University of Mosul

College of Petroleum & Mining Engineering

Industrial Chemistry

Lecture …(1)….

Petroleum and Refining Engineering Department

Catalytic Cycle

- Catalysts facilitate reactions through a cycle, returning to their original state after form

Catalyst + Reactant

↑

Catalyst-Reactant Complex

↑

Catalyst + Product

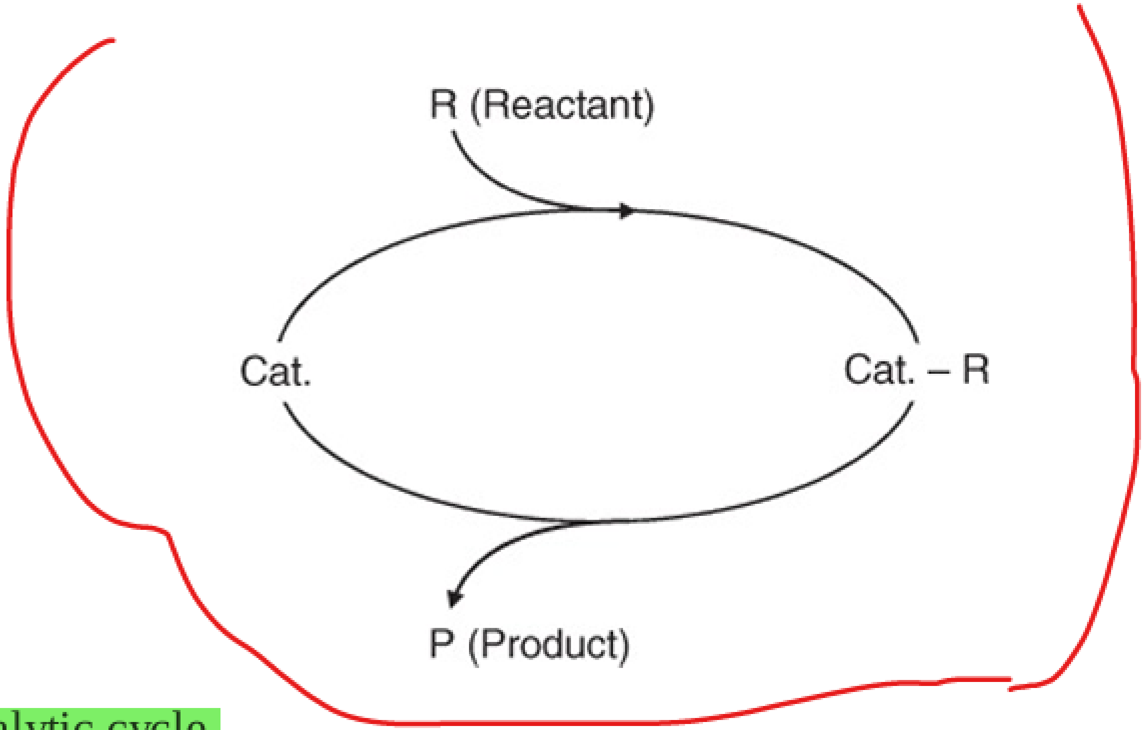


Figure 1.1 Catalytic cycle.

Catalysis Kinetics: Rate Laws and Activation Energy

- • Reaction Rate: $r = -d[A]/dt = k \cdot f(cA)$
- • Arrhenius Equation: $k = k_0 \cdot \exp(-Ea / RT)$

- Where:
- k = rate constant
- Ea = activation energy
- R = gas constant
- T = temperature (Kelvin)

TOF (Turnover Frequency) – Reactions per second per site

Examples:

TOF values for the hydrogenation of cyclohexene at 25 °C and 1 bar (supported catalysts, structure-insensitive reaction) are provided in Table 1.2).

Table 1.2 TOF values for the hydrogenation of cyclohexene [9]

Metal	TOF (s^{-1})	
	Gas phase	Liquid phase
Ni	2.0	0.45
Rh	6.1	1.3
Pd	3.2	1.5
Pt	2.8	0.6

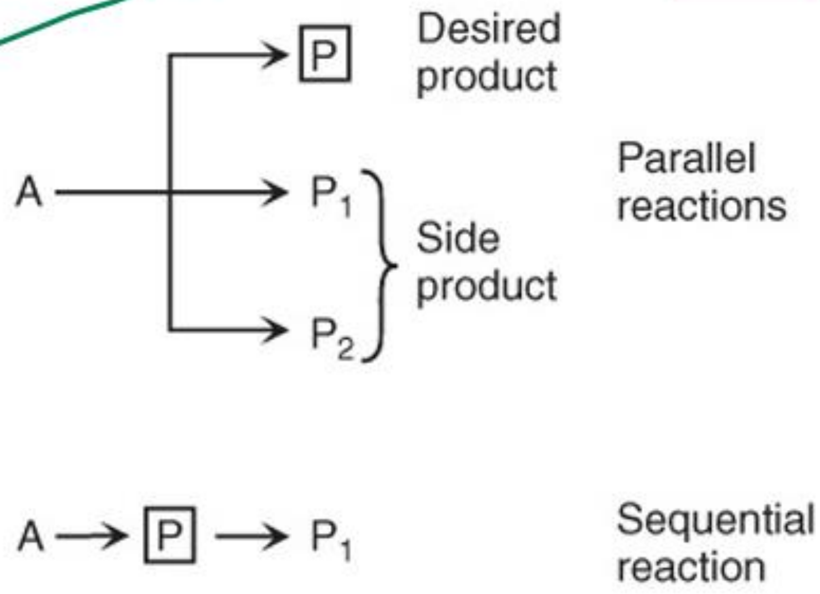
Turnover Frequency (TOF) Comparison

- TOF indicates how many reactions each active site performs per

Metal	TOF (Gas Phase)	TOF (Liquid Phase)
Ni	2.0	0.45
Rh	6.1	1.3
Pd	3.2	1.5
Pt	2.8	0.6

Selectivity

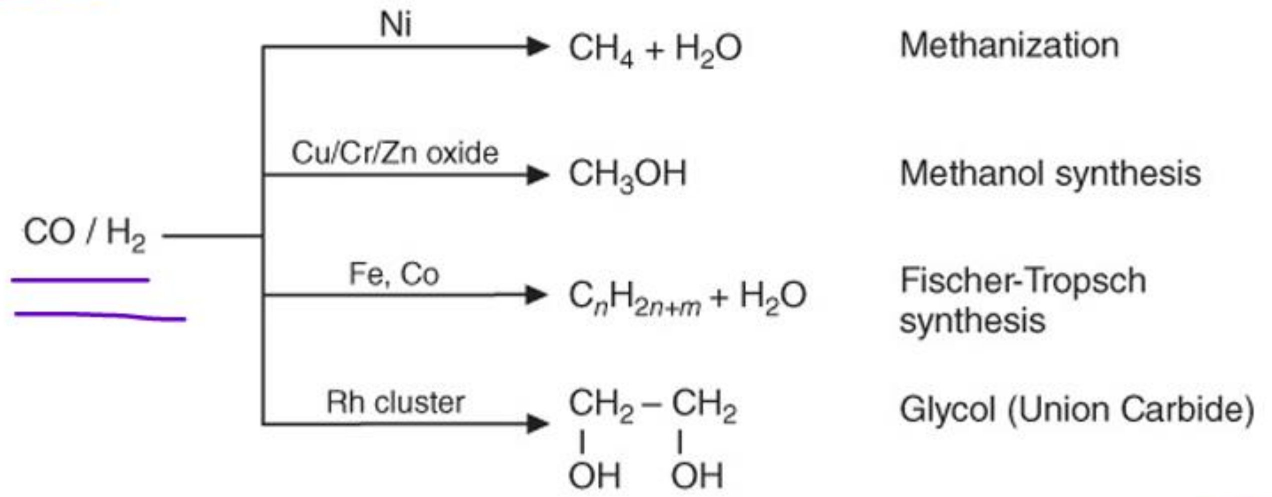
(Scheme 1.1).



Scheme 1.1 Parallel and sequential reactions.

Since this quantity compares starting materials and products, the stoichiometric c

Selectivity



Scheme 1.2 Reactions of synthesis gas.

Selectivity problems are of particular relevance to oxidation reactions.

Example

The methanol synthesis in a laboratory reactor is carried out at 80 bar and 250 °C with the addition of inert gas nitrogen. Under these conditions, the conversion of CO is 30%.

$$CO + 2\,H_2 \rightarrow CH_3OH$$

The feed of the reactor consists of 1 mol/h CO, 2 mol h^{-1} H_2, and 3 mol h^{-1} N_2. In the condenser, it results in 9.2 g h^{-1} liquid methanol.

a. Calculate the composition of the gas phase at the reactor outlet (mol%).
b. Calculate the volume flow rates at the reactor outlet.
c. Which amount of liquid methanol/h should be obtained theoretically?

Solution

(a) At the end of the conversion, there should be obtained

Species	n_i	n_i (mol) gas	%	(b) flow rate (l h^{-1})
CO	$1 - X$	0.7	13.7	15.7
H_2	$2(1 - X)$	1.4	27.5	31.4
CH_3OH	X	—	—	—
N_2	3	3	58.8	67.2

(c) 0.3 mol methanol = 9.6 g CH_3OH/h.

Table 1.4 Comparison of homogeneous and heterogeneous catalysts

	Homogeneous	Heterogeneous
Effectivity		
Active centers	All metal atoms	Only surface atoms
Concentration	Low	High
Selectivity	High	Lower
Diffusion problems	Practically absent	Present (mass-transfer-controlled reaction)
Reaction conditions	Mild (50–200 °C)	Severe (often >250 °C)
Applicability	Limited	Wide
Activity loss	Irreversible reaction with products (cluster formation); poisoning	Sintering of the metal crystallites; poisoning
Catalyst properties		
Structure/stoichiometry	Defined	Undefined
Modification possibilities	High	Low
Thermal stability	Low	High
Catalyst separation	Sometimes laborious (chemical decomposition, distillation, extraction)	Fixed-bed: unnecessary suspension: filtration
Catalyst recycling	Possible	Unnecessary (fixed-bed) or easy (suspension)
Cost of catalyst losses	High	Low

The major disadvantage of homogeneous transition metal catalysts is the difficulty of