

Coke Deposition on Cracking Catalysts Study by Thermogravimetric Analysis

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ABSTRACT

The Beta zeolite is used as an additive the FCC process catalysts, but its efficiency can be affected by the presence of coke in the system, causing pore blockage and a consequent deactivation of active sites. For such regeneration, coke combustion is enhanced with air at high temperatures. Aiming at understanding the mechanism of Beta zeolite regeneration, the kinetic study of coke decomposition was carried out through thermogravimetric tests, using multiple heating rates and integral kinetic models. From the determination of kinetic parameters such as activation energy, rate constants, half-lives, and coke removal time as a function of temperature; it is perceived that the removal of the coke deposited in the zeolite, within one hundred minutes, would require a thermoxidation process at 800 K.

Keywords - Beta zeolite, coke, kinetic study, thermogravimetric, regeneration

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I. INTRODUCTION

Fluid catalytic cracking (FCC) is one of the main oil refining industry's process. It is responsible for the conversion of heavy bottom product fractions from distillation towers into lighter, higher added value feedstock [1, 2].

The active component most used in FCC catalysts is the Y-zeolite. Other additives may be added to these catalysts aiming at increasing gasoline octane rating, forming lighter olefins, or decreasing the sulfur content in fuel [3-5]. The Beta zeolite, also used as an additive, is composed of a three-dimensional system of porous channels confined in 12 tetrahedral rings, directly synthesized with a considerably high Si/Al ratio, besides being very acidic, thermally and hydrothermally stable, and having an ease in diffusing relatively large molecules through its channels [6]. In FCC, the reaction rate is not constant throughout the catalytic process, since the catalyst may suffer from deactivation due to coke formation, active site poisoning by metals and sintering [7].

Coke is a mixture of undesirable substances, mainly composed of carbon, which are physically adsorbed onto the catalytic surface, provoking pore obstruction. However, it also diminishes poisoning when forming a layer on the

catalyst before the attack from metals, allowing their removal along with coke during regeneration [8].

In the FCC process, the catalyst moves between a reactional zone, called riser, and a regeneration zone. The latter is located in the regenerator, where coke combustion occurs using air as oxidizer. In more efficient plants, pure oxygen is used as to enrich vent gases as CO, which eases CO₂ capture. The regenerator operates from 953 K and 1033 K at a pressure of 3 bar, and 5 to 10 minute residence time. Such conditions along with poisoning, and sintering promote lower regenerative yields over time, making the removal of part of the catalyst and injection of some new catalyst every cycle necessary to achieve a constant activity distribution [2, 9].

The coke decomposition study can be done through Thermogravimetric Analysis (TGA), where a sample's mass variation is measured as a function of the programmed temperature, and by Differential Thermal Analysis (DTA), where the temperature difference between the sample and the reference material is portrayed as a function of time or temperature. Kinetic data extracted from such analyses are used for the calculation of kinetic model parameters [10].

Techniques proposed by Ozawa, Flynn, Wall, and Toop can be employed for coke

decomposition study as to acquire catalyst regeneration kinetic parameters, obtained through integrated thermogravimetric curves associated with mathematical models. These techniques provide calculations for activation energy, rate constants, half-lives, and, mainly, coke removal time as a function of temperature [11].

When obtaining a kinetic model, and reaction parameters, coke nature and location on the catalytic surface can be better analyzed, easing the FCC regenerator designing for better operational conditions in the coke decomposition step [12].

This way, the objective of this paper is to study coke thermal decomposition on Beta zeolite by thermogravimetric analysis as for obtaining catalyst regeneration kinetic parameters.

II. MATERIAL AND METHODS

A Zeolyst International commercial Beta zeolite (BEA) (CP814N) in the ammoniacal form with SAR 18 was used for the study. The catalyst was calcined for 4h with synthetic air at 773 K, to reach the proton form.

A standard solution of 100 ppm thiophene in n-hexane was prepared from n-hexane solvents ($\geq 99\%$ A.C.S. reactant, Sigma-Aldrich) and thiophene (99% A.C.S. reactant, Sigma-Aldrich). Thiophene was used as a sulfur source and n-hexane as a paraffinic component of gasoline.

The catalytic cracking of n-hexane containing 100 ppm thiophene was performed in a fixed bed lab reactor, operating at atmospheric pressure at 773 K, with a space velocity of 0.83 s^{-1} . The catalyst was treated with nitrogen at 773 K for 4h before the test.

The thermogravimetric analyses were performed in a DTG-60 Shimadzu with a sample size of approximately 5 mg, which were weighted in open platinum sample pan, introduced in the thermogravimetric oven scale. The reference was an identical sample pan of the same material and weight. The tests occurred in different linear heating rates (β) of 5, 10, and 20 K min^{-1} , in temperature range of 303 K and 1173 K, with a nitrogen flow of 50 mL min^{-1} in a dynamic synthetic air atmosphere with a flow rate of 100 mL min^{-1} , controlled by a gas control system.

Having obtained the thermogravimetric analysis results, which provide sample mass variation as a function of temperature rise related to the heating rate, Origin[®] was used for data analysis through the plotting of adequate graphs, allowing the interpretation of results.

The appropriate integral kinetic models were applied for the study of coke deposition on Beta zeolites through thermogravimetric experiments to determine kinetic parameters such as: activation

energy, rate constants, half-lives, and the necessary time for coke removal.

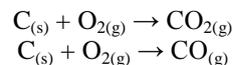
III. RESULTS AND DISCUSSION

The TGA/DTA technique involves a program of linear heating with programmed oxidation temperature and air flow that can allow the assumption of a constant oxygen pressure throughout the experiment. From these thermogravimetric tests, the activation energy of coke decomposition on the Beta zeolite was calculated using the method Ozawa-Flynn-Wall, with the simplified equation 1 [11, 12].

$$E_a \cong -18,2 \frac{d(\log \beta)}{d(1/T)} \quad (1)$$

The kinetic model proposed by Ozawa and developed by Flynn and Wall is an integral method, simple, and widely applicable to kinetic parameter obtention from thermogravimetric studies, being very used in random degradation of polymers and other more complex reactions which cannot be analyzed through other methods [13, 12].

Employing the DTG derived curves, obtained for the studied conditions at different heating rates, we observed a loss in mass, without affecting the zeolite structure, resulting from coke decomposition:



As the heating rate decreases, the DTG temperature for coke burning switches to a lower value [12]. However, this change was not significant, and regeneration occurred in temperature intervals similar for all heating rates. Nevertheless, at the rate of 10 K min^{-1} , the DTG curve peak is more visible and easier to interpret. We verify that coke oxidation is maximum at the temperature range from 553 K to 951 K, Fig. 1.

In the temperature analysis of regeneration as a function of lost mass percentage for the different heating rates (Fig. 2), it was noted that the thermal region of coke removal is a direct function of the employed heating rate, and the similarity in coke burning temperature was confirmed among the tests. In FCC catalysts, low heating rates are used when coke is in the core instead of in the pores [14].

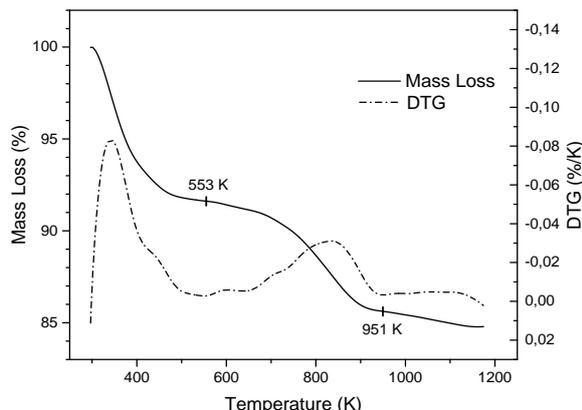


Figure 1: Differential thermogravimetric curve for the Beta zeolite impregnated with coke at a heating rate of 10 K min⁻¹.

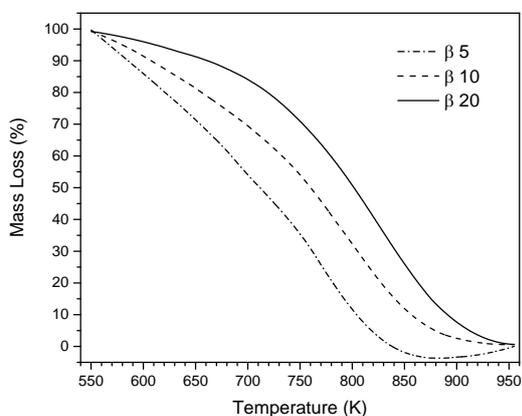


Figure 2: Multiple thermogravimetric curves in the coke impregnated Beta zeolite oxidation zone at different heating rates (β).

The linearity observed when the heating rate logarithmic is plotted as a function of reciprocal temperature, for several degradation rates of coke (Fig. 3), confirms that the kinetic model can be used to evaluate catalyst coke removal. From the first derivative of such curves, sufficient parameters are obtained for determining activation energy through equation 1, reaching a value of 72,4 kJ mol⁻¹.

We perceived that, for different coke degradation rates, the combustion profile changes. This occurs due to the nature of deposited coke, and the complex structure and composition of the zeolite. Therefore, we must assume activation energy for regeneration as the sum of coke combustion steps in several fractions for different heating rates [12].

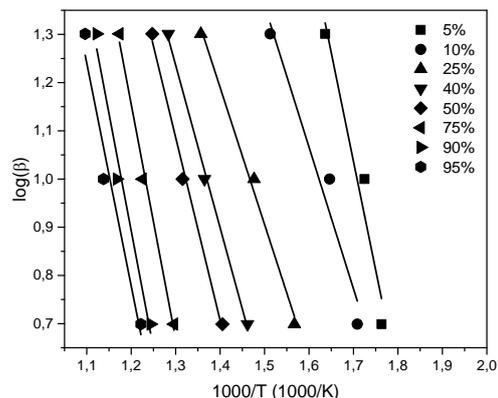


Figure 3: Heating rate logarithmic versus reciprocal temperature for different coke degradation rates.

From the Arrhenius equation (equation 2) [14], we note that curve of kinetic constant presents small variation until 700 K, where there is an exponential increase, indicating that thermoxidation velocity increases in the same way past this (Fig. 4).

$$k = A \cdot e^{-\frac{E_a}{RT}} \quad (2)$$

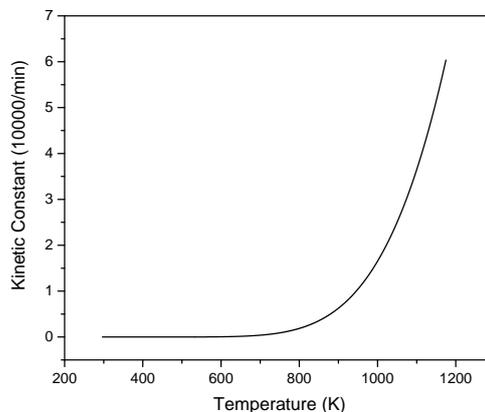


Figure 4: Kinetic constant versus coke thermoxidation temperature on the Beta zeolite.

Conversion is related to the time function for all heating conditions (Fig. 5). We note that, with the increase in heating rates, higher conversions are obtained in smaller process time spans. Therefore, this allows the comparison of the coke decomposition profile for different analysis conditions and verify the influence of heating rates in the coke oxidation reaction on the Beta zeolite.

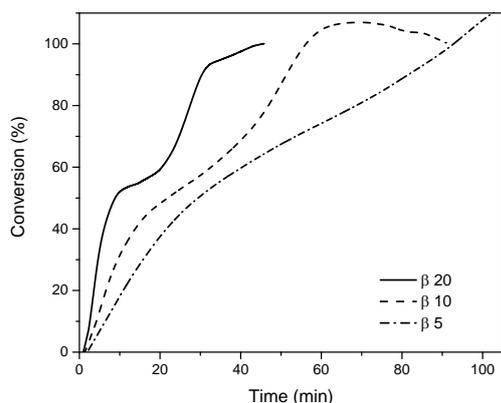


Figure 5: Conversion of coke with time for different heating rates.

From the Toop relation, equation 3, it is possible to plot lifetime versus regeneration temperature, predicting when time will lead to remove coke at certain temperature [13] shown in Fig. 6. In order to remove 99% of coke from the zeolite within one hundred minutes, for example, a process of thermoxidation at 800 K would be necessary, with an air flow of 100 mL min⁻¹.

$$T_c = \frac{E_a/R}{\ln t_c - \ln \left[\frac{E}{\beta \cdot R} \cdot P \left(\frac{E}{R \cdot T_p} \right) \right]} \quad (3)$$

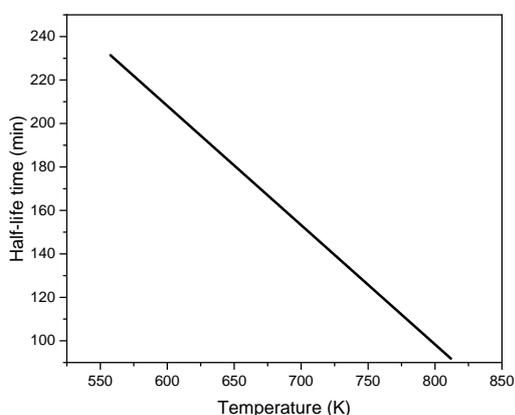


Figure 6: Coked Beta zeolite regeneration time for determining temperature.

According to data for coke decomposition evaluation in different zeolites found in literature, distinct behaviors were presented. This can be attributed to complex structures and chemical characteristics of the catalysts, besides a wide spectrum of operational conditions. Therefore, the kinetic combustion of coke depends on several factors.

IV. CONCLUSION

The reaction of coke deposition onto the

Beta zeolite is a process that requires an activation energy equal to 72,4 kJ mol⁻¹. For TGA analysis, under lower heating rates, the thermoxidation temperature decreases.

The kinetic constant rate increases as a function of temperature, representing an increase in reaction velocity as a consequence of larger amount of available energy to the molecules. This is confirmed in conversion as a function of temperature analysis, which are directly proportional.

The thermogravimetric tests under different conditions along with the kinetic models demonstrated to be efficient for the establishment of parameters and analysis of coke decomposition in the Beta zeolite.

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