— University of Mosul —

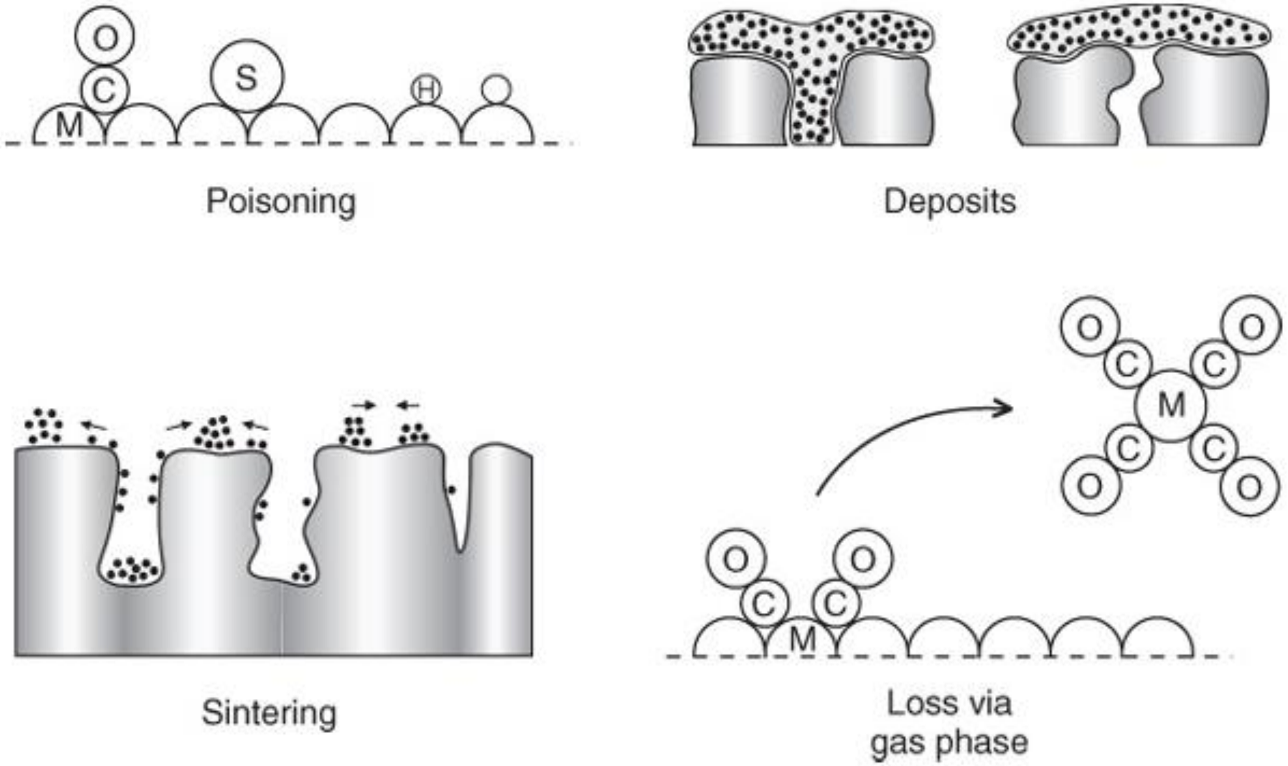
College of Petroleum & Mining Engineering

Industrial Chemistry

Lecture …(5)….

Petroleum and Refining Engineering Department

Catalyst Deactivation



Poisoning

Deposits

Sintering

Loss via gas phase

Figure 5.32 Mechanisms of catalyst deactivation (M = metal) [6].

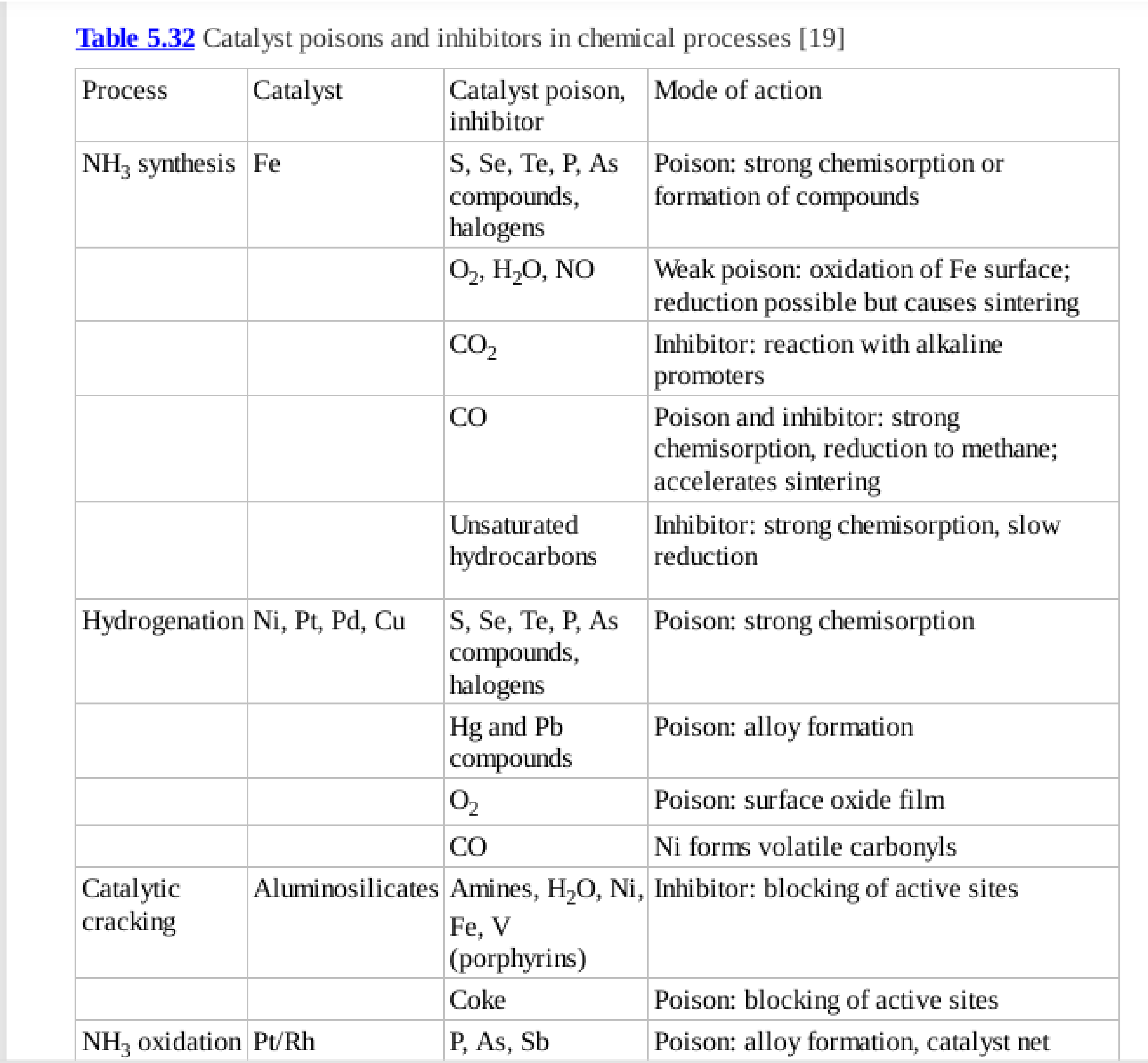


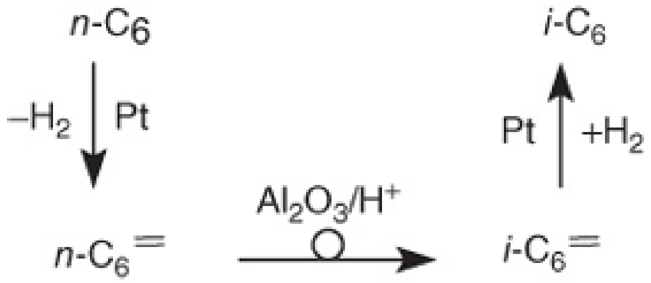
Table 5.32 Catalyst poisons and inhibitors in chemical processes [19]

Process	Catalyst	Catalyst poison, inhibitor	Mode of action
NH_3 synthesis	Fe	S, Se, Te, P, As compounds, halogens	Poison: strong chemisorption or formation of compounds
		O_2, H_2O, NO	Weak poison: oxidation of Fe surface; reduction possible but causes sintering
		CO_2	Inhibitor: reaction with alkaline promoters
		CO	Poison and inhibitor: strong chemisorption, reduction to methane; accelerates sintering
		Unsaturated hydrocarbons	Inhibitor: strong chemisorption, slow reduction
Hydrogenation	Ni, Pt, Pd, Cu	S, Se, Te, P, As compounds, halogens	Poison: strong chemisorption
		Hg and Pb compounds	Poison: alloy formation
		O_2	Poison: surface oxide film
		CO	Ni forms volatile carbonyls
Catalytic cracking	Aluminosilicates	Amines, H_2O, Ni, Fe, V (porphyrins)	Inhibitor: blocking of active sites
		Coke	Poison: blocking of active sites
NH_3 oxidation	Pt/Rh	P, As, Sb	Poison: alloy formation, catalyst net

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.

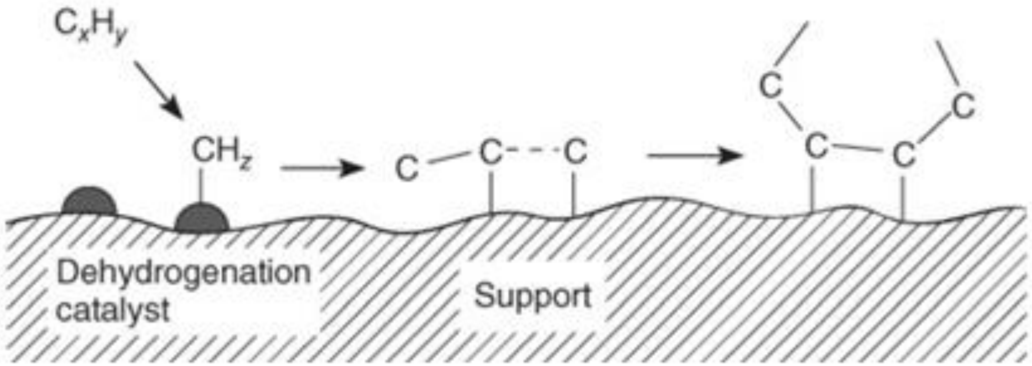


Figure 5.33 Dehydrogenative coking.

Dehydrogenative coking mainly occurs in catalytic reforming, HDS, and in cases of metal contamination of the starting materials. In catalytic reforming processes, bimetallic catalysts are successfully used. Addition of Re to Pt greatly increases the stability of the catalyst, as depicted schematically in Figure 5.34.

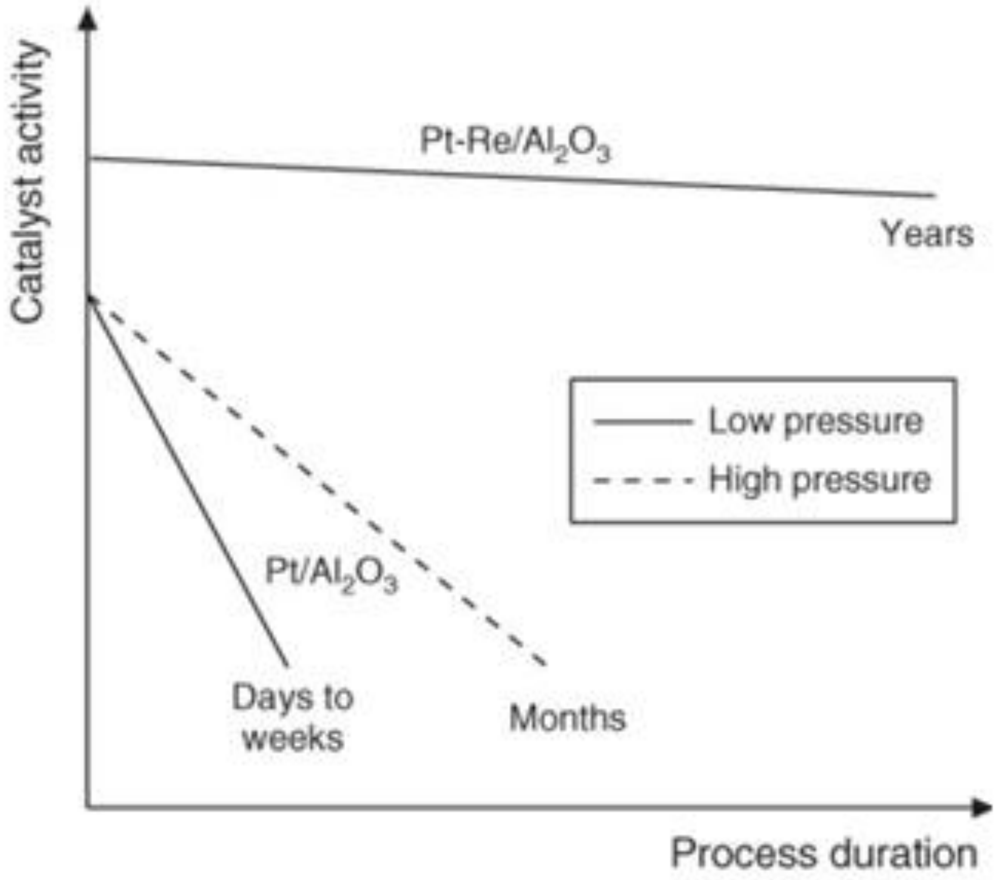


Figure 5.34 Catalyst deactivation in reforming processes [8].

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

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.

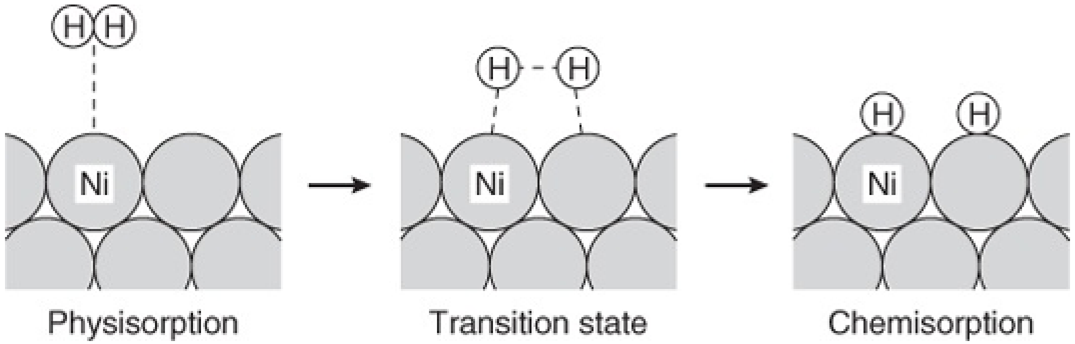
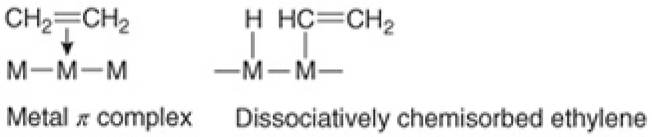


Figure 5.12 Dissociative adsorption of hydrogen on nickel surfaces.

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:



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:

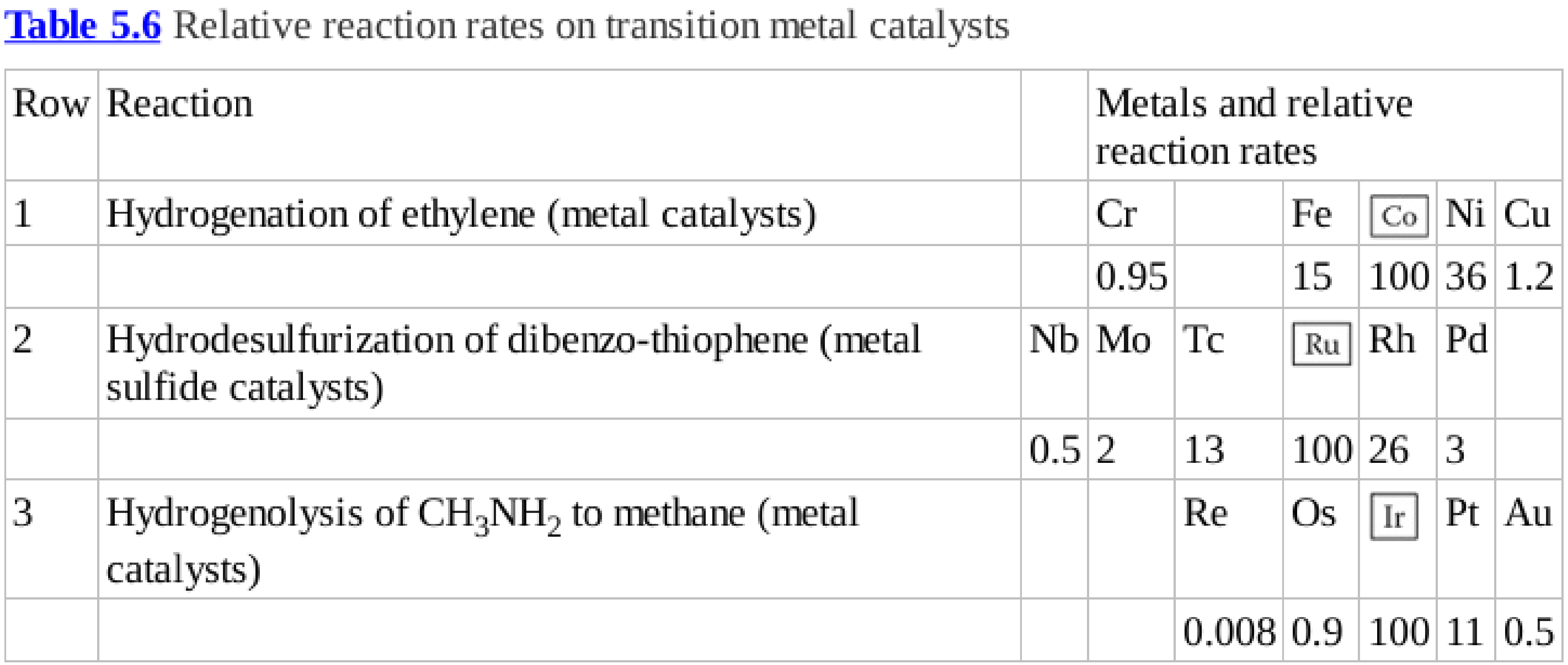


Table 5.6 Relative reaction rates on transition metal catalysts

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

Regenerationand Recycling of Heterogeneous Catalysts

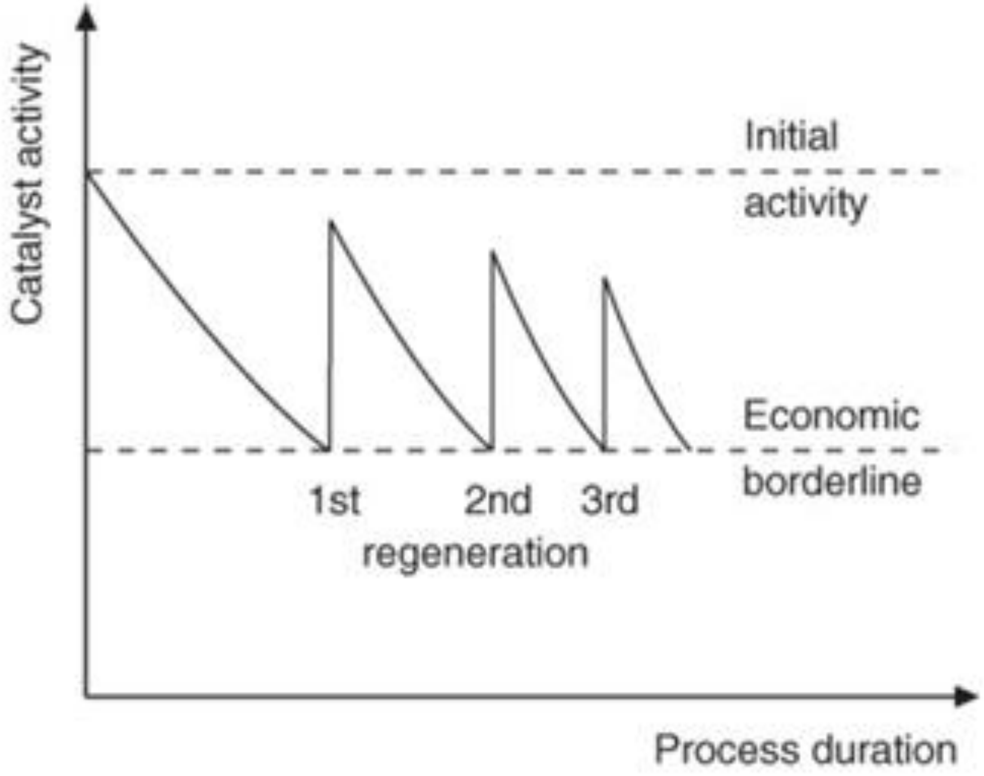


Figure 5.35 Catalyst regeneration and loss of activity during a process.