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Heterogeneous catalysis – conversion of methanol to hydrocarbons over acidic zeolites

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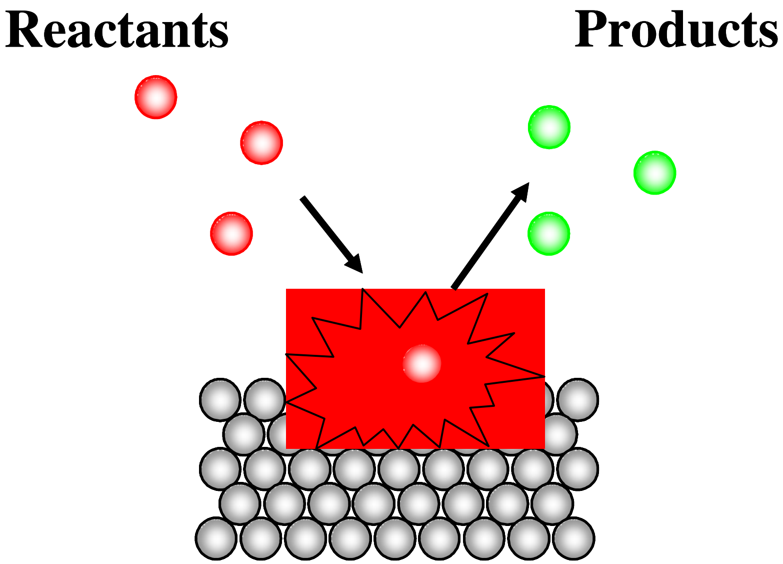
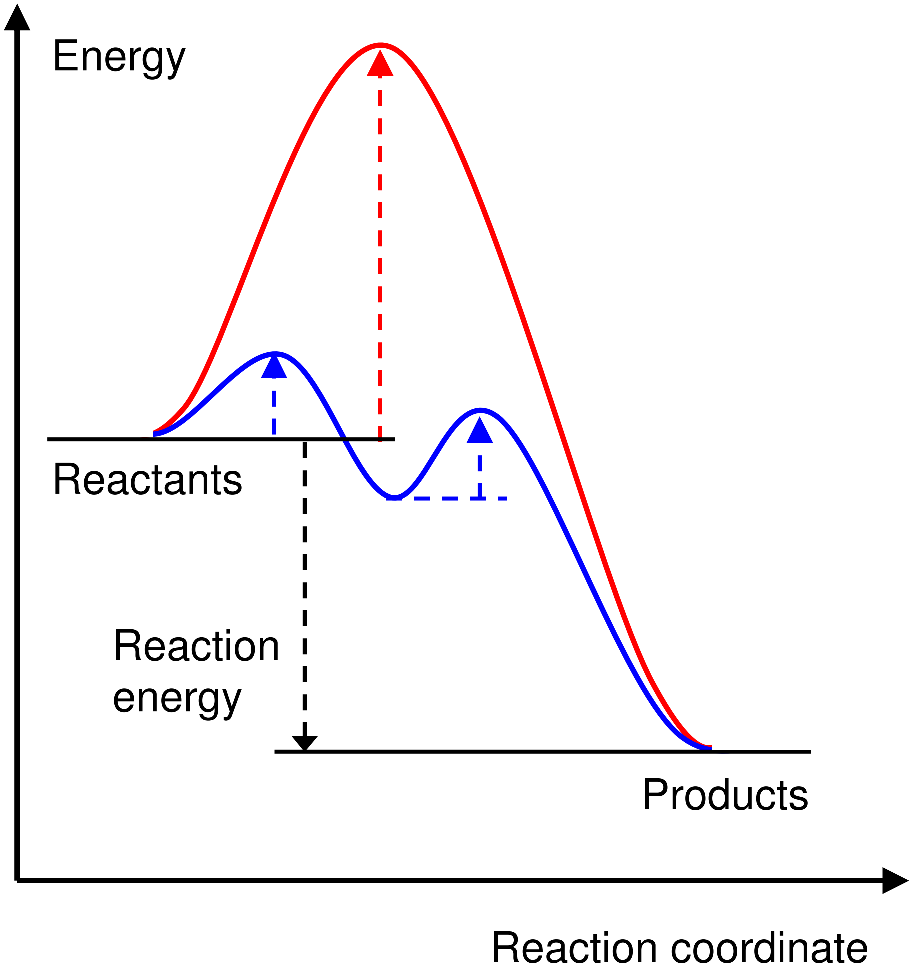
Outline

- ✓ Definition of catalysis
- ✓ Concepts in catalysis
  - ✓ Catalyst types, main reactions, reactor types, adsorption on the catalyst surface
- ✓ Acidic zeolite catalysts
- ✓ Conversion of methanol to hydrocarbons
- ✓ Determining the activation energy of a catalyzed reaction
- ✓ Summary

What is catalysis?





- ✓ “Chemical marriage brokers”
- ✓ The precense of a catalyst facilitates reactions that would be kinetically impossible or very slow without a catalyst
- ✓ The catalyst does not alter the overall thermodynamics of the reaction

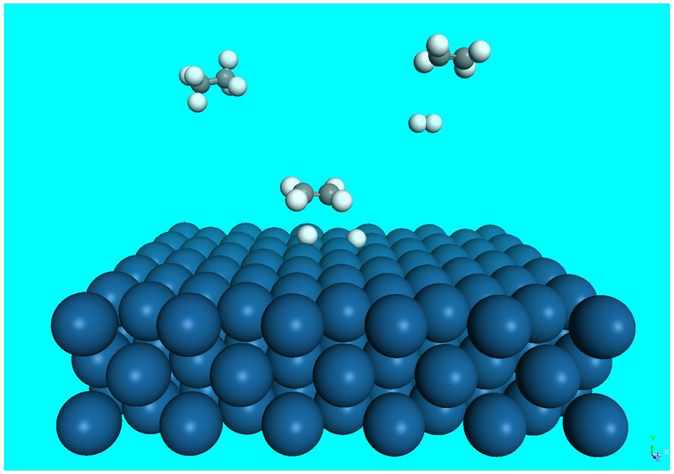
Homogeneous versus heterogeneous catalysis

- ✓ Heterogeneous catalysis
    - ✓The catalyst is in one phase, normally solid, while the reactants and products are in another phase. Separation of catalyst and products is easy, but the reaction is often less selective, because the catalyst material is not homogeneous.
- ✓ Homogeneous catalysis
    - ✓The catalyst, reactants and products are all in one phase, normally the liquid phase. The reactions proceed over a metal complex and are often highly selective, but separation of the products and the catalyst is difficult.

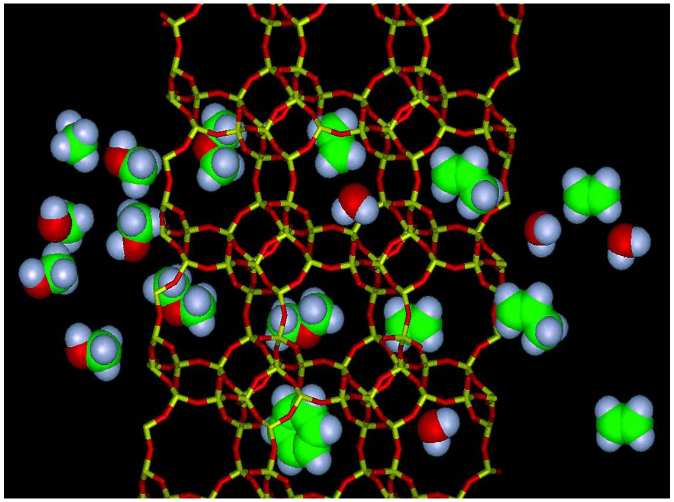
Most industrial processes are based on heterogeneous catalysts, and the rest of this lecture will be devoted to heterogeneous catalysis.

Two main classes of heterogeneous catalysts

- ✓ Red-ox catalysts
    - ✓ *Electron transfer*
    - ✓ Metal
    - ✓ Metal/support



- ✓ Acid-base catalysts
    - ✓ *Proton transfer*
    - ✓ Phosphorous acid/support
    - ✓ Zeolites



Largest industrial processes based on heterogeneous catalysis:

Reaction	Catalyst
Catalytic cracking of crude oil	Zeolites
Hydrotreating of crude oil	Co-Mo, Ni-Mo, Ni-W (sulfidic form)
Reforming of nafta to gasoline	Pt, Pt-Re, Pt-Ir
Alkylation	H_2SO_4, HF, solid acids
Polymerization of ethylene, propylene etc.	Cr, $TiCl_x/MgCl_2$
Water-gas shift reaction	Fe(oxide), Cu-ZnO
Ammonia synthesis	Fe
Ammonia oxidation to NO and HNO_3	Pt-Rh

The importance of catalysis

- ✓ More than 70 % of all existing processes on an industrial scale rely on catalysis
  - ✓More than 99 % of the world gasoline production occurs via catalytic cracking of oil fractions and other catalytice processes
- ✓ More than 90 % of all *new* industrial processes are catalytic
- ✓ Enzymatic catalysis
  - ✓Enzymes are catalysts that fascilitate complex reactions with 100 % selectivity at extremely mild reaction conditions, *i.e.* in our bodies
  - ✓The chemical precision displayed in enzymatic reactions is a source of inspiration for all catalysis chemists.

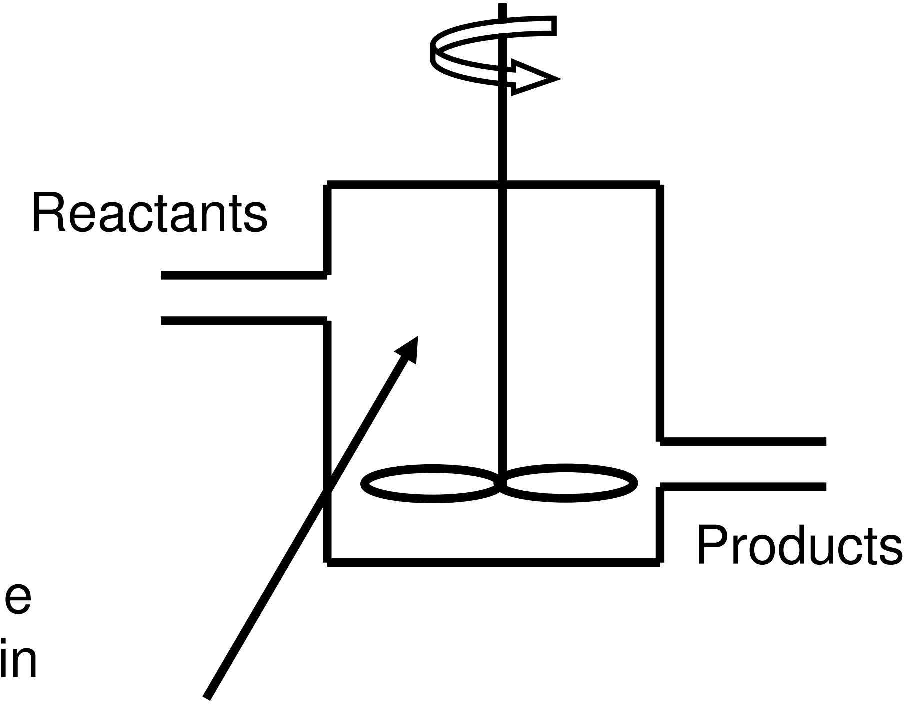
Reactor types in catalysis

- ✓ Three main types of reactors in which heterogeneously catalyzed reactions are carried out
- ✓ Reactants and products are gases or liquids
- ✓ Catalysts in the solid state
    - ✓Stirred tank reactor
    - ✓Fixed bed reactor
    - ✓Fluidized bed reactor

Industrial scale fluidized bed catalytic cracker for gasoline production

Stirred tank reactor

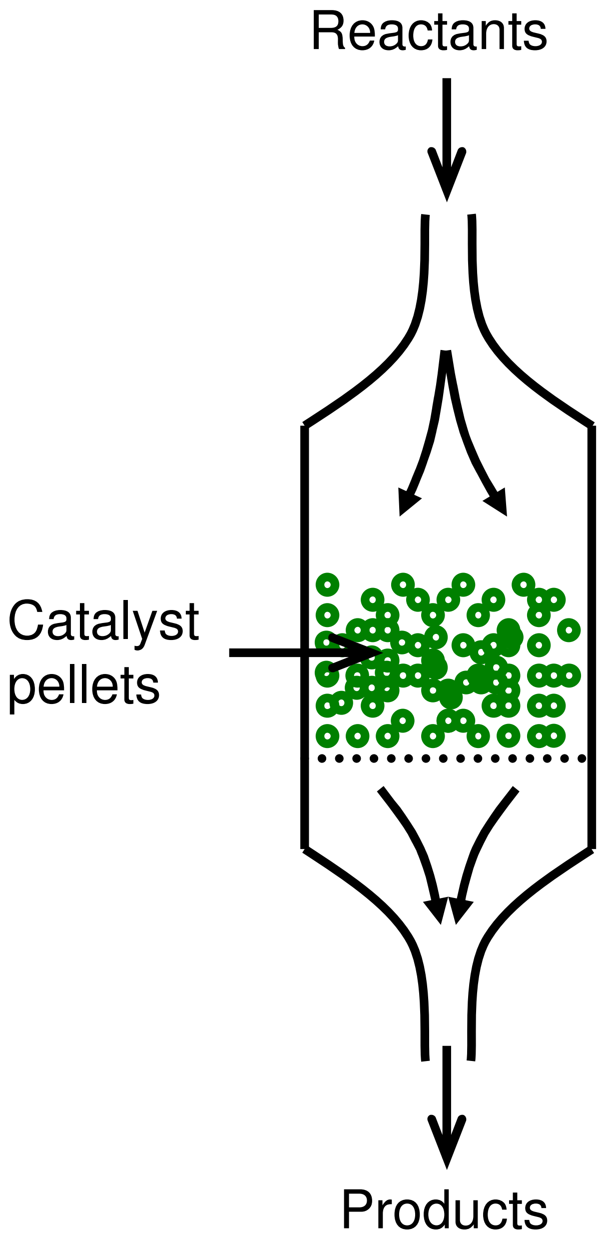
- ✓ Stirring:
  - ✓Good contact between catalyst and reactants
  - ✓Good temperature control
- ✓ May be operated in continous flow or batch mode
- ✓ Often used in homogeneous catalysis
- ✓ For comparable conditions, the conversion will be lower than in a *fixed bed reactor*



Reactants, products and catalyst (solvent)

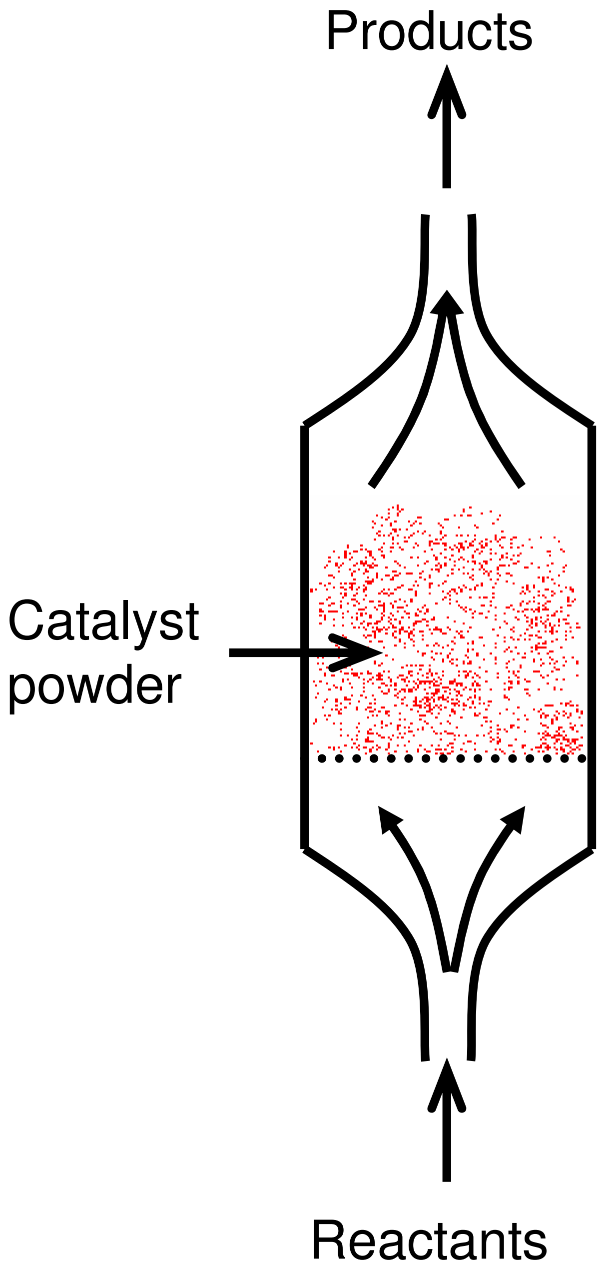
Fixed bed reactor

- ✓ The catalyst is resting on a grate while the reactant gases pass through the catalyst bed from the top
- ✓ Simple engineering (cheap)
  - ✓Often used in labs
- ✓ Often many paralell tubes rather than one big tube
- ✓ The main disadvantage is to control the reactor temperature for exothermic reactions
- ✓ Pressure drop



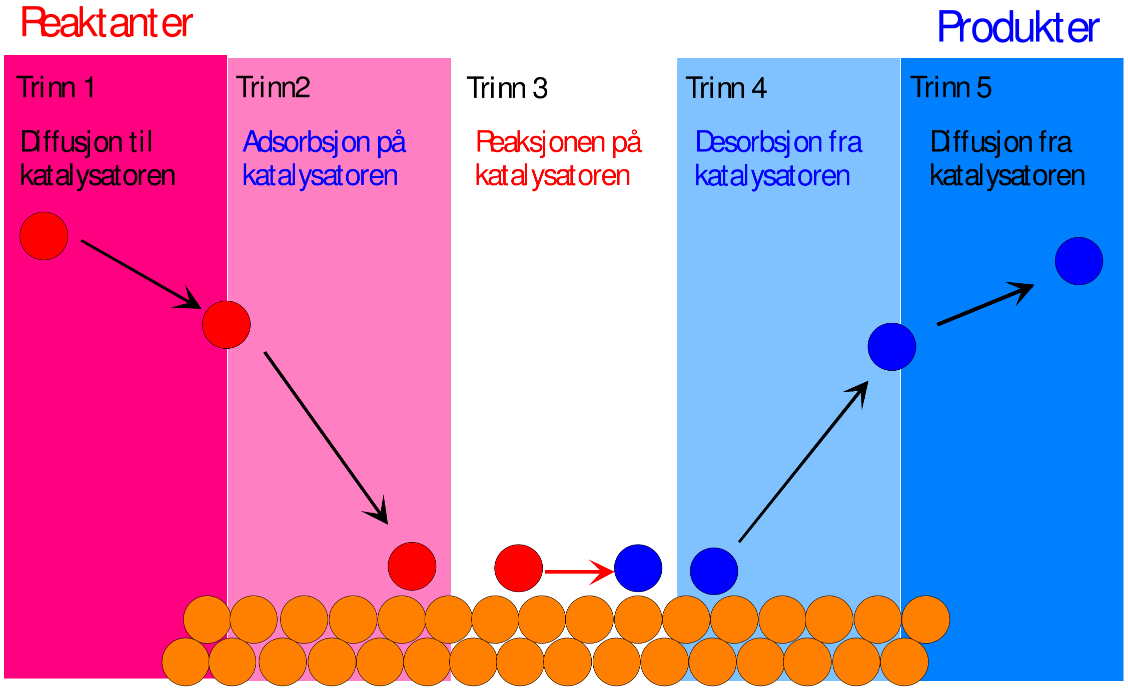
Fluidized bed

- ✓ The reactors enter from the bottom of the reactor
- ✓ Small catalyst particles are suspended by the reactant gas into a *fluidized bed*
- ✓ Complex engineering (expensive)
  - ✓Rarely used in labs
- ✓ Good temperature control
- ✓ Good mixing of catalyst and reactants
- ✓ Some catalyst powder may escape from the top of the reactor



Heterogeneous catalysis takes place in five steps

1. Diffusion from bulk to catalyst surface
2. Adsorption on active site
3. Surface reaction
4. Desorption from active site
5. Diffusion from catalyst surface to bulk



Reaktanter

Produkter

Trinn 1
Diffusjon til katalysatoren

Trinn2
Adsorbsjon på katalysatoren

Trinn 3
Reaksjonen på katalysatoren

Trinn 4
Desorbsjon fra katalysatoren

Trinn 5
Diffusjon fra katalysatoren

What's important?

✓ Laboratory experiments are designed to avoid the constraints of diffusion

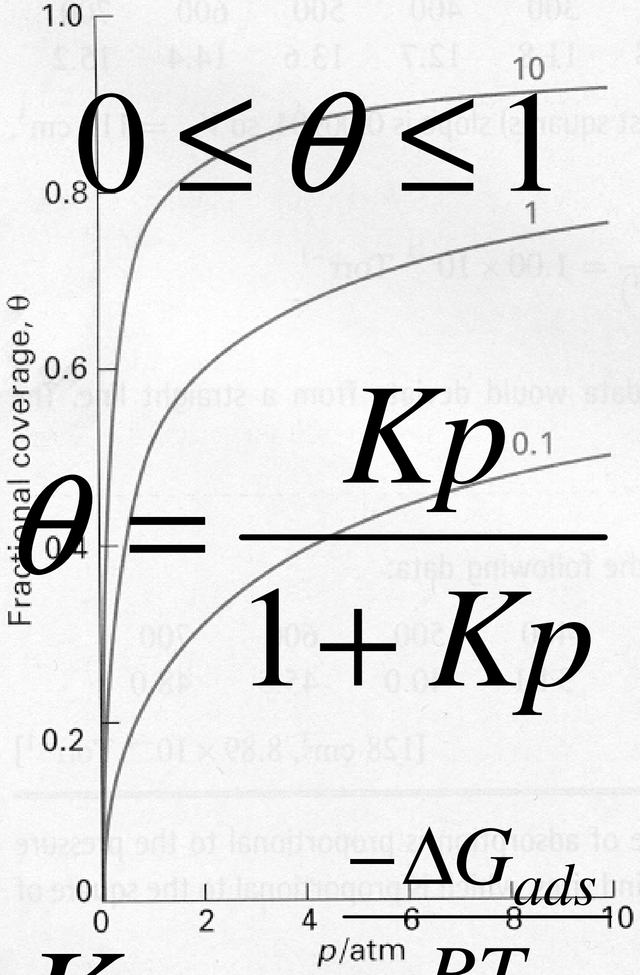
✓ The reaction rates of industrial processes are (almost) always limited by diffusion

  ✓Schmidt's corollary: A reactor that is not mass transfer limited is improperly designed.

✓ *Adsorption* on the catalyst surface, characterization of active site(s) and *reactions occuring on the active site(s)*

Adsorption on the surface

- ✓ The simplest mathematical model of adsorption is called the Langmuir isotherm
    - ✓Only one type of adsorption sites
    - ✓Only monolayer coverage
    - ✓Non-dissociative adsorption
    - ✓ΔG_{ads} independant of coverage
- ✓ The surface coverage depends on the pressure of the adsorbate and the equilibrium constant



$$0 \le \theta \le 1$$

$$\theta = \frac{Kp}{1+Kp}$$

$$K = e^{\frac{-\Delta G_{ads}}{RT}}$$

28.25 The Langmuir isotherm for non-dissociative adsorption for different values of K.

$$\theta = \frac{Kp}{1 + Kp}$$

Langmuir adsorption – two extremes

- ✓ Strong adsorption or high pressures

$$Kp >> 1 \Rightarrow \theta = 1$$

- ✓ Weak adsorption or low pressures

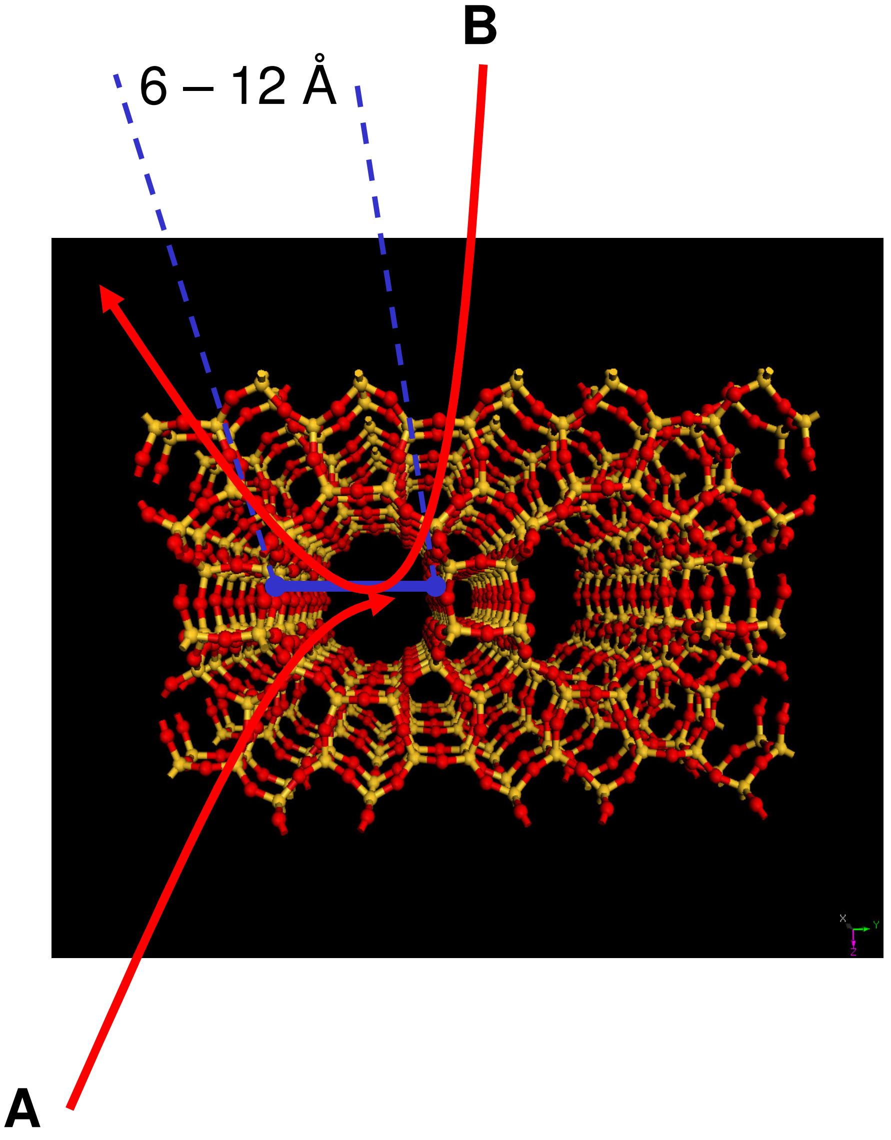
$$Kp << 1 \Rightarrow \theta = Kp$$

- ✓ The rate of a bimolecular surface reaction: 1 + 2 → Product

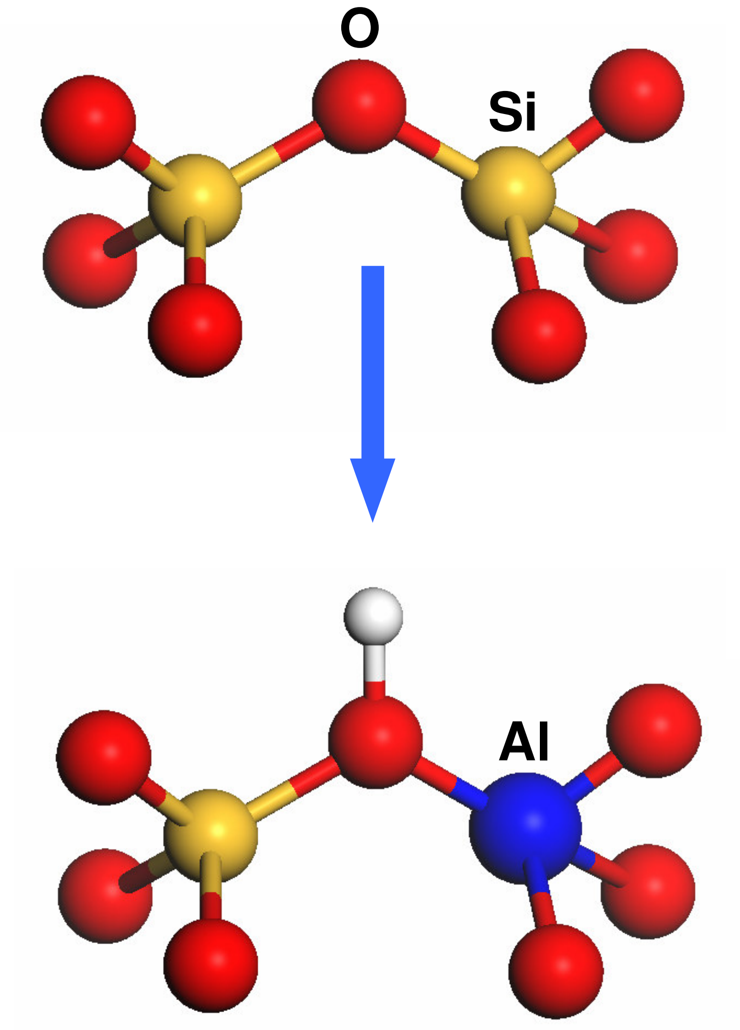
$$r = k_{reaction}\theta_1\theta_2 \;= k_{reaction}K_1 p_1$$

Zeolites

- ✓ Highly porous (high surface area), crystalline aluminosilicates
- ✓ Framework based on SiO_4 and AlO_4 tetrahedra
- ✓ Framework charge balanced by mobile non-framework cations
- ✓ Brönsted acidic properties
- ✓ Sharply defined pore structures
  - ✓Shape selective
  - ✓Molecular sieves



Charge balancing cations in zeolites



No framework charge

One negative excess charge per Al

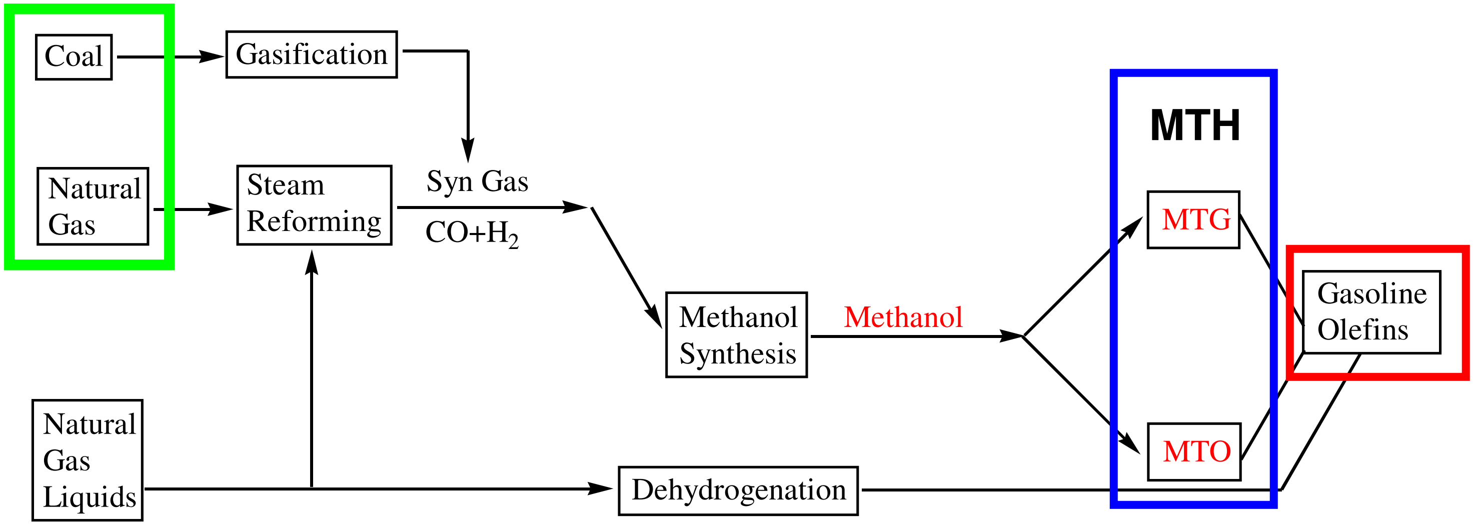
Compensating cations to ensure overall neutrality

Protons give zeolites Brönsted acidic properties

$$\mathrm{CH_3OH} \rightarrow \text{”}\mathrm{CH_2}\text{”} + \mathrm{H_2O}$$

Conversion of methanol to hydrocarbons

The methanol-to-hydrocarbons (MTH) technology represents a route for formation of olefins or gasoline from natural gas/coal



Coal

Gasification

Natural Gas

Steam Reforming

Syn Gas

$CO+H_2$

Methanol Synthesis

Methanol

MTH

MTG

MTO

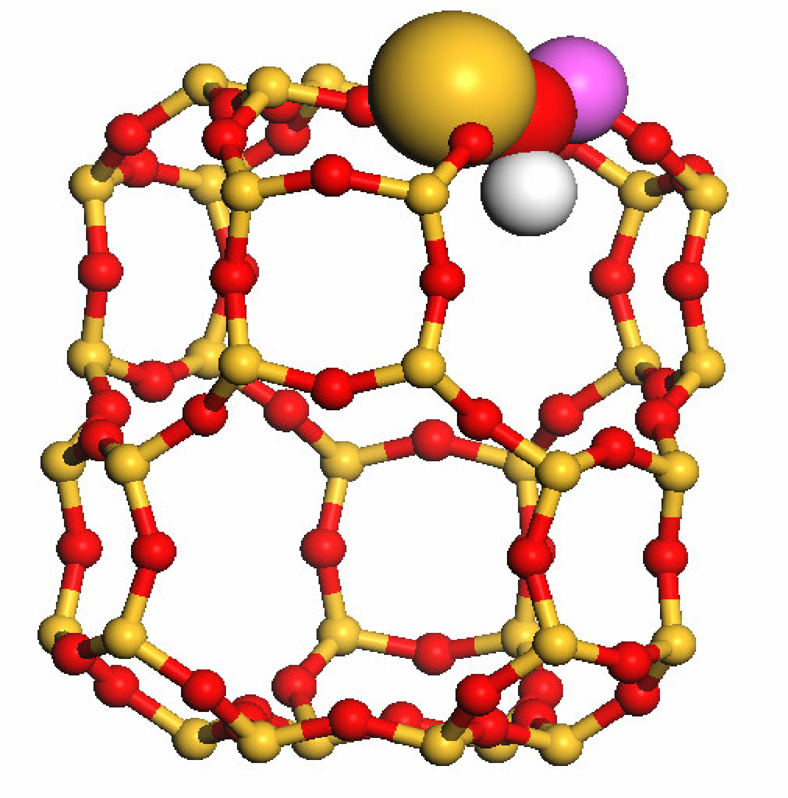
Gasoline Olefins

Natural Gas Liquids

Dehydrogenation

Conversion of methanol over SAPO-34

- ✓The SAPO-34 catalyst has narrow 8-ring cage windows (3.8 × 3.8 Å)
- ✓Due to these fairly small pore openings, the product distribution is infuences by diffusion
- *✓This catalyst yields mainly C2 and C3*



Zeolite H-ZSM-5

- ✓ Larger, 10 membered rings
- ✓ Zeolite framework consisting of straight and zig-zag pores
- ✓ Fairly large voids at the intersections
- ✓ The larger pores allow larger molecules to escape

- ✓ *Yields a high octane gasoline mixture*

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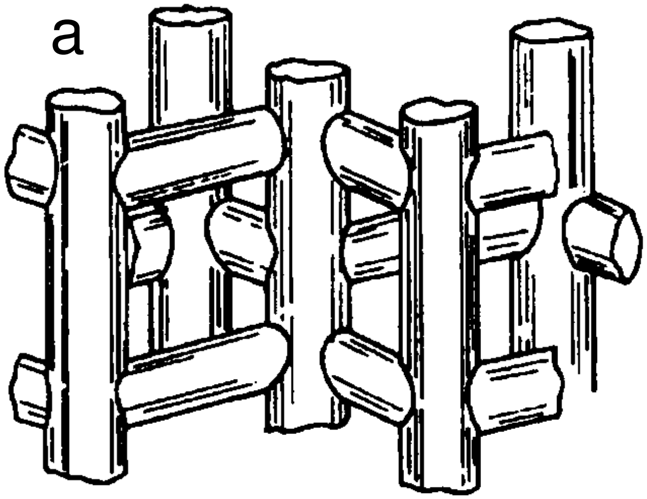

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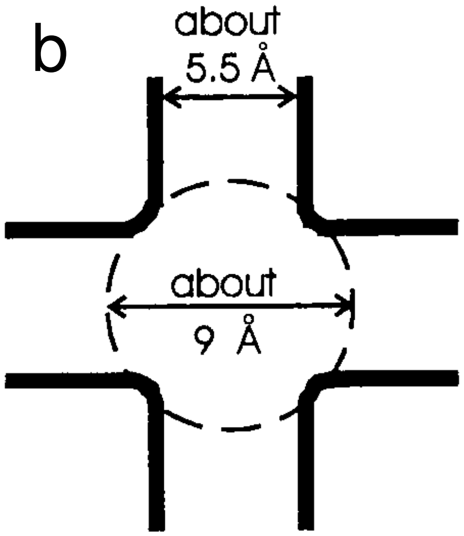
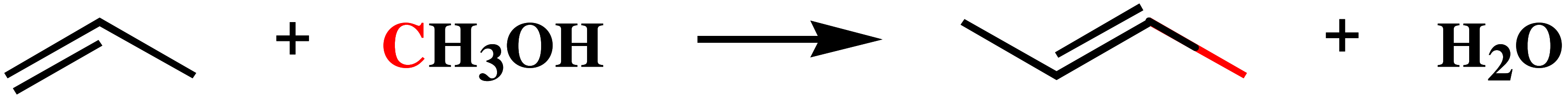


Experimental studies of alkene methylation

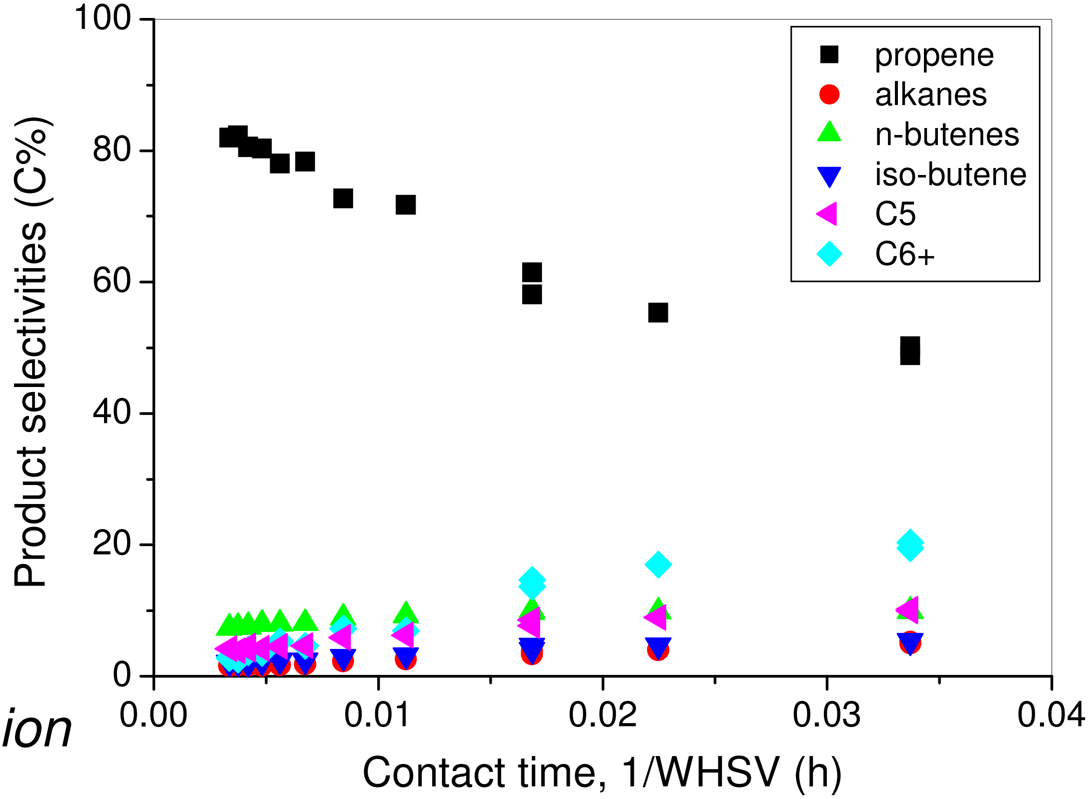
- ✓ ^{13}C MeOH + ^{12}C alkenes
- ✓ Typically 350 °C
- ✓ Commercial H-ZSM-5 catalyst, Si/Al = 45; two acidic sites per unit cell
- ✓ Experiments performed at high feed rates
  - ✓ WHSV ~ 300 h^{-1}
- ✓ The effects of many reaction parameters were studied
  - ✓Feed rate
  - ✓Partial pressures (reaction orders)
  - ✓Reaction temperature (Arrhenius plots)



S. Svelle, P.O. Rønning, S. Kolboe, *J. Catal.* 224 (2004) 115.

S. Svelle, P.O. Rønning, U. Olsbye, S. Kolboe, *J. Catal.* 234 (2005) 385.

Product distribution, ethene + methanol



Low conversion

High conversion

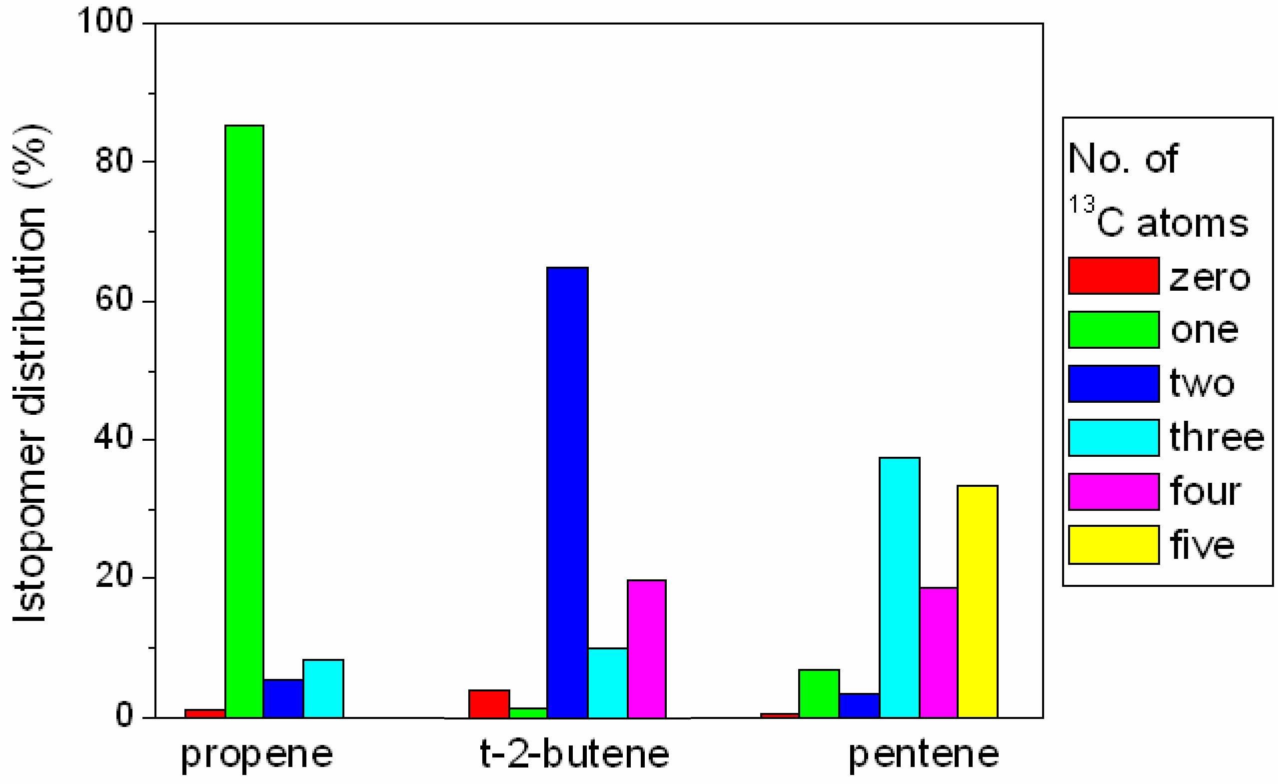
T = 350 °C

50 mbar ethene

50 mbar methanol

- ✓ Propene is dominating among the products at high feed rates
- ✓ Sufficient suppression of side-reactions
- ✓ Minor amounts of other products are always detected

Isotopic distribution, ethene + methanol



The ethene selectivity is about 80 C%

Methylation is the main mode of product formation

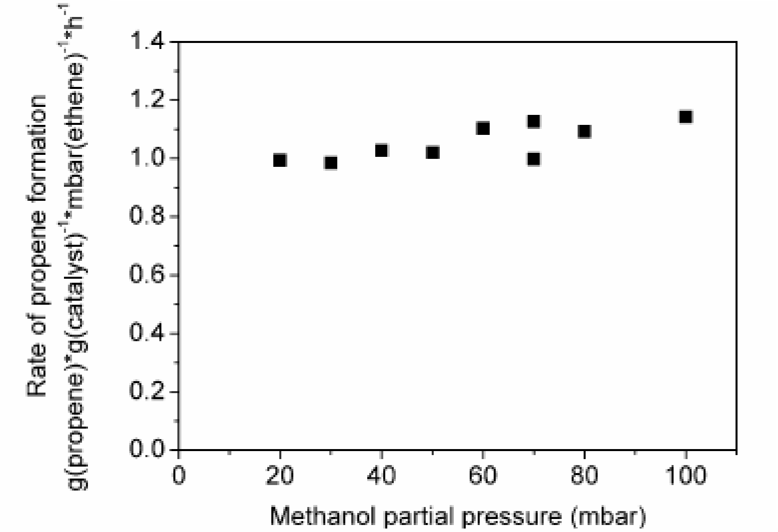
Partial pressures, ethene + methanol

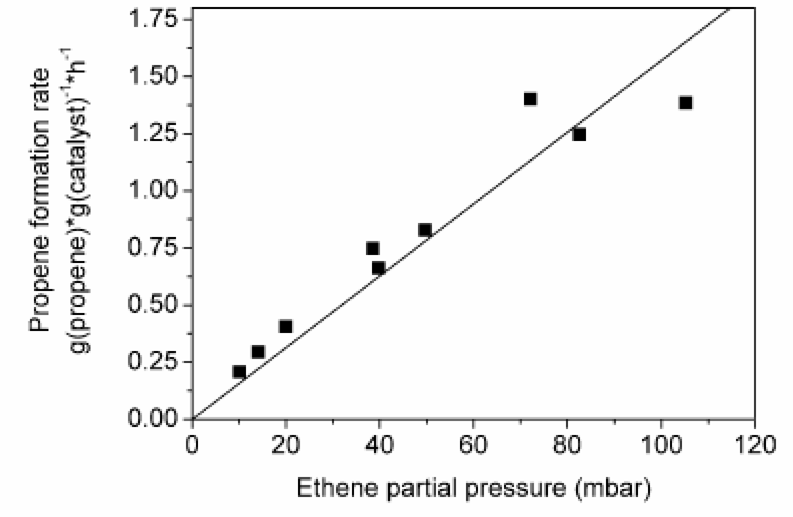
- ✓ Zero order with respect to methanol
  - ✓Θ ~ 1
- ✓ First order with respect to ethene:
  - ✓Θ ~ 0

$$r = k_{reaction}\theta_1\theta_2 \;= k_{reaction}K_1 p_1$$

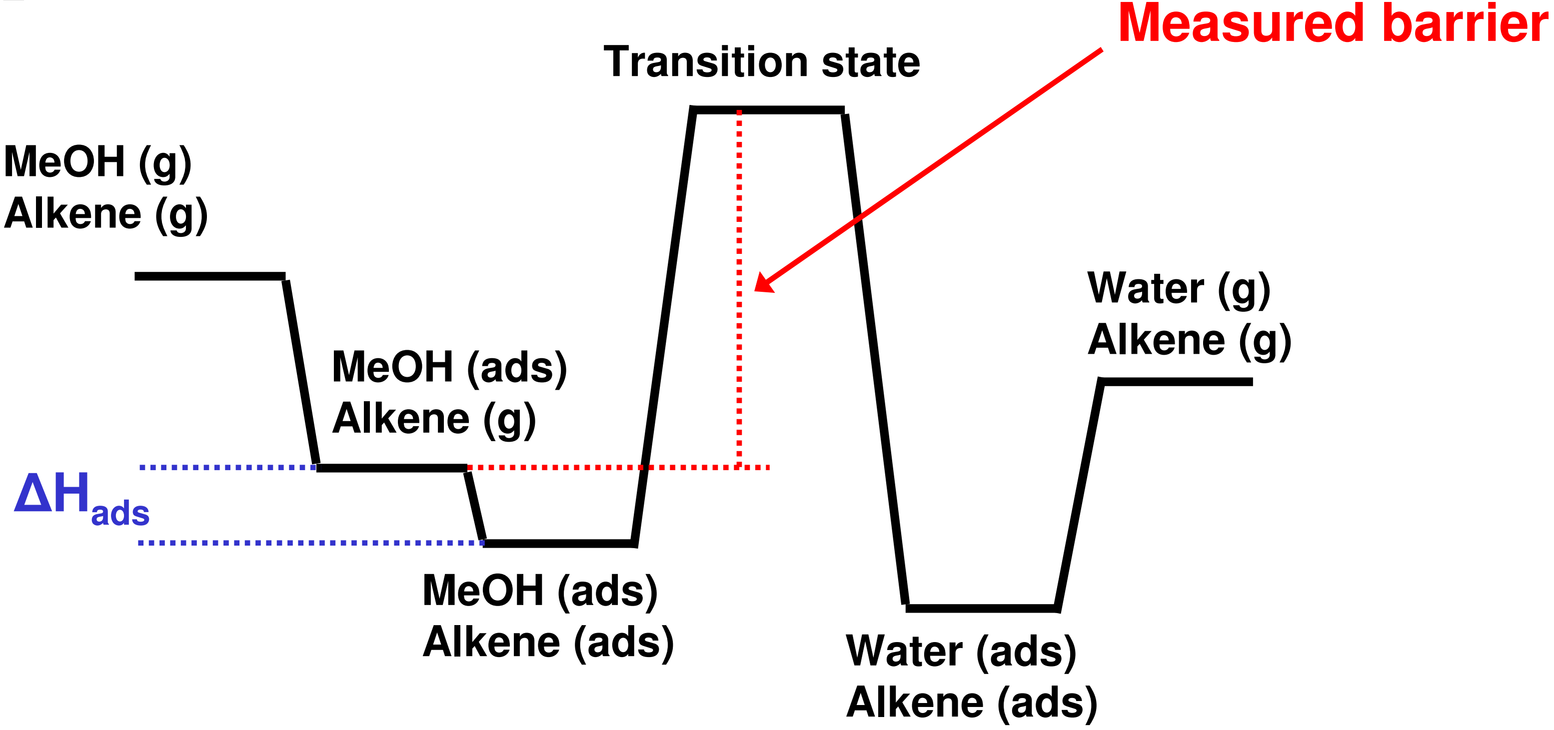
- ✓ This iless clear when propene or n-butene are co-reacted with methanol, stronger alkene adsorption

- ✓ Also, the larger alkenes display greater rectivity and the data are more obscured by side reactions





Apparent vs. intrinsic barriers



- ✓ The measured barrier...
- ✓ ...must be corrected with the heat of alkene adsorption...
- ✓ in order to get the intrinsic barrier

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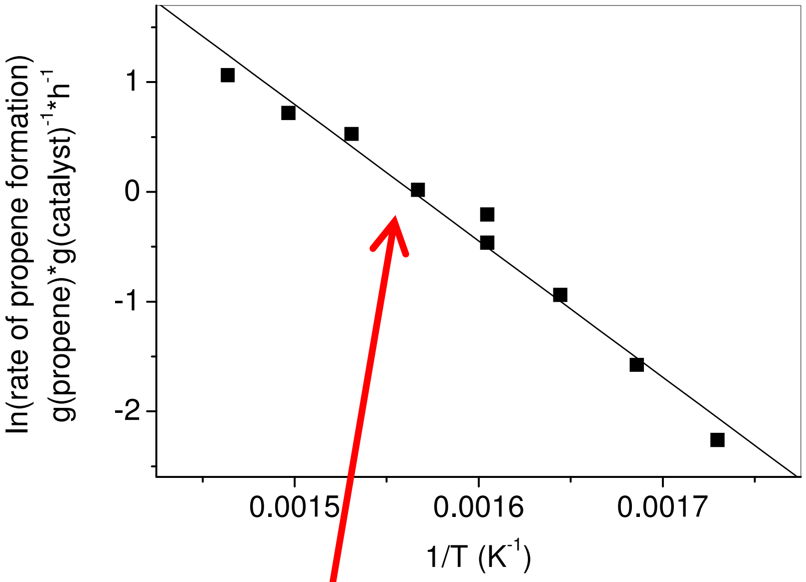
Reaction temperature

$$k_{reaction} = Ae^{-\frac{E_{activation}}{RT}}$$

- ✓ The barries is determined by varying the reaction temperature
- ✓ When corrected for the heat of alkene adsorption, the following estimates for the ”true” activation barriers are found:
- ✓ Ethene
  - ✓110 + 25 = 135 kJ/mol
- ✓ Propene
  - ✓70 + 40 = 110 kJ/mol
- ✓ n-Butene
  - ✓45 + 45 = 90 kJ/mol



Arrhenius plot for the formation of mono-labeled propene, temperature range: 305 – 410 °C

Slope: $-\frac{E_{activation}}{R}$

P. Pascual *et al.*, *J. Phys. Chem. B* 108 (2004) 393

V.R. Choudhary and S. Mayadevi, *Zeolites* 17 (1996) 501

Conclusions

- ✓ Catalysts enhance the rate with with a chemical reaction approaches equilibrium
- ✓ Two main types of heterogeneous catalysts: Metals (on supports) and acidic materials
- ✓ Diffusion, adsorption and reaction needs to be considered when studing heterogeneously catalyzed reactions
- ✓ Experimental determination of activation energies is fascilitated by the use of isotopical labelling

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