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Effect of zeolite, kaolin and alumina during cracking of heavy petroleum residue evaluated by thermogravimetry

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Abstract This work evaluates the effect of the FCC catalyst components—Y zeolite, kaolin and alumina—on the formation of coke during the cracking of heavy residue (HR) of petroleum. The Y zeolite, kaolin and alumina were mixed with a HR at a ratio of approximately 1:4. The effect was studied using dynamic thermogravimetry at a heating rate of 50 K min^{-1}, with N_2 (between 35 and 700 °C) and air (in the 700–1,000 °C temperature range). The HR analyzed in these conditions formed 8.1% of coke. All the mixtures presented larger coke formation than that observed in pure HR. The Y zeolite presented fourfold larger coke formation, while kaolin and alumina showed twofold higher formation than pure HR. The major focus of this study was to verify the sensitivity of the TG technique in providing information about coke formation in the fluid catalytic process of refineries.

Keywords Catalyst · Zeolite · Alumina · Kaolin · Coke · Thermogravimetry

Introduction

The fluid catalytic cracking (FCC) is one of the most important and most profitable processes in the petroleum refining industry [1]. FCC process plays an important role in heavy oil upgrading, converting heavy petroleum fractions into valuable light products such as gasoline and diesel [2]. Over the years, many improvements have been made in the FCC process. Since FCC is a catalytic and heat integration process, efforts have been dedicated to establishing the FCC feedstock specification to meet process constraints such as catalyst deactivation and heat load requirements. To satisfy these requirements, carbon residue (coke) formed during the process of feedstock are kept at certain levels.

A fluid catalytic cracking catalyst is a porous microsphere containing Y zeolite dispersed in a clay matrix—kaolin and alumina. Y zeolite is the rate-controlling constituent during the process of catalyst cracking and the matrix performs both physical and catalytic functions [3, 4]. The detailed properties of the matrix can have a profound impact on the properties and performance of a cracking catalyst.

Y zeolites have been used extensively in catalytic cracking since 1962. Unfortunately, the majority of the active sites are located within the Y zeolite pore structure [5–7]. The activity of the cracking catalyst declines rapidly because of the accumulation of carbonaceous deposits on the catalyst surface. During the FCC process, a significant portion of the feedstock is converted into coke. This coke temporarily deactivates the active sites of the catalyst by pore blockage [8] resulting in an important activity loss.

In order to recover the activity, the FCC catalyst continuously circulates between the riser (FCC reactor) and the regenerator vessel. For the catalytic cracking of petroleum heavy residue, coking is inevitable and important. Coking has significant influence on heat balance of the whole catalytic pyrolysis process. Coke deposited on catalysts is burnt off in the regenerator, providing the heat for the whole system. However, coking will reduce the activity of

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catalysts and result in the variation of product distribution [9]. This phenomenon has a very significant economic importance and has therefore been the subject of a number of studies [10].

The purpose of this work was to employ the thermogravimetric technique (TG) to evaluate the influence of each catalytic component—Y zeolite, kaolin and alumina—in the formation of coke during the FCC process of petroleum heavy residue.

Experimental

Samples

Y zeolite, kaolin and alumina samples were selected for this study. All of them with pellets about 60 µm diameter. A sample of Brazilian petroleum heavy residue 12 API (HR) with 7.3% of asphaltenes was used to prepare the mixtures with each component in the proportions of one part of HR sample to four parts of catalyst component (1:4).

The mixture of each component with the HR sample was prepared by heating the catalyst components in a furnace at 550 °C for 2 h. They were then mixed in proportions of one part of HR sample, previously dissolved in 50 mL of dichloromethane, to four parts of the prepared component catalyst. The solvent was evaporated in a vapor-rotational device and the samples were stored in closed vials. This ratio was selected on the basis of what is applied in the catalytic refining process of heavy fractions of oils.

Thermogravimetry

All the experiments were conducted in a Netzsch STA-Luxx 409 thermal analyzer, using alumina crucibles (300 µL), applying a heating rate of 50 K min^{-1} and an initial sample mass of 80 mg, in a dynamic atmosphere of N_2 at 50 mL min^{-1} from 35 to 700 °C and in a dynamic atmosphere of air at 50 mL min^{-1} from 700 to 1,000 °C. The temperature was calibrated with $RbNO_3$, $KClO_4$ and CsCl.

Results and discussion

In a preliminary experiment, the petroleum HR was analyzed by TG to observe the thermal behavior with respect to mass variation and coke formation. The resulting TG and DTG curves (Fig. 1) showed one large mass loss between 320 and 550 °C, indicating its thermal degradation. A little shoulder (320–400 °C) is observed in DTG curve showing that two thermal decomposition processes are occurring. The temperature for the maximum rate of reaction during the thermal degradation is 475 °C. The carbonaceous material formed during thermal degradation was burned in an air atmosphere introduced at 700 °C.

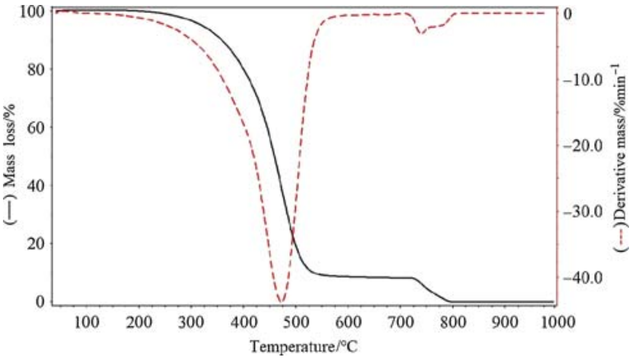

Fig. 1 TG and DTG curves of HR at 50 K min^{-1} in N_2 flow (35–700 °C) and air (700–1,000 °C)

Six replicates of HR samples were processed under the same TG conditions (mass = 20 mg, $\beta = 50$ K min^{-1} and N_2 and air flow rate = 50 mL min^{-1}) to determine the reproducibility of coke formed after HR thermal cracking. Table 1 describes the carbonaceous content taken from TG curves. The coke formed after the thermal process was 8.1%.

Y zeolite, kaolin and Al_2O_3 were analyzed by TG in the same conditions of HR sample. Figure 2 showed the resulting TG curves of each one. Y zeolite (a) indicated that the sample underwent only one mass loss (120–400 °C) due to the evolution of bound water. The kaolin TG curve (b) and alumina TG curve (c) underwent two different events. The first loss was caused by the evolution of bound water (120–400 °C) and the second by the release of the strongly bound water [11]. No mass loss was observed after introducing air (700–1,000 °C).

Before mixtures preparation all types of water were eliminated by heating each catalyst component in a furnace at 550 °C for 2 h. The mixtures of Y zeolite, alumina and kaolin with petroleum heavy residue were prepared as described at experimental part, and analyzed by TG under the same conditions. The TG mixtures curves are showed

Table 1 Replicates of HR (20 mg initial mass, $\beta = 50$ K min^{-1})

Replicates	Cracked material/%	Coke/%
1	92.3	7.4
2	91.8	8.5
3	90.7	8.3
4	91.3	7.7
5	91.3	8.1
6	91.2	8.5
Medium	91.4	8.1

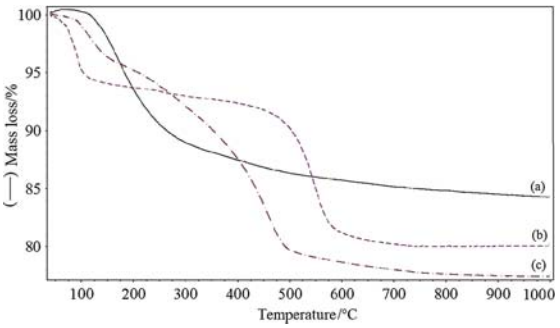

Fig. 2 TG curves of (a) Y-zeolite, (b) kaolin and (c) Al_2O_3 samples at 50 K min^{-1} in N_2 (35–700 °C) and air (700–1,000 °C)

in Fig. 3. The coke was quantified in TG curves after introducing air (700–1,000 °C) and the residual mass at 1,000 °C represents the amount of each component present in the mixture.

The TG curve of zeolite + HR (Fig. 3a) showed three mass losses. The first and largest is at 150 °C. Y zeolite is a material with a high capacity for adsorption; therefore, we believe that the first mass loss was due to water adsorbed during the preparation of the mixture. To confirm this hypothesis, a blank experiment was done, i.e., a certain amount of zeolite was treated at 550 °C and then mixed with dichloromethane. After solvent evaporation in vapor-rotational device, the resulting TG curve is illustrated in Fig. 4. The same mass loss occurred at 150 °C, confirming that the manipulation of Y zeolite after drying, caused water absorption.

The other mass losses in the TG curve of Y zeolite + HR are clearly visible in the DTG curve between 220–350 and 350–550 °C (Fig. 5a). The coke was quantified in TG curve after introducing air (700–1,000 °C) and the residual mass at 1,000 °C represents the amount of Y zeolite in the mixture. Excluding the amount of water, the mass loss between 220 and 550 °C corresponds to the HR in this mixture.

Table 2 shows the results obtained from six replicates of zeolite + HR samples under the same TG conditions. Note that the mixture was obtained as prepared, i.e., with one part of HR and four parts of Y zeolite.

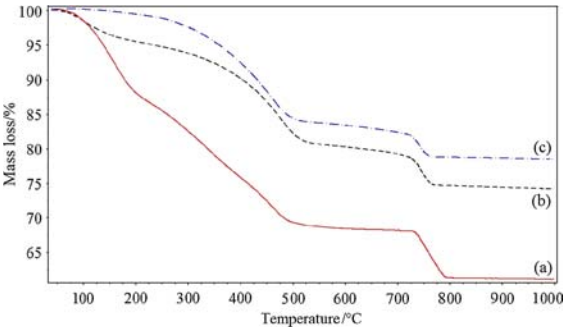

Fig. 3 TG curves of mixtures (4:1): (a) Y zeolite + HR, (b) Al_2O_3 + HR and (c) kaolin + HR at 50 K min^{-1} in N_2 (35–700 °C) and air (700–1,000 °C)

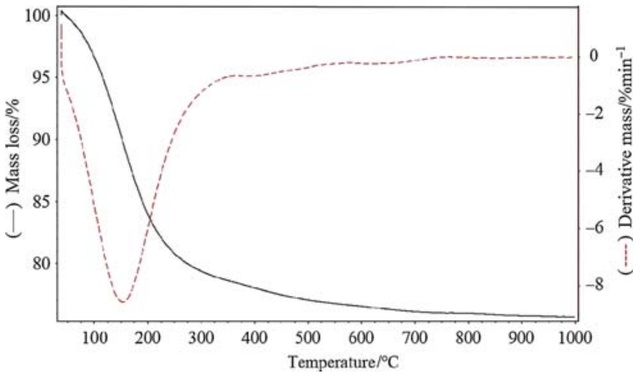

Fig. 4 TG and DTG curves of Y zeolite blank test—prepared by heating at 550 °C for 2 h, mixed with dichloromethane 50 mL that was evaporated before TG analysis

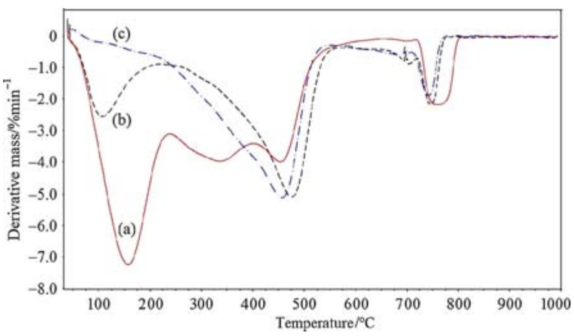

Fig. 5 DTG curves of mixtures (4:1): (a) Y zeolite + HR, (b) Al_2O_3 + HR and (c) kaolin + HR at 50 K min^{-1} in N_2 (35–700 °C) and air (700–1,000 °C)

The TG and DTG curves of Y zeolite (Figs. 3a, 5a) also show that HR cracking in the presence of Y zeolite occurred at lower temperatures (220 and 420 °C) than that observed in the thermal decomposition of HR (300 and 475 °C). This was expected, since Y zeolite is the rate-controlling constituent in the catalyst and is its active component. The amount of coke formed during the cracking of HR mixed with Y zeolite was about 5.5%, corresponding of 17% of HR. Normalizing to 100% of HR, 32% of coke formation would be expected. This amount corresponds to four times more than that observed in thermal treatment of HR without Y zeolite.

The TG curve of Al_2O_3 + HR mixture (Fig. 3b) showed little mass loss at 120 °C, indicating the presence of adsorbed water, though in a smaller amount than that observed in the mixture with Y zeolite. Two mass losses occurred at 320 and 475 °C, the same temperatures observed in the TG curve of HR thermal cracking. The residue at 1,000 °C revealed that the mixture was in the proportion of 4:1 (Table 3). The coke formed in this mixture was 3.8%, which is equivalent to 22% of HR,

Table 2 TG results from replicates of zeolite + HR (80 mg initial mass, $\beta = 50$ K min^{-1})

Replicates	Adsorbed water/%	Cracked material/%	Coke/%	HR/%	Zeolite/%
1	14.9	11.6	5.5	17.1	67.6
2	14.8	11.4	5.4	16.9	67.9
3	15.3	11.5	5.3	16.8	67.4
4	14.7	12.1	5.4	17.5	67.6
5	14.2	11.3	5.7	17.0	68.5
6	14.3	11.7	5.4	17.1	68.3
Medium	14.7	11.6	5.5	17.1	67.9

Table 3 TG results from replicates of Al_2O_3 + HR (80 mg initial mass, $\beta = 50$ K min^{-1})

Replicates	Adsorbed water/%	Cracked material/%	Coke/%	HR/%	Al_2O_3/%
1	3.2	18.1	4.5	22.5	75.0
2	2.9	18.5	3.5	21.9	75.8
3	1.8	18.4	3.4	21.8	76.6
4	2.8	17.9	3.5	21.3	76.0
5	3.4	18.2	3.5	21.7	74.9
6	4.1	17.3	4.7	22.0	73.9
Medium	3.0	18.1	3.8	21.9	75.3

Table 4 TG results from replicates of kaolin + HR (80 mg initial mass, $\beta = 50$ K min^{-1})

Replicates	Adsorbed water/%	Cracked material/%	Coke/%	HR/%	Kaolin/%
1	0.4	15.7	2.6	18.3	81.4
2	1.2	16.1	2.3	18.5	80.8
3	0.3	20.2	3.4	23.6	76.6
4	0.2	15.9	2.4	18.3	82.3
5	0.2	15.8	3.3	18.9	81.7
6	0.2	15.4	2.4	17.8	82.7
Medium	0.4	16.5	2.7	19.2	80.9

while the amount expected for 100% of HR would be 17%. Six replicates of Al_2O_3 + HR mixture were obtained under the same TG conditions.

The kaolin + HR mixture was analyzed in the same way as the two above mentioned mixtures. The TG and DTG curves (Figs. 3c, 5c) showed no loss of adsorbed water, but mass losses occurred at 320 and 475 °C. Table 4 shows the results obtained from six replicates of kaolin + HR samples under the same TG conditions. The residue at 1,000 °C confirmed that the mixture had a proportion of 4:1 (Table 4). The coke formed in this mixture was 2.7%, which represents 19% of HR, while the amount of coke expected from 100% of HR would be 14%.

Conclusions

Based on our TG evaluation, the three basic catalyst components (Y zeolite, kaolin and alumina), used in the refinery fluid catalytic cracking process promoted greater coke formation than the thermal process of petroleum heavy residue.

The Y zeolite, which is the rate-controlling constituent in the catalyst, when mixed with HR, presented fourfold greater coke formation, while kaolin and alumina showed twofold higher coke formation than thermal cracking of pure HR.

It was verified that TG technique has the sensitivity in providing information about coke formation in the catalyst used in fluid catalytic process of refineries as well as to evaluate the influence of each component in the formation of coke during the catalytic refining process of petroleum heavy residues.

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