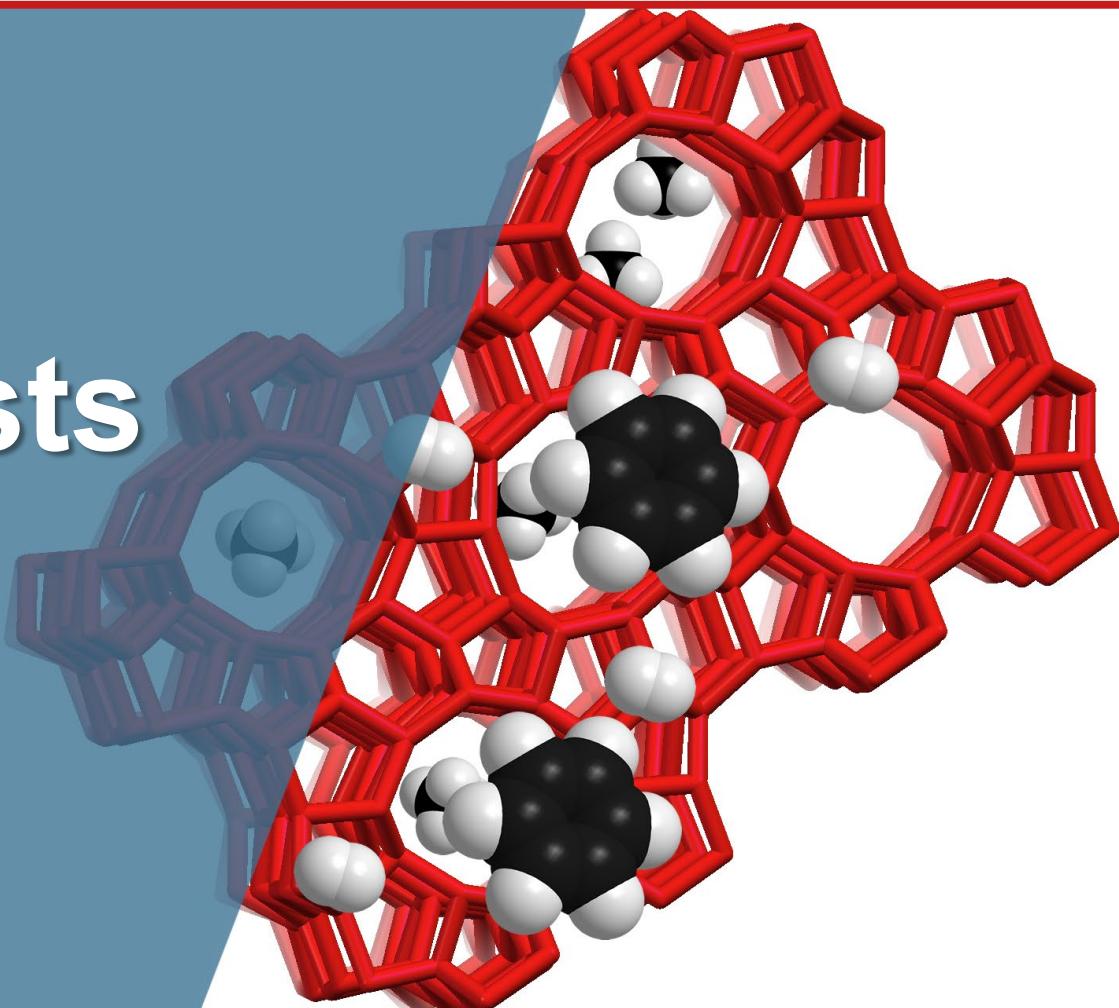


# Microporous Catalysts



6EMAC2  
Modern concepts in catalysis  
14<sup>th</sup> March, 2025

# Intermediate quiz 4

- Go to [Canvas](#) → 6EMAC2 → Quizzes → Intermediate Quiz 4
- 10 questions
- 15 minutes
- For some questions more than one correct answer is possible
- Good luck!

# Previously on 6EMAC2

- Concepts of catalysis
- Existing and future catalytic processes
- Mechanisms of catalytic reactions
- Characterization in catalysis
- Synthesis of catalysts

# Today

- Zeolites

*Porous materials*

*Structural features of zeolites*

*Important zeolite structures (BEA, CHA, FAU, LTA, MFI, MOR)*

*Brønsted and Lewis acidity*

*Synthesis of zeolites*

*Stabilizing transition metal sites in zeolites*

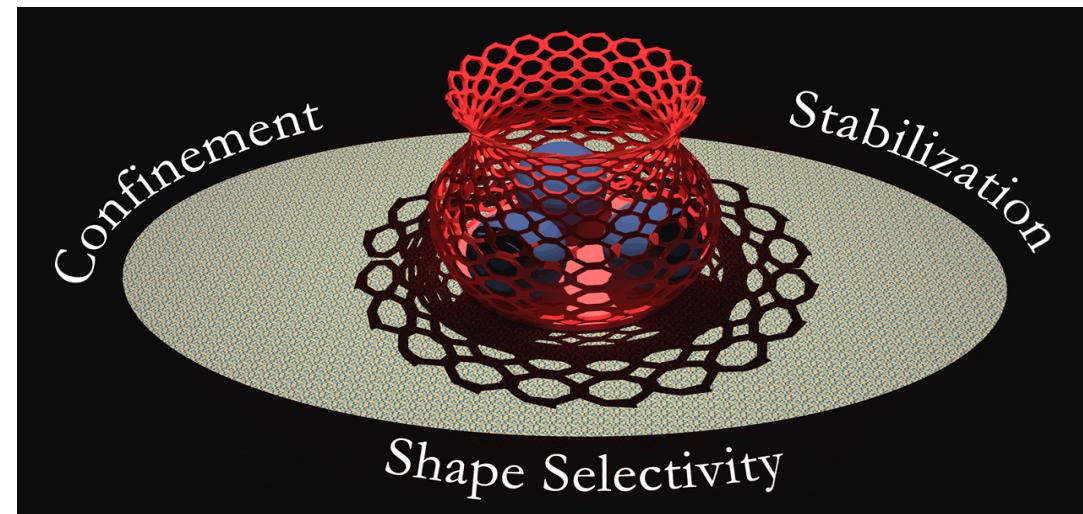
*Shape selectivity and confinement effects*

*Catalytic applications of zeolites*

- Methanol-to-hydrocarbons (MTH)

*Reaction mechanism*

*Chemistry of MTH catalysts*



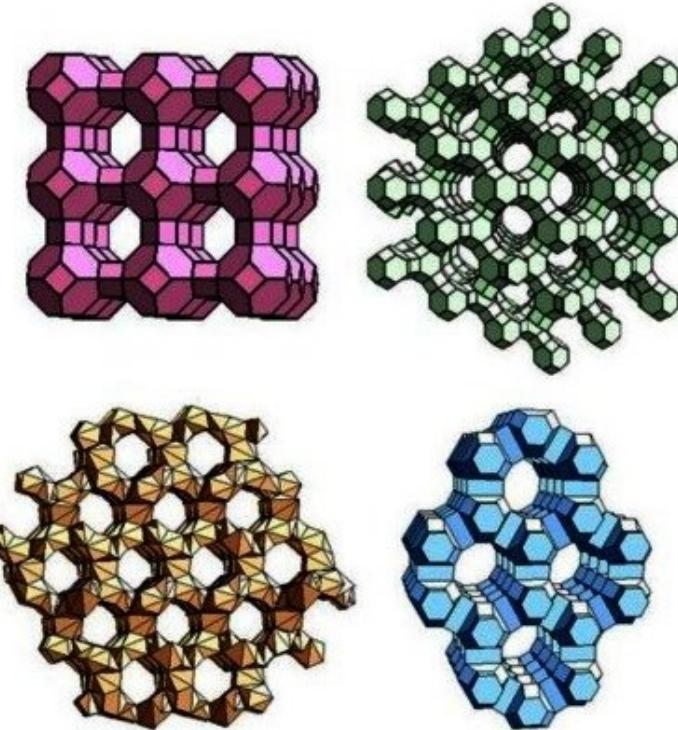
# Learning outcomes

- Categorize different types of porous materials and explain the appearance of corresponding adsorption isotherms
- Classify various silica polymorphs and explain their structure
- Define zeolites and their main properties, provide examples of zeolite topologies with pore dimensions and structural features
- Explain the phenomena of shape selectivity and confinement
- Explain phenomena of Lewis and Brønsted acidity in zeolites and principles of acidity characterization
- Outline the conditions of zeolite synthesis and effect of organic template
- Categorize and explain synthetic strategies to diminish diffusion limitations in zeolites
- Explain the hydrocarbon pool mechanism of zeolite-catalyzed processes (MTH reaction as an example)
- Analyze the effects of reaction parameters (catalyst, temperature, contact time) on the product distribution of MTH reaction

# Porous materials

Indispensable for catalysis applications:

- High surface area (50 – 3000 m<sup>2</sup>/g)
- Accessibility and stabilization of active centers
- Adsorption of reactant to enhance the activity
- Overall (mechanical, chemical) stability of catalyst



# Types of porosity

The classification is based on different mechanisms of pore filling upon adsorption

- **Micropores < 2 nm**

**Micropore filling**

Size of pores is similar to the size of molecules – very strong adsorption

- **Mesopores 2 – 50 nm**

**Capillary condensation**

Medium adsorption strength

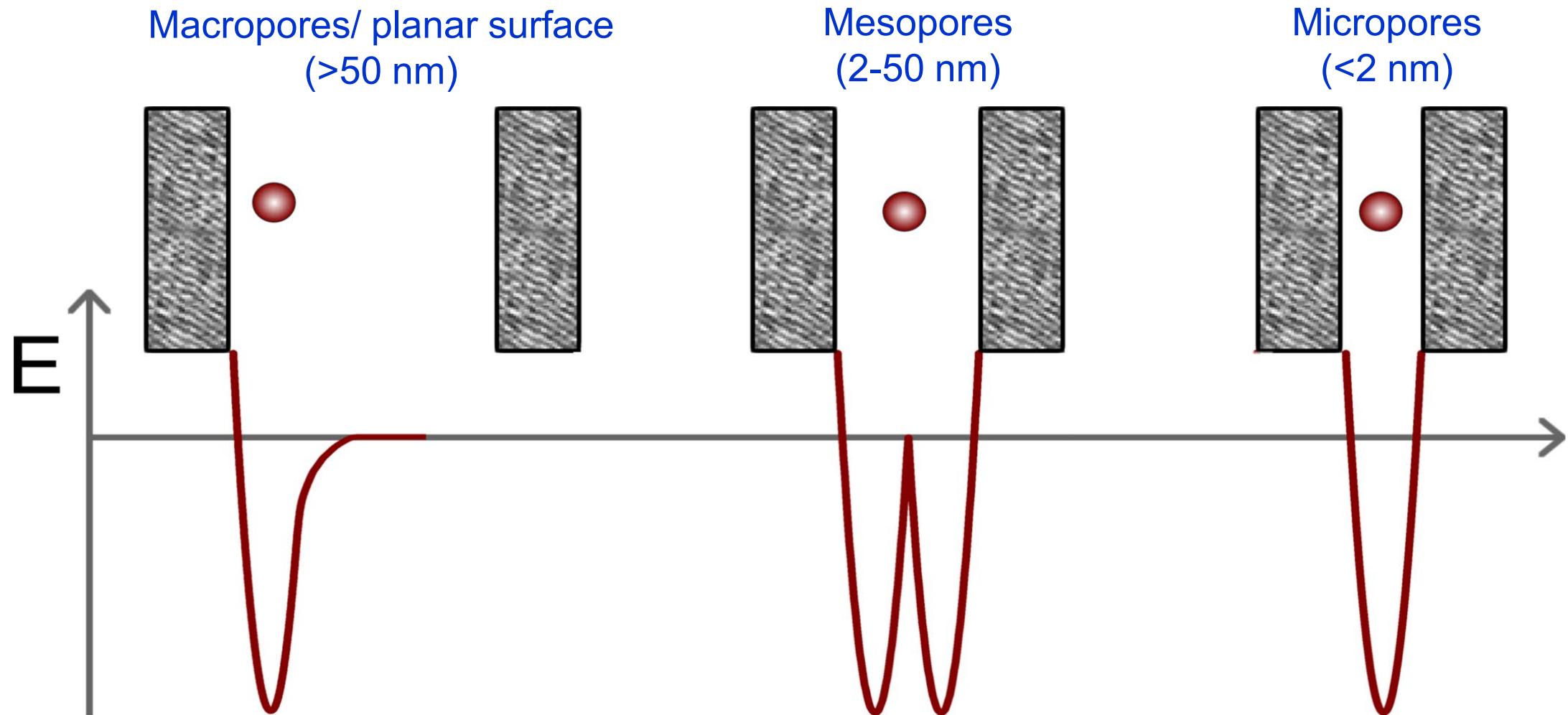
- **Macropores > 50 nm**

**Multilayer adsorption**

Similar to open external surface – weak adsorption

# Types of porosity

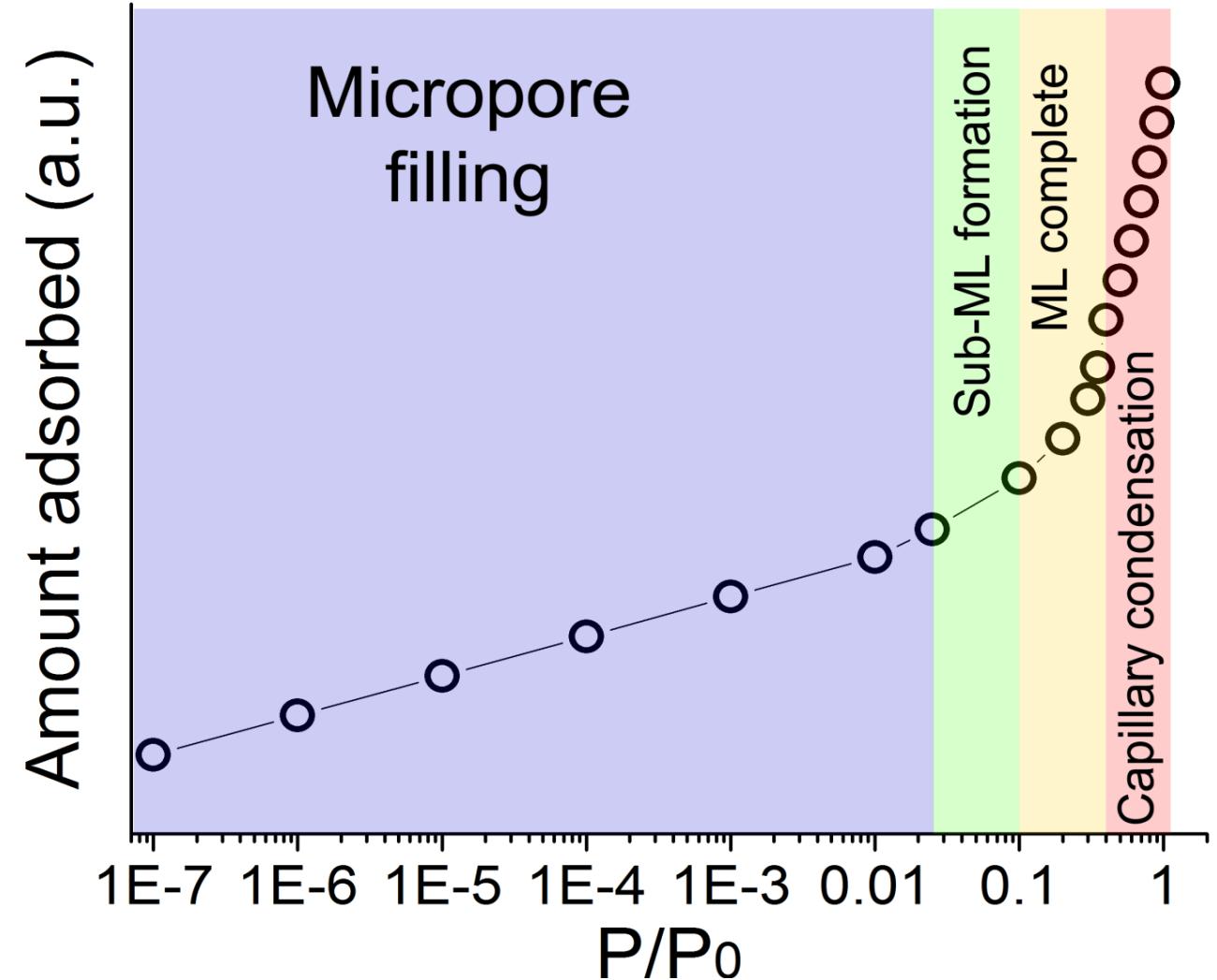
The classification is based on different mechanisms of pore filling upon adsorption



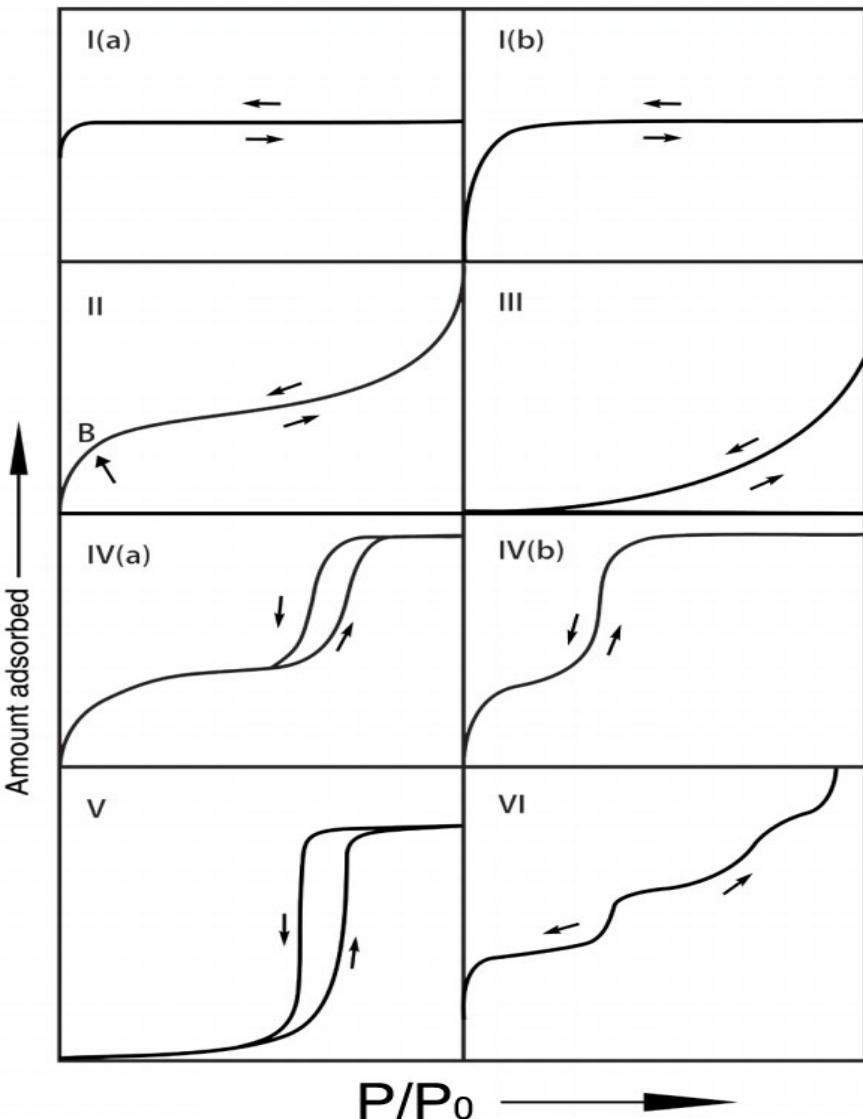
# Characterization of porous solids – adsorption isotherms

P/P <sub>0</sub> range	Process
1×10 <sup>-7</sup> – 0.02	Micropore filling
0.01 – 0.1	Sub-monolayer formation
0.05 – 0.3	Monolayer complete
>0.1	Multilayer formation
>0.35	Capillary condensation
0.1 – 0.5	Capillary filling

Surface area, micro- and meso-pore volumes, and pore size distribution can be derived from adsorption data



# Characterization of porous solids



$N_2$  (Ar) adsorption isotherms measured at 77 K (88 K)

Type I – Microporous materials (strong adsorption)

Type II – Non-porous and macroporous materials (point B showing monolayer coverage)

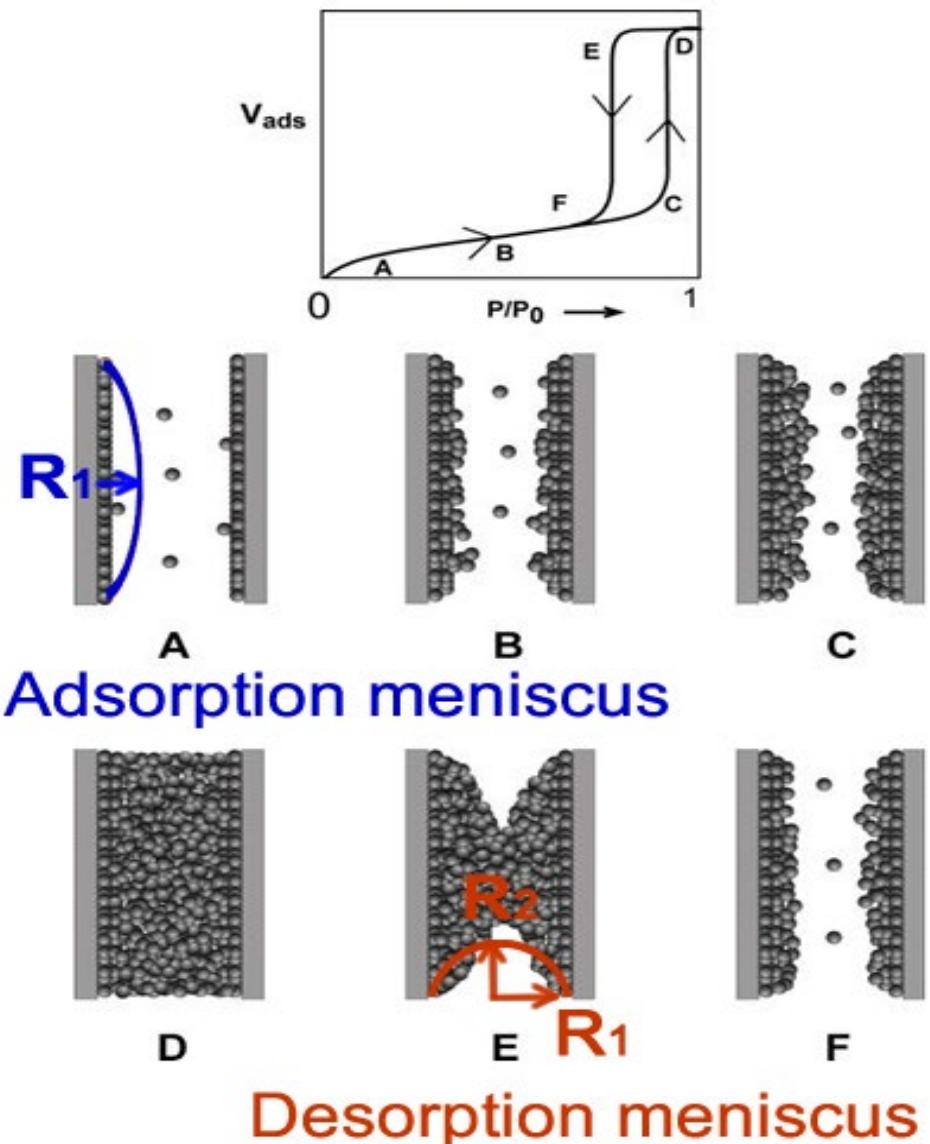
Type III – Non-porous materials with weak adsorbent-adsorbate interaction (no monolayer formed)

Type IV – Mesoporous materials (hysteresis if mesopores are  $> 4$  nm)

Type V – Mesoporous materials with strong adsorbate-adsorbate interactions (water on hydrophobic materials)

Type VI – Layer-by-layer adsorption on uniform non-porous surface

# Nature of hysteresis



Capillary condensation is governed by Kelvin equation:

$$RT \ln \frac{P}{P_0} = \gamma V_m \left( \frac{1}{R_1} + \frac{1}{R_2} \right)$$

$\gamma$  – surface tension

$V_m$  – molar volume of adsorbate

$R_1 = R_2$  for a spherical meniscus

$R_2 = \infty$  for a cylindrical meniscus

Different pressure is necessary to start the adsorption and desorption due to different shapes of menisci

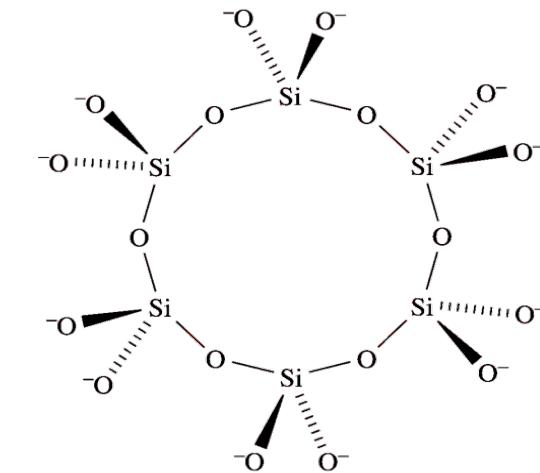
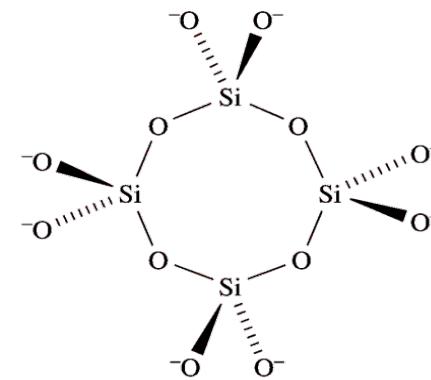
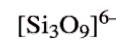
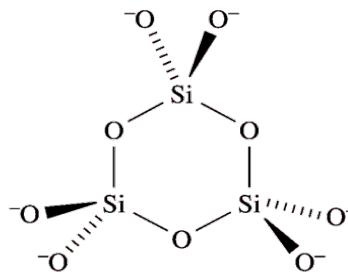
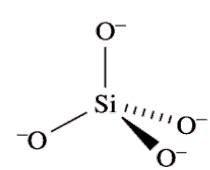
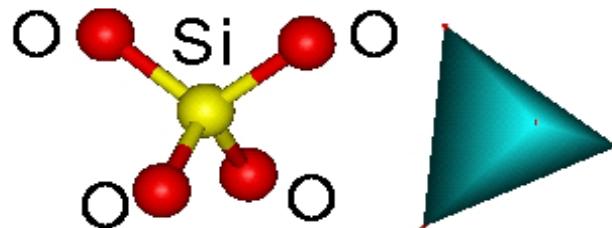
# Porous materials commonly used in catalysis

Support	Price	Surface area (m <sup>2</sup> /g)	Main porosity (other porosity)	Preparation
Silica gel	Low	100 - 800	Meso (micro, macro)	Condensation of alkali silicates
Fumed silica	Medium	50 - 400	Meso (micro)	Flame pyrolysis
$\gamma$ -alumina	Low	200-300	Meso (micro)	Precipitation in aqueous soluton
$\alpha$ -alumina	Low	50-150	Macro	Heat treatment of oxides (>1100°C)
Activated carbon	Low	500 - 3000	Micro (meso, macro)	Pyrolysis of natural materials
Titania	Medium	20 - 100	Macro	Chloride process
CeO <sub>2</sub>	Medium	20 - 100	Macro	Heat treatment of cerium salts
Zeolites	Medium	200 - 700	Micro	Hydrothermal synthesis
Metal-organic frameworks (MOFs)	High	300 - 2500	Micro (meso)	Hydrothermal synthesis

# **Silicon dioxide**

# $\text{SiO}_2$ – most abundant form Si

Basic Unit

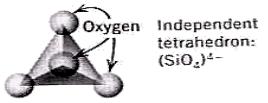


- Silicon oxide typically **tetrahedral** coordination of Si by O
- Amorphous silicas (no atomic ordering of silica network = no XRD reflections)
- Crystalline silicas (atomic ordering of Si-occupied oxygen tetrahedra)
  - quartz, cristobalite (dense)
  - clathrasils, zeolites (porous)
  - clays (layered)

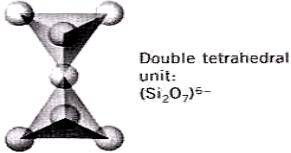
# Different arrangements in space

Nesosilicates  
(0D monomers)

Olivine, Zircon  
Staurolite



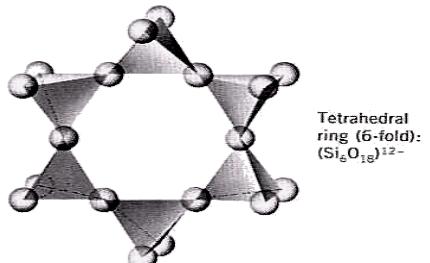
Sorosilicates  
(0D dimers)



Epidote

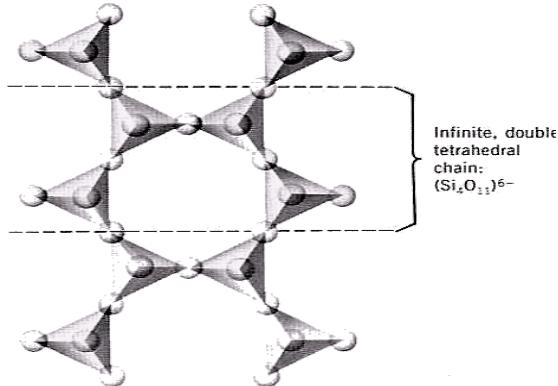
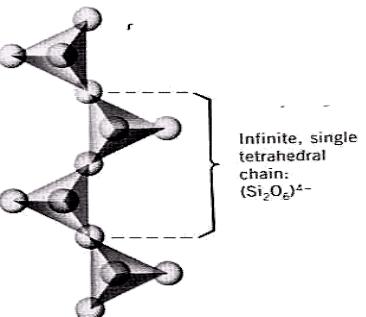
Cyclosilicates  
(0D cycles)

Beryl  
Tourmaline



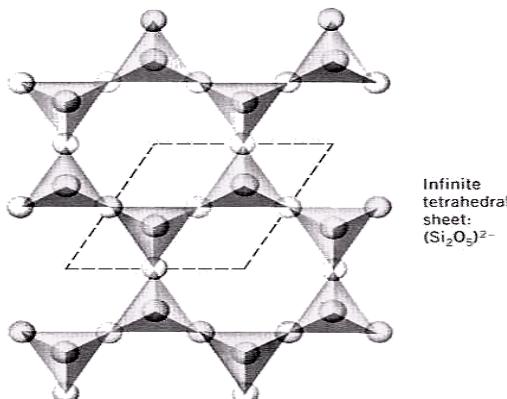
Inosilicates  
(1D single chain)

Pyroxenes



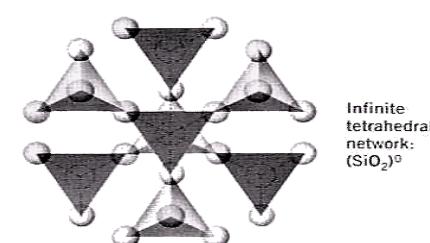
Inosilicates  
(1D double chain)

Amphiboles



Phyllosilicates  
(2D sheets)

Micas, clays  
Serpentine  
Chlorite

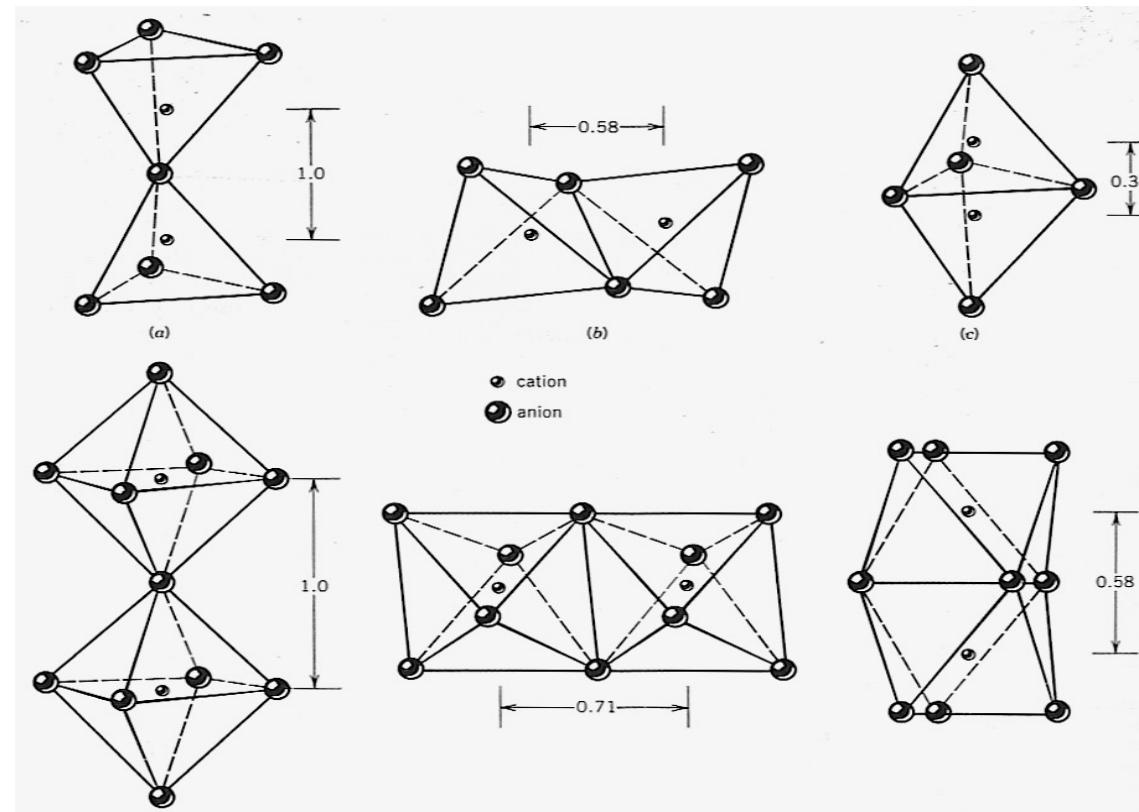


Tectosilicates  
(3D frameworks)

Quartz group,  
Feldspars  
Feldspathoids  
Zeolites

# Corner-sharing of silicates

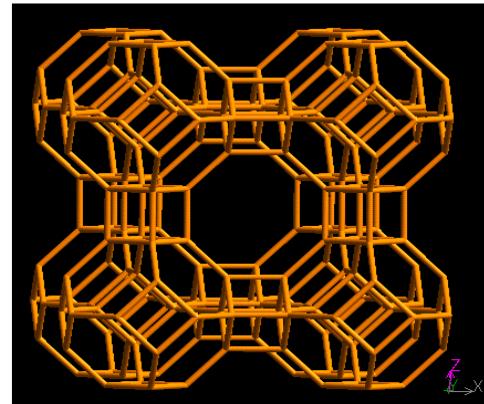
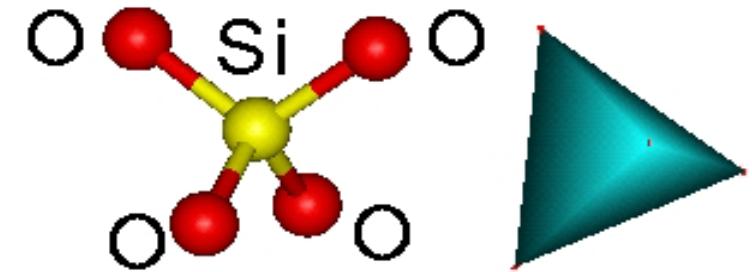
- Oxygens can share electrons with **two silicons**
- **Adjacent silicon tetrahedra can share corners**, but because of the high repulsive charge of  $\text{Si}^{+4}$  cations, they will not share edges or faces. These shared corners are called **bridging oxygens**.



# **Zeolites**

# Zeolites

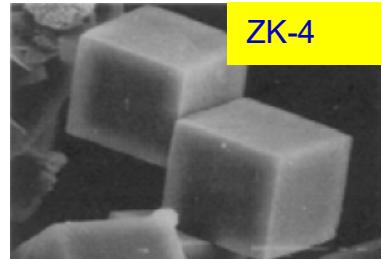
- Microporous crystalline **aluminosilicates**
- ζέω (zeō) = "boil" and λίθος (lithos) = "stone" (Axel Cronstedt, 1756)
- Built up **from tetrahedral  $\text{SiO}_4$  and  $\text{AlO}_4$  units** ( $\text{Si}^{4+}$  and  $\text{Al}^{3+}$ )
- Micropores between 2 and 20 Å (0.2 – 2 nm)
- **Molecular sieving** properties – sorting of molecules based on their size
- High surface area and pore volume
- High thermal and chemical stability
- Strong Brønsted and Lewis **acidity**
- Ion-exchange properties



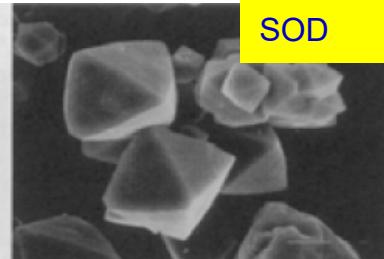
- Water softening (detergents)
- Separation
- Adsorption
- Catalysis

# Zeolites in Catalysis

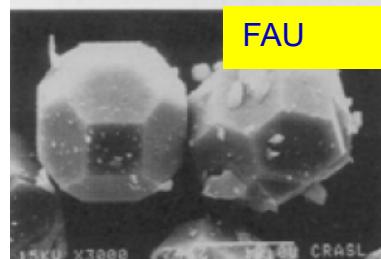
There are **>255** existing zeolite topologies and thousands more are theoretically possible



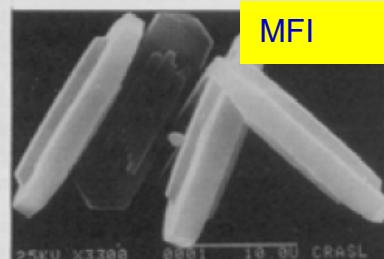
ZK-4



SOD



FAU



MFI

The interface features a blue header with a repeating hexagonal pattern. The title "Database of Zeolite Structures" is at the top right. Below it are links for "IZA-SC", "All Codes", "Intergrowths", "Advanced Search", "Tools", and "Other Links".

Home > Codes

Help Credits

## Zeolite Framework Types

Search for a Framework Type Code or Intergrowth Family

Enter one to three characters to search for a code or  
three or more to search for a code or material name

or select one from the tables below:

ABW	ACO	AEI	AEL	AEN	AET	AFG	AFI	AFN	AFO	AFR	AFS	AFT	AFV	AFX
AFY	AHT	ANA	ANO	APC	APD	AST	ASV	ATN	ATO	ATS	ATT	ATV	AVE	AVL
AWO	AWW	BCT	BEC	BIK	BOF	BOG	BOZ	BPH	BRE	BSV	CAN	CAS	CDO	CFI
CGF	CGS	CHA	-CHI	-CLO	CON	CSV	CZP	DAC	DDR	DFO	DFT	DOH	DON	EAB
EDI	EEI	EMT	EON	EOS	EPI	ERI	ESV	ETL	ETR	ETV	EUO	EWF	EWO	EWS
-EWT	EZT	FAR	FAU	FER	FRA	GIS	GIU	GME	GON	GOO	HEU	-HOS	IFO	IFR
-IFT	-IFU	IFW	IFY	IHW	IMF	-ION	IRN	IRR	-IRT	-IRY	ISV	ITE	ITG	ITH
ITR	ITT	-ITV	ITW	IWR	IWS	IWV	IWW	JBW	JNT	JOZ	JRY	JSN	JSR	JST
JSW	JSY	JZO	JZT	KFI	LAU	LEV	LIO	-LIT	LOS	LOV	LTA	LTF	LTJ	LTL
LTN	MAR	MAZ	MEI	MEL	MEP	MER	MFI	MFS	MON	MOR	MOZ	MRT	MSE	MSO
MTF	MTN	MTT	MTW	MVY	MWF	MWW	NAB	NAT	NES	NON	NPO	NPT	NSI	OBW
OFF	OKO	OSI	OSO	OWE	-PAR	PAU	PCR	PHI	PON	POR	POS	PSI	PTF	PTO
PTT	PTY	PUN	PWN	PWO	PWW	RFE	RHO	-RON	RRO	RSN	RTE	RTH	RUT	RWR
RWY	SAF	SAO	SAS	SAT	SAV	SBE	SBN	SBS	SBT	SEW	SFE	SFF	SFG	SFH
SFN	SFO	SFS	SFW	SGT	SIV	SOD	SOF	SOR	SOS	SOV	SSF	-SSO	SSY	STF
STI	STT	STW	-SVR	SVV	SWY	-SYT	SZR	TER	THO	TOL	TON	TSC	TUN	UEI
UFI	UOS	UOV	UOZ	USI	UTL	UWY	VET	VFI	VNI	VSV	WEI	-WEN	YFI	YUG
ZON														

A "-" sign preceding a three-letter code indicates that the framework is interrupted. That is, not all T atoms are 4-connected.

<http://www.iza-structure.org/databases/>

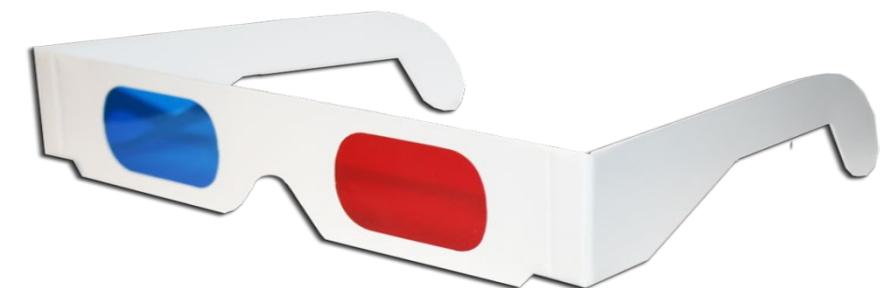
# Prominent zeolite types – “the big six”

- **MFI** – Mordenite Framework Inverted (ZSM-5, mineral mutinaite, silicalite-1, TS-1)
- **FAU** – mineral Faujasite (Linde Type X, Linde Type Y, X, Y)
- **LTA** – Linde Type A (zeolite A, ITQ-29)
- **MOR** – mineral Mordenite
- **BEA** – polymorph Beta of mineral Tschernichite
- **CHA** – mineral Chabazite (SSZ-13, SAPO-34)

For better understanding of these structures check out a set of short 3D movies:

<https://www.youtube.com/playlist?list=PLy5PvMUltEGtwF6kEm92Pn5ls9TUUuz17L>

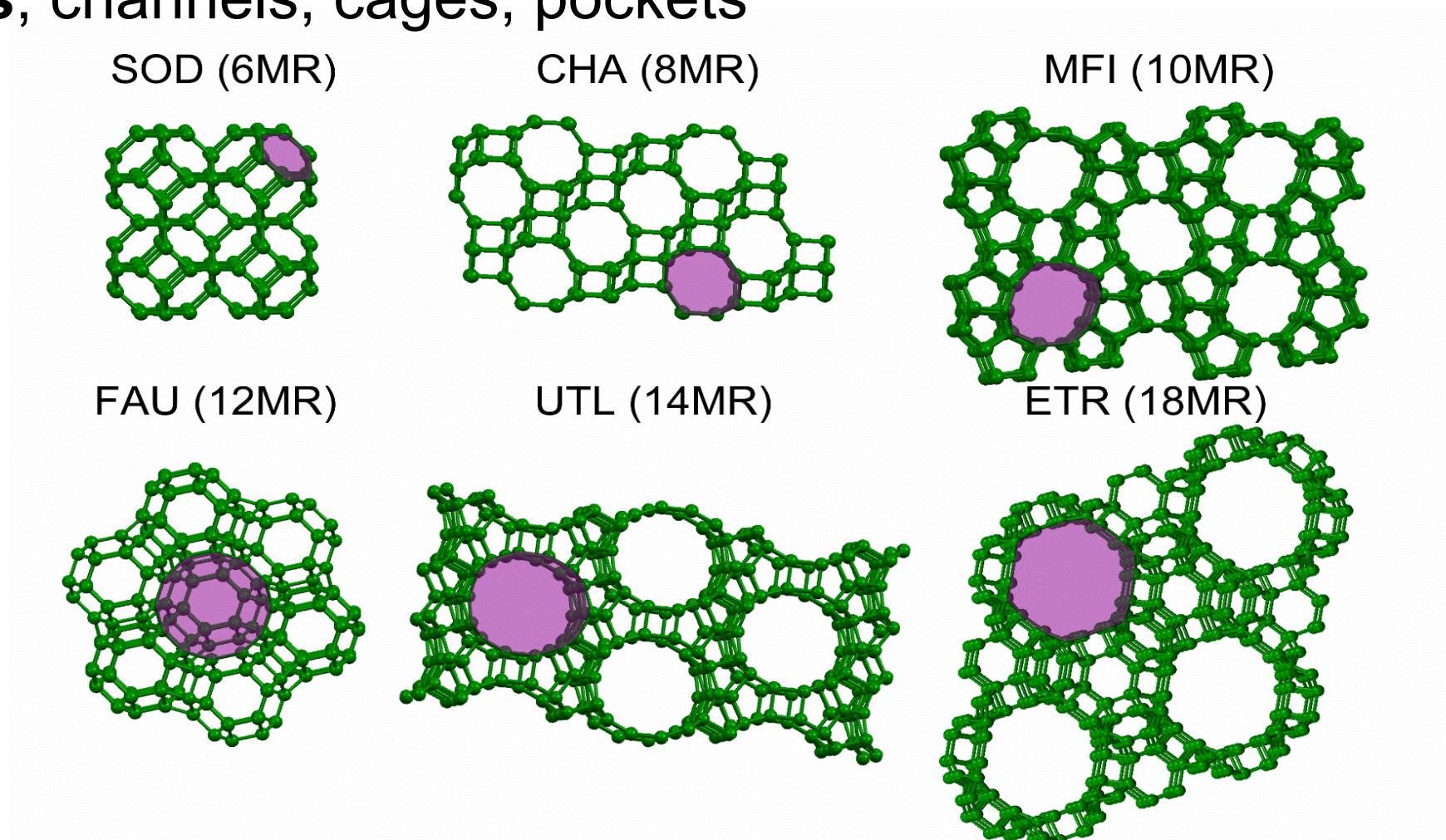
*The structures are also described on the appendix slides for this presentation*



# **Structural features of zeolites**

# Zeolite structural features

- Pores, channels, cages, pockets

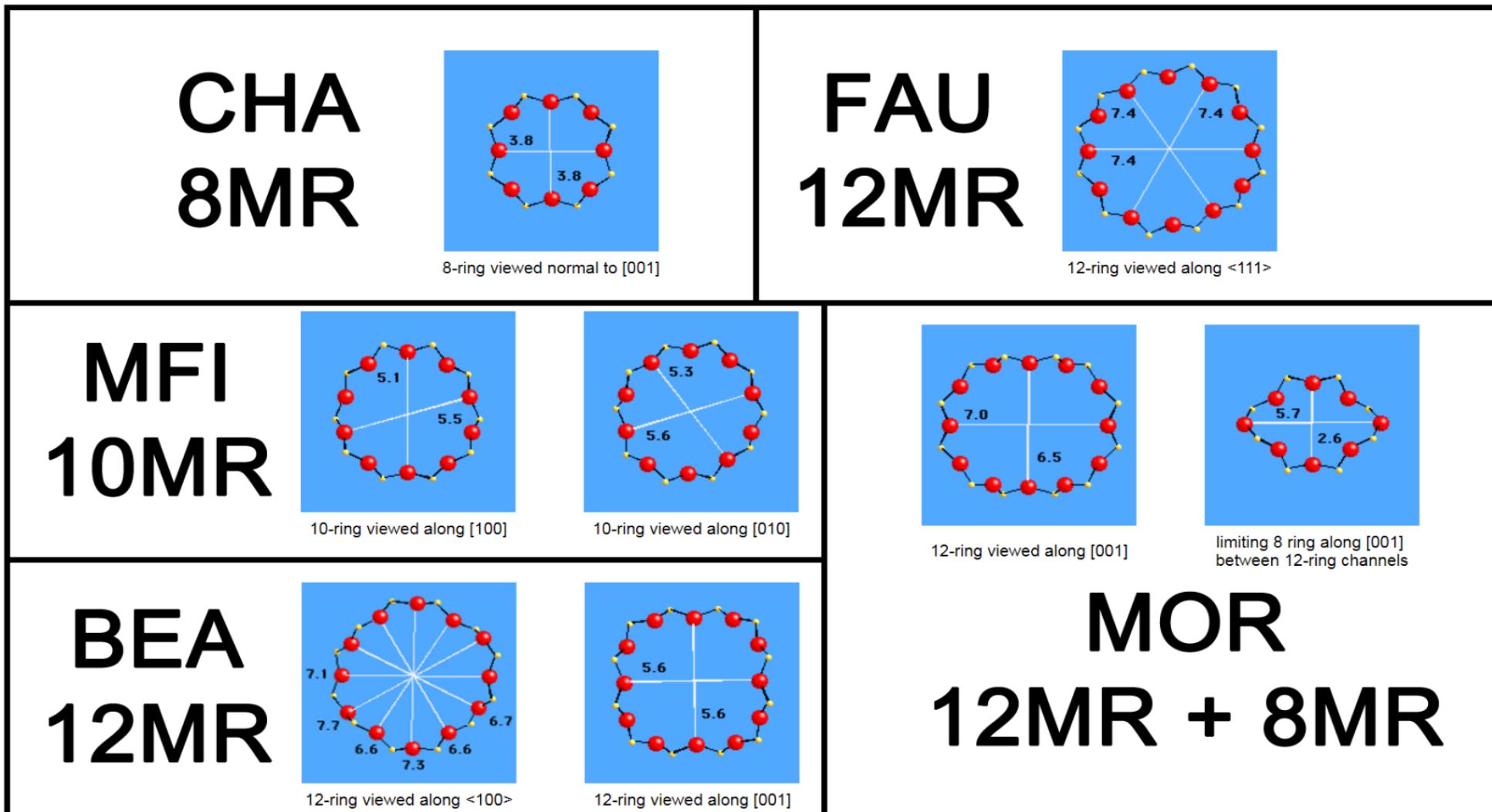


**MR** – membered ring: number of T ( $\text{Si}, \text{Al}$ ) atoms (oxygen excluded) in the pore opening

# Zeolite structural features

- Pores, channels, cages, pockets

MR – membered ring: number of T (Si,Al) atoms (oxygen excluded) in the pore opening



# Zeolite structural features

- Pores, channels, cages

Pore opening	Size, Å
6MR	2.5
8MR	3.5 – 4
10MR	5 – 6
12MR	6 – 8
14MR	8 – 9
16MR	9.5 – 10.5
18MR	11 – 12.5

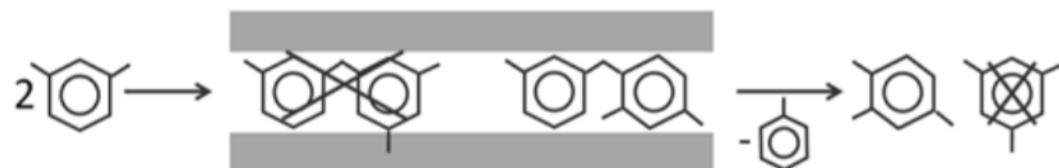
Molecule	Kinetic diameter, Å
H <sub>2</sub> O	2.65
CO <sub>2</sub>	3.3
CH <sub>4</sub>	3.8
C <sub>2</sub> H <sub>6</sub>	3.9
n-C <sub>6</sub> H <sub>14</sub>	4.3
C <sub>6</sub> H <sub>6</sub>	5.85
o-xylene/p-xylene	6.8/5.9

Pore opening size defines the molecular sieving effect

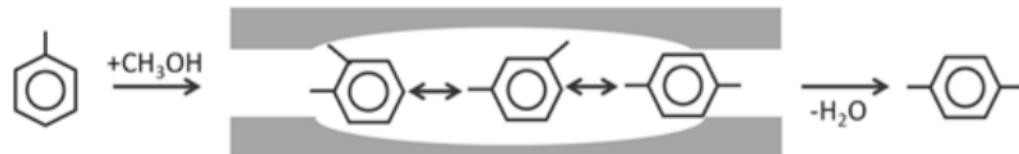
# Shape selectivity (molecular sieving)



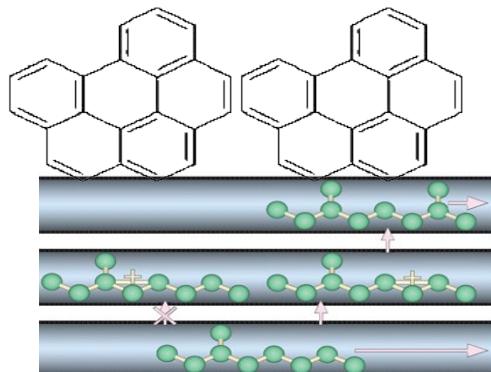
**Reactant selectivity**



**Transition state selectivity**



**Product selectivity**



**Preventing coke formation  
in micropores**

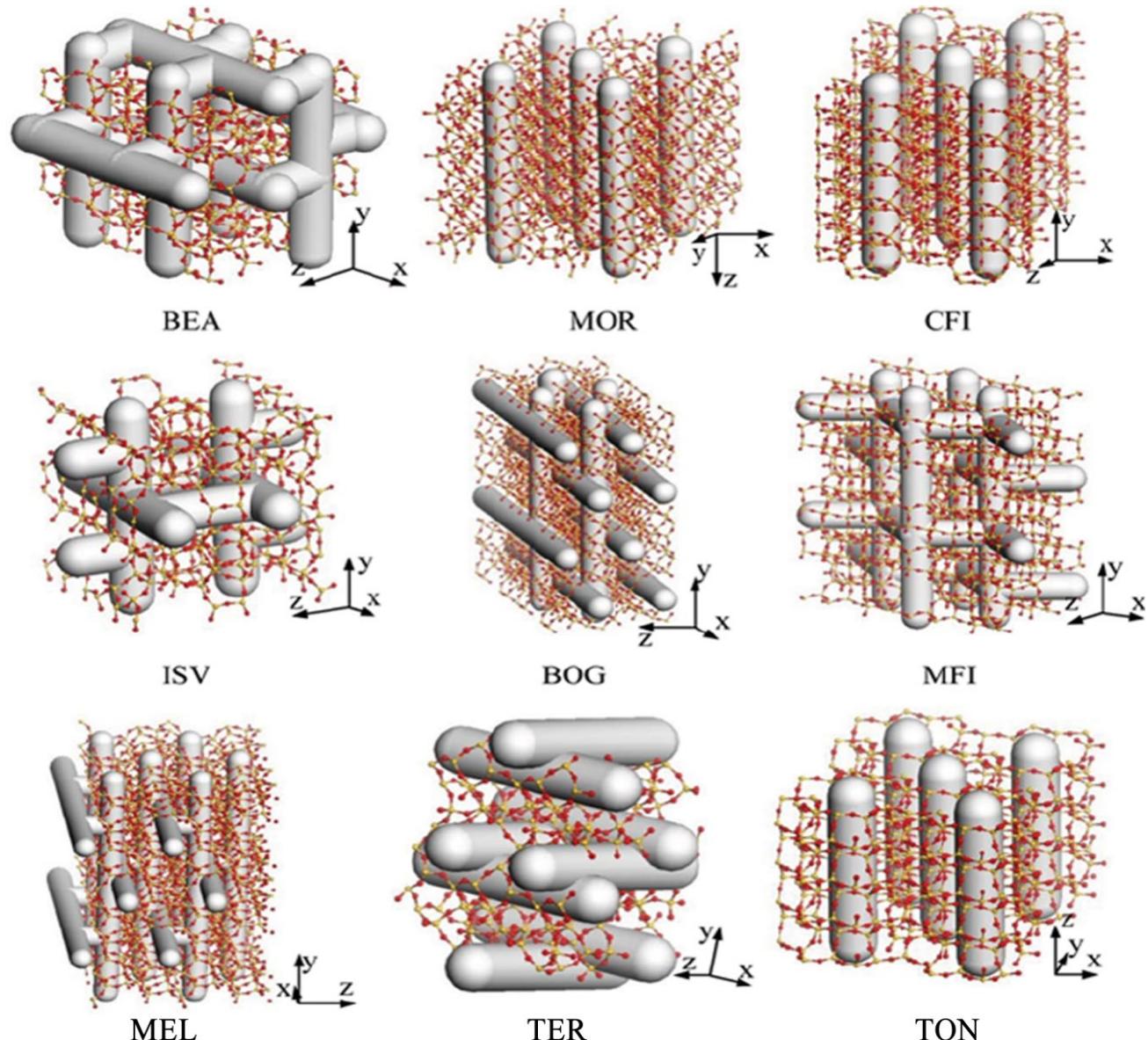
# Zeolite structural features

- Pores, **channels**, cages

Only >6 MR channels allow diffusion

0D, 1D, 2D, 3D zeolite structures based on number of **connected** channel directions

Dimensionality and connectivity of channels governs diffusion properties

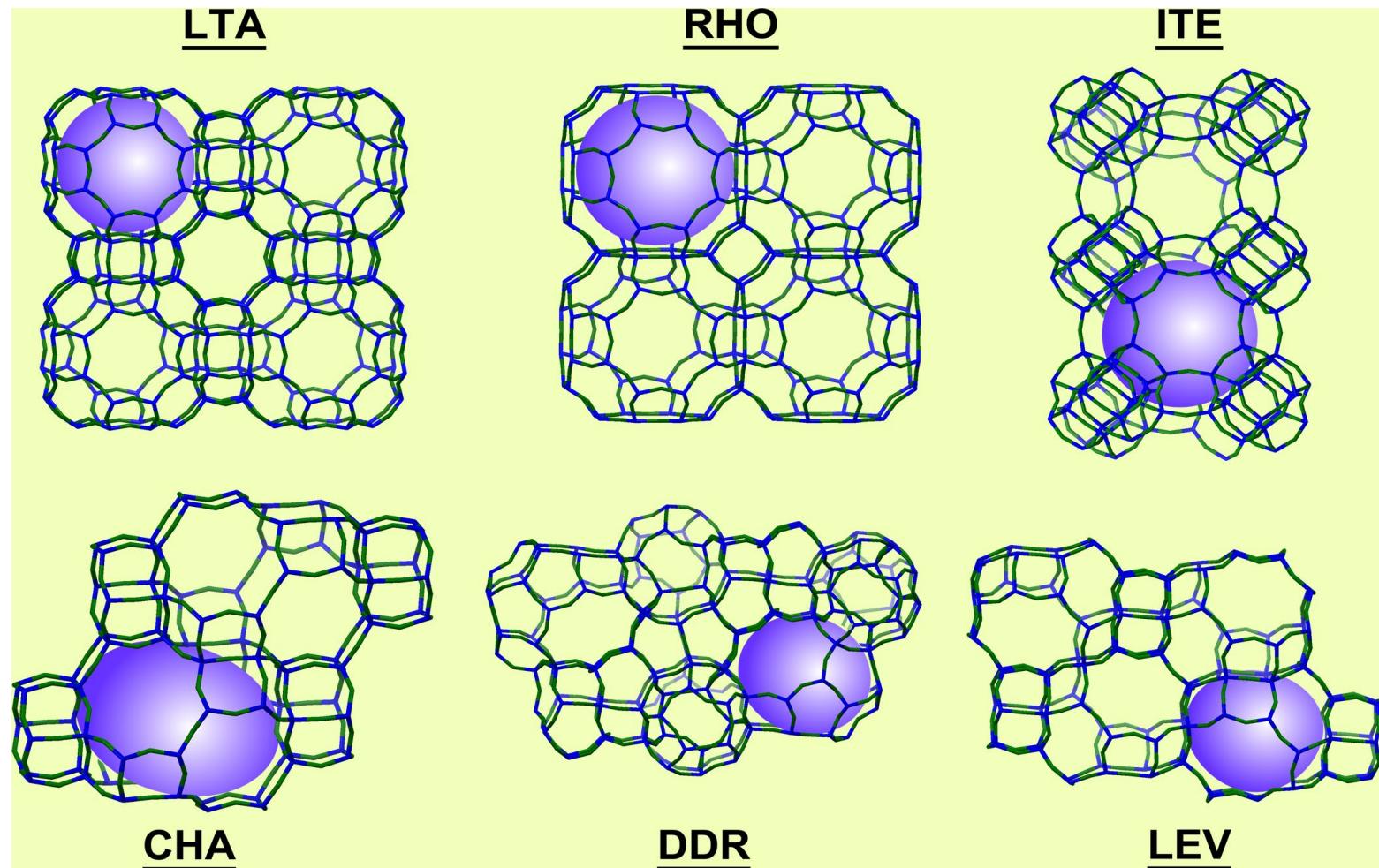


# Zeolite structural features

- Pores, channels, **cages**

Cages of different dimensions (0.8 – 2 nm), accessibility and connectivity

Cages of proper geometry allow stabilization of otherwise unstable intermediates



# **Synthesis of zeolites**

# Synthesis of zeolites

## Hydrothermal synthesis

- **Silicon** source (Cabosil, waterglass =  $\text{Na}_2\text{SiO}_3$ , alkoxy silanes)
- **Aluminium** source (aluminium sulphate,  $\text{AlOOH}$ , sodium aluminate)
- **Base** ( $\text{pH} \sim 12$ ,  $\text{NaOH}$ ,  $\text{KOH}$ , alkylammonium hydroxides), mineralizing action (catalyzing condensation/hydrolysis reactions)
- **Template (structure-directing agent SDA)**: organic cations, hydrated inorganic cations provides scaffold for porous aluminosilicates
- **Temperature**: 50 – 200 °C (typically 150°C)
- **Time**: 1 h – 1 year (typically few days)

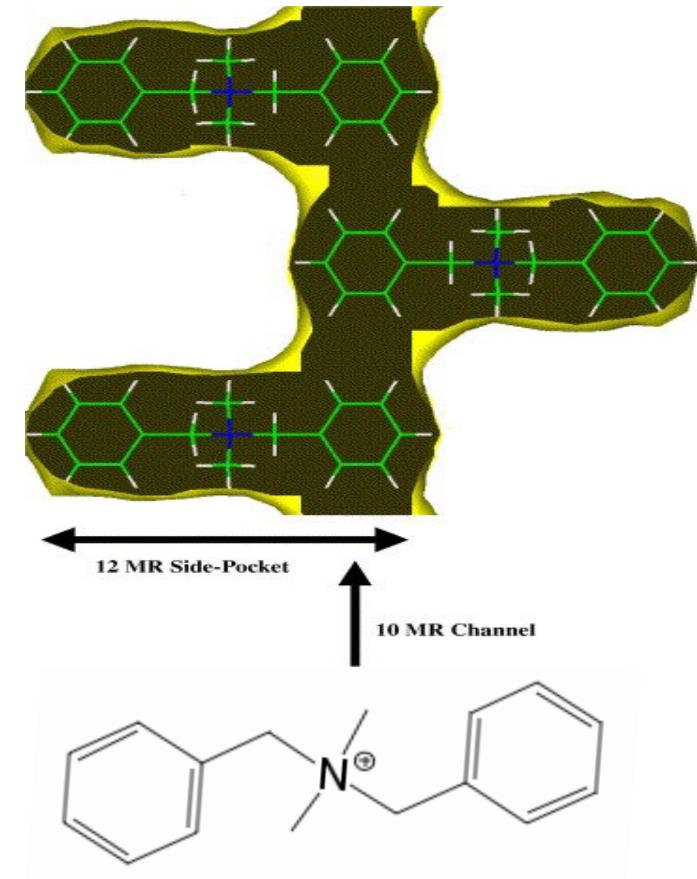


# Templates (SDA) for zeolite synthesis

## Bulky organic molecules (typically ammonium cations)

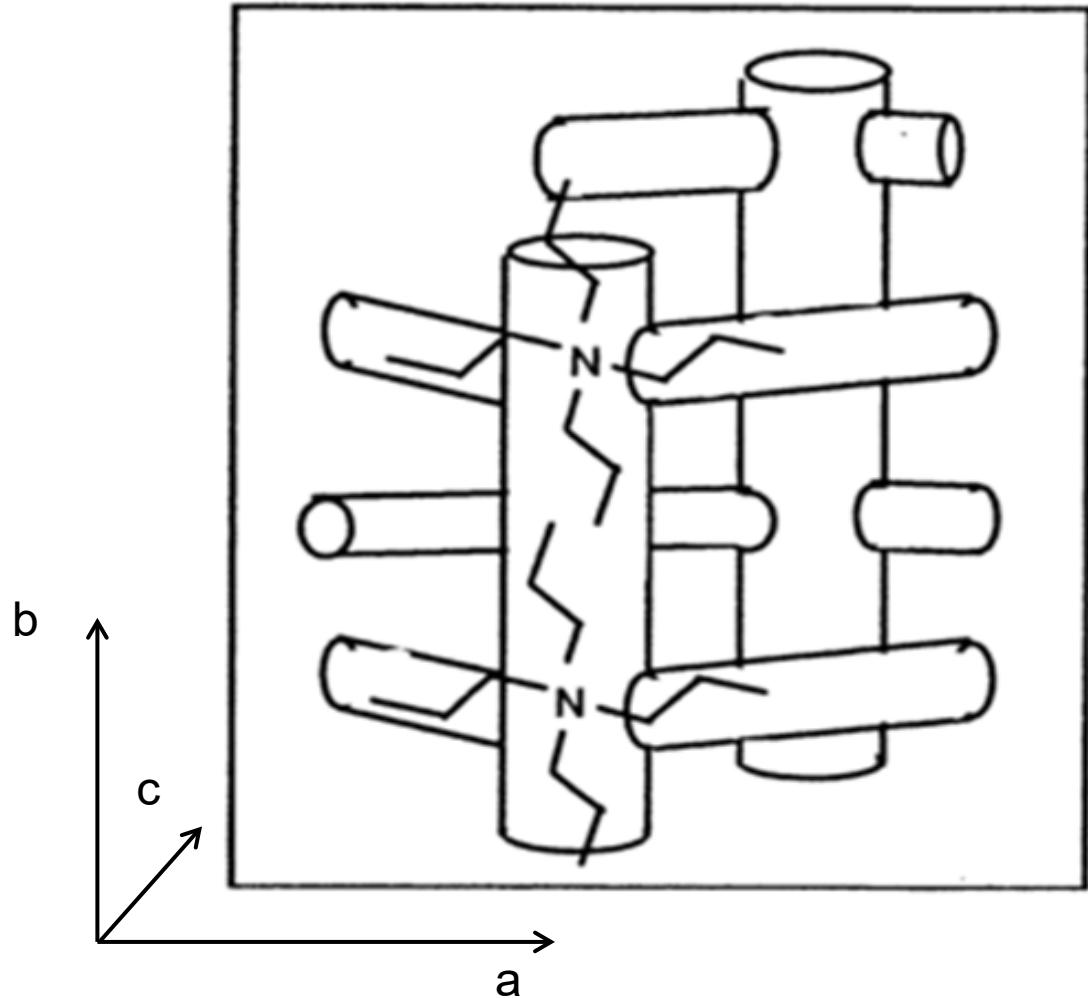
- Match the zeolite features in geometry (**host-guest interactions**)
- Provide **electrostatic stabilization** (presence of Al and silanol defects negatively charges silicate frameworks)
- Presence of **template** enhances the crystallization rate and determines the selectivity to a desired zeolite structure
- Often use of different **ammonium cations** under otherwise the same conditions results in completely different zeolite structures
- Zeolites are **kinetic products** (thermodynamic product – quartz)!

*Dibenzylidemethylammonium ions in EU-1 (EUO) channel system*

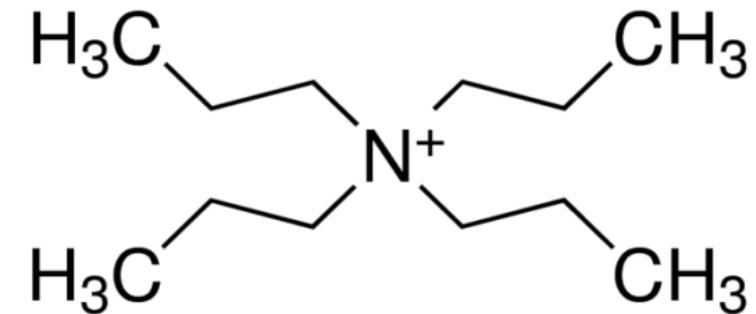


# Templates (SDA) for zeolite synthesis

MFI (ZSM-5)

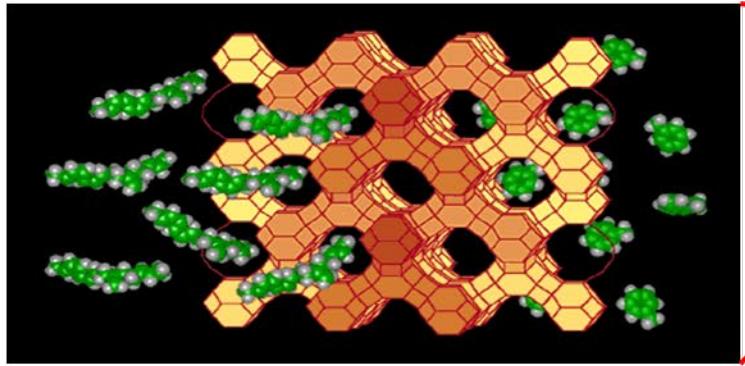


*TetraPropylAmmonium (TPA)*



- TPA occupies the intersection of straight and sinusoidal channels of MFI
- Exactly one TPA molecule per intersection in as-synthesized MFI

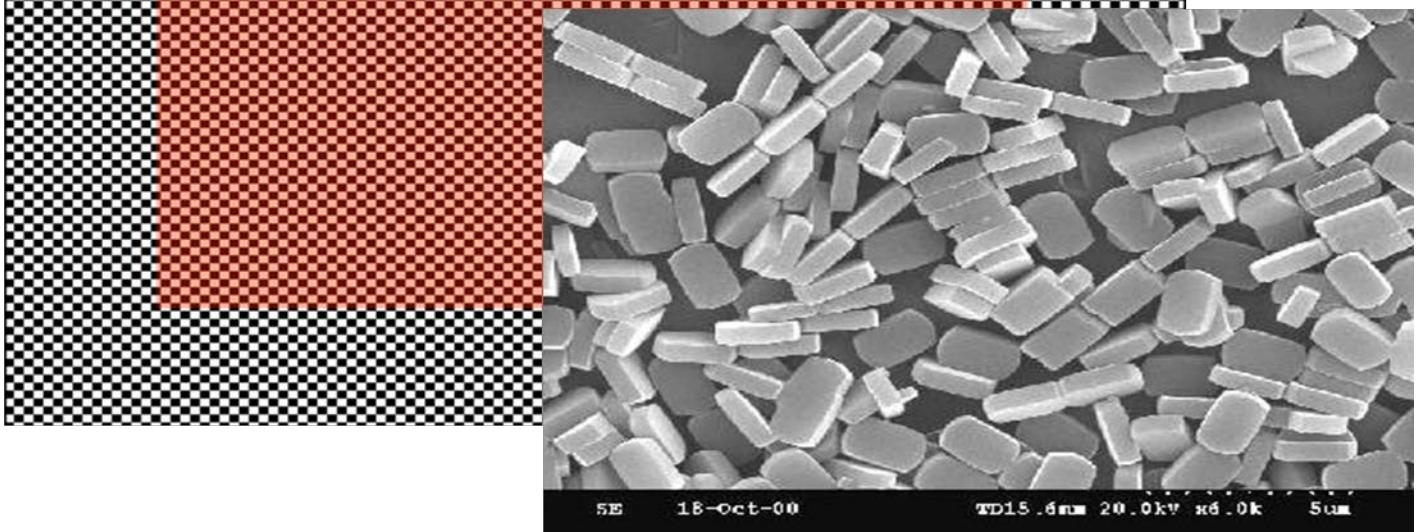
# Diffusion limitations



For large molecules:  
pores are too narrow



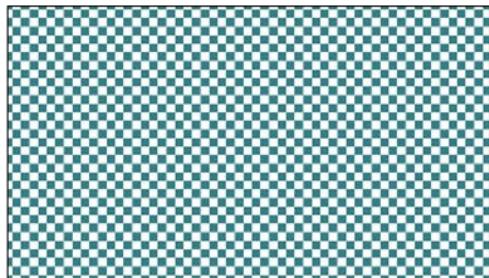
Even for smaller molecules:  
due to slow diffusion, outer zone of crystal is  
mainly utilized in catalytic reactions  
→ low catalytic activity &  
coke formation near the external surface  
→ fast deactivation



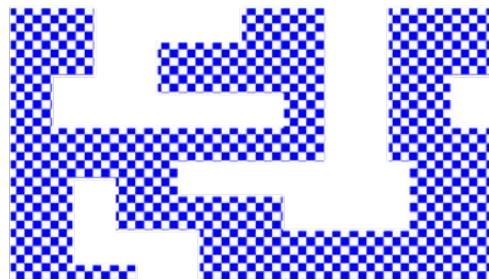
# Hierarchically porous zeolites: top-down approach

Dealumination of FAU zeolite

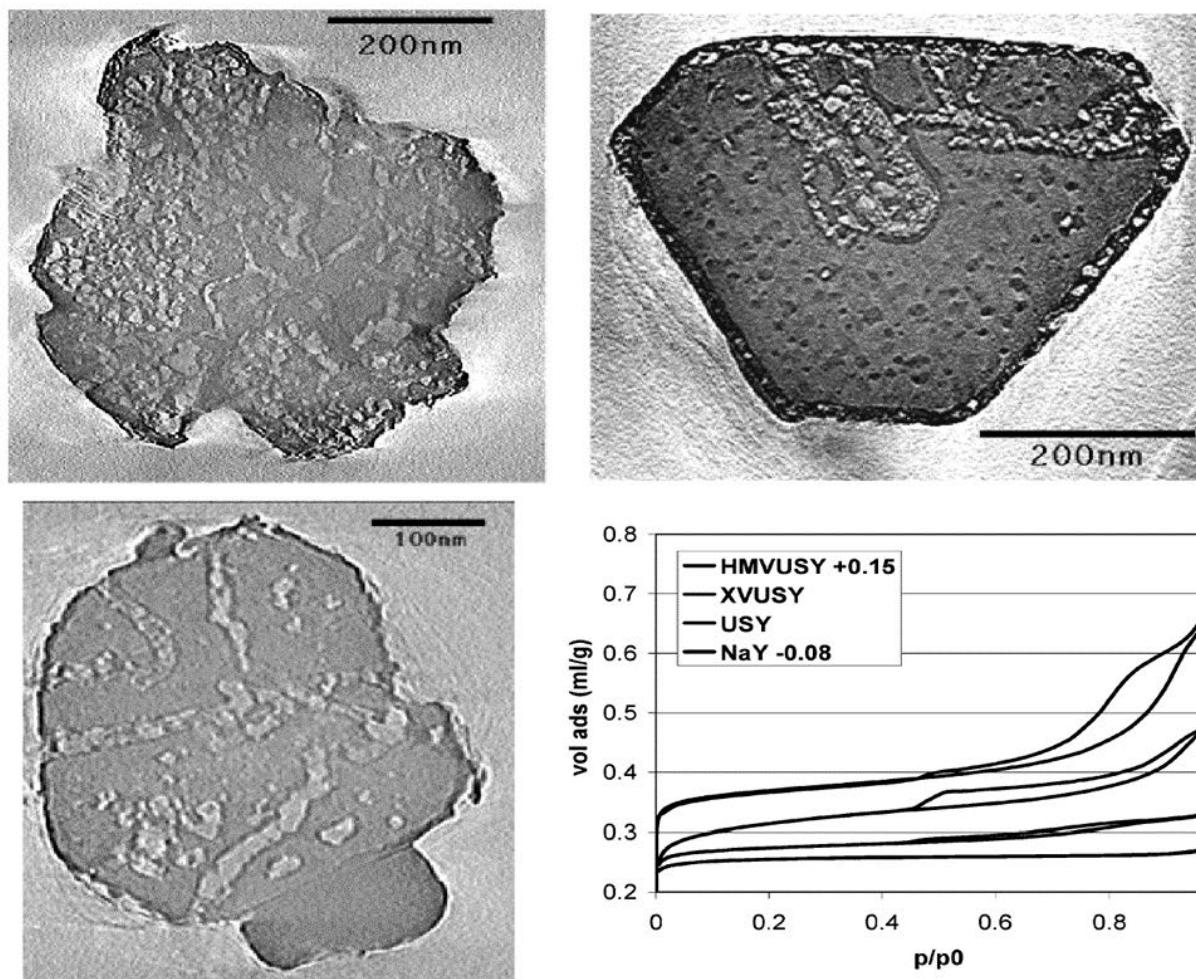
Bulk crystal



HCl treatment

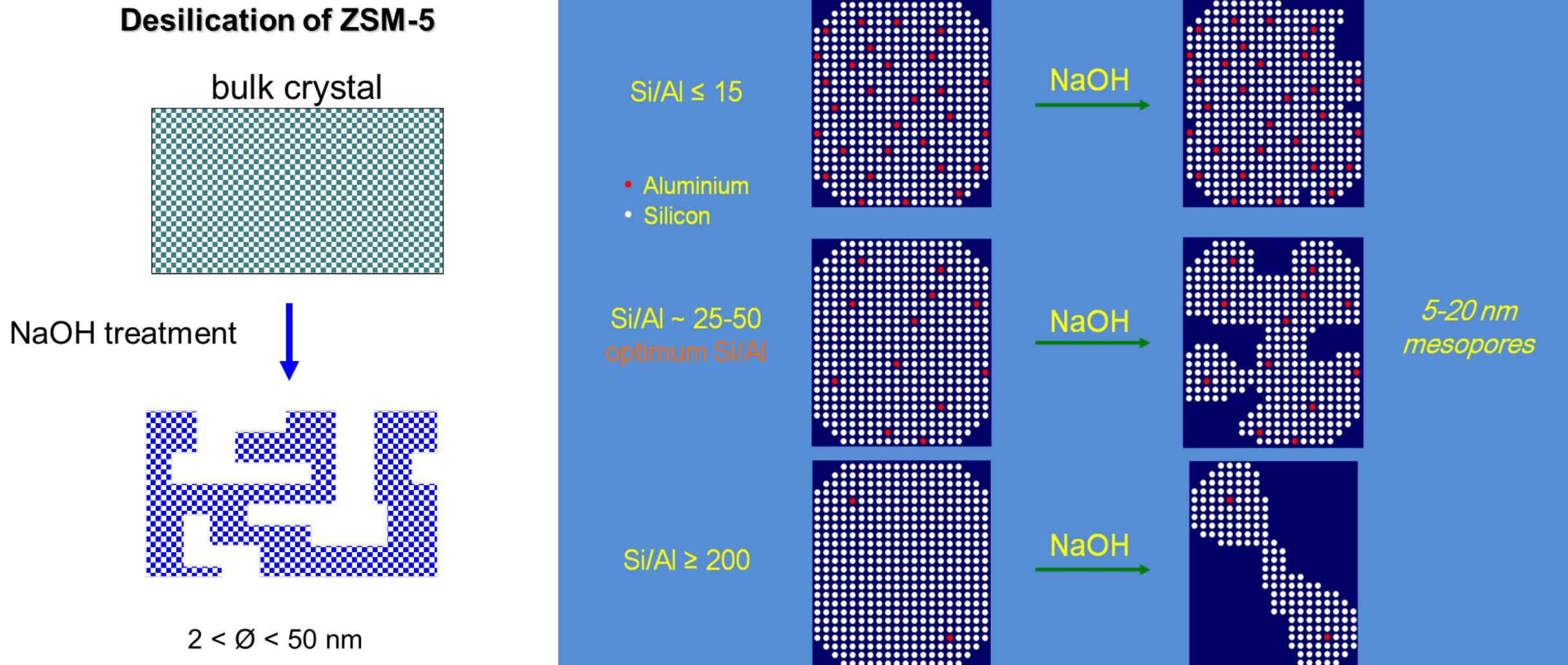


$2 < \emptyset < 50 \text{ nm}$



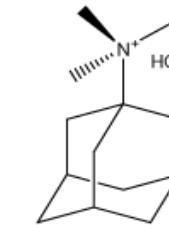
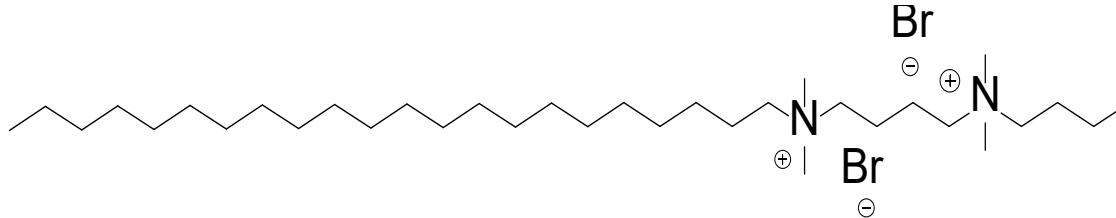
Only for low-silica zeolites

# Hierarchically porous zeolites: top-down approach



# Hierarchically porous zeolites: bottom-up approach

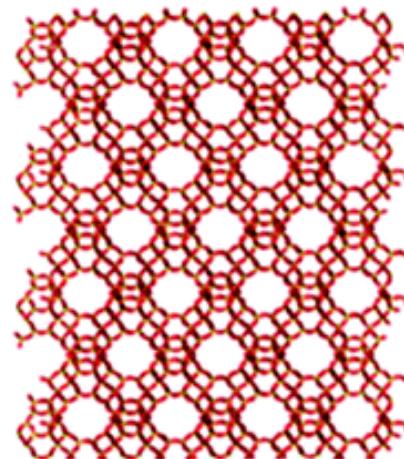
Amphiphilic surfactant  $C_{22-4-4}Br_2$  (mesoporogen)



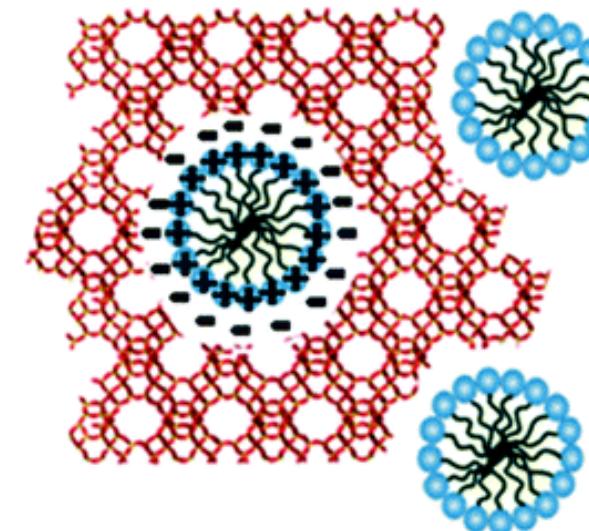
TMAdaOH (microporogen)

Large surfactant molecules interact with the growing zeolite structures and form intracrystalline micelles

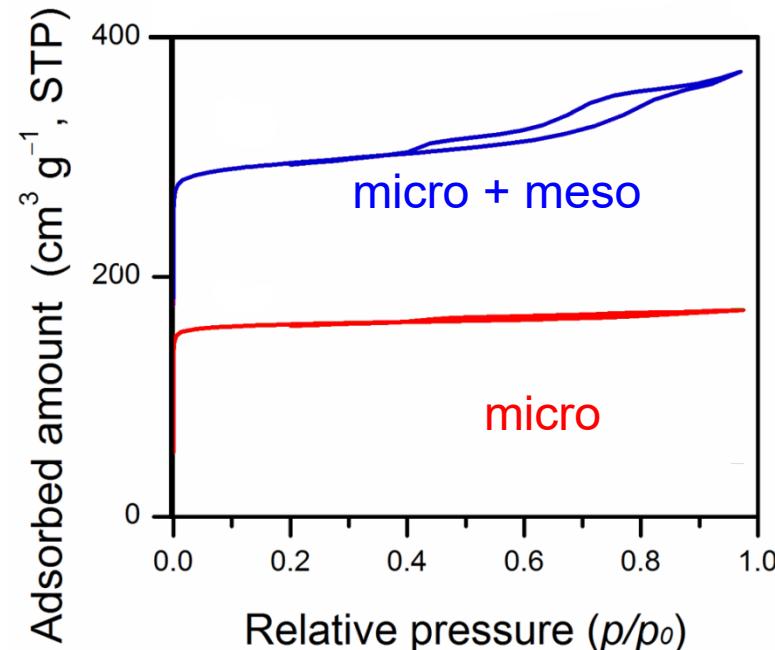
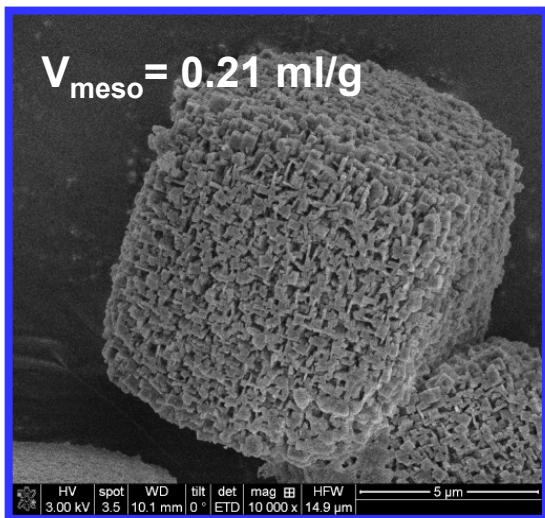
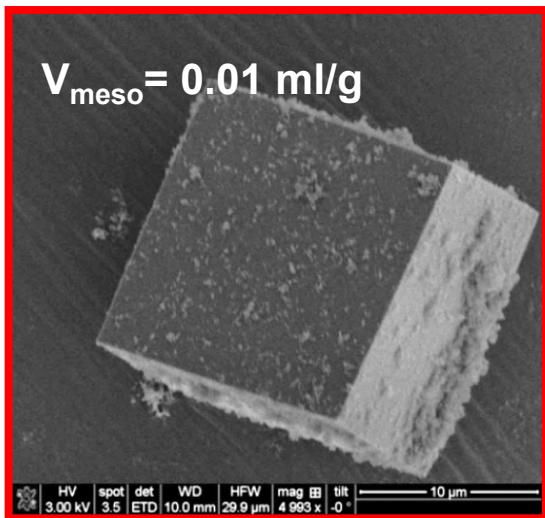
TMAdaOH



TMAdaOH +  $C_{22-4-4}Br_2$

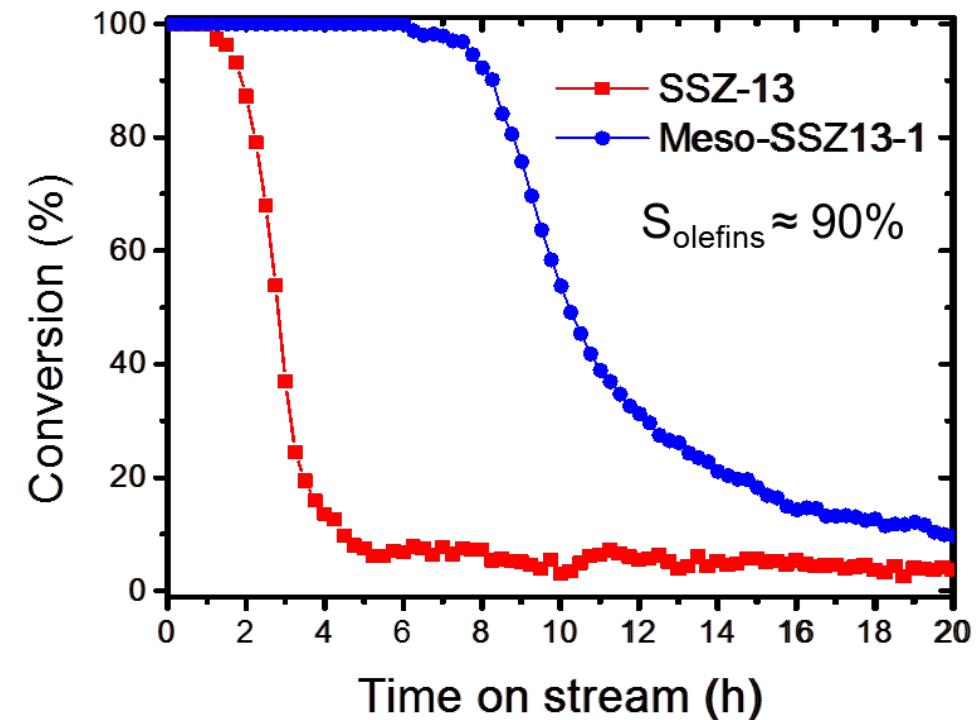


# Hierarchically porous zeolites: bottom-up approach



Mesopores make the difference for methanol-to-hydrocarbons (MTH) stability

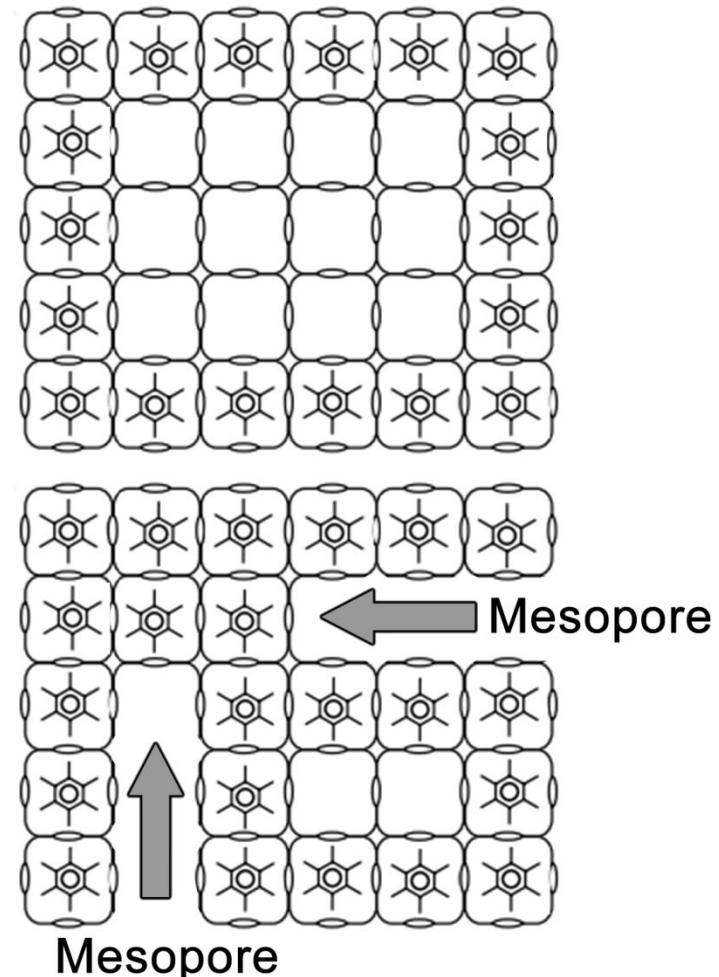
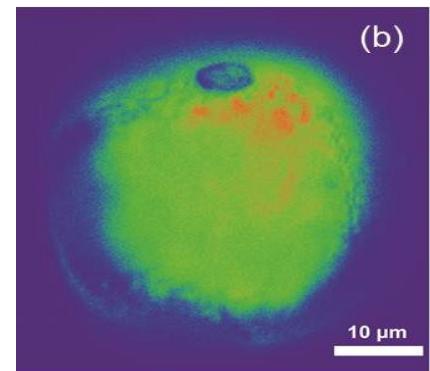
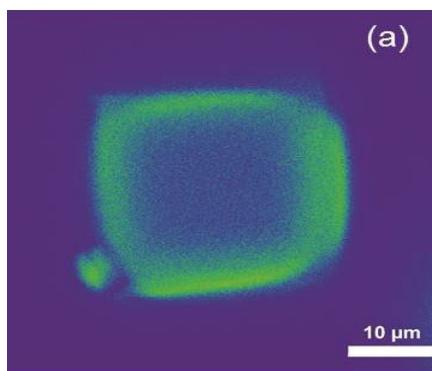
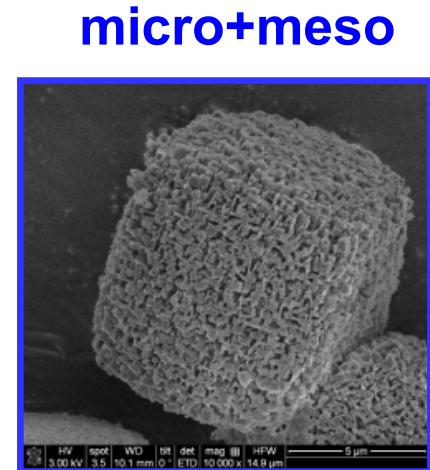
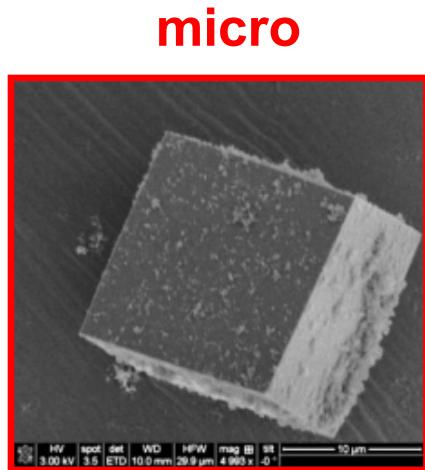
The same acidity, crystallinity, XRD structure but different textural properties



# Hierarchically porous zeolites: bottom-up approach

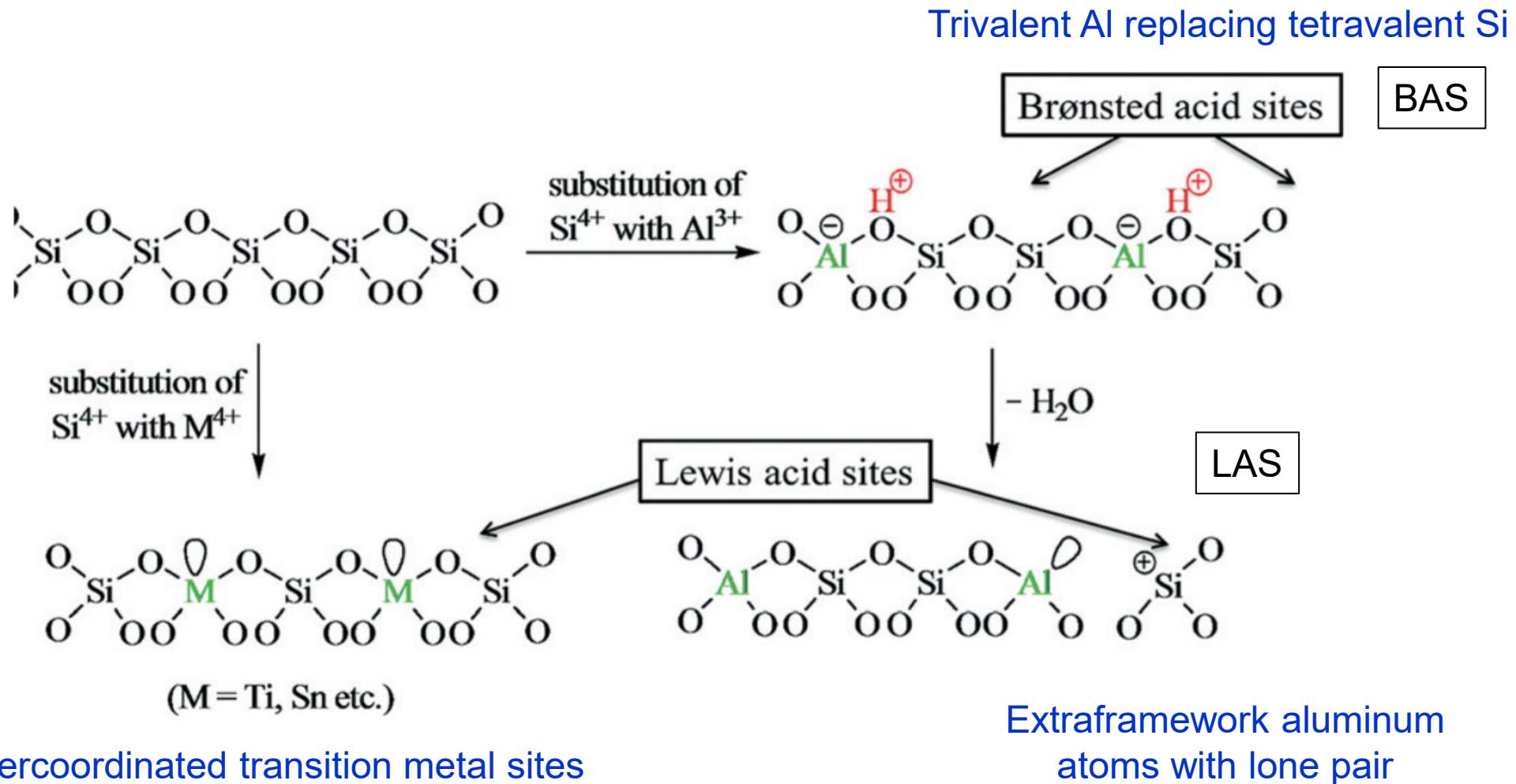
Fluorescence microscopy analysis of reaction intermediates

Improved **crystal utilization** degree



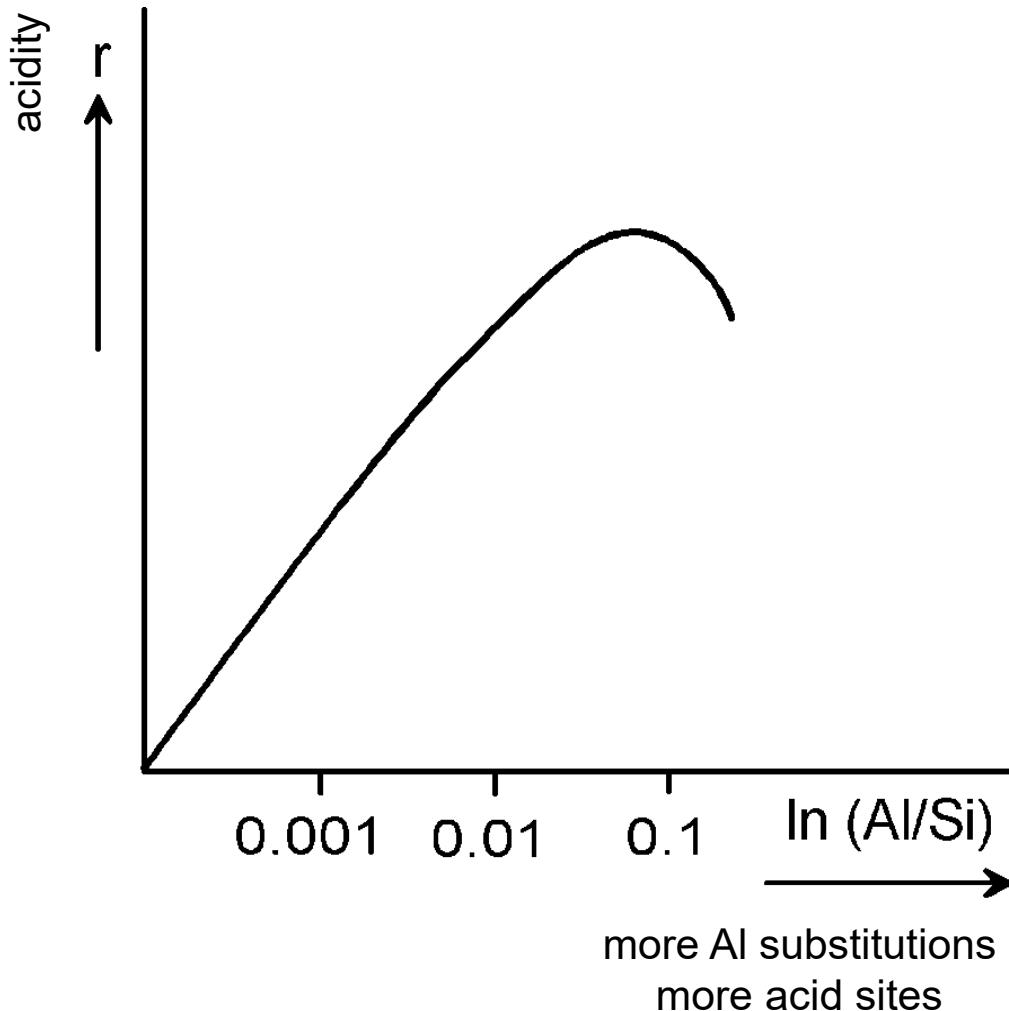
# **Acidity in zeolites**

# Brønsted and Lewis acidity



Undercoordinated transition metal sites

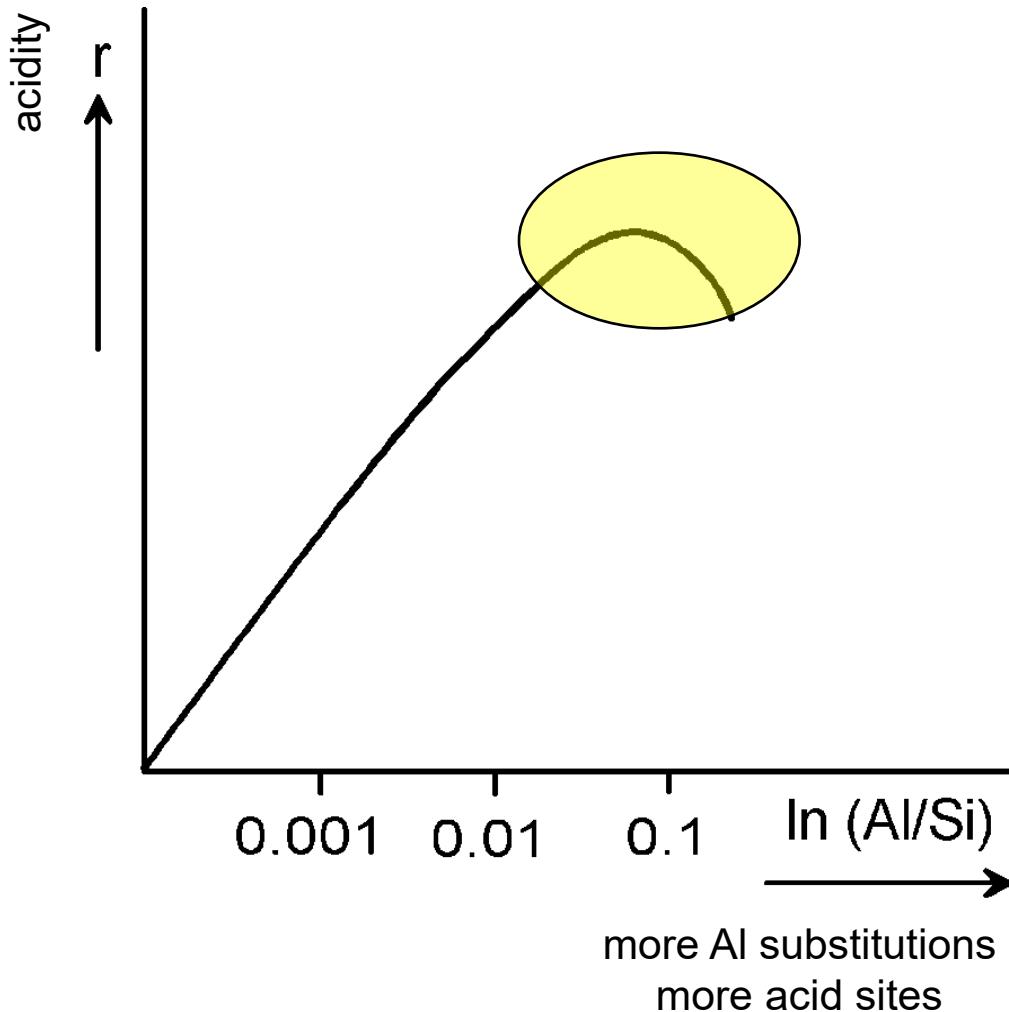
# Effect of Al content of zeolite on Brønsted acidity



## Löwenstein's rule:

- Whenever two **tetrahedra** are linked by **one oxygen bridge**, the center of only one of them can be occupied by **aluminium**; the other center must be occupied by silicon or by another small ion of electrovalence 4 or more (e.g. P)
- Whenever two **aluminium ions** are neighbours to the same oxygen anion, at least one of them must have a **coordination number larger than 4** (i.e. 5 or 6) towards oxygen – the aluminium ion that has a coordination number larger than 4 is not considered part of the zeolite framework and is called '**extraframework**'
- Limits the Al content of framework to  $\text{Si/Al} = 1 - \infty$

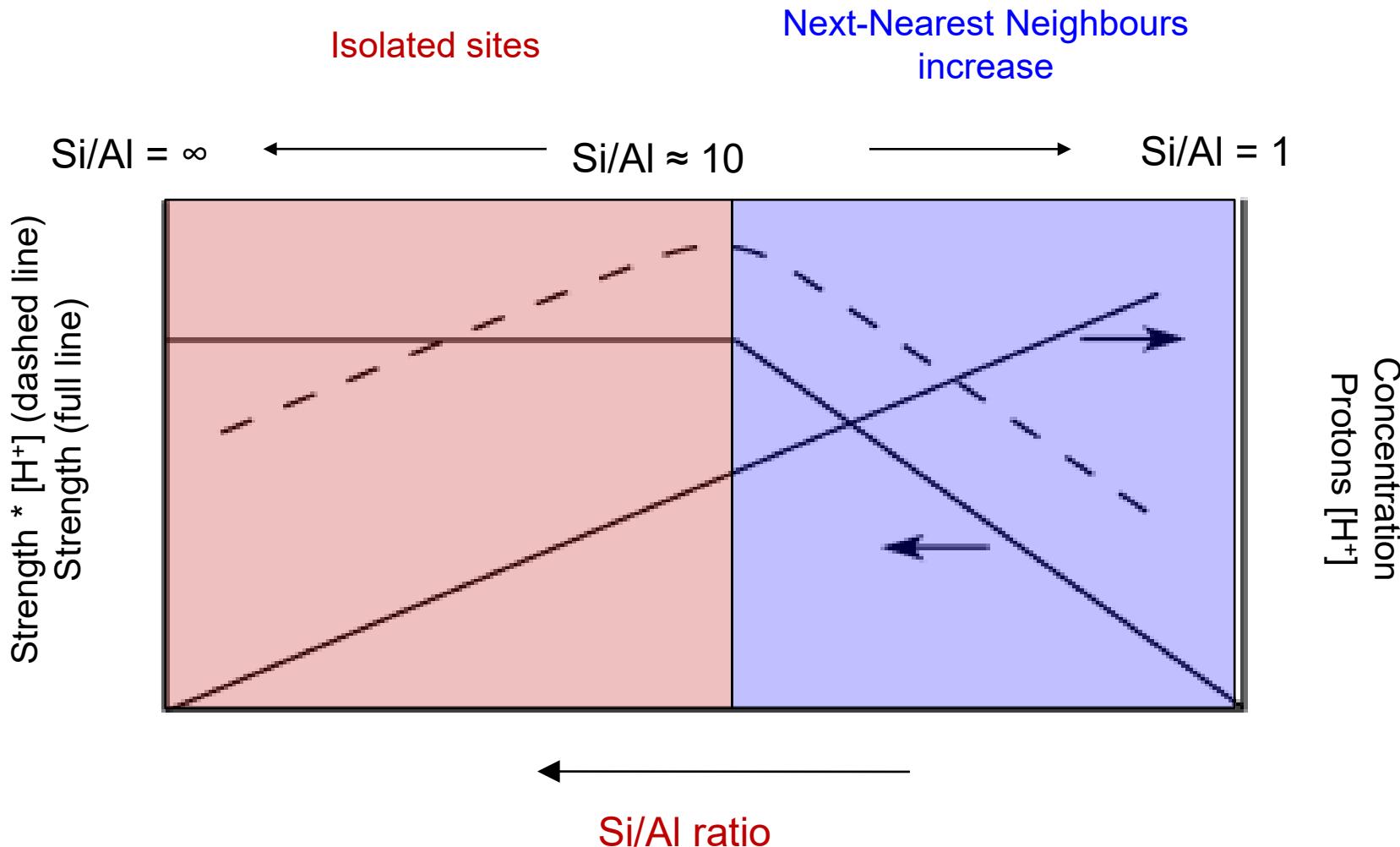
# Effect of Al content of zeolite



## Next-Nearest Neighbour (NNN) model

- Presence of neighbouring Al-occupied oxygen tetrahedra limits the intrinsic acidity of acid site
- Relevant for aluminium-rich zeolite such as faujasite
  - $\text{Si/Al} < 5$  weak acid due to NNN interactions
  - $\text{Si/Al} > 5$  strong acid acid sites sufficiently diluted

# Effect of Al content of zeolite



# How to measure acidity in zeolites?

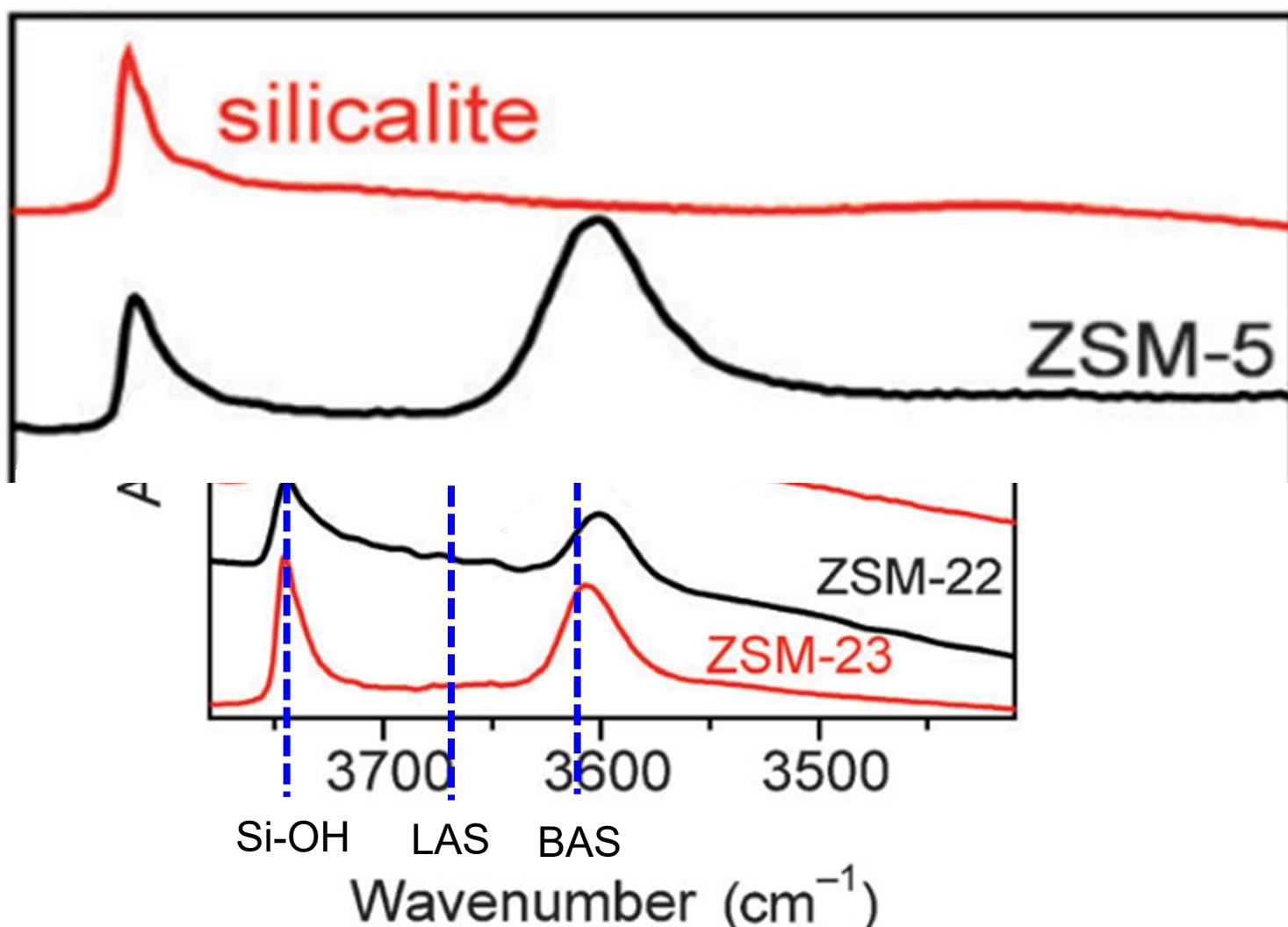
- **FTIR spectroscopy**

Direct observation of OH stretching vibrations in  $3400 - 3800 \text{ cm}^{-1}$  region

Semi-quantitative

Semi-qualitative

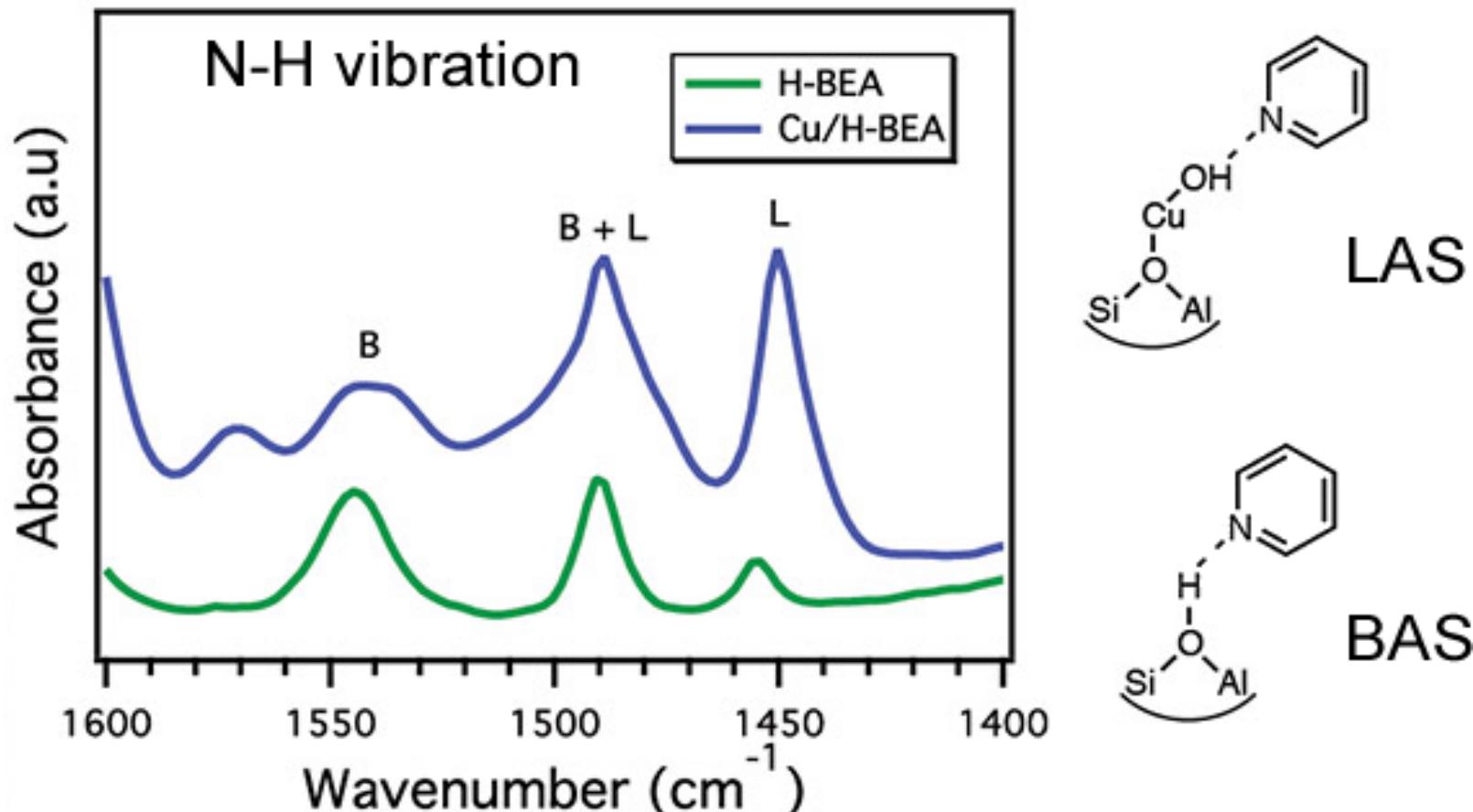
*Why silanol is observed at higher wavenumber than BAS?*



# How to measure acidity in zeolites?

- FTIR spectroscopy of adsorbed probe molecules – quantitative and qualitative

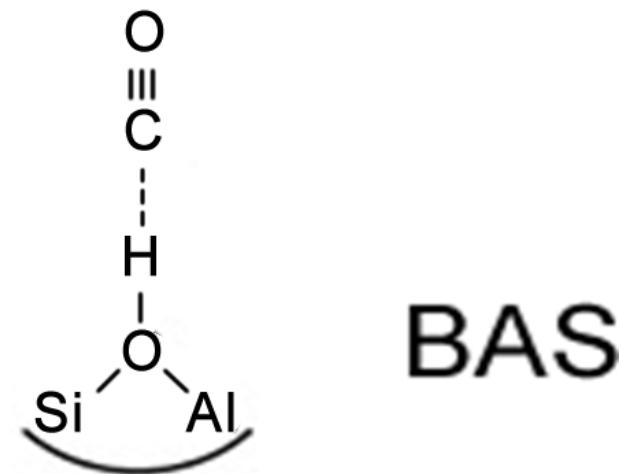
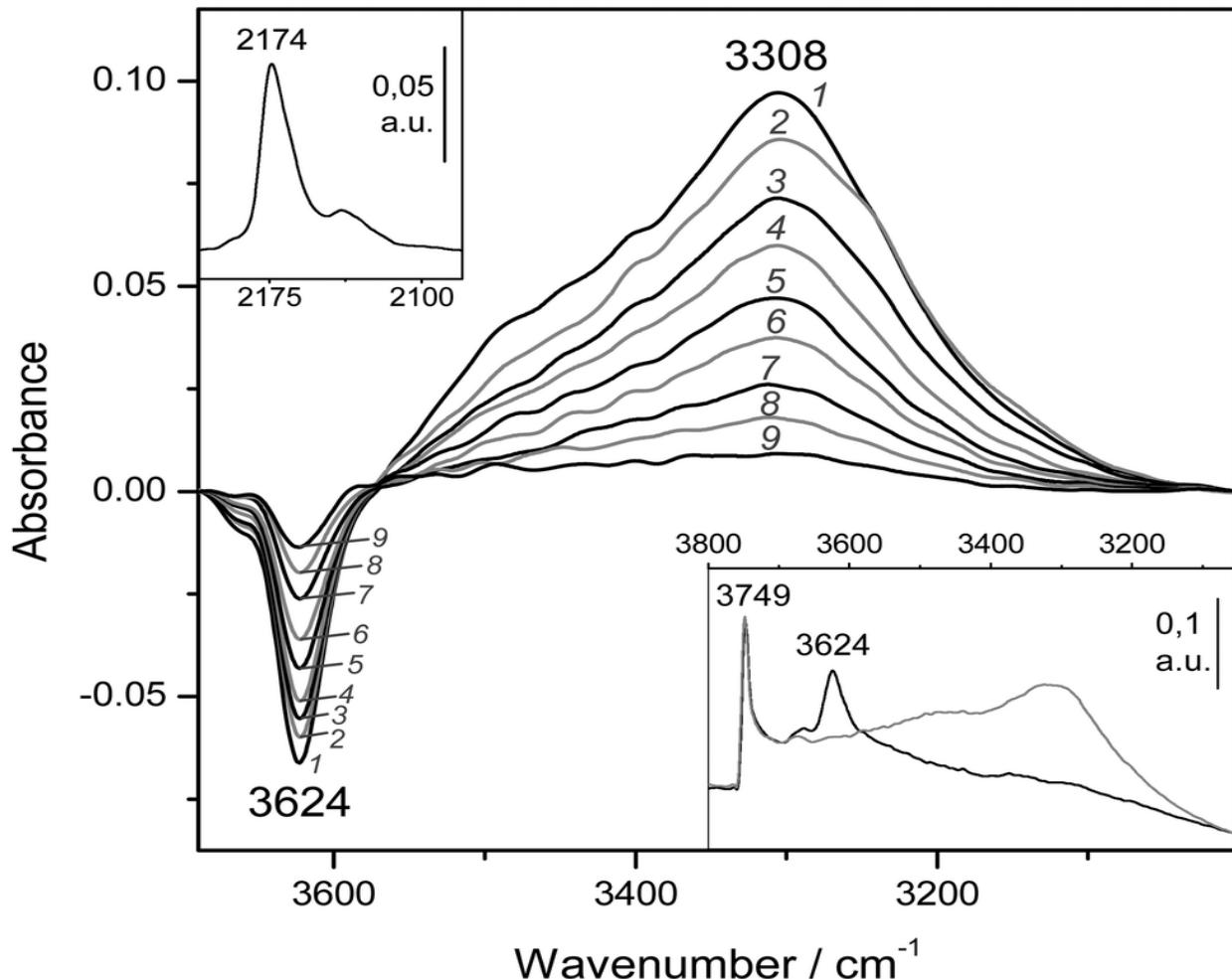
*Adsorption of pyridine (strong base)*



# How to measure acidity in zeolites?

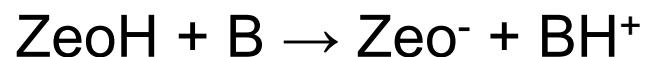
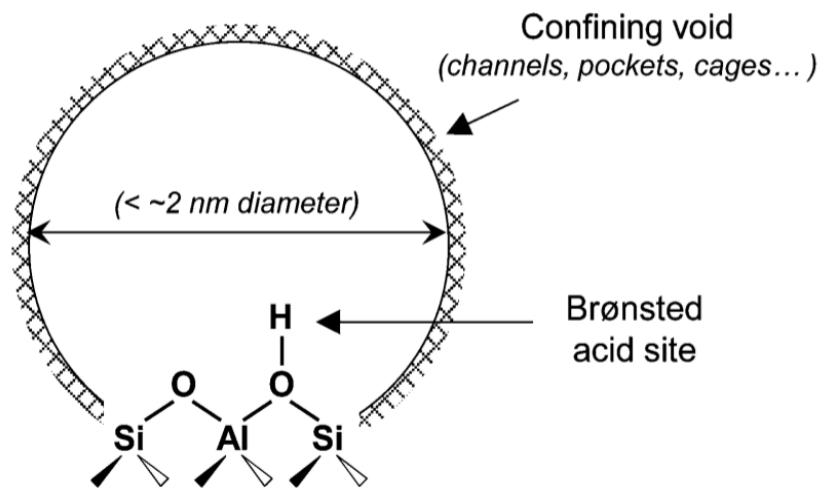
- FTIR spectroscopy of adsorbed molecules – quantitative and qualitative

*Adsorption of CO (weak base)*

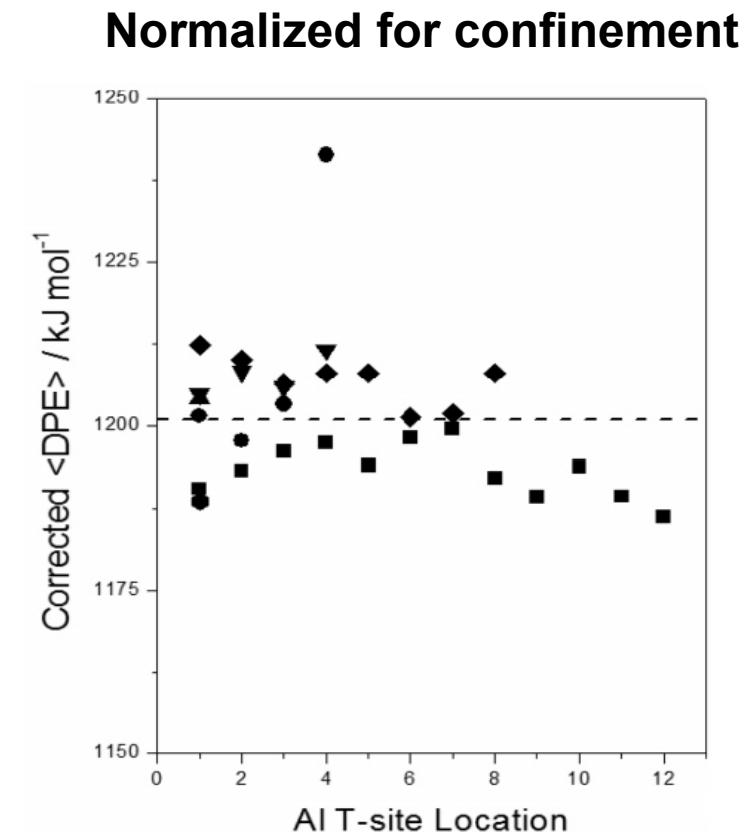
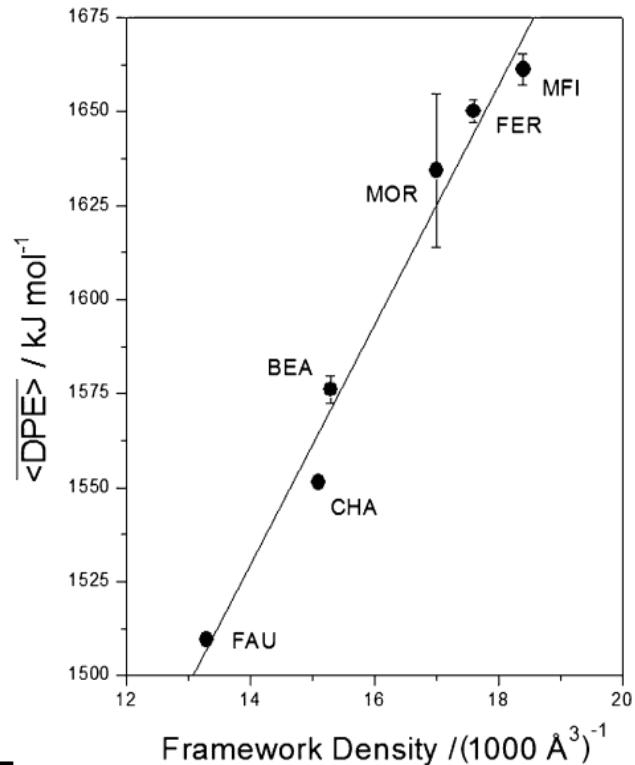


- Modulation of O-H bond vibration and position of carbonyl C-O vibrations (2100 – 2200 cm<sup>-1</sup>) shows the strength of acid sites

# Confinement effect on acidity strength



$$\text{Deprotonation Energy (DPE)} = E_{\text{Zeo}^-} + E_{\text{BH}^+} - E_{\text{ZeoH}} - E_{\text{B}}$$

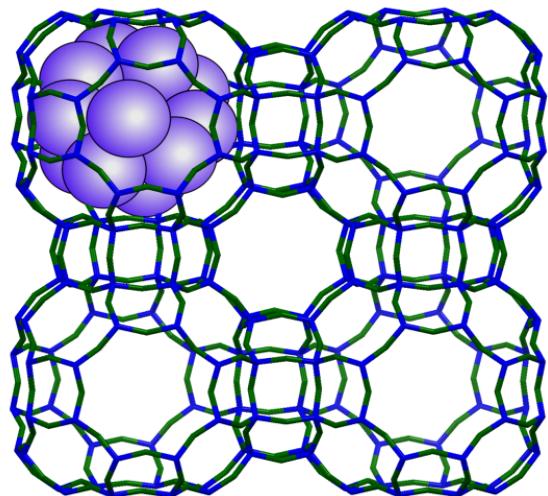


Acid sites  $[\text{Si}(\text{OH})\text{Al}]$  are chemically the same  
Confinement stabilizes the protonated base!

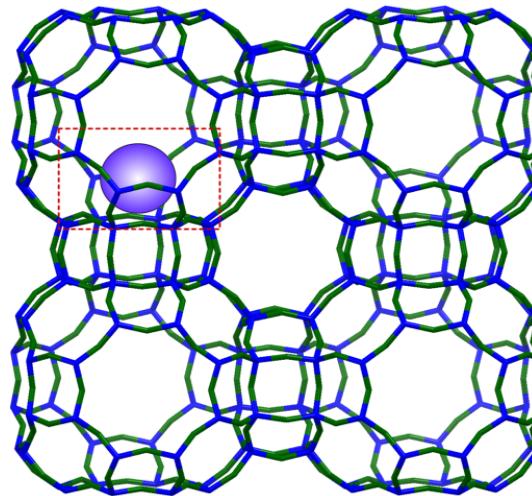
# **Catalysis with Zeolites**

# Stabilization of metal sites

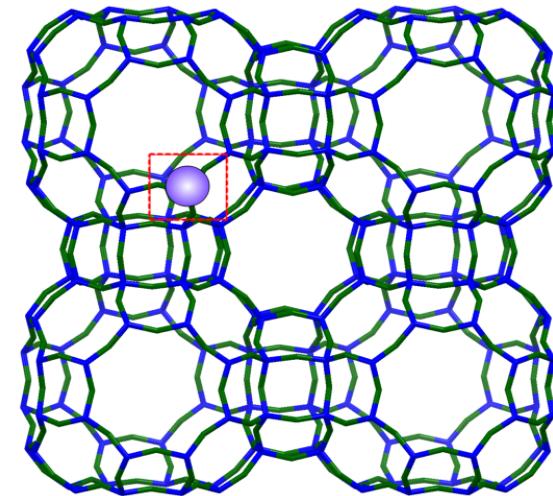
Isolated clusters  
(nanoparticles)



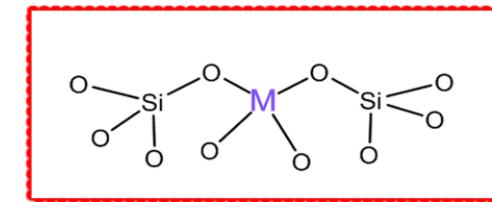
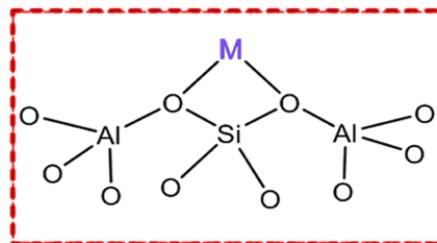
Ion-exchanged cations



Single atoms  
incorporated in the framework



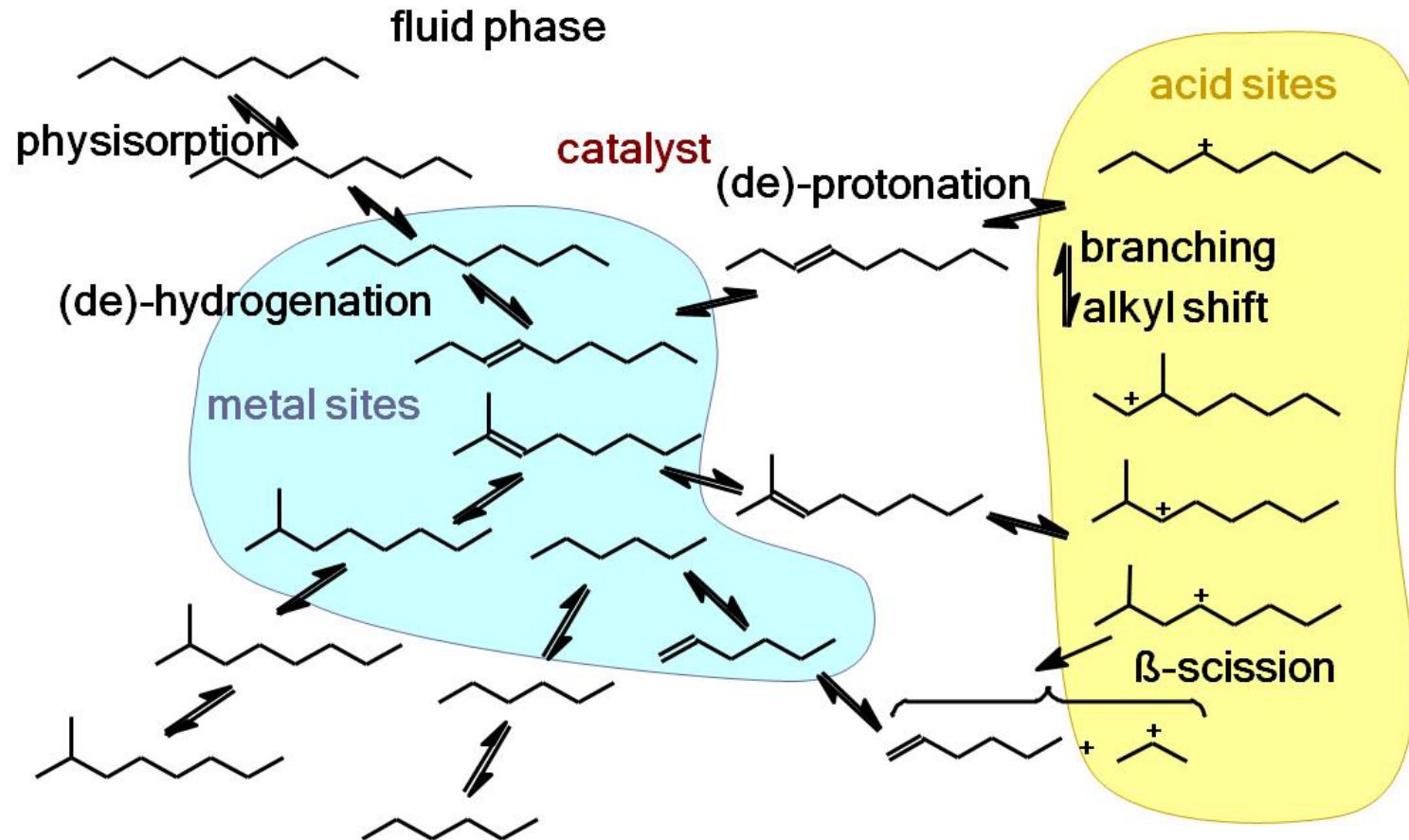
- Chemical stabilization
- Mechanical stabilization
- Shape selective environment
- Combination of metal and acidic catalysis



# Conversion of hydrocarbons

## Transition metal sites:

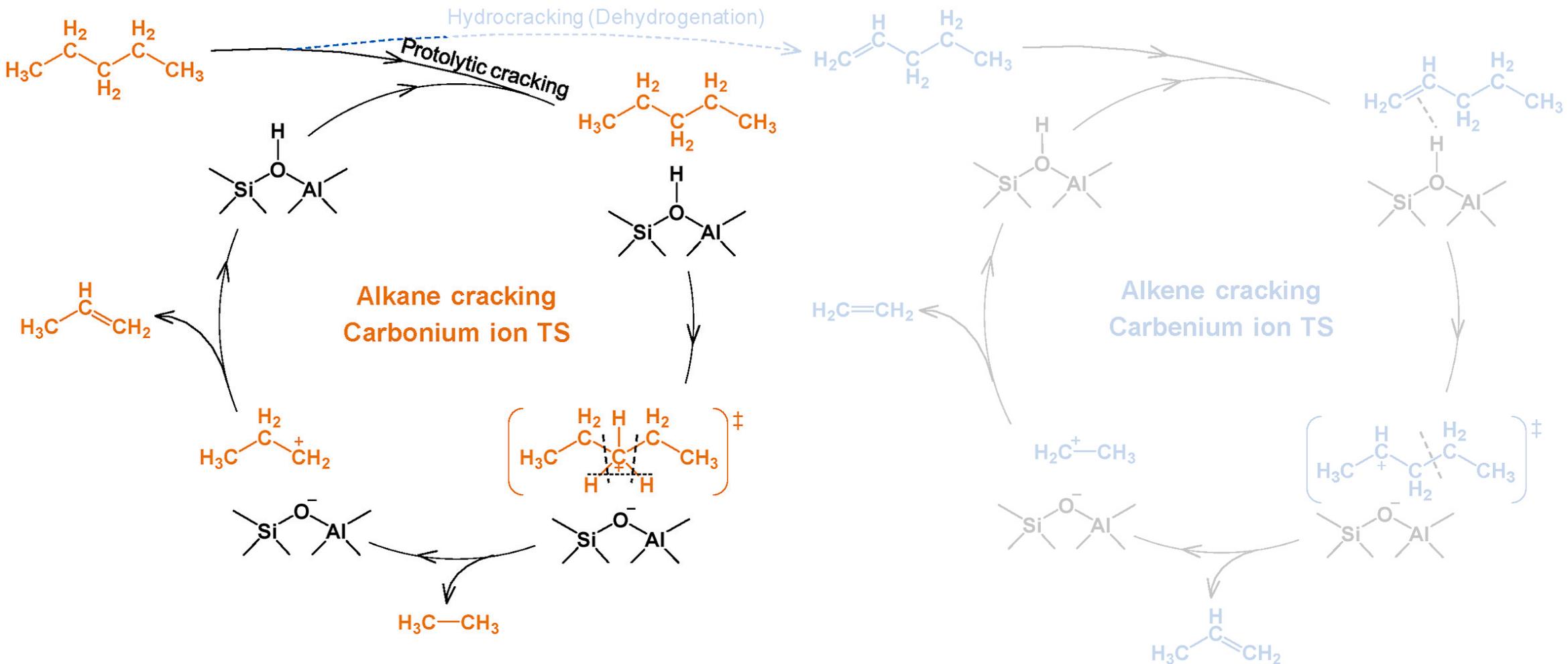
Oxidation  
Hydrogenation  
Dehydrogenation  
C-C coupling  
...



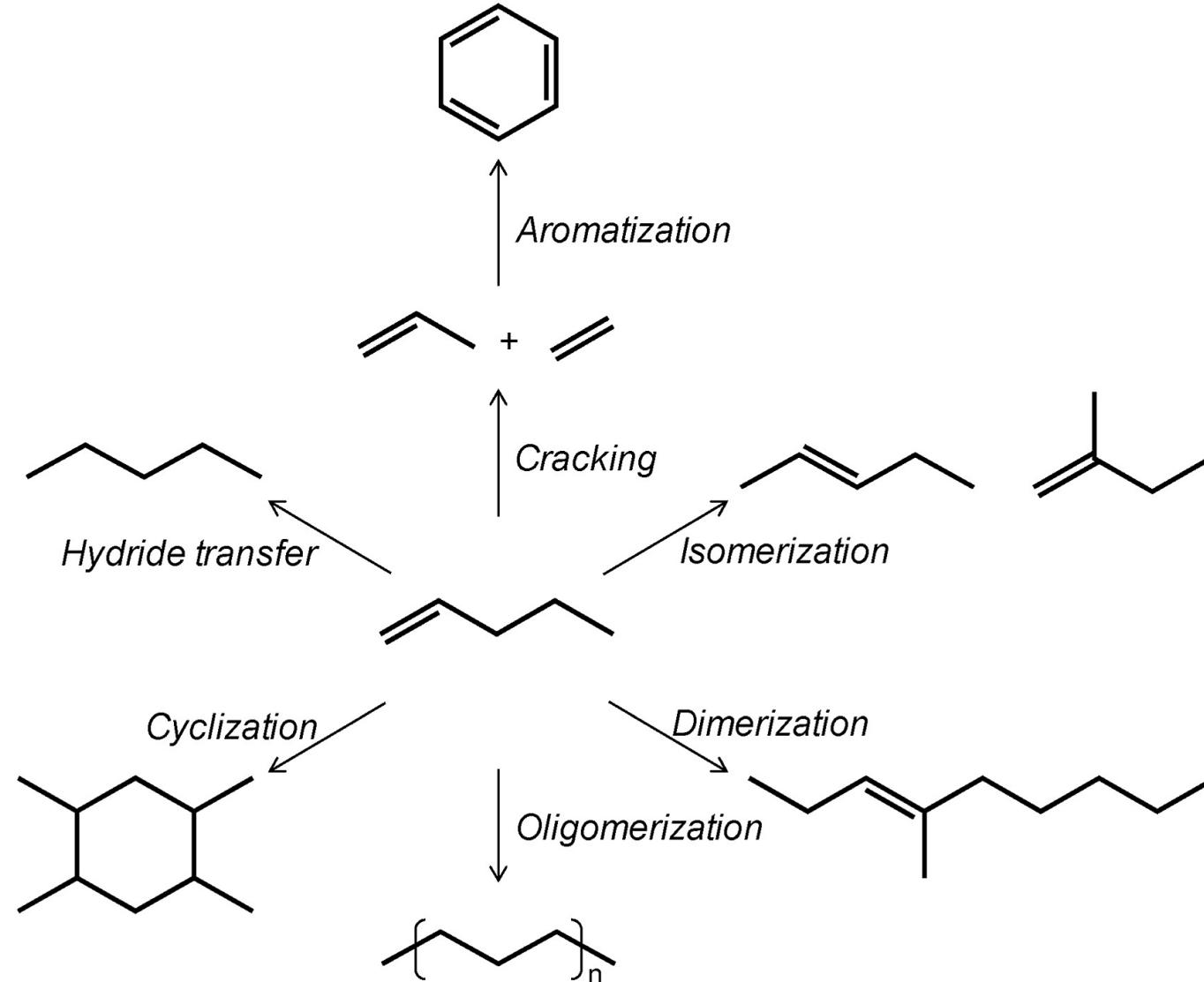
## Acid sites:

Cracking  
Alkylation  
Alkyl shift  
Hydrogen transfer  
...

# Cracking of hydrocarbons: alkanes vs alkenes

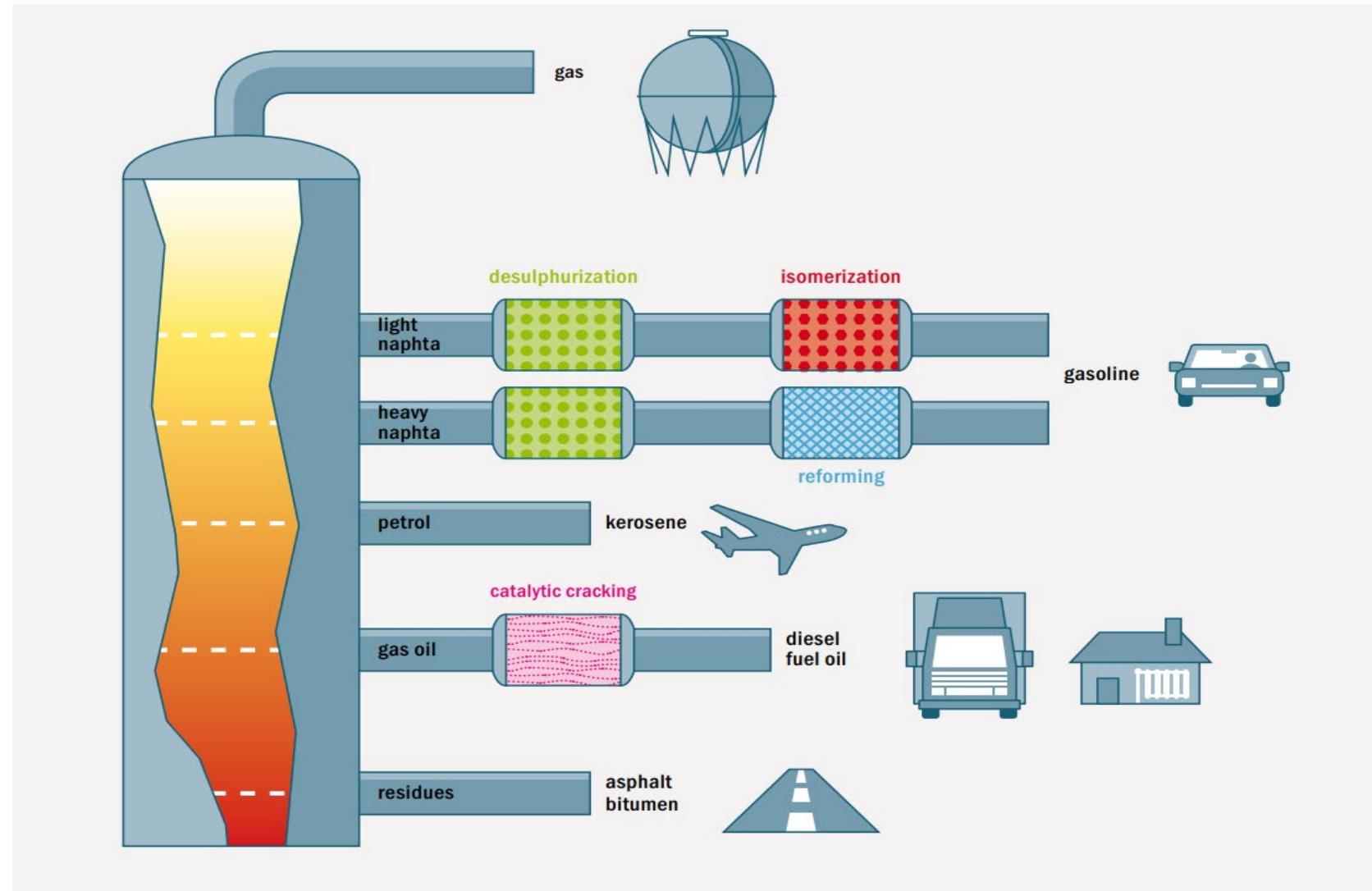


# Conversion of hydrocarbons: other acid-catalyzed reactions



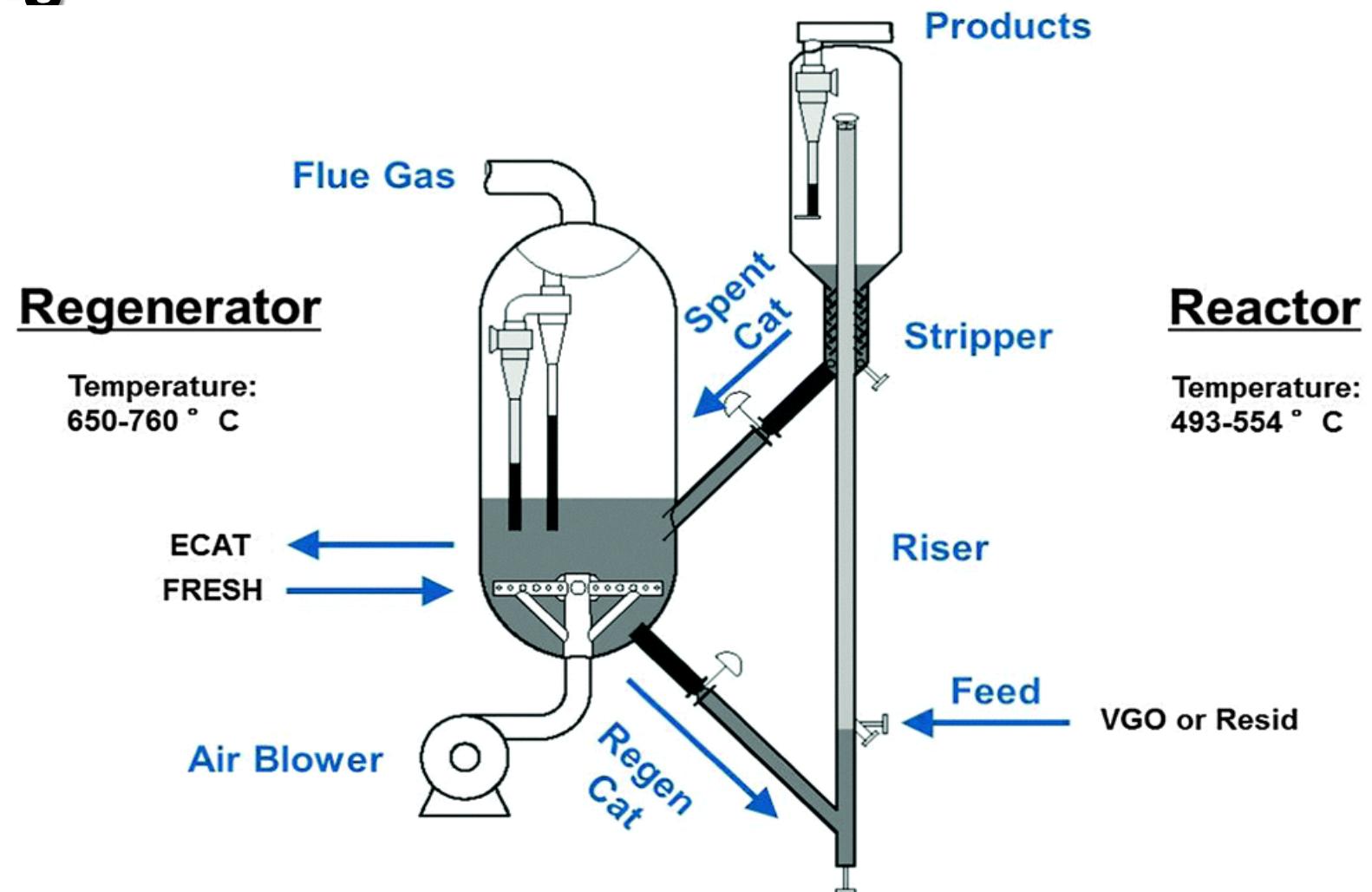
# Fluid catalytic cracking

Production of gasoline, diesel and olefin gases from heavy fraction of petroleum crude oil



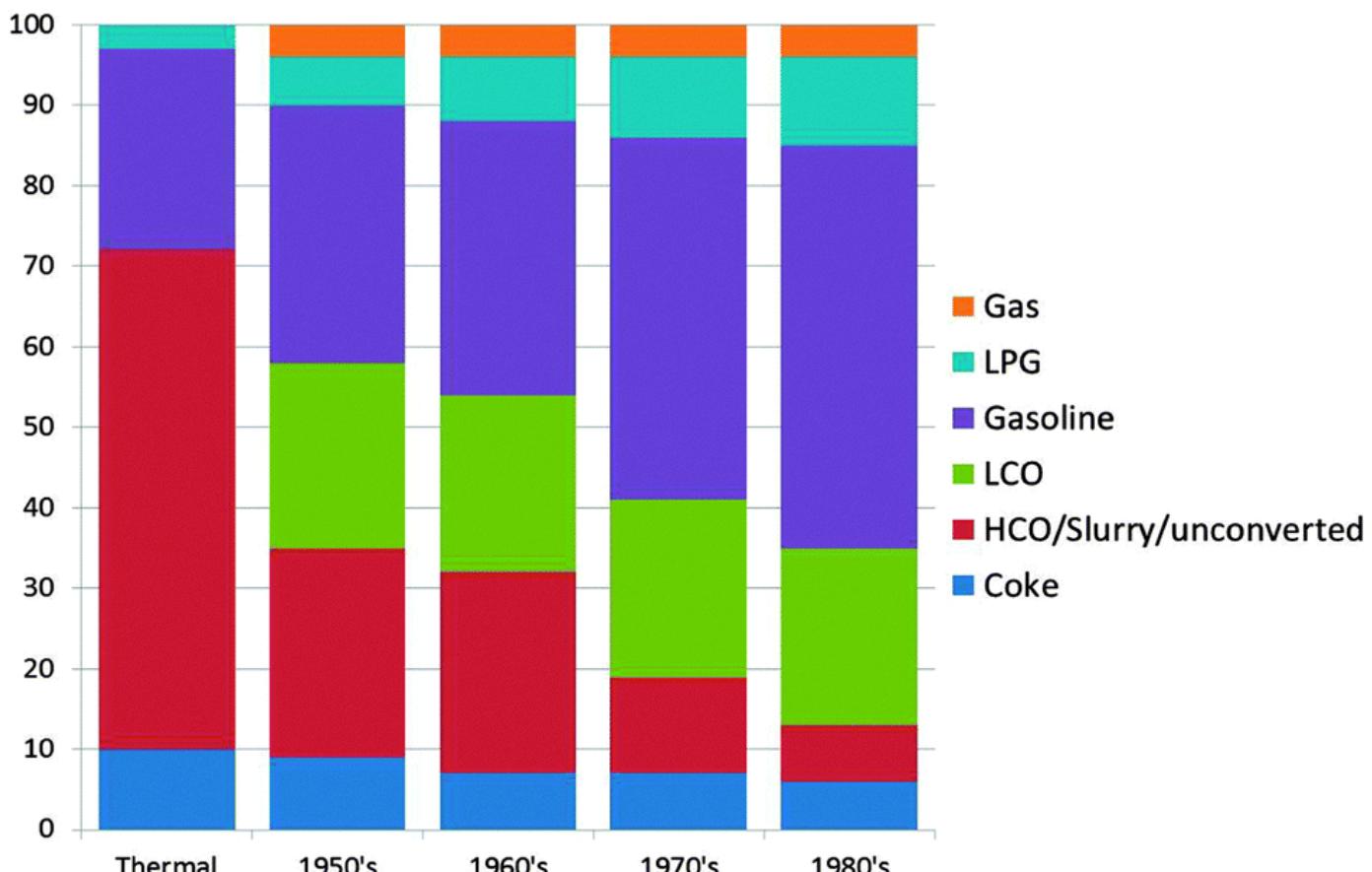
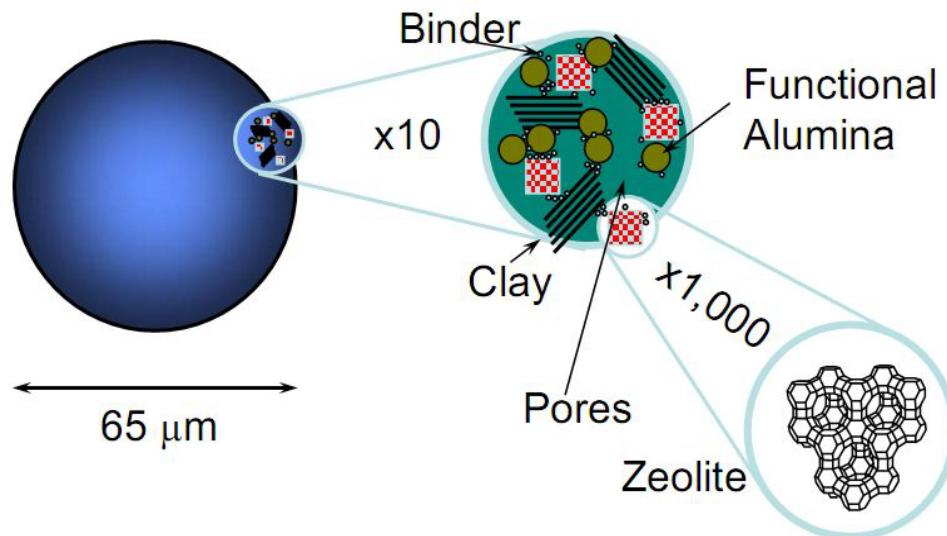
# Fluid catalytic cracking

Schematic depiction of the fluid catalytic cracking (FCC) process, including reactor and regenerator



# Fluid catalytic cracking

Zeolite-based acidic catalysts  
LPG and petrol



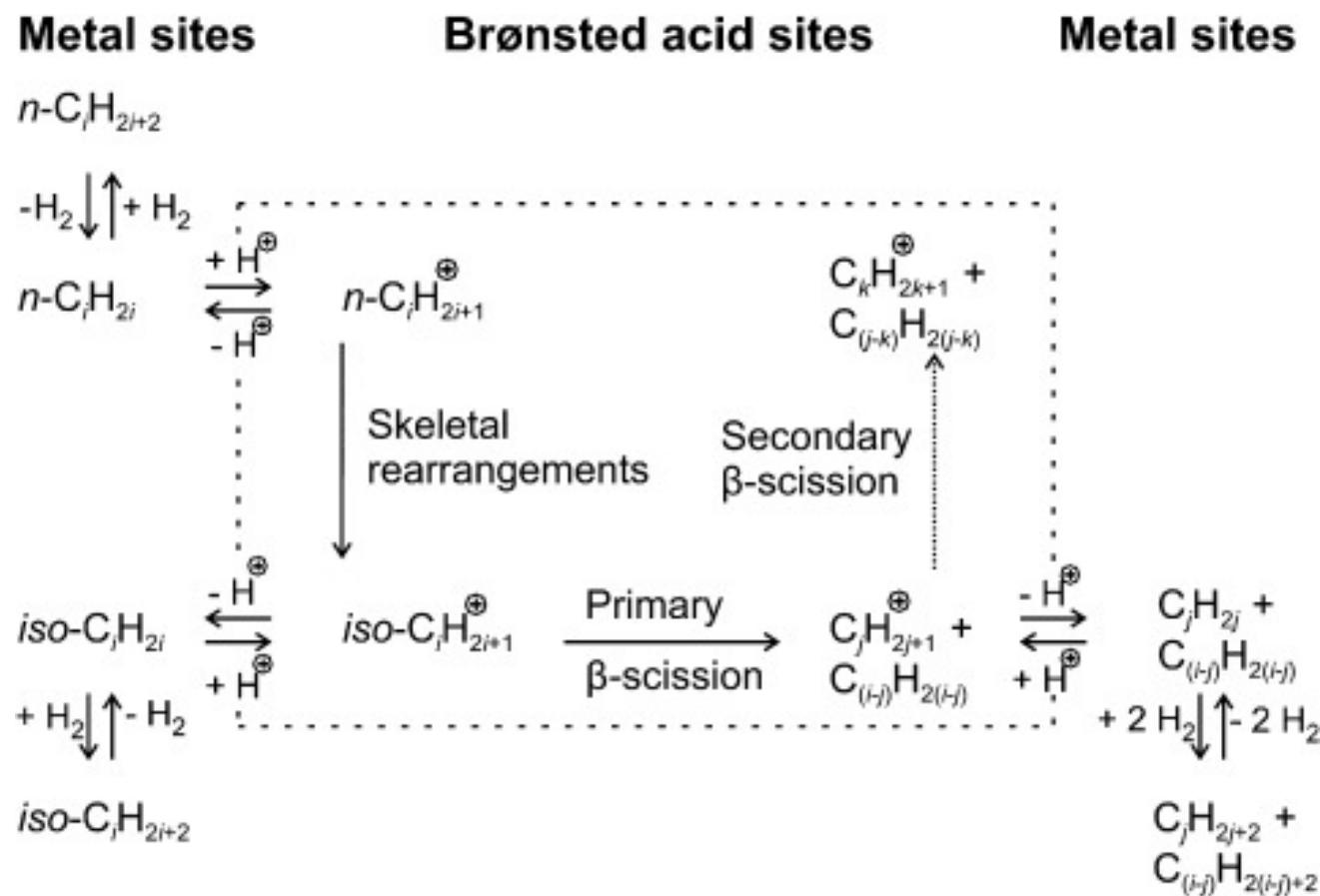
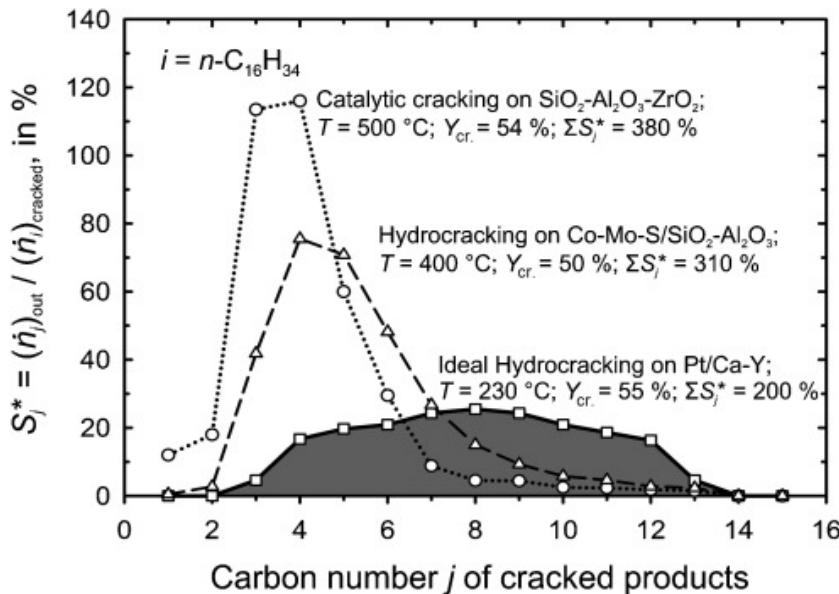
The effect of improving reactor and catalyst technology on the selectivity of FCC

# Hydrocracking

Zeolite-based acidic catalysts + noble metal catalysts

**Jet fuel, diesel, naphtha**

- High hydrogen pressure
- Noble metal co-catalyst
- Lower temperature ( $\approx 250$  °C)
- Much lower degree of cracking



**Cracking of alkenes instead of alkanes**

# **Methanol-to-hydrocarbons reaction**

# Methanol economy

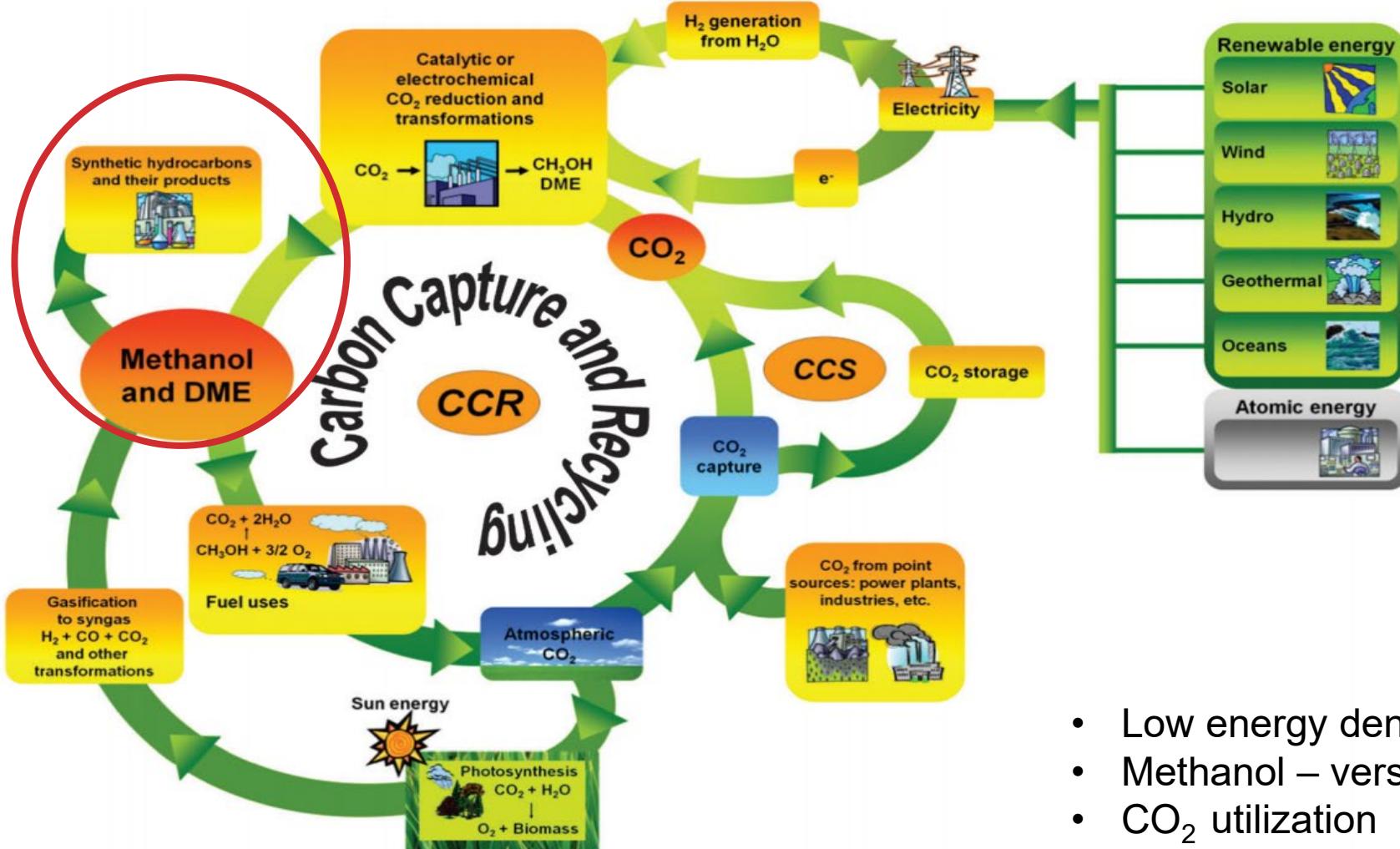


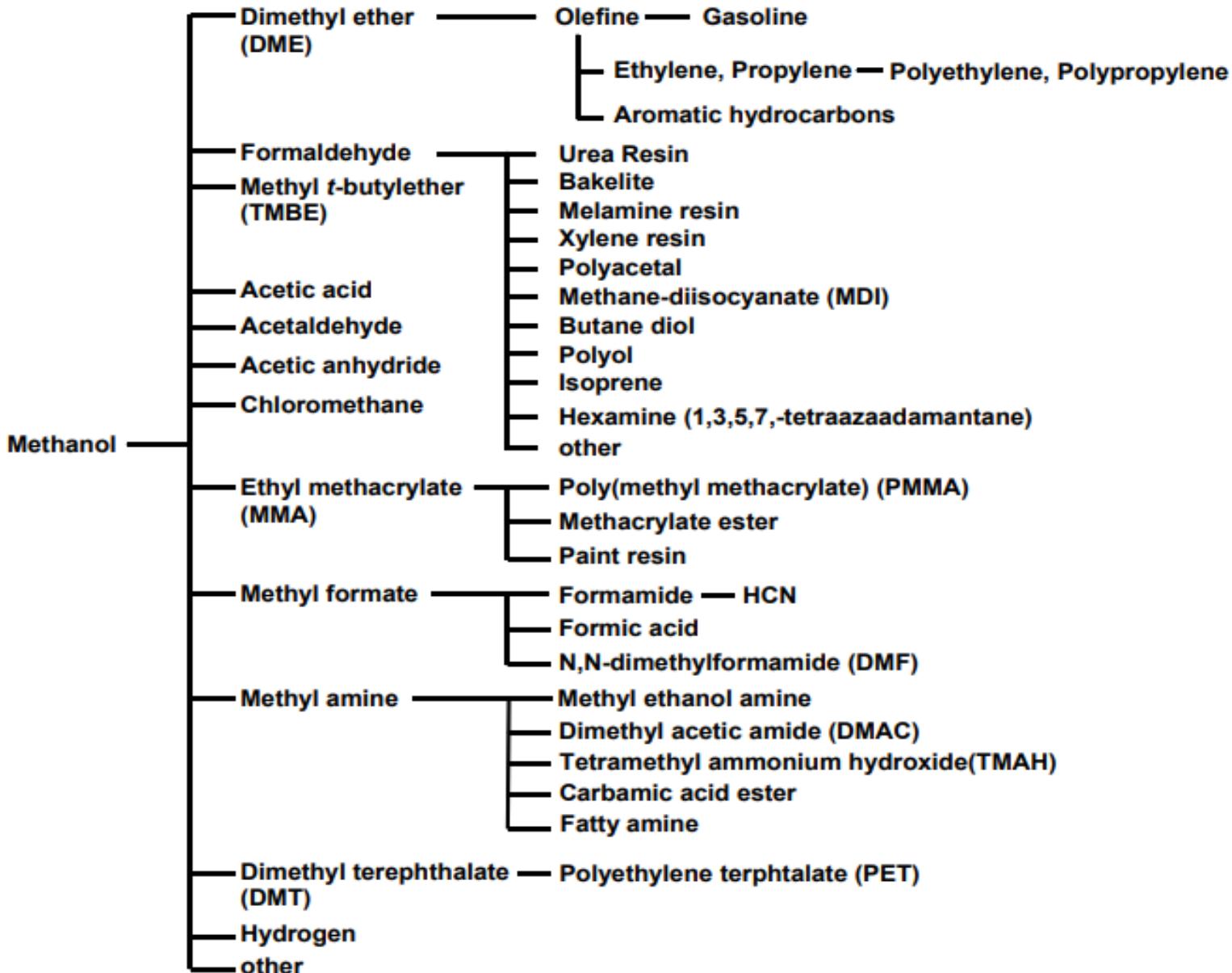
Photo from the Nobel Foundation archive.

George A. Olah (1927-2017)

The Nobel Prize in Chemistry 1994 was awarded to George A. Olah "for his contribution to carbocation chemistry"

- Low energy density of hydrogen
- Methanol – versatile chemical platform
- CO<sub>2</sub> utilization

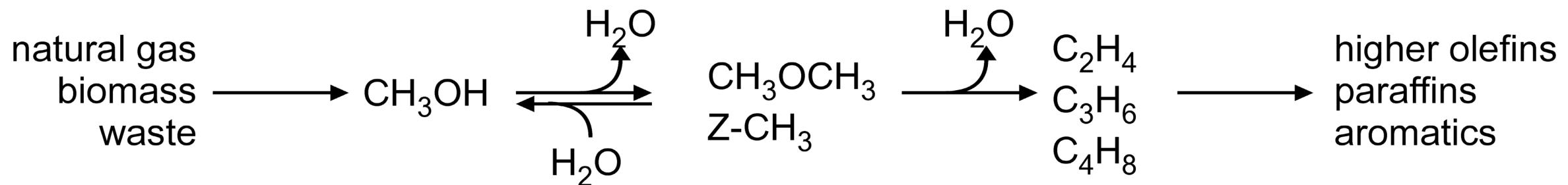
# Methanol conversion routes



# Methanol-to-hydrocarbons (MTH)

- Discovered in 1977 in Mobil
- Commercialized in 1985 (New Zealand)
- Possible to produce:
  - ethylene/propylene (**MTO**)
  - Light olefins (<C6) (**MTO**)
  - Gasoline range hydrocarbons (**MTG**)
  - Aromatics (benzene, toluene, xylene) (**MTA**)
- Zeolite catalysts
- 350-450 °C
- 1-15 atm

# Methanol to X Processes



- Any gasifiable carbonaceous material can be converted to methanol
  - Methanol can serve as the base to products which can replace the crude oil route
- 
- Megaplant Inner Mongolia, China: 500,000 tons polyolefins/year
  - Many plants under construction
  - Cheap coal gasification; methanol synthesis; MTO



# Methanol-To-Olefins catalysts - SAPO

Si substitution for P in AlPO<sub>4</sub> → Brønsted acid sites

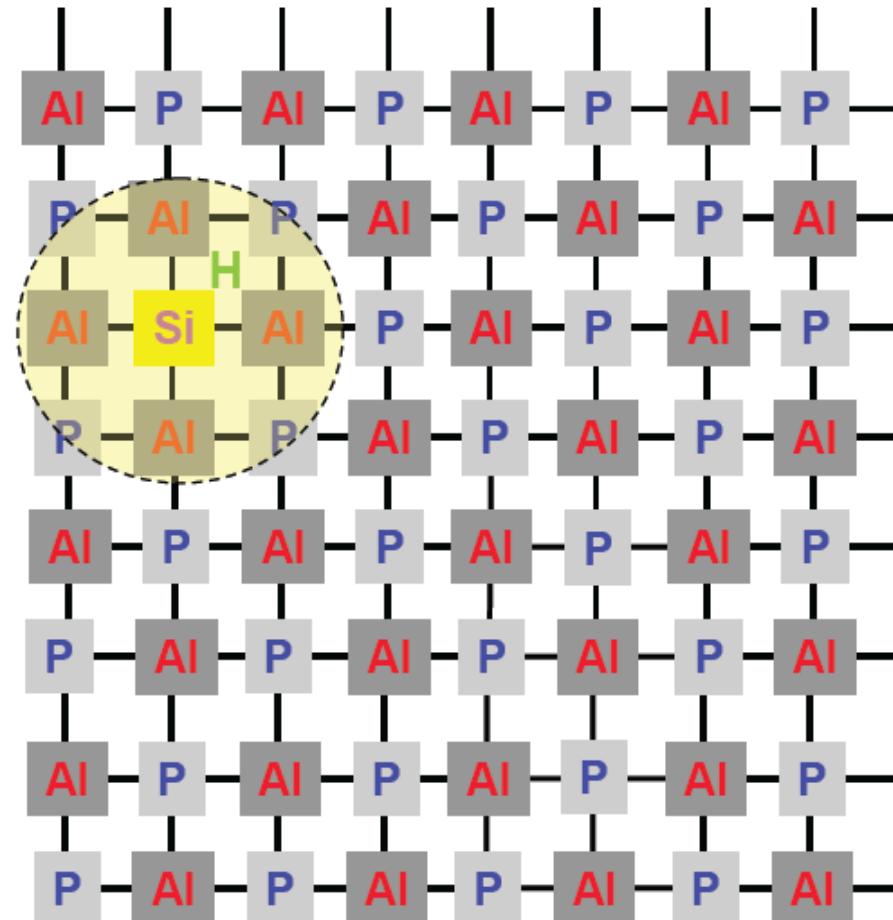
Isolated Si: Si<sup>+4</sup> → P<sup>+5</sup>

Negative framework charge

Template decomposition → H<sup>+</sup>

No Si-O-P

No P-O-P



Silicoaluminophosphate (SAPO) frameworks are much more polar than aluminosilicate frameworks  
– [weaker acidity of SAPO materials](#)

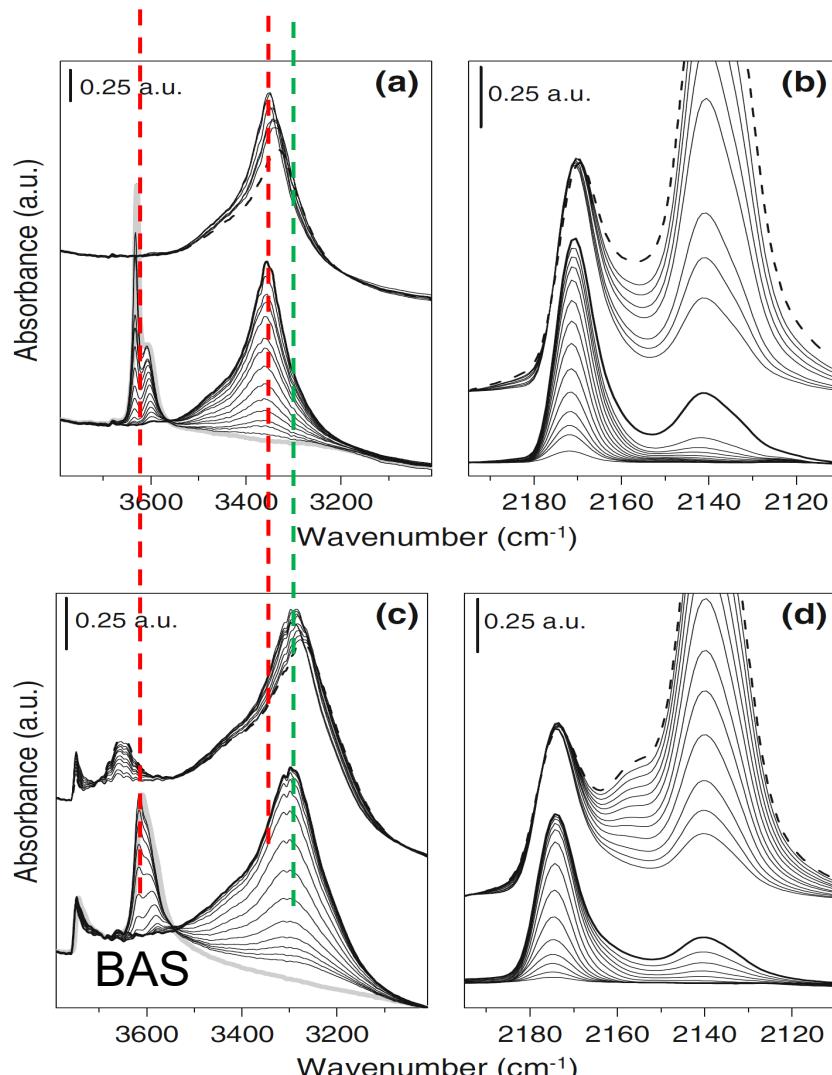
# Methanol-To-Olefins

H-SAPO-34

weaker acid

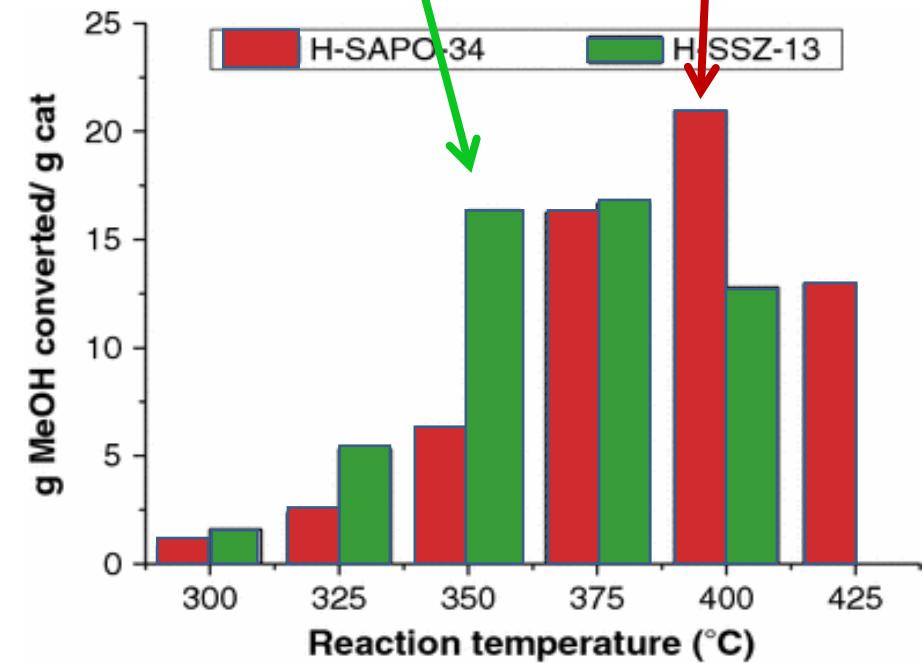
H-SSZ-13

CO adsorption on BAS



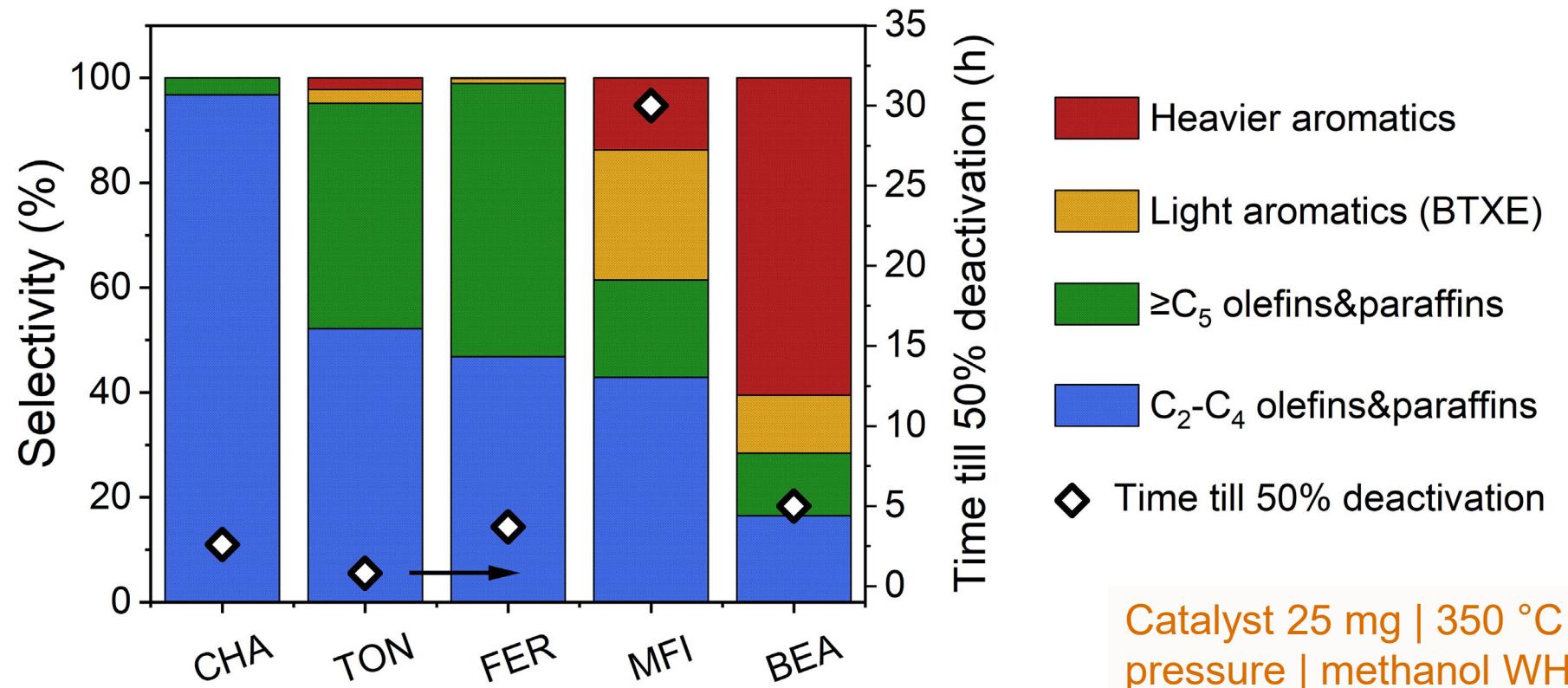
H-SSZ-13 lower  
temperature  
possible

H-SAPO-34  
less coke  
formation at high  
temperature

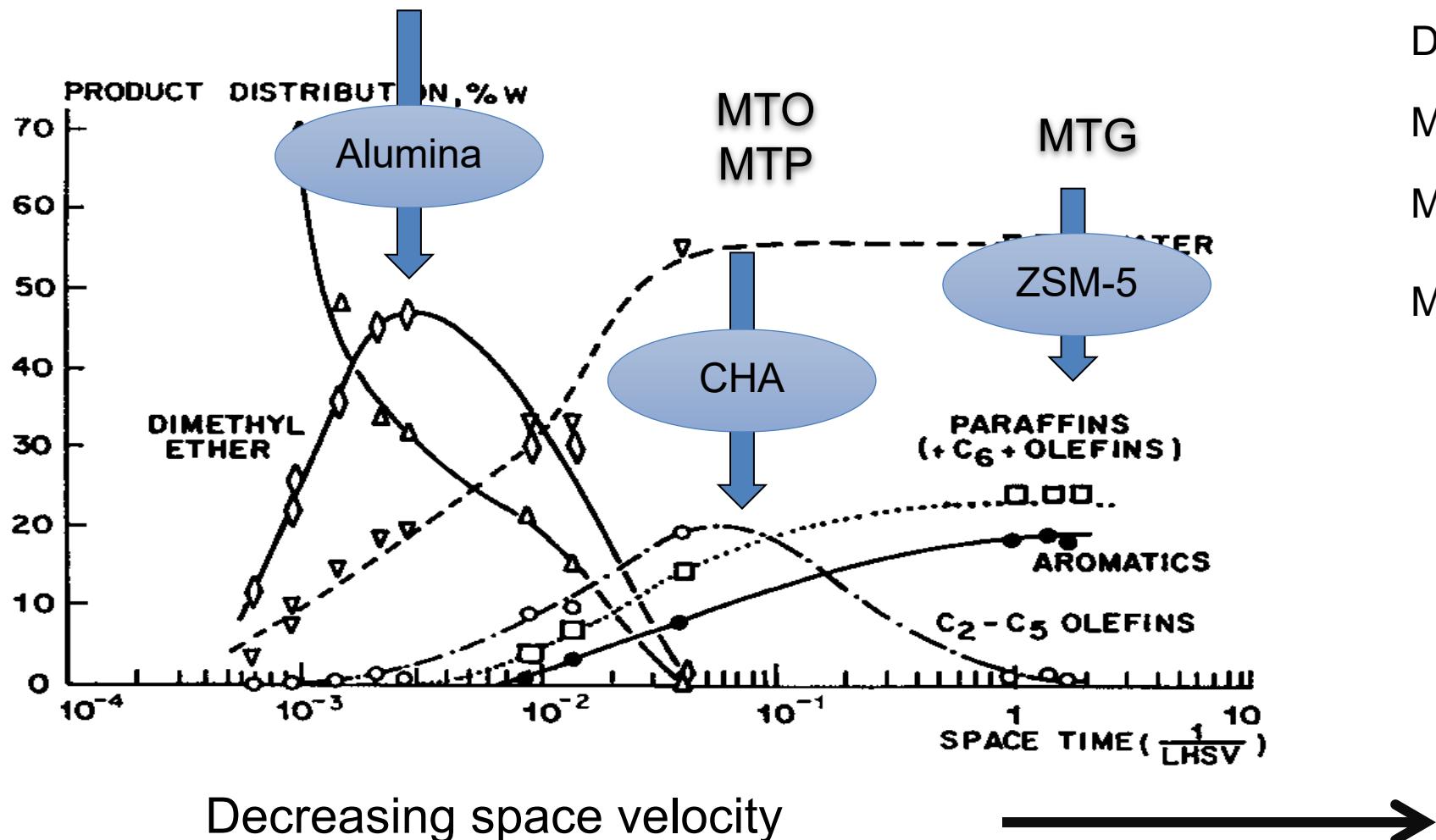


# **Mechanism of MTH**

# Pore geometry determines the performance



# Reaction path



DME = dimethylether

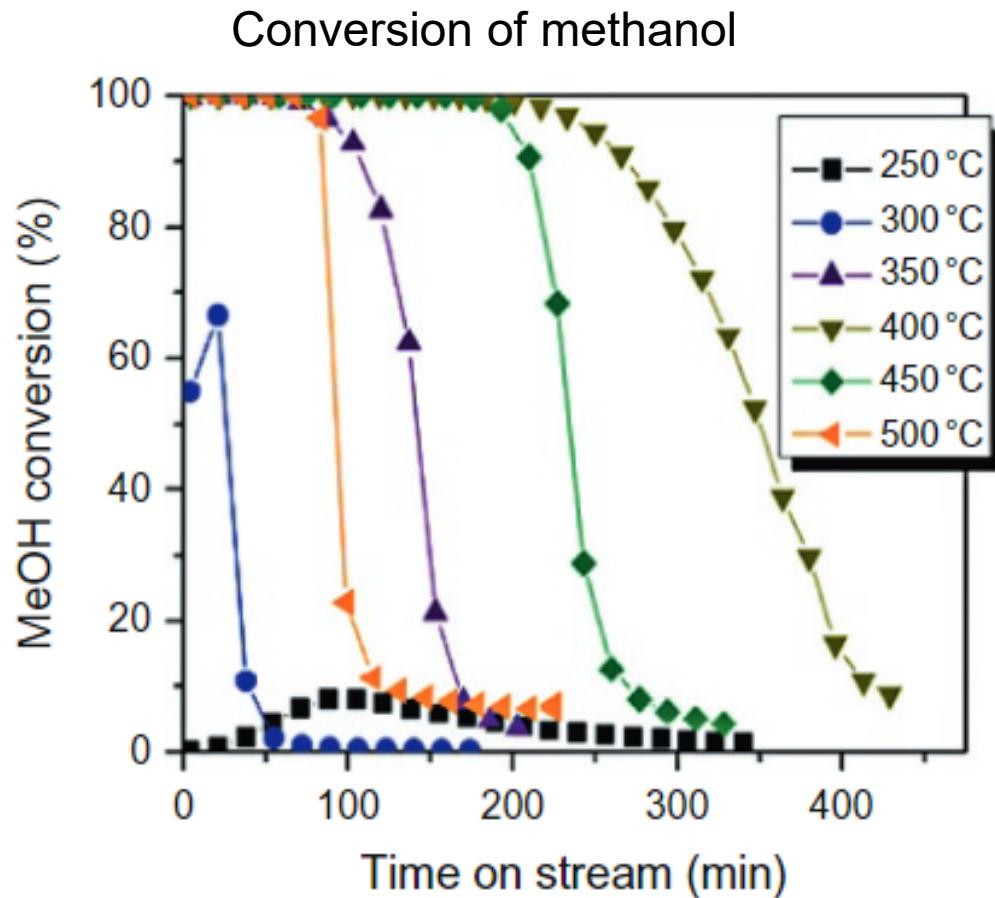
MTO = methanol to olefins

MTP = methanol to propylene

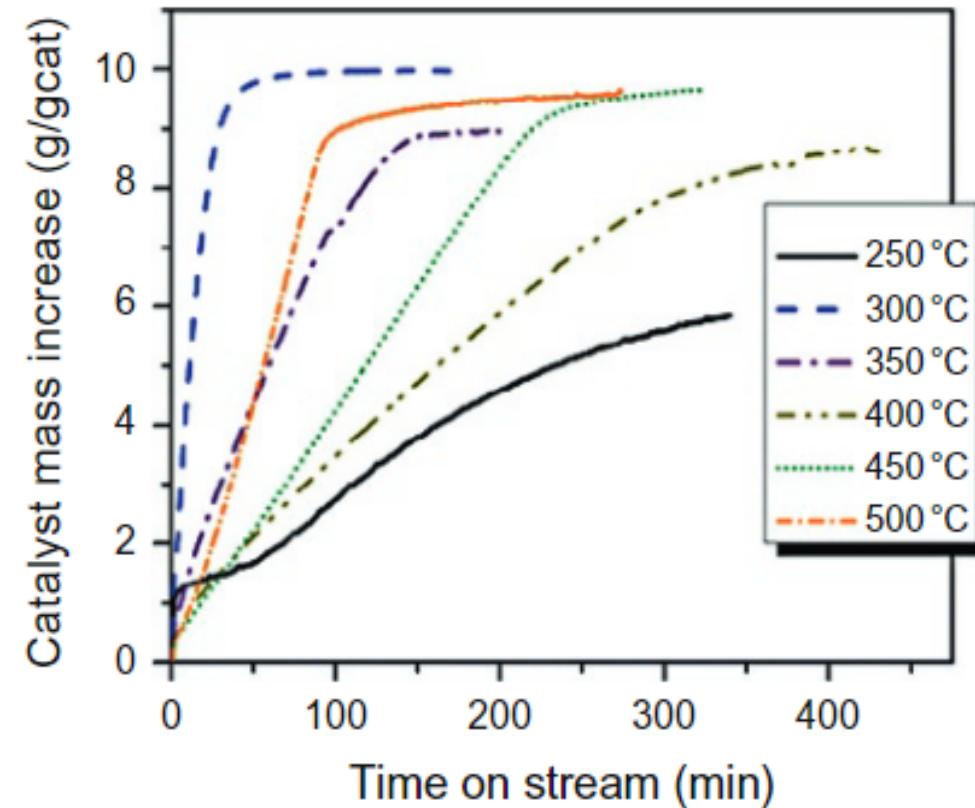
MTG = methanol to gasoline

# Narrow temperature window of MTH

SAPO-34



Real-time increase of catalyst weight



- Coking deactivation
- Nature of coke depends on temperature

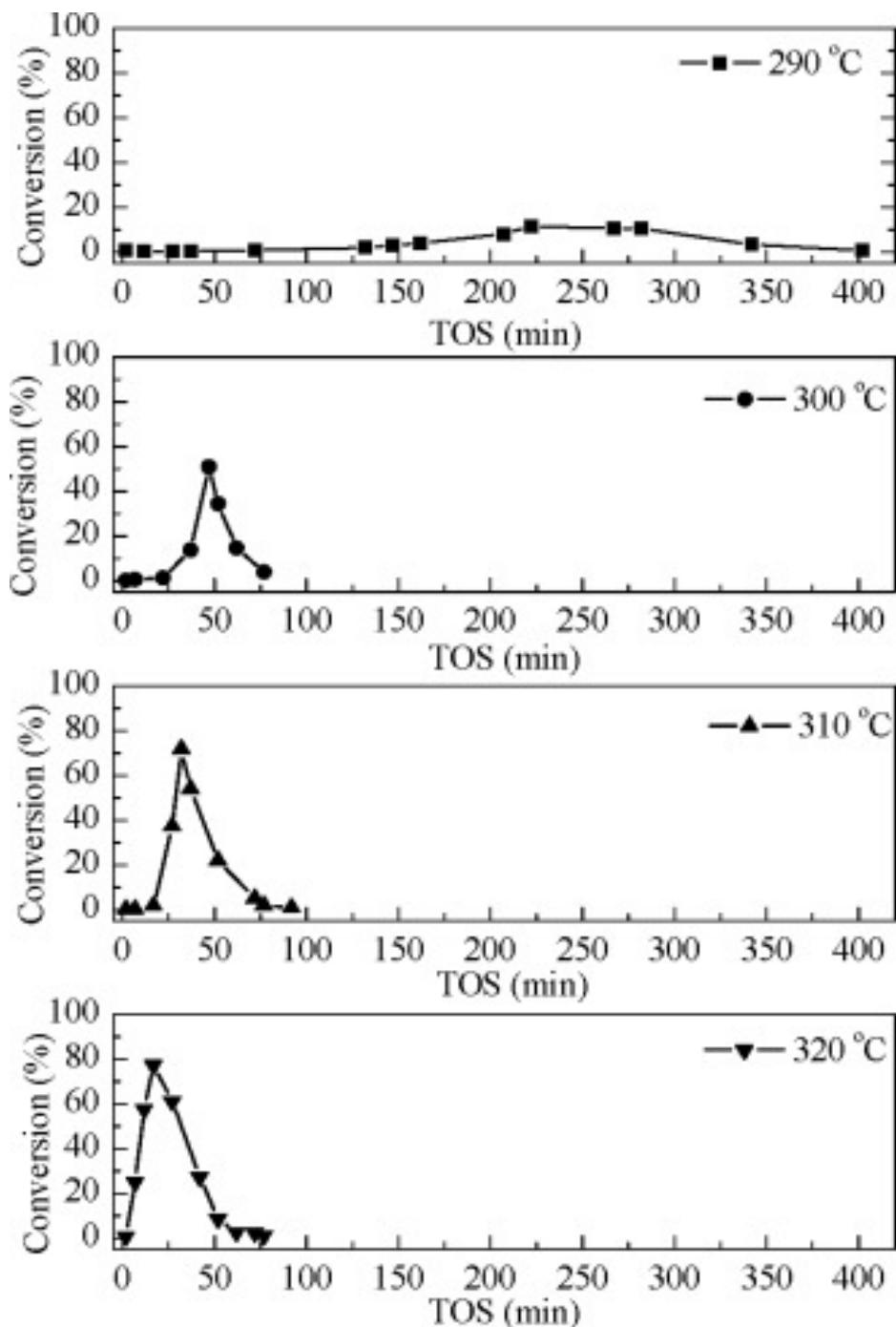
Optimum: 350 – 450 °C

# Induction period

SAPO-34

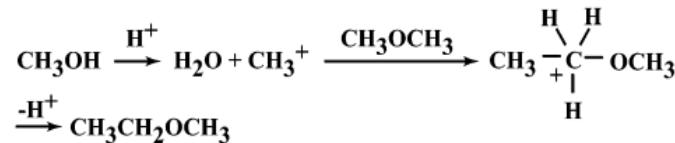
MTH is an **autocatalytic** reaction

Reaction rate increases with time on stream (TOS)

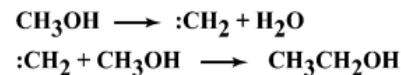


# Proposed mechanisms

How is first C-C bond made?



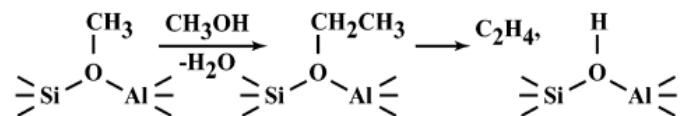
Carbenium ion to carbonium ion



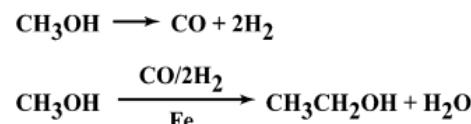
Carbene coupling



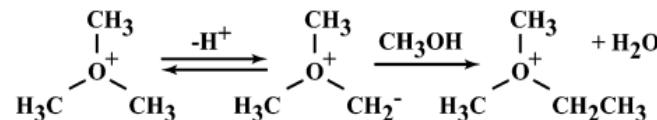
Free radical routes



Methoxy coupling

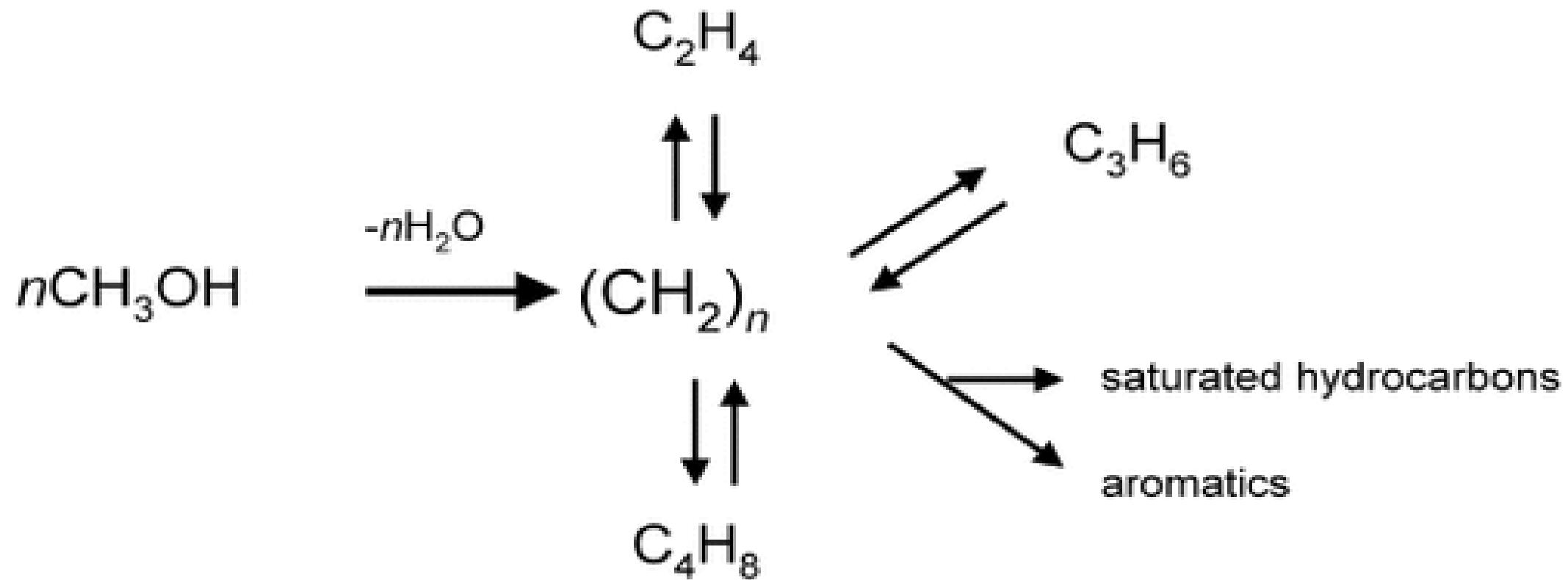


Decomposition to syngas followed by Fischer-Tropsch on Fe impurities



Oxonium-ylide route

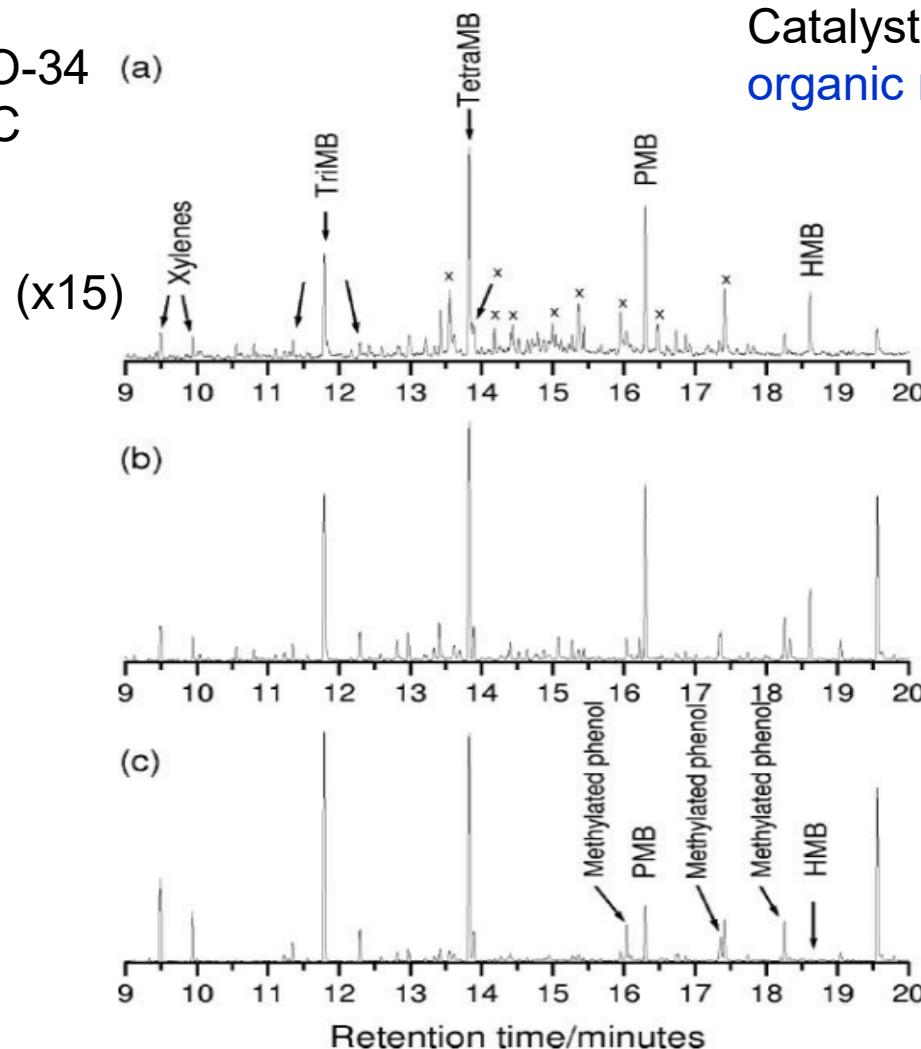
# Hydrocarbon pool hypothesis



Hydrocarbon species, confined inside the pores, react with methanol to produce olefins

# Chemistry of hydrocarbon pool?

SAPO-34 (a)  
325°C



Catalysts at different stages of reaction are dissolved in HF, occluded organic molecules are extracted and analyzed by GC-MS

30 sec on stream

120 sec on stream

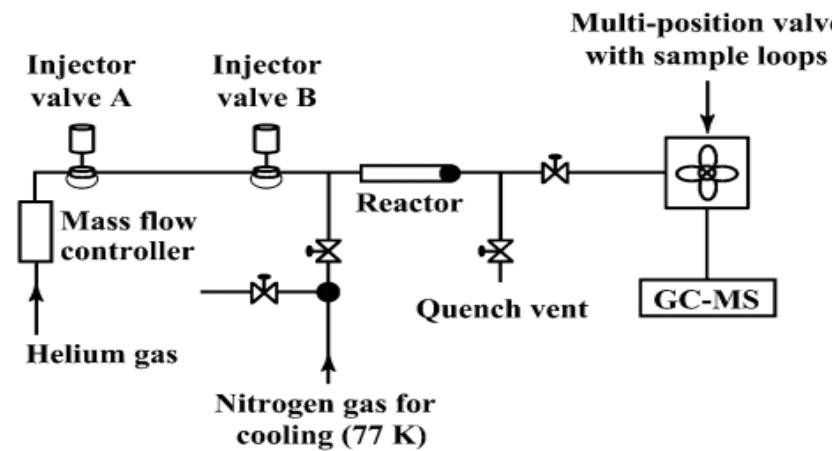
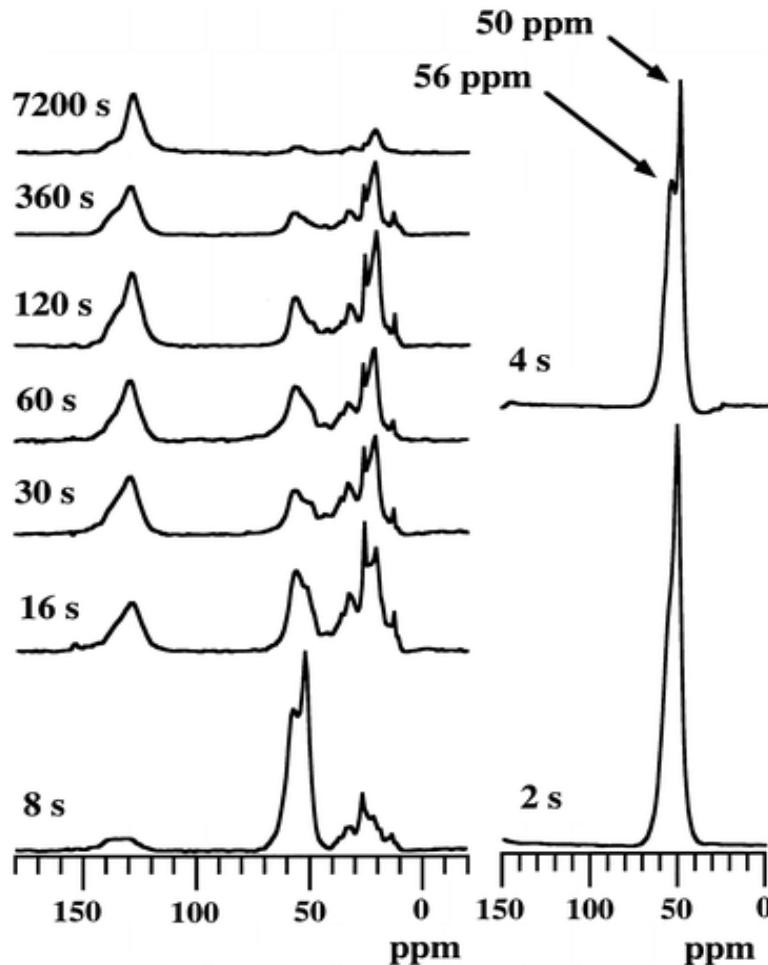
120 sec on stream +  
flushing with He for 160 s

Methylated benzenes  
are the main confined  
species

# Chemistry of hydrocarbon pool?

SAPO-34  
400°C

Methanol is pulsed to a catalyst and then the reaction is quenched by instantly cooling the catalyst with liquid nitrogen.  $^{13}\text{C}$  NMR spectra of obtained samples are measured

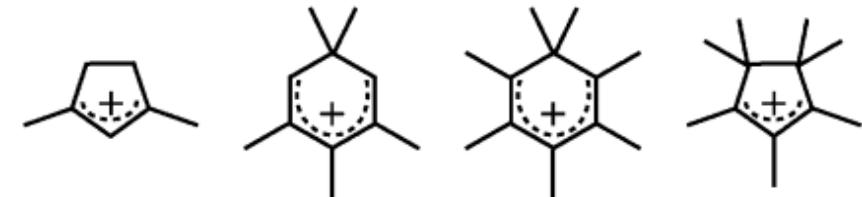
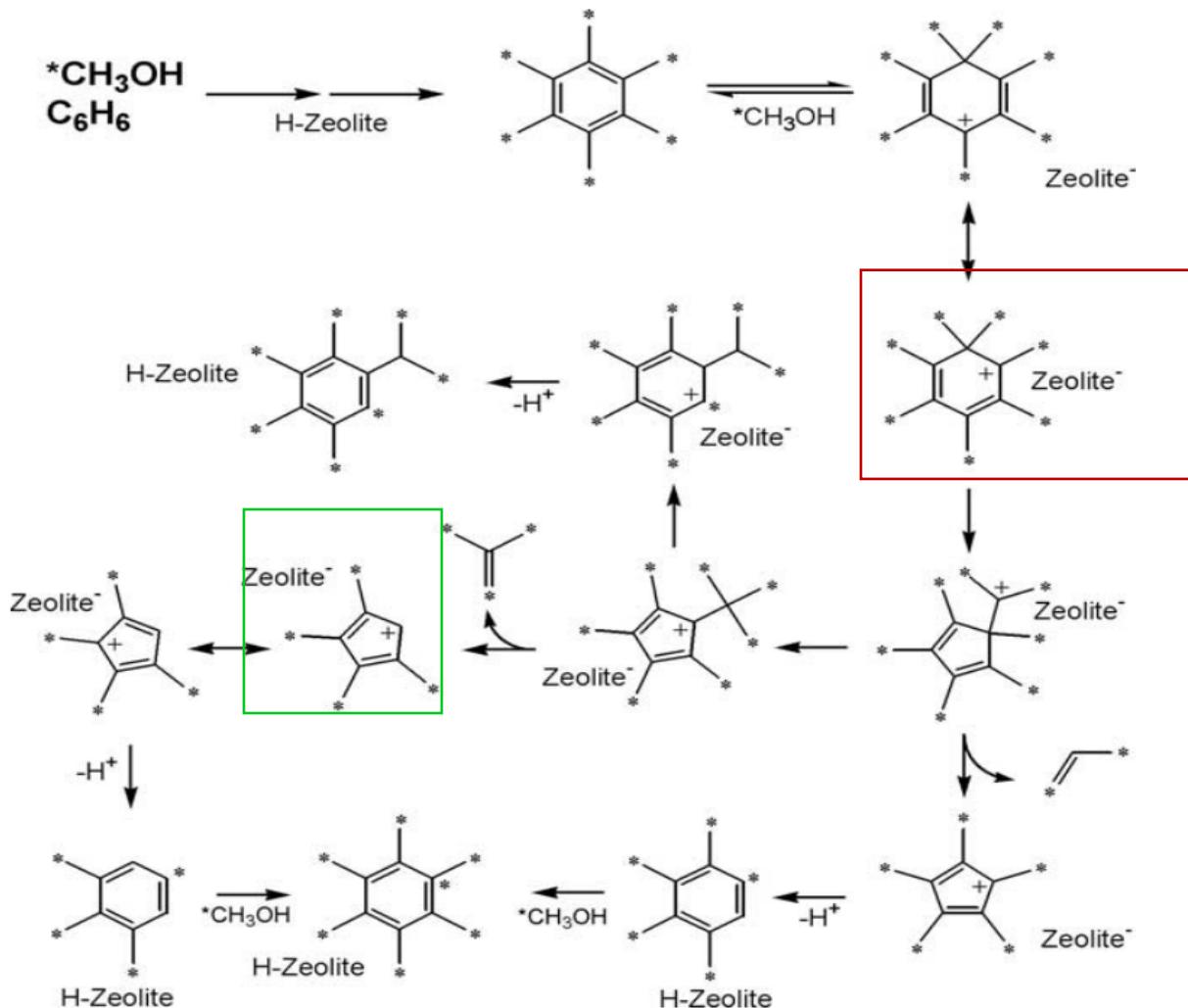


**50 ppm** – adsorbed methanol  
**56 ppm** – methoxy species on acid sites

**129 ppm** – aromatic  $\text{sp}_2$  carbon  
**134 ppm** – alkyl-substituted aromatic  $\text{sp}^2$  carbon  
**20 ppm** – methyl groups on aromatic rings

**Methylated benzenes are the main confined species**

# Chemistry of hydrocarbon pool?



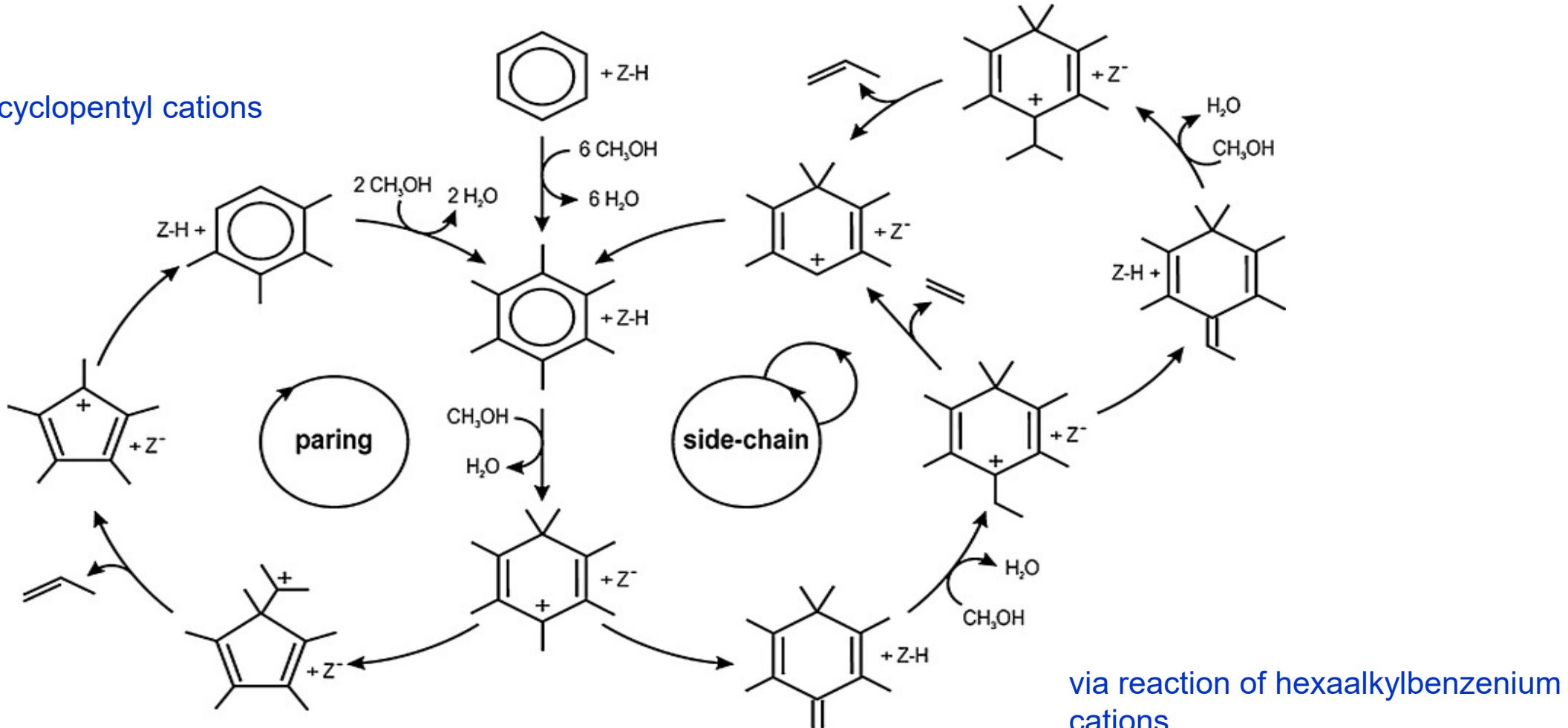
Co-feeding of  $^{13}C$  labelled methanol with unlabeled benzene and careful NMR analysis revealed presence of aromatic cations

heptamethylbenzenium  
cyclopentenyl cations

# Chemistry of hydrocarbon pool?

Paring or side chain mechanisms

via "shaving off" cyclopentyl cations



# Chemistry of hydrocarbon pool?

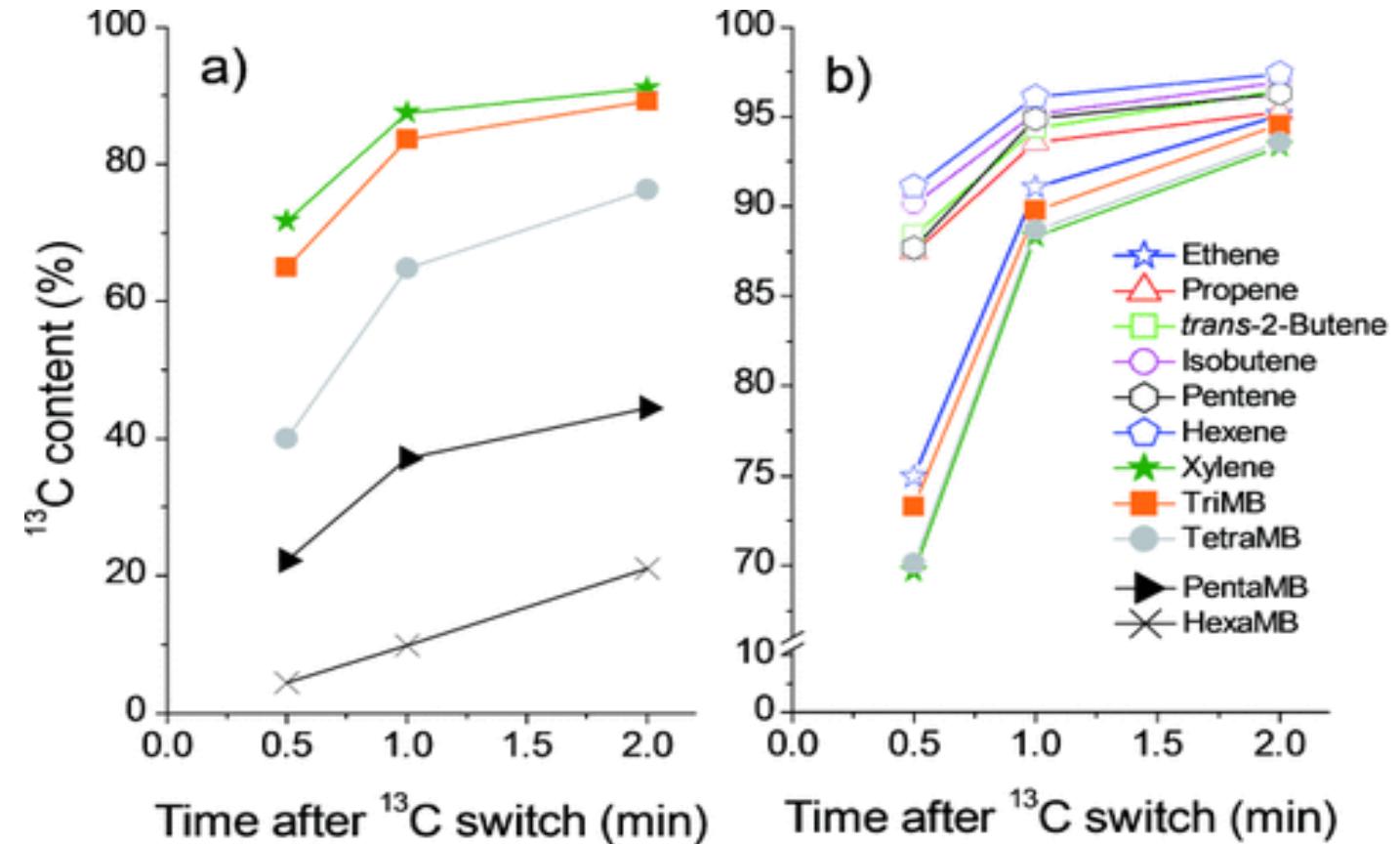
- Pairing and side chain mechanisms only explain the products obtained on SAPO-34 (ethylene and propylene)

Isotope labeling experiment



Ethylene is mechanistically separated from other alkenes on ZSM-5 and is linked to methylated benzenes!

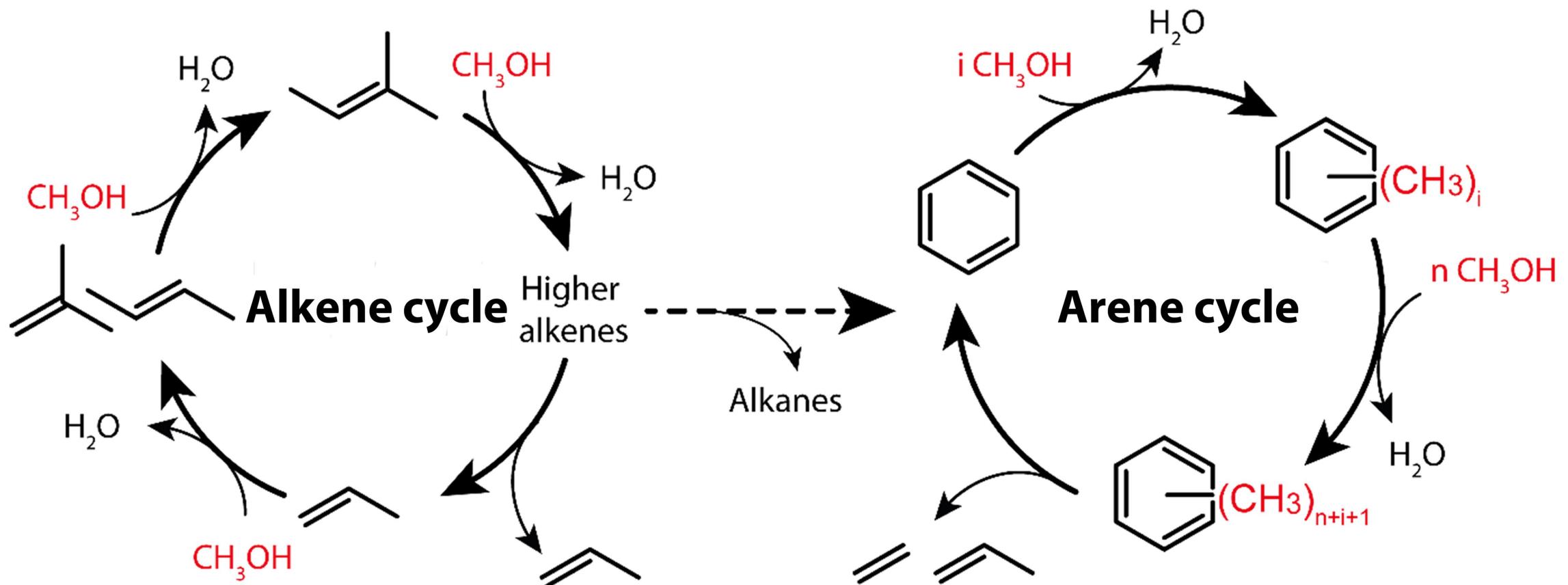
- Aromatic cycle – ethylene
- Cracking of olefins – higher aliphatics



Transient  $^{12}\text{C}/^{13}\text{C}$  methanol switch experiment carried out using H-ZSM-5 ( $\text{Si}/\text{Al}=140$ ).  $^{12}\text{C}$  methanol was fed for 18 min before switching to  $^{13}\text{C}$  methanol and reacting further for a predetermined time.

# Dual cycle mechanism

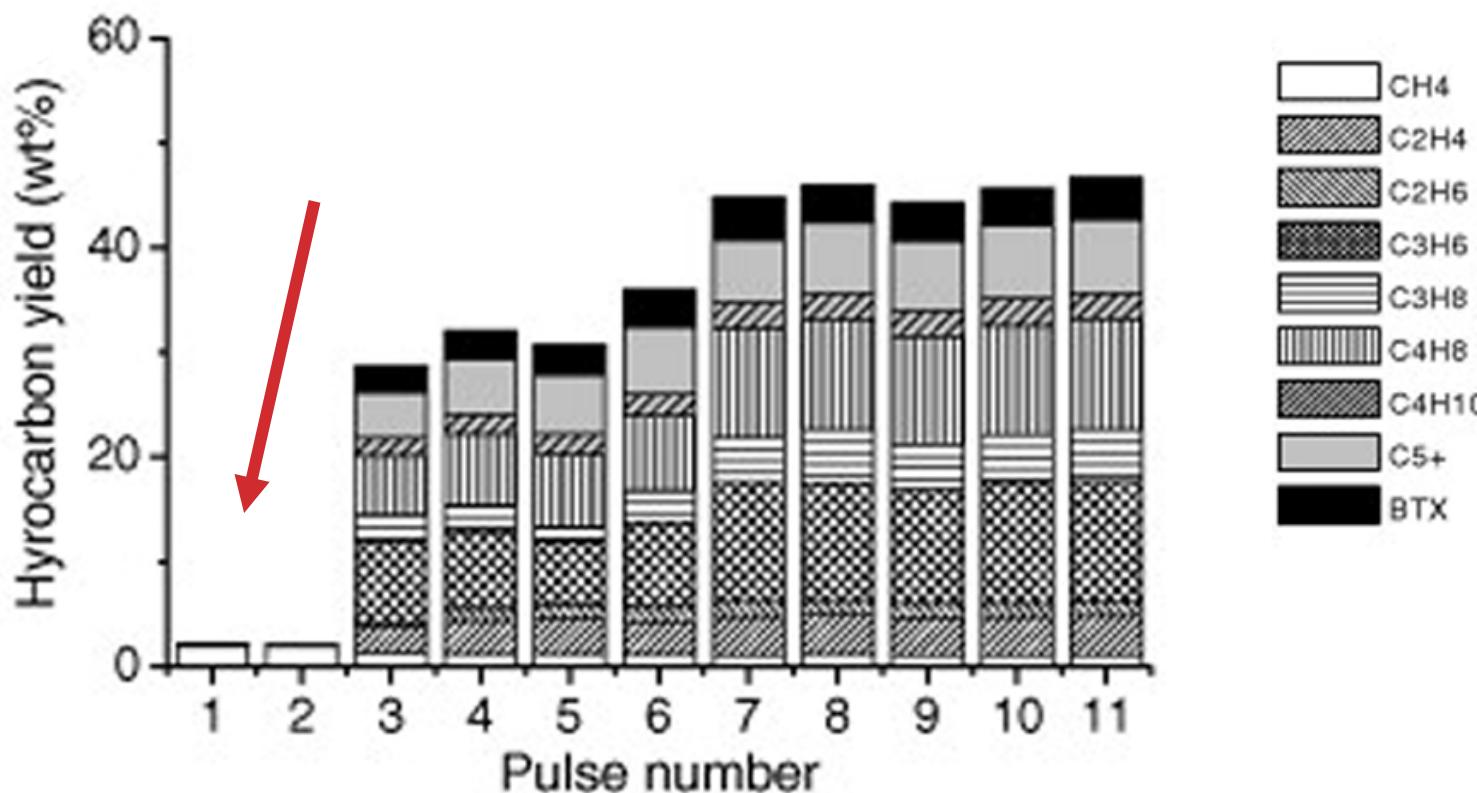
Paring and side chain mechanisms only explain the products obtained on SAPO-34 (ethylene and propylene)



- State-of-the art understanding
- Explains all experimental observations

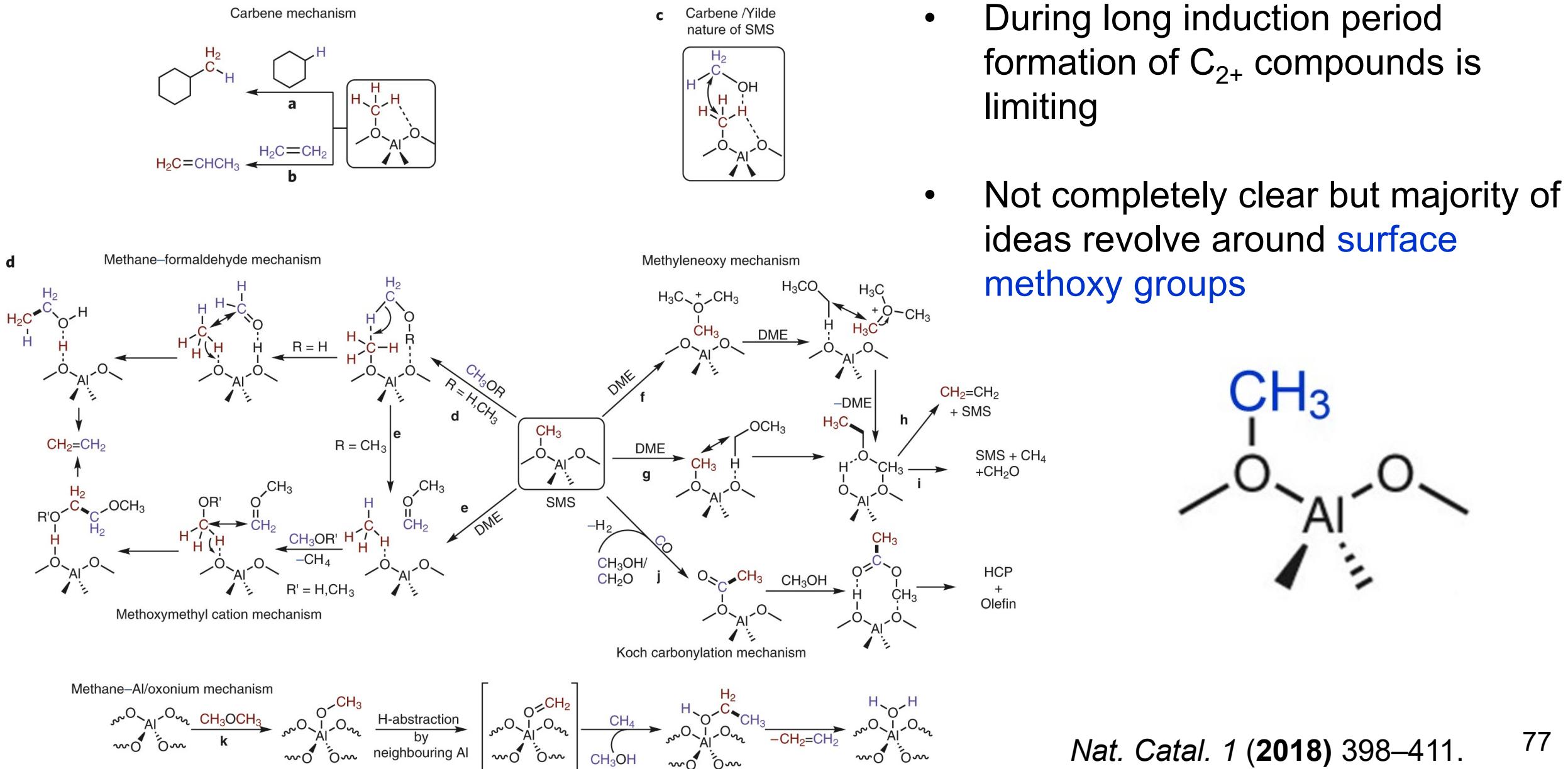
# Formation of the first C-C bonds: pulse study

HZSM-5, 400 °C, 0.09 mg methanol pulses

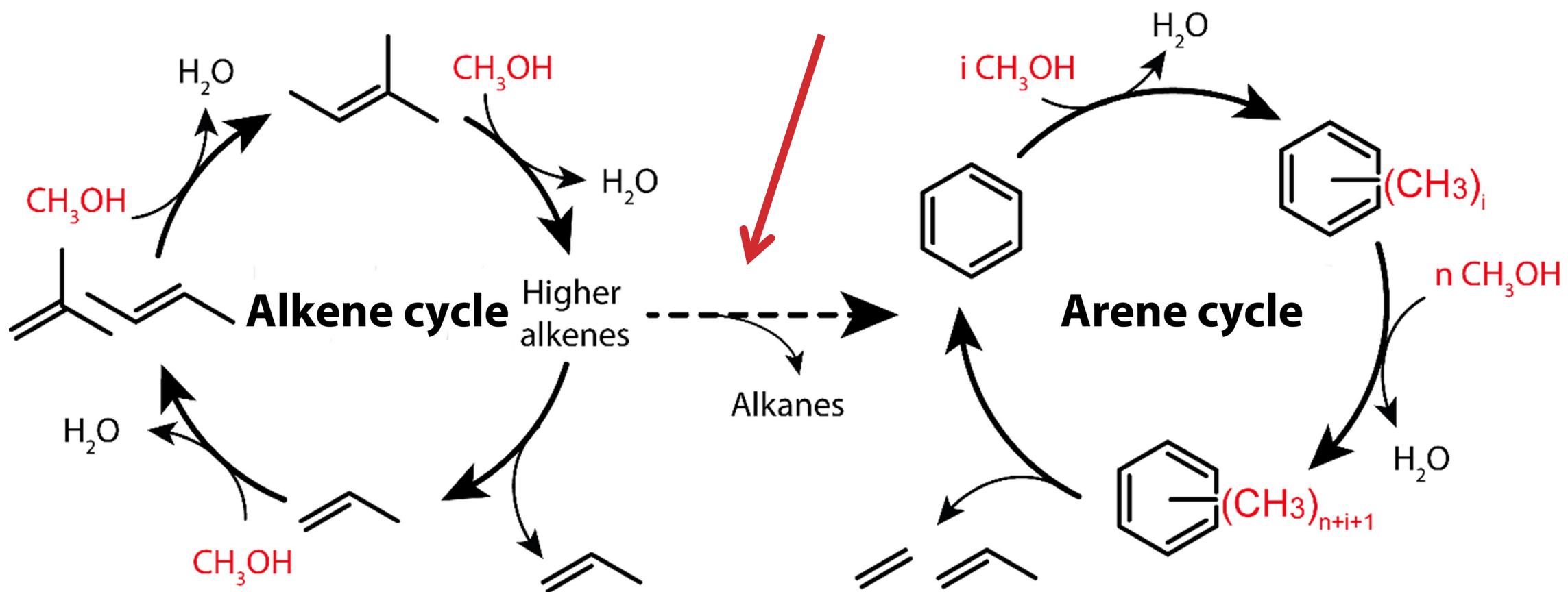


- Development of hydrocarbon pool during the initial induction period
- How do aromatic and olefin hydrocarbon pool components are formed from methanol?

# Formation of the first C-C bonds

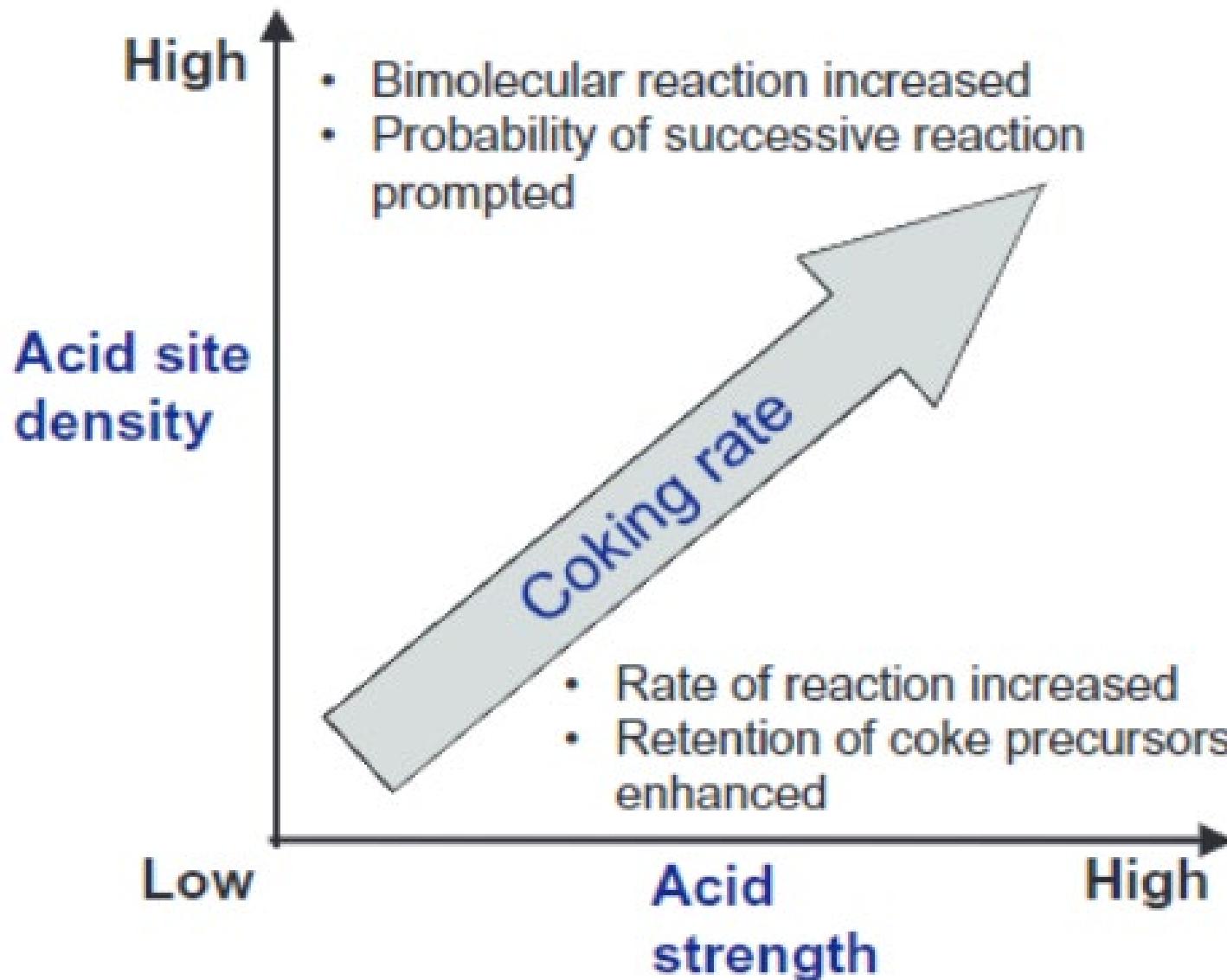


# Hydrogen transfer



- “Disproportionation” of higher olefins to aromatics and alkanes
- Bridges the two cycles together

# Hydrogen transfer

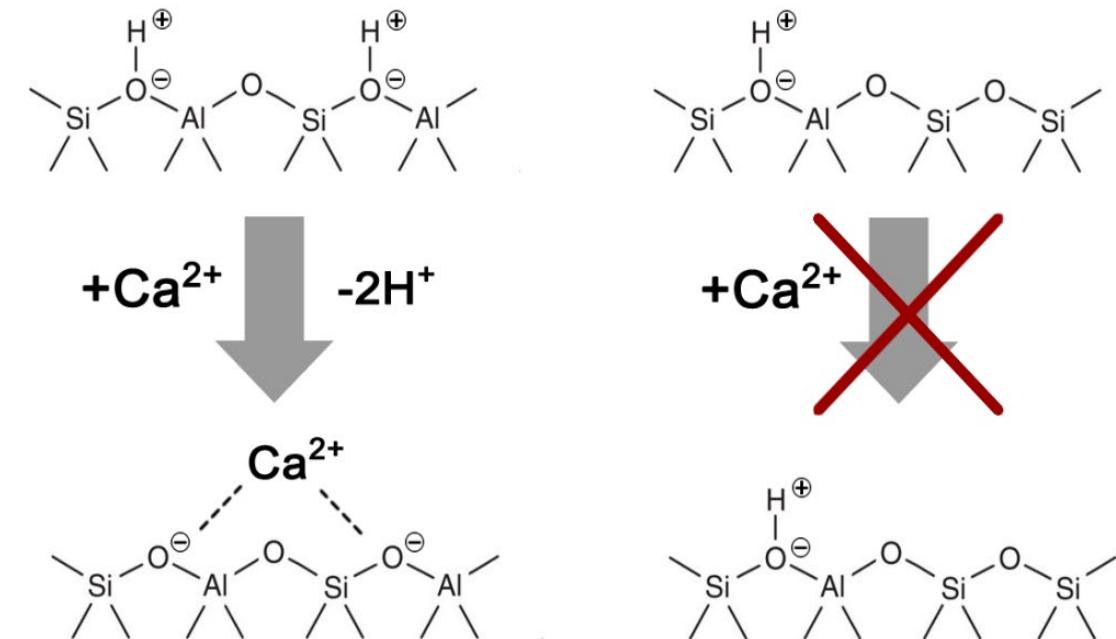


Bimolecular reaction: rate increases with decreasing contact time and increasing the concentration of acid sites

# Density of acid sites governs the hydrogen transfer

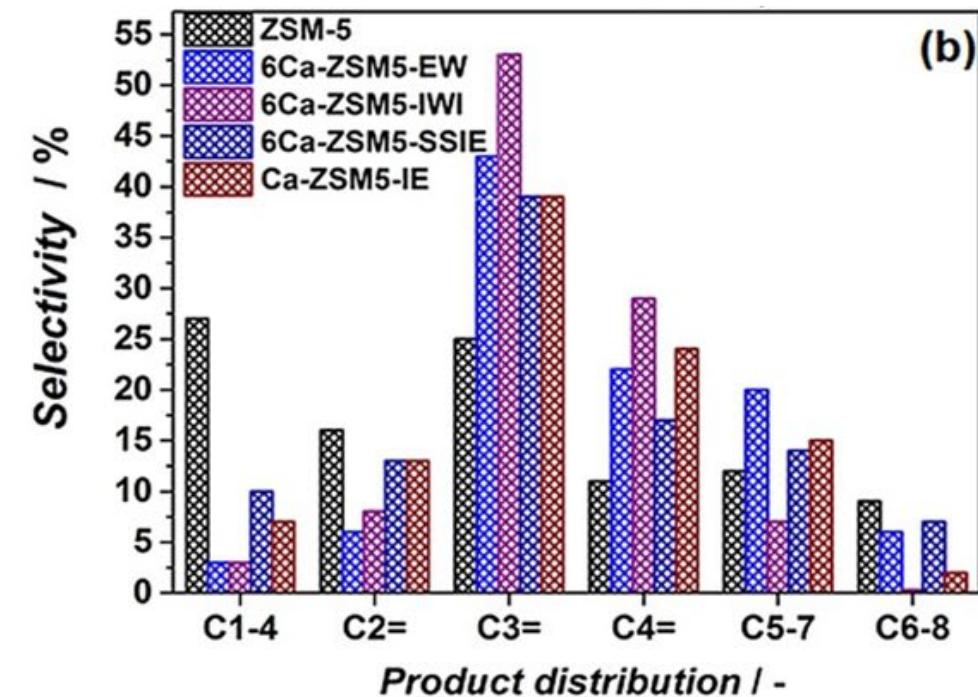
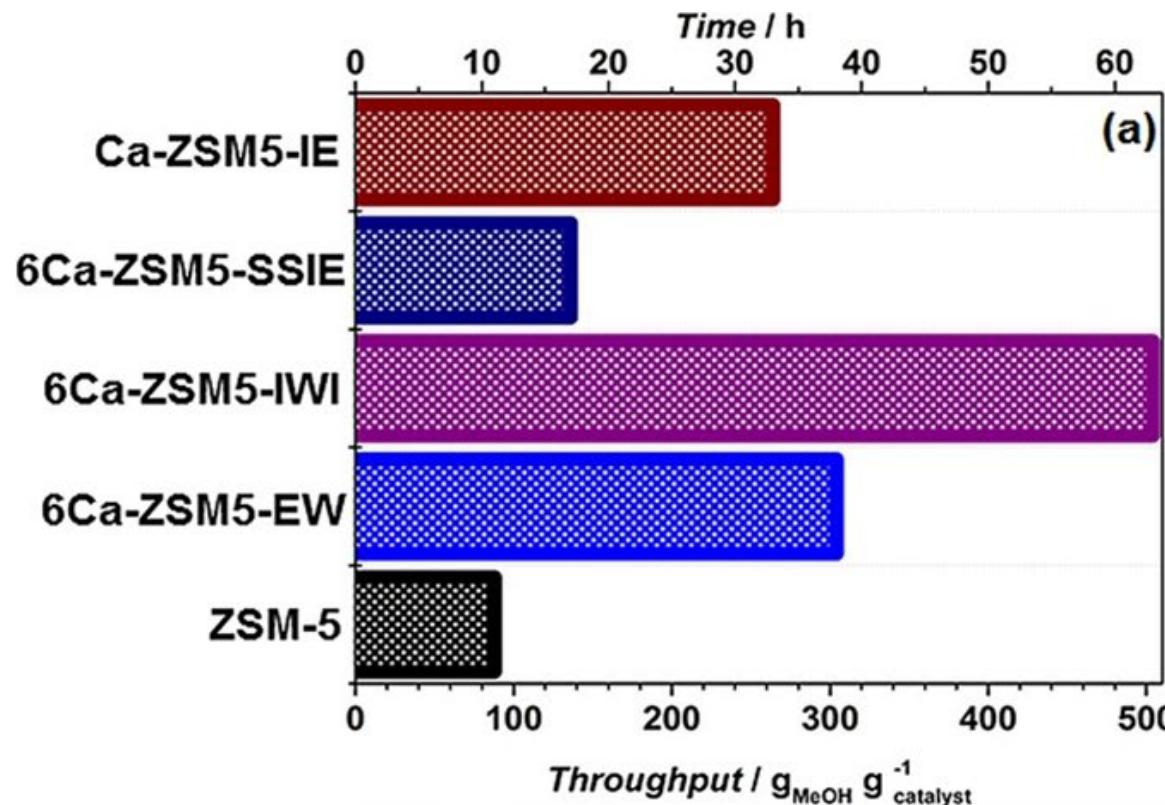
Substitution of some Brønsted acid sites  
with Ca Particularly effective for Al pairs

Sample	Concentration of BAS ( $\mu\text{mol/g}$ )
ZSM-5	232
Ca-ZSM-5-IE	138
6Ca-ZSM-5-SSIE	128
6Ca-ZSM-5-EW	38
6Ca-ZSM-5-IWI	29



- IE      – Ion exchange
- SSIE    – Solid-state ion-exchange
- EW      – Wet impregnation
- IWI     – Incipient wetness impregnation

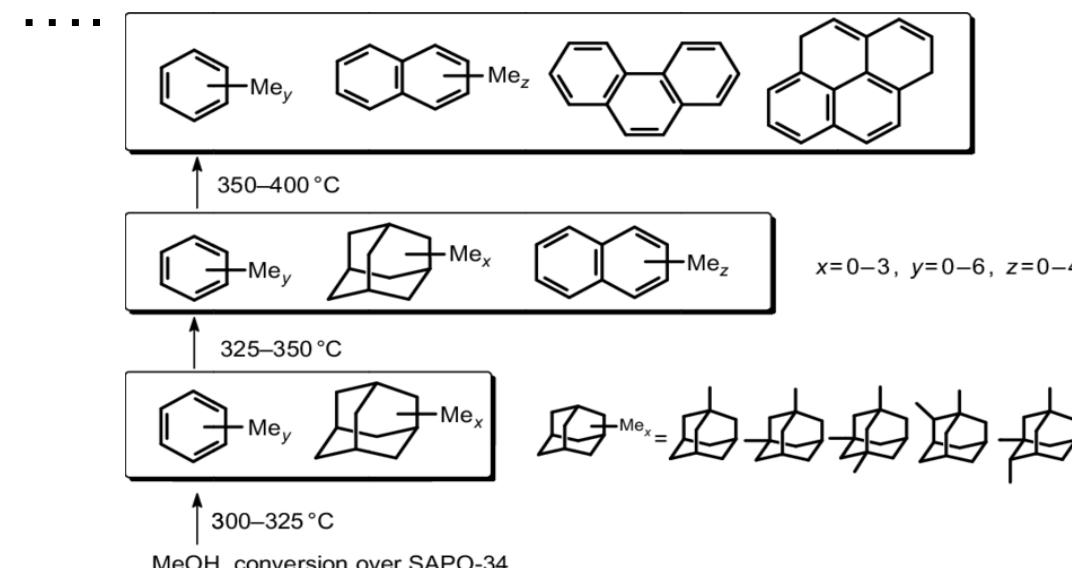
# Density of acid sites



- Removal of excessive acidity helps to suppress the aromatic cycle
- Coke species are the products of the aromatic cycle – longer lifetime

Concentration of acid sites ↓ –  
Hydride transfer ↓

# How to deal with hydrogen transfer?



Alkanes and less saturated olefins (aromatics eventually)

Proton-deficient coke species  
block the pores and deactivate the catalyst

MTO coke species

Polyaromatics (naphthalene, anthracene, pyrene derivatives)

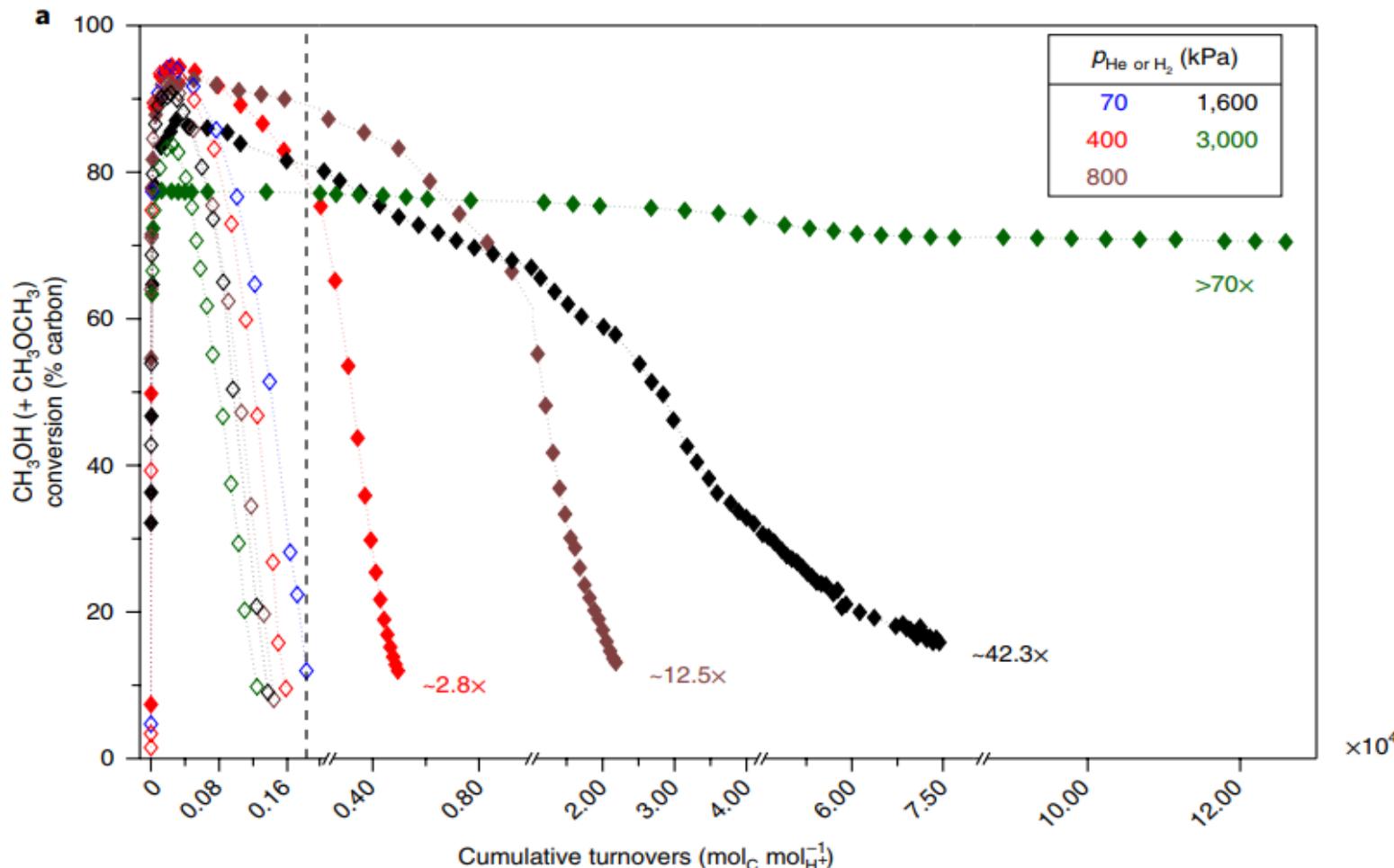
Bulky adamantane-based molecules

# How to deal with hydrogen transfer?

Formation of coke is an equilibrium limited reaction:



High enough pressure of hydrogen can reverse this reaction

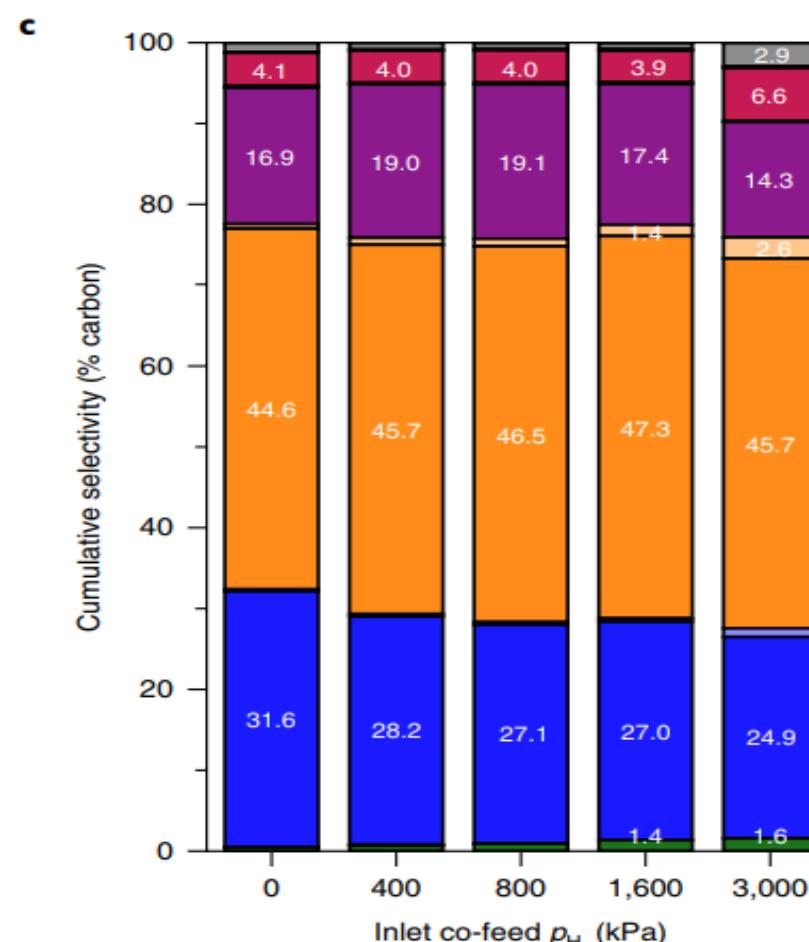
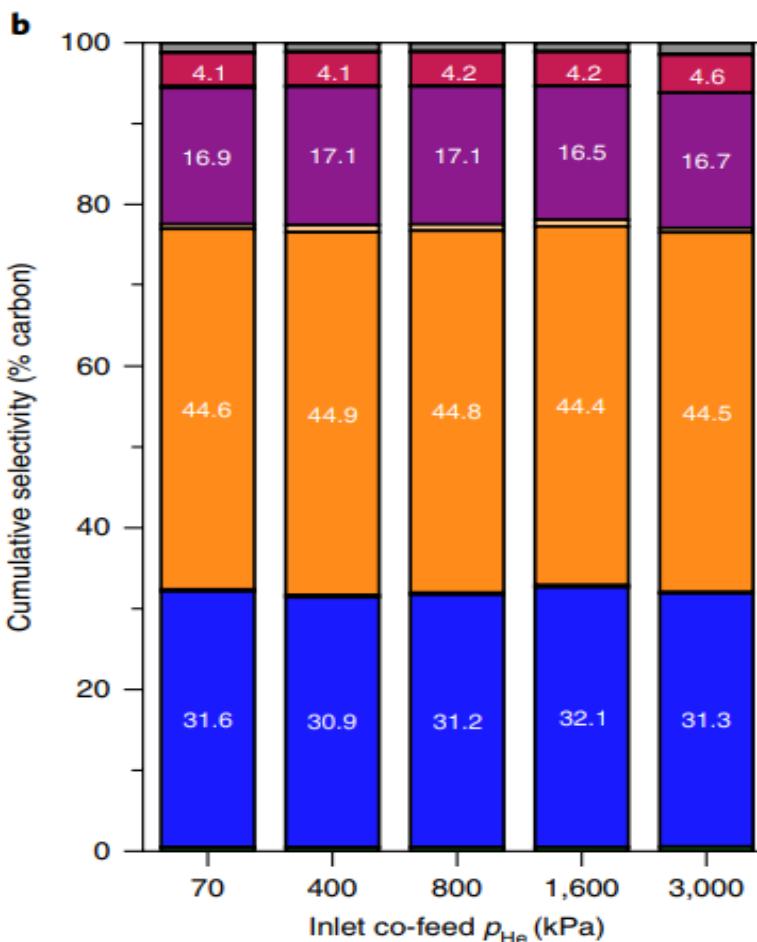


Performing MTO under pressure of hydrogen (30 bar) improves the total conversion capacity **>70 times**

Much higher atom economy!

# How to deal with hydrogen transfer?

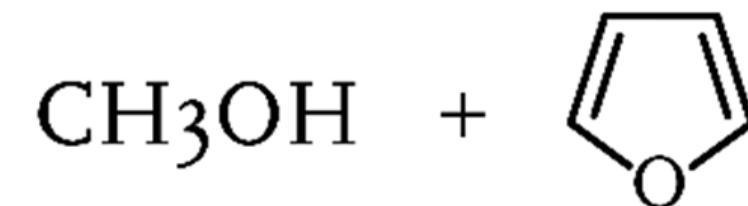
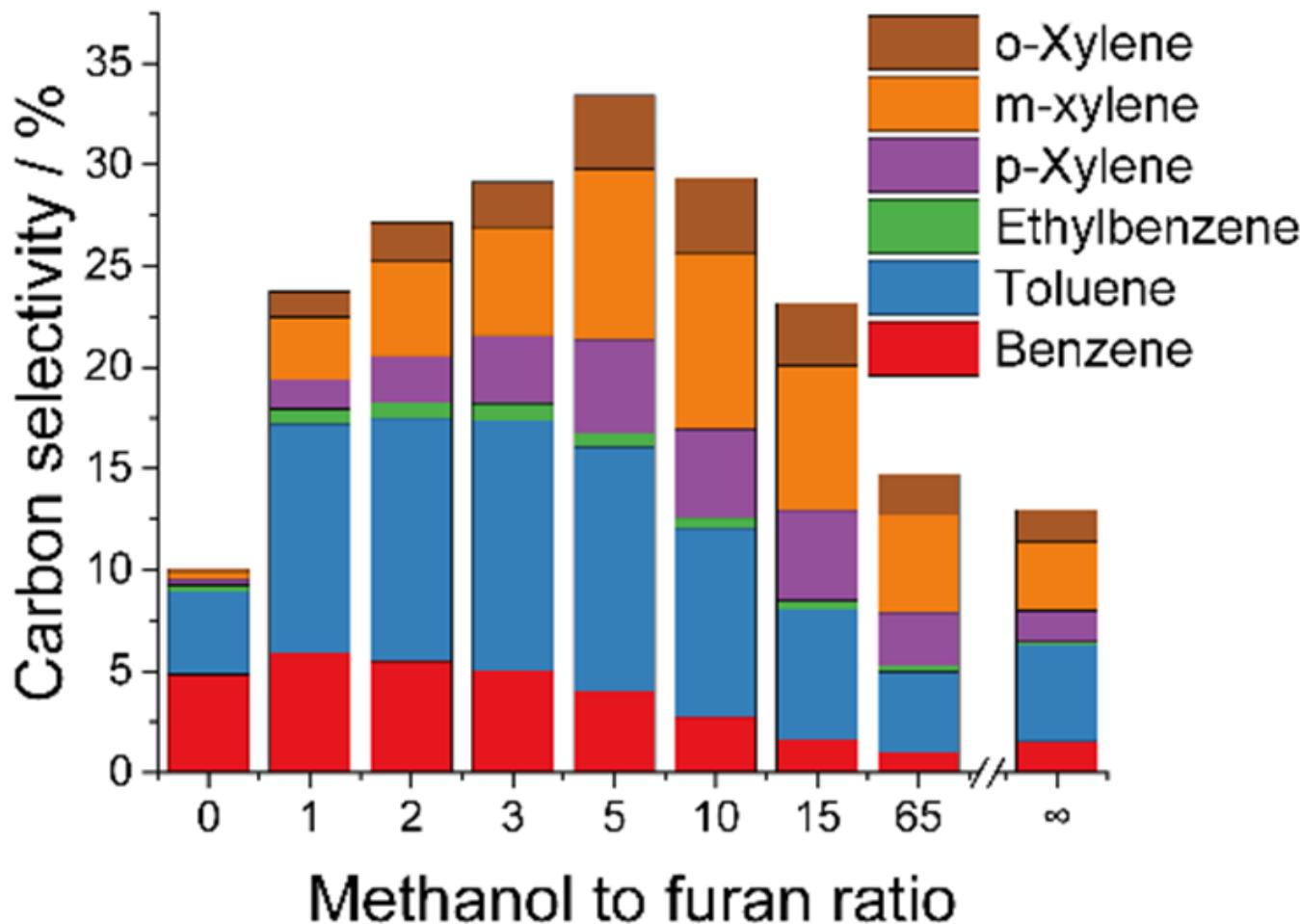
Formation of coke is an equilibrium limited reaction:



Identical product distribution

MTO itself does not produce hydrogen so no influence of hydrogen pressure!

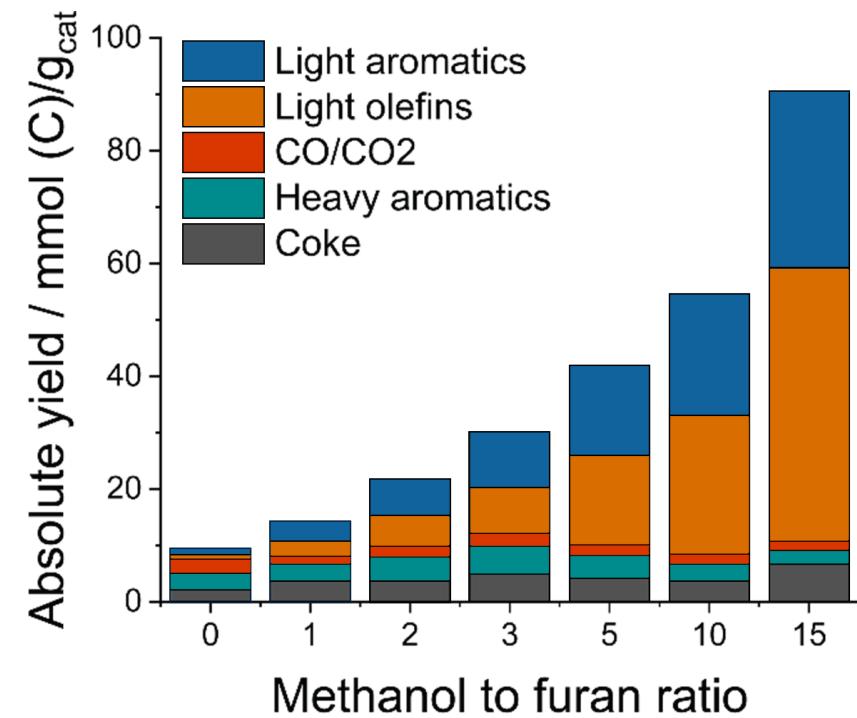
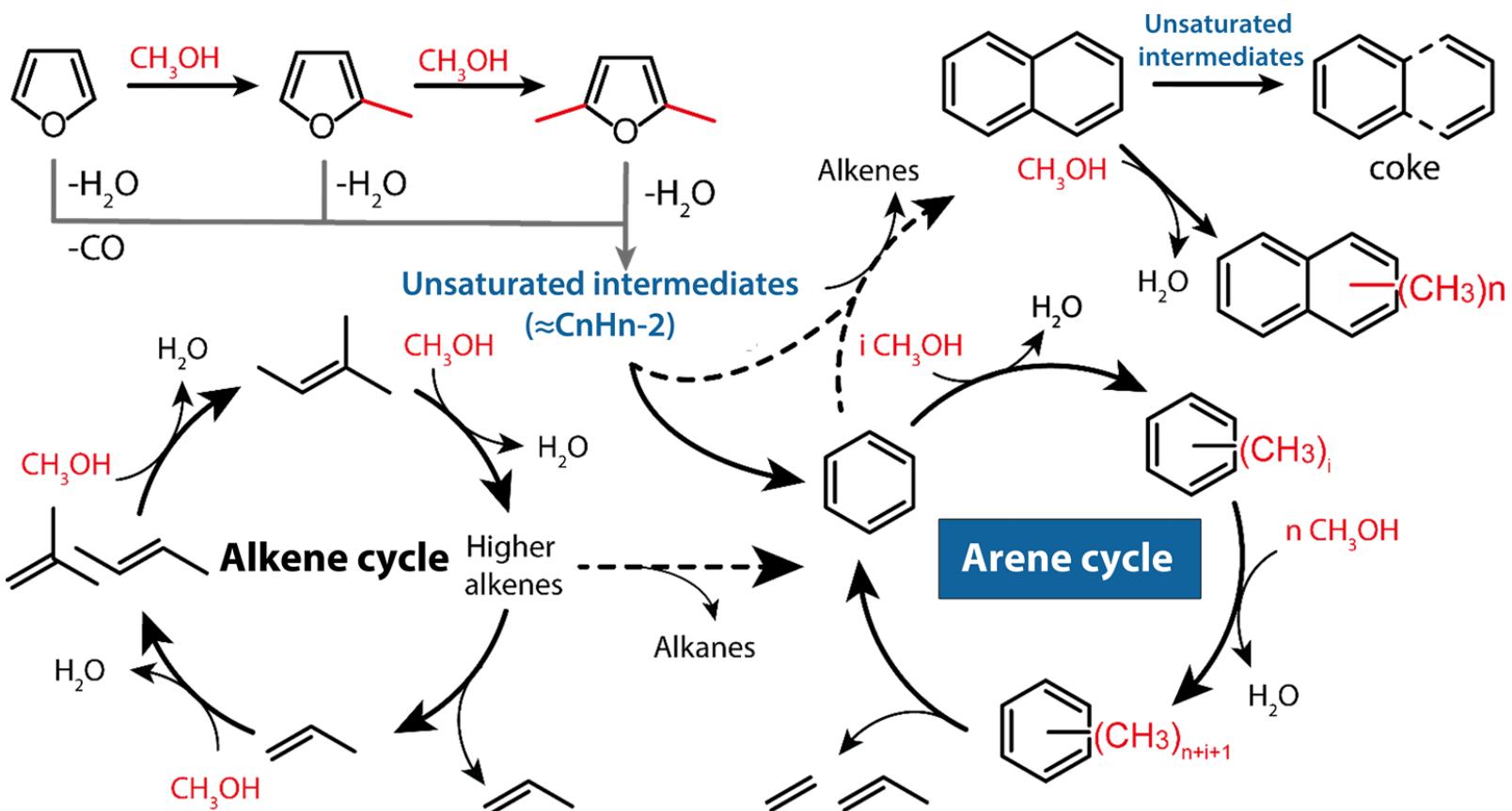
# What if we need more aromatics?



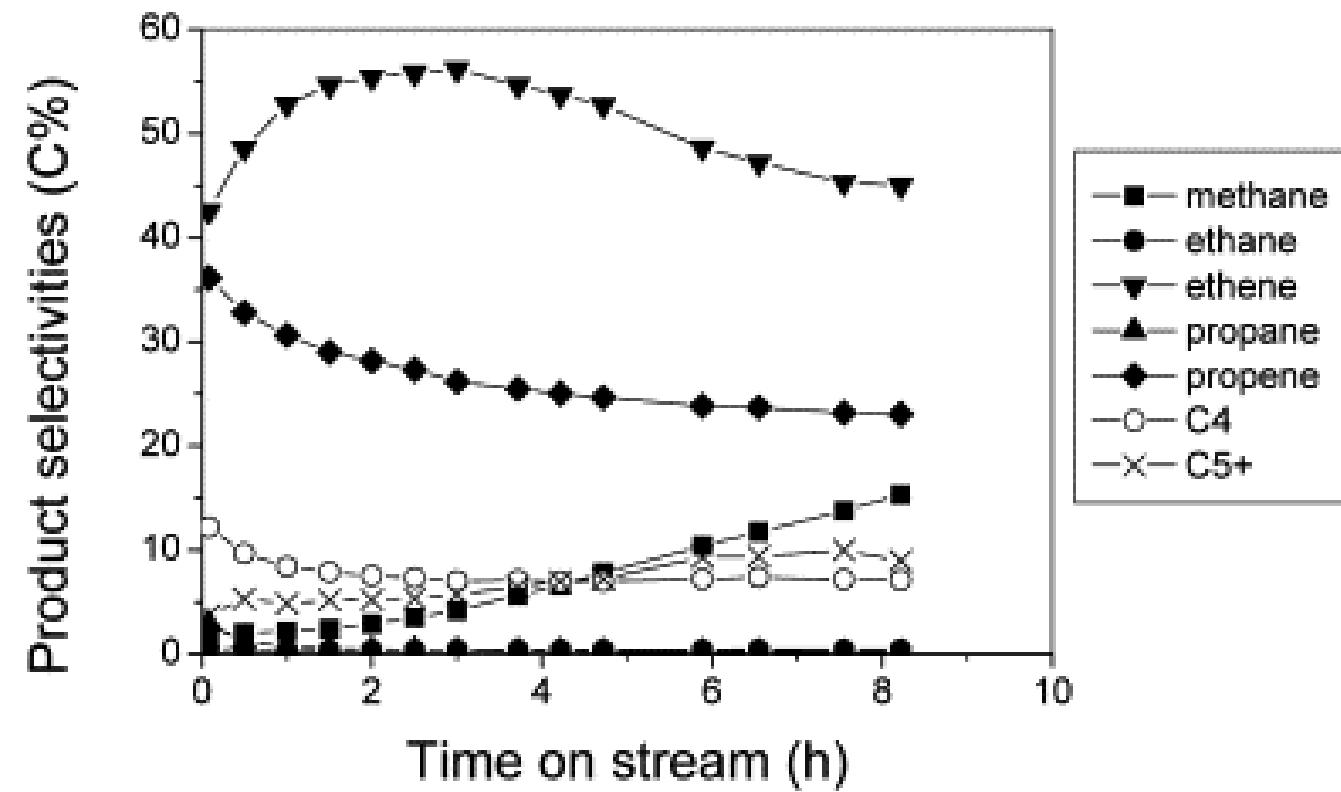
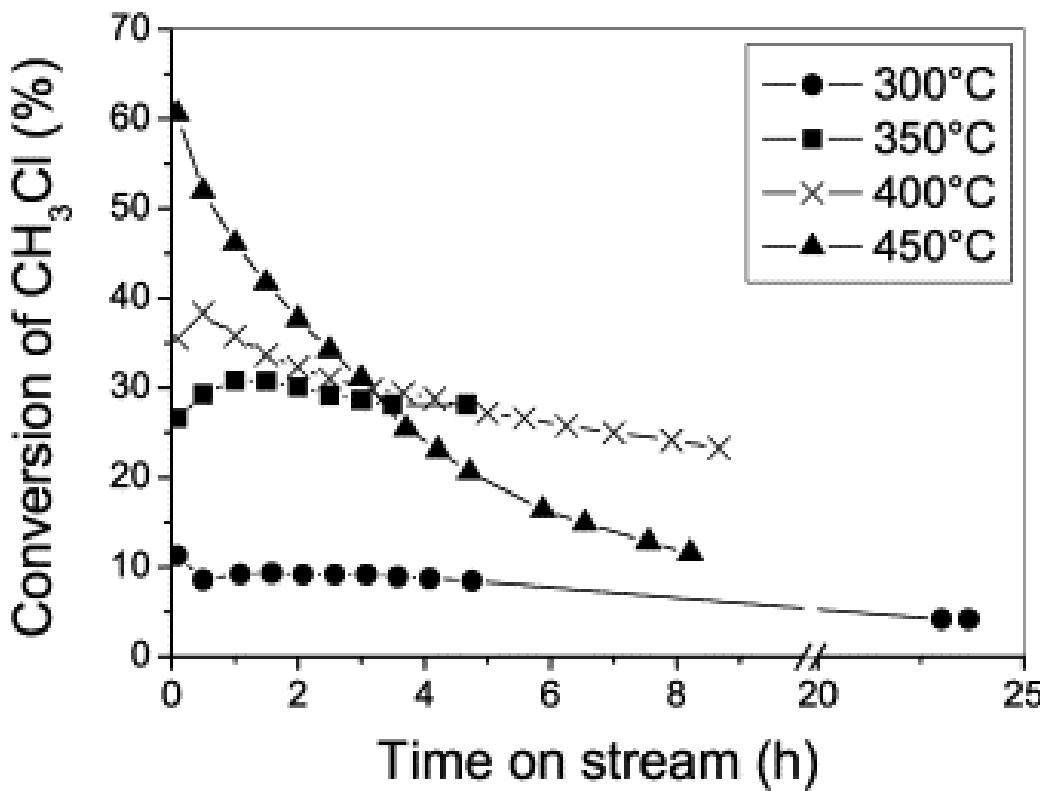
- Co-aromatization of furan and methanol
- Furan and its derivatives are abundant products of biomass valorization
- Highly proton-deficient upon deoxygenation

# What if we need more aromatics?

Co-aromatization of methanol with furanic compounds **promotes the aromatic cycle** and **increases the selectivity and cumulative yield of BTX**



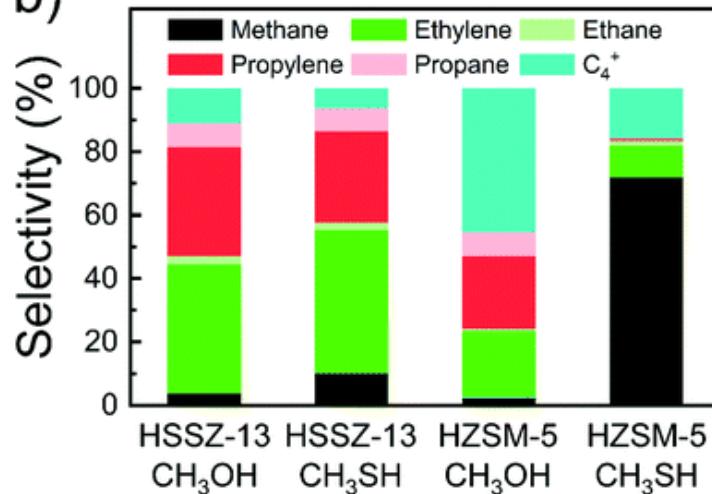
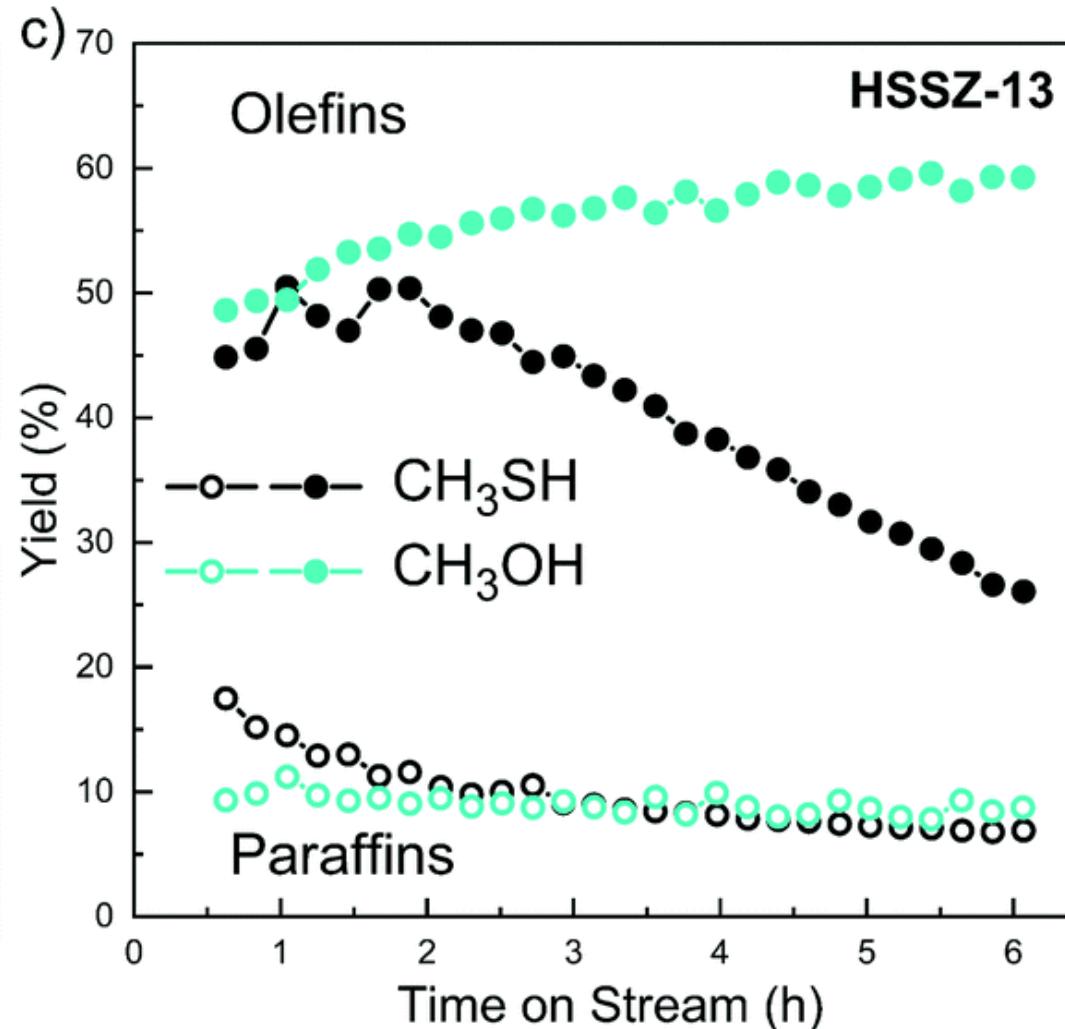
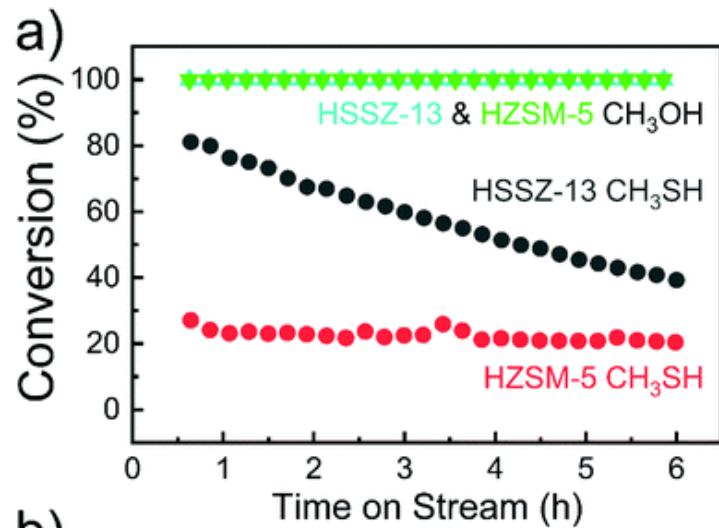
# Not only methanol



# Not only methanol



Methanethiol conversion over HZSM-5 and HSSZ-13 at 450 °C

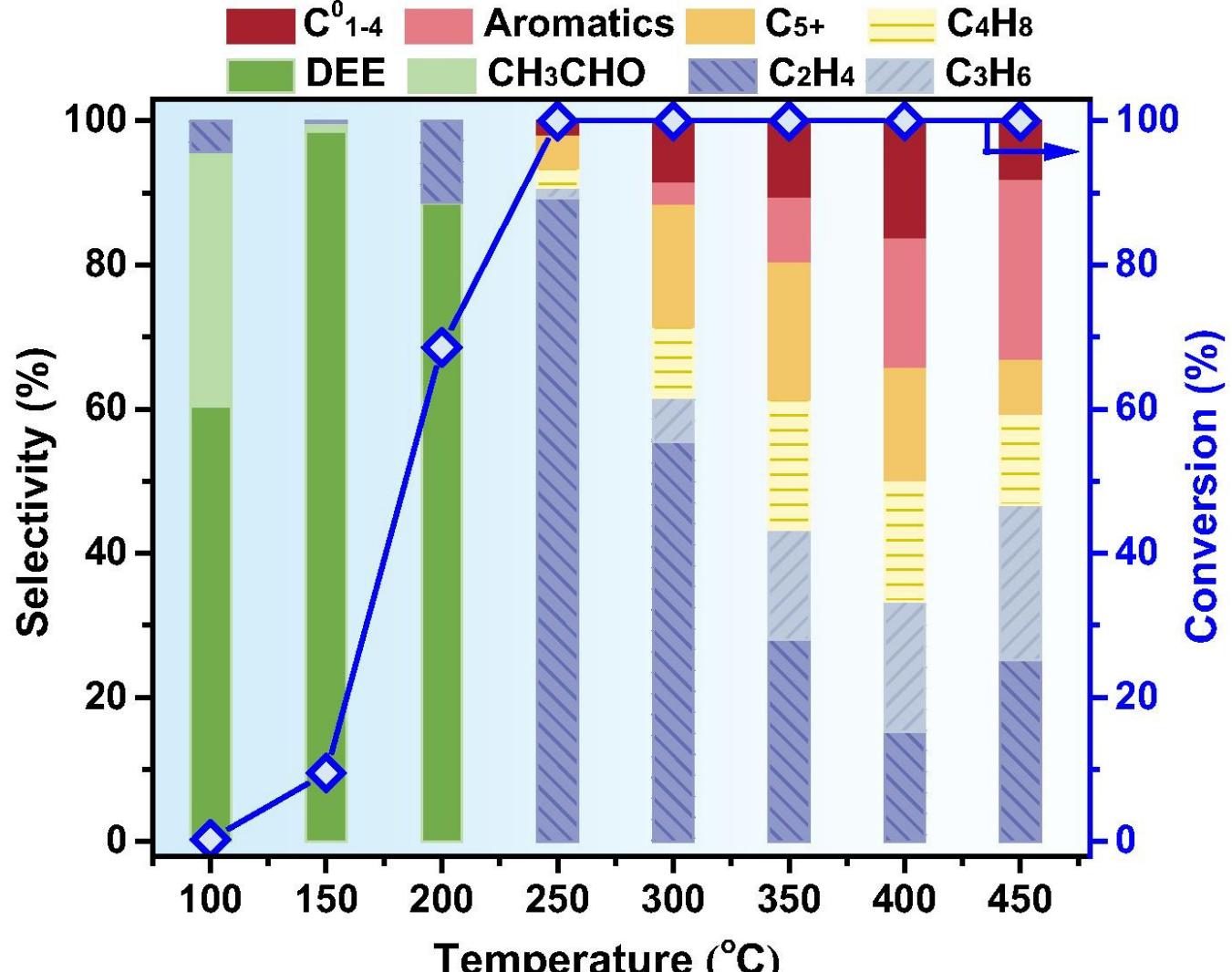


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# Not only methanol

$C_2H_5OH$

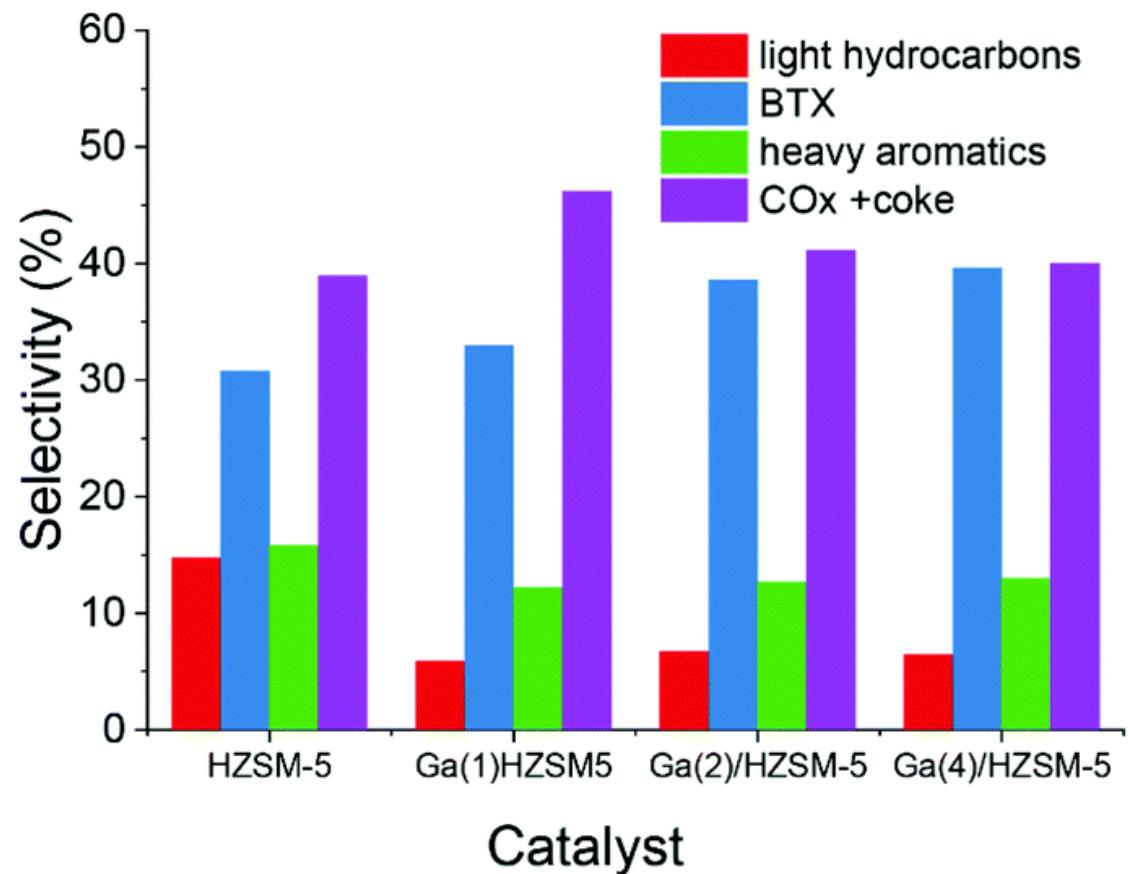
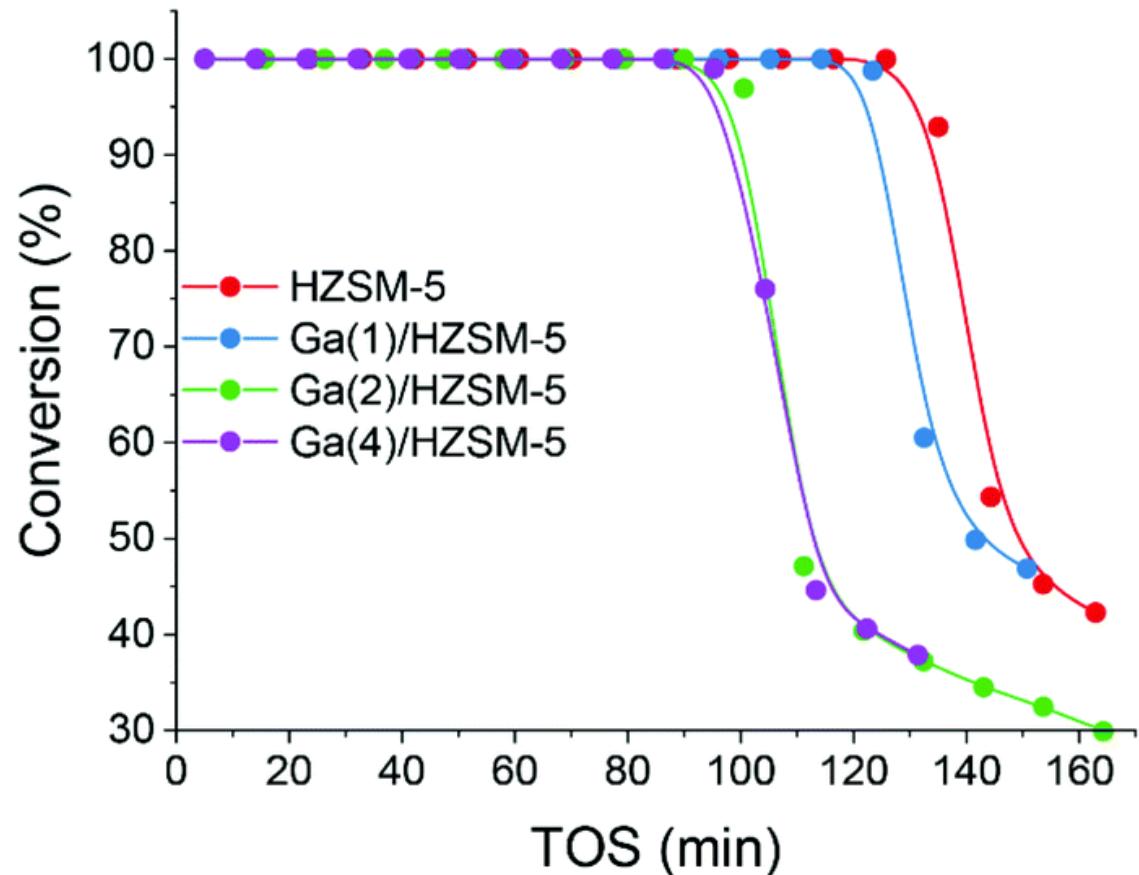
Ethanol conversion over HZSM-5



# Not only methanol

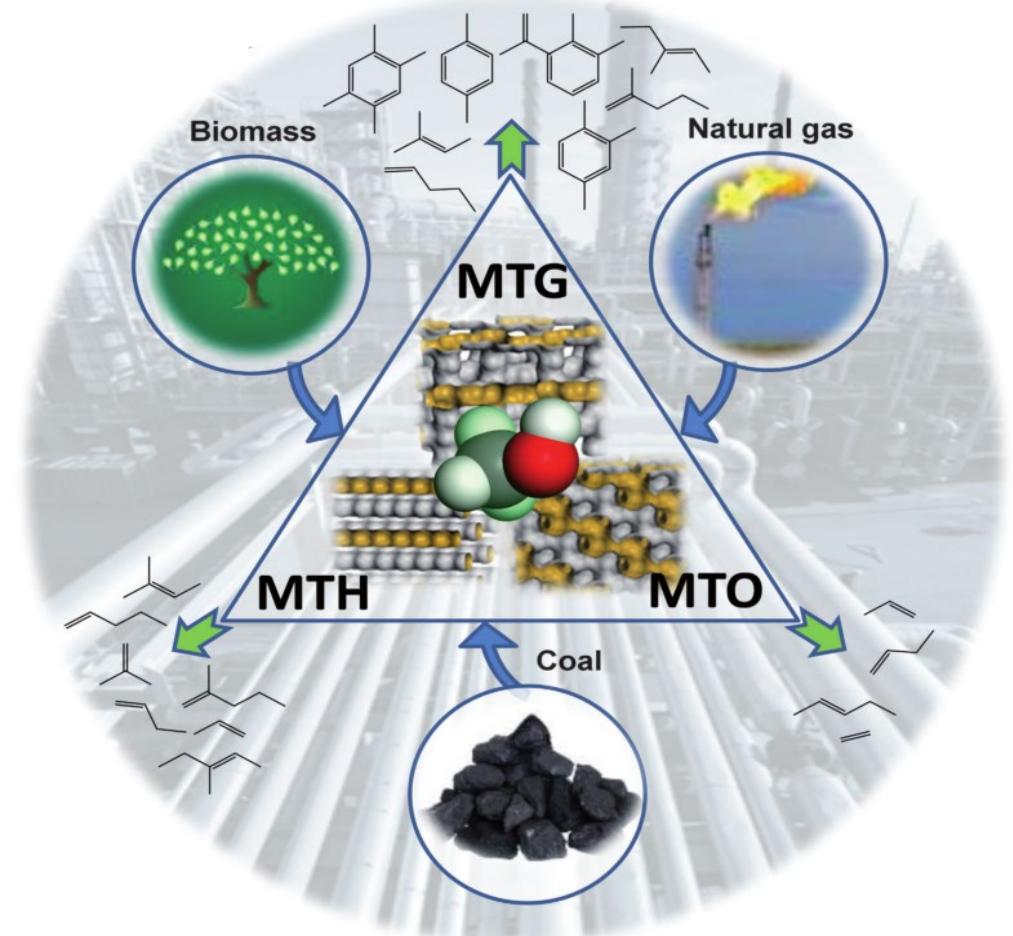
2,5-DMF

2,5-dimethylfuran conversion over HZSM-5 and Ga-modified HZSM-5 at 450 °C

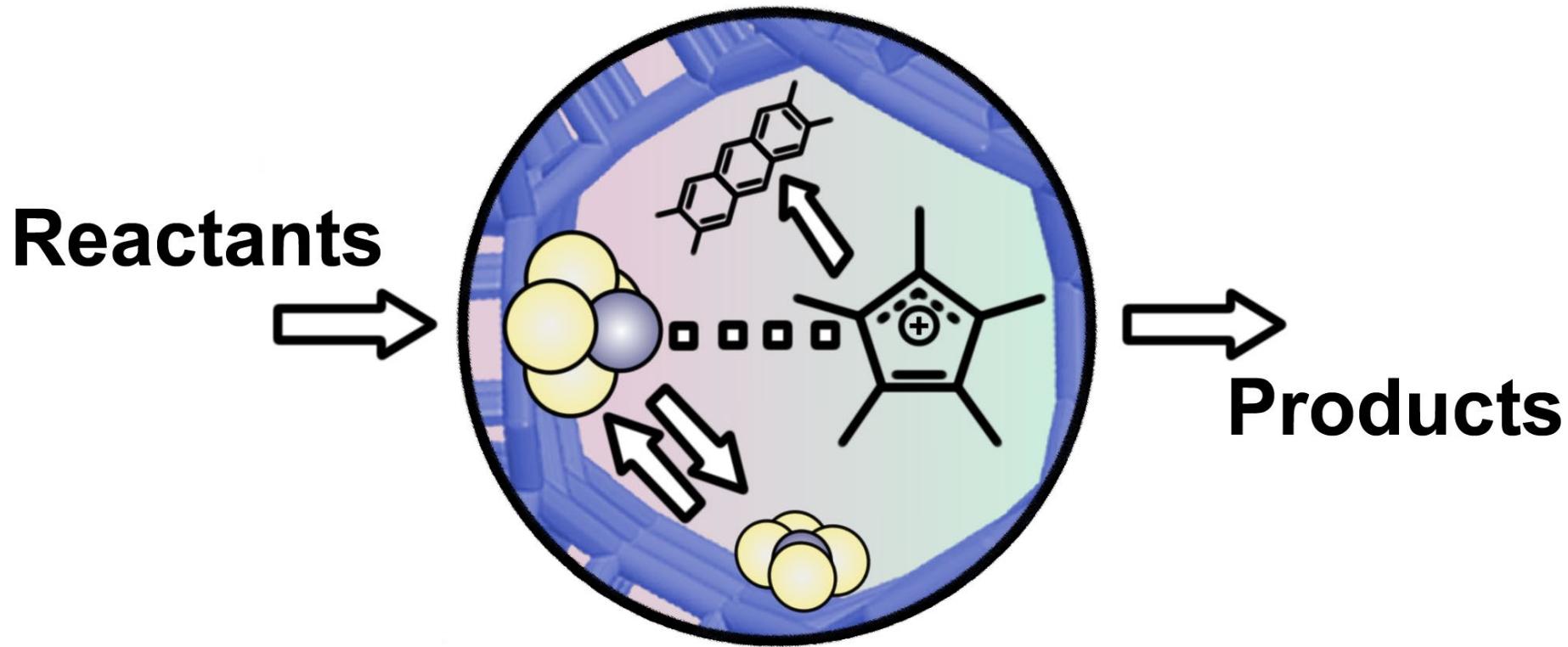


# MTH - Summary

- Selective route from various carbon sources (via syngas) to light olefins (polymers), C<sub>4</sub>-C<sub>10</sub> olefins/ paraffins (fuels), aromatics (chemical building blocks)
- Fascinating chemistry of inorganic-organic hybrid catalysts
- Controlled by pore architecture and textural properties
- Further progress with hierarchically porous materials and alternative feedstocks



# Zeolites as crystalline nanoreactors

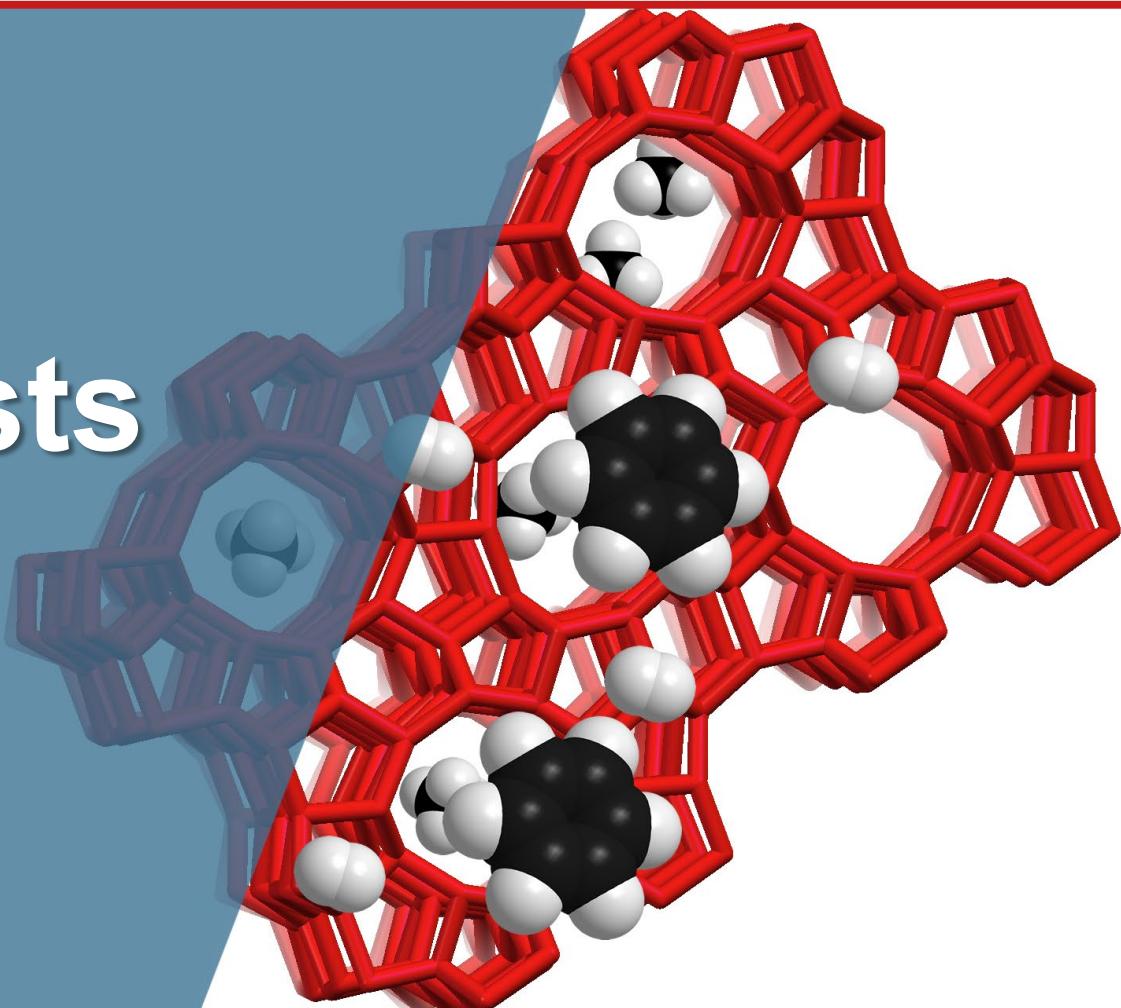


- Unique reactivity and selectivity in various reactions
- Complex interplay of diffusion, active sites, co-catalytic intermediates, deactivating species in nanoconfinement

# Further reading available in Canvas

- Conversion of Methanol to Hydrocarbons - How Zeolite Cavity and Pore Size Controls Product Selectivity
- Engineering of Transition Metal Catalysts Confined in Zeolites
- Zeolites and Catalysis

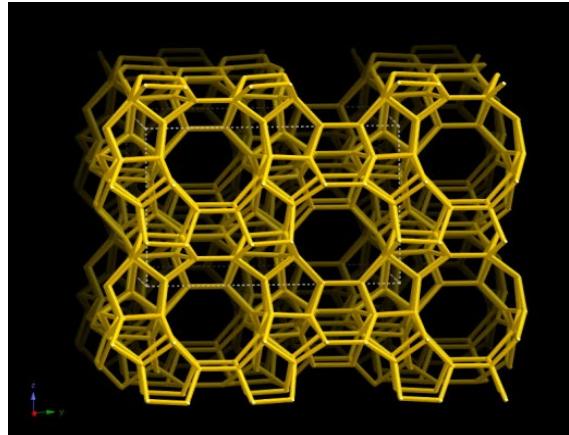
# Microporous Catalysts



6EMAC2  
Modern concepts in catalysis  
14<sup>th</sup> March, 2025

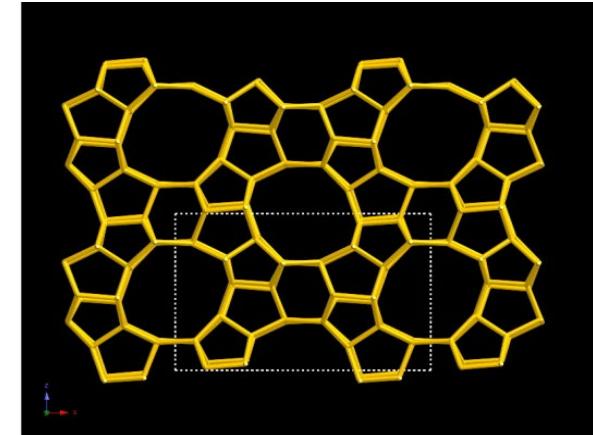
# MFI

Pores	<b>10MR x 10MR</b>
Dimensionality	<b>2D</b>
Framework Density (T/1000 Å <sup>3</sup> )	<b>18.4</b>
Accessible volume	<b>9.81%</b>
Si/Al	<b>9 - ∞</b>



**[100] direction**

Sinusoidal channels

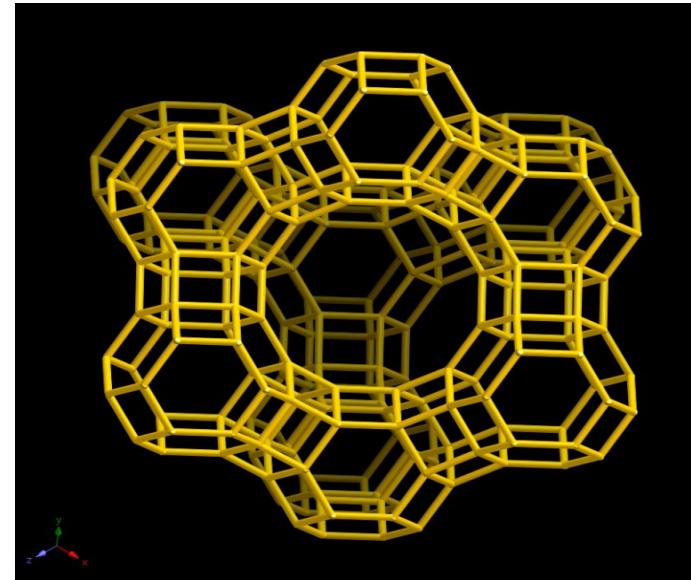


**[010] direction**

Straight channels

- Fluid catalytic cracking
- Dewaxing
- Aromatization of light alkanes/alkenes
- Alkylation of aromatics (p-xylene, cumene, ethylbenzene)
- Oligomerization
- Methanol-to-gasoline
- Isomerizatrion of aromatics (o-xylene to p-xylene)

Pores	<b>12MR</b>
Dimensionality	<b>3D</b>
Framework Density (T/1000 Å <sup>3</sup> )	<b>18.4</b>
Accessible volume	<b>27.42%</b>
Si/Al	<b>1 - 30</b>



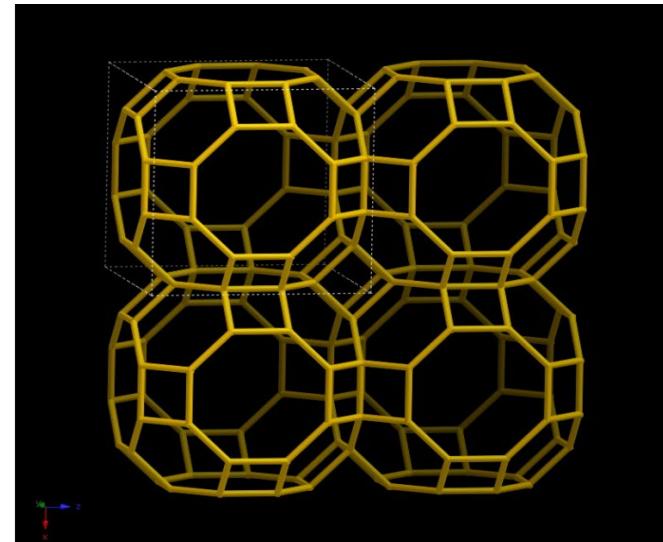
**[111] direction**

- Fluid catalytic cracking
- Hydrocracking
- Olefin/paraffin alkylation
- Alkylation of aromatics (p-xylene, cumene, ethylbenzene)

Straight channels + supercage (~1.5nm)

# LTA

Pores	<b>8MR</b>
Dimensionality	<b>3D</b>
Framework Density (T/1000 Å <sup>3</sup> )	<b>14.2</b>
Accessible volume	<b>21.43</b>
Si/Al	<b>1 - ∞</b>



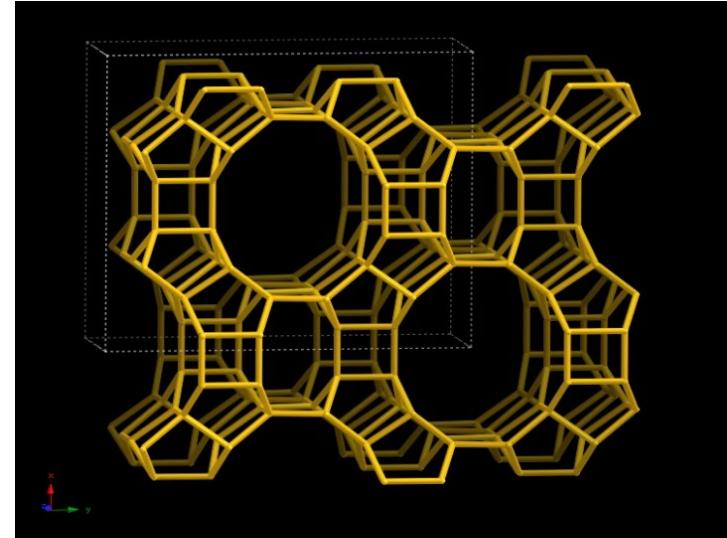
## [100/010/001] directions

Straight channels + LTA cage (~1nm)

- Water softening (detergents)
- Encapsulation of transition metal nanoparticles (hydrogenation, dehydrogenation, oxidation)
- Cu/LTA – effective deNOx catalyst
- Methanol-to-olefins

# MOR

Pores	<b>12MR &amp; 8MR</b>
Dimensionality	<b>1D</b>
Framework Density (T/1000 Å <sup>3</sup> )	<b>17.0</b>
Accessible volume	<b>12.27</b>
Si/Al	<b>5 - 11</b>



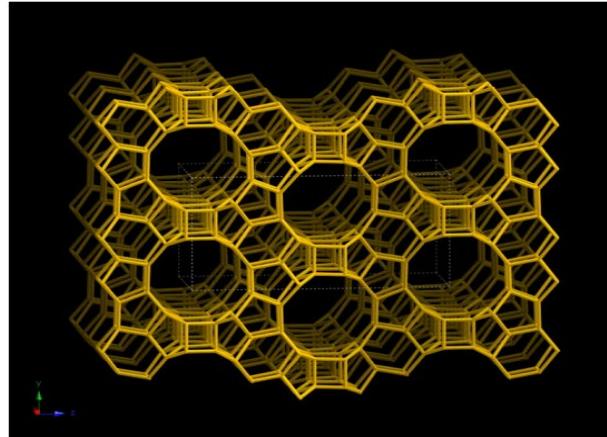
**[001] direction**

12MR and 8MR channels in one direction

- Pt(Pd)/MOR – hydrocracking and hydroisomerization
- Alkylation and acylation of bulky molecules
- C<sub>4</sub> isomerization
- (Trans)alkylation of aromatics
- Cu/MOR – catalyst for direct oxidation of methane to methanol

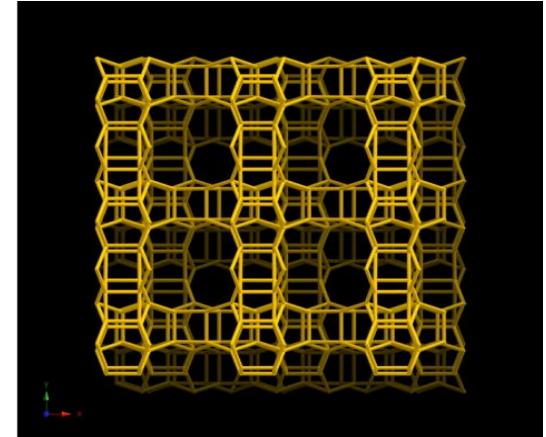
# BEA

Pores	<b>12MR x 12MR</b>
Dimensionality	<b>3D</b>
Framework Density (T/1000 Å <sup>3</sup> )	<b>15.1</b>
Accessible volume	<b>20.52</b>
Si/Al	<b>8 - ∞</b>



**[100/010] directions**

Straight channels



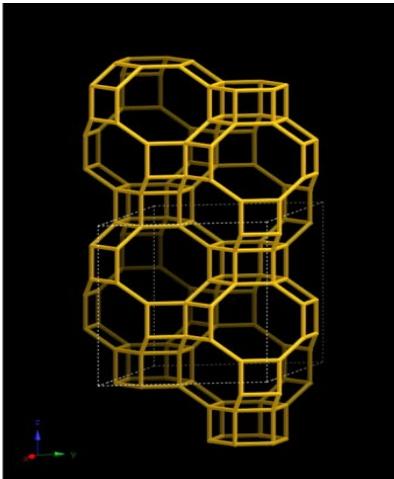
**[001] direction**

Sinusoidal channels

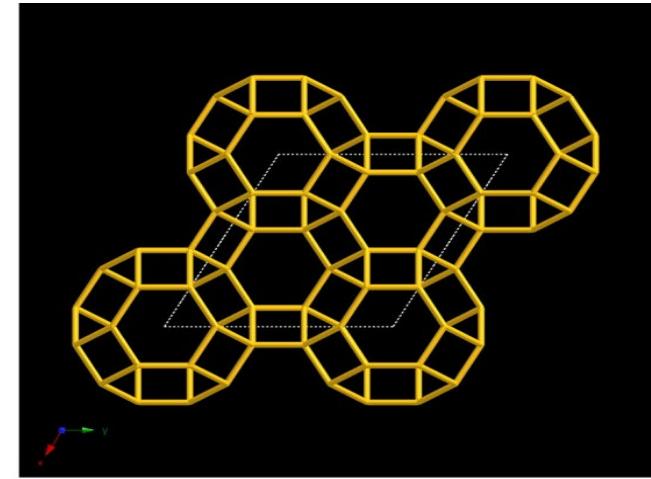
- Dewaxing
- Aromatic alkylation and transalkylation
- Sn/Beta - Lewis acid catalyst active in:
  - Selective oxidation (Baeyer-Villiger and Meerwein-Ponndorf-Verley-Oppenauer reactions)
  - Isomerization of glucose to fructose

# CHA

Pores	<b>8MR</b>
Dimensionality	<b>3D</b>
Framework Density (T/1000 Å <sup>3</sup> )	<b>15.1</b>
Accessible volume	<b>17.27%</b>
Si/Al	<b>2 - ∞</b>



**[100] direction**



**[001] direction**

Large 1.3 nm cages connected by straight channels

- Methanol-to-olefins
- Amination
- Cu/CHA – DeNO<sub>x</sub> catalyst