Deactivation
of heterogeneous catalysts

- Industrial aspects
- Types of deactivation
- Kinetics of deactivation
- Illustration of deactivation for the methanation of C0 on a supported Ni-catalyst
- Simulation of the deactivation process within a tubular reactor packed with porous pellets
- (Catalyst activation and regeneration)
- (Catalyst surface and bulk characterization; e.g. TEM, S_{BET}, XRD, XPS, IR, ...)

Industrial aspects of deactivation

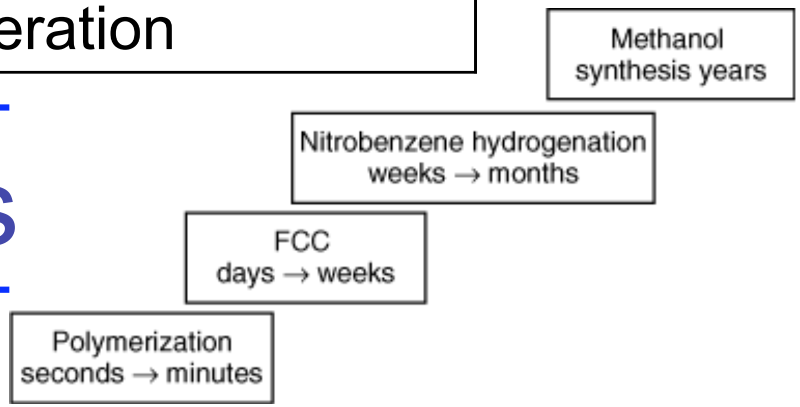
- Life time of catalysts
- Loss of activity and possibly selectivity
- Interruption of process operation for either replacement or regeneration of catalysts

  + loss of time for production

  + loss of investment

Time-scale of deactivation	Typical reactor type
Years	Fixed-bed reactor, usually no regeneration
Months	Fixed-bed reactor, regeneration while reactor is off-line
Weeks	Fixed-bed reactors in swing mode, moving-bed reactor
Minutes–days	Fluidized-bed reactor, slurry reactor; continuous regeneration
Seconds	Entrained-flow reactor (riser) with continuous regeneration

Life time of catalysts



Types of Deactivation

- **Poisoning**

  contaminants in the reactor feed

- **Fouling**

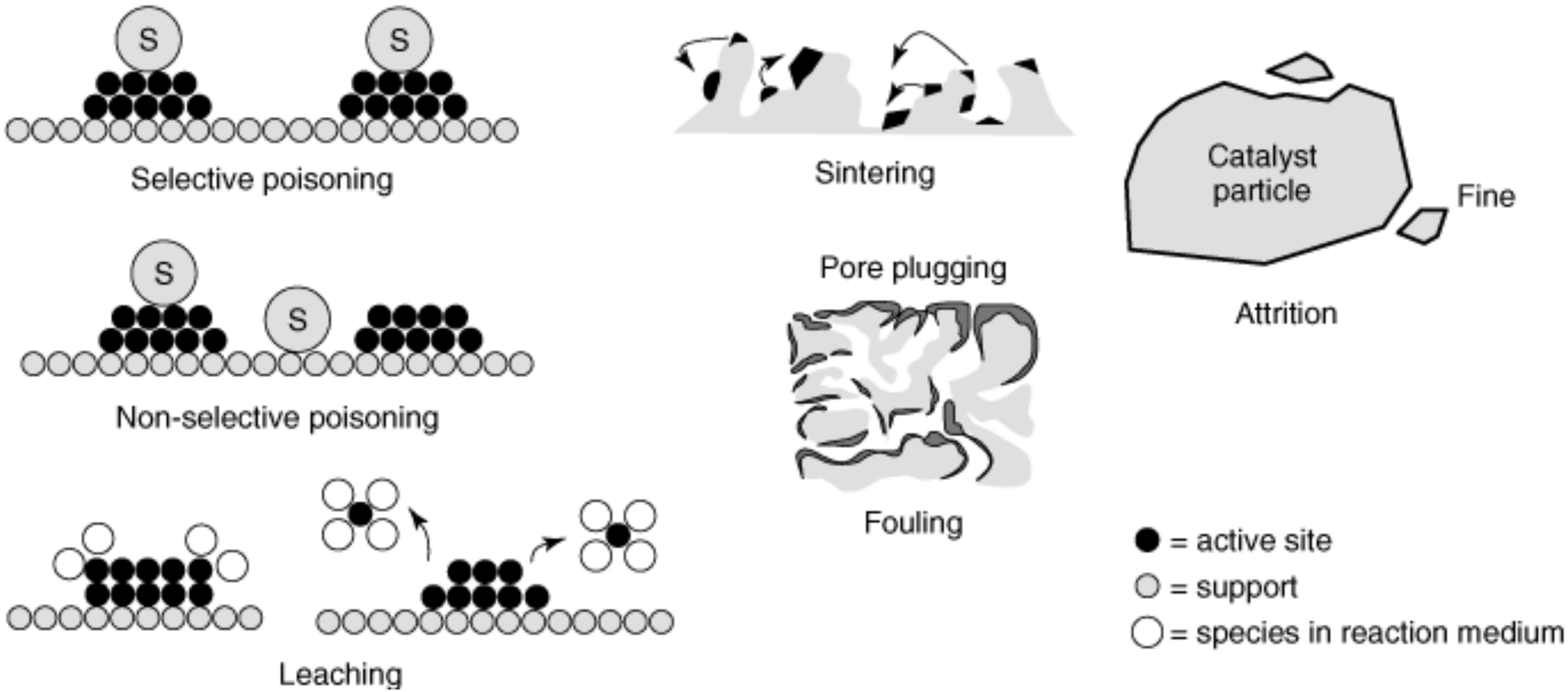
  thermal degradation (sintering, evaporation, volatilization), leaching by the reaction mixture

- **Coking** *(formation of deposits)*

  coverage of the surface by coke or carbon from undesired reactions of hydrocarbon reactants, intermediates, and products

- **Mechanical damage**

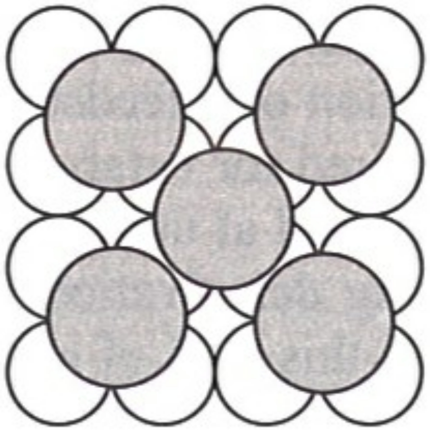
Major types of deactivation in heterogeneous Catalysis



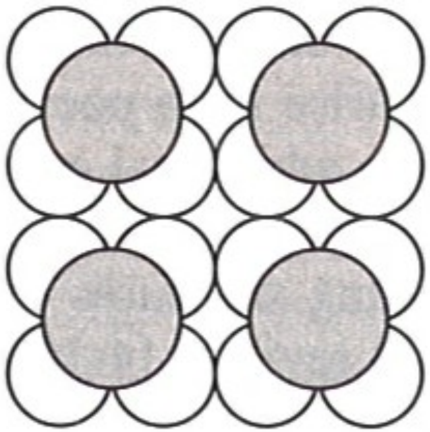
According to J.A. Moulijn et al.

Different geometric structures of sulphur adsorption on Pt(100)

a: c(2x2); b: p(2x2)



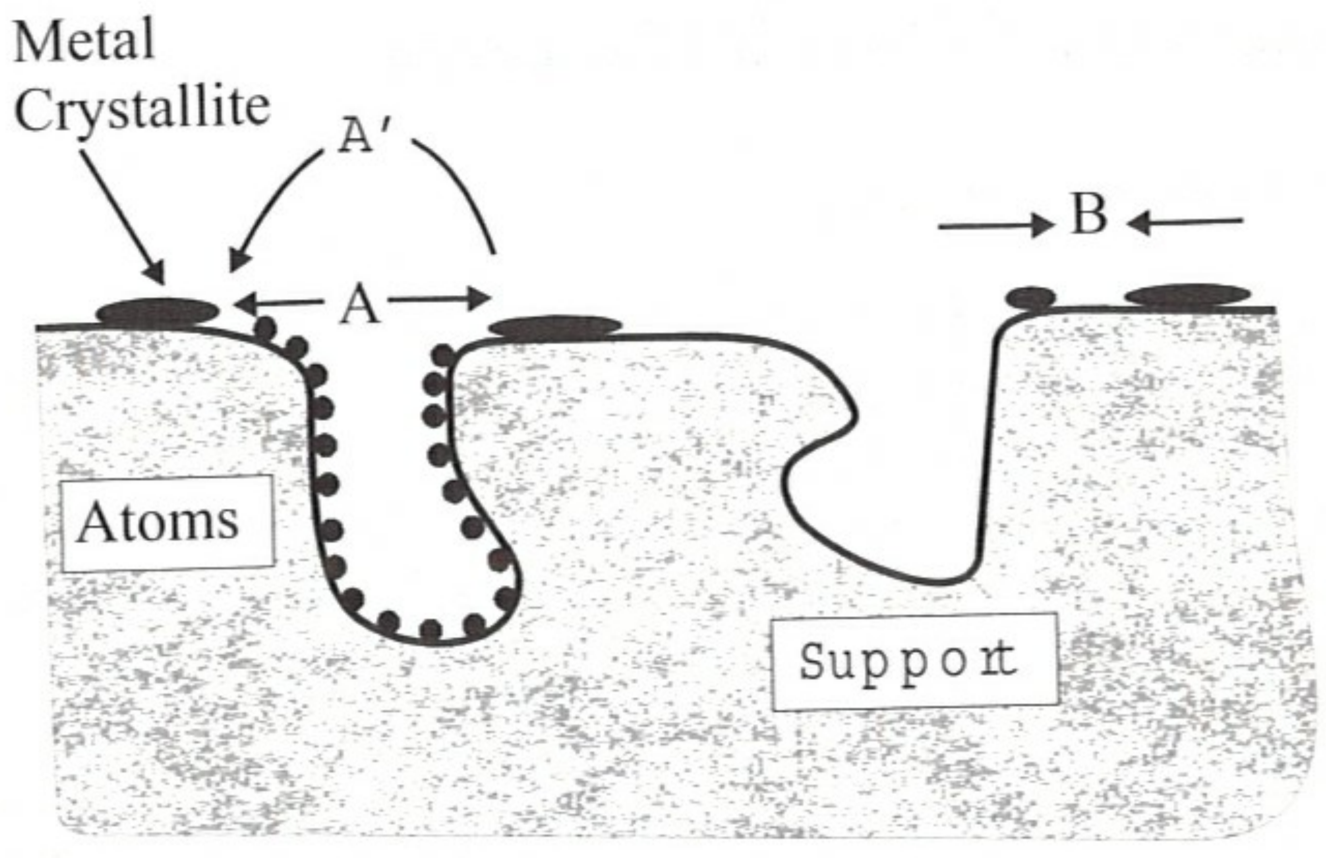
a



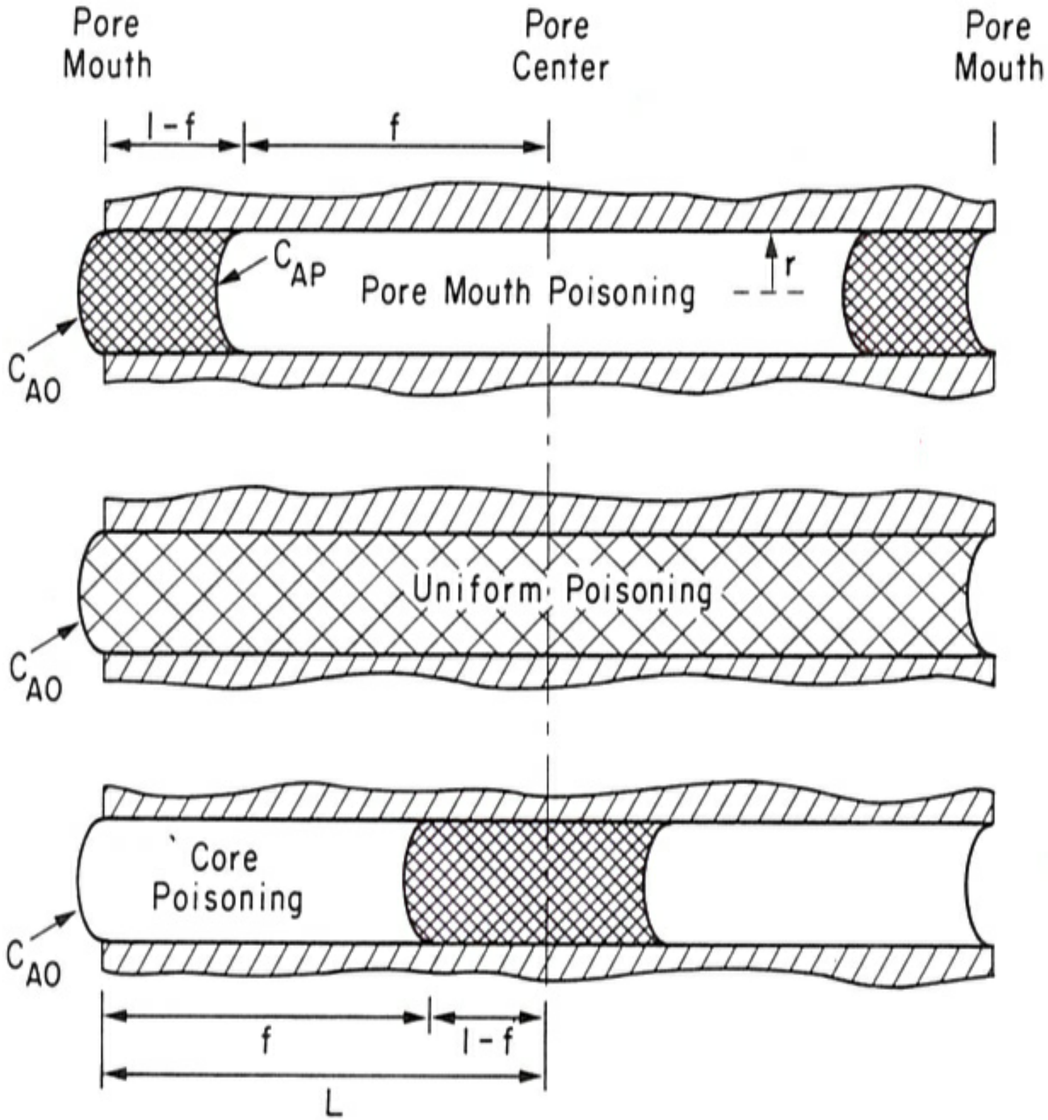
b

Models for crystalline growth due to sintering by movements of atoms

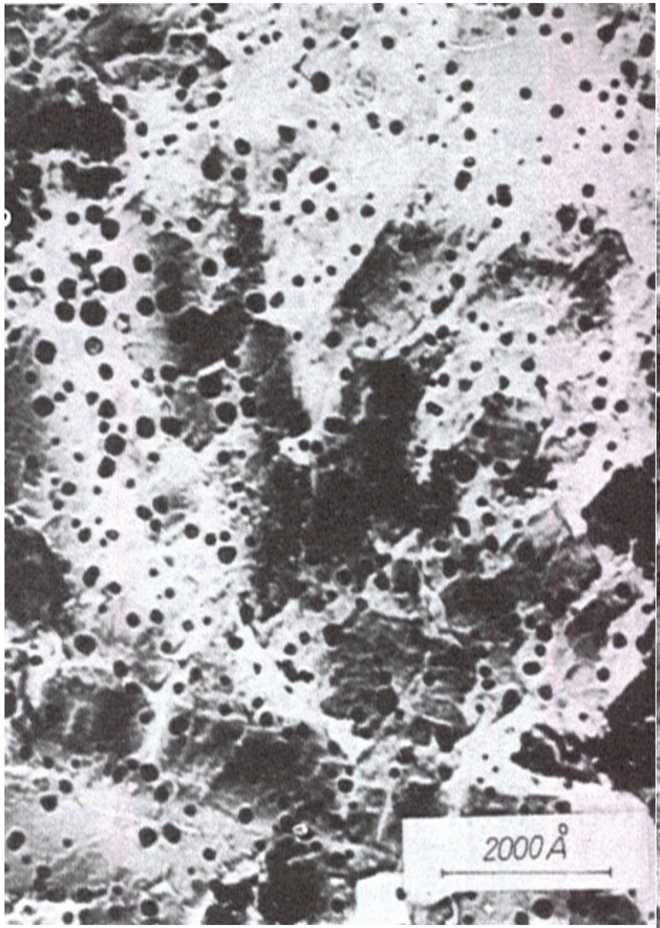
A: migration; A‘: volatilization; B: migration of particles

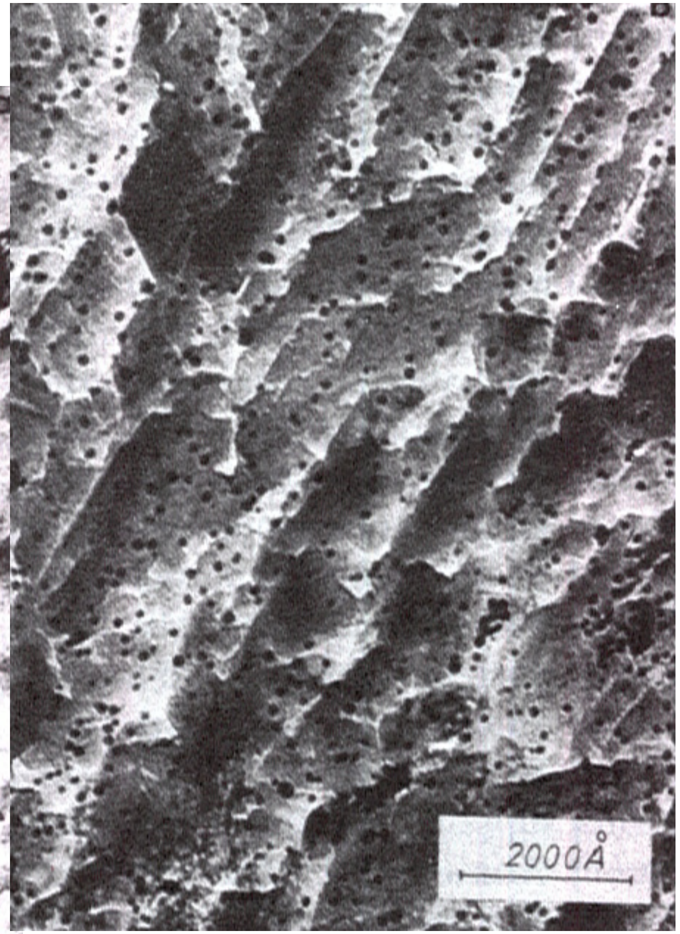


Three limiting cases of Poisoning
(from E.E. Petersen, Exp. Methods in Catalysis)



TEM of Pt crystallites on a γ-Al_2O_3 film support

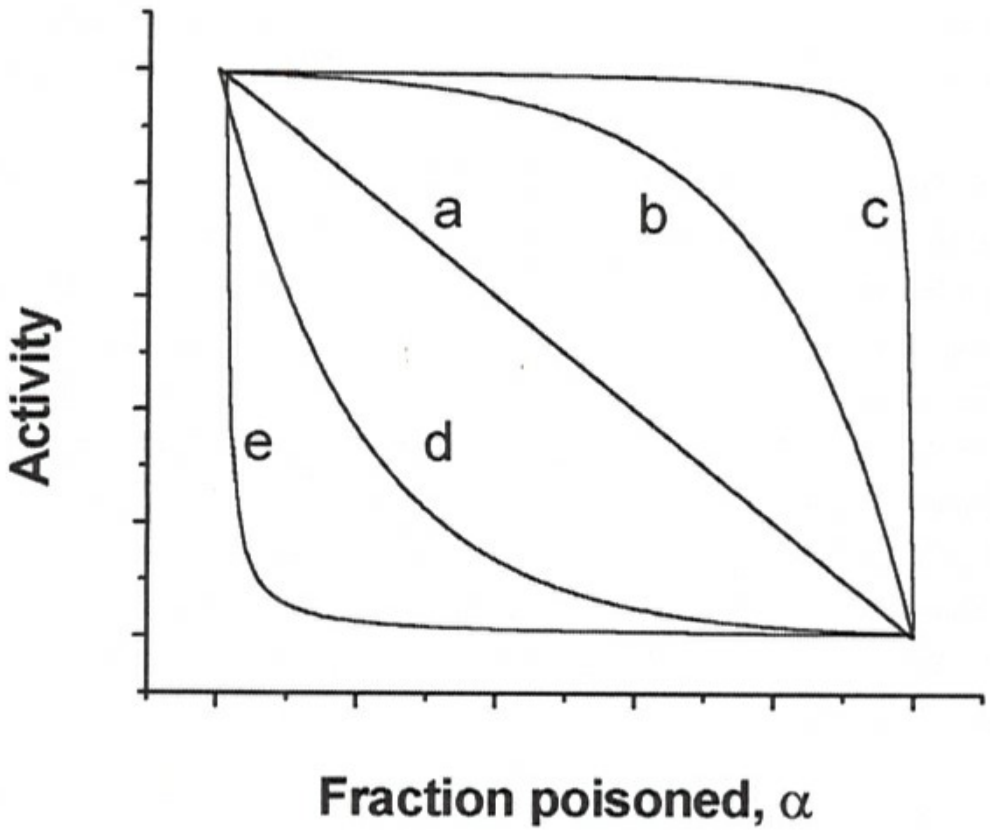


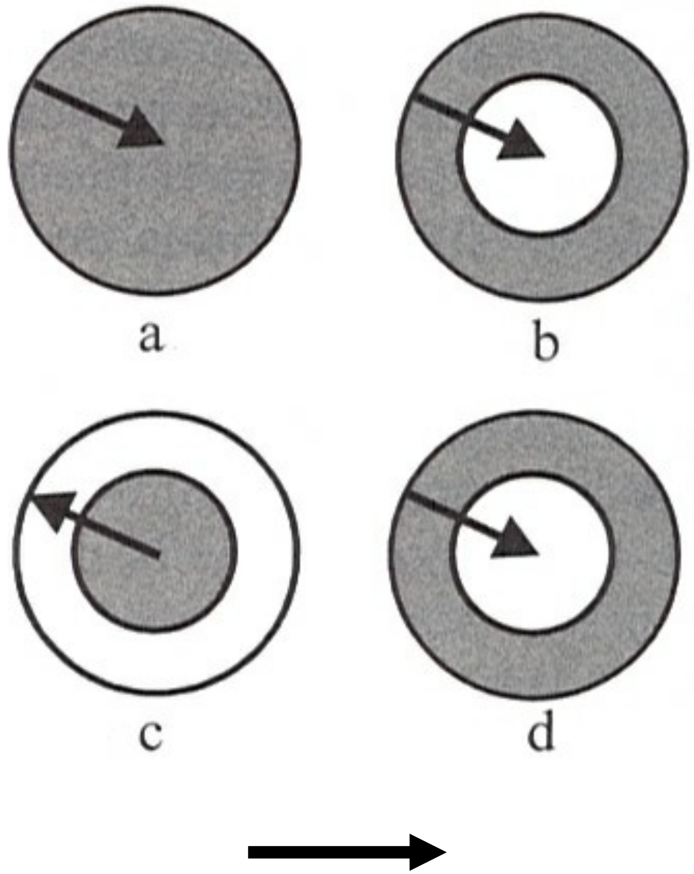


Ruckenstein et al. Acad. Press

as prepared (10.7) → 500 C for 24 h (4.3) 400 C for 24 h (8.3)

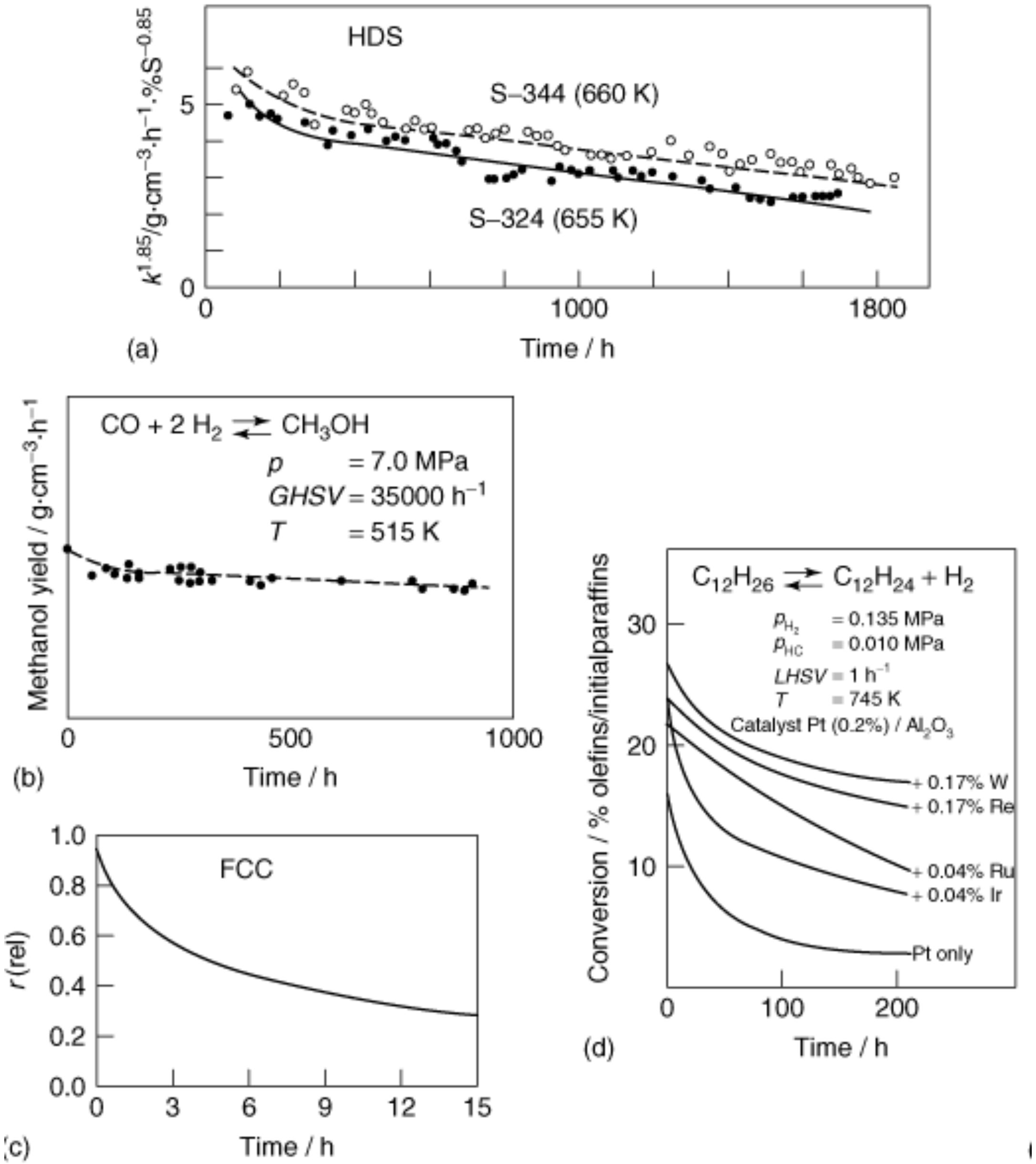
Progress of Poisoning in a catalysts sphere





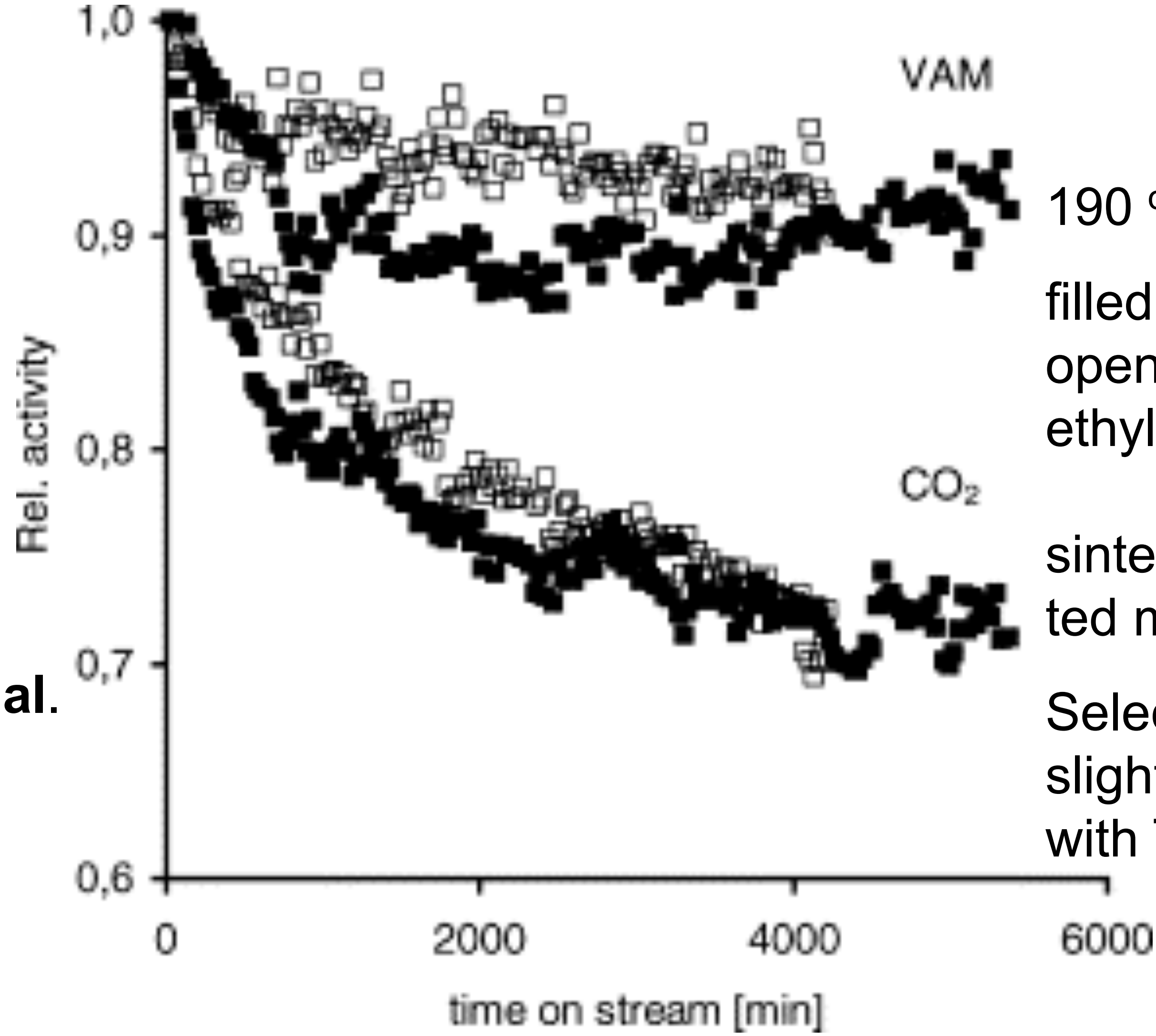
Direction of poisoning

Deactivating catalysts for various reactions



Deactivation of vinyl acetate catalysts

Catalyst: Pd,Au/SiO_2 with potassium acetate promoter



O.Smejkal et.al.

190 ^{o}C, 900 ka

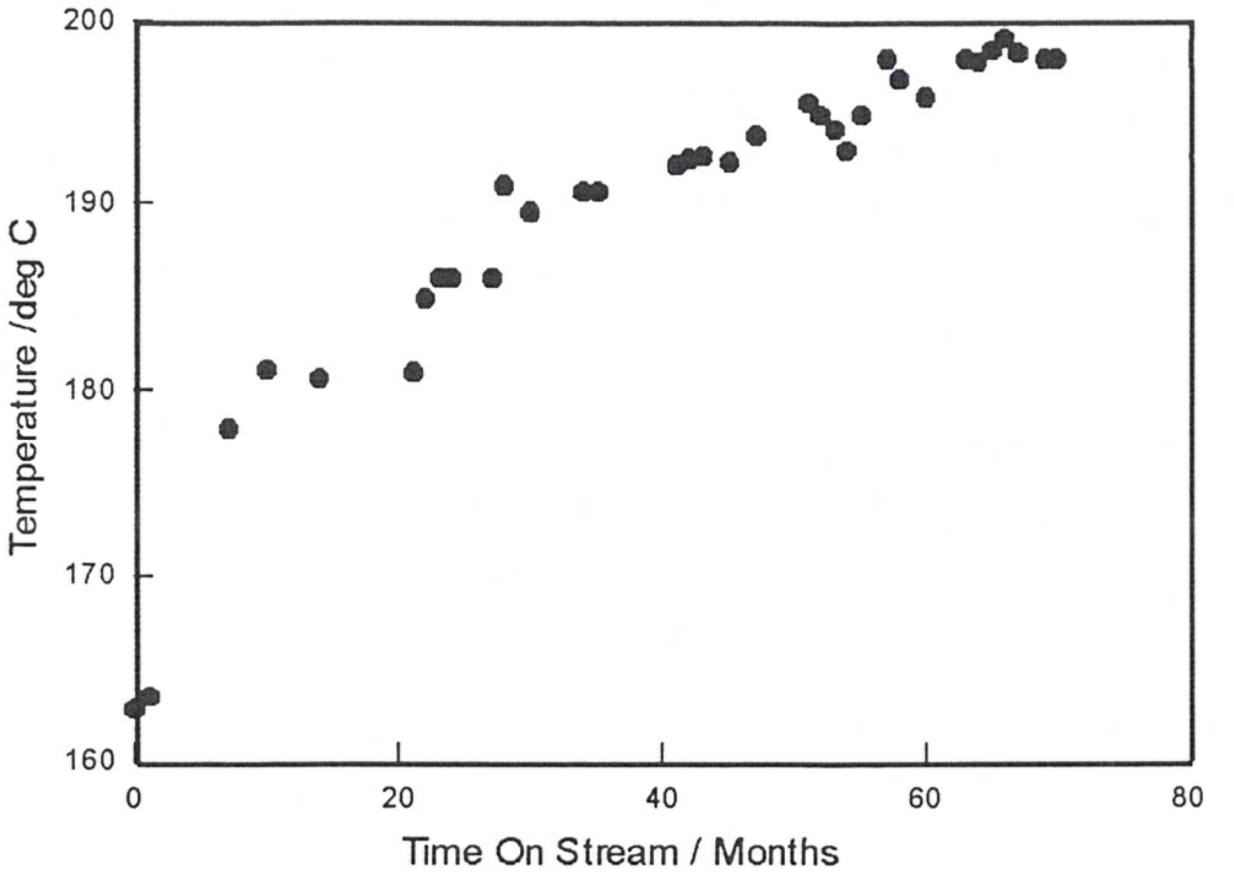
filled symbols 41%
open symbols 30%
ethylene

sintering of suppor-
ted metal catalyts

Selectivity of VAM
slightly increases
with ToS

Isothermal Reactor Operation over Catalyst life

Iso-Conversion over time of operation



Ethylene to ethylene oxide

Compensation for loss of activity by increasing reaction temperature

Deactivation of supported nickel-catalyst pellets and operation of an adiabatic tubular reactor

Reaction: methanation of CO in excess of H_2

$$CO + 3\,H_2 \longrightarrow CH_4 + H_2O$$

Type of deactivation: surface migration of nickel carbonyls

Needs: Kinetics of catalytic reaction and of deactivation

Pore-diffusion processes

Reactor model

Simulation procedure

Reaction Engineering Simulation

Deactivation mechanism of Ni catalyst

No loss of Ni as nickel carbonyls in the presence of CO

Formation of surface cabonyls with the ability to migrate

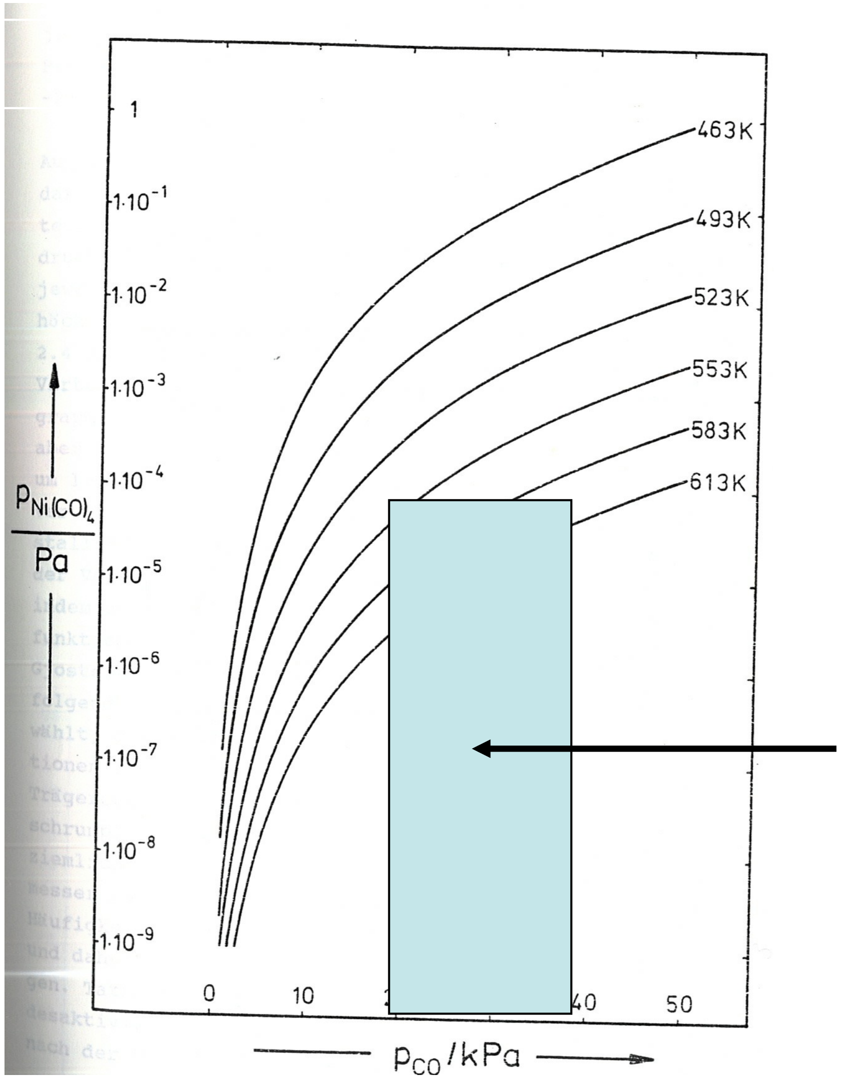
Rate of deactivation

Measurement of the temporal change of rate of methanation in a gradientless controlled recyle reactor (T, p_i : controlled and constant)

activity $a(t) = R_{CO,t} / R_{CO,t=0}$

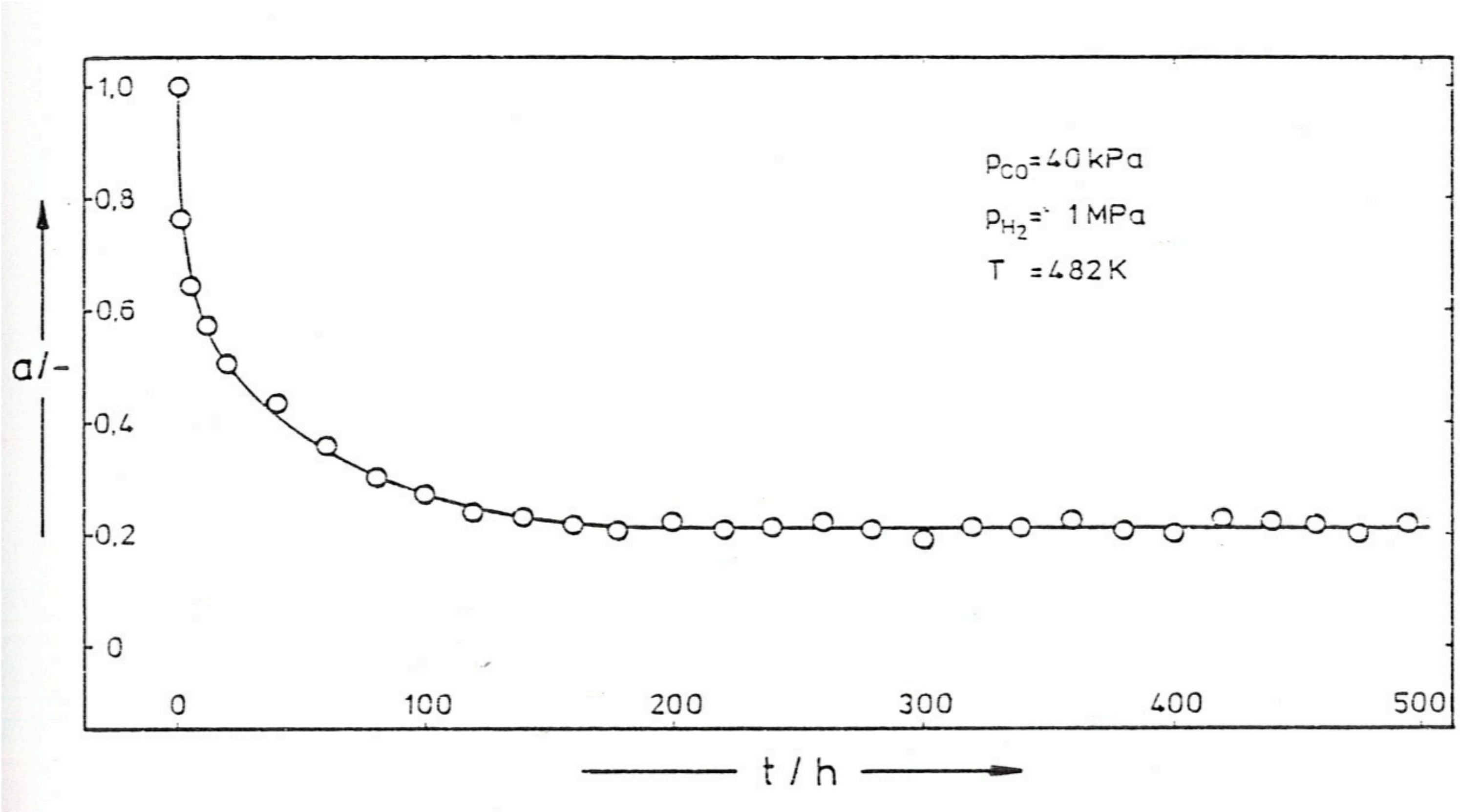
Rate of deactivation: da / dt

Thermodynamics of $Ni(CO)_4$ formation as a function of p_{CO} and T



Range of reactor operation

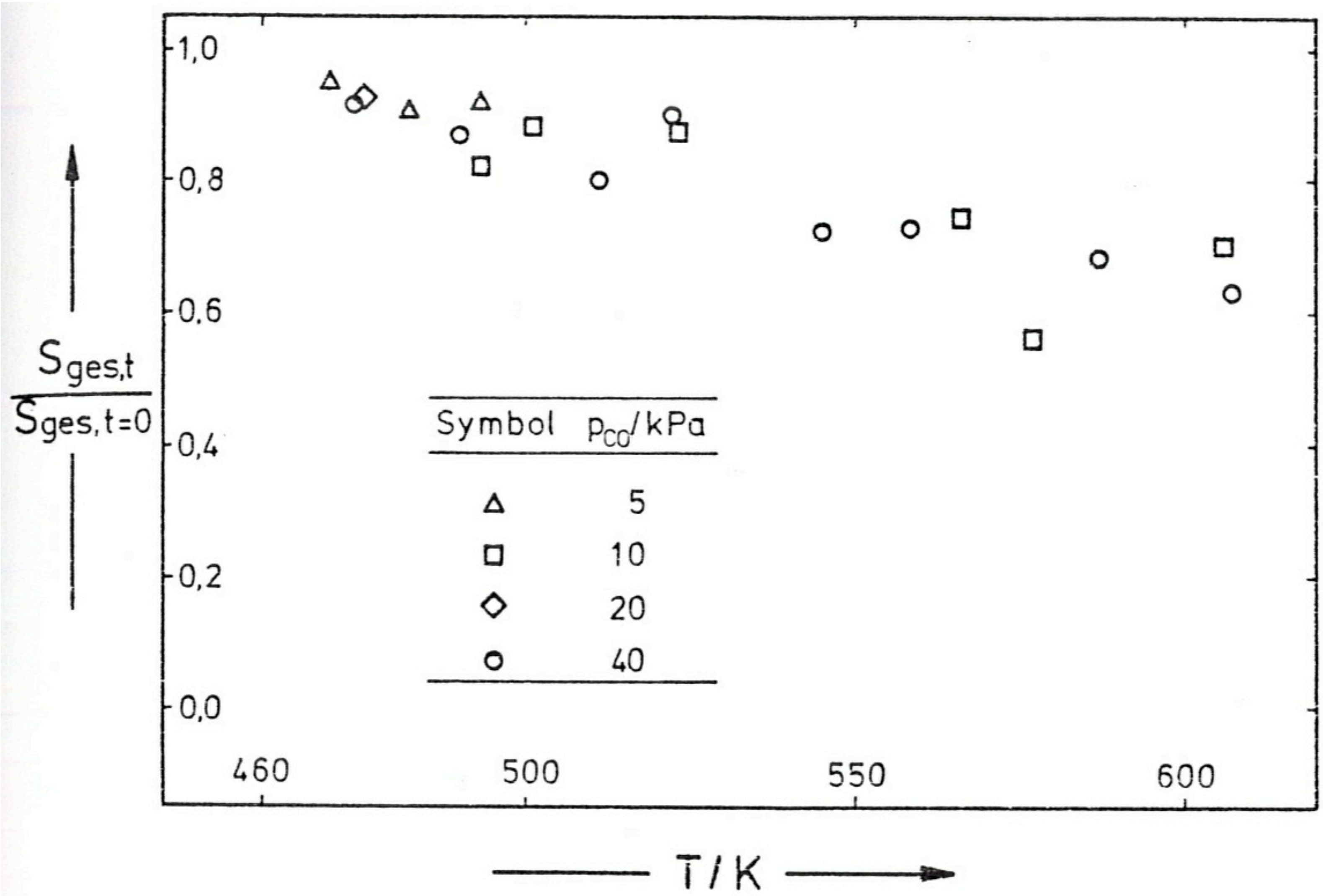
Activity of Ni catalyst particles without diffusional limitation as a function of time on stream



Steady-state activity $\mathbf{a_{ss}}$ after about 150 to 200 hrs of operation

(see surface area of Ni)

Change of total surface area of a supported Ni-catalyst



Rate of Deactivation

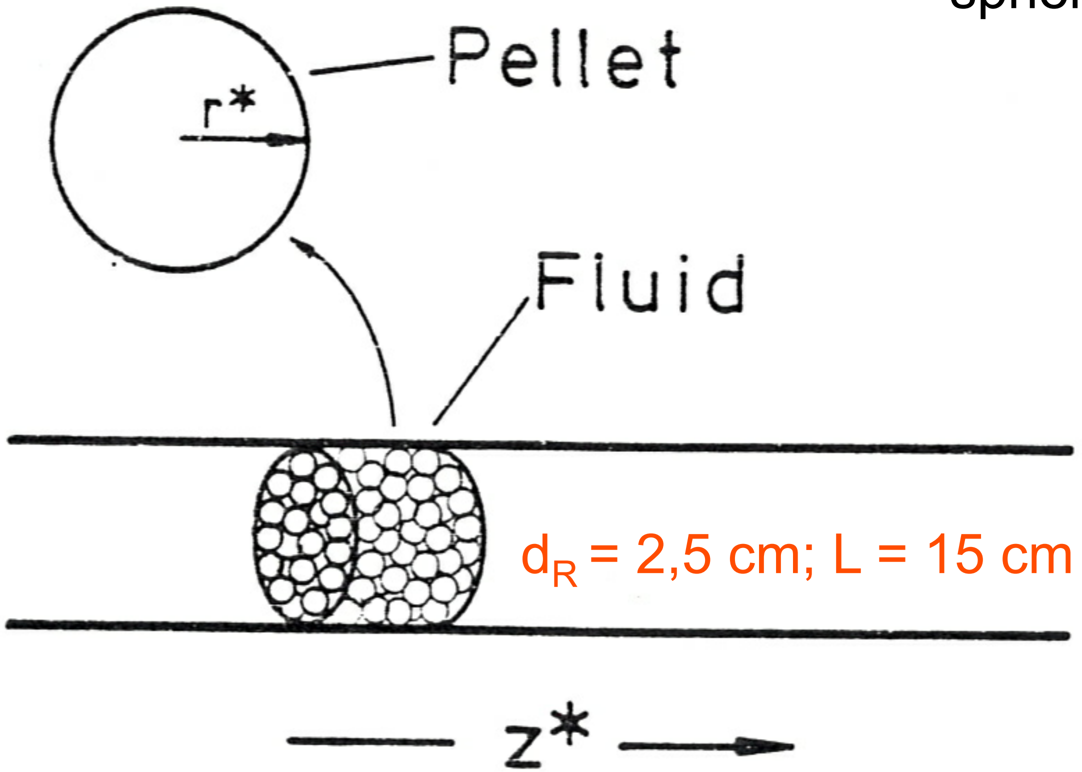
$$da / dt = - k'_D (a - a_{ss})^p$$

$$dS_{ni} / dt = - k_D \; S(Ni)^p$$

$$k'_D = k_D \Pi (p_i)^m$$

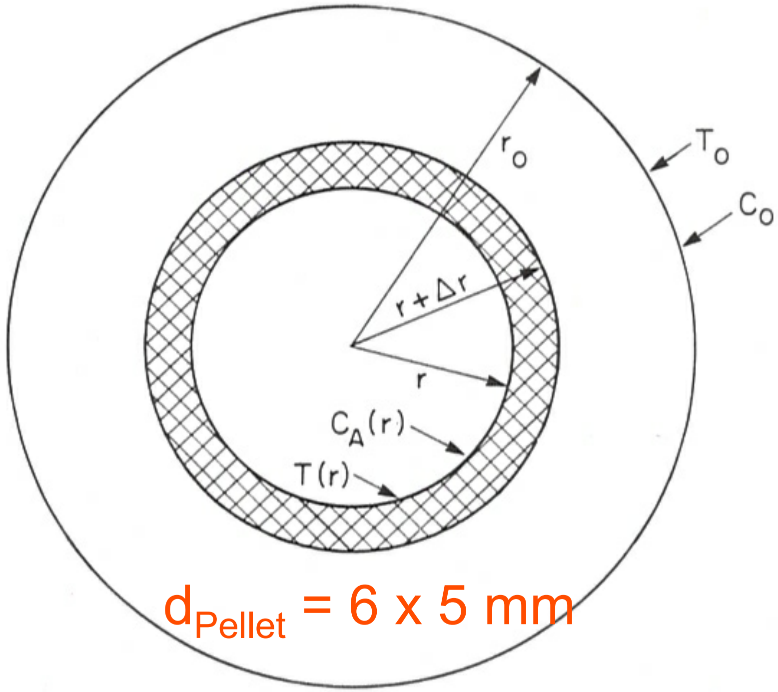
Basis of Reactor Modelling

sphere equivalent to cylindric pellet



d_R = 2,5 cm; L = 15 cm

Reactor model



d_{Pellet} = 6 x 5 mm

Fig. 6-1. A spherical catalyst pellet.

Pellet model

Strategy

Setting up **differential balances** describing

+ the change of mass of the reactants in the convective flow within a small volume element in the reactor, and

+ the change of mass of the reactants in the pellet by **catalytic reaction** and **pore diffusion**

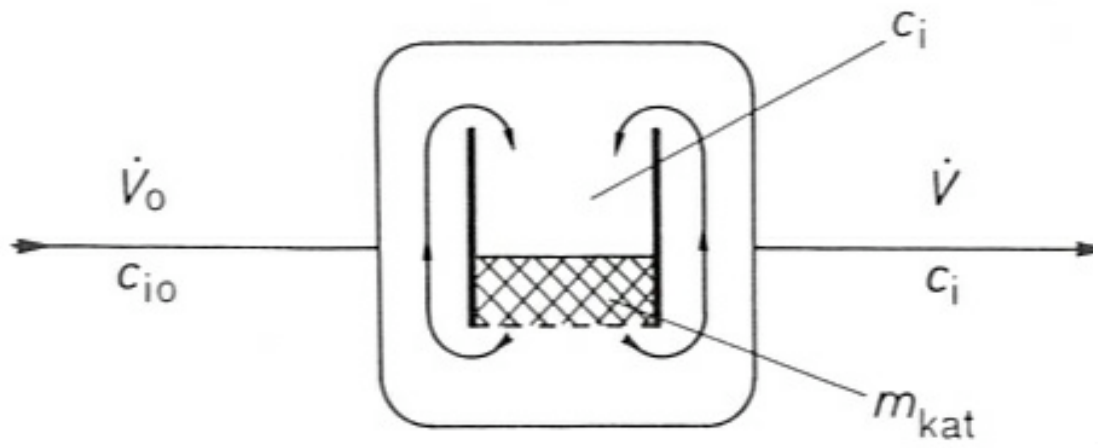
Simultaneous integration of the respective mass balances and including heat balances leads to concentration profiles along the reactor and to ist outlet concentrations.

Rate equation of methanation and ist parameters

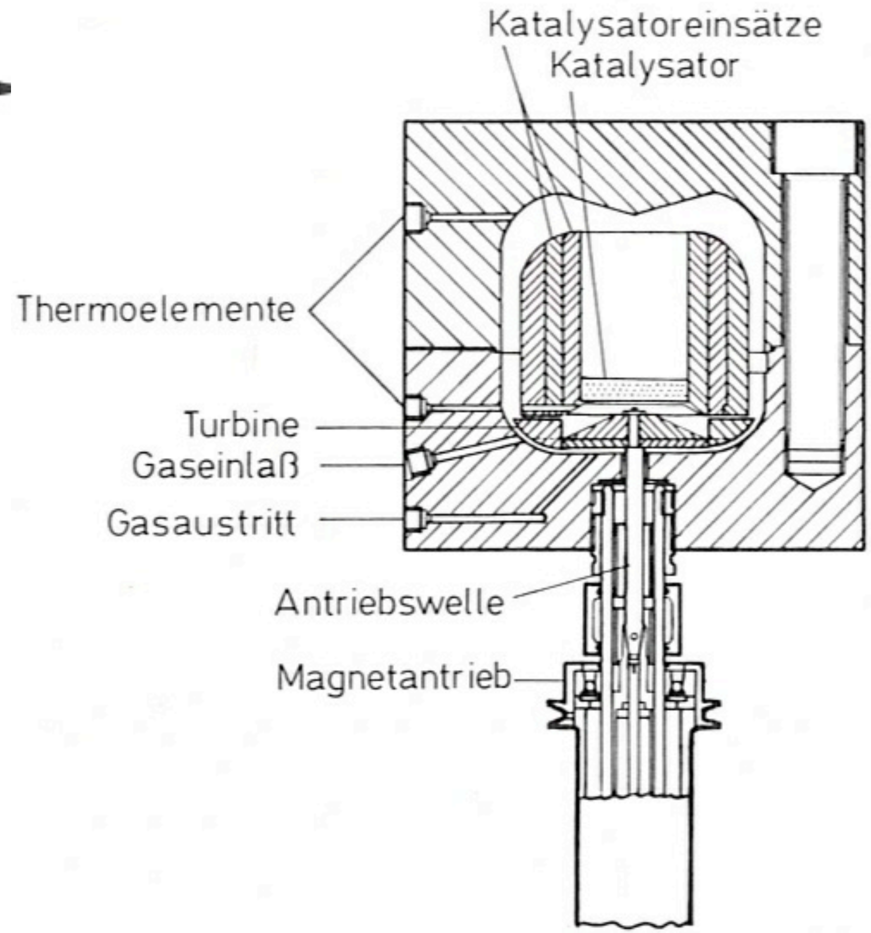
$$- R_{co} = \frac{k_{CH2}(t)\, K_C\, (K_H)^2\, (p_{CO})^{0.5}\, p_{H2}}{(1 + K_C\, (p_{CO})^{0.5} + K_H\, (p_{H2})^{0.5})^3}$$

Parameter	Wert	Dimension
K_C^o	$5.77 \cdot 10^{-4}$	bar
ΔH_C	-42	kJ/mol
K_H^o	$1.60 \cdot 10^{-2}$	bar
ΔH_H	-16	kJ/mol
$k_{CH_2}^o$	$4.80 \cdot 10^{9}$	mol/h g
E_{CH_2}	103	kJ/mol

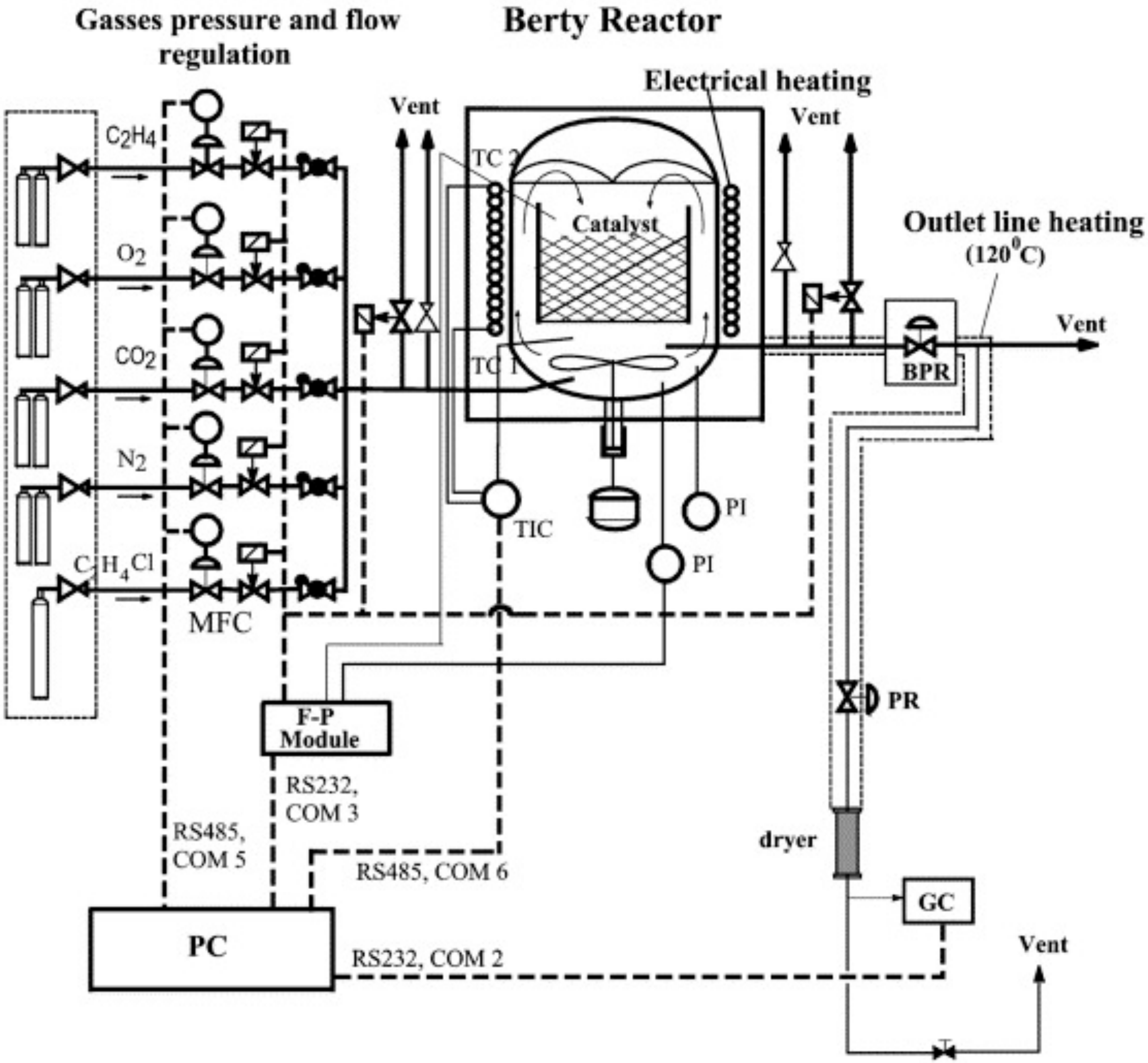
Measurement of methanation rates of CO by means of a gradientless recycle reactor



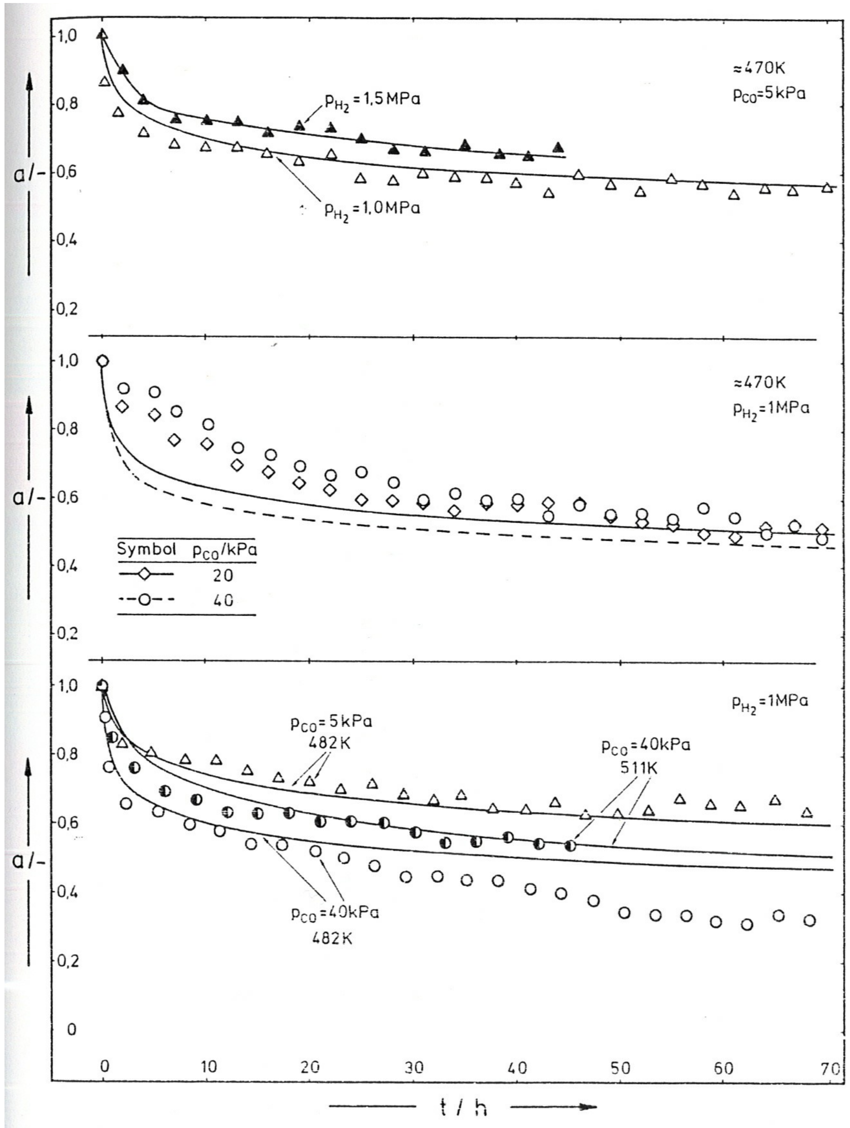
$$\frac{\dot{V} c_i - \dot{V}_0 c_{io}}{\nu_i \, m_{kat}} = r\,(\mathrm{mol} \cdot \mathrm{s}^{-1} \cdot \mathrm{g}_{kat}^{-1})$$



Concentration-controled gradientless recycle reactor



Activity as a function of TOS for a powdered catalyst
No pore-diffusional limitation (symbols exp.; a(t)-rate equation)

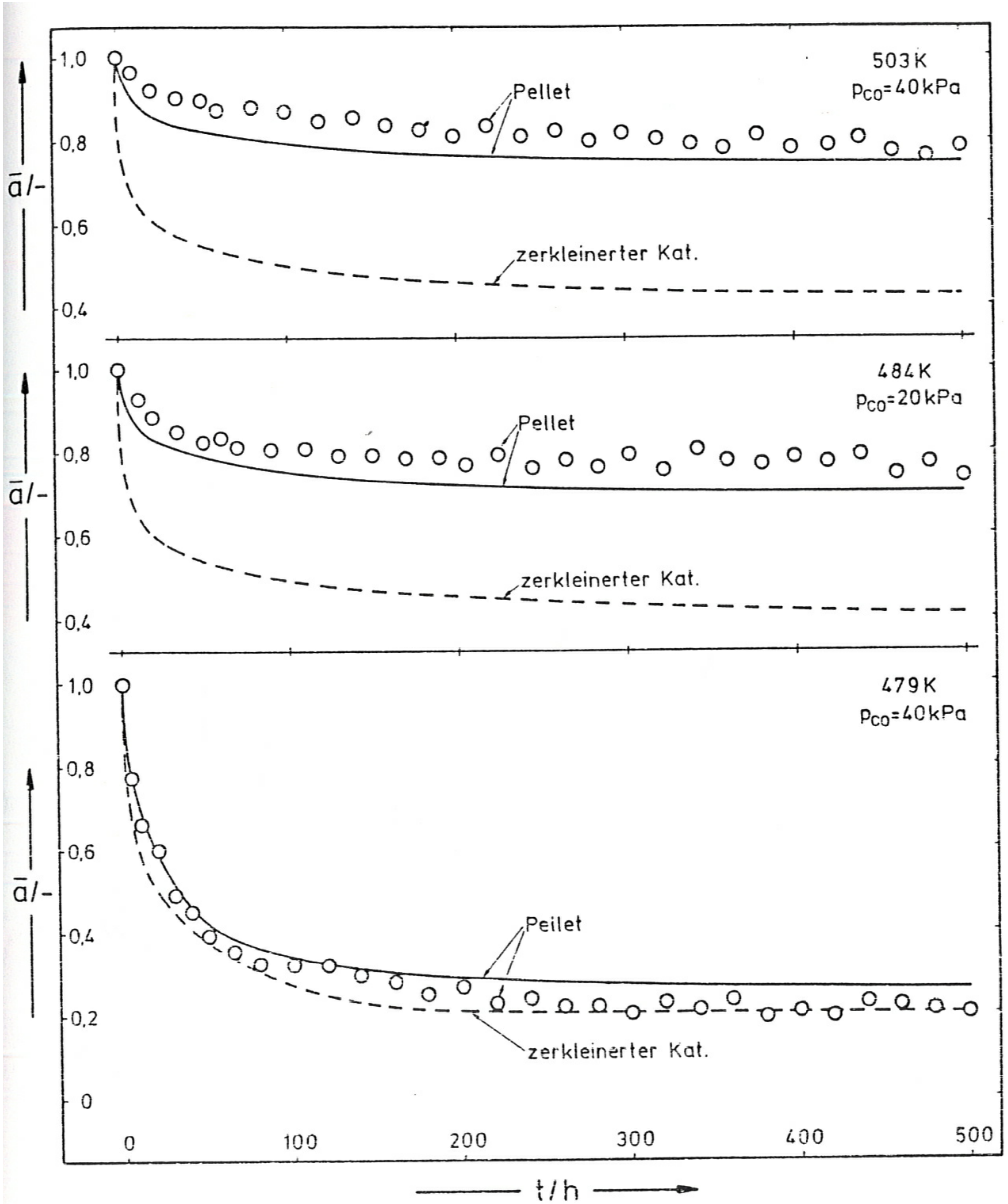


Small particle size no diffusional resistence

Activity as function of time on stream (pellets and powder)

Lines -----, ———

--- rate equ. cat.reac.
— model for overall process



O pellet

--- powder

Concentration profiles within catalytic pellet

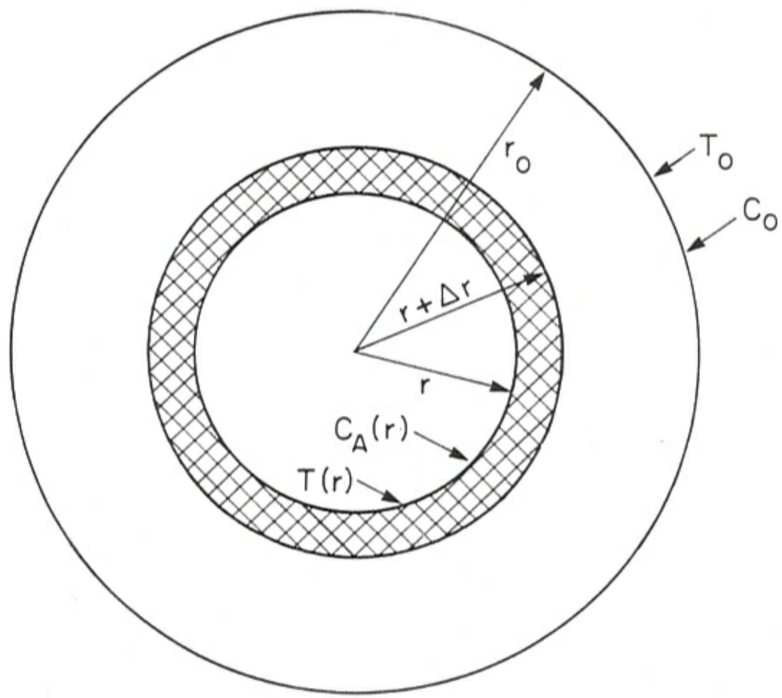
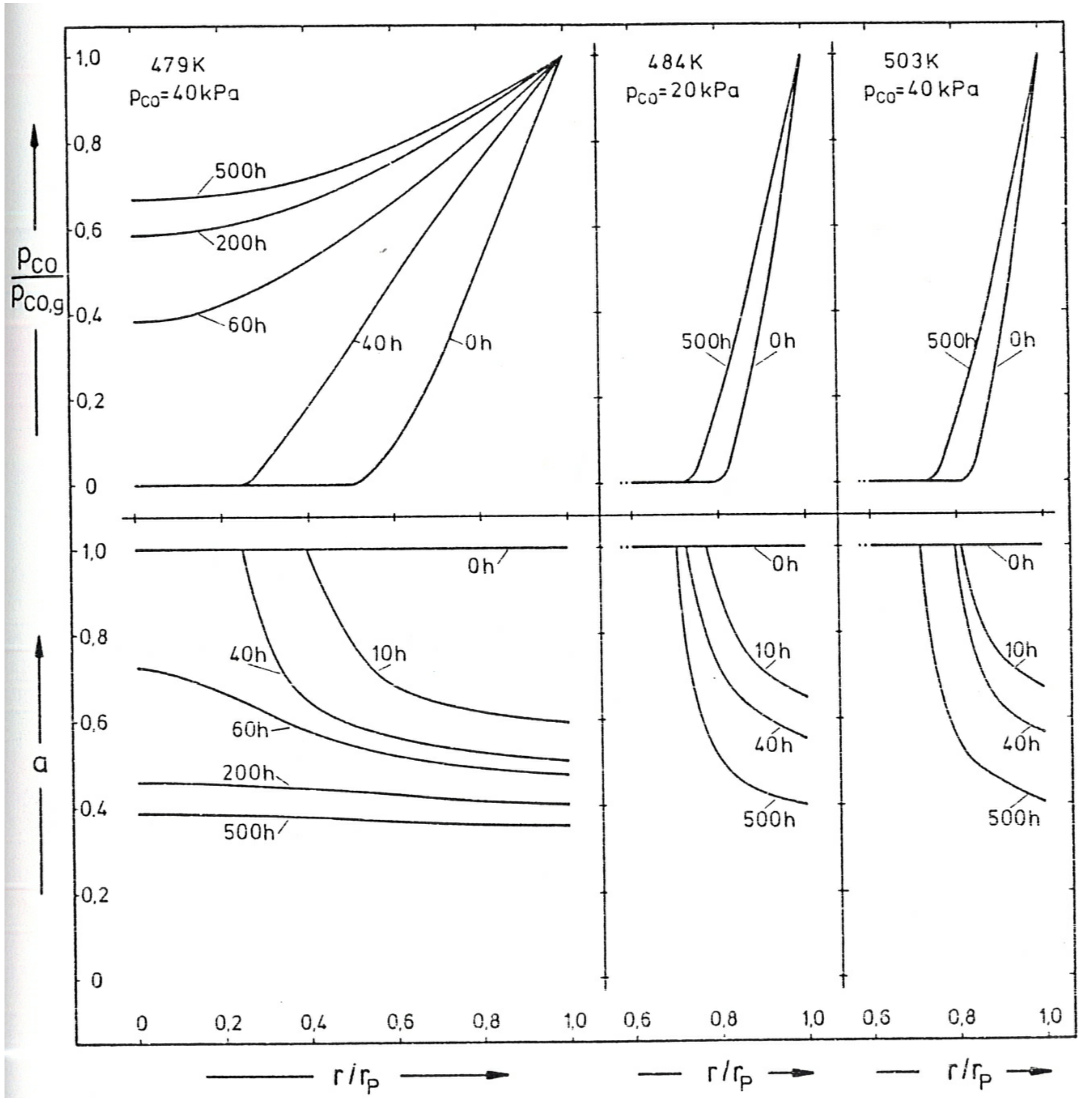


Fig. 6-1. A spherical catalyst pellet.

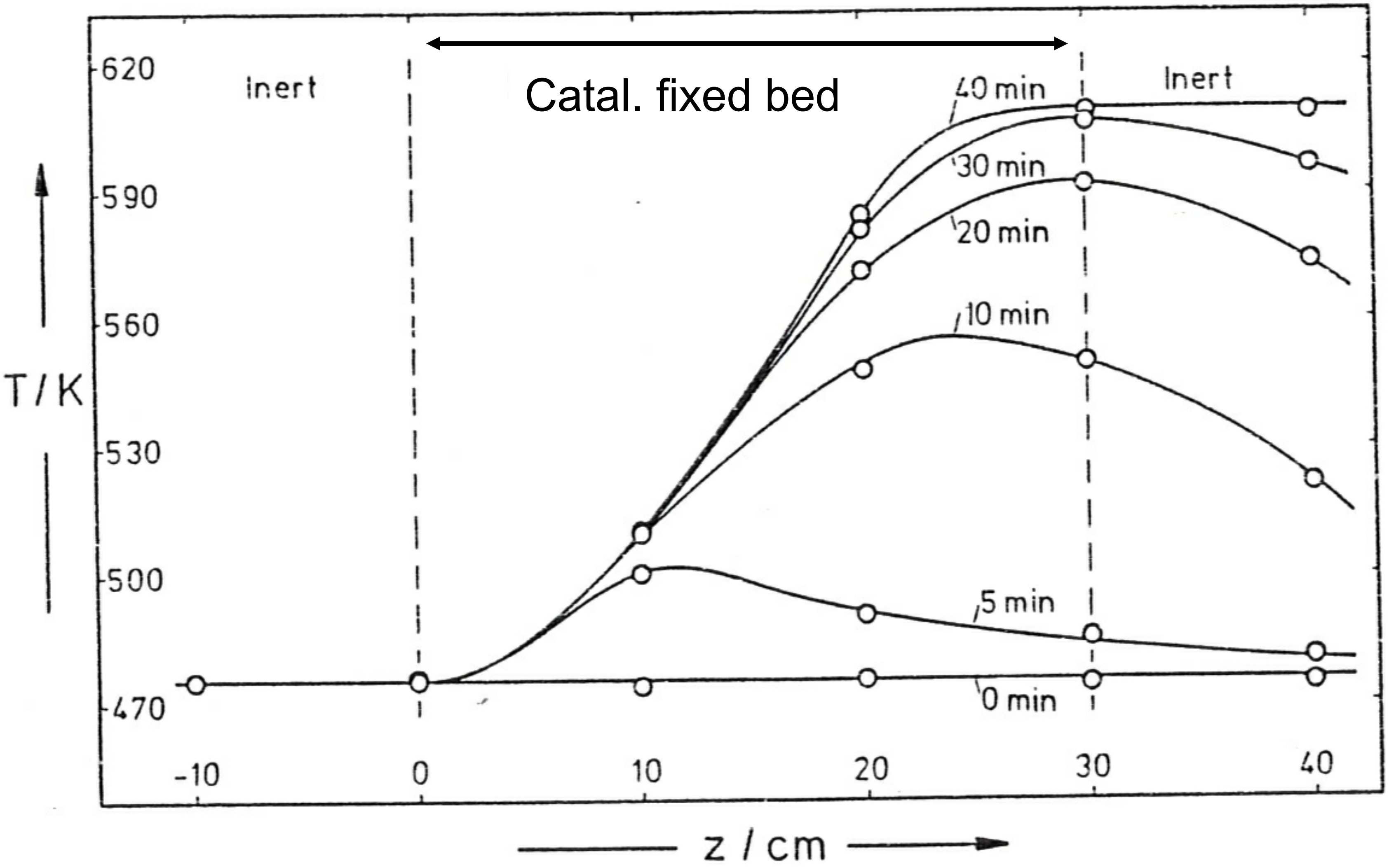
Profiles of CO and activity a within a pellet as f(ToS)

p_{CO}

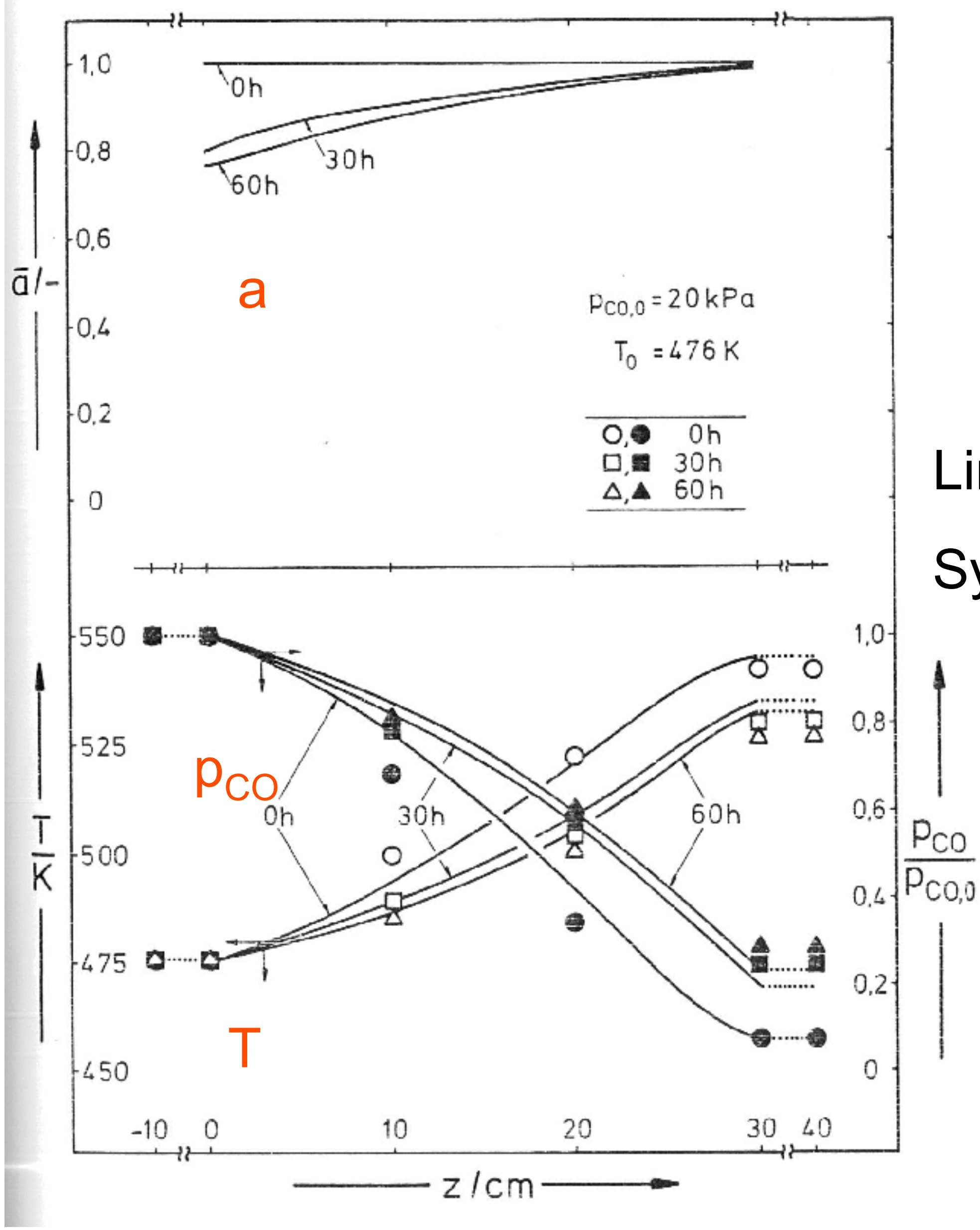
a



Adiabatic catalytic fixed bed reactor
Experimental phenomenon: T profile as f(ToS)



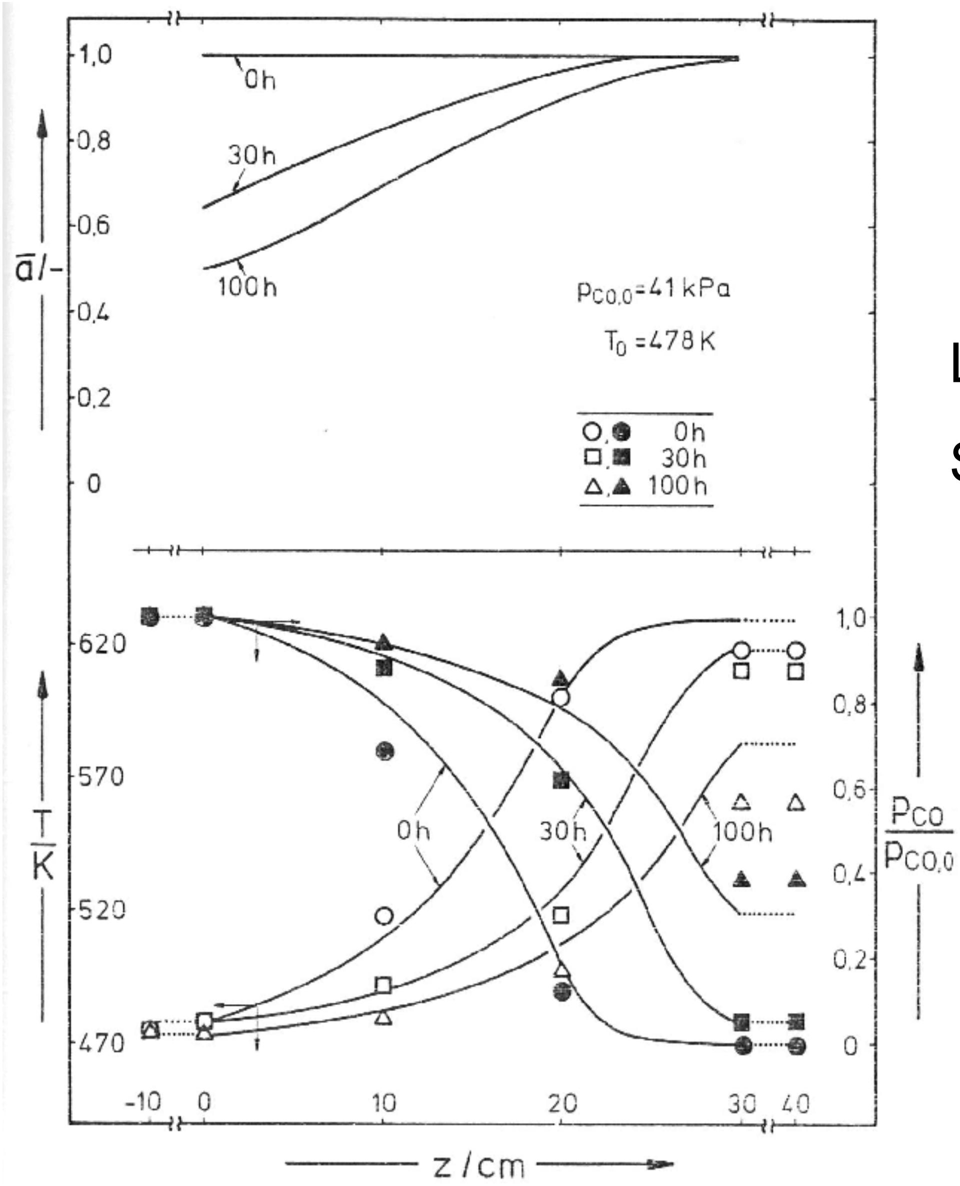
Axial profiles of T, p_{CO} average activity a in a tubular reactor



Lines: simulation

Symbols: experim.

Axial profiles of T, p_{CO} average activity a in a tubular reactor



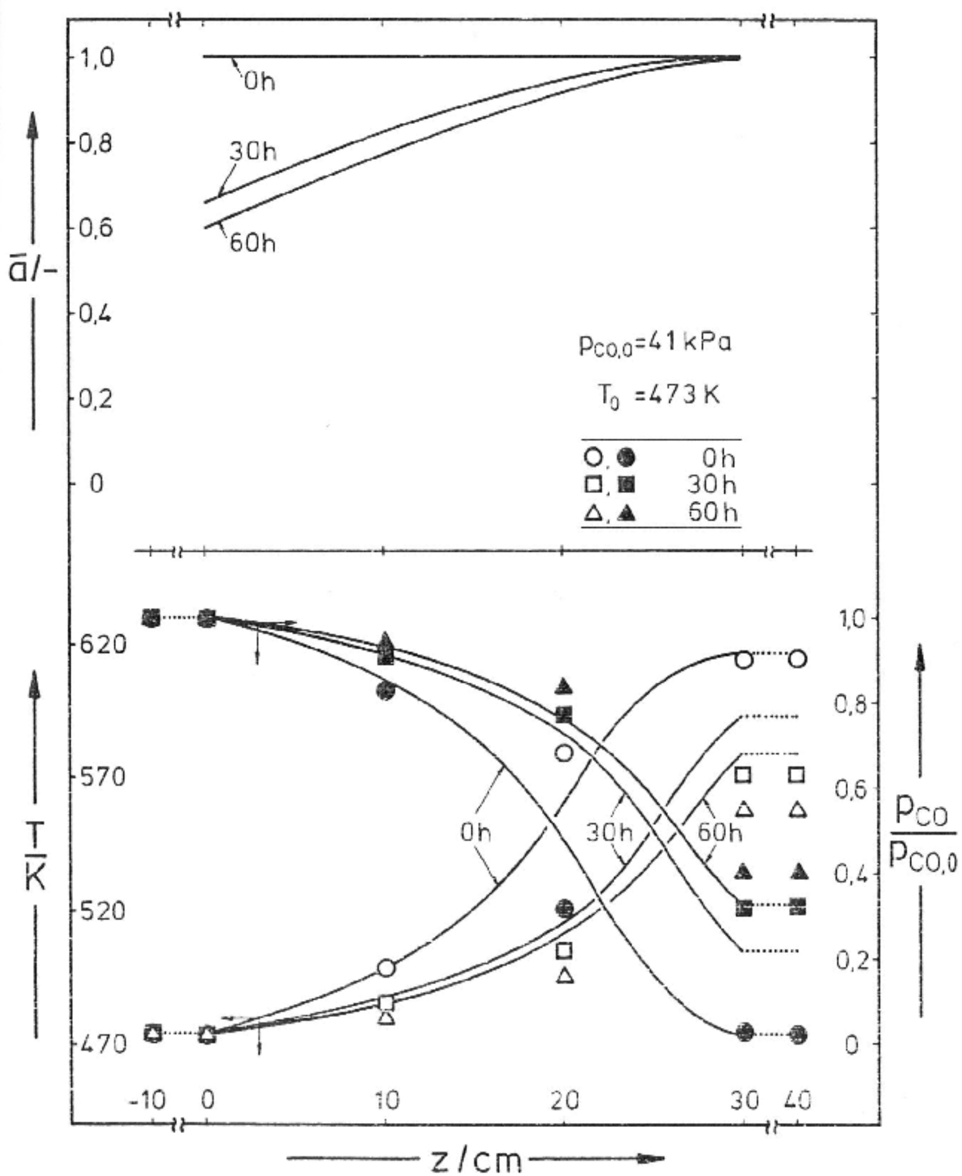
Lines: simulation

Symbols: experim.

Axial profiles of T, p_{CO} average activity a in a tubular reactor

Lines: simulation

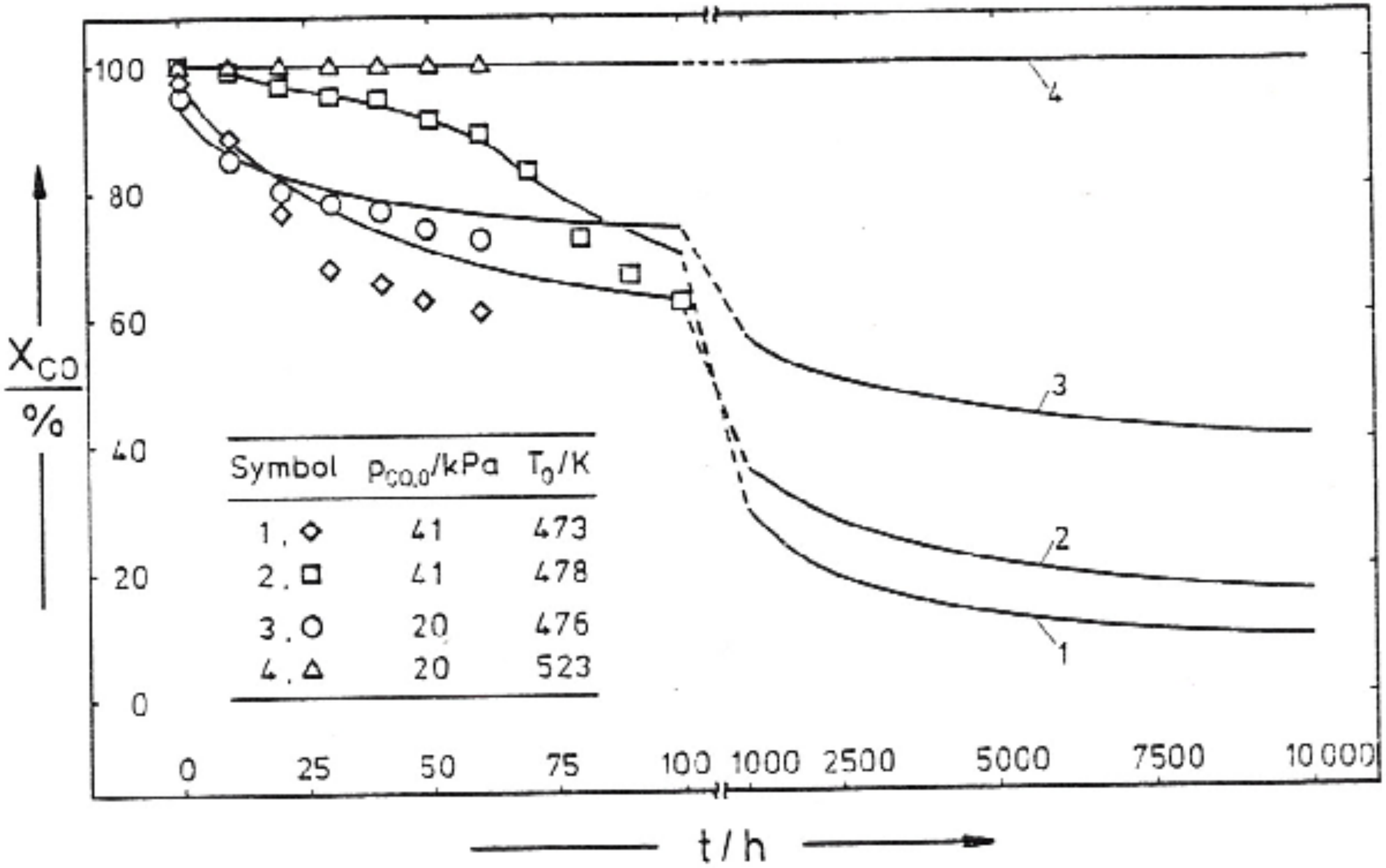
Symbols: experim.



Reproducibility

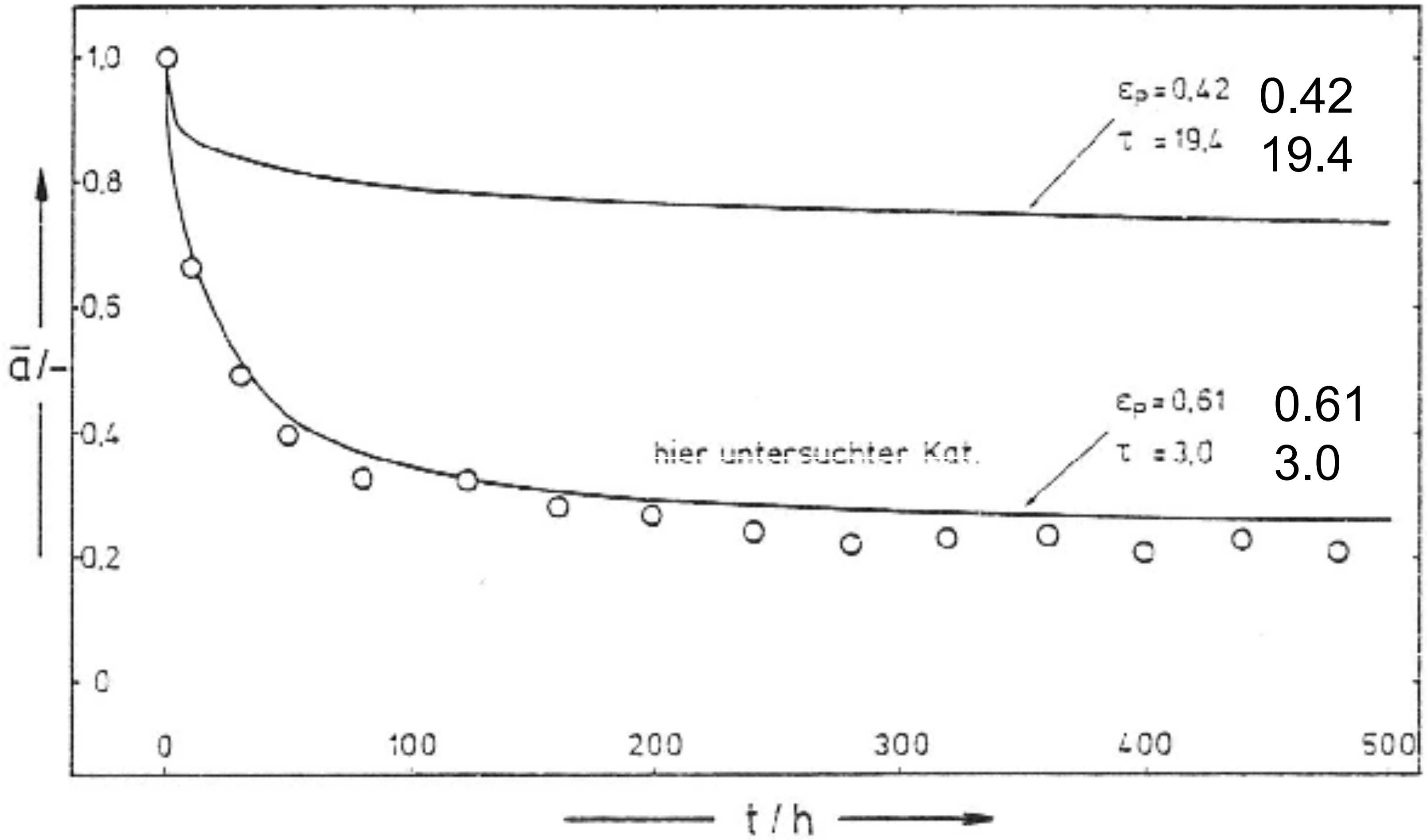
Degree of CO conversion X_{CO} at the reactor outlet

(close to industrial conditions)



Prediction of the effect of porosity parameters

- Tortuosity and porosity -



Lecture Series *"Catalysis"* at FHI/AC **2010/2011**

Catalyst Deactivation
by M. Baerns January 21, 2011

References for advanced reading

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Source: JOURNAL OF CATALYSIS Volume: 224 (2004), Issue: 1, Pages: 187-196.