

CHEMICAL REACTOR DESIGN

CHENG 323

Dr Shaker Haji

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Catalysis & Catalytic Reactors

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In this Chapter

□ Basic information about catalysis:

- Definitions
- Properties
- Deactivation
- Classifications
- Steps involved in catalytic reactions

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Catalysts

- Catalysts have been used by humankind for over 2000 years.
- The first observed uses of catalysts were in the making of cheese and bread.
- It was found that it was always necessary to add small amounts of the previous batch to make the current batch.
- However, it wasn't until 1835 that Berzelius suggested that small amounts of a foreign source could greatly affect the course of chemical reactions.

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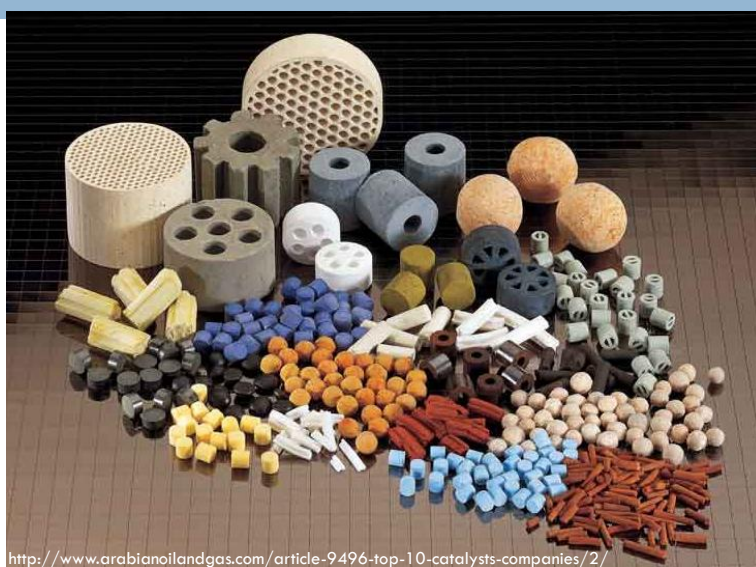
Catalysts

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- This mysterious force attributed to the substance was called catalytic.
- In 1894, Ostwald expanded Berzelius' explanation by stating that catalysts were substances that accelerate the rate of chemical reactions without being consumed.
- In over 150 years since Berzelius' work, catalysts have come to play a major economic role in the world market.
- In the United States alone, sales of process catalysts in 2007 was estimated to be over \$3.5 billion, the major uses being in petroleum refining and in chemical production.

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Catalysts



<http://www.arabianoilandgas.com/article-9496-top-10-catalysts-companies/2/>

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Shapes of Industrial Catalysts


Irregular granule


Sphere


Pellet


Extruded cylindrical


Ring


Minilith


Wagon wheel

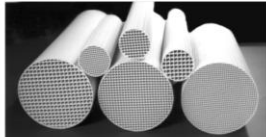

Trilobe


Monolith ceramic


Monolith metallic


Foam

Monoliths



Comparison of Catalyst Shapes

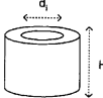
Spheres	Hydrodesulphurisation Methanation Impregnated noble-metal	Low manufacturing costs Relatively high pressure drop Large diffusion length
Granules	Ammonia synthesis Silver cat. For formaldehyde	Not common Low-surface-area catalysts
Pellets	Carbon monoxide shift Hydrogenation	Regular shape; Most common Good mechanical strength
Extrudates	Hydrodesulphurisation	Low pressure drop; Poor strength
Rings	Steam reforming Ethylene oxide production	High strength; Low pressure drop Small diffusion length
Monoliths	Exhaust gas cleaning	Low pressure drop; Insensitive to dust; Small diffusion length
Gauzes	Ammonia oxidation Other high-T processes	Low-surface-area catalysts

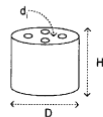
<http://slideplayer.com/slide/5208098/>

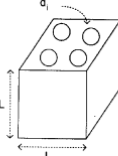
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a) sphere


b) cylinder


c) single channel cylinder


d) multi channel cylinder


e) multi channel cube

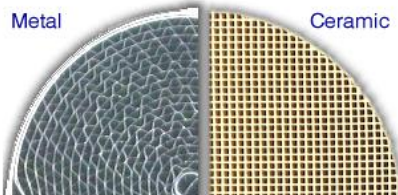
CATALYST SHAPE AS A DESIGN
PARAMETER—OPTIMUM SHAPE FOR
METHANE-STEAM REFORMING CATALYST

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Figure 7. Various shapes of the catalyst pellets.

Metal

Ceramic



https://www.dieselnet.com/tech/cat_substrate.php

Figure 1. Monolithic Catalyst Substrates

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Catalysts



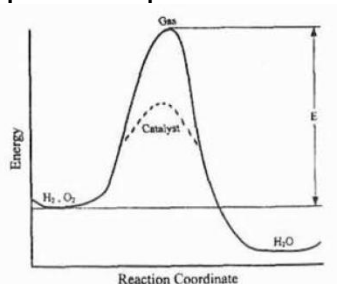
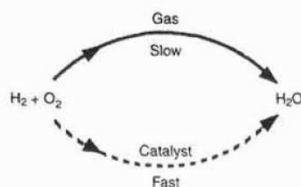
- The photo above shows a variety of different solid catalysts used in industry.
- Those on the front row consist of porous substrate material coated or impregnated with catalyst.
- The two samples on the back row are fine powders with large surface areas.

Courtesy of Prof. David Rockstraw, New Mexico State University.

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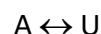
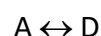
Definitions

- A catalyst is a substance that affects the rate of a reaction but emerges from the process unchanged.
- A catalyst usually changes a reaction rate by promoting a different molecular path (mechanism) for the reaction.
- For example, gaseous H_2 & O_2 are virtually inert at room T , but react rapidly when exposed to platinum.



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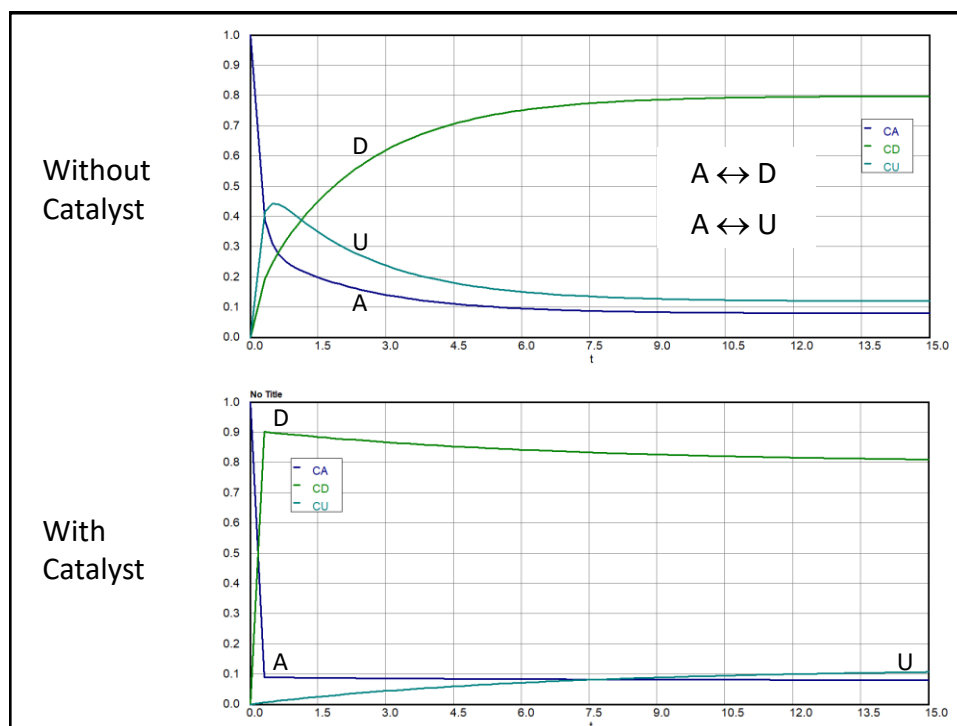
Definitions



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- Normally when we talk about a catalyst, we mean one that speeds up a reaction, although strictly speaking, a catalyst can either accelerate or slow formation of a particular product species.
- Because a catalyst makes it possible to obtain an end product by a different pathway with a lower energy barrier, it can affect both the yield and the selectivity.
- A catalyst changes only the rate of reaction; it does not affect the equilibrium.

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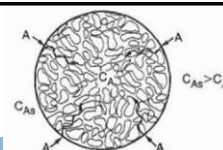
Definitions

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- Homogeneous catalysis concerns processes in which a catalyst is in solution with at least one of the reactants.
- A heterogeneous catalytic process involves more than one phase: usually the catalyst is a solid and the reactants and products are in liquid or gaseous form.
- A heterogeneous catalytic reaction occurs at or very near the fluid-solid interface.

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Properties of Catalysts



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- Because a catalytic reaction occurs at the fluid-solid interface, a large interfacial area is almost always essential in attaining a significant reaction rate.
- In many catalysts, this area is provided by an inner porous structure.
- The area possessed by some porous materials is surprisingly large.
- A typical silica-alumina cracking catalyst has a pore volume of $0.6 \text{ cm}^3/\text{g}$, an average pore radius of 4 nm , and a surface area of $300 \text{ m}^2/\text{g}$.
- A catalyst that has a large area resulting from pores is called a **porous catalyst**.

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Properties of Catalysts

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- Sometimes pores are so small that they will admit small molecules but prevent large ones from entering.
- Materials with this type of pore are called **molecular sieves**.
- These sieves can form the basis for quite selective catalysts.

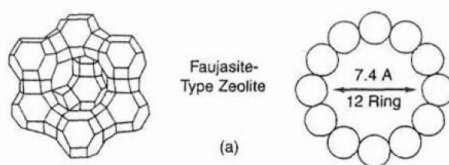


Fig 10-2: Framework structures of two types of zeolites. Faujasite-type zeolite has a 3D channel system with pores at least 7.4 Å in diameter. A pore is formed by 12 oxygen atoms in a ring.

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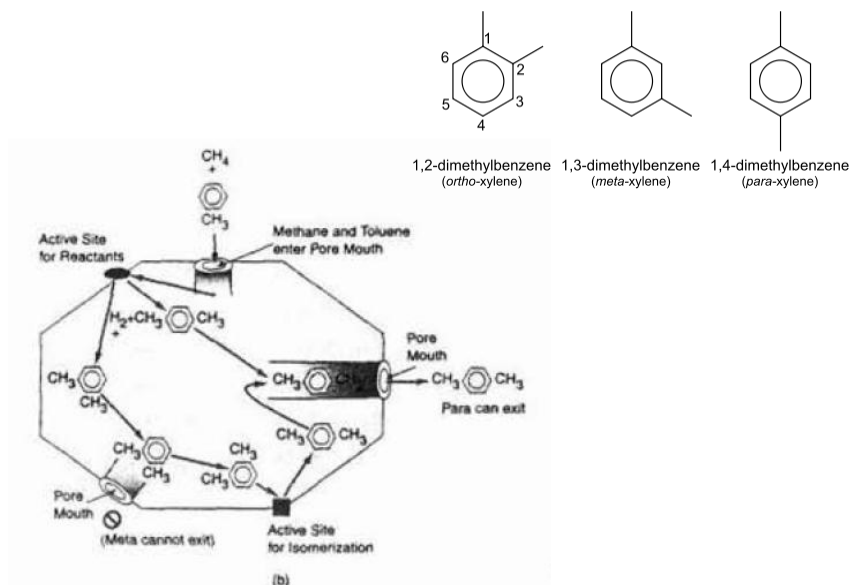


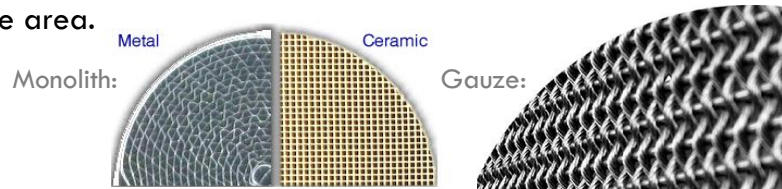
Fig 10-2: reaction of methane with toluene.

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Properties of Catalysts

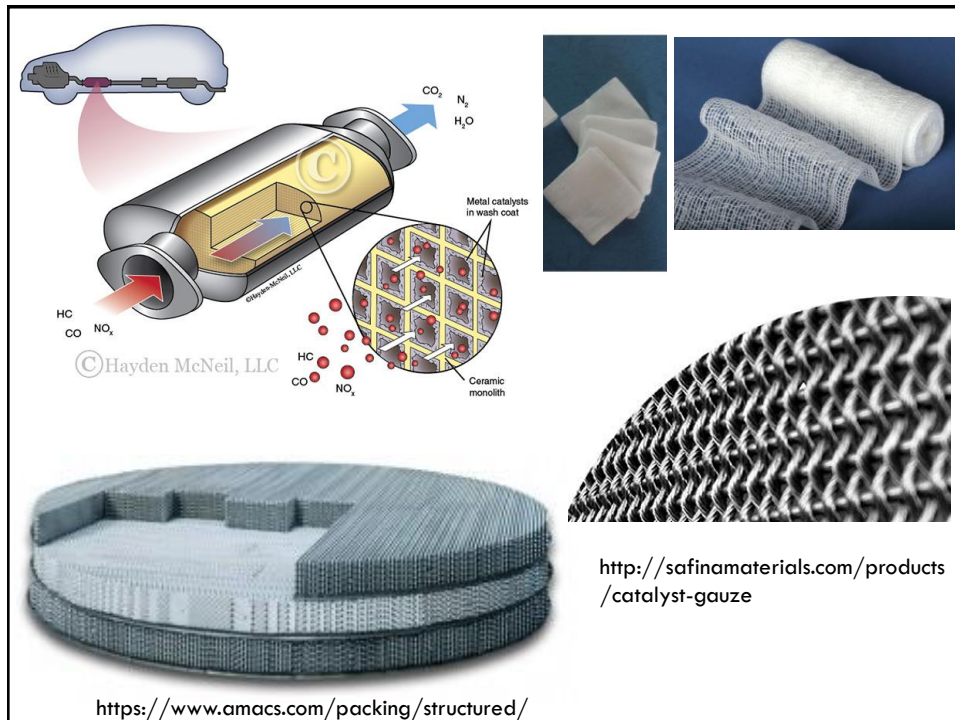
18

- For processes where pressure drop and heat removal are major considerations, the use of beds packed with porous catalysts is sacrificed.
- In such cases monolithic or wire gauze catalysts are used, but need to be very active to compensate for the relatively lower surface area.



- Examples:
 - ▢ Pt gauze reactor used for ammonia oxidation
 - ▢ Pt monolithic catalytic converters used to oxidize pollutants in automobile exhaust gas.

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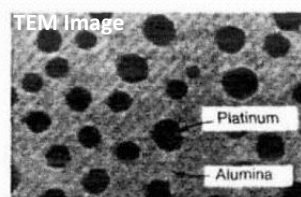


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Supported vs. Unsupported Catalysts

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- In some cases a catalyst consists of minute particles of an **active material** dispersed over a less active substance called a **support**.
- The active material is frequently a pure metal or metal alloy.
- Such catalysts are called **supported catalysts**,



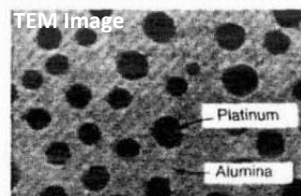
Supported Catalyst: Pt/ Al_2O_3
 Support: Al_2O_3 .
 Active material: Pt.
 (Petroleum Reforming)

20

Supported vs. Unsupported Catalysts

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- In some cases a catalyst consists of minute particles of an **active material** dispersed over a less active substance called a **support**.
- The active material is frequently a pure metal or metal alloy.
- Such catalysts are called **supported catalysts**, and distinguished from **unsupported catalysts**.
- Catalysts can also have small amounts of active ingredients added called **promoters**, which increase their activity.



Supported Catalyst: Pt/ Al_2O_3
 Support: Al_2O_3 .
 Active material: Pt.
 (Petroleum Reforming)



Unsupported Catalyst:
 Iron catalyst (NH_3 synthesis)
 Promoted with: K_2O ,
 MgO , CaO ..etc

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Non-porous metal active sites



Pt nano-particle radius = 10 nm

Surface Area = 628.3 nm²

V = 2094.4 nm³

↓ Do we gain surface area?



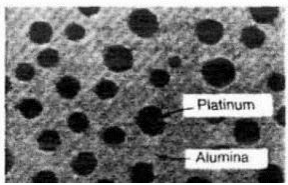
Pt nano-particle radius = 7.94 nm

Surface Area = 791.6 nm²

V = 2094.4 nm³

Yes We Do

Significant increase, 26% increase



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Supported vs. Unsupported Catalysts

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- **Examples of supported catalysts are:**
 - ▣ catalytic converter used in automobiles
 - ▣ platinum-on-alumina catalyst used in petroleum reforming
 - ▣ vanadium pentoxide on silica used to oxidize sulfur dioxide in manufacturing sulfuric acid.
- **Examples of unsupported catalysts are:**
 - ▣ platinum gauze for ammonia oxidation
 - ▣ promoted iron for ammonia synthesis
 - ▣ silica-alumina dehydrogenation catalyst used in butadiene manufacture

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Properties of Catalysts

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- One parameter used to quantify the activity of a catalyst is the **turnover frequency** (TOR, f).
- It is the number of molecules reacting per active site per second at the conditions of the experiment.
- It has a unit of s^{-1}
- When a metal catalyst such as platinum is deposited on a support, the metal atoms are considered active sites.
- The **dispersion** (D) of the catalyst is the fraction of the metal atoms deposited that are on the surface.

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Properties of Catalysts

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- Most catalysts do not maintain their activities at the same levels for indefinite periods.
- They are subject to **deactivation**, which refers to the decline in a catalyst's activity as time progresses.
- Catalyst deactivation may be caused by:
 - ▣ Sintering or aging
 - ▣ Fouling or coking
 - ▣ Poisoning

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Catalyst Deactivation

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1. Sintering or Aging:

- ▣ due to a loss of active surface area resulting from the prolonged exposure to high gas-phase temperatures.
- ▣ The active surface area may be lost either by:
 - crystal agglomeration and growth of the metals deposited on the support, or
 - by narrowing or closing of the pores inside the catalyst pellet.

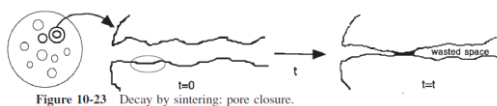


Figure 10-23 Decay by sintering: pore closure.

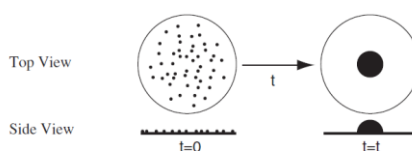


Figure 10-24 Decay by sintering: agglomeration of deposited metal sites.

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Catalyst Deactivation

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2. Fouling or Coking:

- ▣ It results from a carbonaceous (coke) material being deposited on the surface of a catalyst.
- ▣ Hence, this mechanism of decay is common to reactions involving hydrocarbons

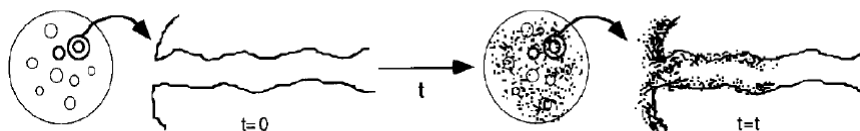


Figure 10-25 Schematic of decay by coking.

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Catalyst Deactivation

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2. Fouling or Coking:



(a) Fresh catalyst



(b) Spent catalyst

Figure 10-26 Decay by coking. (Photos courtesy of Engelhard catalyst, copyright by Michael Gaffney Photographer, Mendham, N.J.)

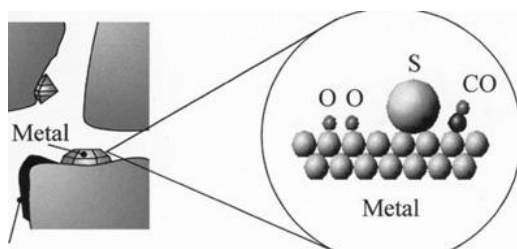
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Catalyst Deactivation

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3. Poisoning:

- ❑ Occurs when the poisoning molecules become irreversibly chemisorbed to active sites.
- ❑ Thereby, reducing the number of sites available for the main reaction.

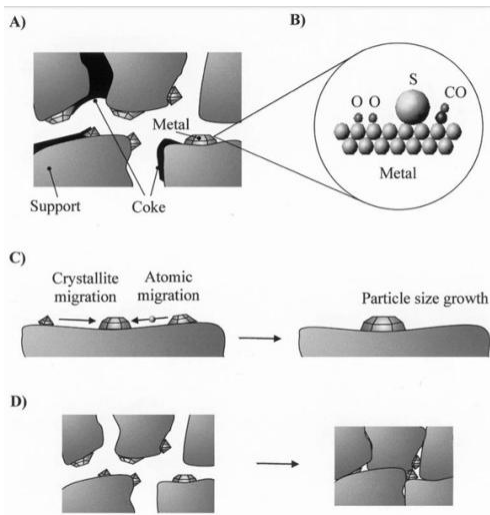


<http://anujasawant.com/tag/chemical/>

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Catalyst Deactivation

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<http://anujasawant.com/tag/chemical/>

Deactivation mechanisms:

- A) Coke formation
- B) Poisoning
- C) Sintering of the active metal particles
- D) Sintering and solid-solid phase transitions of the washcoat and encapsulation of active metal particles

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Commercial Break

فاصل إعلاني

Now you are ready
to read this article:



Applied Catalysis A: General 212 (2001) 3–16



www.elsevier.com/locate/apcata

Catalyst deactivation: is it predictable?
What to do?

J.A. Moulijn, A.E. van Diepen*, F. Kapteijn

*Department of Chemical Process Technology, Section of Industrial Catalysis, Faculty of Applied Sciences,
Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands*

Available on Blackboard.

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Classifications of Catalysts

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No	Reaction	Example	Catalysts
1	Halogenation-Dehalogenation	$\text{CH}_3\text{CH}_2\text{OH} + \text{HCl} \rightarrow \text{CH}_3\text{CH}_2\text{Cl} + \text{H}_2\text{O}$	ZnO, CuCl_2 , AgCl, Pd
2	Hydration-Dehydration	$\text{CH}_2=\text{CH}_2 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CH}_2\text{OH}$	Al_2O_3 , MgO
3	Alkylation-Dealkylation	$\text{C}_6\text{H}_6 + \text{C}_2\text{H}_4 \rightarrow \text{C}_6\text{H}_5\text{C}_2\text{H}_5$	AlCl_3 , Pd, Zeolites
4	Hydrogenation-dehydrogenation (R = alkyl, aryl)	$\text{RCH}=\text{CH}_2 + \text{H}_2 \rightarrow \text{RCH}_2\text{CH}_3$ (R = alkyl, aryl)	Co, Pt, Cr_2O_3 , Ni
5	Oxidation	$\text{CH}_2=\text{CH}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{C}_2\text{H}_4\text{O}$	Cu, Ag, Ni, V_2O_5
6	Isomerization	<i>n</i> -pentane $\rightarrow$ <i>i</i> -pentane	AlCl_3 , Pt/ Al_2O_3 , Zeolites

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Insight into the steps involved in a catalytic reaction:

- Reactants External Diffusion:** Mass transfer (diffusion) of reactants from the bulk fluid to the external surface of the catalyst pellet.
- Reactants Internal Diffusion:** Diffusion of reactants from the pore mouth through the catalyst pores to the immediate vicinity of the internal catalytic surface.
- Reactants Adsorption:** Adsorption of reactant(s) onto the catalyst surface.
- Reaction:** Reaction on the surface of the catalyst (e.g., $\text{A} \rightarrow \text{B}$)
- Products Desorption:** Desorption of the products from the surface.
- Products Internal Diffusion:** Diffusion of the products from the interior of the pellet to the pore mouth at the external surface
- Products External Diffusion:** Mass transfer of the products from the external pellet surface to the bulk fluid.

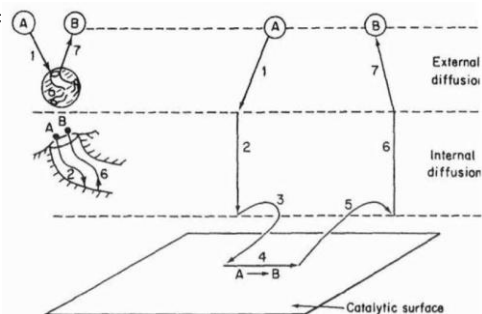


Figure 10-6 Steps in a heterogeneous catalytic reaction.

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Test Yourself

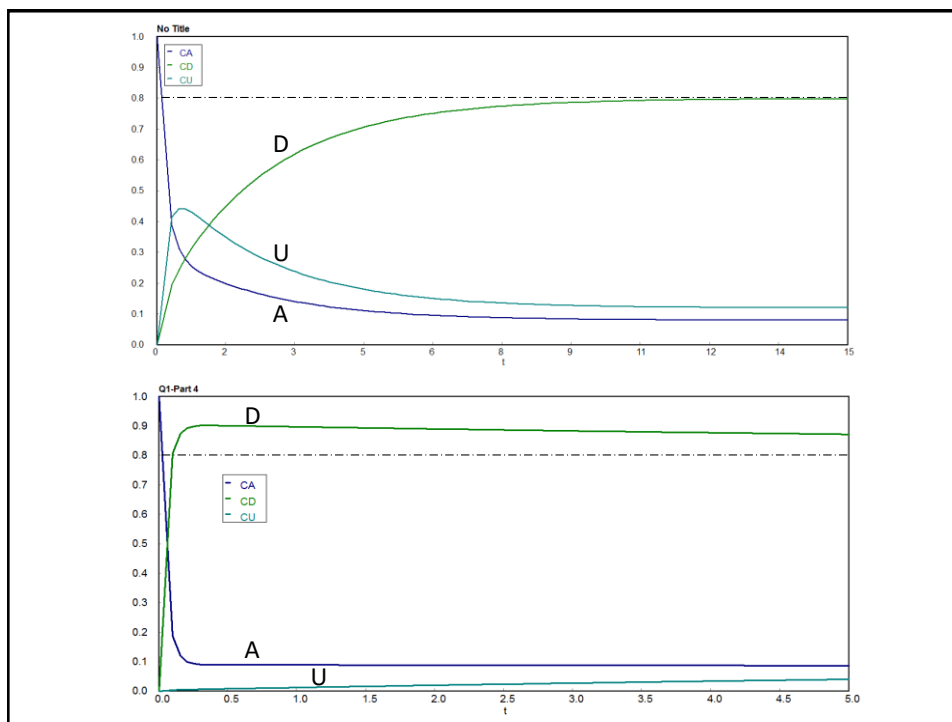
The following liquid-phase reversible reactions



take place in a batch reactor operated isothermally with C_{A0} of 1 mol/L.

- 1) Plot C_A , C_D , and C_U vs. t as well as X vs. t .
- 2) Calculate the overall selectivity, overall yield, and conversion when maximum concentration of the desired product (D) is achieved.
- 3) What are the equilibrium concentrations of A, D, and U?
- 4) When is the maximum concentration of U achieved? (i.e. find t)
- 5) At the given conditions, can a catalyst be used to increase the maximum achievable concentration of D? Explain your answer.

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