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Kinetic study of thermal and catalytic pyrolysis of Brazilian heavy crude oil over mesoporous Al-MCM-41 materials

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Abstract This study aimed to evaluate the activity of Al-MCM-41, as mesoporous heterogeneous catalyst, for the thermal and catalytic degradation of a Brazilian heavy crude oil (14°API), via thermogravimetry. The American Petroleum Institute gravity (°API) is a measure of how light of heavy petroleum is when compared to water. The API value is an inverse measure of the relative density of a petroleum liquid, and it is used to compare the relative densities of petroleum samples. The catalytic activity was investigated as a function of different concentration of Al-MCM-41 (1, 3, 5, 10 and 20 mass%) added to the oil, as well as the apparent activation energy relative to degradation process. The TG runs were carried out at temperature range of 30–900 °C, at heating rates of 5, 10 and 20 °C min^{-1}, under nitrogen atmosphere. From TG/DTG tests, the material presented effective catalytic activity when added to the heavy oil at concentration higher than 5 mass%. This property was clearly evidenced by the activation energy values. By the application of Ozawa–Flynn–Wall kinetic model, it was observed that when the amount of catalyst was increased, the value of the apparent activation energy decreased from 103 kJ mol^{-1} (without catalyst) to 70 kJ mol^{-1} (with 20 mass% of catalyst).

Keywords Mesoporous catalyst · Al-MCM-41 · Heavy crude oil · Thermogravimetry · Ozawa–Flynn–Wall

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Introduction

In the last decade in Brazil, the oil industry has been growing steadily. New oil fields were discovered, farms underwater were built, and new pipelines were opened. The expansion was observed in all areas: exploration, refining and transportation, especially regarding the petroleum from pre-salt. Oil production in Brazil increased by 3.8 % in April 2014, reaching approximately 1.92 million barrels per day (bbl day^{-1}), according to the National Agency of Petroleum, Natural Gas and Biofuels (ANP) and the pre-salt increased by 2.3 % to 295.2 mil bbl day^{-1} of oil and 9.9 million cubic meters per day (m^3 day^{-1}) of natural gas, totaling 357.6 mil barrels of oil equivalent per day (boe day^{-1}).

This increase is due to a variety of hydrocarbons and non-hydrocarbons which may occur in the oil composition and which have physical properties quite different from each other. This can vary according to the predominant type of hydrocarbon present. This diversity can be further increased by the chemical transformation of existing refineries. The heavy oils extracted from Brazilian wells need better processing since raw materials are considered of high energy. Thus, the optimization aims at obtaining value-added fractions such as gasoline, diesel and kerosene. The residue from atmospheric distillation and/or vacuum is also being widely investigated in order to optimize the achievement of lighter fractions.

Thus, some researchers [1–3] investigated materials with potential application in catalytic route of a refinery; among these materials are mesoporous materials, such as MCM-41, Al-MCM-41 and Al-SBA-15, with diameter ranging from 2 to 30 nm, presenting surface area ranging from 700 to 1,000 $\mathrm{m}^2\ \mathrm{g}^{-1}$ and a high ion-exchange capacity, since the presence of exchange sites allows to functionalize the surface of these materials for specific applications.

In order to better understand the catalytic performance of the material, the chemical kinetics study has been applied, to determine the reaction rates and activation energy [4]. In a chemical reaction, the reaction rate depends on variables such as pressure, temperature and the presence of catalysts. In many cases, it is possible to achieve better rates with appropriate choice of reaction conditions. For reactions with petroleum, the chemical kinetics can be an important tool as the choice of the best conditions for obtaining larger quantities of oil derivatives with commercial value [5].

Therefore, the thermogravimetric analysis has been a wide technique used for the determination of kinetic parameters, due to a range of information that can be obtained by their experiments. The thermal stability of a reaction can be evaluated by kinetic parameters such as activation energy, reaction order and the speed, which can be fast or slow depending on the conditions under which such a reaction occurs [6, 7]. Thermal characterization, combustion and kinetics of different origin crude oils have been reported [8, 9], as well as the combustion characteristics and kinetic analysis of crude oils and their SARA fractions by thermal techniques [10, 11].

Thus, this study aims to develop and evaluate a high-quality Al-MCM-41 mesoporous catalyst, in order to apply it in a Brazilian heavy crude oil via thermogravimetry, and evaluate the behavior of this oil when catalyst is added at concentrations from 1 to 20 mass% to the oil, and determine the kinetic parameters, such as apparent activation energy, for this decomposition reaction. Recently, the effect of different clay concentrations on crude oil combustion kinetics by thermogravimetry has been reported [12–14]. This contribution shows the importance of determining the concentration of mesoporous catalyst, temperature and activation energy for processing heavy oil. These parameters are important for maximizing the formation of valuable products in a refinery.

Experimental

The mesoporous materials Al-MCM-41 were synthesized according to the procedure previously described [15]. The material was synthesized using a gel with molar composition: CTMABr: 2NaOH: 4SiO_2: 200 H_2O: $x$$Al_2O_3$, where $x = 0.08$, which was adjusted for obtain Si/Al molar ratio equal to 50. CTMABr represents the cetyltrimethylammonium bromide, which is a surfactant and which was used as a template for the sample; NaOH was used as a source of sodium; SiO_2 (Silica gel) corresponded to the source of silicon; H_2O was used as the solvent; and Al_2O_3 (pseudoboehmite) was used as a source of aluminum. The first solution was prepared by mixing silica gel, sodium hydroxide, a source of aluminum and the solvent, keeping the mixture stirred (400 rpm) for 2 h at 60 °C. The second mixture containing the template and the solvent was kept under stirring for 30 min. These two solutions were mixed and aged for 30 min under constant stirring. Then, this mixture was placed in a Teflon stainless steel autoclave and was afterward kept over a period of 5 days at a temperature of 100 °C. The pH corrections were done daily for values about 9–10, with a solution of 30 vol% of acetic acid. After the hydrothermal synthesis, the material was filtered and washed with distilled water to remove possible ion bromine and sodium waste. After this procedure, the material was dried at 100 °C for 4 h and then calcined at 500 °C, in nitrogen for 1 h, and in air for additional 4 h, for remotion of organic template.

The study of the catalytic activity of Al-MCM-41 was performed using a thermobalance TA Instruments, model SDT Q600-1110. Approximately 10 mg of sample of heavy crude oil with °API equal to 14.0 (signed P2) was analyzed in alumina crucibles. The sample was prepared taking into account the percentage by mass of catalyst (% m/m) tested in each experiment. The samples were prepared by adding percentages of 1, 3, 5, 10 and 20 mass% of Al-MCM-41 catalyst to the heavy crude oil. For this procedure, the initial oil sample was weighed, and for each sample, the percentage of catalyst was calculated for the final equivalent mass to the oil for the mixture. The Ozawa–Flynn–Wall (OFW) kinetic study was performed using three heating rates ($\beta = 5, 10$ and 20 °C min^{-1}) via thermogravimetric analysis (TG/DTG), nitrogen (60 mL min^{-1}) and temperature range from 30 to 900 °C. In order to have accuracy of the experiments, each run was repeated two times.

Results and discussion

The Al-MCM-41 material was successfully synthesized according to procedure described. In order to determine the incorporation of aluminum on the mesoporous structure, the calcined Al-MCM-41 material was analyzed by X-ray fluorescence, using an EDX 800 equipment, from Shimadzu. From the results of elementary chemical analysis, it was confirmed that the Al-MCM-41 material showed high concentration of silica (SiO_2) and low concentration of alumina (Al_2O_3) in the mesoporous material, with a Si/Al molar ratio of 46.4, or $SiO_2/Al_2O_3 = 23.2$. After calcination, a small reduction in the Si/Al molar ratio was observed, suggesting that part of aluminum was not introduced in the structure under the hydrothermal method used.

Figure 1 shows the thermogravimetric curve (TG/DTG) obtained from the thermal degradation of the P2 heavy

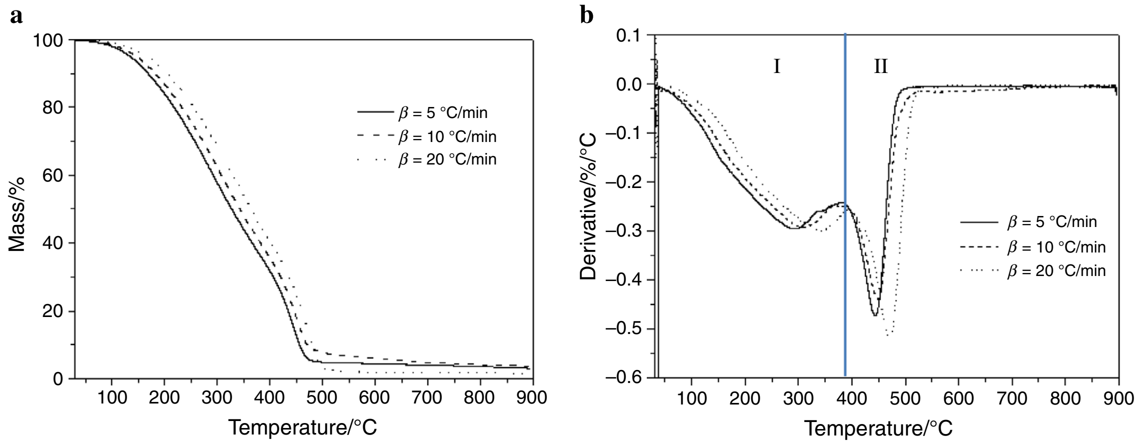

Fig. 1 **a** TG and **b** DTG curves of the heavy oil (P2), showing stages (*I*) and (*II*) of decompositions

crude oil sample, which was subjected to the dynamic non-isothermal method. In this method, the variation of heating rate (β) causes in the material analyzed appreciable differences in initial and final temperature of thermal degradation, as well as the maximum peaks of DTG, decreasing or increasing these temperatures, as the heating is more or less slow, that is, the power supply to the breaking of chemical bonds is provided as a gradual or faster degradation way. When the material was exposed to high temperatures, it undergoes changes in chemical structure and thus the physical properties. Therefore, the curve of thermal degradation in non-isothermal conditions shows the profile of resistance or thermal stability that the material exhibits when subjected to a temperature scan.

The P2 showed two events of mass loss: the first occurring between 100 and 400 °C and the second between 400 and 600 °C. The first event is probably due to the evaporation of light compounds instead of cracking, and the second is due to the breakdown of high molecular weight compounds that exist in this type of material [16, 17]. Table 1 shows the temperatures and mass losses for each event in the thermal degradation of heavy crude oil P2 pure (without catalyst).

In the first event, considering the heating rate of 5 °C min^{-1}, the percentage of mass loss ranged from 60.9 % corresponding to the decomposition of significant amounts of saturated hydrocarbons. The second event with loss of mass equal to 31.8 % was attributed to the removal of other components present with high molecular weight such as aromatic and resins, and also sulfur compounds, such as thiophene, benzothiophene and dibenzothiophene.

For other heating rates, the behavior is repeated, with slight degradation compounds in event (I) and at the event (II) of heavy compounds. The amount of coke formed at the end of each experiment was also analyzed, and it was concluded that there is a greater amount of asphaltenes [18], as well as acidity related to the number of total acidity index on the naphthenic acid content of the oil due to the chemical composition as shown in Table 2.

Figures 2–6 show the TG/DTG curves P2 oil with their respective quantities by mass of catalyst Al-MCM-41, in the case of 1, 3, 5, 10 and 20 mass%. The results were associated with the catalytic activity of Al-MCM-41 in heavy crude oil P2.

Evaluating the TG/DTG curves at the same heating rates, it was observed that when the amount of catalyst was increased, the initial and final temperature ranges were decreased [13, 14]. Also, was verified an increase in the percentage of mass loss in the cracking region (step II), indicating that the catalyst has acted, producing light volatile compounds and carbonaceous materials (coke) were formed during thermal cracking. Table 3 can improve the understanding of this statement. Furthermore, there was stage III,

Table 1 Values of temperatures and mass losses for each event of thermal degradation of pure oil P2

Heating rate	Temperature range/°C				Maximum peak DTG/°C		Residual coke/%
	Stage I	Mass/%	Stage II	Mass/%	Stage I	Stage II	
5 °C min^{-1}	31–380	60.9	380–505	31.8	291	441	7.2
10 °C min^{-1}	33–378	55.9	378–514	33.5	309	451	10.7
20 °C min^{-1}	45–395	56.1	395–545	40.0	341	470	3.8

Table 2 Chemical composition of heavy crude oil P2

Chemical composition	P2 (°API = 14.0)
Hydrocarbons (% m/m)	
Saturated	47.8
Aromatics	27.9
Resins	23.3
Asphaltenes	1.0
Sulfur/mg kg^{-1}	28.0
Total acidity/mg KOH/g	9.5

only the ratio of 10 °C min^{-1}, which can be defined as a delay in the degradation of asphaltenes, which is most responsible for the formation of pyrolysis residue [18].

The amount of coke formed on the oil + catalyst samples was greater than with pure oil. This is probably due to the action of catalyst in step cracking (event II), whose molecules are heavier—typically asphaltenes and aromatics, leaving residual coke more carbonaceous and denser.

The TG/DTG curves relative to the (P2 + cat 20 mass%) sample, did not show the stage III (see Fig. 6). This showed clearly the activity of the catalyst. The activity is a measure of the efficiency in transforming the solid reactant molecules to product molecules. In this case, catalytic activity was greater in the cracking zone, probably due to the presence of aluminum in the structure of the mesoporous ordered material and the nanostructured Si–O–Al arrangement [19]. In order to corroborate the results found with the thermogravimetric analysis, we used data obtained from TG/DTG curves and applied the kinetic model non-isothermal OFW model [20, 21]. In equations were used iso-conversional integral data of the TG curves at different ratios linear heating (5, 10 and 20 °C min^{-1}), where E_a values were estimated for each degree of conversion (α) selected from the TG curve. Thus, the rate of

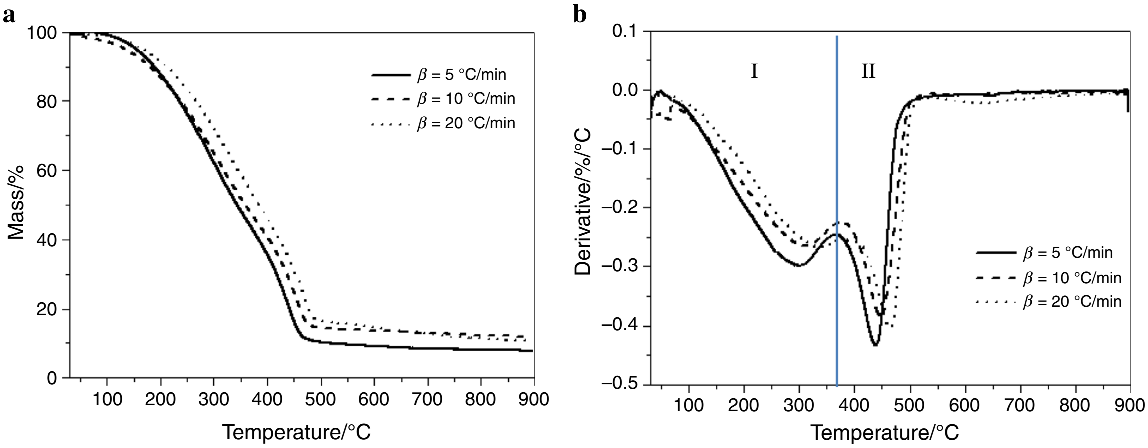

Fig. 2 *Left* (TG) and *right* (DTG) curves of the heavy oil (P2) + 1 % in mass of Al-MCM-41, showing stages (*I*) and (*II*) of decompositions

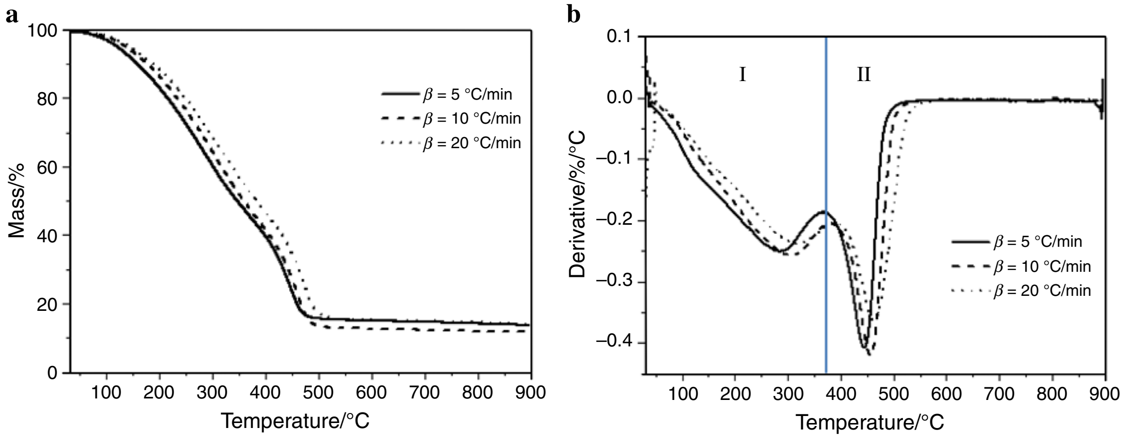

Fig. 3 *Left* (TG) and *right* (DTG) curves of the heavy oil (P2) + 3 % in mass of Al-MCM-41, showing stages (*I*) and (*II*) of decompositions

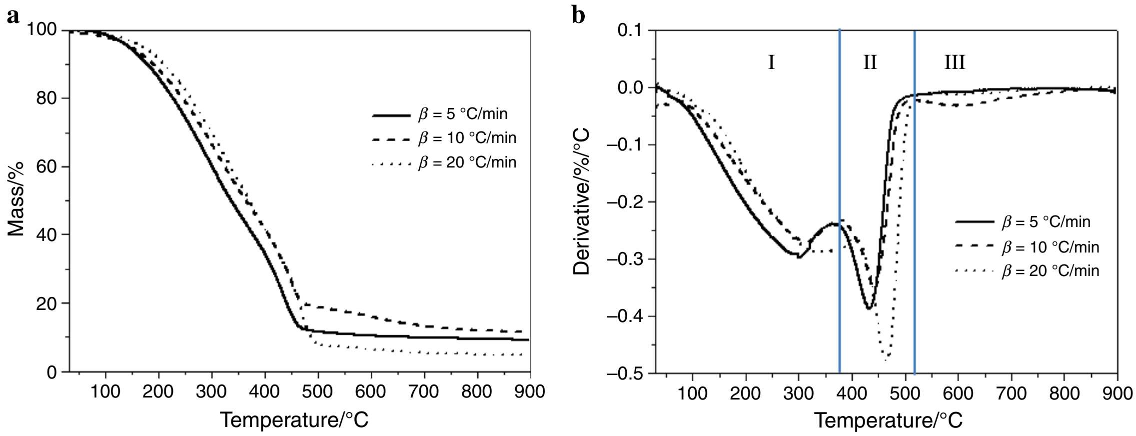

Fig. 4 *Left* (TG) and *right* (DTG) curves of the heavy oil (P2) + 5 % in mass of Al-MCM-41, showing stages *I* and *II* of decompositions

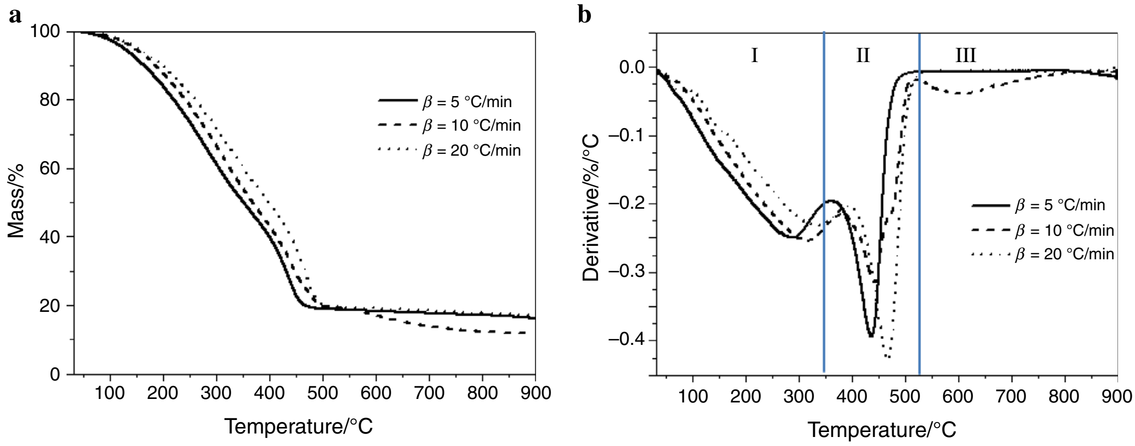

Fig. 5 *Left* (TG) and *right* (DTG) curves of the heavy oil (P2) + 10 % in mass of Al-MCM-41, showing stages (*I*) and (*II*) of decompositions

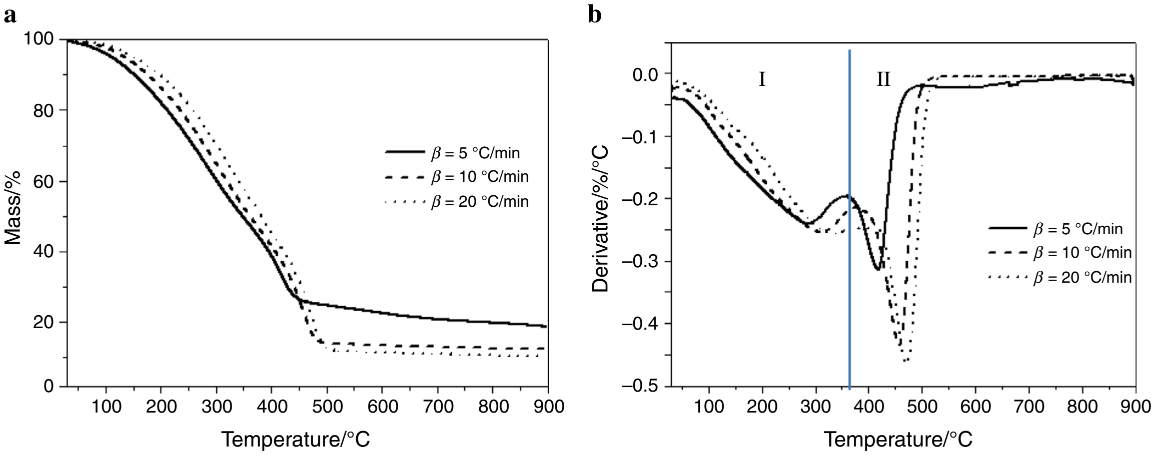

Fig. 6 *Left* (TG) and *right* (DTG) curves of the heavy oil (P2) + 20 % in mass of Al-MCM-41, showing stages (*I*) and (*II*) of decompositions

decomposition of oil depends on parameters such as conversion (α), temperature (T) and reaction time (t) in each process where the reaction rate is given as a conversion function $f(\alpha)$ [22, 23]. Therefore, E_{α} is obtained from the slope of the graph $\log\beta$ versus $1/T$ in a fixed value of α, using the OFW model, with at least three different heating reasons. Therefore, we used Eq. (1) to obtain the experimental values of E_{a} and their graphs:

Table 3 TG and DTG data extracted for the thermal and catalytic degradation of pure oil (P2) and (P2 + catalysts) at heating rate of $\beta = 10$ °C min^{-1}

Sample	Temperature range/°C				Maximum peak DTG/°C		Residual coke/%
	Stage (I)	Mass (%)	Stage (II)	Mass (%)	Stage (I)	Stage (II)	
P2	33–378	55.8	378–514	33.5	309	451	10.7
P2 + 1 %	34–376	51.6	376–522	32.0	312	451	16.4
P2 + 3 %	37–381	53.3	381–530	32.3	308	455	14.3
P2 + 5 %	35–376	51.4	376–515	28.9	312	447	19.7
P2 + 10 %	33–380	51.6	380–514	27.8	311	440	14.3^{a}
	–	–	514–726^{a}	6.3	–	–	
P2 + 20 %	33–376	51.9	376–516	32.8	309	455	15.3

[a] Referred to the Stage III

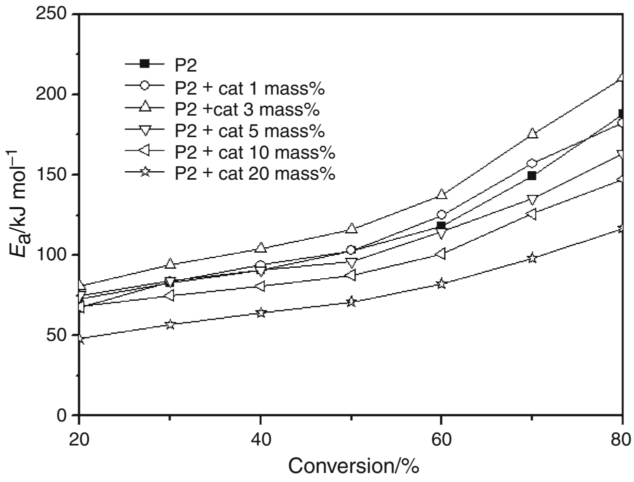

Fig. 7 Curve of apparent activation energy versus conversion (α) for P2 pure and mixed with of different amount of Al-MCM-41 catalyst

$$E_a \cong -18.2 \frac{\partial \log \beta}{\partial (1/T)} \tag{1}$$

where β is the heating rate, T is the absolute temperature (K) and E_a is the apparent activation energy (kJ mol^{-1}). Figure 7 shows the curves of apparent activation energies obtained from the application of equation derived from the OFW model, depending on the conversion α.

According to Fig. 7, for 1 and 3 % of Al-MCM-41, the value of the apparent activation energy was higher compared to pure oil [24, 25]. This result suggests that these concentrations of materials were not sufficient for developing the catalytic activity, being ineffective values. The increase in the value of E_a for 1 and 3 % compared to pure P2 should be due to the presence of another material, obtaining a nanocomposite based on oil-aluminosilicate material, increasing the amount of energy used to complete degradation.

Starting from 5 % in mass of Al-MCM-41 added to the heavy crude oil, it was observed a decrease in the values of the apparent activation energy as compared to the pure P2, which is characterized as the minimum amount of added catalyst for degradation of the heavy crude oil. When the proportion added was increased to 10 and 20 % in mass, were obtained lower values of the energy used for the degradation process, respectively. The function of the catalyst is to provide an alternative way for the reaction whose activation energy should be below. Table 4 shows the values of the apparent activation energies for $\alpha = 50 \pm 10$ %.

Table 4 Values of apparent activation energy (E_a) for pure oil (P2) and mixed with Al-MCM-41 (P2 + catalyst). The value of $\alpha = 50 \pm 10$ %

Sample	E_a/kJ mol^{-1}
P2	103.0
P2 + cat 1 mass%	102.8
P2 + cat 3 mass%	115.8
P2 + cat 5 mass%	96.2
P2 + cat 10 mass%	87.7
P2 + cat 20 mass%	70.9

The correlation coefficients obtained for all samples provided the degree of linearity and reliability of the kinetic model OFW with respect to heavy crude oil samples. From them, we confirmed the adequacy of the model OFW applied to oil. The use of iso-conversional method enabled the calculation of reliable values of E_a without having to take a previously defined kinetic model for the mechanism of the reaction studied. Thus, it was considered that the conversional fractions should be examined within a range of $0.3 \leq \alpha \leq 0.7$ whose deviations are approximately 10 % in the values of E_a [23].

In view of these results, it was found that the degradation of the oil produces lighter fractions such as gasoline, naphtha and gasoil [26]. Thus, analyzing the activation energy of the catalytic process, it is suggested that the best amount of catalyst Al-MCM-41 required for use should be higher than

5 % in mass in a refining unit. Also it demonstrated the performance of this mesoporous material as efficient catalyst for degradation process of heavy crude oil.

Conclusions

It was concluded that the Al-MCM-41 showed effective catalytic activity when added to Brazilian heavy oil (°API = 14), which was well demonstrated by thermogravimetry analysis followed by the application of kinetic model of Ozawa–Flynn–Wall, wherein as the amount of catalyst increased, the value of the apparent activation energy decreased from 103 kJ mol^{-1} for pure heavy oil (P2) until 70 kJ mol^{-1} for heavy oil mixed with 20 % in mass of Al-MCM-41 (P2 + cat 20 mass%). The high-quality Al-MCM-41 nanostructured material was synthesized successfully in accordance with the results obtained by physicochemical characterizations, showing the formation of the mesoporous structure. Thermogravimetry was the main technique used, which can be used satisfactorily to monitor the effective activity of Al-MCM-41 as a catalyst in the degradation process of heavy petroleum. The activity of the material should be due to the nanopore system with its hexagonal arrangements of the pores, and the acidity associated with the presence of aluminum on the structure surface. Thus, the Al-MCM-41 seems to be a good catalyst for processing heavy crude oil, suggesting that it may be used in the refineries in a near future.

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