EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research, Development and Education

MINISTRY OF EDUCATION, YOUTH AND SPORTS

9. Kinetics of catalytic reactions

- **homogeneous catalysis**

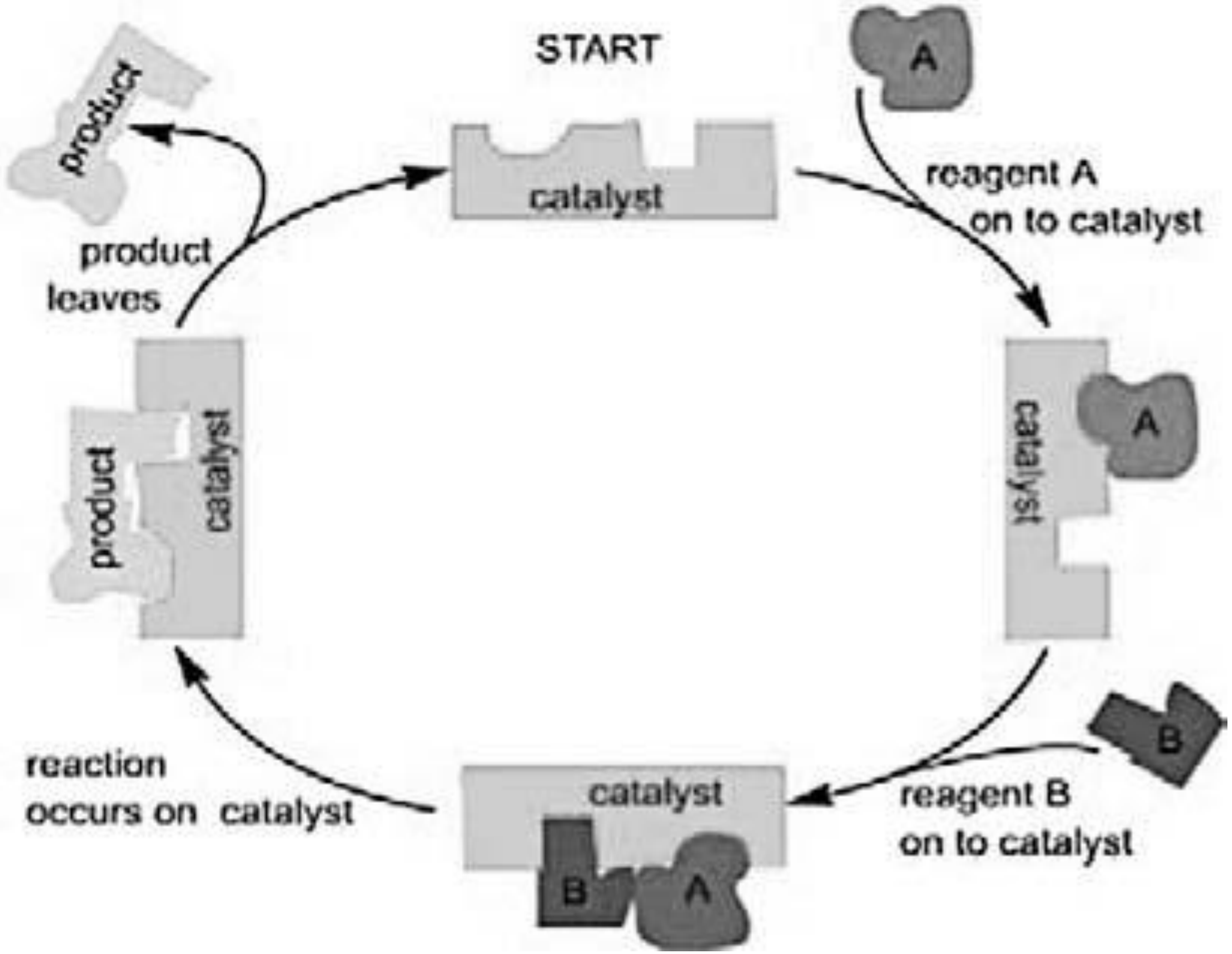
➢ **Ozone decomposition in the presence of Cl**
➢ **SO_2 oxidation by NO_x**
➢ **Esterification catalyzed by acids or bases**
➢ **Enzymatic catalysis**

$$O_3 + Cl \Rightarrow ClO + O_2$$
$$ClO + O_3 \Rightarrow Cl + 2O_2$$
$$2O_3 \Rightarrow 3O_2$$

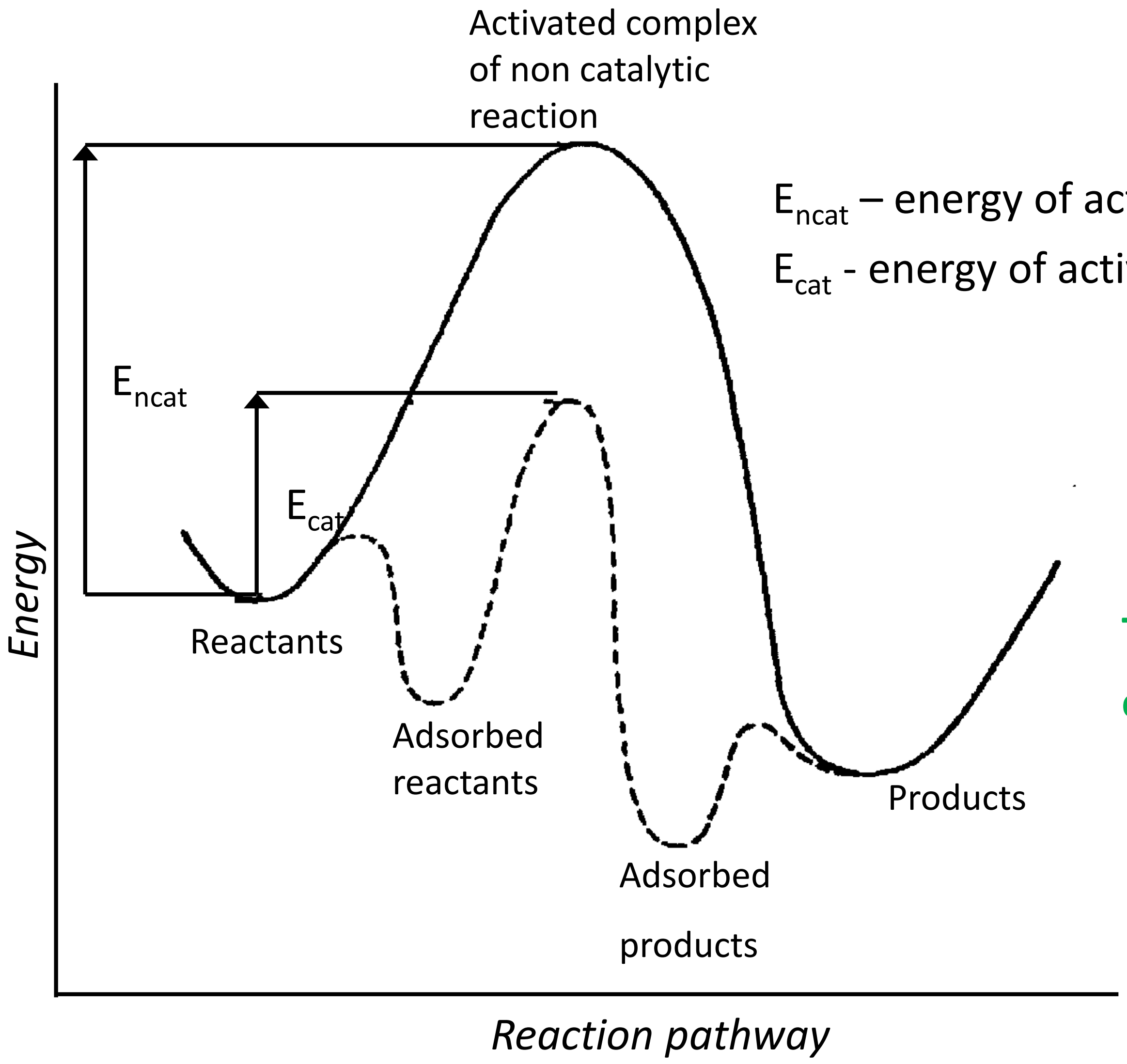
- **heterogeneous catalysis**

➢ **NH_3, CH_3OH production**
➢ **SO_2 to SO_3 oxidation**
➢ **HDS, HDN processes**
➢ **Fluid Catalytic Cracking**
➢ **Hydrogenation**
➢ **Polymerization (Ziegler-Natta catalysts, metallocens)**

Catalytic cycle



Non catalytic x catalytic reaction



E_{ncat} – energy of activation for non catalytic reaction

E_{cat} - energy of activation for catalytic reaction

$$r_i \sim e^{-\frac{E_i}{RT}}$$

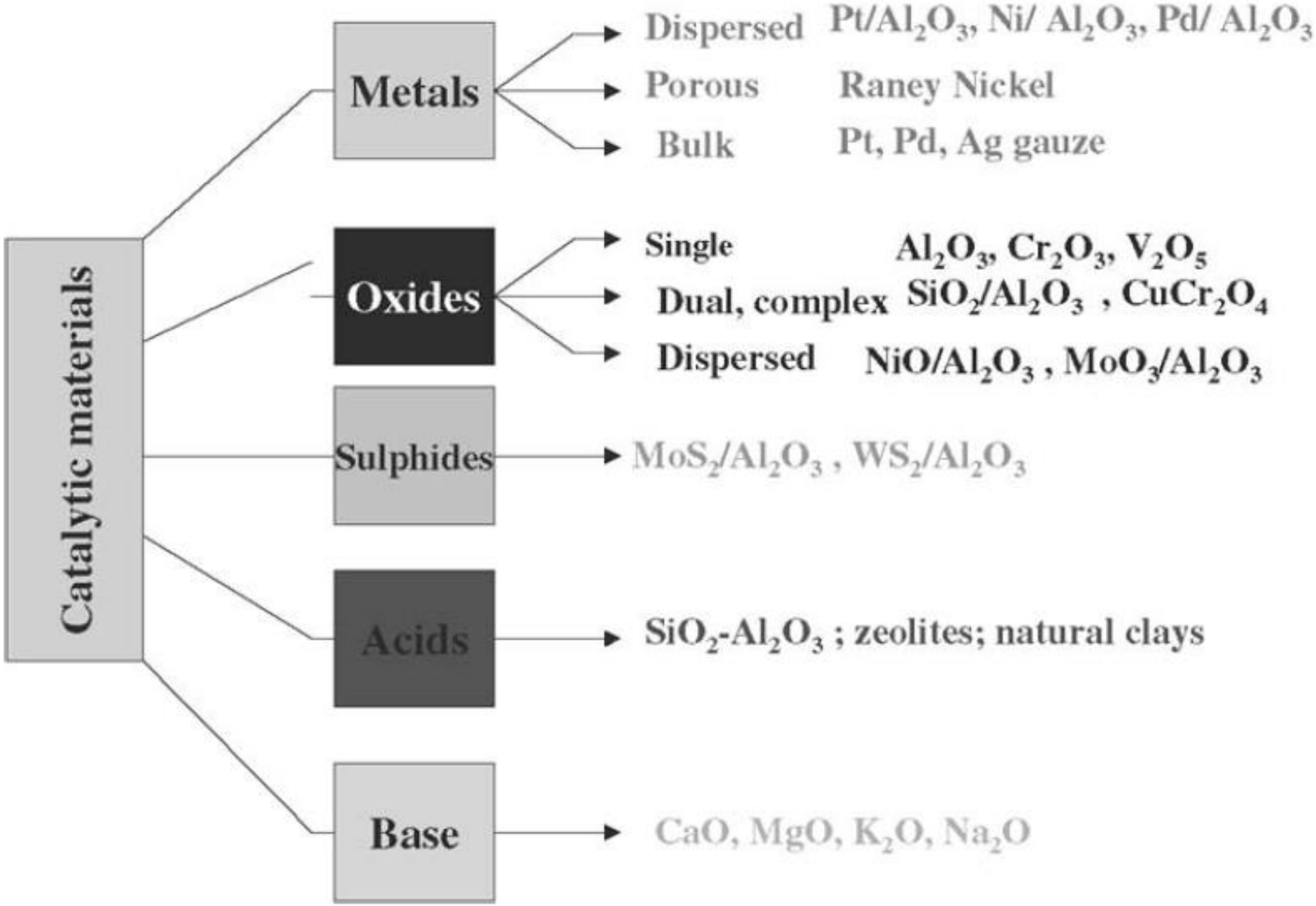
$$\Downarrow$$

The multi-step catalytic reaction can be faster than one-step reaction

Homogeneous x Heterogeneous Catalysts

		Homogeneous	*Heterogeneous*
Active sites		All atoms	Surface atoms
	Concentration	Low	High (variable)
	Diffusion disguises	No	Important
	Reaction conditions	50-200 ^{o}C	200-1000 ^{o}C
	Application	Limited	Large
Characterization	Structure, composition	Well defined	No clear defintion
	Modification	Easy	Difficult
	Temperature stability	Low	High
Separation		Difficult	Easy packed beds
Recycling		Feasible	Feasible

Reactant(s)	Product	Typical catalyst(s)	Global Production/t year^{-1}
Crude oil	Hydrocarbon fuels	Platinum/silica-alumina Platinum/acidic alumina Metal-exchanged zeolites	1*10^{9}
SO_2, O_2	Sulphuric acid	V_2O_5	1.4*10^{8}
N_2, H_2	Ammonia	Fe	9*10^{7}
NH_3, O_2	Nitric acid	Pt/Rh	2.5* 10^{7}
CO, H_2	Methanol	Cu/ZnO	1.5*10^{7}
C_2H_4, O_2	Ethylene oxide	Ag	1*10^{7}
Unsaturated vegetable oils, H_2	Hydrogenated vegetable oils	Ni	8*10^{6}
C_2H_4	Polyethylene	Cr(II), Ti(III)	6*10^{6}
CH_3OH, O_2	Formaldehyde	Mixed Fe, Mo oxides	5*10^{6}
C_3H_6, NH_3, O_2	Acrylonitrile	Mixed Bi, Mo oxides	3*10^{6}
o -Xylene, O_2	Phthalic anhydride	V_2O_5	4*10^{6}
n-Butane, O_2	Maleic anhydride	V_2O_5	4*10^{5}

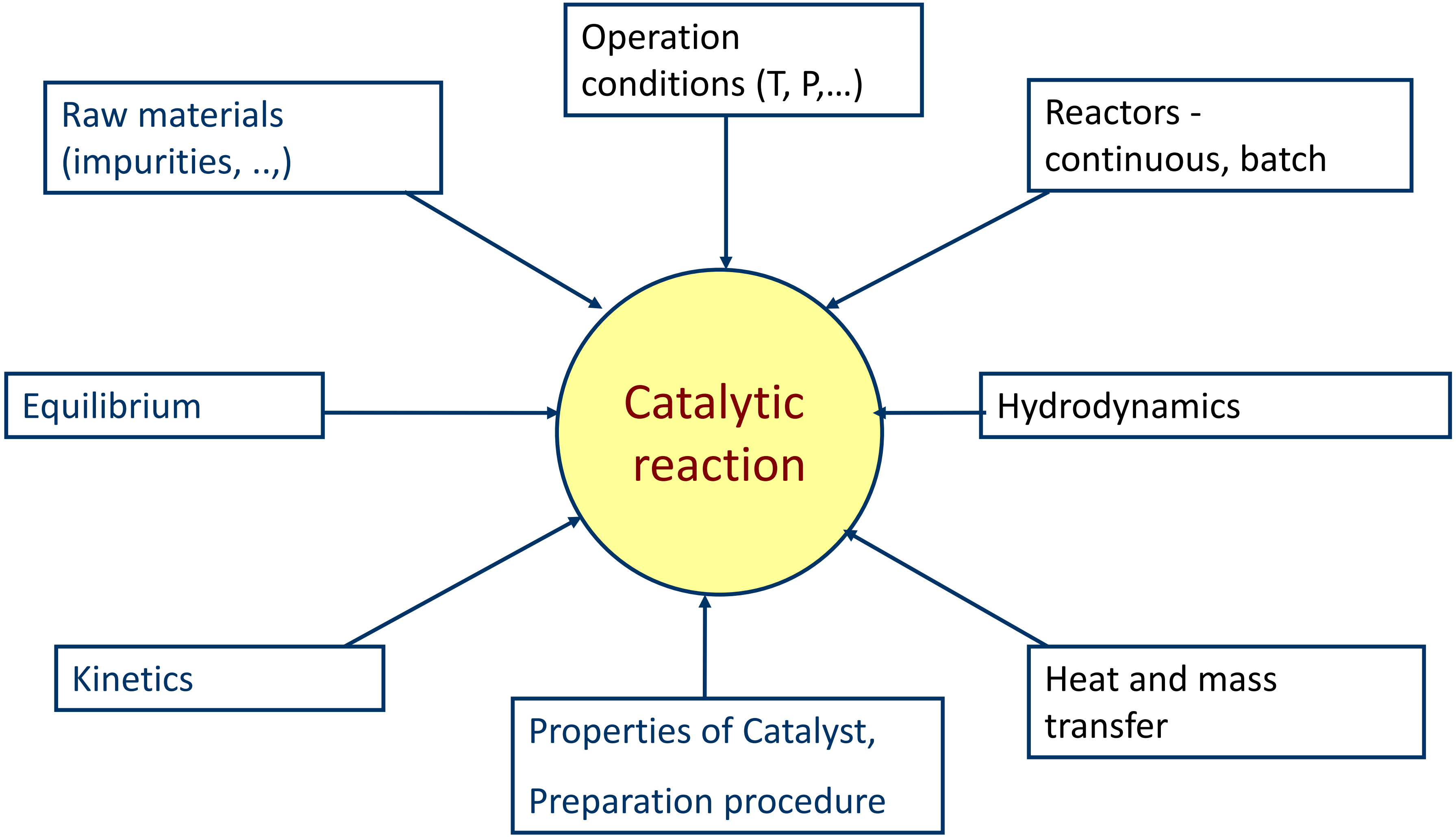


Catalytic materials

- **Metals**
  - Dispersed Pt/Al_2O_3, Ni/ Al_2O_3, Pd/ Al_2O_3
  - Porous Raney Nickel
  - Bulk Pt, Pd, Ag gauze
- **Oxides**
  - Single Al_2O_3, Cr_2O_3, V_2O_5
  - Dual, complex SiO_2/Al_2O_3 , $CuCr_2O_4$
  - Dispersed NiO/Al_2O_3 , MoO_3/Al_2O_3
- **Sulphides**
  - MoS_2/Al_2O_3 , WS_2/Al_2O_3
- **Acids**
  - SiO_2-Al_2O_3 ; zeolites; natural clays
- **Base**
  - CaO, MgO, K_2O, Na_2O

Catalyst	Reaction
Metals (e.g., Ni, Pd, Pt, as powders or on supports) or metal oxides (e.g., Cr_2O_3)	C=C bond hydrogenation, e.g., olefin + $H_2 \longrightarrow$ paraffin
Metals (e.g., Cu, Ni, Pt)	C=O bond hydrogenation, e.g., acetone + $H_2 \longrightarrow$ isopropanol
Metal (e.g., Pd, Pt)	Complete oxidation of hydrocarbons, oxidation of CO
Fe (supported and promoted with alkali metals)	$3H_2 + N_2 \longrightarrow 2NH_3$
Ni	$CO + 3H_2 \longrightarrow CH_4 + H_2O$ (methanation)
Fe or Co (supported and promoted with alkali metals)	$CO + H_2 \longrightarrow$ paraffins + olefins + H_2O + CO_2 (+ other oxygen-containing organic compounds) (Fischer-Tropsch reaction)
Cu (supported on ZnO, with other components, e.g., Al_2O_3)	$CO + 2H_2 \longrightarrow CH_3OH$
Re + Pt (supported on η-Al_2O_3 or γ-Al_2O_3 promoted with chloride)	Paraffin dehydrogenation, isomerization and dehydrocyclization

Catalyst	Reaction
Solid acids (e.g., SiO_2-Al_2O_3, zeolites)	Paraffin cracking and isomerization
γ-Al_2O_3	Alcohol $\longrightarrow$ olefin + H_2O
Pd supported on acidic zeolite	Paraffin hydrocracking
Metal-oxide-supported complexes of Cr, Ti or Zr	Olefin polymerization, e.g., ethylene $\longrightarrow$ polyethylene
Metal-oxide-supported oxides of W or Re	Olefin metathesis, e.g., 2 propylene → ethylene + butene
Ag(on inert support, promoted by alkali metals)	Ethylene + 1/2 O_2 → ethylene oxide (with CO_2 + H_2O)
V_2O_5 or Pt	$2\ SO_2 + O_2 \rightarrow 2\ SO_3$
V_2O_5 (on metal oxide support)	Naphthalene + 9/2O_2 → phthalic anhydride + 2CO_2 +2H_2O
Bismuth molybdate	Propylene + 1/2O_2 → acrolein
Mixed oxides of Fe and Mo	$CH_3OH + O_2$ → formaldehyde (with CO_2 + H_2O)
Fe_3O_4 or metal sulfides	$H_2O + CO \rightarrow H_2 + CO_2$



Operation conditions (T, P,…)

Raw materials (impurities, ..,)

Reactors - continuous, batch

Equilibrium

Catalytic reaction

Hydrodynamics

Kinetics

Properties of Catalyst,

Preparation procedure

Heat and mass transfer

Steps in a catalytic reaction

1) Mass transfer of reactants to the external surface of catalyst
2) Mass transfer of reactants in porous structure of catalyst
3) *Adsorption of reactants*
4) *Surface reaction (+ migration)*
5) *Desorption of products*
6) Mass transfer of products in porous structure of catalyst
7) Mass transfer of reactants from the external surface of catalyst

The transport steps (1,2,6,7) depend on T, P, composition, flow rates, pore size, ...

The chemical steps (3,4,5) are dependent on T, P, composition.

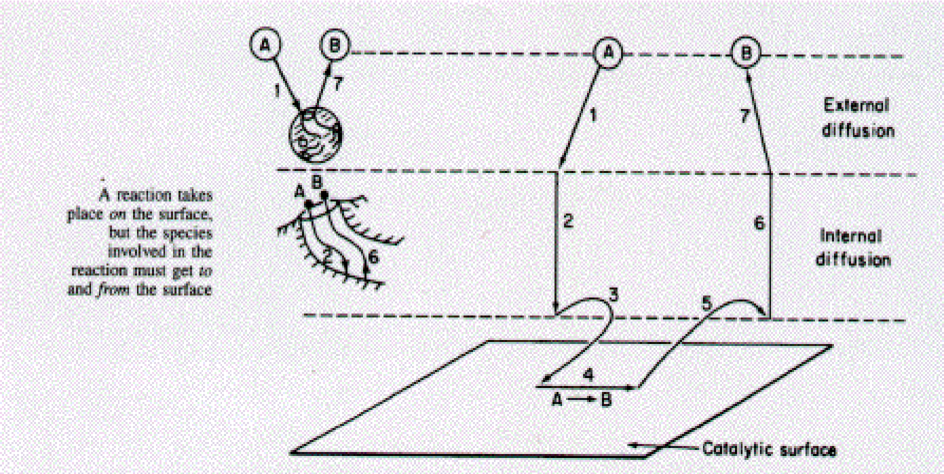
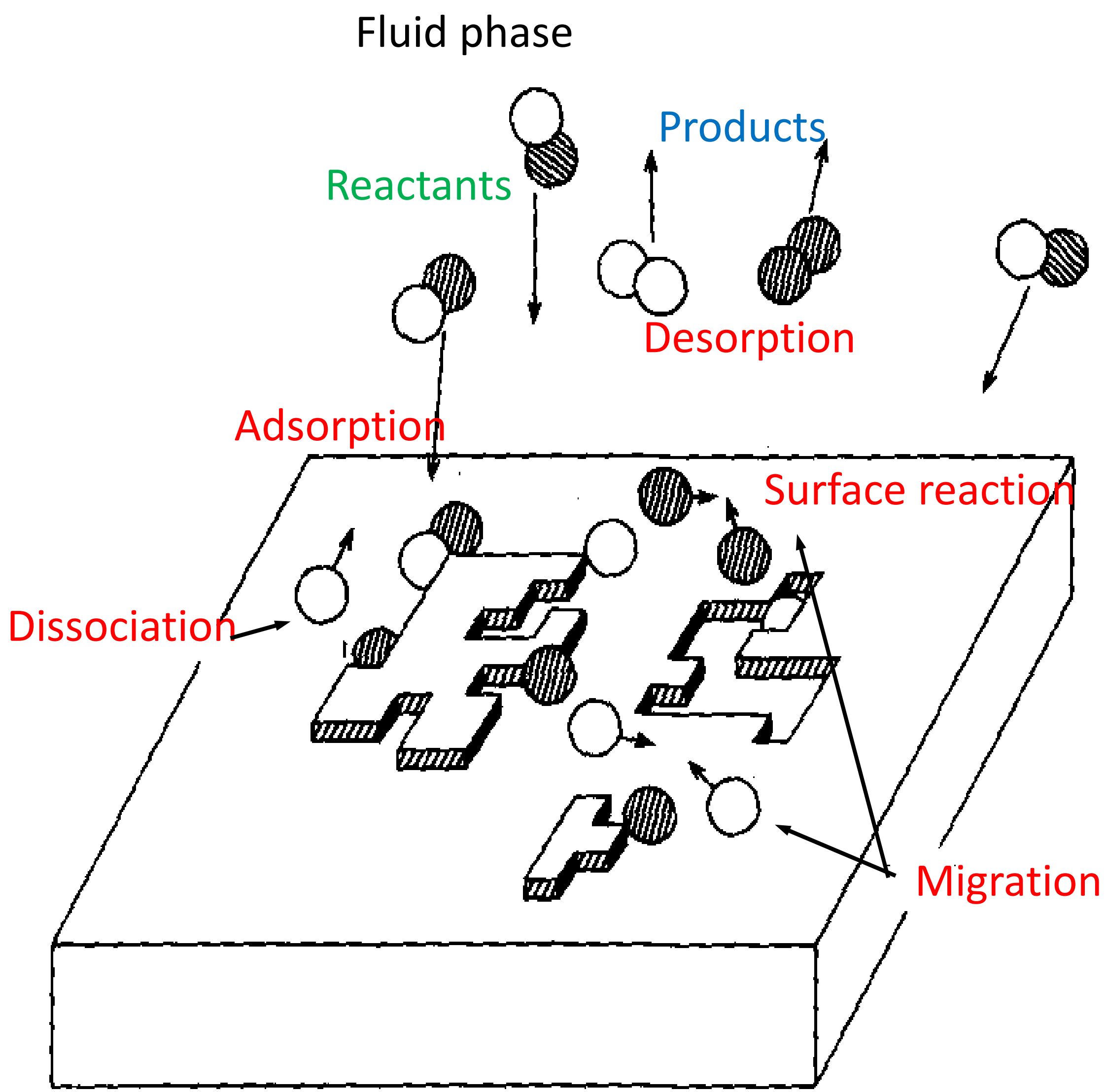

A reaction takes place *on* the surface, but the species involved in the reaction must get *to* and *from* the surface

Figure 10-6 Steps in a heterogeneous catalytic reaction.

Elementary steps of catalytic reaction



Fluid phase

Reactants

Products

Desorption

Adsorption

Surface reaction

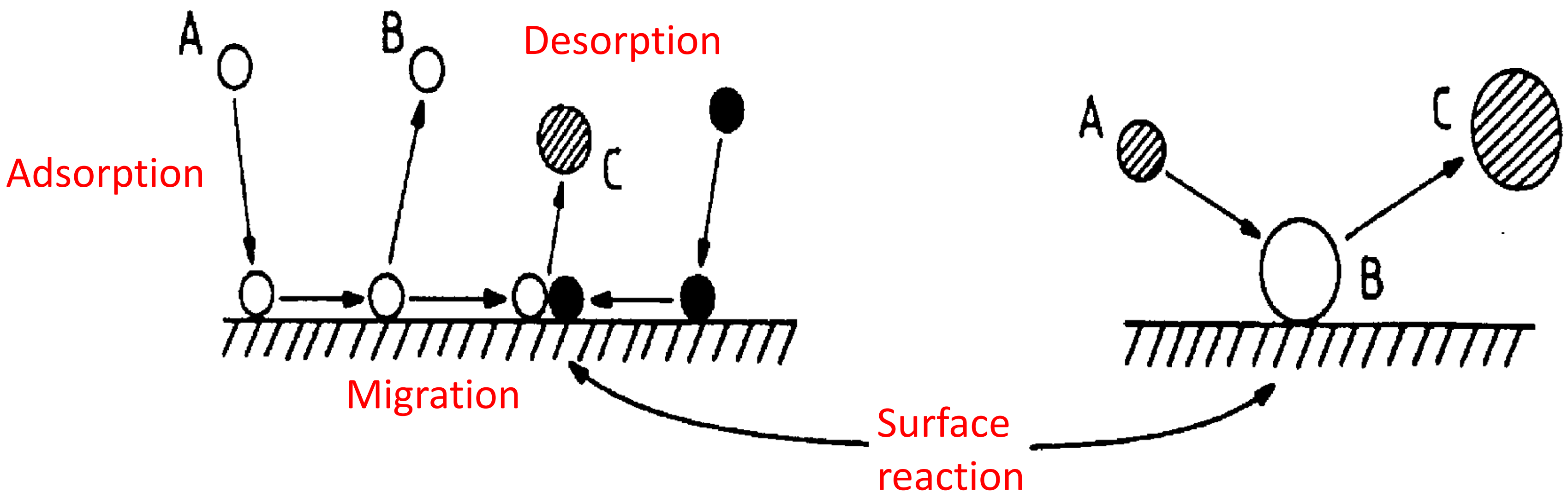
Dissociation

Migration

Mechanisms in heterogeneous catalysis

Langmuir-Hinshelwood

Rideal-Eley

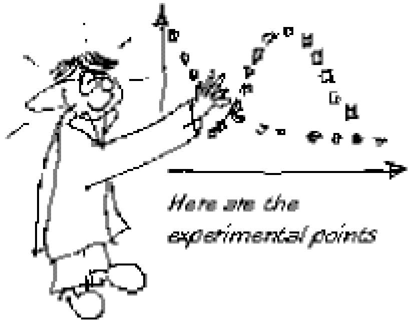


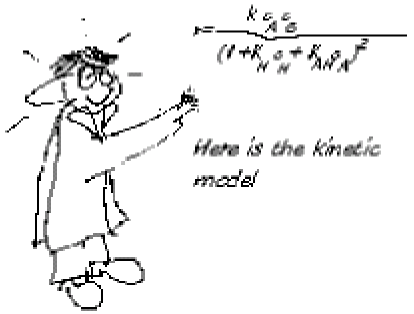
Desorption

Adsorption

Migration

Surface reaction

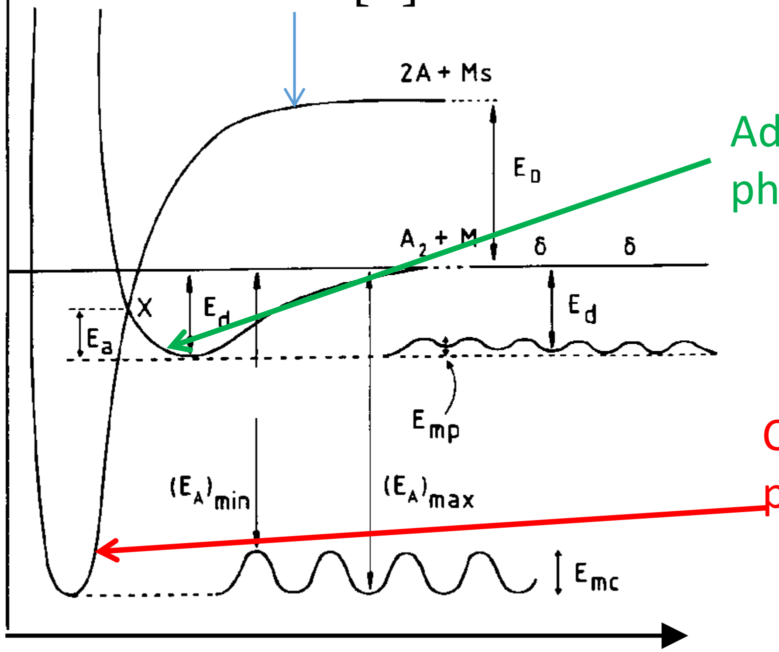




Adsorption x Chemisorption

$$2A + 2[*] \rightleftarrows 2A^*$$

$$A_2 + 2[*] \rightleftarrows 2A^*$$



Adsorption (physical phenomenon)

Chemisorption (chemical phenomenon)

Energy of biatomic molecule A_2

Distance from catalyst surface

E_{mc}, E_{mp} – activation energy of migration in adsorbed and chemisorbed state

E_D – energy of dissociation of molecule A_2

E_d – energy of desorption of A_2

E_a – energy of activation of transition from adsorbrd to chemisorbed state

Adsorption x Chemisorption

	Adsorption	*Chemisorption*
Principal	van der Waals forces no electron transfer !	covalent or ionic bonds electron transfer
Adsorbent	all solids	specific sites
Adsorbat	gases $T < T_c$	reactive components
Temperature	low	higher
Enthalpy	10-40 kJ/mol	80-600 kJ/mol
Rate	high	depends on T
Activation energy	low	high
Occupancy	multilayer	monolayer
Reversibility	YES	YES but …
Use	BET method pore size distribution	surface concentration of active sites

Chemisorption of fluid phase molecule (adsorbat)

Surface occupancy(Θ)

$$\Theta_i = \frac{\text{Number of sites occupied by i-th component}}{\text{Total number of sites}}$$

$$0 < \Theta_i < 1$$

Associative x Dissociative chemisorption

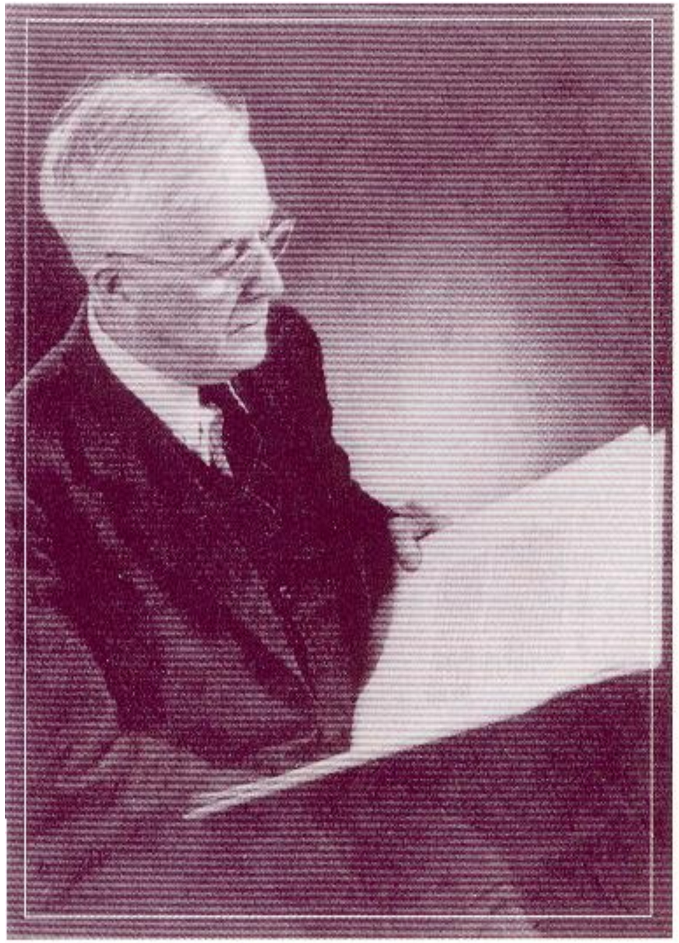
Adsorption (chemisorption) isotherm – Surface occupancy as a function of partial pressure of given component at constant temperature

Irving Langmuir

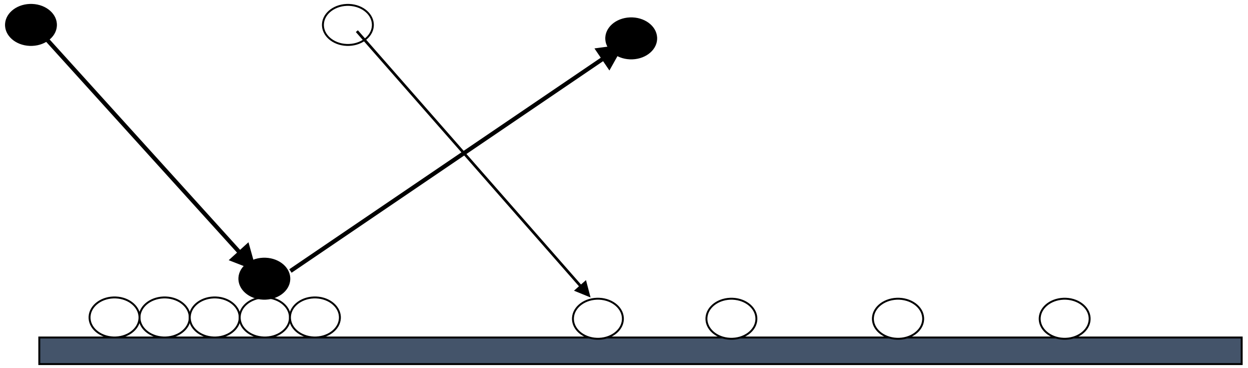
1920 - adsorption isotherm

- kinetics of catalytic reactions on ideal surfaces

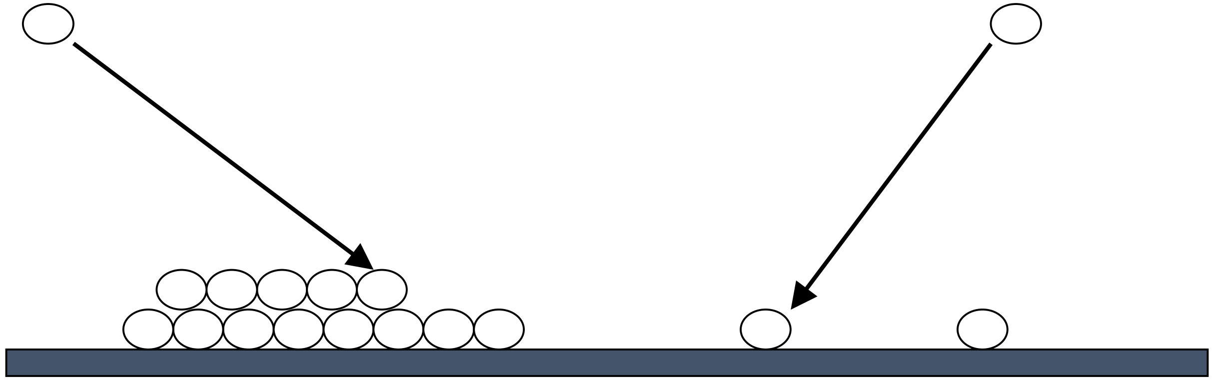
1932 - Nobel Prize



Langmuir adsorption isotherm



Brunauer-Emmett-Teller (BET) adsorption isotherm



Associative adsorption on ideal catalytic surface

$$A_{(g)} + * \underset{k_d}{\overset{k_a}{\rightleftarrows}} A*$$

Rate of chemisorption = $k_a \,.\, P_A \,.\, (1 - \Theta_A)$

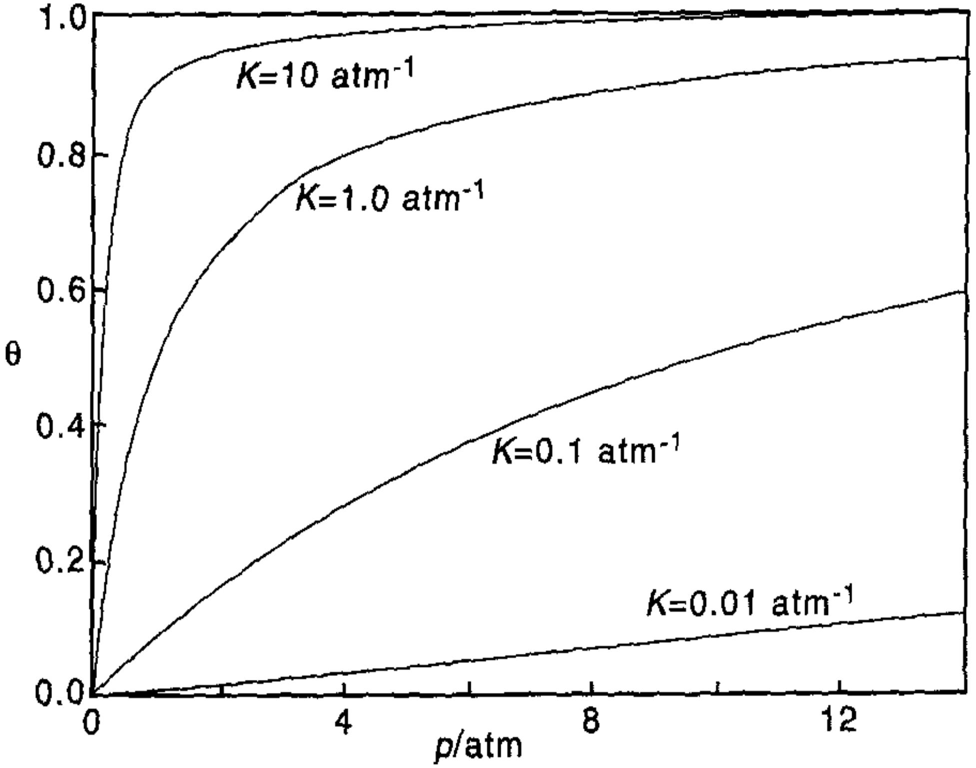
Rate of desorption = $k_d \,.\, \Theta_A$

At equilibrium

$$k_a \,.\, p \,.\, (1 - \Theta_A) = k_d \,.\, \Theta_A \qquad (K_A = k_a/k_d)$$

$$\frac{\Theta_A}{(1 - \Theta_A)} = K_A \,.\, P_A \quad \Rightarrow \quad \Theta_A = \frac{K_A P_A}{1 + K_A P_A}$$

Asociative chemisorption



Langmuir adsorption (chemisorption) isotherm

Multicomponent associative chemisorption on ideal catalytic surface

$$A_{(g)} + * \underset{k_d}{\overset{k_a}{\rightleftarrows}} A^* \qquad B_{(g)} + * \underset{k_d}{\overset{k_b}{\rightleftarrows}} B^*$$

Occupancy of A

$$\Theta_A = \frac{K_A.p_A}{1 + K_A.p_A + K_B.p_B}$$

Occupancy of B

$$\Theta_B = \frac{K_B.p_B}{1 + K_A.p_A + K_B.p_B}$$

$K_A = k_a / k_d$ $K_B = k_b / k_d$

Irreversible chemisorption → atalyst poisoning

Dissociative chemisorption on ideal catalytic surface

$$A_{2(g)} + 2\,* \underset{k_d}{\overset{k_a}{\rightleftarrows}} 2A\,*$$

Rate of chemisorption = $k_a \cdot P_A \cdot (1 - \Theta_A)^2$

Rate of desorption = $k_d \cdot \Theta_A{}^2$

At equilibrium

$$k_a \cdot p \cdot (1 - \Theta_A)^2 = k_d \cdot \Theta_A{}^2 \qquad (K_A = k_a/k_d)$$

$$\frac{\Theta_A{}^2}{(1 - \Theta_A)^2} = K_A \cdot P_A \quad ⇨ \quad \Theta_A = \frac{\sqrt{K_A P_A}}{1 + \sqrt{K_A P_A}}$$

Isotherms

Langmuir

(chemisorption, adsorption, monolayer, micropores)

$$\frac{(n_A)_{adsorbed}}{(n_*)} = \Theta_A = \frac{K_A P_A}{1 + K_A P_A}$$

Henry

(chemisorption, adsorption, low occupancy)

$$\frac{(n_A)_{adsorbed}}{(n_*)} = \Theta_A = K_A P_A$$

Freundlich

(chemisorption, adsorption, non ideal)

$$\frac{(n_A)_{adsorbed}}{(n_*)} = \Theta_A = K_A (P_A)^{\frac{1}{n}}$$

Temkin

(chemisorption, non ideal)

$$\frac{(n_A)_{adsorbed}}{(n_*)} = \Theta_A = \alpha_A \ln(\beta_A P_A)$$

Brunauer-Emmett-Teller (BET)

(adsorption, multilayer)

$$\frac{P_A}{(n_A)_{ads}(P_A^o - P_A)} = \frac{1}{n_m C} + \frac{(C-1)}{n_m C}\frac{P_A}{P_A^o}$$

Virial

(adsorption, multilayer)

$$\frac{P_A}{\mathbf{R}.T} = \Theta_A(1 + a_1\Theta_A + a_2\Theta_A^2 + \ldots)$$

Brunauer-Emmett-Teller (BET)

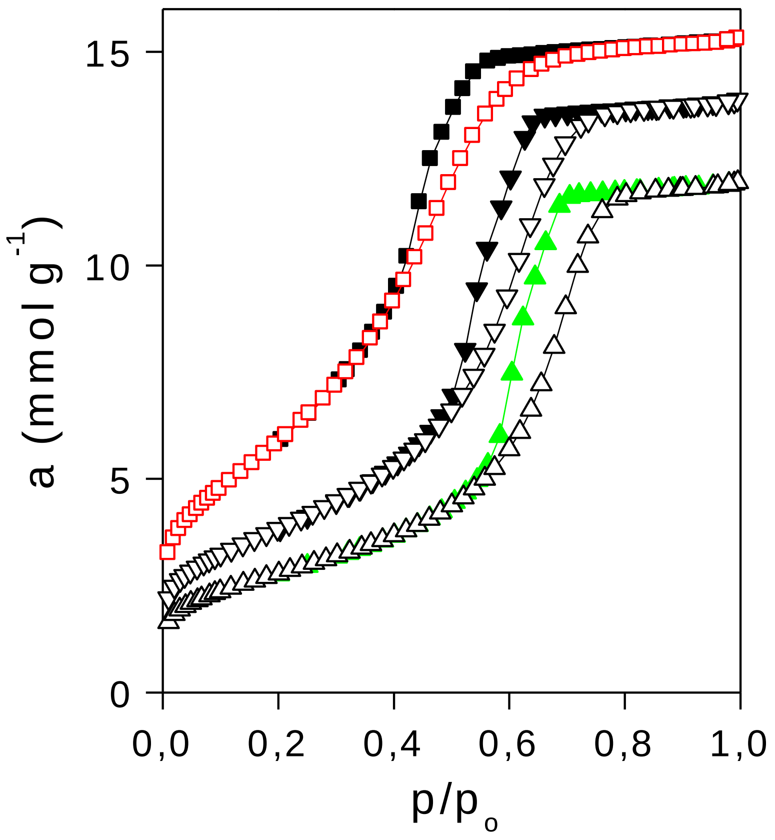
Extention of Langmuir model

Assumptions:

- adsorption in multilayer s, 1st layer interaction between adsorbent and adsorbat, in 2nd and further layers condensation-like interaction

$$\frac{P_A}{(n_A)_{ads}(P_A^o - P_A)} = \frac{1}{n_m C} + \frac{(C-1)}{n_m C}\frac{P_A}{P_A^o}$$

Mesoporous alumina



Temperature od calcination : 3,3 nm (450 ^{o}C) - 4,5 nm (600 ^{o}C) - 5,1 nm (800 ^{o}C)

Reaction rate per mass

$$r_M = \frac{1}{m} r = \frac{1}{m}\frac{d\xi}{dt} = \frac{1}{m}\frac{1}{\nu_i}\frac{dn_i}{dt} \qquad \text{mole.kg}^{-1}.s^{-1}$$

$$r_{M,k} = \frac{1}{m} r_k = \frac{1}{m}\frac{d\xi_k}{dt}$$

Reaction rate per surface

$$r_S = \frac{1}{S} r = \frac{1}{S}\frac{d\xi}{dt} = \frac{1}{S}\frac{1}{\nu_i}\frac{dn_i}{dt} \qquad \text{mole.m}^{-2}.s^{-1}$$

$$r_{S,k} = \frac{1}{S} r_k = \frac{1}{S}\frac{d\xi_k}{dt}$$

Reaction rate per active center (turnover number)

$$r_{RS} = \frac{1}{n_{RS}} r = \frac{1}{n_{RS}} \frac{d\xi}{dt} = \frac{1}{n_{RS}} \frac{1}{\nu_i} \frac{dn_i}{dt} \qquad \mathrm{s}^{-1}$$

$$r_{RS,k} = \frac{1}{n_{RS}} r_k = \frac{1}{n_{RS}} \frac{d\xi_k}{dt}$$

Reaction rate of catalytic reactions

Langmuir-Hishelwood ideal surface

⦿Rate of elementary steps

⦿Rate determining step x steady state hypothesis

Reaction rate of catalytic reactions

Langmuir-Hishelwood ideal surface

- Rate of elementary steps
- Rate determining step x steady state hypothesis

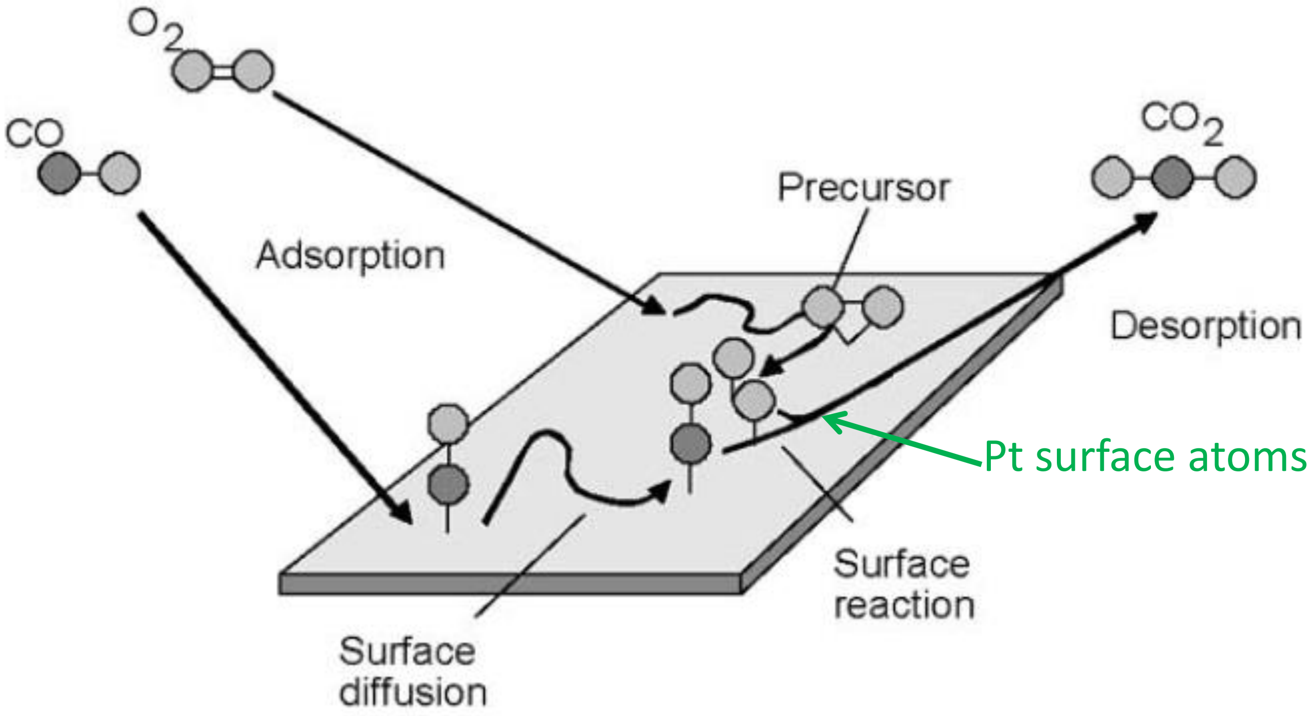
CO oxidation on Pt

Overall reaction ($\Delta G_r^o < 0$)

$$2CO_{(g)} + O_{2(g)} \rightarrow 2CO_{2(g)}$$

nebo

$$2CO_{(g)} + O_{2(g)} \rightarrow 2CO_{2(g)}$$



Elementary steps of catalytic CO oxidation on Pt

1. CO chemisorption

$CO_{(g)} + [*] \leftrightarrow CO*$	$r_1 = k_{f,1} P_{CO} \Theta_* - k_{b,1} \Theta_{CO}$

2. O_2 dissociative chemisorption

* - Pt surface atoms = Catalytic active centre

$O_{2(g)} + 2[*] \leftrightarrow 2O*$	$r_2 = k_{f,2} P_{O_2} \Theta_*^2 - k_{b,2} \Theta_O^2$

3. Surface reaction between CO* and O*

$CO* + O* \leftrightarrow *CO_2 + *$	$r_3 = k_{f,3} \Theta_{CO} \Theta_O - k_{b,3} \Theta_{CO_2} \Theta_*$

4. CO_2 desorption into gas phase

$*CO_2 \leftrightarrow CO_{2(g)} + *$	$r_4 = k_{f,4} \Theta_{CO_2} - k_{b,4} P_{CO_2} \Theta_*$

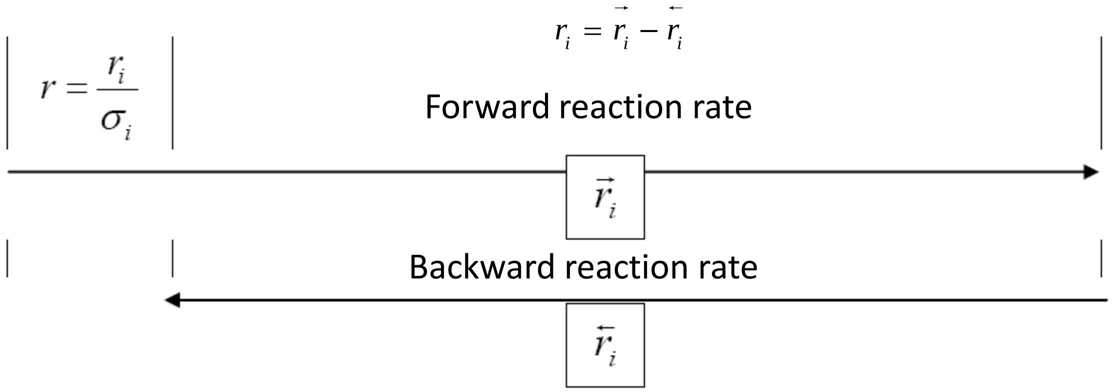
P_i – partial pressures of gaseous components [Pa]

Θ_i - occupancy (coverage) of the i-th species [-]

$k_{f,j}, k_{b,j}$ - reaction rate constants

r_j – rate of the j-th elementary step [mol/kg katalyzátoru/s
mol/molPt/s= 1/s]

Rate determining step in steady state



$r_i = \vec{r}_i - \overleftarrow{r}_i$

$r = \frac{r_i}{\sigma_i}$

Forward reaction rate

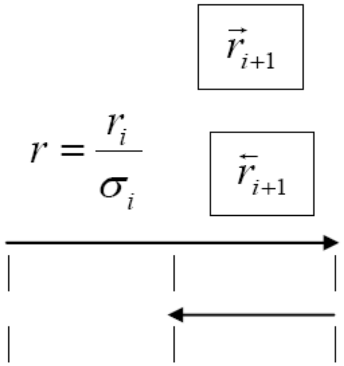
$\boxed{\vec{r}_i}$

Backward reaction rate

$\boxed{\overleftarrow{r}_i}$

Fast step

$\vec{r}_i \cong \overleftarrow{r}_i \Rightarrow$ step is close to the equilibrium



$\boxed{\vec{r}_{i+1}}$

$r = \frac{r_i}{\sigma_i}$

$\boxed{\overleftarrow{r}_{i+1}}$

Slow step =
Rate determining step

Relation between overall reaction rate and the rate of i-th elementary step determines the stoichiometric number σ_i
(do not confuse with stoichiometric coefficient !)

$$r = \frac{r_i}{\sigma_i}$$

	σ_i
$\mathbf{CO_{(g)} + [*] \leftrightarrow CO*}$	**2**
$\mathbf{O_{2(g)} + 2[*] \leftrightarrow 2O*}$	**1**
$\mathbf{CO* + O* \leftrightarrow *CO_2 + *}$	**2**
$\mathbf{*CO_2 \leftrightarrow CO_{2(g)} + *}$	**2**
$\mathbf{2CO_{(g)} + O_{2(g)} \rightarrow 2CO_{2(g)}}$	

M. Boudart, 1968, in “Kinetics of Chemical Processes”:
The stoichiometric number of i-th elementary step, σ_i *is the number of times that this elementary step, as written, must be repeated, in the closed sequence, in order to obtain by summation of all steps the overall stoichiometric equation for reaction, as written.*

Rate determining step: surface reaction

$$K_{CO} = \frac{k_{f,1}}{k_{b,1}} = \frac{\Theta_{CO}}{P_{CO}\Theta_*} \qquad K_{O2} = \frac{k_{f,2}}{k_{b,2}} = \frac{\Theta_O^2}{P_{O_2}\Theta_*^2} \qquad K_{CO_2} = \frac{k_{b,4}}{k_{f,4}} = \frac{\Theta_{CO_2}}{P_{CO_2}\Theta_*}$$

$$\Theta_* + \Theta_{CO} + \Theta_O + \Theta_{CO_2} = 1$$

$$\Theta_* = \frac{1}{1 + K_{CO}P_{CO} + \sqrt{K_{O_2}P_{O_2}} + K_{CO_2}P_{CO_2}}$$

$$\Theta_{CO} = \frac{K_{CO}P_{CO}}{1 + K_{CO}P_{CO} + \sqrt{K_{O_2}P_{O_2}} + K_{CO_2}P_{CO_2}}$$

$$\Theta_O = \frac{\sqrt{K_{O_2}P_{O_2}}}{1 + K_{CO}P_{CO} + \sqrt{K_{O_2}P_{O_2}} + K_{CO_2}P_{CO_2}}$$

$$\Theta_{CO_2} = \frac{K_{CO_2}P_{CO_2}}{1 + K_{CO}P_{CO} + \sqrt{K_{O_2}P_{O_2}} + K_{CO_2}P_{CO_2}}$$

Reaction rate as a function of measurable variables

$$r_3 = k_{f,3}\Theta_{CO}\Theta_O - k_{b,3}\Theta_{CO_2}\Theta_* = \frac{k_{f,3}K_{CO}\sqrt{K_{O_2}}P_{CO}\sqrt{P_{O_2}} - k_{b,3}K_{CO_2}P_{CO_2}}{\left[1 + K_{CO}P_{CO} + \sqrt{K_{O_2}P_{O_2}} + K_{CO_2}P_{CO_2}\right]^2}$$

Example

$$C_2H_5OH_{(g)}\ (A_1) \rightarrow CH_3CHO_{(g)}\ (A_2) + H_{(g)}\ (A_3)$$

catalysts: CuO, CoO a Cr_2O_3
(Franckaerts J., Froment G.F., Kinetic study of the dehydrogenation of ethanol, Chem. Eng. Sci. 19 (1964) 807-818).
Kinetics

$$r_M = \frac{kK_1\left(P_1 - P_2P_3 / K_{eq}\right)}{\left(1 + K_1P_1 + K_2P_2\right)^2}$$

r_M (mol.g^{-1}.hod^{-1}), P_i (bar), k (mol.g^{-1}.hod^{-1}), K_{eq} (bar), K_i (bar^{-1}).

Task: to estimate on the basis of experimental data kinetic and adsorption parameters k, K_1, K_2

EXPERIMENTAL SET-UP

Franckaerts J., Froment G.F., Kinetic study of the dehydrogenation of ethanol, Chem. Eng. Sci. 19 (1964) 807-818

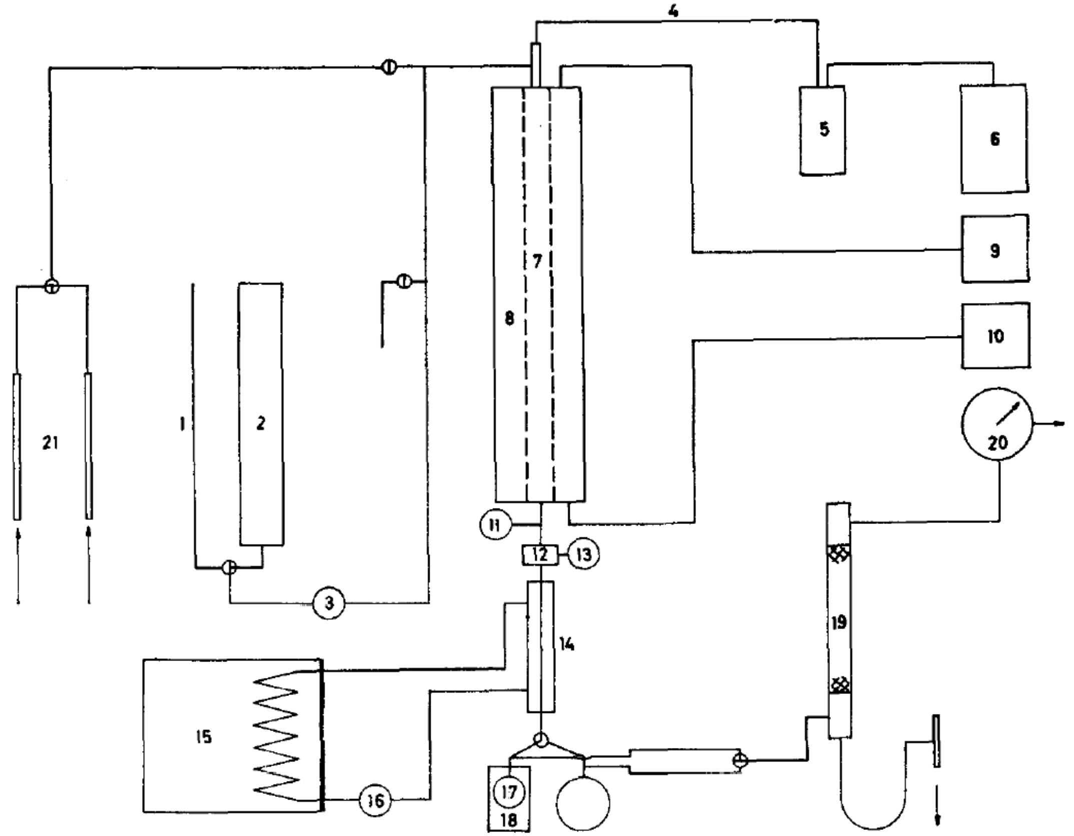


FIG. 1. Apparatus: 1,2, feed burettes; 3, metering pump; 4, thermocouples; 5, ice-bath; 6, mV-recorder; 7, reactor; 8, reactor-mantle; 9,10, variable transformers; 11,13, manometers; 12, pressure regulating device; 14, cooler; 15, cooling unit; 16, circulating pump; 17, sampling flask; 18, liquid air trap; 19, saturator, eventually also absorber in periods between sampling; 20, wet test meter; 21, flowmeters for air and nitrogen.

EXPERIMENTAL DATA

W / F_1^o [g.hod/mol]	P [bar]	y_1^o [−]	y_4^o [−]	y_2^o [−]	T [°C]	X_1 [−]
1,60	7,0	0,865	0,135	0,0	225,0	0,066
0,80	4,0	0,865	0,135	0,0	225,0	0,083
0,40	3,0	0,865	0,135	0,0	225,0	0,055
1,0	1,0	0,865	0,135	0,0	225,0	0,118
1,0	1,0	0,750	0,130	0,119	225,0	0,052
0,40	1,0	0,865	0,135	0,0	225,0	0,060
1,0	1,0	0,732	0,167	0,101	225,0	0,052
0,40	10,0	0,865	0,135	0,0	225,0	0,038
1,60	7,0	0,865	0,135	0,0	250,0	0,149
0,80	4,0	0,865	0,135	0,0	250,0	0,157
0,40	3,0	0,865	0,135	0,0	250,0	0,108
1,0	1,0	0,865	0,135	0,0	250,0	0,218
1,0	1,0	0,672	0,145	0,183	250,0	0,123
0,60	1,0	0,865	0,135	0,0	250,0	0,152
0,80	1,0	0,672	0,145	0,183	250,0	0,106
0,60	10,0	0,865	0,135	0,0	250,0	0,094
1,60	7,0	0,865	0,135	0,0	275,0	0,254
0,80	4,0	0,865	0,135	0,0	275,0	0,262
0,40	3,0	0,865	0,135	0,0	275,0	0,20
1,0	1,0	0,865	0,135	0,0	275,0	0,362
1,0	1,0	0,672	0,145	0,183	275,0	0,230
0,20	1,0	0,865	0,135	0,0	275,0	0,118
0,40	10,0	0,865	0,135	0,0	275,0	0,148
0,40	1,0	0,865	0,135	0,0	275,0	0,196

Solution:

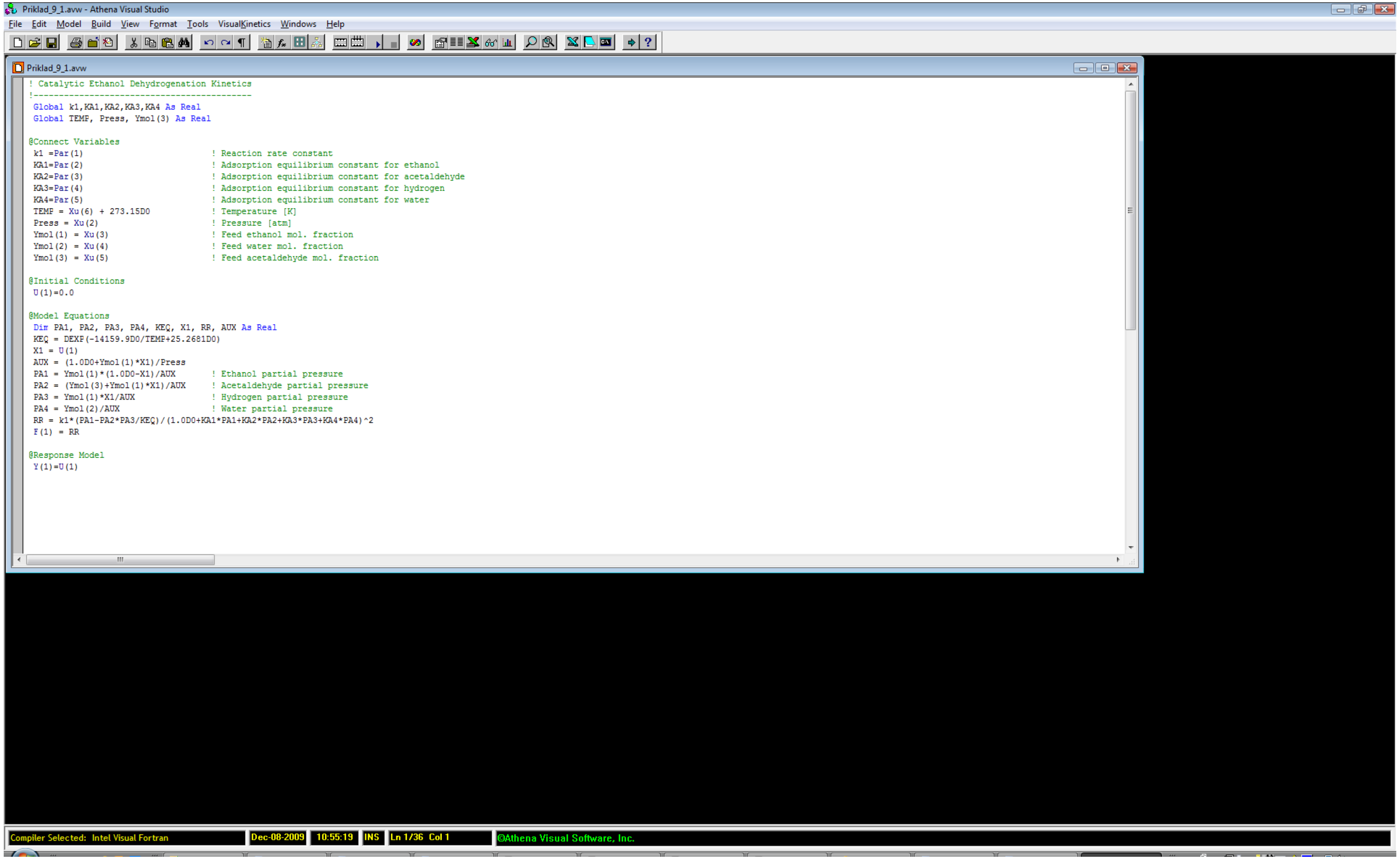
Minimize the objective function:

$$\Phi(k, K_1, K_2) = \sum_{i=1}^{NEXP} \left[X_{1,i}^{\exp} - X_{1,i}^{\mathrm{mod}}(k, K_1, K_2) \right]^2$$

$X_{1,i}^{\mathrm{mod}}(k, K_1, K_2)$ calculated from isothermal catalytic PFR model:

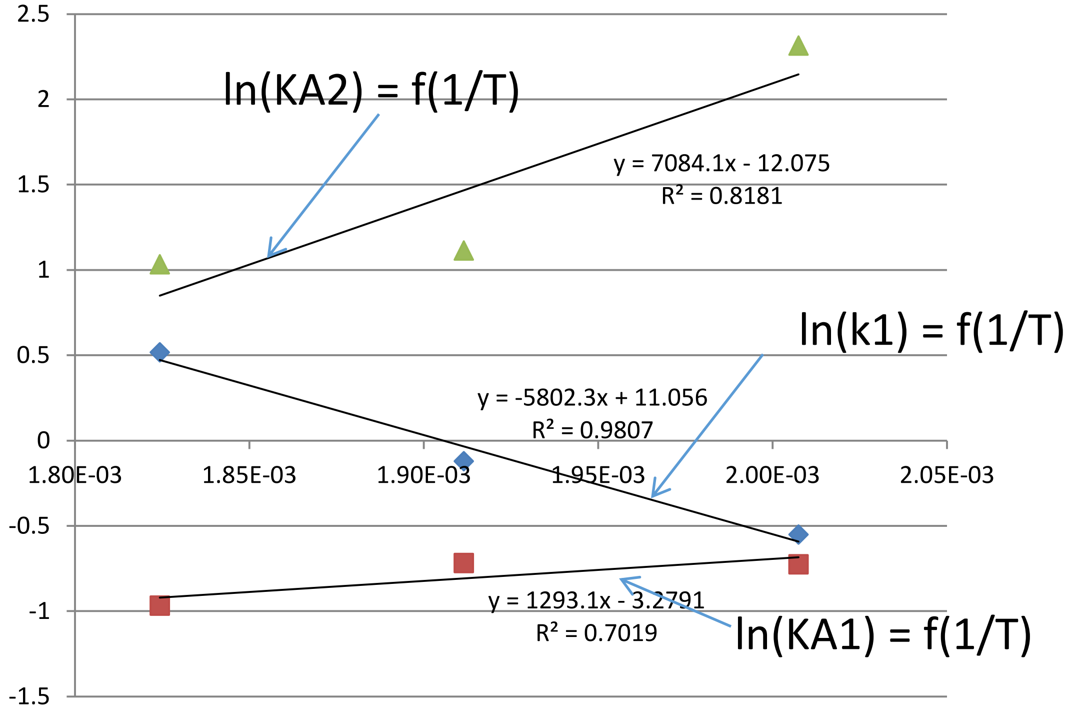
$$\frac{dX_1}{d\left(W / F_1^o\right)} = r_M(X_1) \qquad W / F_1^o = 0, X_1 = 0$$

ATHENA Visual Studio.



```
! Catalytic Ethanol Dehydrogenation Kinetics
!--------------------------------------------
 Global k1,KA1,KA2,KA3,KA4 As Real
 Global TEMP, Press, Ymol(3) As Real

@Connect Variables
 k1 =Par(1)                         ! Reaction rate constant
 KA1=Par(2)                         ! Adsorption equilibrium constant for ethanol
 KA2=Par(3)                         ! Adsorption equilibrium constant for acetaldehyde
 KA3=Par(4)                         ! Adsorption equilibrium constant for hydrogen
 KA4=Par(5)                         ! Adsorption equilibrium constant for water
 TEMP = Xu(6) + 273.15D0            ! Temperature [K]
 Press = Xu(2)                      ! Pressure [atm]
 Ymol(1) = Xu(3)                    ! Feed ethanol mol. fraction
 Ymol(2) = Xu(4)                    ! Feed water mol. fraction
 Ymol(3) = Xu(5)                    ! Feed acetaldehyde mol. fraction

@Initial Conditions
 U(1)=0.0

@Model Equations
 Dim PA1, PA2, PA3, PA4, KEQ, X1, RR, AUX As Real
 KEQ = DEXP(-14159.9D0/TEMP+25.2681D0)
 X1 = U(1)
 AUX = (1.0D0+Ymol(1)*X1)/Press
 PA1 = Ymol(1)*(1.0D0-X1)/AUX       ! Ethanol partial pressure
 PA2 = (Ymol(3)+Ymol(1)*X1)/AUX     ! Acetaldehyde partial pressure
 PA3 = Ymol(1)*X1/AUX               ! Hydrogen partial pressure
 PA4 = Ymol(2)/AUX                  ! Water partial pressure
 RR = k1*(PA1-PA2*PA3/KEQ)/(1.0D0+KA1*PA1+KA2*PA2+KA3*PA3+KA4*PA4)^2
 F(1) = RR

@Response Model
 Y(1)=U(1)
```

	225 oC	**250 oC**	**275 oC**
k1	5.767986E-01 +- 4.112E-01	8.863130E-01 +- 1.668E-01	1.675828E+00 +- 4.225E-01
KA1	4.839934E-01 +- 3.591E-01	4.876108E-01 +- 9.443E-02	3.803293E-01 +- 1.473E-01
KA2	1.011693E+01 +- 7.376E+00	3.044445E+00 +- 9.054E-01	2.812096E+00 +- 1.078E+00



ln(KA2) = f(1/T)

ln(k1) = f(1/T)

ln(KA1) = f(1/T)