

Life cycle stability of ULSD catalysts

Accelerated ageing test methods allow refineries to gather an unprecedented amount of information about catalysts

FLORIAN HUBER and IOAN-TEODOR TROTUŞ
hte GmbH

Industrial hydroprocessing applications rely on the continuous operation of catalysts for time periods on a scale of years. In consequence, catalyst selection for such applications is the result of intricate evaluation processes as this decision will impact profitability for the whole operational life cycle. The catalyst needs to operate in a certain window of activity and to give a desired spectrum of product selectivities and qualities, and it must meet these performance criteria while maximising the length of the life cycle.

Ultra low sulphur diesel (ULSD) production has a very small margin for error. Here the feeds can contain four orders of magnitude more sulphur than the product. If a batch of product has a too high sulphur content, blending it with a batch of lower sulphur content is only of limited use in compensating sub-optimal catalyst operation because the limits of acceptable sulphur content are very low (<10 ppm). At the same time, exchanging the catalyst out of schedule is undesirable because this is a costly, time-consuming operation

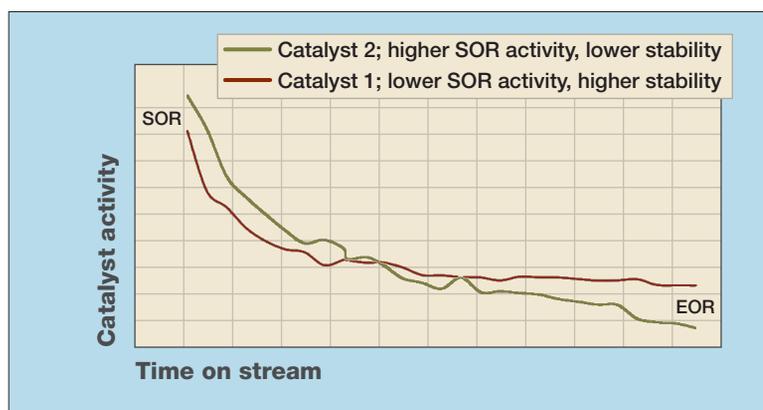


Figure 1 Relative activity ranking of two catalysts with different deactivation rates. Figure given only for illustrative purposes; there is no guaranteed general link between catalyst activity and stability. This must be determined for each catalyst individually

with increased safety concerns, which disturbs refinery production.

For the reasons outlined above, catalysts for ULSD production need to be very resilient. Stability over long periods of operation, but also the ability to function over a wide range of operating conditions and feedstocks, and the ability to withstand and recover from occasional unforeseen extreme conditions that might arise during an operating cycle are required attributes for a catalyst in this application.

Conventional catalyst testing relies on comparing the activity

of start-of-run (SOR) catalysts using experimental plans which are relatively short when compared with the lifetime of industrial catalysts but nevertheless operate under conditions (temperature, pressure, feed, and so on) that are very close to those of normal industrial operation. This approach is suitable for finding the most active SOR material but in most cases offers limited information for comparing the relative stability of the catalysts being tested.

The deactivation rates of different catalysts are not necessarily identical: a highly active catalyst can deactivate more

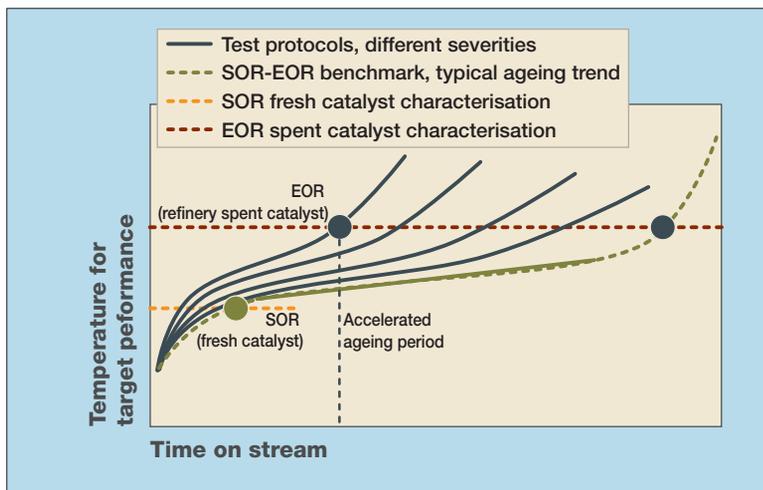


Figure 2 Schematic representation of the concept of accelerated ageing

quickly than a catalyst with lower initial activity. Also, with different deactivation rates, it is possible that a highly active SOR material (Catalyst 2 in **Figure 1**) can have a higher activity at the beginning of its operation when compared to another material (Catalyst 1 in **Figure 1**) but during operation the activity ranking would be reversed.

Considering the long lifetime of industrial catalysts (1-2 years) in diesel desulphurisation, a test under standard operating conditions with the aim of evaluating relative catalyst stability would hardly be feasible, simply due to time constraints. To address these limitations of conventional catalyst testing, hte has developed a testing method in collaboration with MOL based on accelerated ageing for ULSD catalysts.¹ This testing method speeds up the loss of catalyst activity, which would normally occur in periods of 1-2 years or more, to just 1-2 months.

In general, coke formation by condensation of polynuclear aromatic compounds is considered one of the major causes of

catalyst deactivation in diesel hydrotreating.² Coke deposition typically increases with increasing operation temperature. Hence, operating under conditions that favour coke deposition on the catalyst will increase the rate of catalyst deactivation. But simply running a set of catalysts at unrealistically high temperatures for a short time and then measuring which one retained the most activity after this treatment does not provide a convincing accelerated ageing method. This one-dimensional approach would most likely over-simplify the impact of coke formation and neglect the impact of additional root causes on deactivation.³

The challenge in designing an accelerated ageing protocol lies in relating the accelerated deactivation process to the catalyst deactivation observed in actual industrial operation and thus gaining pertinent industrial information from such a test.

hte's testing method relies on the use of a reference SOR catalyst and a corresponding reference end-of-run (EOR) catalyst that has seen a normal

cycle of industrial operation. As displayed in **Figure 2**, the accelerated ageing protocol is validated by comparing the activity of the EOR industrial catalyst with the SOR catalyst aged at an accelerated rate. In this way the accelerated ageing is validated against the normal ageing observed in a real industrial process. This comparison ensures that the extent of ageing applied to the SOR catalyst is industrially relevant. Additionally, this procedure allows the comparison of various product properties between the refinery EOR catalyst and the SOR catalyst aged under conditions of increased severity.

There are two more common ways of performing accelerated ageing: one is at constant temperature, the other at constant sulphur level.⁴ The constant temperature approach is suitable for comparing very similar materials, but when highly active catalysts are compared to catalysts of low activity, one would end up either with the low activity catalyst operating below its required temperature and giving a product with a much higher sulphur content than targeted, or with the high activity catalyst operating above its temperature window and being subjected to a needlessly high temperature, which it would never actually see during its normal operation. The constant sulphur level is more suitable for comparing catalysts of different activities.

In ULSD production, the target is to reach a sulphur concentration below 10 ppm. Under normal industrial operation, the reactor is heated to the temperature needed to reach that target sulphur level. As

the catalyst ages, the temperature must be increased until the point where a further increase in temperature is no longer desirable and the catalyst must be changed out. An accelerated ageing protocol should retain some characteristics of this mode of operation to be realistic. From this point of view, it also becomes obvious why the constant sulphur mode is more adequate.

Nevertheless, under industrial operation reactor heating rates are in the order of several degrees per month.⁵ Under accelerated ageing, the heating rate would consequently be 10-20 times higher than under normal operation. Because the heating rate is determined by the ageing and the ageing is determined by the heating rate, and it is also the ageing that must be determined, hte chose to develop an accelerated ageing protocol that increases the severity of multiple process parameters and the temperature is selected to give a product sulphur concentration close to 5 ppm at the start of the ageing protocol. This method ages the catalyst at a constant temperature, but chooses a relevant temperature for each catalyst, thus making the best of both the constant temperature and the constant sulphur approach. The severity of each individual process parameter is tuned to match realistic parameters from industrial operation, thus increasing the severity of all relevant process parameters, but maintaining all these parameters in a realistic operation window. In other words, hte's ageing protocol could be defined as a 'constant initial sulphur level – constant age-

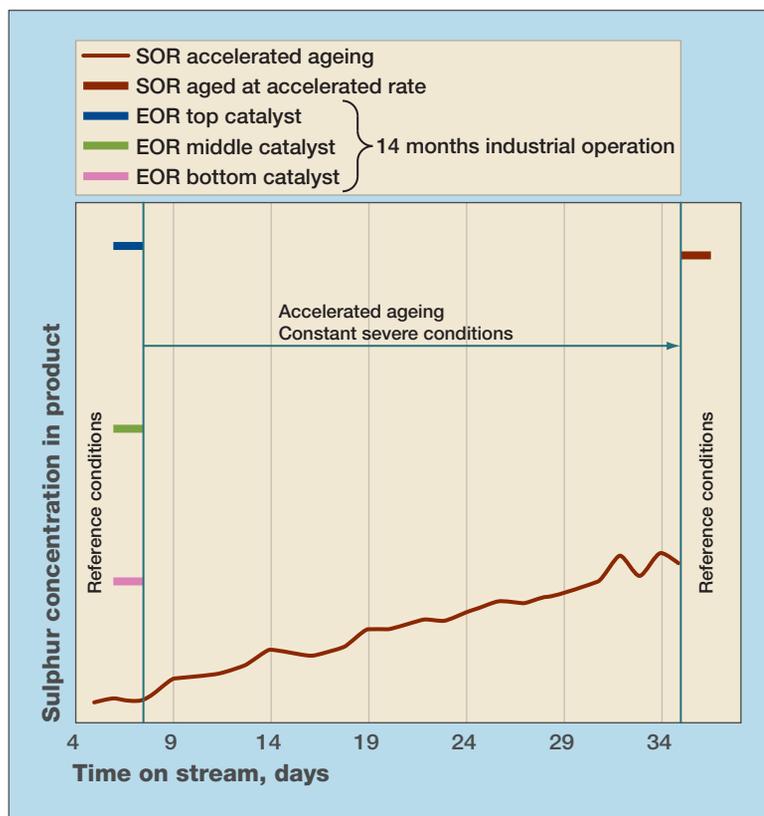


Figure 3 Schematic representation of hte's accelerated ageing with additional illustration of the behaviour of EOR materials sampled from different levels in the industrial reactor when compared to the SOR material

ing temperature' protocol. This allows the study of catalysts with considerable activity differences, as is required given the numerous hydrotreating catalyst options available on the market.

Figure 3 shows a schematic representation of hte's accelerated ageing protocol for the comparison of product sulphur levels with an illustration of the behaviour of EOR materials from different levels in the industrial reactor compared to the SOR material and the lab-aged EOR catalyst material. As a quality control measure, detailed analyses of the reaction products obtained from the catalysts aged with hte's accelerated ageing protocol (Aged-SOR) are

performed and these are compared with the properties of the products obtained from an EOR catalyst. With hte's accelerated ageing testing protocol, the differences between EOR and Aged-SOR in all the relevant ULSD product properties are minimal, as can be seen from **Table 1**.

One crucial aspect of this testing protocol is the industrial reference catalyst. Industrial reactors contain catalyst in the order of hundreds of cubic metres, while a bench-scale unit from hte uses several tens of millilitres of catalyst and a high throughput unit from hte uses only several millilitres of catalyst per reactor. For this reason, the sample of spent cat-

alyst from the industrial reactor must be selected carefully, considering that deactivation does not occur homogeneously throughout a fixed catalyst bed.² In **Figure 3** we illustrate the sulphur concentrations of the products obtained when testing EOR material sampled from different levels in the industrial reactor. It can easily be observed that the three EOR materials sampled from different levels in the industrial catalyst bed have significantly different activities. The EOR catalyst from the top of the bed shows the lowest activity. This part of the catalyst bed comes directly into contact with the unprocessed feed. Hydrotreating, in particular aromatic saturation, is an exothermic process with significant temperature increase in the top of the bed. Hence conditions favouring coke formation from the large fraction of polyaromatics still present. Going down through the catalyst bed, sulphur and nitrogen are split from the hydrocarbon backbones and aromatics and olefins become more and more saturated, so the lower levels of the catalyst bed only come into contact with a feed that has much less potential to deactivate the catalyst.

The catalyst in the middle or bottom of the catalyst bed never comes into direct contact with the unconverted feed throughout the entire run and suffers much less deactivation over the operating period. Moreover, maintaining a moderate operation temperature down the catalyst bed throughout the run helps to suppress coke formation. As a consequence, when comparing the EOR materials along the bed, the material at the top

Compared product properties, EOR vs Aged-SOR

Catalyst	EOR top catalyst >420	Aged-SOR HDS catalyst
Days on oil		37
Density at 15°C	0.8311	0.8319
Sulphur content of product at reference condition	46	46
Simdist T-10% (ASTM D2887)	211.18	210.8
Simdist T-50% (ASTM D2887)	273.04	272.85
Simdist T-90% (ASTM D2887)	330.97	330.75
Cetane Index (ASTM D4737 - 10)	57.7	57.7
Cloud point (ASTM D2500)	-15.5	-15.5
Pour point (ASTM D97)	-22	-20
Flash Point (ASTM D3828)	94	100.5
Yield (Diesel), %	96.7	96.7
Monoaromatics, %	23.5	23.8
Diaromatics, %	1	1.1
Tri+Aromatics, %	0.1	0

Table 1

of the industrial reactor had lost the most activity, the EOR in the middle was more active than the EOR at the top, and the EOR at the bottom was the most active of all at the end of the cycle length.

In general, when selecting an EOR reference for the ageing protocol, one should have an idea of the deactivation profile inside the industrial reactor and a strategy for taking into account the inhomogeneous

Compared activation energies (calculated for HDS reaction order n=1.3) of EOR catalysts from different reactor heights and of the Aged-SOR

Catalyst	Activation energy, kcal/mol
EOR-top	30.4
EOR-middle	32.3
EOR-bottom	32.2
Aged-SOR	31.4

Table 2

deactivation pattern. One strategy could be to use a representative sample from the top third of the industrial reactor to simulate ageing. This means taking the material that has suffered the most ageing as a reference to observe the evolution of the properties of the tested catalysts over the entire range of deactivation that is observable under industrial operation. Another more sophisticated strategy could include kinetic reactor modelling to compose the overall catalyst deactivation in the industrial reactor based on the inhomogeneous deactivation pattern. A necessary prerequisite of this modelling approach would be to generate lab EOR corresponding to different EOR locations in the industrial reactor, hence utilising protocols with different ageing severity.

When comparing the HDS activation energies of the EOR catalysts from different heights of the industrial reactor (see **Table 2**) to the activation energy of the catalyst aged with the accelerated ageing protocol, one can observe that the differences are within the experimental error for determining activation energies, despite the different activity level of the industrial EOR samples in particular. This indicates that the deactivation is caused by a reduction in the number of active sites or a structural change to the active phase. Such deactivation may be caused by coke deposits covering the active centres and making them less accessible, or by a structural change in the sulphide phase. These deactivating phenomena are not blocking the pores of the catalyst to an extent that can noticeably limit the mass trans-

fer through the catalyst's pores. This kind of deactivation would have no significant impact on the activation energy.

With coke deposition being a major cause of deactivation, the factors that favour coke deposition will also accelerate deactivation. The most obvious parameter that can be adjusted when designing an accelerated ageing process is temperature, because an increase in this parameter will accelerate all reactions, including the formation of coke deposits that block access to the active site of the catalyst. Another relevant parameter is hydrogen partial pressure. As this gets lower the rate of hydrogenation reactions decreases and in consequence increased amounts of unsaturated molecules come into contact with the catalyst. Unsaturated molecules are required to form the polymeric species that constitute the layers of coke blocking the active sites. The third relevant parameter is the amount of polyaromatic hydrocarbons passed through the reactor. This is dependent both on the polyaromatic content of the feed and on the feed rate. Polyaromatic hydrocarbons work as coke precursors and increasing their availability in the system will favour coke formation. Temperature and hydrogen pressure should be kept, to a reasonable extent, close to realistic operating conditions to ensure that the coke species formed on the catalyst are similar to those that form in the industrial reactor. For the flow rate and polyaromatics content of the feed, the limits are less strict, as long as the temperature and hydrogen pressure are chosen reasonably.

Not all feeds are identical, so the interplay of these parameters must be considered when designing such a test. The use of an industrial catalyst that has endured an entire operational cycle as a reference ensures that the deactivation protocol is relevant for comparing the stability of catalysts under industrially relevant conditions.

Conclusion

The application of high throughput experimentation technology and tools is essential for comparing many catalysts that the market has to offer under accelerated ageing conditions. As a result of such an accelerated ageing test protocol, the ranking of SOR catalysts would be determined based on their activity under the reference conditions, similar to conventional testing. In addition, such a test would give the added benefit of clearly indicating the ranking of catalyst stability for an industrially relevant life span. The results of the test would also allow a semiquantitative estimation of the lifetime of several catalysts when compared to the industrial reference EOR catalyst. Conventional testing can give a rough lifetime assessment assuming similar deactivation rates by comparing the activity difference of the SOR catalysts. However, it is clear that the assumption of constant deactivation rates may be an over-simplification of reality taking into account the ageing dependency on catalyst material, operation conditions and feedstock properties.

With all the uncertainties about long term catalyst stability inherent in classical catalyst testing, accelerated ageing test

methods provide the next step in catalyst testing technology and allow refineries to gather an unprecedented amount of information about catalysts from their studies with a modest amount of additional effort.

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Ioan-Teodor Trotuş is Project Manager R&D Solutions with hte GmbH – the high throughput experimentation company, Heidelberg, Germany. He joined hte as a project manager in the field of hydroprocessing and biofeed conversion and previously studied chemistry and materials science at the University of Bucharest, then joined the Max Planck Institute for Coal Research for a doctorate in chemistry. *Email: ioan-Teodor.Trotus@hte-company.de*

Florian Huber is Team Lead and Senior Scientist for R&D Solutions with hte GmbH – the high throughput experimentation company, working in the field of hydroprocessing and biofeed conversion. He previously worked on developing catalysts in the R&D department of Haldor Topsøe. He holds a MSc in chemical engineering from the University of Erlangen-Nürnberg and a PhD in chemical engineering from the University of Trondheim, Norway. *Email: Florian.huber@hte-company.de*