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

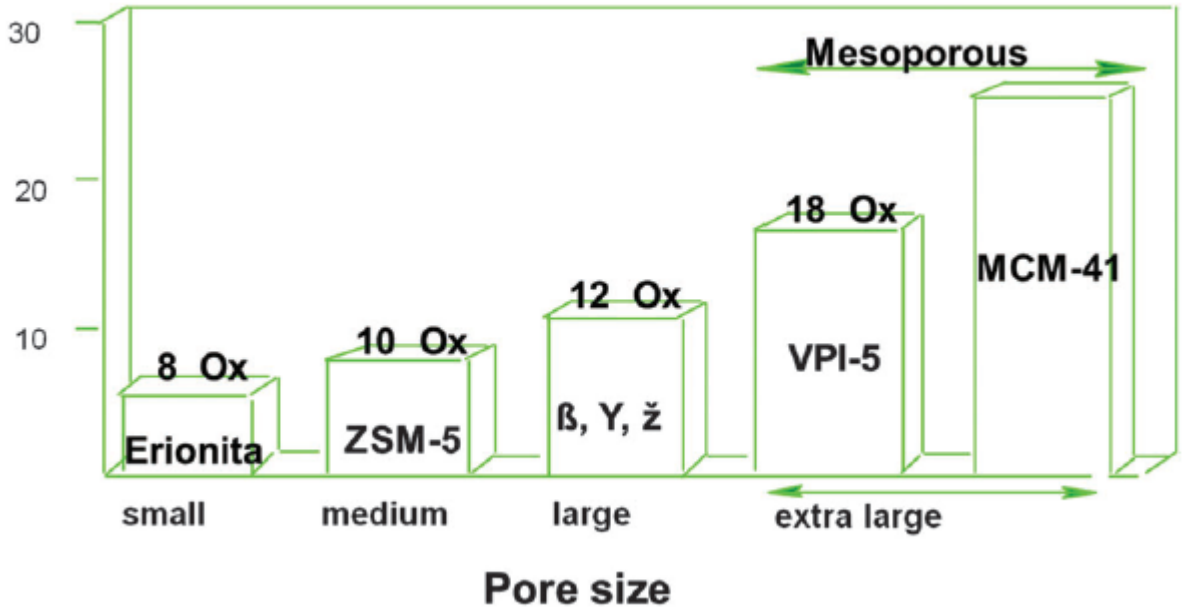
- **Reaction mixture:** Na_2SiO_3, Al_2O_3, quarternary ammonium salt (=structure directing agent), water

  - 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**

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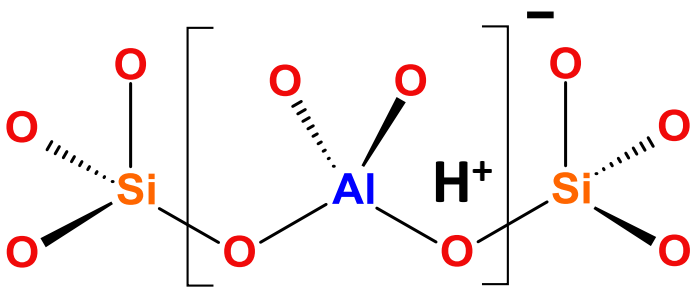
Zeolites - acidity

- **Brønsted:** …
  - Structure:

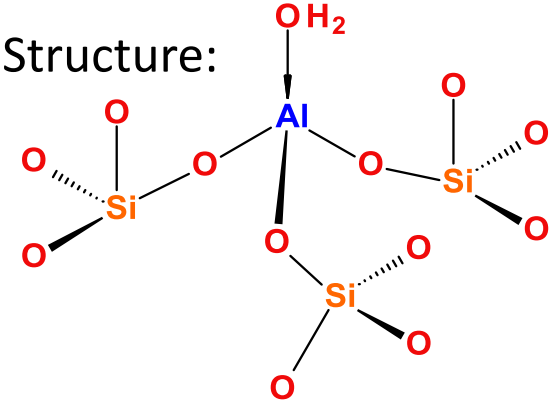
- **Lewis:** …
  - Structure:

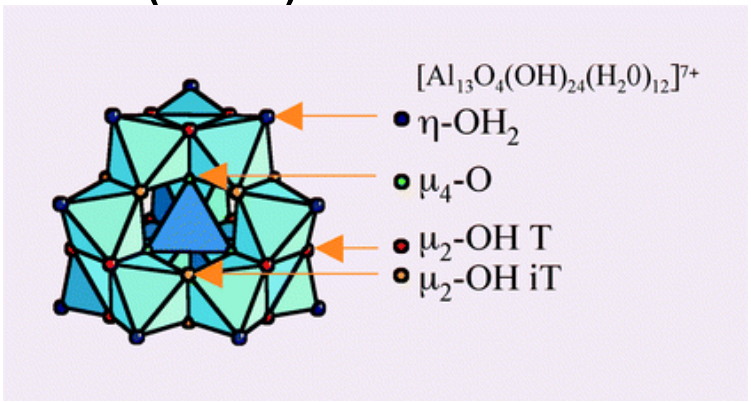
Zeolites - acidity

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



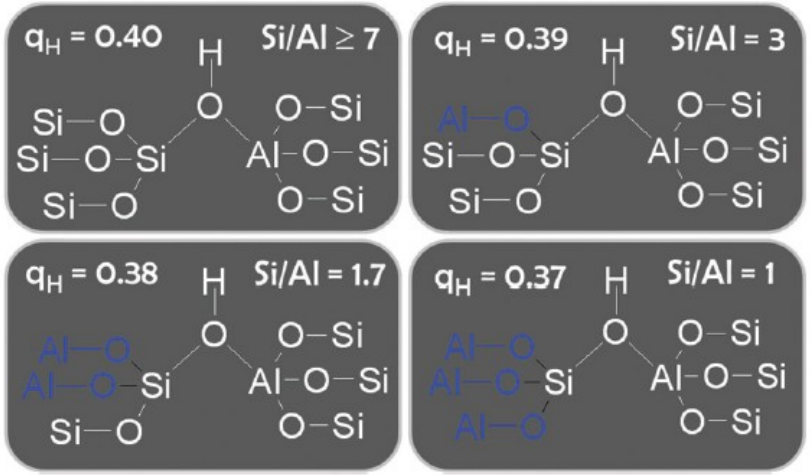
- **Lewis:** Al atoms that are not embedded in the aluminosilicate net (e.g. surface species, amorphous stuff, alumina particles) = extraframework aluminum species (EFAL)
  - Structure:





Zeolites - acidity

- **Brønsted:** 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

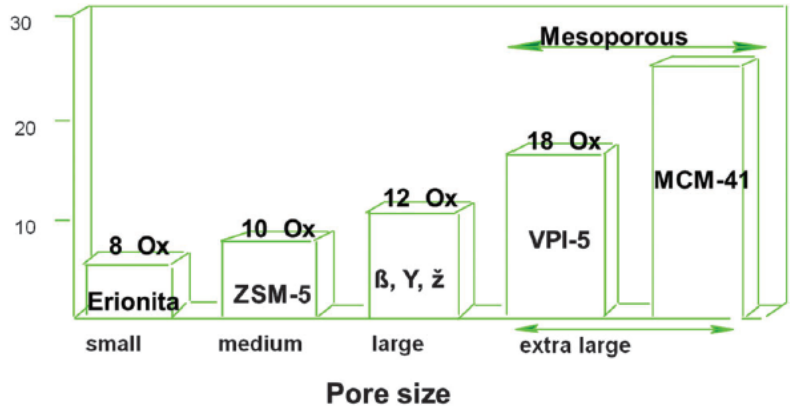
Zeolites - acidity

- **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

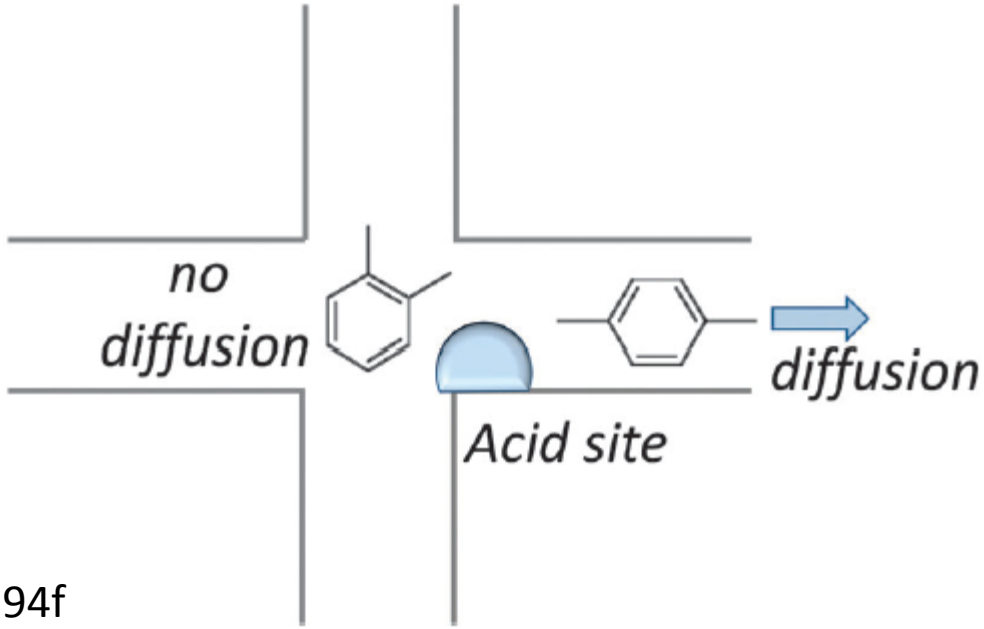
- **Confinement effect**



- **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**



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Zeolites in oil refinement

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

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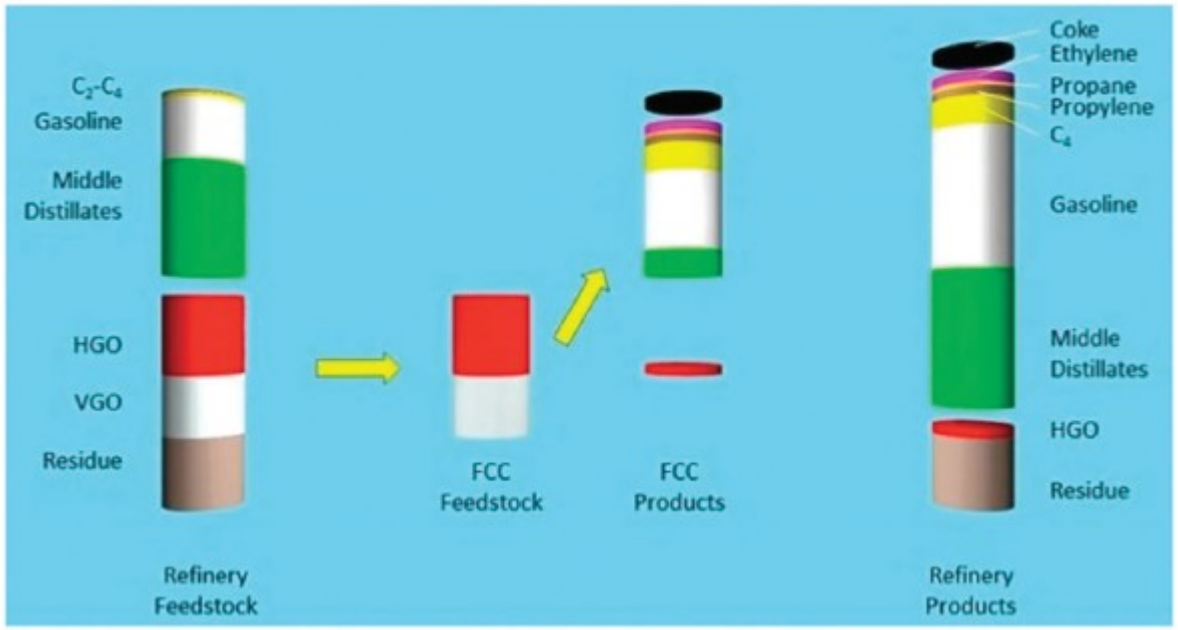
Zeolites in oil refinement

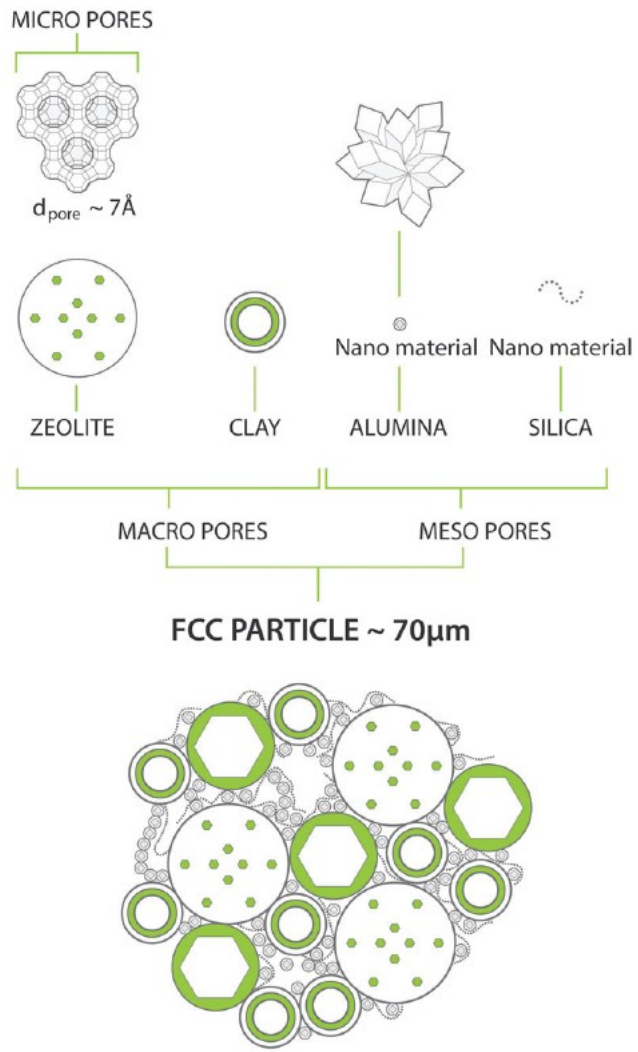
- **Fluid catalytic cracking**



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



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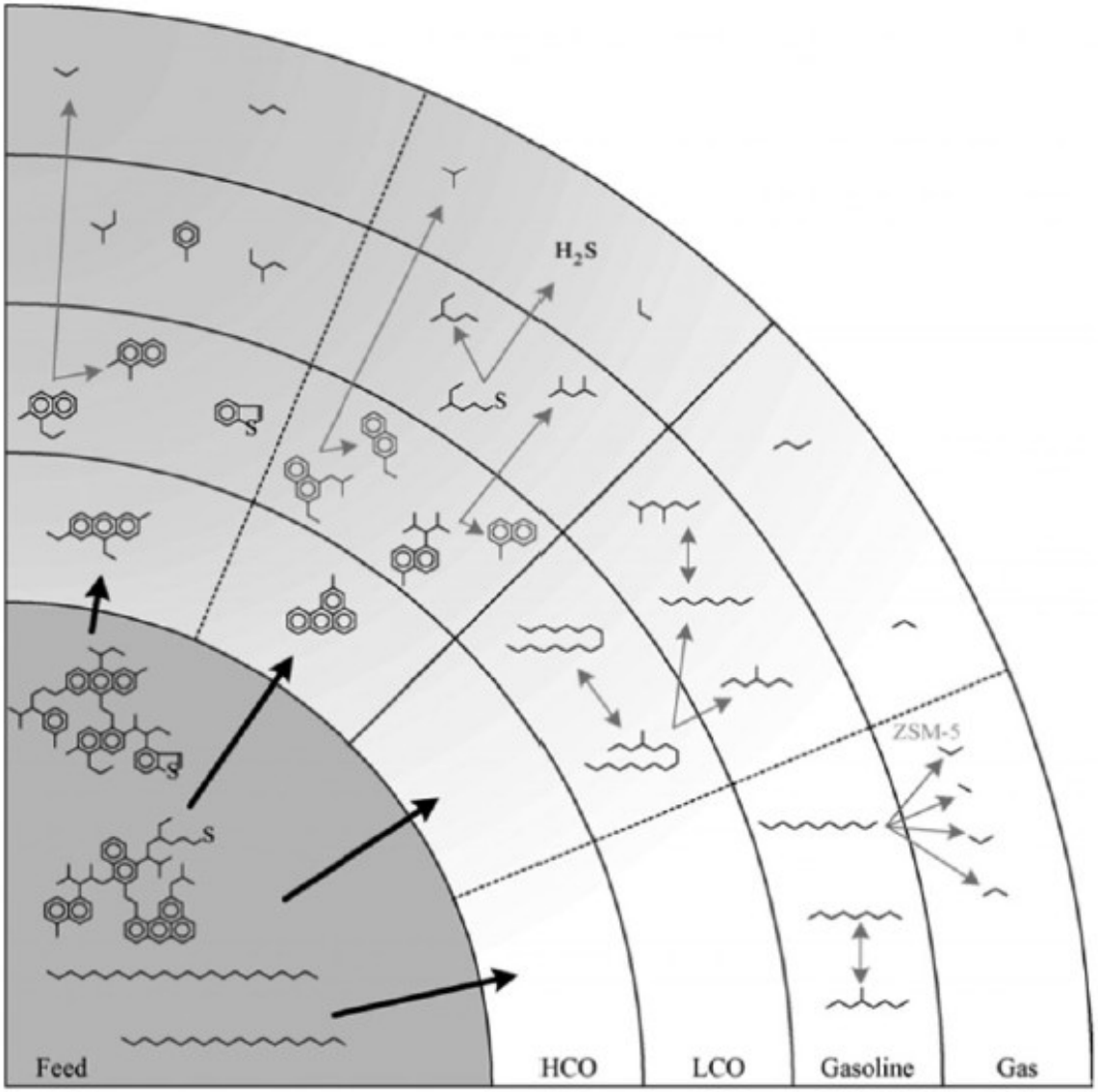
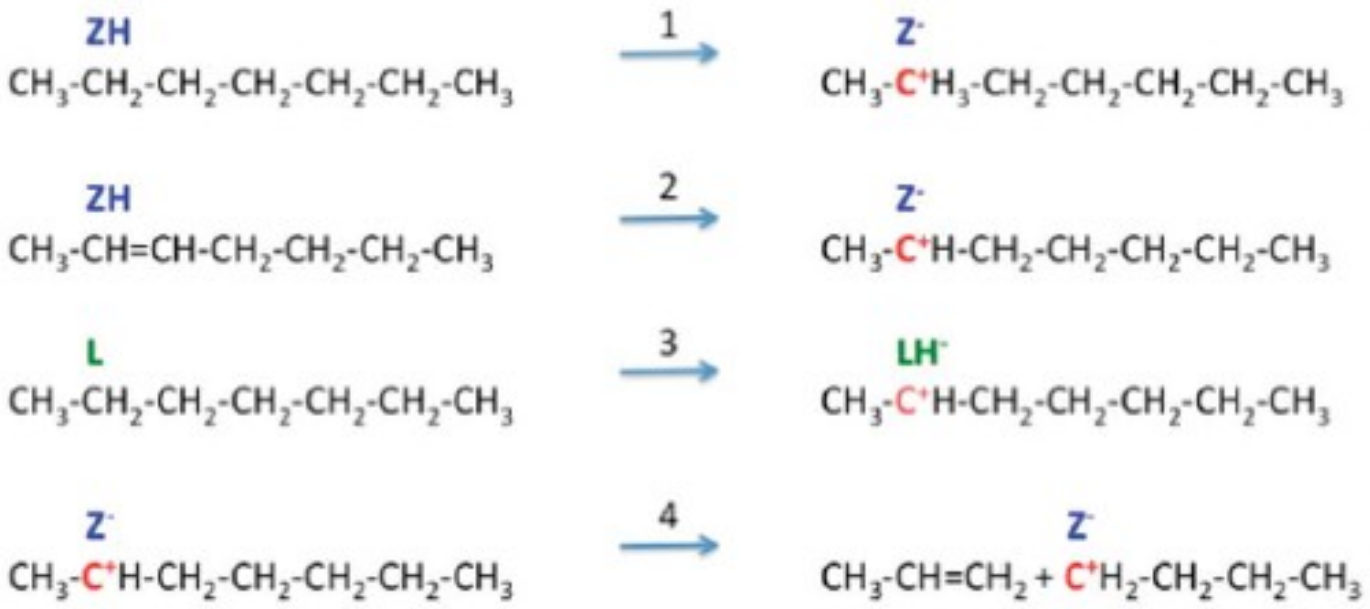
Zeolites in oil refinement

- **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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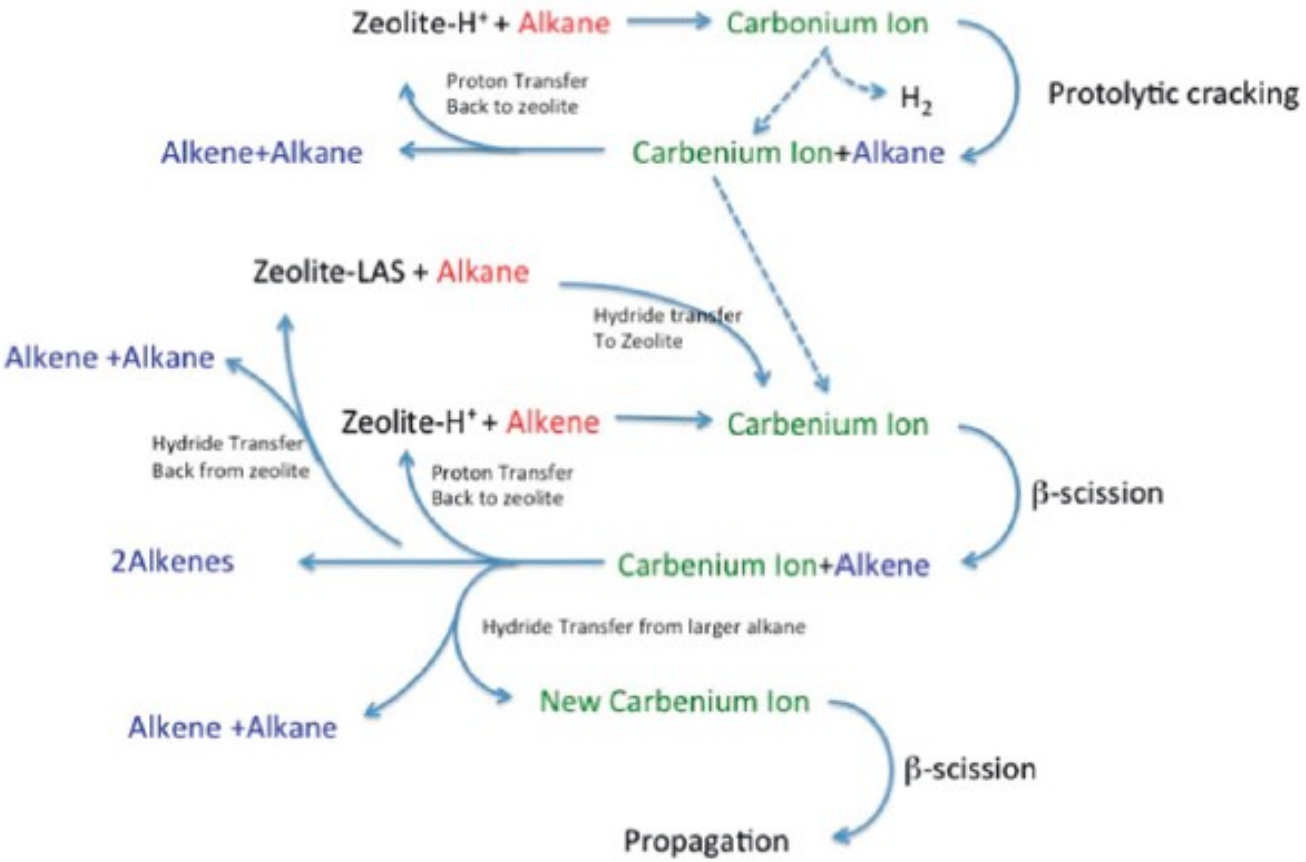
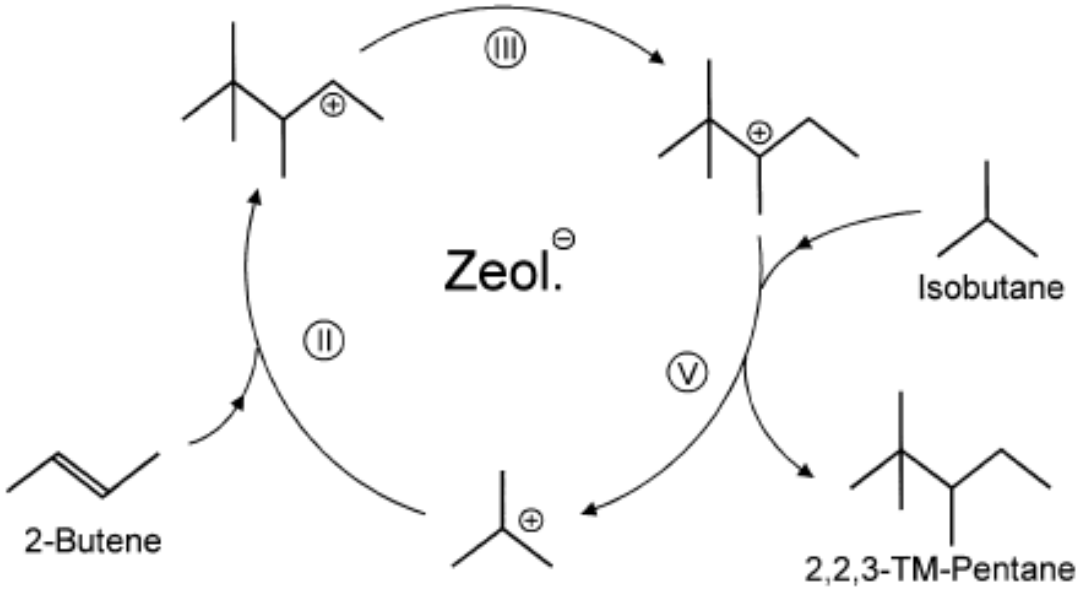


Zeolites in oil refinement

- **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

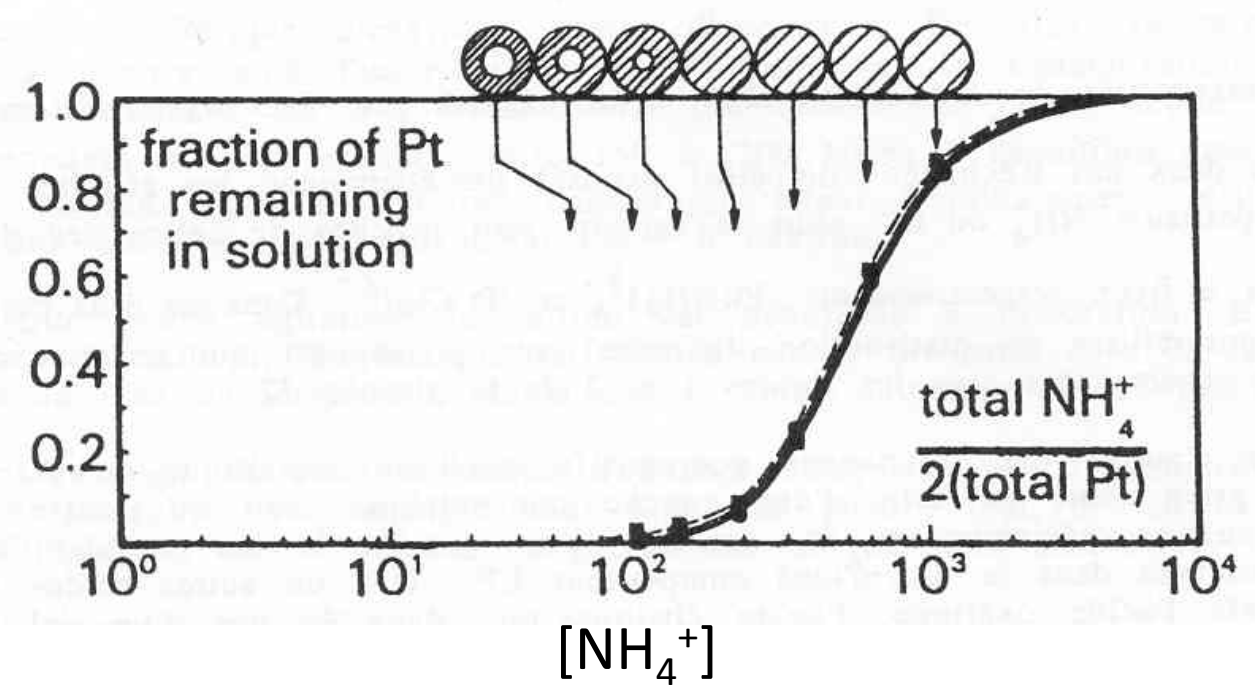
- **Linear paraffin isomerization**
  - Linear C8 (C7) → branched C8 (C7)
  - Requires strong Brønsted acidity and hydrogenation/dehydrogenation activity (Pt(Ni) on mordenite)
  - Mordenite – large pore, monodirectional pores
  - Mordenite – dealuminated (strong H^+), acid washed (low EFAL)
  - Protonation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

Zeolites in oil refinement

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

Zeolites in oil refinement

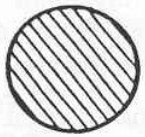
- **Linear paraffin isomerization**
  - Pt, Pd, Ni on mordenite
  - Electrostatic interaction = **Ion exchange**
    - Competitive ion exchange



Zeolites in oil refinement

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

ISOMERIZATION OF N-HEXANE ON Pt/HUSY

T (°C)	$10^4 v_i$ (mole h^{-1} g^{-1} of Pt/HUSY)		$\frac{V_{i\,GD}}{V_{i\,PD}}$
	G.D. 	P.D. 	
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