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But will it last until the shutdown? Deciphering catalyst decay!

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Abstract

This paper is concerned with the study of decay of industrial catalysts, both in the plant and in the laboratory. Techniques are described for deciphering the characteristics of catalyst decay in the industrial plant, using plant performance data and post-mortem characterization. Simulated examples are used to show how such data can be used to construct simple decay models. The detailed investigation of decay kinetics in the laboratory usually requires the use of gradientless reactors. However, even studies in a single-tube, plug-flow reactor can provide useful insight into decay kinetics, especially if segmental catalyst discharge and recharge is possible. With parallel testing in multi-tubular catalyst test units there are even greater possibilities. Accelerated decay techniques are frequently used in industry for comparative evaluations of catalyst performance. Accelerated decay is a valuable tool but only if it is used wisely. A simple index is proposed for the purpose of judging the validity of test procedures for accelerated decay.

Keywords: Catalyst life; Activity; Selectivity; Plant; Decay; Deactivation; Aging; Testing; Parallel; Difference; Accelerated; Kinetics; Models

1. Introduction

No catalyst study, industrial or academic, is complete without some description of catalyst stability. Yet, research into catalyst decay receives less attention in the open literature than the discovery of new catalysts, even though most of these will never be commercialized. The study of process catalyst decay is both less glamorous and more difficult than new catalyst discovery. It requires multi-disciplinary skills, suitable equipment, detailed knowledge of process conditions and feedstock, and, in most cases, time and patience. Yet, the pay-back time for industrial research into process catalyst decay can be very short.

The cost of decay is not simply the cost of a replacement catalyst charge, which is usually a small fraction of the overall unit manufacturing cost. It also includes increased raw material and energy usage and the shut-down costs and lost production during the catalyst change. The environmental costs of increased by-product waste and waste catalyst disposal may also be considerable.

In industrial research there is generally more interest in the kinetics of catalyst decay than in the detailed surface mechanism. In order to make progress and to meet deadlines, approximate descriptions of the decay tendencies of several alternative catalysts will often be more useful than a laborious, detailed study of a single catalyst that could turn out to be unsuitable. Studies of catalyst decay may be concerned with selection of the most suitable catalyst for the plant or for the next stage of development, with prediction of the expected life in the plant, or with the optimization of catalyst life. Life prediction and optimization require monitoring of the catalyst performance in the process, and hence the title of this paper. The aim is to present some useful techniques for interpreting the impact of catalyst decay. The focus is mainly on approximate techniques,

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suitable for industrial research, but some techniques will also be applicable in academic research.

Solid catalysts are used in a wide range of industrial processes, e.g., catalyst pellets in fixed beds, powders in fluidized beds and slurry reactors. The systems can be two-phase (l–s or g–s) or three-phase (g–l–s). The reaction conditions can be oxidising or reducing, the temperature and pressure can vary from mild to severe. The feedstocks may include very pure, individual components or complex mixtures of variable composition. The timescale for industrial catalyst decay can vary from fractions of a second, in between the regeneration cycles of fluidized catalytic cracking, to several years for catalysts in fixed beds. The scope of catalyst decay is therefore very wide and so the examples presented in this paper are necessarily limited to some of the most common situations.

2. Kinetics of catalyst decay

The kinetics of catalyst decay can be studied at three levels, fundamental, semi-empirical and empirical. In a fundamental study, the decay kinetics is related directly to changes in the active sites of the catalyst, e.g., use of Langmuir–Hinshelwood expressions for the kinetics of the main reaction and a parallel poisoning decay reaction [1]. In a semi-empirical study, the actual decay kinetics is related by an empirical expression to the rate of some measurable change on the catalyst, e.g., increase in carbon content [2]. In an empirical study, the decay kinetics is described directly in terms of the local reaction environment by empirical power-law expressions [3a,3b]. In practice, most industrial studies of catalyst decay are semi-empirical or empirical.

The principle of separability is frequently assumed in studies of catalyst decay so that the kinetics of the main reaction and the kinetics of the decay reaction can be resolved. The term 'separability' was first used by Szépe and Levenspiel [3c]. According to this principle, the rate r_t of the main reaction at any time t is the product of two separable terms

$$r_t = f_1(C, T) f_2(a) \tag{1}$$

Function f_1 describes the kinetics of the catalytic reaction and is time-independent. Function f_2 describes the current activity a (relative to some standard condition a_0) and is time-dependent. The physical basis of this principle is that there is negligible effective linkage between f_1 and f_2; the decay reaction reduces the number of active sites for the main reaction but causes no other change to its kinetics.

The principle of separability has been applied to a large number of decay studies and its validity has been assumed in the categorization of decay kinetics, described below. In general, authors agree that the assumption is adequate for most cases but there are circumstances where this assumption is not justified. The terms could be non-separable due to the physical non-equivalence of active sites, e.g., non-homogeneous surfaces containing sites which have a significant range of activity and which decay at different rates [4], or to non-linearity in the site balance equation [4,5,6]. Eq. (1) would also not apply if the decay reaction results, not in the total deactivation of the active site, but in some modification that causes a change to $f_1(C, T)$, e.g., a change in the activation energy E_r of the main reaction.

Following Levenspiel's approach [3a,3b], the deactivation kinetics of solid catalysts can be described by simple power-law expressions of the general form

$$-\frac{\mathrm{d}a}{\mathrm{d}t} = k_\mathrm{d}\{C_1^{n1} C_2^{n2} \cdots C_i^{ni}\} a^m \tag{2}$$

where k_d is the deactivation rate constant, a the activity at time t relative to fresh catalyst, m the order of the deactivation, C_1–C_i the concentrations of components of the fluid phase, n_1–n_i the orders of the concentration dependencies. E_d (see later) is the corresponding activation energy for decay.

Levenspiel described four main categories of decay kinetics: (a) parallel, (b) series, (c) side-by-side and (d) independent [3a,3b]. Types (a)–(c) have concentration dependency on, respectively, reactants, products, and feedstock poisons. Independent decay has no concentration dependency. More complex cases could have mixed concentration dependency (reactants, products and/or impurities), e.g., decay reactions within reaction networks, or even the depletion of feed components (concentration dependency with negative order).

Power-law expressions have been found to be suitable for a wide variety of decay reactions. They are generally applied to a single mechanism for activity decay although in some cases different decay processes may predominate simultaneously in different parts of the catalyst bed. More complex expressions may be required if different decay processes are interdependent in some way.

Obviously, if the principle of separability is not an adequate approximation then the above expressions will not apply and more complex expressions will be required to fit observed decay data, e.g., dependence on quantity of accumulated coke or changing deactivation order with degree of deactivation for single site poisoning and multiplet site adsorption [5,6]. Likewise, if the function $f_1(C, T)$ changes significantly during deactivation then additional terms will be needed in the above decay equations.

In some deactivations, the activity does not decay to zero. A decay expression which seems adequate for decay over short periods may need to be modified if test data extend over a longer timescale. One example is the sintering of supported metals but the phenomenon of a residual or steady-state activity is reported to occur more generally [7]. In generalized power-law expressions, the activity a is replaced with a–a' where a' represents a limiting, steady-state value [7]. It is important that the decay is studied for a sufficiently long period to justify the additional parameter a'. Otherwise, there is the danger that the additional parameter might simply compensate for poor experimental data, an unsuitable power-law expression, or even non-separable kinetics. However, the lack of a term for the steady-state value can also be compensated by unusual features of the power law. In some cases, the use of generalized power-law expressions has been found to lead to a reduction in the apparent deactivation order m, implying simpler, and hence, more plausible deactivation kinetics [7]. In the case of sintering, the meaning of a' can be interpreted in terms of the surface equilibrium particle size distribution [8].

Note that independent decay kinetics cannot be assumed for catalysts that decay due to sintering processes. The kinetics of sintering of supported metal particles and the equilibrium metal dispersion may both be influenced by the fluid composition [9a,9b] and so catalyst deactivation may show dependence on concentration terms, e.g., C_{H_2O}, C_{O_2}, C_{H_2}. The sintering rates of oxide supports may also depend on fluid composition, especially C_{H_2O}.

The study of selectivity decay (or even, in some cases, selectivity gain) adds a further degree of complexity to catalyst decay and this is discussed later in more detail.

3. Influence of composition and temperature gradients on decay

3.1. Pore resistance

If the pore resistance to diffusion is significant compared to the reaction rate then concentration gradients for reactants and products will occur within catalyst pellets (Fig. 1). Decay types (a)–(c) are affected differently by pore diffusion resistance [3a,3b,10,11]. Decay type (a), parallel deactivation, tends to occur close to the pellet exterior where most of the main reaction takes place. The decay front may occupy a thin shell at the outside of the pellet, moving inwards as the catalyst deactivates. Decay type (b), series deactivation, occurs more in the pellet interior where the product concentration is higher, leading to development of a decay front from the inside of the pellet outwards.

For decay type (c), feedstock poisoning, the influence of pore resistance is potentially more complex [11]. Either the main reaction or the deactivation reaction may be influenced by the pore resistance or both may be influenced to similar or different extents, depending on their respective reaction and diffusion rates within the pellet. For a fast poisoning reaction with high diffusion resistance the decay occurs mainly at the pellet exterior, i.e., pore-mouth deactivation. The main reaction may experience increasing diffusion limitation as an increasing proportion of the

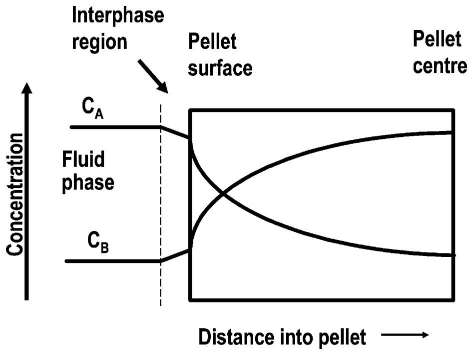


Fig. 1. Schematic intra-pellet concentration gradients of reactant A and product B due to pore diffusion resistance.

remaining active sites are situated deeper inside the pellets. Pore-plugging is an extreme case of pore-mouth deactivation in which access into the pores for the reactants becomes completely blocked, leading to a catastrophic loss of activity. At the other extreme, for a slow poison reaction the impact of pore diffusion resistance will be low and the decay will occur uniformly throughout the pellet.

Decay processes with more complex fluid composition dependence may likewise vary throughout the pellet. However, decay type (d), being independent of fluid composition, should be invariant throughout the pellet unless there are temperature gradients as well.

The optimum pellet design for catalyst life thus depends on the decay kinetics. For series decay, low pore resistance may be desirable to minimize the internal concentration of reaction product. Strong pore-resistance to a reactive feedstock poison may help to protect the activity of the pellet interior for the main reaction. The optimum design may require a more subtle balance between the respective reaction rates and diffusion rates in the pellet for the main reaction and a poisoning reaction.

The empirical power-law expressions described earlier are frequently applied to catalyst pellets without allowance for any effect of pore-resistance on decay rate. The parameters determined by fitting these expressions to observed decay data might be influenced by these effects and, if so, the values determined for crushed catalyst pellets will not be valid for whole pellets without some further allowance for the effect of intra-pellet gradients. Likewise, the parameters determined from accelerated decay tests might also be affected by changes to the composition gradients within pellets (see later).

3.2. Axial gradients

Concentration and temperature gradients within the catalyst bed affect decay types (a)–(d) differently. Parallel deactivation is more severe in regions of the bed where the concentration of reactants, and hence the rate of the main reaction, is high, e.g., initially at the front of isothermal beds, maybe closer to the peak temperature zone of non-isothermal beds. During the catalyst decay, the zone of peak activity and the deactivation front both move down the bed, sometimes leading to a sudden drop in conversion when the active catalyst is exhausted. The change in the overall catalyst performance over time is then a combination of integral reaction kinetics with mean-bed, integral decay kinetics. This is illustrated for an isothermal case in Fig. 2a and b. An observer following performance from the exit conversion might conclude that this catalyst was stable for 12 months and then started to decay. An observer following performance from the mid-bed conversion would realize that the catalyst was decaying right from the start. Similar considerations apply to the observed selectivity, as discussed further below. In non-isothermal cases, where a peak temperature zone moves along the bed, the fall-off in conversion at end of life will be even more abrupt.

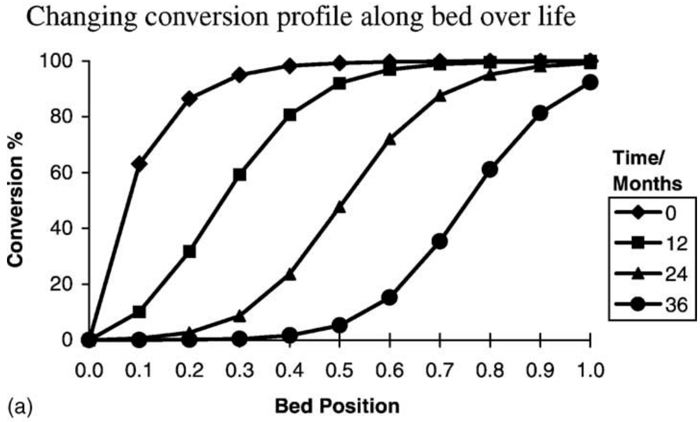
Series deactivation increases towards the end of isothermal and adiabatic reactor beds where the product concentration is greatest and, for adiabatic beds, the temperature is also greatest. For non-isothermal beds it may be most severe in the peak-temperature zone. The profile of side-by-side (feed poison) deactivation along the bed will show a peak at the front of the bed for very reactive poisons or be more uniform along the bed, depending on the kinetics of the deactivation reaction.

4. Process design and reaction engineering

Industrial processes are designed to achieve the target process capacity over the design catalyst life, i.e., the time between planned shutdowns. The reactor design (type, size, number of tubes or vessels) should allow for suitable reaction conditions for both the target capacity and the target catalyst life. This implies control of temperature and composition gradients.

The reaction kinetics and the decay kinetics are frequently known only approximately. Petersen [12] has commented “I have always been impressed by the success that an intelligent engineer can achieve with limited data when it is supplemented by an indefinable intuition and a few model calculations. This works largely because the magnitude of the reactor design integral is not terribly sensitive to the exact shape of the rate function so long as it has approximately the right general shape”.

One disadvantage of approximation is that reactors may be oversized in order to allow for uncertainty. In general, better knowledge of catalyst decay leads to


Changing conversion profile along bed over life

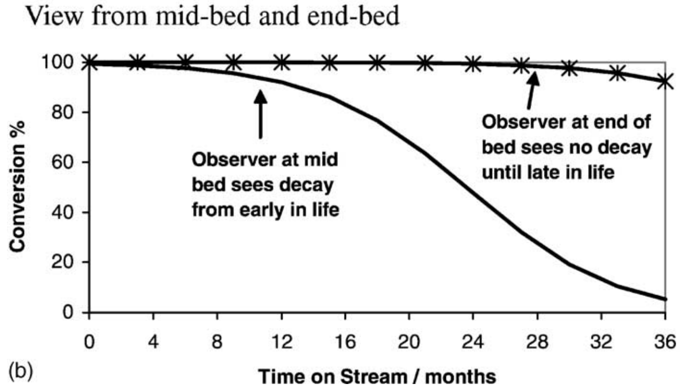

View from mid-bed and end-bed

Fig. 2. Parallel deactivation in an isothermal bed.

better reaction engineering and to longer catalyst life, but, as mentioned already, there is usually a compromise to be made between the detail and the deadlines.

There are many ways in which the catalysis and the reaction engineering can be integrated to reduce catalyst decay. The aim is to achieve a suitable combination of reaction conditions and catalyst formulation. The reaction temperature can be controlled, for catalyst life as well as for reaction control, by selection of an isothermal reactor, or the temperature rise can be limited by the use of several adiabatic reactors in series with inter-cooling or intermediate injection of cold feedstocks. The reactant concentrations can be controlled by use of multiple feedstock injection points in single fixed beds, or of intermediate injection points for reactors in series. The exposure of catalyst to reaction product can be limited by operation at low conversion or by avoidance of excessive catalyst volume at the start of life (a reserve secondary bed can be brought into operation when the catalyst in the main bed has partially decayed). The use of guard beds (absorbents, hydrotreaters, etc.) to protect from poisons is well-known.

As discussed above, the design of the catalyst pellet is important and, self-evidently, the nature and composition of the catalyst is crucial. A non-uniform catalyst composition may even be preferred. If the decay process is especially severe in one region of the bed then it may be better to use a special, decay-resistant catalyst formulation in that region, and a different formulation in the rest of the bed. This approach has been adopted for the steam reforming of hydrocarbons; an alkalized Ni/Al_2O_3 catalyst is used in the upper bed to provide better resistance to carbon lay-down, and a non-alkalized formulation is used in the rest of the bed [13]. Different catalysts with quite different functions can even be combined with novel reaction engineering (inter-zone feed and partial product removal) into a single reactor, e.g., hydrodesulphurization followed by catalytic hydrogenation as in the Synsat process [14].

In some processes the catalyst decay is so rapid that the process is designed around the decay by incorporation of on-line regeneration and/or partial catalyst replacement (e.g., FCC).

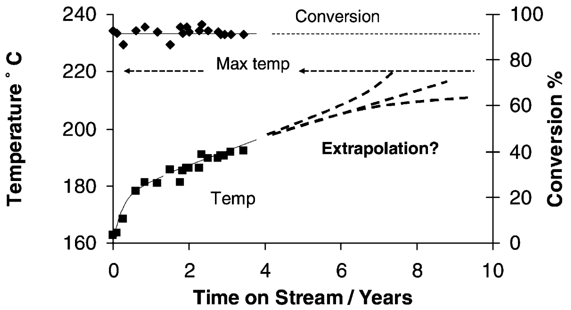
5. Process catalyst monitoring

The ultimate test of a catalyst is its performance in the process. Frequently more information can be derived from the study of plant catalysts than is possible in a research study. The monitoring and study of in-plant catalyst performance is an important but sometimes neglected part of process optimization.

Ideally, monitoring should commence with sample-testing of fresh catalyst for uniformity. The charging procedure for the plant reactor should be monitored to ensure careful handling and even loading. Clumsy loading can cause broken pellets, excessive dust formation and uneven packing, all of which can lead to uneven flow patterns and, consequently, uneven catalyst decay. The activation and start-up behaviour should be recorded, at least as evidence of proper operation in case the subsequent catalyst performance is disappointing.

Process data should be available from plant log-sheets or automated data collection systems, e.g., feed rates and compositions, reactor temperature profiles, analyses (in situ or remote) of the crude product stream and any inter-reactor streams, possibly even in situ analyses of the intra-reactor fluid composition. It is important to design the plant reactor instrumentation so that catalyst decay can be monitored. Adequate provision should be made for measurement devices such as temperature sensors, in situ analytical probes, catalyst sampling devices (for powder catalysts), etc.

In simple cases the plant catalyst can be monitored directly from plant data. An example is shown in Fig. 3 for a supported Ni catalyst that was used in the manufacture of ethylamines from ethanol and ammonia. The catalyst was operated isothermally in a multi-tubular reactor with gradually increasing temperature over life to maintain overall activity and hence constant conversion. The catalyst had previously been replaced after ∼4.5 years in the plant. Could it last for longer? The activity was expressed in terms of the required operating temperature to achieve target ethanol conversion at a set ethanol feed rate. The observed temperature trend from plant operating data could be extrapolated linearly but there was no knowledge about the actual decay profile within the catalyst beds. There was a risk that the required temperature might start to increase more rapidly and exceed the plant maximum value, leading to an unplanned shutdown for a catalyst change. The catalyst performance was monitored carefully over the next 5 years. Ultimately, this catalyst outlasted the plant. Note that the relative selectivity to the three amine products and to by-products was important as well.



Notes: proprietary ethylamines catalyst (Ni/ kieselguhr);
data selected at constant feedrate and target conversion.

Fig. 3. Monitoring catalyst decay directly from plant data. Variation of isothermal reactor temperature over catalyst life.

More complex, non-isothermal cases may require the periodic return to standard operating conditions or the use of a reactor model. These studies can provide valuable background information, depending on the available data, e.g., change in activity with position in the bed. If the activity of a powder (slurry) catalyst is not rate-limiting during early life then its initial decay will have no impact on reaction rate. The decay might not become obvious until the catalyst is almost spent, again leading to an unplanned plant shut-down. In order to monitor the decay it may be necessary to remove samples of the catalyst periodically throughout its life for ex-reactor measurements of activity. Alternatively, an in situ analytical probe could be set up to detect the first signs of reaction limitation due to catalyst decay.

Table 1
Physical and chemical characterization of catalyst decay

Sample size: average local bed values vs. inter-pellet variability
Depth profiles within pellets (analysis at pore-mouth vs. interior)
Catalyst properties
- Bulk chemical analysis: catalyst and deposits
- Phase identification, morphology: XRD, TEM, SEM
- Surface area: sorption techniques
- Crystallite size: XRD; TEM/SEM + particle counting
- Pore structure: porosimetry, sorption techniques
- Surface composition and structure: XPS, SAM, etc.

6. Post-mortem characterization

The aim of post-mortem characterization of discharged plant catalyst is to determine where, why and by how much it has decayed. Inspection of the catalyst beds and representative sampling of catalyst from carefully defined locations should be planned as part of the discharge schedule. Catalyst activity and selectivity can be measured in standard tests for samples from each location. Other diagnostic reaction tests may be used to measure particular catalyst functions, e.g., alkane cracking activity for Bronsted acidity, nitrobenzene reduction activity for hydrogenation. The decay profile can then be related to the operational conditions during life and the observed performance changes. Important physical and chemical properties should also be characterized and the results correlated with catalytic performance. This should provide powerful diagnostic evidence of the causes of decay.

Some catalysts, e.g., high area Ni hydrogenation catalysts, require deactivation by oxidation before discharge and so the decay profile cannot easily be measured. However, the chemical and physical state of discharged samples can usually be characterized to some extent. There are many measurable physical and chemical characteristics of catalysts (see Table 1). The full characterization of a catalyst bed is usually a major undertaking. It is important to identify and focus effort onto those characteristics that are the most relevant to the decay process.

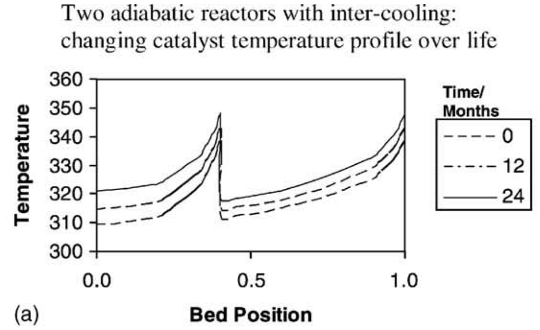
7. Prediction of the plant catalyst performance

In order to predict the plant catalyst performance it is necessary to have some knowledge of the decay mechanism and the decay kinetics, or better still, a plausible decay model. There are two sources of data for the model parameters: experimental investigation and plant data.

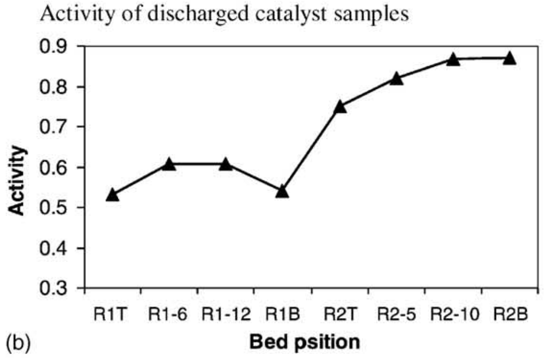
The use of plant catalyst operating data combined with post-mortem catalyst characterization to construct a simple decay model is illustrated by a simulated example for parallel catalyst decay. The example is based on two adiabatic reactors in series, with intercooling. The reactors are operated to maintain constant conversion and equal exit temperatures. The simulated temperature profile over life is shown in Fig. 4a, based on first-order reaction kinetics and simple first-order decay kinetics. The inlet temperature for R1 starts off lower than that for R2 but increases faster. The changing temperature profiles immediately suggest either parallel decay or feed poisoning (side-by-side) decay.

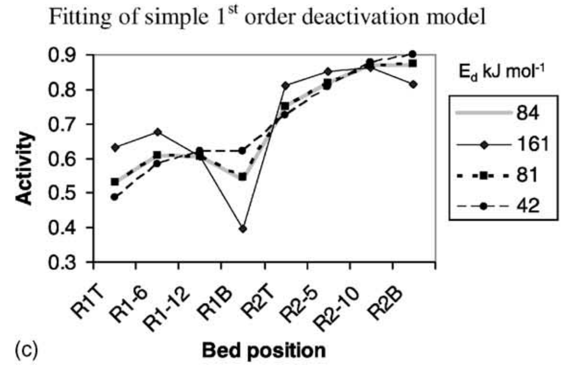
After discharge of the catalyst the activities of eight samples, which have been collected from well-defined points along the two catalyst beds, are measured experimentally. See Fig. 4b. These are the ‘product’ samples of the decay reaction, each with a unique history of temperature and composition during its time in the plant. If additional samples can be collected during mid-life shutdowns, then time can be a variable as well. Just as other sets of reaction ‘products’ can be fitted to reaction models, these decay data can be fitted by trial and error to a decay model. In this example, the plant temperature profiles and the inter-reactor conversion values over life have also been included in fitting the decay model. The model was based on Eq. (4) with one reactant concentration term and $n = 1$. The parameters A_d and E_d were optimized to give the best-fit to the observed decay profile. See Fig. 4c. The parameters which gave the best-fit were close to the values selected in the original simulation.

The above example was idealized but this approach works in real cases. Decay profiles can provide approximate decay kinetics, provided that sufficient data are available. For feedstock poisoning, however, this approach can only work if the poison concentration is either constant or measured throughout the catalyst life. Moreover, it might not be possible to distinguish between parallel and feed-poison decay. Obviously, modelling will be considerably more difficult if there is more than one type of decay, i.e., poisoning at the front of the bed, sintering at the rear. The estimated



Basis: spreadsheet approximation, multiple finite elements, 1st order exothermic reaction, simple 1st order parallel decay.





Basis: known bed temperature profile and inter-reactor conversion data over life of catalyst; post-mortem activity data available for catalyst retrieved from 8 positions; numerical fitting, beds divided into multiple finite elements; select values for E_d and optimize value of A_d to minimize objective function $\Sigma(a_{obs}-a_{calc})^2$. See equation 4 for definitions of E_d and A_d. Note: shaded line represents simulated discharge sample set generated with $E_d = 84$ kJ mol-1.

Fig. 4. Simulated use of plant data and post-mortem characterization for simple decay modelling.

parameters might not be very accurate or precise due to the cumulative effect of errors in plant data, sampling locations and experimentally determined activity values. Moreover, A_d and E_d tend to be mutually compensating in model-fitting. However, the approximate model from one plant charge can be improved with data from later catalyst charges, particularly if these are used for different times in the plant.

Even an approximate model can provide sufficient insight to suggest process improvements. In the above example, the lifetime performance might be improved if the R1 inlet temperature is kept constant and R2 is made to take up progressively more workload over life. Maybe the reaction engineering could be modified, e.g., the relative sizing of R1 and R2. Maybe the process could be improved by development of different catalyst formulations for R1 top and bottom and R2. If selectivity decay can also be modelled then it may be possible to optimize the overall lifetime selectivity. Even if the model is too approximate to provide definitive answers then it may at least provide sufficient financial incentive to justify an experimental programme to develop a more accurate model.

8. Measurement of catalyst decay in the laboratory

Industrially relevant catalyst decay data can be measured in the laboratory but the test conditions must be considered carefully. Most decay processes are slow and so require either long experiments or accelerated conditions. The reactor design must be suitable for the purpose, as discussed in more detail below. It may be possible to make valid and useful measurements on crushed pellets or it may be essential to use whole pellets. This decision requires some knowledge of the decay kinetics and mechanism and the influence of the pore properties and pellet size on decay rate.

In some cases it is essential to use feedstock obtained from the plant but in other cases a mixture of laboratory-grade reagents may be preferred for control and reproducibility. Some plant feedstocks are very pure and so trace impurities in laboratory reagents could cause the measured decay rate to be exaggerated. Some plant feedstocks contain complex impurities which influence decay processes and these must be present for realistic investigations of decay. Other impurities, which cause an additional, minor decay process at the top of the plant catalyst bed, may be disregarded in the laboratory. Some plant feedstocks may even contain impurities that do not affect the decay in the plant but could do so in a laboratory unit. In one study each catalyst charge in the laboratory unit decayed abruptly after exposure to a similar, cumulative quantity of plant feedstock. This did not happen on the plant. A trace polymeric impurity, which was retained in a plant vapourizer, was fed to the catalyst in the laboratory unit, causing a new decay process that was of no relevance to the plant operation. This was proven by comparing the results from (a) plant feedstock (b) plant feedstock passed through a guard-bed of inert absorbent (c) part-distilled plant feedstock (d) research grade reagents. The decay rates for (b), (c) and (d) were all slower compared to (a). It is necessary to confirm that the decay characteristics are similar for decay at plant scale and at laboratory scale and also that the physical and chemical changes, measured in post-mortem testing, are similar in nature. This may be difficult. For instance, the extraction and identification of the polymeric impurity, referred to above, were very difficult. The test with the guard-bed was the main break-through.

9. Measurement of decay kinetics

Returning to the general decay expression in Eq. (2), it is apparent that the measurement of detailed catalyst decay kinetics is a complex problem if there is any concentration dependence. For independent decay there is no concentration dependence and it is possible to determine the kinetic parameters of the decay reaction from integral measurements in a plug-flow reactor [3a,3b]. If the independent decay is not first-order then parameters must be determined from the integral data by trial and error until the best-fit is found [3b].

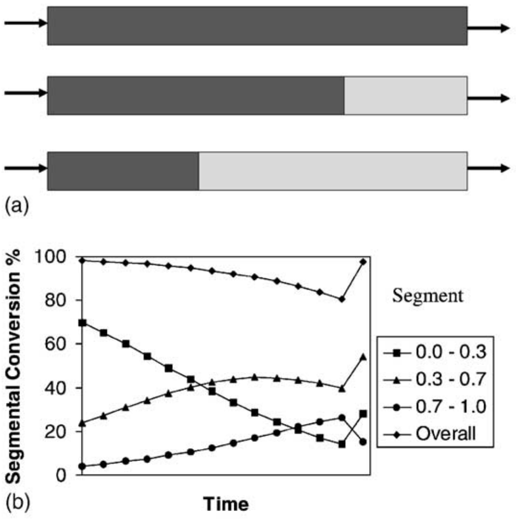
For exact studies of concentration-dependent, catalyst decay kinetics it is necessary to decouple the activity and concentration effects in Eq. (2). This requires a gradientless reactor with intensive back-mixing of reactants and products, e.g., the Berty and Carberry designs of autoclave reactor or fixed-bed reactors with external recycle of the fluid phase. Levenspiel describes techniques for the identification of catalyst decay kinetics in gradientless reactors with controlled variation of feed rate to decouple the activity and concentration effects [3]. The feed rate is gradually reduced as the catalyst decays so that the target concentration term (reactant, product or poison) is kept constant. This process can be automated using feedback from analysis of the product stream [4,15]. The deactivation order m is found by trial and error fitting to a series of derived expressions. Once m has been determined, the concentration dependency and E_d can also be determined by suitable experiments. More complex decay kinetics will require appropriate experimental designs, covering multiple concentration dependence.

It is difficult to investigate concentration-dependent catalyst decay kinetics in an integral, fixed bed reactor. Even with operation at fixed conversion, the axial concentration profile causes the catalyst decay rate to vary along the bed and, in consequence, the axial concentration profile also varies over time. The composition at the reactor exit is the net effect of integral reaction kinetics combined with location-dependent, integral decay kinetics. Nevertheless, it is still possible to learn a great deal from approximate studies. One solution is to construct a single reactor with multiple sample ports along its length. This approach was followed at Exxon for the study of the decay of a Pt–Re reforming catalyst [16]. Another possible approach could be to run several tests at different temperatures, discharge the catalysts segmentally, measure the activity changes along the beds in additional post-mortem activity tests, and then fit the results to decay models by trial and error as described earlier for plant catalyst. However, there do not appear to be any published studies of this nature. Segmental discharge from narrow tubes is often difficult and there is a risk of mechanical damage during discharge.

10. Parallel difference testing

If a multi-tube test unit is available then this can be used for parallel difference testing. Parallel testing of different catalyst formulations within multi-tube, fixed-bed test units has become common in recent years although 8-tube units were in use in ICI almost 25 years ago. Multi-tube reactor units can be used to advantage for the study of catalyst decay. For laboratory units the catalyst charge is usually in the form of ground-up particles.

Parallel difference testing of a single catalyst type enables the performance in discrete segments along the bed to be estimated and, hence, the variation of decay rate along the catalyst bed. The basic procedure is as follows. Multiple, fixed-bed reactors are charged with different amounts of catalyst but are operated in parallel under identical conditions of feed composition, flow rate and temperature. The integral performance across the rear segment of a catalyst bed is determined from the difference between its exit composition and the exit composition of the previous segment, as measured in a parallel test with a shorter catalyst bed. The minimum experimental set-up would consist of two beds, one of half length and the other of full length. However, 1/3 or 1/4 unit segments will provide more information. An example with 1/3 segments is shown in Fig. 5a. This technique is suitable only if the initial catalyst properties in each segment are closely matched and so careful pellet grinding and mixing to achieve uniform catalyst samples is necessary.



Notes. 3 simulated beds of 30%, 70% and 100% lengths were used to generate difference plots. First order reaction kinetics, combined with first order parallel decay. All beds receive identical feeds for the entire test except for the final data point for which the feed-rate to the 100% length bed is reduced so as to restore conversion to the initial value of 98% and the feed-rates to the shorter beds are reduced to the same extent.

Fig. 5. (a) Schematic tube loadings for parallel difference testing. (b) Simulated difference plots for parallel decay.

There is an obvious potential for the propagation of error in the difference calculations. Duplication of experiments is desirable, especially for short beds, in order to reduce error due to non-uniform catalyst composition and deviation from plug flow. Obviously, duplicate charges with three bed lengths will require a 6-tube test unit. Alternatively, the data from parallel tests could be incorporated directly into a decay model without difference calculations.

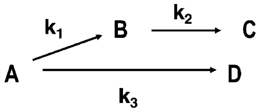
It is necessary to minimize deviation from plug flow due to by-passing and axial dispersion. The generally accepted criterion to minimize the error due to by-passing is $d_R/d_P > 10$ although improved isothermality can justify d_R/d_P ratios as low as 4 [17]. The Mears criterion for <5% error due to axial dispersion in a reactor of length L_R with pellets of diameter d_P is

$$\frac{L_R}{d_P} > 20n\frac{\ln(C_i/C_f)}{Pe_a} \tag{3}$$

where n is the reaction order, C_i and C_f are the initial and final reactant concentrations and Pe_a is the axial Peclet number ($1 < Pe_a < 2$ for gases; lower values for liquids) [17,18]. A similar but less severe criterion ($8n$ instead of $20n$) has been proposed by Gierman [19]. For first-order reactions, $\ln(C_i/C_f)$ increases linearly with bed length and so the criterion will be satisfied equally for all bed segments but for higher order reactions the error due to axial dispersion is more significant for short bed lengths. In order to satisfy these criteria, parallel difference tests are most suited to first order reactions and require long, narrow reactor tubes with small catalyst particles.

The impact of variable feed composition on decay kinetics could also be studied in a parallel test unit with a large number of reactor tubes, equipped for more than one feed composition.

Parallel testing of catalyst beds with variable length provides a simple diagnostic test for the influence of composition gradients on catalyst decay. The example in Fig. 5b has been simulated numerically for the three beds to illustrate typical behaviour. The rate constants for the main reaction and the decay reaction have been set so that after a suitable test period the conversion in the full bed has dropped from 98 to 80%. Then, for the final data point, the feed rate is decreased sufficiently to restore the conversion back to 98%. The characteristic plots of conversion against time provide evidence for the type of decay kinetics



Note: selectivity to B is determined by the degree of conversion of A and the relative rate constants k_1 - k_3 under the reaction conditions.

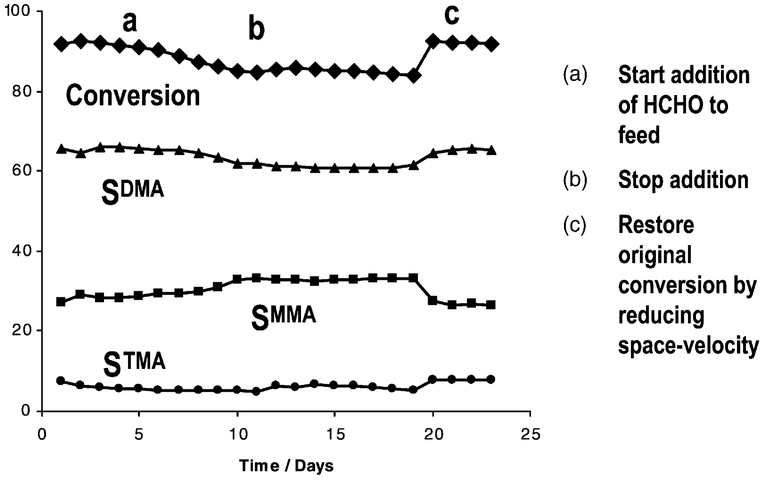
Fig. 6. Influence of parallel and consecutive reactions on selectivity.

but it is not possible to distinguish between parallel decay and feed-poisoning (side-by-side) decay. Note that the presence of a decay gradient along a fixed bed of crushed pellets provides a warning that decay is composition-dependent and so may also be influenced by pellet-size if there is significant diffusion resistance.

11. Selectivity decay

Catalyst selectivity is defined by the relative proportions of feedstock that are converted to the target product and to by-products. This is illustrated in Fig. 6 for a reaction system under kinetic control rather than equilibrium control. As well as the main reaction to product B, additional consecutive and parallel reactions lead to by-products C and D. The selectivity to the main product is determined by the relative values of the rate constants k_1 and k_3 at the reaction temperature and, due to the consecutive reaction of the main product, also by rate constant k_2 and the space time (W/F). The recorded selectivity should therefore be quoted at specified values of temperature and conversion (which depends on activity and space time). Consecutive reactions will continue even after the feedstock conversion is complete and so selectivity recorded at 100% feedstock conversion may have little or no indicative value.

For a complete description of selectivity decay it is therefore necessary to quote selectivity values under equivalent conditions of temperature and conversion. Otherwise, it may be difficult to determine if the observed selectivity decay is intrinsic. In the simplest case, there is no change in the nature of the active sites and an apparent selectivity decay is a secondary consequence of the loss of active sites. When the reaction temperature is increased, in order to maintain the target conversion, the observed selectivity changes due to the differences in activation energy of individual reaction steps, whether parallel or consecutive. In this circumstance, it is possible to tell if the observed selectivity decay is intrinsic by reducing the space velocity (F/W) at constant temperature, so as to keep the overall conversion constant. This is illustrated in Fig. 7 for a commercial zeolite catalyst used for the



Notes. Acid mordenite catalyst (Nitto NZ-87), NH3/MeOH feed ratio 2.0, fixed temperature 297°C. Addition of HCHO (1.4x10^{-4}g/gcat/h) to feed in period (a) causes rapid loss of activity and apparent change in selectivity. Conversion restored to initial value in period (c) by reduction in space velocity.

Fig. 7. Poisoning of methylamines zeolite catalyst by HCHO: selectivity decay due to loss of active sites.

production of methylamines (mono-, di- and tri-) from methanol and ammonia. The catalyst decays rapidly if excessive HCHO is present in the feedstock [20]. In this example, when conversion was restored to the initial value in period (c), the selectivity values for the three methylamines (S^{MMA}, S^{DMA} and S^{TMA}) also returned to their initial values [21]. Therefore, the intrinsic selectivity had not changed and the decay was due simply to the loss of active sites.

In more complex cases, intrinsic selectivity decay occurs due to changes in the nature of a single type of active site or to changes in the relative activities of different types of reaction site. The selectivity decay rate is then not simply coupled to that of activity decay. The combination of different mechanisms of selectivity decay with different types of activity decay kinetics gives many possibilities for selectivity decay kinetics with, potentially, rather complex rate equations. Note also that the commercial meaning of catalyst decay is loss of target performance. During time in use a catalyst can become less active but intrinsically more selective or even more active but intrinsically less selective.

12. Life tests

Much industrial catalyst testing is not concerned with detailed decay kinetics. The aim, more simply, is to measure the catalyst performance under simulated plant reaction conditions over an appreciable portion of its expected life. Such life-tests might be carried out in the laboratory, in a pilot plant or in the plant. Plant tests could involve a side-stream reactor, a single tube from a multi-tubular reactor or a basket of development catalyst contained in the plant reactor. Tests at plant scale have the advantage of exposure to realistic process feedstocks under realistic process conditions. Life tests are usually very slow. Tests at laboratory and pilot scale are frequently limited to the initial part of the catalyst life-cycle. Tests in the plant may need to extend over the entire life-time of the plant catalyst charge.

13. Accelerated decay tests

Accelerated decay tests are frequently used in industry for the comparison of the stability of commercial catalysts, for fast screening of development catalysts, and for process optimization studies. Detailed commercial test procedures are seldom published but typical procedures have been reviewed previously [22]. Accelerated decay tests are most readily applied for comparison of samples of broadly similar composition with a single, dominant decay mechanism. However, they are also used in more complex situations such as test cycles for automobile exhaust catalysts and for FCC catalysts.

Re-expressing Eq. (2) in Arrhenius form

$$-\frac{\mathrm{d}a}{\mathrm{d}t} = A_{\mathrm{d}} \exp\left(-\frac{E_{\mathrm{d}}}{RT}\right)\{C_1^{n1} C_2^{n2} \cdots C_i^{ni}\}a^m \qquad (4)$$

The decay rate can be accelerated by increased temperature and/or changes to concentrations of reactants, products or feedstock impurities, depending on the decay kinetics.

Special caution is needed with accelerated decay tests. The results are only valid for catalysts which follow similar reaction and decay kinetics. Test conditions that are too far outside the normal plant regime could lead to significant changes in the catalyst activation stage, the catalyst steady-state condition and the dominant decay mechanism. Even in a well-designed, accelerated test, the decay profile along the reactor may differ to some extent from the decay profile for an apparently equivalent, integral decay under normal conditions.

For an accelerated test in a fixed bed, both temperature and space velocity may be increased so that the integral conversion is the same as under normal conditions. The initial axial concentration profile for main components will usually be fairly similar to the normal test. In a test at fixed temperature the concentration profile along a fixed bed will change as the catalyst decays. The change in the profile under accelerated conditions will be qualitatively similar but faster compared to the equivalent tests under normal conditions. The same applies to tests in which the temperature is boosted to maintain constant overall conversion.

If space velocity and temperature are increased together so that the exit conversion is unchanged then the rate of deactivation under accelerated and normal conditions (r_{D_2} and r_{D_1}) will vary according to

$$\frac{r_{\mathrm{D}_2}}{r_{\mathrm{D}_1}} = Q^{E_{\mathrm{d}}/E_{\mathrm{r}}} \qquad (5)$$

where the acceleration factor $Q = F_2/F_1$, the ratio of the respective feed rates, and E_d and E_r are the activation energies for the decay process and the main reaction [22,23]. This can be justified as follows, once again denoting a = activity at time t relative to fresh catalyst.

The change in concentration of reactant across any segment dw of the catalyst bed is given by

$$\frac{dC_1}{dw} = -\frac{k_r C_1^{n1} \exp(-E_r/RT)a}{F} \tag{6}$$

For normal and accelerated conditions the change in C_1 is the same. Hence,

$$\frac{1}{T_2} - \frac{1}{T_1} = -\left(\frac{R}{E_R}\right) \ln Q \tag{7}$$

The rate of deactivation r_D at any location in the bed is given by

$$r_D = -\frac{da}{dt} = k_d\{C_1^{n1} C_2^{n2} \cdots C_i^{ni}\} \exp\left(-\frac{E_d}{RT}\right) a^m \tag{8}$$

Comparing accelerated conditions to normal conditions

$$\begin{aligned}\frac{r_{D_2}}{r_{D_1}} &= \exp\left(\left(-\frac{E_d}{R}\right)\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right) \\ &= \exp\left(\left(+\frac{E_d}{R}\right)\left(\frac{R}{E_r}\right) \ln Q\right)\end{aligned} \tag{9}$$

Thus

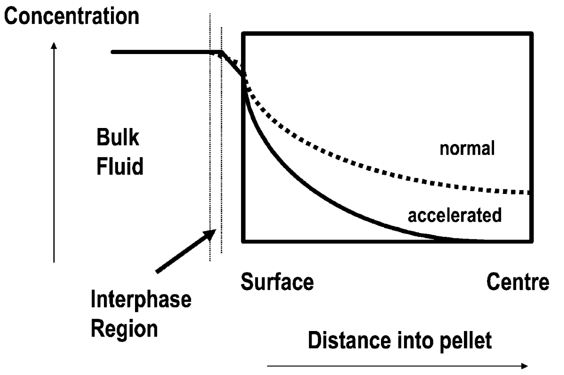
$$\frac{r_{D_2}}{r_{D_1}} = \exp\left(\left(+\frac{E_d}{E_r}\right) \ln Q\right) = Q^{E_d/E_r} \tag{10}$$

Note that this derivation is valid for independent decay, parallel decay and feed-poison decay and also for series decay if the decay process is driven by a main product. The activity profile may vary along the bed with time but the activity decay in any segment and the consequent change in concentration for that segment and for successive segments is simply accelerated compared to normal conditions. If decay is driven by by-products then the concentration terms in Eq. (9) do not cancel out exactly. This is because the concentration profiles of individual by-products along the bed will vary to different extents at different temperatures due to differences in activation energies for individual reaction steps.

If parallel decay is accelerated by means of increased reactant concentration then the relative impact on the reaction rate and the decay rate will depend on the respective kinetics. In some circumstances the axial decay profile in a fixed bed may be different under normal and accelerated conditions for equivalent integral decay. Inspection of the behaviour of parallel decay with second-order concentration dependence suggests that the decay profile for normal and accelerated decay will be similar for equivalent degrees of activity decay. For series decay, the addition of reaction product to the feedstock will cause some modification to the axial decay profile, especially in cases where the front of the catalyst bed is not normally exposed to the reaction product.

Accelerated decay tests may be influenced by pore-resistance. In reactions with significant pellet pore diffusion resistance the impact of the intra-pellet concentration gradient on the intra-pellet decay profile could be magnified under accelerated conditions at high temperature because the reaction rate increases faster with temperature than the diffusion rate. This is expressed schematically in Fig. 8. At high reaction rate the pellet could even become hotter than the bulk phase and it might be necessary to use crushed pellets.

If there is significant pore-resistance to both the main reaction and a poisoning reaction, then accelerated tests at high reaction rate by the combination of increased temperature with increased space velocity could give complex results and so be unsuitable. Under conditions of high rate the main reaction could be pushed into a regime of pore diffusion limitation initially but, once the active area around the pore-mouths



Notes. Rate accelerated by increased temperature & GHSV; film resistance << pore resistance; no change in overall conversion in bulk fluid.

Fig. 8. Intra-pellet reactant concentration gradient under normal and accelerated conditions.

has been deactivated, could move into a regime of pore diffusion control with a change in apparent activation energy [11].

For parallel decay, if there is significant pore-resistance then any increase in reactant concentrations in the bulk phase will be moderated inside the pellet by the intra-pellet concentration gradient, tending to reinforce an inward decay front caused by parallel decay. For series decay, if there is significant pore-resistance, then deliberate addition of product to the feedstock or operation at increased conversion (longer space time) will increase the product concentration in the outer zone of the pellet, and hence also the decay rate. Thus, the accelerated decay will tend to be more uniform throughout the pellet in comparison to the outward decay front caused by normal series decay.

An increased concentration of poison can be used to accelerate a poisoning reaction. If the concentration of a reactive poison is increased too much then the poison profile might penetrate further than normal along the catalyst bed. If there is significant pore-resistance to the poisoning reaction (pore-mouth deactivation), then too great a concentration change could cause the poison profile to penetrate deeper than normal into the pellets. Both of these effects should be considered in the interpretation of the results.

Thus, there is plenty of scope for controversy in the design of accelerated decay tests and the interpretation of the results. The optimum catalyst formulations for normal plant conditions and accelerated test conditions might differ. It is therefore essential to confirm that the accelerated decay process causes similar changes to normal decay by comparing the characteristics of samples from accelerated decay tests to those of reference samples with similar degrees of deactivation from longer periods under normal conditions. They should also be compared to discharged plant samples if these are available. The characteristics to be compared include the reaction performance under normal conditions and relevant physical and chemical properties (Table 1).

The following check-list for accelerated decay tests has been proposed previously [22] but has now been slightly extended.

1. What is the purpose of the test, e.g., decay diagnosis, catalyst development or comparative testing?
2. Which types of decay processes could be significant?
3. Which decay process needs to be accelerated?
4. Which procedure is most appropriate for acceleration of the target decay process without exaggeration of other potential decay processes?
5. What impact can be expected on axial and intra-pellet decay gradients?
6. Can the results be verified against normal decay?
7. Are the results sufficiently reliable to be used predictively?
8. Has there been a significant change in catalyst composition that could invalidate comparisons with previous catalysts?

The validity of the accelerated test procedure can also be expressed as a simple index of the overall risk factor, as shown in Table 2. Multiplication of the appropriate values of four individual risk factors (each in the range 1–5) leads to an overall risk factor in the range 1–625. A carefully designed test procedure on a well-characterized decay process will score a low value. As an approximate guide, if the overall risk factor is in the range 1–20 and no individual factor is greater than 3 then the accelerated decay test is based on a firm foundation of knowledge and suitable caution has been applied in the interpretation of the results. In

Table 2
Accelerated decay validity index[a]

Risk factor	1	3	5
(a) Catalyst type and composition	Single type, single source	Moderate range of composition	Different types, several sources
(b) Decay mechanism	Well known/characterized	Qualitatively characterized	Unknown/not characterized
(c) Test conditions/severity	Range: low to medium severity	Single condition, medium severity	Single condition, high severity
(d) Reason for test	Selection for further evaluation	Plant selection, verification of vendor claims	Plant selection, no vendor information

[a] The overall index (range 1–625) is calculated by multiplying the four individual risk factors (a) × (b) × (c) × (d).

this situation, the accelerated decay test is a valuable tool. For values in the range 20–100 the results should be interpreted with caution. Can the risk factor be reduced with some additional work? If the risk factor is greater than 100 then the results must be interpreted with caution and there is a significant risk that the results of the accelerated decay test could be invalid. For very high index values the use of such tests for predictive purposes is no more than an ill-informed gamble.

14. Concluding remarks

The insight gained from studies of catalyst decay can be applied to optimization of the lifetime catalyst performance, including improvement of the catalyst formulation and the reaction engineering. The study of catalyst decay requires a holistic approach from laboratory to plant scale. The catalyst decay kinetics can be categorized in a rational manner in relation to the kinetics of the catalysed reaction. Once this relationship is known then the variation of catalyst decay rate through a catalyst pellet or along a catalyst bed can be understood. The study of catalyst decay from plant data provides essential information. The post-mortem characterization of discharged catalysts can provide a great deal of insight into the physical, chemical and mechanical causes of decay and, in favourable circumstances, can be combined with lifetime operational data for the construction of a simple decay model. The determination of precise decay kinetics requires careful studies in gradientless test reactors but experiments in fixed beds can provide useful, approximate data. Finally, well-designed, accelerated decay tests are useful for catalyst testing and development but carelessly designed, accelerated decay tests are likely to prove misleading.

Acknowledgements

The idea of comparing the decay in part beds and whole beds (‘parallel difference testing’) was first suggested to me around 1980 by D.W. Johnson of ICI.

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