

THE QUANTITY AND AMORPHICITY DETERMINATION OF OXIDABLE COKE ON THE ZEOLITE-CONTAINING CATALYSTS OF CRACKING

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Abstract

The paper studies the amount and structure of coke on coked and regenerated cracking catalysts used in industrial units. The temperature range of coke oxidation was established (the peak temperature is 515.6°C), which indicates the presence of an amorphous structure on the coked catalyst surface. The coke C/H ratio was determined using the calculation method based on the industrial plant regenerator flue gas composition analysis. This ratio varies in a wide range of 0.57-1.9 units. The efficiency of regeneration was determined by the amount of oxidized coke, which was 78.1 %.

Keywords: *Catalytic cracking; Zeolite-containing catalyst; Coke structure; Regeneration.*

1. Introduction

The development of heavy oil feedstock processing, including catalytic cracking, is largely due to the improvement of catalytic compositions, along with the structural features of industrial units [1]. The world largest cracking catalysts manufacturers are BASF Catalysts, Grace Davison and Albemarle. In Russia there are facilities producing microspherical cracking catalysts equal in performance properties to global manufacturers catalysts. These facilities are Catalysts Ishimbay Specialized Chemical Plant of Catalysts LLC and Sterlitamak Catalysts Plant LLC, which are related to KNT Group (Ishimbay and Sterlitamak, Bashkortostan Republic) and Gazpromneft - Omsk Oil Refinery JSC (Omsk). Catalysts modification with various additives and its composition optimization depending on the processed feedstock features allows to flexibly respond to market needs [2] (maximizing the gasoline, middle distillates, propylene yields, , increasing the gasoline octane number and butylene content in the gas phase, reducing the sulfur content in products, resistance to heavy metals, etc.).

The deactivation of zeolite-containing catalysts under industrial conditions is very important issue, which has a significant impact on the economic efficiency of the process [3]. The loss of catalysts activity and selectivity caused by coke and depositions, heavy metals, attrition, hydrothermal deactivation leads to the target products yield and quality decrease, and increasing of the additional fresh catalyst load in the system [4].

In light of this, today a significant number of studies are aimed at developing new and modernizing existing catalysts for processing heavy petroleum fractions and residual stock that are less tending to reversible and irreversible deactivation [5].

Deactivation of catalysts as a result of coking is a reversible process, since the catalytic properties are partially restored when coke is removed, with the exception of the graphitized coke formation cases. First of all the amount of coke formed depends on the feedstock composition and operating conditions of the catalyst in the reactor-regenerator cycle, as well as catalysts acid and structural properties [6]. With an increase in the density, molecular weight,

aromatic and resins content, etc., the coke content in the process feedstock increases, causing a deactivation effect and the target products yield decrease.

Therefore, the catalyst regeneration stage is important for the industry, since it extends the catalyst service life by reducing the temporary deactivation due to coke formation. The efficiency of the regeneration process depends on a large number of coupled reactor-regenerator system operating parameters, and the amount and structure of coke formed on the catalyst in the reactor [7-8]. In this regard, the valuable data of catalytic processes obtaining directly from industrial units [9-10].

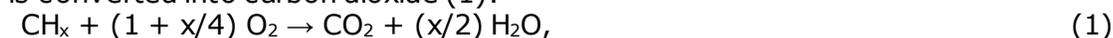
The aim of the work is to establish the amount and structure of coke on coked and regenerated cracking catalysts used in industrial units. The object of the study is a microspherical zeolite cracking catalyst, sampled before and after the regeneration stage. The bulk density of the regenerated catalyst is not less than 0.87–0.88 g/cm³. The technological process is implemented on the C-200 section of the KT-1/1 unit.

Vacuum distillate (fr. 350–500°C) produced by the process of vacuum distillation of fuel oil (C-001) from a mixture of Kazakhstan and West Siberian oil is used as the feedstock of the process. The density of the feedstock at 20°C varies in the range of 880–920 kg/m³, the refraction index is 1.485÷1.500, the sulfur content is not more than 0.15 mass%, the total content of metals (nickel and vanadium) is not more than 3 ppm.

The following methods were used to calculate and experimentally determine the amount and structure of coke on coked and regenerated catalysts:

1. The TGA-DSC method (thermogravimetric analysis and differential scanning calorimetry) [11-12] with the use of NETZSCH STA 449 F3 (temperature range from mines 150°C to 2400°C, accuracy/repeatability of the thermal effect determination is ± 2 %) which allows to simultaneously read off the gravimetric analysis data on the changes in mass and data on the thermal effects that occur with changes in temperature and time. The samples were heated in air atmosphere from 50 to 1200°C at a rate of 10 degree per min in corundum crucible.
2. FG determination method – flue gas composition determination by chemical absorption technique.

Calculation method for determining the oxidized coke amorphicity of by the N/C ratio in coke according to the method [13]. The calculation method is based on the results of the regenerator flue gas composition analysis (volumetric content of CO, CO₂, O₂, N₂) and the total flow rate of the air delivery volume for regeneration. The calculations assume that all carbon is converted into carbon dioxide (1):



where x – the ratio of a mole of hydrogen to 1 mole of carbon

The main stages of calculating the oxidized coke amount and its structure is to determine:

1. Amounts of oxygen consumed and carbon dioxide formed (2), (3):

$$n_{\text{O}_2} = G_v (C_{\text{O}_2}^{\circ} - C_{\text{O}_2}) / 100 / V_m, \quad (2)$$

$$n_{\text{CO}_2} = G_v \cdot C_{\text{CO}_2} / 100 / V_m, \quad (3)$$

where n_{O_2} , n_{CO_2} – is the amount of consumed oxygen and carbon dioxide formed, kmol/h, G_v – is the air consumption, nm³/h, $C_{\text{O}_2}^{\circ}$ – is the oxygen concentration in the air delivery volume, % vol, C_{O_2} – is the oxygen concentration in the regeneration flue gases, % vol, V_m – is the molar volume of gas at standard conditions, m³/kmol, C_{CO_2} – concentration of carbon dioxide in flue gases (total content of CO and CO₂), % vol.

2. The number of carbon and hydrogen atoms in coke (4), (5):

$$N_C = C_{\text{CO}_2}, \quad (4)$$

$$N_H = (n_{\text{O}_2} - n_{\text{CO}_2}) \cdot 4, \quad (5)$$

where N_C – number of carbon atoms in coke, kmol/h; N_H – the number of hydrogen atoms in coke, kmol/h.

3. Mass of oxidized coke (6):

$$M_C = N_C \cdot M_C + N_H \cdot M_H, \quad (6)$$

where M_c – mass of oxidized coke, kg; M_C , M_H – molar mass of carbon and hydrogen, respectively, kg / kmol.

2. Results and discussions

The results of the calculation methodology are presented in Table 1.

Table 1. The oxidized coke amount and C/N ratio determination results for the period from 04/16/2018 to 01/30/2019

| Property | Value |
|--|---------------------|
| CO content in flue gases, % vol. | 0.0–0.4 |
| CO ₂ content in flue gases, % vol. 1 | 10.0–13.6 |
| O ₂ content in flue gases, % vol. 4.0–8.0 | 4.0–8.0 |
| Air flow rate for regeneration, Nm ³ /h | 180 090.5–202 163.5 |
| C/H ratio | 0.57–1.9 |
| Coke mass, kg | 11 587.4–15 664.4 |

Analysis of the regenerator flue gas composition experimental data from a catalytic cracking unit for the period from 04/16/2018 to 01/30/2019 showed that the C/H ratio in coke varies over a wide range from 0.57 to 1.9 units. High C/H ratio values indicate the presence of coke with a low hydrogen index forming as a result of a multiple high-temperature “reaction – regeneration” cycle on the catalyst surface. However, since the calculation method is based on the industrial data of the regenerator operation, the dense structures of coke with a low hydrogen index are oxidized under the conditions of regeneration.

The structure and amount of coke formed on the catalyst depends largely on the feedstock composition, the operating conditions of the catalyst in the reactor and the regenerator [14]. Under repeated conditions of high temperatures in the “reaction – regeneration” cycle, as well as during the processing of high-coking feedstock, the formation of graphitized coke, which irreversibly deactivates the catalyst, is possible.

Under laboratory conditions, thermogravimetric analysis and differential scanning calorimetry were used to establish the structure of coke deposits on coked and regenerated catalysts. This method allows to determine the thermal effects of the processes occurring on the catalyst when heated at a constant rate and the change in mass of the studied samples [15].

The results of experimental determination of the amount and structure of coke on coked and regenerated catalysts by TGA-DSC method are presented in Figure 1.

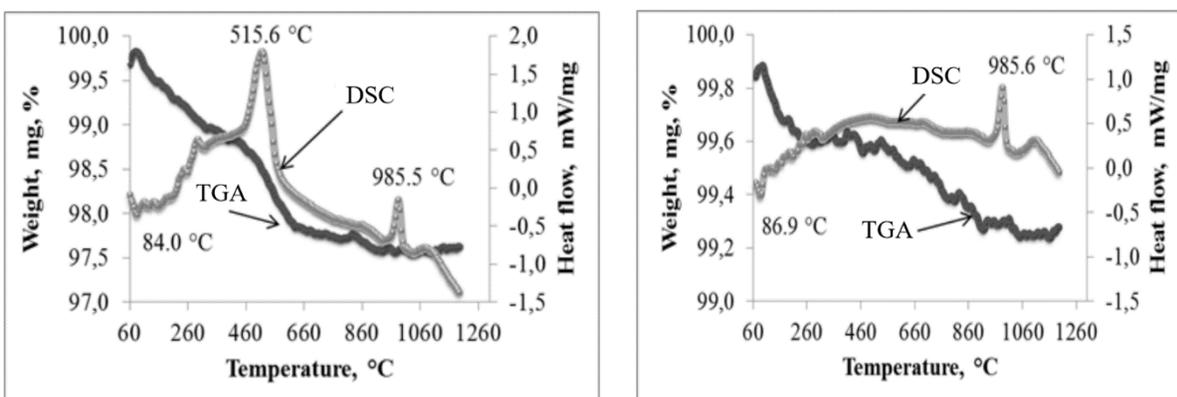


Fig. 1. Thermograms of coked (a) and regenerated (b) catalysts: DSC – differential scanning calorimetry curve; TGA – thermogravimetry curve

There are endo- and exothermic effects, accompanied by a significant mass loss of the samples in the temperature range from 0 to 1200 °C on the DSC curve of coked and regenerated catalysts. There is the endothermic effect at temperature peaks of 84.0 °C for coked catalyst and 86.9 °C for regenerated catalyst which indicates desorption of vapors and hydrocarbons entrained with the catalyst from the desorption zone.

There is a pronounced exothermic maximum at a temperature of 515.6°C on the thermogram of the coked catalyst, which indicates the oxidation of carbon deposits on the surface of the catalyst. Moreover, coke deposits have an amorphous (porous) structure, since the temperature range of 500–600°C specific for oxidation of amorphous coke with a high hydrogen index; at higher temperatures (600–900°C), oxidation of graphitized coke with a low hydrogen index occurs. The results of the analysis showed the absence of a pronounced temperature peak on the regenerated catalyst thermogram (Figure 1b) specific for the amorphous coke oxidation. There is also the catalyst mass loss in this temperature range, probably due to burning of residual coke.

At the same time, it is not possible to detect the presence of a graphitized structure on the coke surface using the thermogravimetry method, since the thermal stability of the catalyst is limited. In some cases, the DSC method is used to control thermal stability. The DSC curve of coked and regenerated catalysts presents a pronounced exothermic peak at temperatures of 985.3–985.5°C, which indicates the destruction of the zeolite-containing catalyst crystalline structure [16] and microcrystals sintering.

Considering that the dehydration and destruction of the zeolite crystalline structure occurs gradually, and not at a strictly fixed temperature, in industrial conditions the regeneration temperature higher than 730°C is not allowed, according to the unit process regulations, to prevent irreversible thermal decontamination due to the exothermic reactions of coke combustion. Moreover, studies conducted by the authors of [17] show that the thermal stability of a zeolite-containing catalyst can vary within 100°C with a change in the content of rare-earth elements up to 10%. For a detailed study of the catalyst samples thermal stability and the graphitized coke presence determination, it is necessary to conduct X-ray phase analysis [18].

The results of conducted studies allow us to indirectly estimate the efficiency of the regeneration process by the amount of oxidized coke on the catalyst relative to the initial content. There is the catalyst mass loss at temperatures under 730 °C specific for industrial conditions. It was 1.9% for the coked catalyst and 0.37% for the regenerated catalyst. Table 2 presents the catalysts thermal analysis results.

Table 2. Catalysts thermal analysis results

| Catalyst type | Pore moisture, % | Amorphous coke content, % | Zeolite crystalline structure destruction temperature, °C |
|----------------------|------------------|---------------------------|---|
| Coked catalyst | 0.85 | 1.05 | 985.5 |
| Regenerated catalyst | 0.14 | 0.23 | 985.3 |

The TGA-DSC results of the regenerated catalyst, shows the coke content on its surface decreased by 4.56 times, the regeneration process efficiency relative to the initial coke content was 78.1%.

3. Conclusions

Experimental studies of zeolite-containing cracking catalysts made it possible to estimate the structure and amount of coke formed on the catalyst during the catalytic cracking process. A temperature peak of coke oxidation was established (515.6°C), which indicates the presence of an amorphous structure on the catalyst coke surface. Using the calculation method based on the analysis of experimental data on the industrial unit regenerator flue gas composition, the C/H ratio in coke was determined, which varies over a wide range of 0.57–1.9 units. Studies of coked and regenerated catalysts made it possible to evaluate the efficiency of regeneration by the amount of oxidized coke, which was 78.1%.

Catalyst state monitoring and feedstock quality control problems can be solved by the method of mathematical modeling. The results of this paper will be used to develop a zeolite-containing catalyst regeneration process mathematical model including the influence of the coke formed on the catalyst structure on the catalyst regeneration stage efficiency. When Operation optimization, it is important to take into account the catalyst coking initial degree and process reactions thermal effects, since a sharp rise in temperature in the regeneration zone can lead to irreversible deactivation as a result of sintering the pore structure. In addition,

as a continuation of the work, it is necessary to investigate the feedstock composition and technological conditions in the lift reactor influence on the rate of coke formation.

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