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ScienceDirect
Catalysis Today 127 (2007) 54–69
CATALYSIS TODAY
www.elsevier.com/locate/cattod

Review on the deactivation of FCC catalysts by cyclic propylene steaming

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Available online 16 July 2007

Abstract

The deactivation of FCC catalysts in small-scale units in the presence of contaminant metals has been the industry workhorse for a number of years due to the robustness and simplicity of such methods.

A major advance in the deactivation of metallated catalysts on a small-scale that better simulated the performance of commercial FCC catalyst, was the introduction of the cyclic propylene steaming (CPS) method. In the CPS protocol, FCC catalyst is impregnated with vanadium and nickel prior to deactivation in reduction–oxidation cycles and the latter provides significant advantages over traditional methods such as the Mitchell approach. In certain situations, however, the contribution of vanadium to catalyst deactivation is over-emphasized in the CPS method, and therefore this method has been developed further.

This paper describes a number of modifications that have been made to the CPS method to further attenuate the destructive effects of vanadium on the FCC catalyst during deactivation. This includes exposing the metallated catalyst to pre-stabilisation steps with reduction-oxidation cycles and changing the ratio of the time the catalyst spends in reducing and oxidising environments during the CPS cycles. The comparison of activity and selectivity data obtained from FCC catalysts having age distribution with those obtained from CPS showed that both scenarios gave the same catalyst ranking.

These investigations have also shown that the use of reduction–oxidation cycles better simulates the deactivation of FCC catalysts in the absence of contaminant metals. These investigations have also shown that the use of reduction–oxidation cycles better simulates the deactivation of FCC catalysts in the absence of contaminant metals ''the part'' than traditional deactivations in a 100% steam atmosphere.

Keywords: FCC catalysts; Laboratory deactivation; Cyclic propylene steaming

1. Introduction

Evaluating fluid catalytic cracking (FCC) catalysts has always been a challenging task. For proper testing, the test methods have to replicate a yield pattern that is as close as possible to commercial FCC units. Catalyst deactivation in its various facets has meanwhile been considered as one of the most difficult parts in FCC catalytic testing since it is the base for each type of FCC catalyst activity and selectivity testing. In broad terms, lab testing of FCC catalysts involves deactivation of metals-free and metallated FCC catalysts depending on the objective targeted.

Various available methods will be discussed throughout this paper.

Catalyst deactivation in the presence of metals is usually done by impregnating the catalysts with vanadium and nickel, which are the predominant contaminants in commercial FCC operation. Vanadium is the more critical of the two metals in lab deactivations because it has two effects: vanadium destroys the zeolite and catalyses dehydrogenation reactions [1,2]. The magnitude of both effects depends on the oxidation state of vanadium [3]. In the +5 state vanadium reacts to form vanadic acid, H_3VO_4, under the hydrothermal conditions in FCC units. Vanadic acid has intraparticle and interparticle mobility [4] and penetrates and destroys the zeolite much more effectively than vanadium at lower oxidation states. Moreover, the formation of hydrogen and coke is exaggerated by vanadium in the +5 state compared with the dehydrogenation activity of nickel [3]. In

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doi:10.1016/j.cattod.2007.05.023

commercial operation vanadium can be in either the +4 or +5 state. The ratio of the time the vanadium is in these two oxidation states depends on regenerator conditions [5], and this complicates lab deactivation. Nickel is less critical because it does not attack the zeolite. It has only a dehydrogenation activity, which is less affected by the oxidation state [3], but this has to be mimicked as well.

The two effects mentioned above, zeolite destruction and dehydrogenation reactions, have a significant impact on FCC performance and refinery economics. For example, in the case of zeolite destruction, as the zeolite becomes more resistant against V-attack, less fresh catalyst has to be added to the FCC unit to maintain activity. This represents lower variable costs to the refinery. In the case of the dehydrogenation reactions, the higher the Ni- and V-passivating potential of the catalyst, the lower the amounts of hydrogen and coke that are produced. Hence considering that the most common bottlenecks of the FCC unit are the wet gas compressor and the regenerator air blower, it is important that the catalyst is deactivated and tested correctly. Improper applications of deactivation protocols will lead to incorrect projections of laboratory data to FCC unit performance, resulting in the selection of a sub-optimised catalyst. As a consequence the refinery would not realise the economic advantages of a more metals-tolerant catalyst. In such a situation the FCC unit would have to process lighter feeds or operate at a lower throughput. Both options represent lost economical opportunities to the oil refinery.

These consequences emphasize that it is of vital importance to apply a deactivation method capable of simulating the equilibration of FCC catalysts in FCC units, and to adjust the test parameters as close as possible to the operational parameters in the FCC unit. The two simplest examples for the latter are: (1) FCC catalysts intended for vacuum gas–oil as well as resid applications are tested in the presence of metals and (2) metals-free testing is performed in cases of hydrotreated feed applications.

Commercially equilibrated FCC catalysts contain continuums of catalyst and metal ages. For the sake of method robustness and simplicity, most laboratories apply deactivation procedures that produce uniformly metallated and deactivated catalysts.

The experiments performed in the body of this work cover the above-described topics; various FCC catalyst deactivation methods incorporating both uniform distribution and age distribution protocols are evaluated. Within this scope it is investigated how the oxidation state of metals affect FCC catalyst performance, and whether uniformly deactivated FCC catalysts give the same ranking as FCC catalysts having age distribution.

2. Background

2.1. Metals deactivation

The first approach for metallation and ageing of FCC catalysts was the Mitchell technique [6]. In this protocol vanadium is in the +5 state continuously, and therefore, this method exaggerates the effects described in Section 1. In order to improve the simulation of commercial deactivation in lab testing, circulating pilot units were designed in which the FCC catalysts were metallated by cracking of vacuum gas-oils spiked with contaminant metals. The metallated catalysts were aged with reduction–oxidation cycles. It was shown that the performance of catalysts deactivated in such units represents commercially equilibrated catalysts much more realistically than the Mitchell technique [7]. However, cyclic metallation and ageing in pilot units is time consuming and the complexity of such units impairs the reproducibility of experiments.

This method was scaled down to the CPS procedure where the catalysts are metallated by the incipient wetness method and deactivated in reduction–oxidation cycles using propylene as the reducing medium [3]. This protocol was equivalent to pilot units in terms of catalyst properties following deactivation, but provided advantages in terms of precision and productivity. Nevertheless, investigations have shown that the effects of vanadium on catalyst performance were often still over-emphasized. In these protocols each reduction-oxidation cycle consisted of a 10 min reduction and 10 min oxidation step separated by 10 min stripping intervals. Consequently, all the vanadium was in the highest oxidation state more than 50% of the total time. The second problem occurs at the first contact of the FCC catalyst with steam. Here, all the vanadium was in the +5 state due to the burning off of the organic components, which originate from the impregnation of the FCC catalysts with organic vanadium and nickel compounds. Because the first CPS step is not a reduction step, the FCC catalyst is exposed to the attack of the total amount of impregnated vanadium in the +5 state. This situation is completely different from commercial operation where only the vanadium deposited during the last cracking step is preferably oxidised in the regenerator, and where in addition the regenerator is not a perfectly oxidising environment. Most of the vanadium from previous cracking steps is passivated in the FCC catalyst for instance as rare-earth and alumina vanadates [8–10]. Hence, much more vanadic acid is formed during the first CPS cycle than in commercial operation, and this together with an overlengthy oxidation-time is responsible for the dominating effects of vanadium during CPS deactivation. The third problem that occurs in CPS deactivations are temperature excursions above the pre-set CPS temperature at the start of steam addition. These excursions are ascribed to the heat released by adsorption of water.

An improved CPS mode emerged from these considerations:

- the sequence of stripping-reduction–stripping-oxidation was changed,
- the ratio of reduction-time to oxidation-time was increased, and
- pre-stabilisation cycles during the heating-up phase were introduced.

2.2. Metals-free deactivation

Historically, when a very low metals feed was used as feedstock to the FCC unit, it was considered appropriate not to

Table 1
AM-1500 deactivation method

Heat-up phase
Room temperature to 811 K at 27.8 K/min, N_2 purge
Keep at 811 K for 3 h, N_2 purge
Heat up to 1089 K at 27.8 K/min, N_2 purge
Stabilise for 1.2 h, N_2 purge
100% Steam at 1089 K for 5 h
Cool down under nitrogen flow

Table 2
CPS-1 deactivation protocol

Heat-up phase
Room temperature to 1006 K with 8.6 K/min; N_2 purge
1006–1061 K with 1.1 K/min; N_2 purge
29 cycles of the cycle described below at 1061 K
10 min, 50% nitrogen + 50% steam
10 min, 50% N_2 (containing 5% propylene) + 50% steam
10 min, 50% nitrogen + 50% steam
10 min, 50%, 4000 ppm SO_2 in air + 50% steam
30th cycle
10 min, 50% nitrogen + 50% steam
10 min, 50% N_2 (containing 5% propylene) + 50% steam
Cool down under nitrogen flow

metallate the FCC catalysts. Therefore, it was thought that the oxidation and reduction cycles would not be of relevance. The protocol used most commonly therefore was the AM-1500 deactivation method. This method is based on the procedure described in ASTM D 4463-96. The protocol used at Grace Davison is shown in Table 1.

This AM-1500 method has several pitfalls that may affect the correct projection of the performance of fresh catalysts to FCC units. The FCC catalyst is not exposed to the high intraparticle temperatures it sees in the FCC units, where the high intraparticle temperatures occur during the burning off of the coke in the regenerator. Such high intraparticle temperatures certainly lead to a pre-stabilisation prior to deactivation. Moreover, the 100% steam atmosphere together with the high temperature of 1089 K may be too severe. In the cases of non-traditional FCC catalysts, e.g. FCC catalysts containing reducible components, the AM-1500 deactivation may not be an appropriate simulation of commercial deactivation since this protocol deactivates in an oxidising atmosphere exclusively. The temperature excursions at the start of the steam addition above the preset temperature described and discussed in the preceding section occurs in the AM-1500 method as well.

Hence, a CPS mode for testing of FCC catalysts in the absence of metals was developed based on these considerations. The CPS mode, as such, is the same as developed for metallated FCC catalysts (see the preceding section). In order to generate high intraparticle temperatures the FCC catalysts were impregnated with a vacuum gas–oil, which was burned off at 973 K prior to CPS deactivation.

3. Deactivation in the presence of metals

Metallation of FCC catalysts prior to CPS deactivations was performed as follows:

The catalysts were calcined for 3 h at 813 K prior to loading with vanadium- and nickel-naphthenates using toluene as solvent. The volume of the impregnation solution was roughly double the amount of the pore volume of the FCC catalysts and the excess of solvent was removed in a rotary evaporator at 393 K. The remaining organics were burned off with air at 523 K for 3 h followed by 973 K for 3 h in a shallow bed.

3.1. CPS-1 method

The method described in this section is referred to as CPS-1 hereinafter (known as Standard-CPS from previous publications [11]). This protocol is illustrated in Table 2 and this method was used as the base case to explore the influence of the modifications described in Section 2.1 on catalyst performance.

The reason for adding SO_2 to the oxidising atmosphere is as follows:

In commercial FCC units sulphur is present in the coke deposited on the FCC catalyst particles during cracking of sulphur containing feeds. This sulphur is oxidised in the FCC regenerator:

$$S_{coke} + O_2 \rightarrow SO_2$$

$$2SO_2 + O_2 \rightarrow 2SO_3$$

Metal oxides (MeO) that have V-trapping functionality react with vanadic acid according to:

$$2MeO + 2H_3VO_4 \rightarrow Me_2V_2O_7 + 3H_2O$$

However, the metal oxides can also react with SO_3 in the FCC regenerator to form stable metal sulphates instead of trapping vanadium

$$MeO + SO_3 \rightarrow MeSO_4$$

Testing of V-traps in the laboratory without SO_2 could falsely indicate a good V-trapping functionality. These traps could fail in commercial operation due to competitive reactions of vanadium and SO_3 with the trap. In order to include sulphur effects in lab deactivation, SO_2 is added to the ''regenerator atmosphere'' in CPS deactivation.

3.2. Development of the CPS-3 procedure

Because of the thresholds described in Section 2.1, it was considered necessary to improve the CPS-1 method. The objective was not only to develop a more realistic and accurate deactivation protocol, but also to maintain the productivity of the CPS method, and therefore the total time of the CPS-1 method was not increased.

3.2.1. Oxidation time after reduction step

The CPS-1 method was modified with the aim of keeping the vanadium in a reduced state as long as possible while at the same time completely burning off the coke formed during the reduction step after each cycle to prevent an accumulation of

Table 3
Variation of the time of the oxidation cycle and thereby of the coked catalyst exposed to air

Heat-up phase
Room temperature to 1022 K at 8.6 K/min; N_2 purge
1022–1077 K at 1.1 K/min; N_2 purge
1 cycle at 1077 K
2 min, 50% nitrogen + 50% steam
30 min, 50% N_2 (containing 5% propylene) + 50% steam
2 min, 50% nitrogen + 50% steam
Different times (0, 3, 4, 5 and 6 min) with 50%, 4000 ppm SO_2 in air + 50% steam
Cool down under nitrogen flow

Table 4
Influence of oxidation time in the first CPS cycle on coke-on-catalyst

Pre-treatment[a]	Coke-on-catalyst (wt.%)	
	Catalyst A	Catalyst B
Variation of oxidation time		
(i) 49.6% air + 0.4% SO_2 + 50% steam: 0 min	0.18	0.14
(ii) 49.6% air + 0.4% SO_2 + 50% steam: 3 min	0.04	0.03
(iii) 49.6% air + 0.4% SO_2 + 50% steam: 4 min	0.02	0.01
(iv) 49.6% air + 0.4% SO_2 + 50% steam: 5 min	0.01	0.01
(v) 49.6% air + 0.4% SO_2 + 50% steam: 6 min	0.01	0.01
30 cycles		
50%, 5% propylene = in N_2 + 50% steam 30 min 50% N_2 + 50% steam 2 min 50% 49.6% air + 0.4% SO_2 + 50% steam 5 min 50% N_2 + 50% steam 2 min	0.01	0.01

[a] 50%, 5% propylene = in N_2 + 50% steam: 30 min; 50% N_2 + 50% steam: 2 min.

coke-on-catalyst during deactivation. The reduction time was increased from 10 to 30 min, the stripping step was reduced from 10 to 2 min and the minimum time necessary to burn off the coke during the oxidation step was determined. This was done by variation of the time the coked catalyst is exposed to air as described in Table 3.

The findings showed that a regeneration time of 6 min is sufficient to burn off the coke, and therefore this time was used in the modified CPS method referred to as CPS-3 hereinafter (also known as Advanced-CPS [11]). The complete CPS-3 procedure is illustrated in Section 5 (Table 15).

The coke on catalyst was measured following the different oxidation-times and the results are given in Table 4. After 5 min of oxidation, the coke was burned off to 0.01 wt.%. Increasing the oxidation time did not reduce the coke further. The same catalysts were run in 30 cycles with 5 min oxidation time, and 0.01 wt.% coke on catalyst was also obtained following the complete CPS deactivation run. These findings suggest that the 0.01 wt.% coke measured after one cycle is located in positions where it cannot be burned off by the regeneration step in the CPS procedure. The results after 30 cycles clearly show that no further coke of this kind accumulates on the catalysts during the CPS cycles. In the following sections, 6 minutes oxidation-time was used to guarantee that the coke is also completely burned off in the case of catalysts that produce more coke than the tested samples.

3.2.2. *Pre-stabilisation cycles during CPS, and modification of the sequence of stripping, reduction and oxidation in the CPS cycles*

As discussed above, the concerns with the current CPS deactivation are (i) the ''fresh 3000 ppm vanadium'' is in the +5 state (due to the burning off of the organic components at 973 K after impregnation) when it has the first contact with steam and (ii) the start of the CPS cycles with the stripping or oxidising step increases the time the catalyst is exposed to the total amount of impregnated vanadium in the +5 state at the start of the hydrothermal treatment.

In order to adjust the CPS procedure to the conditions in FCC units, the sequence of stripping–reduction–stripping–

Table 5
Deactivation during thermal treatments and pre-stabilisation cycles prior to CPS deactivation

Treatments	Metals-free (Thermal)		Metallated: 3000 ppm V + 2000 ppm Ni				
	813 K (3 h)	973 K (3 h)[a]	Thermal (973 K (4 h))	CPS cycles			
				Prestabilisation		1077 K	
				1st cycle	1st + 2nd cycle	1st cycle	32 cycles[b]
Catalyst A (1.0% RE_2O_3 on catalyst)							
Zeolite surface area (m^2/g)	265	261	256	235	219	201	142
Matrix surface area (m^2/g)	43	39	38	40	39	35	31
Unit-cell size (Å)	24.56	24.49	24.48	24.44	24.42	24.37	24.24
Catalyst B (2.8% RE_2O_3 on catalyst)							
Zeolite surface area (m^2/g)	235	237	237	221	214	193	137
Matrix surface area (m^2/g)	84	70	56	69	61	59	47
Unit-cell size (Å)	24.60	24.55	24.55	24.51	24.49	24.43	24.31

Surface areas of catalysts were determined by nitrogen adsorption performed with a Micromeritics ASAP 2000 unit. The zeolite and matrix surface areas were calculated by the *t*-plot method. The unit-cell size of the zeolite was determined by X-ray diffraction (XRD) using a Siemens D-500 automated analyser according to the Standard ASTM D3942-97 procedure.

[a] Impregnated with gas–oil.

[b] 2 Pre-stabilisation cycles (989–1077 K) + 30 cycles at 1077 K.

oxidation was altered to reduction–stripping–oxidation–stripping and two additional cycles during the heating-up phase were introduced. The benefits expected from these modifications were (i) the instantaneous reduction of vanadium at the first contact with steam and (ii) the pre-stabilisation the catalysts experience prior to exposure to the maximum CPS temperature. This pre-stabilisation approach may further reduce the effects the differences between lab and commercial operation could have on catalyst performance.

To investigate the deactivation that the catalysts experience during the pre-stabilisation cycles, unit-cell sizes and surface areas were measured after (i) the burning off of the organic components originating from the impregnation with vanadium and nickel (3 h, 973 K), (ii) the first cycle (989–1033 K) and (iii) the first and the second cycle (989–1077 K). Afterwards, the deactivation during one cycle at 1077 K was determined. The results are summarised in Table 5. During both pre-stabilisation cycles unit-cell sizes decreased about 0.06 Å, whereas in the cycle at 1077 K a unit-cell size drop of about 0.1 Å was obtained. The decline of surface area during pre-stabilisation was also smaller than in the cycle at 1077 K. These data clearly show that the deactivation during the heating up phase is weaker than in the 1st cycle at the final temperature, and therefore, this method is appropriate to achieve a mild pre-stabilisation. The results in Table 5 also reveal a significant decrease in unit-cell size following the burning off of the organic components originating from the impregnation with vanadium and nickel (4 h, 973 K).

In order to investigate whether this observation is attributable to the impregnated vanadium and/or to the thermal treatments following impregnation, FCC catalysts were impregnated with a vacuum gas–oil dissolved in toluene. The excess of toluene was removed in a rotary evaporator, and the organic components remaining on the catalysts were burned off with the same procedure used for the metallated catalysts (3 h, 973°C). The unit-cell sizes and surface areas of these samples are also given in Table 5. The surface areas did not show any significant changes whereas unit-cell sizes revealed a decline similar to that measured for the vanadium and nickel impregnated catalysts after the burning off step. Therefore, it can be concluded that the deactivation the catalysts experienced prior to CPS is not caused by vanadium but can be attributed to the thermal treatments. These findings suggest that in experiments aimed at evaluating the vanadium tolerance of catalysts, the physical properties should be measured after burning off of the organic components.

The temperature profiles during a CPS-1 and CPS-3 run were recorded and the data are displayed in Fig. 1. A sharp temperature increase above the pre-set maximum CPS-1 temperature of 1061 K was observed at the time of the first contact of the catalyst with steam, and this is ascribed to heat released by water adsorption on FCC catalysts. Fig. 1 demonstrates that this temperature excursion above the pre-set maximum temperature cannot occur in the CPS-3 protocol because of the start of steam addition at the beginning of the pre-stabilisation cycles during the heating up phase. Clearly, the start of steam addition at the lower temperature prevents the

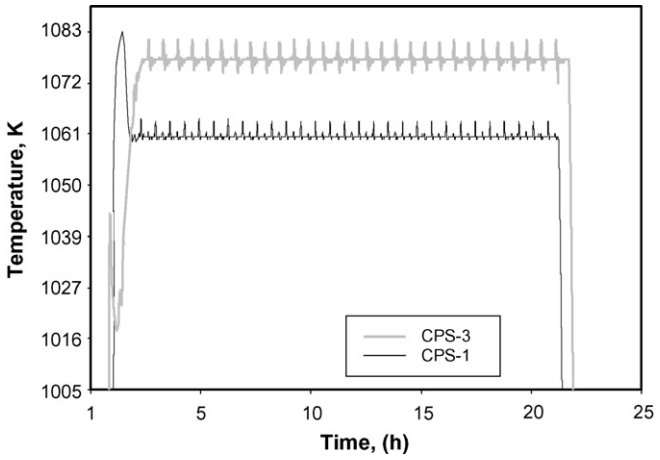

Fig. 1. Temperature profiles during CPS runs.

temperature excursion above the maximum CPS temperature and therefore the CPS-3 method also provides benefits regarding the temperature control during CPS deactivation. The smaller peaks occurring periodically after 40 min were caused by the combustion of coke during the regeneration step. CPS-3 showed larger peaks than CPS-1, which is ascribed to the longer exposure to propylene, i.e. more coke was formed in CPS-3.

Summarising, a prestabilisation step was introduced in order to (i) reduce the destructive effects of the oxidised vanadium at the start of exposure to hydrothermal conditions, and (ii) to prevent temperature excursions above the maximum CPS temperature at the first time of contact of the catalyst with steam.

3.2.3. Variation of reduction-, oxidation- and stripping-time and temperature

Two commercial FCC catalysts containing RE-USY zeolite were deactivated in the CPS-1 protocol and the modifications described before (CPS-3) at 1061 K. Physicochemical properties of the calcined catalysts and following CPS-1 and CPS-3 deactivations are compiled in Table 6. The data show that at 1061 K the effects of vanadium on zeolite destruction are less pronounced in the CPS-3 mode. The weaker deactivation in CPS-3 is attributed to the longer time the vanadium is in a reduced state. Consequently less vanadic acid is formed and therefore the catalyst decay is more governed by hydrothermal deactivation than by vanadium attack, hence less zeolite is destroyed.

In the CPS-1 approach, FCC catalysts containing rare-earth exchanged zeolites are generally equilibrated at physical properties typical for commercially equilibrated catalysts; such a comparison is given in Section 4.4. Therefore the aim was to equilibrate these catalysts in the CPS-3 method to zeolite surface areas and unit-cell sizes obtained by CPS-1 deactivation. To achieve this the CPS-3 deactivations were performed at higher temperatures. The findings obtained at 1077 K were added to Table 6, and the comparison with the values following CPS-1 shows that at this temperature the targeted deactivation severity was obtained.

Table 6
Influence of reduction-time to oxidation-time ratio on the deactivation of metallated (3000 ppm V + 2000 ppm Ni) FCC catalysts

	CPS-1		CPS-3			
	1061 K		1061 K		1077 K	
	Catalyst A	Catalyst B	Catalyst A	Catalyst B	Catalyst A	Catalyst B
RE_2O_3-on-catalyst (wt.%)	1.0	2.8	1.0	2.8	1.0	2.8
Conversion (%)	58	72	62	74	56	71
Zeolite surface area (m^2/g)	142	130	157	147	142	137
Matrix surface area (m^2/g)	32	52	34	52	31	47
Coke-on-catalyst (wt.%)	0.03	0.04	0.10	0.14	0.10	0.12
Unit-cell size (Å)	24.25	24.31	24.26	24.34	24.24	24.31
Zeolite surface area retention (%)[a]	54	55	59	63	52	54

[a] Calculated with zeolite surface area following calcination at 813 K, 3 h.

3.2.4. Activation of FCC catalysts after CPS deactivation

It was shown by Boock et al. [3] that the dehydrogenation activity of nickel and vanadium only has the realistic ratio of 3–4 if CPS ends in a reducing atmosphere. Here the oxidation states of vanadium and nickel are much closer to those on commercially equilibrated catalysts than after ending CPS with an oxidative medium, even when the equilibrium catalysts are taken from FCC units operated in full combustion mode. However, the problem with ending CPS in reduction is the coke-on-catalyst prior to microactivity testing, especially in the CPS-3 protocol. Here the coke-on-catalyst is about three times higher than after CPS-1 due to the longer exposure to propylene. Moreover, the coke-on-catalyst concentrations are different for the individual catalyst families (see Table 6) and this might influence/distort the MAT selectivities measured with such coke-loaded catalysts compared with ''coke-free catalysts''.

It has been shown by several authors that burning off the coke by (i) ending CPS in oxidation and (ii) activation of metallated and deactivated FCC catalysts at high temperatures (973 K) oxidises the vanadium to the +5 state and therefore enhances its catalytic activity [12]. The dehydrogenation activity of V^{+5} was even higher than that of nickel. In this work it was investigated whether these unwanted effects are also obtained at lower activation temperatures. FCC catalysts co-impregnated with vanadium and nickel were run in the CPS-1 and CPS-3 protocols and activated at 773 K for 3 h in a shallow bed. MAT selectivity testing was performed according to the SCT-MAT method on a paraffinic VGO (Feed B) described elsewhere [13] for the activated and non-activated catalysts. The coke-on-catalyst formed by CPS, which was on the FCC catalysts prior to microactivity testing, was subtracted from the coke-on-catalyst measured after gas-oil cracking. The key selectivities are summarised in Table 7. The most important finding was that the activation at 773 K did not boost the formation of hydrogen and coke. In contrast, the activation even lowered hydrogen and coke make.

In order to investigate the contribution of vanadium and nickel to coke and hydrogen formation Catalyst A was divided into two parts. One was impregnated with 3000 ppm vanadium and the second sample was impregnated with 3000 ppm nickel. Each of these samples was activated at 773 K for 3 h following CPS-3 deactivation. Microactivity testing was performed with the non-activated and activated catalysts. Results are summarised in Table 8, and these data suggest that the lower hydrogen yields of the activated catalysts shown in Table 8 can be ascribed to a reduced dehydrogenation activity of nickel. Hydrogen formation by vanadium was not affected by activation. An explanation for these findings could be that the activation at 773 K does not affect the oxidation state of vanadium, whereas nickel is

Table 7
Influence of activation (773 K, 3 h) of V, Ni (3000 ppm, 2000 ppm) co-impregnated and CPS[a] deactivated catalysts on hydrogen and coke formation

Deactivation	CPS-1		CPS-3			
Catalyst	C		D		E	
Pre-treatment	Non-activated	Activated	Non-activated	Activated	Non-activated	Activated
Coke (wt.%)[b]	0.03	0.01	0.10	0.01	0.12	0.01
Conversions at constant catalyst-to-oil ratio (C/O = 3), %	70	70	57	57	78	80
Catalyst-to-oil ratios and yields at 65% conversion						
C/O	2.7	2.6	3.6	3.6	2.0	1.7
H_2 (wt.% ff)	0.50	0.42	0.49	0.43	0.45	0.39
Coke (wt.% ff)	2.8	2.7	2.8	2.6	2.6	2.4
C_4 olefinicity (%)	75.5	78.7	78.4	77.2	73	74.1

[a] CPS ending in reduction.
[b] Coke-on-catalyst after CPS.

Table 8
Influence of activation (773 K, 3 h) of CPS deactivated[a] FCC catalysts on the dehydrogenation activity of vanadium and nickel

	Catalyst A (CPS-3)			
	3000 ppm V[b]		3000 ppm Ni[b]	
	Non-activated	Activated	Non-activated	Activated
Coke (wt.%)[c]	0.05	0.02	0.07	0.01
Conversion at constant C/O ratio (%)	62	66	58	59
C/O and yields at 65% conversion				
C/O	2.6	2.4	2.0	1.7
H_2 (wt.% ff)	0.11	0.11	0.49	0.43
Coke (wt.% ff)	1.6	1.5	2.6	2.5
C_4 olefinicity (%)	70.6	70.0	76.4	74.7

[a] CPS ending in reduction.
[b] Metallation.
[c] Coke-on-catalyst after CPS.

oxidised from Ni(0) to a catalytically less active species, Ni(+2).

4. Further evidence and examples

4.1. V-transfer rates

The rate of interparticle vanadium mobility in different CPS modes was analysed by the V-transfer rate from an FCC catalyst to ''basic oxide'' vanadium traps, which have also been shown to work in FCC units [14].

The V-traps and the FCC catalysts were impregnated separately to 3000 ppm V + 2000 ppm Ni according to the procedure described in Section 3. Blends containing 95% FCC catalyst and 5% V-trap were deactivated in four different scenarios going stepwise from an oxidising to a reducing atmosphere.

(i) hydrothermal oxidising atmosphere: 50% steam +50% N_2, 20 h, 1061 K,
(ii) CPS-1,
(iii) CPS-3,
(iv) hydrothermal reducing atmosphere: 50% N_2 (containing 5% propylene) in N_2, 20 h, 1077 K.

Following these treatments, the blends were separated by density separation in a light and heavy fraction representing the FCC catalyst and V-trap, respectively. A sodium metatungstate solution adjusted to a density between that of FCC catalyst and V-trap was used for these experiments [15]. The fractions were analysed on chemical composition. Vanadium concentrations measured on the light and heavy fractions were normalised to 100% with the vanadium concentration on the blend prior to density separation as base. The V-transfer factor is defined as the ratio of V-on-trap to V-on-FCC catalyst following CPS.

V-transfer factors for the same type of V-traps were determined on commercially equilibrated FCC catalyst and vanadium trap mixtures with the same procedure. These samples were taken from FCC units about 50 days after commencing the V-trap trials. At the time of sampling, the concentrations of V-trap A and B in the FCC unit were similar and rather stable. Hence, the ranking of the commercially deactivated traps and that of the lab findings are comparable.

The corresponding vanadium concentrations obtained for the lab preparations and the commercially equilibrated samples prior to, and following, the density separations are summarised in Table 9.

Table 9
Vanadium transfer from FCC catalyst to vanadium traps in different lab deactivation protocols and in commercial trials

Pre-treatment	FCC catalyst and V trap blend	Heavy fraction (V-trap A)	Light fraction (FCC catalyst)	V transfer factor
Normalised vanadium concentration (ppm) on				
50% steam	2991	19624	2097	9.4
CPS-1	2903	15718	2229	7.1
CPS-3	2946	6780	2790	2.4
PB-CPS	2905	3578	2866	1.2
E-cat	2700	8905	2515	3.5
Pre-treatment	FCC catalyst and V trap blend	Heavy fraction (V-trap B)	Light fraction (FCC catalyst)	V transfer factor
Normalised vanadium concentration (ppm) on				
50% steam	2980	31135	1498	20.8
CPS-1	3101	23178	2044	11.3
CPS-3	3013	8734	2712	3.2
PB-CPS	2887	3101	2876	1.1
E-cat	3136	12474	2645	4.7

Vanadium is known to be mobile in FCCU regenerators. This mobility is dependent on the vanadium being in the +5 oxidation state, [4] and therefore the determination of V-mobility is an indirect measurement of its oxidation state. The V-transfer factors calculated for the different approaches demonstrate that increasing the time the vanadium is exposed to reducing atmosphere significantly reduces the interparticle mobility. The data in Table 9 reveal that compared to the commercially equilibrated FCC catalyst and vanadium trap mixtures, the V-transfer is over-emphasised following the pure hydrothermal deactivation and CPS-1 whilst being to small in the pure hydrothermal reducing atmosphere (mode iv, PB-CPS). The V-transfer factors obtained for the CPS-3 deactivated blend gave the best agreement with the commercially equilibrated FCC catalyst and vanadium trap mixtures, and therefore these findings highlight that the CPS-3 mode generally simulates the deactivation in FCC units better than the CPS-1 deactivation.

4.2. Influence of metal concentration on deactivation

One problem that frequently arises in predicting the performance of commercial catalysts is the variation of deactivation procedure depending on the vanadium and nickel concentrations on the FCC catalysts. Ideally, the metals on the lab-tested catalysts should be tested with the same metals level as the catalyst would contain in the corresponding commercial FCC unit. The operational parameters of the CPS-1 procedure were optimised for vanadium and nickel loadings of roughly 3000 ppm and 2000 ppm, respectively, and here a reasonable deactivation has been achieved. At much higher metal levels the operational parameters have to be modified because of the destructive effects of vanadium, which are in such cases more pronounced in the CPS-1 protocol than in FCC units. In order to investigate the performance of FCC catalysts at different metal levels in the CPS-3 mode, three FCC catalysts with different rare-earth contents and different matrices were impregnated to (i) 3000 ppm V + 2000 ppm Ni, (ii) 5500 ppm V + 3800 ppm Ni, (iii) 7800 ppm V + 5300 ppm Ni and run in the CPS-1 and the CPS-3 protocol. Unit-cell sizes, surface areas and activities measured for these samples and for a catalyst equilibrated in an FCC unit are given in Table 10. These data clearly indicate a stronger catalyst decay in the CPS-1 mode than in CPS-3, especially at the highest metal loading. The comparison with the catalyst equilibrated in the FCC unit showed the CPS-3 data to agree better with commercial operation (Section 4.4), and this is attributed to the lower oxidation states of vanadium in this protocol. As a consequence, less H_3VO_4 is formed and therefore the vanadium is less mobile. Thus, the deactivation is governed more by hydrothermal deactivation rather than by the destructive effects of vanadium. The data indicate that there are still some differences between CPS-3 and commercial equilibration. However, it has to be taken into account that the rate of fresh catalyst addition is used in FCC units to keep the catalyst performance at a desired level. This parameter was not applied for CPS deactivations, hence, we consider the deactivation severity in FCC units and CPS-3 operation to be rather similar.

Table 10
Comparison of CPS-1 and CPS-3 deactivation at different vanadium and nickel concentrations

	Catalyst		
	F	G	H
Metals-free			
Calcination (3 h, 813 K)			
RE_2O_3 (wt.%)	1.1	1.91	3.1
Al_2O_3 (wt.%)	49.8	47.6	46.8
Zeolite surface area (m^2/g)	252	243	246
Unit-cell size (Å)	24.53	24.55	24.58
3000 ppm V + 2000 ppm Ni			
CPS-1			
Unit-cell size (Å)	24.25	24.26	24.32
Zeolite surface area retention (%)	57	51	57
Conversion (%)	59	64	73
CPS-3			
Unit-cell size (Å)	24.26	24.27	24.32
Zeolite surface area retention (%)	62	59	57
Conversion (%)	61	65	76
5500 ppm V + 3800 ppm Ni			
CPS-1			
Unit-cell size (Å)	24.25	24.24	24.29
Zeolite surface area retention (%)	54	50	48
Conversion (%)	54	58	67
CPS-3			
Unit-cell size (Å)	24.25	24.25	24.32
Zeolite surface area retention (%)	61	52	55
Conversion (%)	61	62	71
7800 ppm V + 5300 ppm Ni			
CPS-1			
Unit-cell size (Å)	24.23	24.19	24.25
Zeolite surface area retention (%)	42	38	39
Conversion (%)	50	52	61
CPS-3			
Unit-cell size (Å)	24.25	24.23	24.30
Zeolite surface area retention (%)	67	48	51
Conversion (%)	56	57	72

E-Cat (Catalyst H): RE_2O_3: 2.92 wt.%, vanadium: 6544 ppm, nickel: 2424 ppm; unit-cell size: 24.30 Å, zeolite surface area retention: 50%, conversion: 72%

The data in Table 10 demonstrate that the CPS-3 mode can be used for metals level up to 7800 ppm V + 5300 ppm Ni without changing any operational parameters, in fact even higher metals values than these were used. This advantage certainly simplifies lab-testing.

4.3. Validation against catalysts with age distribution

4.3.1. Background

The physical properties of equilibrium catalyst particles vary from particle to particle as a function of residence time in the FCC unit. This in turn may entail that different slopes of degradation curves are obtained for catalysts of different

Table 11
Catalyst properties

Catalyst	Rare-earth (wt.% db)	Al_2O_3 (wt.% db)	Surface area		Unit-cell size (Å)
			Zeolite (m^2/g)	Matrix (m^2/g)	
I	1.1	50.4	275	57	24.53
J	2.0	46.4	261	57	24.56
K	2.8	47.3	237	41	24.61
L	3.7	46.9	246	60	24.58
M	5.9	45.0	252	53	24.63

stability, and by the same token, different slopes of the corresponding selectivity curves; the curves could even cross. Hence the deactivation severity in laboratory deactivation methods could be decisive for the ranking of FCC catalyst performance.

The piece of work presented by Beyerlein et al. [16] and Palmer and Cornelius [17] have shown that the catalytic performance of an equilibrium catalyst is dominated by the younger fractions. Therefore it can be hypothesized that deactivation methods with moderate severity, i.e. methods that produce fresher catalysts, in relation to equilibrium catalyst may lead to accurate ranking in most cases whilst methods with high severity may not.

4.3.2. Experimental

In order to investigate this issue, FCC catalysts were deactivated with the conventional CPS-3 method and with a modified CPS-3 method producing catalysts with age distribution.

The tested catalysts primarily differed in rare-earth content since the impact of this parameter on catalyst performance is well known [18–21]. The properties of the tested catalysts are listed in Table 11.

The samples with age distribution were produced as follows:

For each catalyst six age fractions were prepared by impregnating the catalysts to six different vanadium and nickel levels followed by CPS-3 deactivations of different durations; the corresponding vanadium and nickel levels and deactivation times are shown in Table 12. The six age fractions of the corresponding catalysts were blended following deactivation to equal parts (16.6% from each fraction).

The samples without age distribution were prepared by impregnation of the catalysts to the average vanadium and nickel levels of the age fractions in one shot and deactivation by a single CPS-3 run for 20 h.

Selectivity testing was performed according to the SCT-MAT method on a paraffinic vacuum gas–oil previously described [13].

Table 12
Metal levels and deactivation times

	Fraction no.						Average
	1	2	3	4	5	6	
V (ppm)	500	1000	2000	3000	4000	5000	2583
Ni (ppm)	150	400	1000	1800	2800	4000	1692
CPS (h)	5	10	20	40	70	110	42.5

4.3.3. Results and discussions

Due to the wealth of data only key findings, and therefore, selected data sets are discussed in this paper.

4.3.3.1. Physical-chemical properties. Unit-cell size and zeolite surface area as a function of CPS deactivation time and metal levels are illustrated in Figs. 2 and 3; the corresponding metal levels to the deactivation times can be seen in Table 12.

These figures exhibit an initially rapid loss of both zeolite surface area and unit-cell size in the 0–5 h regime followed by a slower decline. Both regimes indicate a linear degradation of the catalysts but with different slopes and thus suggest two regimes of first order decay. Hence these data corroborate the studies presented by Wang et al. [22] and Chester and Stover [23] who suggested the same decay kinetics.

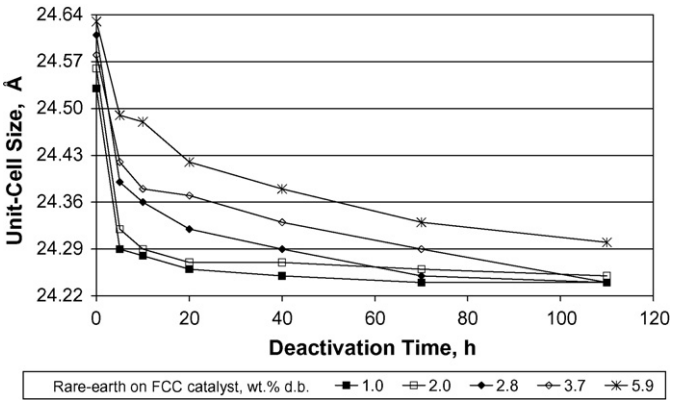

Fig. 2. Unit cell sizes of FCC catalysts of different rare-earth content as a function of deactivation time and metal level.

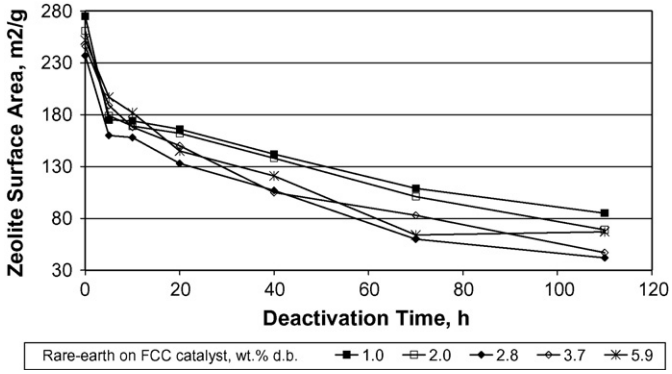

Fig. 3. Zeolite surface areas of FCC catalysts of different rare-earth content as a function of deactivation time and metal level.

Table 13
Catalyst properties with and without age distribution

Catalyst	Rare-earth (wt.% db)	With age distribution			Without age distribution		
		Surface area		Unit-cell size (Å)	Surface area		Unit-cell size (Å)
		Zeolite (m^2/g)	Matrix (m^2/g)		Zeolite (m^2/g)	Matrix (m^2/g)	
I	1.1	141	38	24.26	160	39	24.26
J	2.0	133	33	24.28	153	41	24.28
K	2.8	110	30	24.31	138	32	24.32
L	3.7	124	32	24.34	147	33	24.36
M	5.9	126	29	24.40	115	26	24.46

The average unit-cell sizes and zeolite surface areas of the samples with age distribution (i.e. those of the blends) and the data obtained for the regular CPS-3 deactivated samples are given in Table 13.

The samples with age distribution have lower zeolite surface areas and lower unit-cell sizes compared to those samples without age distribution. Since the catalytic performance of FCC catalysts with age distribution is dominated by the younger fractions, these differences in zeolite surface areas and unit-cell sizes do not allow any conclusions on catalytic consequences.

4.3.3.2. Catalytic results. The catalytic results obtained for the samples with and without age distribution were evaluated from two perspectives; first in terms of differences in the levels of activity and selectivities between the two deactivation modes and second the impact of rare-earth variation on activity and selectivity. For this purpose seven activity/selectivity data sets were selected and these data are illustrated in Figs. 4–10.

In terms of product selectivities, the features of samples with age distribution compared to those without age distribution include:

- lower conversions; cf. Fig. 4,
- less hydrogen; cf. Fig. 5,
- similar coke-on-catalyst; cf. Fig. 6,
- lower gasoline olefinicity; cf Fig. 7,
- less LPG, cf. Fig. 8,
- more gasoline, cf. Fig. 9,
- more LCO; cf. Fig. 10.

The lower activities of the samples with age distribution can be related to their lower zeolite surface areas and unit-cell sizes compared to the samples without age distribution.

The lower hydrogen selectivity of the samples with age distribution is ascribed to the stronger deactivation of most of the vanadium and nickel in the 'age distribution mode'. The similar coke-on-catalyst is ascribed to countercurrent effects of the differences in activity, hydrogen-transfer and metals ageing.

The higher hydrogen-transfer rates of the samples with age distribution (lower gasoline olefinicity) over the samples without age distribution can be ascribed to the catalytic dominance of the younger fractions in these samples. The higher gasoline selectivity of the samples with age distribution is a consequence of a better gasoline stabilisation by reduction of gasoline olefinicity due to their higher hydrogen-transfer activity, i.e. less gasoline was cracked into the LPG fraction.

Bottoms cracking activity is reflected by the LCO selectivity. This parameter is more pronounced for the samples with age distribution, which is related to the high bottoms cracking potential of the older fractions in these catalysts.

The shifts expected from rare-earth variation, i.e. from unit-cell size variation, were observed for the samples with and without age distribution. With increasing rare-earth content the overall cracking activity increased (cf. Fig. 4). In addition, hydrogen-transfer rates increased with increasing rare-earth

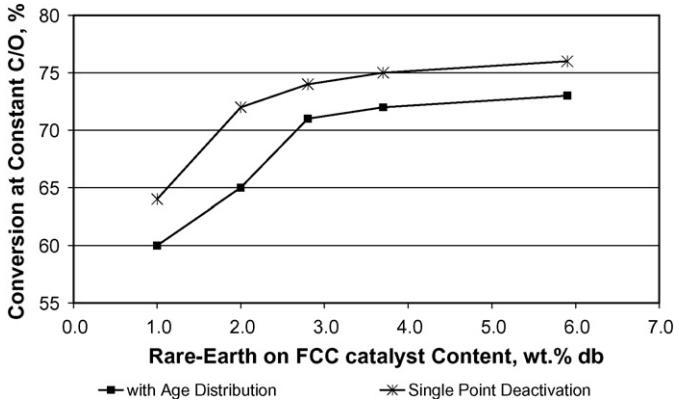

Fig. 4. Conversion for FCC catalysts of different rare-earth content for FCC catalysts deactivated with and without age distribution.

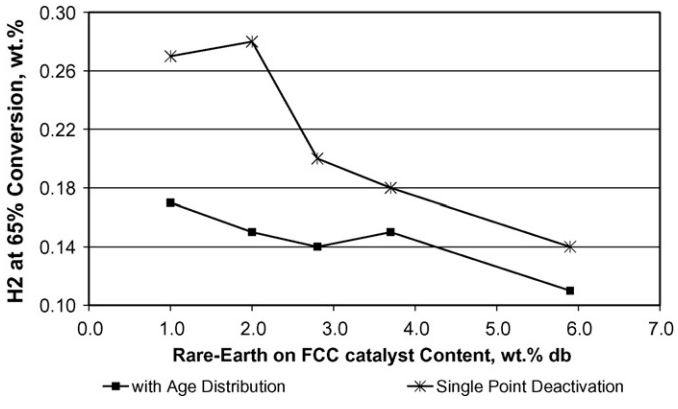

Fig. 5. Hydrogen selectivity of FCC catalysts of different rare-earth content for FCC catalysts deactivated with and without age distribution.

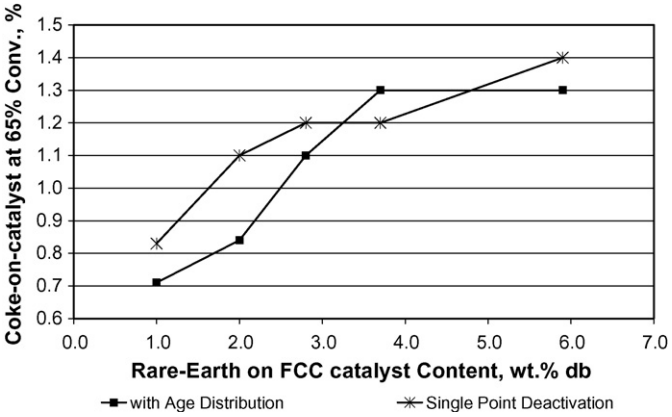

Fig. 6. Coke-on-catalyst of FCC catalysts of different rare-earth content for FCC catalysts deactivated with and without age distribution.

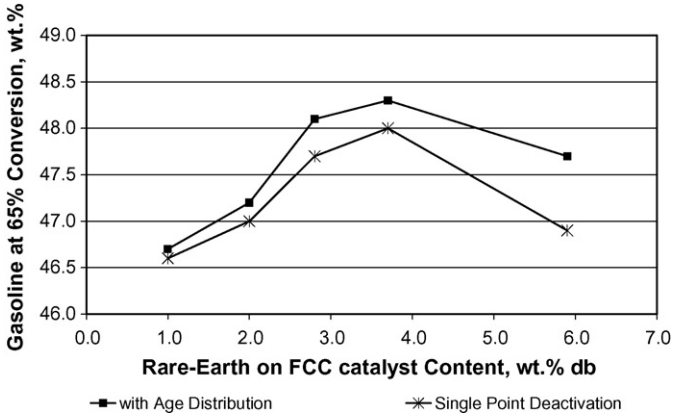

Fig. 9. Gasoline selectivity of FCC catalysts of different rare-earth content for FCC catalysts deactivated with and without age distribution.

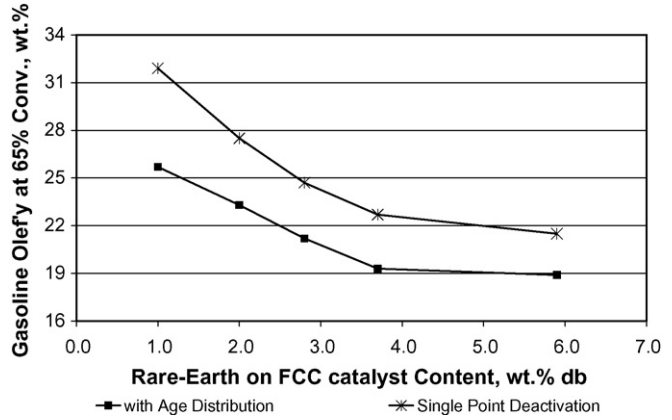

Fig. 7. Gasoline olefinicity of FCC catalysts of different rare-earth content for FCC catalysts deactivated with and without age distribution.

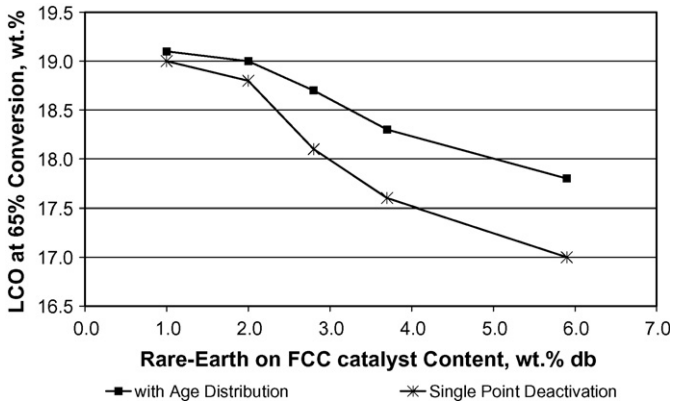

Fig. 10. LCO selectivity of FCC catalysts of different rare-earth content for FCC catalysts deactivated with and without age distribution.

content, (cf. Fig. 7). Gasoline selectivity went through a maximum (cf. Fig. 11) and LPG through a minimum. Bottoms cracking declined with increasing rare-earth levels (cf. Fig. 10). Similar trends were reported in Refs. [18–21].

Gasoline selectivity of catalysts with different rare-earth content as a function of hydrogen-transfer (gasoline olefinicity) and deactivation mode is shown in Fig. 11. As described above, the gasoline selectivity goes through a maximum but the inflection point of the samples with and without age distribution occurs at different gasoline olefinicities. These data suggest that not only the degree of hydrogen-transfer activity, i.e. the gasoline olefinicity, but also the method of hydrogen-transfer activity adjustment has an impact on gasoline formation. Hence, the hydrogen-transfer activity ranking of FCC catalysts as a function of unit-cell size can only be compared in the case that the same deactivation method was applied in such a series.

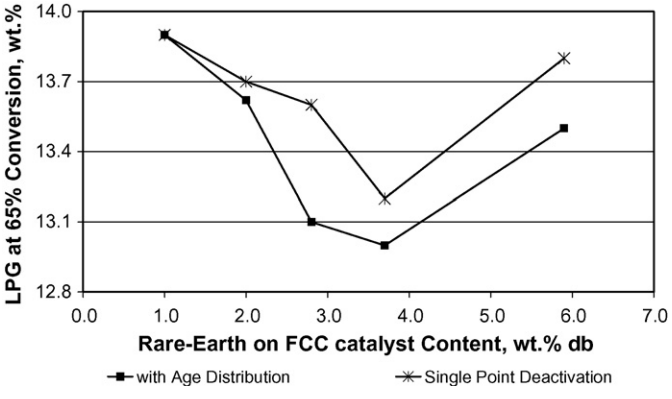

Fig. 8. LPG selectivity of FCC catalysts of different rare-earth content for FCC catalysts deactivated with and without age distribution.

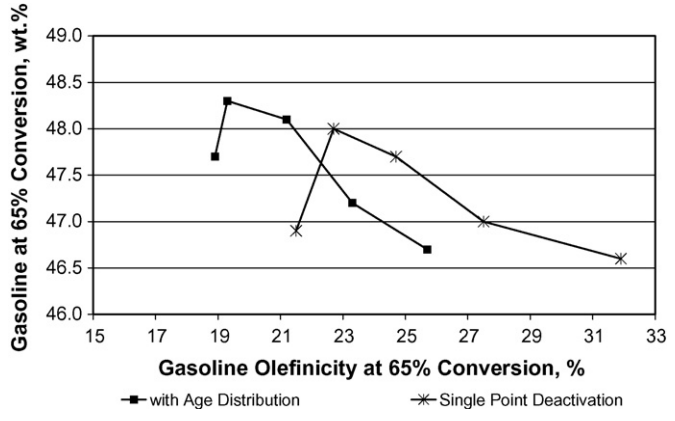

Fig. 11. Gasoline selectivity as a function of hydrogen transfer (gasoline olefinicity) for FCC catalysts deactivated with and without age distribution.

Table 14
Comparison of commercially equilibrated catalysts with CPS-deactivated catalysts

	Refinery A (catalyst N)	Refinery B (catalyst O)	Refinery C (catalyst P)	Refinery D (catalyst Q)
Conversion at constant catalyst-to-oil ratio of 2.8				
E-cat	75	75	67	76
CPS-1	75	81	77	68
CPS-3	75	78	69	79
Catalyst-to-oil ratio at 65% conversion				
E-cat	2.0	2.3	2.7	2.0
CPS-1	2.0	1.8	1.9	2.7
CPS-3	2.0	1.9	2.5	1.8
Unit-cell size (Å)				
E-cat	24.32	24.32	24.24	24.30
CPS-1	24.30	24.33	24.27	24.26
CPS-3	24.29	24.32	24.25	24.33
Zeolite surface area (m^2/g)				
E-cat	96	96	92	124
CPS-1	108	137	119	99
CPS-3	105	122	112	140
Matrix surface area (m^2/g)				
E-cat	24	45	31	28
CPS-1	29	51	37	29
CPS-3	25	55	36	31
Hydrogen, wt.% ff at 65% conversion				
E-cat	0.16	0.25	0.15	0.19
CPS-1	0.31	0.23	0.17	0.43
CPS-3	0.27	0.25	0.26	0.29
Coke, wt.% ff at 65% conversion				
E-cat	1.9	2.3	1.9	2.0
CPS-1	2.5	2.2	1.8	2.5
CPS-3	2.1	2.3	2.3	2.2
V (ppm)	2800	2000	2700	6500
Ni (ppm)	1500	900	1200	2400

In conclusion, the well-established effects of rare-earth variation on catalyst performance were obtained in either scenario, the age distribution mode and the conventional CPS-3 deactivation. Moreover, the differences in selectivity levels between the two deactivation modes agree with our understanding concerning ageing effects and with that reported in the literature so far.

4.4. Comparison of CPS deactivation with catalyst equilibration in FCC units

The performance of four commercially equilibrated catalysts (e-cats) was compared with that of FCC catalysts deactivated in CPS-1 and CPS-3. Selectivity testing was performed according to the SCT-MAT method on a paraffinic VGO (Feed B) described previously [13].

The catalysts for the lab deactivations (lab-cats) were taken from production runs for the corresponding refineries and loaded with vanadium and nickel to the same concentrations as the corresponding e-cat samples. Unit-cell sizes, surface areas, activities and selectivities measured for these samples are summarised in Table 14. Catalysts N, O and P have moderate vanadium and nickel loadings, and catalyst Q represents commercial FCC operation at very high metal levels.

4.4.1. Physical properties

The data analysed for the e-cat samples clearly show e-cats N, O, P and Q to have different properties. E-cats N, O and Q have higher unit-cell sizes than e-cat P. The same ranking was observed for conversion. The zeolite surface areas show e-cats N, O and P to have relatively low surface areas, whilst e-cat Q is significantly higher. In contrast, the CPS-1 protocol deactivated

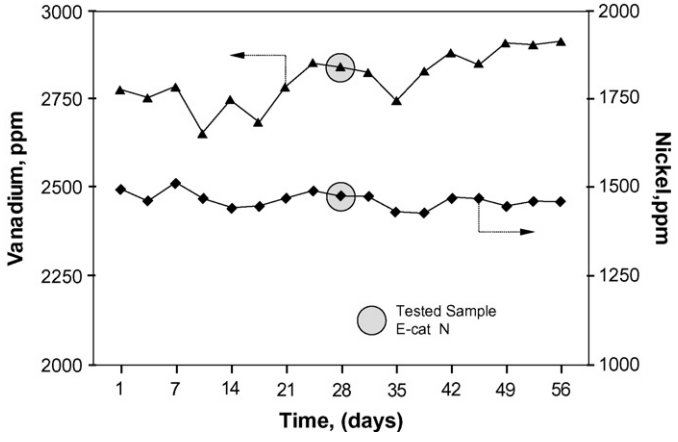

Fig. 12. Vanadium and nickel concentrations on equilibrium catalysts taken from refinery A.

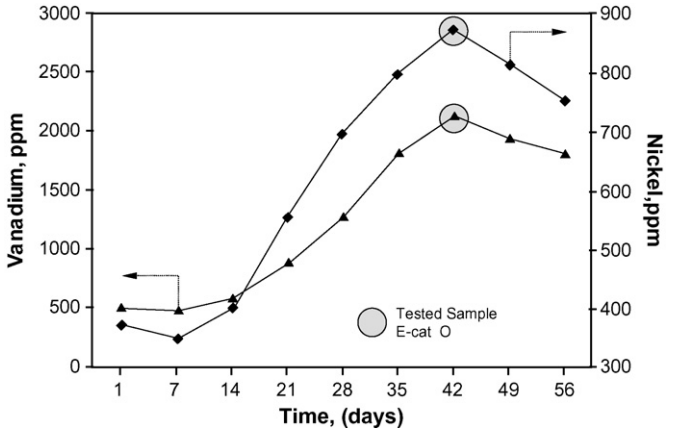

Fig. 13. Vanadium and nickel concentrations on equilibrium catalysts taken from refinery B.

lab-cat P to the second highest conversion and lab-cat Q to the lowest one. The unit-cell size of lab-cat P was also significantly higher than that of e-cat P whereas the unit-cell size of lab-cat Q was significantly lower than the corresponding e-cat value. Following CPS-3, the lab-cats P and Q had the lowest activity and a very high activity, respectively (as did the analogous e-cats). Their unit-cell sizes were also closer to the e-cat data than the CPS-1 findings. Surface areas data show e-cat P and lab-cat P following CPS-3 to have the highest zeolite surface areas, whereas the CPS-1 equilibrated this catalyst to the lowest value.

Apparently the CPS-1 overemphasises the destructive effects of vanadium in the case of catalyst Q, which is loaded with a very high vanadium concentration, and de-emphasises the catalyst decay in case of catalyst P, on which the vanadium level is only moderate. Thus the activity, surface area and unit-cell size data imply that the CPS-3 method is generally better for simulating the commercial FCC operation.

4.4.2. Activity and selectivities

Hydrogen and coke yields of lab-cat O matched those of e-cat O very well following both CPS methods, whereas lab-cats N and Q did not. Lab-cat P matched the corresponding e-cat yields in the case of CPS-1, whereas more hydrogen and coke was produced following CPS-3. The low hydrogen and coke selectivities measured of lab-cat P deactivated by the CPS-1 method is ascribed to its higher activity compared with e-cat P. In this work, the yields were compared at constant conversion. The catalysts compared in this section were of different activity, and in order to enable a comparison of the products at constant conversion the reaction severity had to be varied to obtain the conversion of interest for each catalyst. In the microactivity test employed, the reaction severity was adjusted by the catalyst-to-oil ratio with catalyst mass as the variable. Due to the high activity of lab-cat P, less catalyst mass was used for the cracking experiment of this sample than for e-cat P at constant conversion; hence, less V and Ni was in the reactor resulting in less hydrogen and coke production. In the CPS-3 mode, lab-cat P was equilibrated to an activity similar to that of e-cat P. Consequently, the e-cat and the CPS-deactivated catalysts had similar catalyst quantities in the reactor at constant conversion; therefore, the hydrogen and coke differences to the e-cat were in the range observed for catalysts N and Q following CPS-3.

The O series did not show such a large activity difference between commercial, CPS-1 or CPS-3 deactivation as observed for the series P, i.e. the similar hydrogen selectivities of these catalysts cannot solely be explained by a catalyst-to-oil effect. In this case, the hydrogen findings were more determined by the age of metals on the equilibrium catalyst. The vanadium and nickel concentrations on the e-cats prior to the date the samples were taken from the FCC units are illustrated in Figs. 12–15. E-cats N, P and Q were taken during periods where the metal levels were rather stable, whereas e-cat O was drawn following a period of strongly increasing vanadium and nickel concentrations. It has been shown by Cimbalo et al [24] that the younger the vanadium and the nickel on catalyst are, the higher their dehydrogenation activity is. Due to the strong increase in metal concentration prior to sampling, the metals on e-cat O are younger than on e-cats N, P and Q; hence the similar hydrogen formation in the series O is ascribed to the higher catalytic activity of the fresher metals on e-cat O compared with their age and dehydrogenation activity on e-cats N, P and Q.

Thus, these findings demonstrate that several factors have to be considered for comparisons of commercially and lab

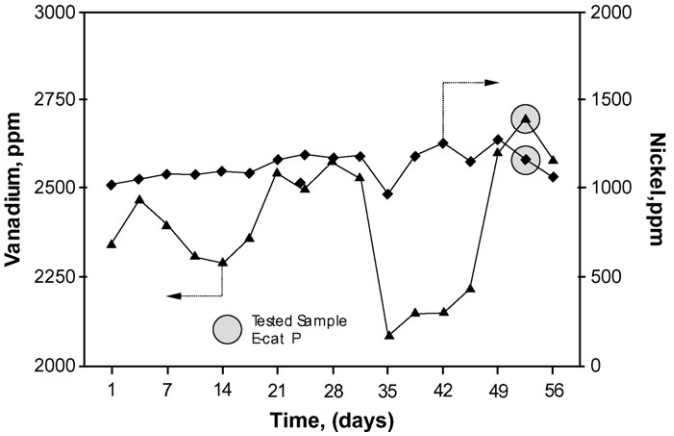

Fig. 14. Vanadium and nickel concentrations on equilibrium catalysts taken from refinery C.

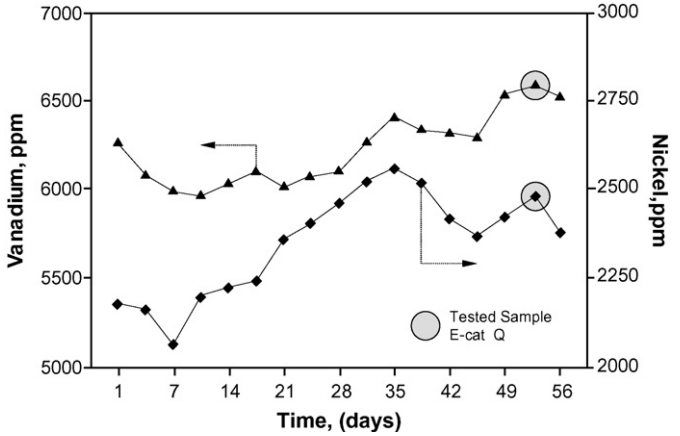

Fig. 15. Vanadium and nickel concentrations on equilibrium catalysts taken from refinery D.

Table 15
CPS-3 deactivation protocol

Heat-up phase
Room temperature to 989 K at 8.6 K/min, N_2 purge
2 cycles during the heating-up phase from 989 to 1077 K at 1.1 K/min
30 min, 50% N_2 (containing 5% propylene) + 50% steam
2 min, 50% nitrogen + 50% steam
6 min, 50%, 4000 ppm SO_2 in air + 50% steam
2 min, 50% nitrogen + 50% steam
29 cycles of the cycle described below at 1077 K
30 min, 50% N_2 (containing 5% propylene) + 50% steam
2 min, 50% nitrogen + 50% steam
6 min, 50%, 4000 ppm SO_2 in air + 50% steam
2 min, 50% nitrogen + 50% steam
30th cycle
30 min, 50% N_2 (containing 5% propylene) + 50% steam
Cool down under nitrogen flow

deactivated catalysts. Firstly, the historical development of vanadium and nickel concentration in the FCC inventory have to be taken into account. Secondly, the catalysts have to be deactivated to an accurate activity. The activities of the lab-cats following CPS-3 deactivation matched better the activities of all the analogous e-cats tested, whereas the CPS-1 did not match the activity of e-cats P and Q, which may distort hydrogen and coke selectivities in some cases.

5. CPS-3 deactivation protocol

All of the previous findings discussed in Sections 3 and 4 show that the modified procedure provides a better simulation of catalyst equilibration in a commercial unit than the CPS-1 protocol. Meanwhile the CPS-3 protocol has also become the industry standard deactivation method. To summarise, the complete details of the CPS-3 are illustrated in Table 15.

6. Testing of catalysts in the absence of metals

In this section, the results obtained with non-metallated catalysts by the different CPS procedures are contrasted with those of the AM-1500 protocol which is the standard deactivation protocol for FCC catalysts in the absence of contaminant metals. This method is thoroughly described in Ref. [25]. Briefly, FCC catalysts were deactivated in a 100% steam atmosphere at 1089 K in a fluidised bed at atmospheric pressure for 5 h (also see Table 1).

For CPS deactivations, both methods described previously, CPS-1 and CPS-3, were applied with the following modifications. In order to generate high intraparticle temperatures the FCC catalysts were impregnated with an aromatic VGO (feed A) described in Ref. [13]), which was burned off at 973 K prior to CPS deactivation.

It has been shown that FCC catalysts containing rare-earth exchanged zeolites equilibrate in the AM-1500 protocol generally at unit-cell sizes and surface areas typical for commercially equilibrated catalysts [25]. Since the destructive effects of vanadium are missing, the deactivation severity for CPS-1 and CPS-3, which should be equivalent to that in the AM-1500 method, had to be adjusted. This was performed by varying the temperatures. Since in the absence of vanadium the catalysts are exclusively deactivated hydrothermally, it was expected that the same temperature can be used for CPS-1 and CPS-3.

Table 16
Comparison of AM-1500, CPS-1 and CPS-3 deactivation in the absence of metals

	Surface area		Unit-cell size (Å)	Conversion (%)
	Zeolite (m^2/g)	Matrix (m^2/g)		
Catalyst R (1.1 wt.% RE_2O_3 on catalyst)				
Calcination[a]	265	43	24.56	
AM-1500	145	38	24.23	63
CPS-1, 1083 K	141	40	24.24	61
CPS-3, 1083 K	140	37	24.25	59
Catalyst S (2.9 wt.% RE_2O_3 on catalyst)				
Calcination[a]	235	84	24.60	
AM-1500	134	56	24.33	77
CPS-1, 1083 K	130	49	24.30	75
CPS-3, 1083 K	133	50	24.31	77
Catalyst P (rare-earth free)				
Calcination[a]	221	35	24.55	
Metals-free				
AM-1500	134	36	24.29	73
CPS-1, 1083 K	128	36	24.28	71
CPS-3, 1083 K	111	37	24.25	64
Metallated				
CPS-1, 1083 K	119	37	24.27	77
CPS-3, 1083 K	112	36	24.25	69
E-cat	92	31	24.24	67

[a] 813 K, 3 h, air.

The unit-cell sizes, surface areas and activities obtained for three FCC catalysts following AM-1500, CPS-1 and CPS-3 at 1083 K are compiled in Table 16. The data obtained for catalyst R and S exhibit that CPS-1 and CPS-3 at 1083 K provide an equivalent deactivation severity to the AM-1500 method. Catalyst P is a non-traditional rare-earth free catalyst and performed differently in the three protocols as in the presence of metals following CPS-1 and CPS-3 (Section 4.4, Table 14). These data together with the data obtained for a commercially equilibrated catalyst were added to Table 16. Clearly catalyst P was more strongly deactivated by CPS-3 than in both CPS-1 in the presence and absence of metals. In the latter, the pure hydrothermal environment gave the weakest deactivation. As seen in the presence of metals, the equilibration of catalyst P in commercial units is also best reflected in the absence of metals by the CPS-3 method. Hence the data suggest this method to be the most appropriate one in the absence of metals as well.

Possible reasons for the more realistic performance in CPS-3 in the absence of metals are:

- the pre-stabilisation of FCC catalysts by the high intraparticle temperatures that the particles are exposed to prior to deactivation when burning off of the organic materials from the vacuum gas–oil impregnation; see also Table 5, Section 3.2.2,
- lower hydrothermal severity,
- reduction–oxidation cycles together with the ratio of the reduction time-to-oxidation time.

7. Conclusions

There are many factors that need to be considered in the evaluation of fluid catalytic cracking (FCC) catalysts, of which deactivation is considered to represent the most decisive parameter in FCC catalytic testing. Various available methods were discussed throughout this paper whereby FCC catalyst deactivations in the presence as well as absence of contaminant metals were covered.

Regarding FCC catalyst deactivation, the investigations were primarily focussed on CPS (cyclic propylene steaming) because, in certain situations, the contribution of vanadium on catalyst deactivation is over-emphasized in the original CPS-1 method. Hence a number of modifications have been made to the CPS-1 method such that the destructive effects of vanadium could be reduced to the levels observed for commercially equilibrated FCC catalysts. This improvement was primarily achieved by exposing the metallated catalyst to pre-stabilisation steps with reduction–oxidation cycles and by increasing the time the catalyst spends in the reducing environment during the CPS cycles. In other words, the catalyst decay in the modified CPS method is governed more by hydrothermal deactivation and less by deactivation from highly oxidised vanadium, especially at high metals levels.

The more real-world deactivation observed in the improved CPS-3 scenario was underlined by the comparison of V-transfer rates between FCC catalyst and vanadium traps in CPS and commercial FCC units, as well as by the comparison to equilibrium catalyst performances at extremely high vanadium, concentrations. In addition, contrasting the activity and selectivity data obtained from FCC catalysts having age distribution with those obtained from CPS-3 deactivation showed that both scenarios gave the same selectivity ranking.

It is shown that the coke-on-catalyst following CPS can be burned off at low temperatures without oxidising vanadium, which would lead to an exaggerated dehydrogenation activity of vanadium relative to nickel. This enables activity and

Table 17
Summary of deactivation methods and their recommended applications

Method	Metals-free		V, Ni			
	AM-1500 (no[a])	CPS-3 (no[a])	Mitchell (no[a])	CPS-1 (no[a])	CPS-3 (no[a])	CPS3 (yes[a])
Operational conditions						
Steam	100%	50%	100%		50%	
Re-Ox-C[b]	No	Yes	No		Yes	
Re-to-Ox[c]	–	Re > Ox	–	Re = Ox		Re > Ox
Ending in[d]	Ox	Re	Ox		Re	
Effects						
Ni: H_2, C	–		High	OK		OK
V: Activity	–		High			OK
V: H_2, C	–		High	OK		OK
Known bias	UCS[e], activity	–	UCS, activity			–
Recommended applications						
w/o V, Ni	No	Yes			–	
with V, Ni	–		No	≤3000[f]		Any

[a] Age distribution.
[b] Reduction–oxidation cycles.
[c] Ratio of reduction-to-oxidation time per cycle.
[d] Deactivation ending in Re (reduction) or Ox (oxidation).
[e] Unit-cell size.
[f] ppm V.

selectivity testing of coke-free catalysts following CPS which certainly improves the accuracy of such experiments.

CPS deactivations were also performed in the absence of contaminant metals. Here, the CPS-3 mode also better simulated the behaviour of FCC catalysts in FCC units than CPS-1 and the traditional steaming in a pure hydrothermal atmosphere. These findings indicate the decisive role of reduction–oxidation cycles together with appropriate operational parameters for each type of catalyst deactivation.

Finally, and as a summary, the following Table 17 has been assembled including all the methods discussed in this paper

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