Lecture 10 Fundamentals of Catalysis and Heterogeneous Kinetics

Goal of the lecture: To study the principles of catalysis, the mechanisms of heterogeneous reactions, and the kinetic models describing catalytic processes on solid surfaces.

Brief lecture notes: This lecture introduces the fundamentals of catalysis — the acceleration of chemical reactions through the participation of a catalyst — with a special focus on heterogeneous systems, where the catalyst and reactants are in different phases. We will explore the mechanistic steps of adsorption, surface reaction, and desorption, analyze kinetic equations such as the Langmuir–Hinshelwood model, and discuss the role of surface structure, active sites, and temperature in determining catalytic efficiency. Additionally, practical aspects of industrial catalysis and rate-limiting steps will be discussed.

Main part

A catalyst is a substance that increases the rate of a chemical reaction without being consumed in the overall process. Catalysis works by providing an alternative reaction pathway with a lower activation energy.

Catalysis can be divided into:

- Homogeneous catalysis: catalyst and reactants are in the same phase (usually liquid).
- Heterogeneous catalysis: catalyst is a solid, while reactants are gases or liquids.

In heterogeneous catalysis, reactions occur on the surface of the solid, making the surface area and active sites critical parameters. Typical examples include:

- Ammonia synthesis on iron (Haber–Bosch process)
- Hydrogenation of alkenes on nickel or platinum
- Catalytic converters in automotive exhaust systems

The overall rate of a catalytic reaction depends on several steps:

1. Diffusion of reactants to the surface
2. Adsorption on active sites
3. Surface reaction (chemical transformation)
4. Desorption of products
5. **Diffusion** of products away from the surface

Kinetic Models of Heterogeneous Reactions

The Langmuir adsorption isotherm forms the basis of heterogeneous kinetic modeling. It assumes monolayer adsorption on uniform active sites and equilibrium between adsorbed and free species:

$$\theta = \frac{KP}{1 + KP}$$

where:

- θ— fraction of surface covered by adsorbate,
- K— adsorption equilibrium constant,
- P— partial pressure of the gas.

The Langmuir–Hinshelwood mechanism describes reactions where both reactants are adsorbed on the surface before reacting:

$$r = \frac{kK_AK_BP_AP_B}{(1 + K_AP_A + K_BP_B)^2}$$

This equation shows that the rate depends on both adsorption and surface reaction kinetics.

Another model, the Eley–Rideal mechanism, assumes that one reactant is adsorbed while the other reacts directly from the gas phase.

Factors Affecting Catalytic Activity

- Surface structure: defects, crystal orientation, and dispersion influence activity.
- Temperature: increases rate but may cause sintering or deactivation.
- Pressure: affects adsorption equilibria.
- Catalyst poisoning: impurities (e.g., sulfur, lead) block active sites.
- Promoters and supports: materials that enhance stability or dispersion of active sites.

Industrial and Environmental Importance

Catalysts play a central role in industrial chemistry, contributing to more than 90% of chemical production processes. Examples include:

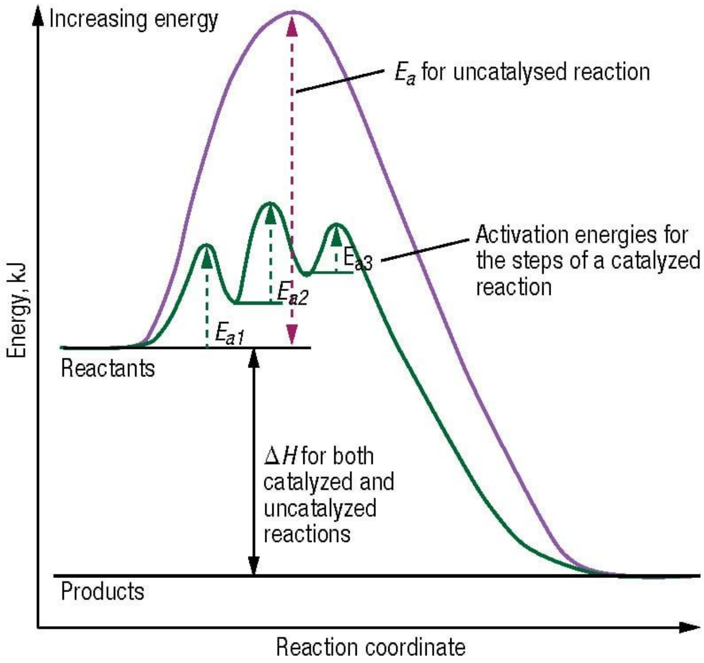
- Ammonia synthesis (Fe catalyst)
- Sulfuric acid production (V_2O_5 catalyst)
- Hydrocarbon reforming (Pt/Al_2O_3 catalyst)
- Emission control (Pt–Rh–Pd converters)

These systems are designed for high selectivity and turnover frequency, minimizing byproducts and energy use.

Table 1. Typical Catalytic Systems and Mechanisms

Reaction Type	Catalyst	Mechanism	Industrial Application
Ammonia synthesis	Fe	Adsorption + surface reaction	Fertilizer production
Hydrocarbon hydrogenation	Ni, Pt	Langmuir–Hinshelwood	Petrochemical industry
CO oxidation	Pt, Pd	Eley–Rideal	Emission control
Sulfuric acid formation	V_2O_5	Redox surface mechanism	Chemical manufacturing
Methanol synthesis	$Cu–ZnO–Al_2O_3$	Langmuir–Hinshelwood	Fuel and chemical synthesis

Figure 1.



Questions for Self-Control

1. What distinguishes heterogeneous catalysis from homogeneous catalysis?
2. Explain the steps of the catalytic cycle in heterogeneous reactions.
3. How does the Langmuir–Hinshelwood mechanism describe surface reactions?
4. What are the main factors affecting catalytic efficiency?
5. Give examples of industrial processes that rely on heterogeneous catalysis.

Literature

1. Atkins P., de Paula J. Physical Chemistry, 11th ed. – Oxford University Press, 2018.
2. Fogler H. S. Elements of Chemical Reaction Engineering, 5th ed. – Prentice Hall, 2016.
3. Boudart M., Djéga-Mariadassou G. Kinetics of Heterogeneous Catalytic Reactions. – Princeton University Press, 1984.
4. Somorjai G. A., Li Y. Introduction to Surface Chemistry and Catalysis, 2nd ed. – Wiley, 2010.
5. Thomas J. M., Thomas W. J. Principles and Practice of Heterogeneous Catalysis. – VCH Publishers, 1997.