Heterogeneous catalysis

Lecture 9

Zeolites in oil refinement

Zeolites - synthesis

- **Reaction mixture:** …, …, …, …

  - pH adjustment, (gelation)
  - Hydrothermal treatment in an autoclave
  - …
  - …

- **Result:** H-zeolite (Brønsted acidic with H^+ ions)

Zeolites - synthesis

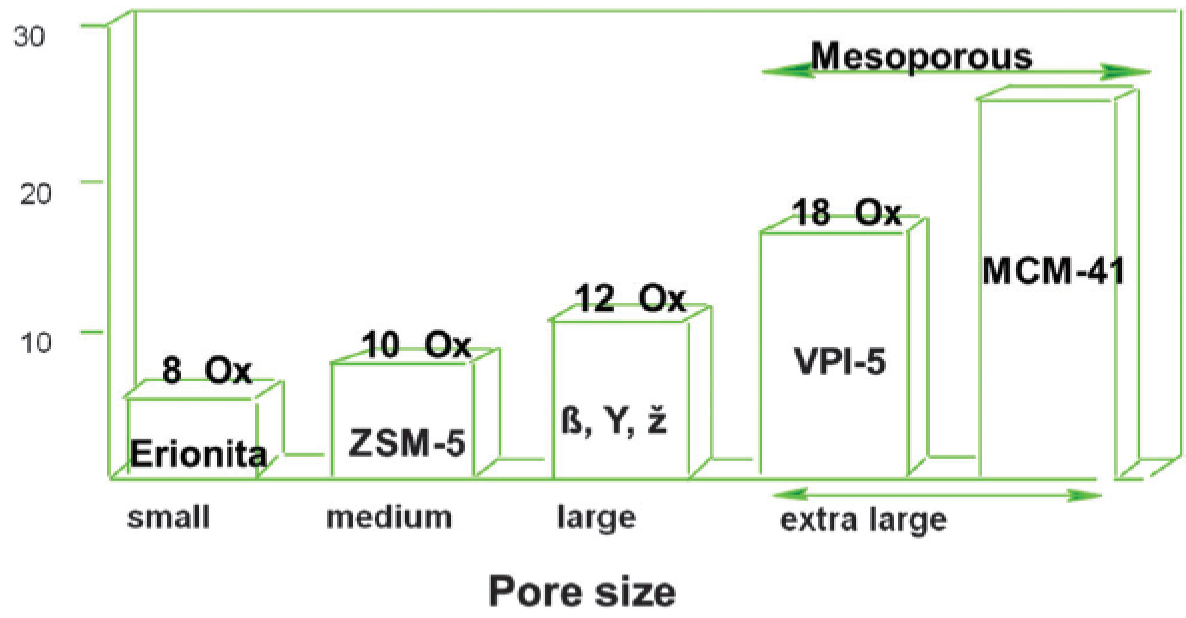
- **Reaction mixture:** Na_2SiO_3, Al_2O_3, quarternary ammonium salt (=structure directing agent), water

  - 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**

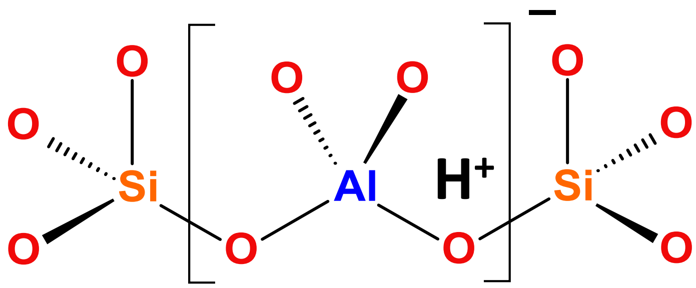
DOI: 10.1039/c3cs60394f

Zeolites - acidity

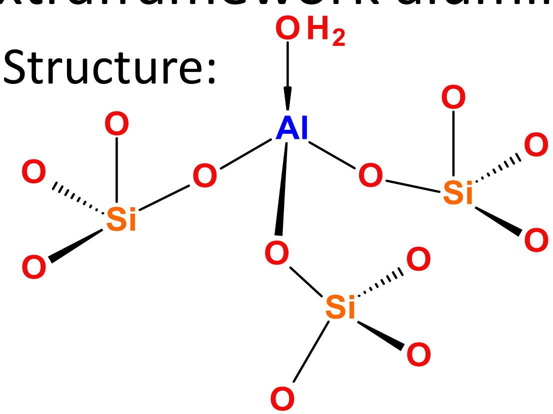
- **Brønsted:** …
  - Structure:
- **Lewis:** …
  - Structure:

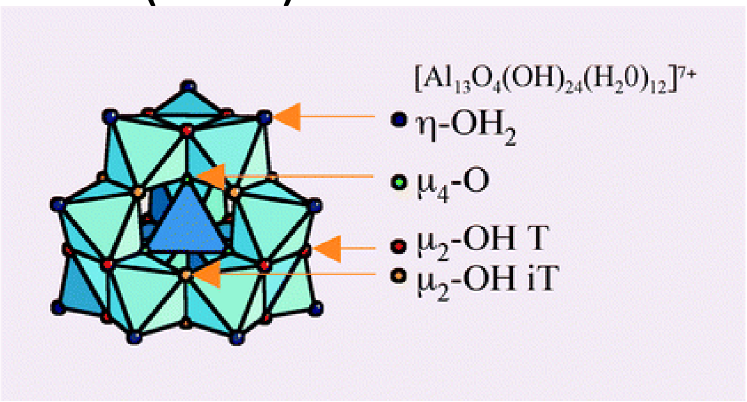
Zeolites - acidity

- **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

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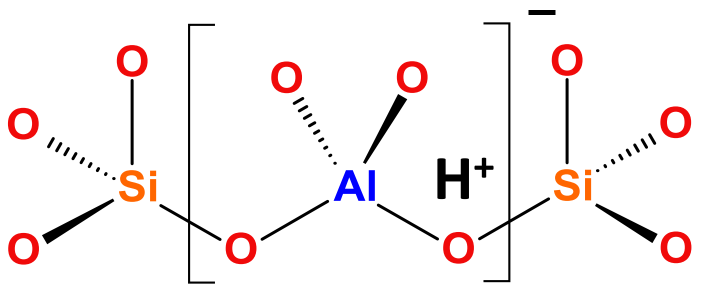
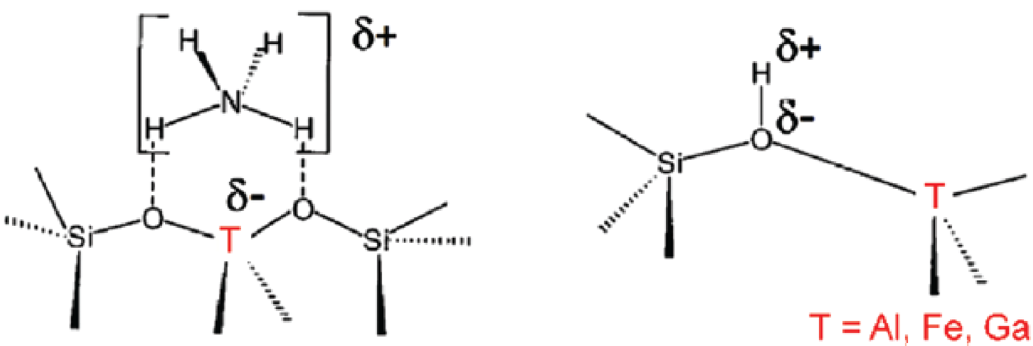
  - Structure:



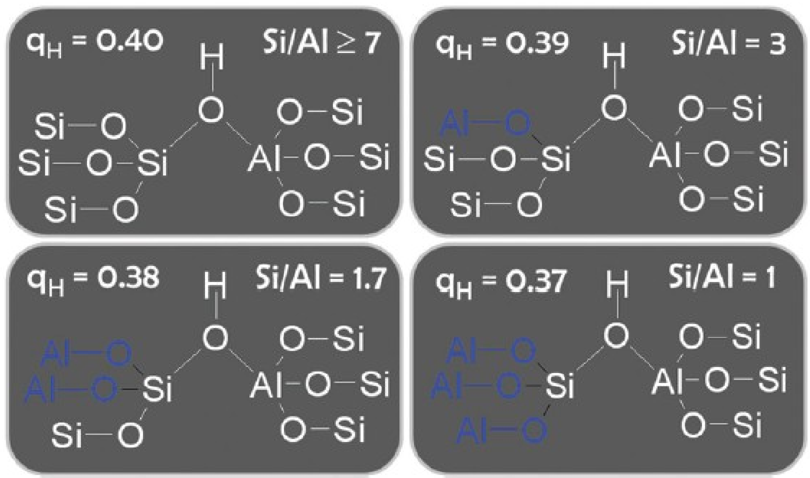


Changes in local Al structure revealed by EXAFS

DOI: 10.1039/C8CS00887F

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

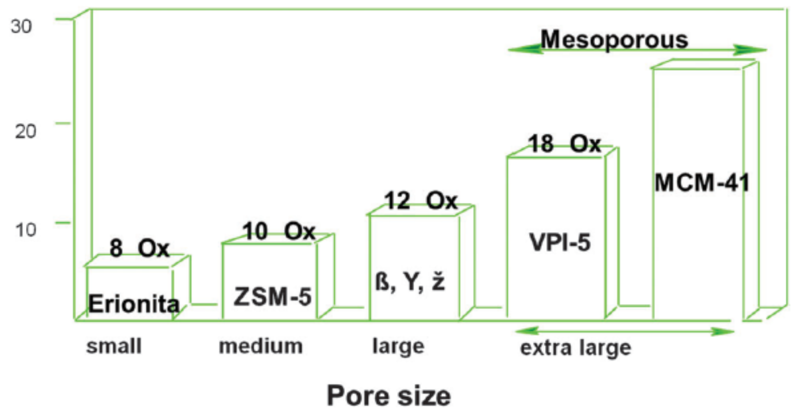
Zeolites - acidity

- **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

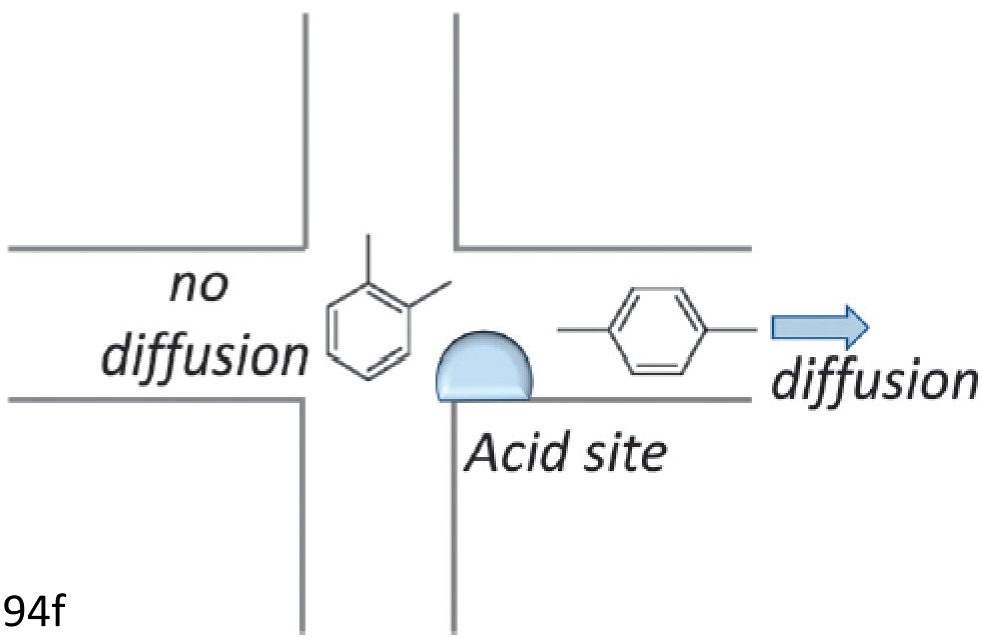
- **Confinement effect**



- **Superacidity**
  - Various probes at RT – acid site strength similar to 70 % H_2SO_4 (=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**



DOI: 10.1039/c3cs60394f

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+}
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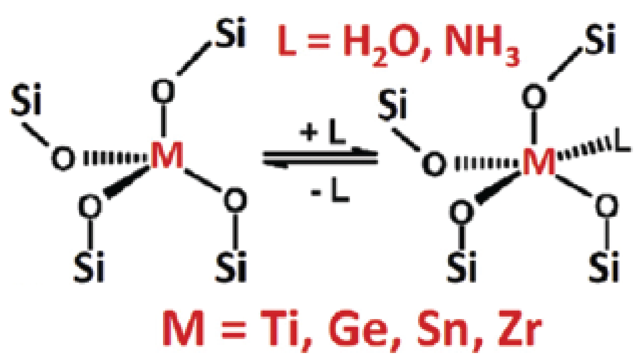
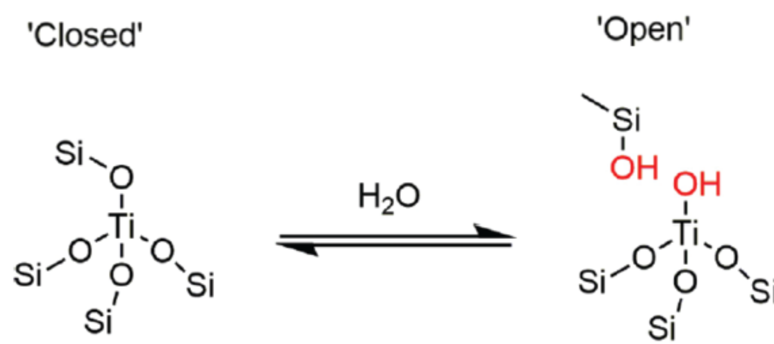


Lewis acidity in non-Al zeolites



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_3OH	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_3OH	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

DOI: 10.1016/j.cattod.2011.02.027

Zeolites in oil refinement

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

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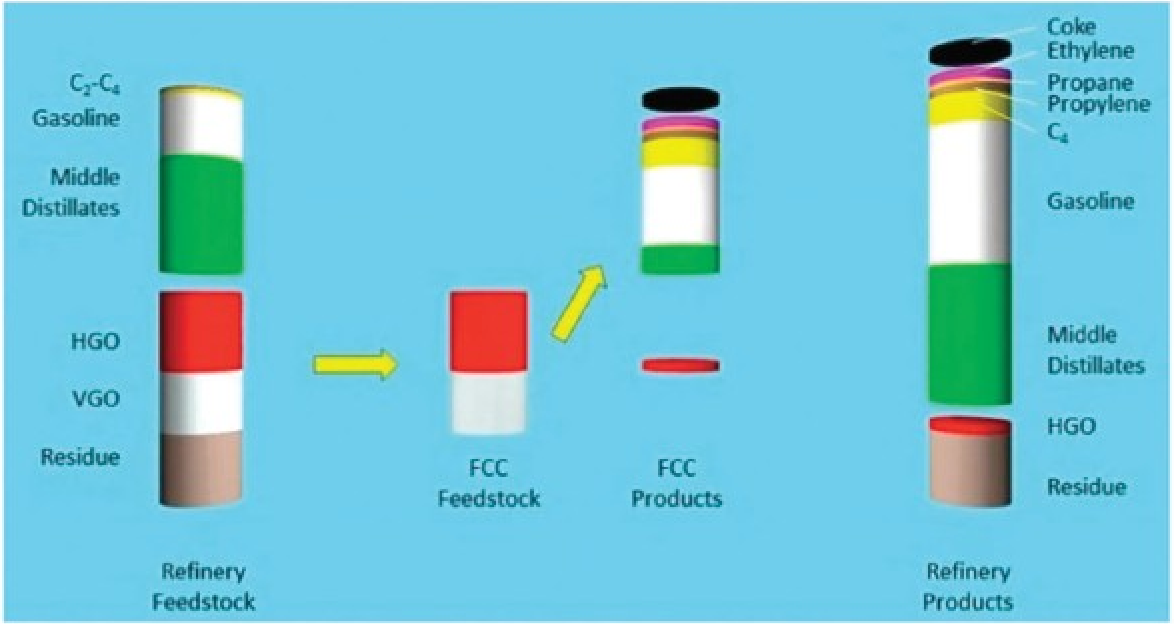
Zeolites in oil refinement

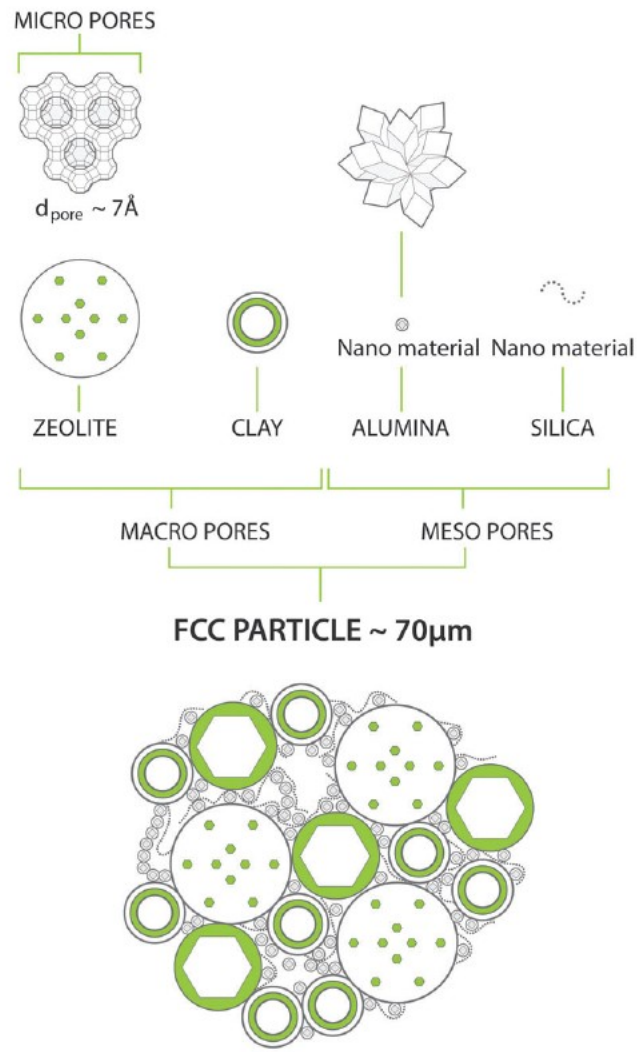
- **Fluid catalytic cracking**



Chem. Soc. Rev., 2015, **44**, 7342–7370

Zeolites in oil refinement

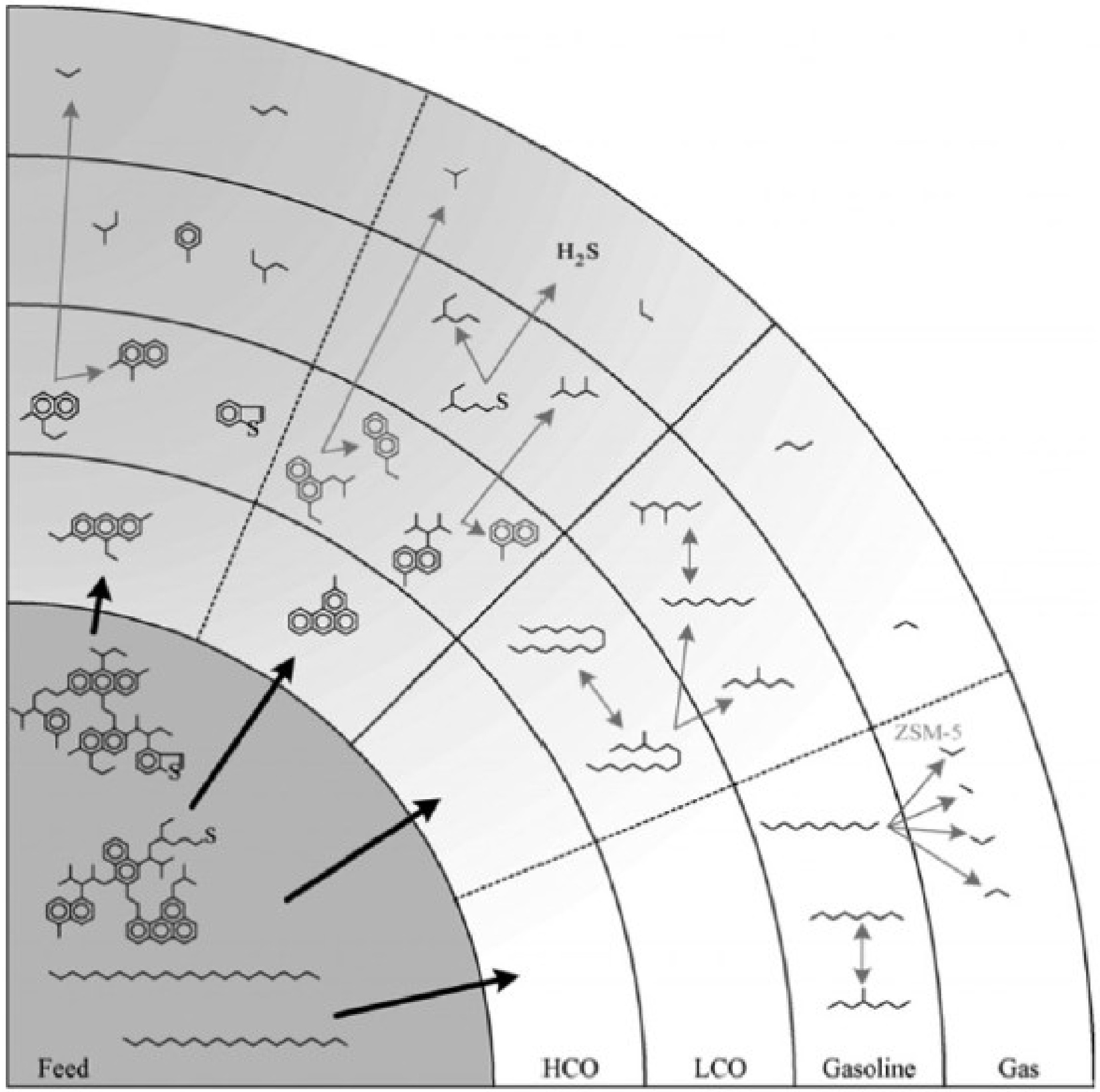
- **Fluid catalytic cracking**
  - Zeolite Y 10-50 wt%
  - Binders 50-90 wt%
  - At the beginning – $AlCl_3$
  - Addition of HZSM-5



Chem. Soc. Rev., 2015, **44**, 7342–7370

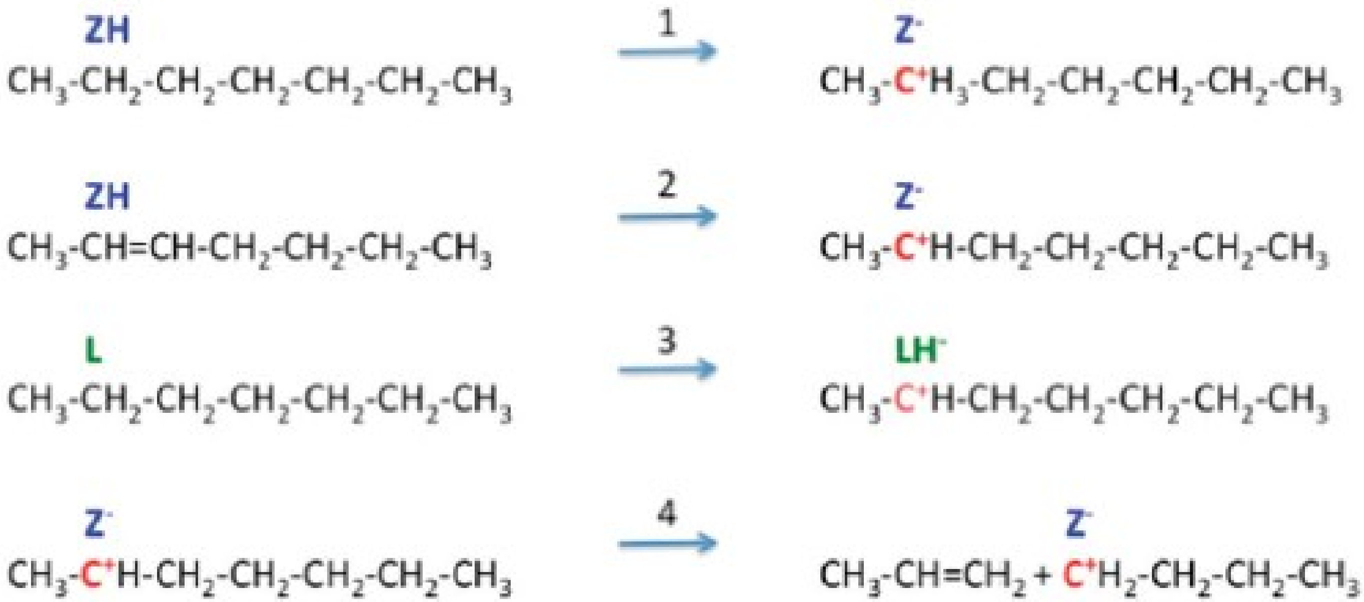
Zeolites in oil refinement

- **Fluid c**
  - Sho
  - Ison
  - „Arc
  - HZS



Zeolites in oil refinement

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



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Zeolites in oil refinement

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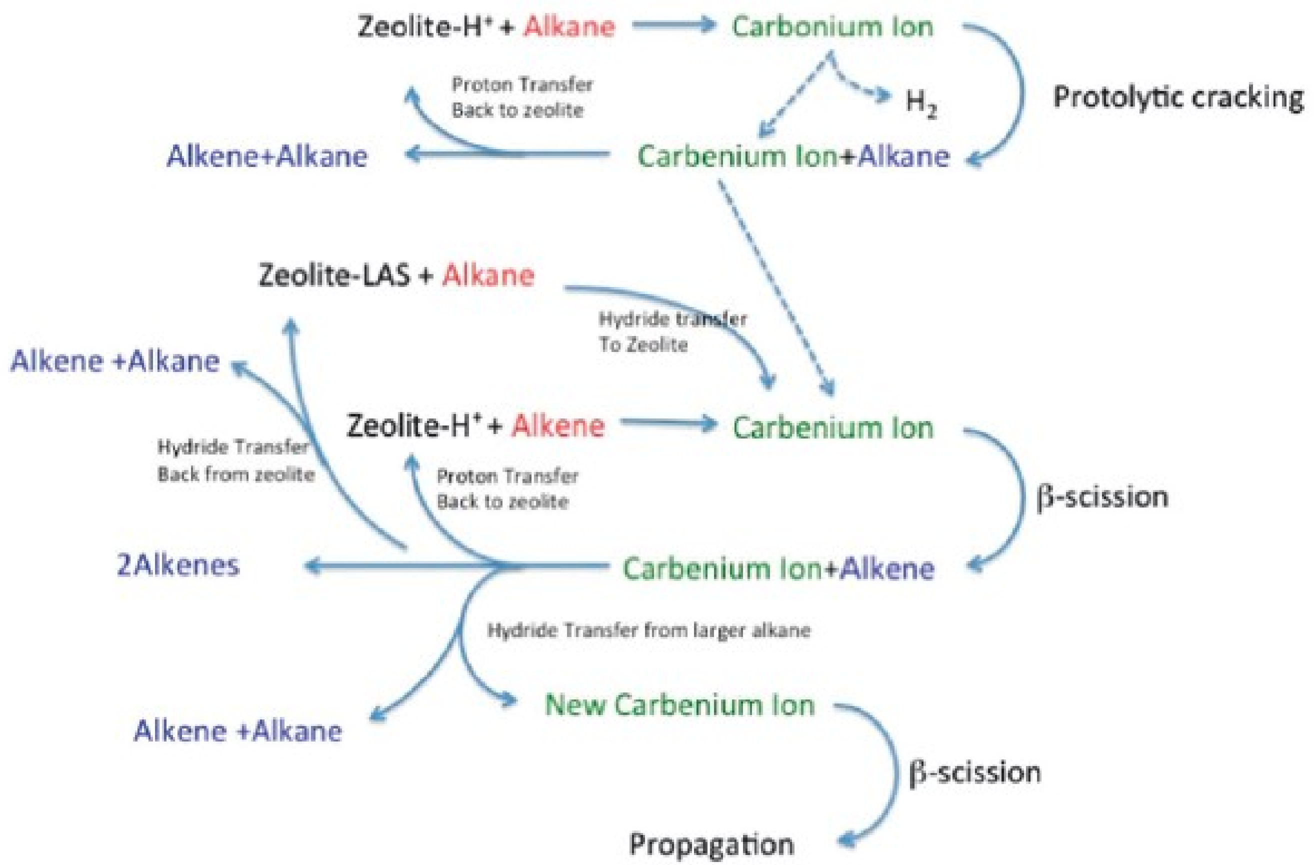
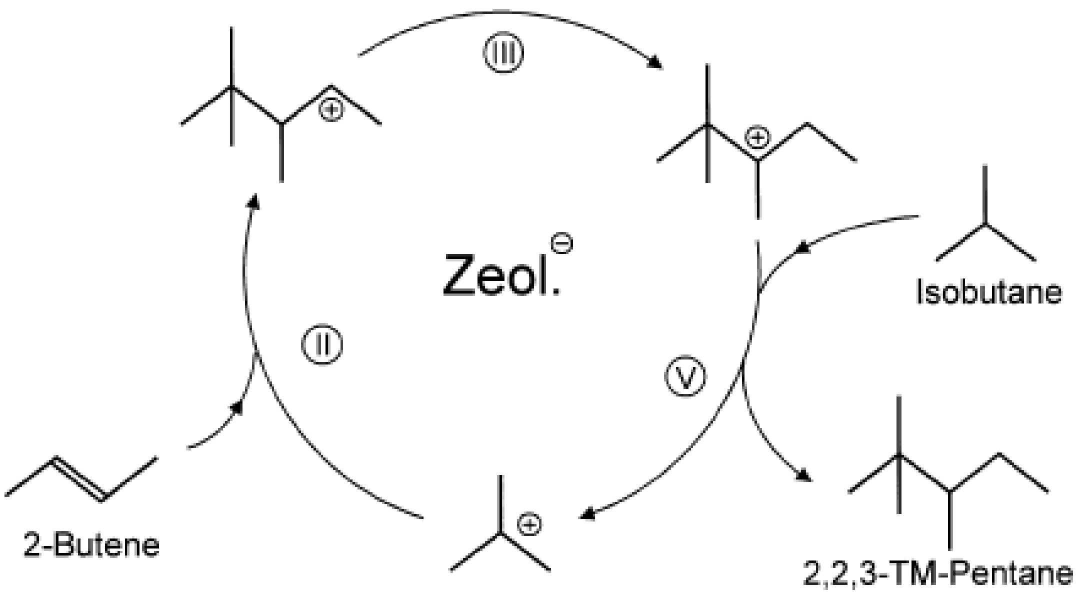


Zeolites in oil refinement

- **Fluid catalytic cracking**
  - Protonation + protolytic cracking
    - We need strong Brøsted 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 H_2SO_4 catalyzed alkylation still running in industry
  - Large pore zeolites as a substitution



Catalysis Today 49 (1999) 193–199

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 Nanoarchitectured 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 Zečević[1], Gina Vanbutsele[2], Krijn P. de Jong[1] & Johan A. Martens[2]

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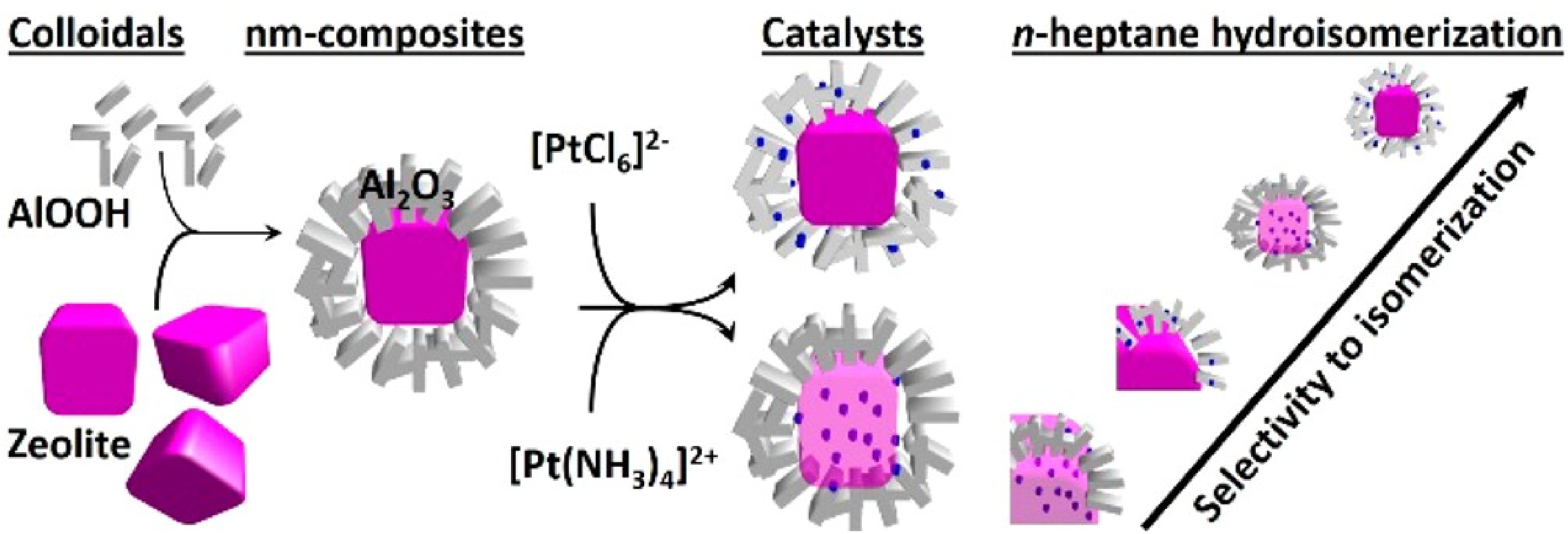


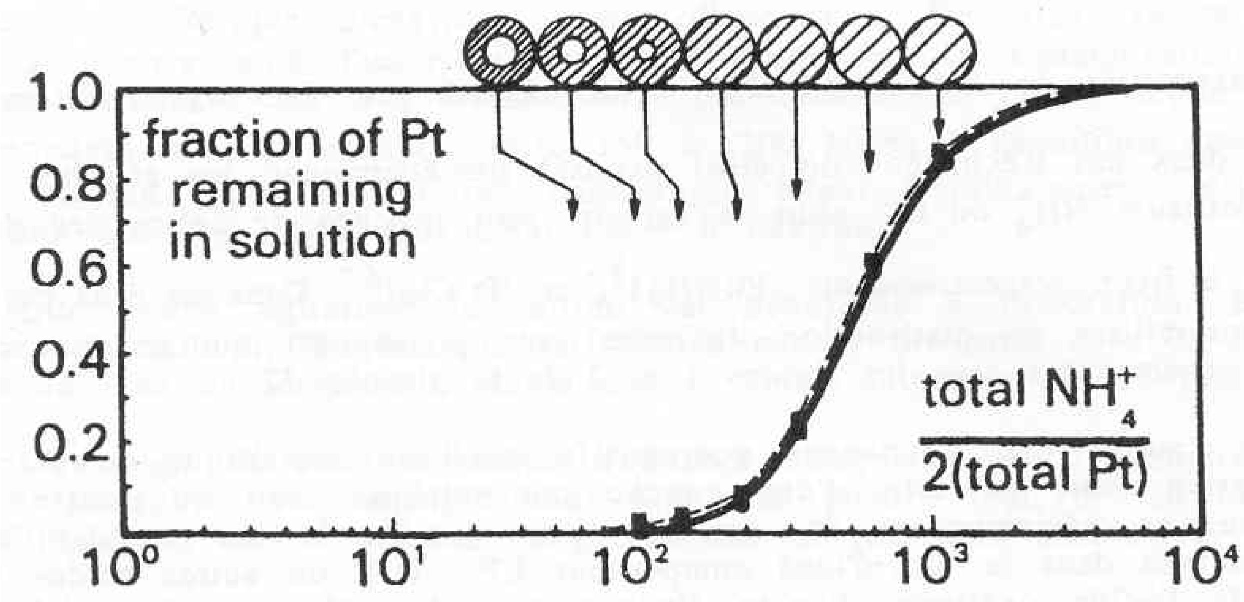
DOI: 10.1021/acscatal.8b01461

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

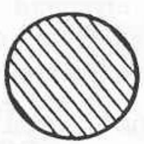


$[NH_4^+]$

Zeolites in oil refinement

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

ISOMERIZATION OF N-HEXANE ON Pt/HUSY

	$10^4 v_i$ (mole h^{-1} g^{-1} of Pt/HUSY)		
T (^oC)	G.D. 	P.D. 	$\frac{V_{i\,GD}}{V_{i\,PD}}$
230	39		
250	180	70	2.6
260	317	140	2.3
270	613	280	2.2
280		540	

G.D. : good distribution
P.D. : poor distribution

Zeolites in oil refinement

- **Hydrocracking (i.e. cracking in the presence of H_2)**
  - 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
  - H_2 as a useful „by-product“
  - Pt on high surface area support, non-acidic
  - Reforming in the presence of H_2O = H_2 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???

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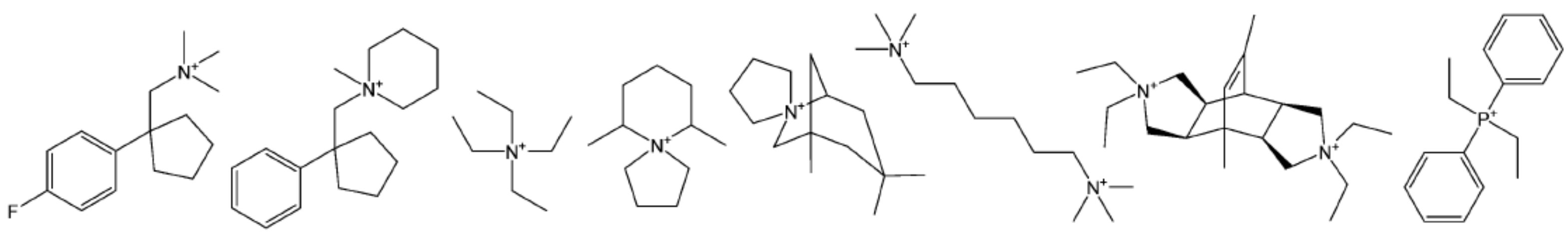
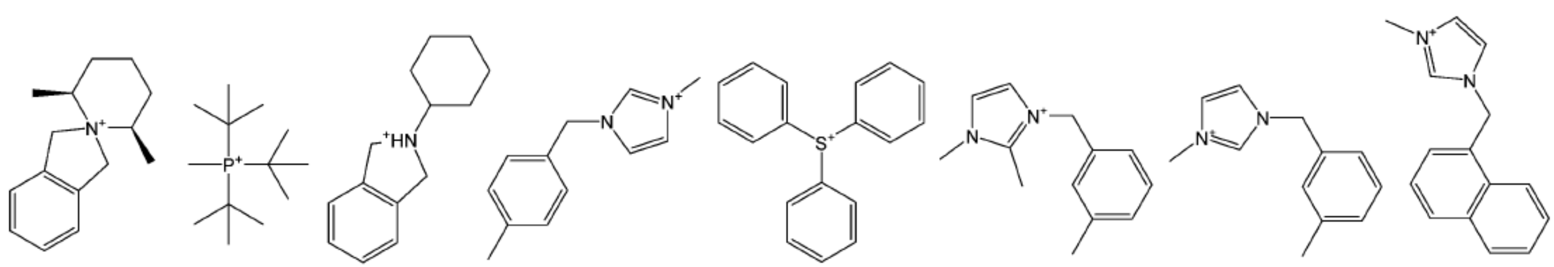
- ~~MCM-41, SBA-15 and other mesoporous silica???~~

Microporosity of zeolites

- **Extra-large pore zeolites**
  - **Ge**rmanosilicates
  - New organic structure-directing agents
  - Ge for Al substitution
  - Assembly-disassembly-organization-reassembly (prof. Čejka, Prague)



1 2 3 4 5 6 7 8

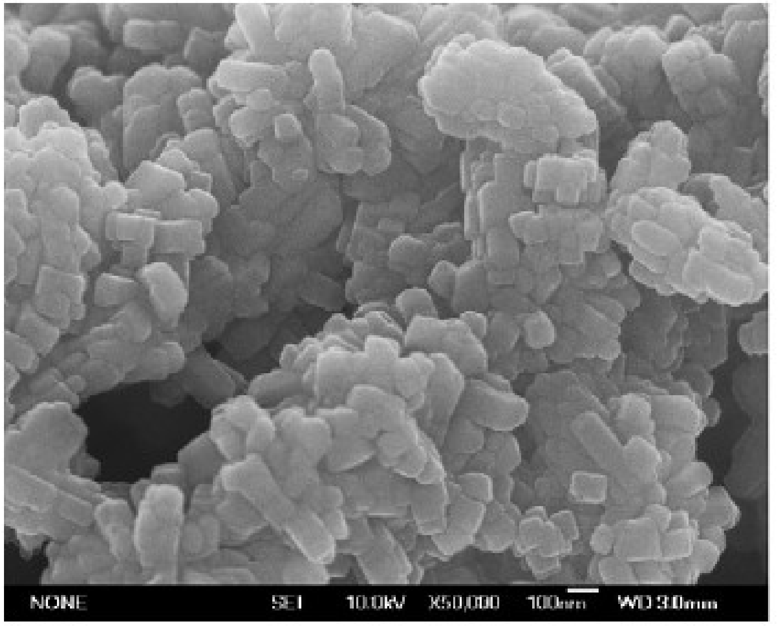


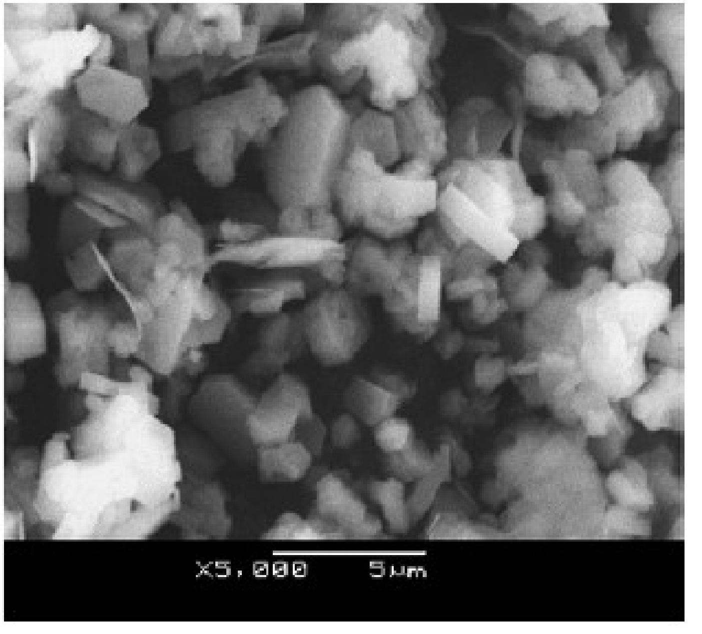
9 10 11 12 13 14 15 16

DOI: 10.1039/C8CS00887F

Microporosity of zeolites

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





DOI: 10.1016/j.cattod.2009.04.016

Microporosity of zeolites

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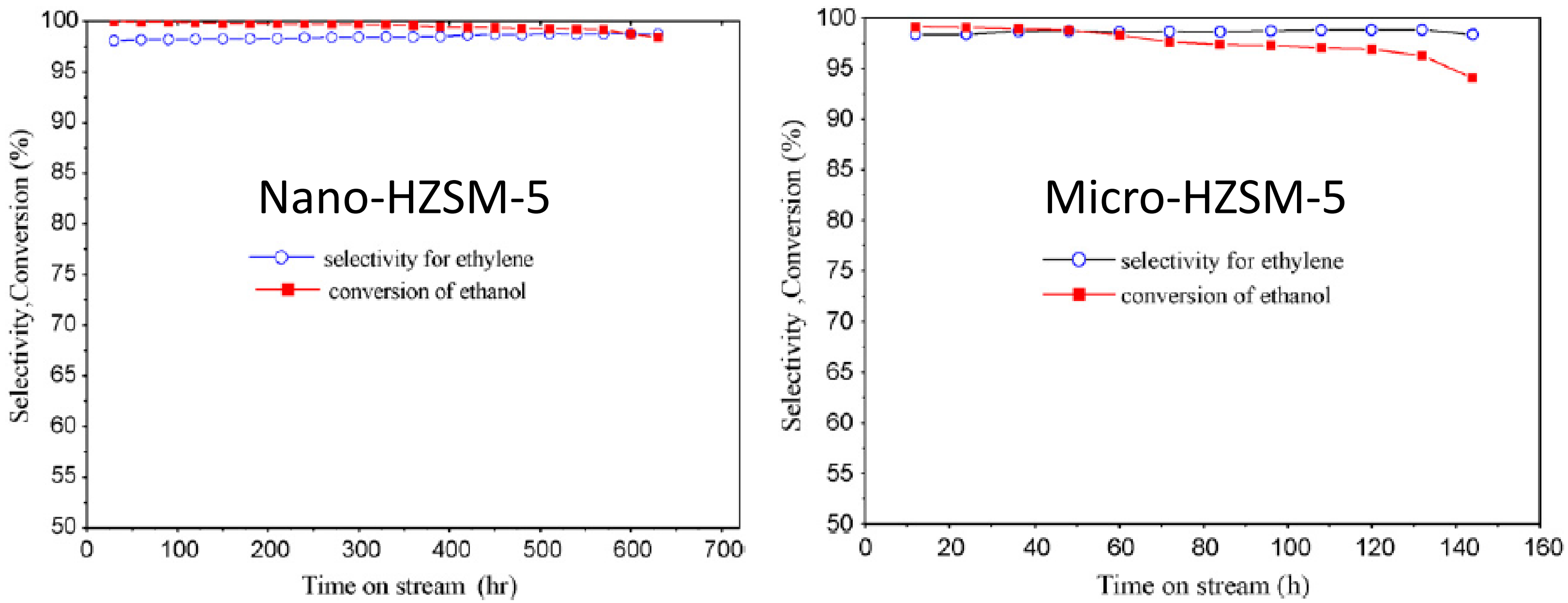
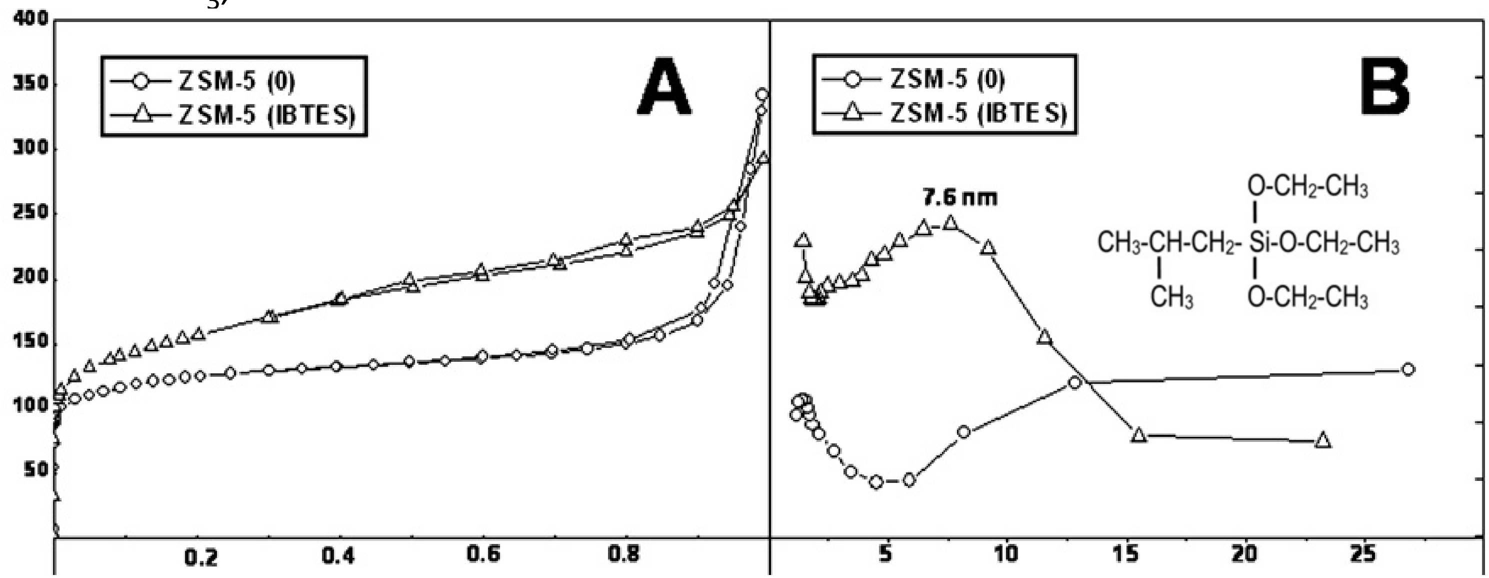


Ethanol dehydration to ethylene

DOI: 10.1016/j.cattod.2009.04.016

Microporosity of zeolites

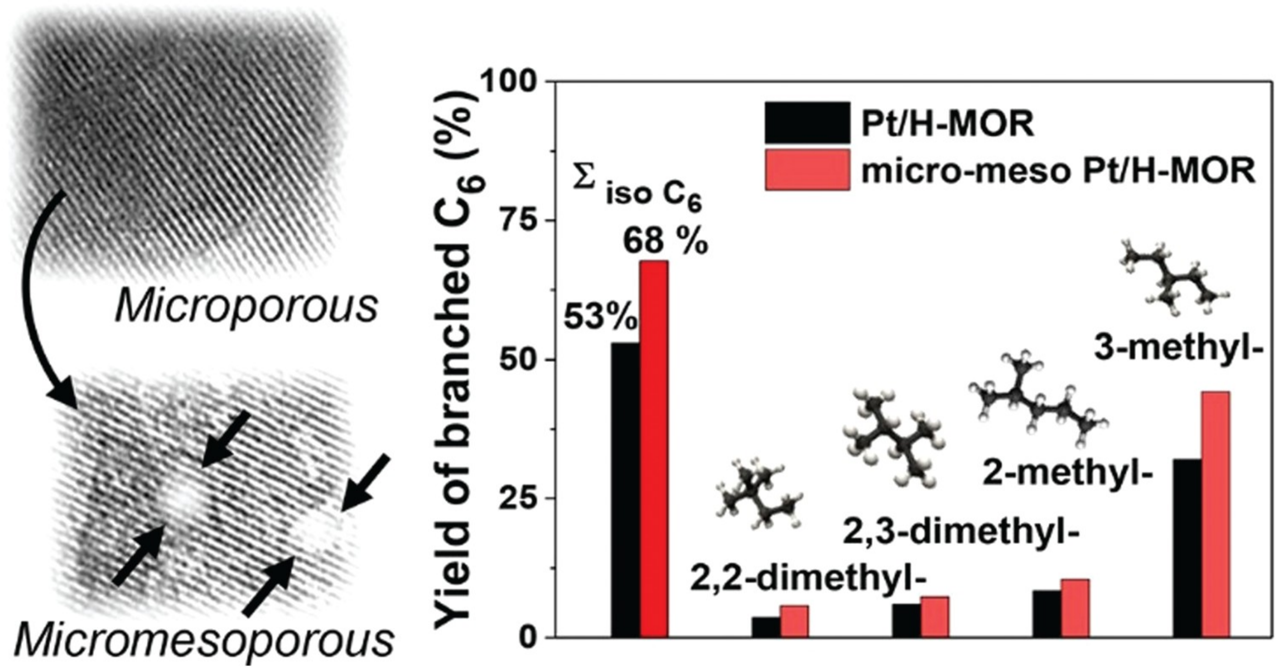
- **Hierarchical zeolites**
  - Add something into the rxn mixture in order to create large pores
    - Hard templates (carbon,…)
    - Soft templates (alkoxysilanes with a long aliphatic chain)
  - Dealumination, desilication
    - HNO_3, NaOH



DOI: 10.1039/B805502E

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)**



DOI: 10.1039/B805502E

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