

COKE CONTENT OF SPENT COMMERCIAL FLUID CATALYTIC CRACKING (FCC) CATALYSTS Determination by temperature-programmed oxidation

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Abstract

Zeolite catalysts are widely used in oil refinery and petrochemical industries. Fluid catalytic cracking (FCC) catalysts used in a refinery consist of Y zeolite, a silica–alumina matrix and a binder. In this study, spent FCC catalysts were prepared by cracking sour imported heavy gas oil (SIHGO) in a microactivity test unit. The total amount of coke and the hydrogen-to-carbon ratio (H/C) in the coke for spent FCC catalysts contaminated with metals were determined using temperature-programmed oxidation (TPO). Total H/C ratios of the coke on FCC catalysts were found to be in the range of 0.4 to 1, indicating the majority of the coke consists of polyaromatic species. H/C ratio decreased with increasing coke contents on the catalysts. This ratio was found to be higher for the catalyst with high metal concentration compared to the catalyst with relatively low metal concentration. The high H/C ratio for highly contaminated FCC catalyst was attributed to the formation of hydrogen rich coke by hydrogenation reactions catalyzed by the contaminant metals on the catalyst. After hydrogen pre-treatment both coke amount and H/C ratio decreased significantly. This was due to the decrease in the hydrogenation activities of the contaminant-metals in their reduced forms.

Keywords: coke measurement, FCC catalysts, metal contamination, temperature-programmed oxidation (TPO)

Introduction

The deposition of metal contaminants (e.g., nickel, vanadium, and iron) from the hydrocarbon feed causes the deactivation of fluid catalytic cracking (FCC) catalyst used in petroleum refining. The metal contaminants on the cracking catalyst promote excessive hydrogen and coke makes at the expense of gasoline [1]. The production of excess coke and hydrogen is a result of dehydrogenation reactions catalyzed by these contaminant metals on equilibrium catalysts.

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Formation of coke that consists of the carbonaceous compounds (polyaromatic or non-polyaromatic) during catalytic cracking reactions causes FCC catalyst to deactivate. The properties of coke such as amount, nature and location are affected by feed composition, catalyst type and reaction conditions. These properties give some idea about the FCC catalyst performance and also play important roles in combustion kinetics during the regeneration process. Therefore, an extensive understanding of coke properties is essential in the development of new FCC catalysts and improvement of present commercial FCC operations. In-situ methods for coke characterization are very practical since the separation of coke from the zeolite portion of the catalyst by conventional extraction methods is not an easy task. In some cases coke concentration on the catalyst can be less than 1%. Therefore, the low levels of coke content on the catalyst makes it necessary to use a very sensitive analytical technique for reproducible and accurate results. Since FCC coke is very complex, usually multiple analytical techniques have to be applied for the determination of coke composition and structure. A technique like TPO combined with either evolved gas or gravimetric analysis can be used for the characterization of coke on the solid catalysts. TPO can determine the total amount of coke, the hydrogen-to-carbon ratio in the coke, and the location of coke deposited on the spent catalyst. Several groups have used the TPO (temperature-programmed oxidation) to characterize the coke on FCC catalysts [2–11]. The information about the coke properties is inferred from TPO profiles through the shape, area and position of each peak. The aromaticity of coke is usually judged by the atomic H/C ratio. This ratio can be easily determined stoichiometrically by measuring the oxygen consumption and carbon dioxide production during the TPO experiment. The decrease in atomic H/C ratio (<1) is accepted as the indication of increasing polyaromatic content of the coke. The H/C ratio of 0.41 was found to be a typical value for spent FCC catalyst from the industrial cracking reactor [12].

In this work, we will demonstrate the coking properties of metal contaminated commercial equilibrium FCC catalysts with or without hydrogen pretreatment. We will examine the coked catalysts by TPO to determine the differences in the amount and nature of the coke.

Experimental

Usually, commercial FCC catalysts are manufactured using 1–2 μm zeolites dispersed on an amorphous silica–alumina matrix forming the 60 μm particles. Zeolites are extremely active especially in hydrocarbon conversion reactions and their regular pore dimensions make them selective as to which molecules are adsorbed or converted. Y-zeolite is the active and the most important component in FCC catalysts.

In this study, the equilibrium FCC catalysts (used catalysts from commercial operation) were supplied by Ashland, Inc. They are named as ECat-LOW 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 at 550°C or pretreated at 700°C with 8% hydrogen in argon for approximately 6 h before they are used in catalytic cracking reaction. 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. The MAT unit, described in ASTM method D-3907, was manufactured by Industrial Automated Systems (Parlin, NJ). Standard test conditions were 5 g of catalyst, 500°C reactor temperature and catalyst/oil ratios of 3 and/or 5. Performing cracking reactions at different catalyst-to-oil ratios allowed us to change the conversions. The catalyst-to-oil ratios of 3 and 5 were obtained by injecting different amounts of cracking feed while keeping the catalyst-amount constant at 5 g. It is quite difficult to obtain exactly the desired catalyst-to-oil-ratios and conversion values. Therefore we have determined the amount of coke for each spent FCC catalysts corresponding different conversion value regardless of the catalyst-to-oil ratio.

Table 1 Nominal properties of equilibrium catalysts from Ashland Inc.

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

The TPO equipment consists of a Hewlett-Packard 5890 gas chromatograph with a thermal conductivity detector (TCD), 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). 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. The CO_2 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.

To determine the coke amount by mass measurements before and after calcination at 560°C for 16 h in a muffle furnace, fused-quartz crucibles obtained from Fisher Scientific Co. were used. These crucibles have airtight self-sealing lids. During the volatile run, the lid automatically rises and the released gases or moisture is expelled as the sample is heated. Then the lid sinks back to restore the seal when the sample is cooled. This self-sealing action prevents sample from being exposed the moisture of the environment, thus eliminate inaccurate weighing caused by the moisture uptake.

Results and discussion

The coke contents of spent catalysts were determined by mass measurements after calcination in the muffle furnace. The results obtained from both TG and mass measurements were found to be in good agreement. This confirmed that mass measurements using quartz crucibles before and after calcination are quite reliable for determination of coke amounts on the spent catalysts. The comparison of quantitative analysis results from TPO and a commercial laboratory was made in the previous study [13]. Agreement between these techniques was satisfactory. Both TPO and mass measurement methods can be used equally well for determination of coke amount on the spent catalysts. However, TPO was found to be very useful since it provides information about the hydrogen-to-carbon ratio and oxidation profile as well. The more detailed results from mass measurements and TPO analysis for the different spent catalysts are tabulated and compared in Table 2. The spent catalysts in this table are either calcined or pretreated with hydrogen prior to the cracking reactions. Therefore some of these results reflect the changes in H/C ratio and coke amount as a result of the pretreatment.

For calcined only or hydrogen pretreated catalysts, the amount of coke on the catalyst was changed by using different catalyst-to-oil ratios during cracking reactions as explained earlier in experimental section. That is why the coke contents of calcined catalyst samples labeled as ECat-HIGH-01 to ECat-HIGH-07 in Table 2 vary in the range of 1.16 to 1.63 %.

H/C ratio was obtained by measuring the oxygen consumption and carbon dioxide production during the TPO experiment. From the coke combustion reaction, the H/C ratio can be calculated as follows:

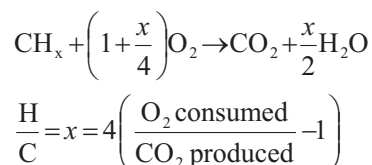


Table 2 Comparisons of results from TPO and mass measurements analyses

Pretreatment	Catalyst ID	TPO results			Mass measurements		Error/%
		Carbon/%	H/C	Hydrogen/%	Coke/%	Coke/%	
Calcined	ECat-LOW-01	1.74	0.45	0.07	1.81	1.89	4.23
	ECat-LOW-02	1.55	0.49	0.06	1.61	1.69	4.73
	ECat-LOW-03	1.41	0.57	0.07	1.48	1.42	-4.23
	ECat-LOW-04	0.97	0.71	0.06	1.03	1.04	0.96
	ECat-LOW-05	1.33	0.60	0.07	1.40	1.41	0.71
Pretreated with H ₂	ECat-LOW-06	1.61	0.47	0.06	1.67	1.71	2.34
	ECat-LOW-07	1.38	0.60	0.07	1.45	1.43	-1.40
	ECat-LOW-08	1.52	0.52	0.07	1.59	1.67	4.79
	ECat-HIGH-01	1.65	0.61	0.08	1.73	1.78	2.80
Calcined	ECat-HIGH-02	1.55	0.65	0.08	1.63	1.66	1.80
	ECat-HIGH-03	1.52	0.69	0.09	1.61	1.51	-6.21
	ECat-HIGH-04	1.39	0.80	0.09	1.48	1.48	0.00
	ECat-HIGH-05	1.53	0.68	0.09	1.62	1.69	4.14
	ECat-HIGH-06	1.47	0.71	0.09	1.56	1.69	7.69
	ECat-HIGH-07	1.07	0.96	0.09	1.16	1.25	7.20
Pretreated with H ₂	ECat-HIGH-08	1.33	0.69	0.08	1.41	1.36	-3.68
	ECat-HIGH-09	1.13	0.86	0.08	1.21	1.29	6.61
	ECat-HIGH-10	1.65	0.54	0.07	1.72	1.82	5.49

Figure 1 shows the changes of overall H/C ratios with respect to coke contents of the spent equilibrium catalysts. If we look at the H/C ratios of calcined equilibrium catalysts at a constant coke amount on the catalyst, the lower H/C ratios were observed for ECat-LOW compared to ECat-HIGH catalysts. This indicates that the coke formed on the catalysts with high metal concentration is less aromatic than the catalyst with relatively low metal concentration for a given coke content. This difference in the nature of the coke can be explained by the way coke is formed. For example, coke formed by hydrogenolysis on the metal portion of the catalyst was found to be richer in hydrogen compared to the coke formed by carbenium ion reactions on the acid sites of the catalyst [14, 15]. The overall H/C ratio becomes greater when the majority of the coke is formed on the metal surface. Usually pretreatments are performed to minimize the coke formed by hydrogenolysis on the metal surface. In our case, spent ECat-HIGH catalysts pretreated with hydrogen demonstrated lower H/C ratios compared to calcined catalysts, indicating that less coke is formed on the contaminant metals after pretreatment. The effect of pretreatment on the H/C ratio of the coke formed during cracking reactions was found to be more significant for ECat-HIGH compared to ECat-LOW. When the metal concentration on the catalyst is high enough, it becomes easier to observe the effect of pretreatment on the nature of coke. As seen from Fig. 1, H/C ratios decrease with increasing coke contents for all the catalysts. Regardless of the zeolite types such as USHY, HZSM5, and HERI, H/C ratio was always found to decrease with increasing coke content [16]. This is consistent with our findings. It is accepted that the coke deposited on the zeolite catalysts is a mixture of highly unsaturated hydrocarbons with an average H/C ratio varying from 0.3 to 1 [17]. This is in good agreement with our finding that total H/C ratios varying

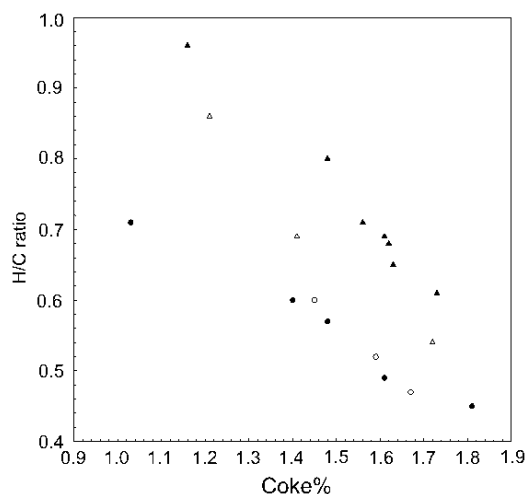


Fig. 1 Hydrogen-to-carbon (H/C) ratios of the coke on spent metal contaminated equilibrium catalysts before and after hydrogen pretreatment; ● – ECat-LOW (calcined), ○ – ECat-LOW (pretreated with hydrogen), ▲ – ECat-HIGH (calcined) and △ – ECat-HIGH (pretreated with hydrogen)

in a range between 0.4 to 1.0, indicating the majority of the coke must consist of polyaromatic species.

Generally the coke is classified as soluble and insoluble coke based on their solubilities in methylene chloride. Soluble coke molecules are usually too volatile and too weakly basic to be located on the outer surface, therefore must be located in the pores. It has been confirmed that insoluble coke is formed as a result of the growth of soluble coke molecules trapped in the pores. Based on this fact, at least part of insoluble coke molecules should be located in the micropores of the zeolite. The components of insoluble coke were found to be polyaromatic with an atomic H/C ratio of 0.4–0.5 for USHY type zeolite [16].

Shape of TPO profiles is affected by the combustion mechanism, which is determined by the properties of coke and the catalyst. Some researchers [12, 18, 19] reported that coke oxidation was practically independent of the coke content and composition. The effect of H/C on oxidation rate is generally considered insignificant, although a high H/C ratio can be an indicator of reactive carbons [12]. The catalytic coke formed on the catalyst can be bonded to the acid sites and contaminant metals as well as other carbon species. Despite of different bonding energies of coke species, the acidity of the catalyst and the combustion promoting effect of the contaminant metal are the most effective parameters, which affect combustion mechanisms. Changes in the shape of TPO profile after pretreatment can be explained by the formation of relatively less coke on the contaminant metals.

Figure 2 shows the TPO spectra of spent ECat-HIGH equilibrium catalysts, which were either calcined (solid lines in Fig. 2a and c) or pretreated with hydrogen (dashed lines in Fig. 2b and d) before cracking reactions. Replicate TPO runs for ECat-HIGH-03 sample in Table 2 give the TPO profiles shown in Fig. 2a and c. Similarly, replicate TPO runs for the sample named ECat-HIGH-08 in Table 2 provide the TPO spectra shown in Fig. 2b and d. As seen from Fig. 2, hydrogen pretreatment has a significant effect on the shape of TPO profile indicating the changes in the amount

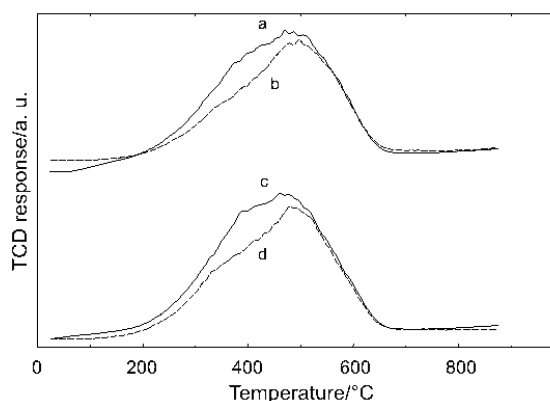


Fig. 2 TPO spectra for spent ECat-HIGH catalysts; a – and c – calcined at 550°C prior to cracking with SIHGO feed (solid lines); b – and d – pretreated at 700°C prior to cracking with SIHGO feed (dashed lines)

of coke formed by contaminant metals. After hydrogen pretreatment, low temperature portion of TPO spectrum shown in Fig. 2b and d disappears considerably in comparison to TPO spectrum shown in Fig. 2a and c. The effect of pretreatment on the TPO spectrum of ECat-LOW was not significant. This was due to relatively low metal concentration on ECat-LOW equilibrium catalyst compared to ECat-HIGH equilibrium catalyst. The changes in TPO spectrum for ECat-HIGH after hydrogen pretreatment can be attributed to the decrease in the dehydrogenation activities of contaminant metals in their reduced forms to produce coke.

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