— University of Mosul —

College of Petroleum & Mining Engineering

Industrial Chemistry

Lecture …(4)….

Petroleum and Refining Engineering Department

Catalyst Performance

Factors Which Affect the Catalyst Performance

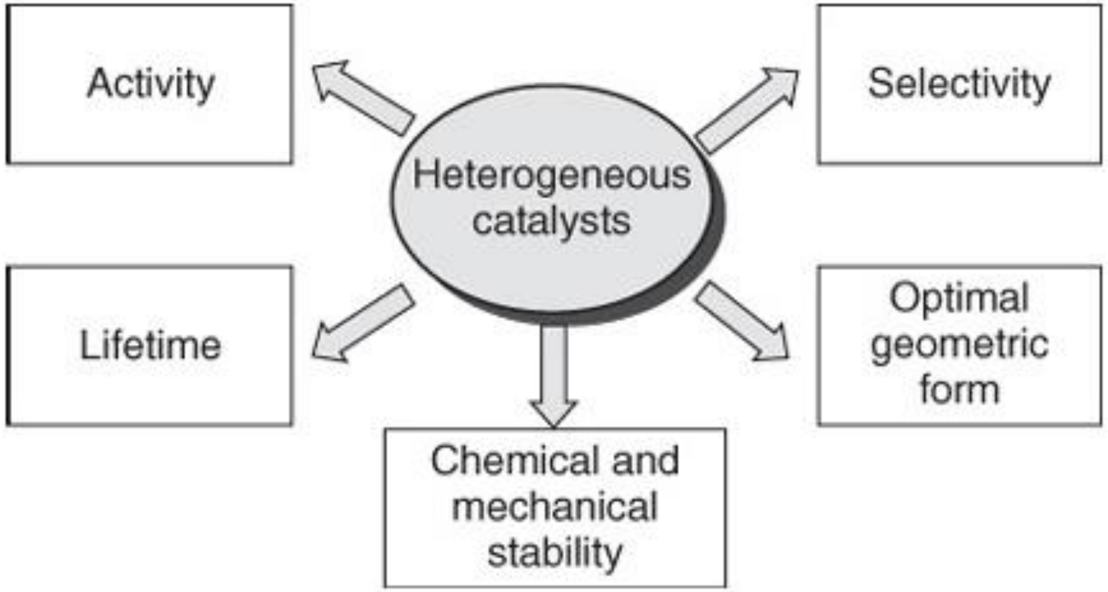


Figure 5.28 Important properties of an industrial catalyst.

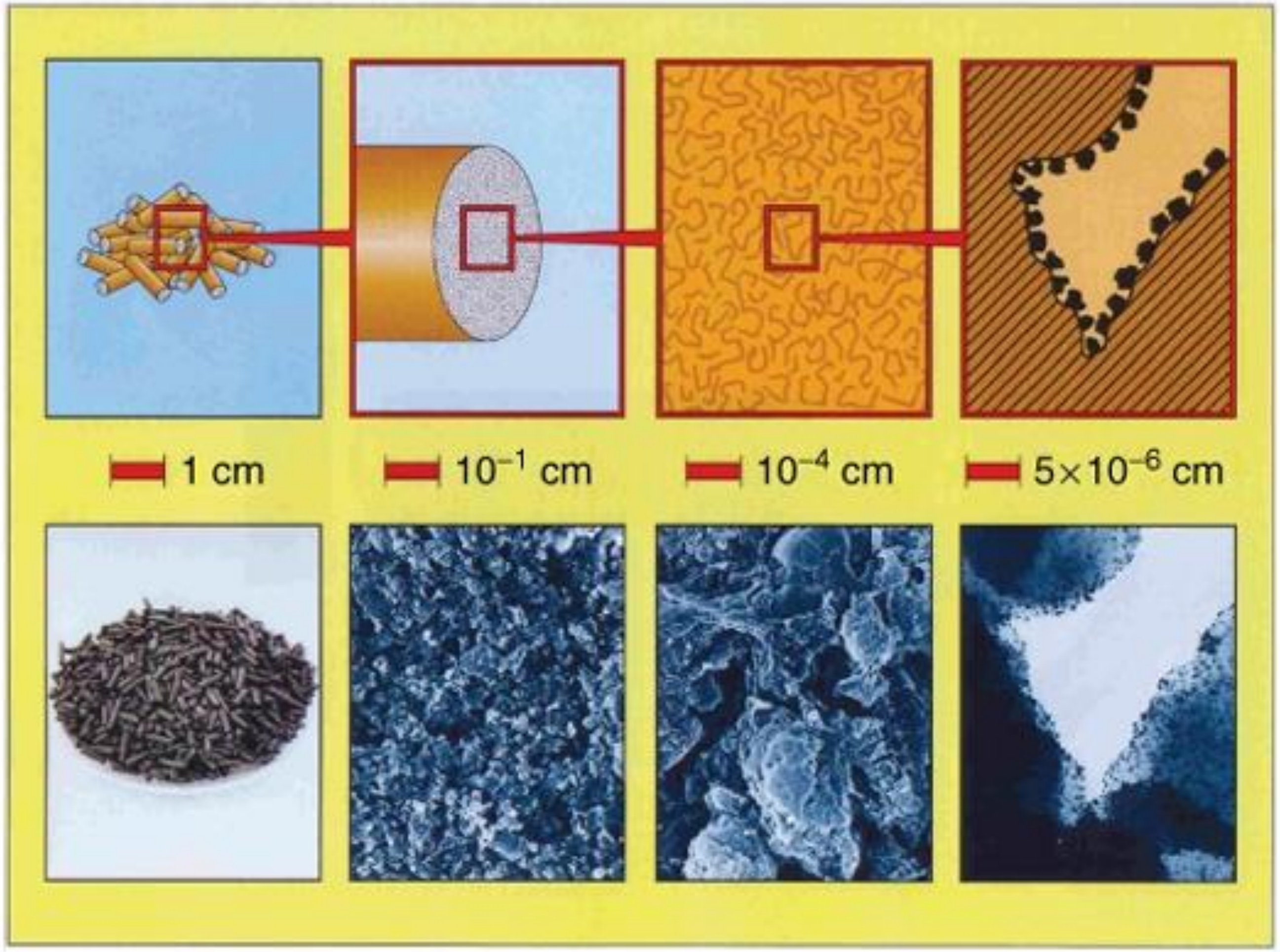
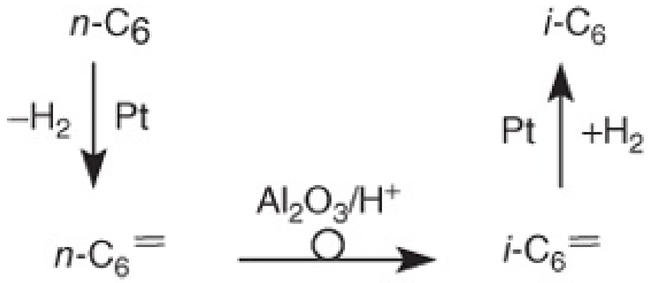


Figure 5.29 Structure of supported catalysts (Fonds der Chemischen Industrie, Frankfurt am Main, Germany, Folienserie Katalyse Nr. 19).

Table 5.29 Influence of support materials on the hydrogenation of CO with rhodium catalysts

Catalyst	Active catalyst	Chemisorption of CO	Products
Rh/SiO_2	Rh(0)	Dissociative	CH_x
Rh/ZrO_2	Rh(0)	Dissociative/	42% ethanol
Rh/ZrO_2	Rh(I)	Associative	12% methanol 32% CH_4
Rh/ZnO Rh/La_2O_3	Rh(I)	Associative	94% methanol

The next example shows how catalyst bifunctionality can arise from the support material. Platinum metal dehydrogenates napthenes to give aromatic compounds, but it is not able to isomerize or cyclize *n*-alkanes. This function is adopted by the Al_2O_3 support with its acidic properties. The cooperation of the two catalyst components is shown schematically for the reforming of *n*-hexane in Scheme 5.5.



Scheme 5.5 Reforming of *n*-hexane on a Pt/Al_2O_3 supported catalyst.

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)

$$\Delta G = -46 + (300 \times 0.068) = -25.6\ \text{kJ mol}^{-1}$$

The probability of reaction is thus extremely high. The diagram also shows that the idea that the H_2 molecule dissociates and is then chemisorbed on the Ni surface is purely hypothetical, and that in fact physisorption precedes chemisorption. The total process can be described schematically as shown in Figure 5.12.

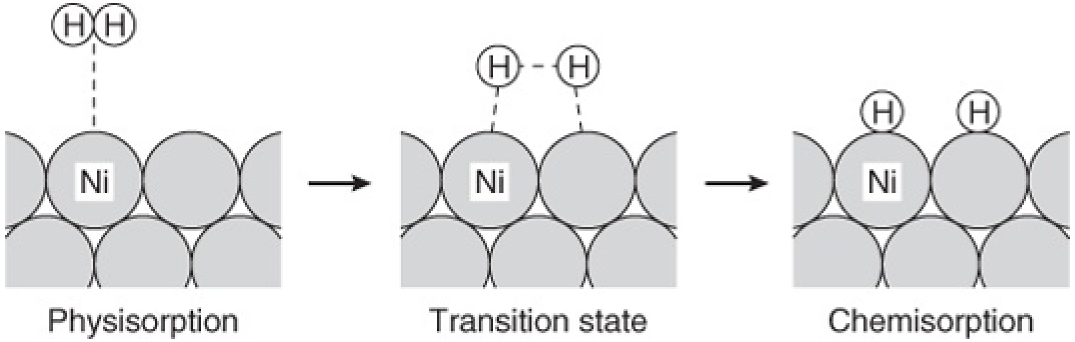
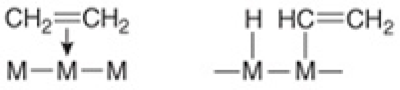


Figure 5.12 Dissociative adsorption of hydrogen on nickel surfaces.

For both types of chemisorption, there are numerous examples that exhibit parallels to organometallic chemistry and therefore homogeneous catalysis.

In the chemisorption of alkenes, other surface complexes can occur, for example, π complexes with a donor–acceptor bond and dissociatively bound complexes:



Metal π complex   Dissociatively chemisorbed ethylene

Dissociative chemisorption occurs preferably with alkenes in which the allylic methyl group is highly activated (e.g., propene). Hydrogen abstraction gives an allyl radical, which can be bound as follows:

Table 5.6 Relative reaction rates on transition metal catalysts

Row	Reaction		Metals and relative reaction rates					
1	Hydrogenation of ethylene (metal catalysts)		Cr		Fe	Co	Ni	Cu
			0.95		15	100	36	1.2
2	Hydrodesulfurization of dibenzo-thiophene (metal sulfide catalysts)	Nb	Mo	Tc	Ru	Rh	Pd	
		0.5	2	13	100	26	3	
3	Hydrogenolysis of CH_3NH_2 to methane (metal catalysts)			Re	Os	Ir	Pt	Au
				0.008	0.9	100	11	0.5

Table 5.30 Examples of promoters in the chemical industry [19]

Catalyst (use)	Promoters	Function
Al_2O_3 (support and catalyst)	SiO_2, ZrO_2, P	Increase thermal stability
	K_2O	Poisons coke formation on active centers
	HCl	Increases acidity
	MgO	Slows sintering of active components
SiO_2/Al_2O_3 (cracking catalyst and matrix)	Pt	Increased CO oxidation
Pt/Al_2O_3 (reforming)	Re	Lowers hydrogenolysis activity and sintering
MoO_3/Al_2O_3 (hydrotreating, HDS, HDN)	Ni, Co	Increased hydrogenolysis of C-S and C-N bonds
	P, B	Increased MoO_3 dispersion
Ni/ceramic support (steam reforming)	K	Improved coke removal
$Cu/ZnO/Al_2O_3$ (low-temperature conversion)	ZnO	Decreased Cu sintering
Fe_3O_4 (NH_3 synthesis)	K_2O	Electron donor, favors N_2 dissociation
	Al_2O_3	Structure promoter
Ag (EO synthesis)	Alkali metals	Increase selectivity, hinder crystal growth, stabilize certain oxidation states

Table 5.31 Causes of deactivation in large-scale industrial processes

Reaction	Reaction conditions	Catalyst	Catalyst lifetime (years)	Deactivation process
Ammonia synthesis $N_2 + 3\ H_2 \rightarrow 2NH_3$	450–550 °C 200–500 bar	$Fe/K_2O/Al_2O_3$	5–10	Slow sintering
Methanization $CO + 3H_2 \rightarrow CH_4 + H_2O$	250–350 °C 30 bar	Ni/Al_2O_3	5–10	Slow poisoning by S and As compounds
Methanol synthesis $CO + 2H_2 \rightarrow CH_3OH$	200–300 °C 50–100 bar	$Cu/Zn/Al_2O_3$	2–8	Slow sintering
Hydrodesulfurization of light petroleum	300–400 °C 35–70 bar	$CoS/MoS_2/Al_2O_3$	0.5–1	Deposits (decomposition of sulfides)
NH_3 oxidation $2NH_3 + 2.5O_2 \rightarrow 2NO + 3\ H_2O$	800–900 °C 1–10 bar	Pt net	0.1–0.5	Loss of platinum, poisoning
Catalytic cracking	500–560 °C 2–3 bar	Zeolites	0.000002	Rapid coking (continuous regeneration)
Benzene oxidation to maleic anhydride $C_6H_6 + O_2 \rightarrow C_4H_2O_3$	350 °C 1 bar	$V_2O_5/MoO_2/Al_2O_3$	1–2	Formation of an inactive vanadium phase

Catalyst deactivation, also known as ***aging***, is expressed by the decrease in catalyst activity with time. Catalyst activity *a* is the ratio of the reaction rate at a given time *t* to the reaction rate at the time that use of the catalyst began ($t = 0$; Eq. (5.76)).

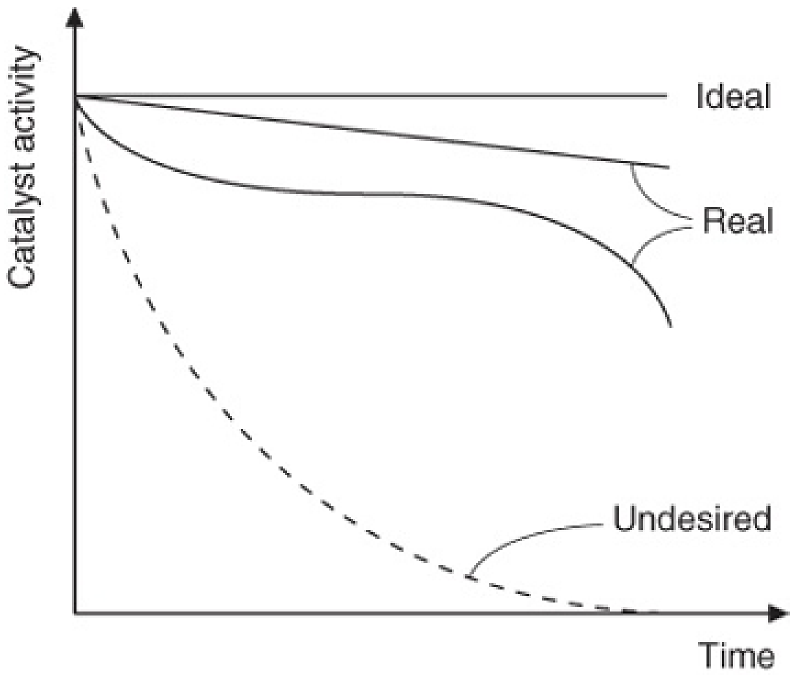


Figure 5.31 Deactivation behavior of catalysts [6].

Not only does the decreasing catalyst activity lead to a loss of productivity, it is also often accompanied by a lowering of the selectivity. Therefore, in industrial processes, great efforts are made to avoid catalyst deactivation or to regenerate deactivated catalyst. Catalyst regeneration can be carried out batchwise or preferably continuously while the process is running.

In this chapter, we will encounter the most important mechanisms of catalyst deactivation and discuss possible methods of catalyst regeneration [8].

The four most common causes of catalyst deactivation are as follows:

- Poisoning of the catalyst. Typical catalyst poisons are H_2S, Pb, Hg, S, and P.