UNIVERSITÄT LEIPZIG

Topical Workshop – MOF Catalysis

„Microkinetics in Heterogeneous Catalysis“

DFG Priority Program 1362

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12.04.2011

Outline

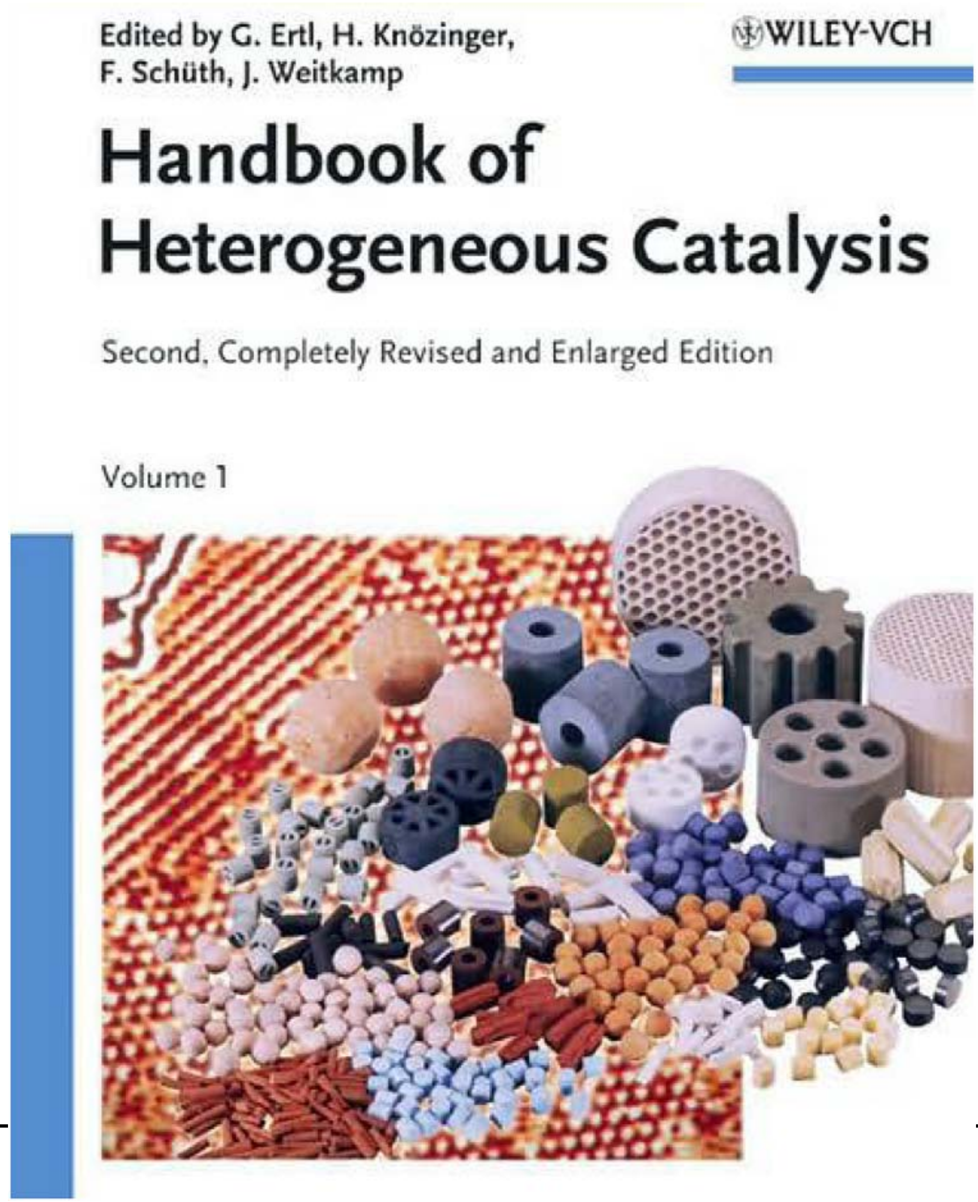
- Introduction
- Microkinetics in Catalysis
  - Fundamentals
  - Kinetics and Reaction Mechnisms: Microkinetic Modelling
  - Examples
- Rate Procurement: Catalytic Testing
  - Testing Reactors and Set-ups
  - Transient Methods
  - Problems and Pitfalls
- Conclusions: MOFs and Microkinetics

References

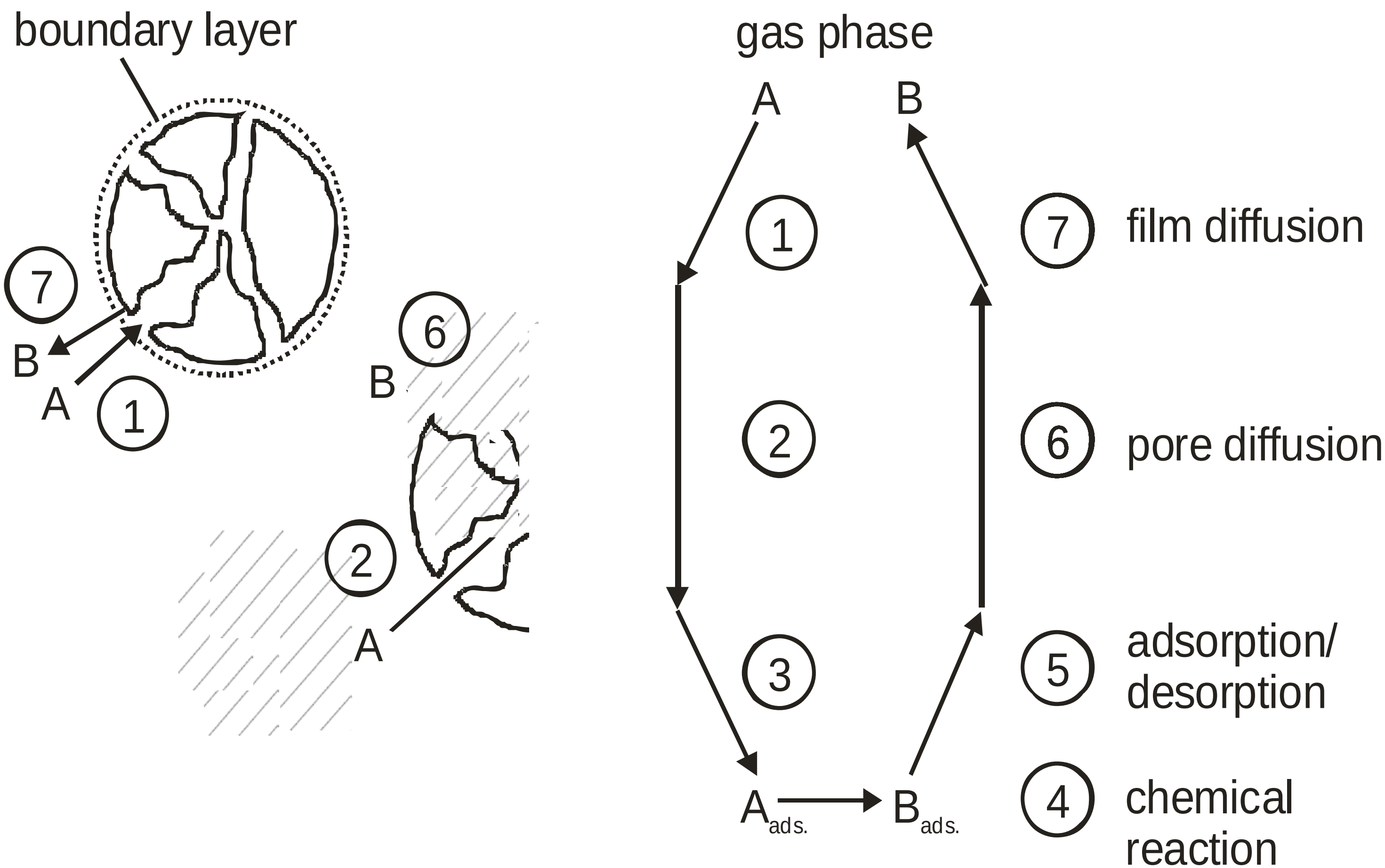
- I. Chorkendorf, J.W. Niemantsverdiet: "**Concepts of Modern Catalysis and Kinetics**", Wiley-VCH, Weinheim (2003).

- "**Handbook of Heterogeneous Catalysis**", G. Ertl, H. Knözinger, F. Schüth, J. Weitkamp, eds., 2nd edition, Wiley-VCH (2008),
  - Chapter 5.2, pp. 1445-1560.
  - F. Kapteijn, R.J. Berger, J.A. Moulijn, Chapter 6.1, pp. 1693-1714.
  - J. Weitkamp, R. Gläser, Chapter 9.2, pp. 2045-2053.

References


Edited by G. Ertl, H. Knözinger,
F. Schüth, J. Weitkamp
WILEY-VCH
Handbook of
Heterogeneous Catalysis
Second, Completely Revised and Enlarged Edition
Volume 1

Steps in Heterogeneous Catalysis

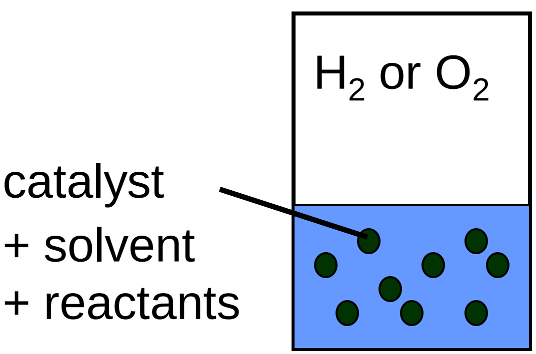


Micro- versus Macrokinetics

Microkinetics = kinetics of the chemical elmentary steps

transport
- mass and heat transfer
- within and across phases
- all reactants and products

Macrokinetics = kinetics of combined reaction and transport

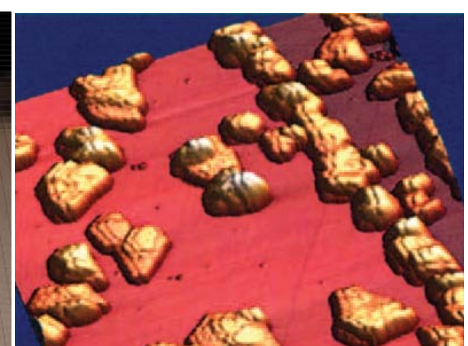


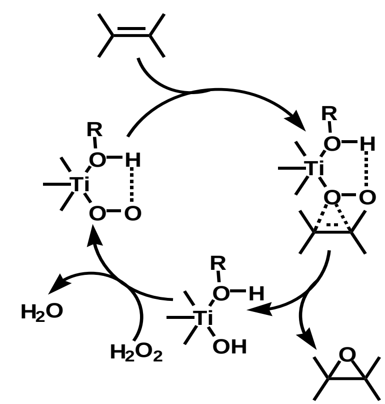
Why Do Microkinetics?

- Catalyst and Reactor Design
  - Nature and utilization of mass, surface area, porosity, active sites
  - Kind and operating conditions of reactors
  - Reaction rate occurs in design equations

➡ Heterogeneous Catalysis Engineering

- Elucidation of Reaction Mechanisms
  - Microkinetic Modelling
  - Falsification rather than proof
  - Requires experimental data of sufficient amount and accuracy





Fundamentals

General reaction equation

$$|\nu_A| A + |\nu_B| B \qquad \nu_C C + \nu_D D$$

$$r = -\frac{d\,c_i}{d\,t}$$

$$r_j = f\left(c_i, T, p, m_{Kat}\right)$$

$$r_j = k(T) \cdot f\left(c_i\right)$$

power rate law

$$r_j = k_j \cdot c_1^a \cdot c_2^b \cdots$$

Arrhenius law

$$k_j = k(T) = k_0 \cdot e^{-\frac{E_A}{R \cdot T}}$$

parallel reactions j

$$R_i = \sum_j \left(\nu_{ij} \cdot r_j\right)$$

Fundamentals (II)

General reaction equation

$$|\nu_A| A + |\nu_B| B \qquad \nu_C C + \nu_D D$$

$$r = -\frac{d\,c_i}{d\,t}$$

→ Problem for heterogeneous catalysis:

c_i at the surface not directly accessible

➢ *concentration at the the surface:*

- loading of sites through adsorption
- coverage Θ → fraction of occupied sites (max. Θ=1)
- for gaseous reactants: Θ only indirectly accessible as a function of the partial pressure

→ **Adsorption models**

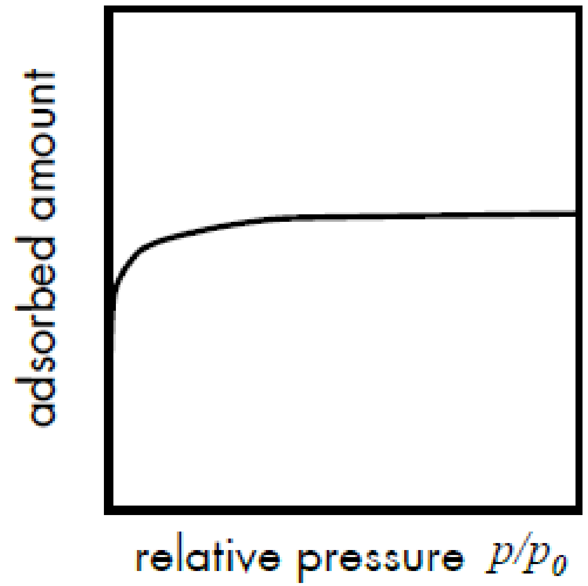
Fundamentals (III)

Adsorption Models – Adsorption Isotherms

Equilibrium loading at constant T in dependence of concnetration or partial pressure

Adsorption capacity of a solid for a given reactant accessible

Several types according to an IUPAC-definition,
often used for kinetic models in heterogeneous catalysis:



→ **Langmuir isotherm**

Fundamentals (IV)

Langmuir Isotherms - Derivation

Treatment of adsorption as chemical equilibrium:

Gas + free adsorption site (AZ) adsorbate cmplex (AK)

Conzentration measures:

- Gas: partial pressure p_A;
- AZ: relative density (on surface);
- AK: relative coverage.

Fundamentals (V)

Langmuir Isotherm – Derivation (II)

Adsorption equilibrium:

$$K_L = \frac{\Theta}{p \cdot \Theta_0} = \frac{\Theta}{p \cdot (1 - \Theta)}$$

↓

$$r = k \cdot \Theta_A \cdot \Theta_B$$

$$K_L \cdot p \cdot (1 - \Theta) = \Theta$$

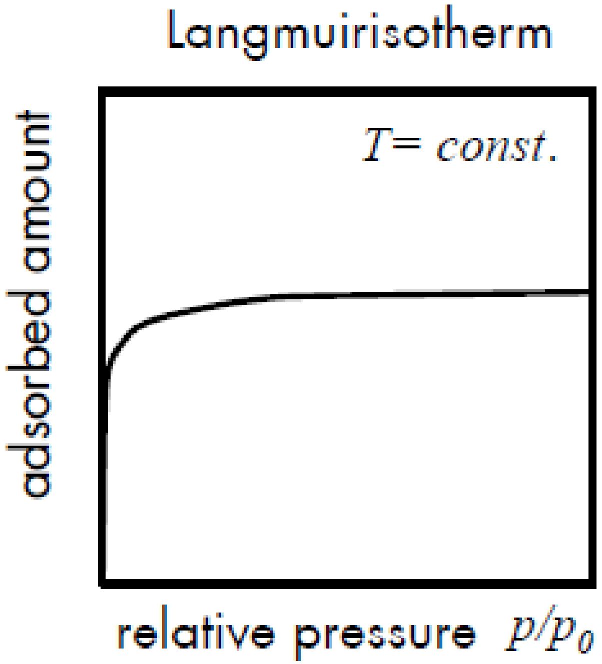
$$K_L \cdot p - K_L \cdot p \cdot \Theta = \Theta$$

$$K_L \cdot p = \Theta \cdot (1 + K_L \cdot p)$$

$$\Theta = \frac{K_L \cdot p}{1 + K_L \cdot p}$$

→

here: K = Langmuir constant K_L



Microkinetic Modelling

Kinetic Models

→ Kinetics of heterogeneously catalyzed reactions often complex

→ simplification:

- *reaction rate is determined by the slowest step; all other steps can be treated as chemical equilibria*

gernerally (Hougen-Watson)

$$r_A = \frac{(\text{rate factor})\,(\text{driving force})}{(\text{inhibition term})^n}$$

- ***rate factor:***
  rate constants of slowest step and adsorption constants
- ***driving force:***
  experimentally accessible concentrations and chemical equilibrium constant
- ***inhibition (adsorption) term:***
  coverage of active sites → inhibition by site blocking

Microkinetic Modelling (II)

Hougen-Watson-Kinetics

Reaction A $\rightarrow$ P

rate-limiting step	driving force	rate factor	inhibition term	n
adsorption A	$p_A - \frac{p_P}{K}$	$k \cdot c_L$	$\left(1 + \frac{b_A \cdot p_P}{K} + b_P \cdot p_P\right)$	1
desorption R	$p_A - \frac{p_P}{K}$	$k \cdot c_L \cdot K \cdot b_P$	$(1 + b_A \cdot p_A + b_P \cdot p_A \cdot K)$	1
surface reaction	$p_A - \frac{p_P}{K}$	$k \cdot c_L \cdot b_A$	$(1 + b_A \cdot p_A + b_P \cdot p_A)$	1
dissociative adsorption of A	$p_A - \frac{p_P}{K}$	$k \cdot c_L \cdot b_A$	$\left(1 + 2 \cdot \sqrt{\frac{b_A \cdot p_P}{K}} + b_P \cdot p_P\right)$	2

$$K = \frac{p_P}{p_A} \qquad p_A - \frac{p_P \cdot p_A}{p_P} \qquad \Theta = \frac{K_L \cdot p}{1 + K_L \cdot p}$$

Microkinetic Modelling (III)

surface reaction is rate-determining

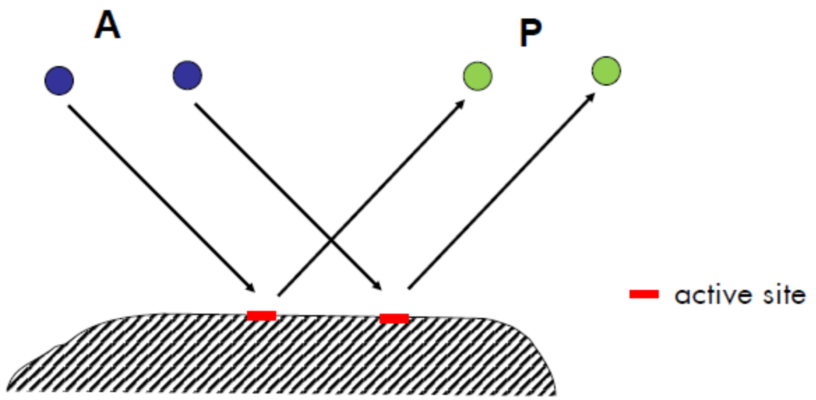
unimolecular reaction

$A \rightarrow P$

→ Fast adsorption and desorption: adsorption equilibrium

→ Langmuir isotherm

$$r_A = \frac{k b_A L \left(p_A - \frac{p_B}{K} \right)}{\left(1 + b_A p_A + b_B p_B\right)}$$

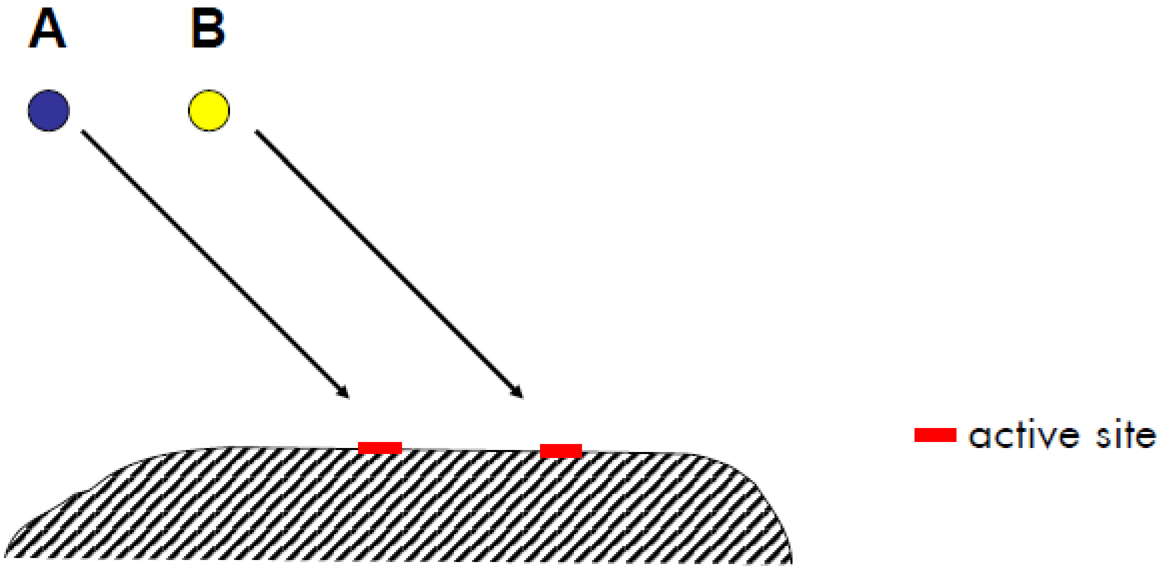


Microkinetic Modelling (IV)

surface reaction is rate-determining

bimolecular reaction

$A + B \rightarrow P$



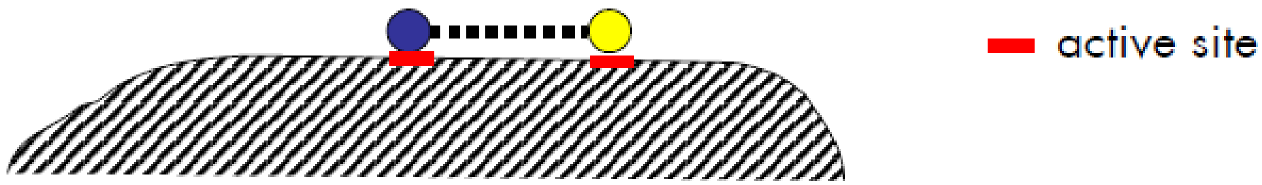
Microkinetic Modelling (V)

surface reaction is rate-determining

bimolecular reaction

$A + B \rightarrow P$

Langmuir-Hinshelwood-Mechanism



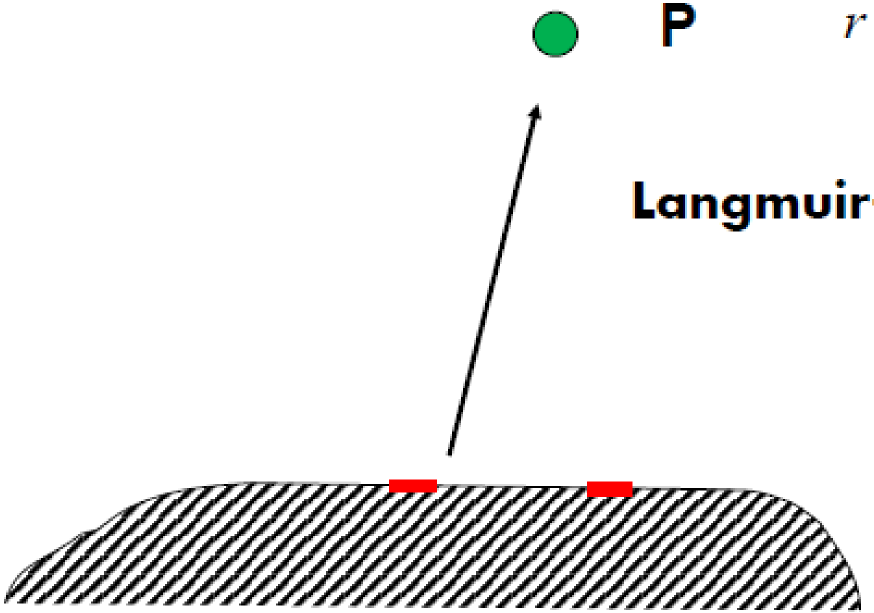
Microkinetic Modelling (V)

surface reaction is rate-determining

bimolecular reaction

$A + B \rightarrow P$

$$r = k \cdot \Theta_A \cdot \Theta_B$$



$$r = \frac{k \cdot b_A \cdot b_B \cdot p_A \cdot p_B}{(1 + b_A \cdot p_A + p_A \cdot p_B + b_P \cdot p_P)^2}$$

Langmuir-Hinshelwood-Mechanism

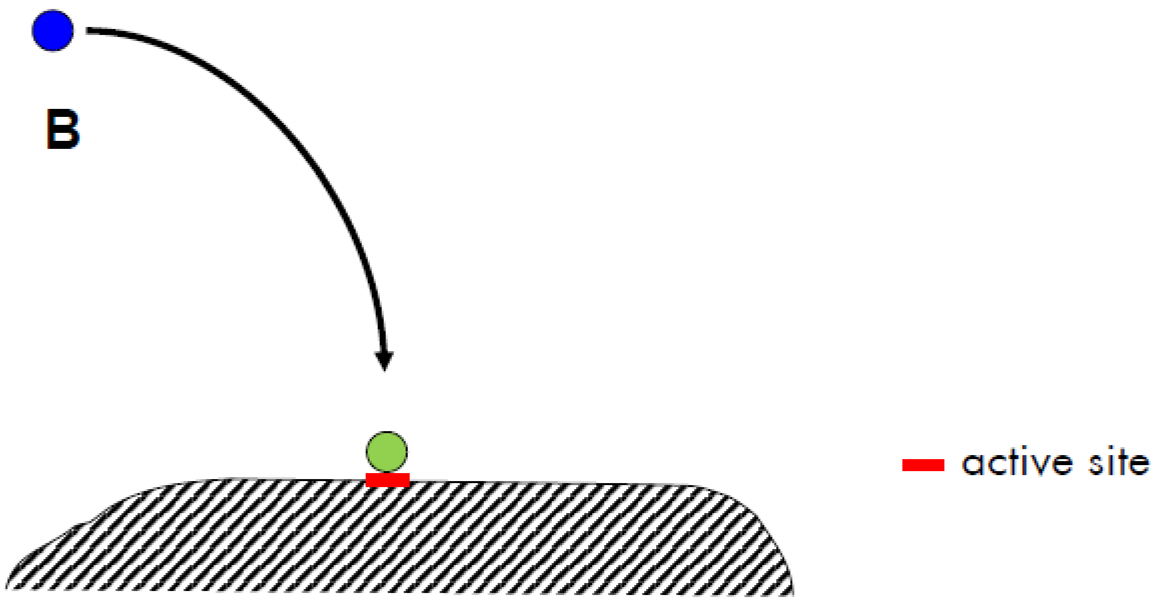
active site

Microkinetic Modelling (VI)

surface reaction is rate-determining

bimolecular reaction

A + B → P



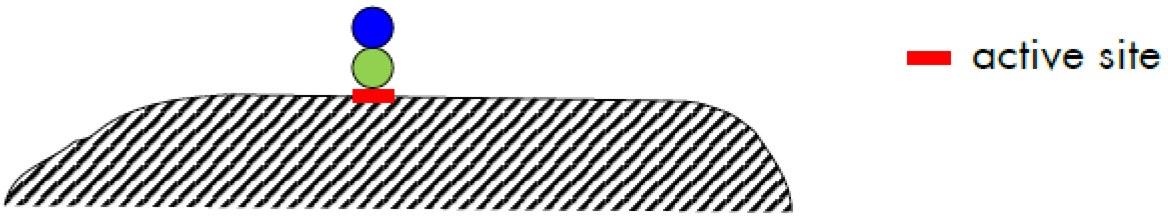
Microkinetic Modelling (VI)

surface reaction is rate-determining

bimolecular reaction

$A + B \rightarrow P$

Eley-Rideal-Mechanism



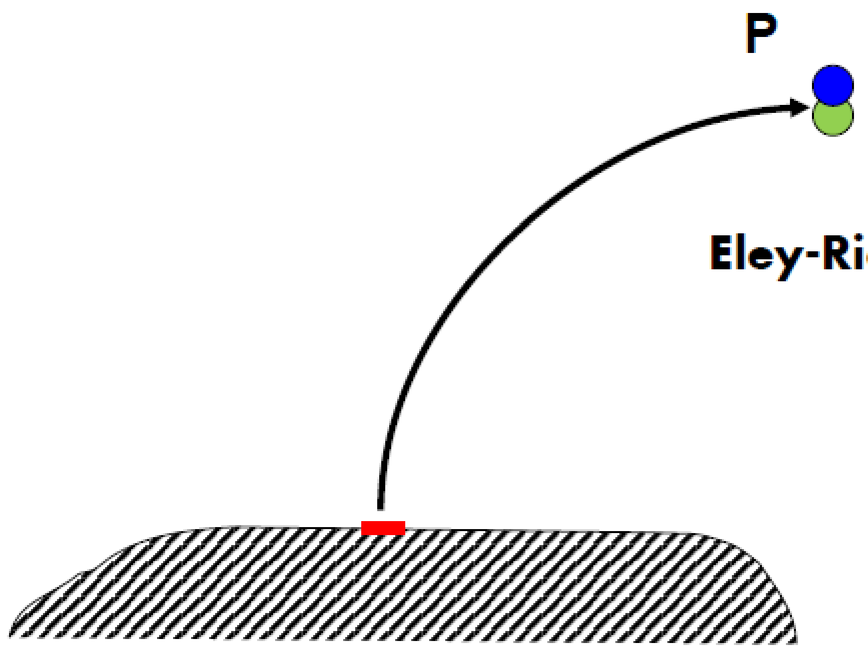
Microkinetic Modelling (VI)

surface reaction is rate-determining

bimolecular reaction

$A + B \rightarrow P$

$$r = k \cdot \Theta_A \cdot \Theta_B$$



$$r = k \frac{k \cdot b_A \cdot p_A \cdot p_B}{1 + b_A \cdot p_A}$$

Eley-Rideal-Mechanism

active site

Terms in Kinetics

	Heterogeneous catalysis	*Biocatalysis*
Kinetics	Langmuir–Hinshelwood	Michaelis–Menten
Rate expression	$r = \frac{kN_T K_A p_A}{1 + K_A p_A}$	$\nu = \frac{kE_0 C_A}{k_M + C_A}$
	K_A = adsorption constant	k_M = Michaelis constant
Linearization	Hougen–Watson	Lineweaver–Burke
Catalytic center	"Active site"	Enzyme
Turnover number		k/s^{-1}
Turnover frequency	$\frac{r}{N_T}/s^{-1}$	
Number of turnovers	No. of molecules converted/No. of active sites	

Example 1: N_2O-Decomposition

$$2N_2O \longrightarrow 2N_2 + O_2$$

elementary steps

$$\begin{array}{lll} 1.\ N_2O + {}^* & \leftrightarrows N_2O^* & |2| \\ 2.\ N_2O^* & \rightarrow N_2 + O^* & |2| \\ 3.\ 2\ O^* & \leftrightarrows O_2 + 2^* & |1| \end{array}$$

$$r_1 = r_{+1} - r_{-1} = k_1 N_T p_{N_2O} \theta_* - k_{-1} N_T \theta_{N_2O}$$

$$r_2 = r_{+2} = k_2 N_T \theta_{N_2O}$$

$$r_3 = r_{+3} - r_{-3} = k_3 N_T s \theta_{O*}^2 - k_{-3} N_T s p_{O_2} \theta_*^2$$

$$r = r_1 = r_2 = 2r_3$$

steady-state assumption

$$0 = \frac{d\theta_*}{dt} = k_{-1}\theta_{N_2O*} + 2k_3 s \theta_{O*}^2 - k_1 p_{N_2O}\theta_* - 2k_{-3} s p_{O_2} \theta_*^2$$

$$0 = \frac{d\theta_{O*}}{dt} = k_2 \theta_{N_2O*} + 2k_{-3} s p_{O_2} \theta_*^2 - 2k_3 s \theta_{O*}^2$$

$$0 = \frac{d\theta_{N_2O*}}{dt} = k_1 p_{N_2O}\theta_* - k_{-1}\theta_{N_2O*} - k_2 \theta_{N_2O*}$$

Example 1: N_2O-Decomposition (II)

site balance

$$N_T = [N_2O^*] + [O^*] + [^*]$$

$$1 = \theta_{N_2O^*} + \theta_{O^*} + \theta_*$$

assumption: step 2 is rate limiting, steps 1, 3 in quasi-equilibrium

$$K_1 = \frac{k_1}{k_{-1}} = \frac{\theta_{N_2O^*}}{p_{N_2O}\theta_*} \Longrightarrow \theta_{N_2O^*} = K_1 p_{N_2O}\theta_*$$

$$K_3 = \frac{k_3}{k_{-3}} = \frac{p_{O_2}\theta_*^2}{\theta_{O^*}^2} \Longrightarrow \theta_{O^*} = \sqrt{p_{O_2}/K_3}\,\theta_*$$

$$r = r_2$$

$$r = \frac{k_2 N_T K_1 p_{N_2O}}{1 + K_1 p_{N_2O} + \sqrt{p_{O_2}/K_3}}$$

Example 2: CO-Oxidation

application: automotive off-gas treatment

active component: noble metals

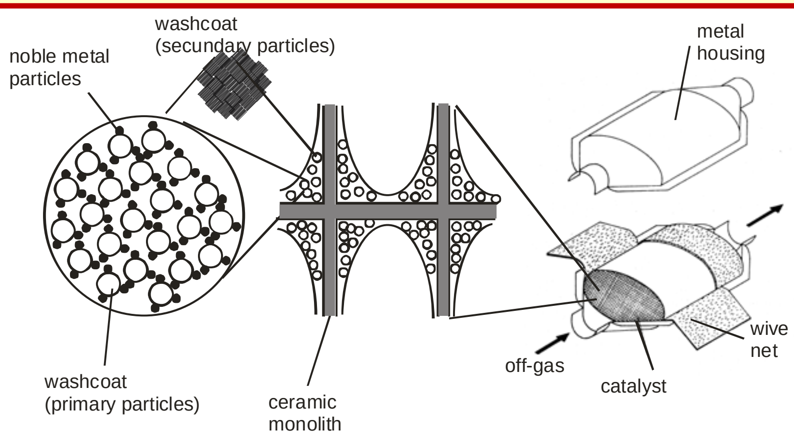
conversions:

a) $C_nH_m + (n + m/4)\ O_2 \longrightarrow n\ CO_2 + (m/2)\ H_2O$

b) $2\ CO + O_2 \longrightarrow 2\ CO_2$

c) $2\ NO + 2\ CO \longrightarrow N_2 + 2\ CO_2$

$2\ (n + m/4)\ NO + C_nH_m \longrightarrow (n + m/4)\ N_2 + (m/2)\ H_2O + n\ CO_2$



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Example 2: CO-Oxidation (II)

elementary steps

$$(1)\quad CO + * \xleftrightarrow{K_1} CO^*$$

$$(2)\quad O_2 + 2^* \xleftrightarrow{K_2} 2O^*$$

$$(3)\quad CO^* + O^* \underset{k_3^-}{\overset{k_3^+}{\rightleftarrows}} CO_2^* + * \ \text{(RDS)}$$

$$(4)\quad CO_2^* \xleftrightarrow{K_4^{-1}} CO_2 + *$$

surface coverages

$$\theta_{CO} = K_1\, p_{CO}\, \theta_*$$

$$\theta_O = \sqrt{K_2\, p_{O_2}}\, \theta_*$$

$$\theta_{CO_2} = K_4^{-1}\, p_{CO_2}\, \theta_*$$

$$\theta_{CO} + \theta_O + \theta_{CO_2} + \theta_* = 1 \Rightarrow \theta_* = \frac{1}{1 + K_1\, p_{CO} + \sqrt{K_2\, p_{O_2}} + K_4^{-1}\, p_{CO_2}}$$

Example 2: CO-Oxidation (III)

rate

$$r = k_3^+ \theta_{CO}\theta_O - k_3^- \theta_{CO_2}\theta_* = k_3^+ K_1 \sqrt{K_2}\, p_{CO} \sqrt{p_{O_2}} \left(1 - \frac{p_{CO_2}}{p_{CO}\sqrt{p_{O_2}}\, K_G}\right)\theta_*^2$$

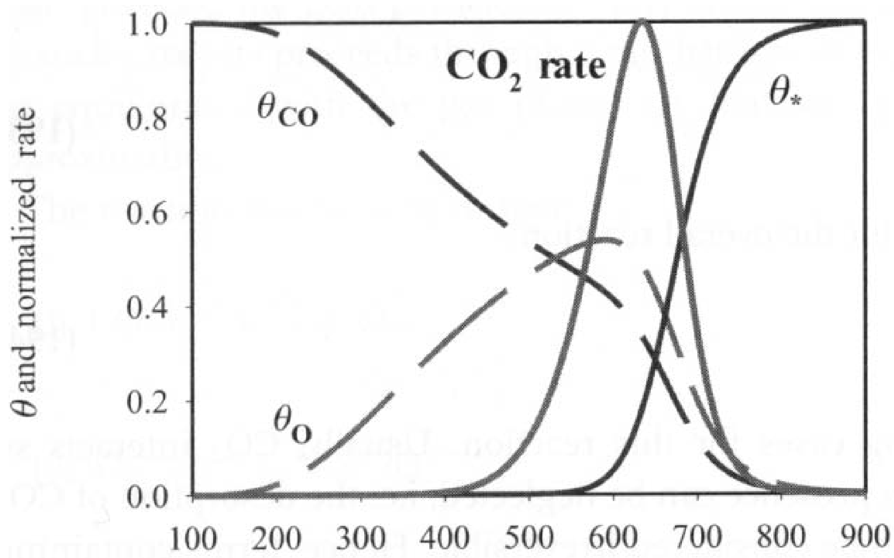
$$K_G = K_1 \sqrt{K_2}\, K_3\, K_4$$

$$r = \frac{k_3^+ \sqrt{K_2\, p_{O_2}}}{K_1\, p_{CO}}$$

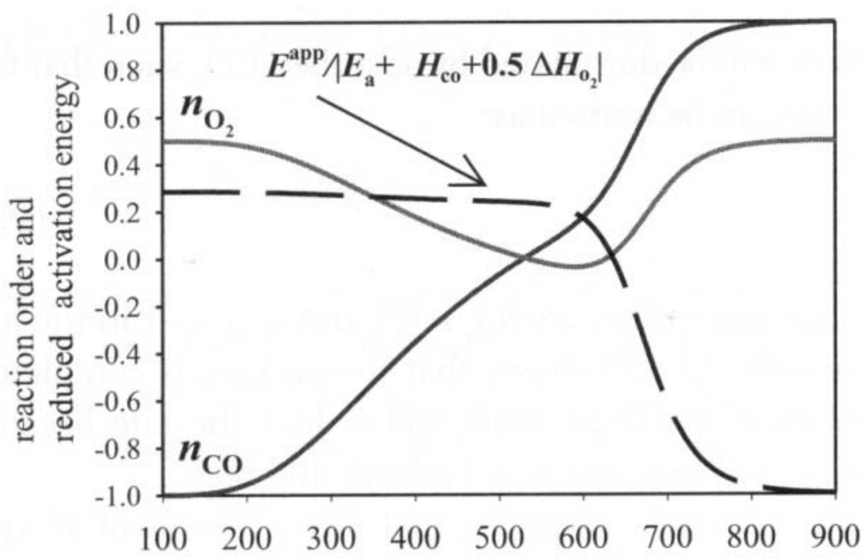
low temperature

$$r = k_3^+ K_1 \sqrt{K_2}\, p_{CO} \sqrt{p_{O_2}}$$

high temperature



temperature / K



temperature / K

Example 3: NH_3-Synthesis

$$N_2 + 3H_2 \leftrightarrow 2NH_3$$

elementary steps

$$N_2 + {}^* \rightleftarrows N_2{}^* \quad \frac{d\theta_{N_2}}{dt} = P_{N_2} k_1^+ \theta_* - k_1^- \theta_{N_2} = 0 \Rightarrow \theta_{N_2} = K_1 P_{N_2} \theta_*$$

$$N_2{}^* + {}^* \xrightarrow{RLS} 2N* \quad r = r^+ - r^- = k_2^+ \theta_{N_2} \theta_* - k_2^- \theta_N^2$$

$$N^* + H^* \rightleftarrows NH^* + {}^* \quad \frac{d\theta_{NH}}{dt} = k_3^+ \theta_N \theta_H - k_3^- \theta_{NH} \theta_* = 0 \Rightarrow \theta_N = \frac{\theta_{NH}\theta_*}{K_3 \theta_H}$$

$$NH^* + H^* \rightleftarrows NH_2{}^* + {}^* \quad \frac{d\theta_{NH_2}}{dt} = k_4^+ \theta_{NH} \theta_H - k_4^- \theta_{NH_2} \theta_* = 0 \Rightarrow \theta_{NH} = \frac{\theta_{NH_2}\theta_*}{K_4 \theta_H}$$

$$NH^* + H^* \rightleftarrows NH_3{}^* + {}^* \quad \frac{d\theta_{NH_3}}{dt} = k_5^+ \theta_{NH_2} \theta_H - k_5^- \theta_{NH_3} \theta_* = 0 \Rightarrow \theta_{NH_2} = \frac{\theta_{NH_3}\theta_*}{K_5 \theta_H}$$

$$NH_3{}^* \rightleftarrows NH_3 + {}^* \quad \frac{d\theta_{NH_2}}{dt} = -k_6^+ \theta_{NH_3} + k_6^- P_{NH_3} \theta_* = 0 \Rightarrow \theta_{NH_3} = \frac{1}{K_6} P_{NH_3} \theta_*$$

$$H_2 + 2^* \rightleftarrows 2H^* \quad \frac{d\theta_H}{dt} = k_7^+ P_{H_2} \theta_*^2 - k_7^- \theta_H^2 = 0 \Rightarrow \theta_H = \sqrt{K_7 P_{H_2}}\, \theta_*$$

Example 3: NH_3-Synthesis (II)

surface coverages

$$\theta_{N_2} = K_1 P_{N_2} \theta_* \equiv a_1 \theta_*$$

$$\theta_N = \frac{P_{NH_3}}{K_3 K_4 K_5 K_6 (K_7 P_{H_2})^{\frac{3}{2}}} \theta_* \equiv a_3 \theta_*$$

$$\theta_{NH} = \frac{P_{NH_3}}{K_4 K_5 K_6 K_7 P_{H_2}} \theta_* \equiv a_4 \theta_*$$

$$\theta_{NH_2} = \frac{P_{NH_3}}{K_5 K_6 \sqrt{K_7 P_{H_2}}} \theta_* \equiv a_5 \theta_*$$

$$\theta_{NH_3} = \frac{1}{K_6} P_{NH_3} \theta_* \equiv a_6 \theta_*$$

$$\theta_H = \sqrt{K_7 P_{H_2}} \theta_* \equiv a_7 \theta_*$$

$$\theta_* = 1 - \sum_i a_i \theta_* \Rightarrow \theta_* = \frac{1}{1 + \sum_i a_i}$$

$$\theta_* = \frac{1}{1 + K_1 P_{N_2} + \frac{P_{NH_3}}{K_3 K_4 K_5 K_6 \sqrt{(K_7 P_{H_2})^3}} + \frac{P_{NH_3}}{K_4 K_5 K_6 K_7 P_{H_2}} + \frac{P_{NH_3}}{K_5 K_6 \sqrt{K_7 P_{H_2}}} + \frac{1}{K_6} P_{NH_3} + \sqrt{K_7 P_{H_2}}} \quad (48)$$

Example 3: NH_3-Synthesis (III)

rate

$$r = r^+ - r^- = k_2^+ \theta_{N_2} \theta_* - k_2^- \theta_N^2$$

$$r = k_2^+ K_1 P_{N_2} \theta_*^2 - k_2^- \left[\frac{P_{NH_3}}{K_3 K_4 K_5 K_6 (K_7 P_{H_2})^{3/2}} \right]^2 \theta_*^2$$

$$r = k_2^+ K_1 P_{N_2} \left(1 - \frac{P_{NH_3}^2}{K_1 K_2 K_3^2 K_4^2 K_5^2 K_6^2 K_7^3 P_{H_2}^3 \, P_{N_2}} \right) \theta_*^2$$

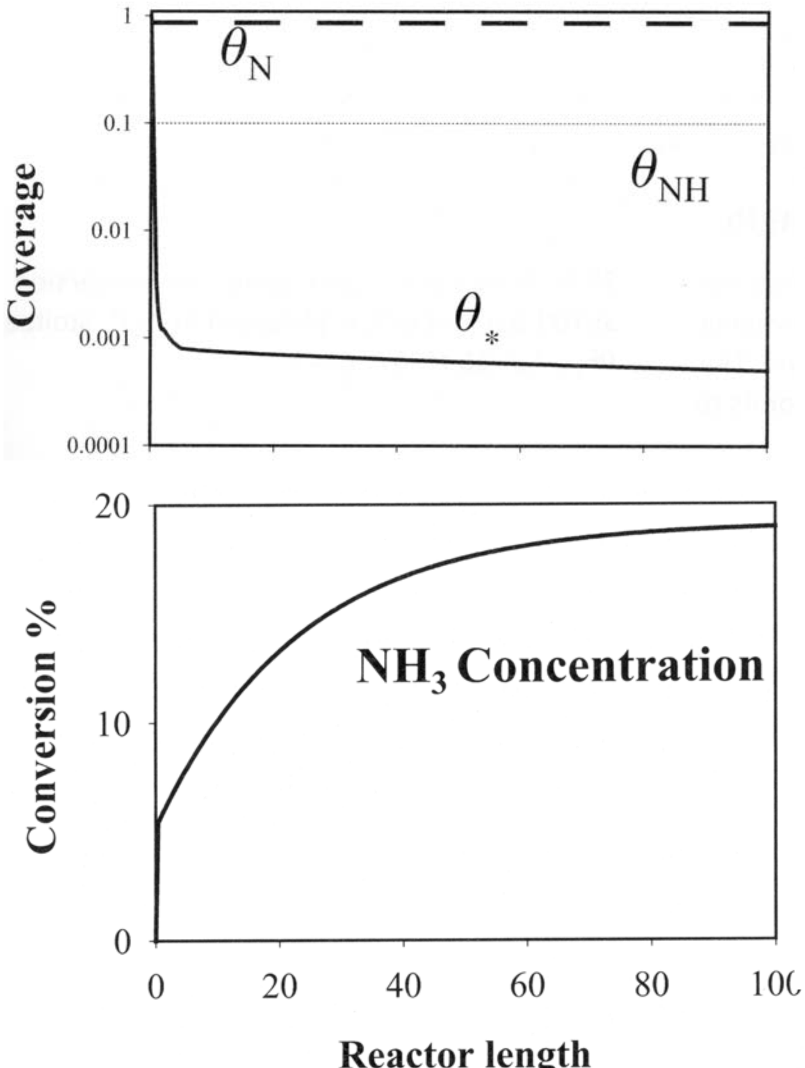
$$r = k_2^+ K_1 P_{N_2} \theta_*^2 - k_2^- \left[\frac{P_{NH_3}}{K_3 K_4 K_5 K_6 (K_7 P_{H_2})^{3/2}} \right]^2 \theta_*^2$$

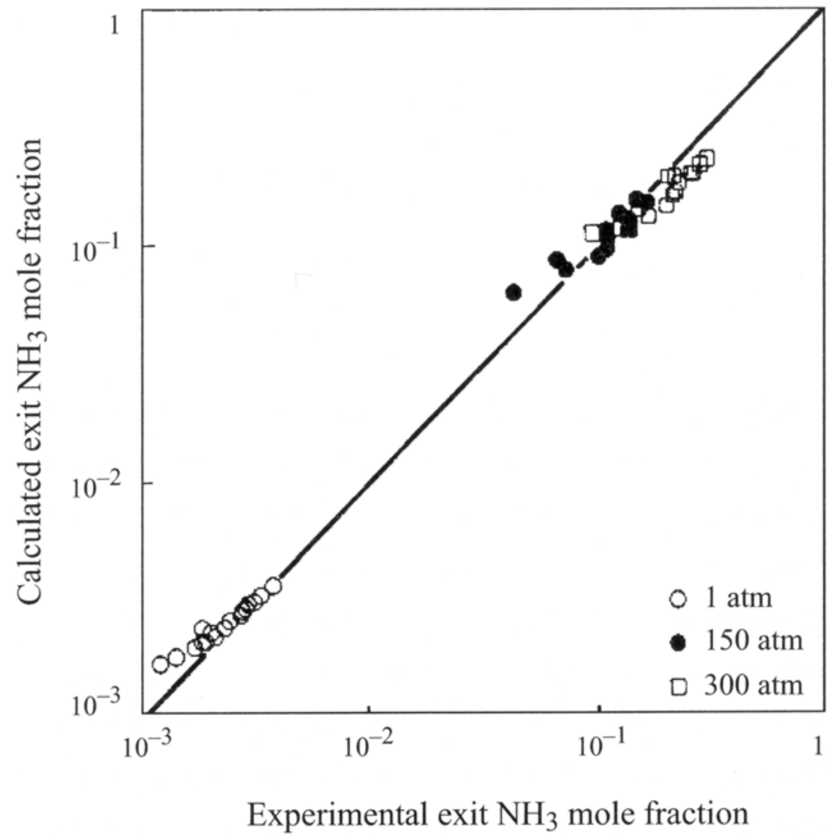
$$\frac{P_{NH_3}^2}{P_{H_2}^3 \, P_{N_2}} = K_1 K_2 K_3^2 K_4^2 K_5^2 K_6^2 K_7^3 = K_G$$

equilibrium condition

$$r = k_2^+ K_1 P_{N_2} \left(1 - \frac{P_{NH_3}^2}{K_G P_{H_2}^3 \, P_{N_2}} \right) \theta_*^2$$

Example 3: NH_3-Synthesis (IV)





Measurement of Reaction Rates

$$\nu_A A + \nu_B B + \ldots \rightleftarrows \nu_P P + \nu_Q Q + \ldots$$

$$\text{PFR: } \frac{dx_A}{d\left(\frac{W}{F_A^0}\right)} = -\nu_A \times r$$

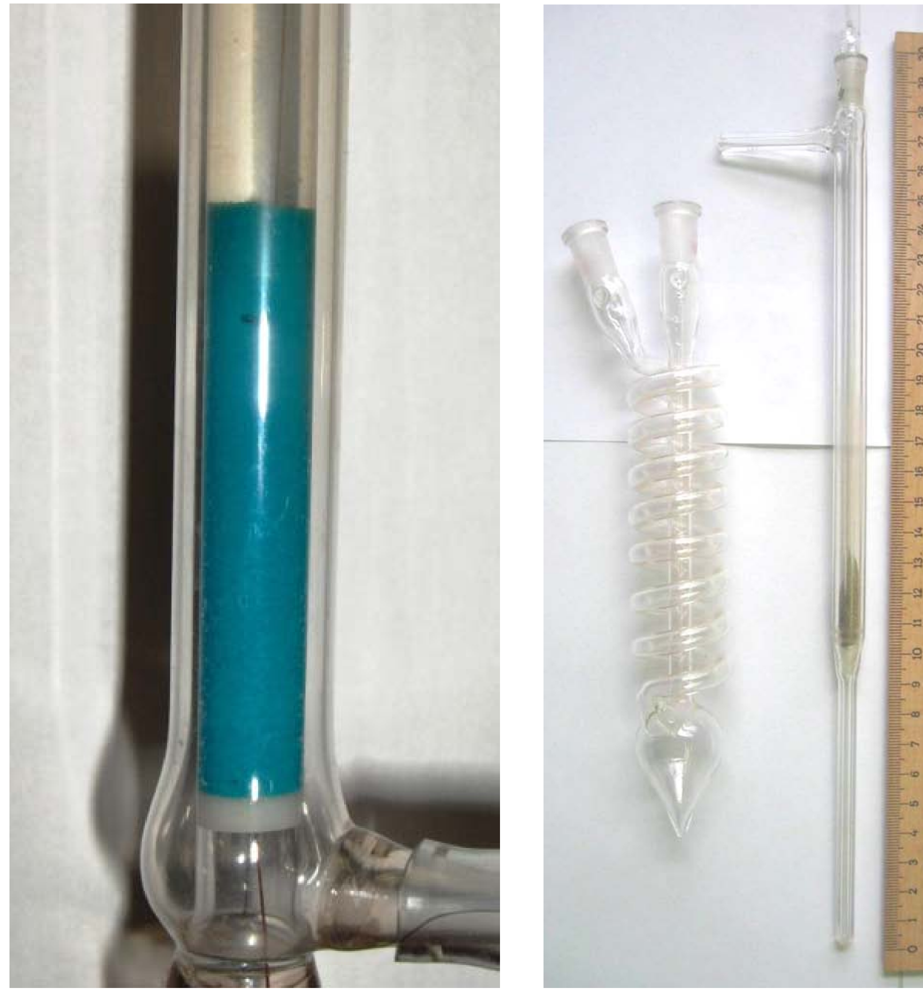
$$\frac{W}{F_A^0} = -\int_0^{x_A} \frac{dx}{\nu_A r}$$

$$\text{CSTR: } \frac{x_A}{\left(\frac{W}{F_A^0}\right)} = -\nu_A \times r$$

$$\text{Batch: } N_A \frac{dx_A}{dt} = -\nu_A \times r$$

Reactors for Catalytic Testing

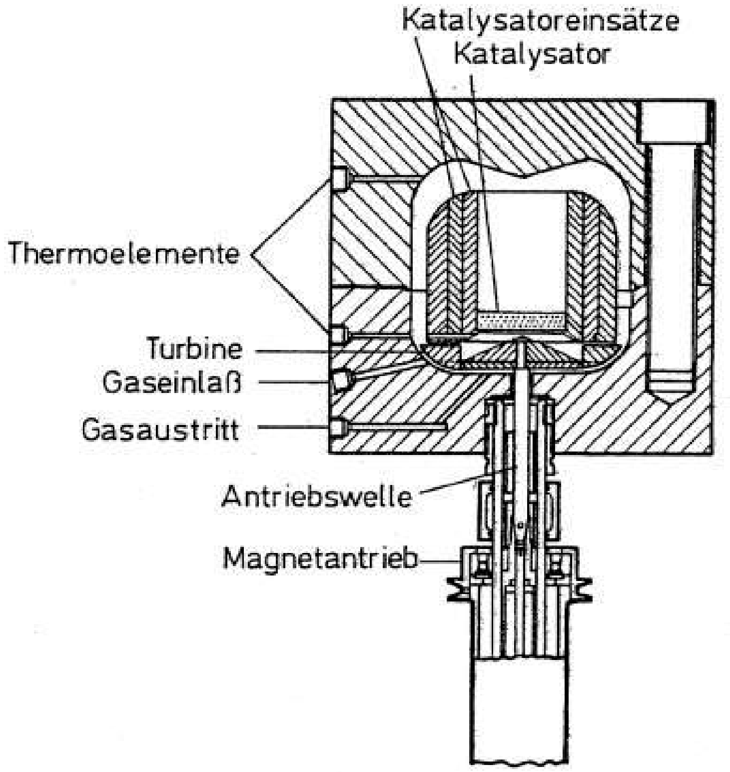
Batch



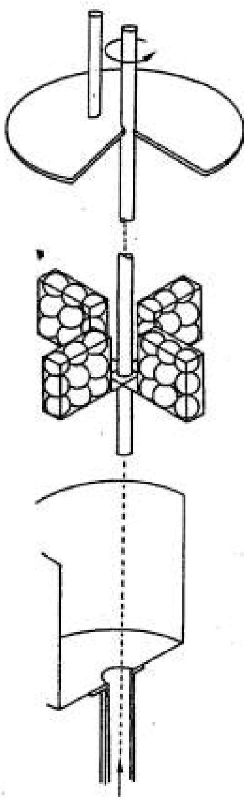
Continuous flow: PFR

Reactors for Kinetic Measurements

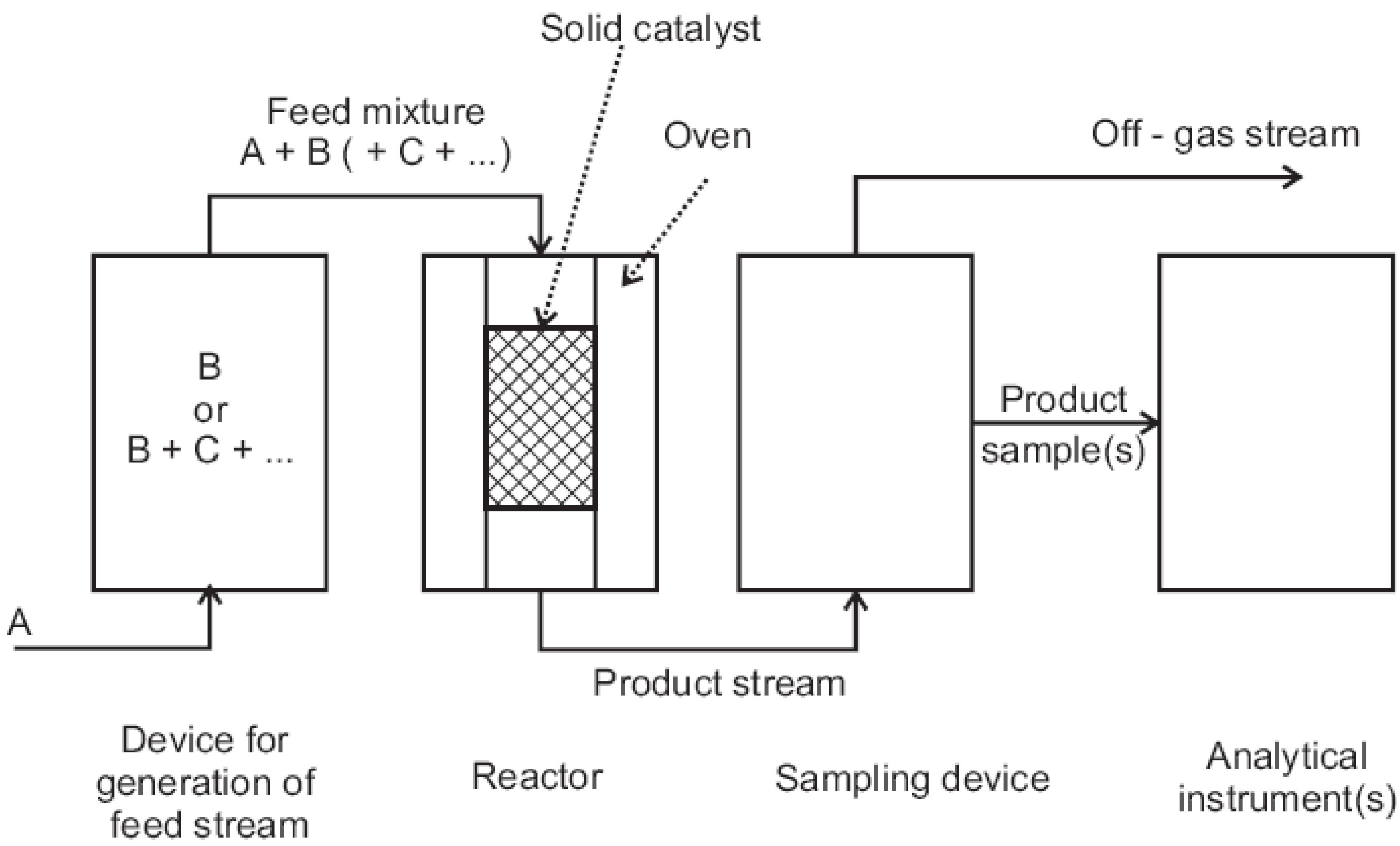
Gradientless reactor
with internal recycling loop



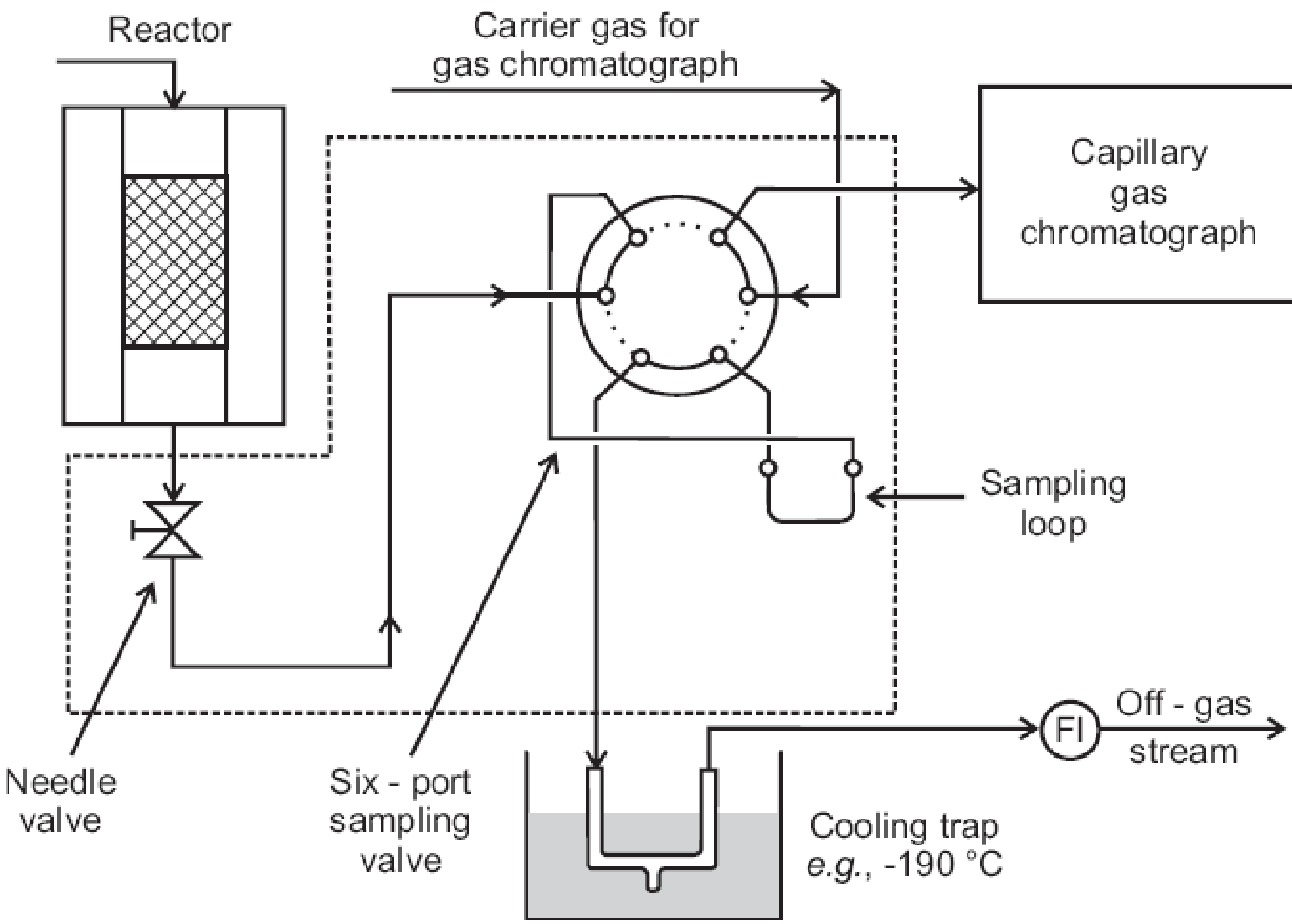
spinning basket reactor



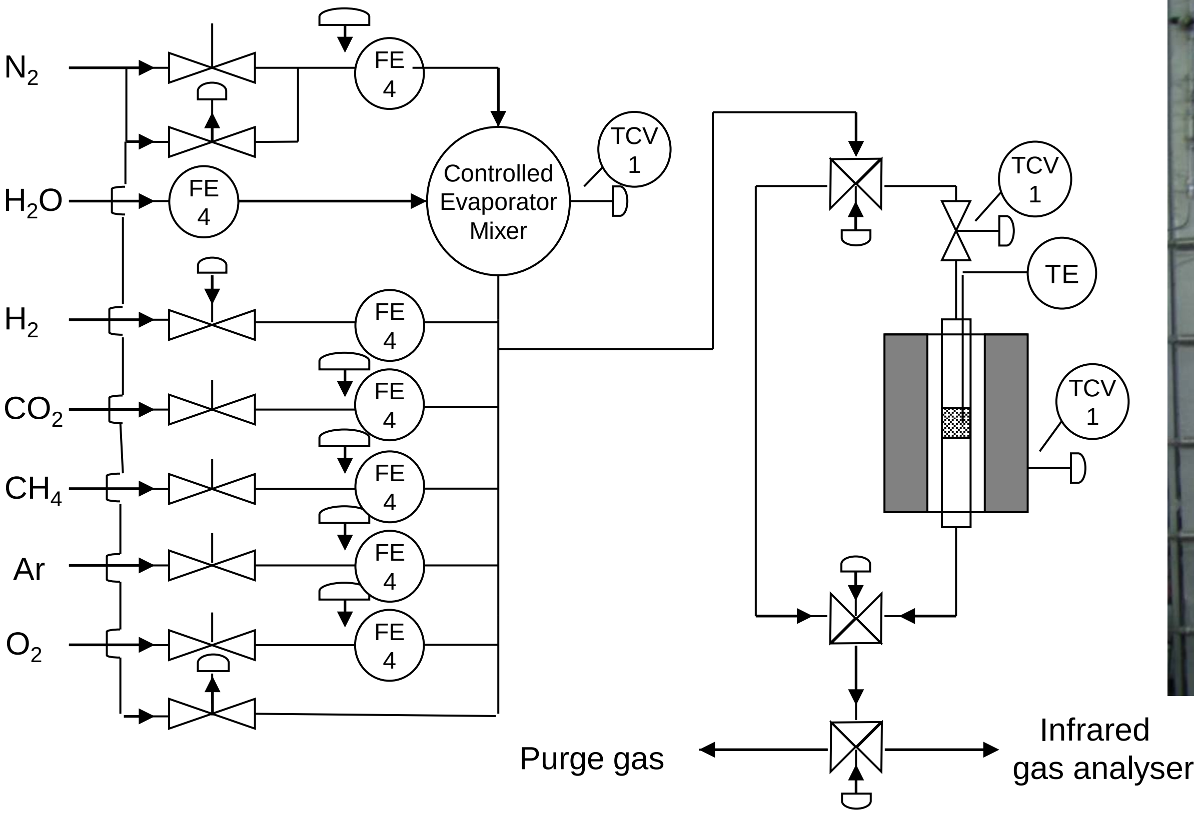
Set-Ups for Kinetic Measurements



Set-Ups for Kinetic Measurements (II)



Set-Ups for Kinetic Measurements (III)



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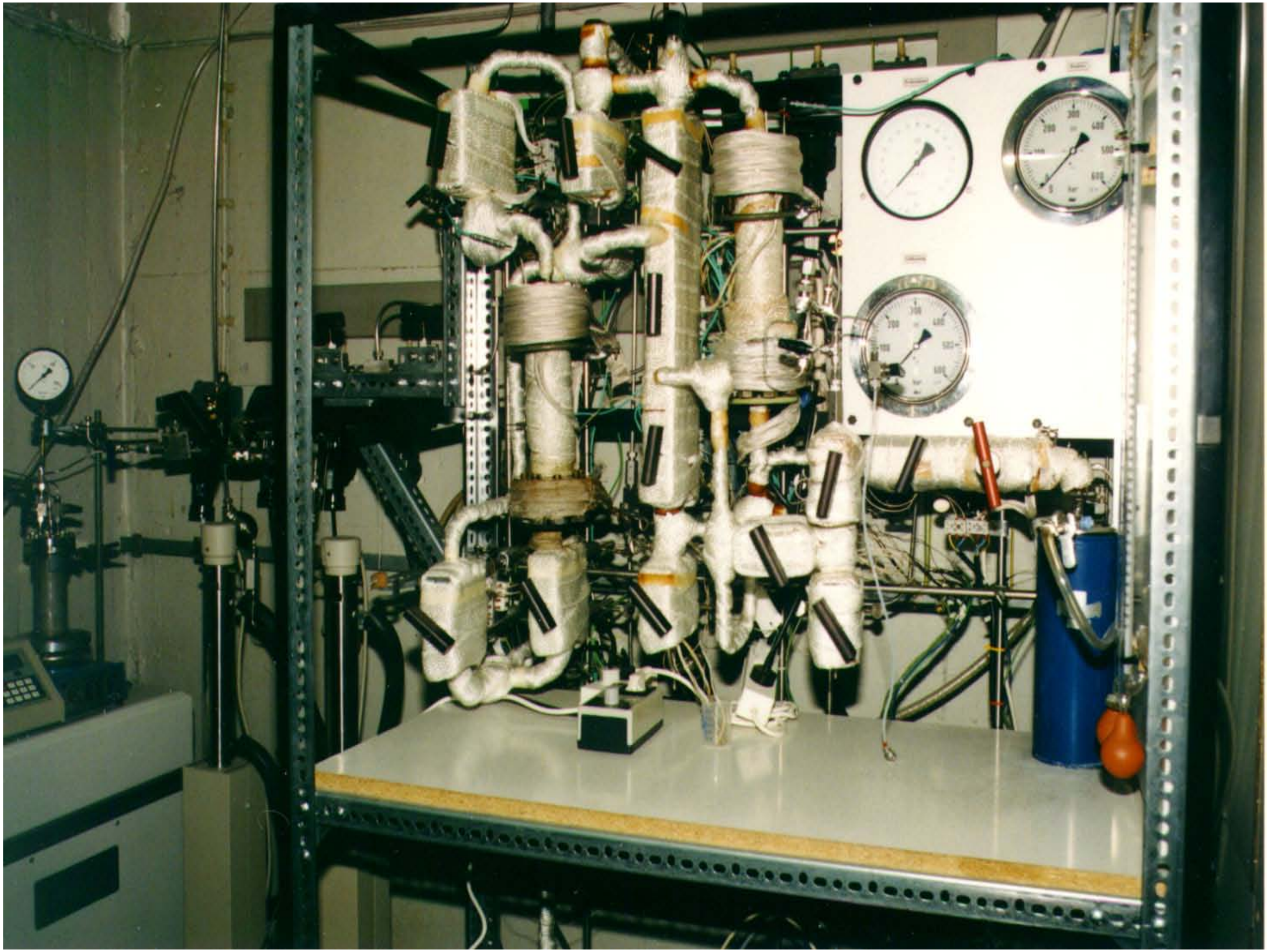
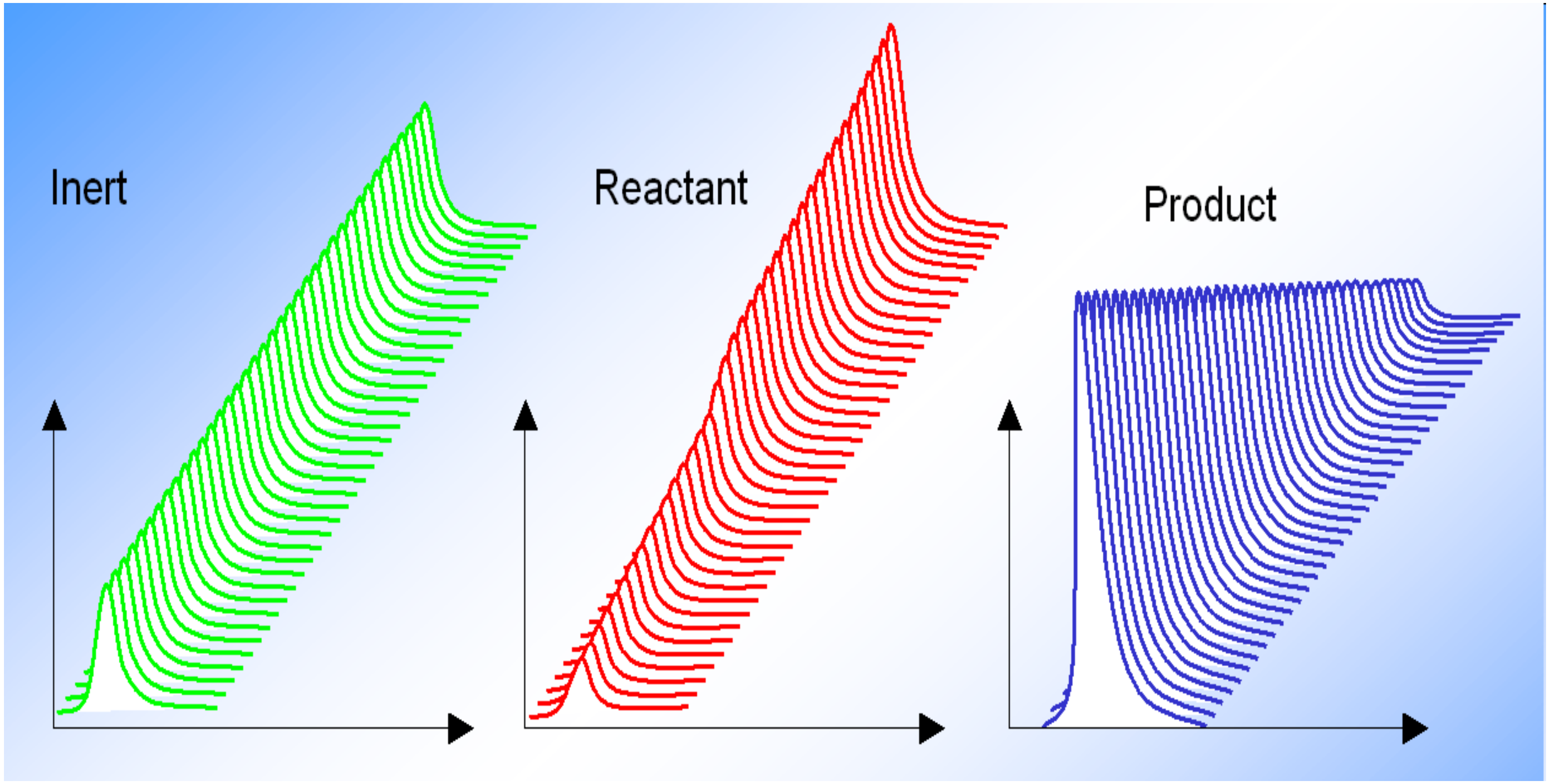
Set-Ups for Kinetic Measurements (IV)



Transient Methods

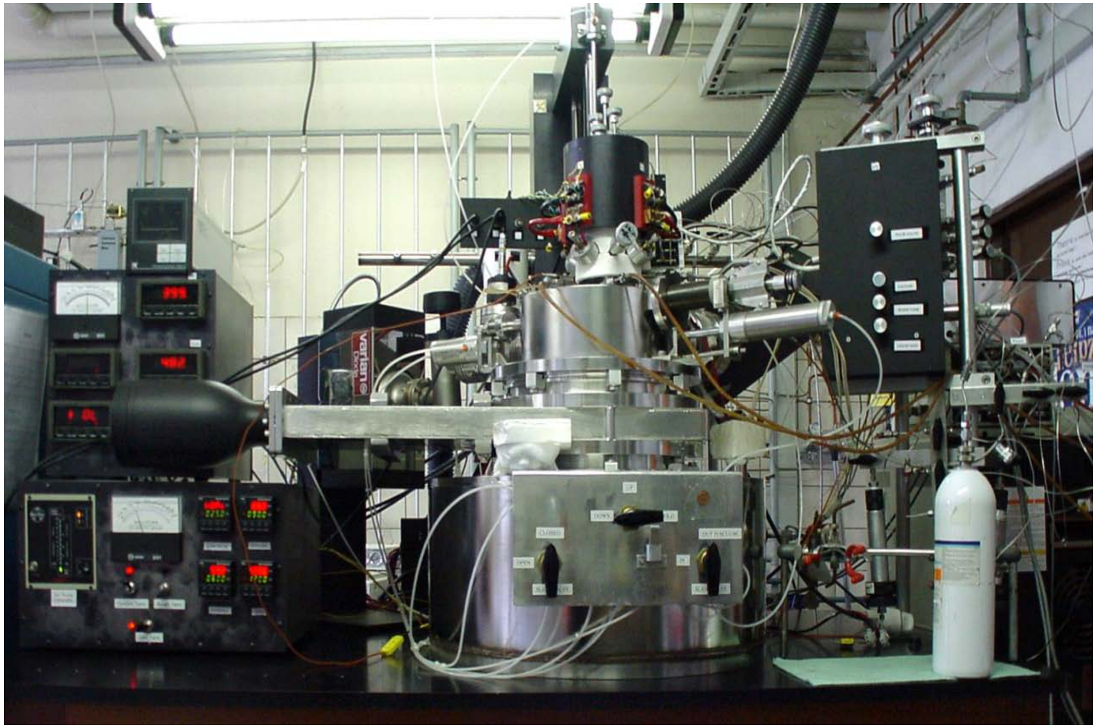
TAP = Temporal Analysis of Products

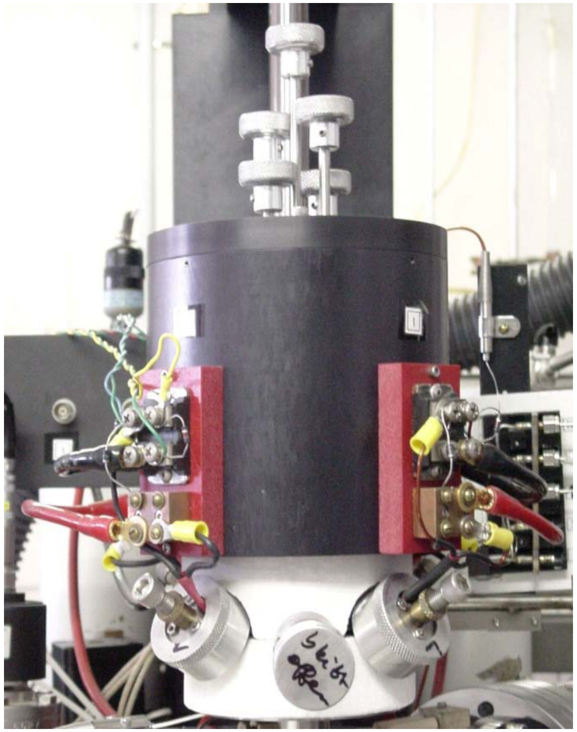


R.J. Berger, F. Kapteijn, J.A. Moulijn, G. B Marin, J. De Wilde, M. Olea, D. Chen, A. Holmen, L. Lietti, E. Tronconi, Y. Schuurman, Appl. Catal. A: General 342 (2008) 3.

Transient Methods (II)

TAP = Temporal Analysis of Products





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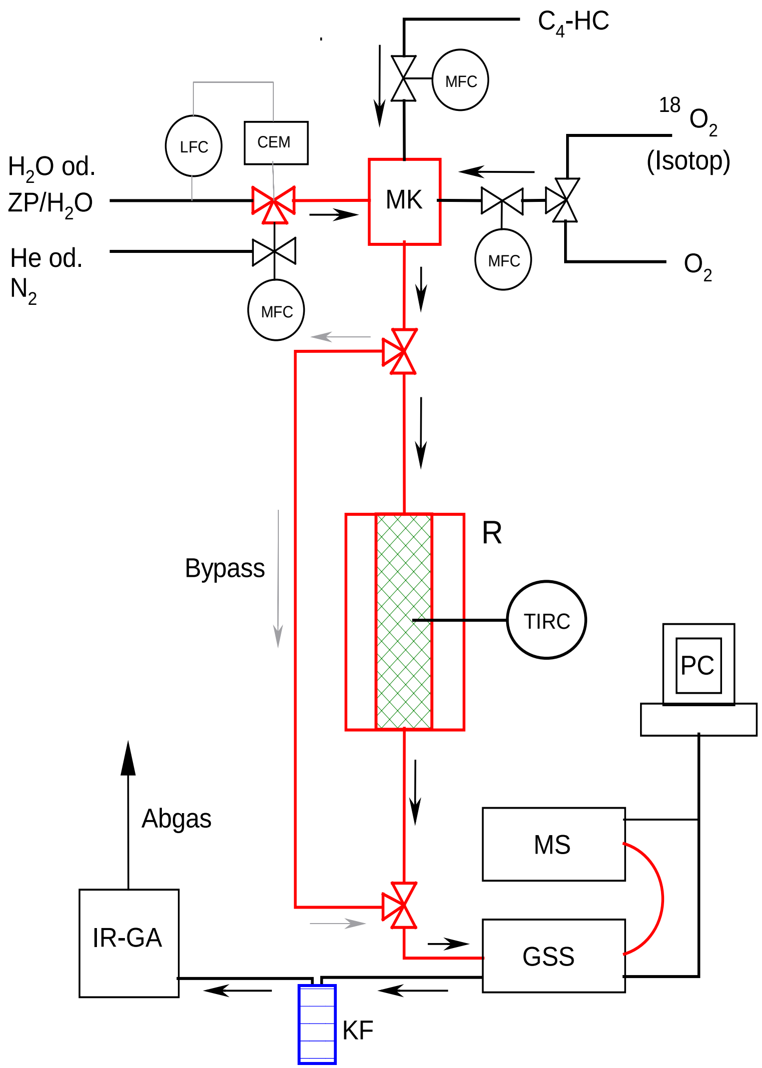
Transient Methods (III)

SSITKA = Steady-State Isotope Transient Kinetic Analysis

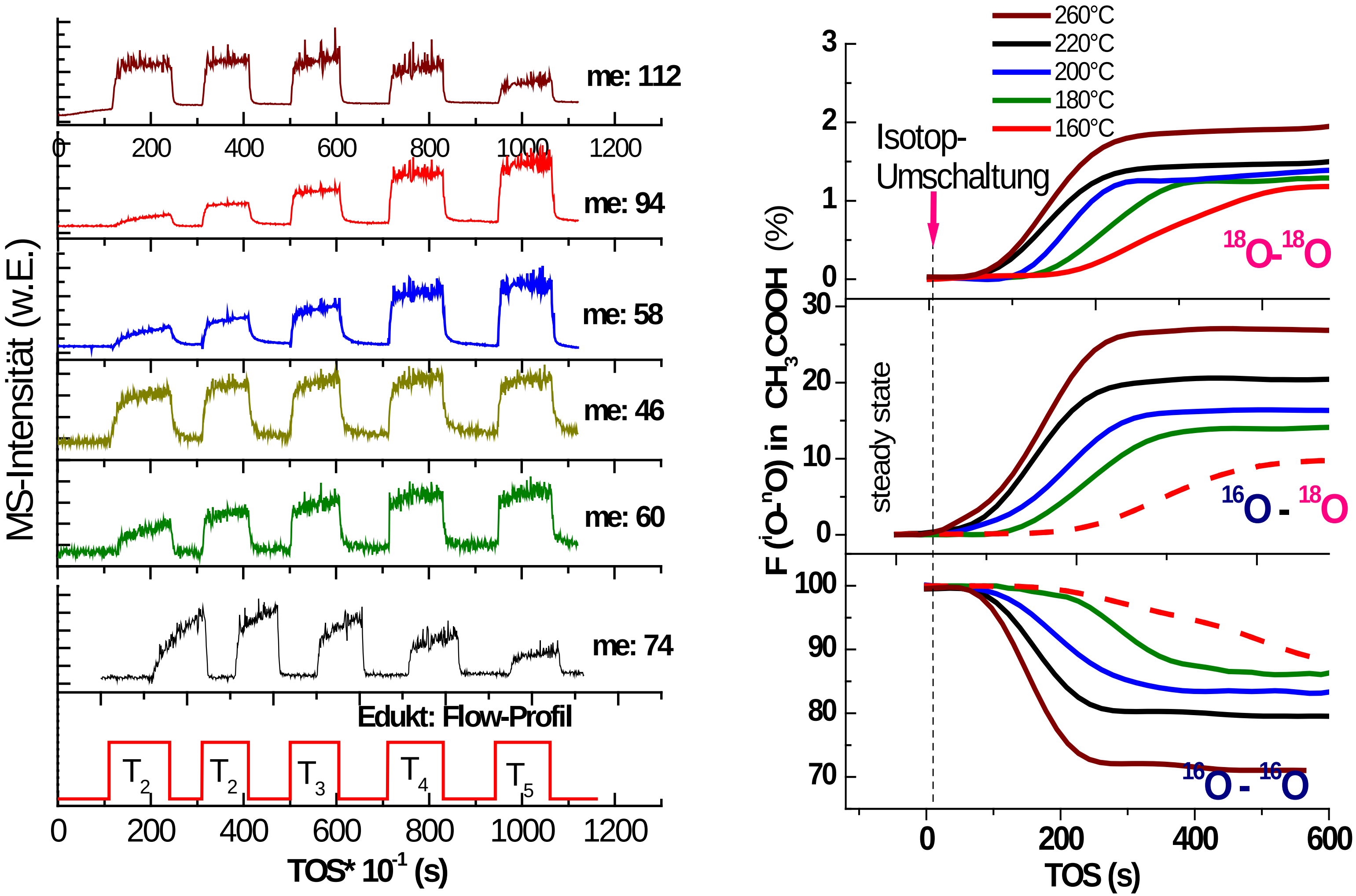


Legende:

MFC	Mass Flow Controler
LFC	Liquid Flow Controler
CEM	Controlled Evaporator Mixer
MK	Mischkammer
MS	Massenspektrometer
GSS	Gas Stream Selector
IR-GA	Infrarot-Gasanalysator
R	Reaktor mit Heizmantel
PC	Computer
TIRC	Steuereinheit zur Regelung und Kontrolle der Temperatur
KF	Kühlfalle

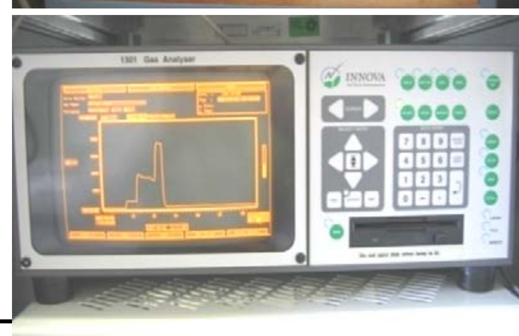
Transient Methods (IV)

SSITKA = Steady-State Isotope Transient Kinetic Analysis



Transient Methods (V)

SSITKA = Steady-State Isotope Transient Kinetic Analysis



Testing: Batch or Continuous

- Batch
  - ✓ Easy to handle
  - ✓ Commonly available and cost efficient
  - ✓ Simple sampling
  - – Reaction and deactivation kinetics coupled
  - – Data analysis difficult

- Continuous-flow
  - – Elaborate handling
  - – Dedicated equipment, partly costly
  - – Sampling often difficult (online analysis)
  - ✓ Reaction and deactivation kinetics uncoupled
  - ✓ Data analysis straight forward

Pitfalls

BATCH

- High initial rates
- Fast deactivation

- Low conversions
- Strong endo- or exothermic reactions
- Low catalyst amounts

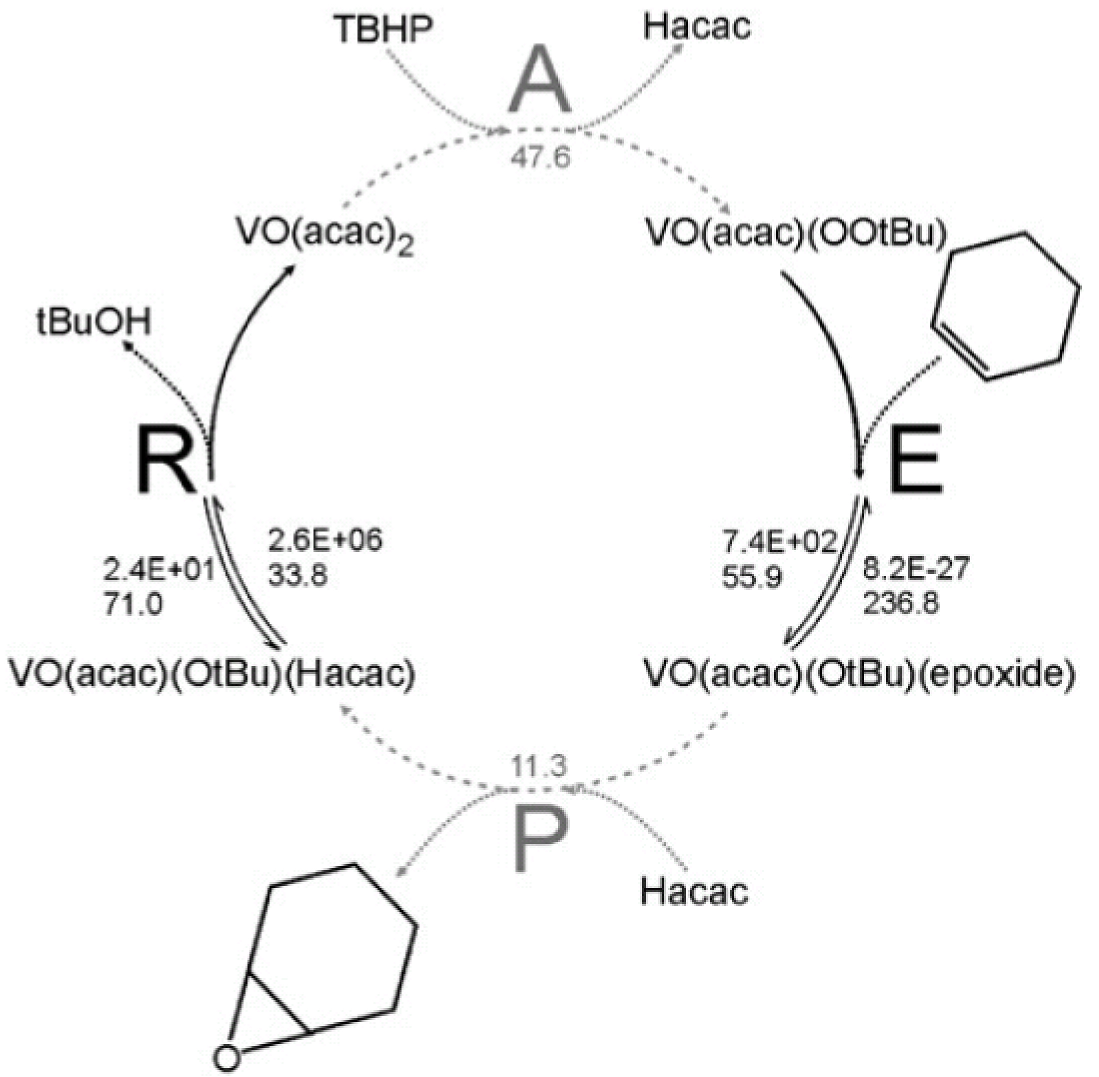
CONTINUOUS

- Varying or unsteady reactant flow
- Changing bed heights
- Changing pressure drop

Ten Commandments for Testing Catalysts

1. Specify objectives
2. Use efficient strategy
3. Chose right reactor type
4. Establish ideal flow patterns
5. Ensure isothermal conditions
6. Minimize transport effects
   - ✓ Small particles
   - ✓ Low conversions
   - ✓ Moderate temperatures
7. Obtain meaningful data
   - ✓ Rate, TOF, space time yield
8. Determine the stability
9. GLP: reproducibility, blank runs, cleanliness
10. Report unambiguously

MOFs and Microkinetics?



K. Leus, I. Muylaert, M. Vandichel, G.B. Marin, M. Waroquier, V. Van Speybroeck, P. Van der Voort, Chem. Commun. 46 (2010) 5085.

Conclusions

- Microkinetics
  - are needed for reactor design
  - can help to elucidate reaction mechanisms
  - require knowledge on elementary steps and active sites
  - might be mathematically challenging
  - are complementary to experimental kinetic data
- … and MOFs
  - only few discussions on catalytic mechanisms
  - further characterization of active sites needed
  - continuous-flow testing essentially absent

… an attractive field for future research!