Catalyst deactivation

Pio Forzatti[*], Luca Lietti

Dipartimento di Chimica Industriale e Ingegneria Chimica "G.Natta", Politecnico di Milano, P.zza Leonardo da Vinci 32, 20133 Milan, Italy

Abstract

The fundamentals of catalyst deactivation are presented in this review. The chemico-physical aspects concerning the various deactivation causes (i.e. poisoning, sintering, coking, solid-state transformation, masking, etc.) have been analyzed and discussed, along with the mathematical description of the deactivation phenomena. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

One of the major problems related to the operation of heterogeneous catalysis is the catalyst loss of activity with time-on-stream, i.e. "deactivation". This process is both of chemical and physical nature and occurs simultaneously with the main reaction. Deactivation is inevitable, but it can be slowed or prevented and some of its consequences can be avoided.

In the following, the causes of catalyst deactivation will be reviewed and the chemico-physical aspects related to the various deactivation processes will be discussed, along with mathematical description of the deactivation phenomena.

1.1. Chemical, physical and kinetic aspects of catalyst deactivation

The knowledge of the chemical and physical aspects of catalyst deactivation is of pivotal impor-tance for the design of deactivation-resistant catalysts, the operation of industrial chemical reactors, and the study of specific reactivating procedures.

Deactivation can occur by a number of different mechanisms, both chemical and physical in nature. These are commonly divided into four classes, namely poisoning, coking or fouling, sintering and phase transformation. Other mechanisms of deactivation include masking and loss of the active elements via volatilization, erosion and attrition. In the following a brief description of the various deactivation mechan-isms will be reported.

1.1.1. Poisoning
Chemical aspects of poisoning. Poisoning is the loss of activity due to the strong chemisorption on the active sites of impurities present in the feed stream. The adsorption of a basic compound onto an acid catalyst (e.g. isomerization catalyst) is an example of poisoning. A poison may act simply by blocking an active site (geometric effect), or may alter the adsorp-tivity of other species essentially by an electronic effect. Poisons can also modify the chemical nature

*Corresponding author. Tel.: +39-02-2399-3238; fax: +39-02-7063-8173
E-mail address: pio.forzatti@polimi.it (P. Forzatti)

of the active sites or result in the formation of new compounds (reconstruction) so that the catalyst performance is definitively altered.

Usually, a distinction is made between poisons and inhibitors [1]. Poisons are usually substances whose interaction with the active sites is very strong and irreversible, whereas inhibitors generally weakly and reversibly adsorb on the catalyst surface.

Poisons can be classified as ''selective'' or ''non-selective''. In the latter case the catalyst surface sites are uniform to the poison, and accordingly the poison chemisorption occurs in a uniform manner. As a result, the net activity of the surface is a linear function of the amount of poison chemisorbed. In the case of ''selective'' poisoning, on the other hand, there is some distribution of the characteristics of the active sites (e.g. the acid strength), and accordingly the strongest active sites will be poisoned first. This may lead to various relationships between catalyst activity and amount of poison chemisorbed.

Poisons can be also classified as ''reversible'' or ''irreversible''. In the first case, the poison is not too strongly adsorbed and accordingly regeneration of the catalyst usually occurs simply by poison removal from the feed. This is the case, for example, of oxygen-containing compounds (e.g. H_2O and CO_x) for the ammonia synthesis catalysts. These species hinder nitrogen adsorption, thus limiting the catalyst activity, but elimination of these compounds from the feed and reduction with hydrogen removes the adsorbed oxygen to leave the iron surface as it was before. However, gross oxidation with oxygen leads to bulk changes which are not readily reversed: in this case the poison-

ing is ''irreversible'', and irreversible damages are produced.

Upon poisoning the overall catalyst activity may be decreased without affecting the selectivity, but often the selectivity is affected, since some of the active sites are deactivated while others are practically unaffected. This is the case of ''multifunctional'' catalysts, which have active sites of different nature that promote, simultaneously, different chemical transformations. The Pt/Al_2O_3 reforming catalysts are typical examples: the metal participates in the hydrogenation–dehydrogenation reactions whereas alumina acts both as support and as acid catalyst for the isomerization and cracking reactions. Hence basic nitrogen compounds adsorb on the alumina acid sites and reduce isomerization and cracking activity, but they have little effect on dehydrogenation activity.

''Selective'' poisons are sometimes used intentionally to adjust the selectivity of a reaction: for example, the new $Pt–Re/Al_2O_3$ reforming catalysts are pretreated in the presence of low concentration of a sulfur compound to limit the very high hydrocracking activity. Apparently, some very active sites that are responsible for hydrocracking are poisoned by S-compounds. This treatment is known as ''tempering'' a catalyst [2].

Table 1 reports a list of the poisons typically encountered in some industrial catalytic processes. In some cases, due to the very strong interaction existing between poisons and the active sites, poisons are effectively accumulated onto the catalytic surface and the number of active sites may be rapidly reduced. Hence, poisons may be effective at very low levels: for instance, the methanation activity of Fe, Ni, Co and Ru

Table 1
Examples of poisons of industrial catalysts

| Process	Catalyst	Poison
Ammonia synthesis	Fe	CO, CO_2, H_2O, C_2H_2, S, Bi, Se, Te, P
Steam reforming	Ni/Al_2O_3	H_2S, As, HCl
Methanol synthesis, low-T CO shift	Cu	H_2S, AsH_3, PH_3, HCl
Catalytic cracking	$SiO_2–Al_2O_3$, zeolites	Organic bases, NH_3, Na, heavy metals
CO hydrogenation	Ni, Co, Fe	H_2S, COS, As, HCl
Oxidation	V_2O_5	As
Automotive catalytic converters (oxidation of CO and HC, NO reduction)	Pt, Pd	Pb, P, Zn
Methanol oxidation to formaldehyde	Ag	Fe, Ni, carbonyls
Ethylene to ethylene oxide	Ag	C_2H_2
Many	Transition metal oxides	Pb, Hg, As, Zn
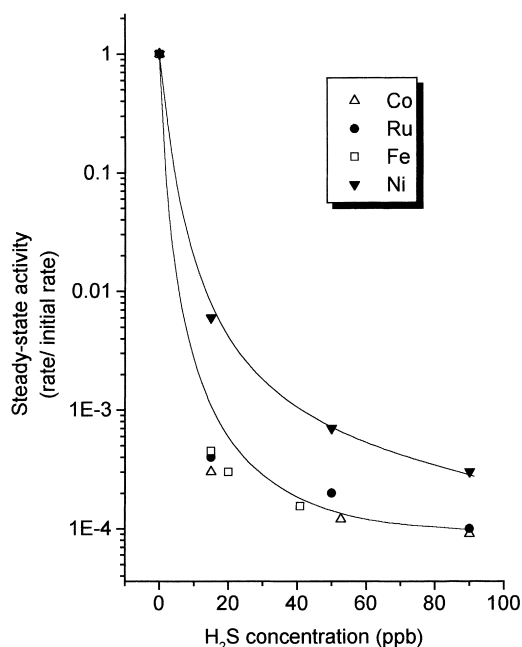
Fig. 1. Effect of H_2S poisoning on the methanation activity of various metals (T=400°C, P=100 kPa, feed: 4% CO, 96% H_2 for Ni; 1% CO, 99% H_2 for others) [3].

catalysts is strongly reduced by H_2S in the range 15–100 ppb [3] (Fig. 1).

It follows that the analysis of poisoned catalysts may be complicated, being the content of poison of a fully deactivated catalyst as low as 0.1% (w/w) or less. Extremely sensitive analysis is then mandatory, and since poisons usually accumulate on the catalyst surface, surface sensitive techniques are particularly useful.

Poisoning of metal-based catalysts. Maxted [4] reported that for metal catalysts of groups VIII B (Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt) and I B (Cu, Ag, Au), typical poisons are molecules containing elements of groups V A (N, P, As, Sb) and VI A (O, S, Se, Te). The surface metal atoms active in the catalytic reactions can be depicted as involved in the chemisorption of the reactants (and of poisons as well) via their ''dangling orbitals''. Accordingly, any chemical species having a ''proper electronic configuration'' (e.g. unoccupied orbitals or unshared electron) or multiple bonds (e.g. CO, olefins, acetylenes, etc.) can be considered as potential poisons. Accordingly several molecules have been classified as having

''shielded'' or ''unshielded'' structures [4,5]: for example As in the form of arsine (AsH_3), having a lone pair, is a strong poison for catalysts such as Pt in hydrogenation reaction, whereas no effect on catalytic activity is observed on the decomposition of H_2O_2, possibly because As under oxidizing conditions is present in the form of arsenate AsO_4^{3-}. Along similar lines the order of increasing poisoning activity for sulfur species, i.e. $H_2S > SO_2 > SO_4^-$, can be explained.

Poisoning of metal oxide-based catalysts. Metal oxide-based catalysts are generally more resistant than metal catalysts to deactivation by poisoning. Acid catalysts (e.g. cracking catalysts) are poisoned by basic materials (alkali metals or basic N-compounds) [6]. Several studies have been reported in the literature concerning the effects of the nature (i.e. Lewis versus Brønsted) and strength of the acid sites and the basic character of the poison on the deactivation of acid catalysts [7–9].

Oxide catalysts other than acid catalysts are also poisoned by several compounds, and often by Pb, Hg, As, Cd. These compounds react with the catalyst active sites usually leading to a permanent transformation of the active sites which thus become inactive.

Preventing poisoning. Poisoned catalyst can hardly be regenerated, and therefore the best method to reduce poisoning is to decrease to acceptable levels the poison content of the feed. This is generally achieved by appropriate treatments of the feed, e.g. catalytic hydrodesulphurization followed by H_2S adsorption or absorption to remove S-compounds, methanation for the elimination of CO_x from the ammonia synthesis feed, adsorption over appropriate beds of solids to remove trace amounts of poisons (e.g. ZnO for H_2S, sulfured activated charcoal for Hg, alkalinized alumina for HCl). In several processes, e.g. low-temperature shift, guard-beds (often constituted by the same catalytic material) are installed before the principal catalyst bed and effectively reduce the poisoning of the catalyst bed. A review of a number of these methods can be found in [10].

Another approach to prevent poisoning is to choose proper catalyst formulations and design. For example, both Cu-based methanol synthesis and low-temperature shift catalysts are strongly poisoned by S-compounds. In these catalysts significant amounts of ZnO are present that effectively trap sulfur leading to the formation of ZnS. The catalyst design (e.g. surface

area, pore size distribution, pellet size) can also modify the poison resistance: these aspects will be briefly discussed in the next section.

Finally, it is noted that the operating conditions also affect the poison sensitivity of several catalysts: for example 5 ppm sulfur in the feed poison a Ni/Al_2O_3 steam reforming catalyst working at $800°C$, less than 0.01 ppm poison a catalyst working at $500°C$, due to the increased strength of S adsorption.

1.1.2. Coking

Chemical aspects of coking. For catalytic reactions involving hydrocarbons (or even carbon oxides) side reactions occur on the catalyst surface leading to the formation of carbonaceous residues (usually referred to as coke or carbon) which tend to physically cover the active surface. Coke deposits may amount to 15% or even 20% (w/w) of the catalyst and accordingly they may deactivate the catalyst either by covering of the active sites, and by pore blocking. Sometimes a distinction is made between coke and carbon. The difference is however somewhat arbitrary: usually carbon is considered the product of CO disproportionation ($2CO \rightarrow C+CO_2$), whereas coke is referred to the material originated by decomposition (cracking) or condensation of hydrocarbons.

Mechanisms of carbon deposition and coke formation on metal catalysts have been detailed in several reviews [11–15]; they differ significantly from those on oxide or sulfide catalysts [16]. For instance, the mechanisms for carbon formation from carbon monoxide over Ni catalysts have been reviewed by Bartholomew [11]. The rate-determining step is presumably the CO dissociation leading to the formation of various carbon forms, including adsorbed atomic carbon (C_α), amorphous carbon (C_β), vermicular carbon (C_ν), bulk Ni carbide (C_γ), and crystalline, graphitic carbon (C_c) [17]. The formation of such species depends on the operating conditions, catalyst formulation, etc. In the case of the steam reforming of hydrocarbons on Ni-based catalysts, three different kinds of carbon or coke species were observed [18], i.e. encapsulated-like hydrocarbons (formed by slow polymerization of C_nH_m on Ni surface at temperatures lower than $500°C$), filamentous or whisker-like carbon (produced by diffusion of C into Ni crystals, detachment of Ni from the support and growth of whiskers with Ni on top), and pyrolitic-type carbon (obtained by cracking

of C_nH_m species at temperatures above $600°C$ and deposition of carbon precursors).

The mechanism of coke formation on oxides and sulfides is rather complex but it can be roughly visualized as a kind of condensation–polymerization on the surface resulting in macromolecules having an empirical formula approaching CH_x, in which x may vary between 0.5 and 1. It has been suggested that the pathway to coke, starting from olefins or aromatics, may involve: (a) dehydrogenation to olefins; (b) olefin polymerization, (c) olefin cyclization to form substituted benzenes, and (d) formation of polynuclear aromatics from benzene [16]. These mechanisms proceed via carbonium ions intermediates and accordingly they are catalyzed by Brønsted acid sites. The details of coke-forming reactions vary with the constituents of the reaction mixture, the operating conditions, and the catalyst used, but one can speculate that the reactive intermediates combine, rearrange and dehydrogenate into coke-type structures via carbonium ions-type reactions, as shown in Fig. 2. Carbonium ions can also crack to form small fragments that can further participate in the coke-forming process as hydrogen transfer agents.

The chemical nature of the carbonaceous deposits depends very much on how they are formed, the conditions of temperature and pressure, the age of the catalyst, the chemical nature of the feed and products formed. Several authors pointed out a direct relationship between the amount of coke deposited and the aromatic and polynuclear aromatic content of the feed [19,20]. Also, it has been reported that coke formation occurs more rapidly when a hydrogen acceptor, such as an olefin, is present [21,22], in line with the hypothesis of a carbonium ion chemistry for coke formation.

Various analytical techniques have been used in order to characterize the nature, amount and distribution of coke deposits. The chemical identity of the carbonaceous deposits has been extensively investigated by IR [23,24]. Other techniques are well suited for this purpose, e.g. UV–Vis, EPR, ^{13}C-NMR. A short review of these methods has been recently reported [25]. The amounts of coke deposited into the catalyst pores may be estimated by burning the coke with air and recording the weight changes via TG-DTA techniques and/or by monitoring the evolution of the combustion products CO_2 and H_2O.
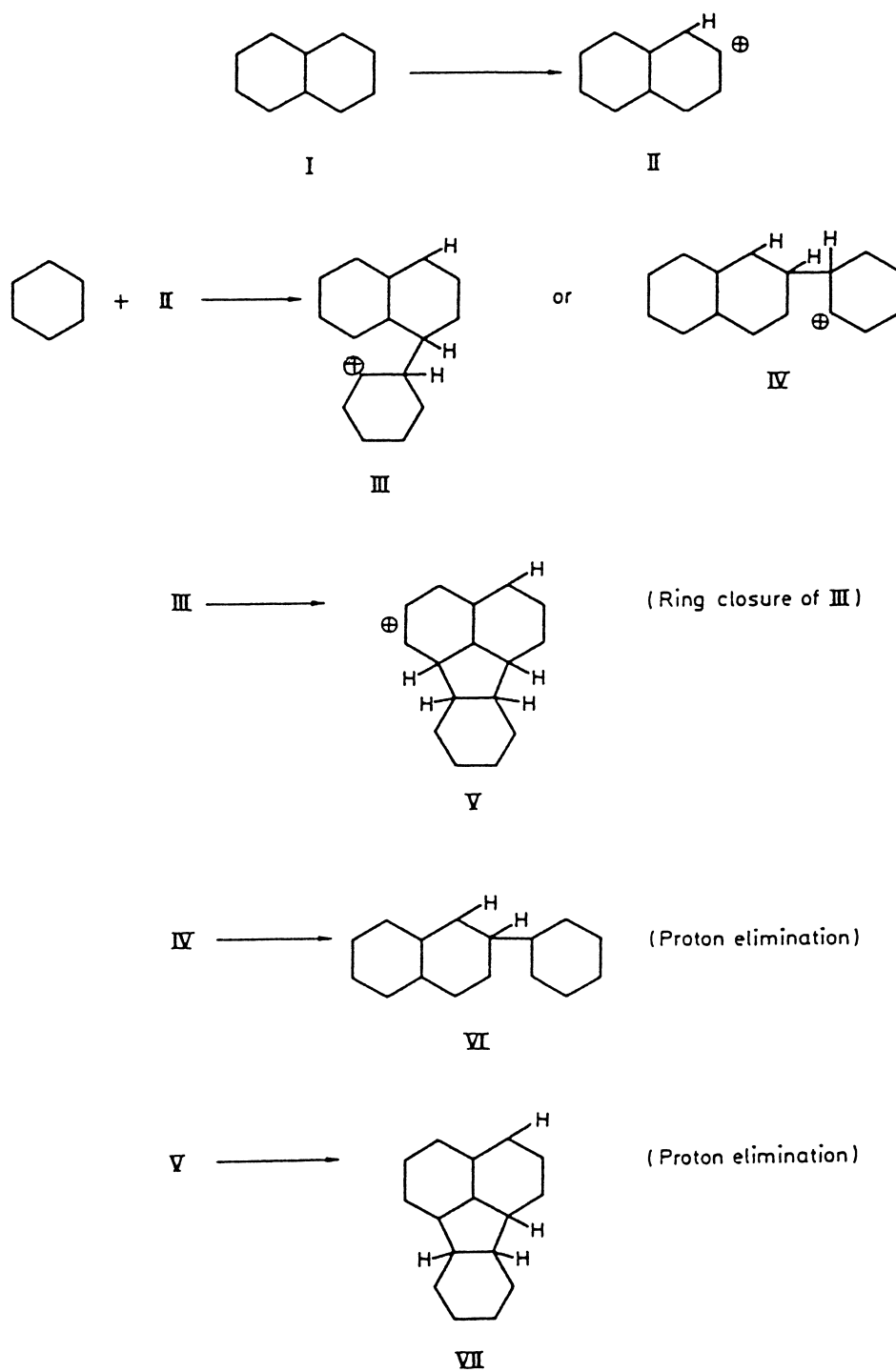
Fig. 2. Carbonium ion mechanism for formation of higher aromatics from benzene and naphtalene [19].

Coke deposits may not be uniformly distributed in the catalyst pellets, and attempts were made to measure the coke concentration profiles by several techniques, including controlled combustion, electron microscopy, ^{1}H- and [129]Xe − NMR, XPS, AES [25,26]. It appears that under certain conditions the coke profile is very non-uniform, with preferential deposition of carbon in the exterior of the particle. The non-uniform coke deposition inside the catalyst pores may be related to the existence of intraparticle diffusional limitation, as reported by Levinter et al. [27]. It is noted that as coke accumulates within the catalyst pores, the effective diameter of the pores decreases, leading to an increase of the resistance to the transport of reactants and products in the pores. If coke is concentrated near the pore mouth it will be more effective as a barrier than the same amount evenly distributed on the pore wall, and eventually pore blockage can occur [26–29].

Preventing coke deposition. In practice, the coke deposition may be controlled to a certain extent by using an optimal catalyst composition and an appropriate combination of process conditions. During the reaction an equilibrium is reached between the rate of coke production and the rate of coke removal by gasifying agents (e.g. H_2, H_2O and O_2 that remove coke as CH_4, CO and CO_x, respectively) so that steady-state conditions, corresponding to a certain level of coke present on the catalyst surface, are eventually reached. Otherwise, if the rate of coke deposition is higher than that of coke removal, a suitable regeneration procedure must be applied. For example, in hydro-desulfurization reactions the catalyst life is roughly proportional to the square of hydrogen partial pressure: hence, in spite of hydrogen cost, process equipment cost (high pressure) and operating costs (compression) still there remains a substantial economic incentive for operating at high H_2 partial pressure. Along similar lines

1. in the catalytic reforming processes high hydrogen partial pressures are usually employed to limit the catalyst deactivation by carbonaceous deposits, and
2. low hydrocarbon/steam ratios are typically employed in steam reforming over Ni catalysts.

In general, in many processes the gas mixture composition is kept as far as possible from conditions under which carbon formation is thermodynamically favored. Obviously this is a necessary but not sufficient requirement in that carbon may form if the carbon forming reactions are inherently faster than the carbon-removal reactions.

The catalyst composition does also affect significantly the coke deposition. Promoters or additives that enhance the rate of gasification of adsorbed carbon or coke precursors and/or depress the carbon-forming reactions minimize the content of carbon on the catalyst surface. For this reason alkali metal ions, e.g. potassium, are incorporated in several catalysts (e.g. Ni-based steam reforming catalysts, Fe_2O_3–Cr_2O_3 dehydrogenating catalysts, etc.). Potassium has several effects: it neutralizes acid sites which would catalyze coke deposition via the carbonium ion mechanism previously mentioned, and catalyzes the gasification of the adsorbed carbon deposits, thus providing an in situ route for catalyst regeneration. Along similar lines, bimetallic Pt–Re/Al_2O_3 reforming catalysts are superior to Pt/Al_2O_3 in view of their greater resistance to deactivation by coking, which allows long activity (up to 1 year) at relatively low H_2 pressures, without regeneration.

1.1.3. Sintering

Sintering usually refers to the loss of active surface via structural modification of the catalyst. This is generally a thermally activated process and is physical in nature.

Sintering occurs both in supported metal catalysts and unsupported catalysts. In the former case, reduction of the active surface area is provoked via agglomeration and coalescence of small metal crystallites into larger ones with lower surface-to-volume ratios. Two different but quite general pictures have been proposed for sintering of supported metal catalysts, i.e. the *atomic migration* and the *crystallite migration* models. In the first case, sintering occurs via escape of metal atoms from a crystallite, transport of these atoms across the surface of the support (or in the gasphase), and subsequent capture of the migrating atoms on collision with another metal crystallite. Since larger crystallites are more stable (the metal–metal bond energies are often greater than the metal–support interaction), small crystallites diminish in size and the larger ones increase. The second model visualizes sintering to occur via migration of the crystallites

along the surface of the support, followed by collision and coalescence of two crystallites.

A number of different rate-limiting steps can potentially be identified in either model, e.g.

1. the dissociation and emission of metal atoms or metal-containing molecules from metal crystallites;
2. the adsorption and trapping of metal atoms or metal-containing molecules on the support surface;
3. the diffusion of metal atoms, metal-containing molecules and/or metal crystallites across support surfaces;
4. the metal particle spreading;
5. the support surface wetting by metal particles;
6. the metal particle nucleation;
7. the coalescence of metal particles;
8. the capture of atoms or molecules by metal particles;
9. the metal atom vaporization and/or volatilization through volatile compounds

As a matter of fact, sintering of supported metals involves complex physical and chemical phenomena that make the understanding of mechanistic aspects of the sintering a difficult task.

Experimental observations showed that sintering rates of supported metal catalysts are strongly affected by the temperature and to a lower extent by the atmosphere. The effect of temperature and atmosphere can be easily derived from constant temperature–variable time data such as those reported in Fig. 3.

The figure shows two different regimes: a rapid, almost exponential loss of surface area during the initial stage and, later on, a slower (almost linear) loss. These data may be consistent with a shift from crystalline migration at low temperatures to atomic migration at high temperatures [30].

Contrasting data are available concerning the effect of the atmosphere on sintering. For Pt-supported catalysts, several authors [31] reported that under oxidizing atmosphere the sintering is more severe than under inert or reducing atmosphere. Bartholomew however observed that this is not a general case, since the rate of dispersion also depends on Pt loading (Fig. 3) [32]. These effects may be related to changes in surface structure due to adsorbed species such as H, O or OH in H_2, O_2 or H_2O-containing atmospheres, respectively. This points out the role of surface energy which depends on the gas composition and on the kinetics of the surface reactions.

Finally, the presence of strong metal–support interactions (SMSI) affect the spreading, wetting and redispersion of the supported metals: accordingly, because of the strong interaction of NiO with oxide supports, NiO/SiO_2 is thermally more stable in air than Ni/SiO_2 in H_2 [32]. Along similar lines, Pd stabilizes Pt in O_2-containing atmospheres, possibly because of strong interactions of PdO with the oxide supports [33].

Other factors affect the stability of a metal crystallite towards sintering, e.g. shape and size of the crystallite [34], support roughness and pore size
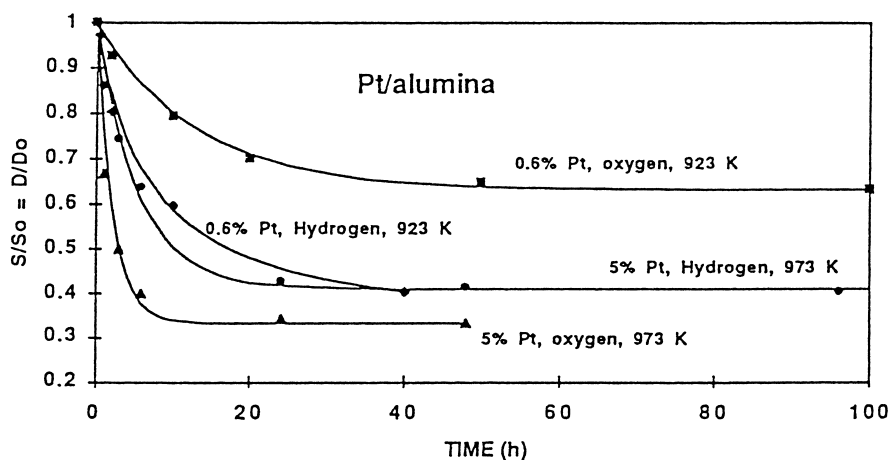

Fig. 3. Effects of H_2 and O_2 atmospheres and of metal loading on sintering rates of Pt/Al_2O_3 catalysts [32].

[35], impurities present in either the support or the metal. Species such as carbon, oxygen, Ca, Ba, Ce or Ge may decrease metal atom mobility, while others such as Pb, Bi, Cl, F or S can increase the mobility. Rare earth oxides such as CeO_2 and La_2O_3 have been suggested to "fix" noble metal atoms in automotive exhaust converters due to a strong, localized chemical interaction [36–38].

The effects of chlorides on the sintering of supported noble metal catalysts has been extensively investigated, since in several cases catalysts are prepared from chlorine-containing precursors (e.g. H_2PtCl_6) or are treated with chlorine-containing compounds to maintain or enhance their acid properties. The presence of chlorine either in the gas-phase or on the support favors the sintering of Pt [39]. However, recently there has been an accumulation of convincing experimental evidences that Cl favors a process opposite to sintering, i.e. redispersion [40]. This process has been explained by either a physical splitting of the metal particles or to a spreading of metal monolayers over the surface. The redispersion is of industrial importance in catalytic reforming over Pt/Al_2O_3 catalysts, where it has been observed that appropriate chlorine treatments in the presence of oxygen during the catalyst regeneration procedures may be useful for Pt redispersion. This treatment, often termed as "oxychlorination", possibly involves the transport of metal oxide or oxychloride molecules through the vapor or along the surface.

Chlorides are also well known to cause severe sintering of Cu in Cu-based methanol synthesis and low-temperature shift catalysts (Fig. 4).

Metal oxide catalysts and supports are also affected by sintering, that is related to the coalescence and growth of the bulk oxide crystallites. The process is
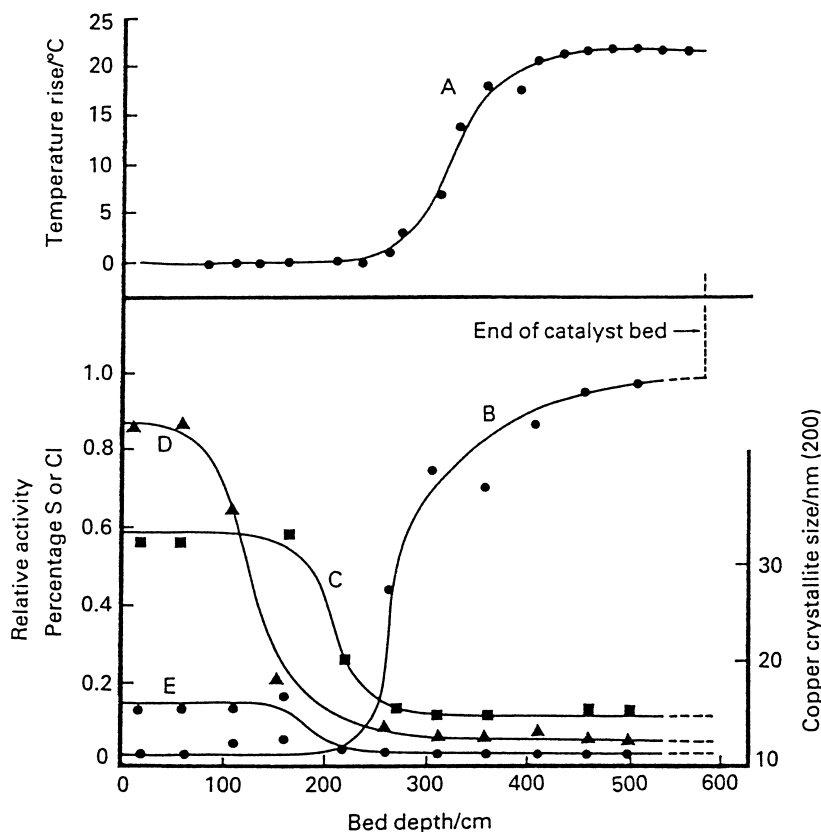

Fig. 4. Temperature rise (A) and variation of catalyst activity (B, from laboratory data), Cu crystal size (C), Cl and S content (E and D, respectively) with reactor depth for an old charge of low-temperature shift catalyst in a commercial reactor [10].

accompanied by an increase of the crystallite dimension leading to a decrease in the surface area and porosity. Like for sintering of supported metal catalysts, also in this case the mechanisms leading to crystallites coalescence and growth are rather obscure. In any case, the actual rate and the extent of sintering depends on many factors, including the metal oxide concerned, the initial crystallite size and the size distribution, the presence of additives that favor or promote sintering, the environment. The key variable is temperature, so that operation at low temperatures greatly reduces the sintering rate. Reaction atmosphere also affects sintering: water vapor, in particular, accelerates crystallization and structural change in oxide supports. Accordingly, over high-surface area catalysts it is desirable to minimize the water vapor concentration at high temperatures during both operation and activation procedures as well. The presence of specific additives is known to reduce the catalyst sintering. For example BaO, CeO_2, La_2O_3, SiO_2 and ZrO_2 improve the stability of γ-alumina towards sintering [41–45], whereas Na_2O enhances its sintering. In addition to a decrease in the surface area, sintering may also lead to a decrease in the pore openings, and eventually the pores close completely making the active species inaccessible to the reactants.

1.1.4. Solid-state transformation

Solid-state transformation is a process of deactivation that can be viewed as an extreme form of sintering occurring at high temperatures and leading to the transformation of one crystalline phase into a different one. These processes may involve both metal-supported catalysts and metal oxide catalysts as well. In the first case we can observe the incorporation of the metal into the support, e.g. incorporation of metallic Ni into the Al_2O_3 support (at temperatures near 1000°C) with formation of inactive nickel aluminate, or reaction of Rh_2O_3 with alumina (in automotive exhaust catalysts) to form inactive $Rh_2Al_2O_4$ during high-temperature lean conditions.

In the case of metal oxide catalysts or supports the transformation of one crystalline phase into a different one can occur, like the conversion of γ- into δ-Al_2O_3 with a step-wise decrease in the internal surface area from about 150 m^2/g to less than 50 m^2/g.

Several of these transformations are limited by the rate of nucleation. This process may occur due to the
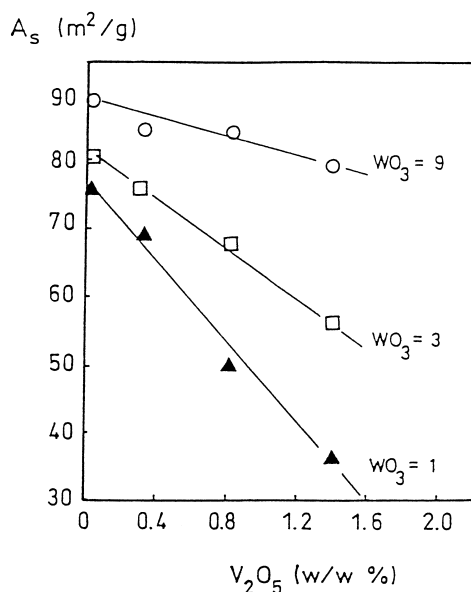

Fig. 5. Effects of vanadia and tungsta loading on the surface areas of TiO_2-supported V_2O_5-WO_3 catalysts [46].

presence of some foreign compounds in the lattice or even on the surface. For example, V_2O_5 has been reported to favor the sintering of the TiO_2-anatase support as well as the anatase-to-rutile transformation in TiO_2-supported V_2O_5 catalysts. On the other hand, WO_3 effectively contrasts this phenomenon (Fig. 5) [46].

1.1.5. Other mechanisms of deactivation

Other mechanisms of deactivation include masking or pore blockage, caused e.g. by the physical deposit of substances on the outer surface of the catalyst thus hindering the active sites from reactants. In addition to the coke deposition already discussed, masking may occur during hydrotreating processes where metals (principally Ni and V) in the feedstock deposit on the catalyst external surface, or in the case of automotive exhaust converters by deposition of P (from lubricants) and Si compounds.

Certain catalysts may also suffer from loss of active phase. This may occur via processes like volatilization, e.g. Cu in the presence of Cl with formation of volatile $CuCl_2$, or Ru under oxidizing atmosphere at elevated temperatures via the formation of volatile RuO_x, or formation of volatile carbonyls by reaction of metals with CO [3].

Finally, loss of catalytic material due to attrition in moving or fluidized beds is a serious source of deactivation since the catalyst is continuously abraded away. Accordingly the availability of attrition-resistant catalysts for fluid-bed catalytic cracking is extremely important since the process operates with regeneration and catalyst recycle. Also, washcoat loss on monolith honeycomb catalysts may occur, especially when the gases are flowing at high linear velocities and/or when rapid changes in temperatures occur. Indeed differences in thermal expansion between the washcoat and the honeycomb lead to a loss of bonding.

2. Kinetics of catalyst deactivation

A quantitative description of deactivating systems is essential in order to optimize the design and operation of catalytic processes, especially for fast deactivating systems.

The activity a of a deactivating catalyst is expressed according to the equation:

$$a = r/r_0, \tag{1}$$

where r_0 is the initial rate of reaction (i.e., the rate of reaction of a fresh catalyst sample) and r is the rate of reaction measured after a determined time-on-stream). r_0 is generally obtained by extrapolation to zero on a rate versus time-on-stream plot.

In general, the rate of reaction depends on the actual reaction conditions as well as on the activity, which is function of the previous catalyst history:
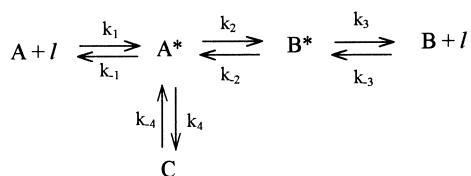
$$r = r(C, T, P, \dots, a). \tag{2}$$

According to the term coined by Szepe and Levenspiel [47], i.e. separability, possibly the rate of reaction may be separated into two terms: a reaction kinetics dependency, which is time-independent, and an activity dependency, which is not:

$$r = r_0(C, T, P, \dots)r_1(a). \tag{3}$$

Usually the separable factor $r_1(a)$ is simply taken as a normalized variable a ($0 \leq a \leq 1$).

Since the activity of a catalyst (and hence the rate of reaction) is related to the population of the active sites on the surface, the catalyst deactivation can be considered as the decrease of the number of active sites on the surface. Accordingly, if N_0 is the number of active sites on a non-deactivated catalyst and N_t is the number of active sites at any stage of deactivation, the fraction of active sites is $\alpha = N_t/N_0$. The goal is now to relate α with a. Butt and Petersen [15] extended the Langmuir–Hinshelwood–Hougen–Watson (LHHW) kinetic approach to the description of systems of changing activity, and considered the dehydrogenation reaction of methyl-cyclohexane (A) to toluene (B) with formation of coke (C) according to the following scheme:

$$A + l \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^* \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} B^* \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} B + l$$

with A^* also reacting via $k_{-4} \upharpoonleft\downharpoonright k_4$ to give C.

By considering the surface reaction $A^* \Leftrightarrow B^*$ as the rate-determining step ($k_{-2} < k_2 < k_1, k_{-1}, k_3, k_{-3}$), and since in most situations the rate of poisoning is small compared to the rate of reaction, i.e. $k_4 < k_{-4} < k_2$, the following rate expression can be obtained:

$$r = \frac{k_2 K_A C_A C_t}{1 + K_A C_A + K_B C_B} e^{-\int_0^t \frac{k_4 K_A C_A}{1 + K_A C_A + K_B C_B} dt}. \tag{4}$$

Only in the case that the coke formation does not depend on the concentrations of the reacting species, then $\int_0^t \frac{k_4 K_A C_A}{1 + K_A C_A + K_B C_B} dt = K't$ and therefore:

$$r = \frac{k_2 K_A C_A C_t}{1 + K_A C_A + K_B C_B} e^{-K't}. \tag{4a}$$

In this example the obtained rate equation clearly satisfies the separability requirement. However, many situations are reported in which this criterion is not fulfilled [15].

In the case of separability of the kinetics, there are several mathematical forms of the deactivation function used in the literature. In all cases, a relationship is searched between a and α and a population balance is used to relate α and time, or empirical forms directly relating a and time, as discussed in the following.

Kinetics of deactivation by coke. Much work has been done on coking, which is a common cause of deactivation for many petroleum refining and petrochemical processes. In a pioneering work, Voorhies [48] empirically described coke formation as a function of time-on-stream via the following

simple equation:

$$C_c = At^n, \tag{5}$$

where C_c is the wt% of coke on the catalyst, t is the time-on-stream, A is a constant depending on the feedstock, reactor type, reaction conditions and n is an exponent with a value close to 0.5. In this equation the amount of coke formed on the catalyst is assumed to be independent of the hydrocarbon feed rate, an hypothesis that has not been confirmed by all authors. In spite of this, the Voorhies correlation has been widely accepted and probably used beyond the original purposes.

A different approach has been developed by Froment and Bishoff [49,50]. These authors relate the rate of coke formation to the composition of the reacting mixture, catalyst temperature and catalyst activity. It has been assumed that coke (C) formation could occur either by a reaction parallel or consecutive to the main reaction:

A ⟷ B
     ↘
       C   A ⟷ B → C

In order to derive a rate expression for the deactivating catalysts, the common A↔B reaction step has been considered first. According to the LHHW approach, by writing the site balance equation in the form:

$$C_t - C_{C^*} = C_1 \cdot (1 + K_A C_A + K_B C_B) \tag{6}$$

and by assuming that the rate of the surface reaction is the rate-determining step, the following expression for the rate of reaction r is obtained:

$$r = \frac{k_r C_t K_A \varphi_A (C_A - \frac{C_B}{K})}{1 + K_A C_A + K_B C_B}, \tag{7}$$

where $\varphi_A = \frac{(C_t - C_{C^*})}{C_t}$ remaining active (deactivation or activity function). Froment and Bishoff [49,50] empirically related φ_A to the coke content of the catalyst C_c, i.e. $\varphi_A = \exp(-\alpha C_c)$ or $\varphi_A = (1 + \alpha C_c)^{-1}$. Accordingly, the problem is now to determine how C_c varies with time. When the coke formation is parallel to the main reaction path, the following equation can be easily obtained:

$$r_C = \frac{k_c C_t K_A \varphi_C C_A}{1 + K_A C_A + K_B C_B}, \tag{8}$$

with $\varphi_C = (C_t - C_{C^*})/C_t$. This deactivation function has one of the forms previously proposed for φ_A, but it is not necessarily identical to φ_A. A rate equation similar to Eq. (8) is obtained when the coke precursor is formed from a consecutive reaction scheme.

Eqs. (7) and (8) form a set of simultaneous equations showing that coking not only depends on the reaction mechanism, but also on the composition of the reaction mixture. This approach differs from that proposed by Wojchiechowsky [51] and Szepe and Levenspiel [47]. The point of divergence is that these authors relate the activity or deactivation functions directly to time with several empirical functions, e.g. $\varphi = 1 - \alpha t$, $\varphi = \exp(-\alpha t)$, $\varphi = (1 + \alpha t)^{-1}$, $\varphi = \alpha t^{-0.5}$ or $\varphi = (1 + \alpha t)^{-N}$. Using $\varphi = f(t)$ instead of $\varphi = f(C_c)$ presents the obvious advantage that the rate equation is directly expressed in terms of time and therefore it is self-sufficient to predict the deactivation rate at any process time. However, this approach is valid only when the coke formation does not depend on the reactants concentration, that looks like unusual. Furthermore, the constant α appearing in $\varphi = f(t)$ depends on the operating conditions determining the coke deposition, so that its application is strictly limited to the conditions prevailing during its determination. On the other hand, Bartholomew [11] argued that the approach followed by Froment and Bishoff may be questionable when several forms of carbon are present, some of which may not contribute to deactivation.

Several cases have been reported in the literature concerning the non-adequacy of the separability approach [52]. However, in spite of these major criticisms, several deactivation kinetics have been accurately described by means of kinetic models involving the separability concept. In some cases this may be related to the number of parameters employed in the kinetic equations leading to a good flexibility of the model and allowing for a nice fit of the experimental data. Accordingly, a certain degree of correlation among the various parameters might be expected, and caution must be considered when gaining physical meaning from the obtained parameters.

The above treatments have been developed for reactions occurring under chemically controlled regime. In real situations the picture is more complicated since the presence of diffusional limitations may significantly affect the results. Furthermore, in the

case of fouling, coke may grow up to block the pore. Beekman and Froment [53,54] used a probabilistic approach to deal with this problem.

Effects of poison or coke non-uniform distribution in the catalyst pellets. Since the 1950s, Wheeler [55] showed that a homogeneous catalyst surface could produce a non-linear curve in a plot of the reaction rate versus fraction of unpoisoned surface even for a non-selective poison. Wheeler assumed that poisons, being strongly adsorbed, tend to collect at the exterior of porous catalyst pellets with a very sharp front proceeding inward as the quantity of poison adsorbed by the catalyst increases. This is the so-called pore mouth poisoning model, and is consistent with the fact that the deposition of several poisons is strongly diffusion limited (Fig. 6). According to this model, the pore can be seen as divided into two zones:

1. a catalytically inactive zone that has already adsorbed its saturation amounts of poison, and
2. an unpoisoned zone.

On the opposite side, poisons with very low sticking coefficients tend to uniformly distribute throughout the porous catalyst pellet (uniform poisoning).

A schematic picture representing these two different situations is shown in Fig. 6, along with the so-
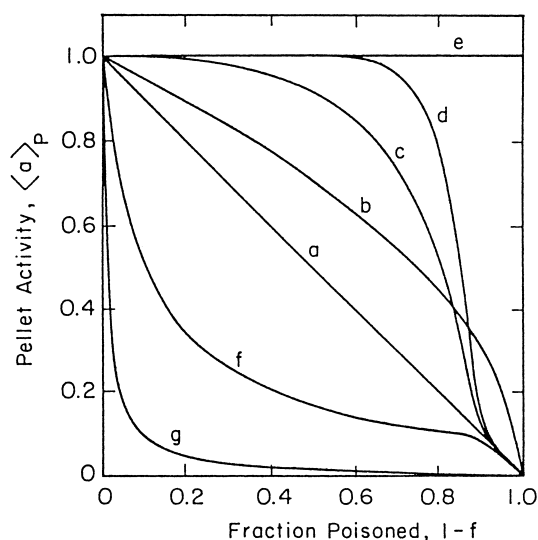

Fig. 7. Decrease in pellet activity with amount of poison for different types of poisoning. (a) All type of poisoning, ϕ (Thiele modulus)$\ll 2$; (b) uniform poisoning, $\phi \gg 2$; (c) core poisoning, $\phi = 3$; (d) core poisoning, $\phi = 5$; (e) core poisoning, $\phi \gg 5$; (f) pore mouth poisoning, $\phi = 10$; (g) pore mouth poisoning, $\phi = 100$ [15].

called core poisoning model that will be discussed below.

In the presence of a "non-selective" poison and under kinetic regime, the activity of the catalyst (in terms of r/r_0) is linear in the amounts of adsorbed poison in both the "pore mouth poisoned" and "uniformly poisoned" model (Fig. 7, curve a). Indeed in these cases the net result of the poisoning is to reduce the number of the catalyst active sites. A different situation holds under internal controlled diffusional regime. In this case, the catalyst with "pore mouth poisoning" will show a more rapid decline in activity with the amounts of adsorbed poison with respect to the case of kinetic regime (Fig. 7, curves f and g). Indeed the reactants must cross the inactive part of the catalyst moving towards the interior unpoisoned zone of the catalyst particle in order to react. This slows down the process much faster than would be expected on the basis of the fraction of the active sites actually removed, since the outer poisoned zone offers an additional resistance to the diffusion of the reactants inside the catalyst pellet.

On the other hand, the activity of a catalyst uniformly poisoned declines less rapidly under diffusional controlled regime than under chemical
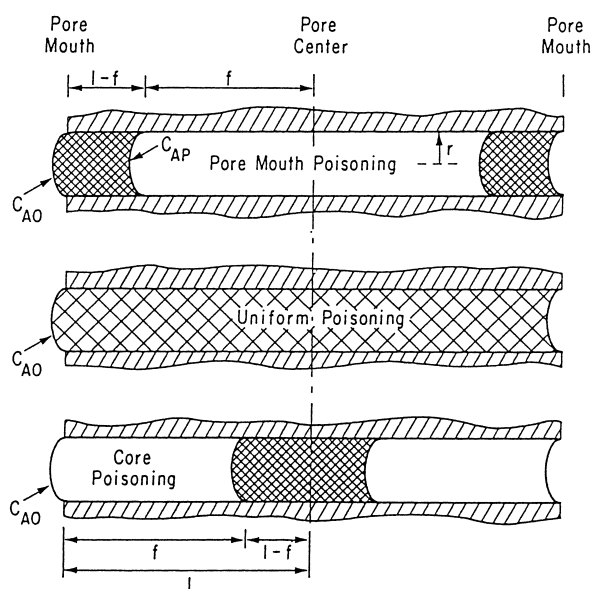

Fig. 6. Three limiting cases of poisoning and/or fouling.

regime (Fig. 7, curve b). Indeed the poisoning of the catalyst decreases the *effective* or *intrinsic* rate of reaction and accordingly the reactants are able to penetrate more deeply into the pores of the catalyst. Therefore they can utilize more surface area than they could initially. The net result is that the activity of the catalyst pellet decreases less rapidly than linearly with the amount of poison in the catalyst. It should be mentioned however that similar behaviors have not been observed in real cases, since poisons usually tend to be adsorbed at the pore inlet.

A third case should be mentioned, not actually common for poisons but representative e.g. for coking processes. This is the *core poisoning* model (Fig. 6), and represents the deactivation of the pores from the inside, possibly with a sharp front. This is for example the case of a coking process in which the foulant precursor is a reaction product that therefore may be formed in the center of the catalyst particle. In this case, in the presence of strong diffusional limitations, no decrease in the catalyst activity is observed, since the reaction takes place in the catalyst outer portion, whereas the foulant accumulate in the catalyst inner portion.

A mathematical analysis of the cases discussed above has been reviewed in [15,56,57]. An interesting practical conclusion deriving from the previous discussion is that a proper catalyst design may improve the pellet efficiency upon poisoning. Indeed since poisoning usually occurs on the outer shell of the catalyst pellet, the use of particularly shaped catalysts or of non-uniform distribution of the catalytic material in the pellet – e.g. eggshell – may favor, in principle, the desired reaction with respect to the poisoning. Several studies have been reported on this subject [58–60]. For example a study of different Pt/Pd distributions in automotive exhaust catalysts and on the use of an outer layer as scavenger for impurity poisons was developed by Hegedus et al. [61,62]. As expected, not a single rule does exist, but the most effective distribution of the catalytic material depends on the manner in which the poisoning (or fouling) process occurs.

Regeneration of coked catalysts and kinetics of coke removal. In general, the oxidation of coke is a very rapid reaction, and in many practical applications it is diffusion limited. On the other hand, intrinsic oxidation kinetics are of interest for several purposes. The

intrinsic kinetics of carbon burning were reported by Bondi et al. [63] to be first-order in the carbon content C_c and in the oxygen partial pressure P_{O_2}, i.e. $r_{ox}=kP_{O_2} C_c$. The validity of this assumption is certainly dependent on the amount of coke present: indeed in the presence of thick coke deposits, oxidation would initially remove an outer coke layer so that the rate of reaction must be zero-order in coke.

Much of the work devoted to the coke burning kinetics is related to the regeneration of catalysts used in catalytic cracking. In this case, a typical amount of coke on deactivated catalysts is near 5% (w/w), and accordingly a sub-monolayer coverage is reasonable. Typical examples of coke rate plots versus τ are reported in Fig. 8 for a SiO_2–Al_2O_3 catalyst; the initial flatten portion of curve B in the figure may be ascribed to the fact that initially not all the surface carbon is accessible to oxygen and kinetically it represents the transition from zero-order to first-order kinetics in C_c.

Kinetics of sintering of supported metal catalysts. A number of workers have attempted to correlate sintering kinetics via power–law expressions (PLE):

$$\frac{d(D/D_0)}{dt} = -k(D/D_0)^n, \tag{9}$$

where D is the metal dispersion and k the activated kinetic rate constant for sintering. Alternative forms of correlation may involve the metal surface area instead of dispersion. In several cases it has been found that application of Eq. (9) leads to values of k varying with sintering time, and hence with dispersion. In particu-
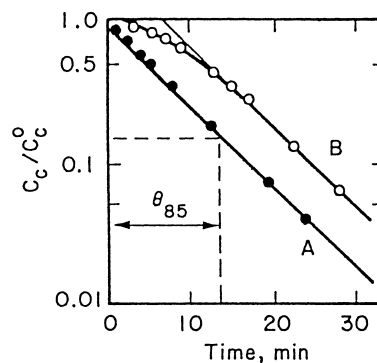

Fig. 8. Typical examples of rate plots of carbon remaining versus burning time; SiO_2–Al_2O_3 in air, 538°C. (●) Normal sample, 3% carbon (A); (○) initial flattening due to partial inaccessibility, mix 7–20% carbon (B) [15].

lar, the values of k at short times are greater than those measured at long times [32]. Thus it is not possible to quantitatively compare kinetic parameters from this rate expression because they are function of time, and this indicates that a simple correlation like Eq. (9) is inadequate to cope with the complexities of sintering kinetics. However some trend may be identified when comparing deactivation rates of different catalysts or of the same catalyst under different environments.

A slightly different expression has been proposed by Fuentes et al. [64]:

$$\frac{\mathrm{d}(D/D_0)}{\mathrm{d}t} = -k(D/D_0 - D_{eq}/D_0)^n, \qquad (10)$$

which adds the term $-D_{eq}/D_0$ to account for the asymptotic approach observed in the typical dispersion versus time curves (Fig. 3). Eq. (10) is known as generalized power law expression, viz. GPLE. It has been found that the various parameters appearing in the equation are modest function of time: accordingly, by the use of this equation it was possible to perform a direct quantitative comparison regarding the effect of temperature, time, atmosphere, metal, support and promoters on the rate of sintering of supported metal catalysts [32].

3. Example of deactivation in catalytic chemical processes: the catalytic cracking

Fluid catalytic cracking (FCC) is used in refineries to produce gasoline and middle distillates from gas oils. The process (Fig. 9) consists of a cracking unit in which a gas oil feed is cracked into lighter components (gasoline) in the presence of a catalyst. During the cracking reactions, very rapid catalyst deactivation occurs (with characteristic times in the order of seconds) by coke deposition. Accordingly the spent catalyst is continuously moved to a regenerator vessel where coke is burned with air. Therefore the FCC process is a representative example of how process solutions and catalyst design have been developed in order to cope with such an unavoidable very rapid decay.

Several reports are available in the literature concerning the development and application of suitable models describing the interaction of reaction kinetics and deactivation applied to the FCC process. Most of
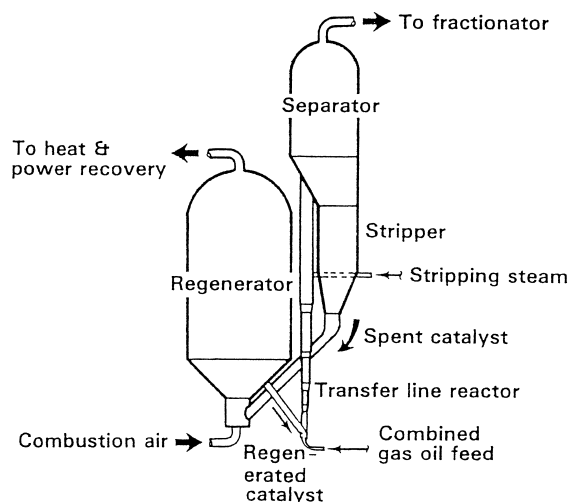

Fig. 9. Fluid catalytic cracking unit.

these studies have been reported by Weekman et al. [65–70].

Due to the complexity of the reacting system (hundreds of individual reactions are involved) a suitable lumped model has been developed, in which a generic class of compounds are treated as a kinetic entity with respect to both the cracking reactions and the deactivation behavior. In this respect, a very simple model has been considered in which the gas oil charge (O) is cracked to a gasoline fraction (G) together with low molecular weight products and coke (X):

$$O \xrightarrow{K_1} G \xrightarrow{K_2} X$$

with $O \xrightarrow{K_3} X$
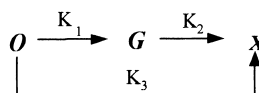
The reaction scheme reported above shows that some undesired products X are formed not only from gasoline G, but also directly from gas oil O. Accordingly, an analysis of the operation of FCC processes requires the development of models for the cracker (riser) reactor and the regenerator.

The cracker reactor can be modeled as a riser-tube reactor, where gas oil O and dispersing steam carry the freshly regenerated catalyst upwards in two-phase (gas–solid) flow. The cracking and coke-forming reactions take place in the riser-tube reactor. Data obtained with representative feedstocks and operating conditions in a fixed bed reactor [65] showed that, disregarding the very rapid initial decay, the net catalyst activity is described in terms of an exponential func-

tion of the time-on-stream, i.e. $\phi = \mathrm{e}^{-\alpha t_m}$ where ϕ is the remaining fraction of the initial activity, α the decay velocity and t_m is the time-on-stream. This exponential model is consistent with a Voorhies-type dependence of the coke content with residence time [67].

Weekman and Nace [65,67,68] developed a simple model for catalytic cracking for fixed, moving and fluid beds. In the case of an isothermal fixed bed, by assuming

1. idealized piston flow;
2. absence of diffusional limitations; and
3. quasi-steady-state approximation.

(i.e. the decay of the catalyst is slow relative to the vapor residence time), the unconverted weight fraction y of gas oil is given by:

$$\frac{\mathrm{d}y}{\mathrm{d}Z} = \frac{\epsilon \cdot \rho_v}{\rho_1 \mathrm{LHSV}}(-r),$$ (11)

where Z is the axial dimensionless coordinate ($Z=z/L$), ϵ the bed void fraction, ρ_v the vapor density, ρ_1 the liquid reactant density, and r is the rate of gas oil consumption and LHSV the liquid hourly space velocity.

Weekman observed that the pseudo-component gas oil O cracks according to second-order kinetics, i.e. $-r = k_0 y^2 \mathrm{e}^{-\alpha t_m}$. Introducing the characteristic decay time $\lambda = \alpha t_m$, which represents the "length" of decay

(i.e. the product of the decay velocity α and the total time of decay, t_m), Eq. (12) is obtained:

$$\frac{\mathrm{d}y}{\mathrm{d}Z} = -Ay^2 \mathrm{e}^{-\lambda\theta},$$ (12)

with $A = \frac{\varepsilon \rho_0 k_0}{\rho_1 \cdot \mathrm{LHSV}} = \frac{K_0}{\mathrm{LHSV}}$, where K_0 is the rate constant for gas oil cracking ($K_0=K_1+K_3$), θ ($\theta=t/t_m$) is the dimensionless time variable and ρ_0 the initial vapor density. The reaction velocity group A is the reaction rate multiplied by the vapor phase residence time and represents the "length" of reaction. Integration of Eq. (12) yields the conversion χ:

$$\chi = 1 - y = \frac{A \cdot \mathrm{e}^{-\lambda\theta}}{1 + A \cdot \mathrm{e}^{-\lambda\theta}}.$$ (13)

The value of gas oil conversion represented by Eq. (13) is an instantaneous one. The time-averaged value of the conversion, $\bar{\chi} = \int_0^1 \chi \, \mathrm{d}\theta = \frac{1}{\lambda} \ln \left[\frac{1+A}{1+A\mathrm{e}^{-\lambda}} \right]$, is reported in Fig. 10 as a function of the decay and reaction groups [65].

Under actual reaction conditions, the reactor is best represented by a moving bed reactor. Accordingly, the residence time of the catalyst in the riser (typically 5–7 s) is the characteristic time for deactivation. The catalyst activity profile is invariant with time, and by assuming plug flow for both the solid and the gas phases basically the same equations employed for fixed beds can be adopted also for moving beds. However, the position in the catalyst bed now replaces
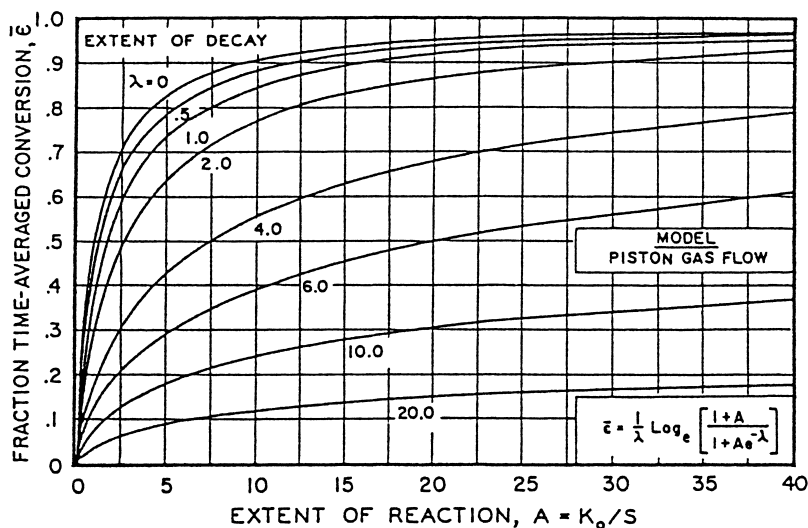

Fig. 10. Time-averaged conversion for fixed beds [65].

the time-on-stream, so that Z will replace θ in the argument of the exponential in the decay function. This means that the "length" of decay λ is now the decay velocity, α, multiplied by the total residence time of the catalyst in the moving bed t_c, i.e. $\lambda = \alpha t_c$. The calculated conversion at the bed exit is:

$$\chi = \frac{A \cdot \left(1 - e^{-\lambda}\right)}{\lambda + A \cdot \left(1 - e^{-\lambda}\right)}. \tag{14}$$

Similar models have also been obtained for fluid beds [65].

Weekman and Nace [65,67,68] demonstrated the validity of the kinetic-deactivation model by application over a wide range of experimental conditions. An interesting application of the Weekman–Nace model is the maximization of the gasoline yield. In this case, by considering the reaction scheme reported above, the gasoline mass–balance equation can be written as:

$$\frac{\mathrm{d}y_G}{\mathrm{d}Z} = \frac{K_1}{\mathrm{LHSV}} \phi \cdot y^2 - \frac{K_2}{\mathrm{LHSV}} \phi \cdot y_G, \tag{15}$$

where y_G is the mass fraction of gasoline, K_1 is the rate constant for gasoline formation and K_2 is the rate constant for gasoline cracking. Eq. (15) shows that gasoline is formed from gas oil (first term on the LHS) and lost by over-cracking (second term on the LHS).
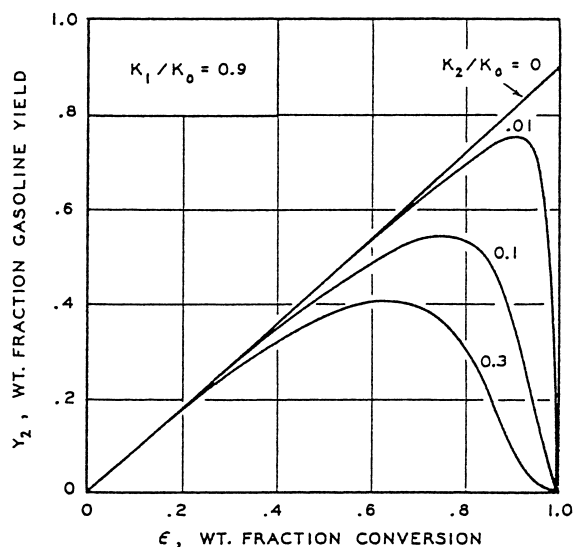
Eq. (15) can be integrated under isothermal conditions and plots can be obtained relating the gasoline yield as a function of gas oil conversion for various K_1/K_0 and K_2/K_0 values (Fig. 11) [67,68,71]. It appears that the overcracking ratio K_2/K_0 must be very low in order to obtain good gasoline yields. The maximum gasoline yield is sensitive to conversion, and therefore the extent of conversion should be limited in the riser. Voltz et al. [70] observed that K_1 is a fraction of K_0, and that these parameters (along with α, the decay velocity) depend primarily upon the aromatics-to-naphthalene ratio of the gas oil.

The detailed reaction engineering of the riser reactor is of course more complex than it has been presented here, although these results are not bad approximations of industrial cracking reactors. In particular, two major complications should be considered:

1. the reactor is not isothermal;
2. the presence of gas-phase axial dispersion lowers the conversion and the yields.

Fig. 11. Effect on selectivity of varying gasoline/gas oil cracking ratio at constant initial selectivity [68].

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