

Catalyst deactivation: is it predictable? What to do?

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Abstract

Catalyst deactivation is usually inevitable, although the rate at which it occurs varies greatly. This article discusses the causes of deactivation and the influence on reaction rate. Methods for minimising catalyst deactivation, by tailoring catalyst properties and/or process operations, are presented, as well as reactor configurations suitable for the regeneration of deactivated catalysts. Alkane dehydrogenation is used as an example to demonstrate the variety of engineering solutions possible. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

What makes a catalyst a good catalyst? Obviously, a good catalyst shows high activity. A high activity allows the use of relatively small reactors and operation at mild conditions. However, activity is not the only crucial property of a catalyst. A high selectivity for the desired products is often of even greater importance. Furthermore, it is important that a catalyst retains its activity and selectivity for some time. Ideally, a catalyst does not change and should have eternal life. In practice, this is not the case. Depending on the process used the catalyst cycle life may vary from a few seconds, as in fluid catalytic cracking (FCC), to several years, as in for instance ammonia synthesis. Catalyst deactivation is highly relevant for the application of catalysis and scientifically it has many challenges. An

excellent introduction is given in the recent book by Bartholomew and Farrauto [1].

The time scale of deactivation has profound consequences for process design. Fig. 1 shows the deactivation time for several processes in the refining and petrochemical industry. The two most important applications in environmental catalysis are also included. This deactivation time refers to the time after which a catalyst has lost so much of its initial activity that it must be regenerated or replaced. Often regeneration is possible, but there is a limit. At the end of the cycle life the catalyst is recycled or, when this is more economical, disposed. It is obvious that disposal should be postponed as long as possible and that recycling is becoming more and more important. Regeneration technology develops with time. Several procedures are in use and besides regeneration milder treatments are used, referred to as rejuvenation.

As can be seen from Fig. 1, the deactivation time varies greatly for the different processes. At the lower end, we find the FCC process with a deactivation time of seconds. Deactivation of a hydrodesulfuri-

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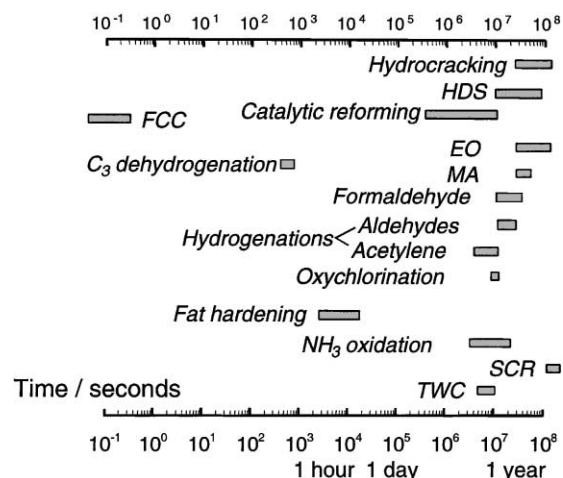


Fig. 1. Time scale of deactivation of various catalytic processes.

sation (HDS) catalyst is much slower, depending on the feed, in the order of months or a year.

The importance of catalyst stability is often underestimated, not only in academia but also in certain sectors of industry, notably in the fine chemicals industry. In bulk chemicals production, its importance generally has been acknowledged. In fine chemicals production, chemists sometimes look upon the catalyst as a reactant: when it does not function anymore, it is disposed and new catalyst is added. So, it is understandable that catalyst stability is not always a point of strong concern. With increasing environmental awareness this attitude will change.

This article will focus on deactivation in heterogeneous catalysis, although catalyst stability is just as important or even more important in homogeneous catalysis, see [2]. Table 1 lists some typical cases of deactivation in industrial processes.

2. Causes of deactivation

Deactivation is a complex phenomenon. Feed molecules might poison active sites, the catalyst might produce intermediates and products that are lethal poisons for the catalyst, the catalyst might not withstand the high temperature applied, etc. The length scale is also relevant: deactivation can be caused by phenomena on a nanometer scale (clusters at the surface, micropores in zeolites), micrometer scale

(macropores), several micrometer–millimeter scale (particles, washcoat) or even meter scale (reactor).

The five main causes of deactivation are poisoning, fouling, thermal degradation (sintering, evaporation) initiated by the often high temperature, mechanical damage and corrosion/leaching by the reaction mixture. In the first two cases, the catalyst might be regenerated in some way. Sintering, evaporation and leaching sometimes also can be cured by redispersing the catalytic material or restoring the active sites by a chemical vapour deposition (CVD) type treatment. It should be noted that the causes listed are often not independent. A good example is the adsorption of sulphur on a platinum catalyst; sulphur poisons the Pt sites, and at the same time causes the Pt clusters to become more mobile leading to sintering. In this issue, Bartholomew [3] discusses the deactivation mechanisms in detail. Fig. 2 shows a schematic representation of the deactivation phenomena inside a catalyst particle.

2.1. Poisoning

Poisoning is defined as deactivation by strong adsorption of, usually, impurities in the feed. Strictly speaking, also reactants and products adsorb at the catalyst surface and the most strongly adsorbing components hinder the adsorption of less strongly adsorbing components. This is not called poisoning but competitive adsorption and it should be incorporated in the rate expression. For instance, Langmuir–Hinshelwood–Hougen–Watson (LHHW) kinetic schemes model this. It is useful to distinguish between temporary and permanent poisoning. In the former situation, the poison can be removed, whereas this is not the case in the latter situation. The distinction between temporary and permanent poisoning is not always this clear: poisons that are strong poisons at low temperature are less harmful in high-temperature processes. Acetylenes and dienes readily polymerise to form carbonaceous deposits on catalysts. Higher temperatures help to remove these deposits by depolymerisation. Analogously, in catalytic combustion due to the high temperatures involved (>1270 K) poisoning by traces of sulphur, halogens, etc. is much less of a problem than in catalytic processes at ‘normal’ temperatures, because these poisons do not adsorb on the catalyst surface at such high temperatures [4].

Table 1
Typical cases of catalyst deactivation and the measures taken to counteract it

Process	Catalyst	Main deactivation mechanism	Time scale of deactivation	Consequences for catalyst	Regeneration	Consequences for process
FCC	Zeolite	Coke	Seconds	Regeneration on seconds scale	Coke combustion	Recirculation catalyst between reactor and regenerator
Oxidative dehydrogenation	Various oxides	Coke	Seconds	Regeneration on seconds scale		Similar schemes as in FCC
Catalytic reforming	Pt/ γ -Al ₂ O ₃	Coke	Months	Alloying	Coke combustion	Fixed bed, swing operation, moving bed
		Cl loss	Days		Cl supply redispersion	
Hydrotreating	Co/Mo/S/Al ₂ O ₃	Coke Metal sulphides	Months Days	Once-through catalyst Adapted porosity	Coke combustion	Fixed bed, slurry, moving bed
Methanol	Cu/ZnO/Al ₂ O ₃	Sintering (Cl)	Years	Stabilisation		Feed purification
Water-gas shift	Cu/ZnO/Al ₂ O ₃	Poisoning (S, Cl)	Years	Stabilisers (ZnO)		Feed purification
Three-way catalyst	Pt, Pd	Sintering, loss of active components, deposits (Zn, P from lubricants)	Years	Noble metals, stabilised alumina (La, Ba)	Rejuvenation by leaching	
Steam reforming	Ni/Al ₂ O ₃	Coke, whiskers		K, Mg gasification catalysts	Coke combustion	Excess steam
Dry reforming	Ni	Coke		S-doping	Coke combustion	Excess steam
Diesel soot	Cu–Cl	Evaporation	Minutes, hours	Select other catalyst		Add catalytic additives to fuel (Ce)
DeNO _x	V ₂ O ₅ /Al ₂ O ₃	Formation surface salts	Months	Select other carrier		
Wacker oxidation	Pd, Cu	Catalyst deposit				Low pH
Xylene oxidation	Co, Mo, Br	Mo, Co deposits		Add new catalyst		Deposits in reactor and downstream
Styrene	Iron oxide	Coke, sintering movement promoters		Structural promoters	Coke gasification in steam	

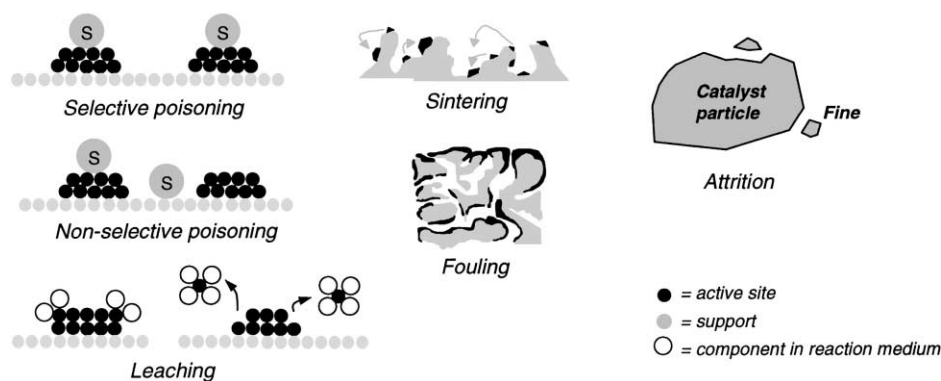


Fig. 2. Major types of deactivation in heterogeneous catalysis.

It is not uncommon that poisoning takes place by strong adsorption of traces of impurities in the feed. As adsorption is a fast process the poison molecules might well be predominantly present in the outer shell of the particle. A so-called egg-shell distribution is obtained. This might be viewed as an example of selective poisoning, but usually this term is limited to selection in terms of chemistry (i.e. preferential adsorption on specific sites). In the case of egg-shell poisoning, the most accessible sites are poisoned and, as a consequence, the observed deactivation behaviour is the same as in selective poisoning. Catalyst poisons exist in various forms, as is illustrated in Table 2.

Poisoning by sulphur compounds, such as H_2S is encountered in many large-scale processes using metal catalysts, such as methanation, steam reforming,

hydrogenations, and even HDS. A good example is sulphur poisoning in catalytic processes in the petroleum refinery. For example, in catalytic reforming the Pt-catalyst adsorbs sulphur very strongly and the process can only operate when the sulphur level is very low. Every catalytic reforming unit is preceded by an HDS unit.

In oxidation, usually air is used as reactant. The purity of the ambient air might be disappointing. Besides air pollution components, nature might also carry undesired components. A good example are coastal areas where the air contains aerosol particles and as a consequence Cl-poisoning might occur.

Metals or compounds that are reducible to metals under reaction conditions may alloy with the active catalyst metal and reduce its effectiveness [5]. Examples are Cu in Ni and Ni or Fe in Pt.

Poisoning can also be advantageous. Addition of a poison gives the option to enhance the selectivity, although usually at the expense of activity. In the upgrading of the products of ethane cracking, acetylene is removed by selective hydrogenation; adding Cu to the Ni catalyst results in selective hydrogenation of acetylene, while leaving ethene unaffected [5]. Similarly, on a palladium catalyst the addition of a small amount of Co can improve the selectivity of acetylene hydrogenation relative to ethene [5]. In such cases, the term modifier better describes the process than poison.

It is also possible that a strongly adsorbing species even leads to an increase in activity. In that case one speaks of a promoter. For instance, in the production of amines from nitriles by hydrogenation, addition

Table 2
Examples of catalyst poisons

Type of poison	Examples
Strong chemisorber	H_2S NH_3
Surface active metal or ion	Cu in Ni Ni in Pt Fe in Pt Pb or Ca in Co_3O_4 Pb in Fe_3O_4
High molecular weight product producer	Fe (from pipes) on Cu or Si–Al Acetylenes Dienes

of a small amount of an alkali hydroxide to the reactant feed improves the activity of the metal catalyst and the selectivity to the desired primary amine [6]. More commonly the promoter is incorporated into the catalyst as it is prepared, e.g. addition of a small amount of alumina to the conventional iron catalyst for ammonia synthesis [7].

2.2. Fouling

Fouling covers all phenomena where a surface is covered with a deposit. Its origin is not always related to processes on the catalyst. An example is the deposition of dust, e.g. from combustion residues like ash or soot or from mechanical wear of upstream equipment. Another example is the presence of colloidal particles in the feed, which leads to deposition, e.g. deposition of asphaltenes in processing of heavy petroleum fractions. In high temperature processes large molecules can be formed by free radical mechanisms and subsequently deposit on the catalyst particles. The injection of ammonia in selective catalytic reduction (SCR) of flue gases may lead to ammonium(bi)sulphate formation due to the presence of sulphur in the fuel.

In the cases above, the catalyst itself probably does not play a major role. More often, however, the catalyst itself is responsible for fouling by undesired by-products that lead to deposits. In petroleum processing fouling is a major concern. In most of the catalytic processes in the petroleum refinery fouling by the deposition of 'coke' plays a major role. Coke is a term that is used in many meanings. Dependent on the conditions (temperature, partial pressure of steam, hydrogen, composition of the liquid phase, etc.) several reactions can occur that lead to coke or in any case to carbonaceous material. At high temperatures poly-aromatic or even graphitic compounds are formed that deactivate catalysts. This coke is produced by unwanted polymerisation and dehydrogenation (condensation) of organic molecules present in the feed or formed as product. These reactions leave a layer of highly hydrogen deficient carbonaceous material on the catalyst surface, making the active sites inaccessible.

In hydropurification of heavy petroleum fractions, besides coke also metal sulphides are deposited, the most important being nickel, vanadium and iron sulphides. A typical plot is given in Fig. 3, which shows

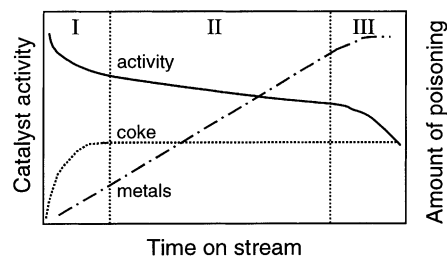


Fig. 3. Typical three stage activity decline of a residue hydrotreating catalyst [8].

the linear increase in metal sulphide deposits and the saturation of the coke deposits. As a result the activity initially declines fast (stage I), both due to coke and metal sulphide deposits, after which a phase of slow deactivation (stage II) is observed due to the continued deposition of metal sulphides. Finally, pore plugging leads to fast and complete deactivation of the catalyst (stage III).

For iron and vanadium in particular the reactions leading to the deposits are fast (and the diffusion rates within the particles are relatively slow) and, as a consequence, non-uniform deposition takes place. Fig. 4 gives examples of profiles measured under industrially relevant conditions [8].

Coke formation is not limited to petroleum processing. For instance, in alkene reactions over acid sites oligomerisation and alkylation reactions will occur. When the products do not desorb deactivation is

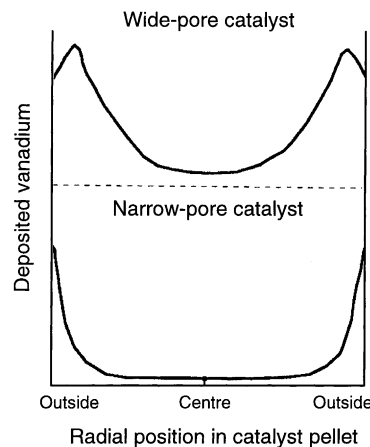


Fig. 4. The influence of the pore size on the vanadium deposition profiles for the hydroprocessing of a heavy industrial feedstock [8].

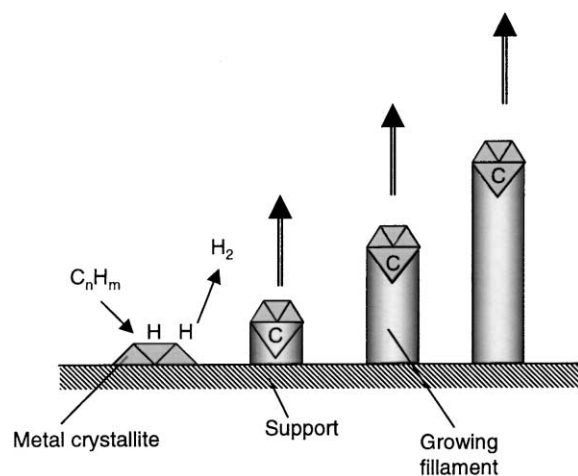


Fig. 5. Schematic of carbon formation on supported metal catalyst.

observed and the deposit might be referred to as 'coke'.

In metal catalysed reactions of hydrocarbons and CO layers of carbonaceous material can be formed, leading to encapsulation of the metal cluster or the formation of whiskers of carbon with the metal particle on top (see Figs. 5 and 6). It is a question of taste whether this is referred to as coke or carbon, although the latter term is most often used. The carbon can have spectacular shapes. Under some conditions hydrocarbons decompose at the metal surface of small crystallites and the carbon diffuses through the metal

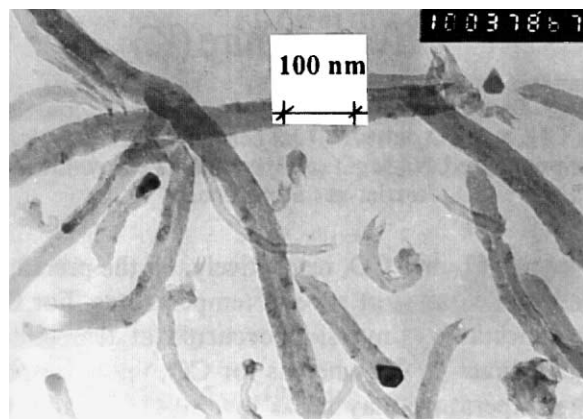


Fig. 6. Carbon filaments resulting from CH_4 decomposition at 873 K on a prereduced Ni/CaO. Reprinted from [9] with permission from Elsevier Science.

and forms a carbon nanotube at the other side of the crystallite. The crystallite is even lifted from the surface and becomes the head of a growing filament. Sometimes the crystallites split up and more filaments are formed. Under hydrogen-rich conditions this process may be reversible. Continued growth can lead to complete destruction of the catalyst particle and even blocking of passages in the reactor. This phenomenon can also occur at metal surfaces and can lead to destruction of piping.

2.3. Thermal degradation

Thermal degradation is a physical process leading to catalyst deactivation because of sintering, chemical transformations, evaporation, etc. Sintering is the loss of catalyst active surface due to crystallite growth of either the support material or the active phase. Fig. 7 shows a schematic representation of this type of deactivation.

Initially, the atoms are supposed to be present as small clusters of atoms (or small metal particles), termed a monomer dispersion. Surface diffusion of the atoms will lead to two-dimensional clusters, and upon further diffusion three-dimensional particles will be formed (Fig. 7a). These particles can grow into larger ones through several mechanisms. Particles might move and coalesce (Fig. 7b) or atoms move from one particle to another, either by volatilisation or by surface migration (Fig. 7c).

The most important mechanism for sintering of small particles often is the movement of atoms rather than particles; depending on the conditions (temperature, type of surface) atoms will move via a hopping mechanism or via surface diffusion. Sintering resembles crystallisation: larger particles grow at the expense of smaller ones. The position of the particle contributes to sintering. A 'valley' position is stable, while an 'on-top' position is highly unstable.

Besides processes on top of the support, also reactions can take place in which the support is directly involved. An example is alumina-supported cobalt oxide. At high temperature (>800 K) solid-state diffusion becomes noticeable and Co ions diffuse into the support generating a spinel [10]. It is not surprising that in this process catalytic activity is lost.

Thermal degradation can occur in all stages of the life cycle of the catalyst. It might occur due to local

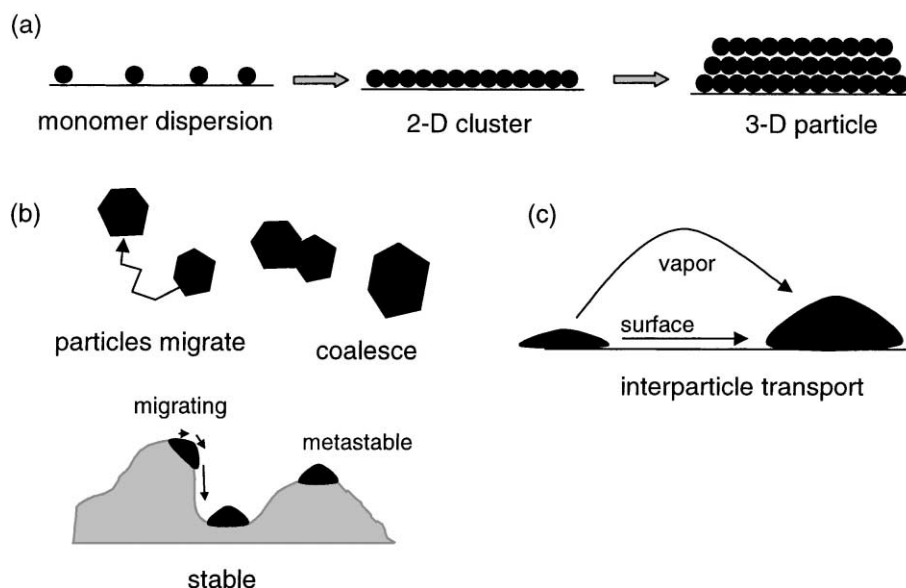


Fig. 7. Schematic of the various stages in the formation and growth of particles from a monomer dispersion.

heating during preparation (calcination), reduction (fresh or passivated catalyst), reaction (hot spots, maldistribution), or regeneration (coke burn-off).

A prediction of the propensity to sintering could help in rational catalyst selection and design. At first sight this might seem an impossible task, even more so because the chemical environment and the presence of promoters also play a role.

Sintering is strongly temperature dependent. The underlying mechanism is surface diffusion, or, at sufficiently high temperature, mobility of larger aggregates. So, it is clear that for a stable system the diffusion coefficients and the partial pressure should be low. This leads to a correlation with characteristic physical properties of the catalyst material.

The melting point plays a central role. It is not illogical that solid-state diffusion becomes faster when the temperature is closer to the melting point. The so-called Tamman and Hüttig temperatures, indicative for the temperature at which sintering may occur, are directly related to the melting temperature. Upon temperature increase the mobility of atoms increases. First, when the Hüttig temperature is reached, atoms at defects will become mobile. Later, when the Tamman temperature is reached, atoms from the bulk will exhibit mobility, and at the melting temperature, the

mobility will be so high that liquid-phase behaviour is observed. The following semi-empirical relations for the Tamman and Hüttig temperatures are recommended for use:

$$T_{\text{Hüttig}} = 0.3T_{\text{melting}} \quad (1)$$

$$T_{\text{Tamman}} = 0.5T_{\text{melting}} \quad (2)$$

Actually, the temperature at which the solid becomes mobile depends on several factors such as texture, size and morphology. $\gamma\text{-Al}_2\text{O}_3$ (highly porous) is much more sensitive to sintering than $\alpha\text{-Al}_2\text{O}_3$ (moderately porous). For small particles the temperature at which mobility occurs may be much lower than that indicated by the Tamman or Hüttig temperature. Table 3 gives data of T_{Tamman} and $T_{\text{Hüttig}}$ for some metals and their compounds. The melting point is not always well-defined, for instance some oxides already begin to decompose before T_{Tamman} or $T_{\text{Hüttig}}$ has been reached.

From Table 3, it can be understood why ceramic supports like alumina and silica are generally used in metal catalysts. They possess high Tamman temperatures and are often referred to as thermostable supports. Moreover, the small metal clusters often are anchored to them by chemical bonds, thus avoid-

Table 3

T_{melting} , T_{Tamman} and $T_{\text{Hüttig}}$ values (K) of metals and their compounds, relevant for heterogeneous catalysis

Compound	T_{melting}	T_{Tamman}	$T_{\text{Hüttig}}$
Pt	2028	1014	608
PtO	823	412	247
PtO ₂	723	362	217
PtCl ₂	854 ^c	427	256
PtCl ₄	643 ^c	322	193
Pd	1828	914	548
PdO	1023 ^c	512	307
Rh	2258	1129	677
Rh ₂ O ₃	1373 ^c	687	412
Ru	2723	1362	817
Fe	1808	904	542
Co	1753	877	526
Ni	1725	863	518
NiO	2228	1114	669
NiCl ₂	1281	641	384
Ni(CO) ₄	254	127	76
NiS	1249	625	375
Ag	1233	617	370
Au	1336	668	401
Cu	1356	678	407
CuO	1599	800	480
Cu ₂ O	1508	754	452
CuCl ₂	893	447	268
Cu ₂ Cl ₂	703	352	211
Mo	2883	1442	865
MoO ₃	1068	534	320
MoS ₂	1458	729	437
Zn	693	347	208
ZnO	2248	1124	675
Al ₂ O ₃	2318	1159	695
SiO ₂ ^a	1986	993	596
SiO ₂ ^b	1883	942	565

^a Cristobalite.

^b Quartz.

^c Decomposes at this temperature.

ing sintering. The so-called structural promoters also reduce sintering by their high stability: they inhibit surface migration of the atoms of the active phase. In a sense, they generate valley positions for the active phase (compare Fig. 7). So, at first sight for metal catalysts the data are not disturbing, except for processes operating at very high temperature, like catalytic combustion and steam reforming. However, the catalyst can react with the surrounding medium, which can lead to formation of relatively volatile compounds.

A well-documented example is the copper catalyst in methanol synthesis. In the past sintering appeared

to be a real problem at reaction temperature (ca. 500 K). It was found that sintering was promoted by traces of chlorine present in the feed, which react with the active surface producing a mobile copper chloride phase [11]. The data in Table 3 corroborate this.

In the oxidation of ammonia into nitric oxide, platinum/rhodium gauzes (90% Pt, 10% Rh) are used, at temperatures up to 1200 K. Table 3 makes it understandable that Pt evaporation via the oxide is a major problem in the process. Rhodium oxide is also formed and the alloy is slowly decomposed by the formation of dendritic morphology leading to physical loss of material. Typically, the gauzes have lives of 50–300 days [12]. The ultimate mobility is evaporation of the active phase leading to catalyst loss.

A good example illustrating the importance of being alert is obtained from the field of catalytic oxidation of diesel soot. In that field the challenge is to find a catalyst that is active at, say, 700 K. A catalyst was discovered with satisfactory activity. It was based on K, Cu and Mo, and as a result of the preparation method used, it contained some Cl. Catalysis in diesel soot oxidation is difficult to realise because the reacting system comprises two solid phases (soot and catalyst) and a gas phase (air). It is not surprising that a prerequisite for catalysis is good contact between the soot and the catalyst. Table 3 suggest that (oxy)chlorides are formed that are highly mobile and even volatile. This explains the high activity, because a good catalyst-soot contact will be realised. Unfortunately, also catalyst evaporation has to be expected. In agreement with this interpretation, it was found that for a series of transition metal chlorides the catalytic activity increases with decreasing melting temperature. This nicely illustrates the power of the correlations used.

Of course, evaporation is most important in high temperature processes, the major examples being steam reforming and catalytic combustion.

In practice, mobility is not always undesired. In fact, it can be applied to regenerate catalysts in certain cases. An elegant example is the redispersion of Pt in reforming catalysts. During reaction the dispersion of Pt decreases. However, by a high-temperature treatment (up to 920 K) in an oxygen-containing gas, platinum is slightly vaporised because of the formation of Pt-oxides. Adsorption on active sites of the support takes place and the dispersion is enhanced.

In the catalyst, always traces of chlorine are present, which allow the formation of oxychlorides [13,14]. These probably also play a role. The values of the Tamman temperature support this interpretation.

2.4. Mechanical deactivation

Mechanical strength is important in giving the catalyst resistance against crushing, e.g. during transport and loading of the catalyst in the reactor. A packed bed of catalyst particles will experience strong stresses in its life cycle: during start up it will be heated and thermal expansion of the tube will occur, whereas during cooling down the opposite will happen. During catalyst regeneration the expansion and contraction of the reactor might even be much larger than during start-up. So, it is no surprise that mechanical degradation is observed: during its life cycle the catalyst is often tortured in an extremely severe way!

In a fluidised-bed reactor attrition will always occur and the fines formed will be carried away with the product flow. It has been well-documented that in the DuPont process for the production of maleic anhydride the development of an attrition-resistant catalyst was a major issue [15,16]. In a fixed-bed reactor (FBR) attrition will be less, but the temperature transients described above should not be underestimated. For a FBR the consequences of even limited formation of fines are very important: enhanced pressure drop and eventually blocking of the bed.

The shape of the catalyst particles influences mechanical strength: a spherical shape is most favourable. Mechanical strength is also related to porosity, for instance, macropores will lead to reduced strength.

In washcoat monoliths the adherence of the coating to the monolith is very important [17]. For instance, the washcoat may be fractured and/or separated from the monolith as a result of thermal stresses. This is particularly relevant in automotive applications, in which the catalyst is subject to a wide range of temperatures during its life, while the temperature change is often very rapid, resulting in sudden expansion or contraction, which in turn can lead to thermal shock. A notable example of the possibility of thermal shock is in the oxidation of soot from diesel engines. A number of techniques have been developed to filter particulates (soot) from the diesel exhaust [18], but removing

the captured material from, for example, a ceramic wall-flow monolith is not so straightforward. The rapid temperature increase resulting from the combustion of the soot may even result in melting of the ceramic [19]. One of the alternatives is the use of a SiC filter, which is highly heat-resistant, coated with a soot oxidation catalyst, so that continuous regeneration can take place.

2.5. Corrosion/leaching

The reaction medium can be quite corrosive. Consider alumina at high or low pH. Above pH = 12 it will dissolve. So, it is not surprising that at a pH approaching 12 corrosion and leaching occur. The same applies for a low pH (<3). For extremely high or low pH carbon should be considered, not alumina.

Another good example is the sulphiding of oxides when H₂S is present in the reaction medium. Oxygen–sulphur exchange will take place leading to a sulphide phase. For example, in hydropurification of petroleum fractions a molybdenum oxide phase will be transformed in a molybdenum sulphide phase.

Particularly in liquid-phase catalysis leaching often is important. This has become painfully clear in the often enthusiastically reported results on heterogenisation of homogeneous catalysts: more often than not the system claimed to be active exhibited leaching and the catalytic activity is due to the leached compounds rather than the solid phase [20]. A good example of leaching is solid-catalysed fat hydrogenation. Nickel is the catalyst of choice, but it is clear that traces appear in the product. This does not apply to palladium, which might be a good reason to replace nickel with palladium.

3. How deactivation influences the reaction rate

In the simplest case, the catalytic activity is proportional to the number of active sites

$$k_{\text{obs}} = N_{\text{T}} k_{\text{intr}} \eta \quad (3)$$

where k_{obs} and k_{intr} are the observed and intrinsic rate constants for the reaction (per active site), N_{T} the total number of active sites, and η the effectiveness factor.

Catalyst deactivation can be caused by (i) a decrease of the number of active sites (N_T decreases); (ii) a decrease of the quality of the active sites (k_{intr} decreases); and (iii) a degradation in accessibility of the pore space (η decreases).

Due to poisoning the number of active sites decreases

$$N_T = N_T(1 - \alpha) \quad (4)$$

where α is the fraction of the sites poisoned.

When poisoning takes place by strong adsorption of impurities in the feed, the poison molecules might well be most predominantly present in the outer shell of the particle, as adsorption is a fast process. This implies that the diffusion limitations increase (η decreases, Eq. (3)) and that catalyst deactivation is stronger than might have been expected.

The intrinsic rate constant, although presented as a constant, may change as a result of catalyst poisoning; When an impurity in the feed interacts with the catalyst, the chemical nature of the catalyst changes, and thus, the rate constant also changes. An example is the interaction of H_2S with transition metals leading to the formation of surface sulphides with a different activity than the original

metal species. The activity of the catalytic site can also be completely destroyed (k_{intr} becomes zero for this site), which results in reduction of the number of active sites. The catalyst effectiveness is also influenced by poisoning: for non-selective poisoning it increases.

Sintering is a function of time and temperature. Empirical correlations have been proposed for the catalyst activity as a function of both

$$\frac{da}{dt} = k_d a^m \quad (5)$$

$$k_d = k_{d0} \exp\left(-\frac{E_a}{RT}\right) \quad (6)$$

in which a is the catalyst activity and k_d the deactivation rate constant. The exponent m in Eq. (5) often has a value of two.

In general, fouling and sintering do not affect the intrinsic rate constant. Fouling results in physical blocking of the active sites and catalyst pores (e.g. by carbon or dust), and hence, affects both the number of active sites and the catalyst effectiveness. Sintering will also affect these variables. Fig. 8 summarises the phenomena responsible for deactivation and their influence on k_{obs} .

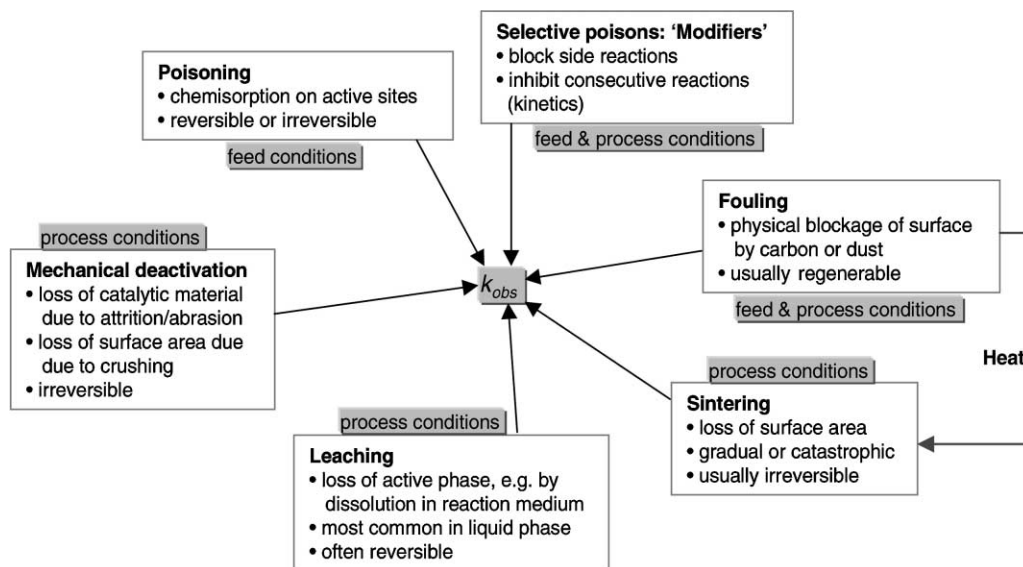


Fig. 8. Deactivation phenomena, their causes and effects.

4. Stability too low; what to do?

High conversions are often achieved with the fresh catalyst, but these conversions drop rather rapidly as the catalyst adjusts to the operating conditions and after that decay subsequent deactivation takes place continuously, although usually at a much slower rate. What options do we have? What can be done to eliminate or in any case reduce the unfavourable decrease in catalytic activity? And if this is not possible, can the activity be restored and how?

First, when the cause of deactivation is understood logical measures can be contrived, to begin with at the catalyst level. Second, a sound reactor and process design should be made, in which the deactivation and its cause are taken into account. Third, good engineering practice will imply optimisation of the operating conditions.

4.1. Measures on the scale of the catalyst particle

With respect to eliminating or limiting deactivation, improving the catalyst is most rewarding. It does not call for additional capital investment, and therefore, it is often economical. When poisoning is the problem, a more robust active phase or support might be selected. A good example is the replacement of alumina by titania in selective catalytic reduction (SRC). Alumina forms a surface sulphate with sulphur oxides, whereas titania is inert. This explains why the former deteriorates and the latter does not.

Another option is to optimise the catalyst texture. In hydrodemetallisation (HDM) of heavy petroleum fractions fouling by metal sulphide deposits results in pore blocking. Therefore, a wide-pore catalyst outperforms a small-pore catalyst, as the catalyst interior particle remains available for reaction longer (see Fig. 4).

Profiling of the active phase can be attractive. An egg-yolk profile will protect the active sites against poisoning and fouling when those processes are diffusion limited and the main reaction is not.

For the formation of carbon filaments the carbide phase might be the intermediate. The formation of this phase can be prevented by tuning the reaction conditions or by alloying the metal particles.

Sintering is easier prevented than cured as it is often irreversible. Sintering can be reduced by structural promoters or stabilisers. For example, the iron catalyst

used in ammonia production contains oxides like calcium oxide. Alloying can also give spectacular results. A good example is the classical catalytic reforming process where addition of Re to the Pt/alumina catalyst leads to strongly improved stability.

As discussed by Bartholomew [3], crushing strengths and attrition resistances of catalysts can be significantly improved, for example by using different preparation methods.

An example where attrition resistance of the catalyst plays a major role is in the production of maleic anhydride from butane [15,16]. From the viewpoint of temperature control (the reaction is highly exothermic) a fluidised-bed reactor is much more suitable than the conventionally used multi-tubular FBR. However, operation in a fluidised-bed reactor requires high attrition resistance. One solution is to incorporate the active catalyst ingredients in a matrix, but this decreases the activity and might lead to lower selectivity. A new technology, developed by DuPont, encapsulates the active material in a porous silica shell. The pore openings of the shell permit unhindered diffusion of the reactants and products, without affecting conversion or selectivity.

4.2. Tailored reactor and process design

4.2.1. Relation between time-scale of deactivation and choice of reactor

It will be clear that the time scale of deactivation influences the choice of reactor and need for regeneration. Table 4 gives a global indication for solid-catalysed processes. Fixed-bed reactors are suitable for catalysts that stay sufficiently active for at least

Table 4
Relationship between time scale of deactivation and reactor type (solid catalysts)

Time scale of deactivation	Typical reactor type
Years	Fixed-bed reactor, no regeneration
Months	Fixed-bed reactor, regeneration while reactor is off-line
Weeks	Fixed-bed reactors in swing mode, moving-bed reactor
Minutes–Days	Fluidised-bed reactor, slurry reactor; continuous regeneration
Seconds	Entrained-flow reactor (riser) with continuous regeneration

a few months. The process must be shut down for catalyst regeneration or for reloading the reactor with fresh catalyst. In that case, whenever possible, regeneration and/or reloading are incorporated in the periodical (partial) revision of the plant.

Fluidised-bed and slurry reactors are suitable for fast deactivation, because continuous catalyst replacement, and possibly regeneration, is easy with these reactors in principle. It should be remarked, however, that in the case of slurry reactors filterability of the catalyst is an important issue, which is often difficult to solve. In addition, attrition of the catalyst plays an important role for both reactor types. For extremely fast deactivation, entrained-flow reactors are employed, with continuous generation of the catalyst by cycling between the reactor and the (fluidised-bed) regenerator, as in FCC.

Exceptions always exist, like the fixed-bed dehydrogenation of propane with a deactivation time in the

order of 15–30 min. This process operates in with a swing reactor.

Depending on the process catalyst stability has to be assessed. For instance, in fine chemicals production the stability requested usually is much more modest than in bulk chemicals production and it generally does not determine reactor choice. The same reasoning applies to the reactor used. In slurry and fluidised-bed reactors the chemical stability is a point of less concern than in FBRs (and monolithic reactors), while the opposite holds for mechanical stability.

4.2.2. Engineering solutions allowing for regeneration

Often, there is not one best engineering solution. This is illustrated by the different reactor and regeneration technologies used in, e.g. catalytic reforming of naphtha [21,22], Fischer–Tropsch synthesis [23,24], and the catalytic dehydrogenation of alkanes for the

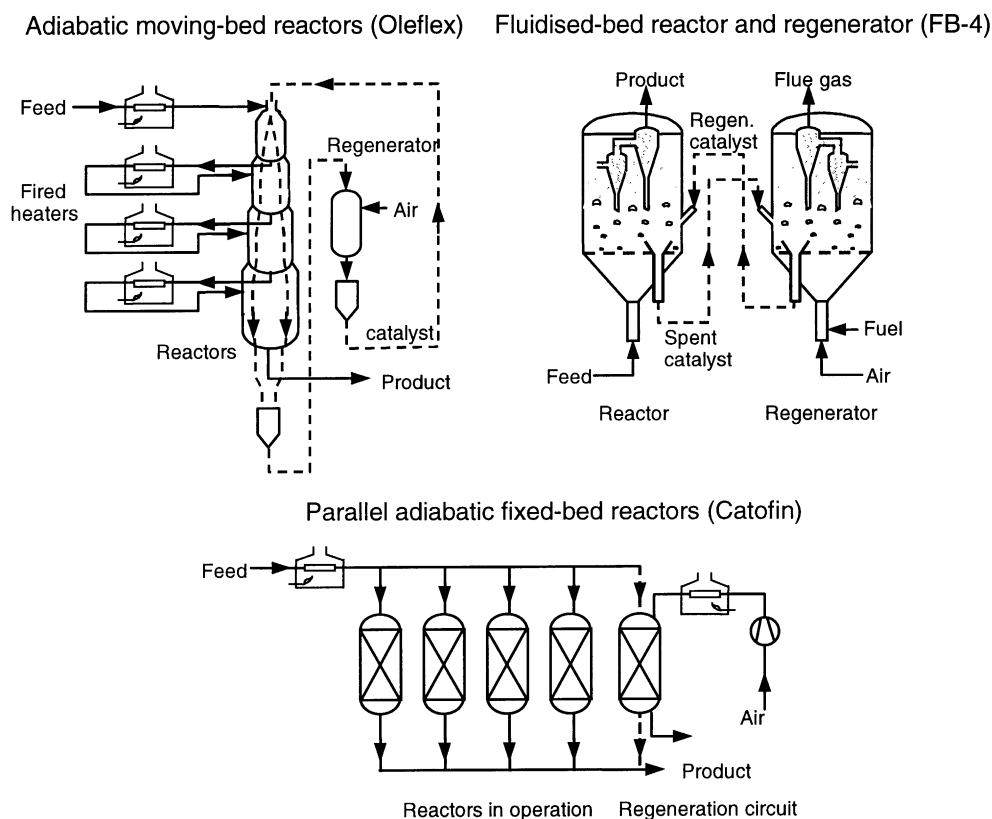


Fig. 9. Commercial technologies for alkane dehydrogenation.

selective production of specific alkenes [21,25–29], see Fig. 9. Because of the fast deactivation by coke formation during the dehydrogenation process, which has to operate at high temperature, different technologies have been developed to enable catalyst regeneration.

The UOP *Oleflex* process [26] uses three or four radial-flow moving-bed reactors, packed with a supported Pt catalyst, in series with interstage heaters, similar to the UOP continuous regenerative reforming process [21,22]. In the regeneration unit the coke is burned off the catalyst, the platinum is redispersed, and excess moisture is removed. The cycle time through the unit is between 2 and 7 days.

A key feature of the Lummus *Catofin* process [27] is the principle of storing the needed reaction heat in the catalyst bed. A supported chromium oxide catalyst is used in this process. Reactors (usually three to eight in parallel) are alternately on stream for reaction and off stream for regeneration by coke burn-off. During regeneration by burning the coke off the catalyst, the bed is heated, while this heat is consumed in the endothermic dehydrogenation reaction during the on-stream period. The cycle time between reaction and regeneration mode is typically between 15 and 30 min [21]. Regeneration in the Phillips steam active reforming (STAR) process [29], which uses multiple catalyst-packed tubular reactors in a firebox (similar to steam reforming processes), is also based on the swing-reactor concept. The catalyst used for dehydrogenation is a supported platinum catalyst promoted with tin. Carbon burn-off is required every 8 h [21].

The Snamprogetti–Yarsintez *FBD-4* design [25] is similar to older FCC units with continuous catalyst circulation between a fluidised-bed reactor and regenerator on a 30–60 min cycle [28]. Catalyst returning from the regenerator, where coke is burned off, to the reactor supplies the reaction heat. The catalyst used is a promoted chromium oxide powder with high attrition resistance.

This example shows that different engineering solutions are possible for the same problem, depending on factors such as choice of catalyst, relation between chosen process conditions and catalyst deactivation, and maybe most importantly, company experience; the processes discussed are all based on technology that was already in use for other processes.

4.3. Good engineering practice

4.3.1. Feed purification

When the feed contains a poison, adequate purification is the answer. Usually this will be done upstream the reactor. It could also be advantageous to profile the reactor by positioning a layer of material that traps the poison on top. In the case of fouling inert porous balls are suitable.

A trivial way of solving the deactivation problem can be to overdesign the bed. As the catalyst itself might well be a perfect trap, after start-up the top layers will be slowly deactivated and in that way protect the remainder of the bed. This procedure is quite common: under quasi steady-state conditions the reactor consists of three parts: a deactivated toplayer, a layer where full conversion is achieved and an active layer that is not yet used for conversion. With increasing time-on-stream the reacting part of the bed moves towards the end while the deactivated part increases in size.

4.3.2. Optimising reaction conditions

Obviously, deactivation very much depends on the reaction conditions. A good example is coke formation in steam reforming. At high excess of steam coke deposition is strongly diminished, mainly due to increased coke removal rate.

The temperature is usually also quite critical. A good example is the Pd/C catalysed selective hydrogenation of CCl_2F_2 into CH_2F_2 . At an $\text{H}_2/\text{CCl}_2\text{F}_2$ ratio of 12 and a pressure of 0.2 MPa extended stability studies were performed. Above 500 K deactivation strongly increased with the temperature. When the temperature was kept below 510 K a satisfactory stability (on a months scale) was observed [30].

4.3.3. Optimal conditions as function of time-on-stream

In practice, the process conditions will be adapted such that during a certain period of time a stationary level of activity is maintained. Usually, this is done by increasing the operating temperature gradually to compensate for activity loss, often at the expense of selectivity. It is unavoidable that the higher temperature results in accelerated deactivation. At a certain time-on-stream (varying from seconds to years),

deactivation cannot be compensated for any more, resulting in a fast decline, as shown in Fig. 3.

5. Concluding remarks

Catalyst deactivation is an important issue in the petroleum refining and chemical industries. It plays an important part in process design and operation. The five main causes of deactivation are: poisoning, fouling, thermal degradation (sintering, evaporation) initiated by the often high temperature, mechanical damage and corrosion/leaching by the reaction mixture. In the first two cases, the catalyst might be regenerated in some way. Sintering, evaporation and leaching sometimes also can be cured, but here usually the best strategy is prevention.

Several measures can be taken to decrease the rate of deactivation, or else, to restore the catalyst activity. The best action is to improve the intrinsic stability by tailoring catalyst properties such as the active phase, the texture, the diffusion length (particle size, active phase profile), reaction conditions and phases present (gas, liquid, near critical). An obvious action is adequate purification of the feed, to prevent poisoning and some types of fouling. When those measures are not sufficient, more chemical reaction engineering solutions can be applied such as dedicated reactor set ups with catalyst moving between a reaction zone and a regeneration zone. This is an example of transient operation [31], i.e. the catalyst is not kept at the same place but cycled between two different environments: in one it acts in the designed way, in the other it is regenerated.

References

- [1] R.J. Farrauto, C.H. Bartholomew, *Fundamentals of Industrial Catalytic Processes*, Blackie, London, 1997, p. 265.
- [2] P.W.N.M. Van Leeuwen, *Appl. Catal. A: Gen.* 212 (2001) 61.
- [3] C.H. Bartholomew, *Appl. Catal. A: Gen.* 212 (2001) 17.
- [4] M.F.M. Zwinkels, S.G. Järås, P.G. Menon, in: A. Cybulski, J.A. Moulijn (Eds.), *Structured Catalytic Reactors*, Marcel Dekker, New York, 1998, p. 149.
- [5] C.S. Satterfield, *Heterogeneous Catalysis in Industrial Practice*, 2nd Edition, McGraw-Hill, USA, 1991 (Chapter 6).
- [6] C. de Bellefon, P. Fouilloux, *Catal. Rev.-Sci. Eng.* 36 (3) (1994) 459.
- [7] C.S. Satterfield, *Heterogeneous Catalysis in Industrial Practice*, 2nd Edition, McGraw-Hill, USA, 1991 (Chapter 4).
- [8] J.P. Janssens, *Characterisation, Testing and Deactivation of Sulfided Catalysts in the Hydrodemetallisation of Vanadyl-Tetraporphyrin*, Ph.D. Thesis, Delft University of Technology, The Netherlands, 1996 (Chapter 8).
- [9] P. Chen, H.-B. Zhang, G.-D. Lin, Q. Hong, K.R. Tsai, *Carbon* 35 (10/11) (1997) 1495.
- [10] P. Arnoldy, J.A. Moulijn, *J. Catal.* 93 (1985) 38.
- [11] G.W. Bridger, M.S. Spencer, in: M.V. Twigg (Ed.), *Catalyst Handbook*, 2nd Edition, Manson Publishing, London, 1996, p. 441.
- [12] M.V. Twigg, D.E. Webster, in: A. Cybulski, J.A. Moulijn (Eds.), *Structured Catalytic Reactors*, Marcel Dekker, New York, 1998, p. 59.
- [13] L.L. Hedegus, R.W. McCabe, *Catal. Rev.-Sci. Eng.* 23 (1981) 377.
- [14] P. Forzatti, L. Lietti, *Catal. Today* 52 (1999) 165.
- [15] J.J. Lerou, P.L. Mills, in: M.P.C. Weijnen, A.A.H. Drinkenburg (Eds.), *Precision Process Technology*, Kluwer Academic Publishers, Dordrecht, 1993, p. 175.
- [16] R.M. Contractor, H.E. Bergna, H.S. Horowitz, C.M. Blackstone, B. Malone, C.L. Torardi, B. Griffiths, U. Chowdhry, A.W. Sleight, *Catal. Today* 1 (1987) 54.
- [17] T.A. Nijhuis, A.E.W. Beers, Th. Vergunst, I. Hoek, F. Kapteijn, J.A. Moulijn, *Catal. Rev.-Sci. Eng.* (2001) in press.
- [18] J.P.A. Neeft, M. Makkee, J.A. Moulijn, *Fuel Process. Technol.* 47 (1996) 1.
- [19] M.V. Twigg, A.J.J. Wilkins, in: A. Cybulski, J.A. Moulijn (Eds.), *Structured Catalytic Reactors*, Marcel Dekker, New York, 1998, p. 91.
- [20] M.V. Twigg, R.A. Sheldon, *App. Catal. A: Gen.* 212 (2001) 175.
- [21] R.A. Meyers (Ed.) *Handbook of Petroleum Refining Processes*, 2nd Edition, McGraw-Hill, 1997.
- [22] S.T. Sie, *App. Catal. A: Gen.* 212 (2001) 129.
- [23] M.E. Dry, *Catal. Today* 6 (3) (1990) 183.
- [24] S.T. Sie, *Rev. Chem. Eng.* 14 (2) (1998) 109.
- [25] P.R. Sarathy, G.S. Suffridge, *Hydroc. Process Feb.* (1993) 43.
- [26] P.R. Pujado, B.V. Vora, *Hydroc. Process March* (1990) 65.
- [27] S. Gussow, R. Whitehead, in: *Paper Presented at the 1991 NPRA Annual Meeting*, San Antonio, TX, 17–19 March 1991.
- [28] N. Calamur, M. Carrera, in: J.I. Kroschwitz, M. Howe-Grant (Eds.), *Kirk-Othmer Encyclopedia of Chemical Technology*, Vol. 20, 4th Edition, Wiley, New York, p. 249.
- [29] R.O. Dunn, F.M. Brinkmeyer, G.F. Schuette, in: *Paper Presented at the 1992 NPRA Annual Meeting*, New Orleans, LA, 22–24 March 1992.
- [30] A. Wiersma, E.J.A.X. van de Sandt, M. Makkee, J.A. Moulijn, *App. Catal. A: Gen.* 212 (2001) 233.
- [31] A. Zwijnenburg, A. Stankiewicz, J.A. Moulijn, *CEP*, November, 1998.