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Acid removal from crude oils by catalytic esterification naphthenic acid catalize by Mg/Al hydrotalcite

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ABSTRACT

The presence of relatively high levels of naphthenic acids in crude oil may cause serious corrosion problem at temperature between 200 °C and 400 °C. One of the viable processes for decreasing acidity is the esterification of the present acids using an alcohol such as methanol. Therefore, the aim of this work is to develop a solid catalyst for the esterification reaction of 3-cyclopentylpropionic acid representative of the naphthenic acids.

The esterification reaction is carried out at 80 °C, 3.5 kg/cm^2 of pressure in a mechanically stirred batch reactor, using Mg-Al hydrotalcite (Mg/Al = 4) with different activation treatments as catalyst. These solids are characterized by N_2 sorptometry and X ray diffraction. The higher concentration of Bronsted basic sites present in uncalcined hydrotalcite would explain the satisfactory performance obtained. TAN decreased 90% by operating at a temperature as low as 80 °C after 60 min of reaction. The catalytic activity is evaluated at different reaction conditions such as, mass of catalyst, stirring speed and reaction temperature. A kinetic study for heterogeneous esterification of 3-cyclopentylpropionic acid with methanol was performed.

1. Introduction

With the growing demand for oil worldwide and the increase in the depth of exploitation of deposits, petroleum with increasing acid content is being discovered. The existence of high levels of naphthenic acids in crude oil causes serious corrosion problems at temperatures between 200 °C and 400 °C, which mainly affects pipes and primary distillation units [1]. Naphthenic acids are mainly monocarboxylic acids [2] where the carboxyl group is linked to a hydrocarbon molecule with a molecular formula R(CH_2) nCOOH where R is generally a cyclopentane or cyclohexane.

The total acid number (TAN) is defined as the number of milligrams of KOH needed to neutralize 1 g of oil. When the TAN is greater than 0.5, the oil is considered acidic and therefore potentially corrosive to the refinery units. Consequently, crude oils with high TAN value are considered of poor quality and their market value is low. High TAN crude oils have been discovered and exploited in California, Venezuela, the North Sea, Canada, West Africa, India, China and Russia [3,4].

The removal of naphthenic acids can be achieved by non-destructive methods, such as solvent extraction or adsorption [5,6]. However, solvent extraction requires several washing steps which consume large amounts of solvent. In addition, the obtained emulsion is difficult to separate increasing the cost of the process [7]. With respect to chemical treatments, the decarboxylation of naphthenic acids, although it is a possibility to process acidic crudes, the disadvantage is that it is necessary to operate at temperatures higher than 250 °C, aggravating corrosion [1,7]. On the other hand, esterification reaction is a promising alternative, since a significant decrease in acidity could be achieved at temperatures below 150 °C, especially when homogeneous catalysts are used. It is known that the homogeneous process occurs at a lower temperature than the heterogeneous one. However, the use of solid catalysts implies a double benefit. First, the formation of emulsions is avoided, and further complex steps are not necessary to remove the excess catalyst.

There are few works published in relation to the esterification of naphthenic acids from acidic crudes using solid catalysts. Some of them [2,7,8], have studied the esterification of naphthenic acids present in a petroleum sample using metal oxide as a catalyst. Among them, Wang et al. [7] studied the influence of operating conditions using SnO/Al_2O_3 as catalyst. In addition, some authors have used zeolites as Amberlite-15 and heteropoly acids supported on silica (HPA/silica) [9,10] as catalyst. The authors reported that as the reaction is relatively slow, to obtain a reasonable conversion, it is required to employ either higher temperature or catalyst mass.

Finally, the researches have evaluated the thermal stability of the esters formed. The results show that the esterification is a reasonable

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method for processing naphthenic acid since the treated crude are thermally stable. It can be emphasized that esterification processes employing basic catalysts occur at lower temperatures than those employing acid catalysts [11,12].

The layered double hydroxide (LDH) play a critical role in the process of catalytic reaction by proton elimination. Hydrotalcites (HTs) are well-known layered double hydroxides (LDH) that have the general formula $[M^{2+}_{(1\text{-}x)}\ M^{3+}_{x}(OH)_2][(A^{n-}_{x/n}).mH_2O]$, where M^{2+} and M^{3+} represents metal components with divalent and trivalent cations, respectively. For the divalent metal component, magnesium is the most common, although many other metal species with a cation size like that of Mg are also available, such as Co, Cu, Ni, Ca, Zn, and Mn. The trivalent metal component is generally occupied by Al, although Fe and Cr can be also employed. Some available anions, such as $CO_3{}^{2-}$, NO^{3-}, Cl^-, $SO_4{}^{2-}$, and OH^-, are located between the interlayer along with water molecules to compensate the excessive positive charges. As a result, HTs have a unique layered structure with positively charged brucite like layers and compensating anions [13,14].

The objective of this work is to develop a solid catalyst based on Mg/Al LDH, which is active at low temperatures in the esterification of 3-cyclopentyl propionic acid, representative of naphthenic acids. Different activation treatments, as calcination or calcination followed by rehydration, were applied to the samples. Additionally, it is an aim to carry out the kinetic study of the esterification reaction is carried out in a batch stirred reactor with a solid catalyst in suspension by agitation.

2. Material and methods

2.1. Catalysts preparation

Mg-Al Hydrotalcite catalysts with an Mg/Al ratio equal to 4 were synthesized to ensure that the obtained solid has basic properties [14]. Hydrotalcite (HT) was synthesized by homogeneous precipitation using the urea hydrolysis method [15]. The method consisted of preparing stock solutions of Al (III) and Mg (II) nitrates (0.5 mol/L, each one) by dissolving $Al(NO_3)_3.9H_2O$ (Merck, purity > 98.5%) and Mg $(NO_3)_2.6H_2O$ (Merck, purity > 99.9%) in distilled water, respectively. A solution of urea ($CO(NH_2)_2$, 2 mol/L) (Sigma-Aldrich, purity > 99%) was also prepared beforehand. Then, these solutions were mixed in appropriate proportions, according to the stoichiometry required in the solid, taking into account that in the generated solution, once the stock solutions were mixed, the urea concentration should be 0.5 mol/L, while the total concentration of cations [Mg(II) + Al(III)] should be 5.0×10^{-2} mol/L and the ratio Al/(Al + Mg) should be 0.2. The solutions containing urea-Mg(II)-Al(III) were aged in a thermostatted bath at 90 °C for 24 h in polypropylene (PP) bottles.

Under these conditions, a homogenous alkalinization rate determined by the rate of urea hydrolysis was reached. The gel was precipitated, centrifuged three times, with alternating washes with cold distilled water, and dried in an oven at 70 °C overnight. Different activation treatments were implemented: 1) only drying, without calcination; 2) calcination at 500 °C and 3) calcination at 500 °C and subsequent rehydration. The solid obtained without further treatment is identified as *Htnot calc*. On the other hand, HT calcined at 500 °C during 5 hs it is identified as *HTcalc*. Finally, *HTcalRH* is designated to calcined and rehydrated HT. The rehydration was carried out by dilution of 1 g of *HTcalc* in 100 mL of distilled water in a bath thermostatted at 80 °C, stirred for 4 h and finally centrifuged for 10 min at 160 rpm. Finally, the largest amount of supernatant water was discarded and the solid obtained was dried in an oven at 90 °C until there were no traces of liquid in the sample. Once the catalysts were synthesized, pellets of approximately 1 cm of diameter were formed by means of a hydraulic press, to subsequently sieve in order to obtain a determined particle diameter.

2.2. Catalysts characterization

The HTs were characterized by means of a N_2 adsorption isotherm at 77 K in an ASAP 2010 apparatus from Micrometics and X-ray diffraction (XRD). The surfaces areas were obtained using BET methodology. Previously the sample were pre-treating under vacuum at 400 °C overnight for *HTcalc* and 120 °C for *HT* and *HTcalcRH*. X-ray diffraction measurements were recorded with Siemens D 5000 equipment with Cu Kα radiation.

2.3. Reaction measurements

The esterification reaction was performed in a mechanically stirred stainless-steel batch reactor of 500 mL. The reagents used were 3-cyclopentyl propionic acid (98% Sigma Aldrich) and methanol (99.8% Cicarelli) diluted in n-heptane (95% Cicarelli).

In all the experiments, the pressure was maintained at 3.5 kg/cm^2 to prevent methanol evaporation from the reactive mixture. The reactor was heated externally by an electric resistance to keep the reaction temperature constant. To ensure efficient mixing a stainless propeller type stirrer driven by a 0.25 HP motor was used.

The compounds 3-cyclopentyl propionic acid, methanol and ester were analysed by gas chromatography using an Agilent Technology GC-7890A chromatograph with flame ionization detector and a non-polar Agilent J & W DB-5 column (30 m length, internal diameter of 0.32 mm and film thickness of 0.5 μm). The concentration of the compounds in each sample was determined using n-octane as internal standard.

The conversion is defined as:

$$x(t) = \frac{c(t=0) - c(t=t)}{c(t=0)}100 \tag{1}$$

Where, $c(t)$ is the acid molar concentration as a function of time.

The procedure used in each experiment consisted in the addition to the reactor of 3-cyclopentyl propionic acid (0.005 M) and methanol in n-heptane (0.04 M) solutions and a determined mass of catalyst with an average particle diameter of 100 μm. Then, N_2 was injected with an on-off valve until a constant pressure of 3.5 kg/cm^2 was reached, increasing the temperature of the reactor up to the corresponding reaction temperature. Once the reaction temperature was reached, this time was recorded as the start of the reaction. The following operating conditions were varied to study the effect of mass of catalyst (0.3 g, 0.5 g and 1.5 g), stirred speed (700, 800 and 900 rpm), temperature (70, 80, 90 °C) and particle diameter (44 μm, 66 μm, 100 μm).

3. Calculations

3.1. Kinetics modelling approach

The kinetic model is based on the following assumptions: a) the contribution of non-catalysed reaction rate was negligible compared to the catalysed reaction rate b) the direct reaction follows the pseudo-n order reaction rate law, while the reverse reaction is neglectable.

$$r_A = -\frac{dc_A}{dt} = k.\ c_A^n \tag{2}$$

It is considered that far from the equilibrium, at the beginning of the reaction, the inverse reaction rate is negligible.

Where c_A: acid molar concentration, k: reaction rate constant, n: reaction order.

$$k = k_0.\ e^{-\frac{Ea}{R.T}} \tag{3}$$

Where Ea is the activation energy, k_0: pre-exponential coefficient, R: gas constant and T: temperature (K).

Applying natural logarithm to both members of Eq. 2, n can be calculated from the slope and the reaction rate constant (k) from the intersection of the linear plot of ln (r_A) against ln (c_A). The activation energy (Ea) can be estimated by Eq. 3 from the slope of the linear graph ln k versus 1/T, for which it was necessary to carry out experiments at different temperatures.

It is known that in a heterogeneous reaction the overall rate can be limited by the rate of mass transfer of reactants between the bulk fluid and the catalytic surface and through the pores within the pellet. In order to determine the specific parameters, it was necessary to operate under conditions controlled by the chemical reaction. This means under conditions where mass transfer limitations are negligible.

The batch reactor model with solids in suspension is described for the following expressions:

$$r_A = k_c\, a_p\, w\, (c_A - c_A^{sup}) \tag{4}$$

$$r_A = \eta\, k_m\, w\, c_A^{sup^n} \tag{5}$$

Where k_c is mass transport coefficient; a_p: external surface area of particle per gram of catalyst; η: effectivity factor; k_m: specific reaction rate constant; w: catalyst concentration.

Considering first order reaction, it is possible to obtain:

$$r_A = \left[\frac{1}{k_C.\, a_p.\, w} + \frac{1}{\eta.\, k_m.\, w}\right]^{-1} c_A \tag{6}$$

$$\frac{c_A}{r_A} = \frac{1}{w}.\left[\frac{1}{k_C.\, a_p} + \frac{1}{\eta.\, k_m}\right] \tag{7}$$

$$\frac{c_A}{r_A} = \frac{1}{w}.\,[r_c + r_r] \tag{8}$$

Where $r_c = 1/(k_c\, a_p)$, represents the external diffusional resistance, and $r_r = 1/(\eta\, k_m)$ represents the combined diffusional and reaction resistances in g.min/L. From Eqs. 7 or 8 we can see that a plot of c_A/r_A as a function of the reciprocal of the catalyst concentration (1/w) should be a straight line where the slope is equal to the specific combined resistance ($r_c + r_r$). To define which of these steps is limiting, the particle size (dp) must be varied and the slope of ln ($r_c + r_r$) vs. lndp must be analysed. As the size of the particle increases, the resistances vary as follows [16]:

a) For sufficiently small particle diameters, ln($r_c + r_r$) becomes independent of particle diameter. Under these operating conditions the chemical reaction control is reached and the slope of the linear plot c_A/r_A vs $1/w$ is $1/k_m$.
b) When particle size increases that internal diffusion limits the reaction, and there is a linear relationship between ln($r_c + r_r$) vs lndp. Under these conditions the overall rate of reaction can be increased by decreasing the particle size. However, the overall rate will be unaffected by the mixing conditions in the bulk liquid.
c) For increasing particle sizes, 2 different behaviours take place:

c1) the particles move with the fluid motion, such that there is no shear between the particle and the fluid. Under these conditions, the external transfer is controlling but the increase in the stirring rate does not affect the conversion. The slope of a plot of ln ($r_c + r_r$) vs. ln dp should be 2.

c2) the particles are sheared by the fluid motion, then external resistance is controlling, and the conversion is affected by the stirring speed. The combined resistance ($r_c + r_r$) is a function of particle diameter to an exponent which varies between 1.5 and 1.7.

4. Results and discussion

4.1. Catalysts characterization

Table 1 shows the specific surface area of the different HTs.

It can be seen a significant increase in the specific surface area (BET) after calcination. This behavior is assigned to the formation of craters through the layers, because the carbonates and water molecules existing in the structure type HT are eliminated as CO_2 and H_2O. The specific surface area of the rehydrated HT (*HTcalcRH*) decreases in comparison with the calcined sample, due to the reincorporation of water molecules in its structure, although its value is higher than that of the *HTnot calc*. This behaviour is assigned, to the rupture of the particles and a marked exfoliation of the layers during the rehydration [17].

Table 1
HTs specific surface area.

Catalyst	Surface area (m^2/g)
$HT_{not\ calc}$	11.7
HT_{calc}	294.0
HTcalcRH	128.2

The XRD spectra corresponding to the HTs are presented in Fig. 1. In the diffraction pattern of the *HTnot calc* (Fig. 1, a) it can be observed the presence of narrow diffraction peaks corresponding to the planes (003) and (006) at low values of 2θ (11-24°), compatible with a double-layer hydrotalcite-like structure (JCPDS 22–700) with a high degree of crystallinity.

After calcination at 500 °C, the characteristic peaks of the layered structure disappear. The calcination generates a change in the structure due to the evaporation of water and the decomposition of carbonate anions present in the interlayer. In the diffraction pattern of calcined HT (*HTcalc*) (Fig. 1, c), wide reflections are observed at 2θ = 43° and 2θ = 63° corresponding to a periclase-like structure (JCPDS 87-0653) revealing the formation of mixed oxides of $Mg(Al)O_x$ [13]. The X ray powder diffractogram of *HTcalcRH* (Fig. 1, b) shows peaks like those of *HTnot calc*. This is indicative of the "memory effect" that the HTs present after rehydration, attributed to the partial reconstruction of HT recovering its original stratified structure. Although, lower intensity and slight shift of the diffraction peaks are observed for *HTcalcRH* respect to *HTnot cal*. This shift is due to the fact that more water molecules were inserted between the layers in the rehydration process.

4.2. Reaction

A mixture of 400 mL of 3-cyclopentyl propionic acid (0.005 mol/L) (TAN 0.3 mg KOH/g of solution) and methanol (0.04 mol/L) (relation 1:8 mol/mol) in n-heptane was added to batch stirred reactor. In a first stage, the activity of the HTs was compared using 1.5 g of catalyst with an average particle diameter of 100 µm. Fig. 2 compares the reaction behavior of the HTs. It can be observed that, the conversion reached 90% for *HTnot calc*, while for *HTcalc* the maximum conversion was 60% after 120 min of reaction. The BET surface area values (Table 1) does not explain the highest conversion obtained for the *HTnot calc*. Instead, X ray powered diffractogram of *HTcalc* (Fig. 1, c) showed that the double laminar hydroxide was converted into a mixed $Mg(Al)O_x$ oxide, where the basic Brönsted (OH^-) sites were replaced by basic Lewis sites [11]. Evidently, the reaction behaviour must be related to the presence of Brönsted basic sites (OH^-), which seem to be more active for esterification than the basic Lewis sites characteristic of the *HTcalc*. The lowest catalytic activity was verified for *HTcalRH*, reaching acid conversion of 30% at 120 min of reaction. Although, the basic sites that were lost during calcination are regenerated in the rehydration process, the high-water content used in rehydration was detrimental, as shown in Fig. 2. It is proposed [14] that the excess of water was adsorbed on the active sites OH^-, evidently favouring the hydrolysis of the ester. There would be, therefore, an optimal volume of water rehydration that would provide OH- free sites for the reaction.

According to the activity results obtained, the OH^- sites would be responsible for the H^+ extraction from methanol with the consequent formation of the alkoxide, followed by the C attack of the carbonyl

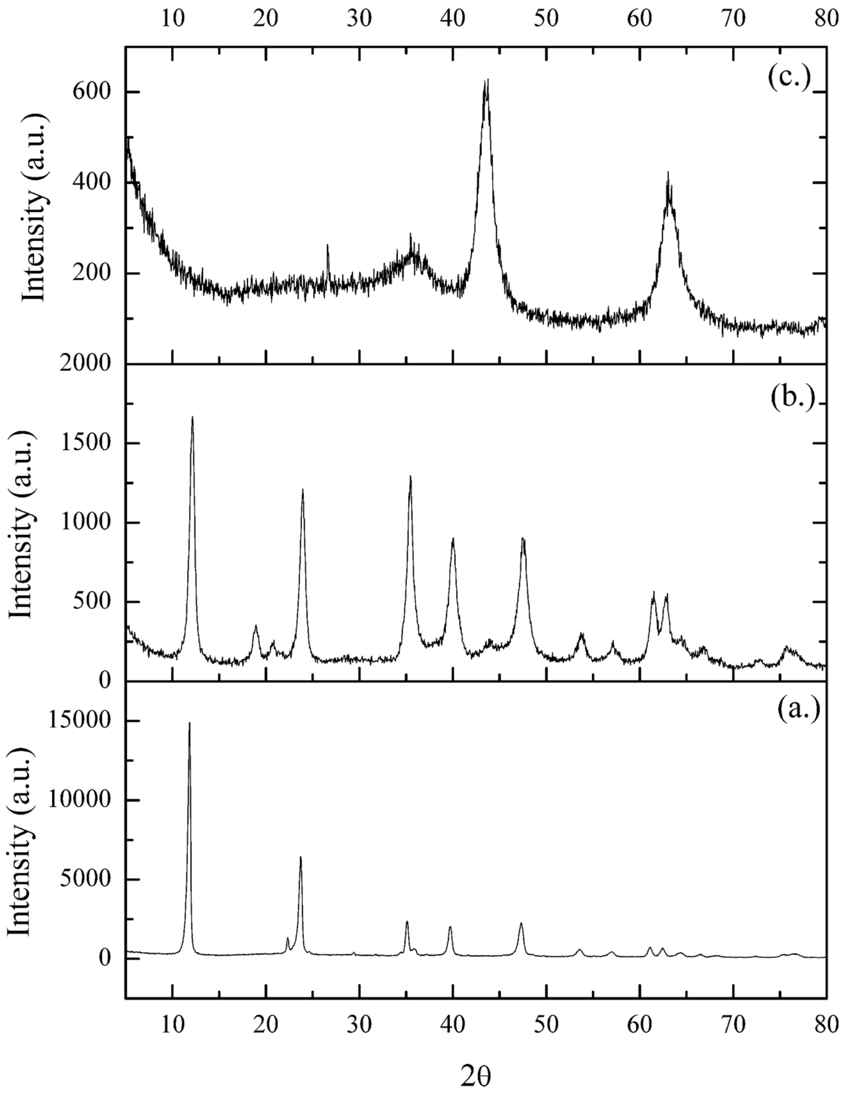

Fig. 1. XRD of: a. *HTnot calc*, b. *HTcalcRH*, c.*HTcalc*.

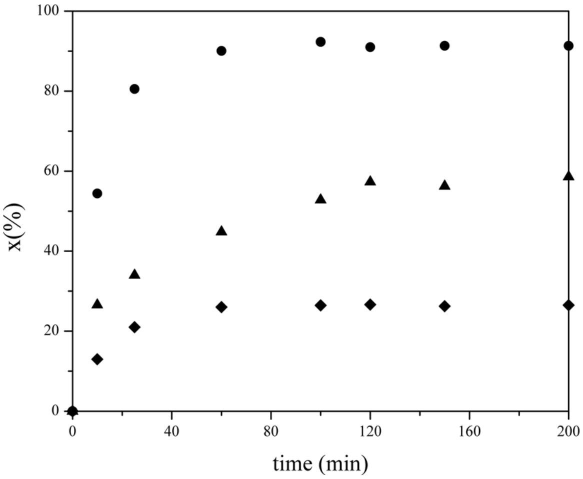

Fig. 2. Acid conversion vs time. *HTnot cal* (●), *HTcalc* (▲), *HTcalcRH* (◆) Mass of catalyst = 1.5 g, dp = 100 μm, T = 80 °C, P = 3.5 kg/cm^2.

group of the acid to give the corresponding ester:

$$CH_3OH + OH^- \leftrightarrow CH_3O^- + H_2O$$

$$RC(OH) = O + CH_3O^- \leftrightarrow RC(OH)OCH_3O^-$$

$$RC(OH)OCH_3O^- \leftrightarrow RC(OCH_3) = O + OH^-$$

As HT without treatment (*HTnot calc*) was identified as the catalyst with the highest activity, the subsequent reaction experiments were carried out using HTnot calc as catalyst.

Fig. 3 shows the effect of the catalyst load on the acid conversion. It can be observed that the increase of the *HTnot calc* mass, increases the acid conversion. After 60 min of reaction, the conversion reached a constant value of 50, 70 and 90%, for 0.3 g, 0.5 g and 1.5 g of catalyst, respectively for 80 °C and 3.5 kg/cm^2 of pressure. Fig. 3 also shows the contribution of non-catalysed reaction. The maximum conversion was 3% without catalyst, which is negligible compared to the conversions achieved with *HTnot calc*.

The following three different stirring speeds of 700, 800 and 900 rpm were tested in the esterification of 3-cyclopentyl propionic acid using 0.5 g of *HTnot calc*. The results are exhibited in Fig. 4.

The increase in stirring speed from 700 to 800 rpm produced an increase in conversion due to the decrease of the mass transfer resistance. When comparing the conversions for 800 and 900 rpm, insignificant difference was obtained, which does not imply that the mass transfer resistance has been eliminated. It is known [16], that if the particle moves with the fluid, the reaction rate is not affected by the stirring (c$_1$- item 3.1)

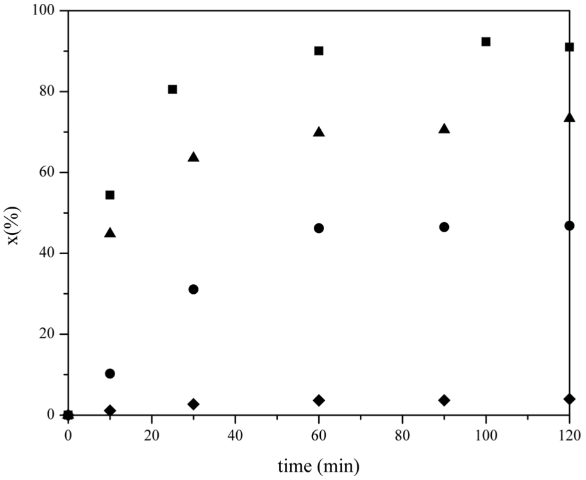

Fig. 3. Effect of *HTnot calc* load. ●0.3 g; ▲0.5 g; ■ 1.5 g, y ◆ without catalyst. dp = 100 μm; T = 80 °C, 800 rpm, P =3.5 kg/cm^2.

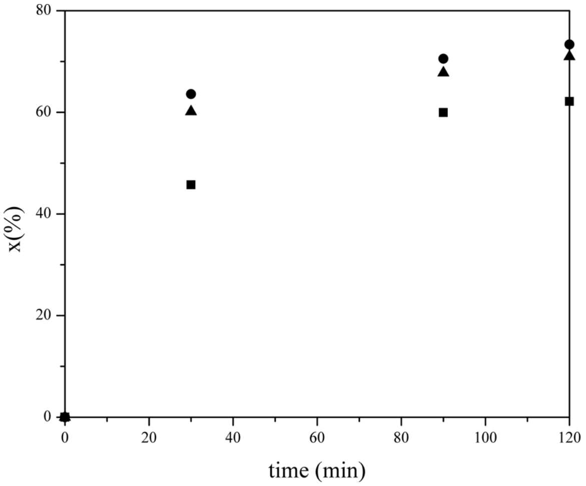

Fig. 4. Effect of the agitation rate. ■700 rpm; ▲800 rpm; ●900 rpm; *HTnot cal,* mass HT = 0.5 g, dp = 100 μm, T = 80 °C; P =3.5 kg/cm^2.

Before identifying the rate controlling step (mass transfer or specific reaction), it is necessary to determine the pseudo reaction order.

A kinetic study for esterification of 3-cyclopentyl propionic acids with methanol in presence of *HTnot calc* was performed. A further analysis of the experimental data in Fig. 4 was completed applying differential method and the results are presented as $ln\ (r_A)$ vs $ln\ (c_A)$. The linear relationship presented a good agreement ($R^2 = 0.98$) for n = 1 and $k = 0.016$, 0.020 and 0.053 1/min for 0.3 g, 0.5 g and 1.5 g of *HTnot calc* catalyst, respectively.

Experiments carried out at different reaction temperatures allowed to determine the activation energy (Ea =25.3 kJ / mol) by Arrhenius equations (Eq. 3). It can be observed in Fig. 5 that the conversion of 3-cyclopentylpropionic acid increased with temperature.

Some authors reported reaction orders equal to 1 or 2 for the acid and Ea like the one found in this work, depending on the catalyst and the solvent employed. Particularly, Yanzhao et al. [19] determined the esterification kinetics of Cyclohexanecarboxylic acid as a model compound. The esterification kinetics followed a second order irreversible reaction with an activation energy of 22.78 kJ/mol over ZnAl-HTlc catalyst in diesel oil solution. Additionally, Li et al. [17] using HT calcined and rehydrated as catalyst in the esterification of naphthenic acid in dewaxed VGO reported a reaction order of 2 and an activation energy of 31.09 kJ / mol. Neuman et al. [18] carried out the kinetic study of the esterification of oleic acid with ethanol using Amberlite 15 as catalyst. They found a reaction order for oleic acid of 2 and Ea =36.62 kJ/ mol. Das et al. [12] employed Zn/Al HTlc as catalyst for esterification of acetic acid with n-butanol, and n-heptane, they reported a first-order reaction to acid.

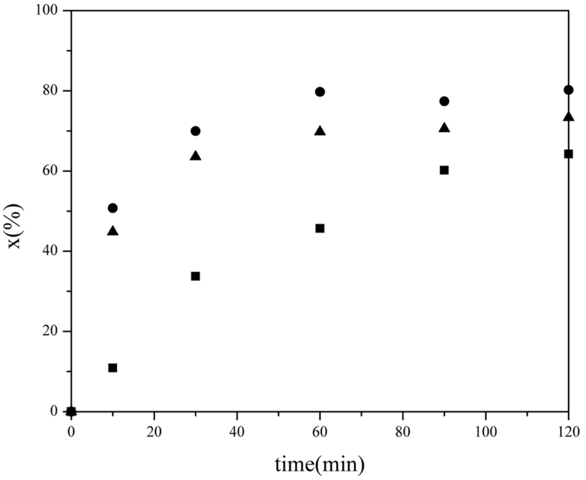

Fig. 5. Effect of reaction temperature, T=70 °C■, 80 °C ▲, 90 °C●. *HTnot cal* Mass HT = 0.5 g, dp = 100 μm, P =3.5 kg/cm^2 and 800 rpm.

Since the reaction order found was 1, the equations developed in item 3.1, valid for agitated reactor model with solid in suspension, was applied to elucidate the controlling step. The results obtained for different loads of HT (Fig. 3) were expressed as c_A/r_A as a function of the reciprocal of the catalyst concentration (1/w). To analyse the effect of particle diameter, kinetic experiments were implemented using three particle diameters (44 μm, 66 μm and 100 μm). The linear relationship of c_A/r_A vs 1/w was verified for the considered particle diameters (Fig. 6). The combined resistance ($r_c + r_r$) was obtained from the slope for each particle diameter of HT.

It can be observed in Fig. 6 that the slopes are the same for the considered particle diameters, indicating that the combined resistance ($r_c + r_r$) is independent of particle diameter. Then it could be concluded that, the control determining step was the reaction, and that both, external and internal mass transfer resistance, were insignificant. Based on these results the reaction coefficient (k_m = 0.02 L/g.min) was determined by least squares method, being R^2 equal to 0.99, confirming the goodness of the fit. Considering that de Ea was 25.3 KJ/mol and applying Arrhenius equations, the preexponential factor can be

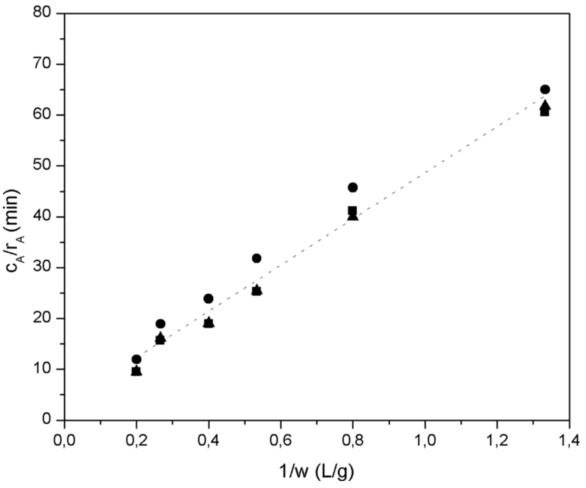

Fig. 6. Analysis of behaviour of batch reactor with solid in suspension for different mass and particle diameter for *HTnot cal*: 66 μm ■, 44 μm▲ and 100 μm●, T = 80 °C, P =3.5 kg/cm^2 and 800 rpm.

calculated being its value equal to 110.9 L/g·min

5. Conclusions

This study reports the process of heterogeneous esterification of 3-cyclopentylpropionic acid representative of the naphthenic acids with methanol and Mg-Al hydrotalcite as catalyst. Mg-Al hydrotalcite with Mg/Al molar ratio of 4 was synthetized by urea method. The samples received different activation treatments, as calcination or calcination followed by rehydration and they were tested in esterification reaction under mild conditions (80 °C and 3.5 kg / cm^2).

The hydrotalcite of MgAl (Mg/Al = 4) without any treatment presents higher conversion compared with the calcined HT at 500 °C. This behaviour is attributed to the greater contribution of OH^- species in HT without calcining. This confirms the role of Brönsted basic sites (OH^-) as active centres in the esterification instead of Lewis basic sites. The Mg/Al hydrotalcite calcined and rehydrated showed poorer catalytic performance due to the excess of water used, which is responsible of the catalyst deactivation by blocking the basic sites OH^-. There would be an optimal volume of water rehydration that would provide OH^- free sites for the reaction, which will be the subject of future investigations

A kinetic study of esterification reaction catalysed by Mg/Al hidrotalcite without any treatment was performed. The kinetic parameters were determined by applying the differential method and the stirred batch reactor model with solid in suspension. The kinetics of esterification was described by the irreversible pseudo first-order reaction rate law. The reaction order was 1 for acid and the activation energy was 25.3 kJ / mol, while the preexponential factor of the specific reaction coefficient k_m was equal to 110.9 L/g.min. The analysis of the stirred batch reactor behavior for different mass and particle diameters of catalyst allowed to determine the absence of external and internal diffusional effects.

In conclusion, the esterification in the presence of Mg/Al hydrotalcite was an efficient method to remove naphthenic acids under mild conditions. equivalent to homogeneous conditions.

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