Part 4. Kinetics of Reactions Involving Solids
Solids in industry (chemical and related)

- minerals and reactants (i.e. raw materials);
- chemicals and functional materials (i.e. target products);
- construction materials (i.e. reaction environment);
- catalysts ...
Solids as components of reaction system:

heterogeneity / phase interfaces

- properties and behaviour of reactants;
- peculiarities of reactant supply;
- structuring of reaction space;
- presence of ‘inert’ admixtures;
- formation of heterophasesic products;
- presence / effect of reactor walls
Solids in chemistry (kinetics):

- solid state chemistry;
- heterogeneous catalysis
Solid State Chemistry:

- topochemistry;
- reactivity of solids
Solid State Chemistry:

- topochemistry
  (from Greek τόπος – locus, position, place)
  describes reactions of solids based on their topological characteristics

- reactivity of solids
  analyses reactions of solids based on their chemical nature, structural features, ...

  strongly interrelated!
Topochemistry (basics):

- reaction is localized on the interface between solid reactant(s) and product(s);
- kinetic features of reaction are determined by the shape and the overall ‘size’ of this interface and their development in time;
- reaction starts from the formation of product nuclei (nucleation) on the surface of solid reactant;
- development of reaction is associated with growth of nuclei;

i.e. nucleation and growth of nuclei are the main stages of the process;

i.e. overall rate is a combination of the two
Topochemistry

\[ \frac{dX}{dt} = k(1 - X)^{2/3} \quad \text{or} \quad 1 - (1-X)^{1/3} = kt \]

contracting sphere (or cube, or volume)
equation
(Roginsky-Schultz equation)


Theory of nucleation (oversaturation theory):

\[ \frac{dN}{dt} \sim \langle \mu \rangle \sim \Delta G \]

rate of homogeneous formation of nuclei, e.g.
precipitation (synthesis of active solid catalysts
and catalytic supports)
Topochemistry

Nuclei – compact areas:

- of chemical composition that corresponds to the solid product

and

- capable of further growing
Topochemistry

Nuclei – compact areas of chemical composition that corresponds to the solid product and capable of further growing

*Example.* NiO + CO → Ni + CO₂
Topochemistry

dN/dt = f(t) – kinetics of nucleation

Important cases:

1. instantaneous nucleation

@ t = 0  \Rightarrow  N = S_{sp.}/\sigma_0

2. constant rate of nucleation (e.g., 1st order)

\begin{align*}
dN/dt &= k(N_0 - N)  \Rightarrow  N = N_0(1 - e^{-kt})
\end{align*}

Uniform and isotropic growth of nuclei (interface propagation) – Roginsky-Schultz equation

\begin{align*}
dX/dt &= k(1 - X)^{2/3}  \quad \text{or}  \quad 1 - (1-X)^{1/3} = kt
\end{align*}
Topochemistry

\[ \frac{dN}{dt} = f(t) \] – kinetics of nucleation

Important cases:

1. instantaneous nucleation

@ \( t = 0 \) \( \Rightarrow \) \( N = \frac{S_{sp}}{\sigma_0} \)

2. constant rate of nucleation (e.g., 1\textsuperscript{st} order)

\[ \frac{dN}{dt} = k(N_0 - N) \] \( \Rightarrow \) \( N = N_0(1 - e^{-kt}) \)

\[ \frac{dX}{dt} = kX^m(1-X)^n[-\ln(1-X)]^p \]

– joint KEKAM equation
Topochemistry

\[ \frac{dN}{dt} = f(t) \] – kinetics of nucleation

Important cases:

1. instantaneous nucleation

\[ @ \ t = 0 \Rightarrow N = \frac{S_{sp}}{\sigma_0} \]

2. constant rate of nucleation (e.g., 1\textsuperscript{st} order)

\[ \frac{dN}{dt} = k(N_0 - N) \Rightarrow N = N_0(1 - e^{-kt}) \]

potential centers of nucleation, i.e. non-uniformity of properties ⇒ reactivity
Reactions Involving Solids

Kinetics of reactions on interfaces

Specific rate of reaction on ‘gas – solid’ interfaces

Bernard DELMON
Бернар ДЕЛЬМОН

А.Я. Rozovsky
Александр Яковлевич РОЗОВСКИЙ
(08.02.1929 - 10.03.2008)
Structural non-uniformity and Reactivity

caused by spatial finiteness of real crystals
Structural non-uniformity and Reactivity

edge dislocation

screw dislocation

+ vacancies; impurities and dopants (atoms, ions, …) in lattice positions and interstitial; adsorbed particles and adlayers, …

⇓

heterogeneous catalysis
Heterogeneous Catalysis and Basic Principles of Chemical Kinetics

Microscopic Reversibility Principle (for Chemistry):
any ‘simple’ (elementary) chemical reaction can proceed in both reciprocally reverse directions

Detailed Equilibrium (or Balance) Principle:
if the state of global equilibrium is reached in some system, any partial equilibria are also achieved

or

at equilibrium each elementary process should be balanced by its reverse process

W.F. Ostwald (1909, thermodynamics and catalysis):
catalyst does not shift equilibrium, but accelerates only thermodynamically allowed (feasible) reactions
Heterogeneous Catalysis and Basic Principles of Chemical Kinetics

Microscopic Reversibility Principle (for Chemistry) – (+)

Detailed Equilibrium (or Balance) Principle – (+)

\textit{catalyst does not shift equilibrium, but accelerates only thermodynamically allowed (feasible) reactions}

Independence Principle (\textit{W.F. Ostwald}):

the Law of Mass Action can be used for each ‘simple’ reaction occurring in the system as if it is the only reaction in given conditions

????????
Heterogeneous Catalysis and Basic Principles of Chemical Kinetics

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Independence Principle –

limited due to (a) spatial constrains and restricted mobility (b) non-uniformity of solids and their surfaces

*must be taken into consideration in kinetic analysis of catalytic reactions !!!*
Thank You for Your Attention!

Lecture Course from Russian Catalytic Society and Haldor Topsoe

Catalysis and Chemical Engineering: Theoretical Bases and Selected Applications

2016-2017