

- Introduction
- Basics of heterogeneous catalysis
  - adsorption
  - surface
  - diffusion
  - kinetic approach
  - experimental methods in heterogeneous catalysis
- Concepts for catalyst classification
  - metals
  - semiconductors
  - insulators
- Examples
  - supported catalysts
  - molecular sieves
- Characterisation of catalysts
- Industrial applications

---

---

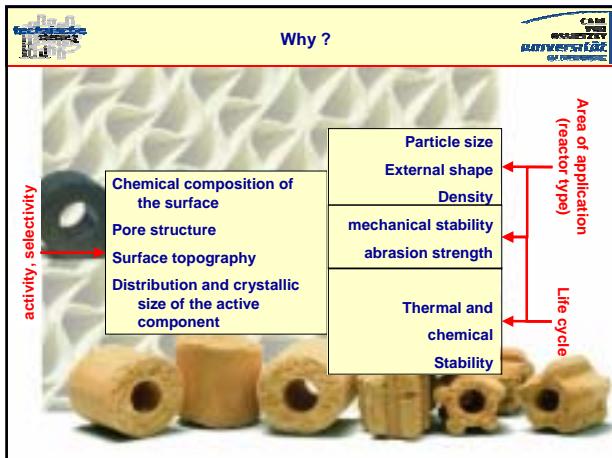
---

---

---

---

---



---

---

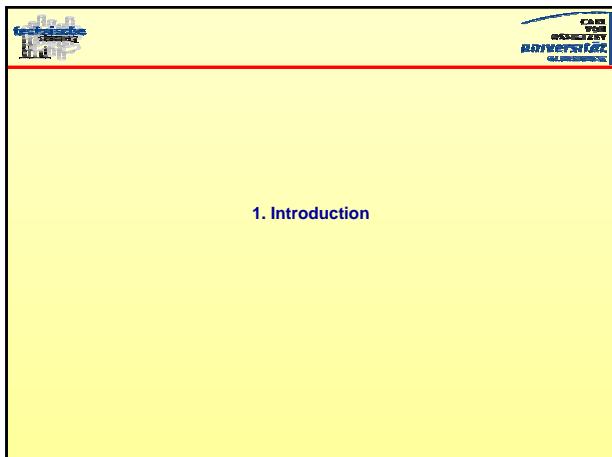
---

---

---

---

---



---

---

---

---

---

---

---

*Es gibt wohl kaum einen Zweig am Baum der  
wissenschaftlichen Erkenntnis, bei dem junge Triebe,  
uplige Blüten und reife Früchte so nahe beieinander  
sind. Das macht die Arbeit auf dem Gebiet der Katalyse  
so reizvoll.*

Hans-Jürgen Quadbeck-Seeger

---

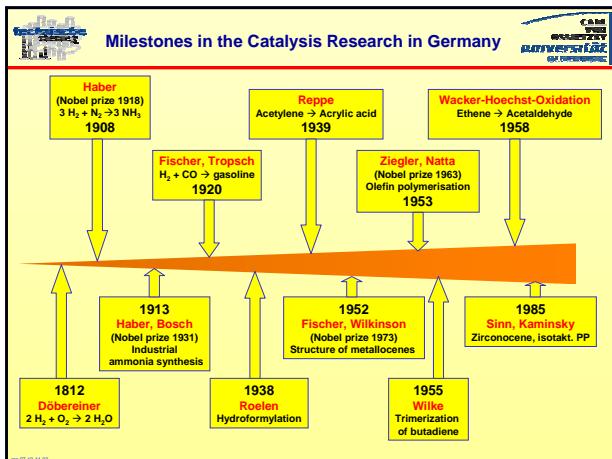
---

---

---

---

---




---

---

---

---

---

---

Short History of Industrial Catalytic Processes

This table provides a historical overview of significant industrial catalytic processes, detailing the year, reaction, catalyst, and discoverer for each.

Year	Catalytic reaction	Catalyst	Discoverer
1806	Sulfuric acid via lead chamber process	$\text{NO}_x$	Desoimes, Clement,
1867	Chlorine production by oxidation of $\text{HCl}$	$\text{CuSO}_4$	Deacon
1875	Sulfuric acid by contact process	$\text{Pt}, \text{V}_2\text{O}_5$	Winkler
1888	Nitric acid by oxidation of $\text{NH}_3$	$\text{Pt/Rh} - \text{nets}$	Knietisch (BASF)
1906			Ostwald,
1907	Fat hardening	Ni	Normann
1913	Synthesis of ammonia	Fe	Mittasch, Haber, Bosch, (BASF)
1920	Oxidation of Benzene or naphthalene to MA and PA	Fe, Mo, Sn	Weiss, Downs
1923	Synthesis of methanol from $\text{CO}/\text{H}_2$	$\text{Zn/Cr}_2\text{O}_3$	Mittasch
1930	Oxidation of ethylene to ethylene oxide	Ag	Lefort
1932	Alkylation of olefins with isobutene to gasoline	$\text{AlCl}_3$	Ipatieff, Pines
1937	Cracking of hydrocarbons	$\text{Al}_2\text{O}_3/\text{SiO}_2$	Houdry

---

---

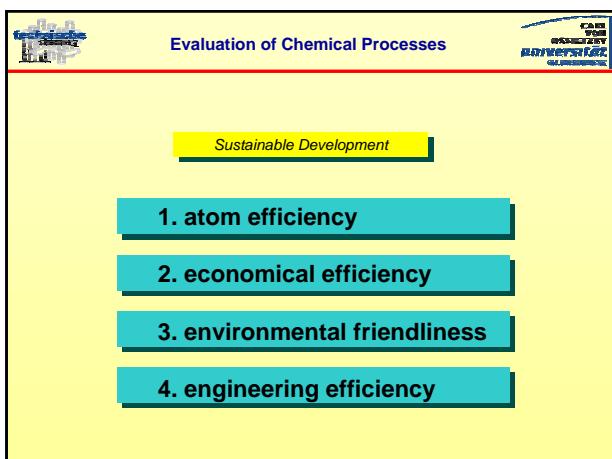
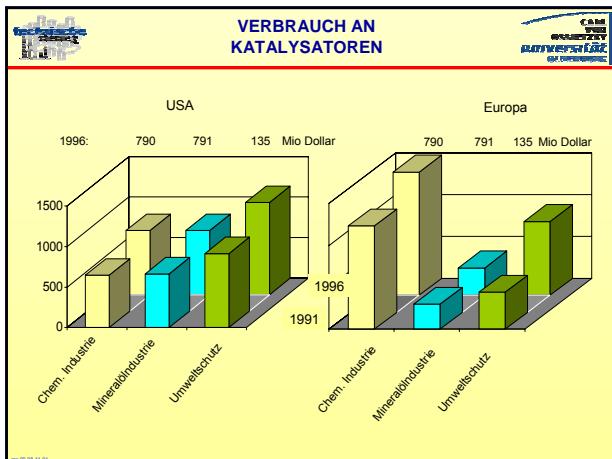
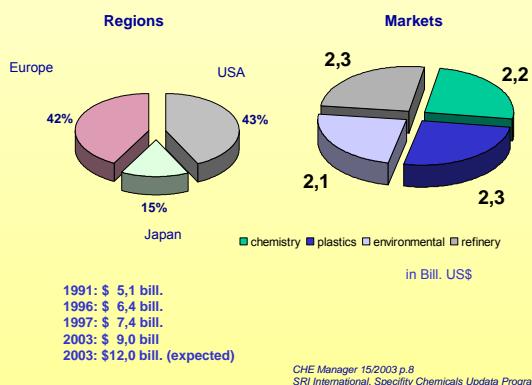
---

---

---

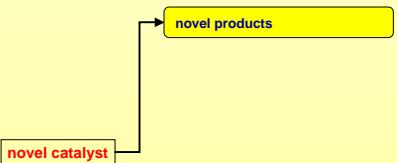
---

## Worldwide Catalyst Demand





## Novel Catalysts - Key for Future Innovation



---

---

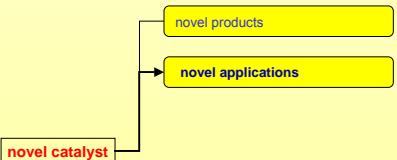
---

---

---



## Novel Catalysts - Key for Future Innovation



---

---

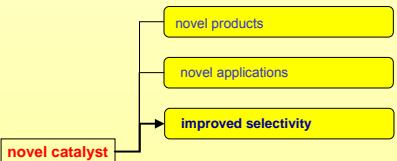
---

---

---



## Novel Catalysts - Key for Future Innovation



---

---

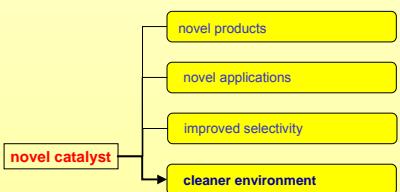
---

---

---



## Novel Catalysts - Key for Future Innovation



---

---

---

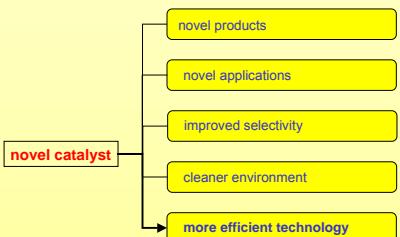
---

---

---



## Novel Catalysts - Key for Future Innovation



---

---

---

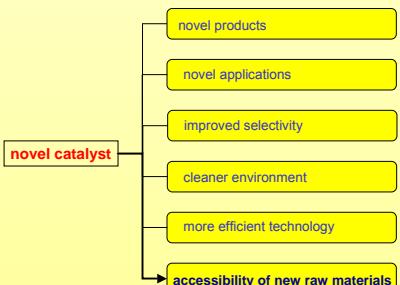
---

---

---



## Novel Catalysts - Key for Future Innovation



---

---

---

---

---

---



## A Selection of Environmental Challenges for Catalysis



- Development of 'zero-waste' processes
- Minimization of hazardous products and 'greenhouse' gases
- Replacement of corrosive liquid acid catalysts by benign solid acid catalysts
- Evolution of sustainable systems
- Reduction in volume of by-products
- Development of processes requiring less 'consumption' of catalysts
- Reformulated transport fuels (containing lower amounts of aromatics and volatile components and larger amounts of more completely combustible additives)

— 09-11-02-01 — J.M. Thomas, W.J. Thomas, Principles and Practice of Heterogeneous catalysis, VCH, Weinheim, 1997, p. 55

---

---

---

---

---

---

---

---



## A Selection of Environmental Challenges for Catalysis I



- Development of (catalytic) automobiles operating on methanol dissociation
- Better catalysts for hydrodesulphurization, hydrodenitrification of light oils and coals and hydrotreatment of heavy oils and tars
- Single-step synthesis of desirable products:
  - acetaldehyde from ethane, aromatics from ethane
  - phenol from benzene, acrolein from propane
  - acrylonitrile from propane by ammoniation
  - acetic acid from methanol
  - 2-methylpropylene from syn-gas
- Better methods for isomerising linear alkanes into branched-chain ones
- Functionalization of light alkanes, especially methane
- Efficient routes to cheaper feed stocks for the chemical and pharmaceutical industries
- Development of robust, re-usable, chiral catalysts

— 09-11-02-01 — J.M. Thomas, W.J. Thomas, Principles and Practice of Heterogeneous catalysis, VCH, Weinheim, 1997, p. 55

---

---

---

---

---

---

---

---



## A Selection of Environmental Challenges for Catalysis II



- New shape-selective catalysts, e.g., for nonthermodynamic ratios of mono- and di-methylamines from methanol and ammonia
- Development of processes using CO<sub>2</sub> as reactant
- Cheaper and safer methods of generating hydrogen
- New catalytic membranes
- Better electrocatalysts for fuel-cell consumption of plentiful hydrocarbons
- Development of modified enzymes, organisms or transgenic plants for 'natural' production of polymers(b)
- Families of solid catalysts for 'tunable' conversion of methanol to either ethylene or propylene
- Fischer-Tropsch catalysts for sharply defined reaction products
- Efficient, safe methods of generating hydrogen peroxide (from H<sub>2</sub> and O<sub>2</sub>)

— 09-11-02-01 — J.M. Thomas, W.J. Thomas, Principles and Practice of Heterogeneous catalysis, VCH, Weinheim, 1997, p. 55

---

---

---

---

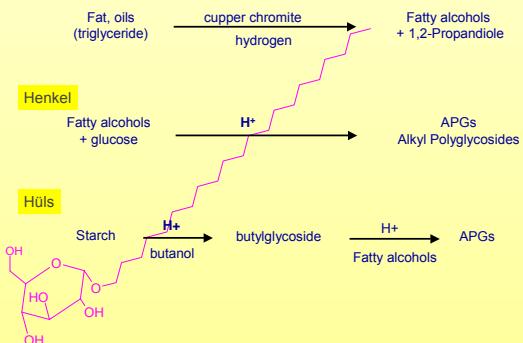
---

---

---

---

## Novel Raw Materials




---

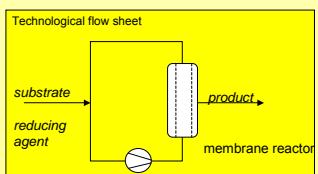
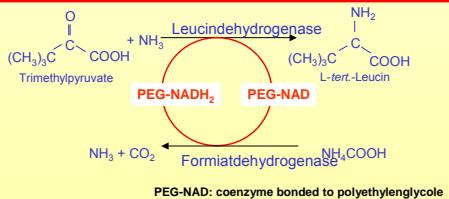
---

---

---

---

## Novel Catalysts – Simpler Processes




---

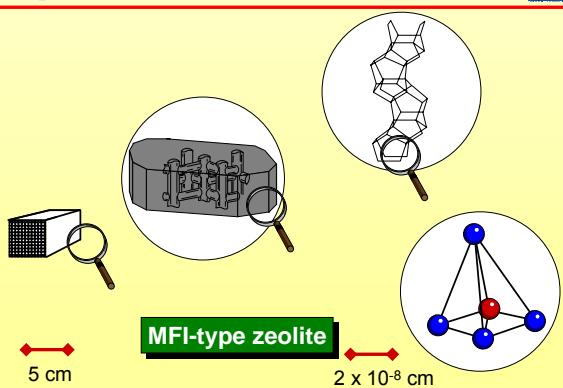
---

---

---

---

## How Look Likes a Zeolite?




---

---

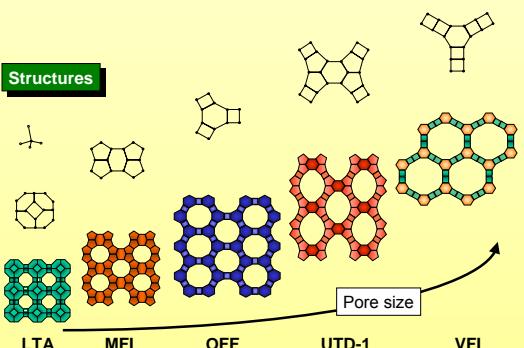
---

---

---

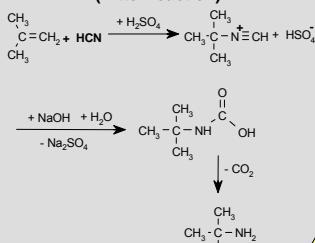
## Variety of Zeolites

### Structures



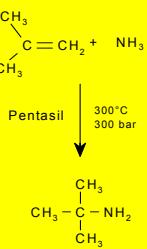
## Novel Catalysts – Simpler Processes

### Old process (Ritter reaction)



4.5 t starting material to produce 1 t *tert*-butylamin  
3.0 t Na<sub>2</sub>SO<sub>4</sub> / t *tert*-butylamin

### BASF- process

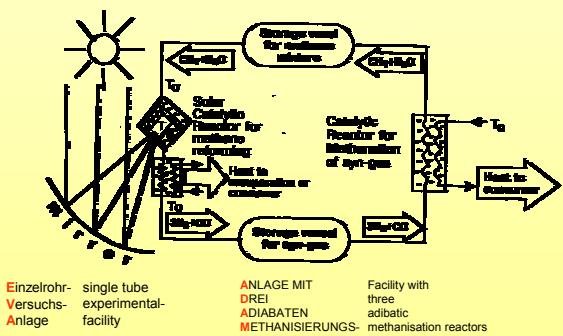


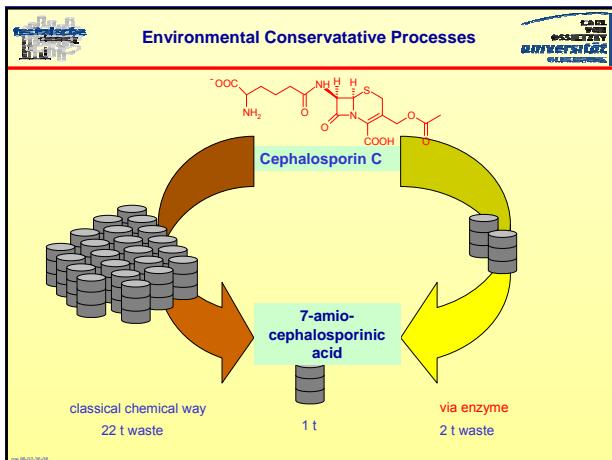
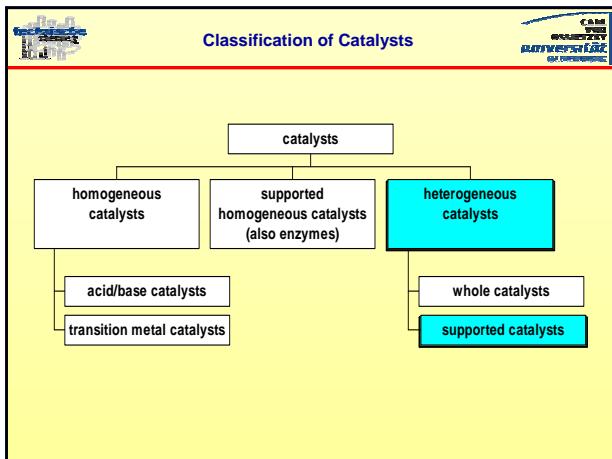
S > 98 %  
NH<sub>3</sub>/C<sub>2</sub>H<sub>6</sub> = 1.3 - 2

W. Hölderich et al. DE 3326579 (Jan. 31, 1985) BASF AG

## Solar-Catalytic Technology Thermochemical ADAM - EVA Cycle

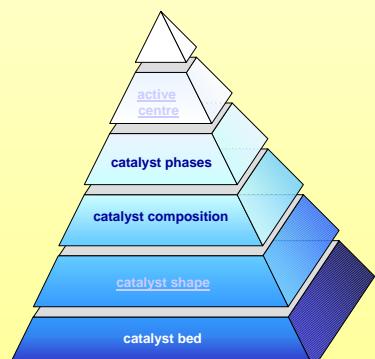
K. I. Zamarajev. Topics in Catalysis, 3 (1996)




iso 9001-2000


	homogeneous	heterogeneous
<b>Effectivity</b>		
active centres	all metal atoms	only surface atoms
concentration	low	high
selectivity	high	lower
mass transfer control	practical no	mass transfer control in dependence on reaction conditions
reaction conditions	50...200 °C	> 250 °C
loss of activity	irreversible reaction with products; poisoning	sintering, poisoning
<b>Properties of catalyst</b>		
structure	defined	undefined
temperature resistance	low	high
catalyst separation	very expensive	in fixed bed reactor not necessarily
costs for catalyst lost	very high	low

iso 9001-2000



---

---

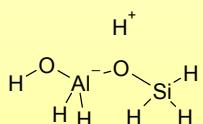
---

---

---

---

### Active Centre



Cluster to be calculated by quantum mechanical methods



---

---

---

---

---

---



---

---

---

---

---

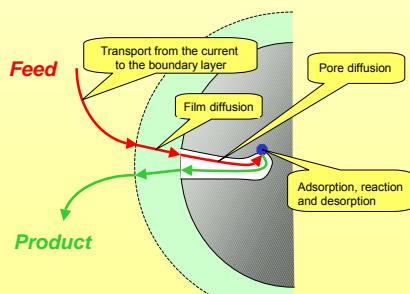
---

CH<sub>3</sub>CH<sub>2</sub>OH

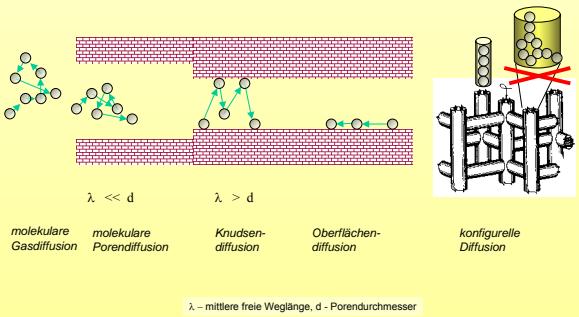
	catalyst	temperature
CH <sub>3</sub> CHO	Cu	250...300
C <sub>2</sub> H <sub>4</sub> + H <sub>2</sub> O	Al <sub>2</sub> O <sub>3</sub>	300...450
C <sub>2</sub> H <sub>6</sub> + H <sub>2</sub> O + H <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub> /ZnO	420...450
CH <sub>3</sub> COCH <sub>3</sub> + H <sub>2</sub> O + H <sub>2</sub>	Cu/Cr <sub>2</sub> O <sub>3</sub>	300
CH <sub>3</sub> COOC <sub>2</sub> H <sub>5</sub> + H <sub>2</sub>	Cu-Ce	300
CH <sub>4</sub> + H <sub>2</sub> + CO	Ni	400
C <sub>2</sub> H <sub>5</sub> OH + H <sub>2</sub> O	Na	350

## 2. Bases of Heterogeneous Catalysis

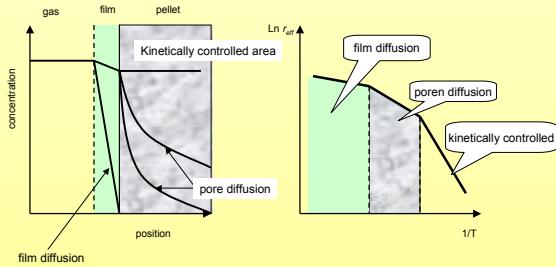
### Steps of Heterogeneously Catalysed Reactions



### Diffusion in der Pore



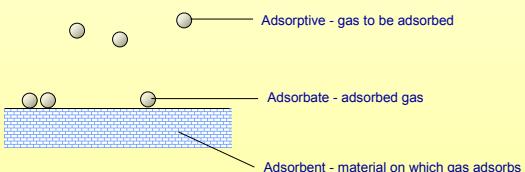
## Dependence of the Concentration on the Site in the Catalyst Pellet



## 2.1 Adsorption

### 2.1.1 Basics

## Basic Terms



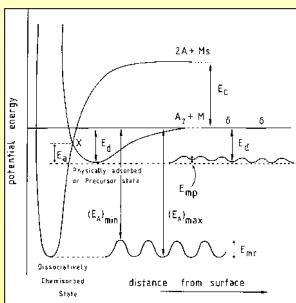
### Roughness



### **Porosity**



## Potential Energy Diagram for the Approach of a Diatomic Molecule Toward a Surface



## ANIMATION

physisorption	Chemisorption
$E_{\text{ad}}$ - activation energy for surface migration in the dissociatively chemisorbed and molecularly physically adsorbed states dissociation energy desorption energy.	

J.M. Thomas, W.J. Thomas, Principles and Practice of Heterogeneous catalysis, VCH, Weinheim, 1997, p. 67

## Physisorption and Chemisorption

	<b>Physical Adsorption</b>	<b>Chemisorption</b>
reason	van der Waals-forces, no electron transfer	covalent/electrostatic forces, electron transfer
adsorbens	all solids	some solids
adsorbate	all gases below critical point, intact molecules	some chemical reactive gases, dissociation into atoms, ions, radicals
temperature range	low temperature	general high temperatures
heat of adsorption	low = melting enthalpy (10 kJ/mol), exothermic	high = reaction enthalpy, 80-200 (600) kJ/mol, commonly exothermic
rate	very fast	strongly depends on temperature
activation energy	low	commonly high
surface coverage	multiplayer	monolayer
reversibility	high reversible	frequently irreversible
importance	determination of surface area	determination of surface concentration of and pore size, active components and of adsorption kinetics, determination of active sites

## What Kind of Molecule ?

METAL	ADSORPTIV	Problems
Fe	H <sub>2</sub> , CO	CO may form various carbonyls or carbides
Co	H <sub>2</sub> , CO	Activated chemisorption, T > 100°C are necessary for full coverage
Ni	H <sub>2</sub>	Rapid equilibration, CO forms Ni(CO) <sub>4</sub>
Cu	NO <sub>x</sub> , Cl <sub>2</sub>	Surface reactions
Ru	H <sub>2</sub>	CO forms Ru(CO) <sub>6</sub> , forms volatile oxide
Rh	H <sub>2</sub> , CO	Adsorption stoichiometry varies with crystallite size
Pd	CO	H <sub>2</sub> can dissolve into the bulk and form bulk hydride
Re	H <sub>2</sub> , O <sub>2</sub>	Forms volatile oxide, H <sub>2</sub> uptake can be low

---

---

---

---

---

---

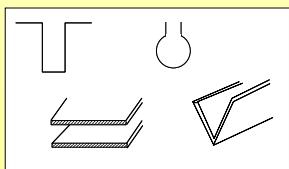
## Pore Size and Shape

## Pore diameter

- micropores (< 2 nm)
- mesopores (2 – 50 nm)
- macropores (~ 50 nm)

## Pore shape

- cylinder
- slit
- ink-bottle
- wedge



---

---

---

---

---

---

## Pore Size and Shape

## Pore Structure



Silica

Carbon

Zeolite

---

---

---

---

---

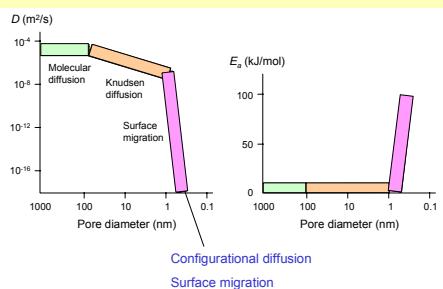
---

## Pore Size and Shape

Why is it important?

it dictates the diffusion process through the material.

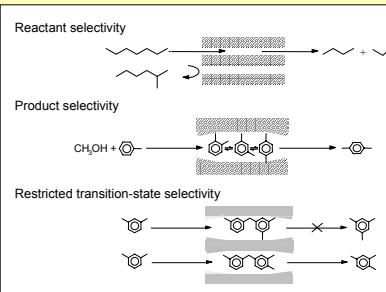
[Start](#)



## Pore Size and Shape

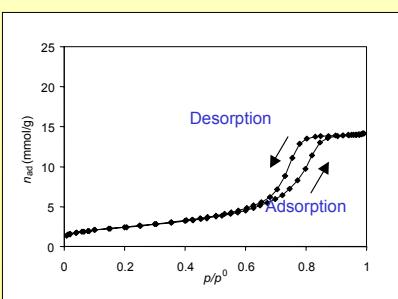
Why is it important?

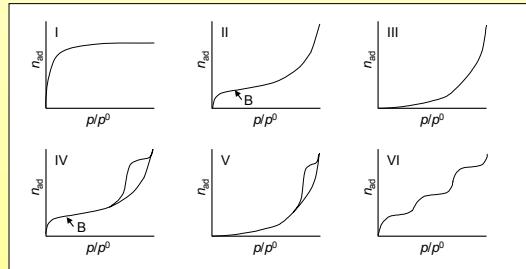
directly affect the selectivity of the catalytic reaction.



## N<sub>2</sub> Physisorption

Adsorption and Desorption Isotherms



**Adsorption and Desorption Isotherms**



---

---

---

---

---

---

**Kinds of Isotherms**

	Name	Equation of Isotherme	Model
1916	Langmuir	$\frac{V}{V_m} = \Theta = \frac{b \cdot p}{1 + b \cdot p}$	chemisorption physisorption <small>multilayer adsorption</small>
	Henry	$V = k \cdot p$	at low coverage
	Freundlich	$V_A = k \cdot p_A^n$	at low coverage
	Temkin	$\frac{V}{V_m} = \Theta = a \cdot \ln b \cdot p$	chemisorption
1938	BET	$\frac{p}{V(p_0 - p)} = \frac{1}{V_m \cdot C} + \frac{C - 1}{V_m \cdot C} \frac{p}{p_0}$	multiplayer adsorption
	Polanyi (1914)	$\varepsilon = RT \cdot \ln(p_0/p)$	physisorption
1946	Dubinin – Radushkevich	$\ln x = \ln(W_0 \cdot p) - D[\ln(p_0/p)]^2$	multiplayer adsorption on microporous solid
	Dubinin – Kaganer – Radushkevich	$x = x_m \cdot \exp(-b \cdot \varepsilon^2)$	physisorption in monolayer
	Virial equation	$\frac{p}{RT} = x(1 + a_1 \cdot x + a_2 \cdot x^2 + \dots)$	multiplayer adsorption on microporous solid

---

---

---

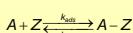
---

---

---

**Type 1  
Langmuir Model**

Model: (i) all adsorption sites are energetically identical, i.e. heats of adsorption is independent on surface coverage  
(ii) monolayer adsorption



A - substance  
Z - Adsorption site

$$R_{\text{A,ads}} = k_{\text{ads}} \cdot p_A \cdot Z_{\text{free}} - k_{\text{des}} \cdot Z_A$$

rate of adsorption reaction                  rate of desorption reaction

R<sub>ads</sub> - rate of adsorption  
k<sub>ads</sub> - rate constant of adsorption  
k<sub>des</sub> - rate constant of desorption  
Z<sub>free</sub> - number of un-occupied sites  
Z<sub>A</sub> - number of occupied sites  
Z<sub>0</sub> - number of all sites  
Θ - coverage

Substitution of Z:  $Z_{\text{free}} = Z_0 - Z_A \quad ; \quad Z_0$

$$\Theta_{\text{free}} = \frac{Z_{\text{free}}}{Z_0}; \quad \Theta_A = \frac{Z_A}{Z_0}$$

$$\Theta_{\text{free}} = 1 - \Theta_A$$

Equilibrium  $R_{\text{A,ads}} = k_{\text{ads}} \cdot p_A \cdot (1 - \Theta_A) Z_0 - k_{\text{des}} \cdot Z_0 \cdot \Theta_A = 0$

---

---

---

---

---

---

## Type 1 Langmuir Model

$$\theta_A = \frac{k_A p_A}{1 + k_A p_A}$$

$$K_{\text{ads}} = Z_0 \cdot k_{\text{ads}}$$

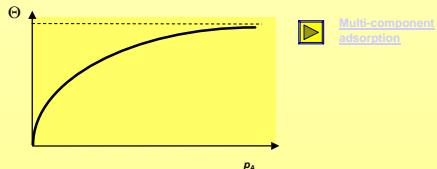
$$K_{\text{des}} = Z_0 \cdot k_{\text{des}}$$

$$k_A = \frac{K_{\text{ads}}}{K_{\text{des}}}$$

### Analysis

1.  $p_A \ll 1$        $\Theta_A = k_A \cdot p_A$       Henry Isotherme

2.  $p_A \gg 1$        $\Theta \rightarrow 1$       independent on  $p_A$



## Extension of Langmuir

Langmuir: no interaction of adsorbed molecules

$$E_{\text{ADS}} \neq \Theta$$

Consideration of adsorbate - adsorbate interaction

Freundlich:

$$E_{\text{ADS}} = f(\Theta) = E_{\text{ADS}}^0 \cdot \ln \Theta$$

$$V_A = k \cdot p_A^n$$

Temkin

$$E_{\text{ADS}} = f(\Theta) = E_{\text{ADS}}^0 \cdot (1 - \text{const} \cdot \Theta)$$

Used as

$$\log V_A = n \cdot \log p_A$$

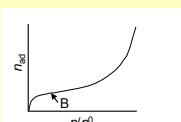


No linearity at low pressure  
No saturation at high pressure



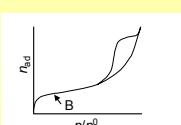
## Isotherms

### Type II



Multilayer adsorption (starting at B)  
Common for pore-free materials

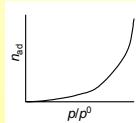
### Type IV



Similar to II at low  $p$   
Pore condensation at high  $p$

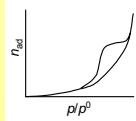
## Isotherms

### Type III



Strong cohesion force between adsorbed molecules, e.g. when water adsorbs on hydrophobic activated carbon

## Type IV



Similar to III at low  $p$   
Pore condensation at high  $p$

## Calculation of Surface Area

## Surface area measurement

The diagram illustrates the relationship between specific surface area ( $m^2/g$ ), monolayer capacity ( $mol/g$ ), and Avogadro's number ( $mol^{-1}$ ). The formula  $S = n_m A_m N$  is central, with arrows pointing to each term:  $n_m$  is labeled 'area occupied by one molecule ( $m^2/molecule$ )';  $A_m$  is labeled 'monolayer capacity ( $mol/g$ )'; and  $N$  is labeled 'Avogadro's number ( $mol^{-1}$ )'.

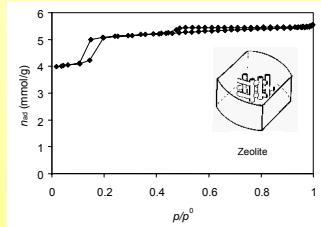
	BET model: $S_{BET}$	$t$ model: $S_t$
Adsorbate	Boiling point K	$A_m$ $\text{nm}^2/\text{molecule}$
N <sub>2</sub>	77.3	0.162
Ar	87.4	1.142
CO <sub>2</sub>	194.5	0.170
Kr	120.8	0.152

Adsorbate	Boiling point K	$A_m$ nm <sup>2</sup> /molecule
N <sub>2</sub>	77.3	0.162
Ar	87.4	1.142
CO <sub>2</sub>	194.5	0.170
Kr	120.8	0.152

## N<sub>2</sub> Physisorption on Zeolite

## Adsorption and Desorption Isotherms

## *Langmuir Adsorption?*



- No:
  - strong adsorption at low  $p$  due to condensation in micropores
  - at higher  $p$  saturation due to finite (micropore) volume

- Modification of Langmuir isotherm
- Both monolayer and multilayer adsorption
- Layers of adsorbed molecules divided in:
  - First layer with heat of adsorption  $\Delta H_{ad,1}$
  - Second and subsequent layers with  $H_{ad,2} = \Delta H_{cond}$

$$\text{BET isotherm: } \frac{p}{n_{ad}(p_0 - p)} = \frac{1}{n_m C} + \frac{C-1}{n_m C} \cdot \frac{p}{p^0} \quad C = \exp\left(\frac{\Delta H_{ad} - \Delta H_{cond}}{RT}\right)$$

- BET equation does not fit entire adsorption isotherm
  - different mechanisms play a role at low and at high  $p$

---

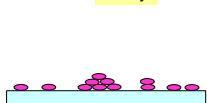
---

---

---

---

**reality**



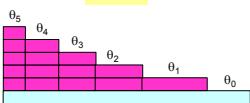
For every layer  
Langmuir model

Assume

$$K_i = K_{i,0} e^{-\frac{\Delta H_{ad,i}}{RT}}$$

$$K_n = K_{n,0} e^{-\frac{\Delta H_{ad,n}}{RT}} \approx K_{n,0} e^{-\frac{\Delta H_{cond}}{RT}}$$

**model**



$$\sum \theta_i = 1 \quad n_{ad} = n_m (\theta_0 + 2\theta_1 + 3\theta_2 + \dots)$$

1<sup>st</sup> layer

$$k_d^0 \theta_0 p = k_d^1 \theta_1 \quad \theta_0 = \frac{k_d^0}{k_d^1} p \theta_0 = K_d p \theta_0$$

n<sup>th</sup> layer

$$k_d^{n-1} \theta_{n-1} p = k_d^n \theta_n \quad \theta_n = \frac{k_d^n}{k_d^{n-1}} p \theta_{n-1} = K_n p \theta_{n-1}$$



$$\frac{n_{ad}}{n_m} = \frac{C}{\left(1 - \frac{p}{p^0}\right) \left(1 + (C-1) \frac{p}{p^0}\right)} \quad \text{with } C = e^{-\frac{\Delta H_{ad} - \Delta H_{cond}}{RT}}$$

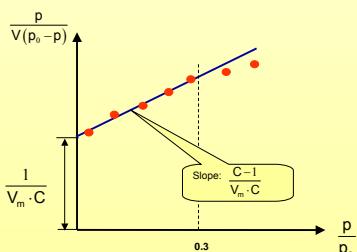
---

---

---

---

---



$$\frac{p}{V_m - V} = \frac{1}{V_m \cdot C} + \frac{C-1}{V_m \cdot C} \cdot \frac{p}{p_0}$$

---

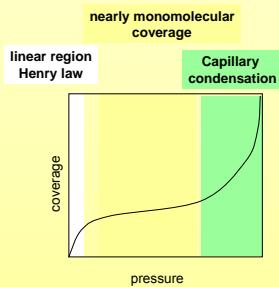
---

---

---

---

## BET Isotherms

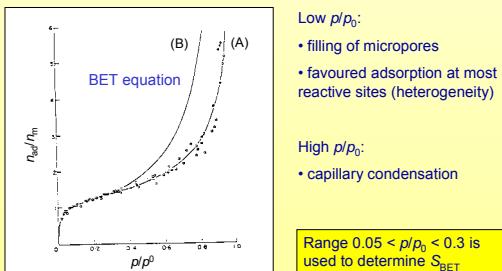


[Animation BET isotherm](#)

[BET Simulation](http://www.rpi.edu/dept/chem-eng/BioTech-Environ/Adsorb/bet.htm)  
(<http://www.rpi.edu/dept/chem-eng/BioTech-Environ/Adsorb/bet.htm>)

## BET Isotherm

### Nonporous Silica and Alumina

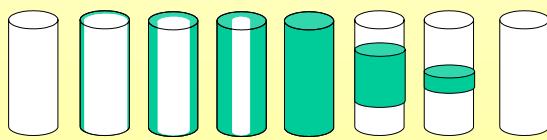


## Pore Size and Surface Area

Material	Mean $d_p$ /nm	$S_{BET}$ / m <sup>2</sup> /g
<b>Catalyst supports</b>		
Silica gel	10	200
	6	400
	4	800
$\gamma\text{-Al}_2\text{O}_3$	10	150
	5	500
Zeolite	0.6 ... 2	400 - 1200
Activated carbon	2	700 - 1200
$\text{TiO}_2$	400 - 800	2 - 50
<b>Catalysts</b>		
MeOH synthesis Cu/ZnO/ $\text{Al}_2\text{O}_3$	20	80
NH <sub>3</sub> synthesis Fe/ $\text{Al}_2\text{O}_3$	100	10
Reforming Pt/Re/ $\text{Al}_2\text{O}_3$	5	250
Epoxidation Ag/ $\alpha\text{-Al}_2\text{O}_3$	200	0.5

## Pore Size Distribution

## Kelvin Equation

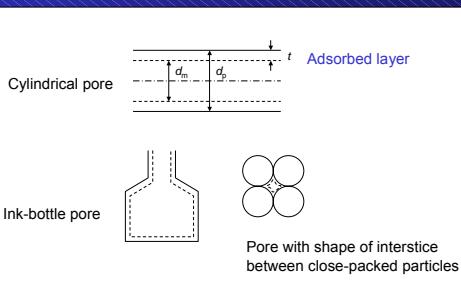


Adsorption

Desorption

## Pore Size Distribution

## Kelvin Equation

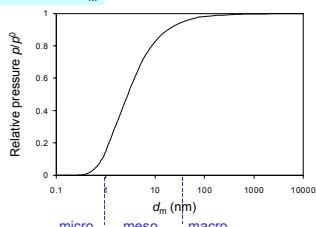


## Kelvin Equation

$$\ln \frac{p}{p^0} = -\frac{2\gamma V_L}{RT} \frac{1}{r_m}$$

$$V_L = 34.68 \cdot 10^{-6} \text{ m}^3/\text{mol}$$

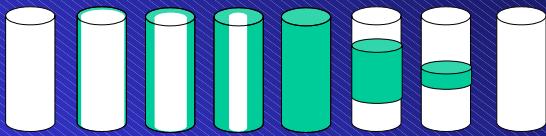
$$\gamma = 8.88 \text{ mN/m}$$



## Kelvin Equation

Pore filling Model

Cylindrical Pore Channel



---

---

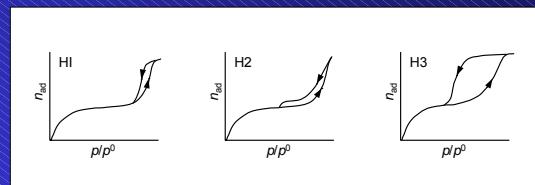
---

---

---

---

## Hysteresis Loop



Information on pore shape

---

---

---

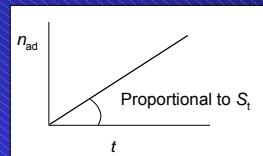
---

---

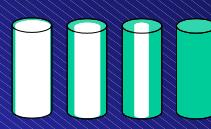
---

## Pore Size Distribution

t-Method



$$t = \frac{n_{ad}}{n_m} \cdot 0.354 \text{ nm}$$



$$S_t = n_m \cdot A_m \cdot N$$

$$\Rightarrow S_t = \frac{n_{ad}}{t} \cdot 0.354 \cdot 10^{-9} \cdot A_m \cdot N$$

$$\Rightarrow S_t = 5.73 \cdot 10^{-6} \cdot \frac{n_{ad}}{t}$$

Note:

$n_{ad}$  is experimental result  
 $t$  is calculated from correlation  $t$  versus  $p$

---

---

---

---

---

---

## Kelvin Equation

### t-Method

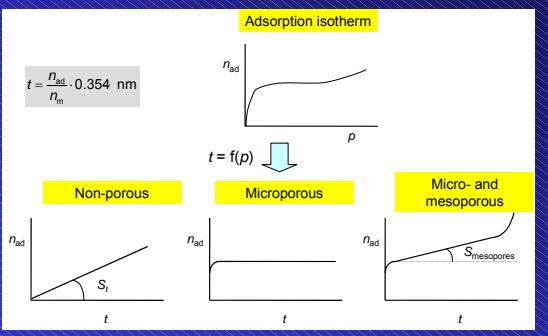
- BET
  - only valid in small pressure interval
  - interpretation not very easy
- thickness ( $t$ ) of adsorbed layer can be calculated



- plot of  $t$  versus  $p$  for non-porous materials is the same (has been checked experimentally)
- $t$ -plot helps in interpretation

## Kelvin Equation

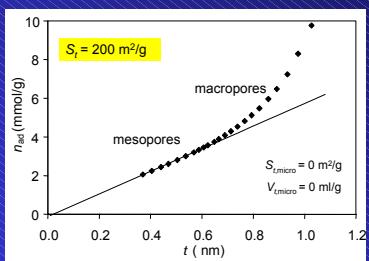
### Shape of t-plots



## Kelvin Equation

### Interpretation of t-Plot

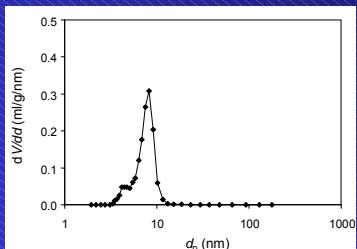
$\gamma$ -alumina



## Kelvin Equation

### Pore Size Distribution

$\gamma$ -alumina



$$r = t + \frac{2\sigma V}{RT \ln \frac{P_a}{P}}$$

## Mercury Porosimetry

### Pore Size Distribution

- Hg does not wet surfaces; pressure is needed to force intrusion
  - From a force balance:
- $$d_p = \frac{14860}{\rho} \quad (d \text{ in nm, } \rho \text{ in bar})$$
- Convenient method for determining pore volume versus pore size

## $N_2$ Physisorption versus Hg Porosimetry

- Hg cannot penetrate small (micro)pores,  $N_2$  can
- Uncertainty of contact angle and surface tension values
- Cracking or deforming of samples

Absorbent	$S_{Hg}$ m <sup>2</sup> /g	$S_{BET}$ m <sup>2</sup> /g	$\theta$ deg
Iron Oxide	14.3	13.3	130
Tungsten Oxide	0.11	0.10	130
Anatase	15.1	10.3	130
Hydroxy Apatite	55.2	55.0	130
Carbon Black (Spheron-6)	107.8	110.0	130
0.5 % Ru/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	237.0	229.0	140
0.5 % Pd/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	115.0	112.0	140
TiO <sub>2</sub> Powder	31.0	25.0	140
Sintered Silica Pellets	20.5	5.0	140
Zeolite H-ZSM-5	39.0	375.0	140
Norit Active Carbon R1 Extra	112.0	915.0	140

## Texture Data on Common Catalysts

	N <sub>2</sub> -physisorption				Hg-porosimetry		
	S <sub>BET</sub> m <sup>2</sup> /g	S <sub>t</sub> m <sup>2</sup> /g	V <sub>p</sub> ml/g	d <sub>p</sub> nm	S <sub>Hg</sub> m <sup>2</sup> /g	V <sub>p</sub> ml/g	d <sub>p</sub> nm
Wide Pore Silica	78	52	0.91	47	80	0.92	54
γ-Alumina	196	202	0.49	10	163	0.49	10
α-Alumina	9	8	0.12	112	12	0.48	150
Active Carbon	105 <sup>a</sup>	28	0.51	2	0.6	0.46	106
Raney Ni	76	-	0.14	5.80	-	-	-
ZSM-5	345	344	0.19	0.58	11	1.1	820 <sup>b</sup>

<sup>a</sup> p/p<sub>0</sub> range of 0.01-0.1 was used in the calculation.

<sup>b</sup> intraparticle voids.

## Hysteresis Phenomenon

Model: cylindrical open pore

Adsorption

1. Process of pore filling → cylindrical concave surface

$$\frac{p}{p_0} = e^{-\left(\frac{\gamma V_m}{r R T}\right)}$$

γ - surface tension  
V<sub>m</sub> - molar volume of condensate  
r - pore radius

2. When the pore is completely filled → formation of a spherical concave meniscus,

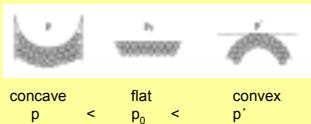
Desorption

Pressure is determined by spherical concave meniscus

$$\frac{p}{p_0} = e^{-\left(\frac{2\gamma V_m}{r R T}\right)}$$

r - pore radius

HYSTERESIS



concave  $p < p_0 < p'$  convex

## Determination of Pore Size



Steep curve (adsorption)  
corresponds radius of pore r<sub>1</sub>

Flat curve (desorption)  
corresponds pore radius distribution r<sub>p</sub>

ln  $\frac{p}{p_0} = -2 * \delta * V_{m0} * \cos\phi$

for N<sub>A</sub> rated to:

$$\ln \frac{p}{p_0} = -\frac{9.77 \text{ \AA}}{r_p}$$

δ - surface tension

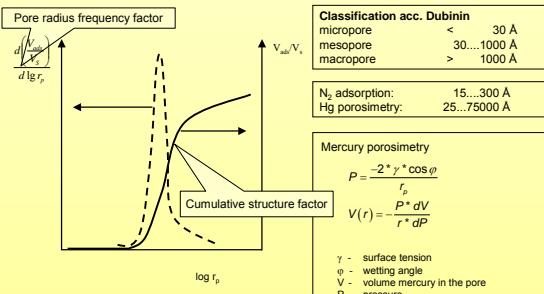
φ - wetting angle

V<sub>m0</sub> - molar volume of adsorbed substance



## Pore Size Distribution

THE  
ASSOCIATE  
UNIVERSITY

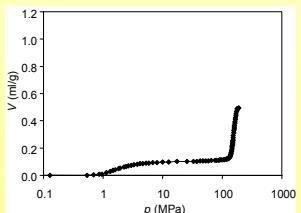


## Mercury Porosimetry

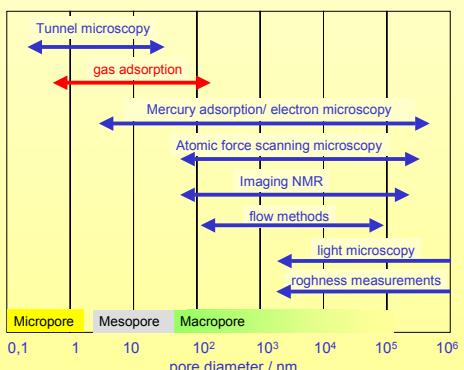
Call  
the  
nearest  
**powerlink**

## Pore Size Distribution

### $\gamma$ -alumina

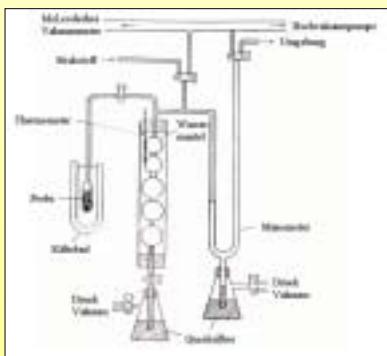


## Experimental Methods for Determination of Surface Area

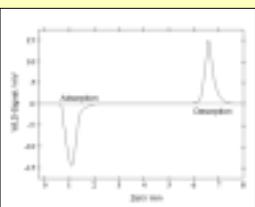
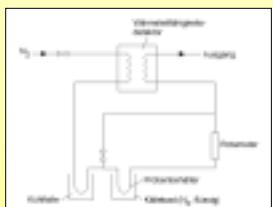


K. Meyer et al., Cryst. Res. Technol. 29 (1994) 203

### Volumetric Method of Determination of Surface Area



### Dynamic Method of Determination of Surface Area



Fixed bed adsorption

Pressure Swing Adsorption

- air separation
- Hydrogen purification for ammonia synthesis

Simulated Moving Bed

---

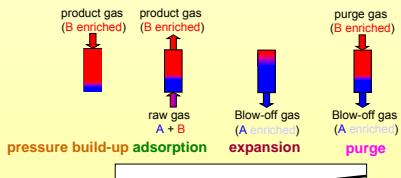
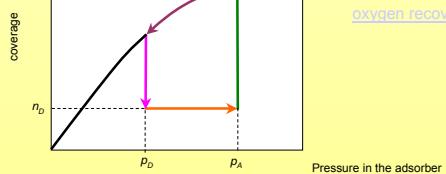
---

---

---

---

---

[Animation](#)[oxygen recovery](#)

BRUNNEN

---

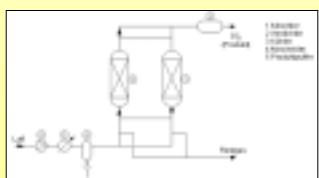
---

---

---

---

---

Kleintechnische Anlage zur N<sub>2</sub>/O<sub>2</sub>-Trennung

---

---

---

---

---

---

---

---

---

---

---

## 2.2. Kinetic of heterogeneously catalysed reaction

---



---



---



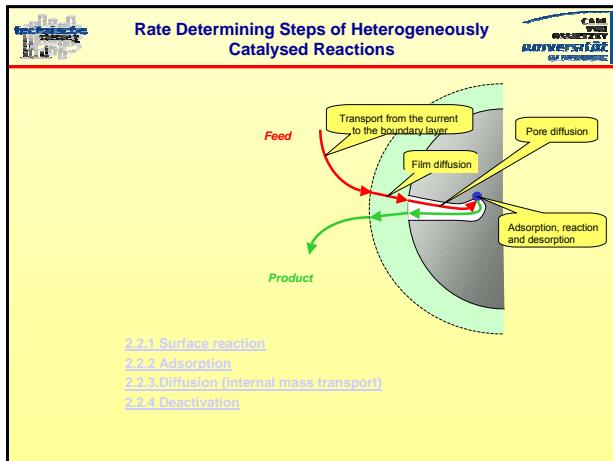
---



---



---




---



---



---



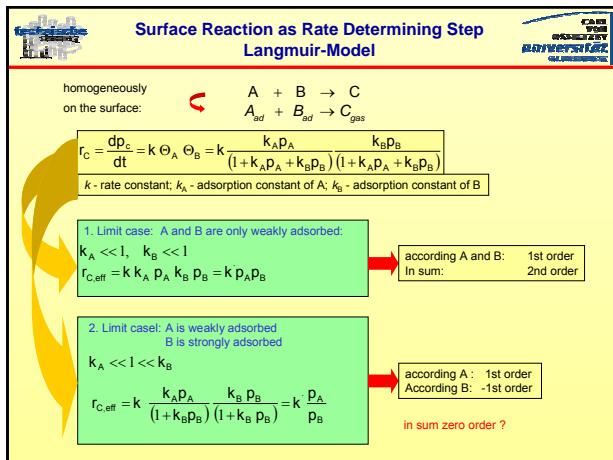
---



---



---




---



---



---



---



---



---

**Surface Reaction as Limiting Step**  
**Eley- Rideal-Model**

The diagram illustrates the Eley-Rideal model. It features a yellow rectangular background representing a surface. On the surface, there are three circular particles: one blue particle labeled 'A' at the bottom center, one teal particle labeled 'B' at the top left, and one green particle labeled 'C' at the top right. Arrows point from both 'B' and 'C' towards the central 'A' particle, indicating that 'B' is adsorbing onto 'A' to form 'C'.

On the surface:  $A_{\text{Adsorb}} + B_{\text{Gas}} \rightarrow C$

$$r_C = -\frac{dp_c}{dt} = k \Theta_A p_B = k \frac{k_A p_A}{(1+k_A p_A)} k_B p_B$$

**Langmuir vs. Eley- Rideal**

**Idea:**  $p_B = \text{const}$

$A_{\text{Adsorb}} + B_{\text{Adsorb}} \rightarrow C$	$A_{\text{Adsorb}} + B_{\text{Gas}} \rightarrow C$
---	--

**Langmuir**

$$1. p_A << 1 \quad r_{\text{eff}} = k \Theta_A \Theta_B = k^* \frac{k_B p_A}{(1+k_A p_A + k_B p_B)^2} = k^* p_A$$

**Eley**

$$2. \Theta_A = \Theta_B \quad r_{\text{eff}} = k \Theta_A \Theta_B = \max$$

$$3. p_A > 1 \quad r_{\text{eff}} = k \Theta_A \Theta_B = k^* \frac{k_B p_A}{(1+k_A p_A + k_B p_B)^2} \approx k^* \frac{1}{p_A}$$

Adsorption as Rate Determining Step I	
Model: surface reaction is very fast Adsorption/desorption is rate determining Adsorption equilibrium of A is not established	$A + B \xrightleftharpoons[k_{-1}]{k_1} C + D$
Surface reaction (in equilibrium):	$k_1\Theta_A\Theta_B = k_{-1}\Theta_C\Theta_D$ $\Theta_A = \frac{k_{-1}\Theta_C\Theta_D}{k_1\Theta_B} = \frac{\Theta_C\Theta_D}{K_c\Theta_B}; \quad K_c = \frac{k_1}{k_{-1}}$
Rate of adsorption and desorption of B are equal (equilibrium of B)	$k_{1B}p_B\Theta_{free} = k_{-1B}\Theta_B$ $\Theta_B = \frac{k_{1B}p_B\Theta_{free}}{k_{-1B}} = K_B p_B \Theta_{free}$
Same approach for C and D	$\Theta_C = K_C p_C \Theta_{free}; \quad \Theta_D = K_D p_D \Theta_{free}$
Balance of all surface sites	$1 = \Theta_A + \Theta_B + \Theta_C + \Theta_D + \Theta_{free}$

## Adsorption as Rate Determining Step II

$$\Theta_{free} = \frac{\Theta_C \Theta_D}{K_C K_B} + \Theta_B + \Theta_C + \Theta_D$$

$$1 = \Theta_{free} + \frac{K_C K_D p_C p_D \Theta_{free}^2}{K_C K_B p_B \Theta_{free}} + K_B p_B \Theta_{free} + K_C p_C \Theta_{free} + K_D p_D \Theta_{free}$$

$$\Theta_{free} = \frac{1}{1 + \frac{K_C K_D p_C p_D}{K_C K_B p_B} + K_B p_B + K_C p_C + K_D p_D}$$

Reaction rate  $r = k_{1,A} p_A \Theta_{free} - k_{-1} \Theta_A$

$$r = k_{1,A} \left( p_A \Theta_{free} - \frac{\Theta_A}{K_A} \right) \quad \Theta_A = \frac{\Theta_C \Theta_D}{K_C K_B} = \frac{K_C p_C \Theta_{free} K_D p_D \Theta_{free}}{K_C K_B p_B \Theta_{free}}$$

$$r = \frac{k_{1,A} \left( p_A - \frac{K_C K_D p_C p_D}{K_C K_B p_B} \right)}{1 + \frac{K_C K_D p_C p_D}{K_C K_B p_B} + K_B p_B + K_C p_C + K_D p_D}$$

If adsorption of A is rate determining

Hougen Hinshelwood Approach  $r = \frac{(\text{kinetical term}) (\text{potential term})}{(\text{adsorption term})^n}$

## Elementarschritte katalytischer Reaktionen an aktiven Oberflächenzentren

Elementarschritt	Aufspaltung / Unterteilung von Reaktionen
Adsorption und Desorption	$\text{H} + \text{H}_2\text{O(g)} \rightarrow \text{H}_2\text{O} \rightarrow \text{H}$ $\text{H} \rightarrow \text{H}_{\text{ads}}$
	$\text{H}_2 + \text{H}_2\text{O(g)} \rightarrow \text{H}_2\text{O} \rightarrow \text{H}_2$
Homogenes Adsorption (wie adsorbierte Reaktionen)	$\text{H}_2 + \text{H}_2\text{O(g)} \rightarrow \text{H}_2\text{O} \rightarrow \text{H}_2$ $\text{H}_2 \rightarrow \text{H}_{\text{ads}}$ $\text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_{\text{ads}}$ $\text{H}_2 + \text{CH}_4\text{O(g)} \rightarrow \text{CH}_3\text{OH} \rightarrow \text{H}_2$ $\text{H}_2 \rightarrow \text{H}_{\text{ads}}$ $\text{H}_2 + \text{CH}_3\text{Cl(g)} \rightarrow \text{CH}_3\text{HCl} \rightarrow \text{H}_2$ $\text{H}_2 \rightarrow \text{H}_{\text{ads}}$ $\text{H}_2 + \text{CH}_3\text{Br(g)} \rightarrow \text{CH}_3\text{HBr} \rightarrow \text{H}_2$ $\text{H}_2 \rightarrow \text{H}_{\text{ads}}$
Homogenes und heterogenes Oberflächenreaktionen	$\text{H}_2 + \text{C}_2\text{H}_5\text{Cl(g)} \rightarrow \text{H}_2\text{C}_2\text{H}_5 + \text{H}_2\text{O(g)}$ $\text{H} \rightarrow \text{H}_{\text{ads}}$ $\text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_{\text{ads}}$
Homogenes Desorption (wie Desorption)	$\text{H}_2\text{O} \rightarrow \text{H}_2\text{O(g)}$ $\text{H}_2\text{O} \rightarrow \text{H}_{\text{ads}}$ $\text{H}_2\text{O(g)} + \text{H} \rightarrow \text{H}_2\text{O}_{\text{ads}}$ $\text{H}_2\text{O}_{\text{ads}} \rightarrow \text{H}_2\text{O(g)}$ $\text{H} \rightarrow \text{H}_{\text{ads}}$ $\text{H}_2\text{O(g)} + \text{H} \rightarrow \text{H}_2\text{O}_{\text{ads}}$ $\text{H}_2\text{O}_{\text{ads}} \rightarrow \text{H}_2\text{O(g)}$ $\text{H} \rightarrow \text{H}_{\text{ads}}$ $\text{H}_2\text{O(g)} + \text{H} \rightarrow \text{H}_2\text{O}_{\text{ads}}$ $\text{H}_2\text{O}_{\text{ads}} \rightarrow \text{H}_2\text{O(g)}$ $\text{H} \rightarrow \text{H}_{\text{ads}}$
Homogenes und heterogenes Reaktionen	$\text{H}_2 + \text{H} \rightarrow \text{H}_2\text{H}$ $\text{H}_2\text{H} \rightarrow \text{H}$ $\text{H}_2 + \text{C}_2\text{H}_5\text{Cl(g)} \rightarrow \text{H}_2\text{C}_2\text{H}_5 + \text{H}_2\text{O(g)}$ $\text{H}_2\text{O} \rightarrow \text{H}_2\text{O(g)}$ $\text{H} \rightarrow \text{H}_2 + \text{H}_2\text{O(g)}$ $\text{H}_2\text{O(g)} \rightarrow \text{H}$ $\text{H}_2 + \text{H}_2\text{O(g)} \rightarrow \text{H}_2\text{O(g)} + \text{H}_2$ $\text{H}_2\text{O(g)} \rightarrow \text{H}_2\text{O}_{\text{ads}}$ $\text{H}_2 + \text{H}_2\text{O(g)} \rightarrow \text{H}_2\text{O(g)} + \text{H}_2$ $\text{H}_2\text{O}_{\text{ads}} \rightarrow \text{H}_2\text{O(g)}$

## Hougen-Watson-Geschwindigkeitsansätze I

$$r = \frac{(\text{kinetischer Term}) (\text{Potentialterm})}{(\text{Adsorptionsterm})^n}$$

Elementare Schritte (in heterogenen Reaktionen)
Adsorption oder Desorption geschwindigkeitsbestimmend für $A_1 + A_2 \rightarrow A_3$
Adsorption von $A_1$ $A_1$
Adsorption von $A_2$ $A_2$ mit $A =$ Geschwindigkeitskonstante der Reaktion
Desorption von $A_3$ $\frac{1}{2}A_3$ , mit $n_3 =$ Anzahl der auf der Reaktion benötigten aktiven Zentren
Desorption von $A_1$ $\frac{n_1}{2}A_1$
Desorption von $A_2$ $\frac{n_2}{2}A_2$
Desorption von $A_3$ $A_3$
Reaktionsschritte geschwindigkeitsbestimmend
Reaktionsschritte $A_1 + A_2 \rightarrow A_3 + A_4 + A_5$ $A_1 + A_2 \rightarrow A_3 + A_4$ $A_1 + A_2 + A_3 + A_4 \rightarrow A_3 + A_4 + A_5$
additionelle
Adsorption von $A_3$ $A_3, A_3$
Desorption von $A_3$ $A_3, A_3, A_3$
Reaktionsschritte $A_1, A_2, A_3 \rightarrow A_4, A_5$ $A_1, A_2, A_3 \rightarrow A_4, A_5$
$A_1$ sehr selektiv $A_1, A_1$
$A_2$ mehrfach selektiv $A_1, A_1, A_1$
$A_3$ nicht selektiv $A_1, A_1, A_1$
$A_4$ chemisch selektiv $A_1, A_1, A_1$

Traditionelle Lösungen für konstante Konzentrationen:					
Adsorptionsrate von $A_1$	$\beta_1 = \beta_1(\bar{P}_A)$	$\beta_1 = \beta_1(\bar{P}_A + \bar{P}_B)$			
Adsorptionsrate von $A_2$	$\beta_2 = \beta_2(\bar{P}_A)$	$\beta_2 = \beta_2(\bar{P}_A + \bar{P}_B)$			
Diffusionsrate von $A_1$	$\beta_{1D} = \beta_{1D}(\bar{P}_A)$	$\beta_{1D} = \beta_{1D}(\bar{P}_A + \bar{P}_B)$			
Diffusionsrate von $A_2$	$\beta_{2D} = \beta_{2D}(\bar{P}_A)$	$\beta_{2D} = \beta_{2D}(\bar{P}_A + \bar{P}_B)$			
Zusammenfassung: $\dot{N}_1 = \beta_1(\bar{P}_A) - \beta_1(\bar{P}_A + \bar{P}_B) = \beta_1(\bar{P}_A + \bar{P}_B)$ und $\dot{N}_2 = \beta_2(\bar{P}_A) - \beta_2(\bar{P}_A + \bar{P}_B) = \beta_2(\bar{P}_A + \bar{P}_B)$ für alle anderen Reaktionsterme gilt das gleiche.					
Wiederholung:	$\dot{N}_1 = \beta_1(\bar{P}_A)$	$\dot{N}_1 = \beta_1(\bar{P}_A + \bar{P}_B)$			
Weitere Abkürzung von $\beta_1$	$\beta_1 = \beta_1(\bar{P}_A)$	$\beta_1 = \beta_1(\bar{P}_A + \bar{P}_B)$			
Weitere Abkürzung von $\beta_2$	$\beta_2 = \beta_2(\bar{P}_A)$	$\beta_2 = \beta_2(\bar{P}_A + \bar{P}_B)$			
Weitere Abkürzung von $\beta_{1D}$	$\beta_{1D} = \beta_{1D}(\bar{P}_A)$	$\beta_{1D} = \beta_{1D}(\bar{P}_A + \bar{P}_B)$			
Weitere Abkürzung von $\beta_{2D}$	$\beta_{2D} = \beta_{2D}(\bar{P}_A)$	$\beta_{2D} = \beta_{2D}(\bar{P}_A + \bar{P}_B)$			
Weitere Abkürzung von $\beta_1$ , $\beta_2$ , $\beta_{1D}$ und $\beta_{2D}$	$\beta_1 = \beta_1(\bar{P}_A)$	$\beta_2 = \beta_2(\bar{P}_A)$	$\beta_{1D} = \beta_{1D}(\bar{P}_A)$	$\beta_{2D} = \beta_{2D}(\bar{P}_A)$	
Weitere Abkürzung von $\beta_1$ , $\beta_2$ , $\beta_{1D}$ und $\beta_{2D}$	$\beta_1 = \beta_1(\bar{P}_A)$	$\beta_2 = \beta_2(\bar{P}_A)$	$\beta_{1D} = \beta_{1D}(\bar{P}_A)$	$\beta_{2D} = \beta_{2D}(\bar{P}_A)$	

### Hougen-Watson-Geschwindigkeitsansätze III

$$r = \frac{\text{(kinetischer Term)} \cdot \text{(Potentialterm)}}{\text{(Adsorptionsterm)}^n}$$

Adsorptionsgeschwindigkeitsansatz für  $A_1 + A_2 + A_3$ :

monomolekulare Adsorption von  $A_1$ :  $n = 1$

monomolekulare Adsorption von  $A_2$ :  $n = 1$

monomolekulare Adsorption von  $A_3$ :  $n = 2$

Oberflächenreaktionsgeschwindigkeitsansatz:

Reaktionszustände:  $A_1 + A_1 = A_1 + A_2 + A_3$ ,  $A_1 + A_2 + A_3 + A_1 = A_1 + A_2 + A_3$ ,  $A_1 + A_2 + A_3 + A_2 = A_1 + A_2 + A_3$

$A_1$  (nur physikalisch adsorbiert):  $1 = 2 = 2 = 2$

$A_1$  chemisch adsorbiert:  $2 = 2 = 1 = 3$

$A_2$  monomolekular adsorbiert:  $1 = 2 = 1 = 2$

$A_3$  monomolekular adsorbiert:  $1 = 2 = 1 = 2$

$A_1$  dimerisch adsorbiert:  $1 = 2 = 1 = 2$

$A_2$  dimerisch adsorbiert:  $1 = 2 = 1 = 2$

$A_3$  dimerisch adsorbiert:  $1 = 2 = 1 = 2$

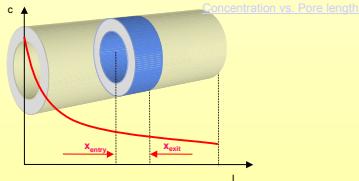
$A_1$  molekulär adsorbiert,  $A_2$  nicht adsorbiert:  $1 = 2 = 1 = 2$

$A_1$  molekulär adsorbiert,  $A_3$  nicht adsorbiert:  $1 = 2 = 1 = 2$

### Pore Diffusion and Reaction

- Model:  
 1. single cylindrical pore  
 2. steady state  
 3. 1<sup>st</sup> order reaction

$$-\frac{1}{S} \frac{dn}{dt} = k_s \cdot c$$



Mass balance:

$$\text{amount on exit} - \text{amount on entry} + \text{amount reacted} = 0$$

$$-\pi r^2 D \left( \frac{dc_A}{dx} \right)_{\text{Aus}} + \pi r^2 D \left( \frac{dc_A}{dx} \right)_{\text{Ein}} + k_s c (2\pi r \Delta x) = 0$$

Surface of pore wall

S - internal surface, r - radius of the pore, D - pore diffusion coefficient,  $c_A$  - concentration of A  
 $k_s$  - rate constant related to surface unit



## Solution of Mass Balance Equation



$$-D\pi r^2 \left( \frac{dc}{dx} \right)_{exit} + D\pi r^2 \left( \frac{dc}{dx} \right)_{entry} + 2\pi r \Delta x k_s c = 0$$

$$\left( \frac{dc}{dx} \right)_{exit} - \left( \frac{dc}{dx} \right)_{entry} - \frac{2\Delta x k_s c}{D r} = 0 \quad | : \Delta x$$

$$\frac{\left( \frac{dc}{dx} \right)_{exit} - \left( \frac{dc}{dx} \right)_{entry}}{\Delta x} - \frac{2k_s c}{D r} = 0$$

for  $\Delta x \rightarrow 0$

$$\frac{d^2 c}{dx^2} - 2 \frac{k_s}{D r} c = 0$$

$$k \cdot V = k_s \cdot S$$

$$k = k_s \frac{S}{V} = k_s \frac{2\pi r \Delta x L}{\pi r^2 \Delta x L} = k_s \frac{2}{r}$$

Integration conditions:

- $c = c_0$  at  $x = 0$
- $\frac{dc}{dx} = 0$  at  $x = L$ , i.e. no flow through the end of pore

$$M_1 = \frac{c_0 e^{-mL}}{e^{mL} + e^{-mL}} \quad M_2 = \frac{c_0 e^{mL}}{e^{mL} + e^{-mL}}$$



## Solution of Mass Balance Equation (cont.)



$$C = \frac{c_0 e^{-mL}}{e^{mL} + e^{-mL}} e^{mx} + \frac{c_0 e^{mL}}{e^{mL} + e^{-mL}} e^{-mx}$$

$$\frac{C}{c_0} = \frac{e^{-mL}}{e^{mL} + e^{-mL}} e^{mx} + \frac{e^{mL}}{e^{mL} + e^{-mL}} e^{-mx}$$

$$\frac{C}{c_0} = \frac{e^{(x-L)m} + e^{(L-x)m}}{e^{mL} + e^{-mL}} = \frac{e^{-(L-x)m} + e^{(L-x)m}}{e^{mL} + e^{-mL}} = \frac{\cosh(m(L-x))}{\cosh(mL)}$$

$$\Phi = L \sqrt{\frac{k}{D}} = L \sqrt{\frac{2k_s}{D}}$$

$$\frac{c}{c_0} = \frac{\cosh(\Phi(1 - \frac{x}{L}))}{\cosh \Phi} \quad \Phi = 0 \quad \frac{c}{c_0} = 1$$

Start

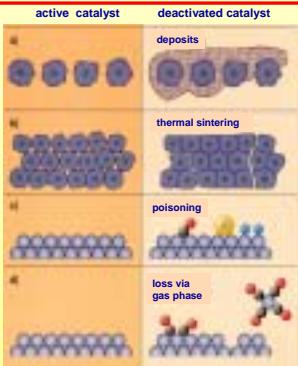
$\lim_{\Phi \rightarrow 0} \frac{c}{c_0} = 1$  reaction proceeds in the whole pore

$\lim_{\Phi \rightarrow \infty} \frac{c}{c_0} = 0$  reaction proceeds on the pore mouth



## 2.4 Deactivation

## Types of Catalyst Deactivation




---

---

---

---

---

---

## Aging of Industrial Catalysts

catalyst / reaction	origin of aging	prevention of aging
Pt/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub> catalytic reforming of naphtha	- deposition of high-molecular hydrocarbons - reduction of platinum dispersion	- increase of operational pressure Pt = 4 - 6 MPa - improvement of stability o dispersion of Pt by alloy formation adding i.e. Re
Zn-acetate / activated coal synthesis of vinyl acetate	- change of pore structure by condensation products of acetaldehyde	- selection of activated coal with determined pore architecture to reduce formation of acetaldehyde
HgCl <sub>2</sub> / activated coal synthesis of vinyl chloride	- sublimation of active compound HgCl <sub>2</sub>	- selection of suitable pore structure to prevent sublime off
V <sub>2</sub> O <sub>5</sub> -TiO <sub>2</sub> / corundum oxidation of o-xylene to phthalic anhydride	- phase transition of TiO <sub>2</sub> anatase $\Rightarrow$ rutile	
Ag / alumina oxidation of ethene to ethylene oxide	- reduction of dispersion of Ag - deposition of polymers of ethylene oxide	- stabilisation of dispersion by addition of promoters like alkaline earth metal oxides (BaO)
V/Mo-mixed oxides / alumina oxidation of benzene maleinic anhydride	- phase transition - sublimation off of MoO <sub>3</sub>	- stabilisation of the phases by promoters like phosphate or sulfate

---

---

---

---

---

---

## Reactors

---

---

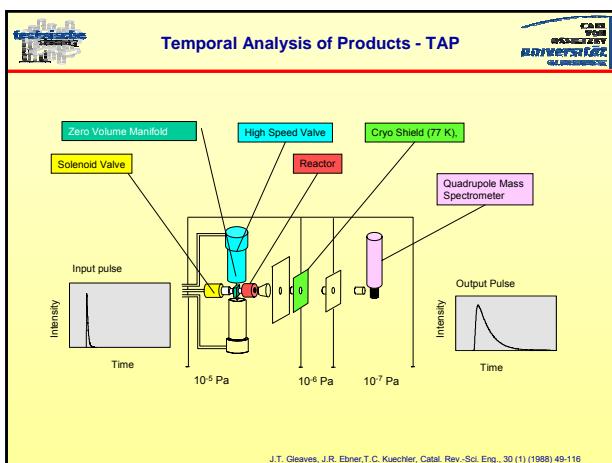
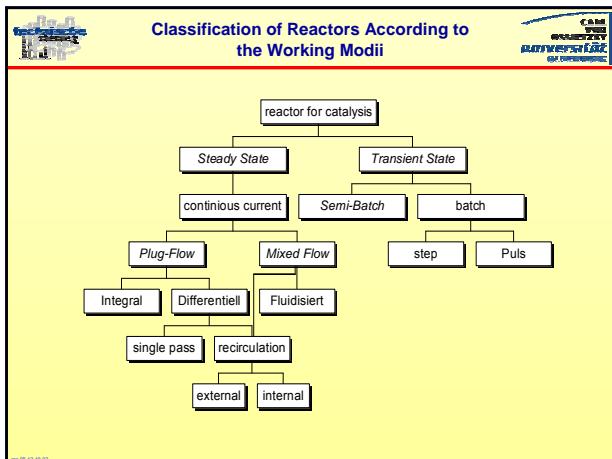
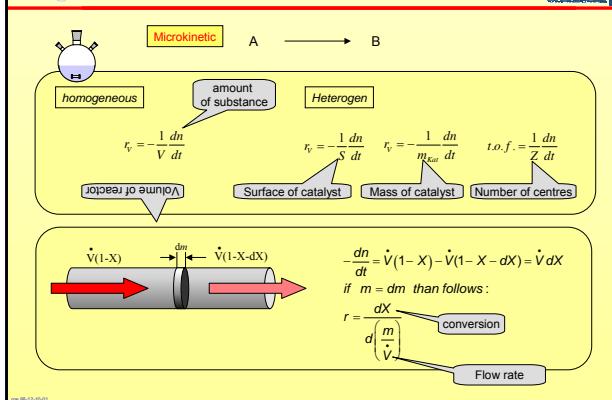
---

---

---

---

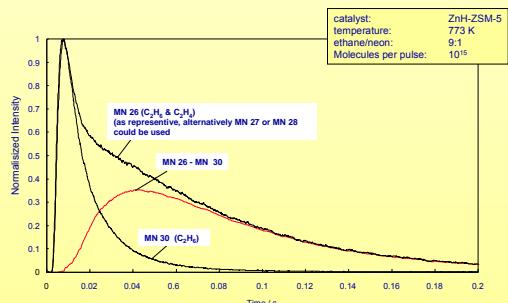
## Kinetic of Heterogenous Reactions





## Single Pulse Experiments Conversion of Ethane

CHEMIE  
WIRTSCHAFT  
UNIVERSITÄT  
REGENSBURG



---

---

---

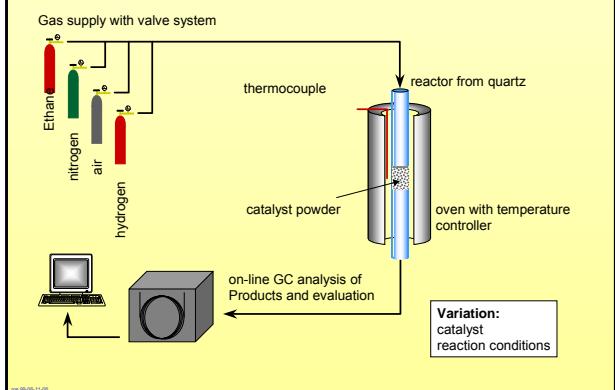
---

---



## Experimental Set-up for Catalytic Measurements

CHEMIE  
WIRTSCHAFT  
UNIVERSITÄT  
REGENSBURG



---

---

---

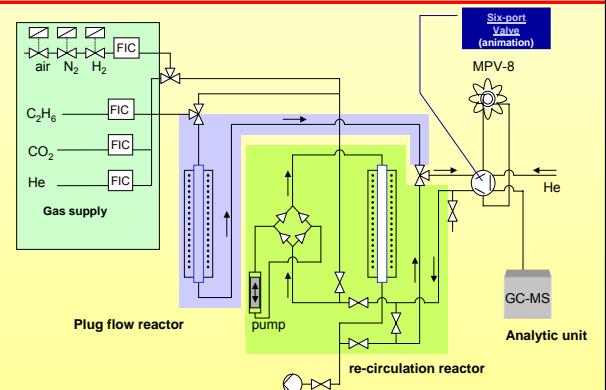
---

---



## Experimental Setup

CHEMIE  
WIRTSCHAFT  
UNIVERSITÄT  
REGENSBURG



---

---

---

---

---



## Laboratory Scale Reactor Unit



---

---

---

---

---

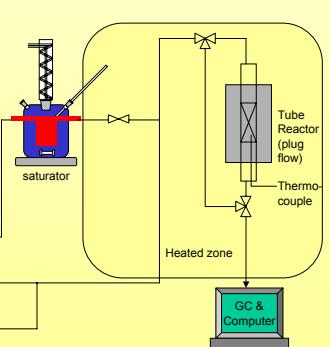
---

---

---



## Flow Sheet for Gas Phase Conversion of Liquids



---

---

---

---

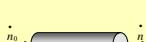
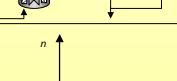
---

---

---



## Strategy of Evaluation for Kinetic Measurements

Batch	continuously differential re-circulation reactor	plug flow reactor
		
		
$(n, t)_0$ , sets of data from <b>one</b> experiment	$(n, t)_0$ , sets of data from <b>n</b> individual experiments	$(X, \frac{t}{\tau})$ , sets of data from <b>n</b> individual experiments
$r = \frac{1}{m_K} \frac{dn}{dt}$	$r = \frac{\dot{n} - \dot{n}_0}{m_K}$	$r = \frac{dX}{d \left( \frac{m_K}{n_0} t \right)}$
Integration of rate equation is necessary !		Integration of rate equation is necessary !

### 3. HETEROGENEOUS CATALYSTS

#### 3.1 Concepts for Catalyst Classification

##### 3.1.1 Energetical Aspects

---

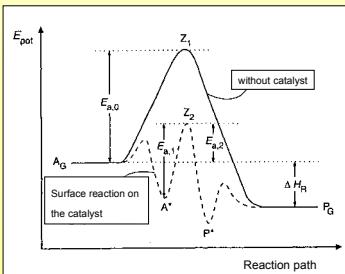
---

---

---

---

### Reaction Path for Heterogeneously Catalysed Gas Phase Reaction



$E_{A,0}$  - activation energy of homogeneous reaction

$E_{A,2}$  - apparent activation energy of the catalysed reaction

$Z_2$  - transition state of surface reaction

$E_{A,1}$  - true activation energy

$Z_1$  - transition state of gas phase reaction

$\Delta H_R$  - Enthalpy of reaction

---

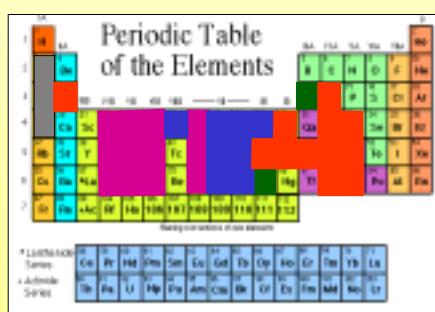
---

---

---

---

### Classification of Metals According their Ability for Chemisorption



---

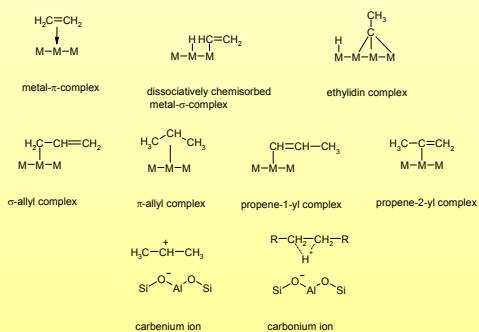
---

---

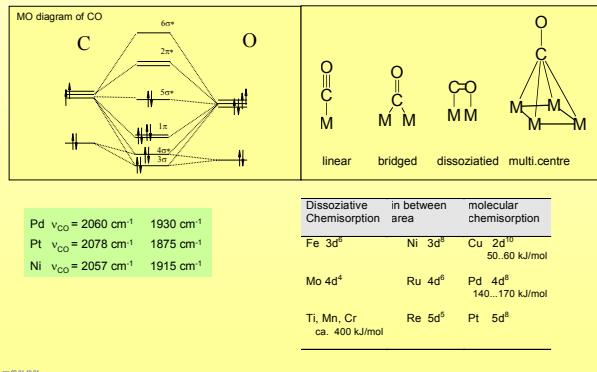
---

---

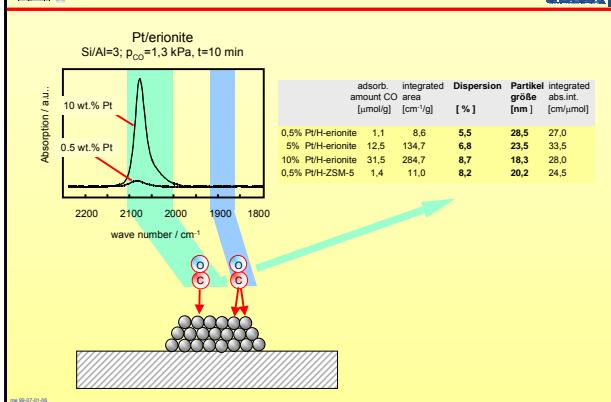
## Surface Compounds of Adsorbed Hydrocarbons



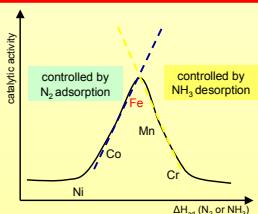
## Surface Complexes of Carbon Monoxide



## Dispersion of Platinum on Erionite

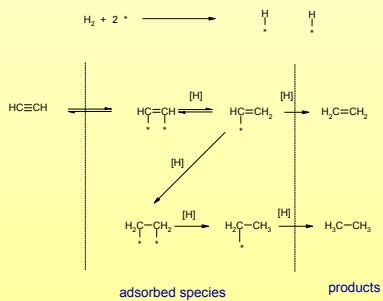


## Vulcano Plots



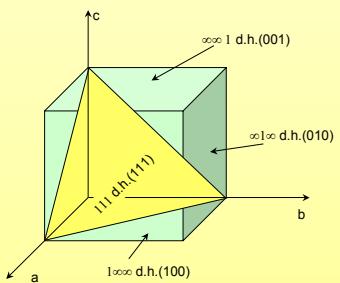
reaction	metals and relative reaction rate				
hydrogenation of ethene on metal catalysts	Cr	Fe	Co	Ni	Cu
	0.95	15	100	36	1.2
hydrodesulfurisation of dibenzothiophene	Nb	Mo	Tc	Ru	Pd
	0.5	2	13	100	26
hydrogenolysis of $CH_3NH_2$ to methane on metal catalysts	Re	Os	Ir	Pt	Au
	0.008	0.9	100	11	0.5

## Mechanism of Hydrogenation of Acetylene



### 3.1.2 Steric Effects

## Miller Indices



---

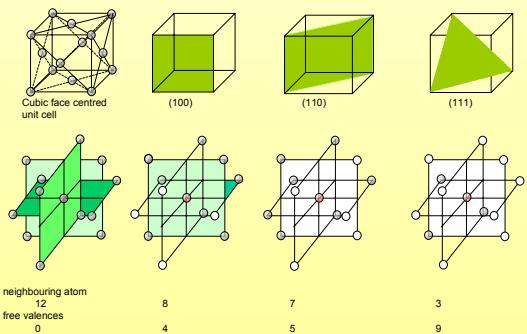
---

---

---

---

## Nickel Atoms in Cubic Face Centred Lattice



---

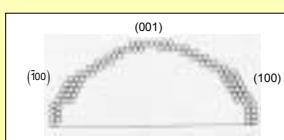
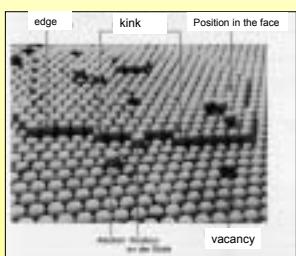
---

---

---

---

## Real Surface of Single Crystals



---

---

---

---

---

### 3.1.3 Electronical factors

---

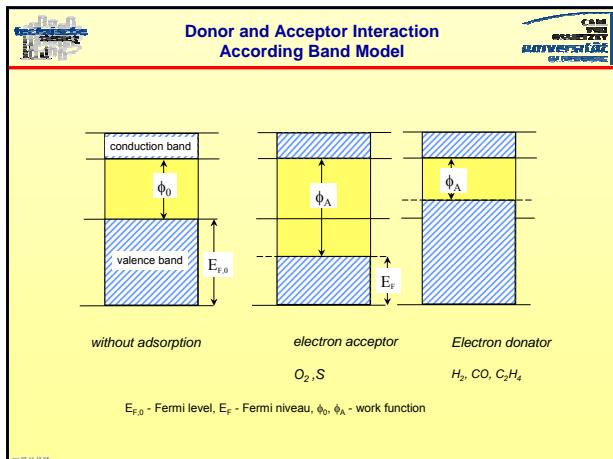
---

---

---

---

---



---

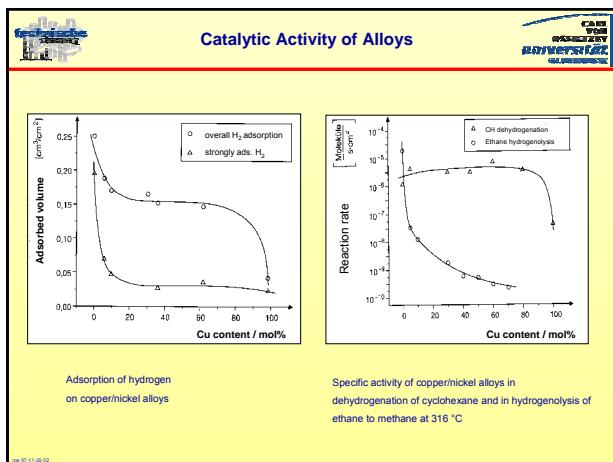
---

---

---

---

---



---

---

---

---

---

---

## Influence of Promotor Metals on the Catalytic Activity

Metal	Promoter	Reaction	Effect of promoter
Pt	5-20% Rh	Ammonia oxidation	increase of NO yield, reduction of Pt loss
Ag	Au	Ethylene epoxidation	Selectivity of Ethylenoxide formation
Ag	10%Au	Cumen oxidation	increase of rate of formation of cumenhydroperoxide
Pt	Ge, Sn, In, Ga	Dehydrogenation and hydrocracking of alkanes	reduction of coke deposition therefore increase of hold-up time
Pt	Sn + Re	Dehydrocyclisation and aromatisation of alkanes	increase of activity and Pt dispersion
Pt	Pb, Cu	Dehydrocyclisation and aromatisation of alkanes	efficiency of aromatisation
Pt, Pd	Au	Oxidative Dehydrogenation of alkanes ( <i>n</i> -butene to butadiene) and of methanol to formaldehyde	increase of selectivity
Ir	Au (Ag, Cu)	Hydroforming of alkanes and cycloalkanes	high yield of aromatics above 500 °C
Pd	Sn, Zn, Pb	Selective hydrogenation of alkenes to alkenes	

## Alloy Formation and Segregation

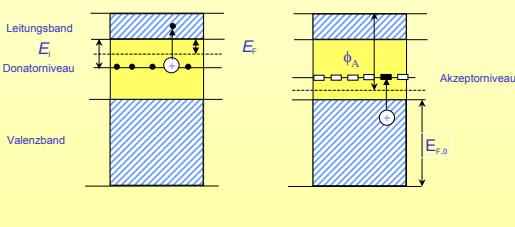
Minority element	bulk
Ru, Ir	Co
Fe, Ru, Rh, Ir, Pt	Ni
Fe, Co, Ni, Cu, Ru	Pt
Fe, Co, Ni,Cu	Pd

Minority element	bulk
Co, Rh, Pd	Fe
Ag, Ir, Pt, Au	Fe
Cu, Ir, Ag, Au	Ni
Au	Pd

Minority element	bulk
Ni, Cu	Fe
C	Co
Cu, Pd, Ag	Ru
Ag, Au	Pt

I. Chorkendorff, J.W. Neemandsverdier, "Concepts of modern Catalysis and Kinetics", Wiley-VCH, 2003, p. 179

## n- UND p-HALBLEITER NACH DEM BÄNDERMODELL



$E_F$  - Fermi-Niveau,  $E_i$  - Ionisierungsenergie  $\phi_A$  - Austrittsarbeit

	n-Typ	p -Typ
Oxide mit Ionen auf Zwischengitterplätzen	ZnO, CdO	UO <sub>2</sub>
Oxide mit Gitterleerstellen	TiO <sub>2</sub> , ThO <sub>2</sub> , CeO <sub>2</sub>	Cu <sub>2</sub> O, NiO, FeO
Art der Leitung	Elektronen	positive Löcher
Addition von (M <sup>+</sup> ) <sub>2</sub> O <sub>3</sub>	erniedrigt Leitfähigkeit	erhöht Leitfähigkeit
Addition von (M <sup>3+</sup> ) <sub>2</sub> O <sub>3</sub>	erhöht Leitfähigkeit	erniedrigt Leitfähigkeit
Adsorption von O <sub>2</sub> , N <sub>2</sub> O	erniedrigt Leitfähigkeit	erhöht Leitfähigkeit
Adsorption von H <sub>2</sub> , CO	erhöht Leitfähigkeit	erniedrigt Leitfähigkeit

---



---



---



---



---



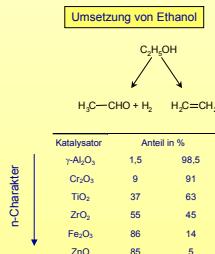
---



---



---




---



---



---



---



---



---



---



---



---



---



---



---



---



---



---



---

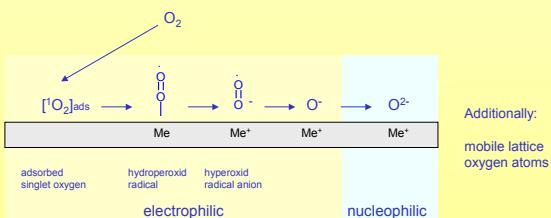
10

## Electrophilic and Nucleophilic Surface Species



### Problem:

**Problem:** two unpaired electrons in antibonding  $\pi$ p orbitals of oxygen  $\rightarrow$  triplet organic molecule  $\rightarrow$  singlet  $\Rightarrow$  Rule of spin conservation



Additionally:  
mobile lattice

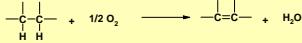
mobile lattice  
oxygen atoms

## Oxidation of Hydrocarbons



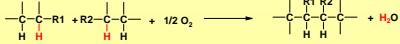
## 1. Intra-molecular oxidative dehydrogenation

- both hydrogen atoms are abstracted from the same hydrocarbon molecule
  - formation of  $\pi$  C-C bond



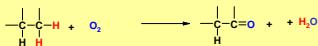
## 2. Inter-molecular oxidative dehydrogenation

- hydrogen atoms are originated from different hydrocarbon molecules
  - formation of new C-C bond



### 3. Oxidation

- first abstraction is followed by addition of an oxygen atom
  - formation of oxygenated hydrocarbon derivatives

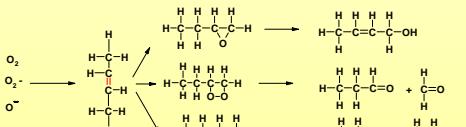


10

## Electrophilic Oxidation

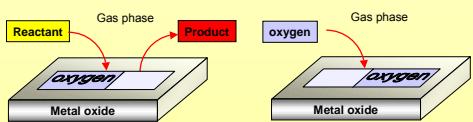


attack of organic molecules in region with highest electron density



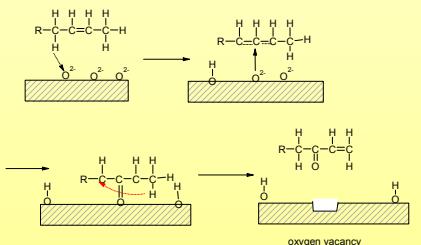
Saturated aldehydes are usually more

unsaturated aldehyde  
↓  
rapid total oxidation


▶ Animation

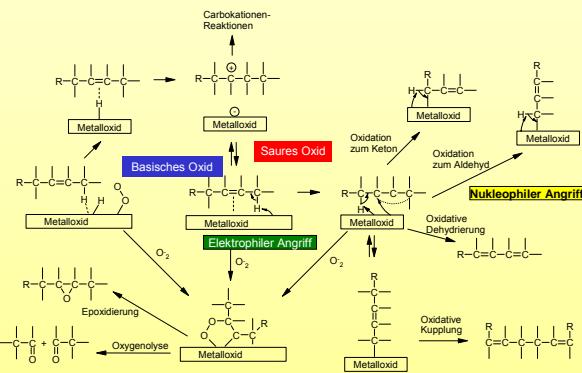
### Nucleophilic Oxidation

$O_2^{\cdot}$  species have no oxidizing properties but are nucleophilic reactants  
 → requirement of hydrocarbon activation



- charge balance by change of the oxidation state of the metal
- formation of vacancies restored by adsorbed oxygen

### Reaktionsnetzwerk für Olefine an Metalloxidoberflächen





## Heterogeneous Oxidation of Hydrocarbons



Electrophilic oxidation		Nucleophilic oxidation	
Reaction type	catalyst	Reaction type	catalyst
Double bond fission		without introduction of heteroatoms	
Oxidation of alkanes to oxides Oxyhydration of alkenes to saturated ketones	$\text{Ag}_2\text{O}$ $\text{SnO}_2\text{-MoO}_3$	Oxidative dehydrogenation of alkanes to diens	$\text{BiPO}_4$
C-C bond fission		Oxidative dehydromerization	
oxidation of alkenes to saturated aldehydes oxidation of aromatics to anhydrides and acids with ring rapture	$\text{V}_2\text{O}_5$ $\text{V}_2\text{O}_5\text{-MoO}_3$	Oxidation of alkenes to unsaturated ketones Ammoxidation of alkenes	$\text{Bi}_2\text{O}_3\text{-MoO}_3$ $\text{Bi}_2\text{O}_3\text{-MoO}_3$
Total oxidation to $\text{H}_2\text{O} + \text{CO}_2$	$\text{Co}_2\text{O}_4$ $\text{CuCo}_2\text{O}_4$		



## Selectivity of Oxidation Reactions



- Carbon dioxide and water are the thermodynamically preferred products in oxidation reactions, i.e. the formation of intermediate products is kinetically controlled.
- Hydrocarbon - oxygen mixtures can react in several reaction pathways including parallel and consecutive reactions. The catalyst has to accelerate the wanted reaction path and should delay the unwanted.
- The C-H bonding in the reactant are usually stronger than in the intermediate, which favours the further fast oxydation.
- All oxidation reactions are strongly exothermically, so that the efficient heat transfer and a strong temperature control should be guaranteed.
- Oxidation of hydrocarbons can also proceed as uncatalysed radical reactions. Therefore, the formation of explosive mixtures is possible.



## Insulators



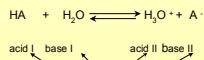
Solid acidic catalysts	Solid basic catalysts
1. metal oxides like $\text{Al}_2\text{O}_3$ , $\text{SiO}_2$ , $\text{TeO}_2$	1. oxides, hydroxides and amides of alkali and earth alkali metals, also supported
2. mixed metal oxides like $\text{Al}_2\text{O}_3\text{-SiO}_2$ , $\text{MgO-SiO}_2$ , $\text{ZrO}_2\text{-SiO}_2$ , heteropolyacids	
3. mineral acids ( $\text{H}_3\text{PO}_4$ , $\text{H}_2\text{SO}_4$ ) supported on solid, porous supports	
4. cation-exchange resins	2. anion-exchange resins
5. salts of O-containing mineral acids, esp. of heavy metals (phosphate, sulphate, tungstate)	3. salts of alkaline and earth alkaline metals of weak acids (carbonate, carbide, nitride, silicate and other)
6. halides of trivalent halides supported on porous supports ( $\text{AlCl}_3$ )	
7. zeolites (H-form)	4. zeolites ( $\text{Me}^+$ -form)
8. superacids: sulphated zirconia ( $\text{ZrO}_2$ ) or titania ( $\text{TiO}_2$ )	5. superbase: $\text{MgO}$ promoted with metallic sodium

iso 97-12/11-02

## Brönsted Acidity



Brönsted (1923)



acid I base I      acid II base II

• proton transfer  
conjugated acid - base pair  
water as reference

Hammett (1932)

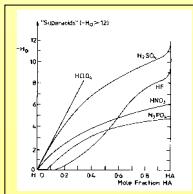
$$\text{HB}^+ \rightleftharpoons \text{B} + \text{H}^+$$

$$K_a = \frac{a_{\text{H}^+} c_{\text{B}} \gamma_{\text{B}^+}}{c_{\text{BH}^+} \gamma_{\text{BH}^+}}$$

$$pK_a = -\log \frac{a_{\text{H}^+} \gamma_{\text{B}^+}}{\gamma_{\text{BH}^+}} - \log \frac{c_{\text{B}}}{c_{\text{BH}^+}}$$

$$pK_a = H_0 - \log \frac{c_{\text{B}}}{c_{\text{BH}^+}}$$

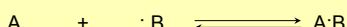
• non-aqueous systems



## Lewis Acidity



Lewis (1923, 1938)



electron pair acceptor

electron pair donor

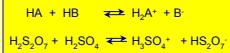
Acids:  
 $\text{H}^+$ ,  $\text{Ag}^+$ ,  $\text{SO}_3^{2-}$ ,  
 $\text{AlCl}_3$ ,  $\text{SnCl}_4$

Base:  
 $\text{OH}^-$ ,  $\text{J}^-$ ,  $\text{SCN}^-$ ,  
 $\text{CH}_3\text{COCH}_3$ ,  $\text{NH}_3$

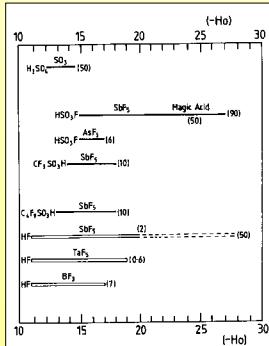
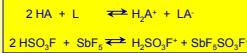
## Superacidity

Conant und Hall (1927):  $-H_o > 12$   
Olah (1985):

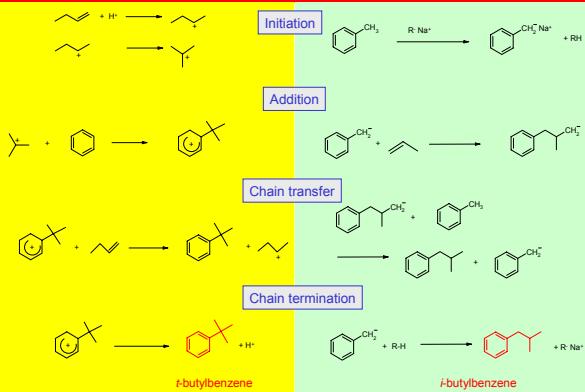
### Brønsted - Brønsted



### Brønsted - Lewis



## SYNTHESIS OF BUTYLBENZENE ACIDIC vs. BASE CATALYSIS



## 3.2 Synthesis of Catalysts

## HETEROGENE KATALYSATOREN

### Mischen



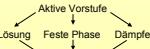
Fällung  
Gemeinsame Fällung  
Komplexierung  
Gelbildung  
Kristallisation

### Umwandeln



Erhitzen  
Verdampfen  
Kneten  
Verbrennen  
Metalle  
Dünne Filme  
Vollkatalysatoren  
Kolloide  
Amorphe Materialien

### Aufbringen



Aktive Vorstufe  
Lösung  
Feste Phase  
Dämpfe  
Ablagerung  
Adsorption  
Chemische Reaktion  
Ionenaustausch  
Verankern  
Imprägnieren

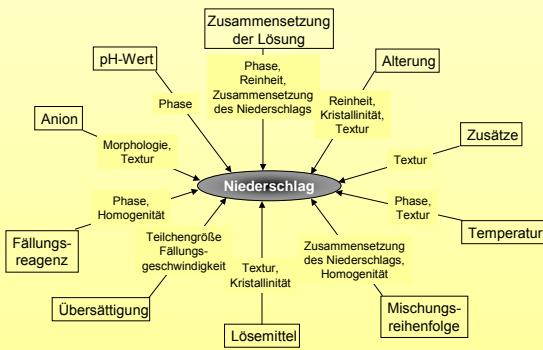
### Kriterien

Aktivität  
Selektivität  
Chemische Stabilität

Morphologie  
Mechanische Stabilität  
Thermische Stabilität  
Regenerierbarkeit

Reproduzierbarkeit  
Originalität  
Kosten

## EINFLUSSFAKTOREN BEI DER FÄLLUNG



## ANWENDUNGSBEISPIELE

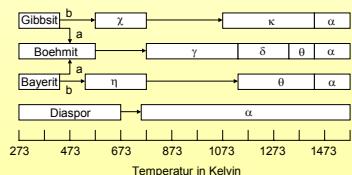
### Industrielle Katalysatoren, hergestellt durch Fällung und Ko-Fällung

Material	Verwendung als	Beispiele
Al <sub>2</sub> O <sub>3</sub>	Träger, Katalysator	Claus-Prozeß, Dehydratisierung von Alkoholen zu Alkenen und Ethern, Träger für 3-Wege-Katalysator
SiO <sub>2</sub>	Träger	Edelmetalle/SiO <sub>2</sub> für Hydrierreaktionen, V <sub>2</sub> O <sub>5</sub> /SiO <sub>2</sub> Schwefelsäureherstellung
TiO <sub>2</sub>	Träger, Katalysator	Hauptkomponente für DeNOx-Katalysator
Cu/ZnO	Katalysator	Methanolsynthese
(VO) <sub>2</sub> P <sub>2</sub> O <sub>7</sub>	Katalysator	Selektivoxidation (z.B. Butan zu Maleinsäureanhydrid)
Bi-Molybdate	Katalysator	Selektivoxidation (z.B. Propen zu Acrolein)

### Industrielle Katalysatoren, hergestellt durch Sol-Gel-Prozeß

Katalysator	Anwendung
Pd/SiO <sub>2</sub>	Hydrierung von Phenylacetylen
Pt/TiO <sub>2</sub>	Co-Oxidation
Übergangsmetall/Al <sub>2</sub> O <sub>3</sub>	Polymerisation und Ko-Polymerisation von $\alpha$ -Alkenen
V <sub>2</sub> O <sub>5</sub> , V <sub>2</sub> O <sub>5</sub> -TiO <sub>2</sub> , V <sub>2</sub> O <sub>5</sub> -TiO <sub>2</sub> -SiO <sub>2</sub>	Selektive katalytische NO-Reduktion durch NH <sub>3</sub>

## Phasenumwandlungen bei der thermischen Behandlung von Aluminiumhydroxiden und Aluminiumoxidhydroxiden



Gibbsite:  $\gamma\text{-Al(OH)}_4$   
 Boehmit:  $\gamma\text{-AlO(OH)}$   
 Bayerit:  $\alpha\text{-Al(OH)}_3$   
 Diaspor:  $\alpha\text{-AlO(OH)}$

Aluminumoxide:  
 χ: chi  
 κ: kappa  
 γ: gamma  
 η: eta  
 θ: theta  
 δ: delta  
 α: alpha

a: Drücke > 1 bar, feuchte Luft,  
 Heizgeschwindigkeiten > 1 K/min, Teilchen > 100 µm  
 b: Drücke um 1 bar, trockene Luft,  
 Heizgeschwindigkeiten < 1 K/min, Teilchen < 10 µm

Aktive Formen!

### 3.3 Examples of Heterogeneous Catalysts

## Application of Heterogeneous Catalysts in the Chemical Industry and Environmental Protection

Industrial process	Catalyst
$\text{H}_2/\text{CO}/\text{CH}_3\text{OH}/\text{NH}_3$	steam reforming CO conversion methylation synthesis of ammonia synthesis of methanol
Hydrogenation	vegetable oil, fat
Dehydrogenation	isobutane from butane styrene from ethylbenzene
Oxidation, ammoniation, Oxychlorination	Ethylenoxid aus Ethen $\text{HNO}_3$ from $\text{NH}_3$ $\text{H}_2\text{SO}_4$ from $\text{SO}_2$ maleic anhydride from butane Phthalic anhydride Ethylchloride
Organic synthesis	Petrochemicals Ethylbenzene Cumene
Polymerisation	Polyethylene Polyvinylchloride Polystyrene Polyurethane
Petrochemistry	catalytic cracking
Environmental catalysis	catalyst for automobile exhaust gas removal of nitric oxides catalytic combustion

### 3.3.1 Transition metal oxides

---



---



---



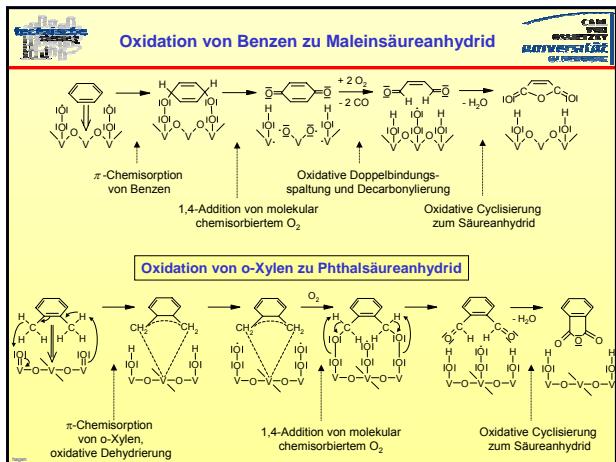
---



---



---




---



---



---



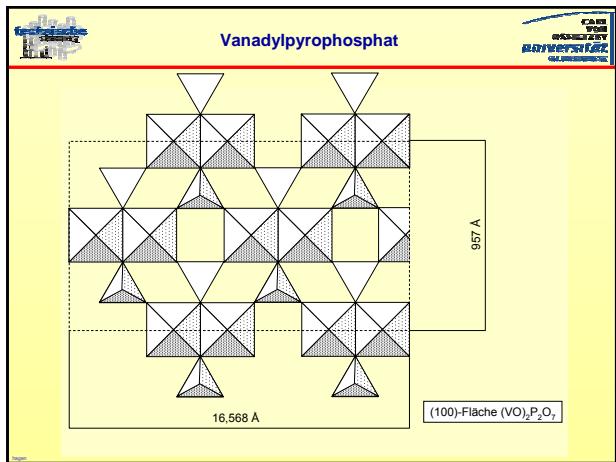
---



---



---




---



---



---



---



---



---

Electrophilic oxidation		Nucleophilic oxidation	
Reaction type	catalyst	Reaction type	catalyst
Double bond fission		without introduction of heteroatoms	
Oxidation of alkanes to oxides Oxyhydration of alkenes to saturated ketones	$\text{Ag}_2\text{O}$ $\text{SnO}_2\text{-MoO}_3$	Oxidative dehydrogenation of alkanes to diens	$\text{BiPO}_4$
C-C bond fission		Oxidative dehydrodimerization	
oxidation of alkenes to saturated aldehydes oxidation of aromatics to anhydrides and acids with ring rapture	$\text{V}_2\text{O}_5$ $\text{V}_2\text{O}_5\text{-MoO}_3$	Oxidation of alkenes to unsaturated ketones Ammoxidation of alkenes	$\text{Bi}_2\text{O}_3\text{-MoO}_3$ $\text{Bi}_2\text{O}_3\text{-MoO}_3$
Total oxidation to $\text{H}_2\text{O} + \text{CO}_2$	$\text{Co}_3\text{O}_4$ $\text{CuCo}_2\text{O}_4$		

### 3.3.2. Silicate and Alumosilicates

#### 3.3.2.1 Layered Silicates

### Application of Layered Silicates

Your Cat knows Minerals Better Than You!  
This is 100% pure Natural Bentonite



With kind permission of Bentonite Division, S&B Industrial Minerals GmbH, Marl (Germany)



## Role of Clays for Health



The history of mineralogy is as old as man.

Clay is a great healer, according to clay expert Ran Knishinsky in *The Clay Cure* (Healing Arts Press, 1998), who quips "I have been eating dirt every day for the past six years." Indeed, in over 200 cultures worldwide, every day people eat or drink clay—the medicinal form of "dirt"—as both a nutritional supplement and detoxifying agent, observes Knishinsky.

[http://www.experiencenetwork.com/a/Bentonite\\_Clay/id/2064](http://www.experiencenetwork.com/a/Bentonite_Clay/id/2064)

With kind permission of Bentonite Division, S&B Industrial Minerals GmbH, Marl (Germany)

---

---

---

---

---

---

---



## Electron Microscopic Image of Layered Silicate



With kind permission of Bentonite Division, S&B Industrial Minerals GmbH, Marl (Germany)

---

---

---

---

---

---

---



## Exploitable Properties of Natural Minerals



- Multi-functional in its physico-chemical properties: (size, shape, porosity)
- High aspect ratio: length/thickness
- Porous structure: molecular sieve effect, gas diffusion and storage
- Inherent catalytic-nature through multiple element content
- Surface functionality: specific interaction with selected molecules
- High surface areas: high adsorption capacities under given conditions
- Generative: could be used in multiple cycles after regeneration
- Abundance and price: Evaluated deposits for longer supply & competitive
- Shaping and stability: could be adapted to diff. gas treatment processes

Their individual properties depend on: structure, Si/Al ratio, pore size, surface nature and the framework density.

---

---

---

---

---

---

---

## What is common to all these minerals?

They are all natural, Si and Al mainly,

Porous in nature, High surface area,

Possibility to functionalize the surfaces

## What are the differences among these minerals?

Different pore sizes and distributions

Different surface reactivities

Different thermal and mechanical stabilities

Different (degree of) pre-treatments needed for pore-deblocking

With kind permission of Bentonite Division, S&B Industrial Minerals GmbH, Marl (Germany)

---

---

---

---

---

---

## Pore-size classification

Class	Pore Width / Å°
Micropores	< 20
Mesopores	20-500
Macropores	> 500

## Internal Pore Classification



a) - "through pores" surface to surface

b) - "interconnected pores"; pores which connect with other pores

c) - "blind pores"; pores with only a single connection to the surface,

---

---

---

---

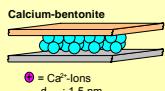
---

---

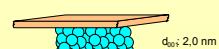
With kind permission of Bentonite Division, S&B Industrial Minerals GmbH, Marl (Germany)

Bentonite Swelling: due to hydration property of Sodium  
This creates the thixotropic property of bentonite suspension

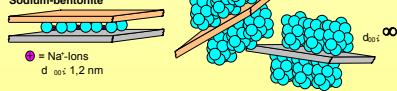
air-dry



after adding water



Sodium-bentonite



With kind permission of Bentonite Division, S&B Industrial Minerals GmbH, Marl (Germany)

---

---

---

---

---

---

## Properties of Clays

- cation-exchange-capacity (CEC) between 70 and 130 meq/100g
- specific surface area between 20 and 90 m<sup>2</sup>/g (BET)
- Smectite content between 60 and 110 % based on an internal standard
- soda content between 0,01 and 2,5 %



Na-bentonite (2g) in water: 32 ml  
Ca-bentonite (2g) in water: 5 ml

With kind permission of Bentonite Division, S&B Industrial Minerals GmbH, Marl (Germany)

---

---

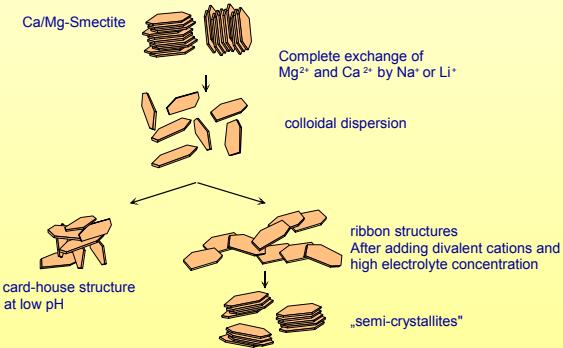
---

---

---

---

## Particle-reciprocal Effect



With kind permission of Bentonite Division, S&B Industrial Minerals GmbH, Marl (Germany)

---

---

---

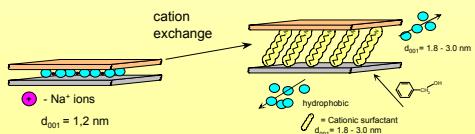
---

---

---

## Organoclay Structure

- Bentonite exchanged with Polymers
- high specific surface area
- higher temperature stability than unmodified Polymers



With kind permission of Bentonite Division, S&B Industrial Minerals GmbH, Marl (Germany)

---

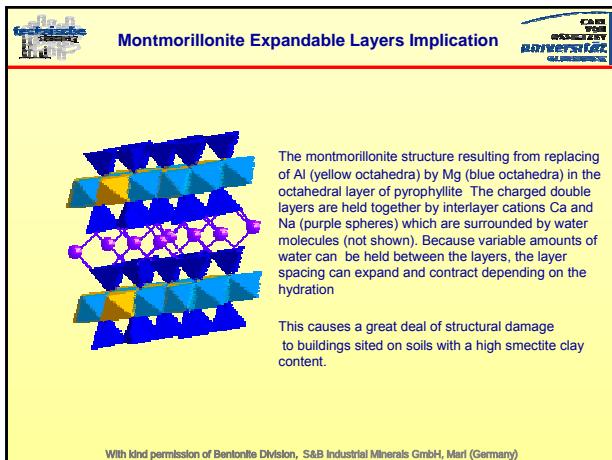
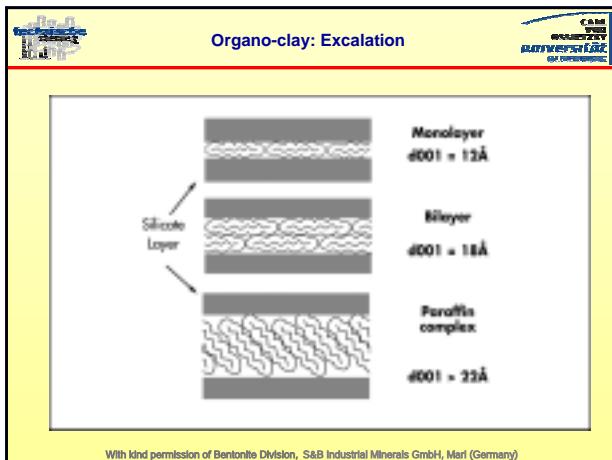
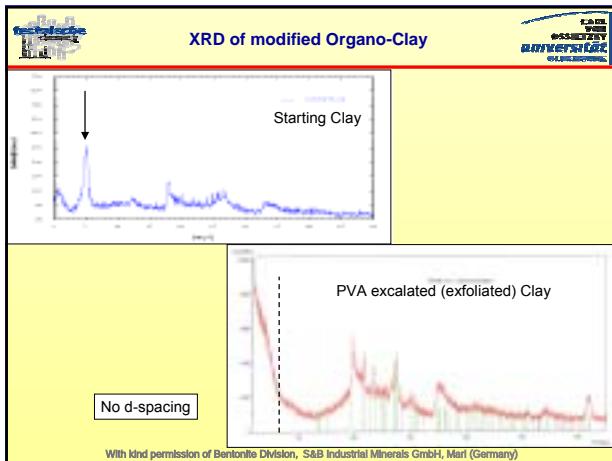
---

---

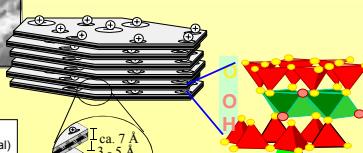
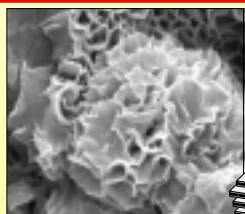
---

---

---



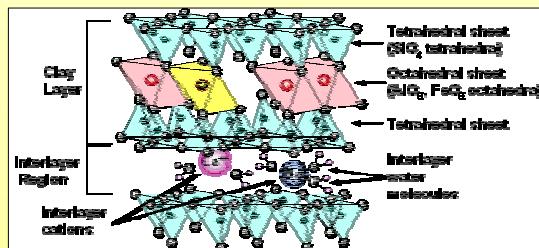
## Structure of Montmorillonite



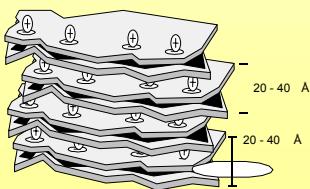
<http://www.geoclassroom.com/mineralogy/montmorillonite.movie.gif>

With kind permission of Bentonite Division, S&B Industrial Minerals GmbH, Marl (Germany)

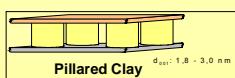
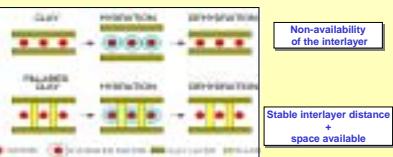
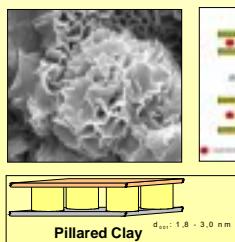
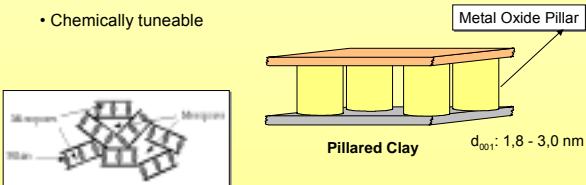
## Montmorillonite: Differs from Zeolite, how? (Electrostatically) Unattached Clay Layers

Acid Clay (Acid treated Montmorillonite)  
Structure

- Bentonite washed with acid
- specific surface area more than 320 m<sup>2</sup>/g (BET)
- very high porosity
- adsorption of odour
- high temperature stability



- Two dimensional mechanically stable, non-swelling porous system with possibility to fix catalytic active centres
- Bentonite pillared with an  $\text{Al}_{13}$  complex
- specific surface area more than  $250\text{m}^2/\text{g}$
- very high porosity
- Chemically tuneable



Retention of porosity in PILC compared to Clay

Material	Spec. Surf. Area, $\text{m}^2/\text{g}$	Spec. Micr. PV, $\text{cm}^3/\text{g}$	Spec. Meso. PV, $\text{cm}^3/\text{g}$
Bentonite	50	0.026	0.070
Pillared Clay	323	0.160	0.180
Zeolite (Untreated)	26	0.013	0.021
Mod. Zeolite	313	0.160	0.100

### 3.3.2. Silicate and Alumosilicates

#### 3.3.2.2 Molecular Sieves

#### 4. Zeolites as Catalysts

---

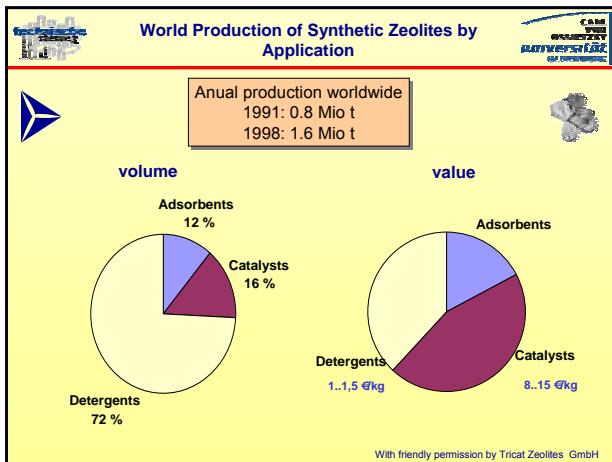
---

---

---

---

---



---

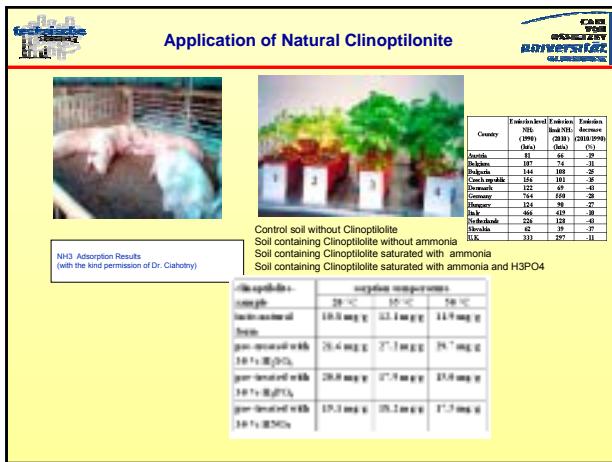
---

---

---

---

---



---

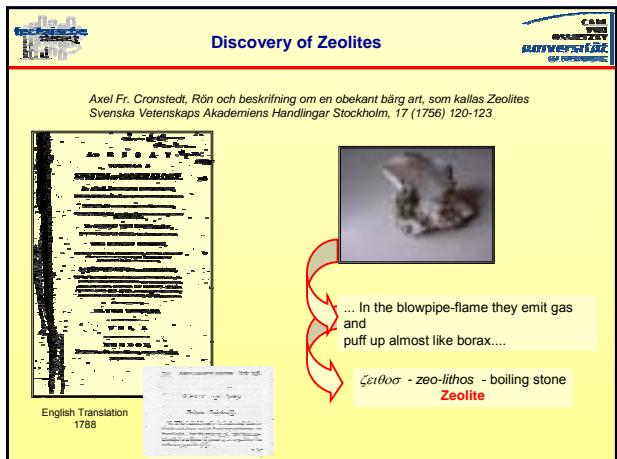
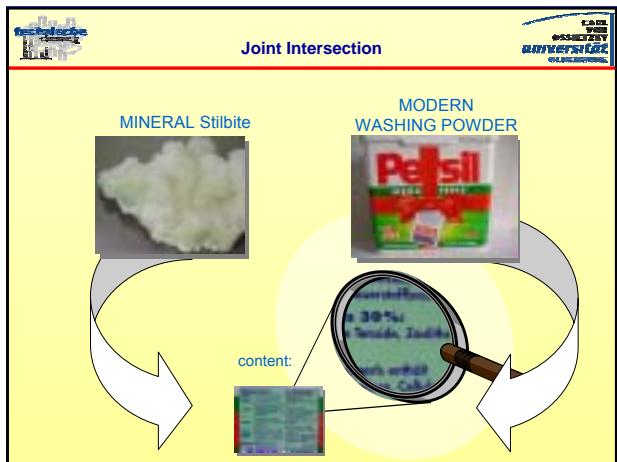
---

---

---

---

---



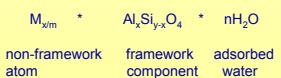
Milestones	Materials	Example
1756	discovery by A. Cronstedt	Stilbit
1934	introduction of the concept of MOLECULAR SIEVE by McBain	
1950 - 1960	aluminium rich zeolites Si/Al : 1...1,5 Si/Al : 2...5	A, X, Y, mordenite, erionite
1959	application of faujasite in process of catalytic cracking	MOBIL
1972	silicone rich zeolites (R. Argauer)	pentasil
80ies	silica molecular sieves aluminophosphate isomorphously substituted zeolites	silicalite AlPO [Me]-ZSM-5
90ies	mesoporous materials	MCM-41

## Modern Definition

### Definition:

3-dimensional linked Si/Al networks  
consisting of  $\text{SiO}_{4\text{-}}$  und  $\text{AlO}_{4\text{-}}$  tetrahedrons  
linked via shared oxygen atoms

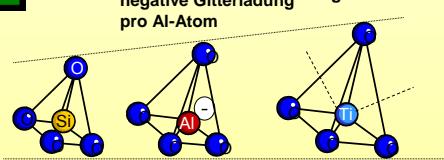
### Formula :



## Vielfalt der Zeolithe

### Chemie

negative Gitterladung pro Al-Atom  
Koordination von zwei weiteren Partnern möglich



Der Einbau unterschiedlicher Atome in das Gitter (auf T-Positionen)  
verändert die räumliche Ausdehnung, die chemischen Eigenschaften,  
die elektronische Umgebung.

Die vorgegebene Zeolithstruktur ist nicht allen denkbaren Atomen  
in beliebigen Mengen gegenüber stabil.  
Die neuen Eigenschaften lassen sich nicht vollständig vorhersagen.

## Structure of Zeolites

primary structure



secondary structure



tertiary structure



3 D structure



erionite

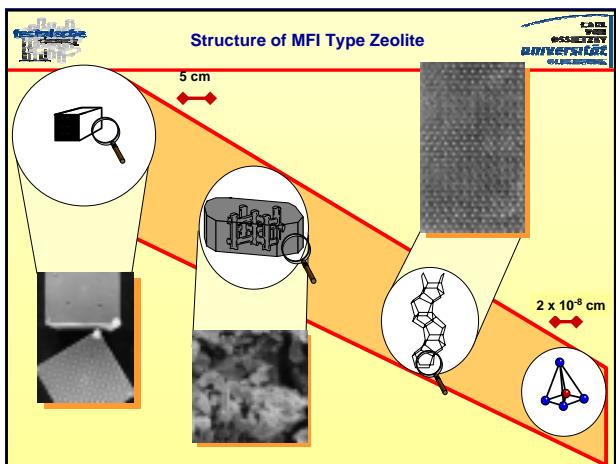
0.36 x 0.52 nm



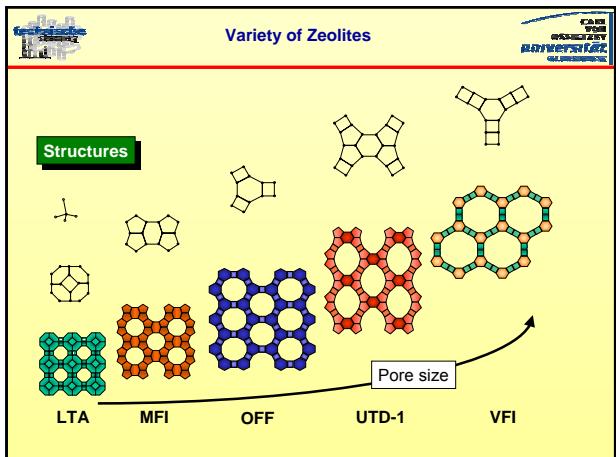
0.51 x 0.54 nm

ZSM-5

0.53 x 0.56 nm

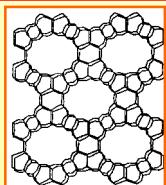
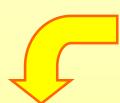


Classification of Zeolites			
<b>Based on morphology:</b>			
Fibre pattern	Lamellar structure	Framework structure	
Natrrolite	Heulandite	Analcim	
Mesolite	Brewsterite	Chabazit	
Thomsonite	Mordenite	Gmelinit	
Edingtonite	Philipsite	Levynit	
	Stilbite	Faujasit	
<b>Based on chemical composition:</b>			
Al-rich	Intermediate	Si-rich	$\text{SiO}_4^4-$ molecular sieves
$\text{Si}/\text{Al}=1\text{-}1.5$	$\text{Si}/\text{Al}=2\text{-}5$	$\text{Si}/\text{Al}=10\text{-}104$	$\text{Si}/\text{Al}=\infty$
A	Y	Datu-Y	Silicalite
X	L	ZSM-5	
Sodalite	Eriomite	Beta	
	Mordenite	ZSM-11	
	Faujasite		
	Omega		
<b>Based on pore size:</b>			
narrow pore (8-ring)	medium pore (10-ring)	wide pore (12-ring)	
A	ZSM-5	Mordenit	
Erionite		Faujasite	
		Beta	





Read the Original Literature !



**NATURE**, VOL 381 23 MAY 1996

... of the *Inova* polymers contain exclusively  
...cyclic polyisobutylene units and 4-MEA and 3-MPA in  
addition to 6-MPA.

The approximate free diameter of the large 14-MR pore in  
UTD-1 is 14 Å, which leads to a geometrically calculated void  
volume ( $V_g$ ) of ~990 Å<sup>3</sup> per unit cell (0.15 g g<sup>-1</sup>). This value is in  
reasonable agreement with the experimentally determined volume  
of 0.15 g g<sup>-1</sup> for UTD-1, based on nitrogen N<sub>2</sub> absorption  
data (isotherm available; see Supplementary Information).  
An estimate of the molecular volume ( $V_m$ ) of the organometallic  
complexes present in UTD-1 gives a value of  $V_m \approx 380 \text{ Å}^3$ . The  
 $V_g/V_m$  ratio value with the available void volume<sup>1</sup>

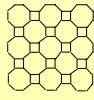


... 1996, PART II  
...r. Lobo of the University of Delaware  
[Nature 381, 295] and UTD-1 are approximately 14 Å in diameter. The calculated void volume of a unit cell is ~990 Å<sup>3</sup> and, per g of material, corresponds to a ratio of 0.15 g g<sup>-1</sup> to the experimentally determined volume<sup>1</sup>.  
The UTD-1 was synthesized using bis-(octamethylcyclotetrasiloxane) as a template. The

C&EN, MAY 27, 1996

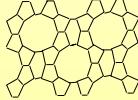
## Structure of Zeolites

8 ring



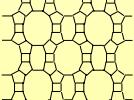
Zeolith A

10 ring

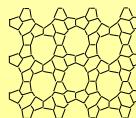


ZSM-22

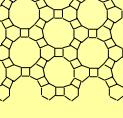
12 ring



Mordenite

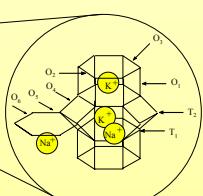
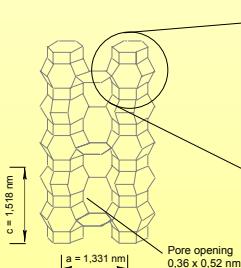


ZSM-23



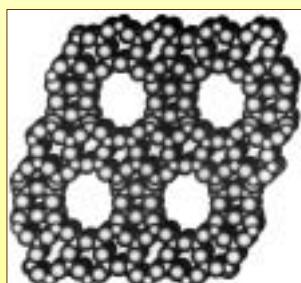
Offretite

## Structure of Erionite





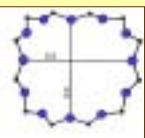
### Zeolite Beta (BEA)



Framework structure viewed along [100]



12-ring pore viewed along [100]



12-ring pore viewed along [001]

---

---

---

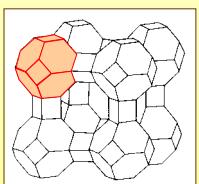
---

---

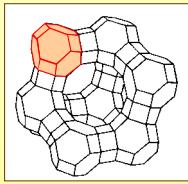
---



### 3D Structure of Zeolite A and Y



Zeolite A



Zeolite Y

---

---

---

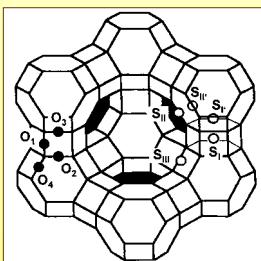
---

---

---



### Crystallographic Structure of Faujasites



Unit cell composition:  
 $M^{2+}_{x/2}[(AlO_4)_x(SiO_4)_{192-x}]^n \cdot H_2O$

16 Positions	Si
32 Positions	Si'
32 Positions	SiII
32 Positions	SiII'
48 Positions	SiIII

All T-positions are identically !

---

---

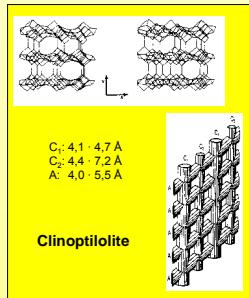
---

---

---

---

### Structure of Clinoptilolite



With kind permission of Bentonite Division, S&B Industrial Minerals GmbH, Marl (Germany)

---

---

---

---

---

---

---

### Structure of Clinoptilolite



---

---

---

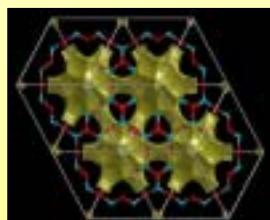
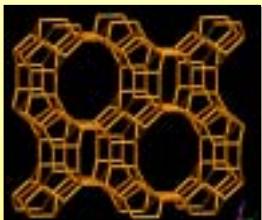
---

---

---

---

### Structure of Mordenite and Chabazite



---

---

---

---

---

---

---

---

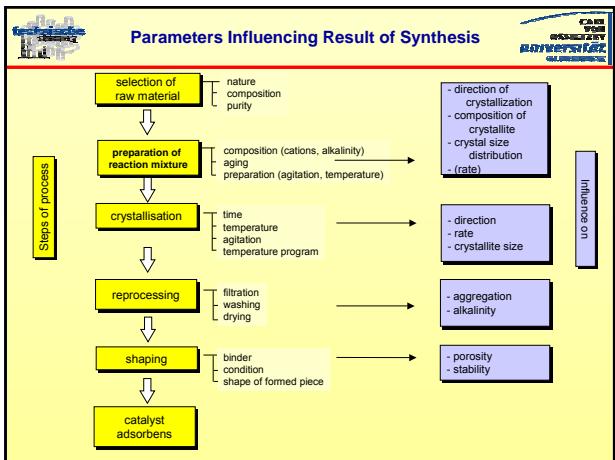
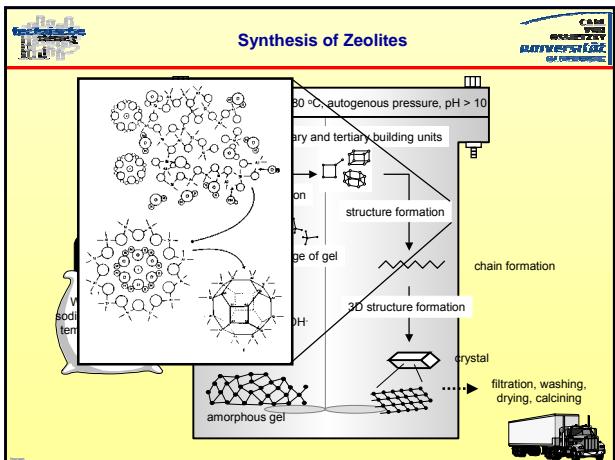
---

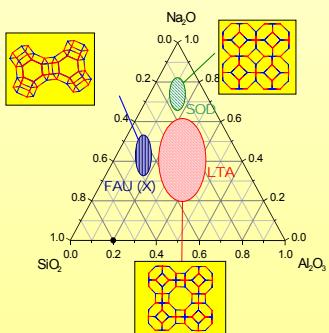
---

---

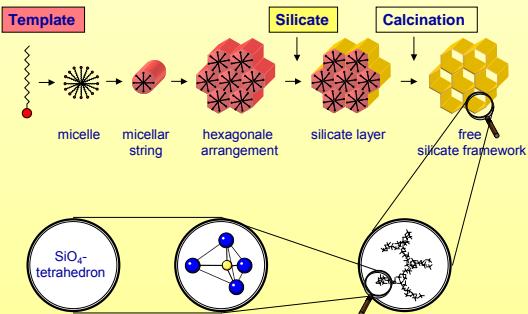
---

### 3.3.2.2 Synthesis

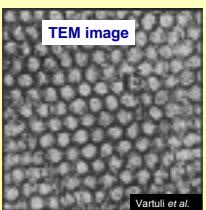




With kind permission of Tricat Zeolites GmbH

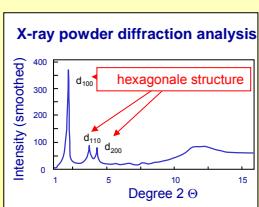


Transmissions Electron Microscopy



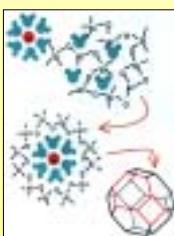
Varutti et al.

X-Ray Powder Diffraction XRD



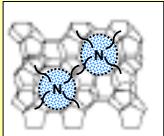
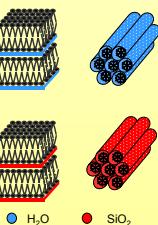
Crystallization from  
the liquid phase

Cation

Template concept  
(FLANIGEN)

Tetrapropylammonium ion Lamellare phase Hexagonale phase

ZSM-5

Molecular arrays  
(STUCKY)

Mit freundlicher Genehmigung von Prof. Schwieger, Universität Erlangen

---

---

---

---

---

### 3.3.2.3 Properties and Modification

- Ion exchange
- Isomorphous substitution
- Formation of acidic sites
- Shape Selectivity
- Supported catalysts

---

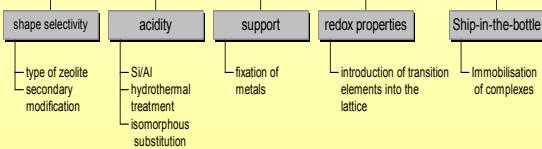
---

---

---

---

Zeolite



---

---

---

---

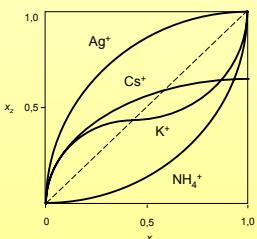
---

## Zeolites as Ion Exchanger

### Ion exchange selectivity on selected zeolites

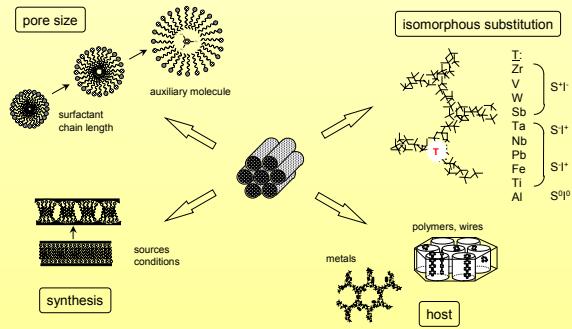
Eryonite                    K > Cs > Rb > Na > Li  
 Clinoptilolite            Cs > K = Rb > Na > Li  
 Stilbite                   Cs > K > Na  
 Zeolite A                Na > K > Rb > Li > Cs  
 Zeolite P                Ba > Ca > Cd > Mg >>Na  
 Cs > Rb >> Na  
 Ba > Ca >> Na

### Ion exchange on Zeolite A



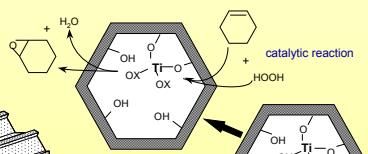
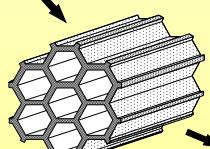
## Mesoporous Materials

### MCM-41



## Grafting of Active Components

Synthesis of the host structure (MCM-41)



Thermal treatment  
⇒ grafting

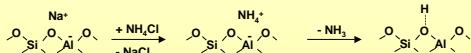
Impragnation with  
titanium alkoxides (X = Et)



## Formation of Acid Sites



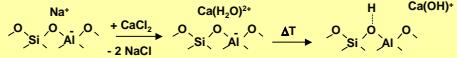
### 1. Thermal decomposition of ammonium ions:



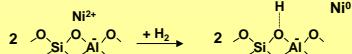
### 2. Ion exchange with mineral acids:



### 3. Ion exchange with polyvalent ions:



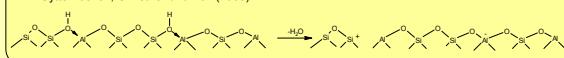
### 4. Reduction of transition metal ions



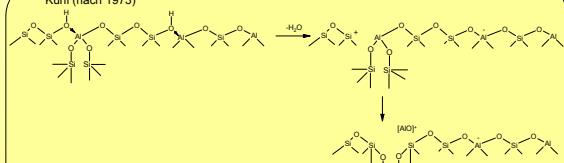
## Formation of Lewis-Acidic Centres during Dehydroxylation of Zeolites



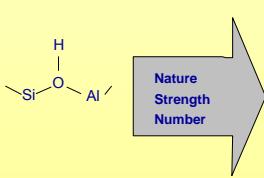
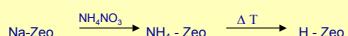
Uytterhoeven, Christner und Hall (1965)



Kühl (nach 1973)

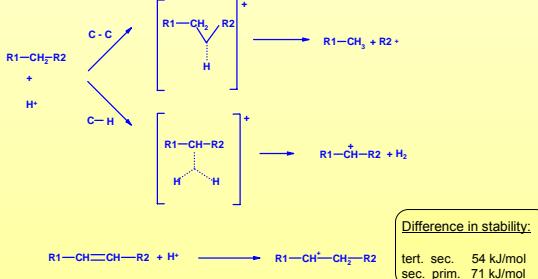


## Properties of Hydroxyl Groups



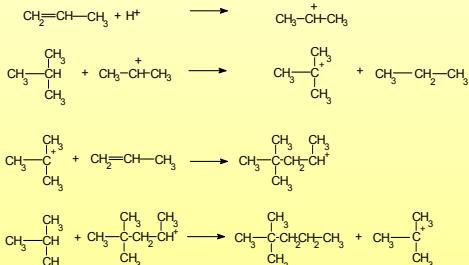
- Acidity**  
 - IR (test molecules)  
 - TPAD  
 - <sup>1</sup>H MAS NMR  
 - H/D exchange
- Accessibility**  
 - IR (test molecules)  
 - catalytic measurements

## Formation of Carbocations



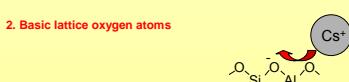
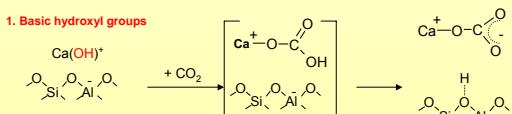
D.S. Santilli and B.C. Gates, in „Handbook of Heterogeneous Catalysis“ ed. by J. Weitkamp et al., Wiley-VCH, 1997, Vol. 3, p. 1133

## Alkylation of Refinery Gases

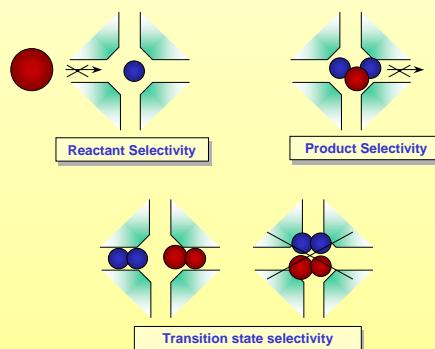


Catalyst: HF,  $\text{H}_2\text{SO}_4$ ;  $T = 0^\circ\text{C}$ ;  $p = 0,1 \text{ MPa}$

## Basic Centers in Zeolites



### Shape Selectivity




---

---

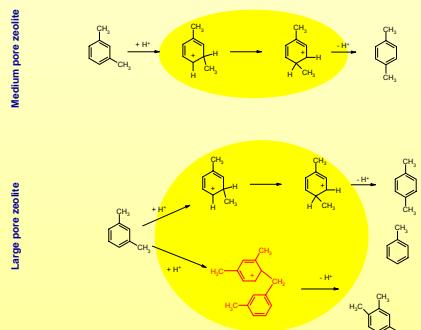
---

---

---

---

### Restricted Transition State Shape Selectivity




---

---

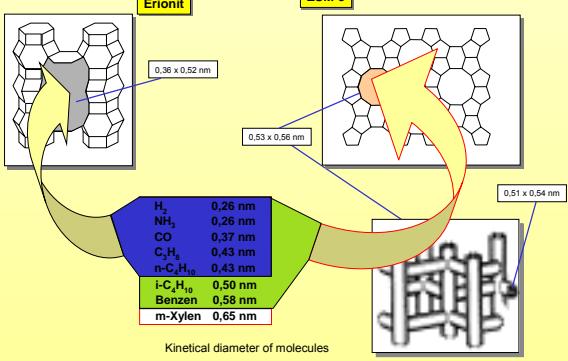
---

---

---

---

### Reactant Selectivity




---

---

---

---

---

---



## Catalytic Test Reactions for Probing for Effective Pore Width Constraint Index - CI



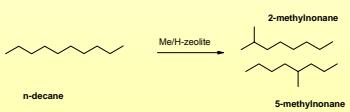
Typical reaction conditions:

$$CI = \frac{k_{n-C_6}}{k_{3-MP}} = \frac{\log(1-X_{n-C_6})}{\log(1-X_{3-MP})}$$

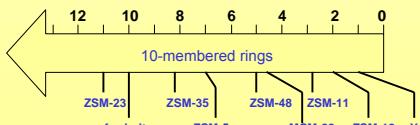
T = 290 – 510 °C  
LHSV = 0.1 – 1.0 h<sup>-1</sup>  
m<sub>cat</sub> = 1.0 g  
10 % n-C<sub>6</sub> + 10 % 3-MP in He

classification	CI	Zeolite	Ring size
large-pore materials CI < 1	0.4	X, Y	12-ring
	0.6 - 2	Beta	
	0.5	mordenite	
medium-pore materials 1 ≤ CI ≤ 12	2.3	ZSM-12	10-ring
	5 - 8.9	ZSM-11	
	6 - 8.3	ZSM-5	
	9.1	ZSM-23	
narrow pores	38	Erionite	8-ring

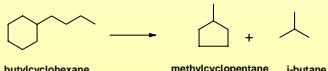
## Catalytic Test Reactions for Probing for Effective Pore Width Modified Constraint Index – CI\*



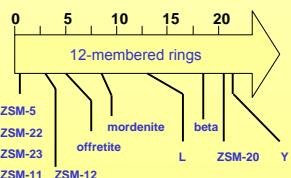
$$CI^* = \frac{Y_{2\text{-methylnonane}}}{Y_{5\text{-methylnonane}}}$$



## Catalytic Test Reactions for Probing for Effective Pore Width Spacious Index – SI

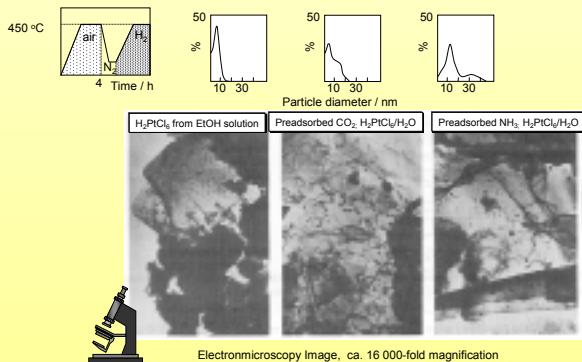


$$SI = \frac{Y_{i\text{-butane}}}{Y_{n\text{-butane}}}$$



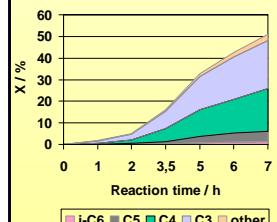
### Platinum Supported on H-ZSM-5 Zeolite

Reduction  $\Rightarrow$  metallic Pt

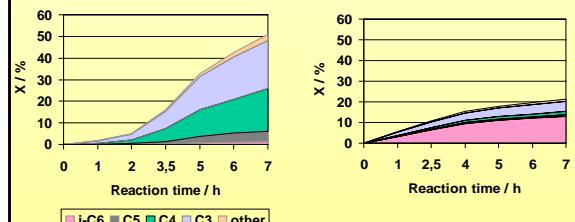


### Cracking of n-Hexan in Hydrogen Atmosphere Effect of Platinum

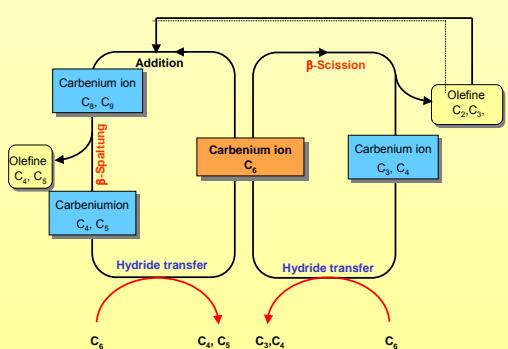
H - Erionite



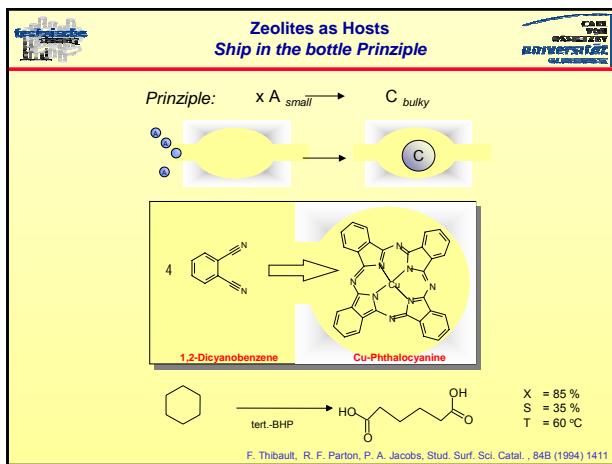
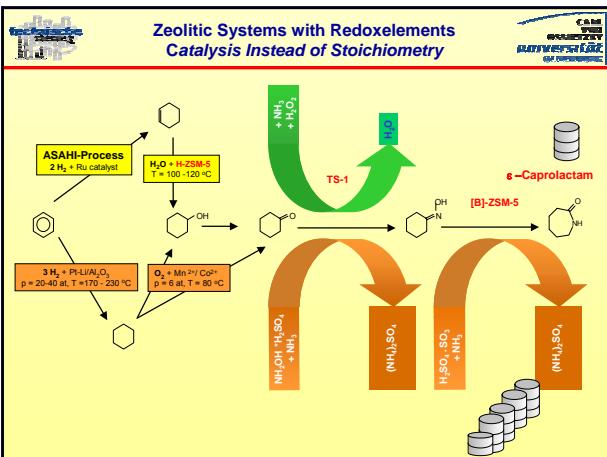
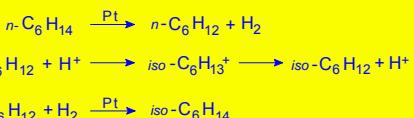
Pt/H - Erionite



### Mechanism of Acid Catalysed Cracking of n-Hexane



G. A. Mills, H. Heinemann, T. A. Milliken and A. G. Oblad, *Ind. Eng. Chem.*, 45 (1953) 134.  
 P. B. Weisz and E. W. Swegler, *Science*, 126 (1957) 31.



## Physical-Chemical Properties of Alumosilicates

---

---

---

---

---

---

### 4. Characterization of Heterogeneous Catalysts

- 4.1 Thermal Methods
- 4.2 Infrared Spectroscopy
- 4.3 UV-Vis Spectroscopy
- 4.4 Magnetic Methods

---

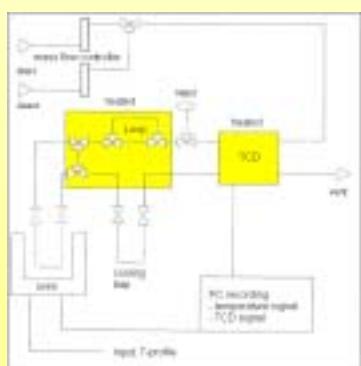
---

---

---

---

---



---

---

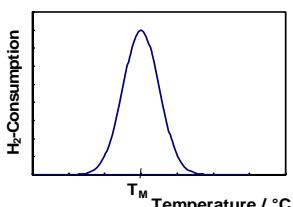
---

---

---

---

## Effects of Experimental Parameters for TPR

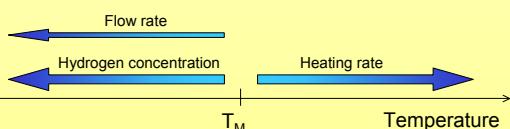


Optimal conditions

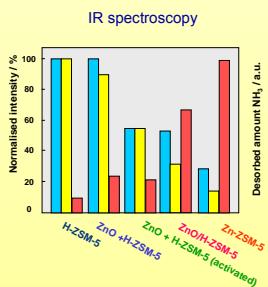
$$P = \frac{\beta \cdot S_0}{F \cdot C_0} \leq 20 \text{ K}$$

$\beta$  - heating rate, K/min  
 $S_0$  - amount of reducible sample, µmol  
 $C_0$  - initial concentration of hydrogen, µmol/g  
 $F$  - flow rate, mL/min

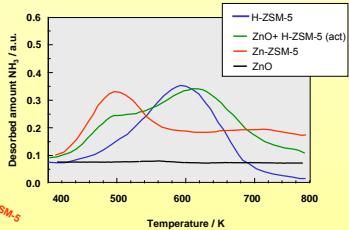
P. Melot, A. Caballero  
*J. Chem. Soc., Faraday Trans. I*, 84 (1988) 2369



## Acidic Properties of Zinc Containing Zeolites

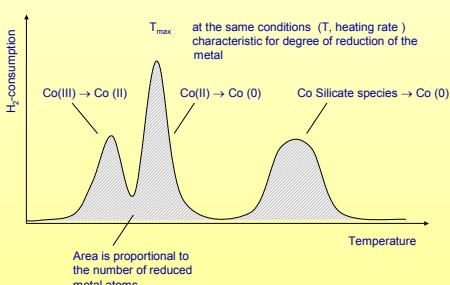


### TPD of ammonia

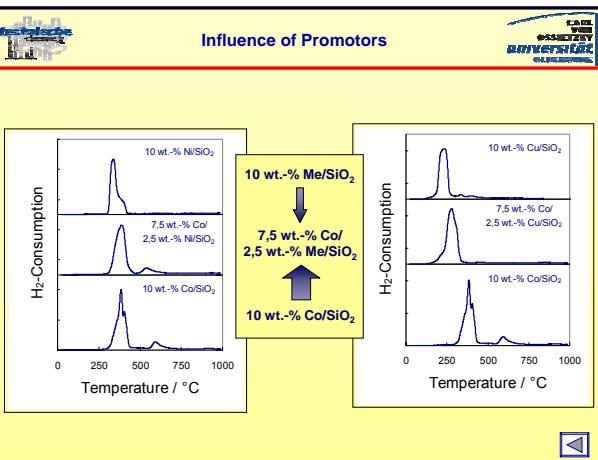


Adsorption:  
 $P_{NH_3} = 1.33 \text{ kPa}$   
 $T_{Ad} = 373 \text{ K}$

## Temperature Programmed Reduction of Co<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>



## Influence of Promoters

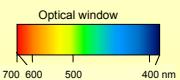


## **Elektromagnetic Radiation**

$$\bar{v} = \frac{1}{\lambda} = \frac{v}{c}$$

v - wave number / cm<sup>-1</sup>  
 λ - wave length / cm  
 c - velocity of light

$$8066 \text{ cm}^{-1} = 1 \text{ eV} = 1,6 \times 10^{-9} \text{ J}$$

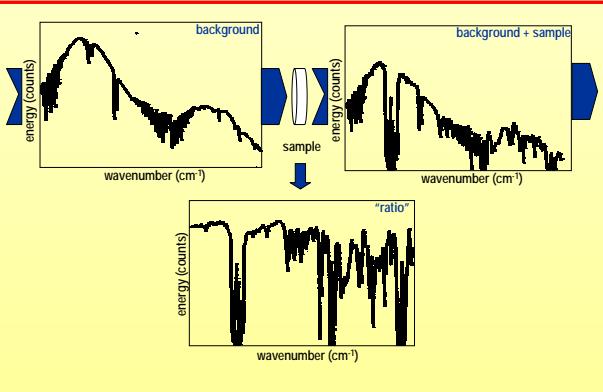


	Radio waves	Mikrowaves	IR	near IR	visible	UV	X-ray	γ-radiation
Wave lenght	> 1 mm	1 mm-25 um	25 - 2.5 μm	2.5 μm 750 nm	750 nm 400 nm	400 nm 1 nm	1 nm 1 pm	< 10 <sup>-12</sup> m
Frequency (Hz)	< 3x10 <sup>11</sup>	3x10 <sup>11</sup> -10 <sup>13</sup>	10 <sup>13</sup> -10 <sup>14</sup>	1...4 x10 <sup>14</sup>	4...7.5x10 <sup>14</sup>	10 <sup>15</sup> -10 <sup>17</sup>	10 <sup>17</sup> -10 <sup>20</sup>	10 <sup>20</sup> -10 <sup>24</sup>
Energy (kJ/Einstein)					160 - 300	300 - 12000		
Transition	nuclear spin change	molecule rotation, electron spin	molecule vibration	molecule vibration	valence electrons	valence electrons	internal electrons	nuclear transition

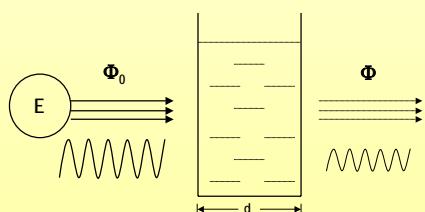
1 Einstein = 1 mol light quant



## Measurement of sample

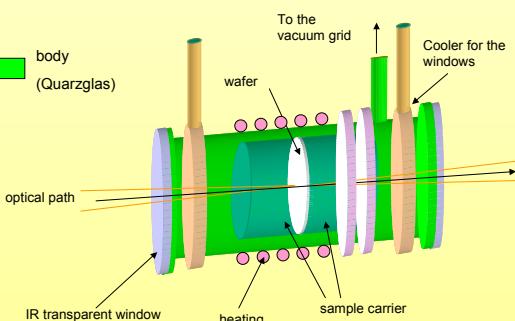


### Transmission

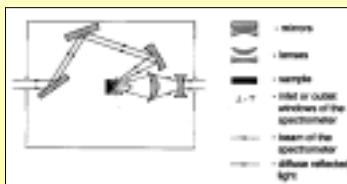


$$T = \frac{\Phi}{\Phi_0}$$

### Set-up of an IR-Transmission Cell



### Diffuse Reflectance Spectroscopy



Schuster-Kubelka-Munk remission function

$$F(R_e) = \frac{K}{S} = \frac{(1-R_e)^2}{2R_e}$$

conversion into transmission units

$$\log F(R_e) = \log K(\lambda) - \log S(\text{const})$$

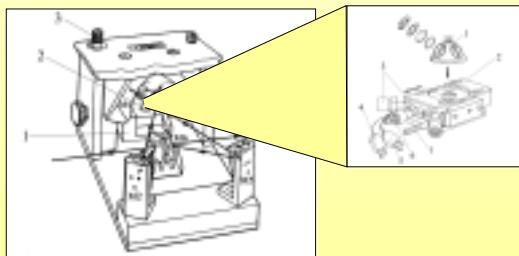
$K$  – adsorption

$S$  – scattering

$R_{\infty}$  – reflectance of a very thick sample with zero background reflectance



## Diffuse Reflectance Unit




---

---

---

---

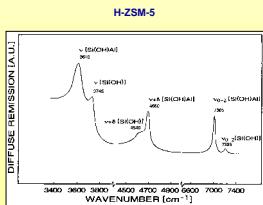
---

---

---



## Application of Diffuse Reflectance Spectroscopy



Measured frequencies	Assignment to combination vibration	Derived assignments cm⁻¹
3614	$\nu(\text{OH}) \text{ Si-OH-Al}$	-
4060	$\nu(\text{OH}) + \delta(\text{OTO})$	$\delta(\text{OTO}): 446$
4340	$\nu(\text{OH}) + \nu_s(\text{TO})$	$\nu_s(\text{TO}): 726$
4661	$\nu(\text{OH}) + \delta(\text{OH})$	$\delta(\text{OH}): 1047$
4760	$\nu(\text{OH}) + \nu_{as}(\text{TO})$	$\nu_{as}(\text{TO}): 1146$
4800	$\nu(\text{OH}) + \delta(\text{OTO}) + \nu_s(\text{TO})$	$\delta(\text{OTO}) + \nu_s(\text{TO}): 1196$
5700	$\nu(\text{OH}) + 2\delta(\text{OH})$	$\delta(\text{OH}): 1043$

Kazansky, V.B., Kustov, L.M., Brovkov V.Y., Zeolites 3 (1983)77

Beck, K., Staudte, B., Pfeiffer H., Microp. Mater. 2 (1993)1

---

---

---

---

---

---

---



## Technical aspects

<b>infrared source:</b> globar =>	siliciumcarbide (conductible ceramics in rod form) diameter: 1 cm length: 1...2 cm
heating by tapping voltage:	typical operating temperature ca. 1500 K
<b>spectral apparatus:</b> decomposition of light in spectral range	<b>detector:</b> DTGS
a) non dispersive	deuterated triglycine sulfate pyroelectric detector
b) dispersive	ferroelectrical properties
[c) interferometer FTIR]	operates at room temperature wide frequency range
a) non dispersive: several filters in range in the optical path	MCT mercury cadmium telluride photodetector
advantage: inexpensively equipment	semiconductor
disadvantage: low resolution	operates at liquid-nitrogen temperature
=> few, special use	more quickly and sensitive than DTGS but limited frequency range and dynamic range used for special applications (fast reactions, kinetic studies)

---

---

---

---

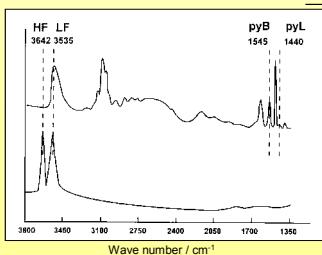
---

---

---

## Determination of Acidic Sites in H-Y Zeolite by Adsorption of Pyridine

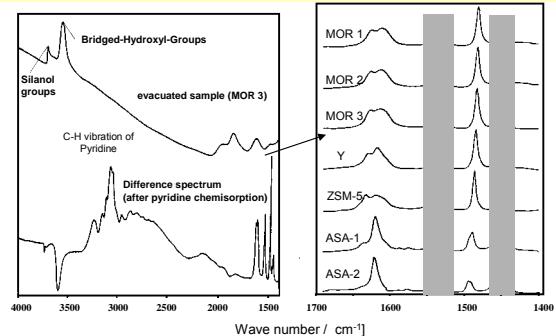
Vibration	Ppy	LPy	BPy	HPy
8a $\nu_{CON}$	1580	1620	1638	1616
8b $\nu_{CON}$	1572	1577	1620	1593
19a $\nu_{CON}$	1492	1490	1490	1490
19b $\nu_{CON}$	1439	1450	1545	1438



PPy - physisorbed pyridine  
LPy - Lewis-site bonded pyridine  
BPy - Brønsted-site bonded pyridine  
HPy - hydrogen bonded pyridine

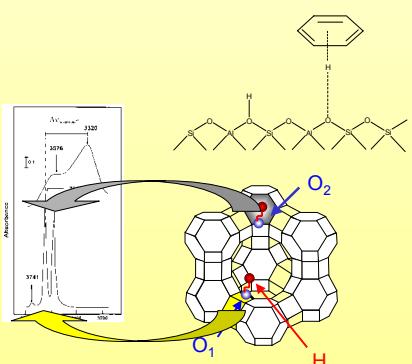
M.R. Basila, Appl. Spectr. Rev., 1 1968 289

## Acidity of Zeolites Chemisorption of Pyridine

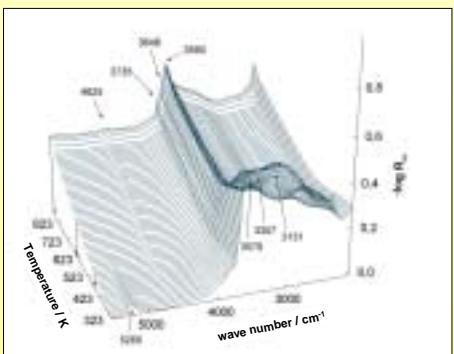


C.A. Emeis, J. Catal. 141 (1993) 347

## OH-vibration of H-Y Zeolite



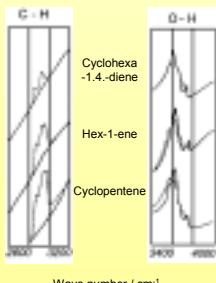
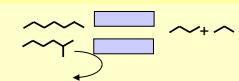
### Dehydratation of H-ZSM-5 Zeolite



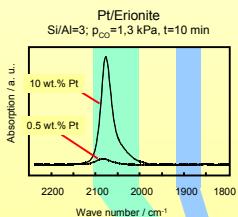
### Shape Selectivity of H-Erionite

Kinetic diameter of molecules:

H <sub>2</sub>	0.26 nm
NH <sub>3</sub>	0.26 nm
CO	0.37 nm
C <sub>2</sub> H <sub>6</sub>	0.43 nm
n-C <sub>3</sub> H <sub>8</sub>	0.43 nm
i-C <sub>4</sub> H <sub>10</sub>	0.50 nm
Benzene	0.58 nm
m-Xylene	0.65 nm



### Dispersion of Platinum



	adsorb. amount CO [µmol/g]	Integrated area [cm²/g]	Dispersion Partial size [%]	integra- tive size, [nm]	integra- tive abs. int., [cm³/µmol]
0.5% H-Erionite	1.1	8.6	5.5	28.5	27.0
5% H-Erionite	12.5	134.7	6.8	23.5	33.5
10% H-Erionite	31.5	284.7	8.7	18.3	28.0
0.5% H-ZSM-5	1.4	11.0	8.2	20.2	24.5

Si/Al=3;  $p_{CO}=1.3$  kPa, t=10 min

10 wt% Pt

0.5 wt% Pt

Wave number / cm⁻¹

2200 2100 2000 1900 1800

Absorption / a.u.

2000 1900 1800

1900 1800

1800

1700

1600

1500

1400

1300

1200

1100

1000

900

800

700

600

500

400

300

200

100

0

1000

2000

3000

4000

5000

6000

7000

8000

9000

10000

11000

12000

13000

14000

15000

16000

17000

18000

19000

20000

21000

22000

23000

24000

25000

26000

27000

28000

29000

30000

31000

32000

33000

34000

35000

36000

37000

38000

39000

40000

41000

42000

43000

44000

45000

46000

47000

48000

49000

50000

51000

52000

53000

54000

55000

56000

57000

58000

59000

60000

61000

62000

63000

64000

65000

66000

67000

68000

69000

70000

71000

72000

73000

74000

75000

76000

77000

78000

79000

80000

81000

82000

83000

84000

85000

86000

87000

88000

89000

90000

91000

92000

93000

94000

95000

96000

97000

98000

99000

100000

101000

102000

103000

104000

105000

106000

107000

108000

109000

110000

111000

112000

113000

114000

115000

116000

117000

118000

119000

120000

121000

122000

123000

124000

125000

126000

127000

128000

129000

130000

131000

132000

133000

134000

135000

136000

137000

138000

139000

140000

141000

142000

143000

144000

145000

146000

147000

148000

149000

150000

151000

152000

153000

154000

155000

156000

157000

158000

159000

160000

161000

162000

163000

164000

165000

166000

167000

168000

169000

170000

171000

172000

173000

174000

175000

176000

177000

178000

179000

180000

181000

182000

183000

184000

185000

186000

187000

188000

189000

190000

191000

192000

193000

194000

195000

196000

197000

198000

199000

200000

201000

202000

203000

204000

205000

206000

207000

208000

209000

210000

211000

212000

213000

214000

## Kubelka-Munk Equation

### Kubelka-Munk-theory:

- description by two constants  
absorption coefficient  $k$   
scattering coefficient  $s$

- simplification:  
diffuse radiant flux as one beam  
 $i_0, j_0$  - light occurring site  
 $j_h, j_d$  - light averting site

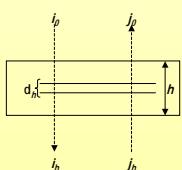
- remission (reflection) degree  $R$

$$R(k, s, h) = \frac{j_0}{i_0}$$

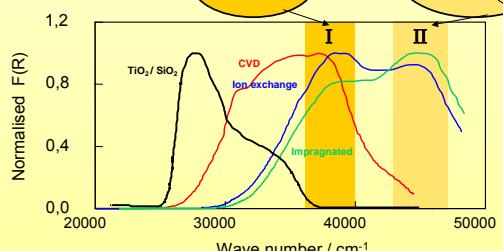
- Kubelka-Munk-function (infinite thickness layer):

$$F(R_\infty) = \frac{k}{s} = \frac{(1 - R_\infty)^2}{2R_\infty}$$

- depends on  $k$  to  $s$  ratio and not on their absolute values

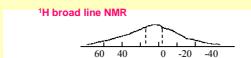


## Study of Grafting of Titanium Complexes using UV-VIS



## 4.4. Magnetic Methods

## <sup>1</sup>H NMR Study of Acidic Centres



### Solid state interactions

$$\hat{H} = \hat{H}_{CSA} + \hat{H}_{DD} + \hat{H}_Q$$

Hamiltonian chemical anisotropic shift  
Hamiltonian dipole-dipole interaction  
Hamiltonian quadrupol interaction

## Hetero-nuclear dipole-dipole interaction

$$\hat{H}_{DD}^{IS} = -\frac{\mu_0 \hbar^2}{4\pi} \frac{\gamma_1 \gamma_2}{2r^3} (3 \cos^2 \Theta - 1) \hat{I}_z \hat{S}_z$$

$\Theta$  - angle between direction of external magnetic field and distance vector

$$3\cos^2 \Theta - 1 = 0$$

i.e.  $\Theta = 54,7^\circ$

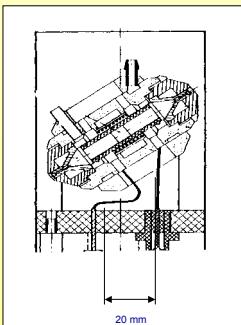
$\Theta$  - angle between direction field and distance vector

$$\hat{H}_{D0} = 0$$

10 of 10

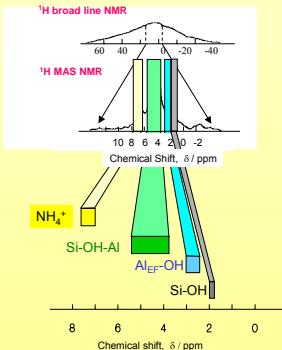
10 of 10

MAS NMR



#### Image of a MAS rotator

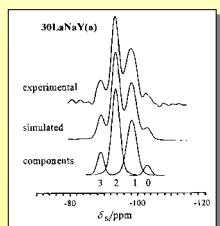
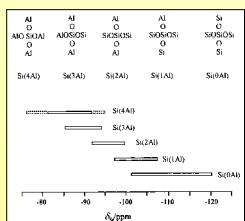
## **<sup>1</sup>H MAS NMR Study of Acidic Centres**





## Solid State NMR

UNIVERSITÄT  
REGENSBURG  
OLDBERG

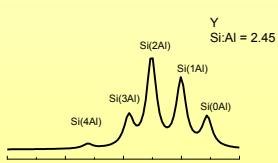
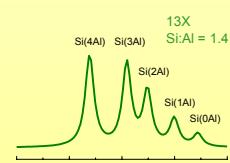
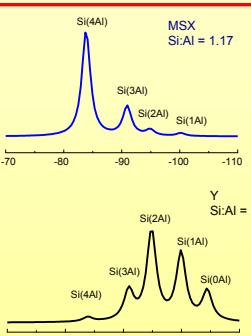
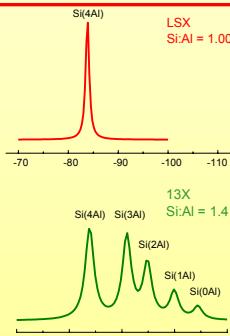


$\delta_{\text{Si}}$  - resonance position referred to the standard tetramethylsilane (TMS)



## <sup>29</sup>Si-NMR Spectra of Faujasite Type Zeolites

UNIVERSITÄT  
REGENSBURG  
OLDBERG

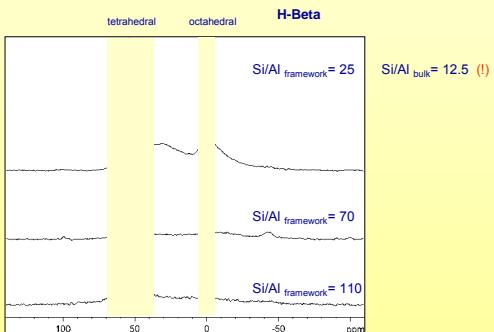


With kind permission of Tricat Zeolites GmbH



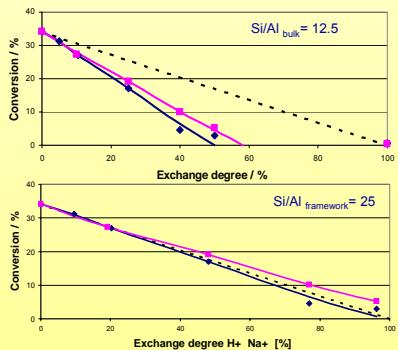
## <sup>27</sup>Al MAS NMR

UNIVERSITÄT  
REGENSBURG  
OLDBERG

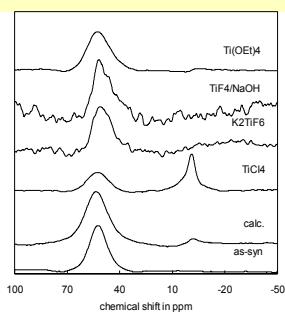




## Fatally Consequences



## $^{27}\text{Al}$ MAS NMR - Ti<sub>x</sub>Al-MCM-41



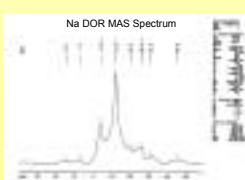
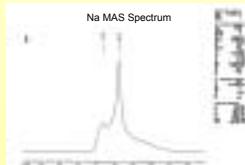
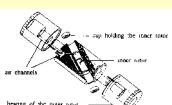
$\text{TiCl}_4$ : 14 hours, 120 °C, autoclave  
 $\text{K}_2\text{TiF}_6$ : 10 hours, 95 °C, reflux  
 $\text{TiF}_4/\text{NaOH}$ : 2 hours, 60 °C, calc. ( $\text{Si}/\text{Al}=60$ )  
 $\text{Ti}(\text{OEt})_4$ : impregnation from ethanolic soln.

Slight dealumination after calcination at 540 °C to remove template

Treatment with  $\text{TiCl}_4$  causes significant removal of Al from framework



## DOR Technique



## 4.5. Microscopic Methods

---

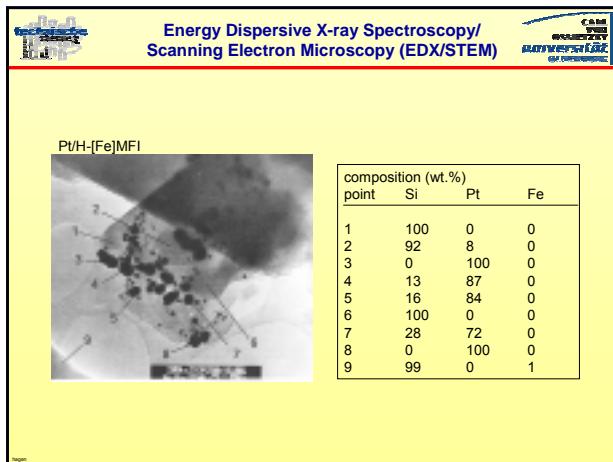
---

---

---

---

---



---

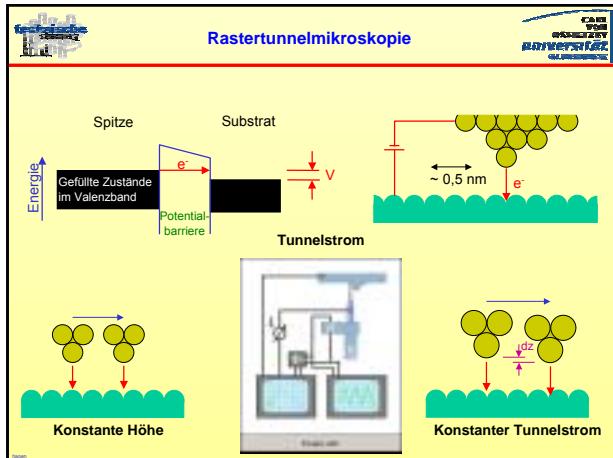
---

---

---

---

---



---

---

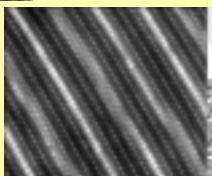
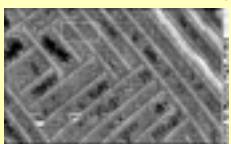
---

---

---

---

Umordnung von Pt-Atomen an der Oberfläche von PtNi(100)  
Institut für Allgemeine Physik, TU Wien



---

---

---

---

---

---

#### 4.6. Surface Methods

---

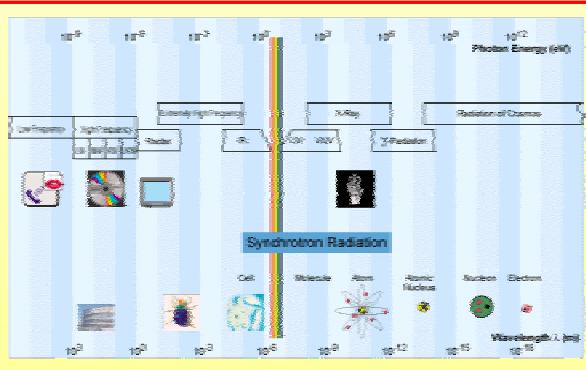
---

---

---

---

---



---

---

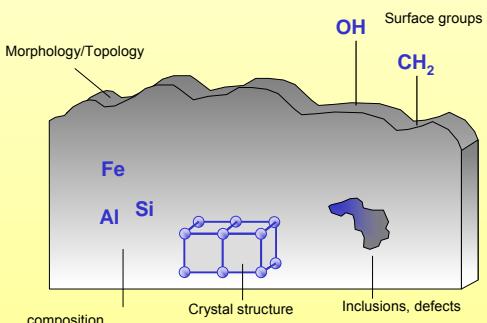
---

---

---

---

## Surface Analytic



---

---

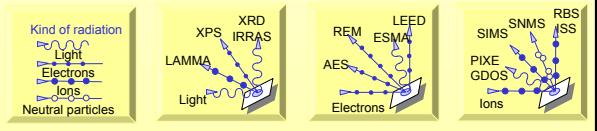
---

---

---

---

## Methods of Surface Analytic



AES	Auger Electron Spectroscopy	PIXE	Particle Induced X-Ray Emission
ESMA	Electron Beam Microanalysis	RBS	Rutherford Backscattering Spectroscopy
GDOS	Glow Discharge Optical Spectroscopy	REM	Sanning Electron Microscopy
IRRAS	Infrared Reflection Absorption Spectroscopy	SIMS	Secondary Ion Mass Spectrometry
ISS	Ion Scattering Spectroscopy	SNMS	Secondary Neutral Particle Mass Spectrometry
LAMMA	Laser Microsond Masspektrometrie	XPS	X-Ray Photoelectron Spectroscopy
LEED	Low Energy Electron Diffraction	XRD	X-Ray Diffraction

---

---

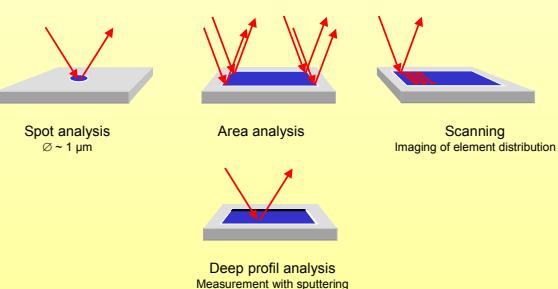
---

---

---

---

## Analysed Areas



---

---

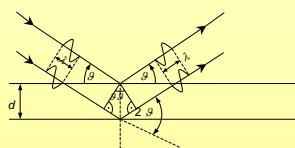
---

---

---

---

Bragg's equation:  $n\lambda = 2d \sin \theta$



### Röntgen-Pulver-Beugung: Anwendung

#### Calced ZSM-5

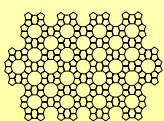
Composition:  $\text{H}_{0.2}(\text{Si}_{10.8}\text{Al}_{0.2}\text{O}_{19.2})$

Structure Type Code: MFI

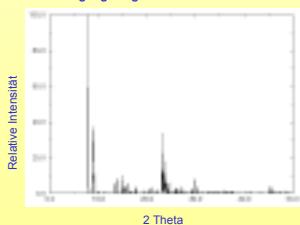
Reference:

H. van Koningsveld, J. C. Jansen and H. van Bekkum, Zeolites 10, 235-242 (1990).  
Wavelength used: 1.54056 Å (CuA1)

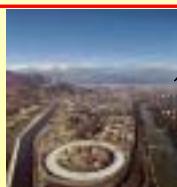
Struktur-Schema



Beugungsdiagramm



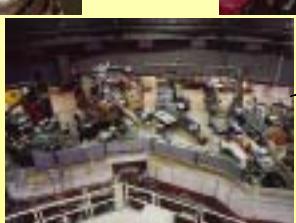
### Synchrotronstrahlung



ESRF Grenoble  
(Foto aus Bauphase)

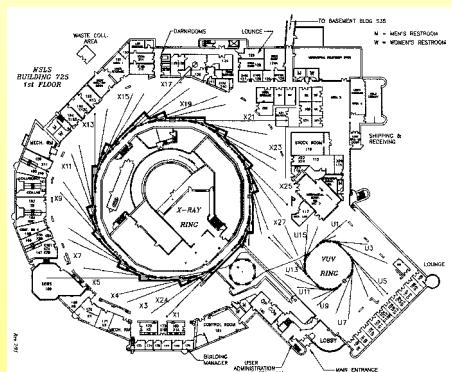


Magnetstruktur bei BESSY:  
Fokussiermagnete (violett),  
Ablenk magnet (orange)

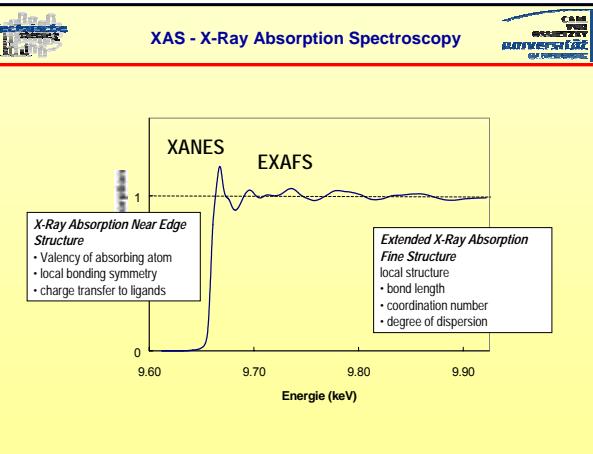


Experimentierhalle bei BESSY:  
Im Vordergrund Abschirmmauer,  
durch welche die Strahlrohre  
zu den Experimenten verlaufen

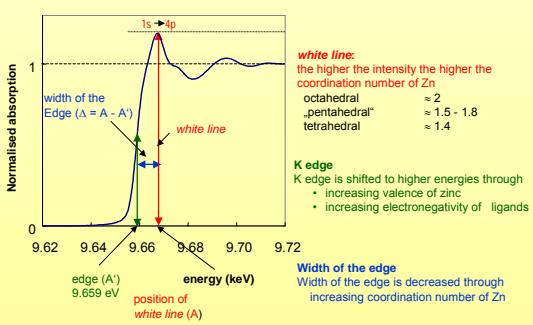
**Synchrotronstrahlung - Experimentierstationen am NSLS (USA)**



XAS - X-Ray Absorption Spectroscopy



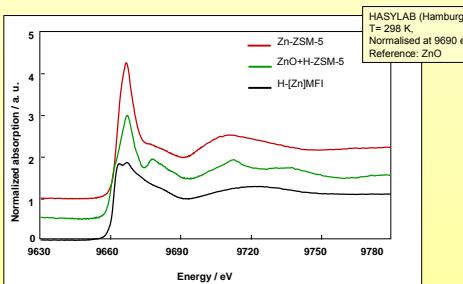
XANES on the Zn<sub>K</sub>-Edge





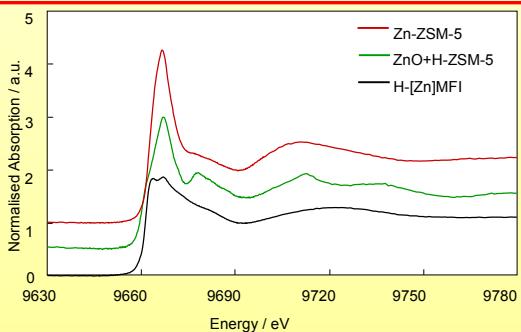
## XANES Studies of Solid State Ion Exchange on Zn containing MFI Zeolites

HASYLAB (Hamburg),  
T= 298 K,  
Normalised at 9690 eV,  
Reference: ZnO



## XANES Spectra - Zinc Containing MFI Zeolite

HASYLAB (Hamburg),  
T= 298 K, Normalised to one at the edge at 9690 eV, Reference: ZnO

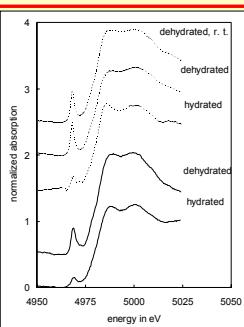


HASYLAB (Hamburg)  
T: 298 K, Normalised to one at the edge at 9690 eV, Reference: ZnO



## XANES - Ti,Al-MCM-41

HASYLAB (Hamburg),  
T= 298 K, Normalised to one at the edge at 5025 eV, Reference: TiO<sub>2</sub>



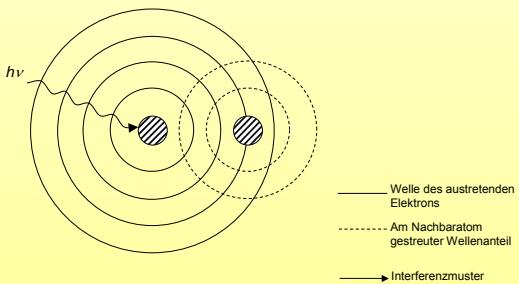
- ⇒ Pre-edge position and intensity indicate octahedral coordination in hydrated samples
- ⇒ Change to lower (probably tetrahedral) coordination upon dehydration
- ⇒ Retaining of low coordination after cooling to room temperature in inert gas flow
- ⇒ No effect in case of samples treated with TiCl<sub>4</sub>, K<sub>2</sub>TiF<sub>6</sub>, TiF<sub>4</sub>/NaOH

Ti/Al-MCM-41, impregnation of Ti(OEt)<sub>4</sub>, dehydrated by heating to 300 °C for 1 hour

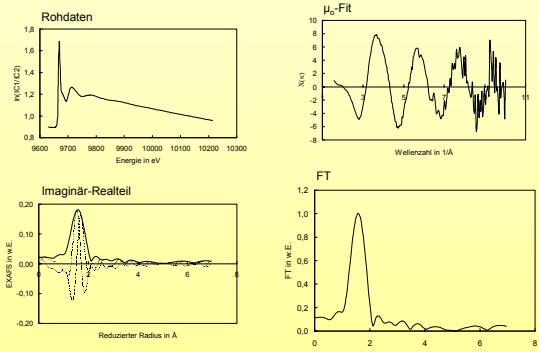
— Si/Al=15, 1 wt.% Ti  
— Si/Al=120, 1 wt.% Ti

CHESS, Cornell University, Ithaca

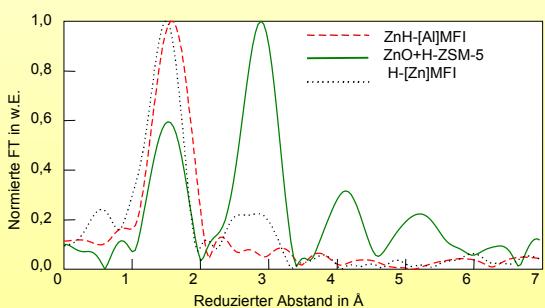
## EXAFS Oszillationen



## EXAFS - Entwicklung der Daten



## EXAFS-Spektrum - Zinkhaltige MFI-Zeolithe

HASYLAB (Hamburg) T: 298 K, Normierung,  $\mu_0$ -Fit, FT ( $k^3$ )

---

---

---

---

---

---

---

---

---

---

---

---

---

---

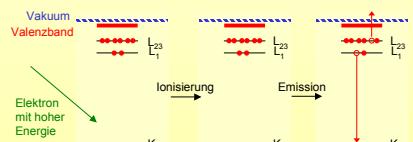
---

---

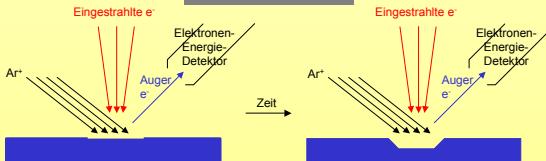
---

---

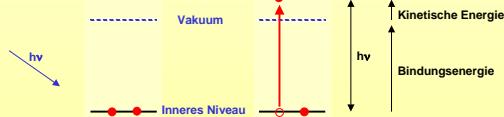
## Auger-Elektronen-Spektroskopie - AES



### AES - Tiefenprofil



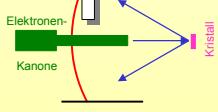
## Elektronenspektroskopie für die chemische Analyse - ESCA



### Analyse der Oberflächengruppen einer Glaskohlenstoff-Elektrode

Bindungsenergie in eV	Element	Gruppe
284,6	C <sub>1s</sub>	Kohlenstoff
286,1	C <sub>1s</sub>	Phenol
287,8	C <sub>1s</sub>	Carbonyl
532	O <sub>1s</sub>	Phenol
533,3	O <sub>1s</sub>	Carbonyl

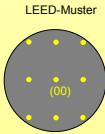
## Low Energy Electron Diffraction - LEED



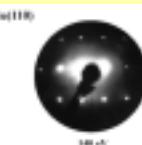
110-Fläche



LEED-Muster



LEED-Aufnahme



Cu(110)  
90 eV      140 eV

Vielen Dank !

---

---

---

---

---

---

#### 6. Industrial Catalytic Processes

- ▶ 6.1    Catalytic Reforming
- ▶ 6.2    Catalytic Cracking
- ▶ 6.3    Hydrocracking
- ▶ 6.4    Alkylation
- ▶ 6.5    Syngas
- ▶ 6.6    Epoxide

---

---

---

---

---

---

#### Antiknock Properties of Fuel Components

$$\text{RON} = \frac{\text{2,2,4 -trimethylpentane (Vol.%)}}{\text{n-heptane (Vol.-%)}}$$

Hydrocarbon	b.p. / K	RON	
Propane	231	111	~
Butane	273	94	~~~~
Hexane	342	25	~~~~~
Heptane	371	0	○
Methylcyclopentane		91	○○
Benzene	353	100	○○○
Cyclohexane	354	83	○○○○
1,1-Dimethylcyclopentane		92	○○○○○
1,3-Dimethylcyclopentane		91	○○○○○○
Methylcyclohexane	373	75	○○○○○○○



---

---

---

---

---

---

