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Effect of metals poisoning on FCC products yields: studies in an FCC short contact time pilot plant unit

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Abstract

In this work the effects of two metal poisons (Ni, V) on FCC products were investigated in an FCC pilot plant. The most important effects of metals were found on the gasoline, coke and H_2 yields. A comparison study of the metal distribution in the catalyst particles aged in the FCC pilot plant, a CDU and an industrial FCCU was also performed using a SEM–EDS method. SEM results showed that the metal profiles from CDU samples simulate more satisfactorily the profiles of the E-cat than that from the FCC pilot plant. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: FCC; Metal poison; SEM–EDS method; Pilot plant unit

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1. Introduction

The detrimental effects of the FCC feedstock metals (and especially Ni and V) have been widely recognized in literature [1–5]. Nickel and vanadium are known dehydrogenation catalysts. Nickel has approximately three to four times more dehydrogenation activity than vanadium, but vanadium destroys also the crystalline zeolite framework of FCC catalyst [5,6]. Although several studies were carried out in literature for the metal effects on FCC product distribution and on metal passivation we consider that the modifications which were performed in FCCU in recent years necessitate a study for the effect of metals poisoning on FCC cracking catalysts. These changes concern the FCC feedstocks, the catalysts and the design parameters. FCC feedstock changes because of the increasing demand for addition of more resid and thus, today there are more than 30% of the European FCCU that run at E-cat Ni + V levels above 3000 ppm [7]. FCC design parameters have also changed since many of the conventional FCC units revamp to the various types of short contact time FCC units (SCT-FCCU). Furthermore, for SCT-FCCU there is a need for new catalyst technologies since the very short residence times can affect the influence of contaminant coke [8]. Contaminant coke is found to be more sensitive to residence time than the catalytic coke [9]. In addition, the contaminant metals, because of the pore blockage, influence more the new SCT catalysts that have high accessibility to active sites [10].

Understanding the behavior of various Ni and V precursors in the FCC process along with the chemical form of metals in the catalyst is necessary in the development of technologies for passivating metal poisons [5,11–13]. Various techniques are now available to overcome the deleterious effects of metal contamination. Among these are the feed hydrotreating, the passivation of metals with various agents (antimony, bismuth, etc.) and the use of additives as metals traps (incorporated into the FCC catalyst or

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as separate particles) [5,12]. However, to develop an efficient passivation process for metal poisons, it is important to clarify how metal poisons are deposited from crude oil to the surface of the zeolite and matrix, and how they migrate between them and to cracking products, under different conditions.

Metal poisoning simulation in the laboratory is also a very complicated task since it demands features of metal profile, metal–catalyst interaction and metal age distribution. This simulation necessitates the development of a protocol for the impregnation of catalyst with metals and following this for the characterization of catalysts. Most of the literature studies [3,8,12,14,15] have been based on laboratory prepared samples, and focused on catalysts artificially contaminated with solutions of Ni or V naphthenates, by the incipient wetness technique (Mitchell method), to concentrations higher than realistic metal loading. Laboratory-testing methods that incorporate more sophisticated aging protocols can get more accurate evaluation of catalytic properties [14].

Several researchers [15–19] have attempted to understand the mechanisms of metal deposition on the catalyst, by observing the distribution of the poisonous metals across the catalyst particles and between the different catalyst components (zeolite, matrix and various additives). Such studies have been conducted mostly by secondary ion mass spectroscopy (SIMS) [15–19]. Some other methods have also been applied: electron microprobe analysis (EPMA) or X-ray photoelectron spectroscopy (XPS) [14]. SIMS is a technique with high sensitivity to most metals found in cracking catalysts. However, the necessary equipment is very scarce and very seldom found in analytical laboratories. Another shortcoming of imaging SIMS measurements is that it is very difficult to quantify them.

The main objective of the present work is to investigate the effects of metal poisons ($Ni + V$) on FCC products using an FCC pilot plant working under very short residence times. Another target was to compare two different methods of artificially depositing contaminant metals on FCC catalysts. The first method is based on the cyclic impregnation in the riser of the FCC pilot plant and the second on the cyclic impregnation in a fixed fluid bed reactor of a cyclic deactivation unit (CDU). The comparison of the two methods was based on the measurement of metal profiles in the catalyst particle of the two units and was performed in relation to an E-cat from the same commercial catalyst. Comparison of product selectivities from the three units will be presented in a future paper. Moreover, one third objective of this work was to apply a new technique for observing the distribution of the poisonous metals, across the catalyst particles, by scanning electron microscopy (SEM) in combination with X-ray energy dispersive spectroscopy (SEM–EDS). Although X-ray EDS is a technique not sensitive to very low elemental concentrations, by using the spot analysis and the linescan option, Ni and V in samples with loading as low as 300 ppm were measured and their distribution across the catalyst particles was determined.

2. Experimental

An FCC pilot plant design, developed by CPERI, was used in this study. The unit operates at a continuous circulating catalyst mode, at pseudo adiabatic conditions and with vapor residence time of about 1 s. The pilot plant is fully automated and consists of a riser, a stripper and a regenerator. A full description of the unit is given elsewhere [20]. The feedstock was a VGO provided by a Greek refinery with the following properties: $S.G = 0.8742$, $S = 0.165$ wt.%, $RI\,(70^\circ C) = 1.4862$, $MeABP = 463^\circ C$. All catalyst samples used in this study were prepared from the same fresh commercial catalyst ($UCS = 24.545$ Å, $SA = 275$ and $SA_{zeo} = 192.5\,m^2/g$).

The work started using a fresh commercial catalyst that was steam deactivated in the regenerator (fluid bed) of the FCC pilot plant unit. The steaming was performed at 1300°F using 70% steam in nitrogen for 30 h. Using the steamed catalyst, pilot plant runs were carried out in order to obtain the base case operation at zero metal concentrations. Following these runs, the Ni and V deposition was taken place. This deposition was performed in the FCC pilot plant unit during the catalyst circulation, using an FCC feedstock spiked with V and Ni-octoates under the following aging protocol: (i) metal deposition up to the desirable concentration level, (ii) runs using the metals-free feedstock, (iii) repeat of the step (i) at a next metal concentration level. All runs in the FCC pilot plant were performed at the following conditions: $T = 970^\circ F$, oil partial pressure = 12 psia, $T_{reg} = 1300^\circ F$. According to the above protocol five set of runs were performed using

Table 1
Origin and metal content of FCC catalyst samples

Sample ID	E3	E14	E23	E33	E58	A4	A3
Ni	350	790	1200	1700	2200	1550	1500
V	330	790	1200	1450	1790	1280	950
Origin	FCC pilot plant	FCC pilot plant	FCC pilot plant	FCC pilot plant	FCC pilot plant	CDU	E-cat

catalyst with five different metal levels. These metal levels are described in Table 1 (samples E3, E14, E23, E33, E58) and were measured by inductively coupled plasma (ICP).

For the comparison of metal profiles in the catalyst aged in the FCC pilot plant the same fresh catalyst was aged using a CDU. The CPERI CDU was constructed by Zytel Company and consists of a fixed fluid bed reactor. The complete CDU run consists of 54 cycles, of which each cycle is formed by the cracking stripping and regeneration steps. The cracking reactions in the CDU take place at 500°C for 50 s and the catalyst regeneration at 788°C for 43 min. For the regeneration a stream of 50 vol.% steam is used [21]. The unit feed tank was filled and spiked with the same organic metal compounds used for the pilot plant tests. Furthermore, for the final comparison of metal profiles an E-cat from the above catalyst sample provided by a Greek refinery was also used.

According to the above described protocols the samples of Table 1 were compared for metal profiles using an SEM method. However, in order to be able to examine the interior of the very small particle of the FCC catalysts (with average size 60 μm), the following method was encountered. Small quantities of sample, as-received, were embedded in epoxy resin blocks, which were initially kept at 60°C under vacuum, to prevent bubble formation, and then hardened for 24 h. The hardened epoxy blocks were then grinded and polished to expose the interiors of the catalyst particles (approximate cross-sections), using silicon carbide paper to 1000 grid and diamond paste to 1 μm, respectively. Prior to data collection the samples were cleaned in an ultrasonic bath in order to remove any embedded grid material. A thin carbon film was deposited on all the samples in order to make them conductive. The morphology and the elemental composition of the catalyst particles were examined with an SEM (Jeol 6300) and an X-ray EDS analyzer (Isis 2000), respectively. Spot analysis and linescanning were the techniques used for the study. Following the spot analysis technique, the catalyst particle image is obtained at the computer screen. Then the points of interest are selected and analysis is performed to each one of them. By selecting points at various distances from the catalyst edge and also at areas with different morphology, one can explore the metals profiles at magnifications from several hundred times to several ten thousand times. Alternatively, for the application of the linescanning technique, a line was drawn that crosses the area of interest and the variations in the concentration of the component elements across this line were studied.

3. Results and discussion

3.1. Metal deposition

The presteamed catalyst used for the metallation procedure had the following properties: UCS = 24.315 Å, total and zeolite surface area 200 and 150 m^2/g, respectively. During the metal deposition the function of Ni and V concentration vs. the number of catalyst cycles was linear and the same for both metals only up to 60th cycle (sample E23, Table 1). Beyond this cycle number the Ni deposition rate was slightly higher and consequently at the cycle 100 higher Ni concentration was achieved (sample E58, Table 1). During the entire metallation period the UCS of the catalyst was not affected in relation to that of the steamed catalyst. The zeolite surface area was slightly reduced, because of the V presence, about 15 m^2/g.

3.2. Metals effects on FCC product yields

The influence of the five different metals concentrations on the FCC product yields was studied during the runs with the metals-free feedstock. For these runs the conversion was varied by changing the catalyst to

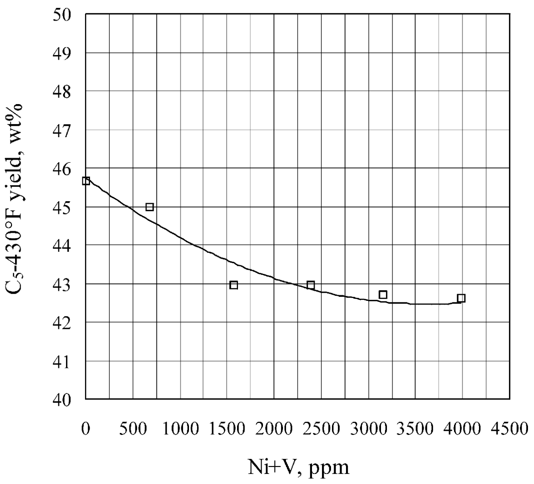

Fig. 1. Effect of Ni + V on gasoline yield at 65% conversion.

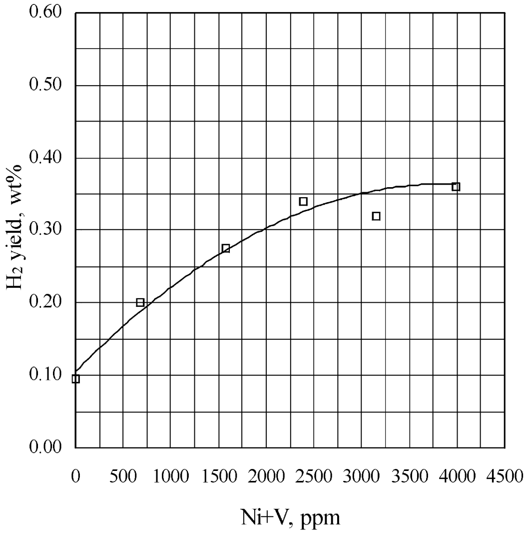

Fig. 3. Effect of Ni + V on H_2 yield at 65% conversion.

oil (C/O) ratio in order to obtain curves of product yields vs. conversion for the five different metal levels. From these curves, by interpolation, the product yields at a constant conversion (65 wt.%) were estimated. The most important effects of metals are on the gasoline, coke and hydrogen yield. The selectivities of these products vs. the Ni + V concentration in the catalyst are given in Figs. 1–3. From Fig. 3 it seems that at a constant conversion (65 wt.%) by increasing the metal level the hydrogen yield increases sharply and reaches values of about 300% higher in relation to that of the steamed catalyst. The effect of metals on H_2 yield is very strong for the catalyst with 2500 ppm Ni + V but beyond this value the effect is weak. It must be pointed out that this small change in dry gases on a weight basis represents a substantial increase in a molar basis. It is known that the hydrogen molar increase has a considerable effect on the performance of the wet gas compressors in the refinery. Coke yield increase is almost parallel to that of hydrogen (Fig. 2). It increases also rapidly up to 2500 ppm and more slowly after this value. It must be also noted that this coke increase is also important since many of the FCCU operate at a heat balance mode and thus, it is necessary to give coke yield in a relatively narrow range. The observed increase of coke and hydrogen yields, due to the metal presence, is at the expense of gasoline and other valuable products. Gasoline yield shows a decline of about 3 units (wt.% on feed) in relation to the steamed catalyst (Fig. 1). As happens with coke and hydrogen, gasoline yield decreases strongly at the initial steps of metal deposition but then remains almost constant.

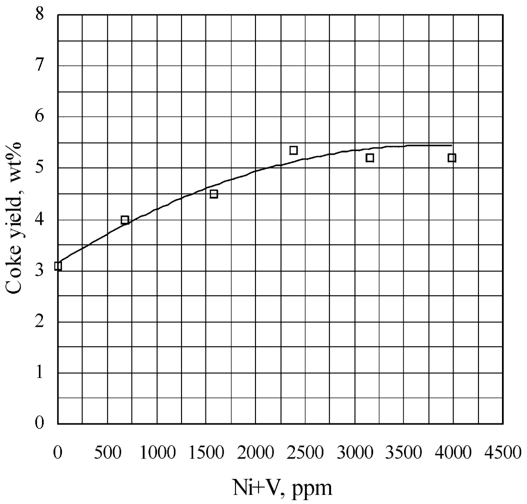

Fig. 2. Effect of Ni + V on coke yield at 65% conversion.

The effect of metals on the other FCC products (at a constant conversion) is not as important as on the gasoline, coke and hydrogen. From the remaining dry gases methane yield seems to increase about 30% in relation to that from the steamed catalyst. The corresponding increase of C_2H_6 is about 16% while C_2H_4 is slightly decreased. This increase of dry gases with metal content is attributed to radical-type nickel catalyzed a-cracking [1,2]. The LPG gases are also very slightly affected although the LPG olefins tend to decrease with the presence of metals while the LPG paraffins increase.

The results obtained in the present study are in a full agreement with literature [1,2,8,9]. This agreement is valid not only for the gasoline, coke and hydrogen yield but also for the other cracking products as well. For example the effect of increasing metals level on the decrease of the LPG olefins was also reported in other pilot plant studies [1,2]. One more interesting result from the present study comes by comparing the incremental changes in gasoline, coke and H_2 with other pilot studies in literature [1,2]. Although different feedstocks and catalysts were used, it seems that the incremental gasoline decline and the corresponding hydrogen and coke increase as metal level increase is somewhat less in the present study than that reported by Cimbalo et al. [1] and Habib et al. [2]. The work in these studies was contacted in risers with longer catalyst residence times. Our pilot unit operates at very low residence time and thus the metals catalyzed dehydrogenation reactions affect less the production of the undesirable coke and hydrogen products.

3.3. Metals profiles

The main constituents of the catalyst, Si and Al, plus quite a few minor components, such as Na, Fe, P, were readily detected by the EDS analysis. Ni and V give very weak peaks when the analysis is performed at a relatively low magnification covering one whole or more than one particle. This happens because the bulk concentrations of these two metals are relatively low, below 2500 ppm, in all samples. During this work, typically 10–20 different images were studied from each sample, to ensure that representative spectra were measured. 5–10 points were measured at the images where the spot analysis technique was used. The results obtained from the study are in general agreement with the previous literature [14–19]. Ni content is, in all cases, very much enhanced near the edges of the catalyst particle, while in the interior of the particle its concentration approaches zero. Vanadium is also enhanced at the particle edges, especially in samples with low loadings (and consequently relatively low number of aging cycles). On the contrary, V profile is much less intense, its concentration in the interior of the particle is not zero and tends to become progressively almost even, as the catalyst ages. On the other hand, no evidence was found that V preferentially accumulates in specific parts of the catalyst, e.g. zeolite, matrix or alumina based additives.

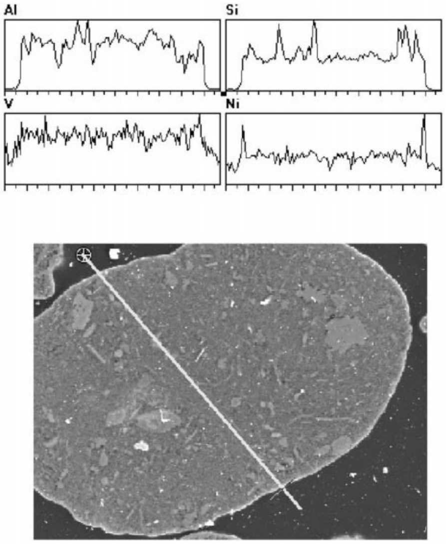

Fig. 4. Linescan across a particle of sample E58.

A typical linescan of a catalyst particle from the FCC pilot plant (sample E58) is shown in Fig. 4. Only the content distribution for the most important elements for this study, Al, Si, V and Ni, are presented, along the line indicated at the catalyst particle image at the lower part of the figure. Variations in the concentration of Si and Al indicate the presence of different components of the catalyst along the line: zeolite particles, aluminosilicate matrix and an Al based additive. Ni presents a very sharp concentration increase near the edges of the particle and a rather uniform, very low, content in the interior of the particle. The V distribution seems to be rather uniform across the particle, not presenting any maxima or minima near the edges.

In order to obtain a closer look to the above phenomena, measurements were made at higher

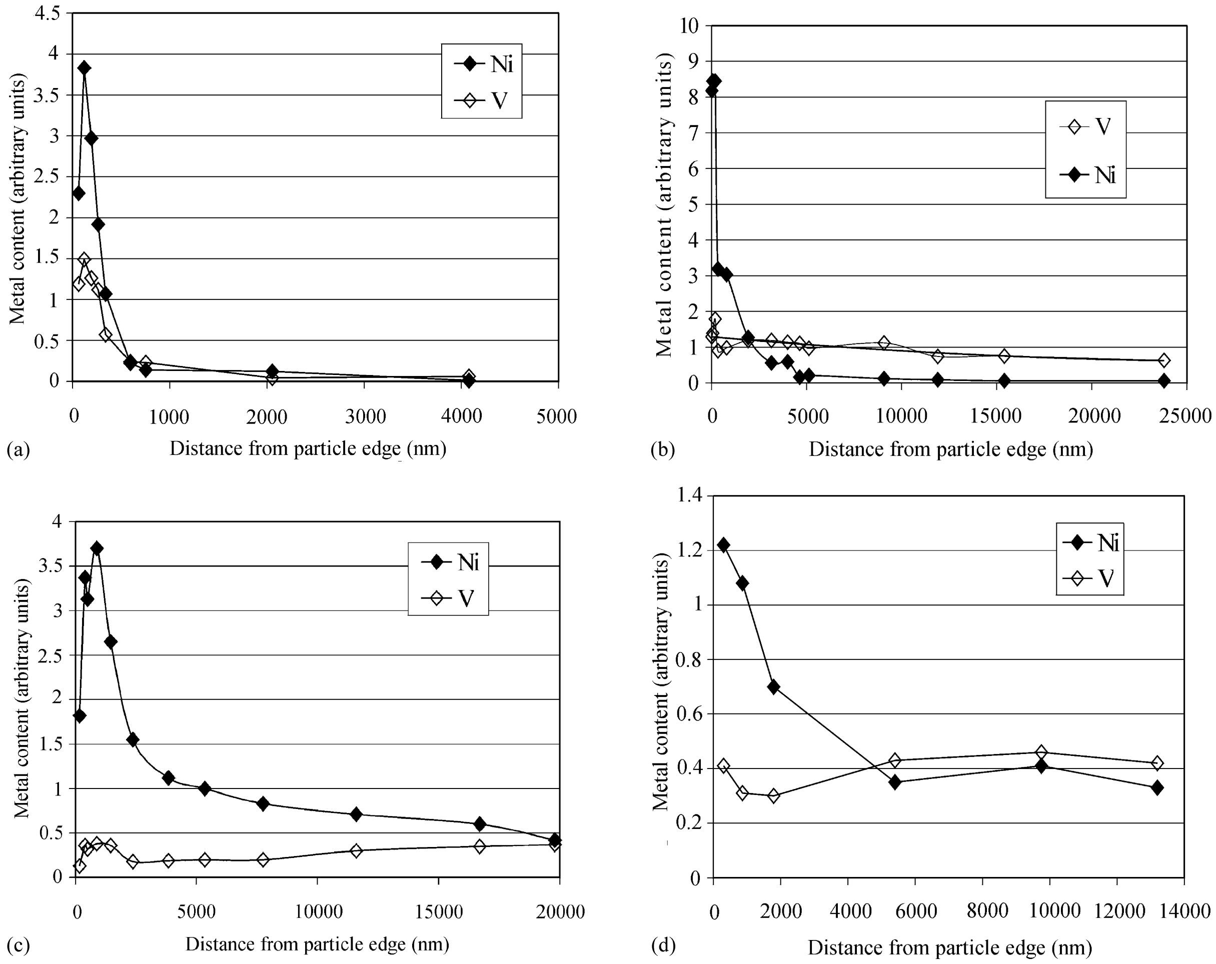

Fig. 5. (a) Ni and V distribution in catalyst sample E3 from FCC pilot plant. (b) Ni and V distribution in catalyst sample E58 from FCC pilot plant. (c) Ni and V distribution of the E-cat. (d) Ni and V distribution in catalyst sample A4 from CDU.

magnifications, by the method of spot analysis. In Fig. 5 typical Ni and V distributions are shown for four different samples. Concentration is given in arbitrary units, which are, however, consistent between all the presented charts. Fig. 5a refers to sample E3, with very low metal loadings, prepared at the FCC pilot plant unit after relatively few reaction–regeneration cycles. Both Ni and V have very sharp profiles near the particle edge and extremely low concentration in the interior of the particle, at distance greater than 500 nm. Ni maximum concentration is about 2.5 times higher than that of V. In Fig. 5b, typical results from sample E58 with the highest metals content and correspondingly the longest time in the pilot plant unit are shown. The Ni maximum value is more than twice the corresponding Ni max of sample E3, while Ni content is significant in depth up to 4000 nm, in the interior of the particle. V maximum at the edge of the particle is much less pronounced although its value is very close to that of sample E3. Furthermore, all the V content is practically in the interior of the particle.

The above results can be explained considering the mechanism by which the two metals are deposited on the catalyst. Initially both metals reside at the catalyst edge, since the big porphyrin molecules from which they originate decompose before entering the narrow pores of the catalyst particle. Thus, in sample E3, which is very poorly aged, practically all the metal loading is accumulated very close to the particle edge. At a second stage, as the particle undergoes more reaction–regeneration cycles, the metals react with the other components of the catalyst. In very good agreement with literature, it was found that V is much more mobile than Ni and proceeds into the interior of the catalyst particle much faster. Thus, in sample E58, V has a nearly uniform concentration profile, slightly declining towards the center of the particle, while Ni retains its initial sharp profile and shows a pronounced shell impregnation profile [5,12,14,22].

Fig. 5c shows Ni and V profiles from the equilibrium catalyst particle of the same commercial catalysts. In an equilibrium catalyst (E-cat), almost every particle has its own history, since fresh catalyst is continuously added while E-cat is withdrawn from the industrial FCCU. Thus, the curves shown in Fig. 5c were drawn after looking at many particles and are at least qualitatively typical of a particle with an average age in the unit. According to the above discussions, it seems that metals in equilibrium catalyst, having undergone greater number of cycles in the FCC unit, are more aged than in the pilot plant samples. The V concentration is almost stable as deeply as the center of the particle, while Ni peek is less steep and Ni content lowers more smoothly.

Fig. 5d presents the Ni and V profiles obtained from the catalyst aged at the CD-unit. A good agreement can be seen in this case with the equilibrium catalyst sample, although this sample has undergone fewer cycles that the pilot plant sample. An explanation of the above results can be based considering the low deactivation severity in the FCC pilot plant regenerator. As it was mentioned in the experimental section, the maximum temperature of the FCC pilot plant regenerator is 705°C while in the CDU is 788°C. The different deactivation severity of these samples is also reflected in the measurements of UCS. The catalyst samples from the CDU and the industrial unit have about the same UCS of about 24.29 Å while the corresponding value from the FCC pilot plant is 24.315 Å. The industrial FCCU operates in a regenerator temperature of 740°C. However, the very high number of catalyst cycles in this unit is simulated more satisfactorily by the higher regeneration temperature of the CDU.

4. Conclusions

An FCC pilot plant unit, working under very low residence times, was used in this study for the investigation of metals effects (Ni, V) on FCC catalysts. A presteamed catalyst was aged with different metal concentrations in this FCC pilot plant during the catalyst circulation. The results showed that under these conditions the metals influence strongly the gasoline, coke and hydrogen yield. At a constant conversion, more than 250% increase in the hydrogen yield is observed when about 4000 ppm Ni + V exist in the catalyst. The corresponding increase of coke is 80%. The same metal concentration decrease the gasoline yield about 7%. The present study showed that the deleterious effects of metals are proportional to metals concentrations only up to certain metal level. After this level the metal effects are not so pronounced. Moreover, by comparing the present results with other pilot plant results from literature, it seems that the operation of the SCT-FCC decreases the influence of the metals.

Ni and V distributions were measured at catalyst samples, with SEM–EDS by the use of the spot analysis and linescan techniques. The catalyst samples were aged at three different units: in the FCC pilot plant, in a CDU and in an industrial unit (E-cat). Bulk concentrations as low as 300 ppm of each metal were measured by the above techniques. The results for the metal profiles in the FCC catalyst particle are in agreement with previous findings. These results can be interpreted according to mechanisms of metals deposition, activity and mobility in the catalyst particle. The main conclusion of this comparison is that the metal profiles in catalyst obtained from CDU simulate better the E-cat than the corresponding profiles from the FCC pilot plant. The low deactivation severity in the FCC pilot plant regenerator is the main reason for this result.

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