Temperature-Programmed Reaction Methods

Temperature-programmed methods are techniques in which a chemical reaction is monitored while the temperature is increased linearly in time. There are used several methods: temperature-programmed reduction (TPR), oxidation (TPO), and sulfidation (TPS).

- Different chemical species react at different temperatures, displaying distinct maxima in the TP profile. The more reactive species react at lower temperatures, and vice versa.
- Although these techniques are older and simpler than the latest spectroscopic methods, they can give important information on the type of bonds and functional groups on the surface.

The equipment for these investigations is relatively simple. The catalyst is placed in a tubular reactor and with TPR the O-releasing catalyst is reduced in a flow of inert gas, usually Ar or N_2 containing a few % of H_2. The off-gases are continuously monitored by a mass spectrometer and the consumption of hydrogen is recorded as a function of the reaction temperature. The reactor is controlled by a processor, which heats the reactor at a linear rate of 0.1 to 20 °C/min. The process is shown schematically in Figure. The complete reduction of a catalyst can be determined by TPR method. Integration of the H_2 consumption signal allows the determination of the total amount of hydrogen used to titrate the reactive oxygen in the catalyst and is expressed in moles of H_2 per mol of metal atoms.

Catalysts for hydrotreatment reactions such as hydrodesulfurization (HDS), based on alumina-supported Mo or W (promoters Co or Ni) are active in the sulfide state. Thus, the oxidic catalyst precursors have to be activated by treating with a mixture of H_2S and H_2. This sulfidation process can be studied by TPS.

Temperature-programmed oxidation is an equally valid technique to determine the amount of reduced species in a catalyst material. The experimental setup of TPO equipment is identical to that of a TPR. Therefore, both techniques can easily be combined. The combination of such a TPR/TPD setup with CO temperature-programmed desorption (TPD), moreover, allows the titration of coordinatively unsaturated metal centers on the catalyst surface as a function of the TPR/TPO pretreatment.

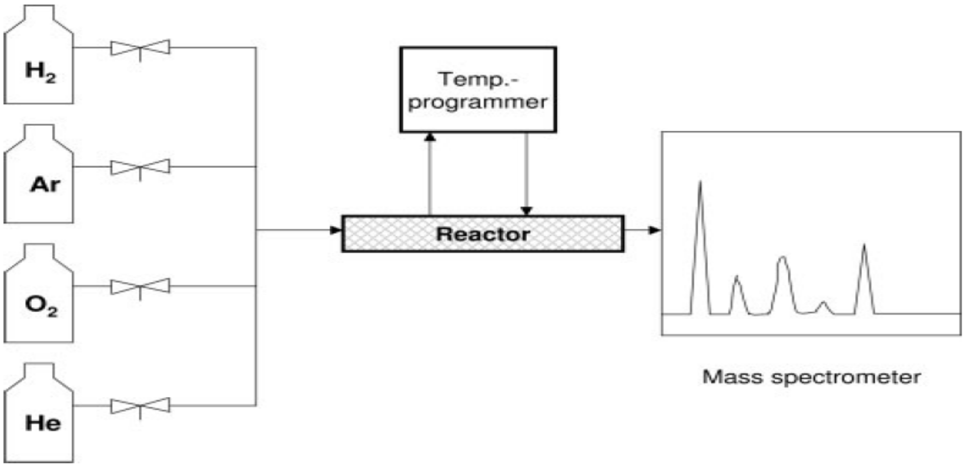


Fig. 5-46 Principle of a device for temperature programmed reduction TPR [45]

Spectroscopy and Microscopy methods:

- This is the fastest-growing area in catalyst characterization. Using a host of methods (and acronyms), samples are bombarded with photons, electrons, and ions, giving chemists large amounts of data on what is happening at the catalyst surface.

- Until recently, many of these methods were restricted to UHV conditions and/or low temperatures, creating a temperature and pressure gap between the study conditions and the real process. However, in situ and operando spectroscopic methods are closing this gap fast, and on-line spectroscopic monitoring of gas/solid catalytic processes is becoming more and more common.

Promoters

Promoters are substances that are themselves not catalytically active but increase the activity of catalysts. The function of these substances, which are added to catalysts in amounts of a few per cent, has not been fully elucidated. There are four types of promoters:

- **Structure promoters** increase the selectivity by influencing the catalyst surface such that the number of possible reactions for the adsorbed molecules decreases and a favored reaction path dominates. They are of major importance since they are directly involved in the solid-state reaction of the catalytically active metal surface.

- **Electronic promoters** become dispersed in the active phase and influence its electronic character and therefore the chemical binding of the adsorbate.
- **Textural promoters** inhibit the growth of catalyst particles to form larger, less active structures during the reaction. Thus they prevent loss of active surface by sintering and increase the thermal stability of the catalyst.
- **Catalyst-poison-resistant promoters** protect the active phase against poisoning by impurities, either present in the starting materials or formed in side reactions.

"A catalyst may contain one active component and one or more promoters."

Inhibitors

An inhibitor is a substance that reduces the rate of a catalytic reaction, often as a result of bonding chemically to the catalyst. Examples are:

- Pt or Pd catalysts on $CaCO_3$, poisoned by Pb (Lindlar's catalyst). They enable selective reduction of triple bonds to double bonds (Eq. 5–82).

$$R-C\equiv CH + H_2 \xrightarrow[100\text{–}150\ ^\circ C]{Pt + Pb/CaCO_3} R-CH=CH_2 \qquad (5\text{-}82)$$

- Aprotic solutions (which act by forming H bonds with catalyst molecules in competition with other reactant molecules).

Catalyst Deactivation and Regeneration

- Catalysts have only a limited lifetime. Some lose their activity after a few minutes, others last for more than ten years. The maintenance of catalyst activity for as long as possible is of major economic importance in industry. A decline in activity during the process can be the result of various physical and chemical factors, for example:
- Blocking of the catalytically active sites
- Loss of catalytically active sites due to chemical, thermal, or mechanical processes.

Catalyst deactivation, also known as ageing, 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. 5-83).

$$a(t) = \frac{r(t)}{r(t=0)}$$

The course of the activity of an industrial catalyst with time can be described by means of several basic types (Fig. 5-37).

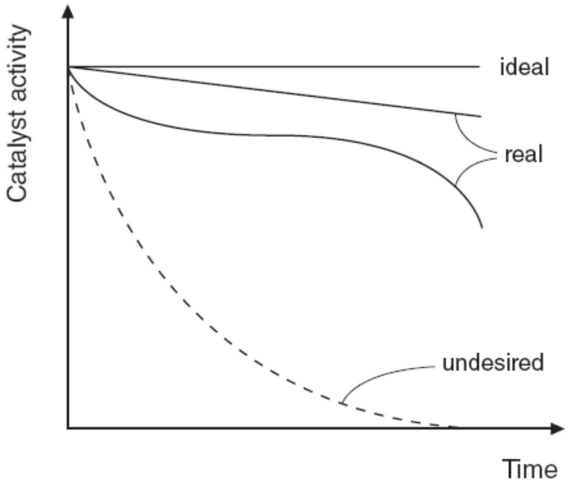


Fig. 5-37 Deactivation behavior of catalysts [8]

An overview of catalyst deactivation in large-scale industrial processes is given in Table 5-41.

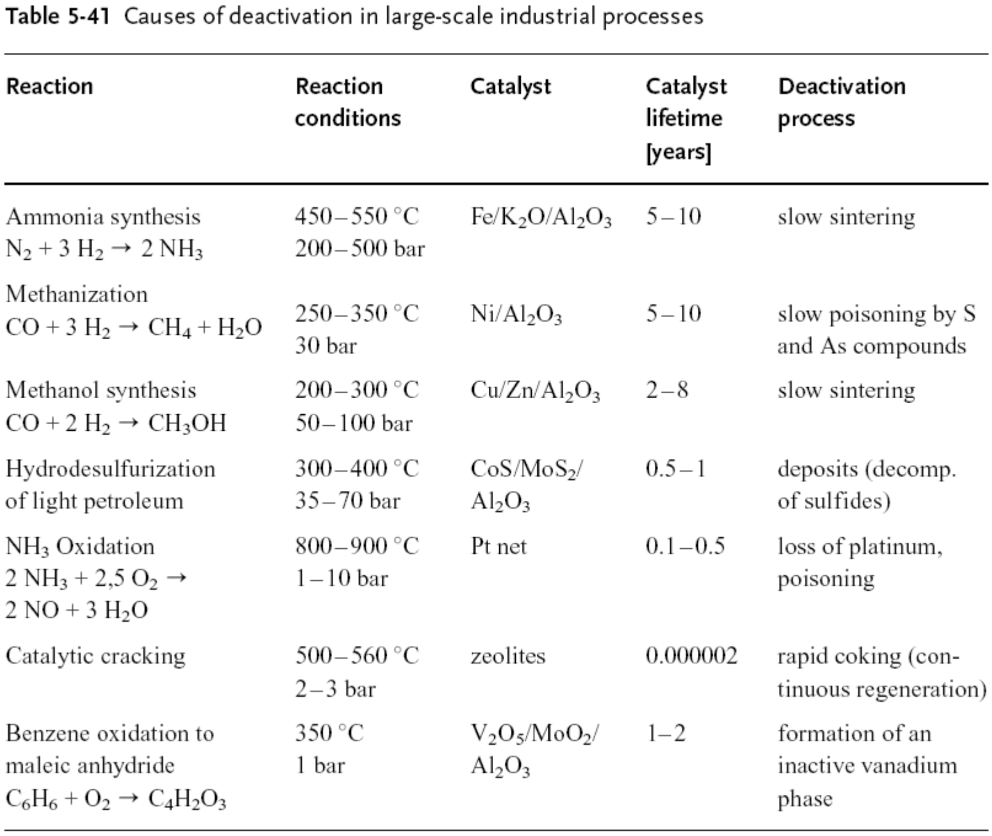


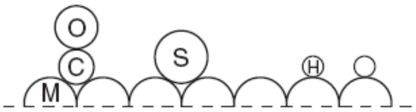
Table 5-41 Causes of deactivation in large-scale industrial processes

Reaction	Reaction conditions	Catalyst	Catalyst lifetime [years]	Deactivation process
Ammonia synthesis $N_2 + 3\ H_2 \rightarrow 2\ NH_3$	450–550 °C 200–500 bar	$Fe/K_2O/Al_2O_3$	5–10	slow sintering
Methanization $CO + 3\ H_2 \rightarrow CH_4 + H_2O$	250–350 °C 30 bar	Ni/Al_2O_3	5–10	slow poisoning by S and As compounds
Methanol synthesis $CO + 2\ H_2 \rightarrow CH_3OH$	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 (decomp. of sulfides)
NH_3 Oxidation $2\ NH_3 + 2{,}5\ O_2 \rightarrow 2\ NO + 3\ H_2O$	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

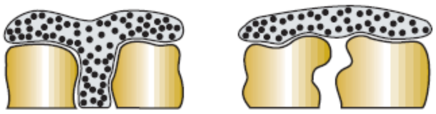
The four most common causes of catalyst deactivation are:

– Poisoning of the catalyst. Typical catalyst poisons are H_2S, Pb, Hg, S, P
– Deposits on the catalyst surface block the active centers and change the pore structure (e. g., coking).
– Thermal processes and sintering of the catalyst lead to a loss of active surface area.
– Catalyst losses by evaporation of components (e. g., formation of volatile metal carbonyls with CO).

These processes are shown schematically in Figure 5-38.



Poisoning



Deposits

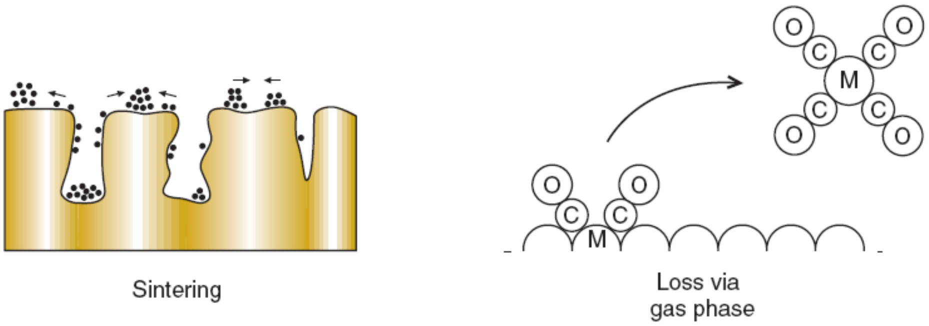


Fig. 5-38 Mechanisms of catalyst deactivation (M = metal) [8]

Catalyst Poisoning

- Catalyst poisoning is a chemical effect. Catalyst poisons form strong adsorptive bonds with the catalyst surface, blocking active centers. Therefore, even very small quantities of catalyst poisons can influence the adsorption of reactants on the catalyst.

- The term catalyst poison is usually applied to foreign materials in the reaction system. Reaction products that diffuse only slowly away from the catalyst surface and thus disturb the course of the reaction are referred as inhibitors.

- Table 5-42 lists some catalyst poisons and inhibitors and the way in which they act.

Poisoning of Metals

- Metal catalysts are highly sensitive to small amounts of certain impurities in the reaction medium. Catalytically active metals make their d orbitals available for adsorption, and this is the key to understanding both their catalytic activity and their sensitivity to poisons.

- Poisons for metals can be classified in three groups:

– **Nonmetallic ions** , the ions of elements of groups 15 (N, P, As, Sb, Bi) and 16 (O, S, Se, Te). The poisoning activity depends on the presence of electron lone pairs, which have been shown to form dative bonds with transition metals on chemisorption.

Poisons: H_2S, thiophene, NH_3, PH_3, AsH_3

Nonpoisons: SO_4^{2-} , NH_4^{+}, PO_4^{3-} , AsO_4^{3-} , sulfones

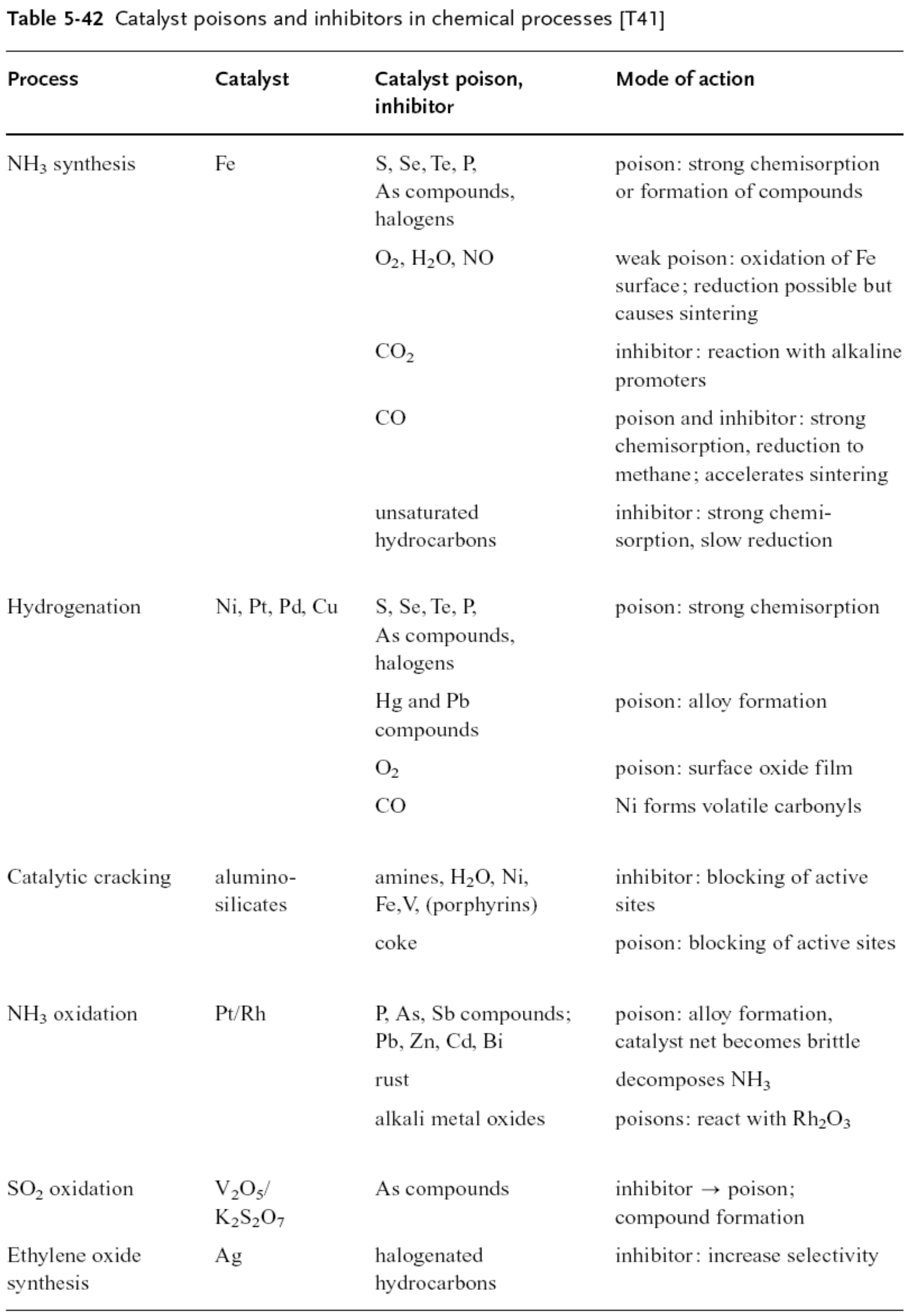
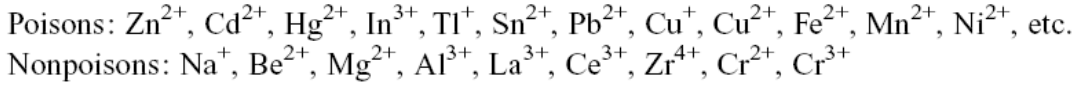


Table 5-42 Catalyst poisons and inhibitors in chemical processes [T41]

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	alumino-silicates	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 compounds; Pb, Zn, Cd, Bi	poison: alloy formation, catalyst net becomes brittle
		rust	decomposes NH_3
		alkali metal oxides	poisons: react with Rh_2O_3
SO_2 oxidation	V_2O_5/ $K_2S_2O_7$	As compounds	inhibitor → poison; compound formation
Ethylene oxide synthesis	Ag	halogenated hydrocarbons	inhibitor: increase selectivity

– **Metal ions ,** The poisoning effect of metal ions depends on the number of d electrons. Metals with an empty d shell, such as alkali and alkaline earth metals, and those with less than three d electrons are nonpoisons,



Poisons: Zn^{2+}, Cd^{2+}, Hg^{2+}, In^{3+}, Tl^{+}, Sn^{2+}, Pb^{2+}, Cu^{+}, Cu^{2+}, Fe^{2+}, Mn^{2+}, Ni^{2+}, etc.
Nonpoisons: Na^{+}, Be^{2+}, Mg^{2+}, Al^{3+}, La^{3+}, Ce^{3+}, Zr^{4+}, Cr^{2+}, Cr^{3+}

– **Unsaturated molecules,** Metals readily adsorb unsaturated molecules such as CO and olefins. If they are adsorbed irreversibly in molecular form, then they act as poisons. If dissociation or decomposition occurs, then this can lead to deactivation by coking.

- Poisoning of metal catalysts can best be avoided by pretreatment of the reactants by:
– Chemical treatment (expensive; can lead to other impurities)
– Catalytic treatment (very effective for organic poisons)
– Use of adsorbers (e. g., ZnO to remove sulfur-containing compounds in natural gas reforming).

Poisoning of Semiconductor Oxides

Because of the presence of electron-donor or electron-acceptor centers with special surface geometries and the fact that redox reactions are favored, general statements about the poisoning of semiconductor catalysts can hardly be made. Any molecule that is strongly adsorbed on the surface is a potential poison.
Up to now there have been no theoretical models of the poisoning of semiconductor catalysts. They are quite resistant to poisoning, the addition of several per cent of foreign materials being required to give a noticeably lower activity.

Poisoning of Solid Acids

- The poisoning of acid centers can easily be explained. Acid centers can be neutralized and thus poisoned by basic compounds such as alkali and alkaline earth compounds and especially organic bases.

- The sensitivity of solid acids towards these poisons correlates directly with their basicity. For example, pyridine, quinoline, amines, and indoles are basic, while pyrrole and carbazole are nonbasic. These poisons are best removed by hydrogenation, together with sulfur and most of the heavy metal poisons.

Deposits on the Catalyst Surface

- The blocking of catalyst pores by polymeric components, especially coke, is another widely encountered cause of catalyst deactivation. In many reactions of hydrocarbons, side reactions lead to formation of polymers. If these are deposited near the pore openings, catalyst activity and selectivity can be influenced due to impaired mass transport into and out of the pores.
-At high temperatures (above 200 ºC) these polymers are dehydrogenated to carbon, a process known as coking. Especially catalysts with acidic or hydrogenating/dehydrogenating properties cause coking.

- The precursors for coke formation are mainly aromatic and olefinic hydrocarbons, which are either contained in the starting materials or are formed as intermediate products in the process.

Thermal Processes and Sintering

- Thermal influences can often affect the catalyst composition. In many cases one or more metastable phases are formed from the active components or the support materials. Phase changes can limit the catalyst activity or lead to catalyst–substrate interactions. We have already dealt with the transformation of γ-Al_2O_3 into α-Al_2O_3 with its lower surface area. Another example is the phase transformation of TiO_2 from anatase to rutile in V_2O_5 / TiO_2 / Al_2O_3 catalysts for the oxidation of *o*-xylene to phthalic anhydride.

The rate of sintering increases with:

- increasing temperature,
- decreasing crystallite size,
- and increasing contact between the crystallite particles.
- Other factors are the amount and type of impurities on the crystallite surface and the support composition in supported catalysts.

- The main effect of sintering is loss of active surface area and the resulting decrease in catalyst activity. However, a change in selectivity can also occur, especially in the case of structure-sensitive reactions.

Catalyst Losses via the Gas Phase

- High reaction temperatures in catalytic processes can lead to loss of active components by evaporation. This does not only occur with compounds that are known to be volatile (e. g., P_2O_5 in H_3PO_4, silica gel, $HgCl_2$/activated carbon), but also by reaction of metals to give volatile oxides, chlorides, or carbonyls. In the oxidation of ammonia on Pt/Rh net catalysts (Ostwald nitric acid process), the catalyst reacts with the gas phase to form volatile PtO_2. Furthermore, porous platinum growths are observed on the surface. This can be prevented by addition of rare earth oxides.

Examples:

- In hydrogenation processes with molybdenum-containing catalysts, too high temperature during regeneration due to the occurrence of hot spots can lead to the formation of MoO_3, which evaporates at temperatures above 800 ºC with irreversible loss of activity.

- the use of nickel catalysts in the methanation of synthesis gas. If the temperature of the catalyst bed drops below 150°C, catalyst is lost by formation of highly toxic nickel tetracarbonyl.

catalyst deactivation:

The catalyst activity varies with time as shown in Figure 5-41. The activity decreases with increasing operating time in a manner that depends on the reaction conditions. First, attempts are made to make the deactivation slower by adjusting the operating parameters (e. g., raising the temperature, increasing the pressure in hydrogenation reactions).

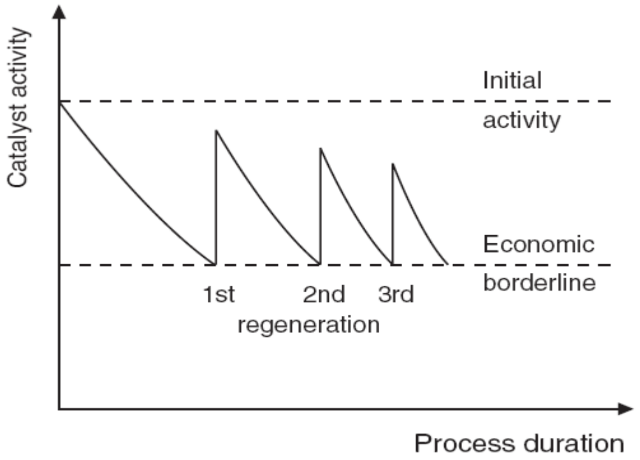


Fig. 5-41 Catalyst regeneration and loss of activity during a process

- The loss of activity can be gradual or very rapid. Examples are the hydrogenative treatment of naphtha, with catalyst lifetimes of several years, and catalytic cracking, in which strong catalyst deactivation occurs after a few minutes.
- In all cases the deactivation reaches an extent at which the conversion or other process parameters are below specification, and the catalyst must be replaced or regenerated.
- In practice, the original activity is not attained due to a permanent secondary deactivation. When regeneration steps are no longer economically viable, the catalyst must be completely replaced.