Elementary Steps in Heterogeneous Catalysis

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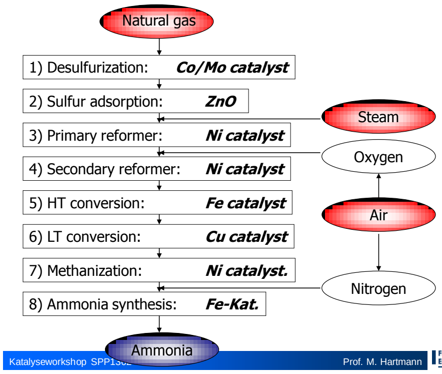
Outline

Principles of Catalysis

- A catalyst accelerates a chemical reaction without appearing in any of the products. An equilibrium is equilibrated faster, but the position of the equilibrium will not be changed.
- Catalysis is of major socio-economic importance for our society. In order to solve the future problems connected with limited resources and energy, as well as environmental protection, there is no way without efficient catalysis.
- Nowadays, more than 80 % of chemicals produced come into contact with a catalyst during their production. The world market for catalysts is estimated to be more than 2×10^9 \$ and the total value of chemicals produced by means of catalysis exceeds 1500×10^9 \$.
- Catalysis is a highly interdisciplinary discipline, bringing together top of the art fields of science and technology.

Ammonia plant – 8 different catalysts



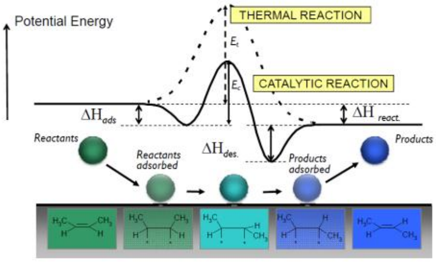
Natural gas

1) Desulfurization:	***Co/Mo catalyst***
2) Sulfur adsorption:	***ZnO***
3) Primary reformer:	***Ni catalyst***
4) Secondary reformer:	***Ni catalyst***
5) HT conversion:	***Fe catalyst***
6) LT conversion:	***Cu catalyst***
7) Methanization:	***Ni catalyst.***
8) Ammonia synthesis:	***Fe-Kat.***

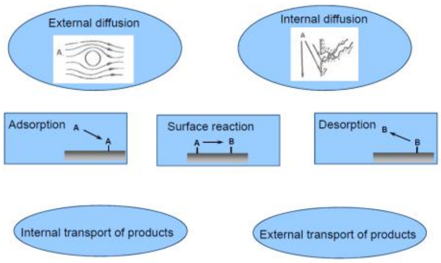
Steam
Oxygen
Air
Nitrogen

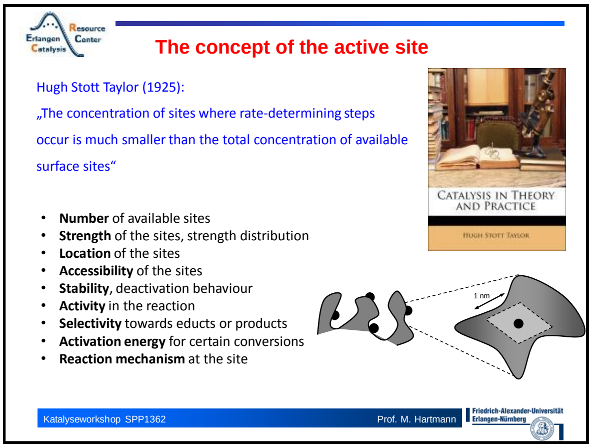
Ammonia

Energy pathway of catalyzed reaction



Elementary steps in Heterogeneous Catalysis





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The concept of the active site

Hugh Stott Taylor (1925):

„The concentration of sites where rate-determining steps occur is much smaller than the total concentration of available surface sites“

- **Number** of available sites
- **Strength** of the sites, strength distribution
- **Location** of the sites
- **Accessibility** of the sites
- **Stability**, deactivation behaviour
- **Activity** in the reaction
- **Selectivity** towards educts or products
- **Activation energy** for certain conversions
- **Reaction mechanism** at the site

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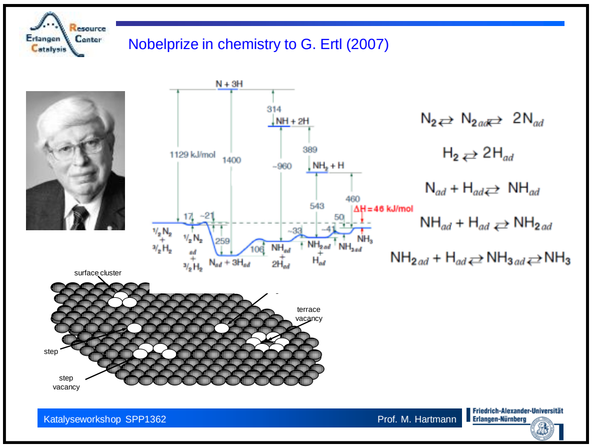

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Nobelprize in chemistry to G. Ertl (2007)

$N_2 \rightleftarrows N_{2\,ad} \rightleftarrows 2N_{ad}$

$H_2 \rightleftarrows 2H_{ad}$

$N_{ad} + H_{ad} \rightleftarrows NH_{ad}$

$NH_{ad} + H_{ad} \rightleftarrows NH_{2\,ad}$

$NH_{2\,ad} + H_{ad} \rightleftarrows NH_{3\,ad} \rightleftarrows NH_3$

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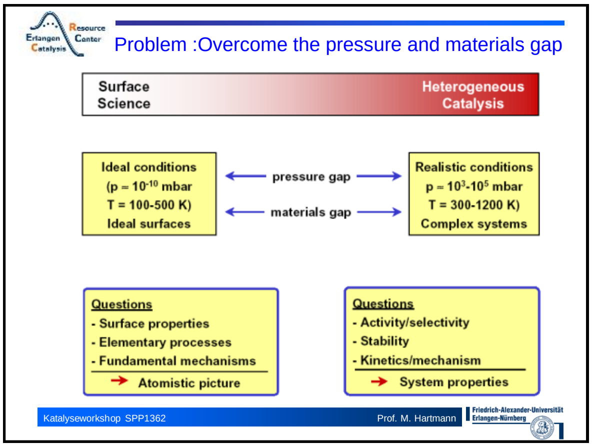

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Problem :Overcome the pressure and materials gap

Surface Science — **Heterogeneous Catalysis**

Ideal conditions		Realistic conditions
(p = 10^{-10} mbar	pressure gap	p = 10^{3}-10^{5} mbar
T = 100-500 K)	materials gap	T = 300-1200 K)
Ideal surfaces		Complex systems

Questions
- Surface properties
- Elementary processes
- Fundamental mechanisms

→ Atomistic picture

Questions
- Activity/selectivity
- Stability
- Kinetics/mechanism

→ System properties

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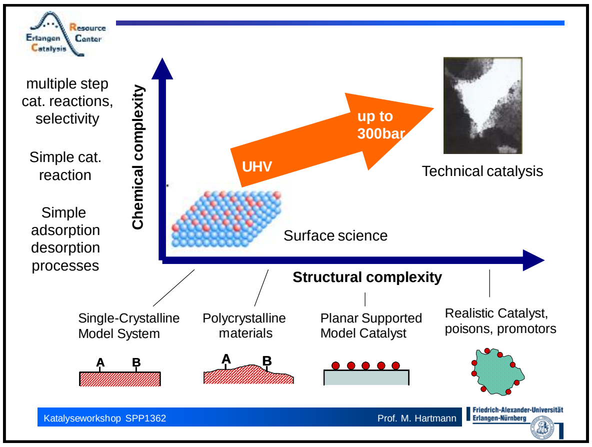

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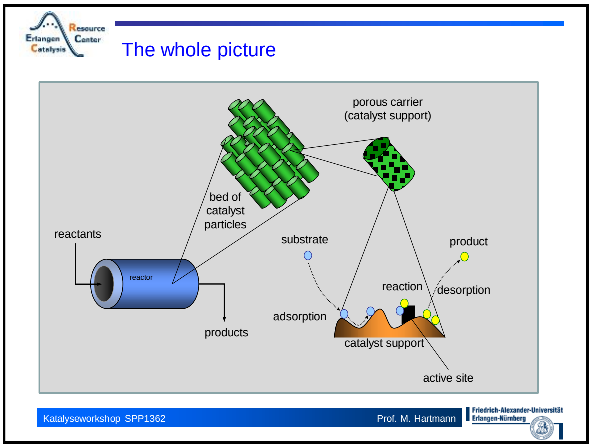

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The whole picture

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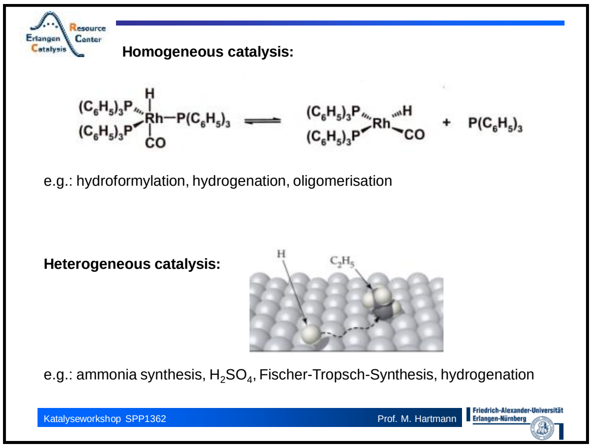

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Homogeneous catalysis:

e.g.: hydroformylation, hydrogenation, oligomerisation

Heterogeneous catalysis:

e.g.: ammonia synthesis, H_2SO_4, Fischer-Tropsch-Synthesis, hydrogenation

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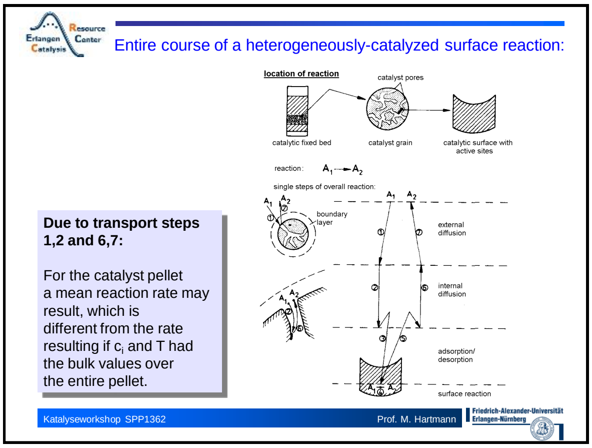
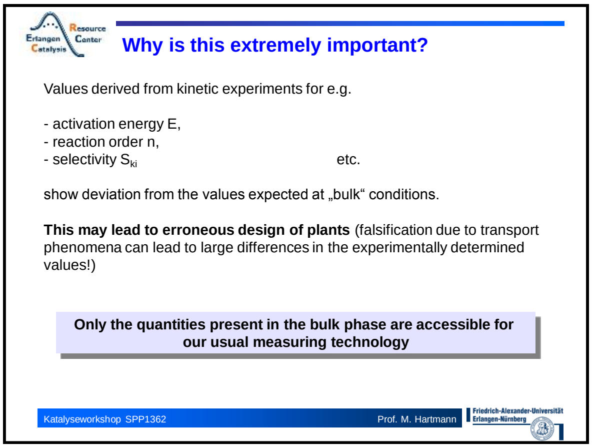


Entire course of a heterogeneously-catalyzed surface reaction:

Due to transport steps 1,2 and 6,7:

For the catalyst pellet a mean reaction rate may result, which is different from the rate resulting if c_i and T had the bulk values over the entire pellet.



Why is this extremely important?

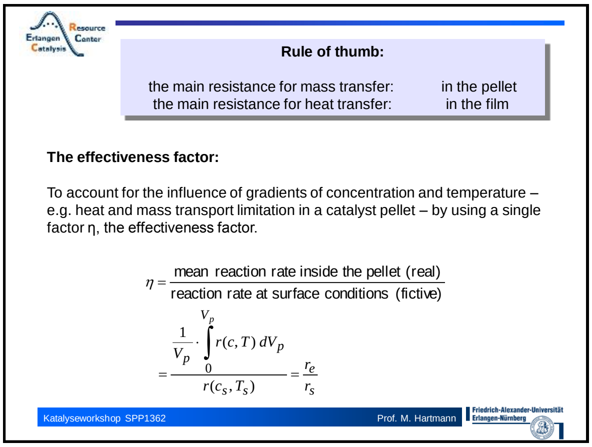
Values derived from kinetic experiments for e.g.

- activation energy E,
- reaction order n,
- selectivity S_{ki} etc.

show deviation from the values expected at „bulk“ conditions.

This may lead to erroneous design of plants (falsification due to transport phenomena can lead to large differences in the experimentally determined values!)

Only the quantities present in the bulk phase are accessible for our usual measuring technology



Rule of thumb:

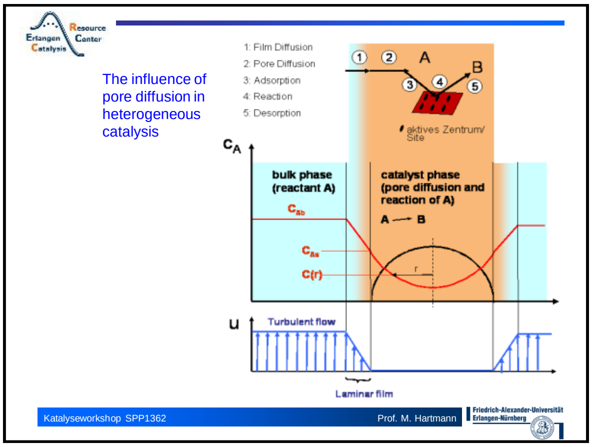
the main resistance for mass transfer:	in the pellet
the main resistance for heat transfer:	in the film

The effectiveness factor:

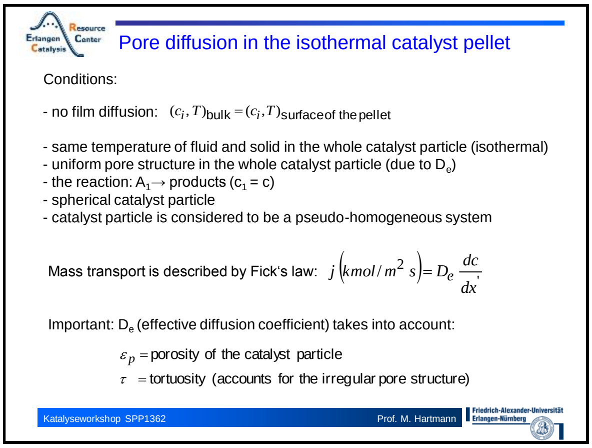
To account for the influence of gradients of concentration and temperature – e.g. heat and mass transport limitation in a catalyst pellet – by using a single factor η, the effectiveness factor.

$$\eta = \frac{\text{mean reaction rate inside the pellet (real)}}{\text{reaction rate at surface conditions (fictive)}}$$

$$= \frac{\frac{1}{V_p} \cdot \int_0^{V_p} r(c,T)\, dV_p}{r(c_s, T_s)} = \frac{r_e}{r_s}$$



The influence of pore diffusion in heterogeneous catalysis



Pore diffusion in the isothermal catalyst pellet

Conditions:

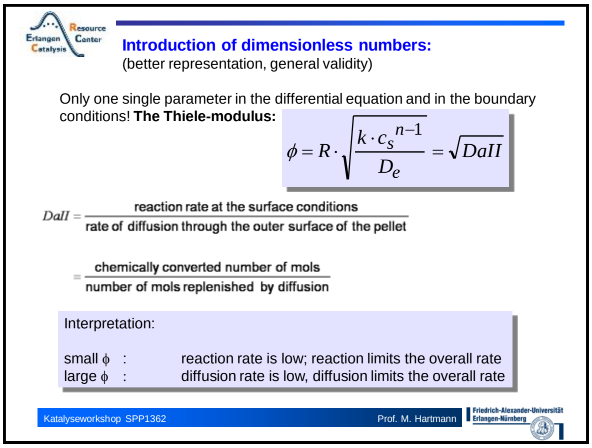
- no film diffusion: $(c_i, T)_{\text{bulk}} = (c_i, T)_{\text{surface of the pellet}}$

- same temperature of fluid and solid in the whole catalyst particle (isothermal)
- uniform pore structure in the whole catalyst particle (due to D_e)
- the reaction: $A_1 \rightarrow$ products (c_1 = c)
- spherical catalyst particle
- catalyst particle is considered to be a pseudo-homogeneous system

Mass transport is described by Fick's law: $j\left(kmol/m^2\, s\right) = D_e \frac{dc}{dx}$,

Important: D_e (effective diffusion coefficient) takes into account:

ε_p = porosity of the catalyst particle
τ = tortuosity (accounts for the irregular pore structure)



Introduction of dimensionless numbers:

(better representation, general validity)

Only one single parameter in the differential equation and in the boundary conditions! **The Thiele-modulus:**

$$\phi = R \cdot \sqrt{\frac{k \cdot c_s^{n-1}}{D_e}} = \sqrt{DaII}$$

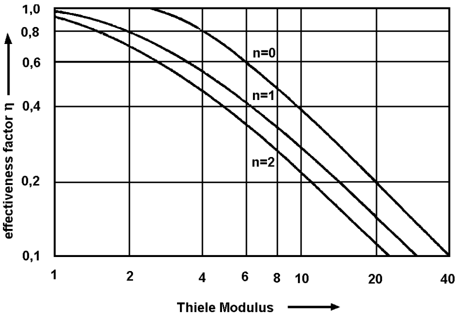
$$DaII = \frac{\text{reaction rate at the surface conditions}}{\text{rate of diffusion through the outer surface of the pellet}}$$

$$= \frac{\text{chemically converted number of mols}}{\text{number of mols replenished by diffusion}}$$

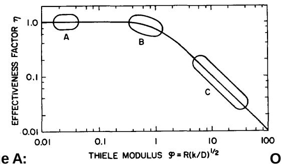
Interpretation:

small ϕ : reaction rate is low; reaction limits the overall rate
large ϕ : diffusion rate is low, diffusion limits the overall rate

Dependence of the effectiveness factor on the Thiele modulus for various reaction orders n



Desired condition for a technical catalytic process:



Operating range A:
(catalyst of low activity,
large D_e – large pores,
small R)

R lower than necessary:
high pressure drop;
activity to low and D_e larger than necessary:
large reactor volume necessary

Operating range B:

desired range of technical operation:

Operating range C:
(very active catalyst,
low D_e – small pores,
large R)

The rate of diffusion determines overall rate; concentration in the center →0:
more rapid deactivation, *shifts in selectivity*

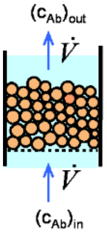
Falsification of kinetic parameters by transport phenomena

For a differential reactor:

$$r_{obs} = \frac{\dot{V} \cdot ((c_{Ab})_{in} - (c_{Ab})_{out})}{m_{cat}}$$

$$r_{obs} = k_{obs} \cdot c_{Ab}^{n_{obs}}$$

$$k_{obs} = k_{0,obs} \cdot \exp(-E_{A,obs} / RT)$$



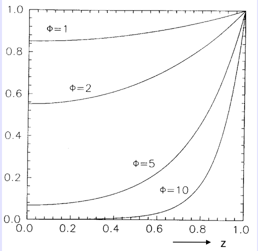
$$r_{true}(r) = k_{true} \cdot c_{Ab}^{n_{true}}(r)$$

$$k_{true} = f(E_{A,true} / RT)$$

We have to expect falsification of measured (observed) kinetic parameters. The measured (observed or effective) parameters may differ strongly from the true (intrinsic) parameters.

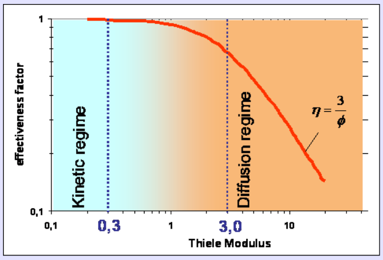
Thiele Modulus: $\phi = R \cdot \sqrt{\frac{k \cdot c_s^{\,n-1}}{D_e}}$

$$f(x) = \frac{c(x)}{c_s}$$



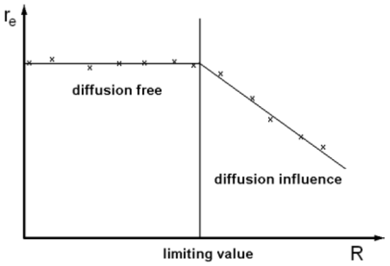
Concentration profile inside the spherical porous catalyst

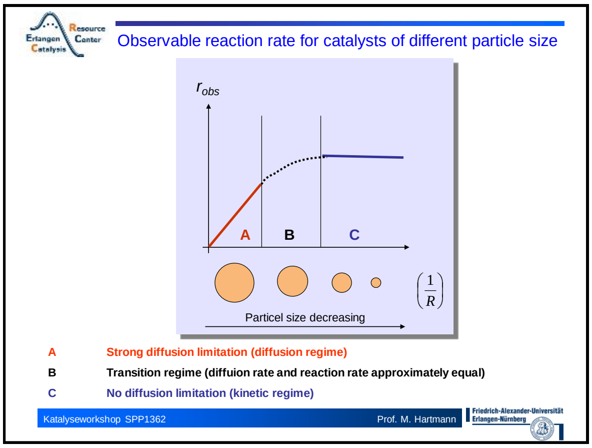
Effectiveness factor: $\eta = \frac{r_{obs}}{r_{true}} = \frac{r_{obs}}{kc_s^n}$



Effectiveness Factor vs. Thiele Modulus

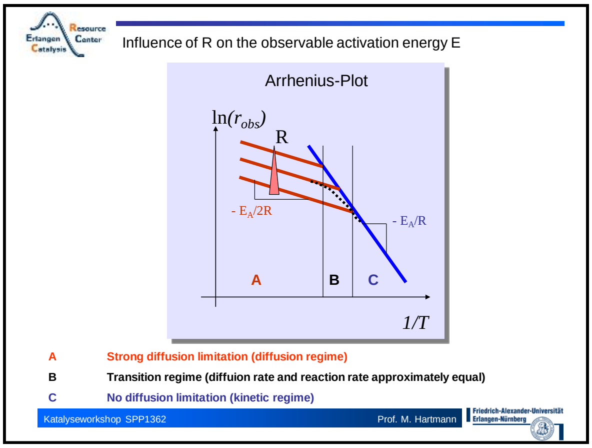
Experimental determination of a limiting value for the pore diffusion influence:





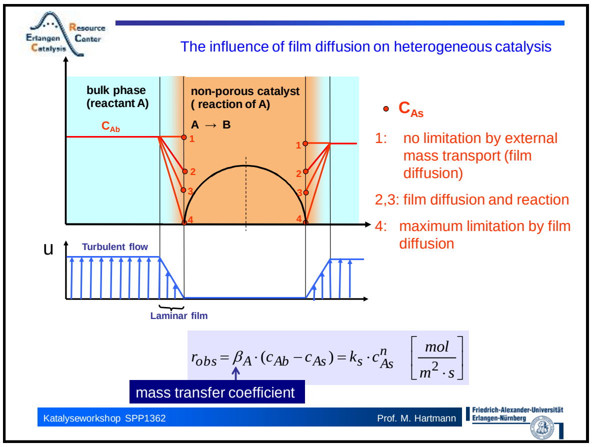
Observable reaction rate for catalysts of different particle size

A	**Strong diffusion limitation (diffusion regime)**
B	**Transition regime (diffuion rate and reaction rate approximately equal)**
C	**No diffusion limitation (kinetic regime)**



Influence of R on the observable activation energy E

A	**Strong diffusion limitation (diffusion regime)**
B	**Transition regime (diffuion rate and reaction rate approximately equal)**
C	**No diffusion limitation (kinetic regime)**



The influence of film diffusion on heterogeneous catalysis

- **C_{As}**

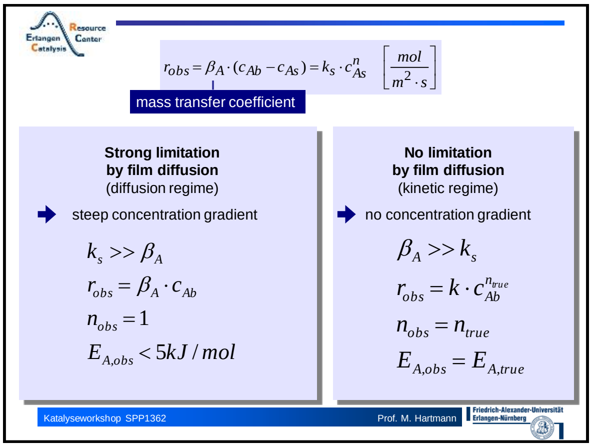
1: no limitation by external mass transport (film diffusion)

2,3: film diffusion and reaction

4: maximum limitation by film diffusion

$$r_{obs} = \beta_A \cdot (c_{Ab} - c_{As}) = k_s \cdot c_{As}^n \quad \left[\frac{mol}{m^2 \cdot s}\right]$$

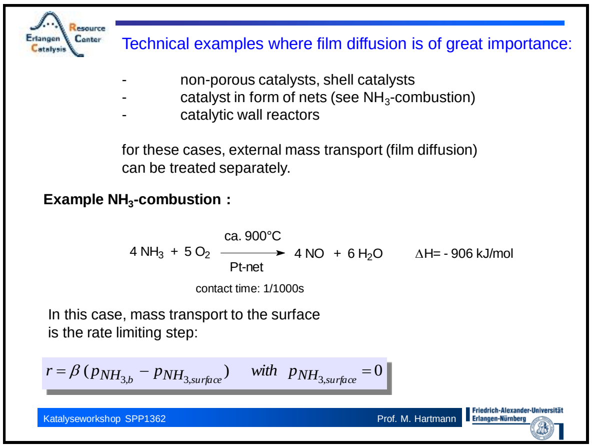
mass transfer coefficient



$$r_{obs} = \beta_A \cdot (c_{Ab} - c_{As}) = k_s \cdot c_{As}^n \quad \left[\frac{mol}{m^2 \cdot s}\right]$$

mass transfer coefficient

Strong limitation by film diffusion (diffusion regime)	**No limitation by film diffusion** (kinetic regime)
➡ steep concentration gradient	➡ no concentration gradient
$k_s >> \beta_A$	$\beta_A >> k_s$
$r_{obs} = \beta_A \cdot c_{Ab}$	$r_{obs} = k \cdot c_{Ab}^{n_{true}}$
$n_{obs} = 1$	$n_{obs} = n_{true}$
$E_{A,obs} < 5kJ/mol$	$E_{A,obs} = E_{A,true}$



Technical examples where film diffusion is of great importance:

- non-porous catalysts, shell catalysts
- catalyst in form of nets (see NH_3-combustion)
- catalytic wall reactors

for these cases, external mass transport (film diffusion) can be treated separately.

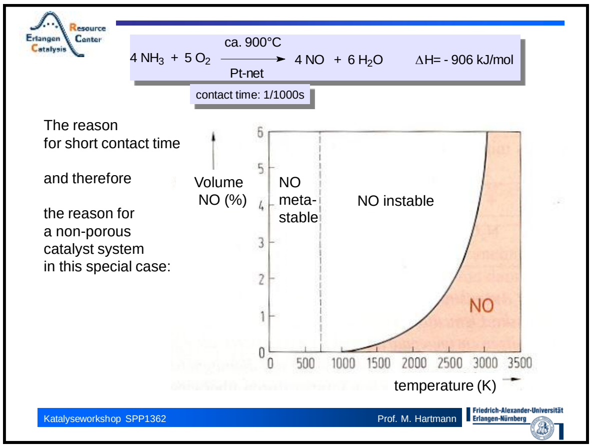
Example NH_3-combustion :

$$4\ NH_3 + 5\ O_2 \xrightarrow[\text{Pt-net}]{\text{ca. 900°C}} 4\ NO + 6\ H_2O \qquad \Delta H = -906\ kJ/mol$$

contact time: 1/1000s

In this case, mass transport to the surface is the rate limiting step:

$$r = \beta\,(p_{NH_{3,b}} - p_{NH_{3,surface}}) \quad with \quad p_{NH_{3,surface}} = 0$$



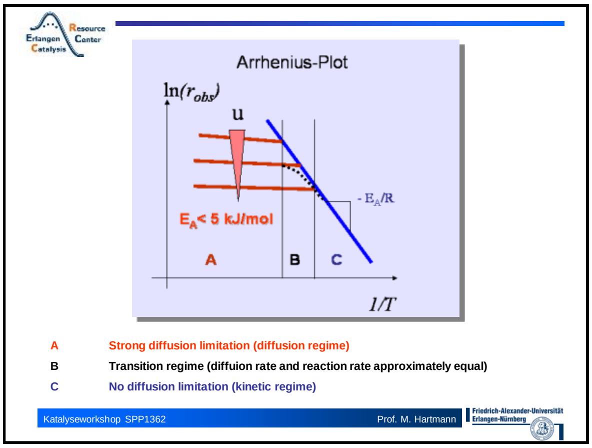
$$4\ NH_3 + 5\ O_2 \xrightarrow[\text{Pt-net}]{\text{ca. 900°C}} 4\ NO + 6\ H_2O \qquad \Delta H = -906\ kJ/mol$$

contact time: 1/1000s

The reason
for short contact time

and therefore

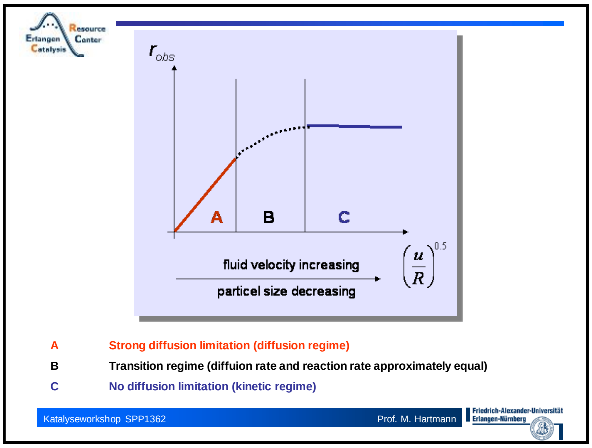
the reason for
a non-porous
catalyst system
in this special case:



A Strong diffusion limitation (diffusion regime)

B Transition regime (diffuion rate and reaction rate approximately equal)

C No diffusion limitation (kinetic regime)



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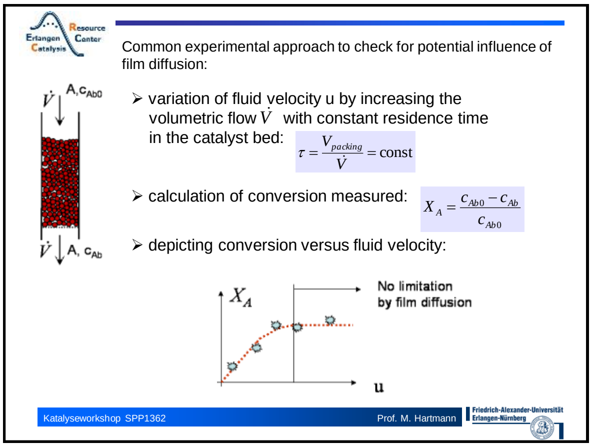
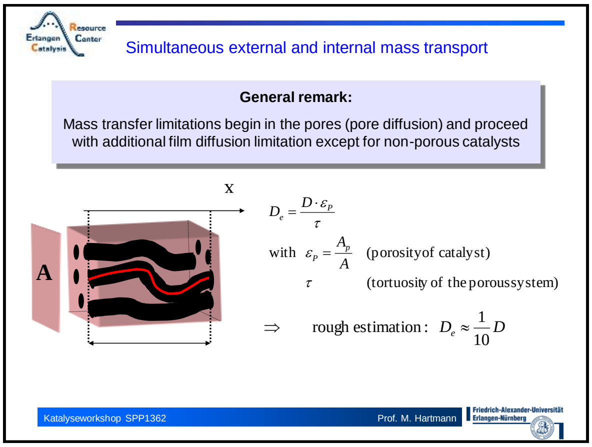


Common experimental approach to check for potential influence of film diffusion:

- variation of fluid velocity u by increasing the volumetric flow $\dot V$ with constant residence time in the catalyst bed: $\tau = \frac{V_{packing}}{\dot V} = \text{const}$
- calculation of conversion measured: $X_A = \frac{c_{Ab0} - c_{Ab}}{c_{Ab0}}$
- depicting conversion versus fluid velocity:



Simultaneous external and internal mass transport

General remark:

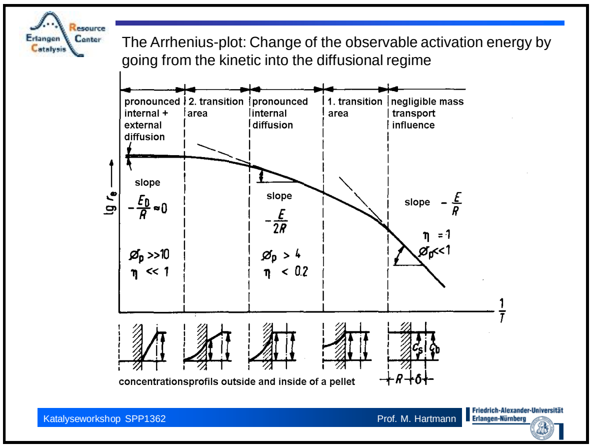
Mass transfer limitations begin in the pores (pore diffusion) and proceed with additional film diffusion limitation except for non-porous catalysts

$$D_e = \frac{D \cdot \varepsilon_P}{\tau}$$

with $\varepsilon_P = \frac{A_p}{A}$ (porosity of catalyst)

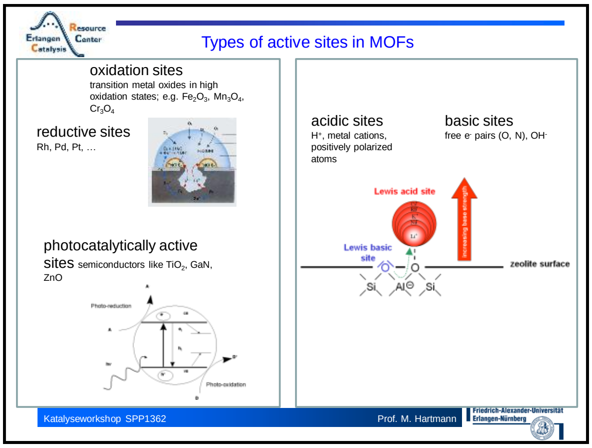
τ (tortuosity of the porous system)

$\Rightarrow$ rough estimation: $D_e \approx \frac{1}{10} D$



The Arrhenius-plot: Change of the observable activation energy by going from the kinetic into the diffusional regime

concentrationsprofils outside and inside of a pellet



Types of active sites in MOFs

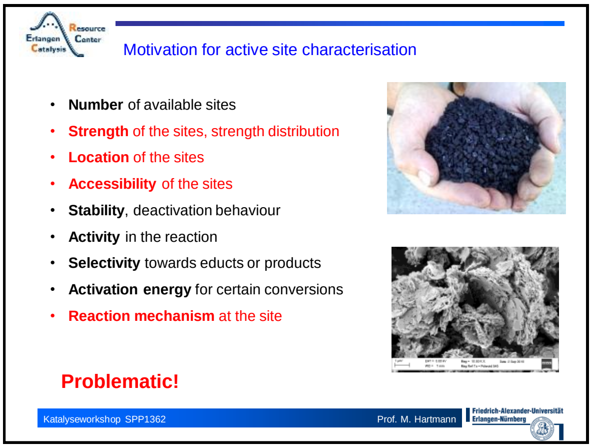
oxidation sites
transition metal oxides in high oxidation states; e.g. Fe_2O_3, Mn_3O_4, Cr_3O_4

reductive sites
Rh, Pd, Pt, …

photocatalytically active sites semiconductors like TiO_2, GaN, ZnO

acidic sites
H^+, metal cations, positively polarized atoms

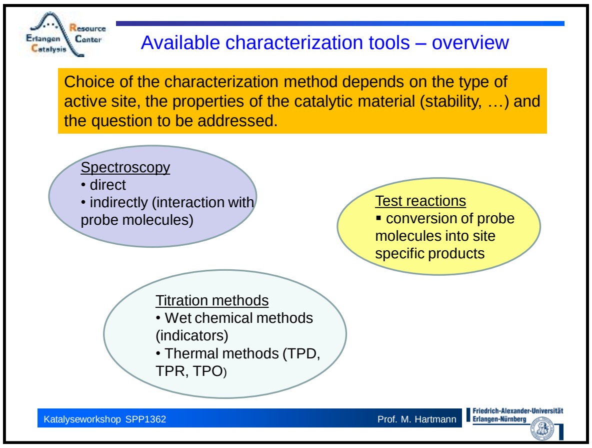
basic sites
free e^- pairs (O, N), OH^-



Motivation for active site characterisation

- **Number** of available sites
- **Strength** of the sites, strength distribution
- **Location** of the sites
- **Accessibility** of the sites
- **Stability**, deactivation behaviour
- **Activity** in the reaction
- **Selectivity** towards educts or products
- **Activation energy** for certain conversions
- **Reaction mechanism** at the site

Problematic!



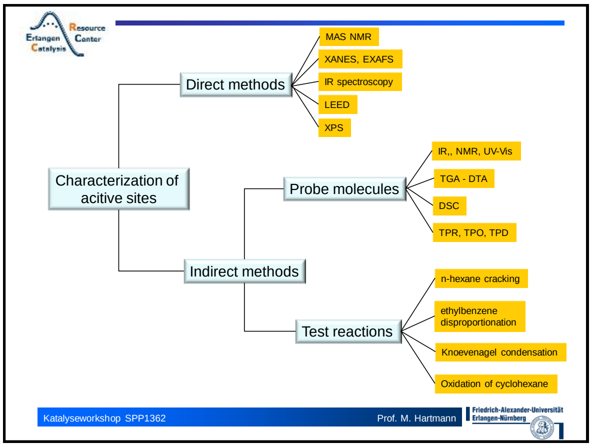
Available characterization tools – overview

Choice of the characterization method depends on the type of active site, the properties of the catalytic material (stability, …) and the question to be addressed.

Spectroscopy
- direct
- indirectly (interaction with probe molecules)

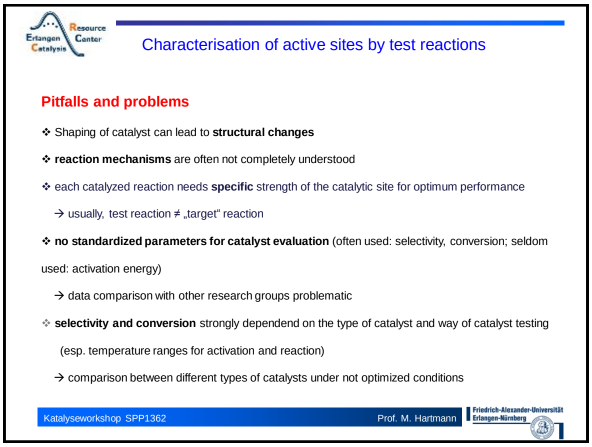
Test reactions
- conversion of probe molecules into site specific products

Titration methods
- Wet chemical methods (indicators)
- Thermal methods (TPD, TPR, TPO)



Characterization of acitive sites

- Direct methods
  - MAS NMR
  - XANES, EXAFS
  - IR spectroscopy
  - LEED
  - XPS
- Indirect methods
  - Probe molecules
    - IR,, NMR, UV-Vis
    - TGA - DTA
    - DSC
    - TPR, TPO, TPD
  - Test reactions
    - n-hexane cracking
    - ethylbenzene disproportionation
    - Knoevenagel condensation
    - Oxidation of cyclohexane



Characterisation of active sites by test reactions

Pitfalls and problems

❖ Shaping of catalyst can lead to **structural changes**

❖ **reaction mechanisms** are often not completely understood

❖ each catalyzed reaction needs **specific** strength of the catalytic site for optimum performance

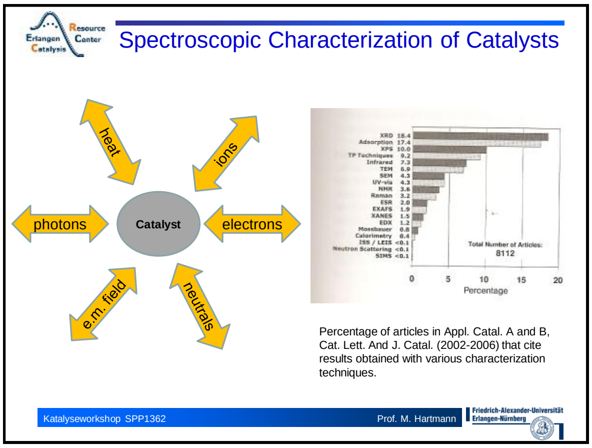
→ usually, test reaction ≠ „target" reaction

❖ **no standardized parameters for catalyst evaluation** (often used: selectivity, conversion; seldom used: activation energy)

→ data comparison with other research groups problematic

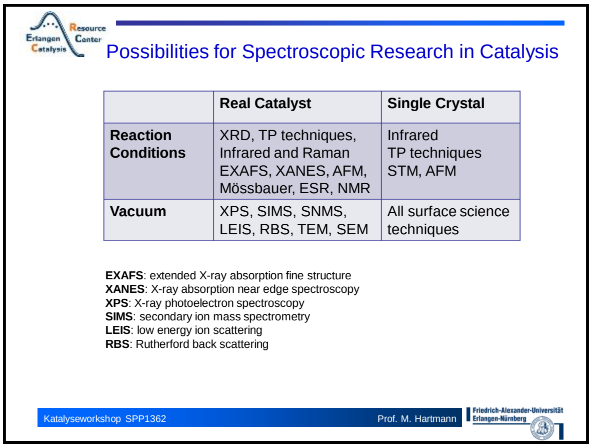
❖ **selectivity and conversion** strongly dependend on the type of catalyst and way of catalyst testing (esp. temperature ranges for activation and reaction)

→ comparison between different types of catalysts under not optimized conditions



Spectroscopic Characterization of Catalysts

Percentage of articles in Appl. Catal. A and B, Cat. Lett. And J. Catal. (2002-2006) that cite results obtained with various characterization techniques.



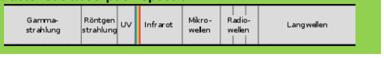
Possibilities for Spectroscopic Research in Catalysis

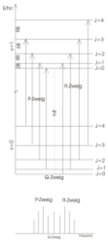
	Real Catalyst	**Single Crystal**
Reaction Conditions	XRD, TP techniques, Infrared and Raman EXAFS, XANES, AFM, Mössbauer, ESR, NMR	Infrared TP techniques STM, AFM
Vacuum	XPS, SIMS, SNMS, LEIS, RBS, TEM, SEM	All surface science techniques

EXAFS: extended X-ray absorption fine structure
XANES: X-ray absorption near edge spectroscopy
XPS: X-ray photoelectron spectroscopy
SIMS: secondary ion mass spectrometry
LEIS: low energy ion scattering
RBS: Rutherford back scattering

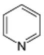
Infrared spectroscopy with probe molecules

Absorption of infrared light leads to molecular rotation and bond vibrations
→Characteristic absorption spectrum

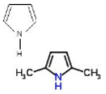




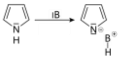
for acidic sites
- pyridine
- CO



for basic sites
- pyrrole (methylated)
- CO_2
- $CHCl_3$
- organic acids



Challanges:



- **Stability of the probe molecule** towards acidic/basic site (decomposition, deprotonation, reaction with the site)
- **size of probe molecule** should be similar to the educt in the catalytic reaction to detect only the accessible sites
- for site strength analysis **high adsorption sensitivity** crucial

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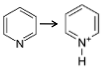
Pyridine IR can distinguish between Lewis and Brönsted acid sites

Brönsted
- protonated probe molecules are formed (pyridinium ion)
- band around **1545 cm^{-1}**



Lewis
just coordination of the probe molecules → absorption band at around **1455 cm^{-1}**

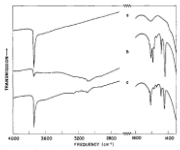
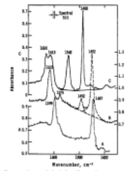
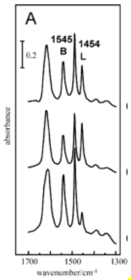


Figure 3. Pyridine adsorbed on silica-alumina: (a) SA calcined and evacuated at 500°; (b) SA exposed to 17 mm. of pyridine at 150° for 1 hr. followed by evacuation for 1 hr. at 150°; (c) evacuated an additional 16 hr. at 150°.



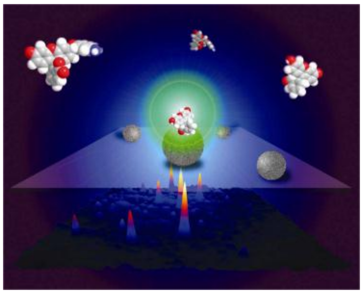


Pyridine is strongly basic
→ no key band shift after adsorption
→To gain information about site strength, less basic molecules like CO necessary (disadvantage CO: adsorption below 100 K necessary to avoid polymer species formation)

In-situ (operando) spectroscopy

Visibility of certain interaction/reaction specific bands →

IR
Raman
NMR
UV-Vis
ESR
…



Andrew J. Foster and Raul F. Lobo, **Identifying reaction intermediates and catalytic active sites through *in situ* characterization techniques,** ***Chem. Soc. Rev.***, 2010, **39**, 4783-4793

(Maybe trivial) Take Home Messages

- Your catalyst is not as well defined as you think (defects,extra-framework species) → thorough characterization of the active site is required!

- Your catalyst is (micro-) porous → transport properties may play an important role.

- MOFs are no the only possible catalysts for the reaction you are interested in → bench marking is required

- Questions to be addressed:

- Is the catalyst stable under the prevailing reaction conditions?
- Is the reaction truly heterogeneous?
- Can the catalyst be recycled?