

Heterogeneous catalysis (C9981)

Lecture 9

Zeolites in oil refinement

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Zeolites - synthesis

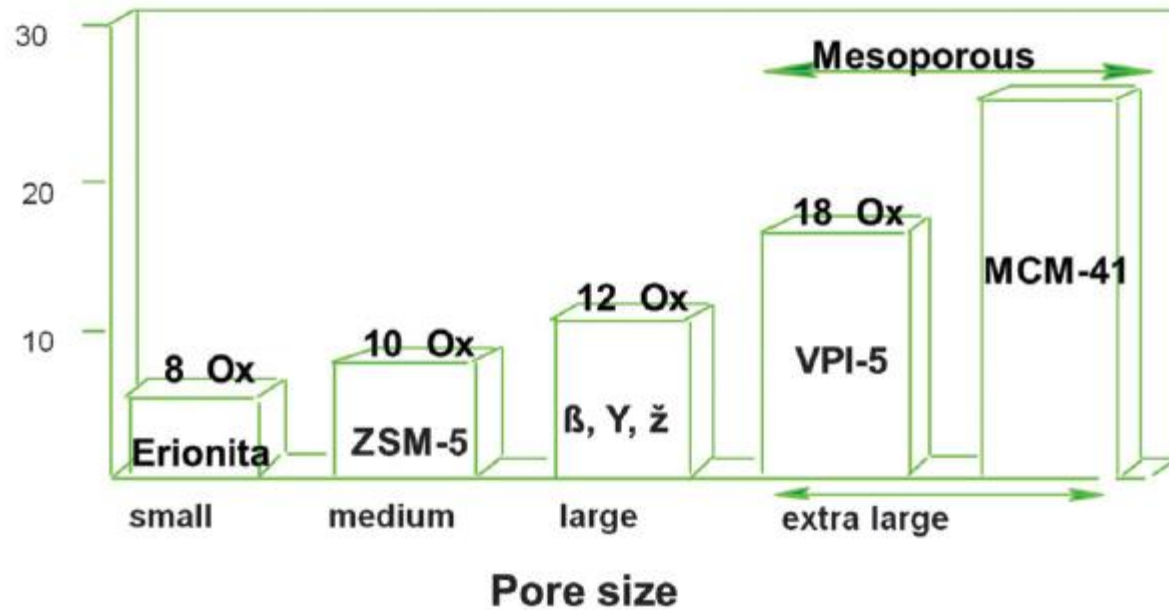
- **Reaction mixture:** ..., ..., ..., ...
 - pH adjustment, (gelation)
 - Hydrothermal treatment in an autoclave
 - ...
 - ...
- **Result:** H-zeolite (Brønsted acidic with H⁺ ions)

Zeolites - synthesis

- **Reaction mixture:** Na_2SiO_3 , Al_2O_3 , quarternary ammonium salt (=structure directing agent), water
 - pH adjustment, (gelation)
 - Hydrothermal treatment in an autoclave
 - Ion exchange (Na^+ for NH_4^+)
 - Calcination (= NH_3 removal)
- **Result:** Crystalline H-zeolite (Brønsted acidic with H^+ ions)

Zeolites - synthesis

- Pore size



- Si/Al ratio ≥ 1

Zeolites - acidity

- **Brønsted:** ...

- Structure:

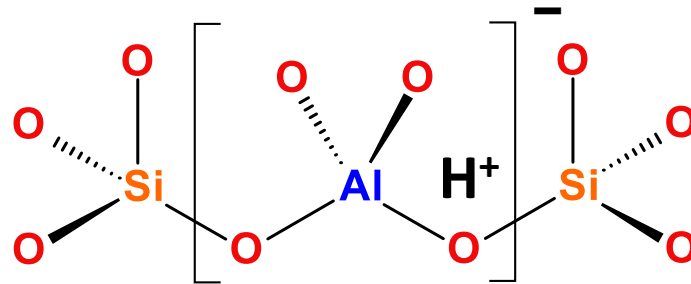
- **Lewis:** ...

- Structure:

Zeolites - acidity

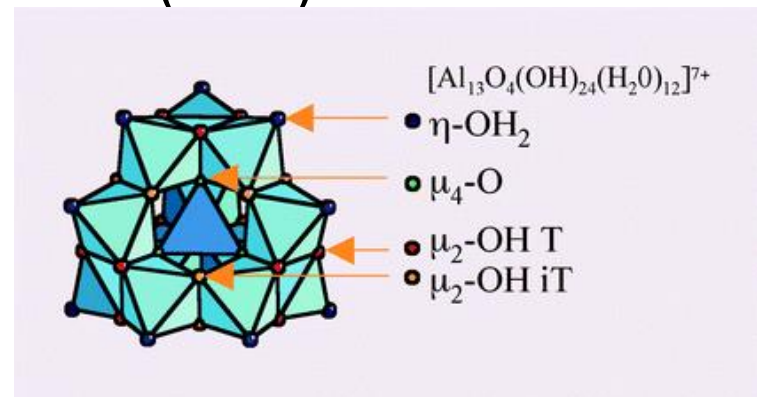
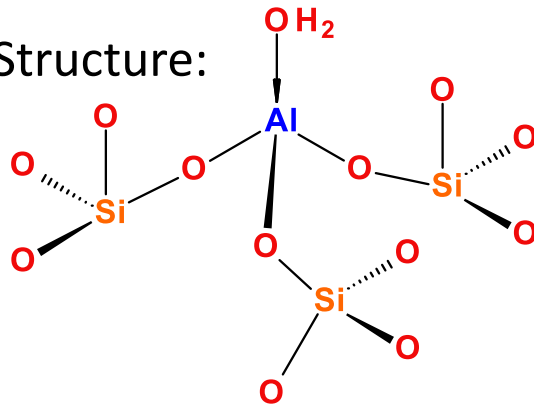
- **Brønsted:** negative charge of the aluminosilicate net balanced by strongly acidic protons

– Structure:



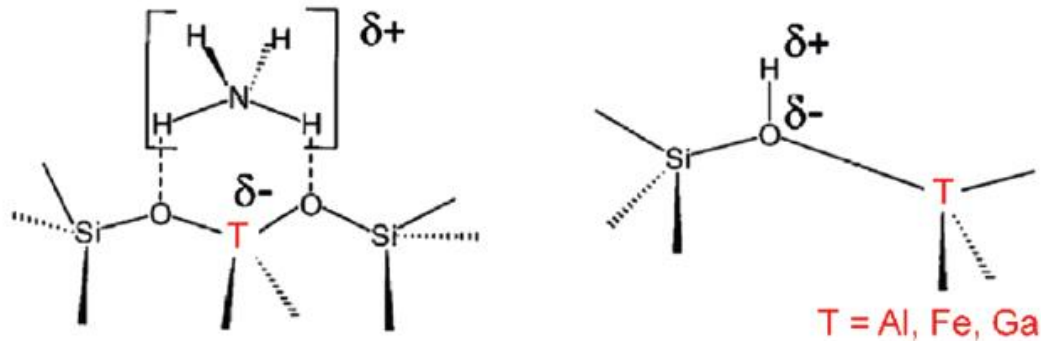
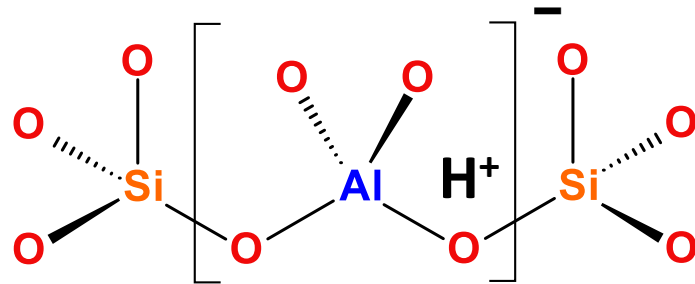
- **Lewis:** Al atoms that are not embedded in the aluminosilicate net (e.g. surface species, amorphous stuff, alumina particles) = extraframework aluminum species (EFAL)

– Structure:



Zeolites - acidity

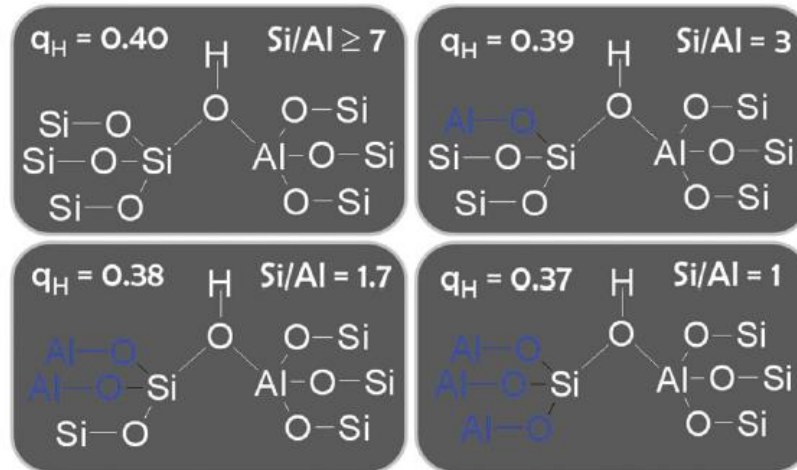
- **Brønsted:** negative charge of the aluminosilicate net balanced by strongly acidic protons
 - Structure:



Changes in local Al structure revealed by EXAFS

Zeolites - acidity

- **Brønsted:** depends on the second coordination sphere (i.e. Si/Al ratio)



- **Lewis:** Extraframework aluminum species (EFAL) depends on
 - Si/Al ratio
 - Aging (time on stream, steaming)
 - Can be washed out (depending on pH – acid washing)

Zeolites - acidity

- **High Si/Al ratio**
 - Strong Brønsted acid sites
 - Weak Brønsted acid sites
 - Strong Lewis acid sites
 - Weak Lewis acid sites

- **Low Si/Al ratio**
 - Strong Brønsted acid sites
 - Weak Brønsted acid sites
 - Strong Lewis acid sites
 - Weak Lewis acid sites

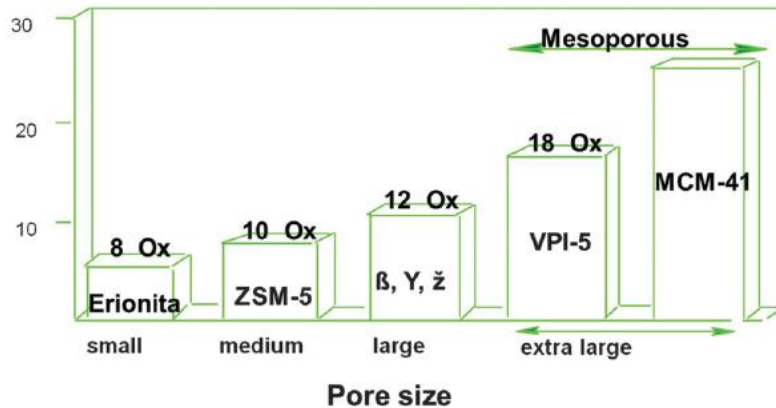
Zeolites - acidity

- **High Si/Al ratio**
 - Strong Brønsted acid sites
 - ~~– Weak Brønsted acid sites~~
 - ~~– Strong Lewis acid sites~~
 - ~~– Weak Lewis acid sites~~

- **Low Si/Al ratio**
 - ~~– Strong Brønsted acid sites~~
 - Weak Brønsted acid sites
 - Strong Lewis acid sites
 - Weak Lewis acid sites

Zeolites - acidity

- **Confinement effect**



- **Superacidity**

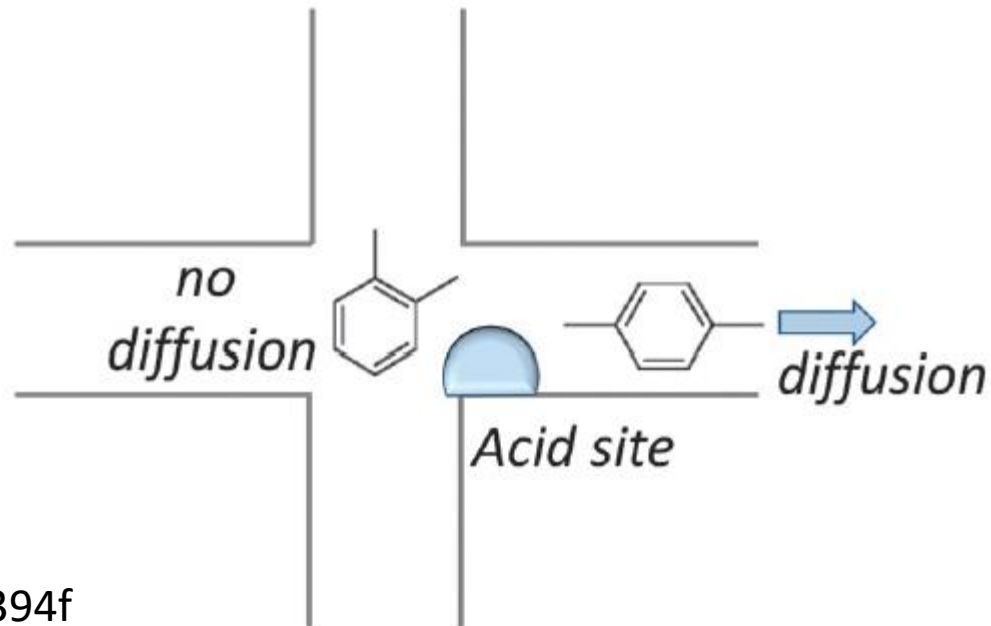
- Various probes at RT – acid site strength similar to 70 % H₂SO₄ (=NO!)
- Ability to protonate hydrocarbons at working conditions (=YES!)
- ?

Zeolites – diffusion/shape selectivity

- **Diffusion**

- Big difference between zeolites with 8 membered vs. 12 membered ring pore openings
- Big difference between zeolites with 1D, 2D, and 3D-connected pore structure

- **Shape selectivity**

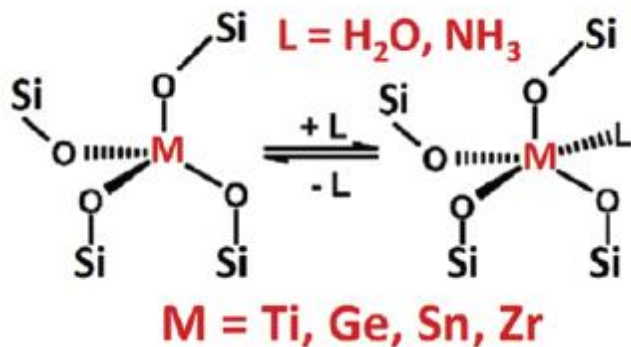


Other microporous frameworks

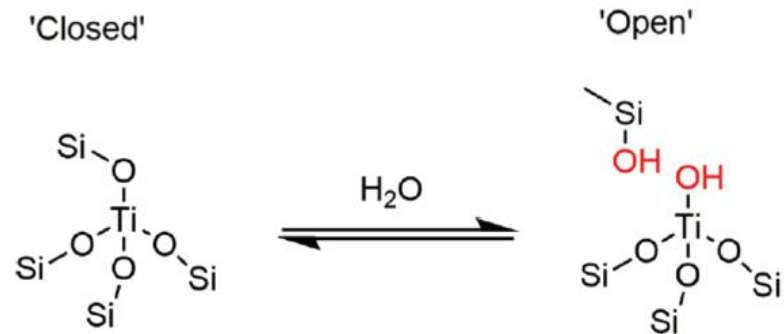
- Non-Al zeolites
 - Be^{2+} , Zn^{2+} , B^{3+} , Ga^{3+} , Fe^{3+} , Ge^{4+} , Ti^{4+} , Sn^{4+}
 - 15 % variation in radius (vs. Si^{4+})
 - ± 0.4 a.u. Pauling electronegativity
- Aluminophosphates (AlPOs)
 - SiO_2 and AlPO_4 and isoelectronic structures
 - No catalytic activity
- M(II) Aluminophosphates
 - Mild Brønsted acids and(or) redox catalysts
- Silicoaluminophosphates (SAPOs)
 - Mild Brønsted acids

Other microporous frameworks

- Non-Al zeolites
 - Be^{2+} , Zn^{2+} , B^{3+} , Ga^{3+} , Fe^{3+} , Ge^{4+} , Ti^{4+} , Sn^{4+}
 - 15 % variation in radius (vs. Si^{4+})
 - ± 0.4 a.u. Pauling electronegativity



Lewis acidity in non-Al zeolites



Open vs. Closed acid sites in non-Al zeolites

Other microporous frameworks

- Aluminophosphates (AlPOs)
 - M(II) Aluminophosphates
 - Silicoaluminophosphates (SAPOs) = milder acidity

Table 1

Methanol conversion and product selectivity of MTO over SAPO-34.

Pulse number	Conversion (%)	Selectivity (C%)							
	CH ₃ OH	C ₁ ⁰	C ₂ ⁻	C ₂ ⁰	C ₃ ⁻	C ₃ ⁰	C ₄	C ₅	C ₆ ⁺
1	40.4	3.5	6.6	0.0	60.8	1.3	15.6	7.6	4.7
15	91.6	0.8	26.8	0.2	42.4	6.8	16.0	5.8	1.2
19	96.0	0.8	27.3	0.2	44.1	4.0	16.0	6.3	1.4

Table 2

Methanol conversion and product selectivity of MTO over ZSM-5.

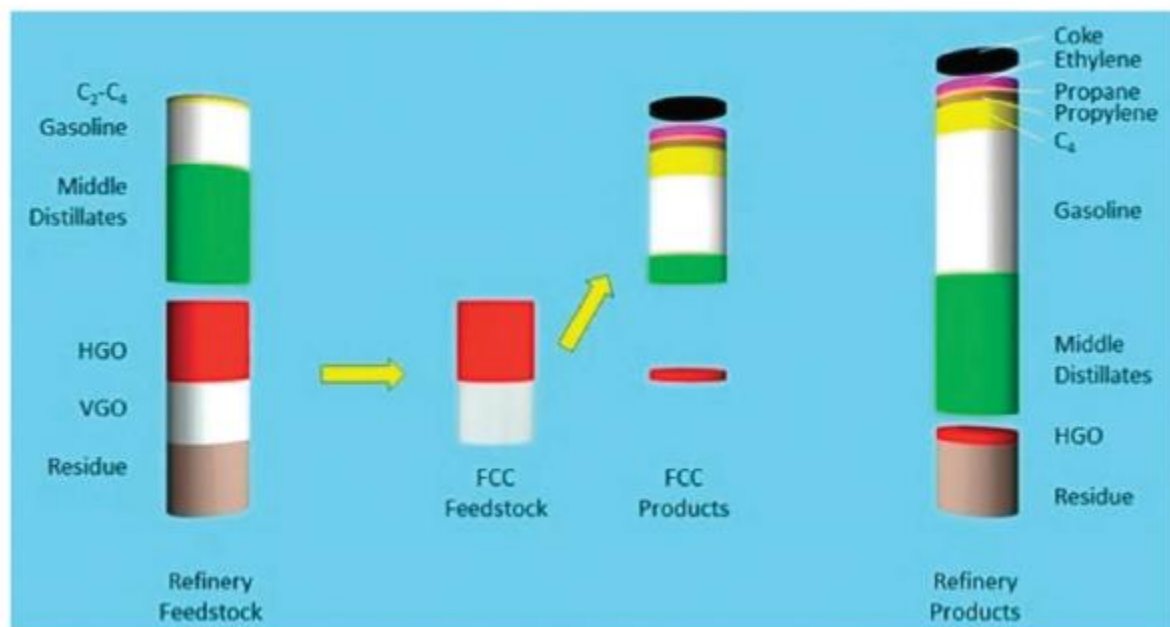
Pulse number	Conversion (%)	Selectivity (C%)							
	CH ₃ OH	C ₁ ⁰	C ₂ ⁻	C ₂ ⁰	C ₃ ⁻	C ₃ ⁰	C ₄	C ₅	C ₆ ⁺
1	76.0	1.8	8.4	0.0	37.3	1.4	15.4	11.1	24.6
15	82.5	2.2	10.8	0.1	36.2	1.2	14.9	8.6	26.0
19	78.5	2.0	9.1	0.1	37.1	1.1	14.5	10.6	25.5

Zeolites in oil refinement

- **Fluid catalytic cracking**
- **Isobutane-butene alkylation**
- **Reforming (+ steam reforming)**
- **Hydrocracking**
- **Linear paraffin isomerization**

Zeolites in oil refinement

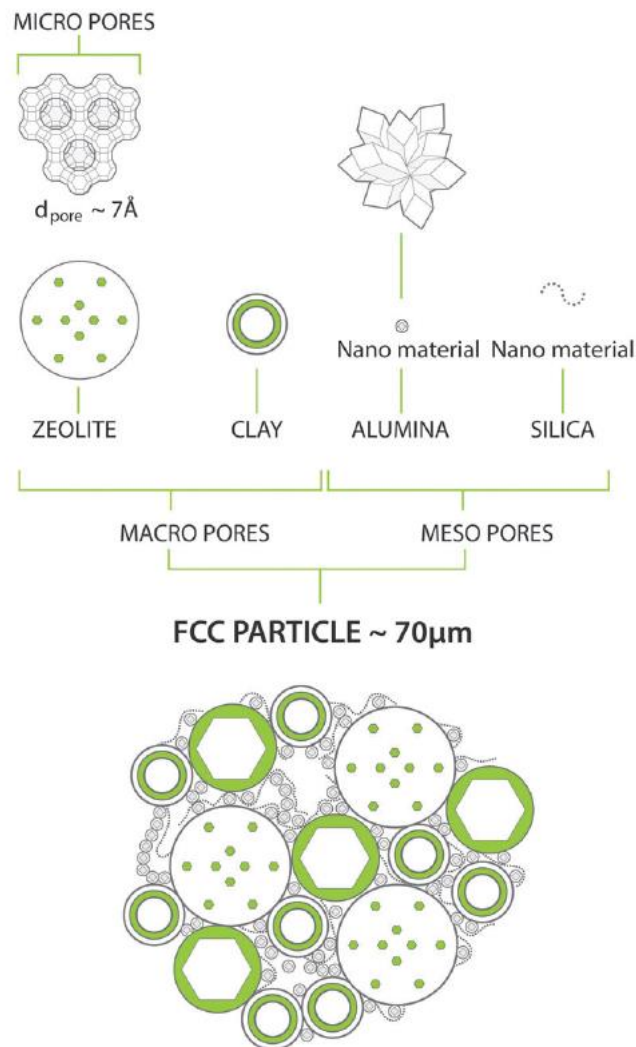
- Fluid catalytic cracking



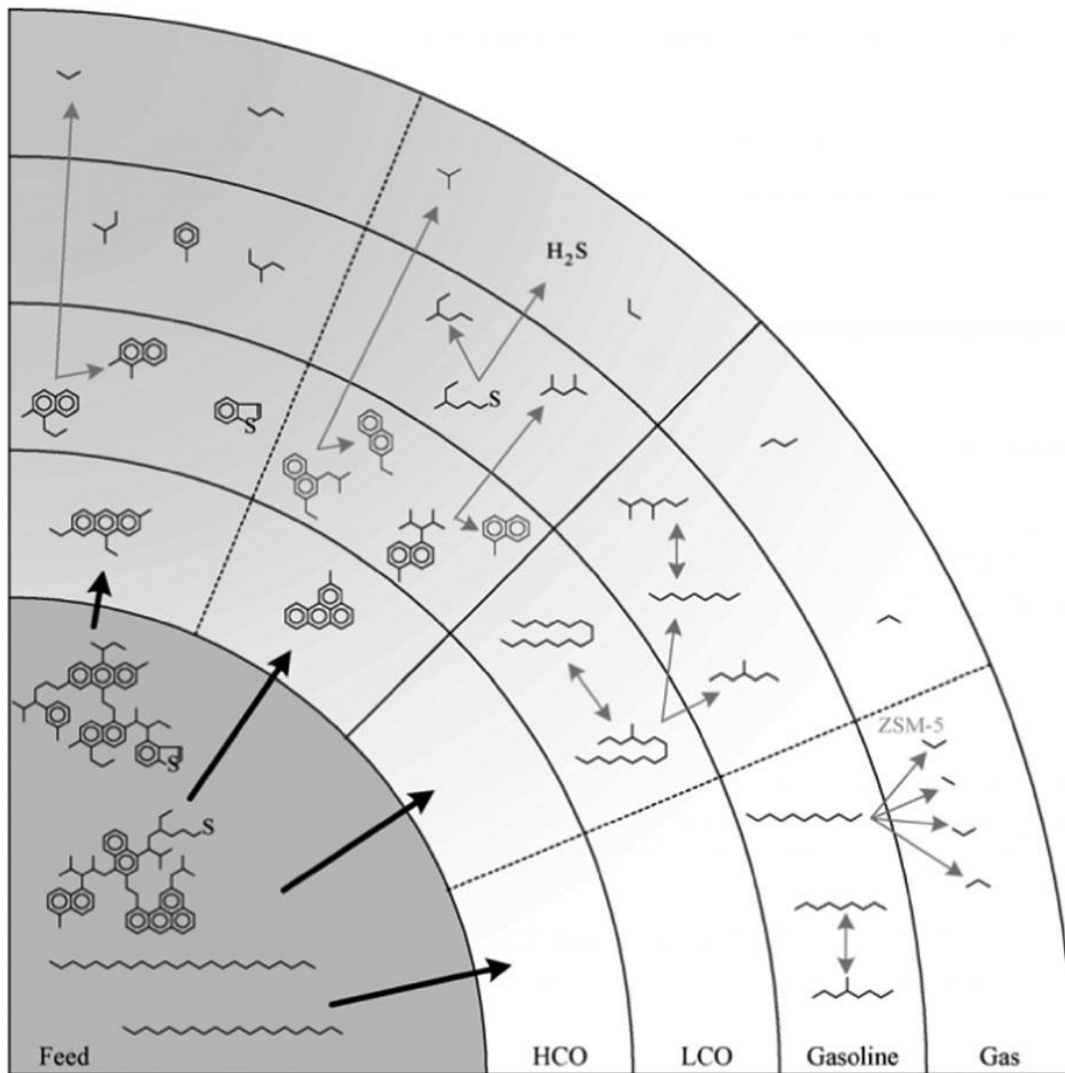
Zeolites in oil refinement

- **Fluid catalytic cracking**

- Zeolite Y 10-50 wt%
- Binders 50-90 wt%
- At the beginning – AlCl_3
- Addition of HZSM-5

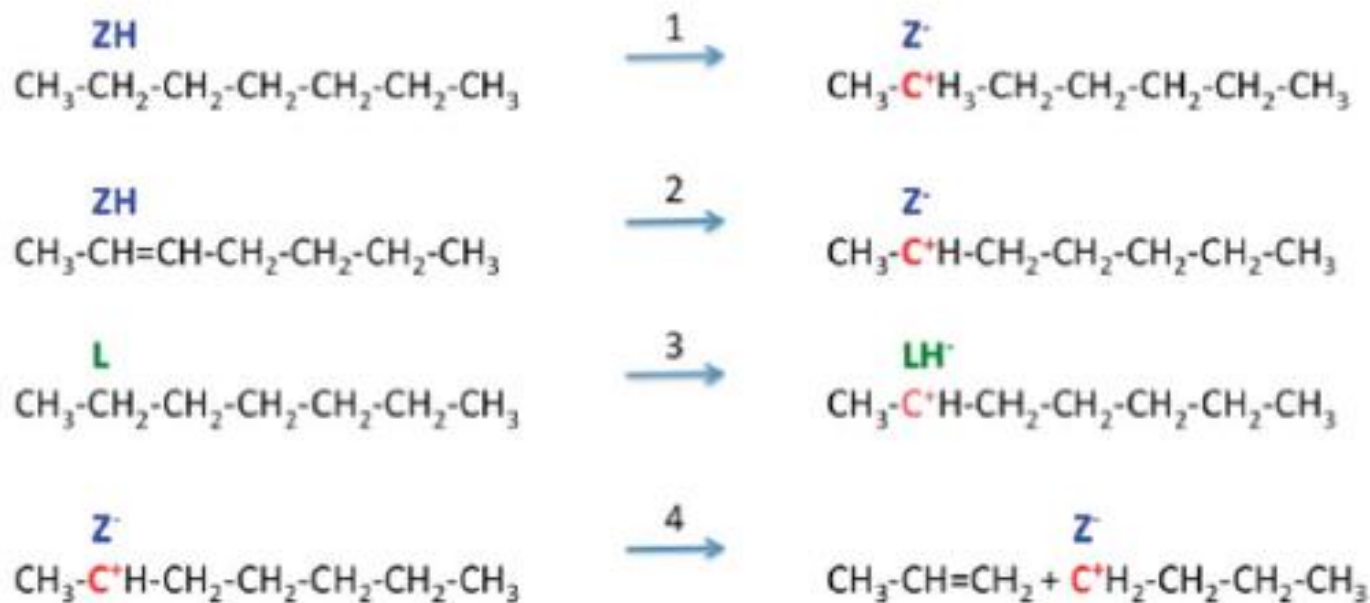


Zeolites in oil refinement



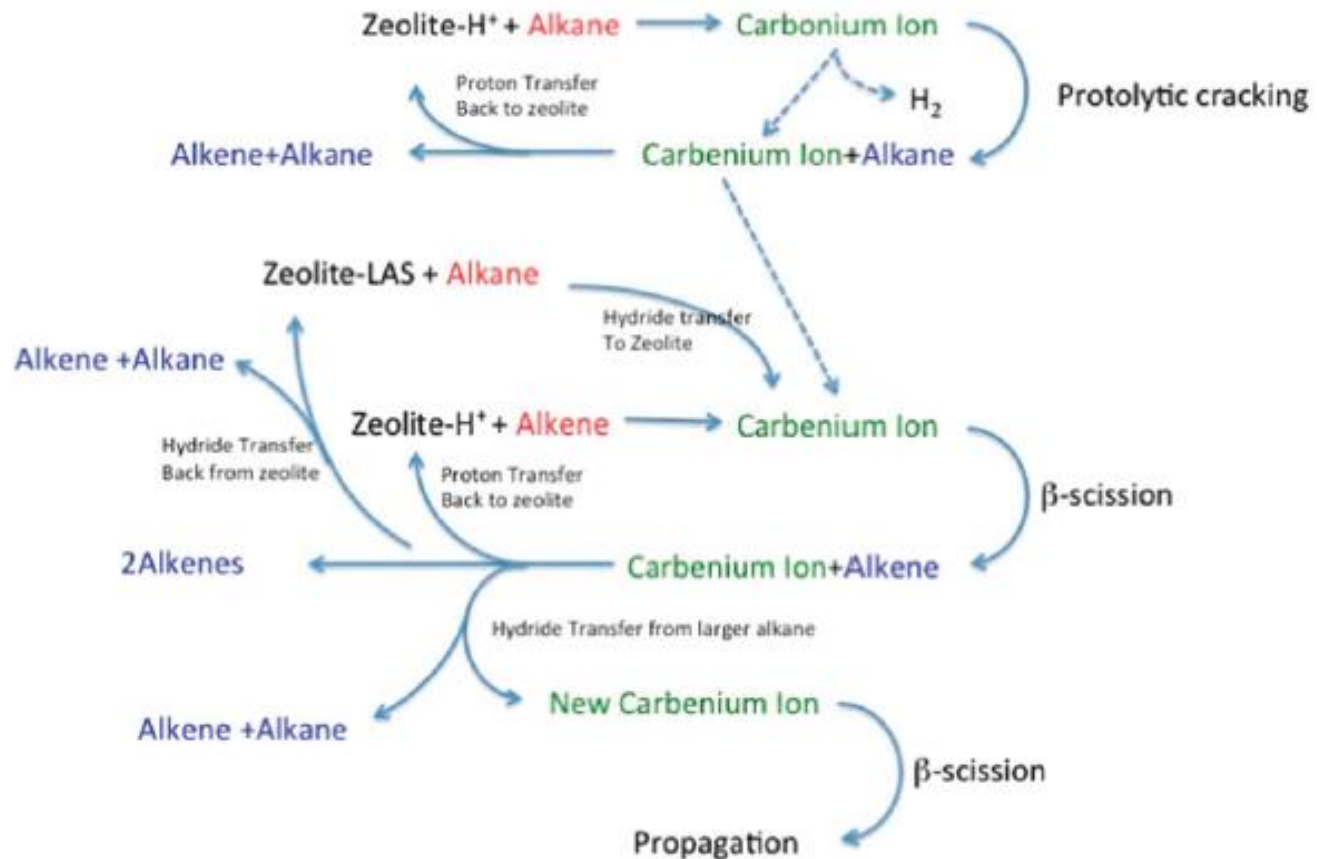
Zeolites in oil refinement

- **Fluid catalytic cracking**
 - Protonation + protolytic cracking
 - H⁺ abstraction + β scission



Zeolites in oil refinement

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Zeolites in oil refinement

- **Fluid catalytic cracking**

- Protonation + protolytic cracking

- We need strong Brønsted acid sites (zeolite Y)

- H⁻ abstraction + β scission

- We need strong Lewis acid sites (steamed/(acid washed) zeolite Y)

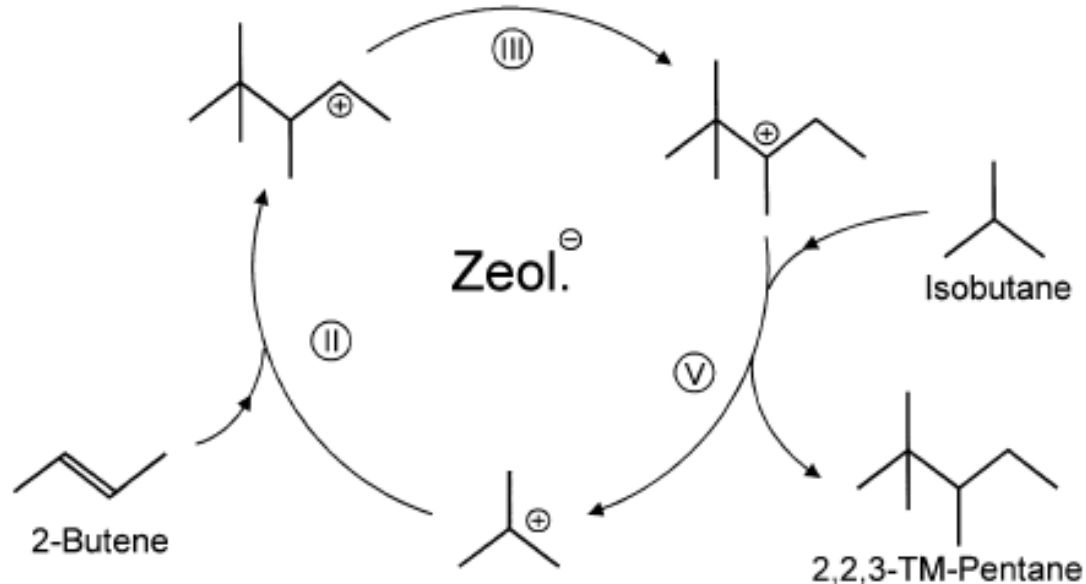
- Long linear hydrocarbons diffusion

- Precracking on alumina and silica-alumina (non-innocent binders)
 - Hierarchical porosity in zeolites (steamed/(acid washed) zeolite Y)

Zeolites in oil refinement

- **Isobutane-butene alkylation**

- We want highly branched C8 hydrocarbons (high octane number)
- HF and H₂SO₄ catalyzed alkylation still running in industry
- Large pore zeolites as a substitution



Zeolites in oil refinement

- **Isobutane-butene alkylation**

- Large pore zeolites as a substitution
- BUT! 2-butene dimerization...oligomerization...coking...deactivation

Table 1 Activity and selectivity of some acid zeolites as alkylation catalysts

Zeolite	USY	Beta	Mordenite	ZSM-5	MCM-22
2-Butene conv. (%)	100	97	94	100	95
C ₈ (wt%)	40.9	50.6	70.2	83.5	33.0
Trimethylpentanes	74.1	76.9	76.9	20.9	36.9
2,2,4-Trimethylpentane	37.7	52.4	57.2	27.3	4.1

Zeolites in oil refinement

- **Linear paraffin hydroisomerization**

- Linear C8 (C7) → branched C8 (C7)
- Requires strong Brønsted acidity and hydrogenation/dehydrogenation activity (Pt(Ni) on mordenite)
- Mordenite – large pore, monodirectional pores
- Mordenite – dealuminated (strong H⁺), acid washed (low EFAL)
- Protonation = carbocations
- Stability of carbocations? Branched hydrocarbons?

Zeolites in oil refinement

- **Linear paraffin hydroisomerization**


- Linear C8 (C7) → branched C8 (C7)
- Requires strong Brønsted acidity and hydrogenation/dehydrogenation activity (Pt(Ni) on mordenite)
- Mechanism???
 - Dehydrogenation of n-alkane to n-alkene on Pt
 - Diffusion???
 - Protonation of n-alkene to secondary carbenium ion on H⁺ zeolite
 - Secondary carbenium ion rearranges to tertiary (more stable) carbenium ion
 - Desorption from acid site produces iso-alkene, H⁺ is restored
 - Diffusion???
 - Hydrogenation of iso-alkene to iso-alkane on Pt

Zeolites in oil refinement

- **Linear paraffin hydroisomerization**

- Researchers interested in the effect of “intimacy” (Pt-acid site)
- Affects mainly selectivity, activity to some extent
- An optimum between “too close” and “too far”

Heteroaggregation and Selective Deposition for the Fine Design of Nanoarchitected Bifunctional Catalysts: Application to Hydroisomerization

Olfa Ben Moussa,^{†,‡} Lionel Tinat,^{†,‡} Xiaojing Jin,[†] Walid Baaziz,[§] Olivier Durupthy,^{*,‡}  Céline Sayag,[†] and Juliette Blanchard^{*,†}

n-Hexadecane hydroisomerization over Pt-HBEA catalysts.
Quantification and effect of the intimacy between metal and protonic sites

N. Batalha^a, L. Pinard^{a,*}, C. Bouchy^b, E. Guillon^b, M. Guisnet^{c,d,*}

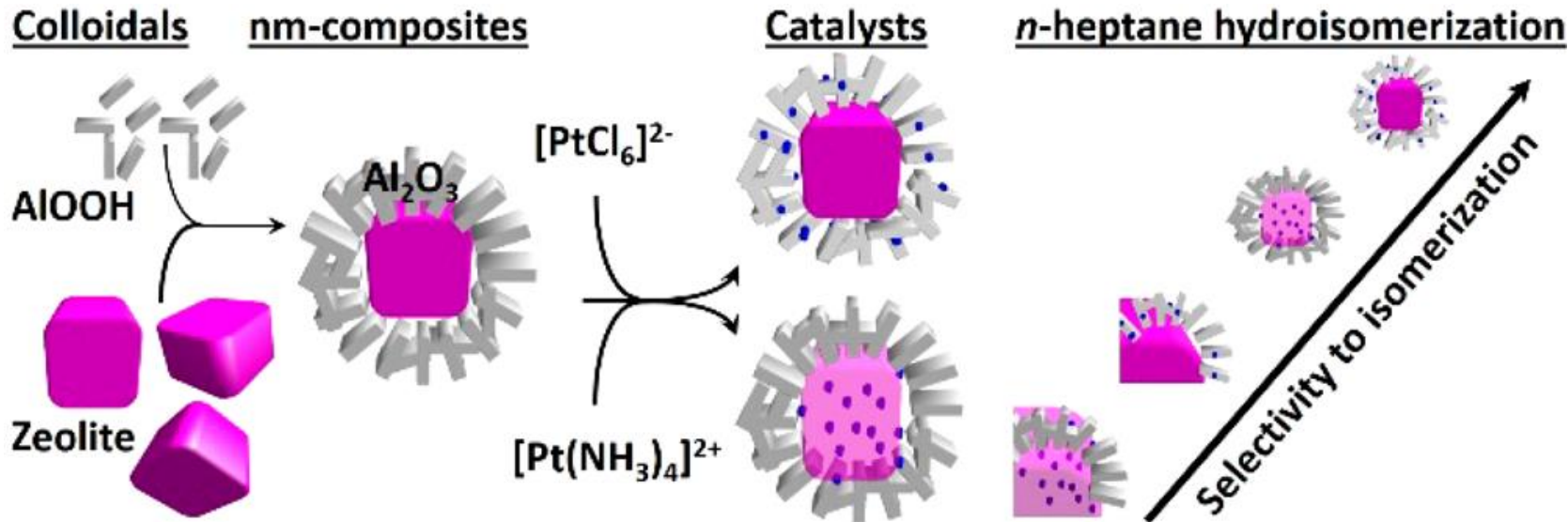
Nanoscale intimacy in bifunctional catalysts for selective conversion of hydrocarbons

Jovana Zečević¹, Gina Vanbutsele², Krijn P. de Jong¹ & Johan A. Martens²

Zeolites in oil refinement

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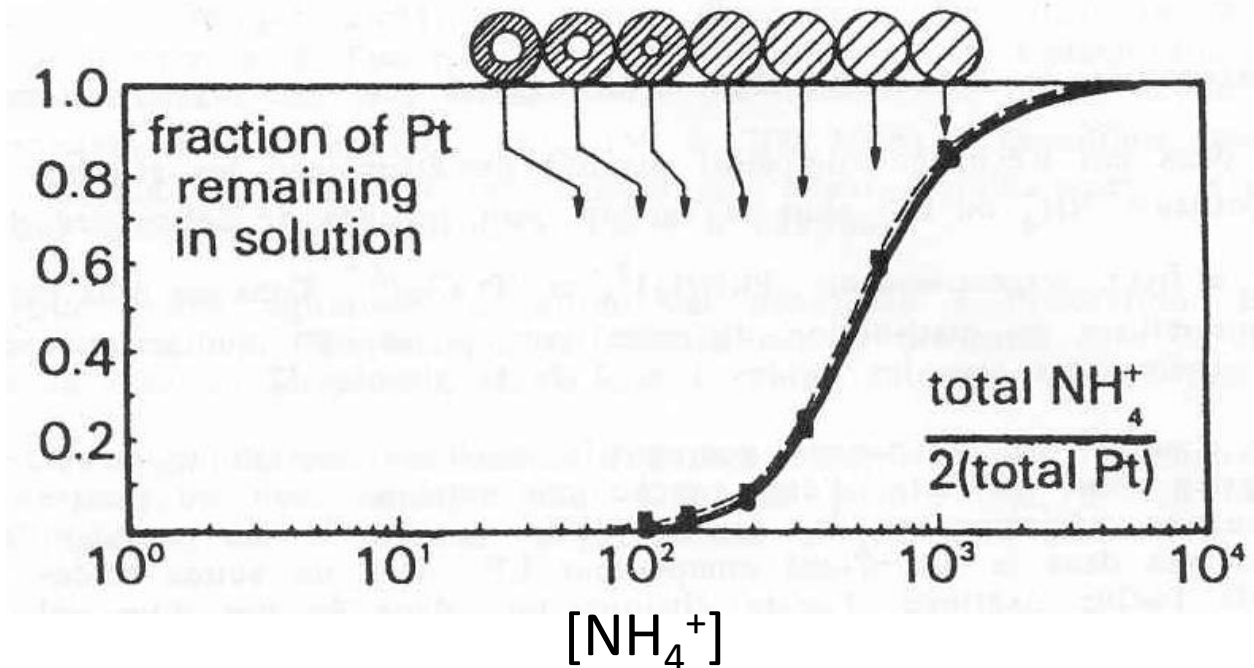


Zeolites in oil refinement

- **Linear paraffin hydroisomerization**
 - Pt(Ni) on mordenite
 - How do we deposit Pt on a zeolite? (Lecture 3)

Zeolites in oil refinement



- **Linear paraffin hydroisomerization**
 - Pt, Pd, Ni on mordenite
 - Electrostatic interaction = **ion exchange**
 - Competitive ion exchange



Zeolites in oil refinement

- **Linear paraffin hydroisomerization**
 - Pt, Pd, Ni on mordenite
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 - Competitive ion exchange

ISOMERIZATION OF N-HEXANE ON Pt/HUSY

T (°C)	$10^4 v_i$ (mole h ⁻¹ g ⁻¹ of Pt/HUSY)		$\frac{v_{IGD}}{v_{IPD}}$
	G.D. 	P.D. 	
230	39	70	2.6
250	180	140	
260	317	280	
270	613	540	
280			

G.D. : good distribution

P.D. : poor distribution

Zeolites in oil refinement

- **Hydrocracking (i.e. cracking in the presence of H₂)**
 - Shortening of long hydrocarbons
 - From linear to branched (alkylation, carbocations,...)
 - Hydrogenation/dehydrogenation
 - Pt, Pd on mordenite (also zeolite Y and β)

Zeolites in oil refinement

- **Reforming and steam reforming**

- Cyclization, isomerization of cyclic compounds to cyclohexene, cyclohexene and its derivatives dehydrogenation to benzene, toluene, xylene (BTX), and other aromatics
- H₂ as a useful „by-product“
- Pt on high surface area support, non-acidic
- Reforming in the presence of H₂O = H₂ production

Microporosity of zeolites

+

- Regular structure
- High stability
- Shape selectivity
- Confinement effect

-

- Diffusion limitations
- Coking
- Fast deactivation

Solution?

- Extra-large pore zeolites
- Nanocrystalline zeolites
- Hierarchical zeolites
- Two-dimensional zeolites
- MCM-41, SBA-15 and other mesoporous silica???

Microporosity of zeolites

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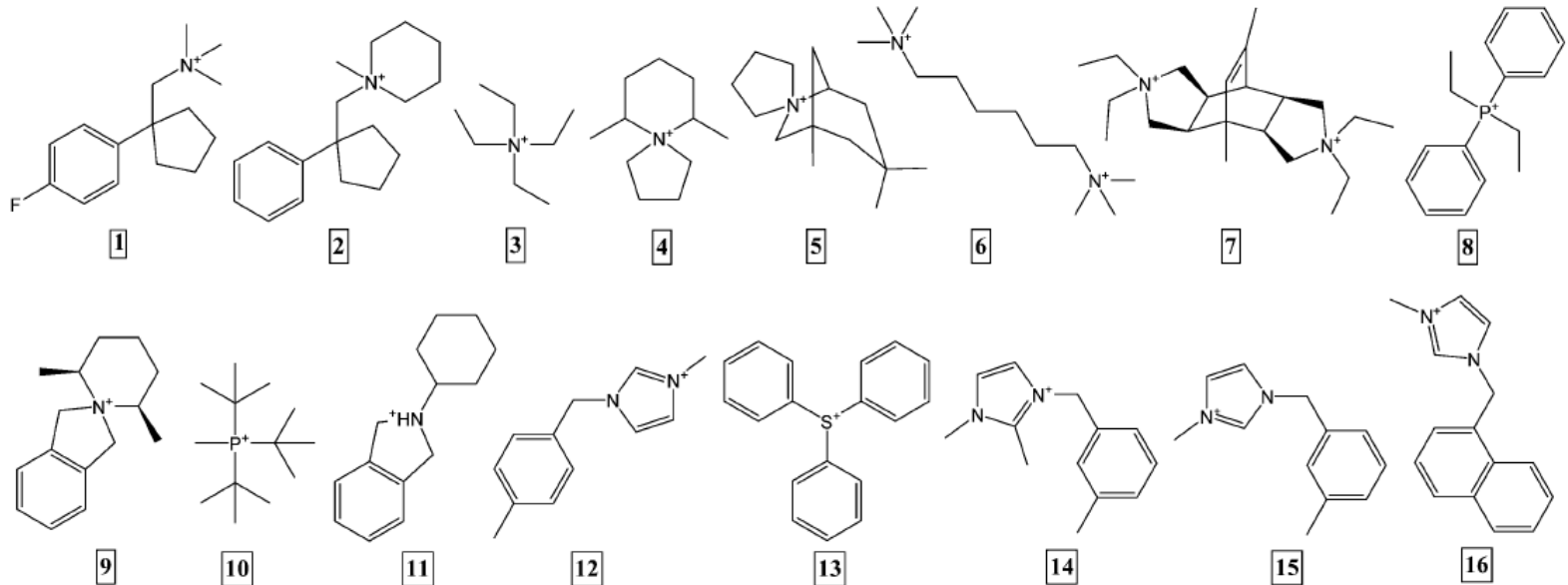
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Microporosity of zeolites

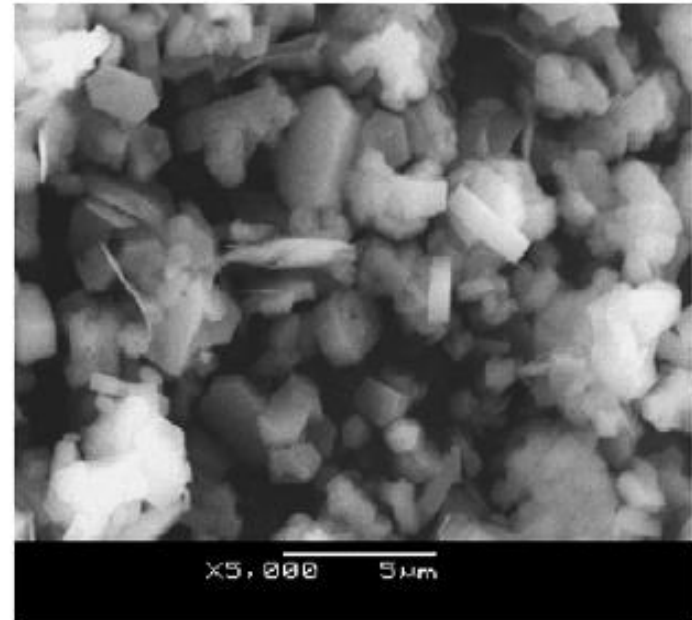
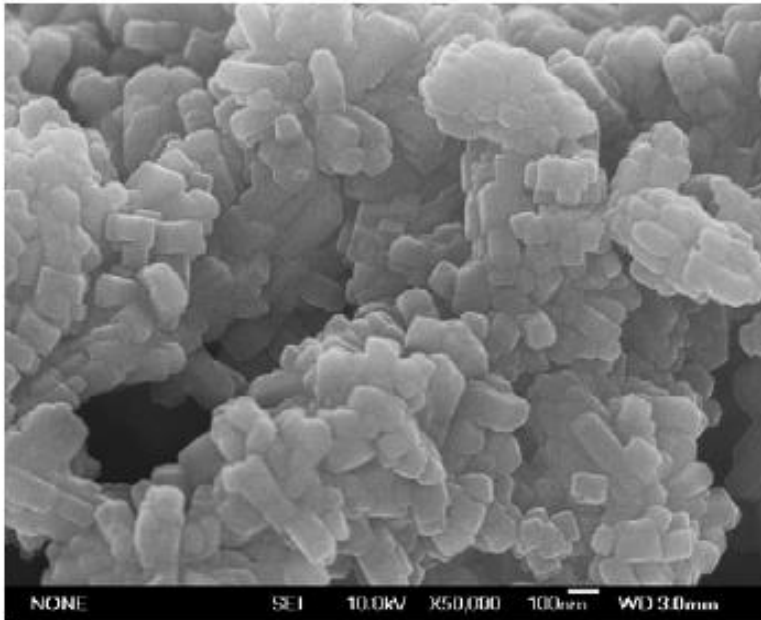
- **Extra-large pore zeolites**

- **Germanosilicates**
- New organic structure-directing agents
- Ge for Al substitution
- Assembly-disassembly-organization-reassembly (prof. Čejka, Prague)



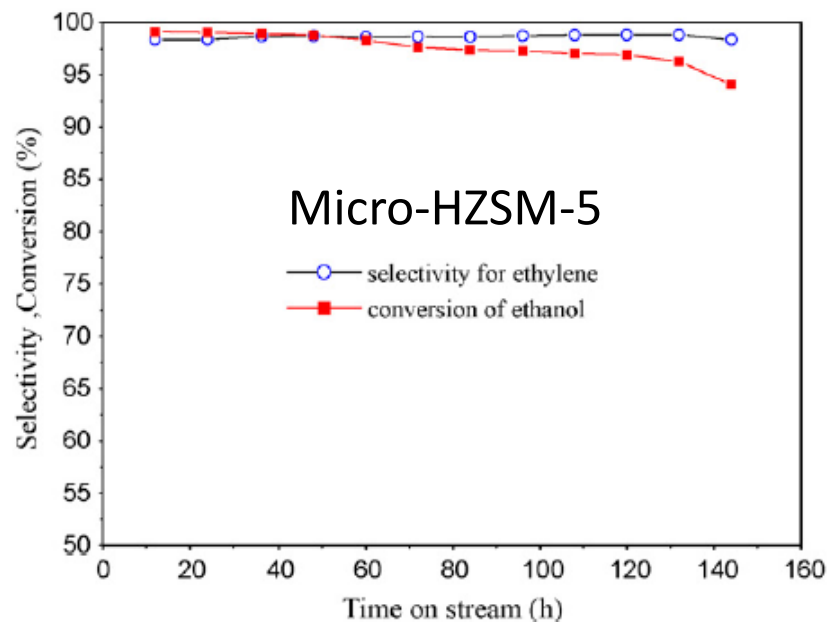
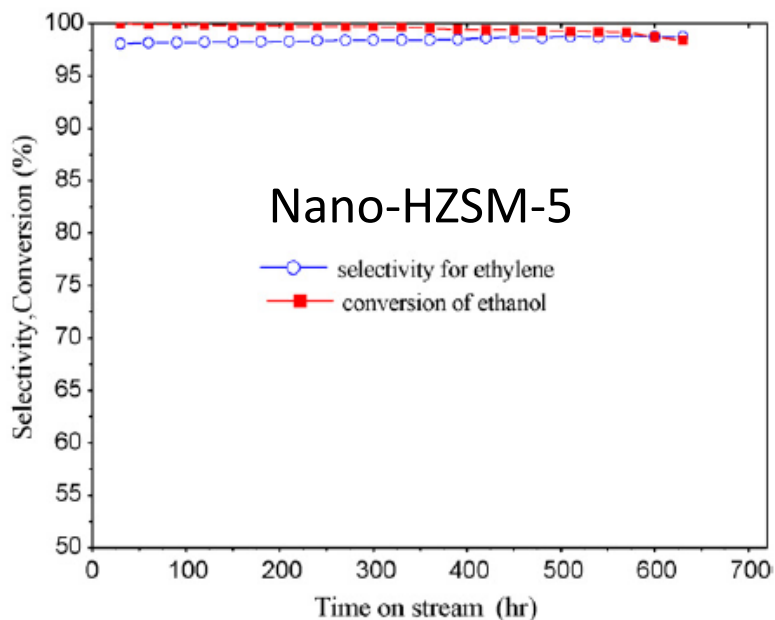
Microporosity of zeolites

- **Nanocrystalline zeolites**
 - Classic hydrothermal synthesis
 - But! Part of Si source = $\text{MeSi}(\text{OEt})_3$



Microporosity of zeolites

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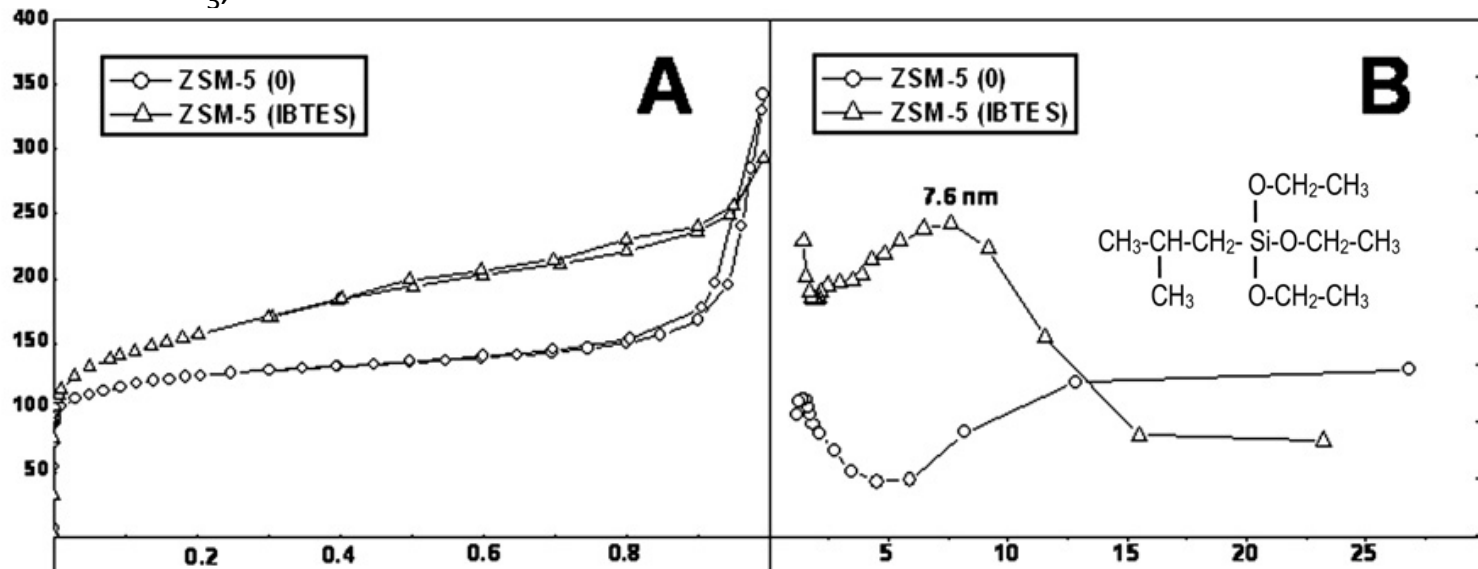


Ethanol dehydration to ethylene

Microporosity of zeolites

- **Hierarchical zeolites**

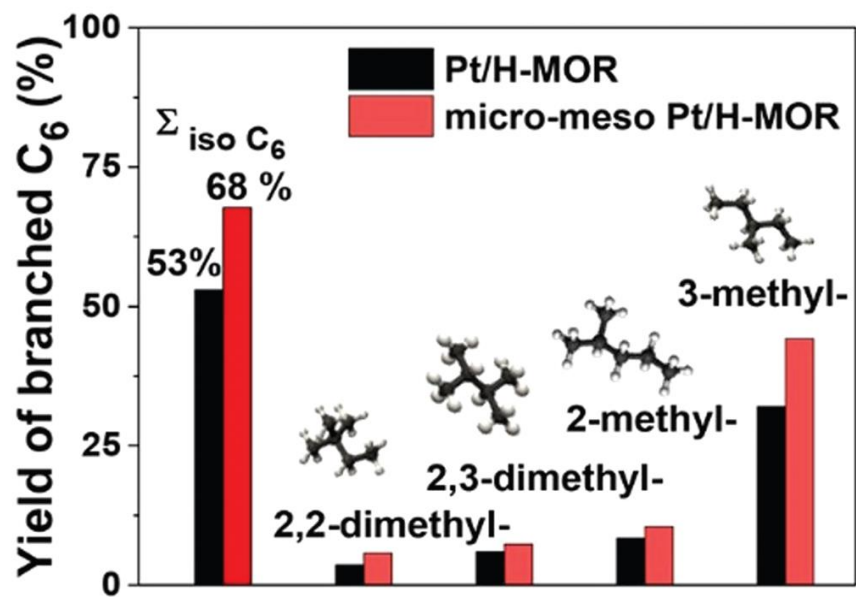
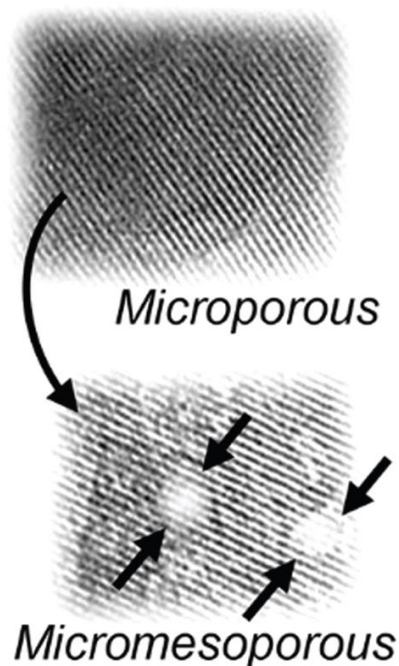
- Add something into the rxn mixture in order to create large pores
 - Hard templates (carbon,...)
 - Soft templates (alkoxysilanes with a long aliphatic chain)
- Dealumination, desilication
 - HNO_3 , NaOH



Microporosity of zeolites

- **Hierarchical zeolites**

- Add something into the rxn mixture in order to create large pores
- Dealumination, desilication: **alkaline–acid, acid–alkaline, and fluorination–alkaline post-synthesis treatments of H-MOR (below)**



Microporosity of zeolites

- **Two-dimensional zeolites**

- Pillaring

- CTMA⁺, sonication, surfactant removal = stacked layers

- Delamination

- CTMA⁺, sonication, TEOS hydrolysis, calcination = layered zeolites with permanently expanded interlayer spaces

