Transient modelling and catalyst deactivation in reaction engineering

Tapio Salmi, Dmitry Murzin, Johan Wärnå,
Esa Toukoniitty, Fredrik Sandelin
Åbo Akademi

Outline

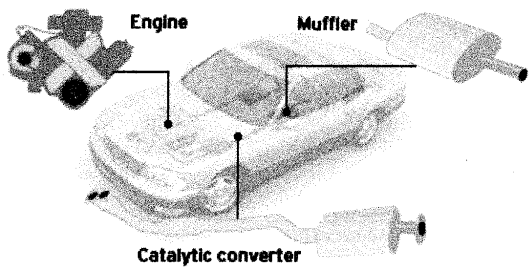
- Modelling of transient experiments
  - Why transient experiment
  - Transient techniques
  - Modelling of transient experiments
  - Results (examples)
- Catalyst deactivation
  - About catalyst deactivation
  - Modelling of catalyst deactivation
  - Case studies

Why transient experiments

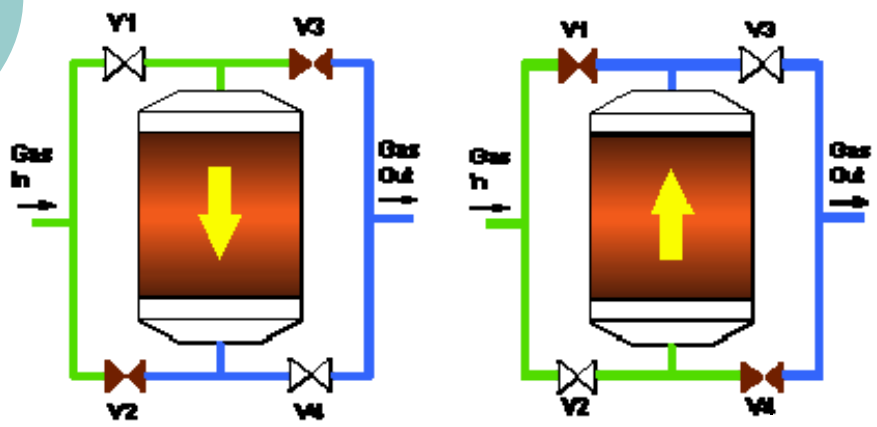
- Obtain more information on mechanism
  - Multiple reactions (sequence of steps, forward and backward rates, etc)
  - Adsorption, reaction, desorption
- Information on dynamic behavior (essential if reactor works in transient regime)
- Information on start-up and shut down behavior

Transient behaviour in chemical engineering

- Start-up and shut down of processes
- Continuous change in conditions, e.g. car exhaust converters



Transient behaviour: Matros reactor

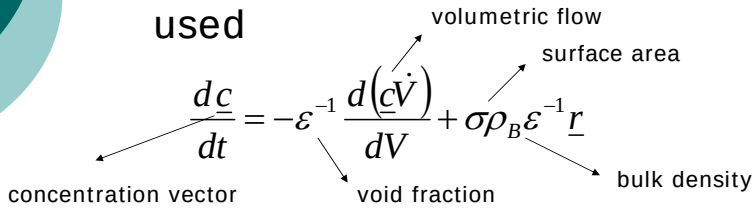


Transient techniques

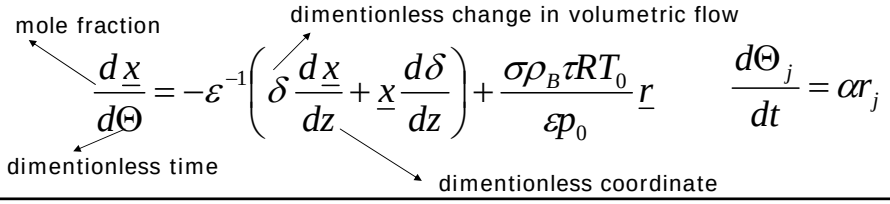
Transient techniques	Instruments	Characterized features
Step response experiments	MS / rapid GC	Inlet parameters are changed in a step
Pulse experiments	MS / GC	Inlet parameters are changed in pulses
Temperature programmed desorption	MS	Desorption is recorded as function of time
Temperature programmed surface reaction	MS	T is changed after each steady-state
Isotope exchange experiments	MS	A molecule is replaced by its isotope
Transient infrared studies	FT-IR	Analysis of composition in bulk phase and on catalyst surface

Modelling transient experiments

- A transient plug flow model can be used



- and in dimensionless form



Modelling transient experiments

- For the surface intermediates

$$\frac{d\underline{c}^*}{dt} = \underline{r}^*$$

- and expressed in surface coverage

$$\frac{d\underline{\theta}}{d\Theta} = \left(\frac{\tau}{c_0}\right)\underline{r}^*$$

Case studies of transient experiments

- Examples from e.g. Rahkama-Tolonen doctoral thesis

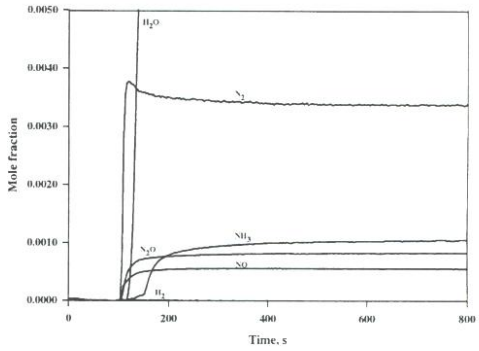
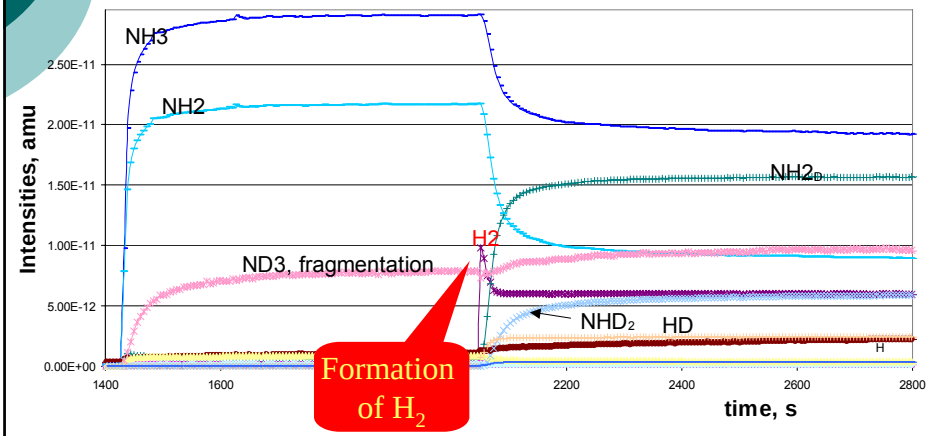


Fig. 2. (1% NO + 1% H_2)/Ar step-response experiment on the Pd catalyst at 165°C.

Transient kinetics: Isotope exchange in NH_3

NH3 -> NH3 + D2

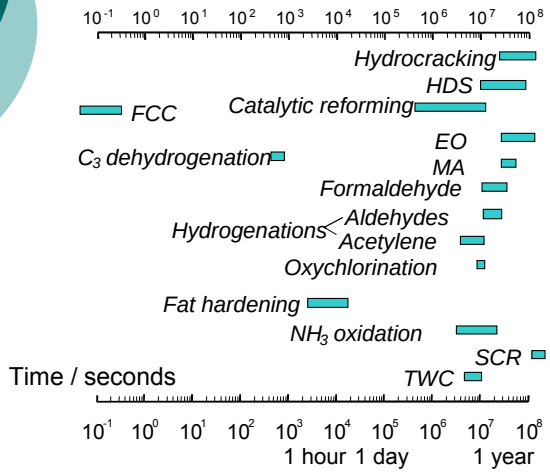
Experiment: Ar -> 1%NH_3 -> 1%NH_3 + 1%D_2 -> 1%NH_3, Pd/modified alumina catalyst at 155 ° C



Catalyst deactivation, general

- All industrial catalysts experience catalyst deactivation
- Rate can vary significantly, from seconds to many years

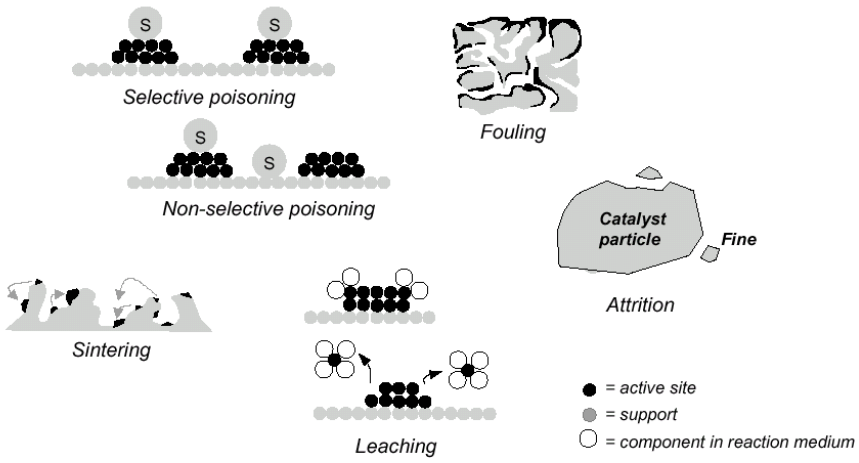
Time-Scale of Deactivation



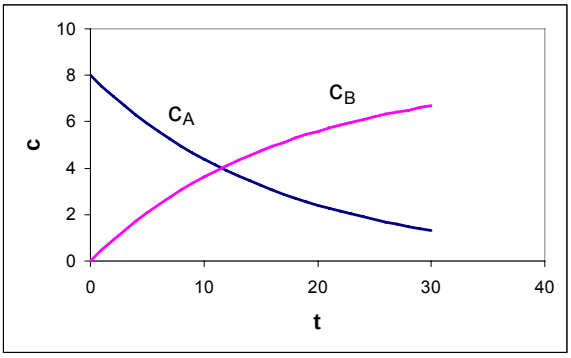
Most bulk processes 0.1-10 year

Batch processes hrs-days

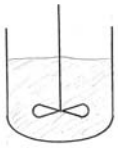
Types of deactivation



Observation of catalyst deactivation



A -> B



- Concentrations as a function of time in a batch reactor. How do you distinguish kinetics from deactivation? Multiple of experiments needed.

Batch reactor

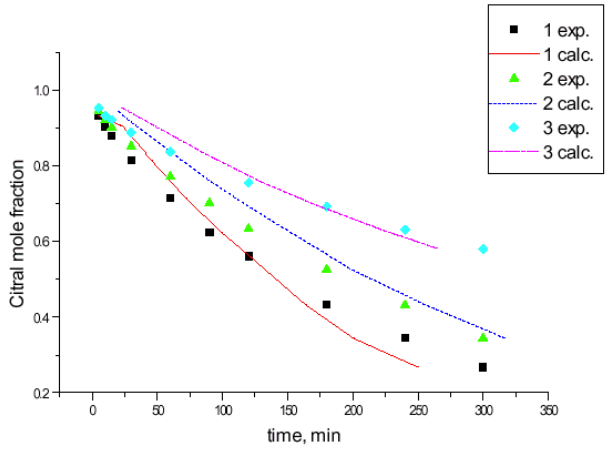
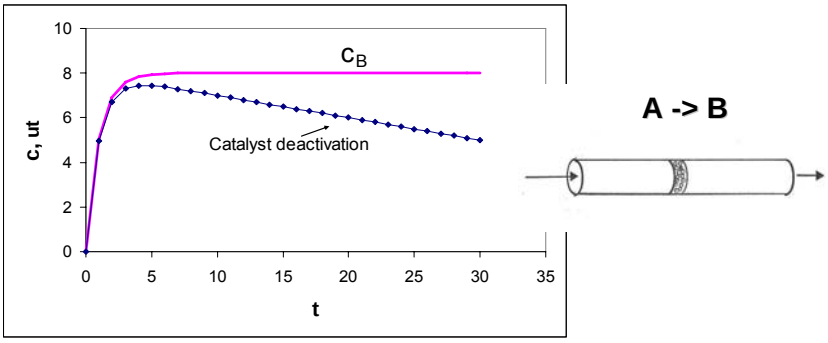


Fig. 1. Citral conversion at 70°C with the fresh (1), once used (2) or twice used (3) Ru/Al_2O_3. Conditions: Initial concentration of citral = 0.05 mol/L, solvent ethanol, citral-to-ruthenium ratio = 10

Observation of catalyst deactivation



- Concentrations as a function of time on stream in a fixed bed reactor. Deactivation observed in activity decay as function of time.

The elements of a reactor model

Catalytic reactor model

Kinetics

- Stoichiometry
- Equilibria
- Rate equations for adsorption, desorption and surface reactions
- Heat effects on rates
- Catalyst deactivation

Mass and heat transfer

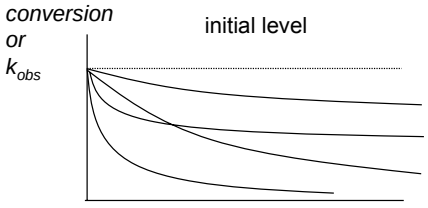
- Mass and heat transfer on reactor level
- Interfacial mass and heat transfer
- Intraparticle mass and heat transfer

Flow pattern

- Continuous or batch
- Degree of backmixing
- Fixed bed, slurry, moving bed or fluidized bed
- Computational fluid dynamics

Mass, energy and impulse balances

Influence of Deactivation on Reaction Rate



$$k_{obs} = k_{intr} \cdot N_T \cdot \eta$$

'constant'

'variable

- loss of surface area
- loss of active sites

variable

- blocking of pores

Fouling

Sintering

Poisoning

Two approaches to catalyst deactivation

Semi-empirical separate function

- Typical approach in the past
- Simple to use and obtain, easy computation

Semi-empirical separate function

- Reaction rate obtained by adjusting initial rate with time dependent function

$$r_i = a(t) r_{0i}$$

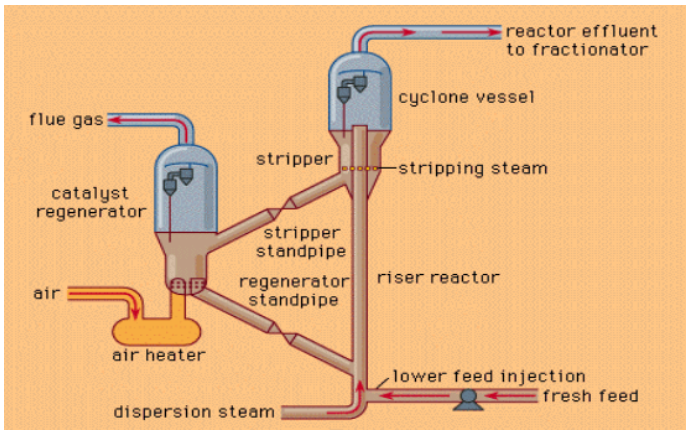
- Semi-empirical functions

$a = 1 - k_d t$ linear, zero order

$a = e^{-k_d t}$ exponential, first order

$a = \frac{1}{1 - k_d t}$ hyperbolic, second order

What to do?



Two approaches to catalyst deactivation

Mechanistic approach (as any reaction)

- Treats deactivation as any reaction in system
- Involves many (complex) reactions in a network
- Dynamic models evolves, demanding to compute
- More information of the system can be obtained.

Mechanistic approach

- Identify reactions e.g. monomolecular reaction and bimolecular coking

$$\mathbf{A^* \rightarrow B^*}$$

$$\mathbf{2A^* \rightarrow C^*}$$

- and develop rate expressions

$$r_{Isom} = k'_{iso} c_A K_A \Theta_V$$

$$r_{Deact} = k'_{dea} \left(c_A K_A \Theta_V \right)^2$$

Mechanistic approach

- Rearrange equations

$$r_{Isom} = \frac{k'_{iso} c_A \left(1 - \Theta_{C^*}\right)}{1 + K\left(c_A + c_B\right)}$$

$$r_{deact} = \frac{k'_{dea} c_A^2 \left(1 - \Theta_{C^*}\right)^2}{\left(1 + K\left(c_A + c_B\right)\right)^2}$$

Mechanistic approach

- Develop mass balances for reactor and for catalyst surface species

$$\frac{\partial c_i}{\partial t} = \frac{1}{\varepsilon}\left(-\frac{w}{L}\frac{\partial c_i}{\partial z} + r_i \rho_B\right)$$

$$\frac{d\Theta_{C^*}}{dt} = \alpha r_{deact}$$

The mass balance for the surface components

- Mass balance for adsorbed surface components

$$\frac{dc_j^*}{dt}\Delta A' = r_j \Delta m_{cat}$$

- and

$$\frac{d\Theta_j}{dt} = \alpha r_j$$

$$\text{where, } \alpha = \Delta m_{cat} / \Delta A' c_0^* \text{ and } \Theta_j = c_j^* / c_0^*$$

Dynamic reactor models

- Axial dispersion model

$$\frac{\partial c_i}{\partial t} = \frac{1}{\varepsilon}\left(-\frac{w}{L}\frac{\partial c_i}{\partial z} + \frac{D_a}{L^2}\frac{\partial^2 c_i}{\partial z^2} + r_i \rho_B\right)$$

- Dynamic plug flow model

$$\frac{dc_i}{dt} = \frac{1}{\varepsilon}\left(r_i \rho_B - \frac{dc_i}{d\tau}\right)$$

- Batch reactor

$$\frac{dc_i}{dt} = \frac{1}{\varepsilon} r_i \rho_B$$

Numerical methods

Dynamic fixed bed	PDE + ODE
Steady state fixed bed	ODE + (N)LE
Batch reactor	ODE

PDE	Partial differential equation
ODE	Ordinary differential equation
(N)LE	(Non-)linear equation

Principle of numerical methods

- The PDEs are solved by discretization
  - With finite differences
  - Ortogonal collocation
- The ODEs are solved with routines suitable for stiff systems
  - Backward differences, BD, e.g. LSODE
  - Runge-Kutta, RK, e.g. SIRK

Solving PDEs by discretization

PDE

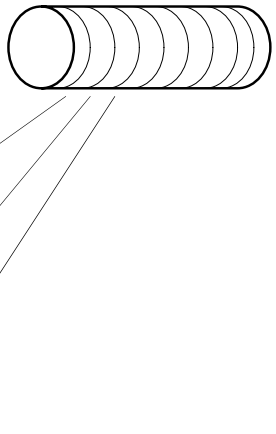
$$\frac{\partial c_i}{\partial t} = \frac{1}{\varepsilon}\left(-\frac{w}{L}\frac{\partial c_i}{\partial z} + r_i \rho_B\right)$$

ODEs

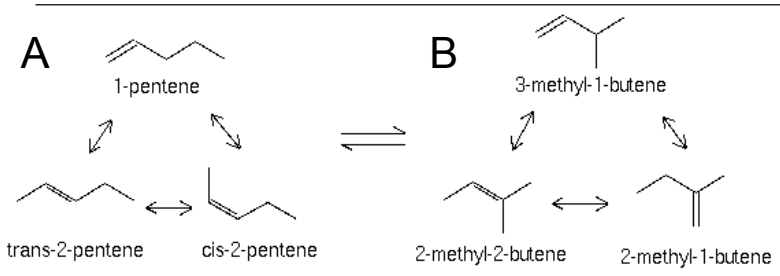
$$\frac{\partial c_i}{\partial t} = \frac{1}{\varepsilon}\left(-\frac{w}{L} c_i(z_1) + r_i \rho_B\right)$$

$$\frac{\partial c_i}{\partial t} = \frac{1}{\varepsilon}\left(-\frac{w}{L} c_i(z_2) + r_i \rho_B\right)$$

•••



Case study I: Skeletal isomerization of 1-pentene



$$\begin{array}{ccccc} & 1 & & 2 & 5 \\ A + * & \leftrightarrow & A* & \rightarrow & B* \leftrightarrow B + * \\ & \downarrow 3 & & \downarrow 4 & \\ & C* & & C* & \end{array}$$

Semi-empirical model

Mechanism reduces to

$$A \rightarrow B$$

Kinetics

$$r_{Isom} = k'' c_A a$$

Semi-empirical model

Deactivation functions

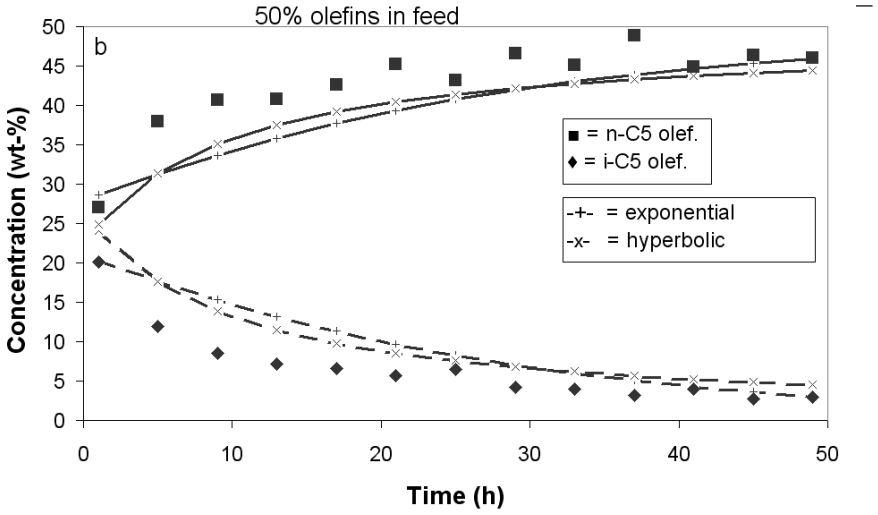
$$a = e^{-k_d t}$$

$$a = \frac{1}{1 + k_d t}$$

Mass balance

$$\frac{dc_i}{d\tau} = r_{Isom}\rho_B$$

Results, semi-empirical model



Mechanistic model

Mechanism

A* → B* II

2A* → C* IV

$$r_{Isom} = k'_{+2} c_A K_A \Theta_V$$

$$r_{Deact} = k'_{+4} \left(c_A K_A \Theta_V \right)^2$$

Mechanistic model

Kinetics

$$r_{Isom} = \frac{k'_{+2} c_A \left(1 - \Theta_{C*}\right)}{1 + K\left(c_A + c_B\right)}$$

$$r_{deact} = \frac{k'_{+4} c_A^2 \left(1 - \Theta_{C*}\right)^2}{\left(1 + K\left(c_A + c_B\right)\right)^2}$$

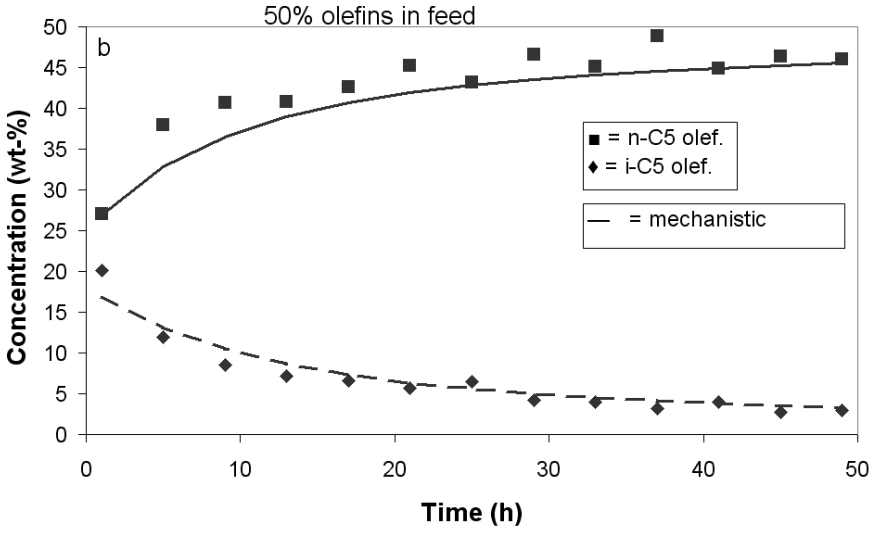
Mechanistic model

Mass balance

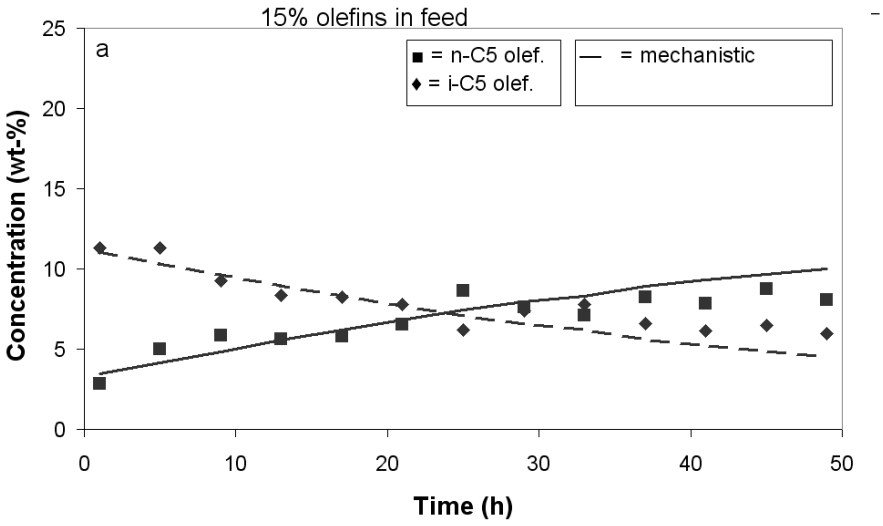
$$\frac{\partial c_i}{\partial t} = \frac{1}{\varepsilon}\left(-\frac{w}{L}\frac{\partial c_i}{\partial z} + r_i \rho_B \right)$$

$$\frac{d\Theta_{C^*}}{dt} = \alpha r_{deact}$$

Results, mechanistic model



Results, mechanistic model



Investigate deactivation mechanisms

Isomerization

A* →B* II

Deactivation mechanisms

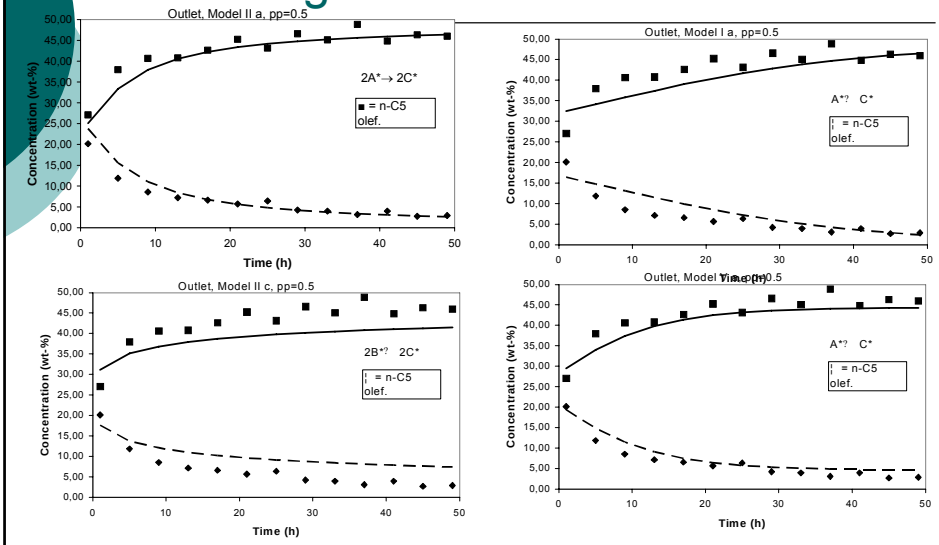
2A* → C* IVa

A* → C* IVb

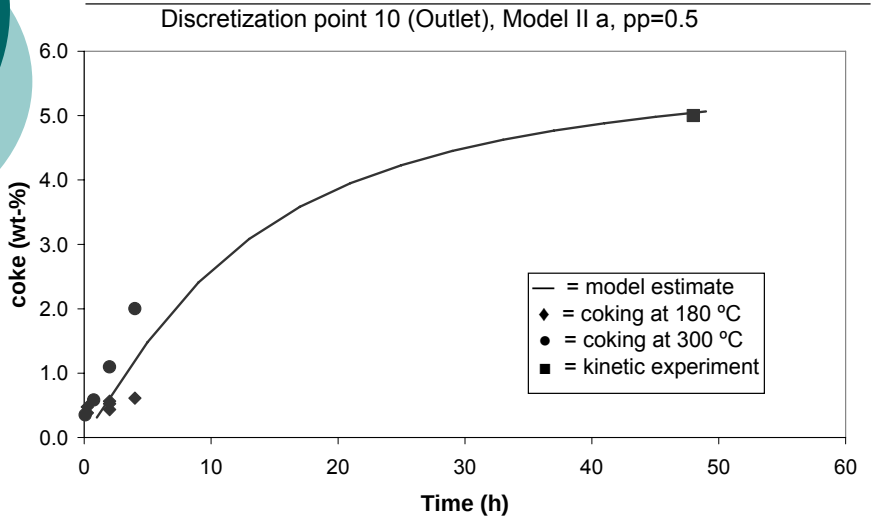
B* → C* IVc

A* ↔ C* IVd

Investigate mechansim



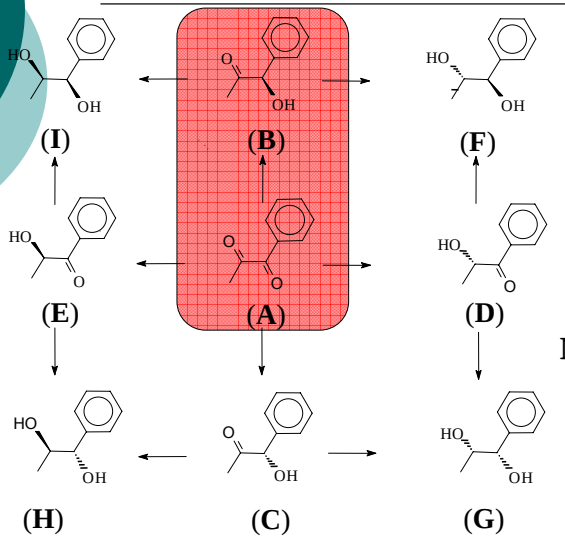
Estimate coke yield



Conclusions

- Deactivation can be accounted for in many ways.
- If understanding of the deactivation phenomenon is desired a more rigorous model is needed.
- Time-on-stream is not allways a good variable for catalyst deactivation
- A dynamic mechanistical model is solvable with modern computational tools.
- The coke on catalyst was modelled and compared to experimental data

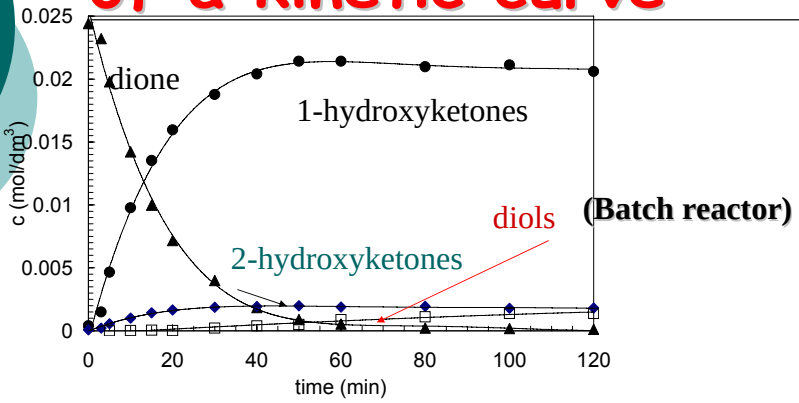
Case study II: dione hydrogenation



$$ee\,(\%) = \frac{|[R]-[S]|}{[R]+[S]} \times 100\,\%$$

Main product is 1 R

General example of a kinetic curve



(Batch reactor)

Multi-centered adsorption model applied
Co-adsorption of organic molecules and catalyst modifier
Adsorption of hydrogen essentially non-competitive
Passive spectators on the catalyst surface

Kinetic model

•Impossible to obtain explicit rate-expressions, but fractional coverages solved numerically

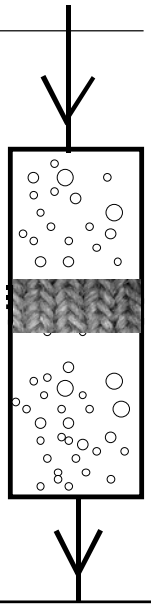
$$c_A(mK_1(1+k_7/k_8)c_0^{(m-1)}\Theta^m + nK_2(1+k_9/k_8)c_0^{(n-1)}\Theta^n) +$$

$$c_M(pK_3c_0^{(p-1)}\Theta^p + qK_4c_0^{(q-1)}\Theta^q) +$$

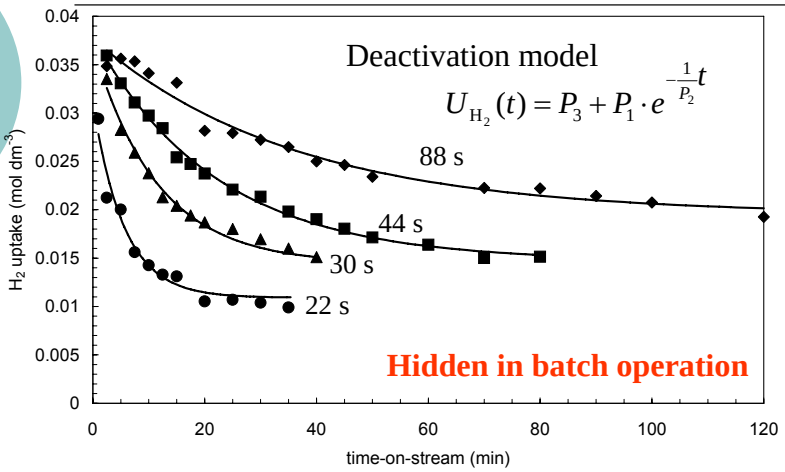
$$(m+p+f)K_1K_3K_5(1+k_{11}/k_{12})c_Ac_Mc_0^{(m+p+f-1)} +$$

$$(n+p+l)K_2K_3K_6(1+k_{13}/k_{14})c_Ac_Mc_0^{(n+p+l-1)} + \Theta = 1$$

Continuous operation



Catalyst deactivation: Dione

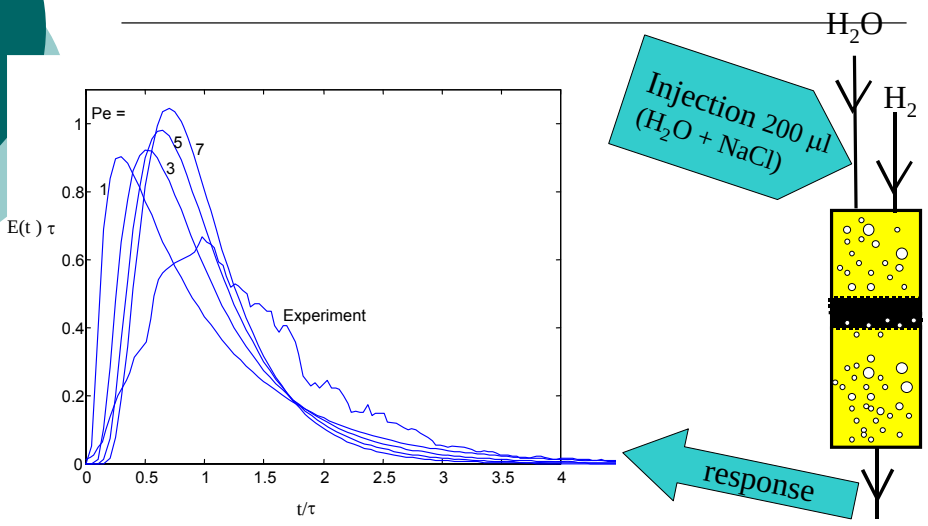


E. Toukoniitty, P. Mäki-Arvela, A. Kalantar Neyestanaki, T. Salmi, D. Yu. Murzin, *Applied Catalysis A: General*, 235 (2002) 125.

Transient modelling: Dione

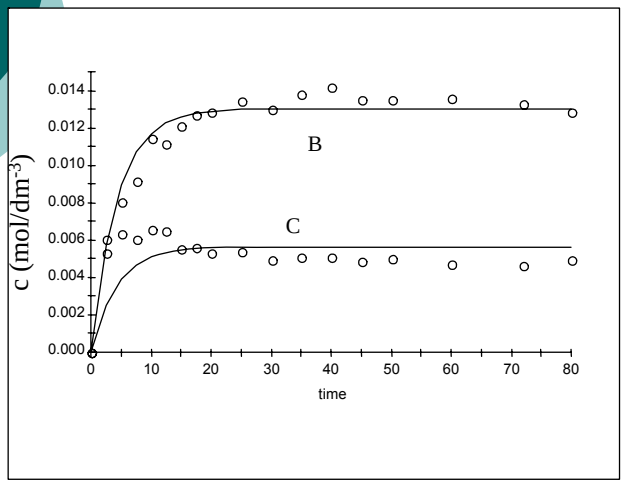
- **Kinetic model : steady or non-steady adsorption?**
  - **adsorption equilibrium**
  - **dynamics of adsorption**
- **Reactor model**
  - dynamic axial dispersion model for tube reactor
  - Peclet number from impulse experiments with inert tracer

Impulse experiments with inert tracer



Transient modelling: Dione

Direct implementation of steady state kinetics

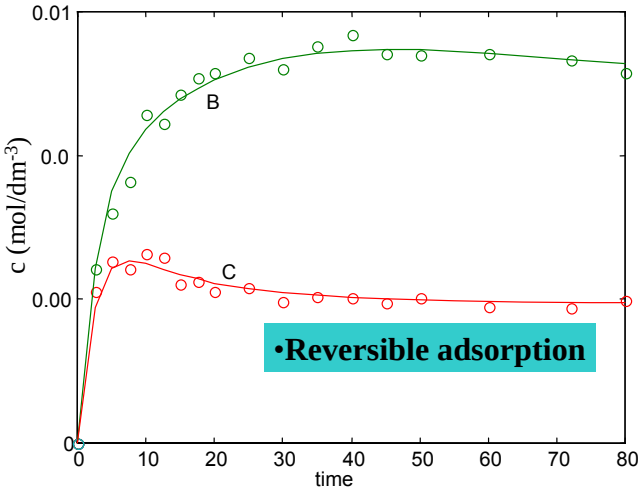


Steady state kinetics:

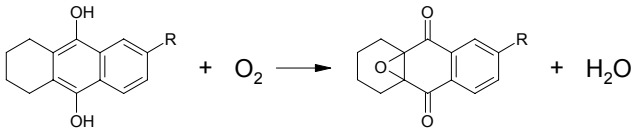
- Describes well batch reactor data
- Adsorption quasi-equilibria
- Addition of hydrogen RDS

Transient modelling: Dione

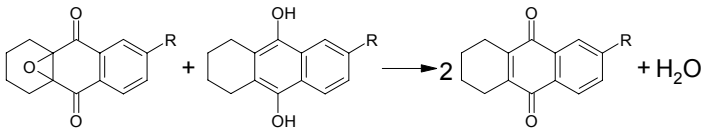
Non-steady state kinetics



Case study III: Transformation of epoxides in the Hydrogen peroxide process

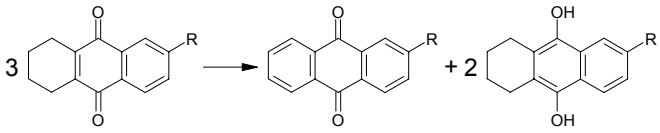


THAAHQ (B) + O_2 ⟶ Epoxide (A) + H_2O (D)



Epoxide (A) + THAAHQ (B) ⟶ 2 THAAQ (C) + H_2O (D)

Case study: Transformation of epoxides in the Hydrogen peroxide process



3 THAAQ (C) ⟶ AAQ (E) + 2 THAAHQ (B)

Mechanism

I	$A + B \rightarrow 2C + D$
IIa	$C + C \rightleftharpoons C' + B$
IIb	$C' + C \rightleftharpoons E + B$
III	$B + E \rightleftharpoons F + C$
IV	$A + F \rightarrow E + C + D$

Kinetics

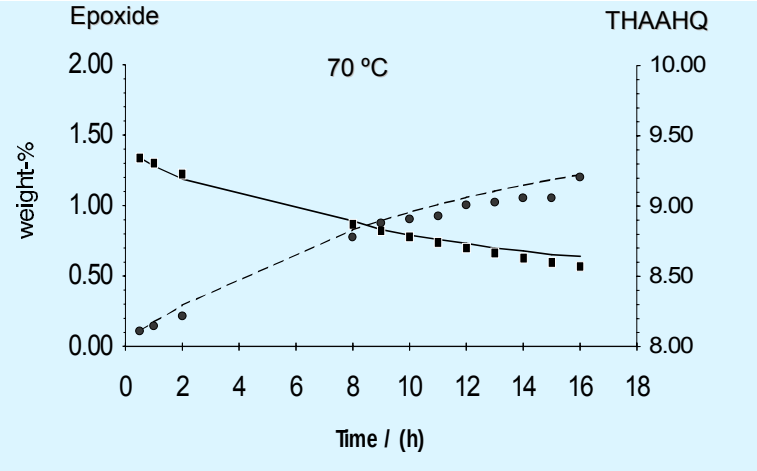
$$r_1 = k'_{+1}\left(c_A c_B - \frac{1}{K'_1} c_C^2 c_D\right)$$

$$r_2 = \frac{k'_{21} c_C^3}{k'_{22} c_B + c_C}$$

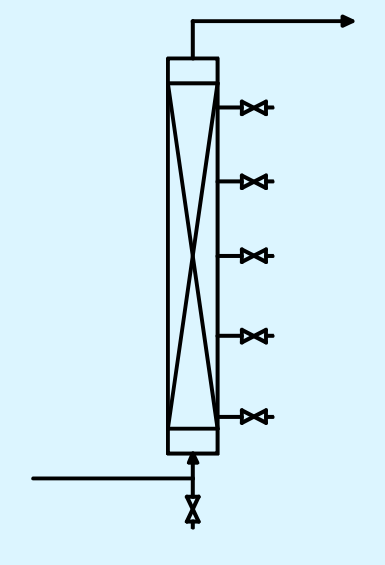
$$k'_{+1} = A_1 e^{-E_1/RT}$$

$$k'_{21} = A_2 e^{-E_2/RT}$$

Modelling results



Modeling of a continuous pilot reactor (packed bed)



Modeling of a continuous pilot reactor (packed bed)

Dispersion model

$$\frac{\partial c_i}{\partial t} = \frac{1}{\varepsilon}\left(-\frac{w}{L}\frac{\partial c_i}{\partial z} + \frac{D_a}{L^2}\frac{\partial^2 c_i}{\partial z^2} + r_i \rho_B\right)$$

Reaction kinetics and deactivation function

$$r_j = a(t) r_{0j}$$

Stoichiometry

$$r_i = \sum \nu_{ij} r_{0j}$$

Semi-empirical description of catalyst deactivation

$$\mathrm{P} + * \rightleftharpoons \mathrm{P}*$$

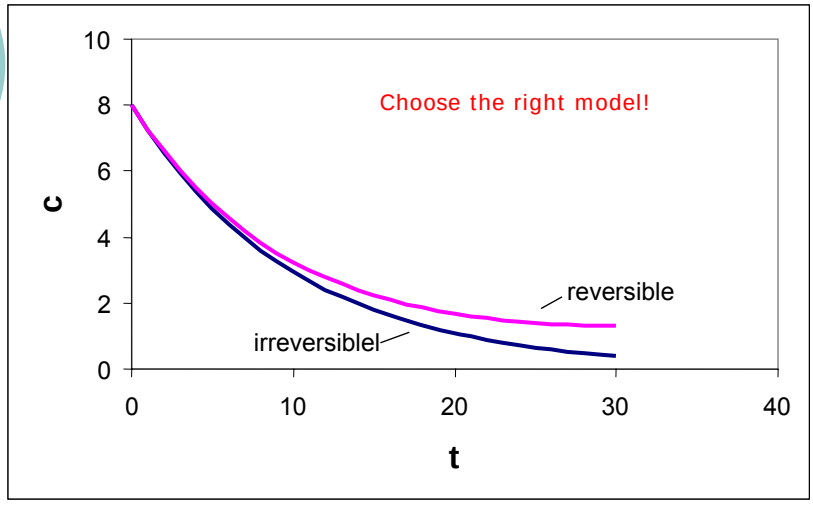
$$r_P = k_+ c_P c_v - k_- c_{P*}$$

$$\frac{da}{dt} = -k'(a - a*)^n$$

$$a(t) = a* + (a_0 - a*)e^{-k't} \qquad , n = 1$$

$$a(t) = a* + \left[(a_0 - a*)^{1-n} + k'(n-1)t\right]^{\frac{1}{1-n}} \qquad , n \neq 1$$

Reversible and irreversible deactivation



Modeling of a continuous pilot reactor (packed bed)