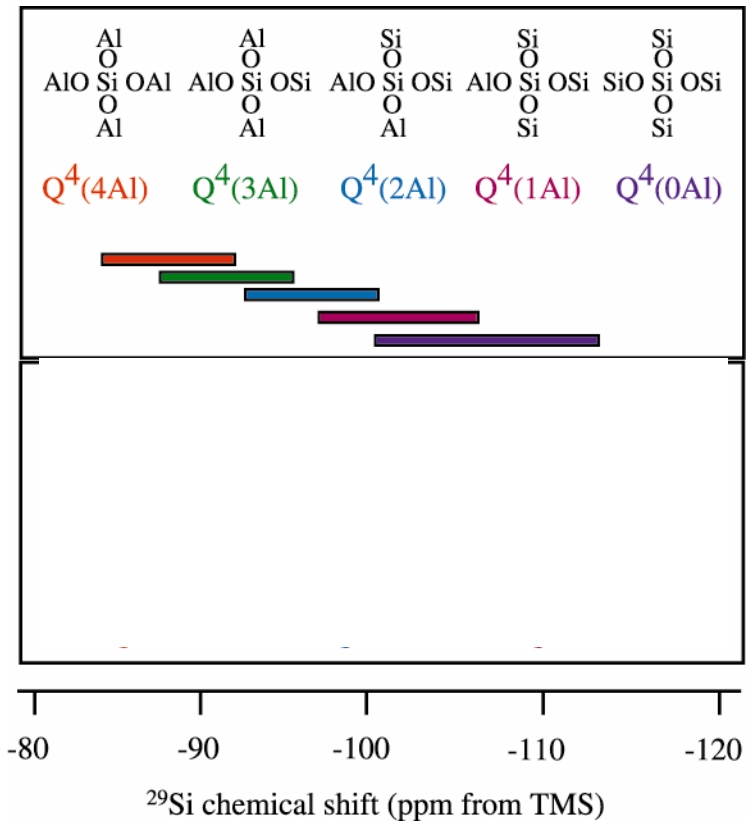
- **Low temp CO adsorption clearly shows strength difference in Brønsted acidity of SAPO and zeolitic materials**

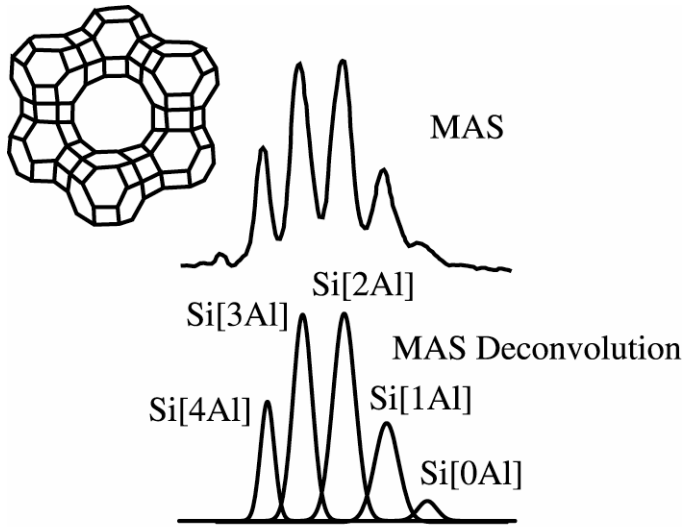




Solid State NMR



Si/Al ratio from ^{29}Si NMR



$$\frac{Si}{Al} = \frac{\sum_{n=0}^{4} I_{Si[nAl]}}{\sum_{n=0}^{4} 0.25\, n\, I_{Si[nAl]}}$$

$$\frac{Si}{Al} = 1.75$$

Engelhardt and Michel (1987); Eckert (1991); Fyfe et al (1991)

^{29}Si NMR of SAPO-34: Effect of Sample Preparation Conditions

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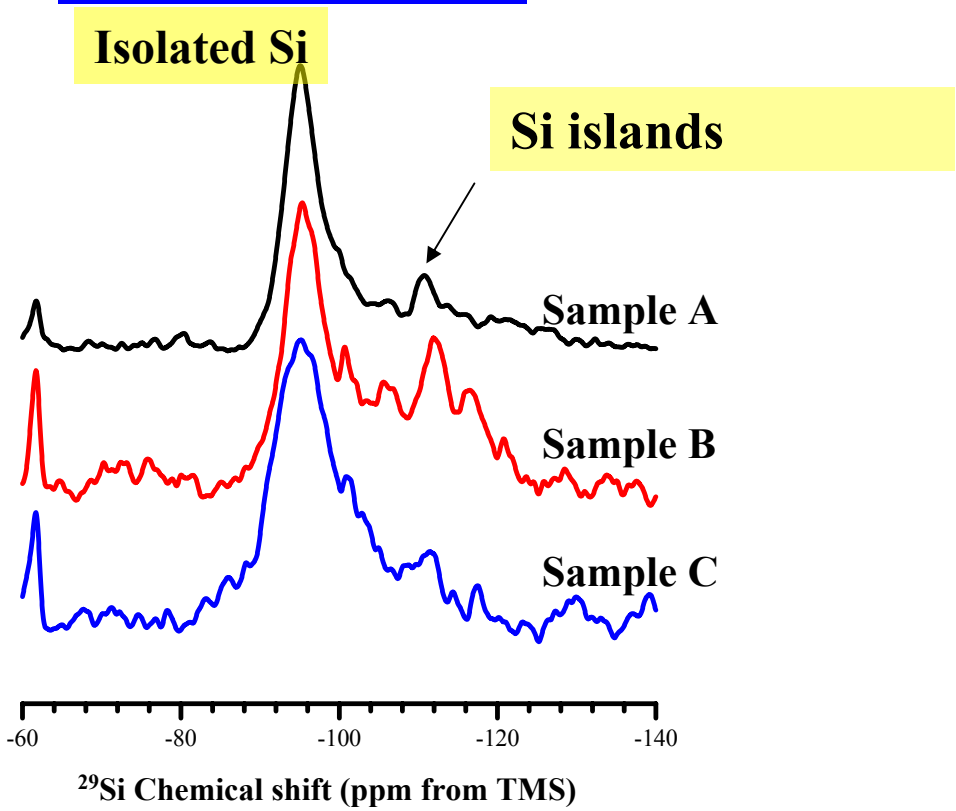
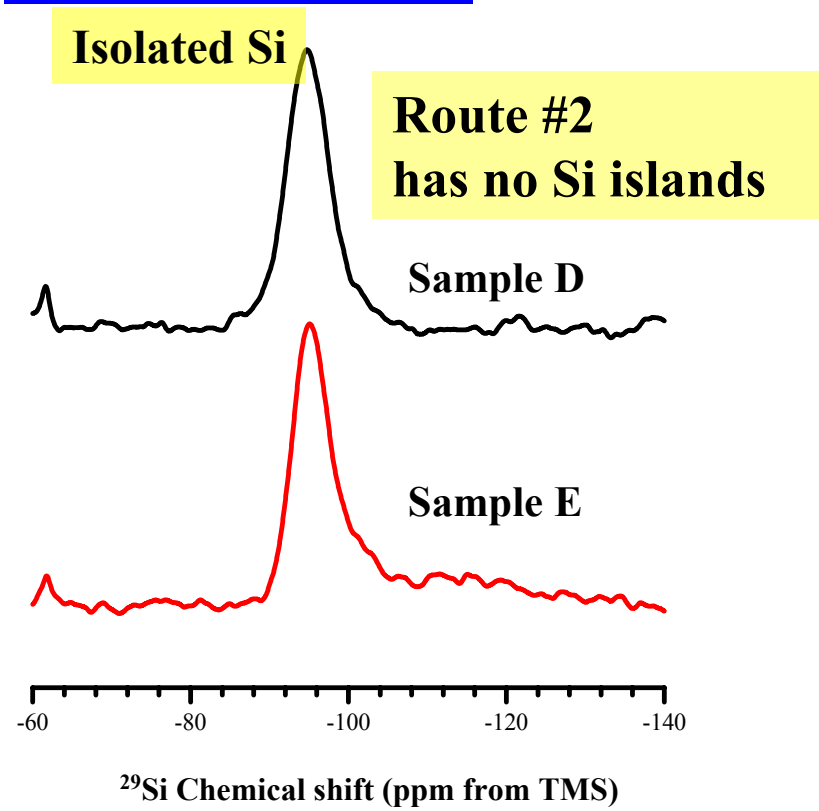
Synthesis Route # 1



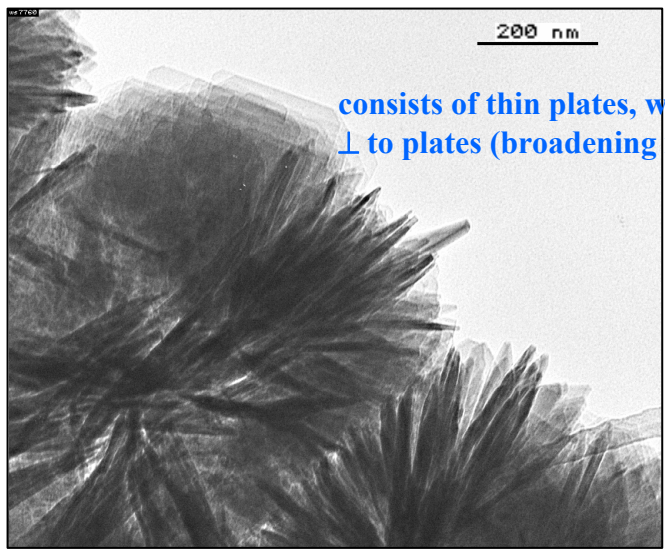
Synthesis Route # 2



- Route #1 produce more silica islands than Route #2
- Silica islands result in lower acidity

High Resolution TEM

- High resolution TEM powerful technique for "visualizing" pore structure and any non-crystalline material in zeolites.
- Can also be used for structure determination using imaging and electron diffraction, e.g. determination of structure of new UOP zeolite UZM-5.
  - UZM-5: Rietveld refinement by XRD was not definitive due to broadening of the peaks due to the morphology of the zeolite (thin plates).

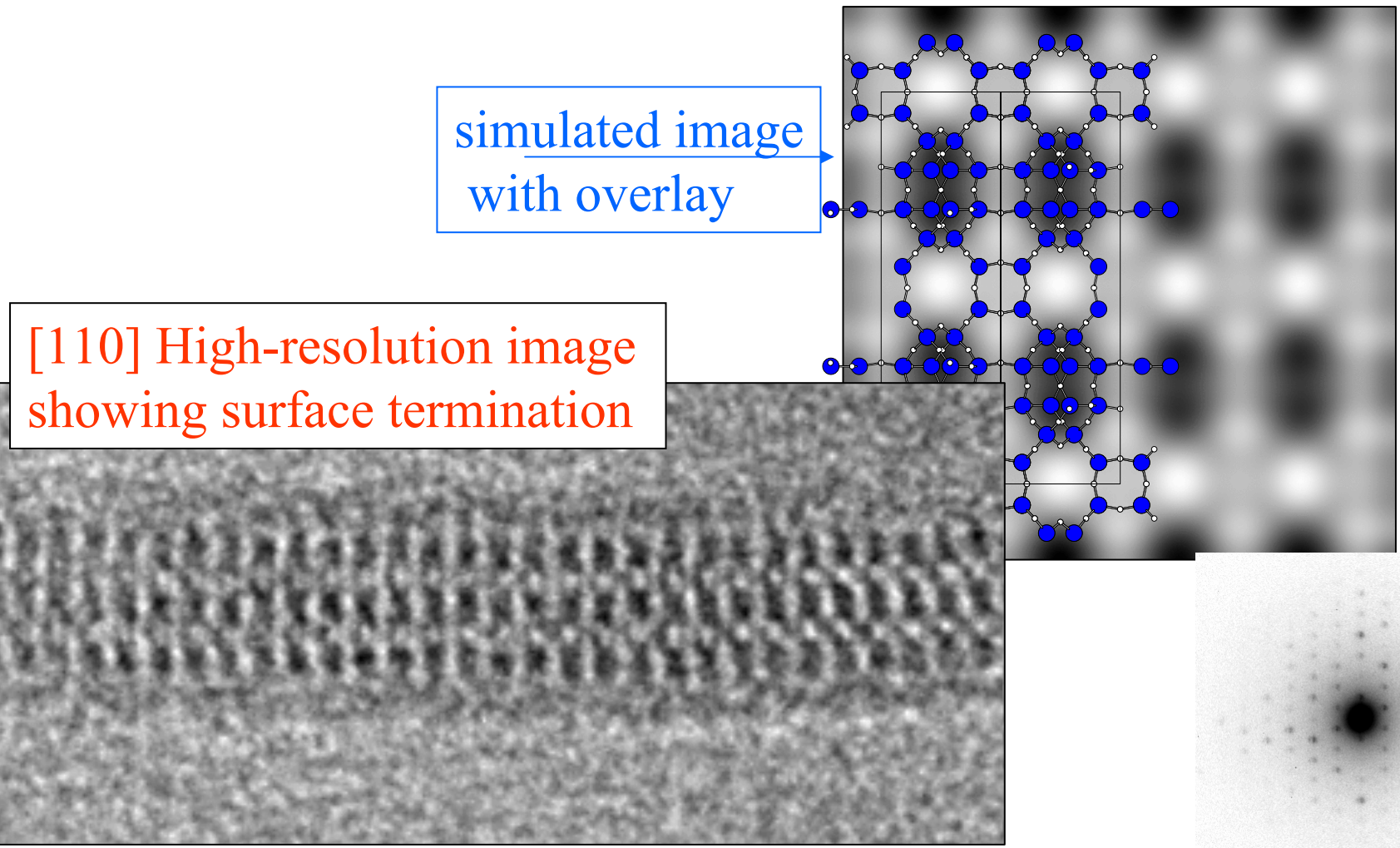


High Resolution TEM

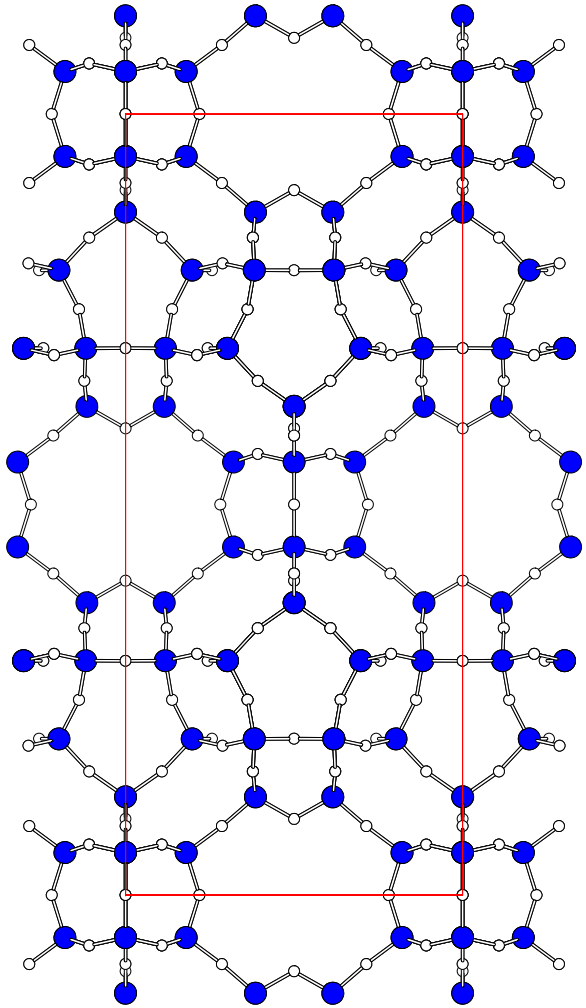
- **Combination of high resolution imaging together with electron diffraction.**

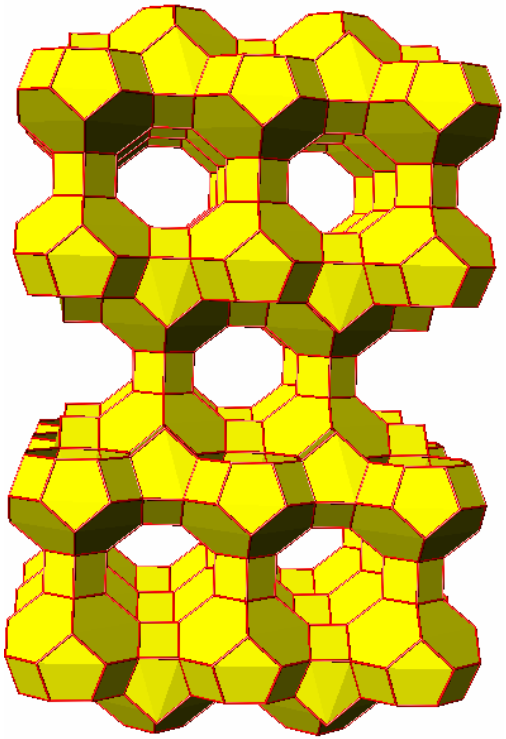
simulated image with overlay

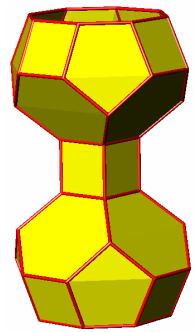
[110] High-resolution image showing surface termination



Structure of UZM-5 (UZF)







"Chalice"

Ang. Chem. Int. Ed. (2003) 42, 1737

Outline

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- Zeolites
- Zeolites as industrial catalysts
- Acid sites in molecular sieves
- Aluminum phosphate ($AlPO_4$) molecular sieves
- Characterization methods for molecular sieves
- **SAPO-34**
- Methanol conversion using zeolites
- Zeolites vs. SAPO's in methanol conversion
- CHA and AEI
- MTO mechanism
- MTO reactor design
- Putting it all together: methanol & natural gas
- Discovery to commercialization

SAPO-34

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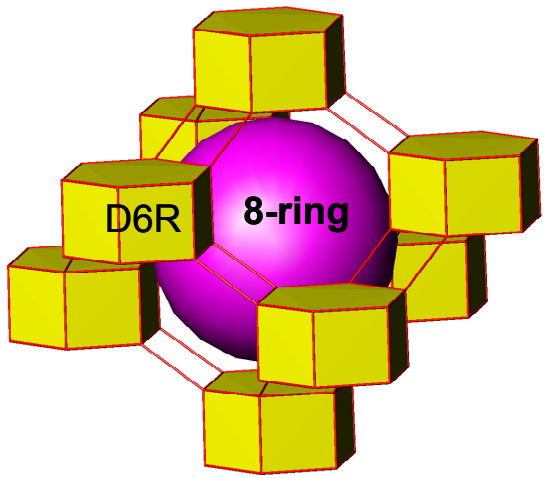
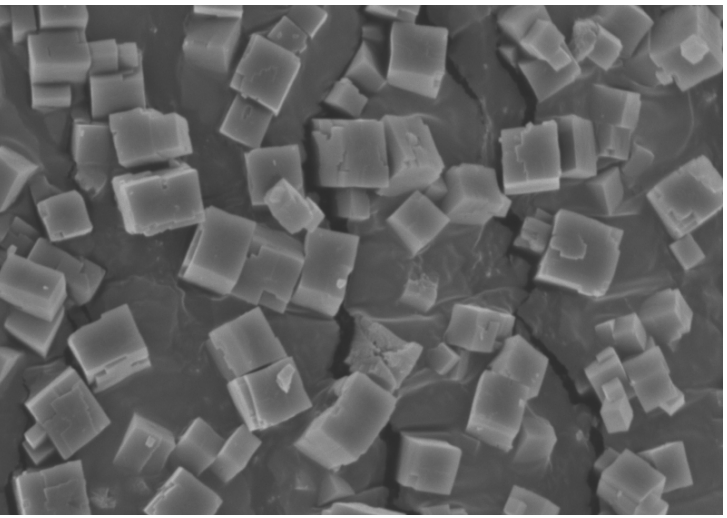
- The particular molecular sieve of interest to the MTO process is SAPO-34.
- This material is structurally analogous to, but compositionally distinct, from the silico-aluminate zeolite mineral chabazite (CHA).
- In chabazite all T sites are occupied by either Si^{4+} or Al^{3+}.
- In SAPO-34 Al and P atoms occupy alternately, and some Si atoms occupy sites normally occupied by P.

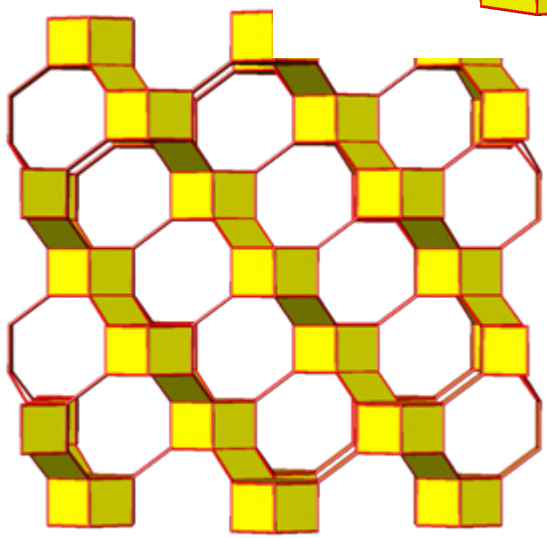
SAPO-34 (CHA) Structure

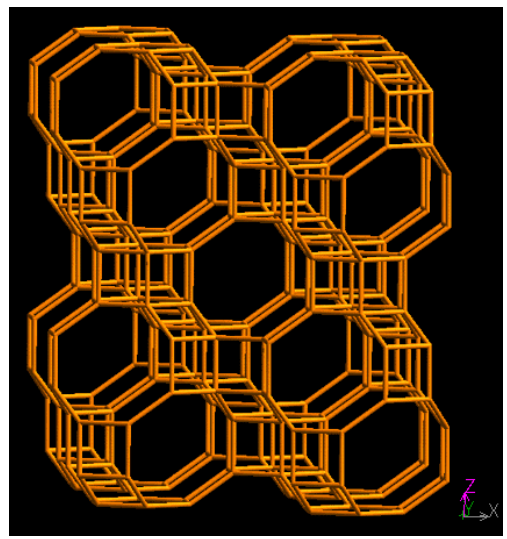
- Three-dimensional pore system consisting of large cavities (about 9.4Å in diameter) separated by small windows (3.8 x 3.8Å)
- Periodic building unit is the double 6-ring layer – connected through 4-rings.





SEM of SAPO-34 crystals
~1 µm





Structural Characteristics of CHA Framework

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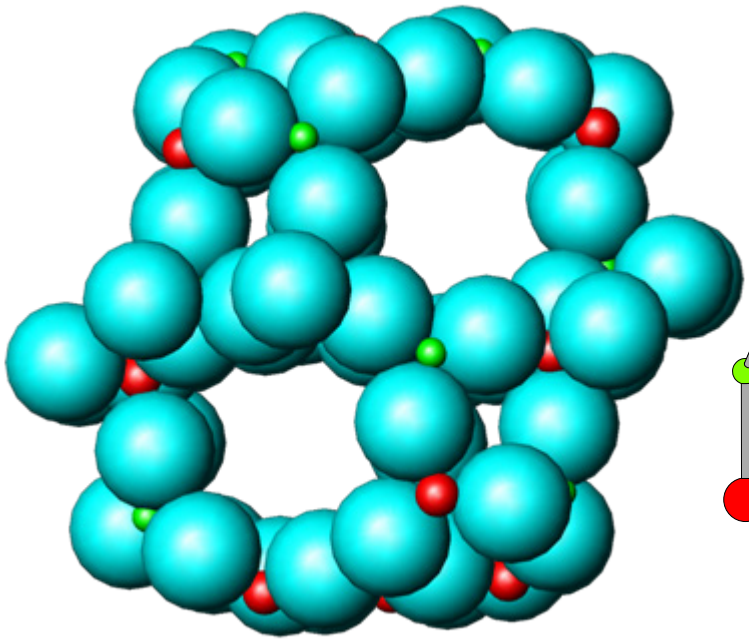
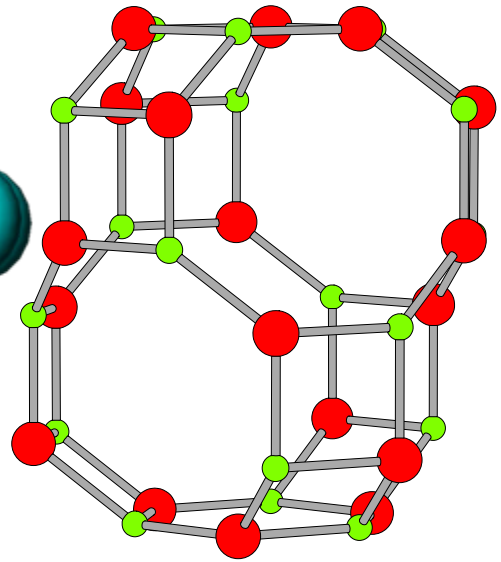
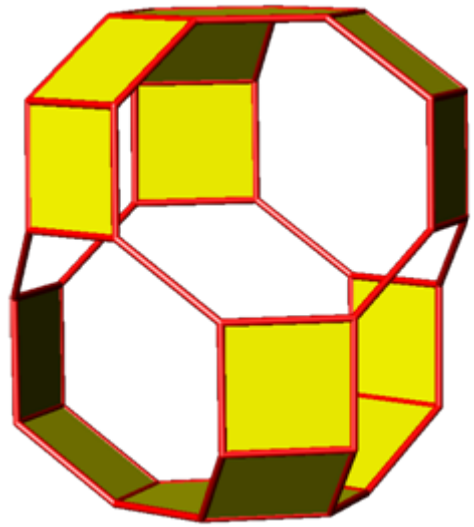
- **The CHA cage.**





4-rings inaccessible to most molecules (door closed)



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

SAPO vs. Zeolite Synthesis

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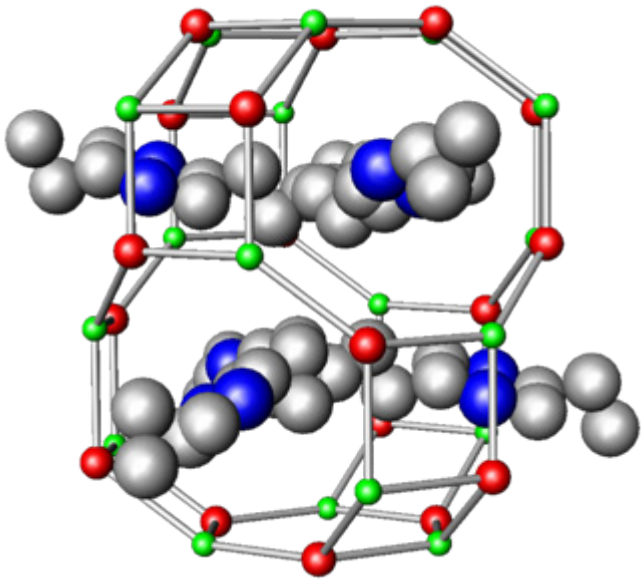
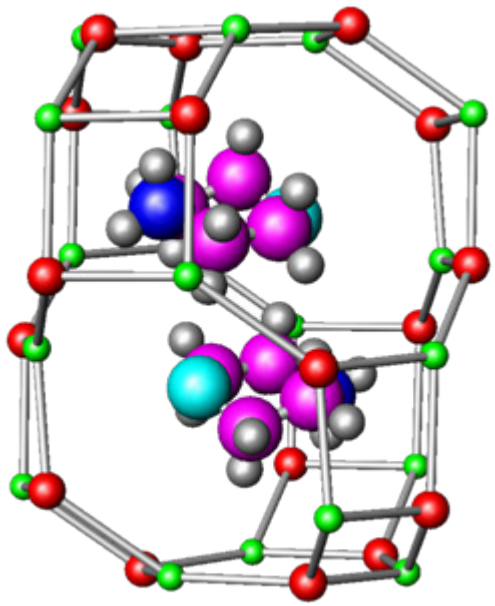
	Zeolite	SAPO
Oxide Reactants	Alumina Silica	Alumina Silica H_3PO_4
Alkali hydroxide	Common	Almost never
Organic structure-directing agent	Common	Required
pH	Usually > 11	Usually < 9
Temperature	25 – 200°C	100 – 200°C
Time	Hours – weeks	Usually < 3 days

Template Packing in SAPO-34

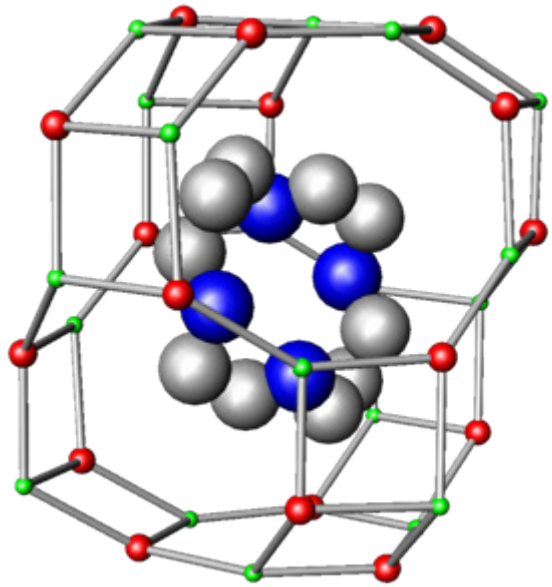
- >30 templates make SAPO CHA framework type.
  - Most not well studied
  - TEAOH is most common



N-Mebutylamine



Morpholine



Cyclam

Calculating Acid Site Density of CHA Framework

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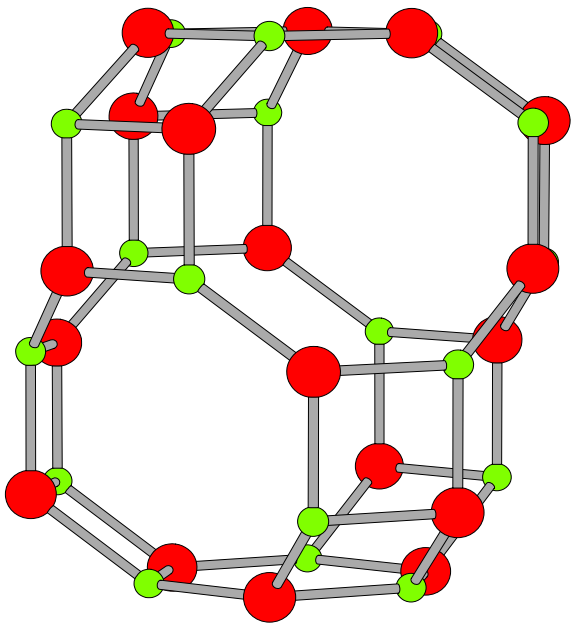
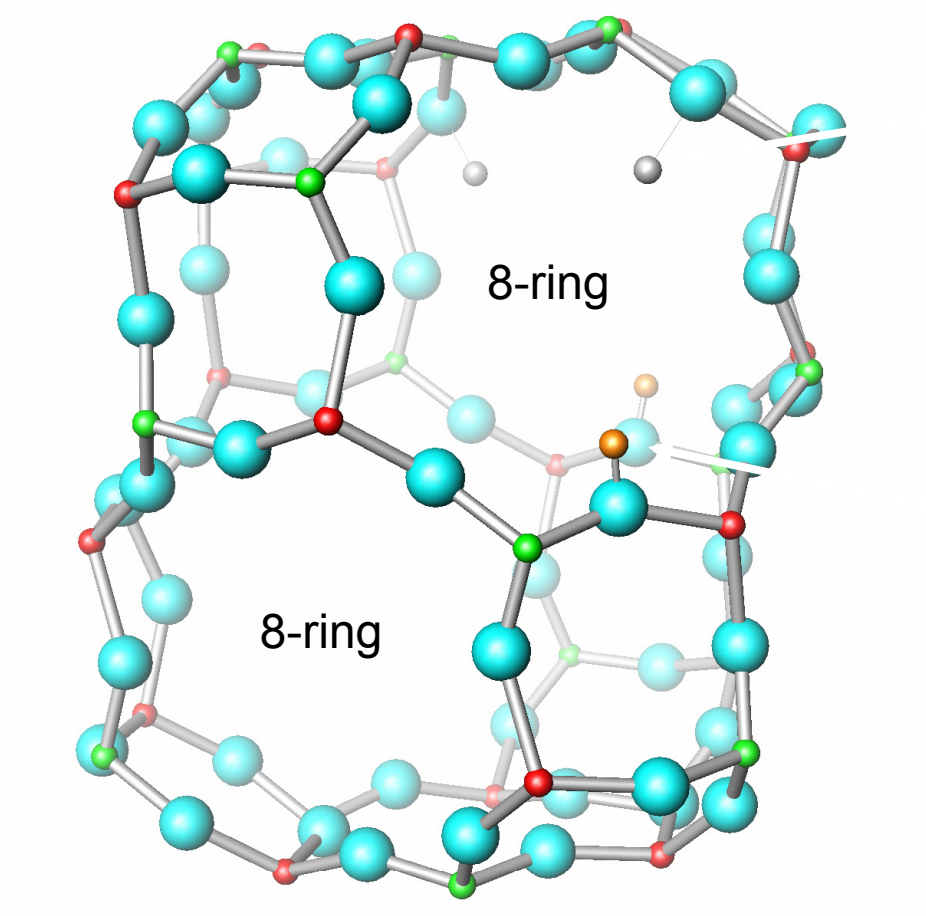
- Elemental analysis of SAPO best expressed as mole fraction:
  - $Si_xAl_yP_zO_2$ where x + y + z = 1.00
- Framework charge = [Al – P] = [Si] if Si is isolated



- Each cage bounded by 36 TO_2
- Each TO_2 is shared by 3 cages
- 1 acid site per cage = 0.03 Si

Acid Site Location: Dehydrated D-SAPO-34

- **Neutron diffraction used to locate the actual position of the acid sites in CHA cage.**



Protons attached to
O4 (4.0% occupancy)
More acidic
3630 cm^{-1}

Protons attached to
O2 (3.4% occupancy)
Less acidic
3601 cm^{-1}

L. Smith et al, Catal. Lett. 1996, 41, 13

Discovery of ALPO and SAPO Materials

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- 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 ……

Discovery of ALPO and SAPO Materials

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- A commitment on part of management to support long-range innovative discovery with no guarantee for commercial success.
- Willingness to take that risk and to assign significant resources to back up that commitment.
- Patience to allow major discoveries to find their place in the commercial world.
- Creating an environment and culture that fostered innovation and that attracted the best scientists and challenged them to their limits.
- Allowing them freedom to dream, and trusting that they would succeed.
- Recognizing and rewarding them when they did succeed.

Outline

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- Characterization methods for molecular sieves
- SAPO-34
- **Methanol conversion using zeolites**
- Zeolites vs. SAPO's in methanol conversion
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- MTO mechanism
- MTO reactor design
- Putting it all together: methanol & natural gas
- Discovery to commercialization

Methanol Conversion using Zeolites

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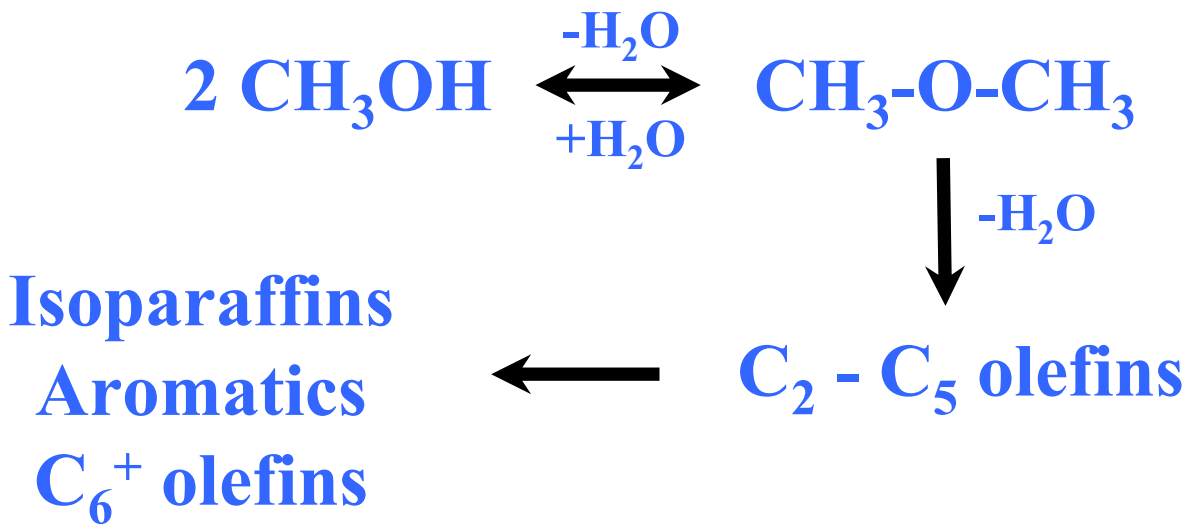
- 1975 – Mobil Oil discloses ZSM-5 catalyst for conversion of methanol to gasoline (MTG)



Chang, Silvestri, and Smith, US 3894103 and 3928483

Methanol Conversion over Zeolites

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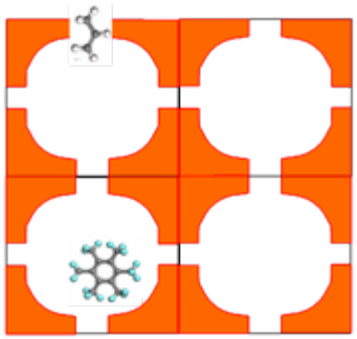
- **Several zeolites with Brønsted acid sites show activity for methanol conversion.**

Pore Size	Examples	Performance (low conversion)	Performance (high conversion)
Small	ERI ERI/OFF KFI	Light olefins	Paraffins
Medium	MFI FER MTT	Olefins	Paraffins Aromatics
Large	MOR FAU		Olefins Aromatics Paraffins

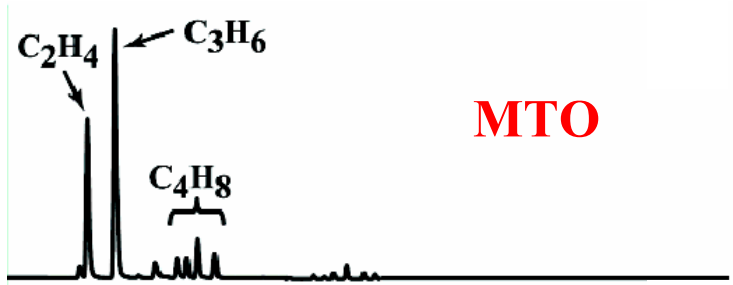
G.F. Froment et al, Catalysis (London), 9, 1 (1992)

Methanol to Hydrocarbons

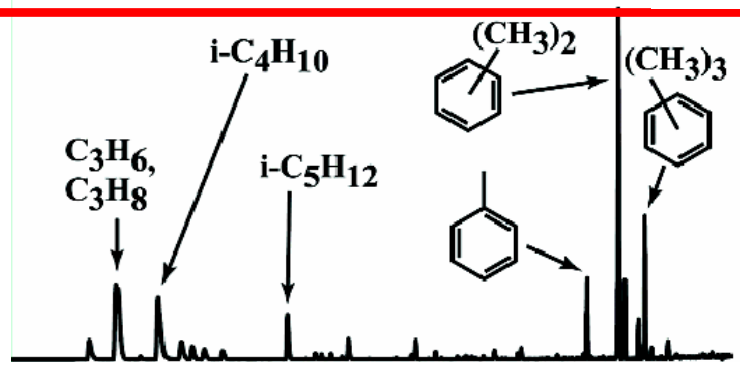
CHA, SAPO-34



8-ring window, only linear hydrocarbons can enter.



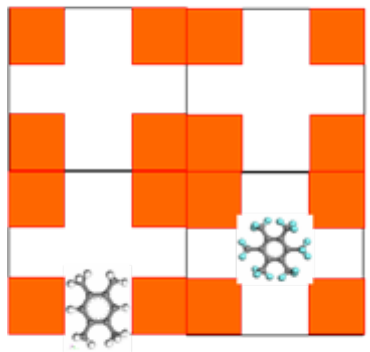
MTO



MTG

ZSM-5, MFI-topology

Cages = Windows



10-ring window, aromatic hydrocarbons can enter.

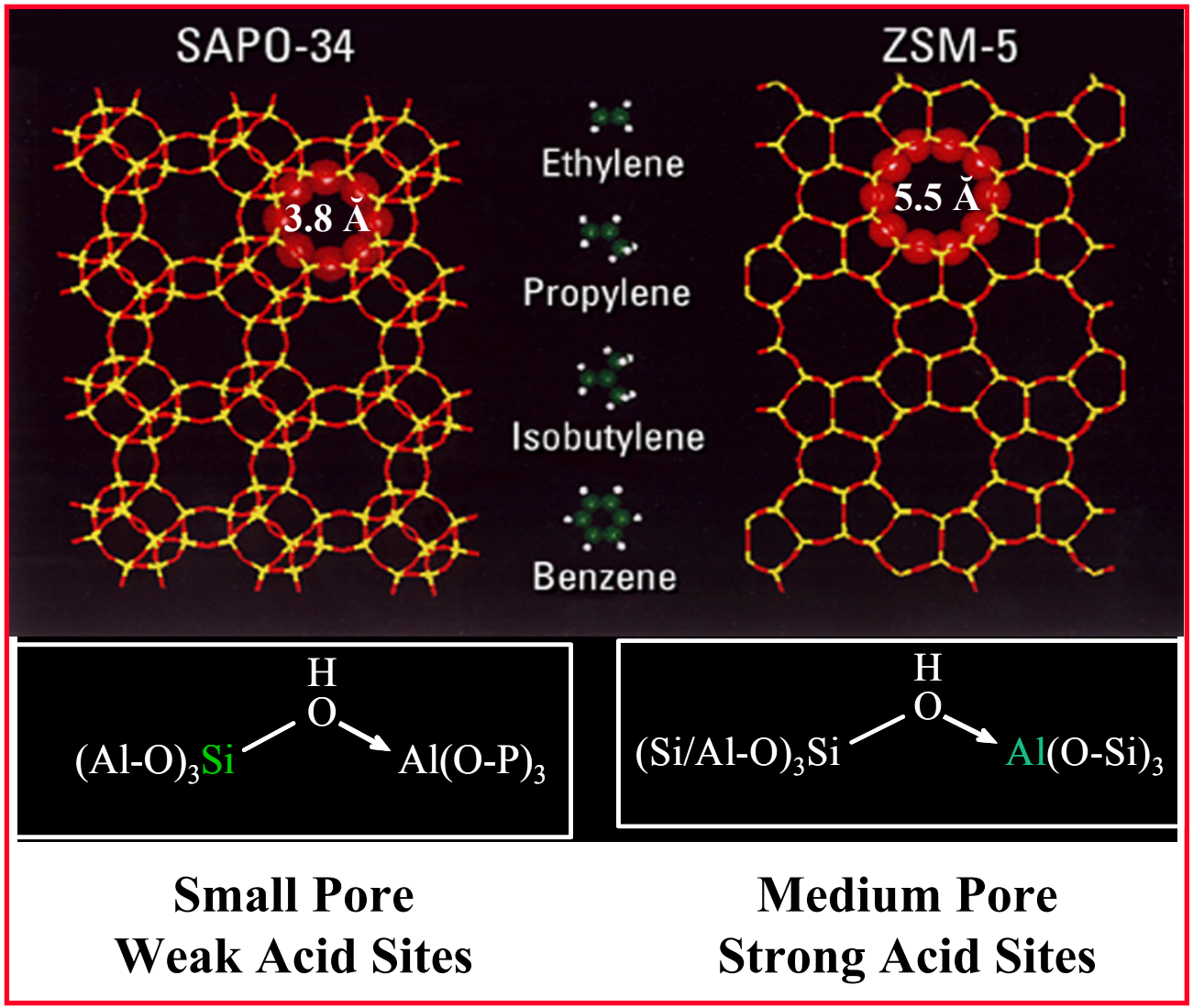
Methanol to Hydrocarbon Catalysis, J. F.Haw, et al., Acc. Chem. Res. 2003, 36, 317

MTO Catalysts

- **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

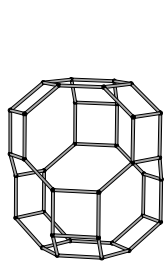
Shape Selectivity

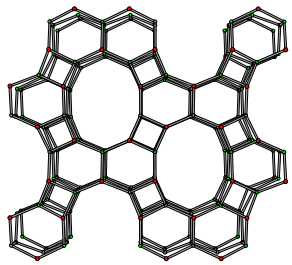
Structural Comparison

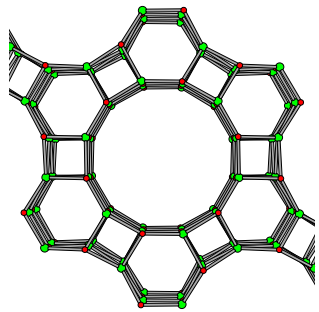


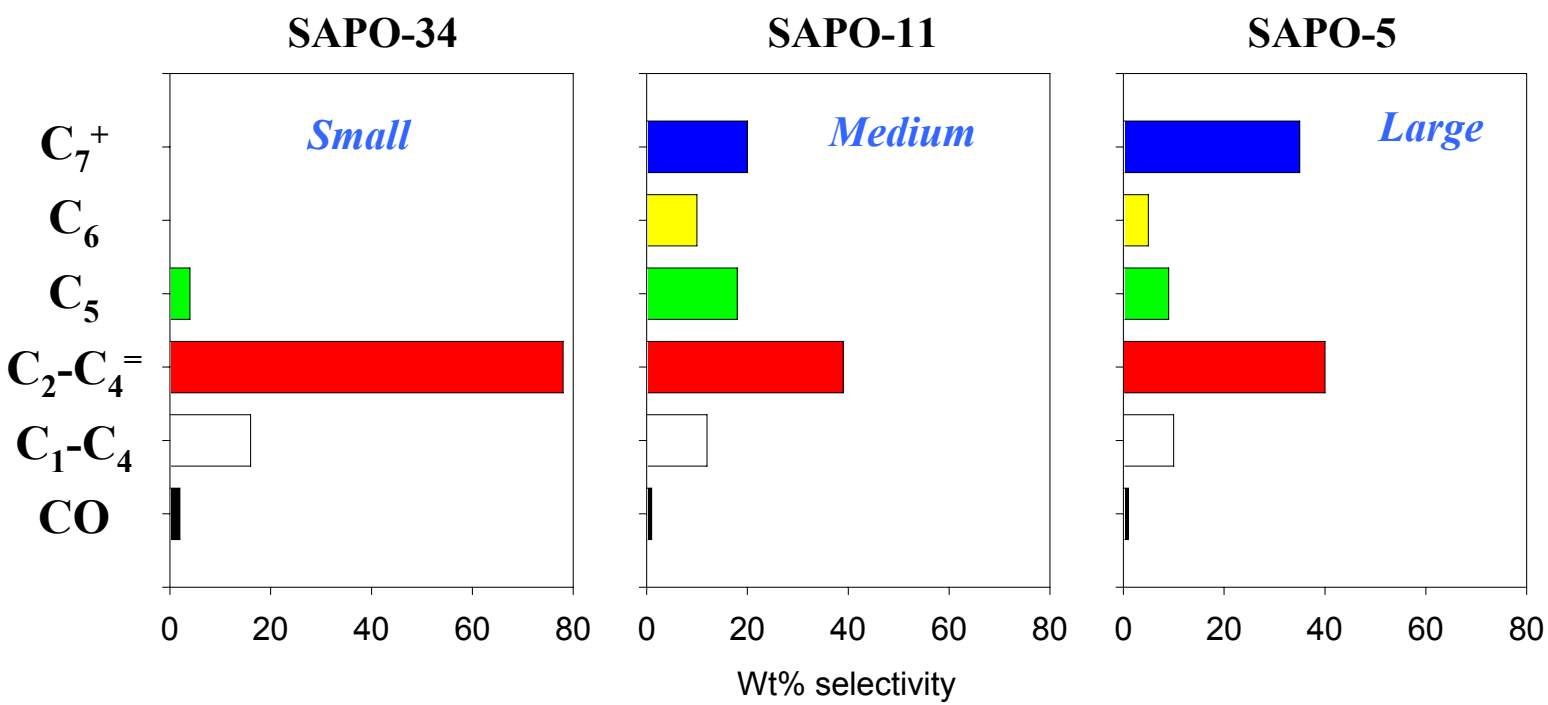
Small, Medium & Large Pore

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









350C, WHSV = 0.3 h^{-1},
MeOH = 0.02 bar, N_2 = 0.98 bar

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

SAPO-34 vs. SSZ-13

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

Material T atom %	SAPO-34 10% Si (gel)	SSZ-13 (Chabazite) 18% Al	SSZ-13 (Chabazite) 10% Al	SSZ-13 (Chabazite) 3.3% Al
Selectivities (2 hr)				
C_2-C_4 olefins	96	69	75	87
CH_4	1.4	3.9		
C_2H_6	0.3	5.4		
C_3H_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

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

Another Twist in the Story…….

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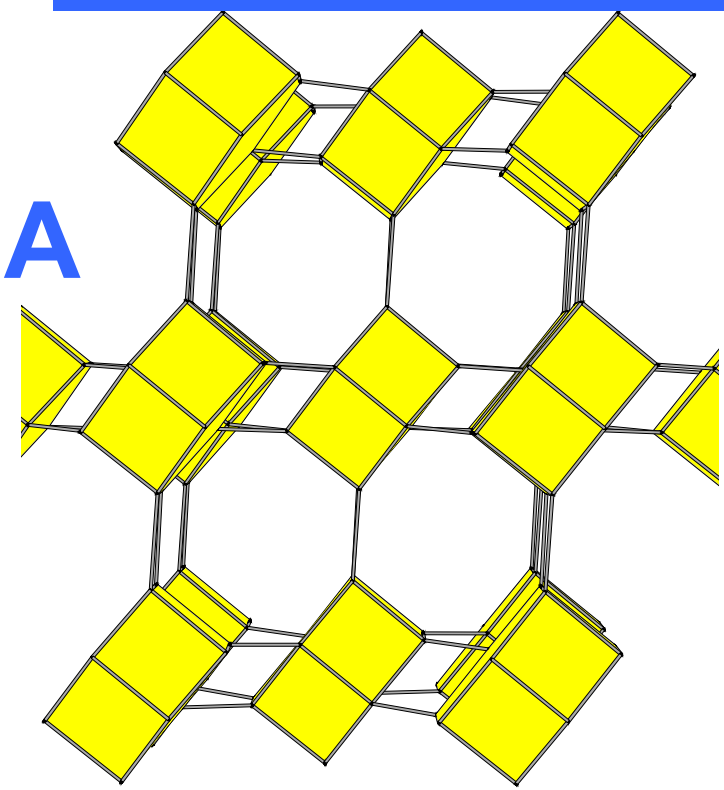
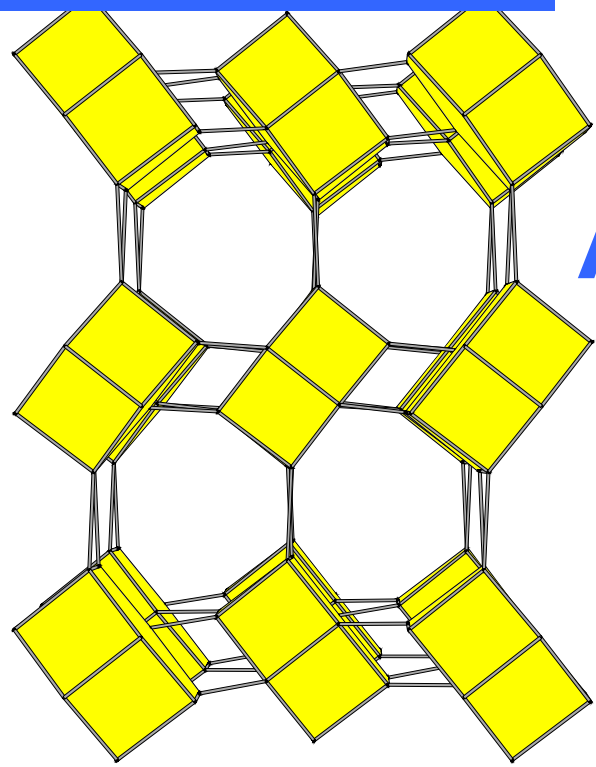
- SAPO-34 has CHA topology. Related framework type is AEI.

Structures depicted as layers of D6R

CHA



Layers of a, a, a

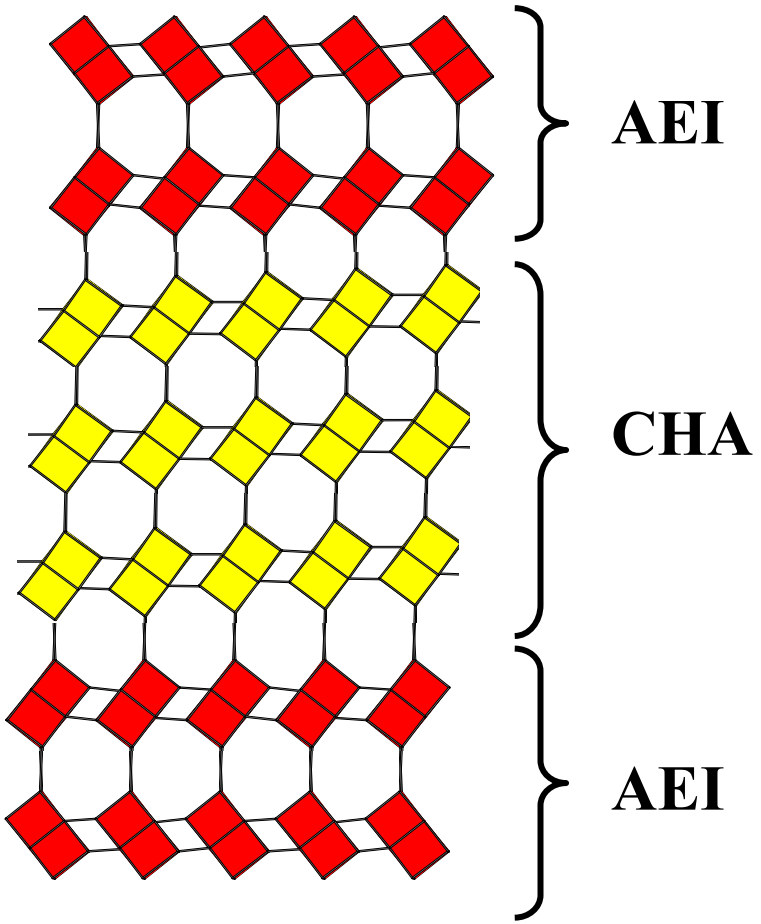


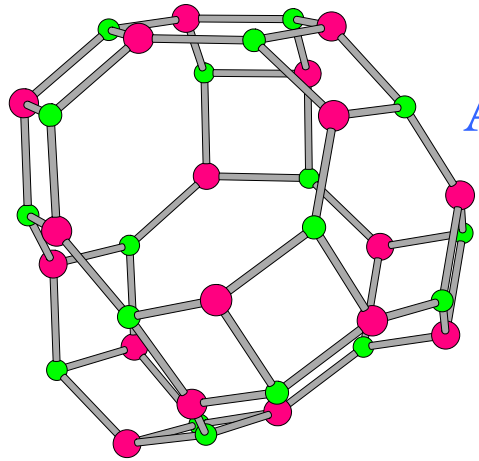
AEI

Alternating layers of b, a, b, a

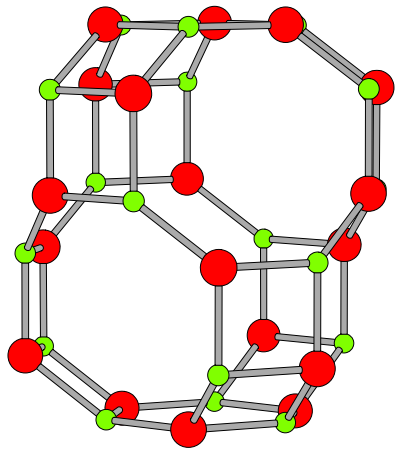
AEI and CHA

- **Exxon and Hydro patents teach that intergrowth of AEI and CHA topology are readily formed and are also active in MTO.**





AEI cage



CHA cage

WO 02 70407 (2002); WO 98/15496 and US 6334994 (2002)

AEI and CHA Intergrowths

A Honeywell Company

Table 3 - Methanol to olefin catalytic performances

Sample	SiO_2/Al_2O_3	AEI/CHA* %CHA	Ethylene selectivity (%)	Propylene selectivity (%)	Ethylene + propylene selectivity (%)	Propane selectivity (%)	C4+ selectivity** (%)	Ethylene to propylene ratio
A (ex. 1)	0.15	0.18 85	34.9	40.8	75.7	1.0	21.4	0.86
B (ex. 2)	0.06	0.33 75	33.6	42.6	76.3	0.4	21.8	0.79
C (ex. 3)	0.09	0.43 70	33.9	42.3	76.2	0.6	21.8	0.80
D (ex. 4)	0.14	0.43 70	34.4	41.1	75.5	0.7	21.9	0.84
E (ex. 5)	0.12	0.43 70	35.1	40.8	75.9	0.9	21.4	0.86
F (ex. 6)	0.16	0.25 80	35.9	40.0	75.9	1.0	21.1	0.90
G (ex. 7)	0.13	0.67 60	34.2	41.4	75.6	0.6	21.1	0.83
Comparative 1 (ex. 2)		9.0 10	29.6	42.5	72.1	0.7	25.0	0.69
Comparative 2 (ex. 8)	0.10	4.0 20	30.0	43.3	73.3	0.9	24.3	0.69

* Determined by DIFFaX

** Selectivity for hydrocarbons having 4 or more carbon atoms

ExxonMobil PCT WO 02/070407

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UOP
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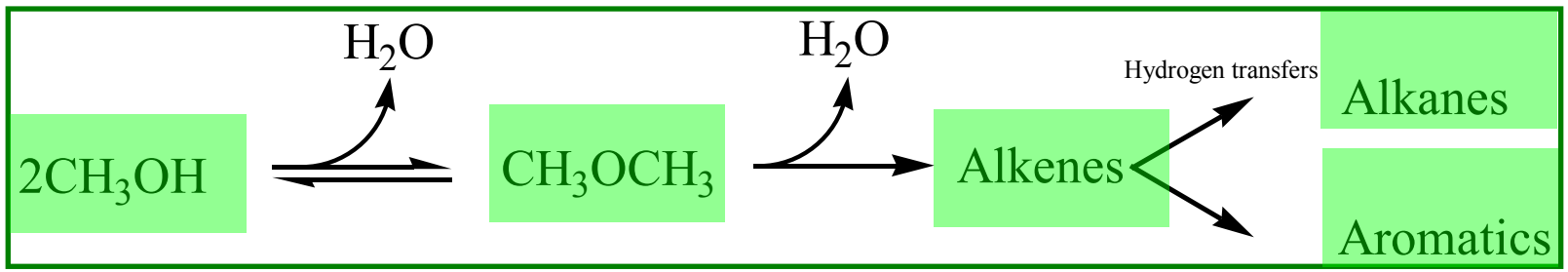
- Characterization methods for molecular sieves
- SAPO-34
- Methanol conversion using zeolites
- Zeolites vs. SAPO's in methanol conversion
- CHA and AEI
- **MTO mechanism**
- MTO reactor design
- Putting it all together: methanol & natural gas
- Discovery to commercialization

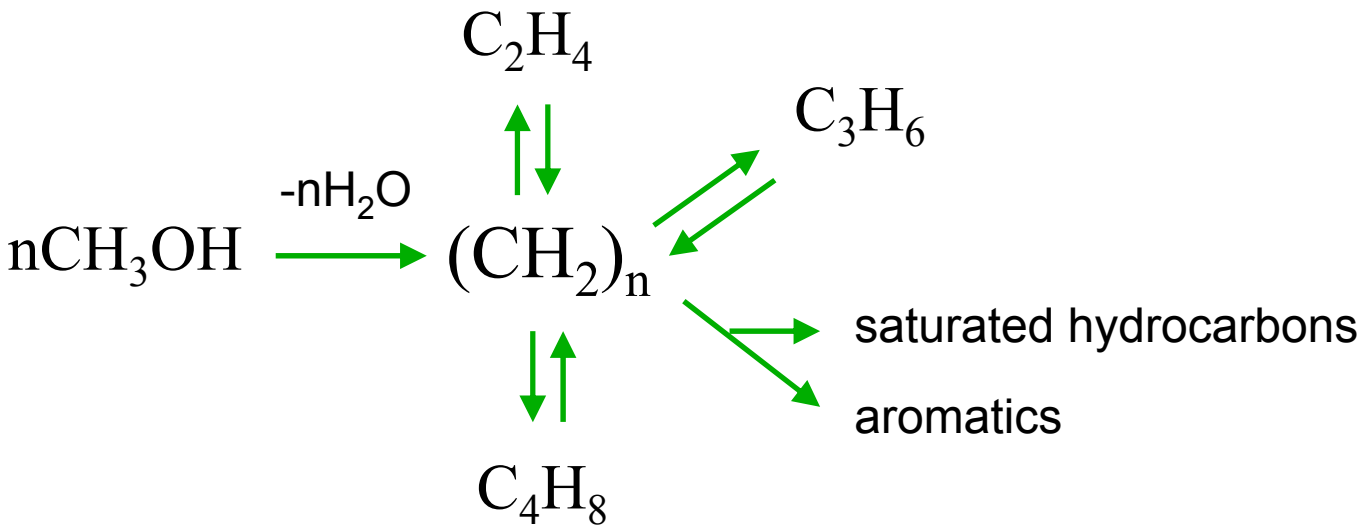
MTO Mechanism

- 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.

Hydrocarbon Pool 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.

Zeolite Beta as a Model System

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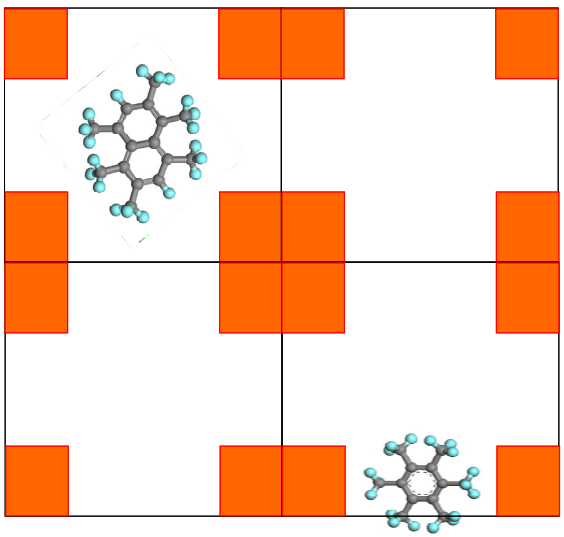
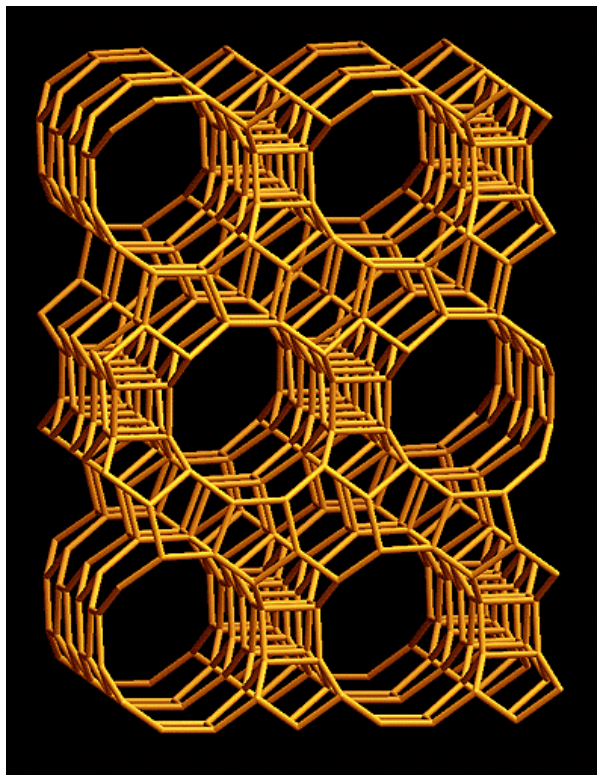
- The beta zeolite is a wide pore zeolite allowing direct introduction of rather large molecules.
- It is not interesting as a commercial catalyst for MTO/MTH chemistry.

Model: Beta, BEA-topology
Cages = Windows

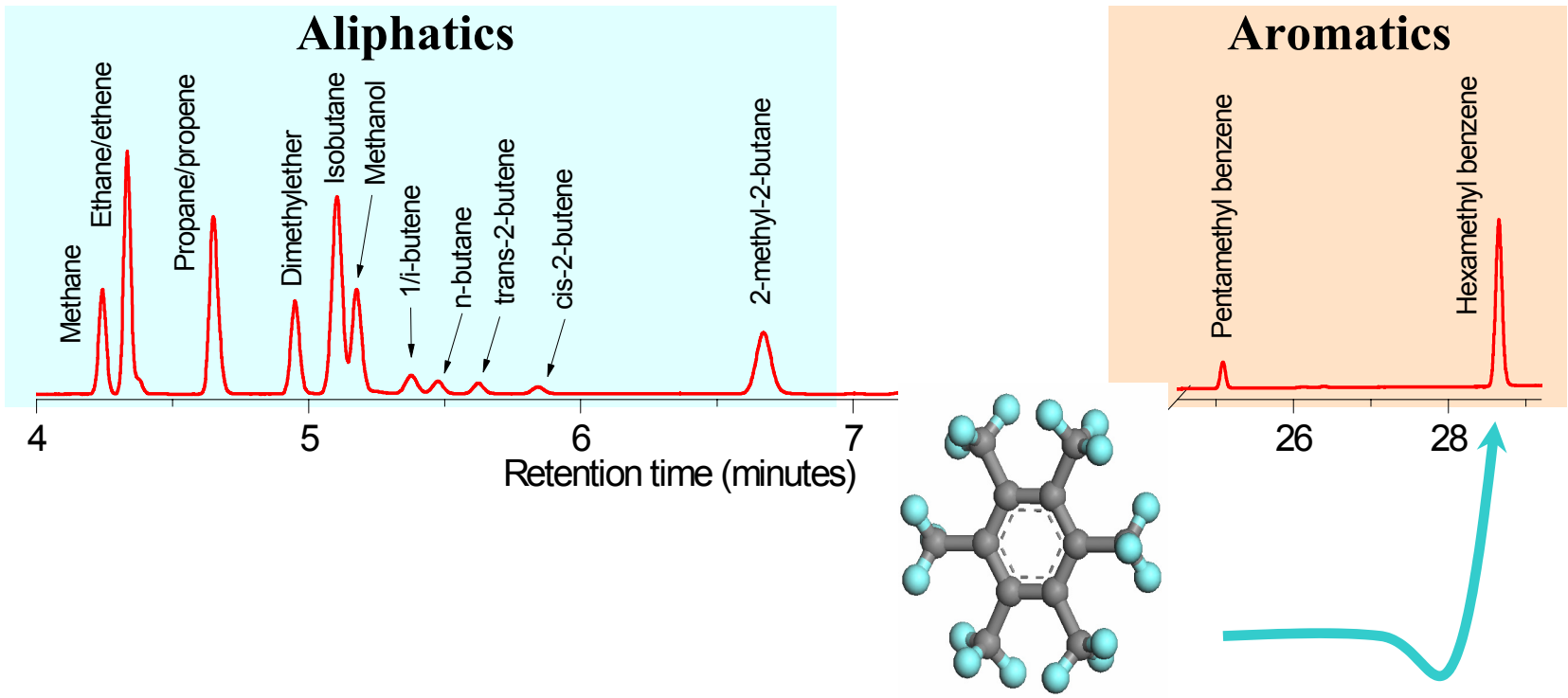


12-ring window, substituted aromatic hydrocarbons can enter.



7.7 x 6.6 Å

Methanol over H-Beta at 400°C

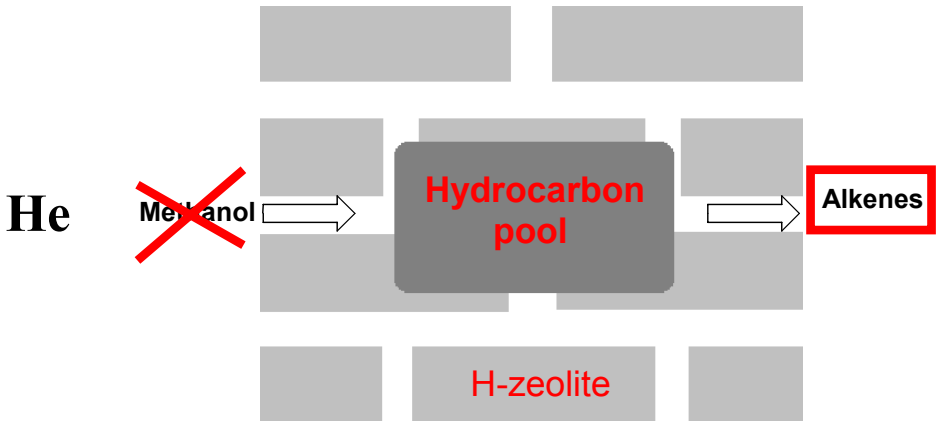


Hexamethylbenzene is a dominant gas phase product

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

Courtesy Unni Olsbye, Univ. Oslo

Hydrocarbon Pool

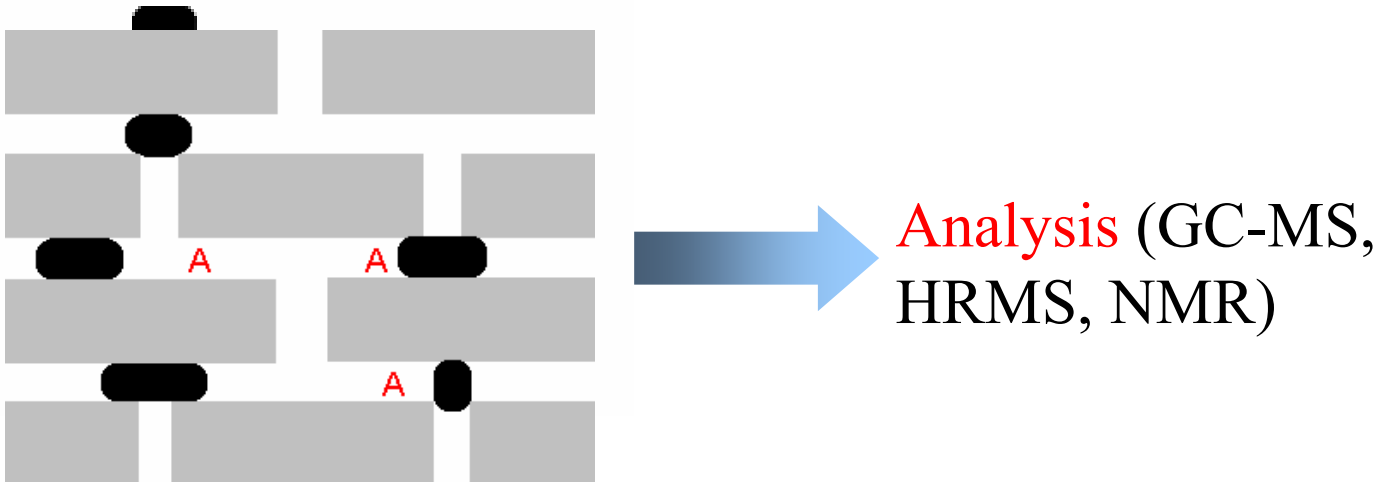


The olefin production goes on for several minutes after the methanol feeding has been terminated

What is the active pool contained inside the zeolite?

Courtesy Unni Olsbye, Univ. Oslo

Hydrocarbons Retained in Zeolite Pores



- ✓ **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, Univ. Oslo

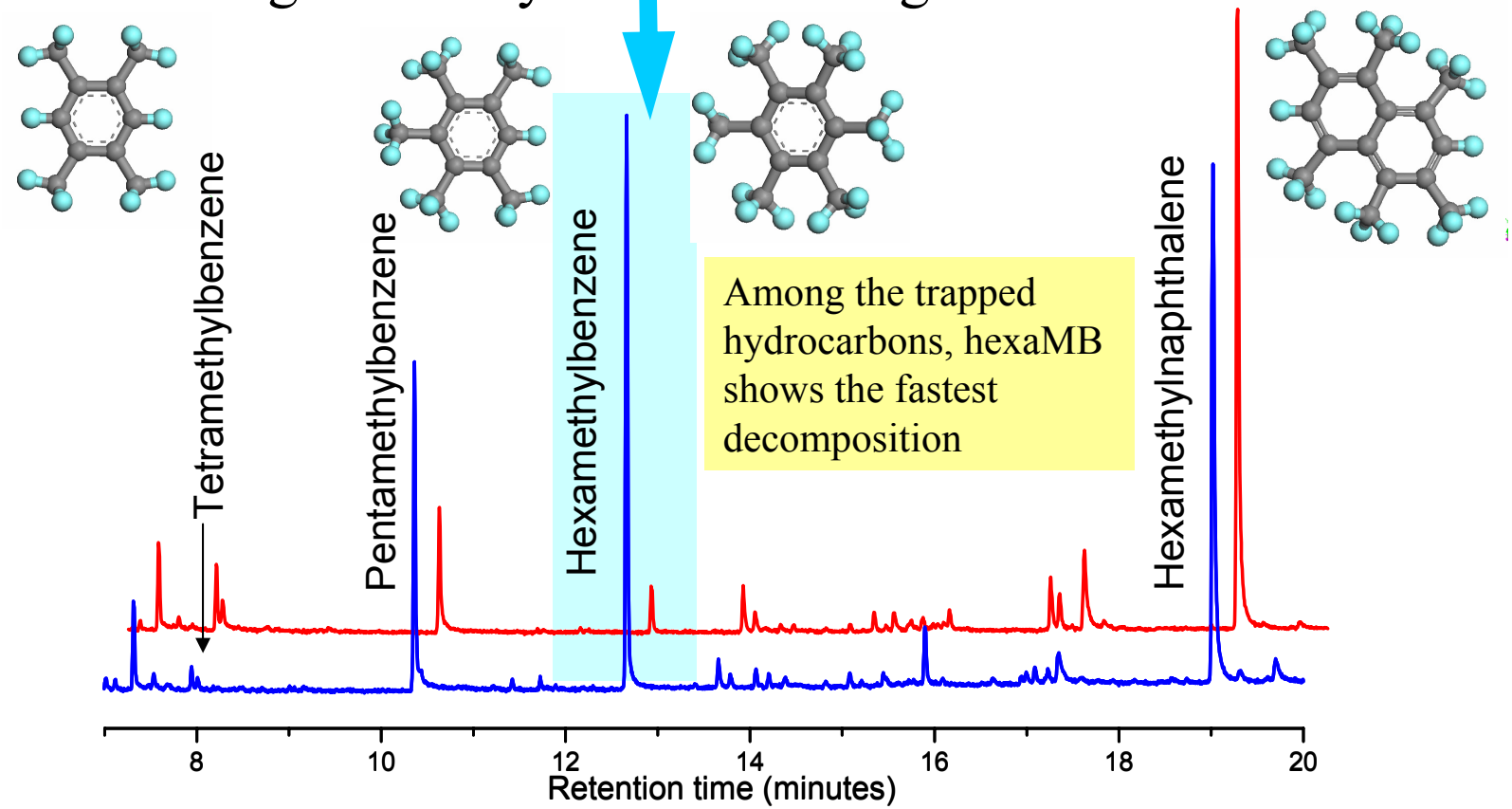
Trapped Hydrocarbons

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

The trapped material is nearly exclusively composed of polymethylated aromatics

Stability of the retained hydrocarbons was probed by stopping the feed and flushing the catalyst with carrier gas for 1 minute

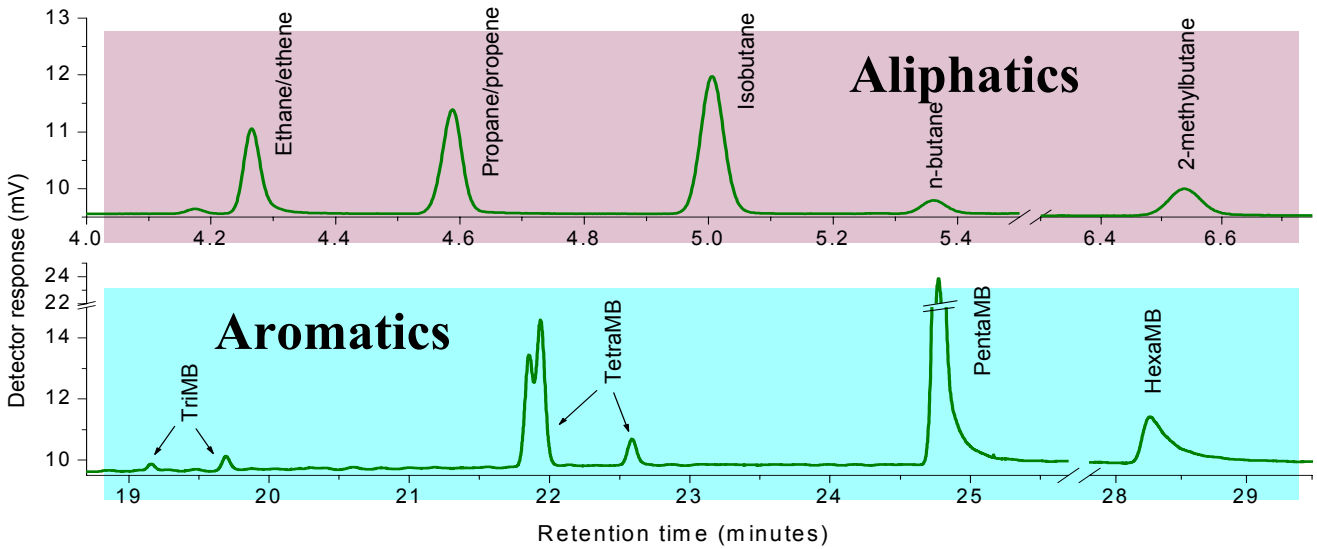
Hexamethylbenzene is a dominant retained species



Courtesy Unni Olsbye, Univ. Oslo

Hexamethylbenzene over H-Beta

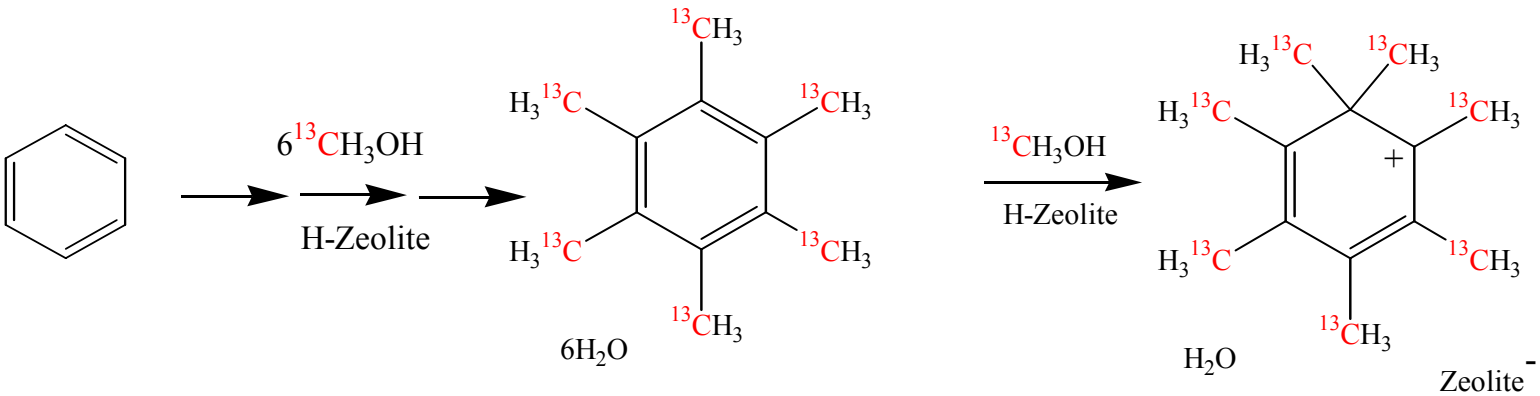
- **The same gas phase products as observed when methanol was reacted**
- **The retained compounds were the same as those obtained from methanol**



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

Courtesy Unni Olsbye, Univ. Oslo

Initial formation of HMB and heptaMP+



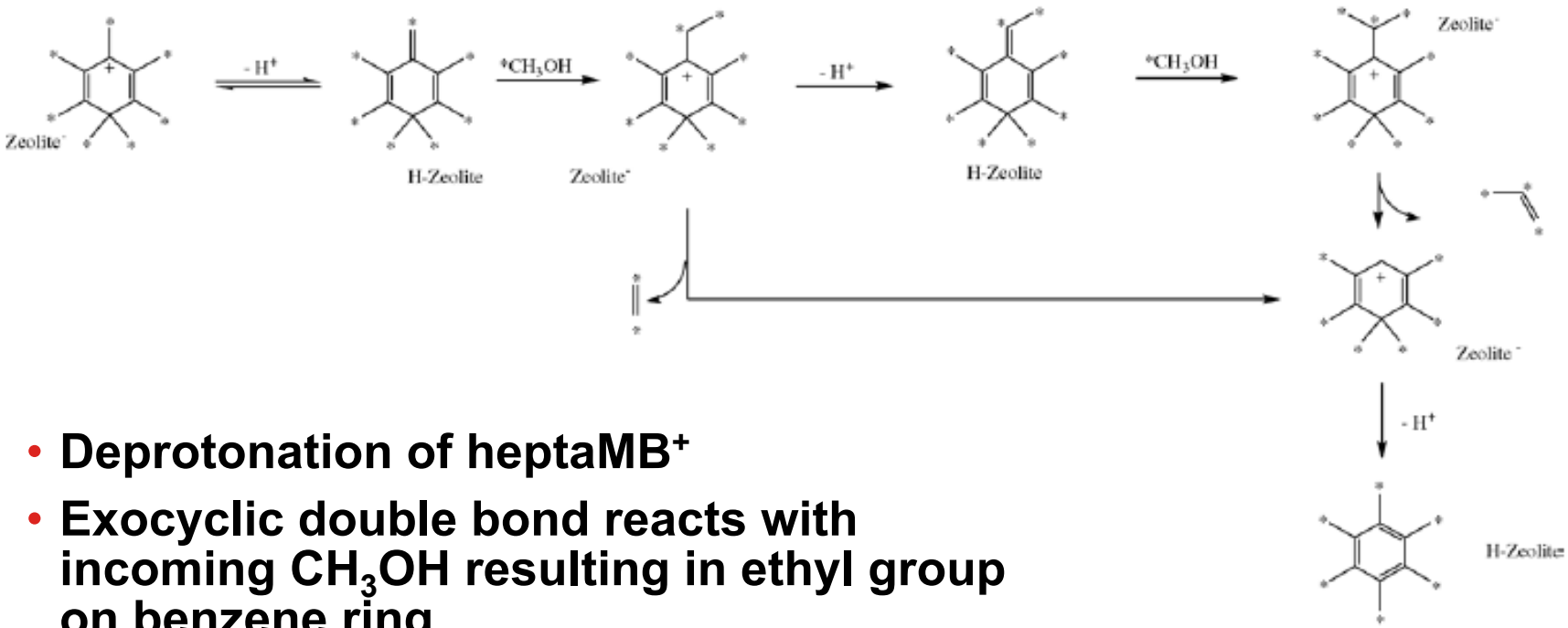
Hexamethylbenzene:
Six labelled atoms

Heptamethylbenzenium:
Seven labelled atoms

Hexamethylbenzene in zeolite pore can take up another CH_3 to form heptamethylbenzenium ion

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

Exocyclic Mechanism



- **Deprotonation of heptaMB⁺**
- **Exocyclic double bond reacts with incoming CH_3OH 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.**

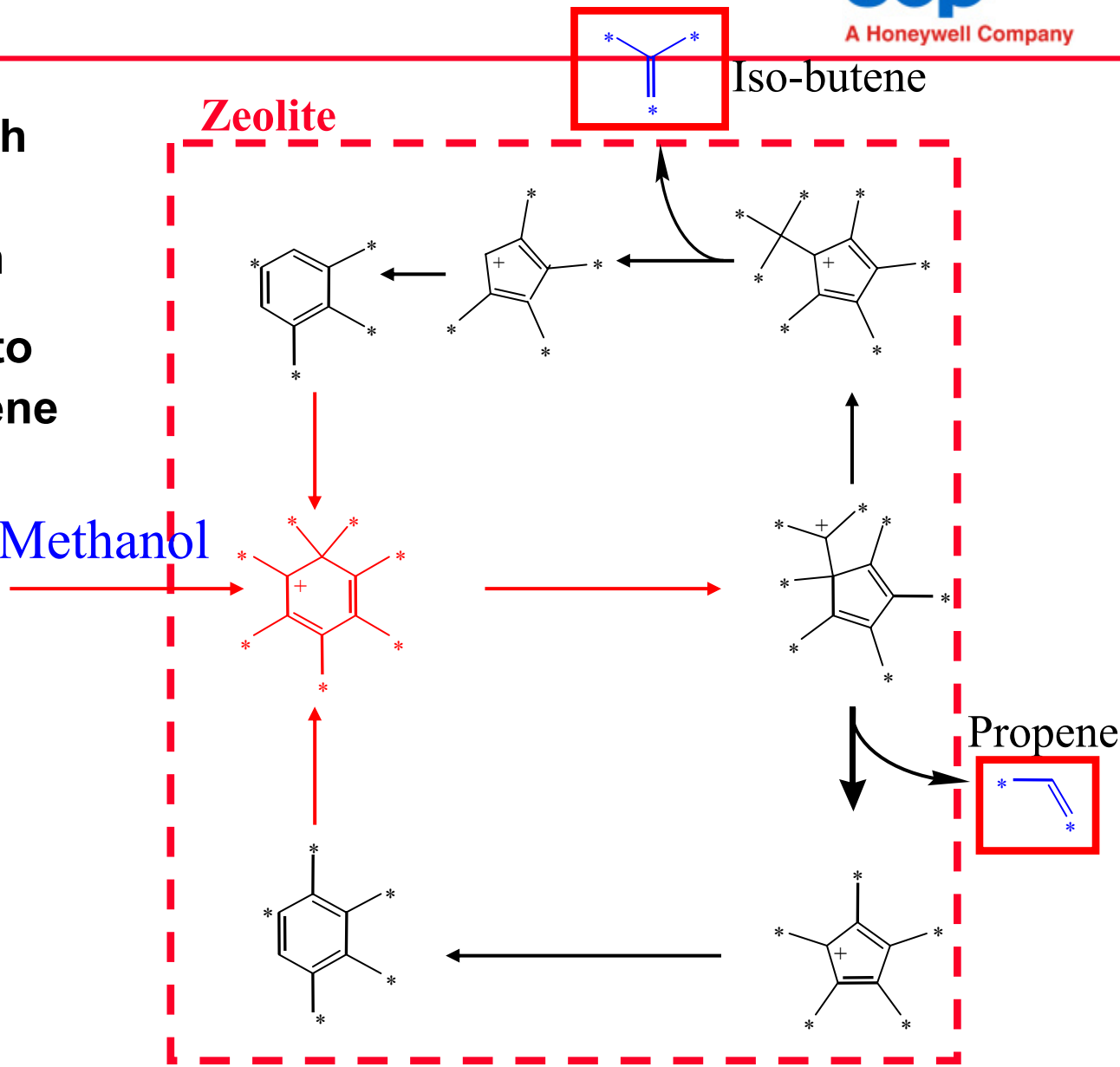
M. Bjørgen, U. Olsbye, D. Petersen and S. Kolboe, ***J. Catal.*** (2004), 221, 1-10.

Paring Mechanism

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.

MTO Site – Organic-Inorganic Hybrid

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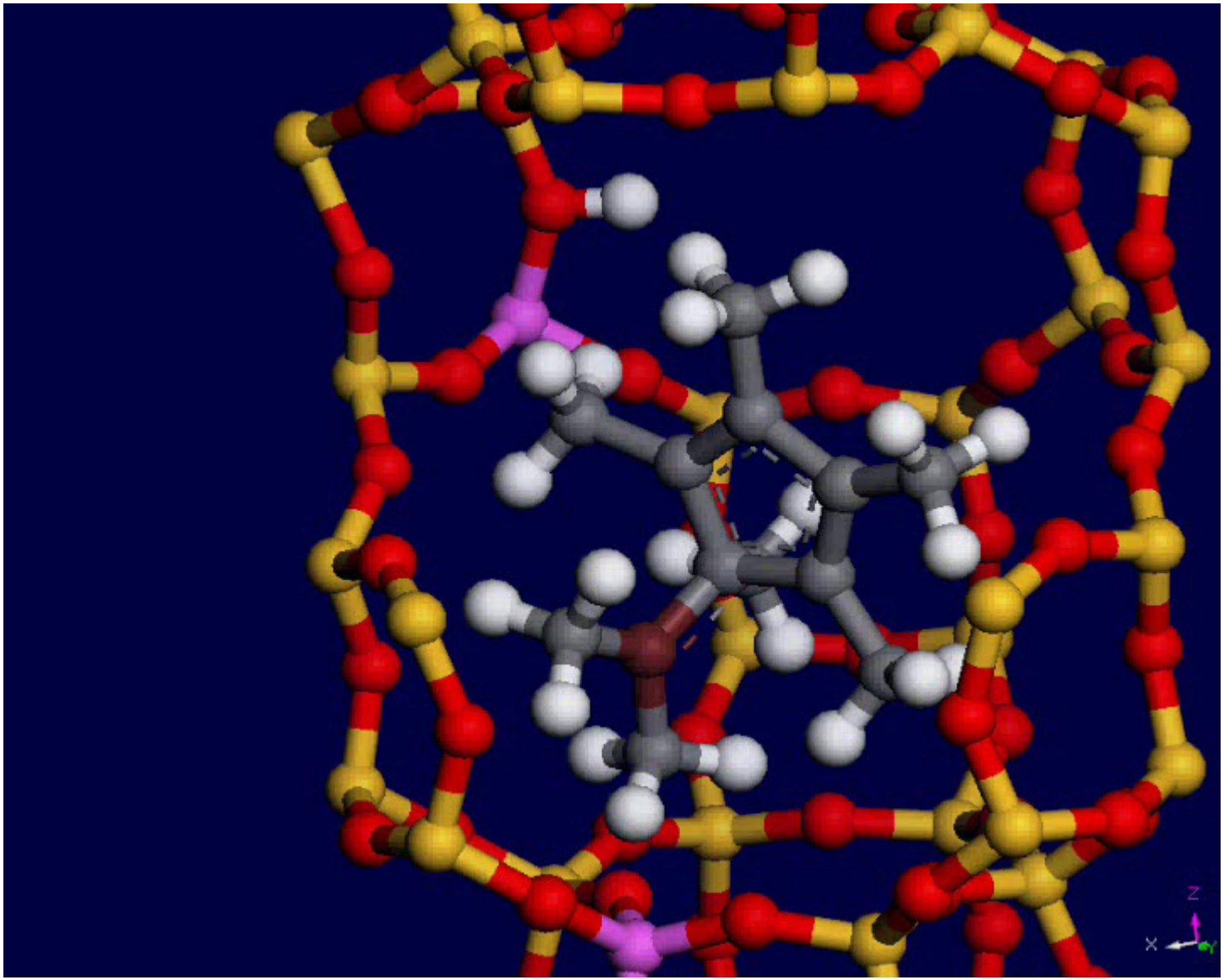
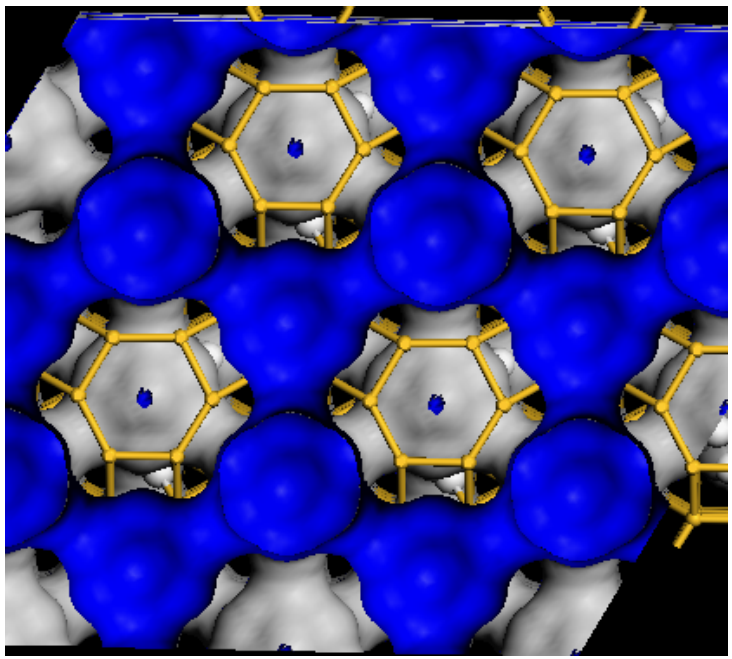
A Honeywell Company



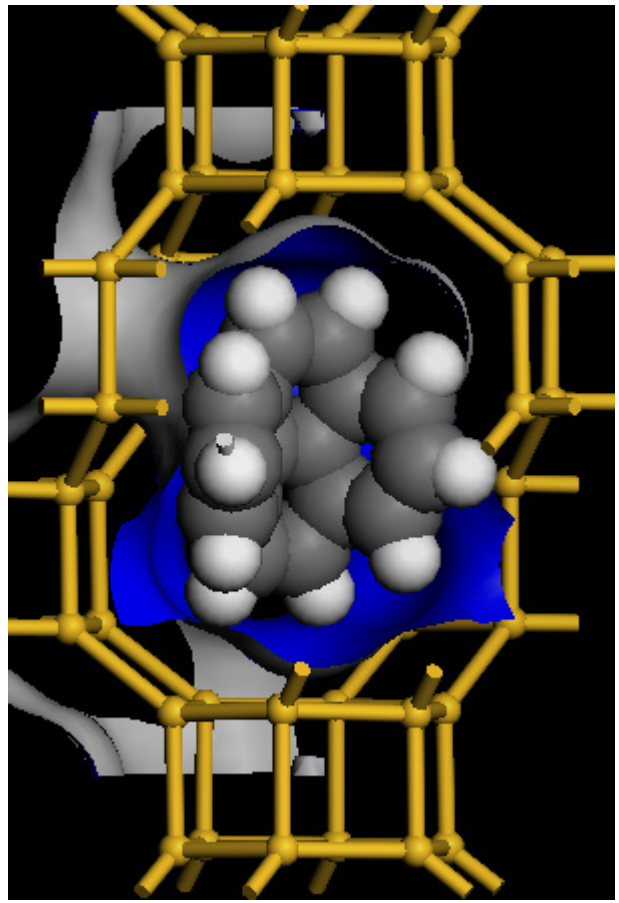
Courtesy Unni Olsbye, Univ. Oslo

SAPO-34

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



(001) projection



Courtesy Unni Olsbye, Univ. Oslo

Outline

UOP
A Honeywell Company

- Zeolites
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- **MTO reactor design**
- Putting it all together: methanol & natural gas
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Fixed Bed MTO Performance

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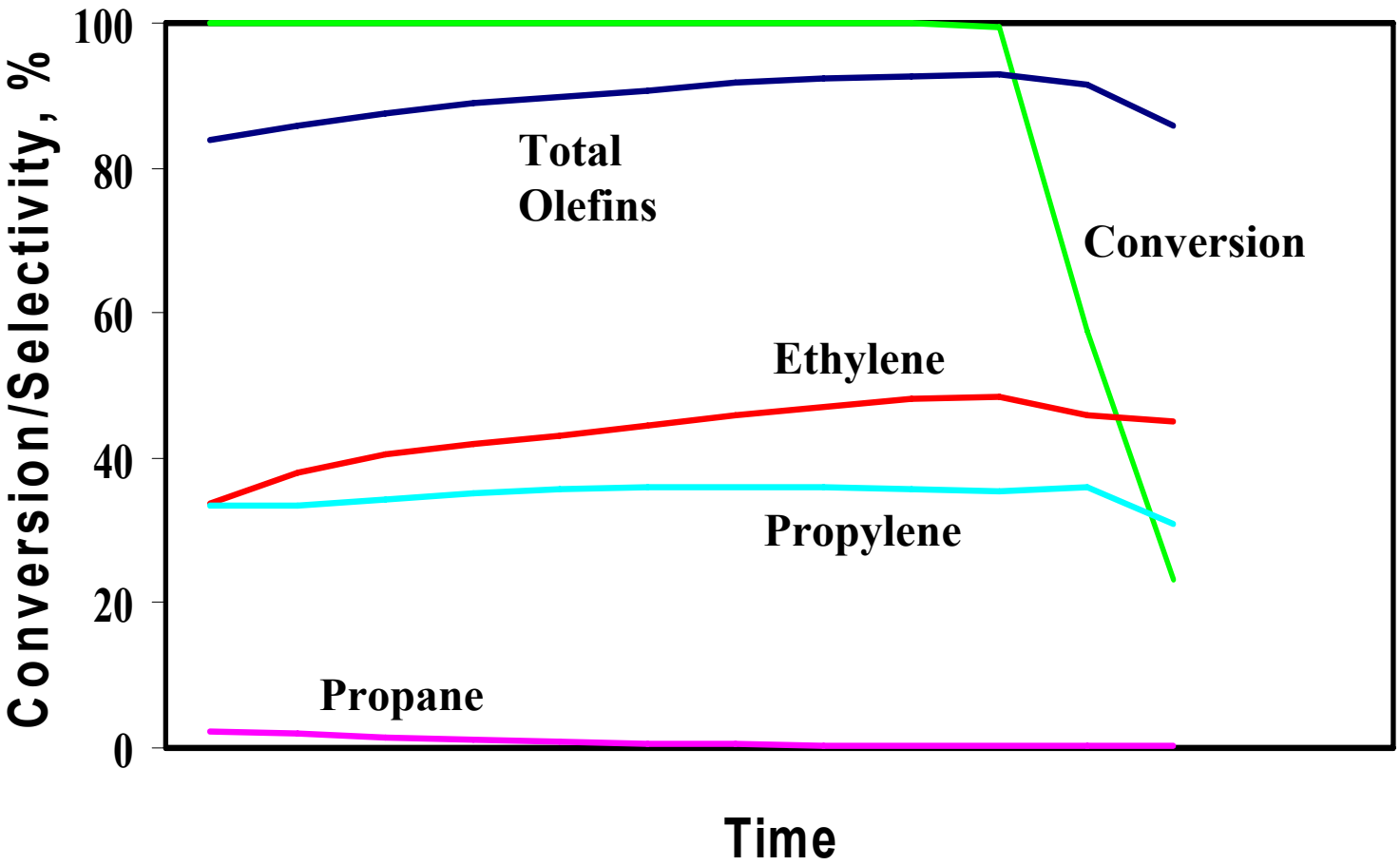
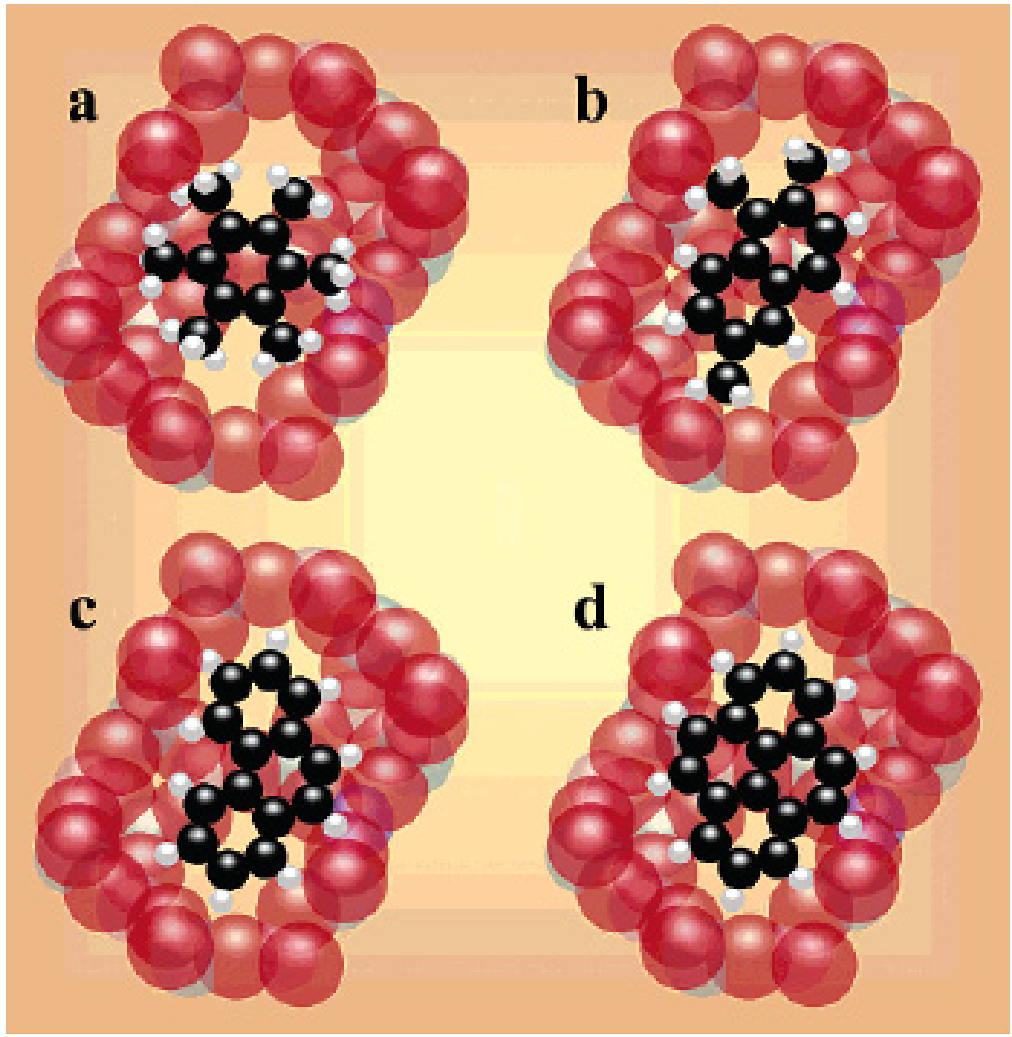
- SAPO-34 catalyst highly active with good selectivity then conversion drops rapidly.



Molecular View of 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

MTO Reactor Design

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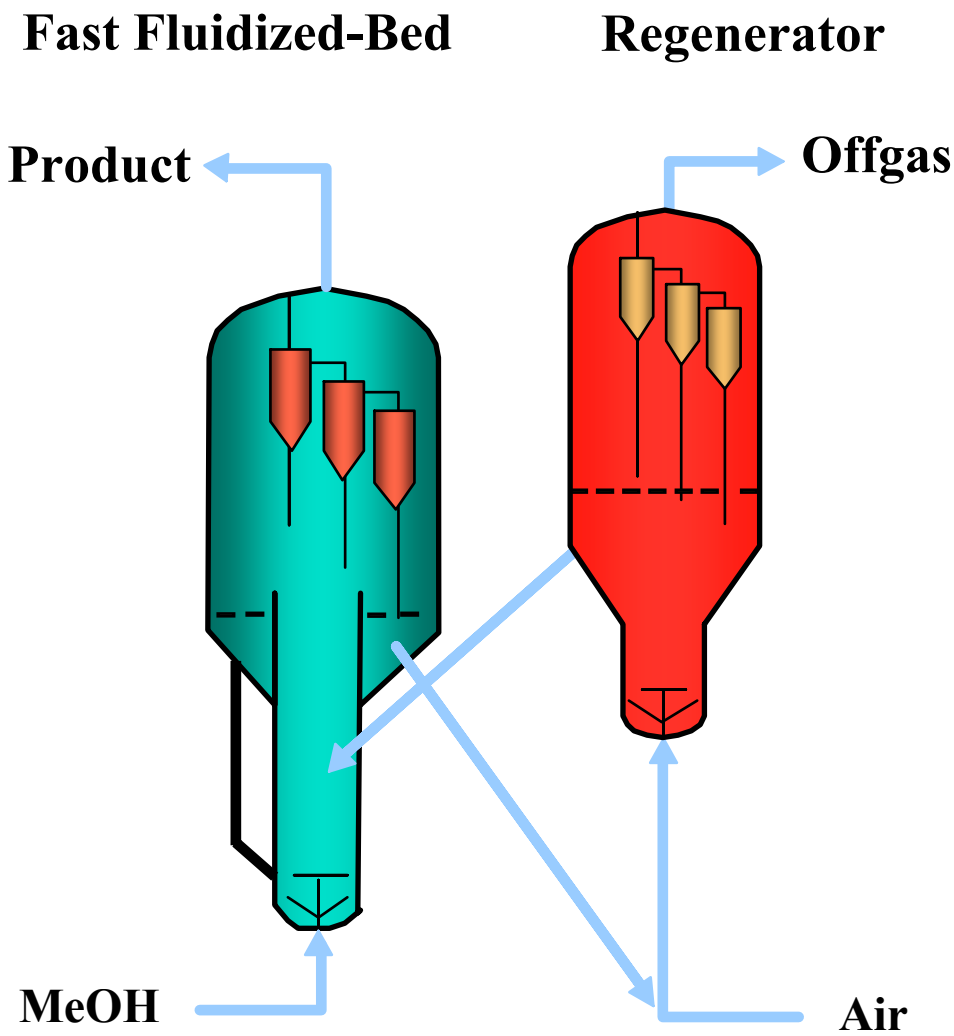
- **Fixed Bed Reactor**
  - rapid deactivation due to coke formation
  - reactor would have to swing between process & regeneration
  - product composition varies with time
  - expensive high-temperature valves required

- **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

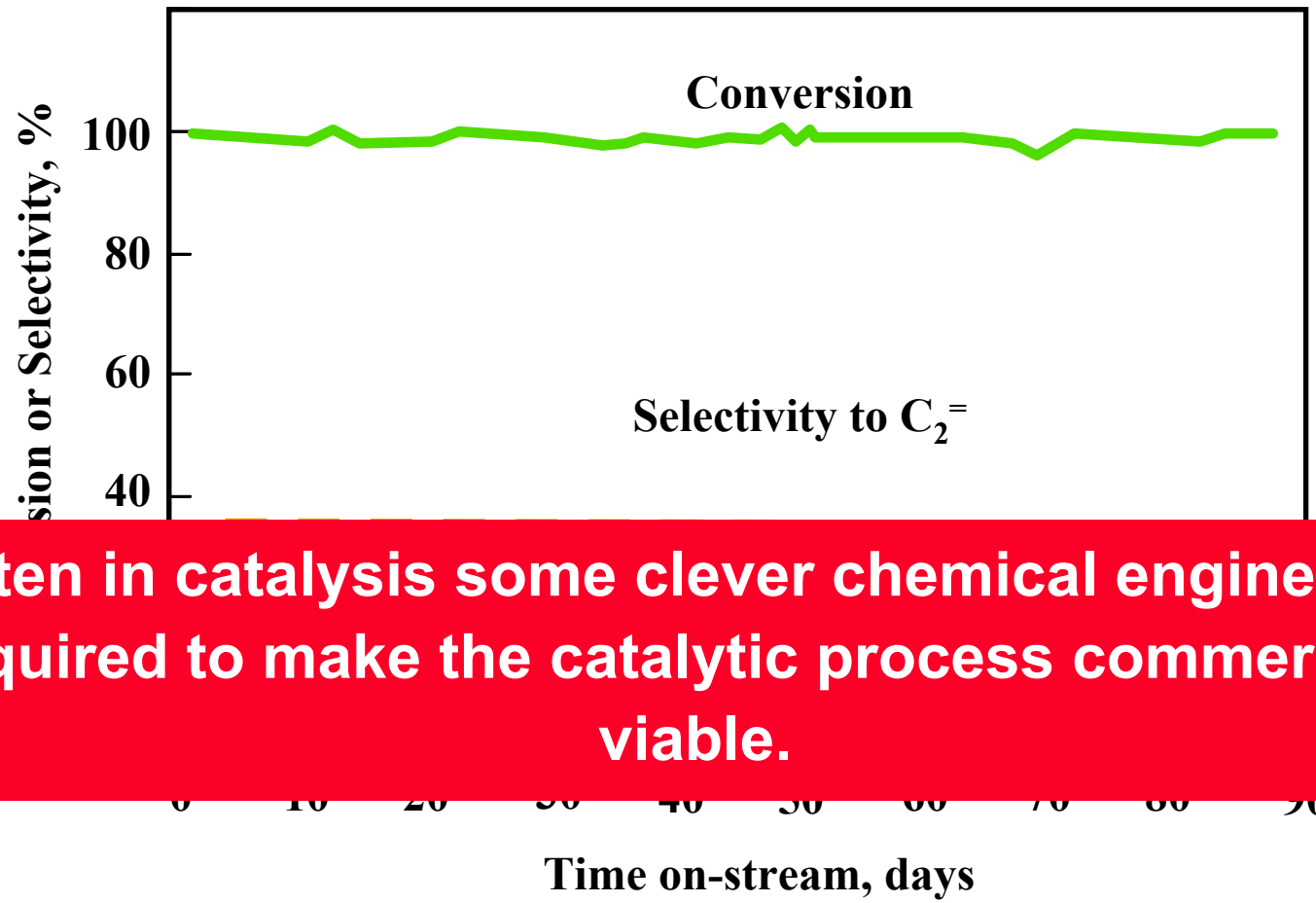
Fluidized Bed Reactor



Fluidized Bed Reactor Results

UOP
A Honeywell Company

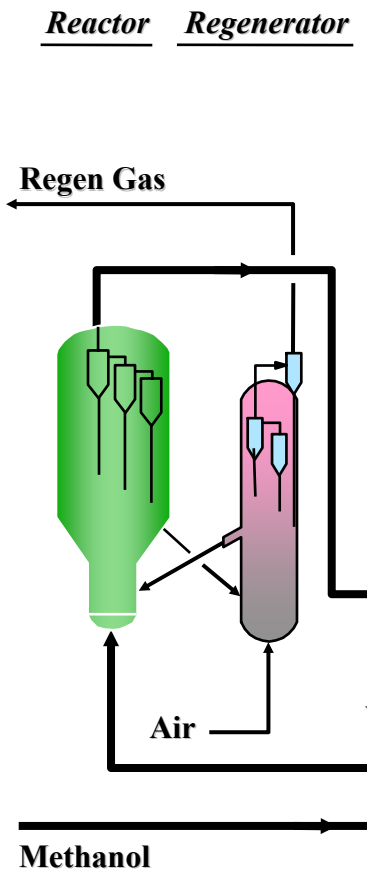
- Conversion and selectivity remain high over months of operation.



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

UOP/HYDRO MTO Process Flow Scheme

- The catalytic reactor is only one small part of the overall process!

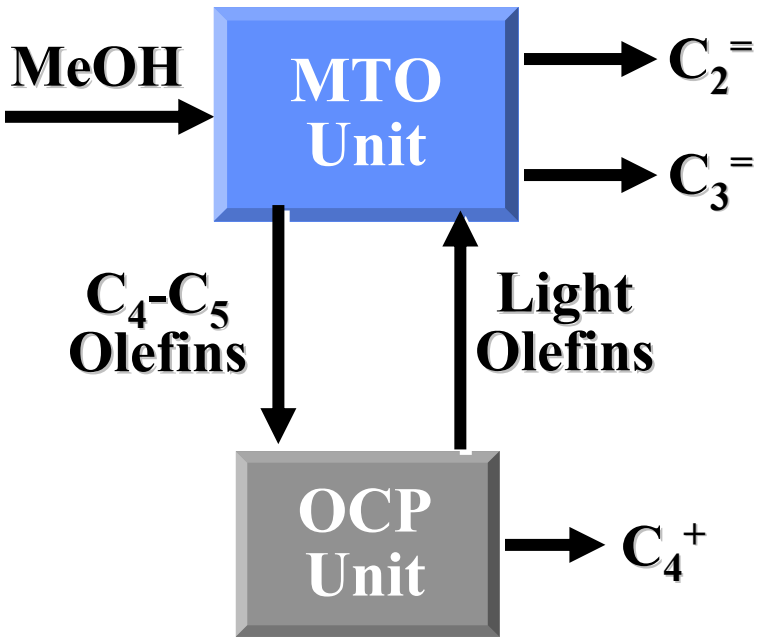


Olefin Cracking Technology

- Another piece of the process…..
- Production of propylene and ethylene from C_4 to C_8 olefins.

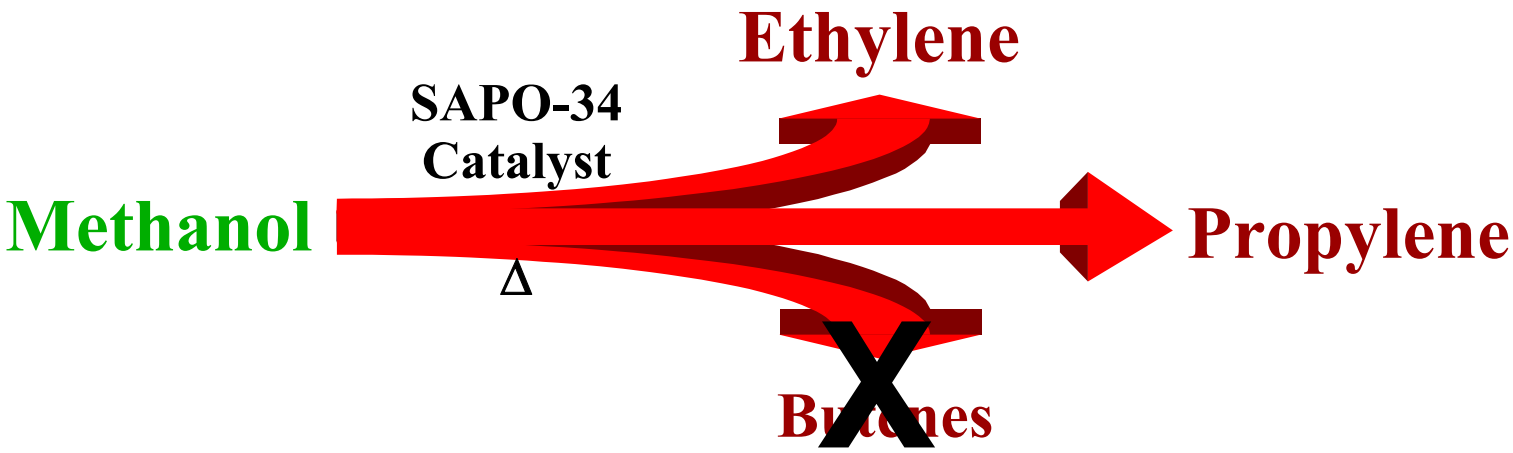
Olefin Cracking integration with MTO

- Upgrade C4+ MTO product to C2= and C3=.



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

MTO Reaction with Olefin Cracking



Other By-Products

H_2O

H_2 , CO_X

C_1-C_5 Paraffins

C_5+

Coke

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- **Putting it all together: methanol & natural gas**
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Why Natural Gas Conversion?

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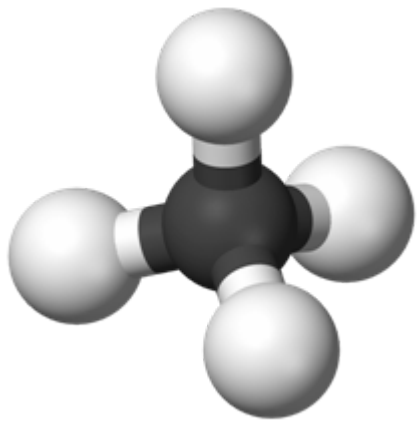
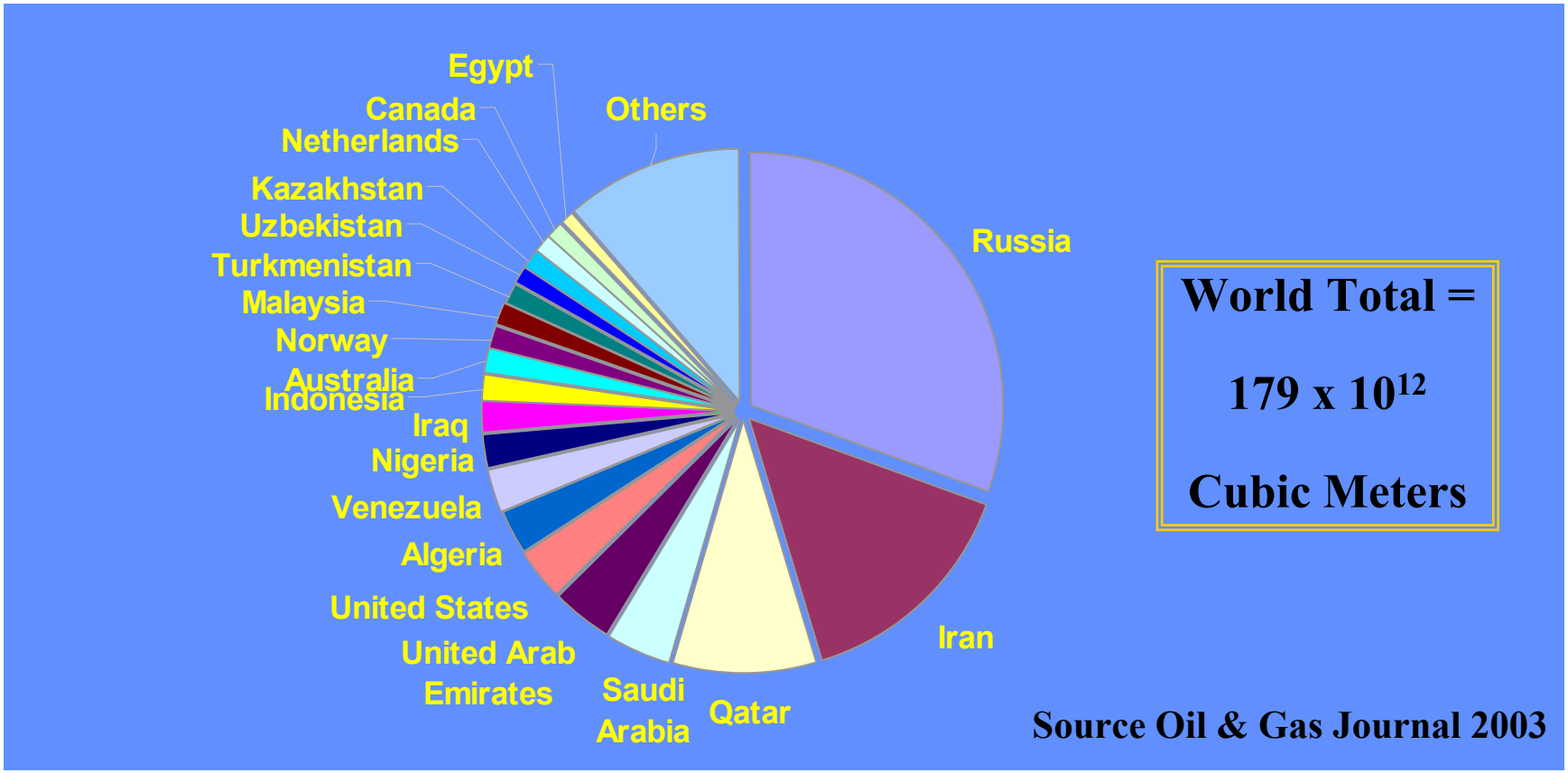
- Large reserves of remote natural gas.
- Environmental need to minimize venting or flaring of associated gas from oil fields.
- Existing technologies for methane conversion limited by market size or marginal economics.



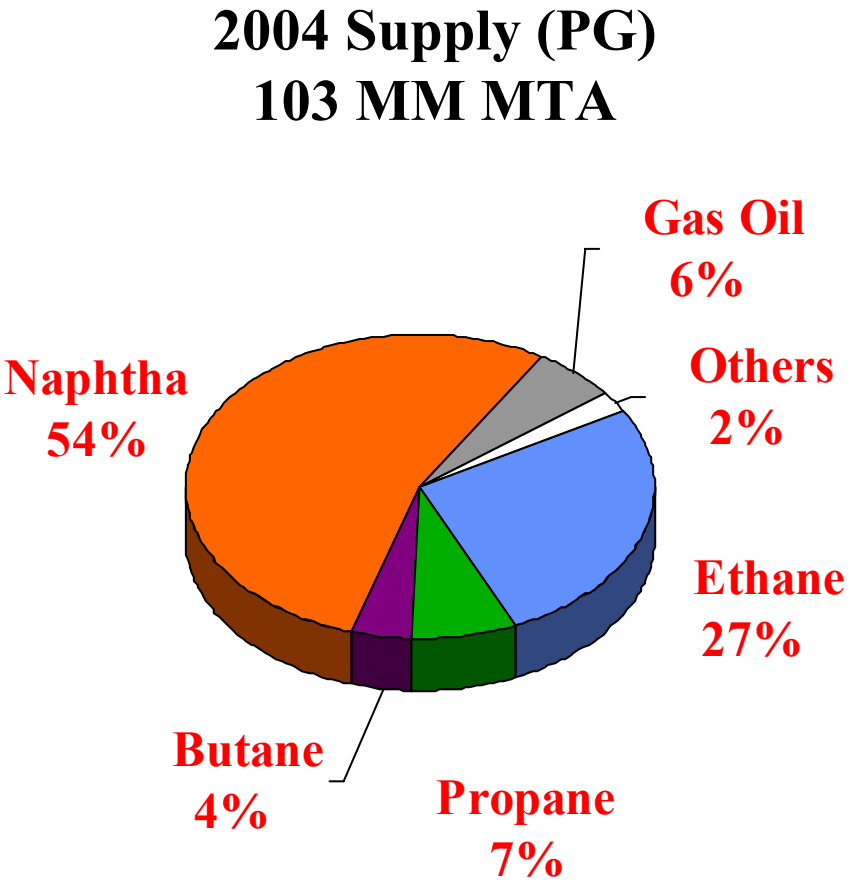
World Natural Gas Reserves



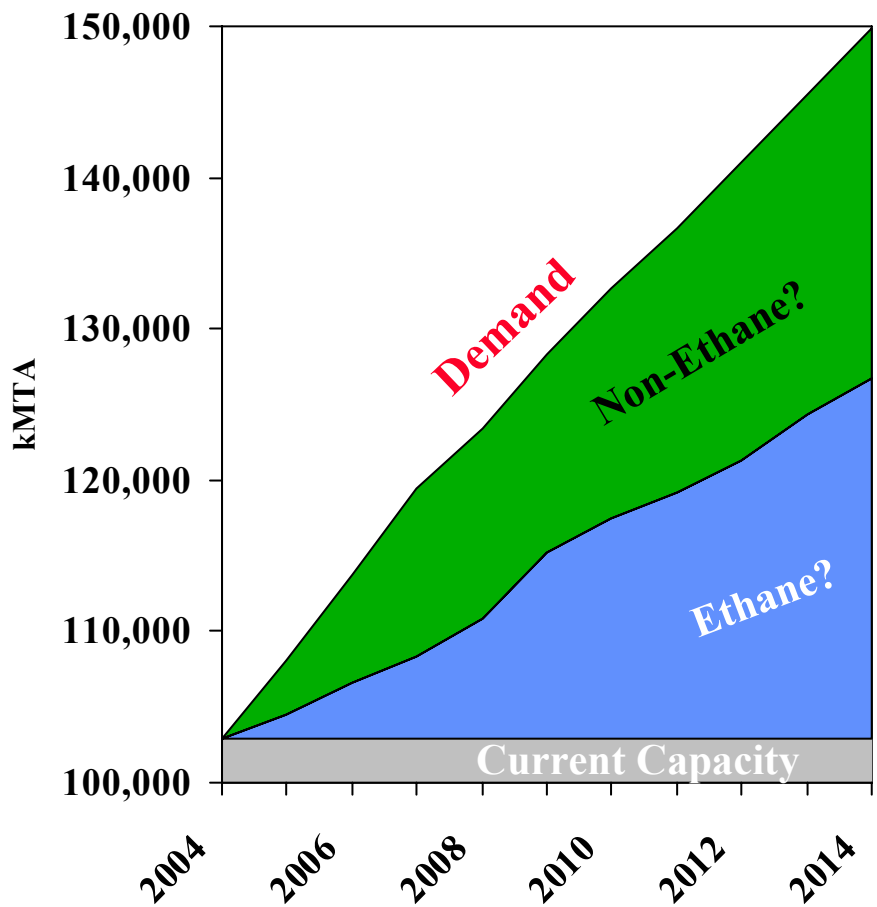
- Natural gas utilization is desired by many companies and nations
  - Monetization of stranded gas reserves
  - Reduced gas flaring
  - Less dependence on crude oil

Ethylene Supply & Demand

- **Demand for ethylene predicted to increase: source will have to come from new capacity.**



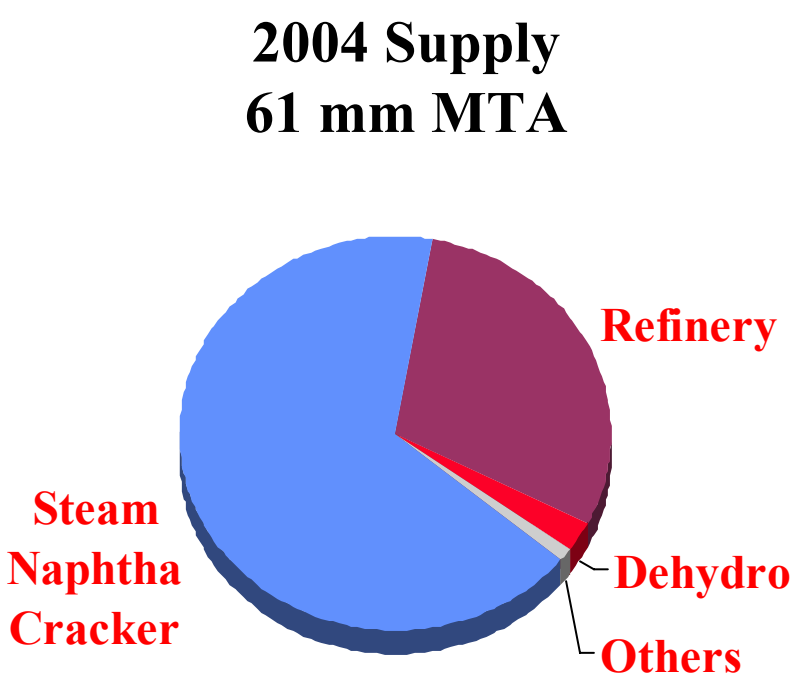
"PG" = polymer-grade

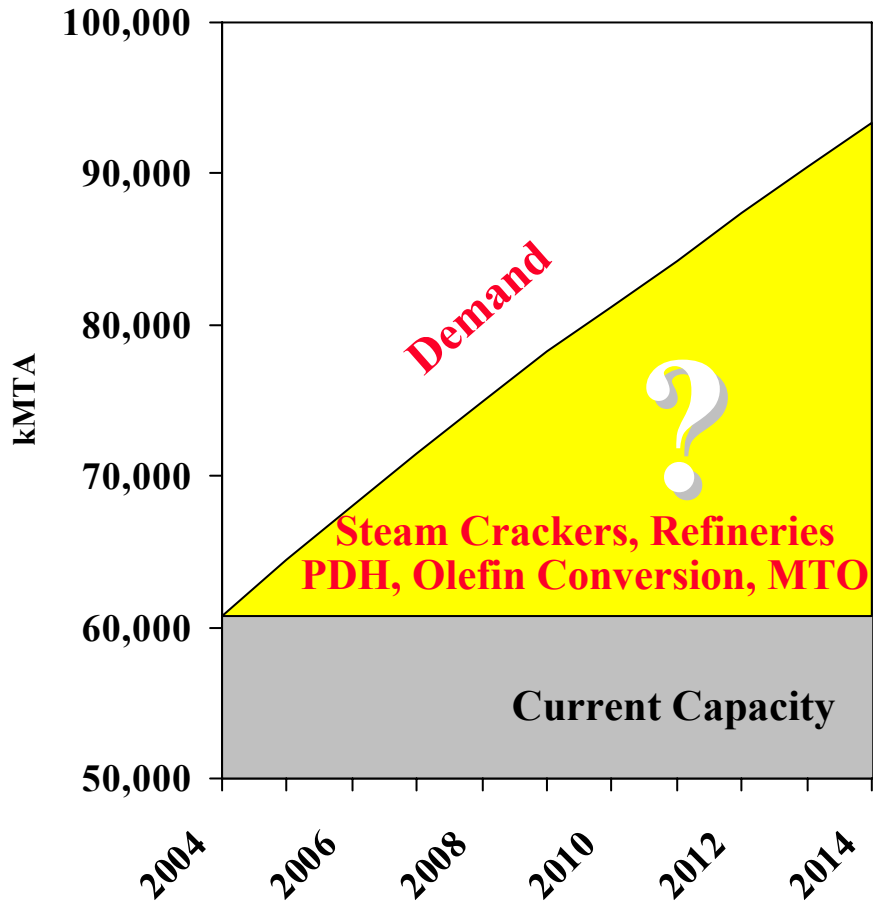


Data Source: CMAI 2005

Propylene Supply & Demand

- Propylene demand also predicted to rise.

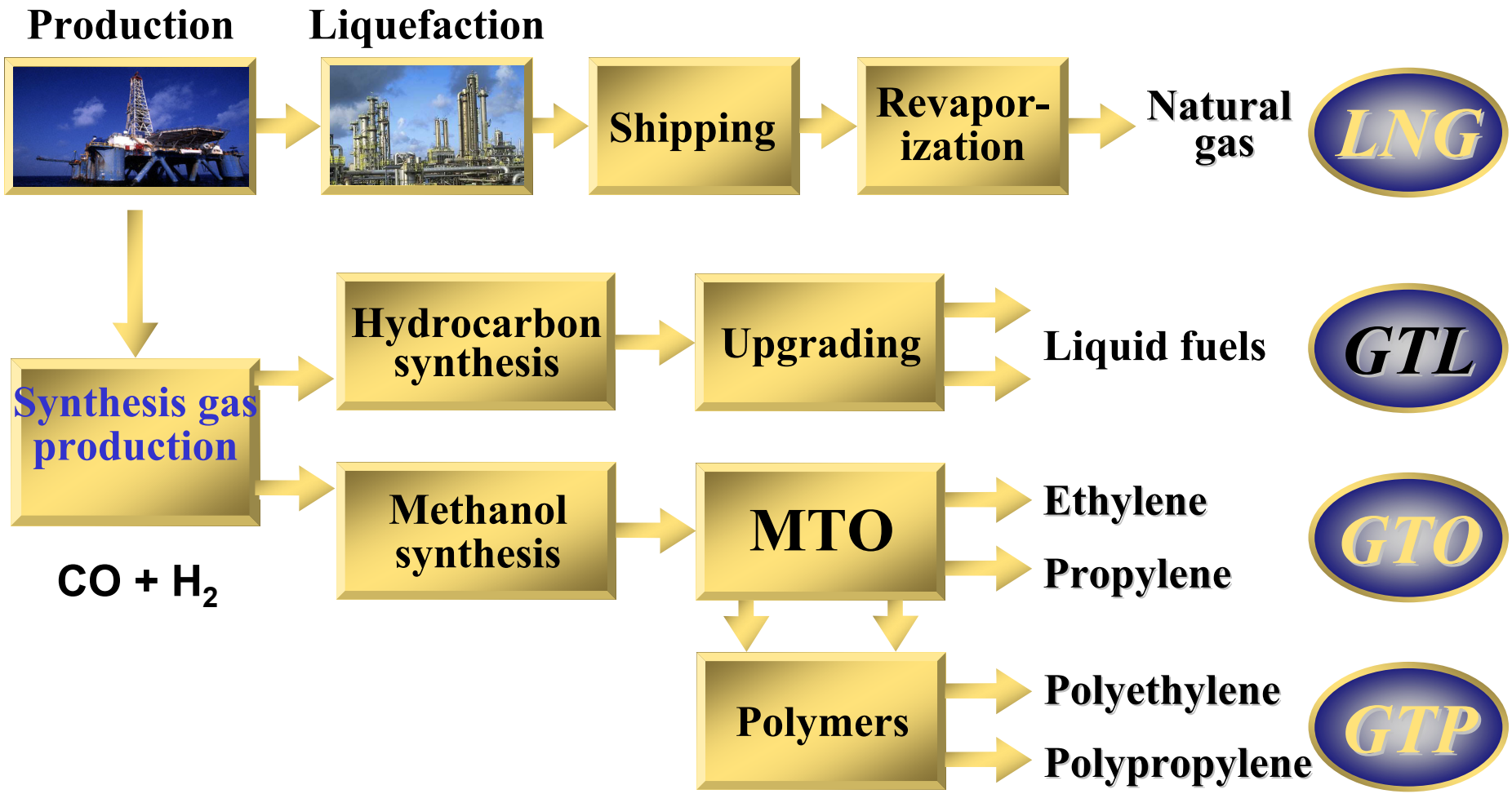




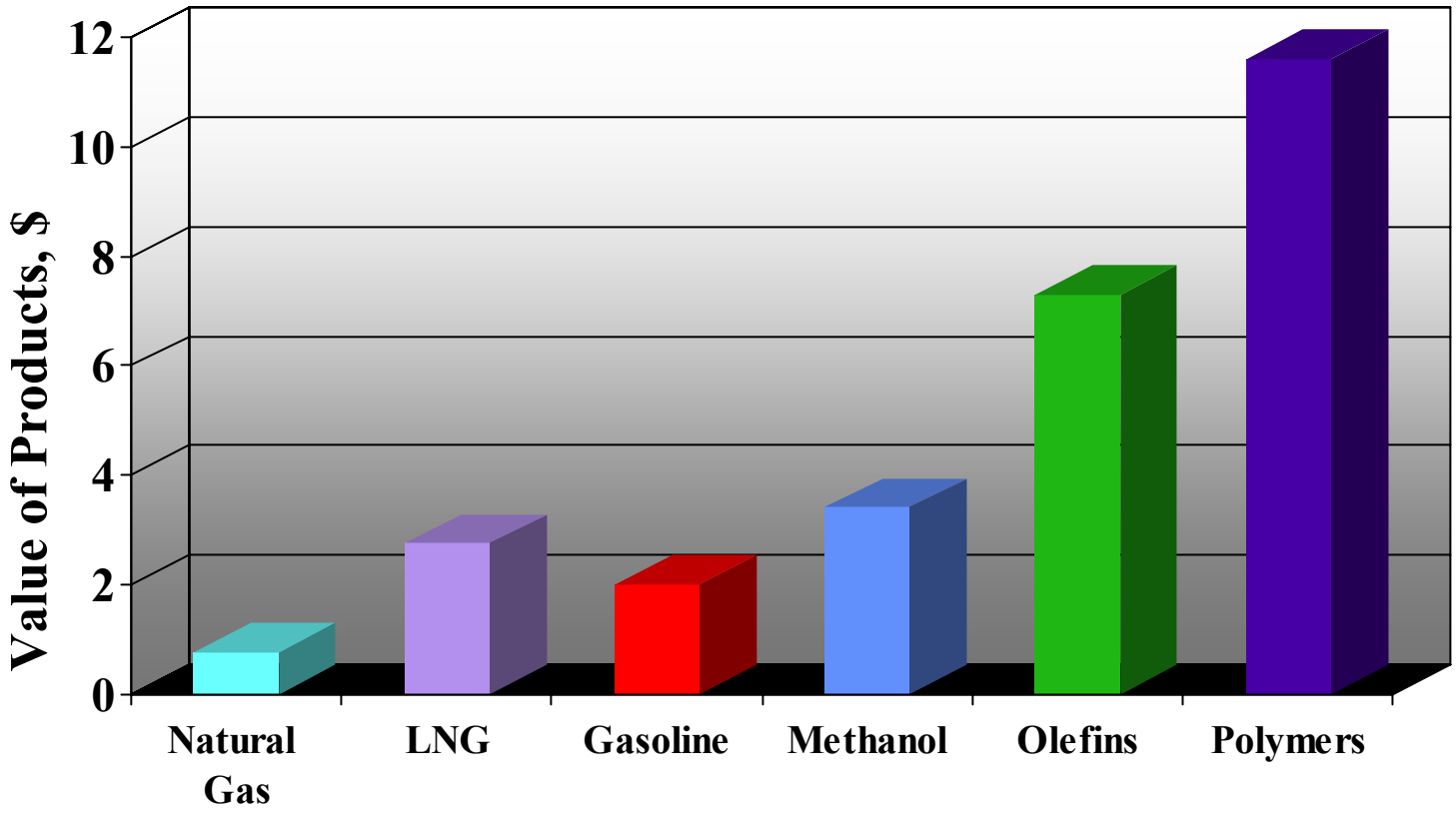
Data Source: CMAI 2005

Stranded Gas Monetization Processes

UOP
A Honeywell Company



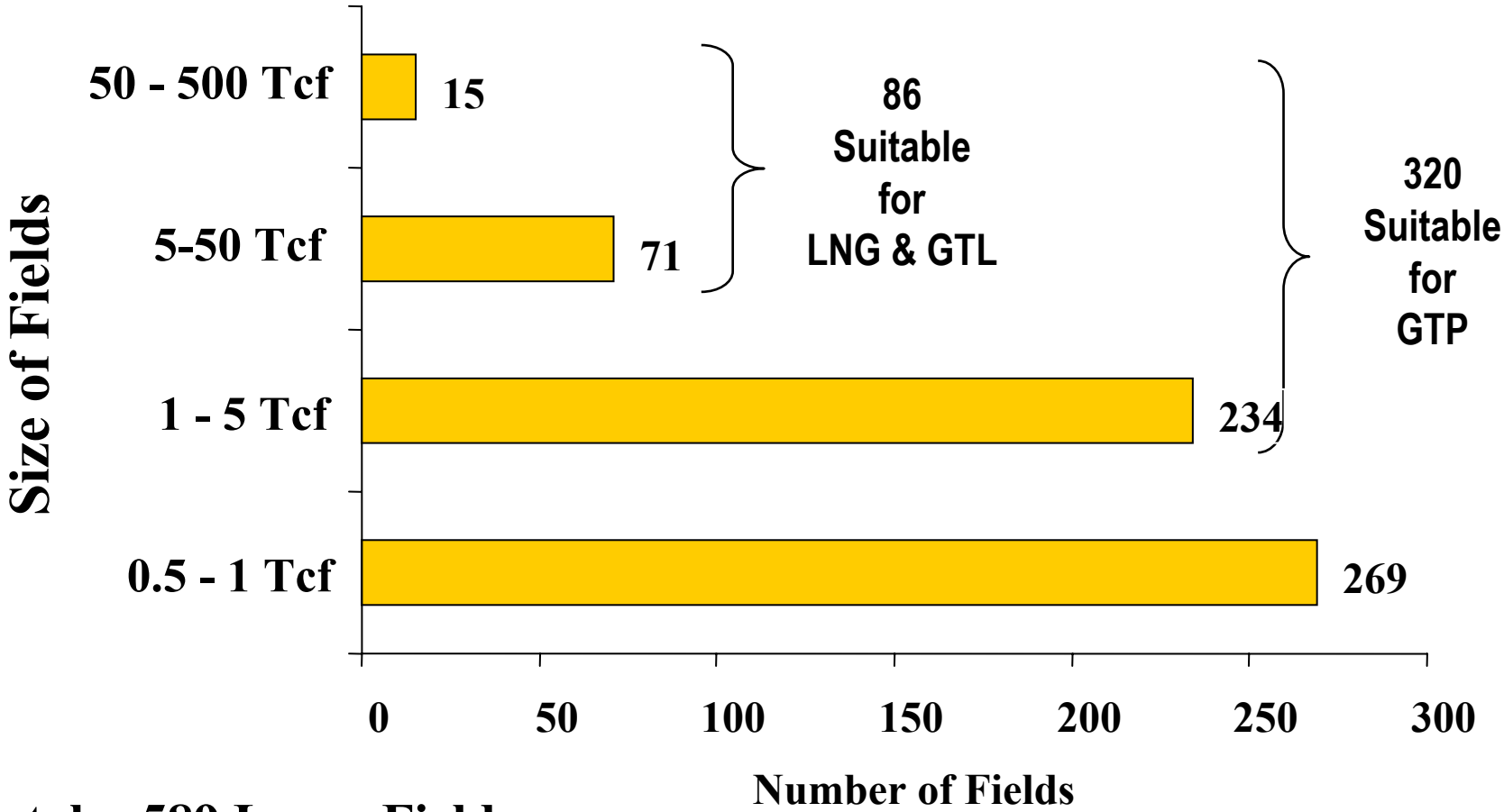
Value of Products Produced from 1 MM BTU of Natural Gas



Polymers are highest value product

Large Gas Fields by Size

- **Substantially more fields economically viable for GTP technology than other technologies.**



Total = 589 Large Fields

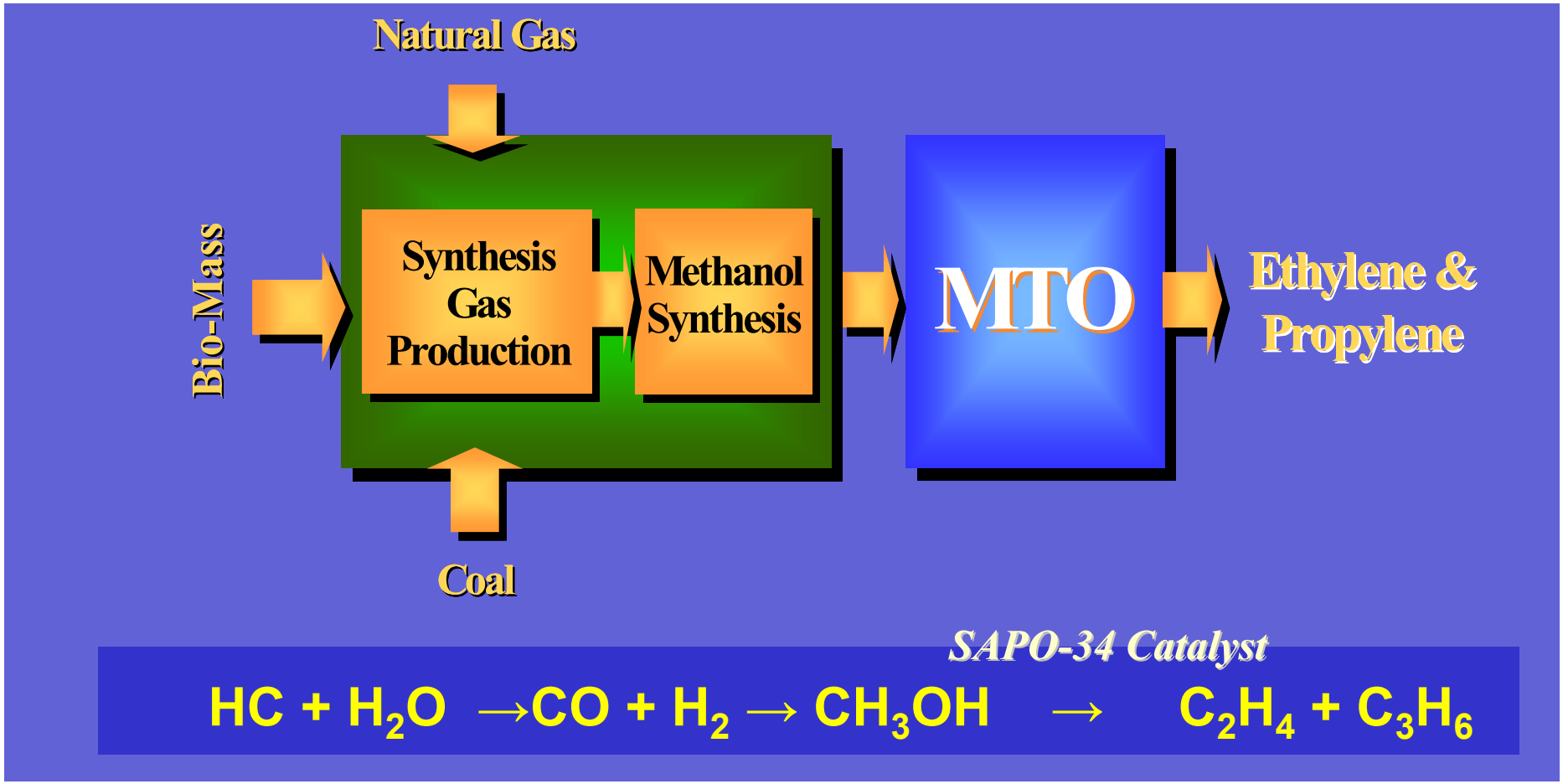
1 Trillion cf = 28.2 BCM

Source: Oil & Gas Journal

Methanol to Olefins Process

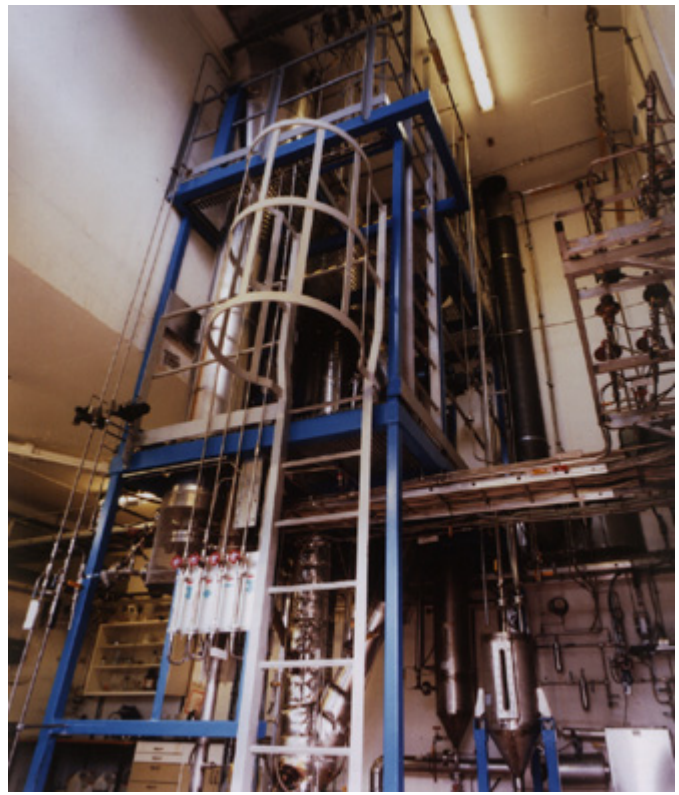
UOP
A Honeywell Company

- **MTO process is new viable route to polymer grade ethylene and propylene.**



MTO Commercial Status

- **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.**



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- MTO reactor design
- Putting it all together: methanol
- **Discovery to commercialization**

SAPO-34 vs UZM's

UOP
A Honeywell Company

- For SAPO-34 it took 20+ years from discovery of the material to its use in a commercial process.
- In 1998 New Materials Group formed at UOP to discover new zeolites.
- UZM-8 discovered in late 2000, patent issued 2004.
- Identified as a candidate for ethylbenzene production.

$$C_6H_6 + C_2H_4 \longrightarrow C_6H_5CH_2CH_3$$

benzene ethylene ethylbenzene

- Performance of UZM-8 allowed for the design of a more economical process.
- New process with new catalyst for EB production offered for sale in late 2006.

6 years to commercialization!

Acknowledgements

- John Chen
- Paul Barger
- Steve Wilson
- Hayim Abreveya
- Edith Flanigen

- Wharton Sinkler
- Sue Wojnicki
- Emmanuelle Siler
- Sesh Prabhakar

- Prof. Unni Olsbye, University of Oslo.