

TEMPERATURE-PROGRAMMED OXIDATION OF EQUILIBRIUM FLUID CATALYTIC CRACKING CATALYSTS

Effects of pretreatment on coke formation

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Abstract

Characterization of coke on equilibrium, fluid catalytic cracking (FCC) catalysts contaminated with metals was investigated using temperature-programmed oxidation (TPO). TPO spectra of spent equilibrium catalysts from cracking of sour imported heavy gas oil (SIHGO) were deconvoluted into four peaks (Peak K, L, M and N). The four peaks were assigned to different types of coke on the catalyst. Peak L in the TPO spectrum was assigned to the 'contaminant' coke in the vicinity of metals. The amount of contaminant coke (Peak L) correlates with metal-contaminant concentration. The size of Peak L which is related to amount of contaminant coke decreased significantly for the spent highly contaminated catalyst pretreated with hydrogen and methane prior to cracking reactions as compared to the non-pretreated catalysts. Since both hydrogen and methane pretreatment can reduce oxidation state of the vanadium that present at high concentrations on the equilibrium catalysts the decrease in the amount of contaminant-coke represented by Peak L was explained by the reduction of the oxidation state of vanadium. Less contaminant coke was produced after the equilibrium catalysts were pretreated using hydrogen and methane gases since reduced vanadium has lower dehydrogenation activity compared to oxidized vanadium.

Keywords: coke characterization, FCC catalysts, pretreatment, temperature-programmed oxidation (TPO), vanadium

Introduction

A common problem in FCC processing is the gradual deterioration of the catalyst due to the deposition of metal contaminants, such as nickel, vanadium and iron, as a non-volatile compound on the cracking catalyst promoting excessive hydrogen and coke makes [1]. The production of excess coke and hydrogen is a result of dehydrogenation reactions catalyzed by the contaminant metals on equilibrium catalysts. It was reported

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that the oxidation state of contaminant-metals, especially vanadium, is very important factor that affects the dehydrogenation activity of a specific metal on FCC catalyst [2]. It is necessary to understand the relationship between the amount coke formed by contaminant metals and the oxidation states of these metals. This task can be achieved by characterizing the coke on spent catalysts using temperature-programmed techniques along with appropriate pretreatment prior to cracking reactions. Coke on several catalyst systems has been characterized with respect to its reactivity towards oxygen (temperature-programmed oxidation, TPO) [3–8]. TPO is a practical tool for characterizing coke on spent catalysts. TPO can determine the total amount of coke, and the hydrogen-to-carbon ratio in the coke deposited on the spent FCC catalyst [9]. The location and nature of coke on spent catalyst affect the coke oxidation kinetics, which are important factors in optimizing catalyst regeneration.

Several researchers have reported the metal effects on the TPO spectra of coked supported-metal catalysts [10–12]. Using TPO analysis, coke located on or near metal particles can be distinguished from coke away from metals on the catalyst support. As addressed in the previous publication [8], TPO spectra of spent equilibrium catalysts from cracking of sour imported heavy gas oil (SIHGO) can be deconvoluted into four peaks (Peak K, L, M and N). The four peaks have been assigned to different types of coke on the catalyst. The sizes of the TPO peaks are proportional to the amount of coke on catalyst. The Peak K is produced by hydrocarbons desorbing from the coke. The Peak L is contaminant coke produced by contaminant-metal reactions. The Peak M is conversion coke produced by acid-catalyzed reactions. A graphite-like coke that is related to both feedstock properties and catalyst activity produces the Peak N.

In the earlier study, effect of hydrogen pretreatment prior to cracking reactions on the amount and nature of coke deposited on the metal-contaminated FCC catalysts was determined [9]. After hydrogen pretreatment both coke amount and hydrogen-to-carbon ratio decreased significantly. The present study focuses on the influence of hydrogen and methane pretreatment applied prior to cracking reactions on the TPO spectra of spent, equilibrium FCC catalysts by deconvoluting the TPO spectra. Three different equilibrium catalysts are used with low, medium and high concentrations of nickel+vanadium. Spent catalysts are prepared by cracking sour imported gas oil (SIHGO) feed in a micro-activity test unit. The TPO spectra of spent catalysts that are calcined only and pretreated with hydrogen or methane prior to cracking reactions are deconvoluted into multiple Gaussian peaks. By comparing the shape of overall TPO profile and the sizes of individual deconvoluted peaks, the effects of pretreatment on the formation of contaminant-coke during cracking reactions are determined.

Experimental

In this study, three equilibrium FCC catalysts (used catalysts from commercial operation) were supplied by Ashland, Inc. They are named as ECat-LOW, ECat-INT and ECat-HIGH based on their contaminant-metals concentration. Characterization data on these equilibrium catalysts are provided in Table 1. These catalysts were either calcined or pretreated before they are used in catalytic cracking reaction. Calcination

was performed at 550°C for 6 h to make sure no coke deposits exist before cracking reactions. Two types of pretreatment using hydrogen and methane were performed in this study. These pretreatments were performed at 700°C for approximately 6 h by using either 8% hydrogen in argon or 8% methane in helium with a quartz reactor in the microactivity test (MAT) unit. These gases were used to reduce the oxidation state of metal contaminants on the catalyst. Spent catalysts were prepared by cracking sour imported heavy gas oil (SIHGO, Davison Chemical) on either calcined or pretreated catalysts in a microactivity test (MAT) unit. Standard test conditions were 5 g of catalyst, 500°C reactor temperature and 3.0 catalyst/oil ratio. Liquid product was collected in a trap at 0°C and vapor product was collected in a glass vessel by downward displacement of water to calculate the extent of conversion and the material balance for the experiment. The MAT unit, described in ASTM method D-3907, was manufactured by Industrial Automated Systems (Parlin, NJ).

Table 1 Nominal properties of equilibrium catalysts from Ashland, Inc.

Catalyst type	ECat-LOW	ECat-INT	ECat-HIGH
BET surface area/m ² g ⁻¹	178	160	115
Matrix surface area/m ² g ⁻¹	63	63	45
Zeolite surface area/m ² g ⁻¹	115	97	70
Metals/ppm			
Nickel	300	900	2600
Vanadium	700	1700	6700
Microactivity	71	69	62

The TPO equipment consists of a Hewlett-Packard 5890 gas chromatograph with a thermal conductivity detector (TCD) and flame ionization detector (FID) in series, and an external furnace connected to a temperature-program controller (Automated Test Systems, Butler, PA). In TPO experiments, samples are exposed to a 3% oxygen-in-helium mixture flowing at 40 mL min⁻¹. The oxygen consumption is measured as a function of time (temperature) in order to obtain the TPO spectrum. In a TPO experiment, a 50 mg spent-catalyst sample is placed in a quartz U-tube reactor and surrounded with quartz chips. The TPO sample forms a fixed bed inside the reactor. The reactor is placed in a furnace where temperature is increased linearly from room temperature to 865°C at a rate of 10°C min⁻¹. On reaching 865°C, the temperature is held constant for about 15 min. The exit stream from the reactor goes directly to the 1% platinum–alumina oxidation catalyst operating at 595°C. The platinum–alumina catalyst converts the CO formed and any desorbing hydrocarbons to CO₂ and H₂O. The product gas mixture from the platinum oxidation catalyst passes through two cold traps in series in order to trap H₂O (dry-ice/acetone trap) and CO₂ (liquid nitrogen trap). The oxygen does not condense in the liquid nitrogen trap because the 3% concentration is an order-of-magnitude below the saturation vapor pressure of oxygen. Since CO and

hydrocarbons are converted to CO₂, and both CO₂ and H₂O are trapped, only oxygen consumption is measured by the thermal conductivity detector. Recorded oxygen consumption provides the TPO profile. At the end of the temperature programming sequence, the liquid nitrogen trap is removed and solid carbon dioxide is allowed to evaporate into the carrier gas flow. This causes a pressure surge and sudden flow increase through the thermal conductivity detector. To dampen this pressure surge, a 0.5 m GC column (Carboxen 1000, Supelco) operating at 50°C is located before the TCD. This column holds the CO₂ long enough for the flow disturbances to disappear before CO₂ is detected. The CO₂ produced by oxidizing the coke deposit is measured. Water produced during the TPO experiment is not measured but remains condensed in the dry-ice/acetone trap until the experiment is over. TPO profiles are deconvoluted using PeakFit software (Jandel Scientific) into four Gaussian type peaks. Quantitative results consisting of individual and total peak areas are tabulated.

Results and discussion

In this work, TPO has been used to characterize coke on metal-contaminated equilibrium FCC catalysts and to see the effects of hydrogen and methane pretreatment on the type of coke formed during cracking reactions. The TPO spectra for spent equilibrium catalysts used for cracking SIHGO feed are shown in the top part of Figs 1–4. TPO profiles usually contain several peaks. In many cases, these peaks are not well resolved. Deconvolution is necessary in order to isolate and identify individual peaks and assign them to various types of coke. In this study, it was practical to deconvolute TPO spectra using Gaussian type peaks. Two or more types of coke were assumed to be present on any spent-catalyst sample. Normally, four peaks were needed to deconvolute TPO spectra. The final analysis used the minimum number of peaks that provided a good fit to the experimental data. Deconvolution results are presented in the bottom part of Figs 1–4. The lowest temperature peak has been designated K and the following peaks at increasing temperature have been labeled L, M and N. The detailed peak assignment was made in our previous study [8]. In this assignment, Peak K is produced by hydrocarbons desorbing from the coke. Traditionally, this is called cat-to-oil coke. Peak L is contaminant coke produced by contaminant-metal reactions. Peak M is conversion coke produced by acid-catalyzed reactions. A graphite-like coke that is related to both feedstock properties and catalyst activity produces Peak N. Quantitative analysis results for the TPO spectra for all three spent equilibrium catalysts are tabulated in Table 2. In this table, the measured area for each peak and the percentage area for each peak (in parenthesis) are listed. These values are the averages of three successive TPO runs under identical conditions. It was confirmed that TPO spectra obtained for the samples from same batch were very similar to each other.

Figures 1 and 2 show the TPO spectra of spent ECat-LOW and ECat-HIGH equilibrium catalysts, which were calcined at 550°C before cracking reactions, respectively. Figures 3 and 4 show the TPO spectra of spent ECat-HIGH after being reduced with 8% hydrogen in argon and 8% methane in helium at 700°C prior to cracking reactions, respectively. When the contaminant-metal concentration increases, the

Table 2 Quantitative results from TPO spectra analyses; the number in parenthesis is the area % for each peak. *LT*: total area of Peaks K and L, *HT*: total area of Peaks M and N

Catalyst (Ni+V/ppm)	Pretreatment	Peak area (area%)							<i>LT</i>	<i>HT</i>	<i>LT/HT</i>	Total area
		Peak K	Peak L	Peak M	Peak N							
ECat-LOW (1000 ppm)	Calcined	21.4 (9.0)	48.2 (20.2)	114.1 (47.9)	54.4 (22.8)	69.6	168.5	0.41	238.1			
	Hydrogen pretreatment	19.8 (8.9)	47.3 (21.3)	103.0 (46.4)	51.7 (23.3)	67.1	154.7	0.43	221.8			
	Methane pretreatment	17.4 (8.4)	41.7 (20.1)	98.0 (47.3)	50.3 (24.3)	59.1	148.3	0.40	207.4			
ECat-INT (2600 ppm)	Calcined	20.2 (8.4)	46.9 (19.5)	126.7 (52.8)	46.3 (19.3)	67.1	173.0	0.39	240.1			
	Hydrogen pretreatment	16.7 (8.1)	40.3 (19.5)	118.5 (57.3)	31.3 (15.1)	57.0	149.8	0.38	206.8			
	Calcined	19.0 (7.9)	82.6 (34.1)	90.2 (37.3)	50.3 (20.8)	101.6	140.5	0.72	242.1			
ECat-HIGH (9300 ppm)	Hydrogen pretreatment	18.9 (9.1)	50.0 (24.2)	88.1 (42.6)	50.0 (24.2)	68.9	138.1	0.50	207.0			
	Methane pretreatment	19.2 (8.3)	59.3 (25.7)	99.9 (43.3)	52.3 (22.7)	78.5	152.2	0.51	230.7			

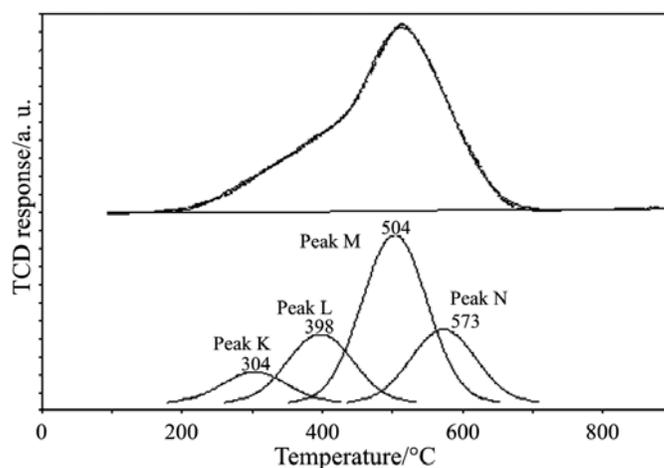


Fig. 1 Analysis of TPO spectrum for ECat-LOW after cracking SIHGO feed: Overlay of experimental curve and composite curve from analysis (top). Individual peaks from analysis (bottom)

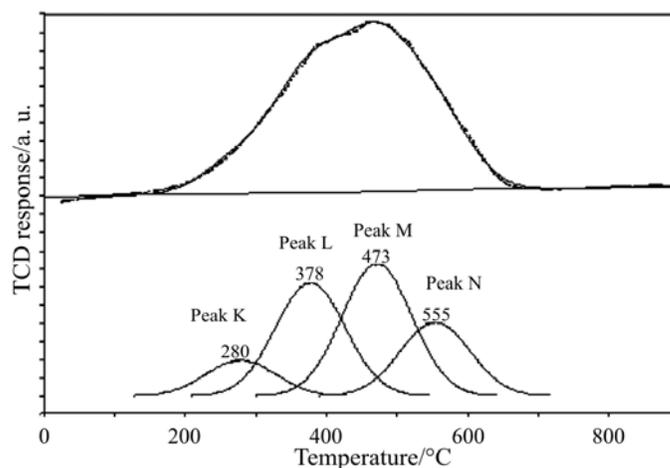


Fig. 2 Analysis of TPO spectrum for ECat-HIGH after cracking SIHGO feed: Overlay of experimental curve and composite curve from analysis (top). Individual peaks from analysis (bottom)

temperature for maximum oxygen consumption decreases from 504 to 473°C (Figs 1 and 2). The location of TPO peaks shifts to lower temperatures with increasing metal concentration on the catalysts. This can be attributed to the catalytic effect of vanadium and nickel on the coke-oxidation reaction. Similar observations have been reported for FCC [8, 13–15] and other catalysts [10–12] with metal contaminants.

Some researchers investigated the effect of inorganic compounds (Fe_2O_3 , ZnO , PbO , CaCO_3 and K_2CO_3) on the blast furnace coke thermal oxidation in the air and in

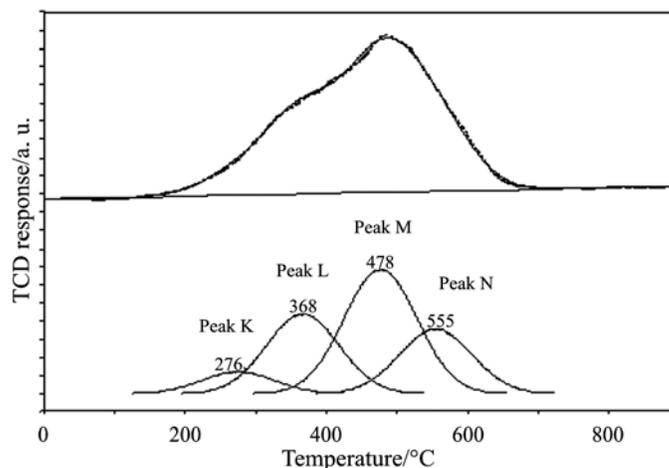


Fig. 3 Analysis of TPO spectrum for ECat-HIGH after cracking SIHGO feed. Pretreated with hydrogen at 700°C prior to cracking reactions. Overlay of experimental curve and composite curve from analysis (top). Individual peaks from analysis (bottom)

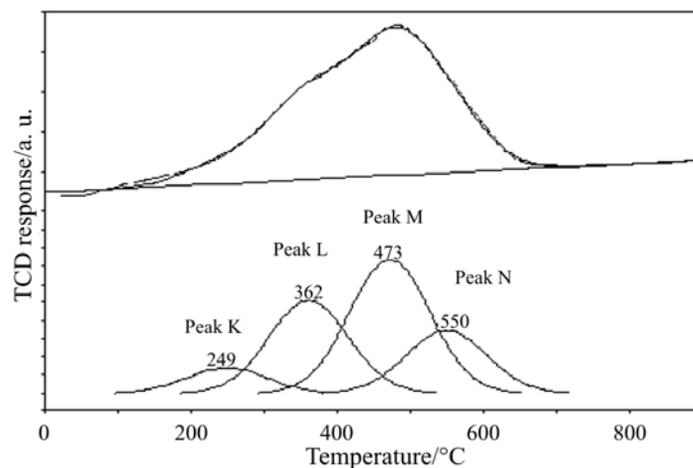


Fig. 4 Analysis of TPO spectrum for ECat-HIGH after cracking SIHGO feed. Pretreated with methane at 700°C prior to cracking reactions. Overlay of experimental curve and composite curve from analysis (top). Individual peaks from analysis (bottom)

the CO₂ atmosphere by means of thermal analysis [16]. A catalytic effect of these compounds caused also a lower oxidation starting temperature and activation energy [16]

The percentage areas for the peaks obtained for calcined catalysts are given in Table 2 as a function of nickel+vanadium concentration. The size of Peak L increases as the contaminant-metal concentration increases, while Peaks K, M and N show no definitive trend. The area of Peak L correlates with metal-contaminant concentration. This peak must be produced by metal catalyzed oxidation of coke residues on the

FCC catalyst. This does not mean that all of the peak area represents coke produced by metal contaminants, only that the peak area relates to metal-catalyzed coke oxidation. The coke that produces Peak L is probably located both on metal contaminants and adjacent to metal contaminants. The coke adjacent to the metal contaminant may have been caused by the metal or by some other function in the catalyst. Therefore, at least, a portion of Peak L is related to the oxidation of contaminant coke.

When Fig. 2 is compared with Figs 3 and 4, it is clear that both hydrogen and methane pretreatment have significant effects on the shape of TPO profiles. This is a good indication that changes occurred in the relative amounts of the certain types of coke represented by deconvoluted peaks in the TPO spectrum. In Table 2, when the relative area of each peak for ECat-LOW and ECat-HIGH spent catalysts, which were either pretreated with hydrogen and methane or calcined only prior to the catalytic cracking reactions, are compared it is clear that the effect of pretreatment on the TPO spectrum of ECat-LOW is not significant. None of the relative areas of individual deconvoluted peaks changed with both hydrogen and methane pretreatment prior to cracking reactions for ECat-LOW. However, relative area of Peak L, which partially represents contaminant coke, decreases significantly with both pretreatment for ECat-HIGH. This can be attributed to the decrease in the catalytic activities of contaminant metals in their reduced forms to produce coke. As seen from Table 2, the changes with pretreatment are minor with both ECat-LOW and ECat-INT spent catalyst samples. This can be due to the relatively low metal concentrations on ECat-LOW and ECat-INT equilibrium catalysts compared to ECat-HIGH equilibrium catalyst. The ratios of area of low temperature peaks (Peaks K and L) to the area of high temperature peaks (Peaks M and N), LT/HT , are given for all TPO profiles in Table 2. By looking at these ratios, it is possible to determine quantitatively whether changes occur in the low temperature or high temperature section of a TPO profile. This ratio remained almost constant around 0.40 before and after pretreatment for ECat-LOW and ECat-INT. On the other hand, this ratio decreased significantly from 0.72 to 0.50 for ECat-HIGH, indicating the changes in the low temperature part of the TPO profile after hydrogen and methane pretreatment. All of the TPO spectra presented in Figs 1 to 4 were obtained from the cracking of SIHGO at a catalyst-to-oil ratio of 3. The comparison of relative areas of each peak for ECat-HIGH spent catalysts, which were either pretreated with hydrogen and methane or calcined only prior to the catalytic cracking reactions at catalyst-to-oil ratios of 5 and 8 was also studied. It seems that there was no significant effect of catalyst-to-oil ratio on the shape of TPO profiles (not shown). Similarly, Peak L, which represents contaminant coke, decreases significantly with pretreatment.

The results above explain why one can observe higher gasoline and lower coke yields using pretreated ECat-HIGH equilibrium catalyst with the highest metal concentration, compared to calcined ECat-HIGH equilibrium catalyst. Our MAT results also showed that there were no significant changes in the catalyst performances before and after pretreatment for ECat-LOW and ECat-INT, except ECat-HIGH equilibrium catalyst. The results from MAT units will be explained in another paper.

Lee [17] studied catalytic cracking in the presence of hydrogen. They found that the presence of hydrogen improved the performance of metal contaminated catalyst. Part of the improvements in performance of metal contaminated catalyst in the presence of hydrogen was attributed to metal reduction similar to hydrogen pretreatment.

The improvement of catalyst performance with hydrogen or methane pretreatments can be explained by the oxidation states of metals such as vanadium and nickel on these equilibrium catalysts. Under FCC conditions, nickel is present in either the +2 or zero valence state. It is known that nickel at zero valence state is more active for promoting dehydrogenation reactions causing coke and hydrogen production [18]. In the zero oxidation state, nickel is mobile and agglomerates under reducing conditions found in FCC reactor. Agglomeration reduces the available surface and decreases the dehydrogenation activity of nickel. Nickel in +2 valence state is less likely to agglomerate into large particles and on a surface like alumina, can embed itself in the alumina structure forming nickel aluminate. In this case, nickel can stay highly dispersed during many redox cycles. Cadet *et al.* [18] have shown that nickel aluminate can also promote dehydrogenation reactions, although its dehydrogenation rate was found to be less than the rate for nickel metal.

Vanadium can also exist in several oxidation states between +3 and +5. However, vanadium does not exist at zero valence state under FCC conditions. It is now known that vanadium has a dehydrogenation activity and this dehydrogenation activity is closely related to its oxidation state [18, 20, 21]. It was found that oxidized vanadium produces more coke and hydrogen compared to reduced vanadium, indicating its high dehydrogenation activity [22, 23]. In our equilibrium FCC catalysts vanadium exists at its +5 state in large quantities. Both hydrogen and methane have the ability to reduce vanadium oxides present on the catalysts. Once the vanadium oxides are reduced during the catalyst pretreatment procedure, their catalytic activity to promote dehydrogenation reactions decreases significantly. Less coke, which is designated Peak L in TPO spectrum, is produced by the contaminant-metal on the equilibrium FCC catalyst.

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