Advanced Reactor Design

Week 6

Catalyst Deactivation

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Introduction

- • Definition of Catalyst Deactivation
- • Importance in Industrial Processes
- • Impact on Reaction Efficiency and Cost
- • Real-world Examples (e.g., petroleum refining, environmental catalysis)

Topics to be Covered

- 1. Basics of Catalyst Deactivation
- 2. Types of Catalyst Deactivation Mechanisms
- 3. Causes of Catalyst Deactivation
- 4. Methods to Prevent or Mitigate Deactivation
- 5. Case Studies in Industry

Objectives

- • Understand the fundamentals of catalyst deactivation
- • Identify different mechanisms and causes
- • Explore strategies to prevent or mitigate deactivation
- • Analyze real-world case studies for practical insights

Catalyst Deactivation

- Catalyst deactivation: the loss over time of catalytic activity and/or selectivity
- Catalyst deactivation is a great problem in industrial catalytic processes: costs $B's per year
- All catalysts deactivate, in scale seconds to decades
- Poor operation conditions can lead to carbon filaments and catastrophic failure in hours

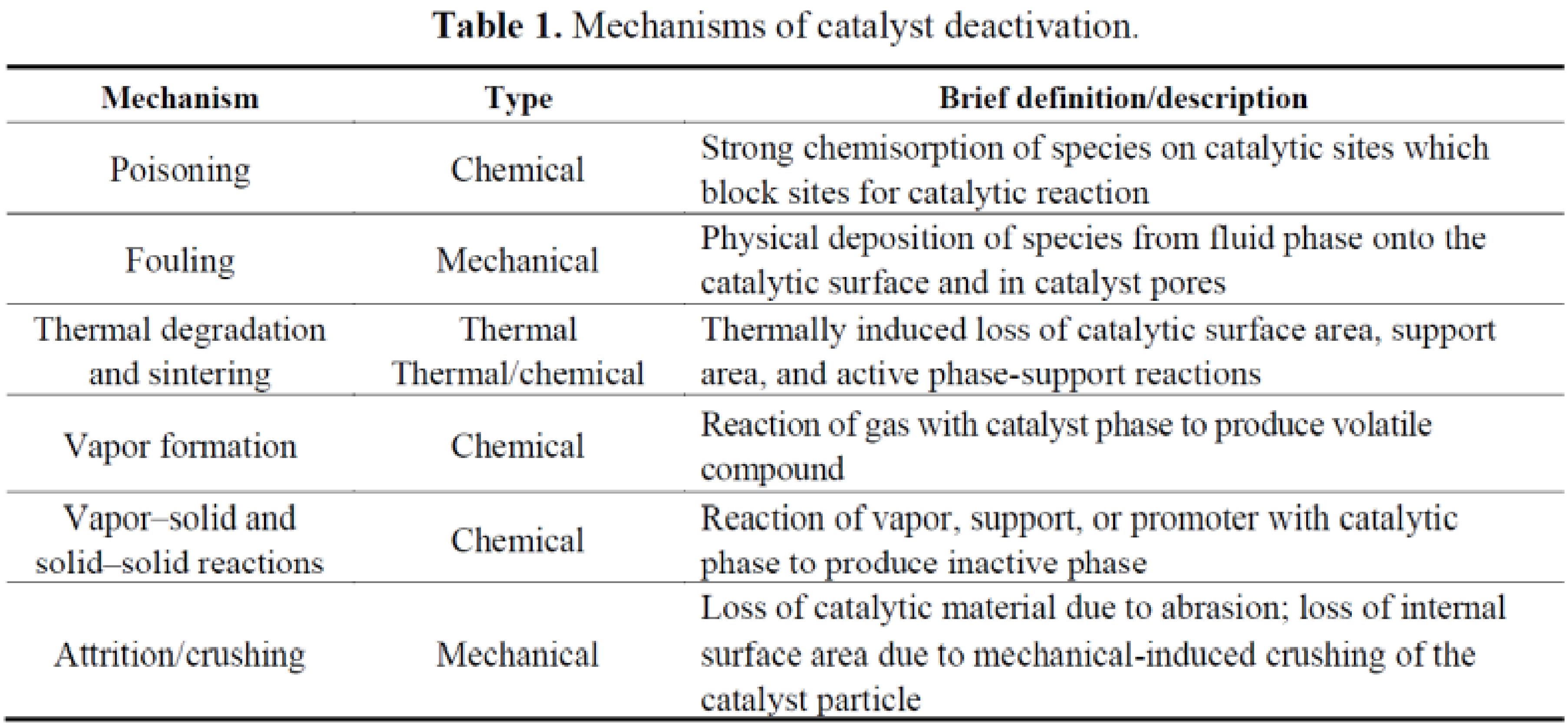

Table 1. Mechanisms of catalyst deactivation.

Mechanism	Type	Brief definition/description
Poisoning	Chemical	Strong chemisorption of species on catalytic sites which block sites for catalytic reaction
Fouling	Mechanical	Physical deposition of species from fluid phase onto the catalytic surface and in catalyst pores
Thermal degradation and sintering	Thermal Thermal/chemical	Thermally induced loss of catalytic surface area, support area, and active phase-support reactions
Vapor formation	Chemical	Reaction of gas with catalyst phase to produce volatile compound
Vapor–solid and solid–solid reactions	Chemical	Reaction of vapor, support, or promoter with catalytic phase to produce inactive phase
Attrition/crushing	Mechanical	Loss of catalytic material due to abrasion; loss of internal surface area due to mechanical-induced crushing of the catalyst particle

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lecture

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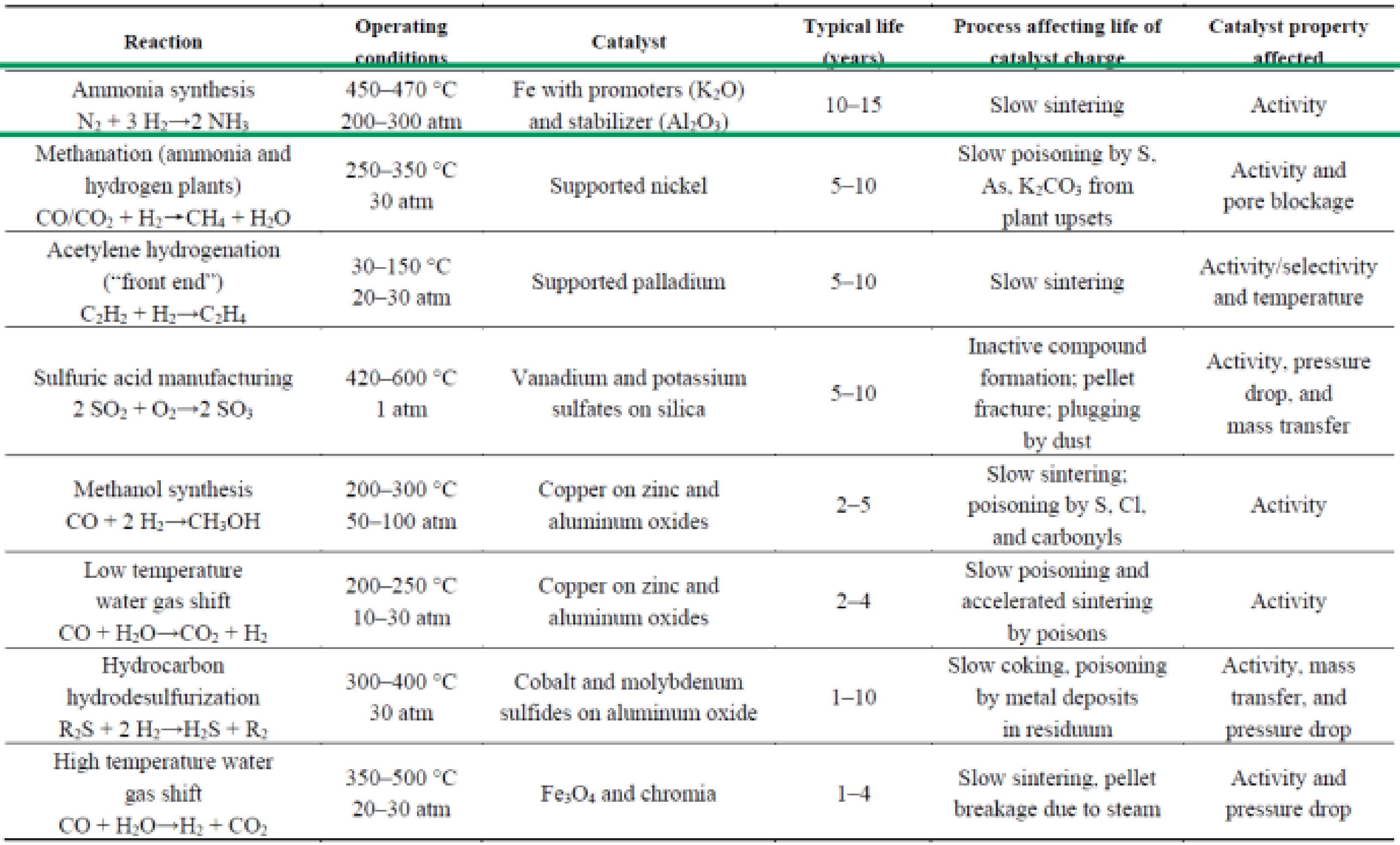
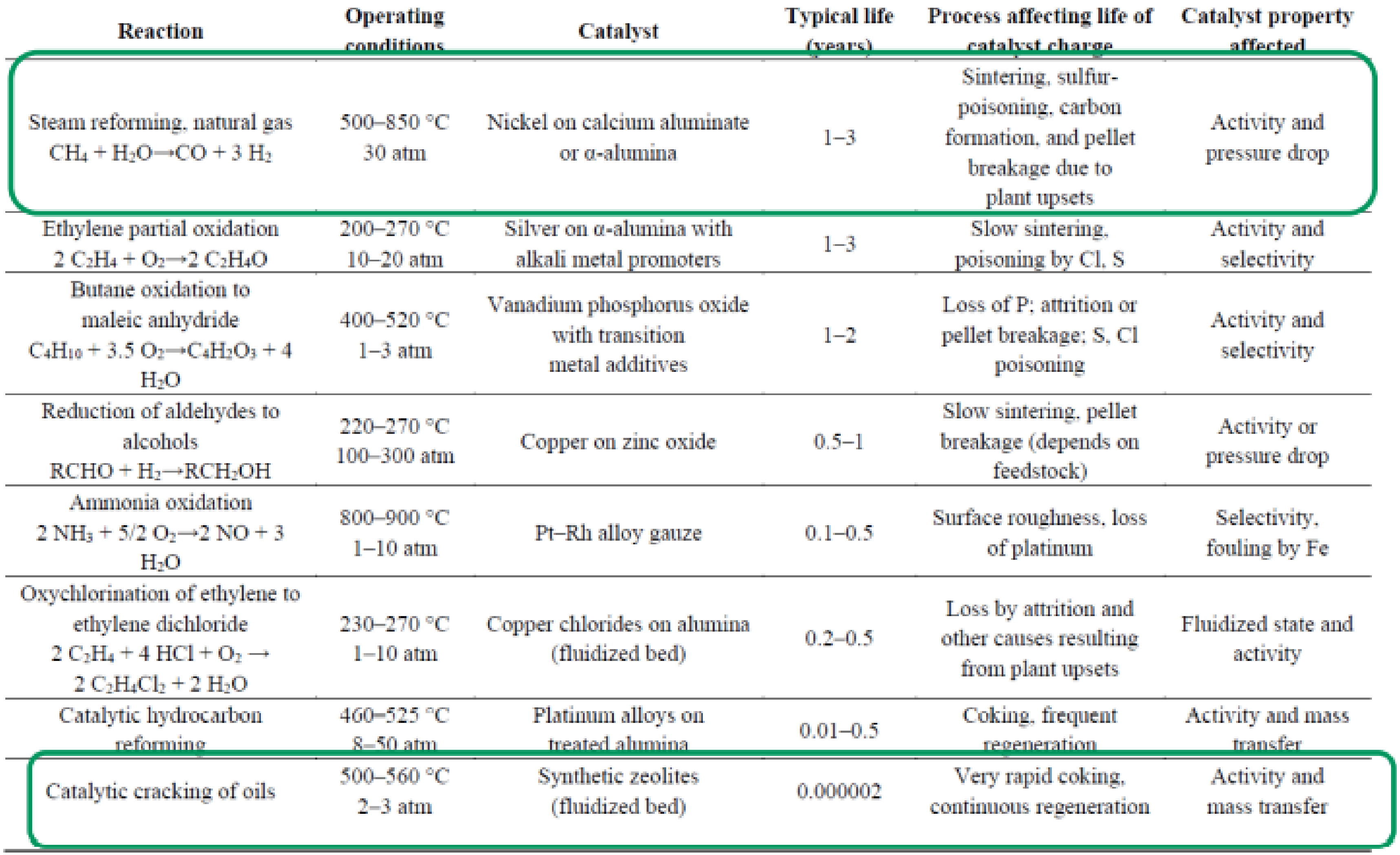
Examples

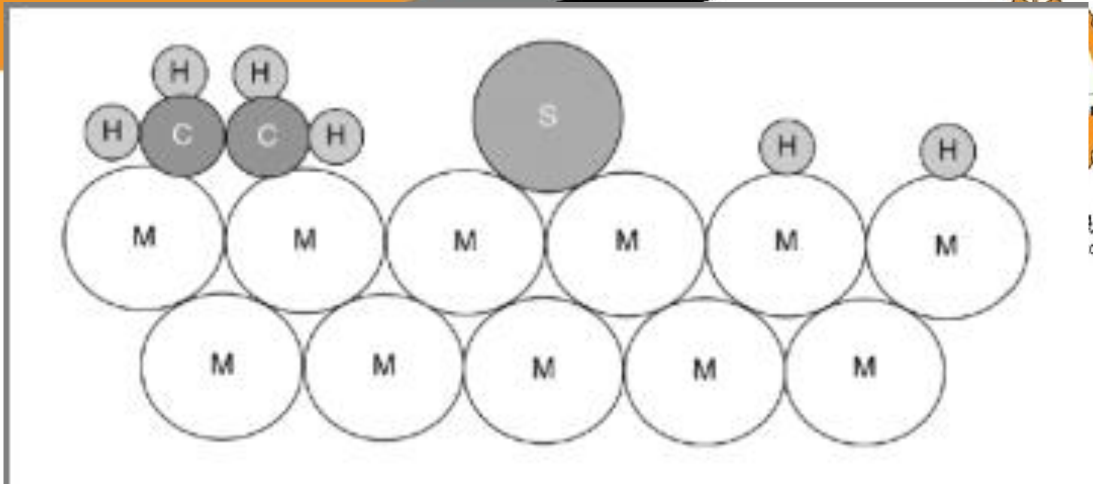


Reaction	Operating conditions	Catalyst	Typical life (years)	Process affecting life of catalyst charge	Catalyst property affected
Ammonia synthesis $N_2 + 3\ H_2 \rightarrow 2\ NH_3$	450–470 °C 200–300 atm	Fe with promoters (K_2O) and stabilizer (Al_2O_3)	10–15	Slow sintering	Activity
Methanation (ammonia and hydrogen plants) $CO/CO_2 + H_2 \rightarrow CH_4 + H_2O$	250–350 °C 30 atm	Supported nickel	5–10	Slow poisoning by S, As, K_2CO_3 from plant upsets	Activity and pore blockage
Acetylene hydrogenation ("front end") $C_2H_2 + H_2 \rightarrow C_2H_4$	30–150 °C 20–30 atm	Supported palladium	5–10	Slow sintering	Activity/selectivity and temperature
Sulfuric acid manufacturing $2\ SO_2 + O_2 \rightarrow 2\ SO_3$	420–600 °C 1 atm	Vanadium and potassium sulfates on silica	5–10	Inactive compound formation; pellet fracture; plugging by dust	Activity, pressure drop, and mass transfer
Methanol synthesis $CO + 2\ H_2 \rightarrow CH_3OH$	200–300 °C 50–100 atm	Copper on zinc and aluminum oxides	2–5	Slow sintering; poisoning by S, Cl, and carbonyls	Activity
Low temperature water gas shift $CO + H_2O \rightarrow CO_2 + H_2$	200–250 °C 10–30 atm	Copper on zinc and aluminum oxides	2–4	Slow poisoning and accelerated sintering by poisons	Activity
Hydrocarbon hydrodesulfurization $R_2S + 2\ H_2 \rightarrow H_2S + R_2$	300–400 °C 30 atm	Cobalt and molybdenum sulfides on aluminum oxide	1–10	Slow coking, poisoning by metal deposits in residuum	Activity, mass transfer, and pressure drop
High temperature water gas shift $CO + H_2O \rightarrow H_2 + CO_2$	350–500 °C 20–30 atm	Fe_3O_4 and chromia	1–4	Slow sintering, pellet breakage due to steam	Activity and pressure drop

Examples

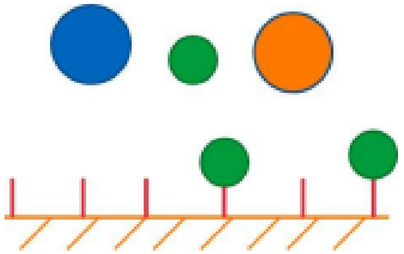


Reaction	Operating conditions	Catalyst	Typical life (years)	Process affecting life of catalyst charge	Catalyst property affected
Steam reforming, natural gas $CH_4 + H_2O \rightarrow CO + 3\ H_2$	500–850 °C 30 atm	Nickel on calcium aluminate or α-alumina	1–3	Sintering, sulfur-poisoning, carbon formation, and pellet breakage due to plant upsets	Activity and pressure drop
Ethylene partial oxidation $2\ C_2H_4 + O_2 \rightarrow 2\ C_2H_4O$	200–270 °C 10–20 atm	Silver on α-alumina with alkali metal promoters	1–3	Slow sintering, poisoning by Cl, S	Activity and selectivity
Butane oxidation to maleic anhydride $C_4H_{10} + 3.5\ O_2 \rightarrow C_4H_2O_3 + 4\ H_2O$	400–520 °C 1–3 atm	Vanadium phosphorus oxide with transition metal additives	1–2	Loss of P; attrition or pellet breakage; S, Cl poisoning	Activity and selectivity
Reduction of aldehydes to alcohols $RCHO + H_2 \rightarrow RCH_2OH$	220–270 °C 100–300 atm	Copper on zinc oxide	0.5–1	Slow sintering, pellet breakage (depends on feedstock)	Activity or pressure drop
Ammonia oxidation $2\ NH_3 + 5/2\ O_2 \rightarrow 2\ NO + 3\ H_2O$	800–900 °C 1–10 atm	Pt–Rh alloy gauze	0.1–0.5	Surface roughness, loss of platinum	Selectivity, fouling by Fe
Oxychlorination of ethylene to ethylene dichloride $2\ C_2H_4 + 4\ HCl + O_2 \rightarrow 2\ C_2H_4Cl_2 + 2\ H_2O$	230–270 °C 1–10 atm	Copper chlorides on alumina (fluidized bed)	0.2–0.5	Loss by attrition and other causes resulting from plant upsets	Fluidized state and activity
Catalytic hydrocarbon reforming	460–525 °C 8–50 atm	Platinum alloys on treated alumina	0.01–0.5	Coking, frequent regeneration	Activity and mass transfer
Catalytic cracking of oils	500–560 °C 2–3 atm	Synthetic zeolites (fluidized bed)	0.000002	Very rapid coking, continuous regeneration	Activity and mass transfer



Poisoning

- *“Poisoning* **is the strong chemisorption of reactants, products, or impurities on sites otherwise available for catalysis.”**
- Whether a species acts as a poison depends upon its adsorption strength relative to the other species competing for catalytic sites.



- **Example: oxygen can be a reactant** in partial oxidation of ethylene to ethylene oxide on a silver catalyst
  and a poison in hydrogenation of ethylene on nickel.
- In addition to physically blocking of adsorption sites, **adsorbed poisons may induce changes in the electronic or geometric structure of the surface**.
- **Poisoning may be reversible or irreversible** (typically it is irreversible).

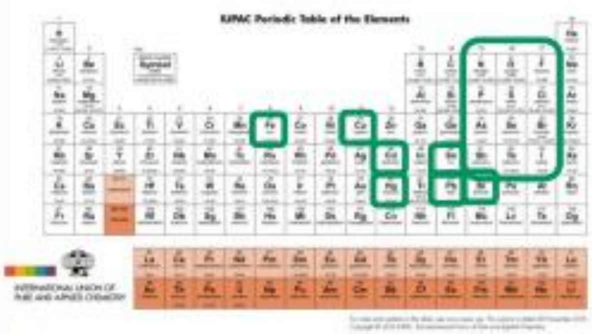
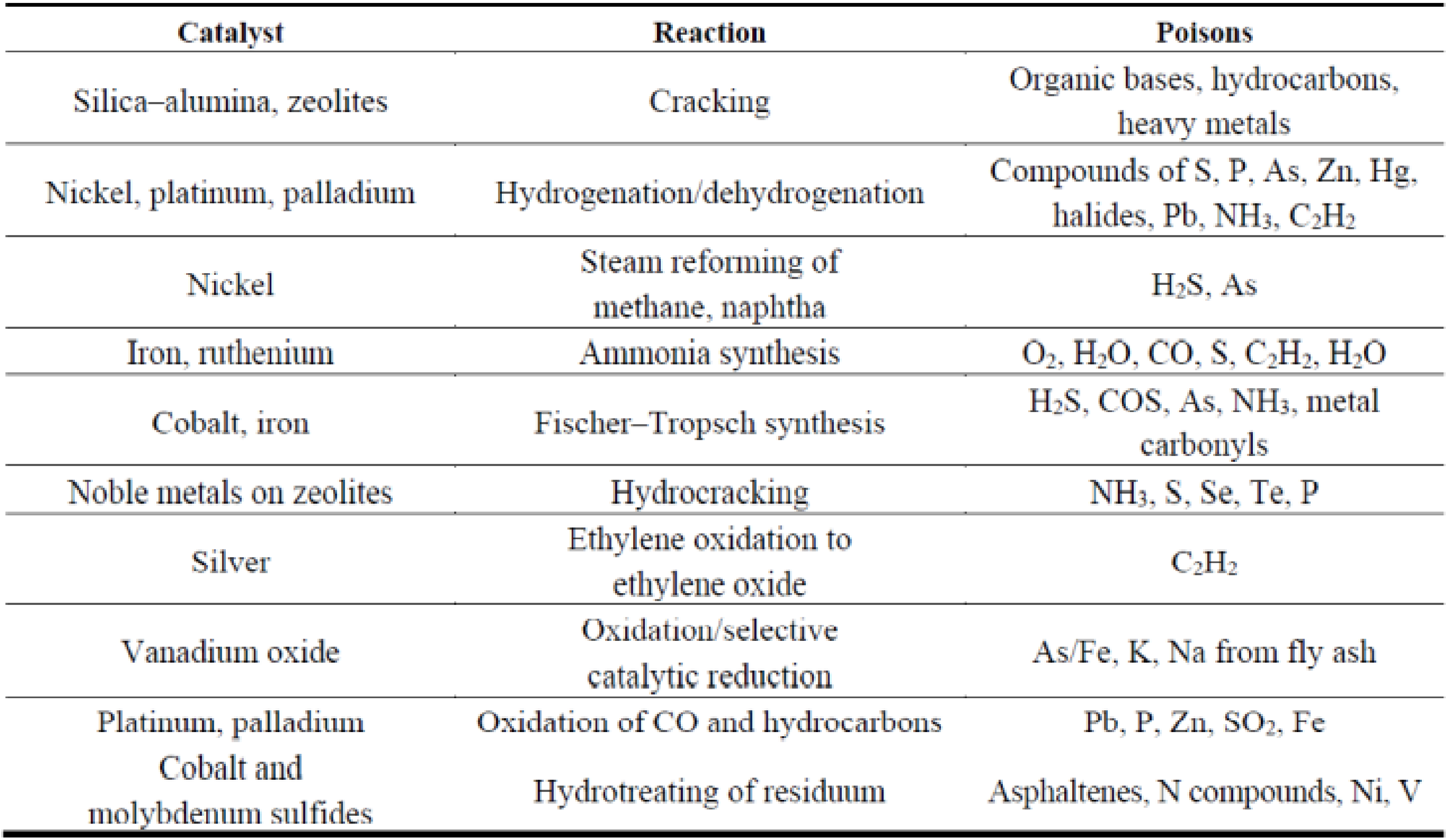


Table 2. Common poisons classified according to chemical structure.

Chemical type	Examples	Type of interaction with metals
Groups VA and VIA	N, P, As, Sb, O, S, Se, Te	Through *s* and *p* orbitals; shielded structures are less toxic
Group VIIA	F, Cl, Br, I	Through *s* and *p* orbitals; formation of volatile halides
Toxic heavy metals and ions	As, Pb, Hg, Bi, Sn, Cd, Cu, Fe	Occupy *d* orbitals; may form alloys
Molecules that adsorb with multiple bonds	CO, NO, HCN, benzene, acetylene, other unsaturated hydrocarbons	Chemisorption through multiple bonds and back bonding

Table 3. Poisons for selected catalysts in important representative reactions.



Catalyst	Reaction	Poisons
Silica–alumina, zeolites	Cracking	Organic bases, hydrocarbons, heavy metals
Nickel, platinum, palladium	Hydrogenation/dehydrogenation	Compounds of S, P, As, Zn, Hg, halides, Pb, NH_3, C_2H_2
Nickel	Steam reforming of methane, naphtha	H_2S, As
Iron, ruthenium	Ammonia synthesis	O_2, H_2O, CO, S, C_2H_2, H_2O
Cobalt, iron	Fischer–Tropsch synthesis	H_2S, COS, As, NH_3, metal carbonyls
Noble metals on zeolites	Hydrocracking	NH_3, S, Se, Te, P
Silver	Ethylene oxidation to ethylene oxide	C_2H_2
Vanadium oxide	Oxidation/selective catalytic reduction	As/Fe, K, Na from fly ash
Platinum, palladium	Oxidation of CO and hydrocarbons	Pb, P, Zn, SO_2, Fe
Cobalt and molybdenum sulfides	Hydrotreating of residuum	Asphaltenes, N compounds, Ni, V

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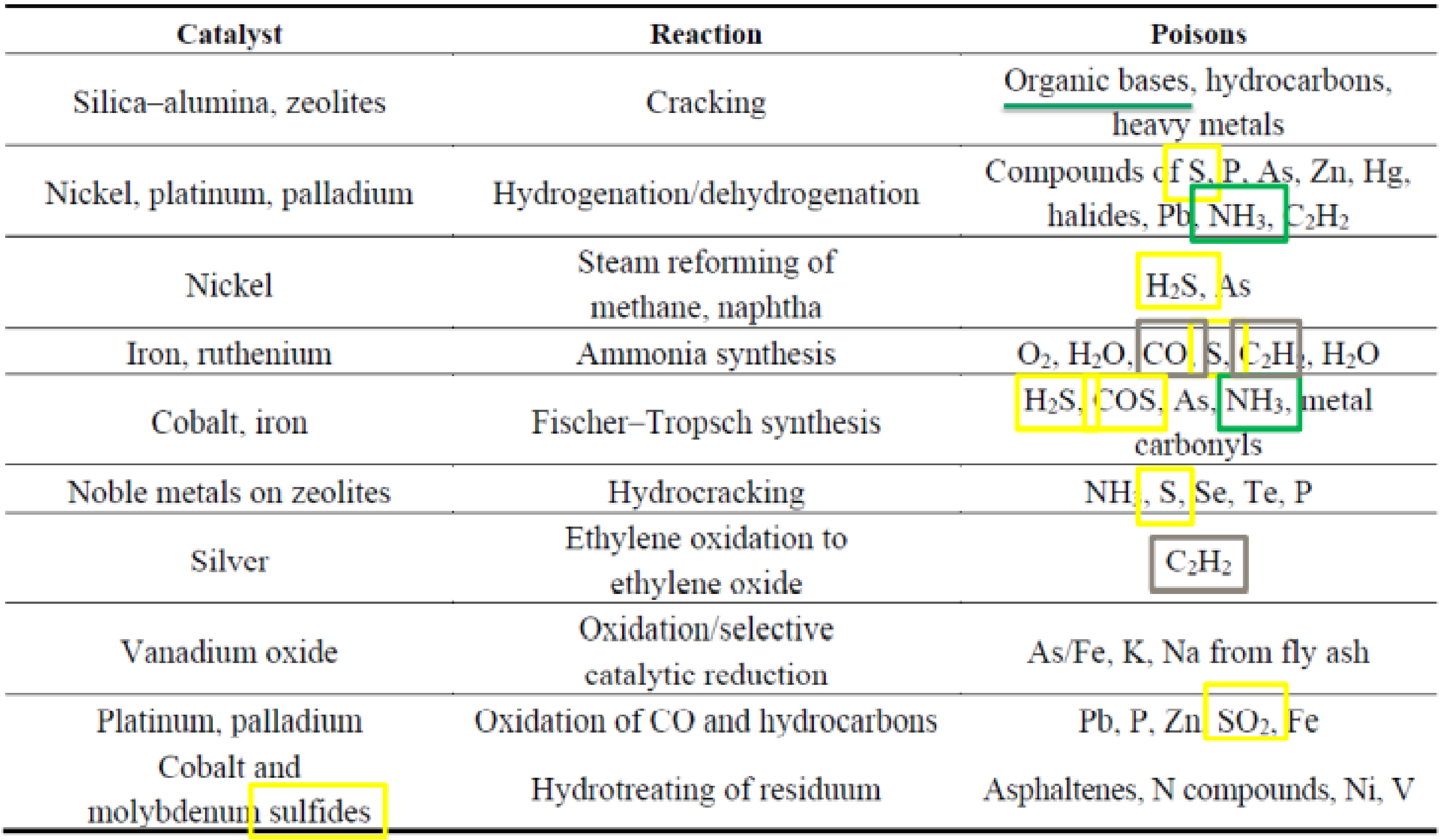

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Cobalt, iron	Fischer–Tropsch synthesis	H_2S, COS, As, NH_3, metal carbonyls
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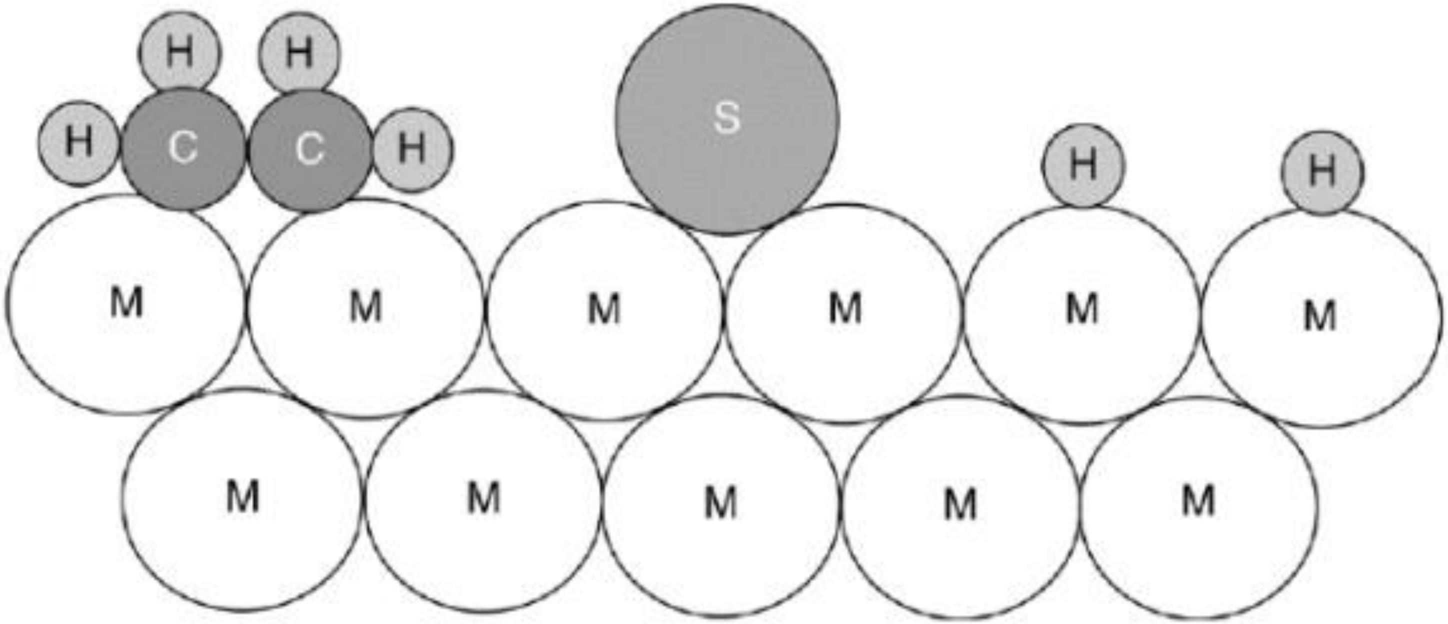
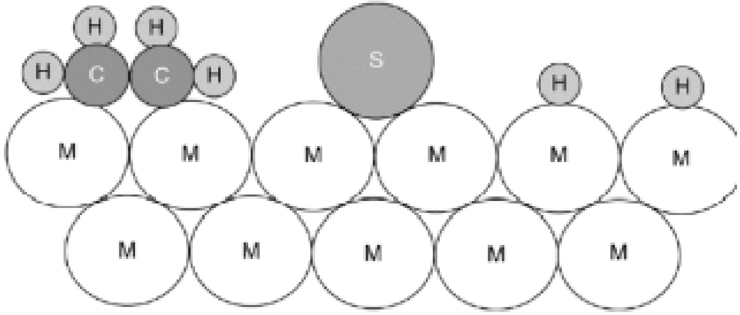


Conceptual two-dimensional model of poisoning by sulfur atoms of a metal surface during ethylene hydrogenation

Five poisonous effects



Adsorbed poison:

1. Physically blocks several adsorption/reaction sites on the metal surface.
2. Through its strong chemical bond, electronically modifies its nearest neighbor metal atoms (and possibly further), modifying their abilities to adsorb and/or dissociate reactant molecules.
3. Potential restructuring of the surface, possibly causing dramatic changes in catalytic properties, for reactions sensitive to surface structure.
4. Blocks access of adsorbed reactants to each other
5. Prevents or slows the surface diffusion of adsorbed reactants.

Poisoning of Ni catalysts by S has been widely studied

1 nm^{-2} = 10^{14} cm^{-2}

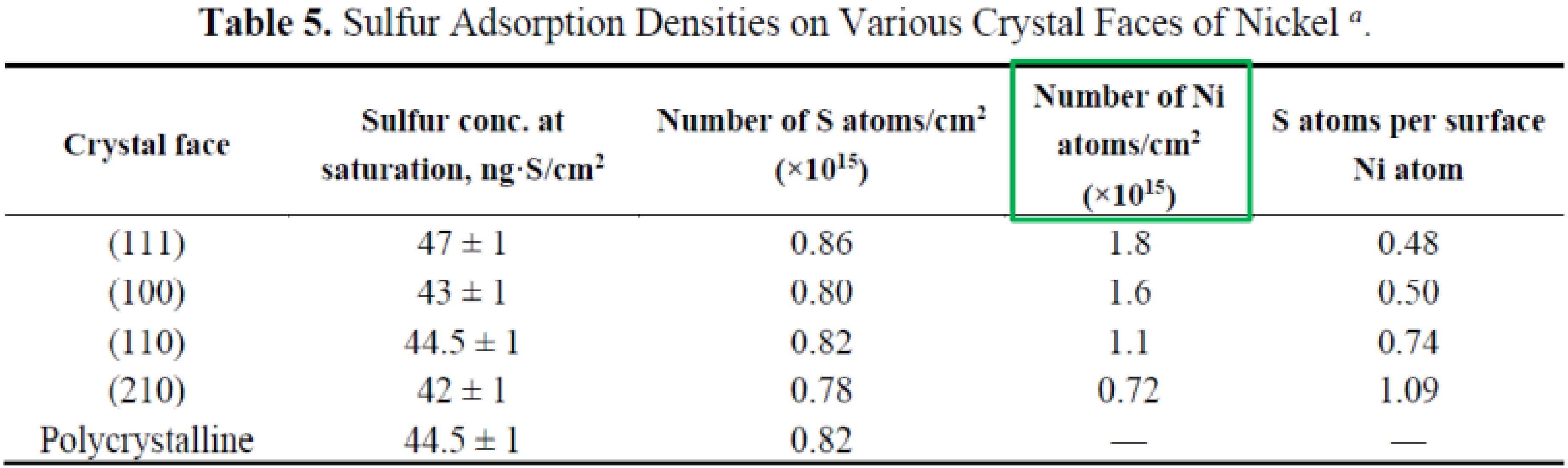
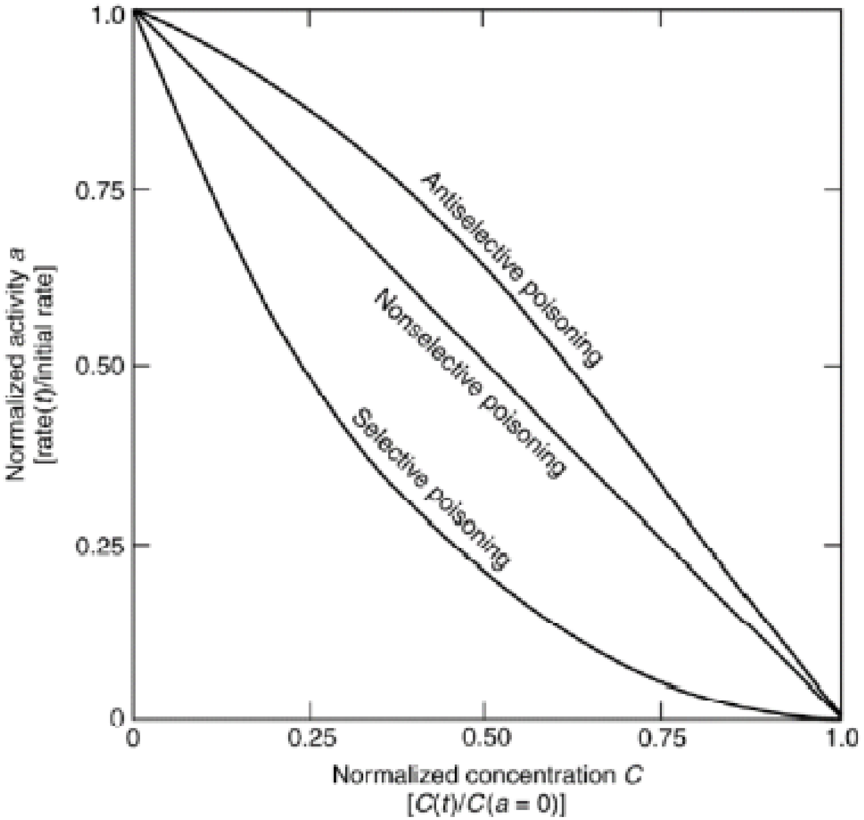


Table 5. Sulfur Adsorption Densities on Various Crystal Faces of Nickel [a].

Crystal face	Sulfur conc. at saturation, ng·S/cm^2	Number of S atoms/cm^2 (×10^{15})	Number of Ni atoms/cm^2 (×10^{15})	S atoms per surface Ni atom
(111)	47 ± 1	0.86	1.8	0.48
(100)	43 ± 1	0.80	1.6	0.50
(110)	44.5 ± 1	0.82	1.1	0.74
(210)	42 ± 1	0.78	0.72	1.09
Polycrystalline	44.5 ± 1	0.82	—	—

At saturation always about 8 S/nm^2



- Selective poisoning: the most active sites are blocked at low poison concentrations
- Antiselective poisoning: sites of lesser activity are blocked first
- Non-selective poisoning: loss of activity proportional to poison concentration

Highly selective poisoning: methanation on Ni, Co, Fe and Ru catalysts

- **Sulfure tolerance extremely low as H_2S concentration on ppb level**
- **Sulfur resistance depends on catalyst metal and composition, reaction conditions…**

- **It is possible to improve sulfur resistance with additives or promoters**
  - e.g. Mo or B on Ni, Co or Fe

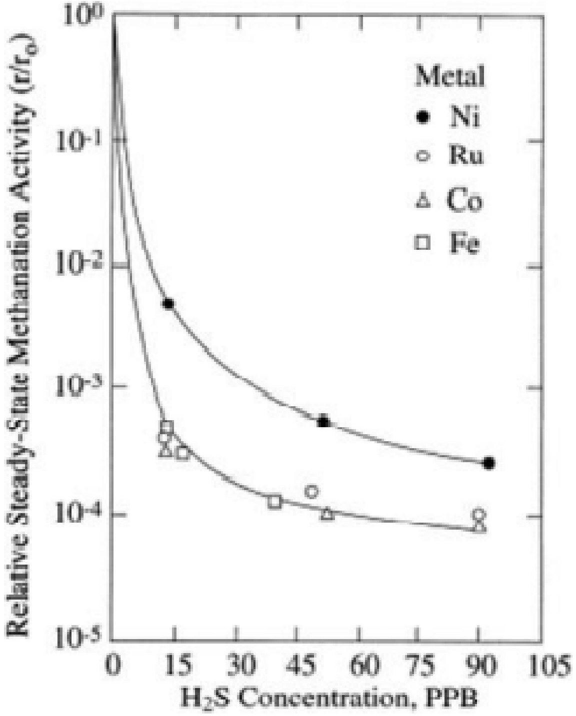


Fig. 8. Relative steady-state methanation activity profiles for Ni (•), Co (△), Fe (□), and Ru (○) as a function of gas phase H_2S concentration. Reaction conditions: 100 kPa; 400° C; 1% CO/99% H_2 for CO, Fe and Ru; 4% CO/96% H_2 for Ni [26].

Poisoning

Poisoning is sometimes used to improve the system, e.g. selectivity

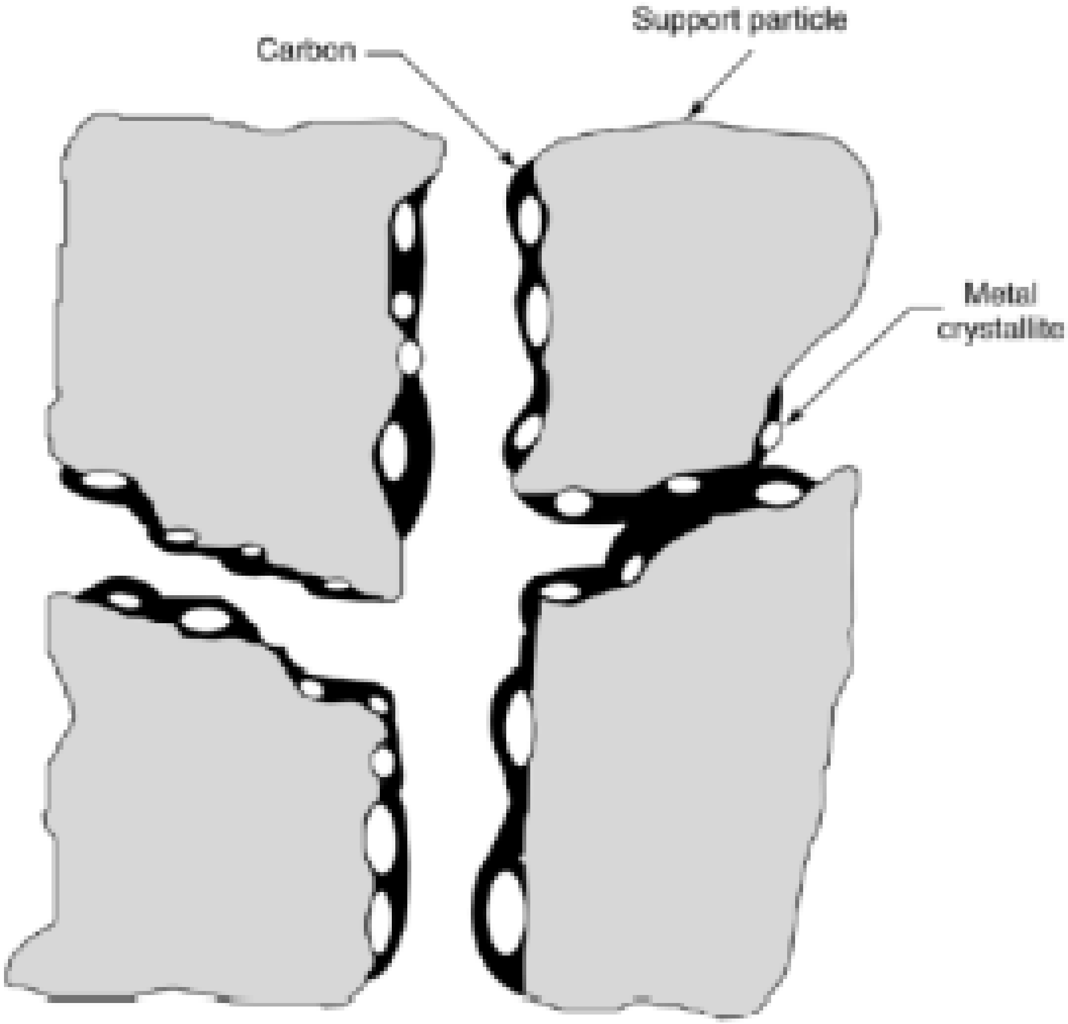
Naphta catalytic reforming Pt catalyst in oil refining:

- Pre-sulfidation to prevent unwanted cracking reactions

Diesel emission catalysts

- V_2O_5 added to Pt to suppress SO_2 oxidation to SO_3

Fouling, coking



- ***Fouling*** **is the physical (mechanical) deposition of species from the fluid phase onto the catalyst surface, which results in activity loss due to blockage of sites and/or pores.** In its advanced stages, it may result in disintegration of catalyst particles and plugging of the reactor voids.
- Important examples include mechanical deposits of carbon and coke in porous catalysts, although carbon- and coke-forming processes also involve chemisorption of different kinds of carbons or condensed hydrocarbons that may act as catalyst poisons.

“The definitions of carbon and coke are somewhat arbitrary and by convention related to their origin.”

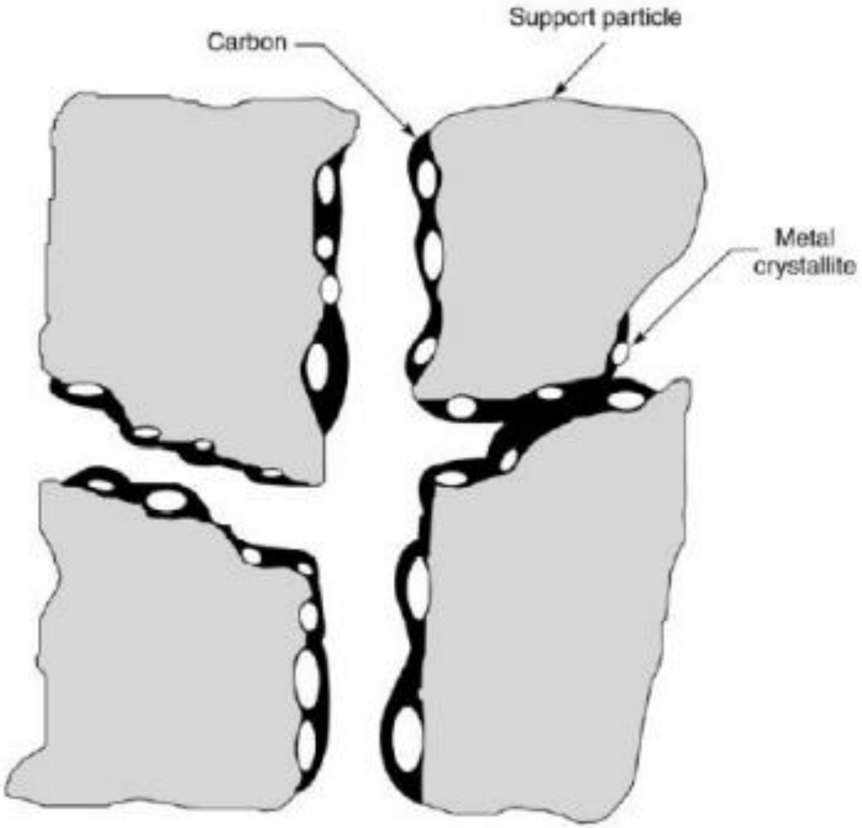
- Carbon is typically a product of CO disproportionation, while
- coke is produced by decomposition or condensation of hydrocarbons on catalyst surfaces and typically consists of polymerized heavy hydrocarbons.

Analogously to structure-sensitive and structure-insensitive reactions…

- In coke-sensitive reactions, unreactive coke is deposited on active sites, leading to activity decline
  - Examples: catalytic cracking and hydrogenolysis
- in coke-insensitive reactions, relatively reactive coke precursors formed on active sites are readily removed by hydrogen (or other gasifying agents).
  - Examples: Fischer–Tropsch synthesis, catalytic reforming, and methanol synthesis

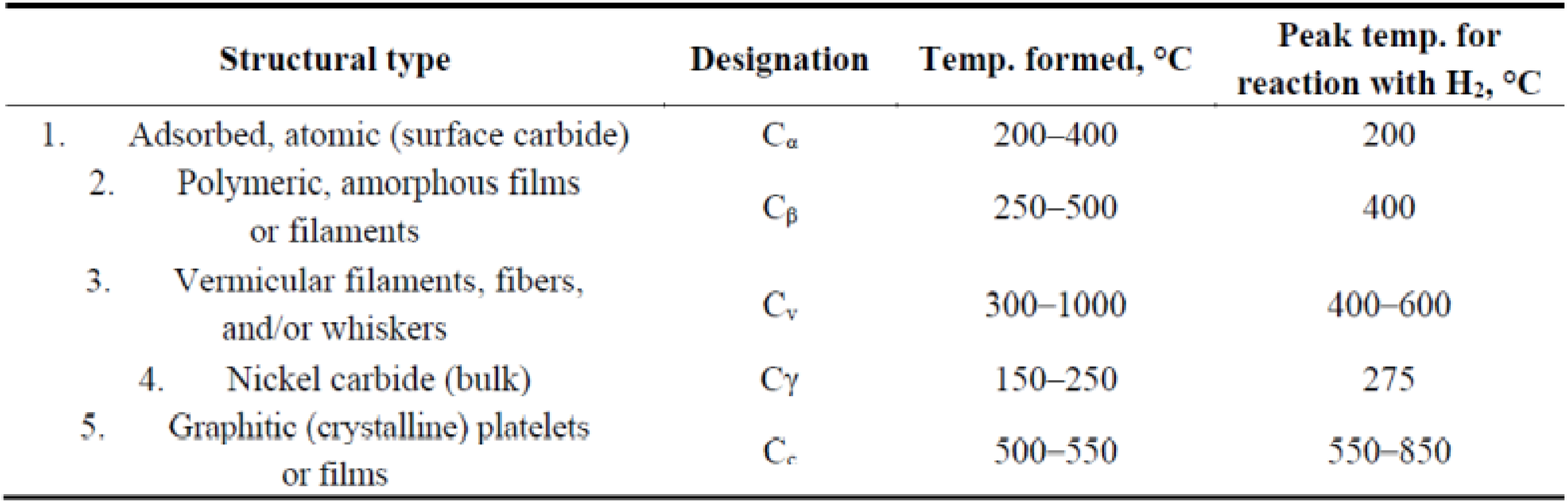
Mechanism of formation?

- metal catalyst?
- metal oxide catalyst (or sulfide, sulfides being similar to oxides)?
- Thermal, radical-based process?

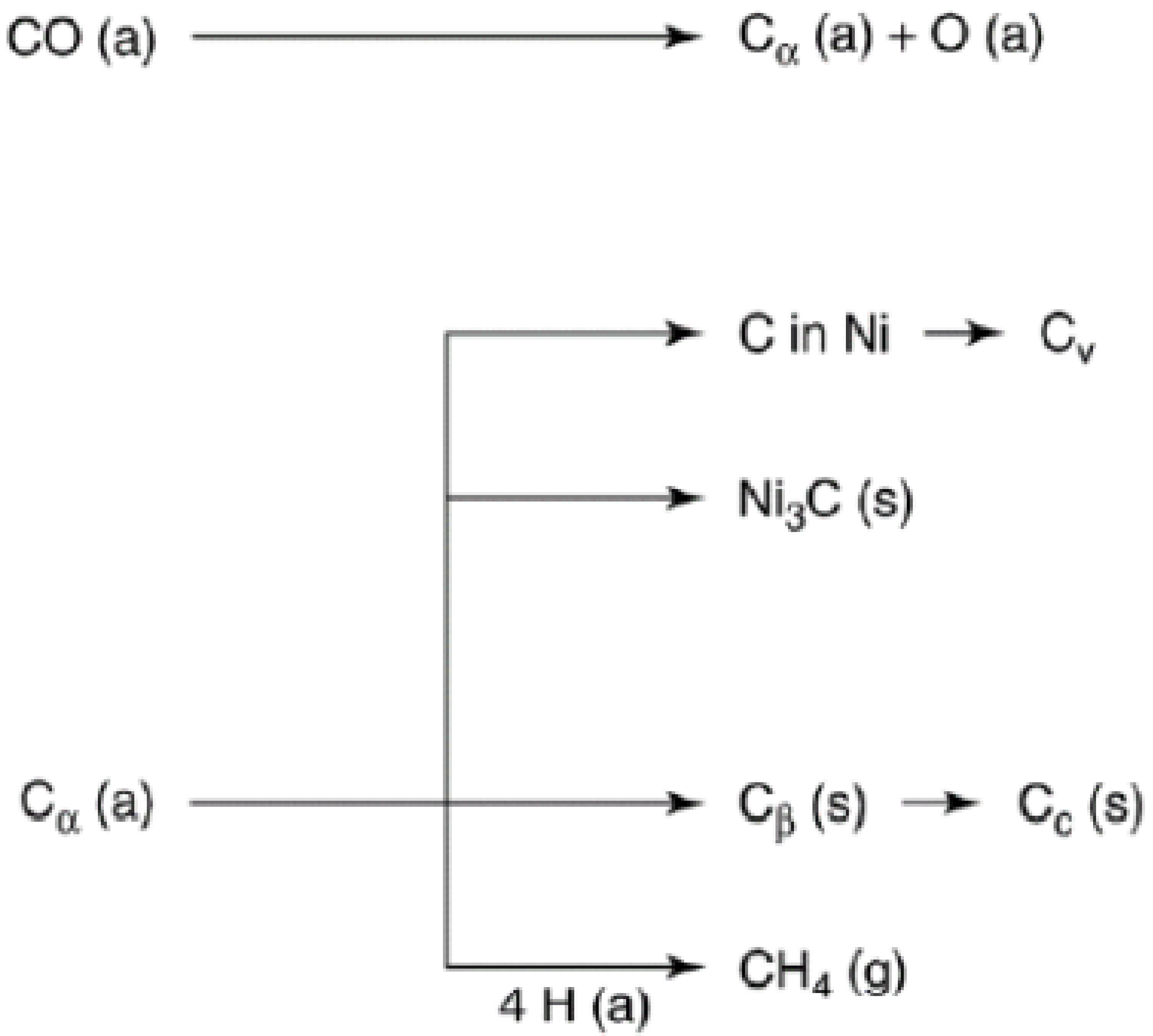


Conceptual model of fouling, crystallite encapsulation, and pore plugging of a supported metal catalyst owing to carbon deposition.

Table 6. Forms and Reactivities of Carbon Species Formed by Decomposition of CO on Nickel [a].



	Structural type	Designation	Temp. formed, °C	Peak temp. for reaction with H_2, °C
1.	Adsorbed, atomic (surface carbide)	C_α	200–400	200
2.	Polymeric, amorphous films or filaments	C_β	250–500	400
3.	Vermicular filaments, fibers, and/or whiskers	C_v	300–1000	400–600
4.	Nickel carbide (bulk)	$C\gamma$	150–250	275
5.	Graphitic (crystalline) platelets or films	C_c	500–550	550–850



$CO\,(a) \rightarrow C_{\alpha}\,(a) + O\,(a)$

Atomically adsorbed

$C_{\alpha}\,(a) \rightarrow C \text{ in } Ni \rightarrow C_v$

vermicular

$C_{\alpha}\,(a) \rightarrow Ni_3C\,(s)$

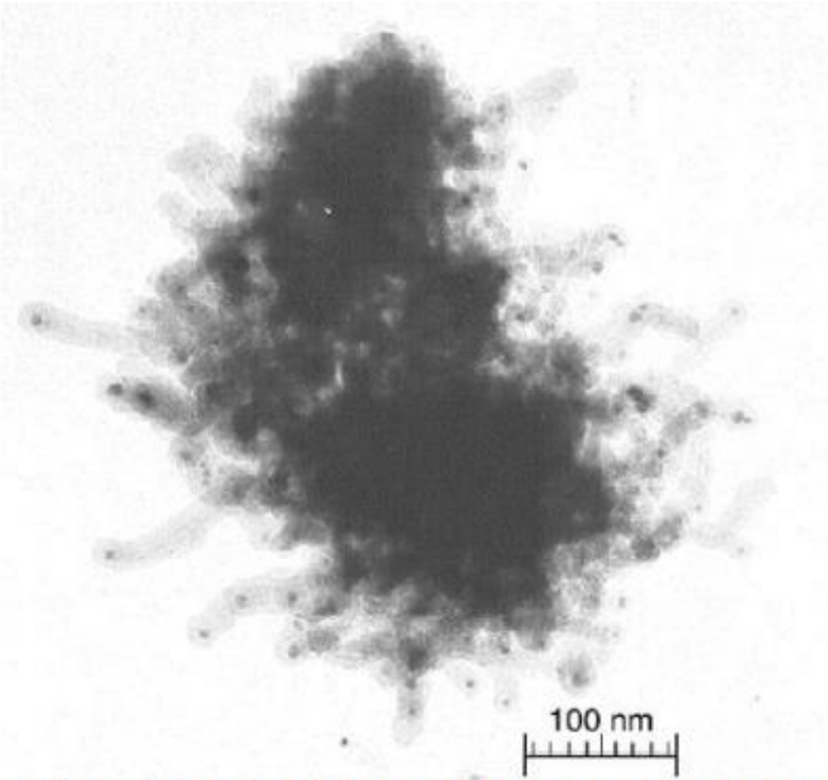
carbide

$C_{\alpha}\,(a) \rightarrow C_{\beta}\,(s) \rightarrow C_c\,(s)$

Polymeric films/filamets → graphitic

$C_{\alpha}\,(a) + 4\,H\,(a) \rightarrow CH_4\,(g)$

(gasified)



Vermicular carbon C_v

Electron micrograph of 14% Ni/Al_2O_3 having undergone extensive carbon deposition during CO disproportionation at 673 K, P_{CO} = 4.55 kPa (magnification of 200,000). Courtesy of the BYU Catalysis Laboratory.

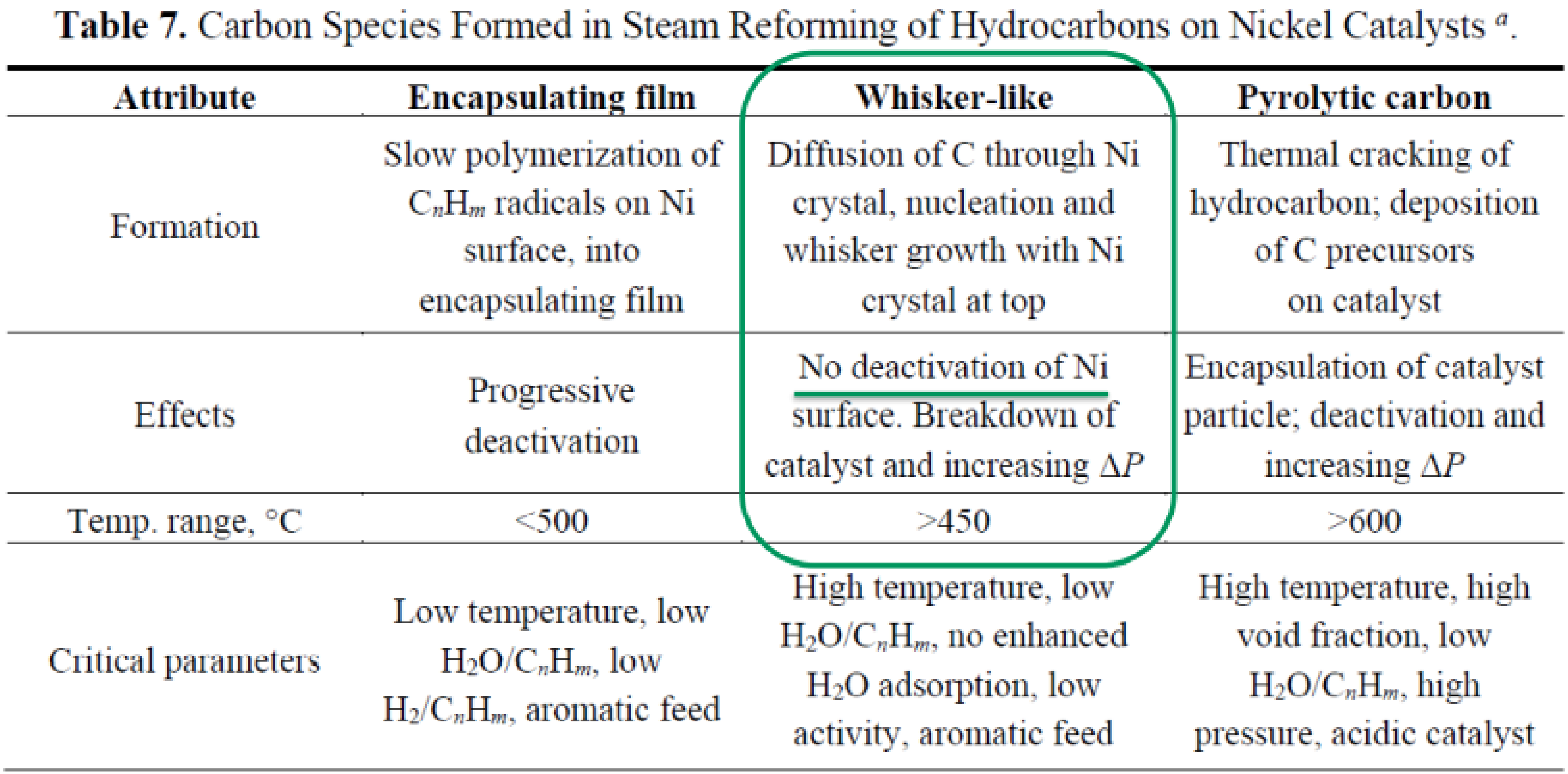
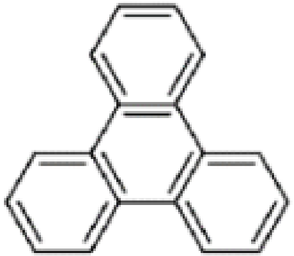


Table 7. Carbon Species Formed in Steam Reforming of Hydrocarbons on Nickel Catalysts [a].

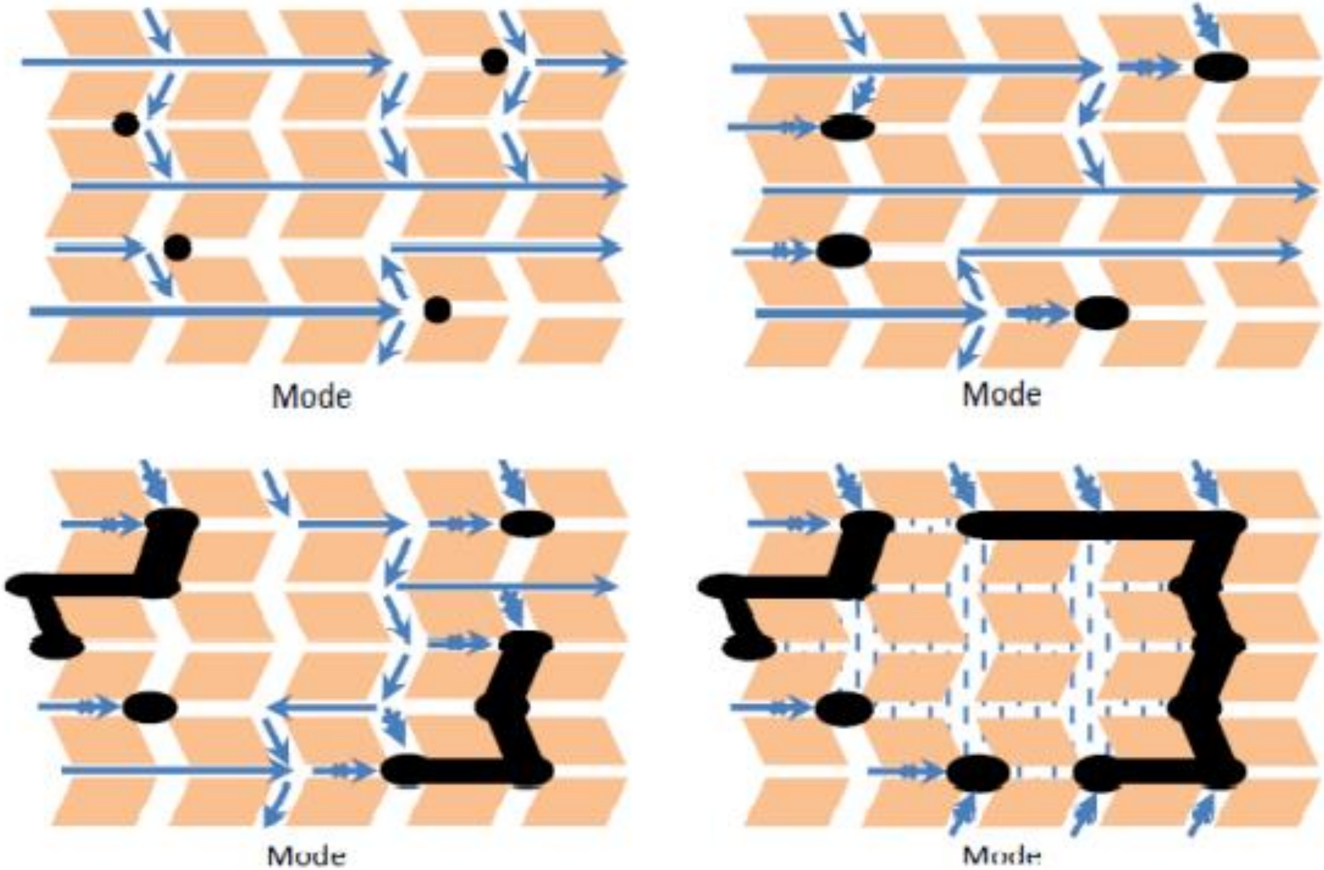
Attribute	Encapsulating film	Whisker-like	Pyrolytic carbon
Formation	Slow polymerization of C_nH_m radicals on Ni surface, into encapsulating film	Diffusion of C through Ni crystal, nucleation and whisker growth with Ni crystal at top	Thermal cracking of hydrocarbon; deposition of C precursors on catalyst
Effects	Progressive deactivation	No deactivation of Ni surface. Breakdown of catalyst and increasing ΔP	Encapsulation of catalyst particle; deactivation and increasing ΔP
Temp. range, °C	<500	>450	>600
Critical parameters	Low temperature, low H_2O/C_nH_m, low H_2/C_nH_m, aromatic feed	High temperature, low H_2O/C_nH_m, no enhanced H_2O adsorption, low activity, aromatic feed	High temperature, high void fraction, low H_2O/C_nH_m, high pressure, acidic catalyst

On oxides and sulfides: coke formation catalyzed by acid sites



- Coke precursors: typically olefins or aromatics
- Dehydrogenation and cyclization reactions of carbocation intermediates formed on acid sites lead to aromatics, which react further to higher molecular weight polynuclear aromatics that condense as coke
- Because of the high stability of the polynuclear carbocations, they can continue to grow on the surface for a relatively long time before a termination reaction occurs through the back donation of a proton

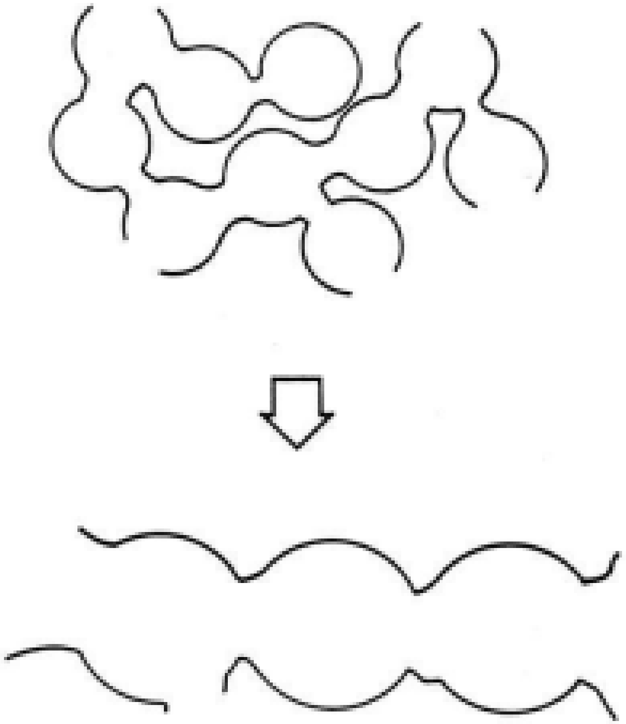
→ **PAH, polyaromatic hydrocarbon**

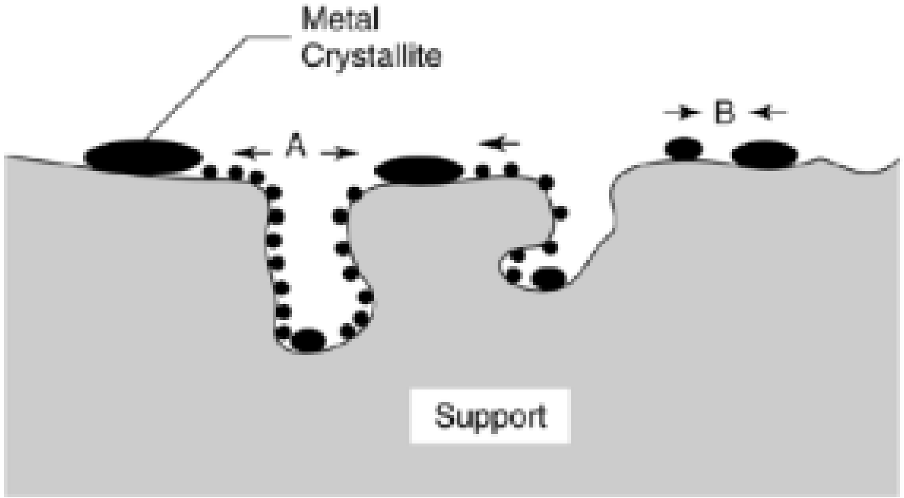


Schematic of the four possible modes of deactivation by carbonaceous deposits in HZSM-5: (1) reversible adsorption on acid sites, (2) irreversible adsorption on sites with partial blocking of pore intersections, (3) partial steric blocking of pores, and (4) extensive steric blocking of pores by exterior deposits.

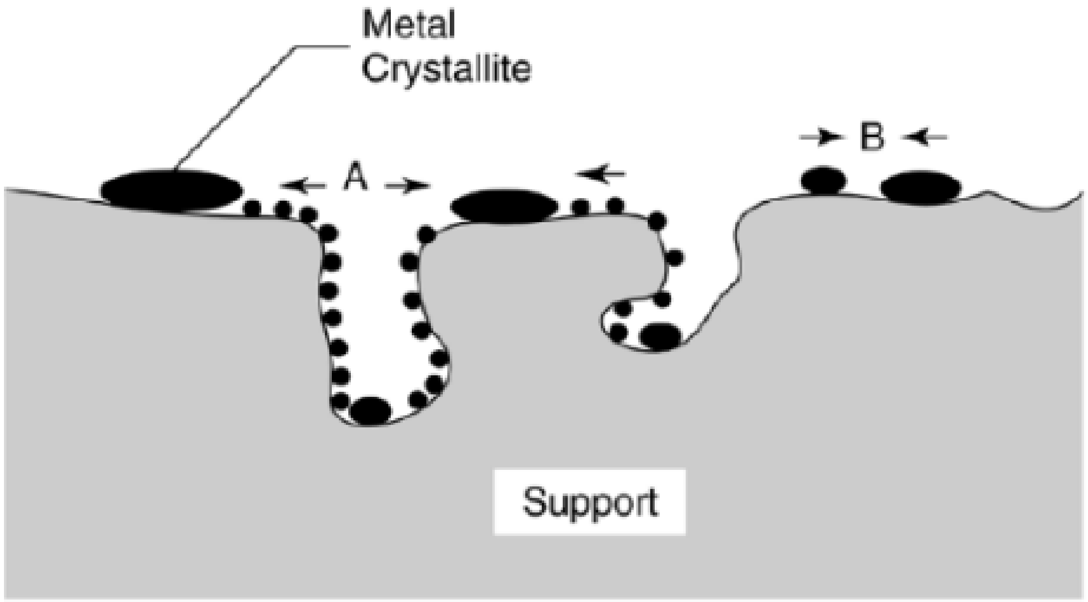
- the order of reactivity for coke formation: polynuclear aromatics > aromatics > olefins > branched alkanes > normal alkanes.
- In coking reactions involving heavy hydrocarbons (complex); different kinds of coke may be formed and they may range in composition from **CH to C**
- In bifunctional catalysts, different types of coke on metal & support.
  - ”Soft coke” on the metal sites (”high” H/C ratio)
  - ”Hard coke” on the acid sites (”low” H/C ratio)

Sintering





Sintering of the active component



Two conceptual models for crystallite growth due to sintering by

(**A**) atomic migration or

(**B**) crystallite migration.

(Also possible: C: vapor transport, at high temperatures, e.g. RuO_4)

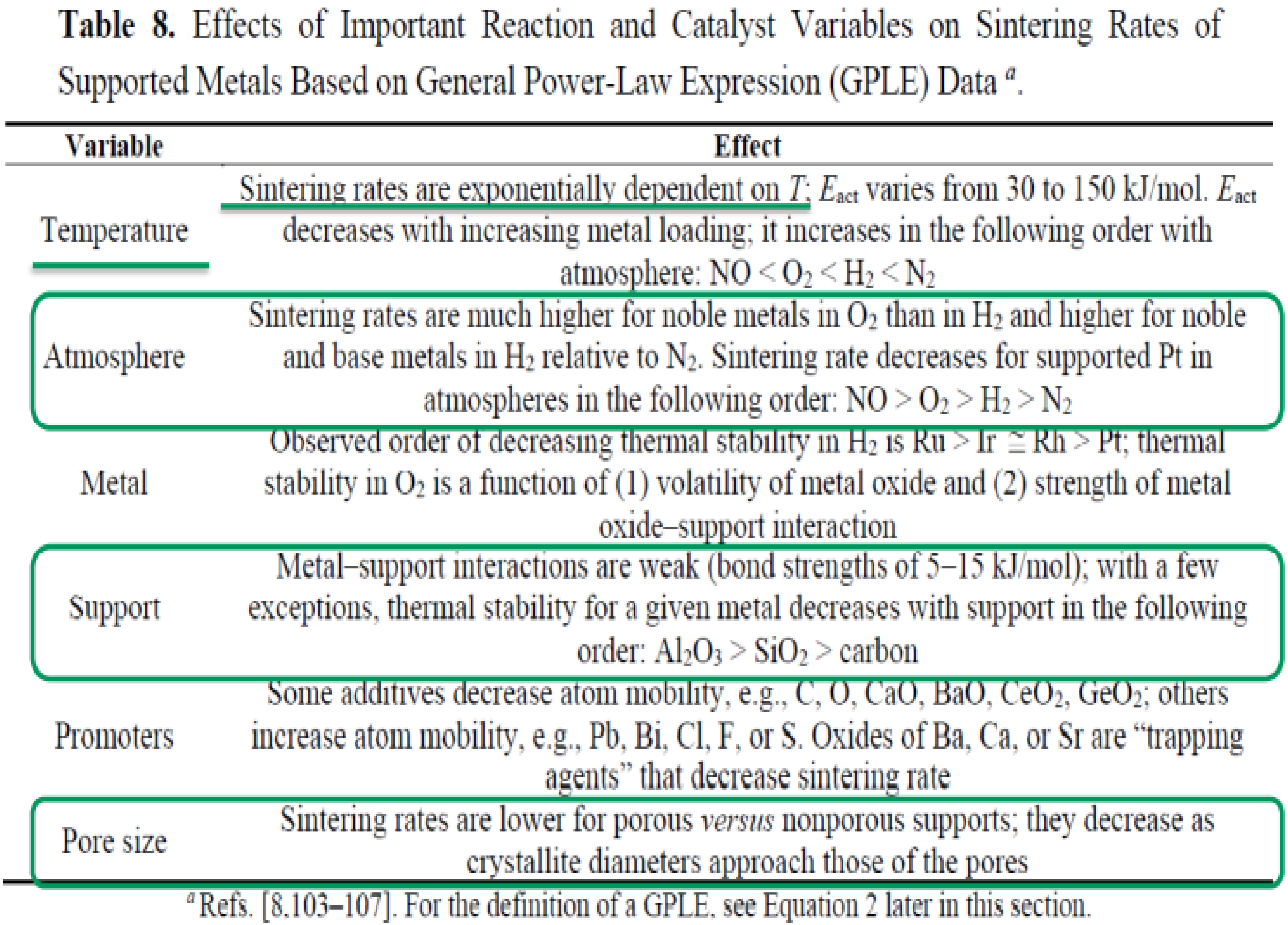
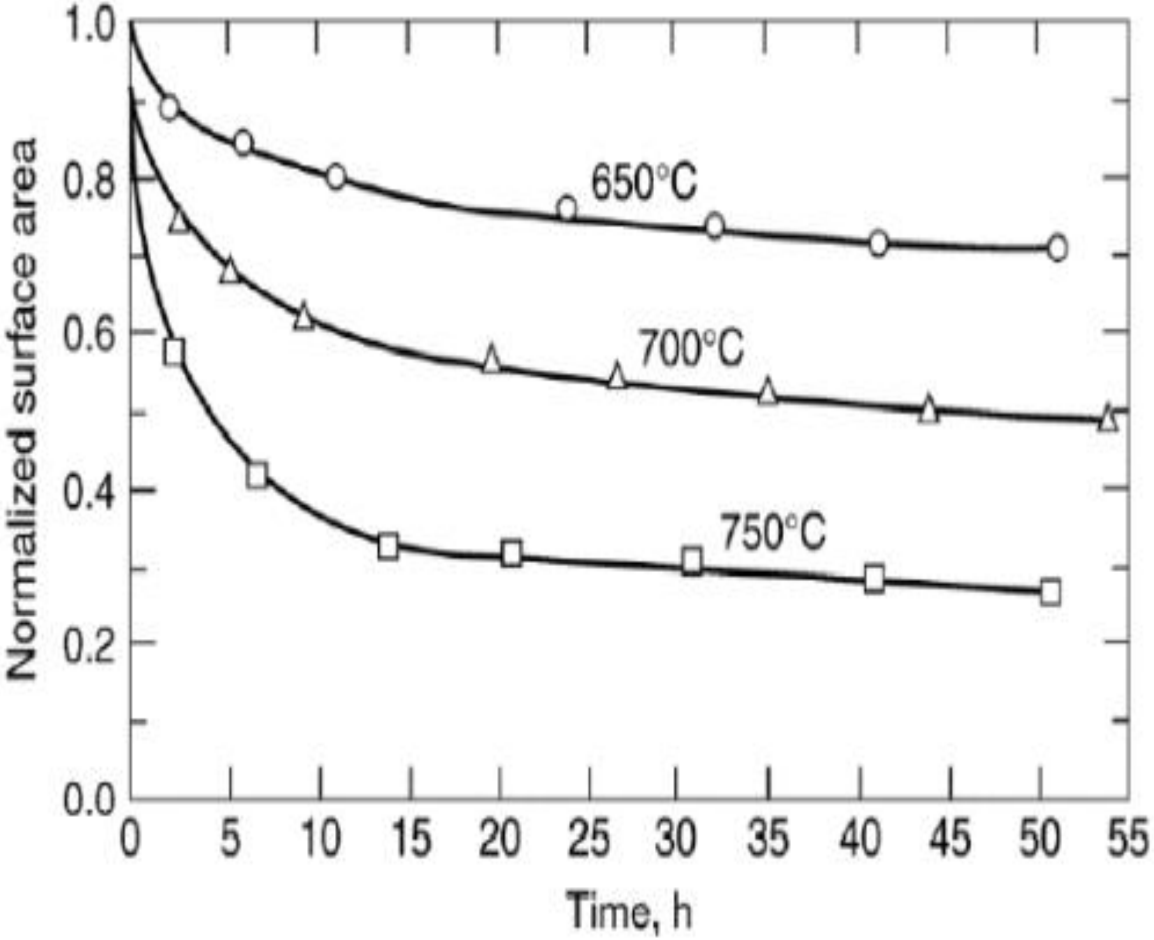


Table 8. Effects of Important Reaction and Catalyst Variables on Sintering Rates of Supported Metals Based on General Power-Law Expression (GPLE) Data [a].

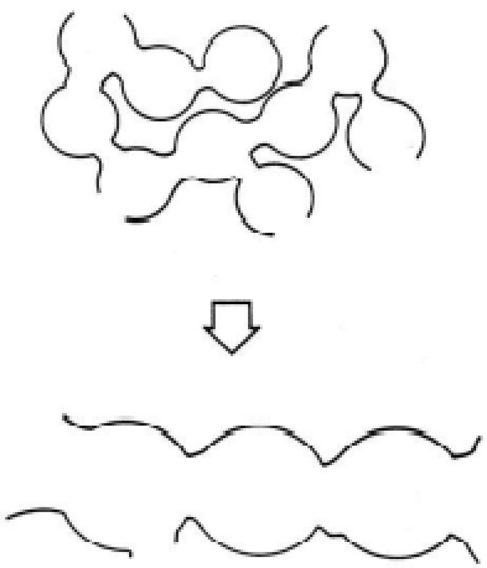
Variable	**Effect**
Temperature	Sintering rates are exponentially dependent on *T*; E_{act} varies from 30 to 150 kJ/mol. E_{act} decreases with increasing metal loading; it increases in the following order with atmosphere: $NO < O_2 < H_2 < N_2$
Atmosphere	Sintering rates are much higher for noble metals in O_2 than in H_2 and higher for noble and base metals in H_2 relative to N_2. Sintering rate decreases for supported Pt in atmospheres in the following order: $NO > O_2 > H_2 > N_2$
Metal	Observed order of decreasing thermal stability in H_2 is $Ru > Ir \cong Rh > Pt$; thermal stability in O_2 is a function of (1) volatility of metal oxide and (2) strength of metal oxide–support interaction
Support	Metal–support interactions are weak (bond strengths of 5–15 kJ/mol); with a few exceptions, thermal stability for a given metal decreases with support in the following order: $Al_2O_3 > SiO_2 >$ carbon
Promoters	Some additives decrease atom mobility, e.g., C, O, CaO, BaO, CeO_2, GeO_2; others increase atom mobility, e.g., Pb, Bi, Cl, F, or S. Oxides of Ba, Ca, or Sr are "trapping agents" that decrease sintering rate
Pore size	Sintering rates are lower for porous *versus* nonporous supports; they decrease as crystallite diameters approach those of the pores

[a] Refs. [8,103–107]. For the definition of a GPLE, see Equation 2 later in this section.



Normalized nickel surface area (based on H_2 adsorption) *versus* time data during sintering of 13.5% Ni/SiO_2 in H_2 at 650, 700, and 750 ° C. Reproduced from [108]. Copyright 1983, Elsevier.

Sintering of the porous support



- **Sintering is irreversible**
- **”Sintering is more easily prevented than cured”**

Sintering of single-phase oxide carriers, five processes:

(1) surface diffusion,

(2) solid-state diffusion,

(3) evaporation/condensation of volatile atoms or molecules,

(4) grain boundary diffusion, and

(5) phase transformations.

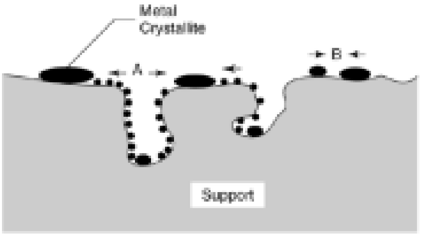
- “In oxidizing atmospheres, γ-alumina and silica are the most thermally stable carriers;
- in reducing atmospheres, carbons are the most thermally stable carriers.”

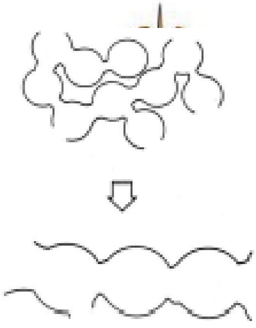
- Additives and impurities affect the thermal properties of carriers by occupying defect sites or forming new phases.
  - Alkali metals accelerate sintering; while
  - calcium, barium, nickel, and lanthanum oxides form thermally stable spinel phases with alumina.
- Steam (H_2O) accelerates support sintering by forming mobile surface hydroxyl (-OH) groups.
- Dispersed metals in supported metal catalysts can also accelerate support sintering; for example, dispersed nickel accelerates the loss of Al_2O_3 surface area in Ni/Al_2O_3 catalysts.

Approximate surface areas of alumina phases

Phase	specific surface area, m^2/g
Boehmite	400
Gamma-alumina	200
Sigma-alumina	120
Theta-alumina	50
Alpha-alumina	1

Effects of sintering on catalytic activity





Specific activity (based on catalytic surface area) can

- **Increase or decrease with increasing metal crystallite size**
  - Structure-sensitive reactions
  - Examples: ethane hydrogenolysis, ethane steam reforming
- **Be independent of metal crystallite size**
  - Structure-insensitive reactions
  - Decrease in mass-based activity proportional to the decrease in metal surface area
  - Example: CO hydrogenation on supported Co, Ni, Fe, Ru

Prevention of catalyst decay

It is often easier to prevent than cure catalyst deactivation

- Many poisons and foulants can be removed from feeds using guard beds, scrubbers, and/or filters.
- Fouling, thermal degradation, and chemical degradation can be minimized through careful control of process conditions,
  - *e.g., lowering temperature to lower sintering rate or*
  - *adding steam, oxygen, or hydrogen to the feed to gasify carbon or coke-forming precursors.*

Multilayer strategy in three-way catalysts

(Bartholomew view)

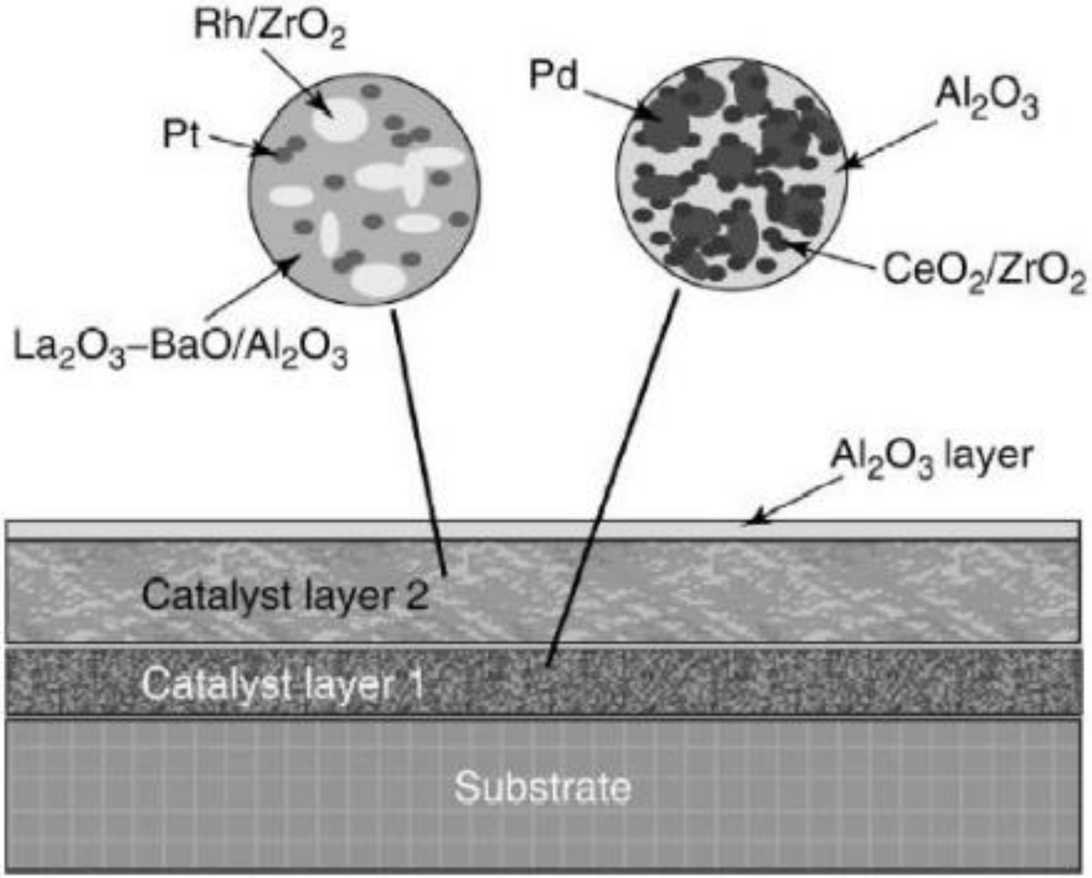


Table 16. How Deactivation Mechanisms Affect the Rate of a Catalyzed Reaction and the Rapidity and Reversibility of Deactivation Process.

	Effects on reaction rate			Deactivation process	
Deactivation mechanism	**Decrease in number of active sites**	**Decrease in intrinisic activity (k_{intr})**	**Decrease in effectiveness factor (η)**	**Fast or slow [a]**	**Reversible**
Chemical degradation	×	×	× [b,c]	Varies	No
Fouling	×	×	-	Fast	Yes
Mechanical degradation	×	-	-	Varies	No
Poisoning	×	×	-	Slow	Usually
Thermal degradation/Sintering	×	× [b,d]	× [b,e]	Slow	Sometimes
Vaporization/leaching	×	× [b,f]	-	Fast	Sometimes

Regeneration of Poisoned Catalysts

- **Supported Ni-based steam reforming catalysts (low surface area): up to 80% of sulfur can be removed, 700C in steam**
- **(High-surface-area catalysts cannot tolerate the same treatment without sintering)**

$$\text{Ni-S} + H_2O \rightarrow NiO + H_2S$$

$$H_2S + 2H_2O \rightarrow SO_2 + 3H_2$$

- **Regeneration of sulfur-poisoned noble metals in air rather than steam, although this is frequently attended by sintering**

Regeneration of Catalyst Deactivated by Coke or Carbon

- **Carbonaceous deposits can be removed by gasification**
  - order of decreasing reaction rate of $O_2 > H_2O > H_2$
- **Rates of gasification of coke or carbon are greatly accelerated by the same metal or metal oxide catalysts upon which carbon or coke deposits.**

Regeneration of Catalyst Deactivated by Coke or Carbon

Examples:

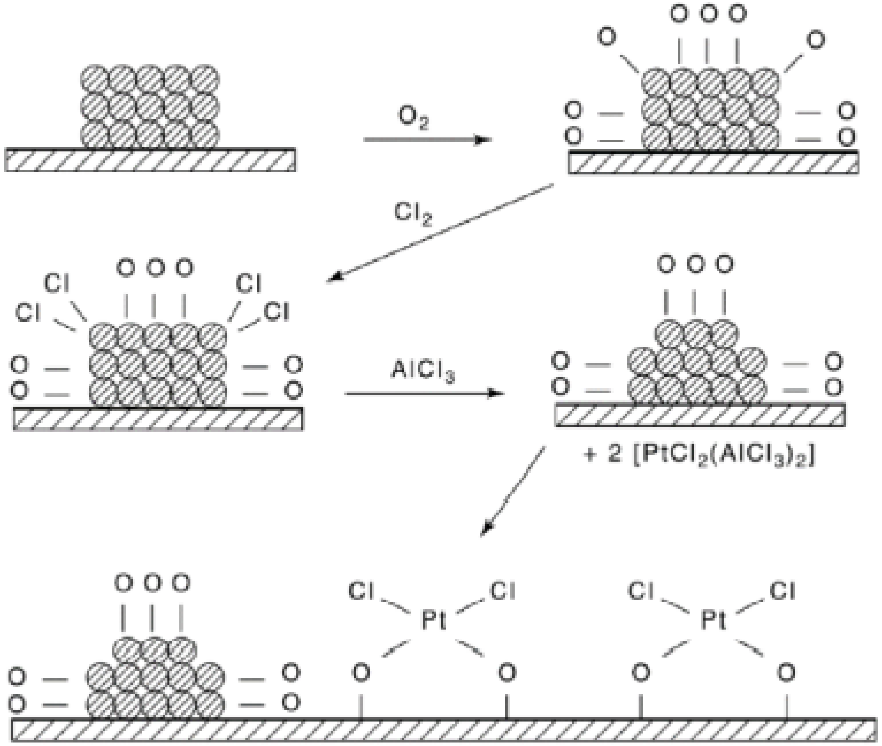
- **metal-catalyzed coke removal with H_2 or H_2O can occur at a temperature as low as 400 ° C;**
- **β-carbon can be removed with H_2 in a few h at 400–450 ° C and with oxygen in 15–30 min at 300 ° C.**
  - Potential hot spots in the catalyst bed with oxygen
- **Gasification of more graphitic or less reactive carbons or coke species in H_2 or H_2O may require temperatures as high as 700–900 ° C,**
  - → catalyst sintering.

Redispersion of Sintered Catalysts

- Extensive patent literature; mechanistic research called for

Example: supported Pt/alumina

- In catalytic reforming of hydrocarbons: 1-nm clusters to 5–20-nm crystallites
- Redispersion by “oxychlorination:” HCl or CCl_4 at 450–550 ° C in 2–10% oxygen for 1–4 h
- Dispersion from 0.25 to 0.81



Catalyst Deactivation

Thus far, we assumed the total conc. of active sites on the surface was constant, which means the catalyst's activity is constant throughout its lifetime

In reality, there is a gradual loss of catalytic activity (active sites on surface of the catalyst) as the reaction takes place

- Main types of catalyst deactivation
    - Sintering (aging): loss of active surface due to high temperature
    - Coking or fouling: carbonaceous material (coke) deposits on surface
    - Poisoning: molecules *irreversibly* bind to the active site

We will evaluate the kinetics of general catalyst deactivation and these specific types

Catalyst Deactivation Kinetics

- Adjustments for catalyst decay need to be made in the design of reactors
- Catalyst activity *a*(*t*) is used as a quantitative specification

Reaction rate for catalyst used for time t

Catalyst activity at time t: $$a(t) = \frac{-r_A'(t)}{-r_A'\big|_{t=0}}$$

Reaction rate for fresh, unused catalyst

$$0 \le a(t) \le 1$$ For fresh, unused catalyst, $$a\big|_{t=0} = 1$$

Rate of consumption of reactant A on catalyst used for time t is:

$$-r'_A = a(t)\,k(T)\,fn(C_{A,} C_B, \ldots.etc)$$

a(t): time-dependent catalyst activity   k(T): T-dependent specific rate constant

fn(C_A, C_B…etc): function of gas-phase conc. of reactants, products & contaminants

Functionality of r_d on reacting species conc. h=1: no conc dependence; h=C_j: linearly dependent on concentration

Function of activity

Rate of catalyst decay: $$r_d = -\frac{da}{dt} = \overbrace{p\left[a(t)\right]}\underbrace{k_d(T)}\overbrace{h(C_A, C_B, \ldots, etc)}$$

Temperature-dependent specific decay constant

Sintering (Aging)

- Loss of active surface area resulting from the prolonged exposure to high gas-phase temperatures
- Active surface area is lost by
  - Crystal agglomeration and growth of metals deposited on support
  - Narrowing or closing of pores inside the catalyst pellet
  - Surface recrystallization
  - Elimination of surface defects (active sites)
- Sintering is usually negligible at temperatures below 40% of the melting temperature of the solid
- Second-order decay of reaction rate with respect to present activity:

$$r_d = k_d a^2$$

Catalyst activity at time t: $$a(t) = \frac{1}{1 + k_d t}$$

Sintering decay constant: $$k_d = k_d(T_0)\exp\left[\frac{E_d}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right]$$

Coking (Fouling)

- Common to reactions involving hydrocarbons
- A carbonaceous (coke) material is deposited on surface of catalyst

Concentration of carbon on surface (g/m²): $C_C = At^n$

A & n are fouling parameters

Catalyst activity at time t: $a(t) = \frac{1}{1 + k't^m}$

(one of many different expressions for a(t))
m is a fouling parameter

- Coking can be reduced by running at high pressure & hydrogen-rich feeds
- Catalyst deactivated by coking is often regenerated by burning off the carbon

Poisoning

- Poisoning molecule is ***irreversibly*** chemisorbed to active sites
- Reduces number of active sites available for reaction
- Catalyst can be poisoned by reactants, products, and impurities

For the overall reaction:

$$A + S \rightarrow B + S$$

poisoning by reactant: $A + S \xrightarrow{k_d'} A \cdot S$

posioning by product: $B + S \xrightarrow{k_d'} B \cdot S$

poisoning by impurity: $P + S \xrightarrow{k_d'} P \cdot S$

$$r_d = -\frac{da}{dt} = a(t)k'_d C_P$$

a(t): time-dependent catalyst activity
k_d: specific decay constant
C_P: Concentration of the poison

Example 10–5 Calculating Conversion with Catalyst Decay in Batch Reactors

The first-order isomerization

$$A \longrightarrow B$$

is being carried out isothermally in a batch reactor on a catalyst that is decaying as a result of aging. Derive an equation for conversion as a function of time.

Solution

1. **Design equation:**

$$N_{A0}\frac{dX}{dt} = -r'_A W \qquad \text{(E10-5.1)}$$

2. **Reaction rate law:**

$$-r'_A = k'a(t)C_A \qquad \text{(E10-5.2)}$$

3. **Decay law.** For second-order decay by sintering:

$$a(t) = \frac{1}{1+k_d t} \qquad \text{(10-98)}$$

4. **Stoichiometry:**

$$C_A = C_{A0}(1 - X) = \frac{N_{A0}}{V}(1 - X) \qquad \text{(E10-5.3)}$$

5. **Combining** gives us

$$\frac{dX}{dt} = \frac{W}{V} k' a(t)(1-X) \qquad \text{(E10-5.4)}$$

Let $k = k'W/V$. Then, separating variables, we have

$$\frac{dX}{1-X} = ka(t)\, dt \qquad \text{(E10-5.5)}$$

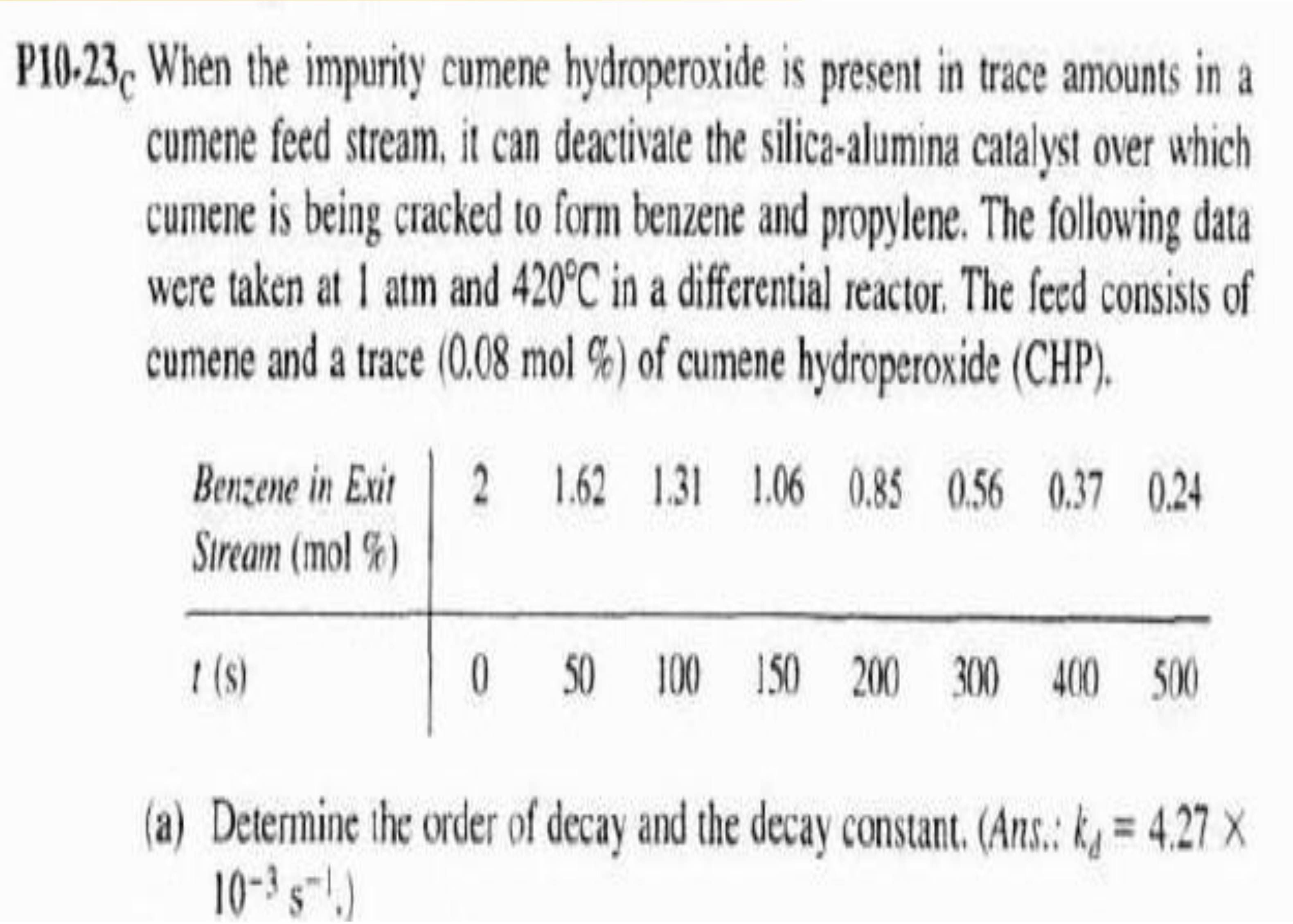
Substituting for a and integrating yields

$$\int_0^X \frac{dX}{1-X} = k \int_0^t \frac{dt}{1+k_d t} \qquad \text{(E10-5.6)}$$

$$\ln \frac{1}{1-X} = \frac{k}{k_d} \ln(1 + k_d t) \qquad \text{(E10-5.7)}$$

6. **Solving** for the conversion X at any time t, we find that

$$X = 1 - \frac{1}{(1+k_d t)^{k/k_d}} \qquad \text{(E10-5.8)}$$

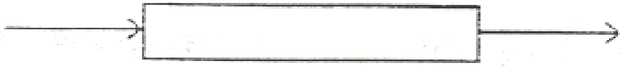


P10-23$_C$ When the impurity cumene hydroperoxide is present in trace amounts in a cumene feed stream, it can deactivate the silica-alumina catalyst over which cumene is being cracked to form benzene and propylene. The following data were taken at 1 atm and 420°C in a differential reactor. The feed consists of cumene and a trace (0.08 mol %) of cumene hydroperoxide (CHP).

Benzene in Exit Stream (mol %)	2	1.62	1.31	1.06	0.85	0.56	0.37	0.24
t (s)	0	50	100	150	200	300	400	500

(a) Determine the order of decay and the decay constant. (*Ans.:* $k_d = 4.27 \times 10^{-3}\ s^{-1}$.)

P10-23 (a)



Design equation: $r = \frac{F_{A0}X}{W}$

Assume W = 1g $\therefore$ $r = F_{A0}X$

$$\underset{F_{A0}(1-X)}{\underset{(A)}{\text{Cumene}}} \longrightarrow \underset{F_{A0}X}{\underset{(R)}{\text{Propene}}} + \underset{F_{A0}X}{\underset{(S)}{\text{Benzene}}}$$

The amount of cumene hydroperoxide does not contribute significantly to the total number of moles.

$$y_S = \frac{F_{A0}X}{F_{A0}(1-X) + F_{A0}X + F_{A0}X} = \frac{X}{1+X} \quad \text{or} \quad X = \frac{y_S}{1-y_S}$$

$$\therefore r = F_{A0}\left(\frac{y_S}{1-y_S}\right)$$

$$a = \frac{r}{r_0} = \frac{\left(\frac{y_S}{1-y_S}\right)}{\left(\frac{y_S}{1-y_S}\right)_{t=0}}$$

X	.0204	.0165	.0133	.0107	.00857	.00563	.00371	.00241
a	1	.809	.652	.5245	.420	.276	.182	.118
t	0	50	100	150	200	300	400	500

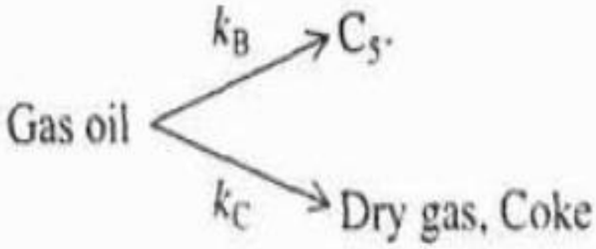
ln a vs. t gives the best fit $a = e^{-\alpha t}$

$\alpha = 4.27 \times 10^{-3}$ (sec^{-1})

Therefore, decay is first order with decay constant of 4.27×10^{-3} (sec^{-1})

Example 10–7 Catalytic Cracking in a Moving-Bed Reactor

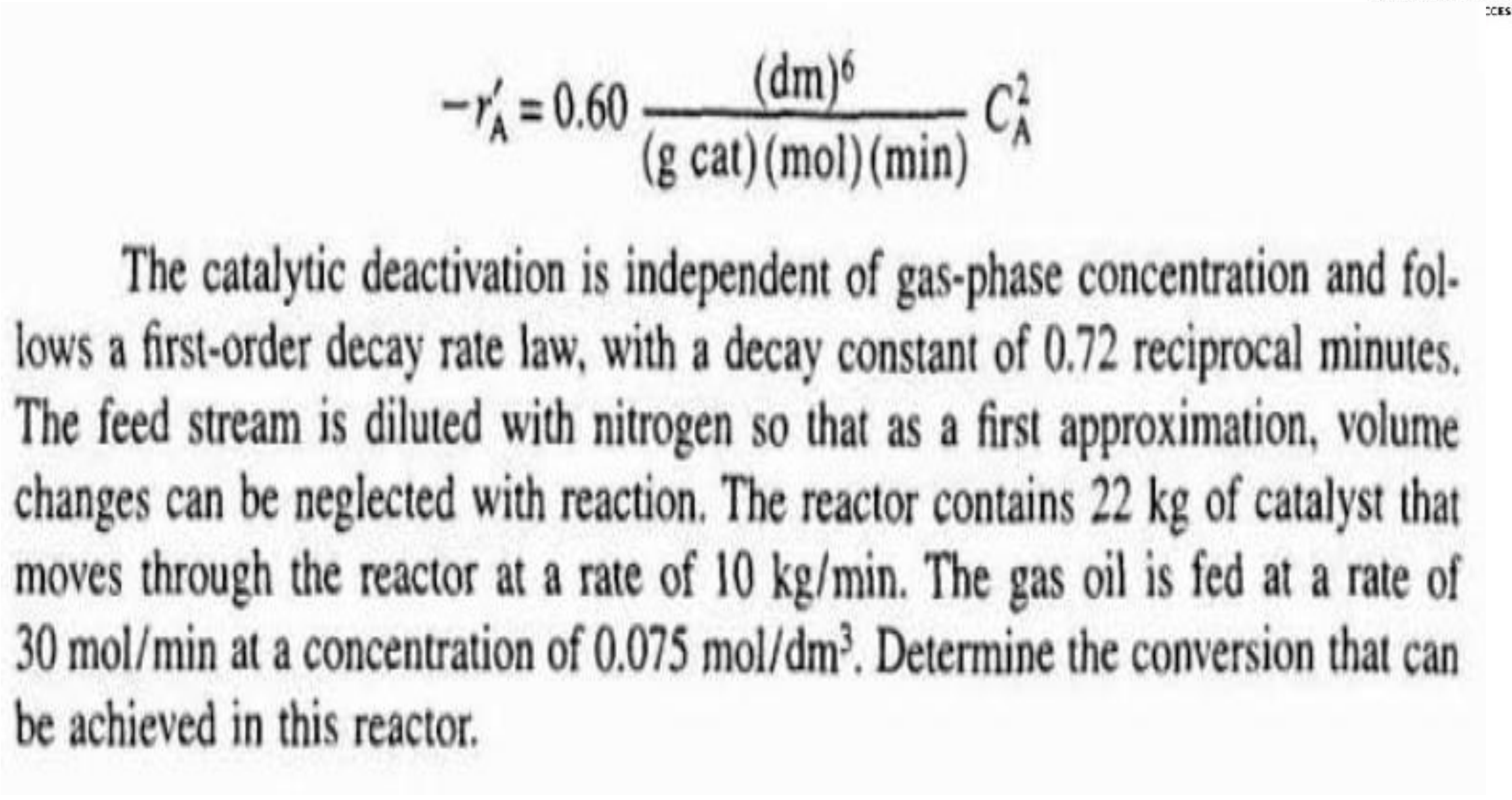
The catalytic cracking of a gas oil charge, A, to form C_5+ (B) and to form coke and dry gas (C) is to be carried out in a screw-type conveyor moving-bed reactor at 900°F:



This reaction can also be written as

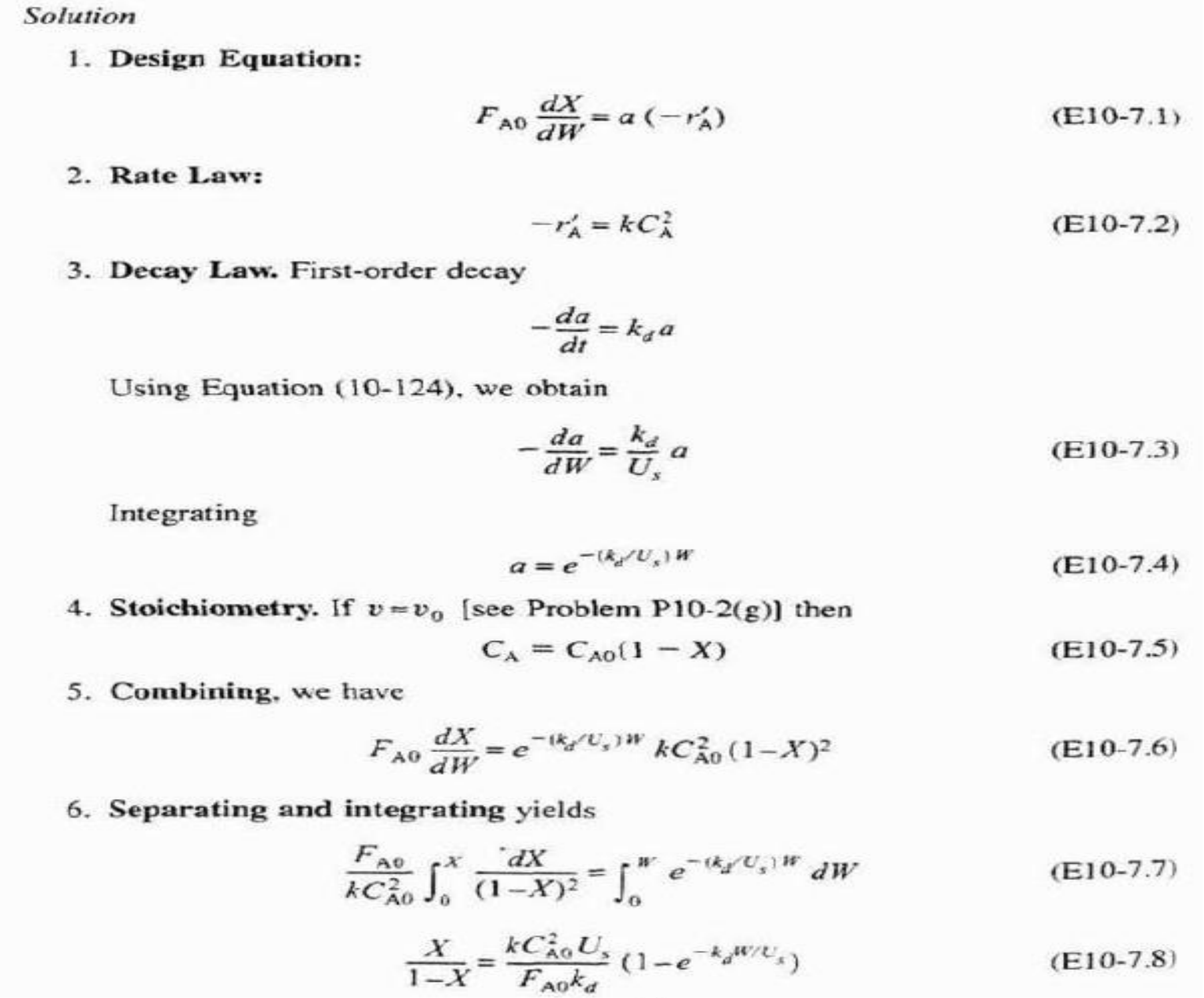
$$A \xrightarrow{k_1} \text{Products}$$

While pure hydrocarbons are known to crack according to a first-order rate law, the fact that the gas oil exhibits a wide spectrum of cracking rates gives rise to the fact that the lumped cracking rate is well represented by a second-order rate law (see Problem CDP5-H_B) with the following specific reaction rate:[32]



$$-r'_A = 0.60 \frac{(\text{dm})^6}{(\text{g cat})(\text{mol})(\text{min})} C_A^2$$

The catalytic deactivation is independent of gas-phase concentration and follows a first-order decay rate law, with a decay constant of 0.72 reciprocal minutes. The feed stream is diluted with nitrogen so that as a first approximation, volume changes can be neglected with reaction. The reactor contains 22 kg of catalyst that moves through the reactor at a rate of 10 kg/min. The gas oil is fed at a rate of 30 mol/min at a concentration of 0.075 mol/dm^3. Determine the conversion that can be achieved in this reactor.



Solution

1. **Design Equation:**

$$F_{A0}\frac{dX}{dW}=a\,(-r'_A) \qquad \text{(E10-7.1)}$$

2. **Rate Law:**

$$-r'_A=kC_A^2 \qquad \text{(E10-7.2)}$$

3. **Decay Law.** First-order decay

$$-\frac{da}{dt}=k_d\,a$$

Using Equation (10-124), we obtain

$$-\frac{da}{dW}=\frac{k_d}{U_s}\,a \qquad \text{(E10-7.3)}$$

Integrating

$$a=e^{-(k_d/U_s)W} \qquad \text{(E10-7.4)}$$

4. **Stoichiometry.** If $v=v_0$ [see Problem P10-2(g)] then

$$C_A=C_{A0}(1-X) \qquad \text{(E10-7.5)}$$

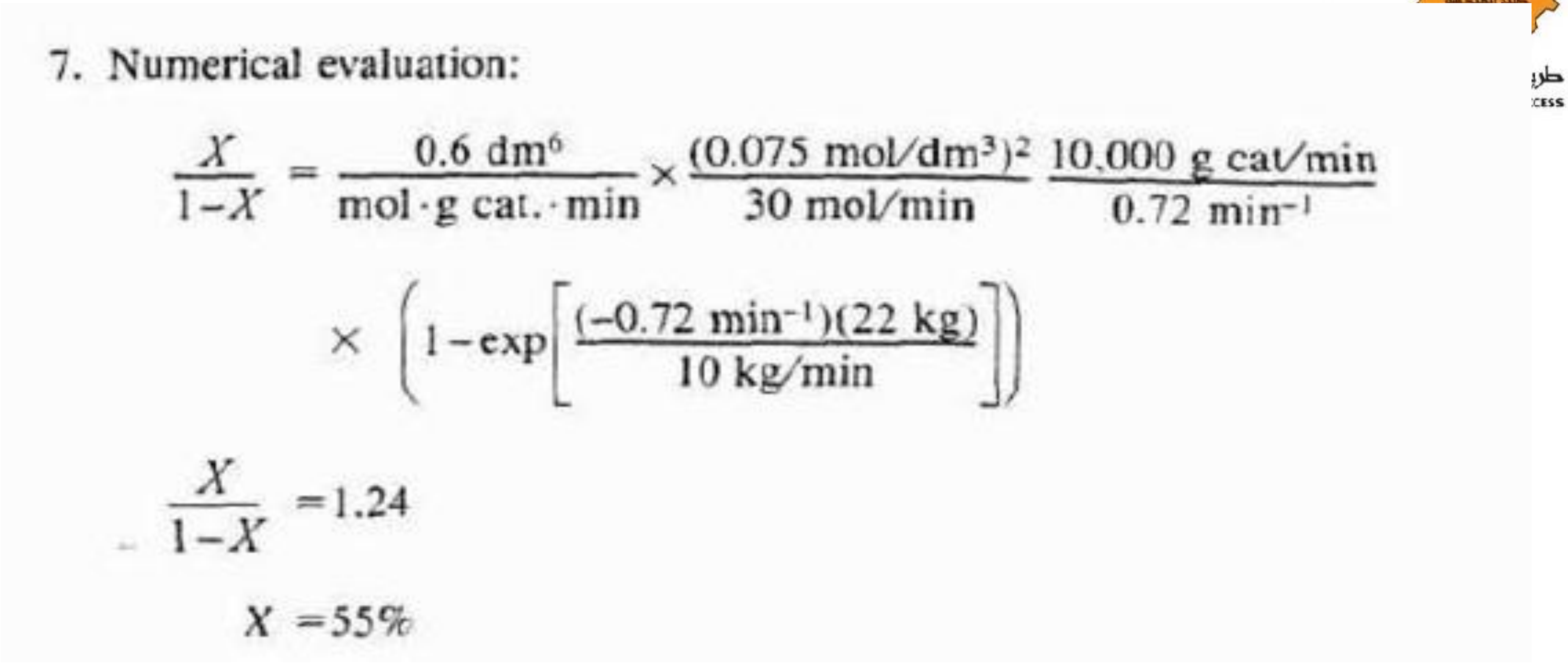
5. **Combining**, we have

$$F_{A0}\frac{dX}{dW}=e^{-(k_d/U_s)W}\,kC_{A0}^2(1-X)^2 \qquad \text{(E10-7.6)}$$

6. **Separating and integrating** yields

$$\frac{F_{A0}}{kC_{A0}^2}\int_0^X\frac{dX}{(1-X)^2}=\int_0^W e^{-(k_d/U_s)W}\,dW \qquad \text{(E10-7.7)}$$

$$\frac{X}{1-X}=\frac{kC_{A0}^2U_s}{F_{A0}k_d}\left(1-e^{-k_dW/U_s}\right) \qquad \text{(E10-7.8)}$$



7. Numerical evaluation:

$$\frac{X}{1-X} = \frac{0.6\ \text{dm}^6}{\text{mol}\cdot\text{g cat.}\cdot\text{min}} \times \frac{(0.075\ \text{mol/dm}^3)^2}{30\ \text{mol/min}}\ \frac{10{,}000\ \text{g cat/min}}{0.72\ \text{min}^{-1}}$$

$$\times \left(1-\exp\left[\frac{(-0.72\ \text{min}^{-1})(22\ \text{kg})}{10\ \text{kg/min}}\right]\right)$$

$$\frac{X}{1-X} = 1.24$$

$$X = 55\%$$

What if you were asked to sketch the temperature–time trajectories and to find the catalyst lifetimes for first- and for second-order decay when $E_A = 35$ kcal/mol, $E_d = 10$ kcal/mol, $k_{d0} = 0.01$ day^{-1}, and $T_0 = 400$ K?

$$\boxed{t = \frac{1 - \exp\left[\dfrac{E_A - nE_A + E_d}{R}\left(\dfrac{1}{T} - \dfrac{1}{T_0}\right)\right]}{k_{d0}(1 - n + E_d/E_A)}} \qquad (10\text{-}119)$$

For a first-order decay, Krishnaswamy and Kittrell's expression [Equation (10-119)] for the temperature–time trajectory reduces to

$$t = \frac{E_A}{k_{d0}E_d}\left[1 - e^{(E_d/R)(1/T - 1/T_0)}\right] \qquad (10\text{-}120)$$

For $E_A = 10$ and $E_d = 35$, for first order decay we rearrange Eq 10-120 to:

$$\ln\left(1-\frac{k_{d0}tE_d}{E_A}\right)=\frac{E_d}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)$$

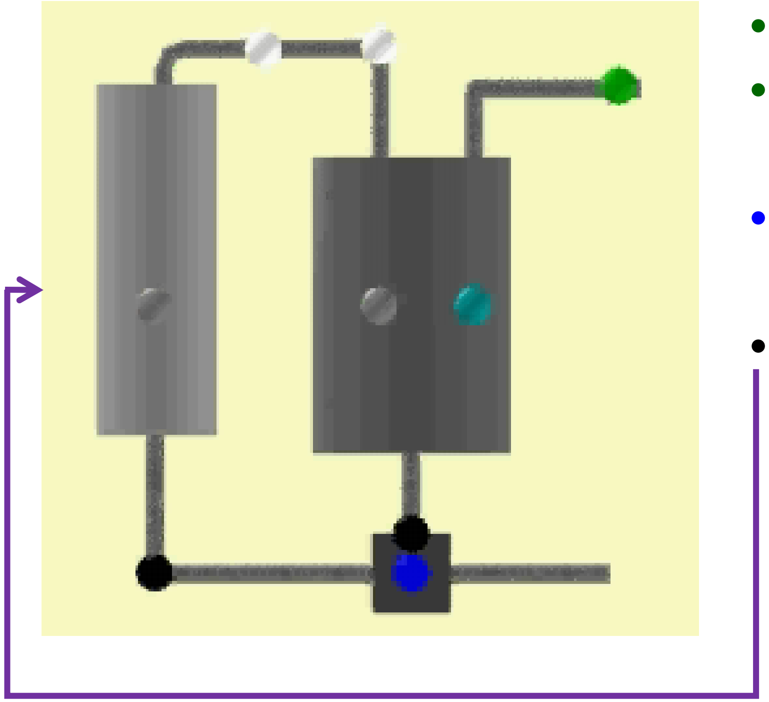
$$\ln\left(\frac{1}{1-\frac{k_{d0}tE_d}{E_A}}\right)=\frac{E_d}{R}\left(\frac{1}{T_0}-\frac{1}{T}\right)$$

$$\frac{R}{E_d}\ln\left(\frac{1}{1-\frac{k_{d0}tE_d}{E_A}}\right)=\frac{1}{T_0}-\frac{1}{T}$$

$$T=\frac{T_0}{1-\frac{T_0R}{E_d}\ln\left(\frac{1}{1-\frac{k_{d0}tE_d}{E_A}}\right)}=\frac{400}{1+0.07948\ln\left(\frac{1}{1-0.00286t}\right)}$$

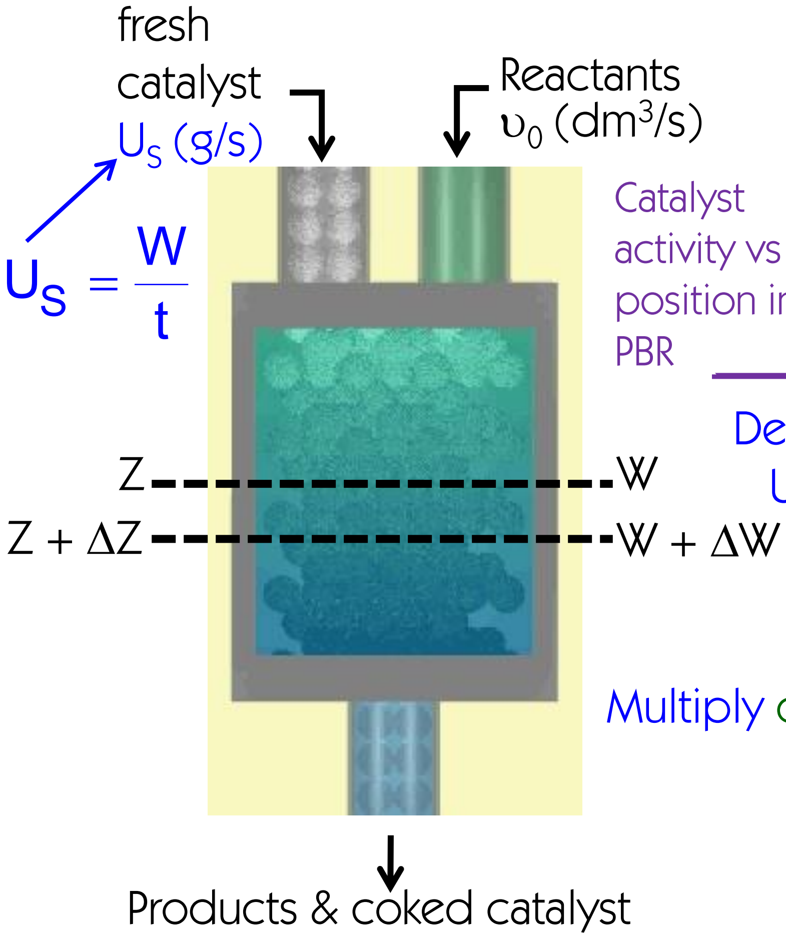
Moving-Bed Reactor

- When catalyst decay occurs at a significant rate, they require frequent regeneration or replacement of the catalyst
- Moving-bed reactor enables continuous regeneration of spent catalyst
- Operates in the steady state, like a PBR



- Reactant & [redacted]ter at top of reactor
- Reactant & c[redacted]w down the length of the reactor together as a plug
- Product and spent catalyst (black) flow out of reactor outlet
- Spent catalyst is regenerated by passing it through a separate regeneration unit, and newly regenerated [redacted]ck into the top of the reactor

Moving-Bed Reactor Design



$$U_S = \frac{W}{t}$$

Catalyst activity vs position in PBR

Catalyst flow U_S << reactant flow υ_0

As far as the reactants are concerned, reactor acts like a PBR: $F_{A0}\frac{dX_A}{dW} = -r'_A$

Assume the decay rate law is: $\frac{-da}{dt} = k_d a^n$

Decay rate must be in terms of W (da/dW) not t (da/dt)

U_S relates W to t→ use U_S to convert da/dt to da/dW

Relate t to U_S: $t = \frac{W}{U_S} \rightarrow dt = \frac{dW}{U_S} \rightarrow \frac{dt}{dW} = \frac{1}{U_S}$

Multiply dt/dW by -da/dt to get –da/dW:

$$\frac{-da}{\cancel{dt}}\left(\frac{\cancel{dt}}{dW}\right) = k_d a^n \left(\frac{1}{U_S}\right) \rightarrow \underbrace{\frac{-da}{dW} = \frac{k_d}{U_S} a^n}$$

Integrate to get a(W)

If the rate of consumption of A for catalyst used for time t: $-r'_A = a(W)k(T)fn(C_j)$

$$\frac{dX_A}{dW} = \frac{-r'_A}{F_{A0}} \rightarrow \frac{dX_A}{dW} = \frac{a(W)k(T)fnC_j}{F_{A0}}$$

$$\rightarrow \int_0^{X_A} \frac{F_{A0}dX_A}{k(T)fnC_j} = \int_0^W a(W)dW$$

A→B Given constant T, pure A in feed, and 1st order ki s for reaction & catalyst deactivation, find $X_A(t)$ in a fluidized batch reactor of constant volume

Rate of rxn: $-r_A = akC_A$ Rate of deactivation: $r_d = \frac{-da}{dt} = k_d a$

Solve the batch reactor design eq for X_A. The batch reactor design eq must be combined with the rate eq. The rate eq contains ‘a’, so we need to use the rate of deactivation to find how ‘a’ varies w/ time. We will determine how ‘a’ varies with time by integrating the rate of deactivation eq & solving for ‘a’:

$$r_d = \frac{-da}{dt} = k_d a \quad \rightarrow \int_{a=1}^{a} \frac{da}{a} = \int_0^t -k_d dt \quad \rightarrow \ln a = -k_d t \quad \rightarrow a = e^{-k_d t}$$

Insert a into the rate eq: $-r_A = kC_A e^{-k_d t} \quad \rightarrow -r_A = kC_{A0}(1-X_A)e^{-k_d t}$

Batch reactor design eq: $N_{A0}\frac{dX_A}{dt} = -r'_A W \rightarrow N_{A0}\frac{dX_A}{dt} = kC_{A0}(1-X_A)e^{-k_d t} W$

Integrate & solve for X_A

$$\rightarrow \int_0^{X_A}\frac{dX_A}{(1-X_A)} = \frac{C_{A0}W}{N_{A0}}\int_0^t k e^{-k_d t} dt \quad \rightarrow \ln(1-X_A) = \frac{C_{A0}W}{N_{A0}}\left[\frac{k}{-k_d}e^{-k_d t}\right]_0^t$$

$$\rightarrow \ln(1-X_A) = \frac{C_{A0}W}{k_d N_{A0}}k\left(1-e^{-k_d t}\right) \quad \rightarrow 1-X_A = e^{\left(\frac{C_{A0}W}{k_d N_{A0}}\right)(k)\left(1-e^{-k_d t}\right)}$$

$$\boxed{\rightarrow X_A = 1-e^{\left(\frac{C_{A0}W}{k_d N_{A0}}\right)(k)\left(1-e^{-k_d t}\right)}}$$

Summary

- Catalyst deactivation significantly affects process efficiency
- Multiple mechanisms contribute to deactivation
- Preventive and mitigation strategies are essential
- Continuous monitoring and innovation improve catalyst longevity