

## ACID ACTIVATION OF NATURAL ALGERIAN CLAY AND ITS USE AS A CATALYST OF ACETIC ACID ESTERIFICATION

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*Herein, preparation, characterization, and catalytic testing of a catalyst based on Algerian clay are presented. The Algerian bentonite is activated in a separated manner following three different acids ( $H_2SO_4$ ,  $HNO_3$  and  $HClO_4$ ). The effects of the nature and the concentration of the activation acid, and the activation temperature were evaluated. The obtained catalyst samples were characterized by X-ray diffraction, infrared spectroscopy, and thermogravimetric analysis. All the prepared catalysts have revealed a high catalytic activity for the esterification reaction of acetic acid along with five different alcohols (methanol, ethanol, propanol-1, butanol-1, and tert-butanol). The catalyst prepared by activation with 3 M  $H_2SO_4$  at 70 °C showed the highest catalytic activity with about 84, 25%.*

**Keywords:** Clay, Acid activation, Esterification, catalyst

### 1. Introduction

The bentonite clay of Maghnia region (Algeria) was used as raw material to be acid activated. Its structural features make it an important material for catalysis and adsorption. In nature, the Maghnia clay could be found as a clayey rock, belonging to phyllo-silicates formed by lamellar leaflet stacks organized in two-dimensional planar layers of tetrahedral unit structures, and octahedral structures connected by their tops [1]. The chemical composition of this clay rock is well known, unlike to its hydration level, which meanwhile varies following the mineralogical source and the climate [2]. Importantly, the activation of the bentonite is generally undertaken in a chemical or thermal manner [3, 4, 5].

The use of the mineral acid along with heating for the chemical activation is a complex process, involving series of chemical reactions which provide the

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formation of protonated clay, developing thus acidic sites of Bronsted and Lewis types with a high specific surface. The mechanisms of clay activation by using sulphuric acid have been well documented [6]. The cations, such as  $\text{Al}^{3+}$ ,  $\text{Mg}^{2+}$  and  $\text{Fe}^{3+}$  are extracted from the octahedron layer, and are substituted by protons acting in solution, as salts of mineral acid [7]. The montmorillonite activated by an acid was successfully applied as a cracking catalyst [8]. Also, the utilization of chemically modified clay in the heterogeneous catalysis of oleic acid esterification in presence of methanol has shown a selectivity of about 100% towards the formation of methyl oleate [9].

Using of the activated clay with whitening colza oil acid showed an elevation in the purification capacity of this oil [10]. Thus, the present study was aimed to compare the preparation process, the physico-chemical characterization and the catalytic activity of Algerian clay catalysts activated by three different acids ( $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$  and  $\text{HClO}_4$ ). Here, investigations of the effects of concentration of activation acid, the activation temperature and the nature of the activation solution were basically used in this study. Noteworthy, the catalytic activity was evidenced through the esterification of acetic acid with four different alcohols (1-butanol, ethanol, methanol, 1-propanol and tert-butanol). Three reacting parameters were studied: the chemical nature of catalyst, class of alcohol and catalyst involved mass.

## 2. Preparation of activated clay

The material, by which we performed our study, is a natural clay of Maghnia region (Algeria) with particle size  $\leq 75\mu\text{m}$  and composed of 60.4%  $\text{SiO}_2$ , 17.33%  $\text{Al}_2\text{O}_3$ , 0.81%  $\text{K}_2\text{O}$ , 3.56%  $\text{MgO}$ , 1.19%  $\text{Fe}_2\text{O}_3$ , 1.60%  $\text{CaO}$  and 0.33%  $\text{Na}_2\text{O}$ . In brief, 10 g of this clay was suspended in distilled water, followed by constant stirring for few minutes. Then, the clay becomes activated in a separated manner by using of three activation solutions and three different acids, which are sulphuric acid (Biochem Chemo-Pharmia, 97 %), nitric acid (AnalaR NORMAPUR, 65%), and perchloric acid (CPR RECTAPUR, 70%). The modification of the described bentonite was performed under the effect of four parameters: the nature of the activation acid, temperature of 25 °C and 70 °C, and concentration of the acidic solutions of 1 M, 2 M and 3 M, respectively. The clay was kept in contact with reaction medium during a well-determined time for being afterwards, separated by centrifugation. The activated clays were washed several times by distilled water to remove the excess acid. The samples were then placed in oven at 105 °C for 6 hours, and after drying step the activated clays were crushed and sieved, noticing that only the fractions having diameter lower than 75  $\mu\text{m}$  are kept, suitable to carry out heterogeneous catalysis.

### 3. Structural characterization

The absorption infrared spectra of the natural and activated clays were recorded by using Perkin Elmer (Spectrum One FTIR) spectrometer. The X-ray spectra of the natural and activated clays were obtained using a diffractometer (Bruker, model D8), with monochromatic radiation ( $K_{\alpha}$ ) of copper ( $\lambda=1.54056$  Å). Also, the thermal stabilities of the natural and activated clays were evaluated by thermogravimetric analysis (TGA), using a 2050 TGA apparatus of TA Instruments.

### 4. Esterification Reaction

The catalytic activity of the prepared catalysts was tested through the esterification reaction of acetic acid along with five different alcohols: methanol, ethanol, 1-propanol, 1-butanol, and tert-butanol. Every test of esterification reaction was elaborated with a quantity of 300 mg of synthesized catalysts. In a 250 mL spherical glass reactor, topped by a coolant and Dean-Stark (water scavenger), were introduced 15 mL of acetic acid (GPR RECTAPUR, 99.8%), 20 mL of alcohol (Merck, 98%) and 0.3 g of catalyst. In addition, the mixture was stirred, and then was heated to a temperature of 98 °C, which is kept constant until the reaction is complete. In the same experimental condition, several esterifications are launched separately in order to preserve a constant liquid/solid ratio. The progress of the reaction is controlled by the determination of the remaining acetic acid. A reaction sample of 3 mL is removed from reactor at well-determined time intervals, it was centrifuged and titrated thrice with 0.1 N NaOH solution. The conversion of acetic acid was calculated by applying the equation :

$$\text{Conversion(}\%) = \frac{A_0 - A_1}{A_0} \quad (1)$$

Here  $A_0$  and  $A_1$  are the initial number of moles and number of moles at reaction time ( $t$ ) of acetic acid. After cooling process, the solid catalyst becomes separated from the reaction products by centrifugation and it was washed with water and dried.

## 5. Results and discussion

### 5.1. Parameters of activation

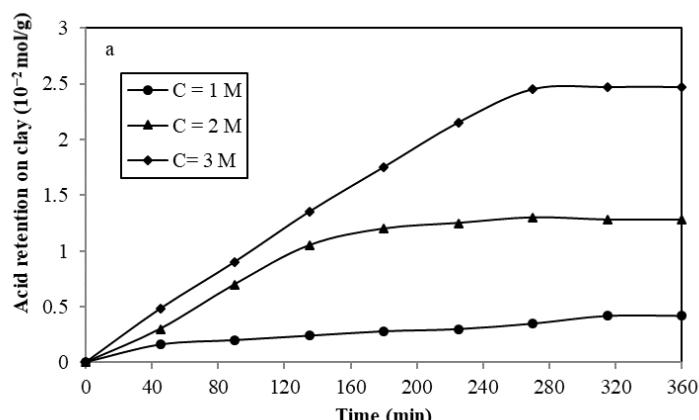
#### 5.1.1. Effect of the concentration of acid on activation of natural clay

*Table 1*  
The acronyms of the activated clays: X is the concentration of activation acid and T is the activation temperature.

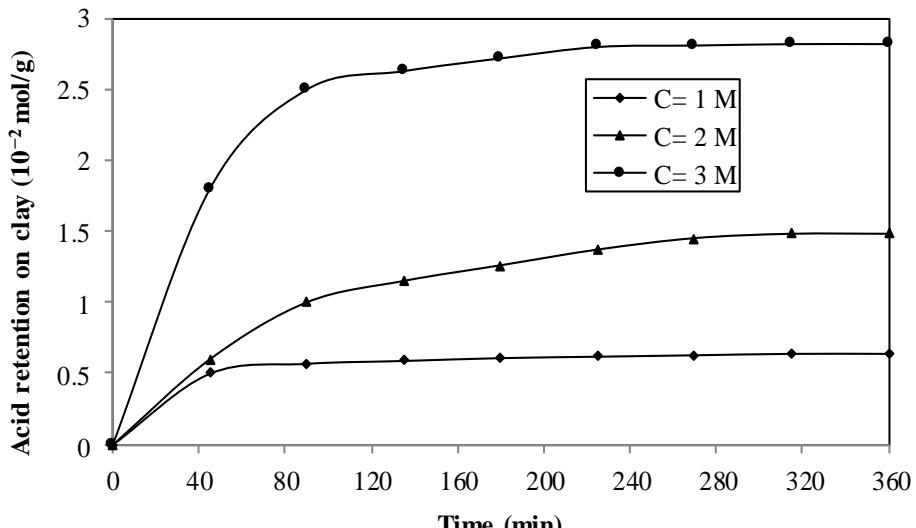
Activation acids	$\text{H}_2\text{SO}_4$	$\text{HNO}_3$	$\text{HClO}_4$
Catalysts	Mont-HSXMT	Mont-HNXMT	Mont-HCLOXMT

The preparation of catalysts from Algerian natural clay was carried out by activation with three acids (sulphuric acid, nitric acid and perchloric acid) in a separated manner, taking into account the required concentrations of their solutions (1 M, 2 M, 3 M). The evolution of clay activation was monitored through samplings in a well-determined period for an activation time of 6 hours. The results illustrated in Figs. 1a, 1b and 1c show a progressive retention of acids on clay. The maximum retention increases with the increase in the concentration of the attack acid solution. Sulphuric acid exhibits a maximum retention on the clay surface of 0.0248 mol/g for an initial concentration of the attack solution (3 M), the nitric acid solution of 3 M shows a maximum retention of 0.0282 mol/g and conversely, the activation by an initial concentration of 3 M of perchloric acid has shown a maximal retention of 0.0175 mol/g. The clay minerals are characterized by the non-neutral electrical surface, and hence there are two charge types [12]. One is the net negative electric charge due to layers arising from the isomorphic substitution of  $\text{Fe}^{2+}$  with  $\text{Al}^{3+}$  in the octahedral structure and  $\text{Al}^{3+}$  with  $\text{Si}^{4+}$  in the tetrahedral sites. The second is a variable surface charge accordingly to pH of medium, related to chemical reactions produced at the mineral surface or following the adsorption of positive or negative sign entities.

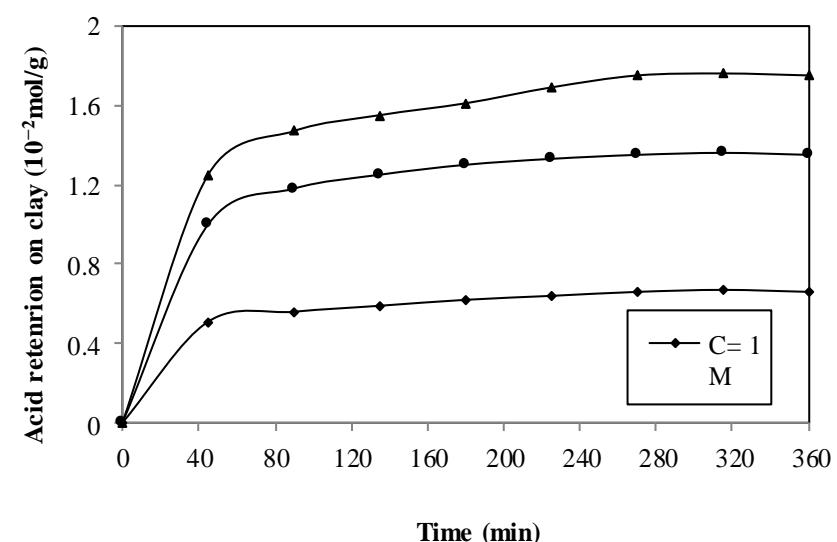
The charge of clay mineral structure, already highly variable, was further modified by its decomposition upon acid or alkaline treatment. At high pH, the clay exhibits an anionic exchanging capacity, where the protons of  $\text{H}^+$  are better bound with clay than  $\text{OH}^-$ , meanwhile a positive charge could be developed. At high level of acidity, the cationic exchanging capacity (CEC) of clay leads to the higher anionic binding of  $\text{OH}^-$  than of proton  $\text{H}^+$ , therefore the negative charge could be developed [13].



(a)



(b)



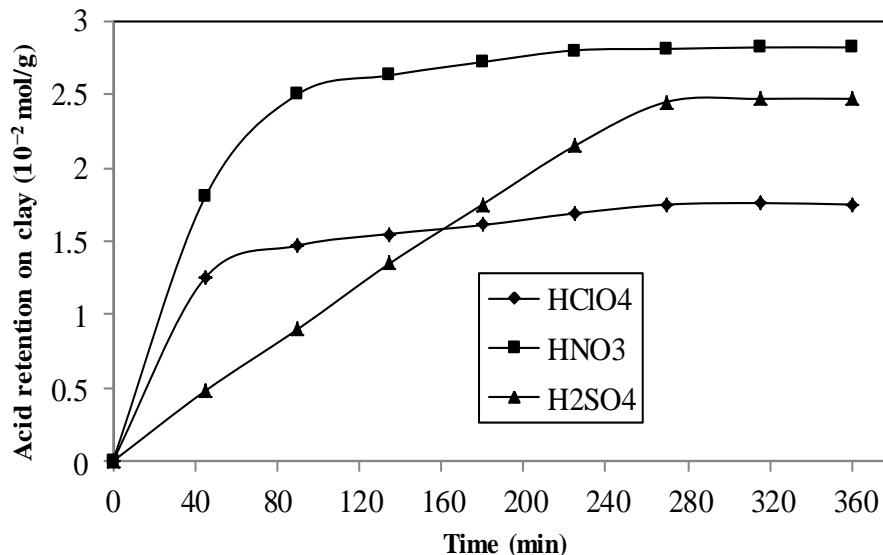
(c)

Fig.1. The effect of acid concentration on the acid retention on clay at 25 °C activated with:  
 (a)  $\text{H}_2\text{SO}_4$ ; (b)  $\text{HNO}_3$ ; (c)  $\text{HClO}_4$ .

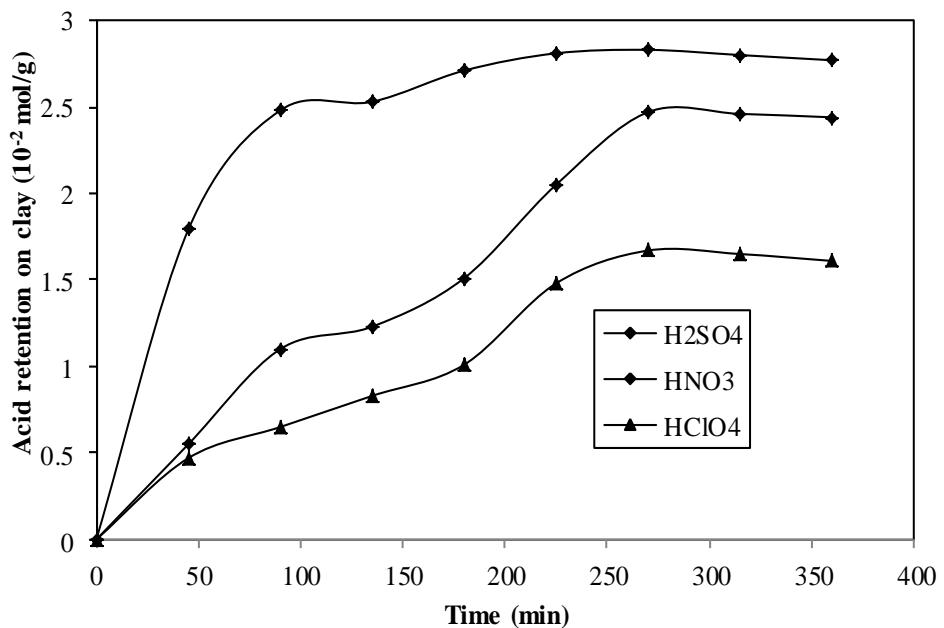
### 5.1.2. Effect of the activation temperature

To explain better the temperature effect, three activation assays using Algerian clay were performed at temperatures of 25 °C (Fig. 2a) and 70 °C

(Fig.2b), for which the same concentration 3 M was considered for all the attack acids and the activation time of 6 hours.



(a)



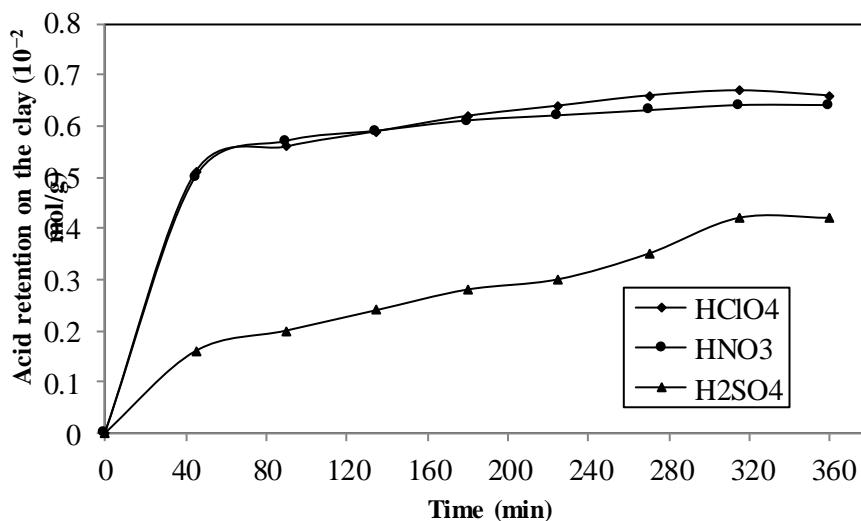
(b)

Fig.2. The effect of the temperature on the acid retention on clay at:  
 (a) 25 °C and (b) 70 °C.

The experimental values show that the retention of the activation acid was done by the same manner for the two temperatures, along with slight difference, promoting the activation at 25 °C. Acid treatment of clay minerals with strong inorganic acids resulted in solid products containing unaltered layers amorphous three-dimensional cross-linked silica, depending on the extent of acid activation and on the heating method. At a temperature of 70 °C, the cation exchange capacity decreased [14].

### 5.1.3. Effect of the nature of the activation solution on the preparation of catalysts

Figs. 3a, 3b and 3c show the results of retention of the attack solutions of each concentration separately. For the initial concentration 1 M of all activation solutions, a concurrence between the nitric acid and the perchloric acid was noticed, since the values of the sulphuric acid solution are very weak. Moreover, the initial concentration 3 M of the attack solutions show that the best activation is obtained by using nitric acid solution for a maximum retention value of 0.0282 mol.g<sup>-1</sup>. The attack mechanism [8] of various acids is similar, and also, it can be noted that HNO<sub>3</sub> and HClO<sub>4</sub> are slightly more effective as an activating agent at low concentration than H<sub>2</sub>SO<sub>4</sub>. Consequently, the location of H<sup>+</sup> on the clay surface leads to the development of Brønsted acid sites, since the other part presented by the anions of the three acids leads to the generation of Lewis acid sites through the bounds established with metals, showing the octahedral layer (Al<sup>3+</sup>, Fe<sup>3+</sup> and Mg<sup>2+</sup>) [7, 15].



(a)

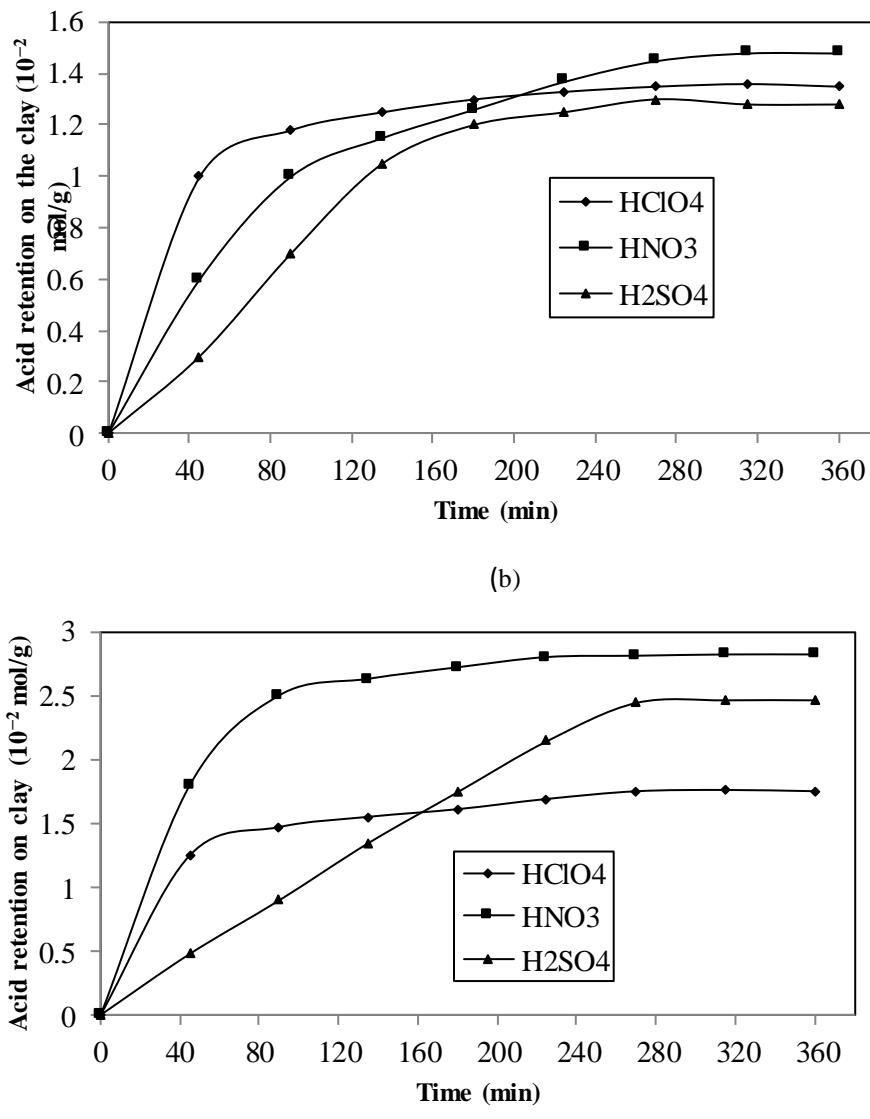


Fig.3. The effect of the nature of the activation acids on acid retention on clay at 25 °C and different initial concentration of the acids: (a) 1 M; (b) 2 M; (c) 3 M.

## 5.2. Characterization by X-ray diffraction

The diffractogram of natural clay shows a basal (001) reflection, specific to montmorillonite at  $2\theta=6.8^\circ$  [16], confirming that Algerian clay is mostly composed of montmorillonite along with other impurities, such as quartz with a specific peak of  $2\theta=18.8^\circ$ . Furthermore, the most important modification on catalyst spectrums is that observed on the ray d(001), and attributed to the

motmorillonite. The intensity of the peak at  $2\theta=6.8^\circ$  decreased for the mont-HClO<sub>3</sub>M70 spectrum and disappeared on that of mont-HS3M70. The existence of this peak on the natural clay spectrum is an evidence of the laminar and crystalline structures of this clay. Also, the attenuation or disappearance of d(001) and the diminishing of the peak  $2\theta=18.8^\circ$  explain that the clay crystallinity was affected by the sulphuric acid activation, and thus the breakdown of the structure appears as a semi-crystalline form for the activated clay. The XRD pattern of the mont-HN3M70 is almost similar to that of the natural clay, showing that the clay structure is not affected by the nitric acid activation.

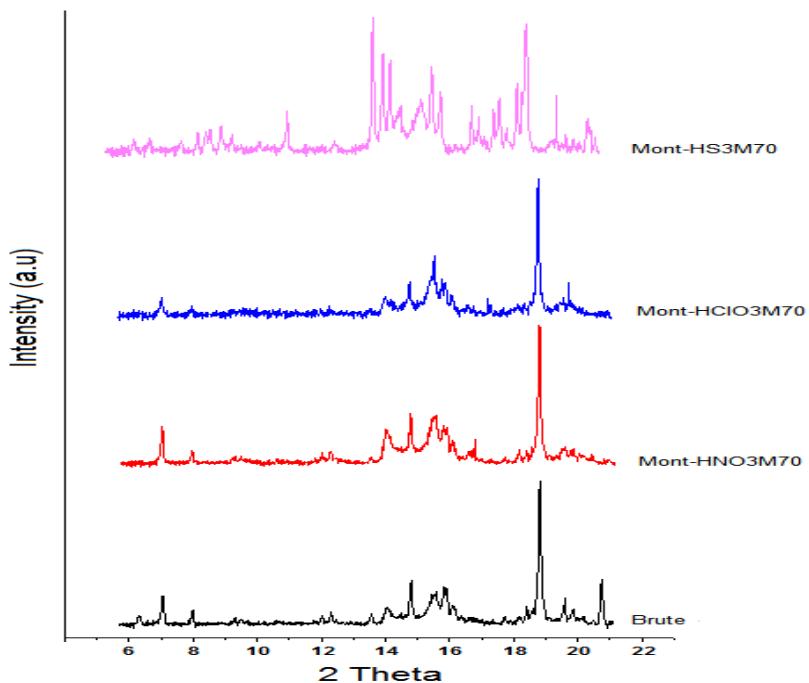


Fig.4. The XRD patterns of natural bentonite and acid activated bentonite.

### 5.3 Infrared spectroscopy characterization of activated clay

The bands presented on the natural clay spectrum (Fig.5) are specific to montmorillonite clay.

The band  $3600\text{ cm}^{-1}$  is not quite larger for investigated bentonite than that observed in the previous works [4,5], and this studied clay was found to be less hydrated.

The infrared spectroscopy applied on the mineral clays allowed us to differentiate between the molecules of water hydration and the hydroxyl groups of the constitution, as well as to monitor the structural changes during the acid activation [17].

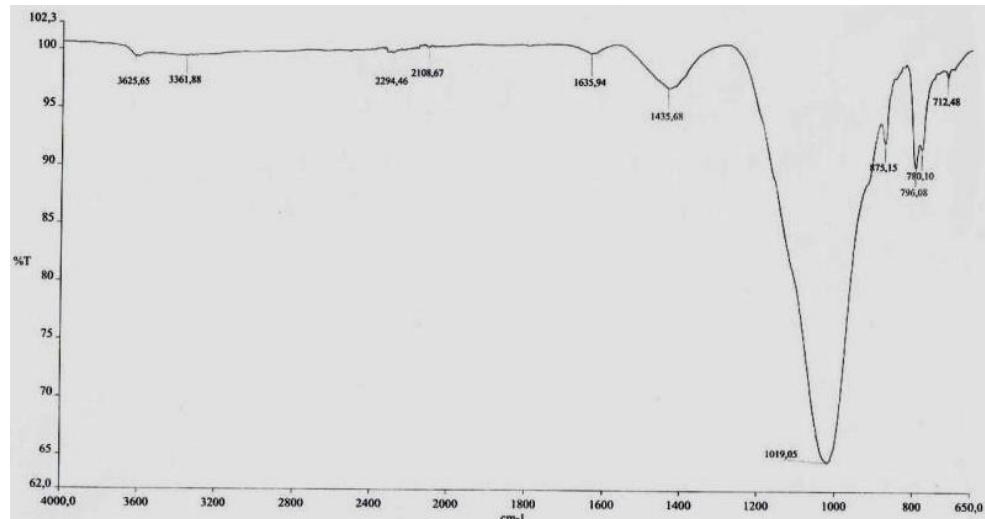
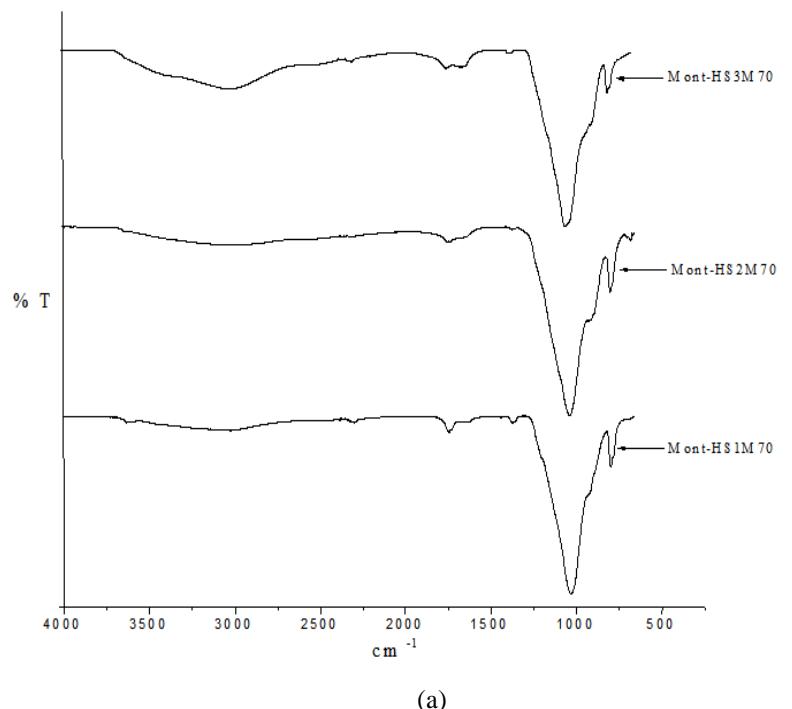


Fig.5. Infrared spectrum of the natural clay

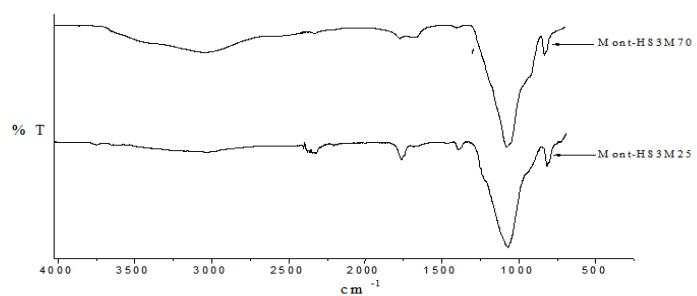
The bands at  $875\text{ cm}^{-1}$  on the natural clay spectrum are assigned to the vibrations AlAlOH, AlMgOH and AlFeOH [11]. These bands disappeared on all the spectrum of the activated clays, indicating that the octahedral layer of natural clay has been attacked [18].

The valence band at  $1635\text{ cm}^{-1}$  is that of OH groups of physisorbed water on the natural clay spectrum. This band exhibits a highly pronounced regression on the spectrum of the activated clay, when the activation temperature equals  $70\text{ }^{\circ}\text{C}$  and the concentration of the activation acid is about 3 M. This is likely due to the dissolution of the octahedral layer that has lost the bound physisorbed water at this layer. The spectrum of the natural bentonite has also shown bands between  $1019\text{ cm}^{-1}$  and  $797\text{ cm}^{-1}$ , representing vibrations in Si–O valence, whilst the band toward  $1435\text{ cm}^{-1}$  corresponds to the calcite. In addition, the increase and the movement of the band at  $1019.05\text{ cm}^{-1}$ , characterizing the vibrations in Si–O valence are due to octahedral and tetrahedral layer attacks, leading to the progressive release of the silica and aluminum ions ( $\text{Al}^{3+}$ ), and hence this phenomenon regresses on the spectrum of the prepared catalysts at  $25\text{ }^{\circ}\text{C}$ . The IR spectrum belonging to the catalysts obtained through Mont-HS3M70 sulphuric acid activation (Fig.6), and Mont-HClO<sub>3</sub>M70 perchloric acid activation (Fig. 8) show that the valence bands of AlAlOH at  $3625\text{ cm}^{-1}$  were moved to the band of  $3009\text{ cm}^{-1}$  and  $3025\text{ cm}^{-1}$ , respectively, on the spectrum of Mont-HS3M70 and Mont-HClO<sub>3</sub>M70. This is probably due to the interactions between the activation acids and ALALOH [19]. Of note, the action of the acid concentration, activated

at high temperature on the clay structure was noticed as a very interesting parameter.



(a)



(b)

Fig.6. Infrared spectrum of the prepared catalysts by the sulphuric acid activation.

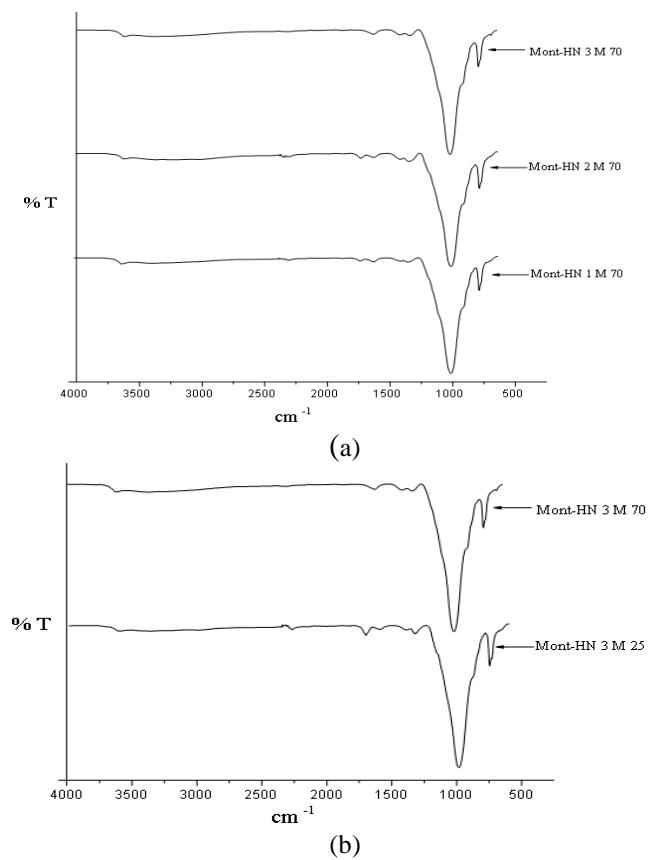
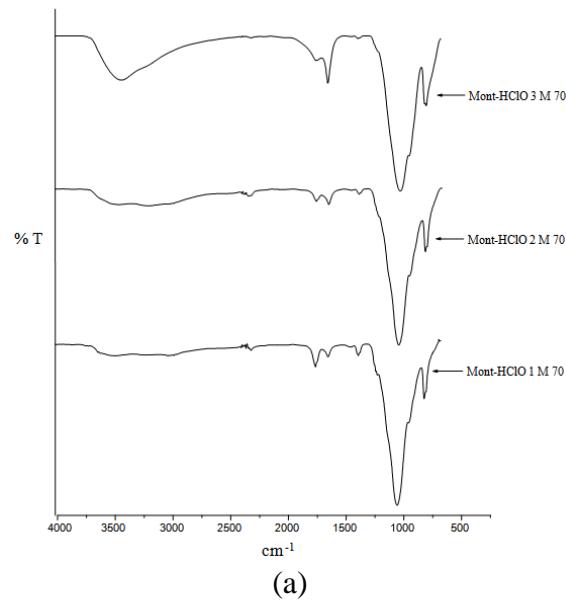
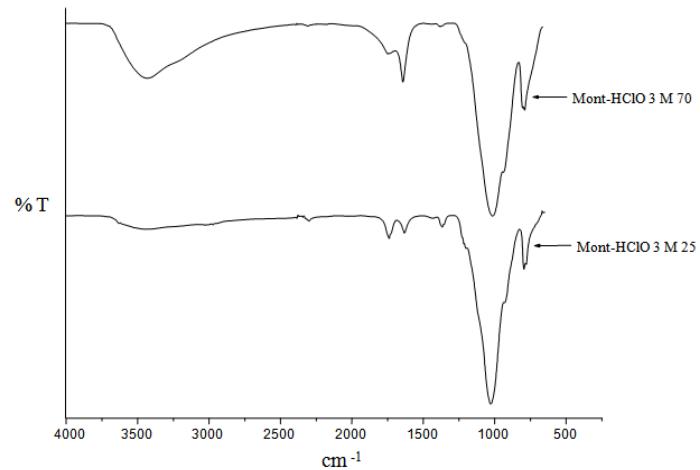


Fig.7. Infrared spectrum of the prepared catalysts by the nitric acid activation.



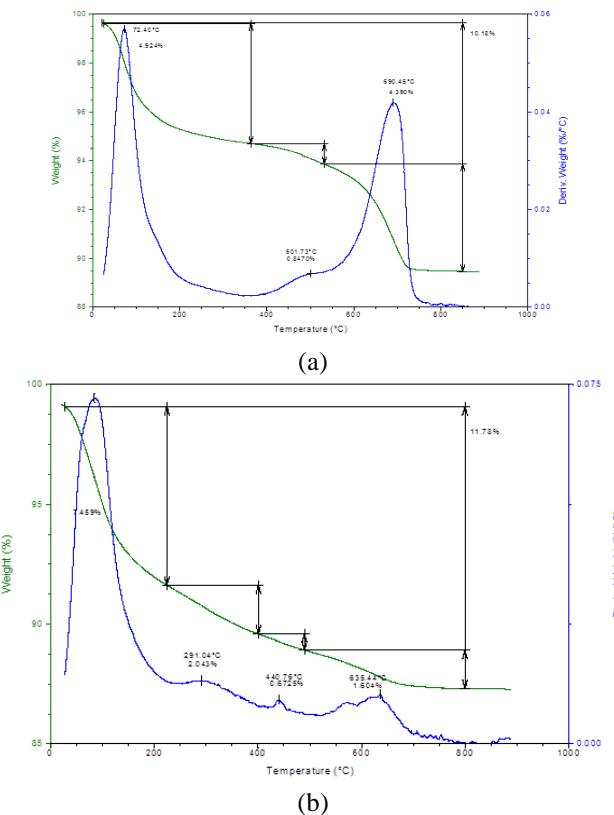


(b)

Fig.8. Infrared spectrum of the prepared catalysts by the perchloric acid activation.

#### 5.4. Thermal analysis

The Figs. 9 show the TGA thermograms for the natural and three activated clays.



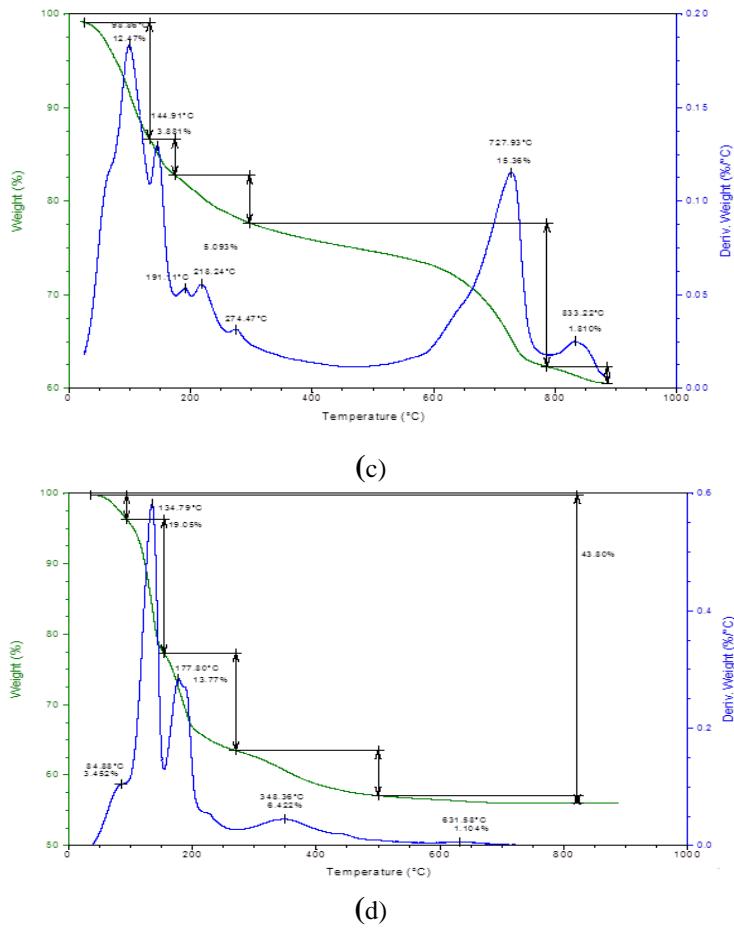


Fig.9.TGA thermograms: a) natural clay, b) Mont-HN3M70, c) Mont-HS3M70 and d) Mont-HClO3M70.

As seen in Fig. 9a, a weight loss of 4.9 resulting from the humidity water loss was noticed at 72 °C, whereas the second weight loss of 5.2% due to the clay dihydroxylation was observed for a temperature of 690 °C [20]. The total loss of natural clay mass in the explored interval is estimated at 10.2%. The thermogram of natural clay provides a reference for the thermal stability study of the activated clay. Additionally, the thermogravimetric analysis curve of Mont-HN3M70 catalysts is indicated in Fig. 9b, showing unlike behavior to that observed in the natural clay. The first mass loss relative to humidity water is about 7.5% at a temperature of 84 °C, meanwhile the second weight loss of 2% was found at a temperature of 291 °C, and it has been attributed to the depart of the absorbed and the inter foliar waters. Also, a weight loss of 2.3% resulting from the breakdown of  $\text{NO}_3^-$  was noticed at 400 °C. The peak at 640 °C corresponds to dehydroxylation of clay materials. In addition, the total loss of Mont-HN3M70 catalyst was found to be about 11.8% [21]. The change in the rate of free, bound

and crystallized waters are affected by chemistry of the hydration solution, and thus the excellent water absorption capacity can be observed, in the case when the monovalent cations ( $H^+$  activation issue) could be found in interlayer space, and this is reflected to the high repulsion force undertaken between leaves [22,23]. In contrast, the repulsion energy becomes weak when the divalent cations are found in the inter-foliar space, and subsequently the absorption capacity becomes also weak [24]. The thermogravimetric analysis curve of Mont-HS3M70 catalysts is presented in Fig.9c. Two mass losses were noticed in this study; the first one is considered as important loss of 21.5% weight appeared in the domain from 90 °C to 220 °C, and this corresponds to the loss in absorbed and interlayer waters. The second one is a weight loss in a temperature ranging from 720 °C to 840 °C, equals to 17.2% and corresponds depart of the crystalline water and the structural reorganization of the material. The total mass loss of Mont-HS3M70 catalyst is very important, and equals to 38.6%, confirming therefore the discussion given on the role of monovalent cation ( $H^+$ ) for Mont-HN3M70, obtained by activation of the clay with sulphuric acid. Here, every mol of sulphuric acid can free two moles of  $H^+$  in the inter-foliar space, proving therefore the increase of the lost weight. The presence of these cations leads to increase the thermal stability of Mont-HS3M70, noting also that maximum dehydration was observed at 833.2 °C. The thermogram of Mont-HClO<sub>3</sub>M70 sample shows a very important weight loss of about 36.4% in a temperature varying from 80 °C to 200 °C, corresponding to the depart of important quantities of free and inter-foliar waters. A peak of 348 °C indicates a weight loss at about 6.42% in association to the breakdown of ClO<sub>4</sub><sup>-</sup> group.

#### 5.4. Catalytic activity

The esterification reaction is a very slow reaction, based on the electrophilic character of carboxyl group, and therefore it requires activation by a catalyst to achieve higher conversion [25-30]. The monitoring of the acetic acid conversion in presence of various alcohols and catalysts is illustrated in Figs. 10, 11 and 12. The allure of different curves indicate that the synthesized catalysts have an interesting catalytic activity.

The catalytic performance of the acid-activated clay is evaluated via the conversion of acetic acid, separately with four alcohols (ethanol, methanol, 1-propanol and 1-butanol) at an esterification temperature of 98 °C and a ratio acetic acid/alcohol equals 1. The comparison of obtained results show that the most performant catalysts are those synthesized by acid activation at a temperature of 70 °C.

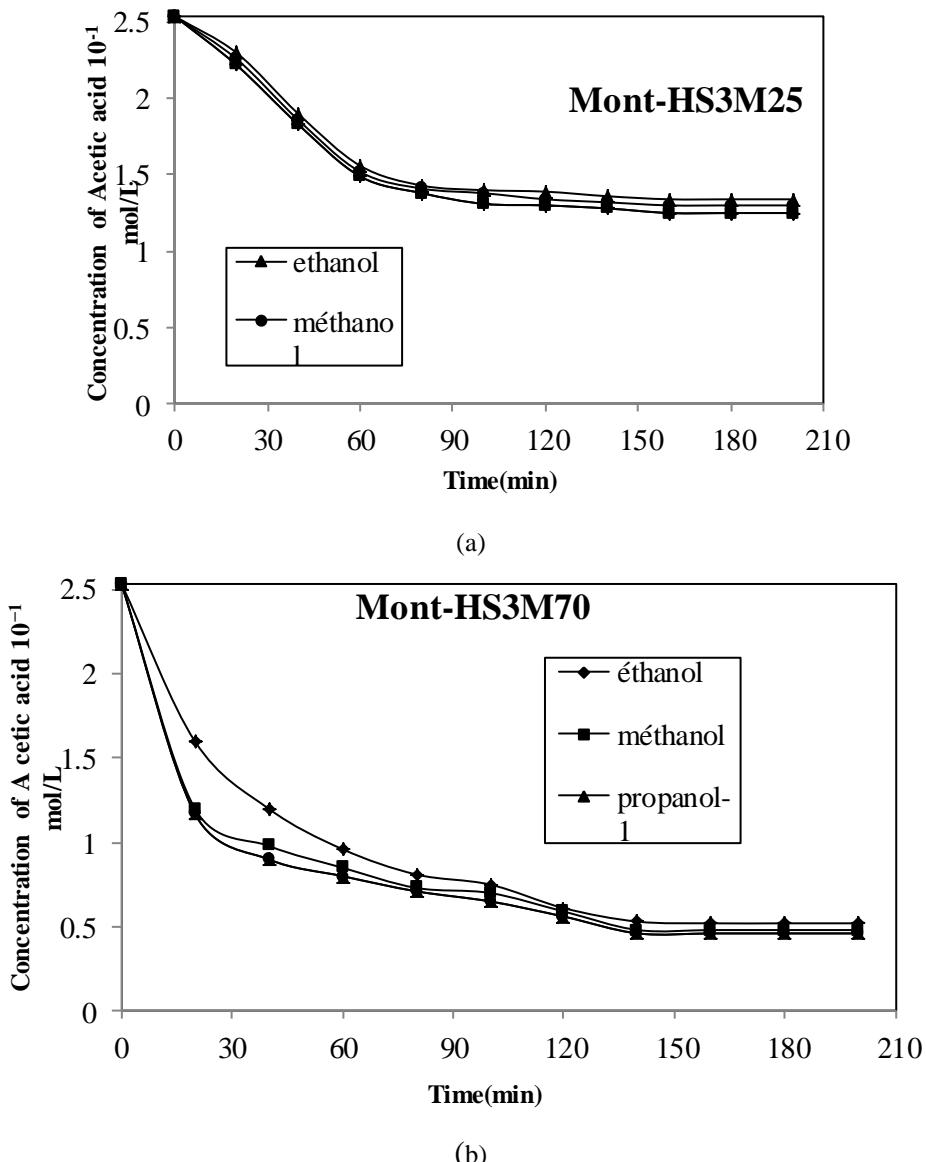


Fig.10. Effect of the nature of catalyst on the acetic acid esterification with four different alcohols for; a) catalyst: Mont-HS3M25; b) catalyst: Mont-HS3M70

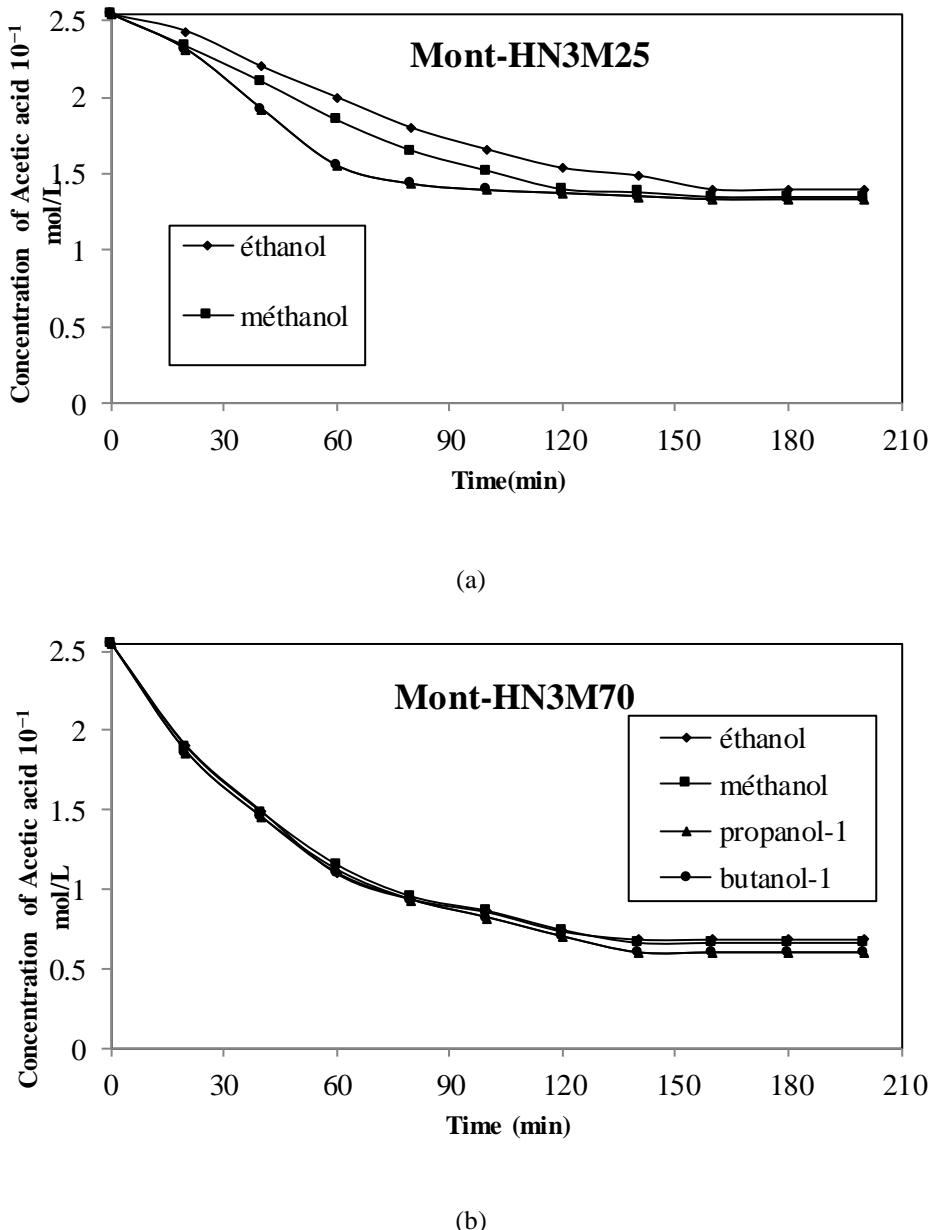


Fig.11. Effect of the nature of catalyst on the acetic acid esterification with four different alcohols  
for: a) catalyst: Mont-HN3M25; b) catalyst: Mont-HN3M70

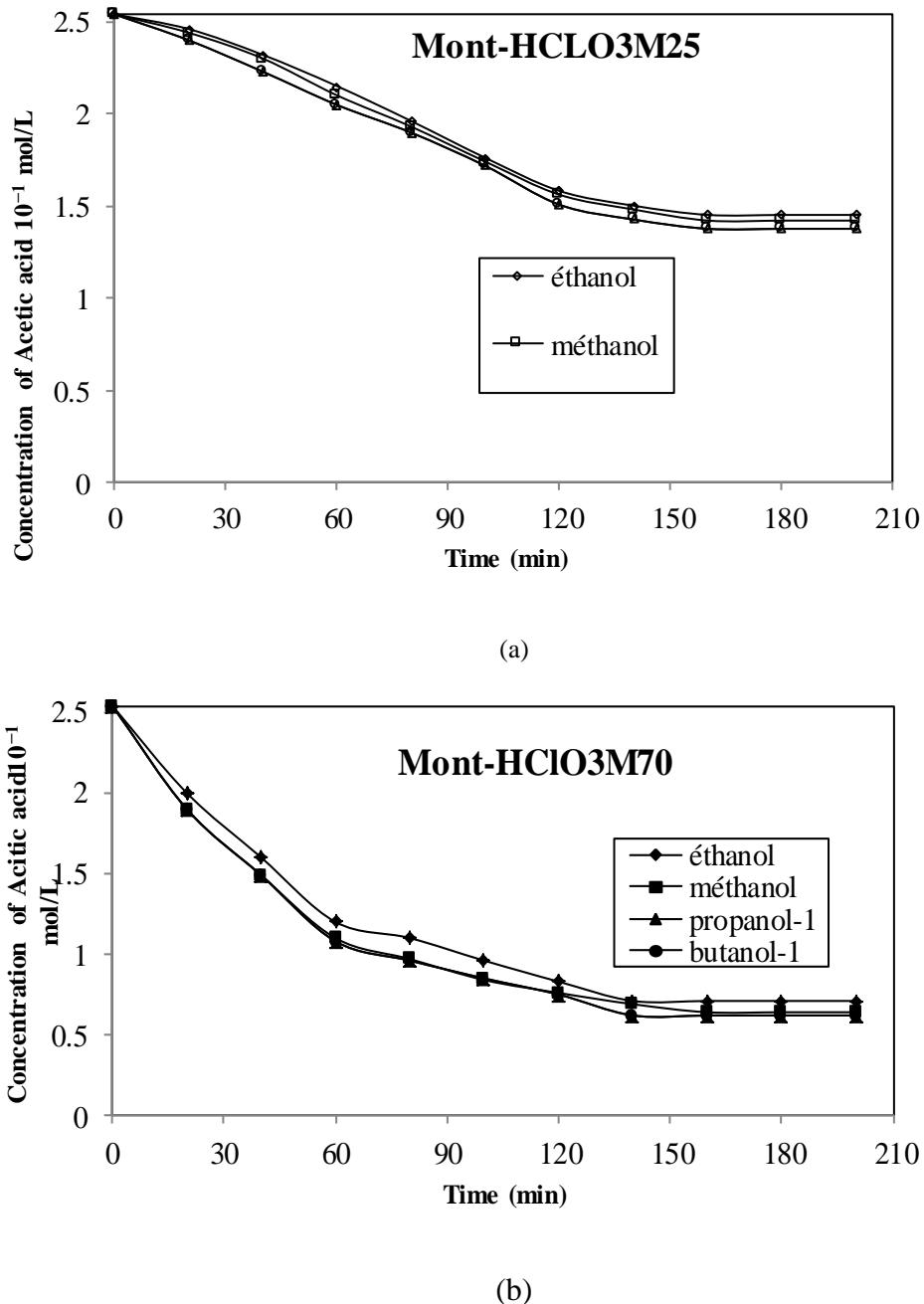


Fig.12. Effect of the nature of catalyst on the acetic acid esterification with four different alcohols;  
 a) catalyst: Mont-HClO3M25, b) catalyst: Mont-HClO3M70

Indeed, the increased temperature during the activation leads to stable binding of hydrogen proton  $H^+$ [31], resulting from the simultaneous attack of

octahedral and tetrahedral layers promoted in the predict conditions [32]. Also, a such thing provides liberation of  $\text{Al}^{3+}$  and  $\text{Si}^{4+}$  along with cationic exchange between the clay and the attack acid, resulting in an important binding of  $\text{H}^+$  proton inside the clay. Interestingly, the reaction time is the same in all the occurred reactions, and it is about 200 min, whilst the low residual concentration of the acetic acid was obtained following its esterification reaction with methanol in presence of Mont-HS3M70 catalyst. In order to show the catalytic role of Mont-HS3M70, three other reaction parameters (alcohol class, reagent ratios and used catalyst quantity) have been studied.

#### 5.4.1. Influence of the alcohol class

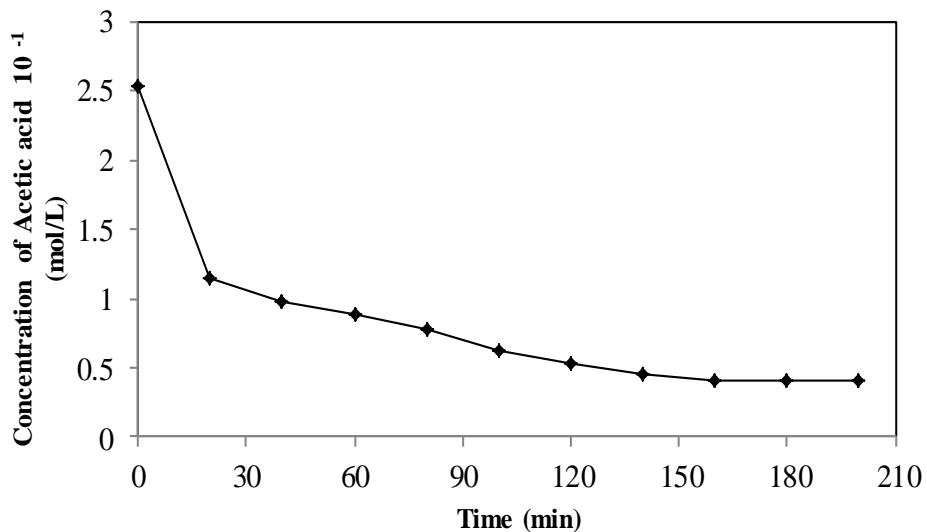


Fig.13. Effect of Mont-HS3M70 on the acetic acid esterification in presence of tert-butanol

The alcohol class is defined as a parameter which may diminish the reaction yield of esterification. However, a clear improvement in the acetic acid conversion could be observed in the case of its esterification reaction with tert-butanol in presence of Mont-HS3M70, acting as a catalyst at 98 °C, as well as a ratio of acetic acid /tert-butanol equal to 1 (Fig. 12). The ratio increase is likely due to the important number of the acid sites present on the inner surface of catalyst, promoting a rapid protonation of tert-butanol, resulting a stable carbonation of this alcohol after departing of the water molecules. This step is followed by the acetic acid attraction on the carbonation to ensure its conversion.

#### 5.4.2. Influence of reagent ratios

The diminution in the reagent ratios of acetic acid /tert-butanol from 1 to 0.8 increased the rate of acetic acid conversion through its esterification reaction

at 98 °C. The new ratio of the reagents was obtained by using alcohol excess, and the same acid quantity. This result confirms the data of the previous mentioned parameter versus the effect of acid sites on the surface of catalysts on the formation of alcohol carbonation and acid conversion.

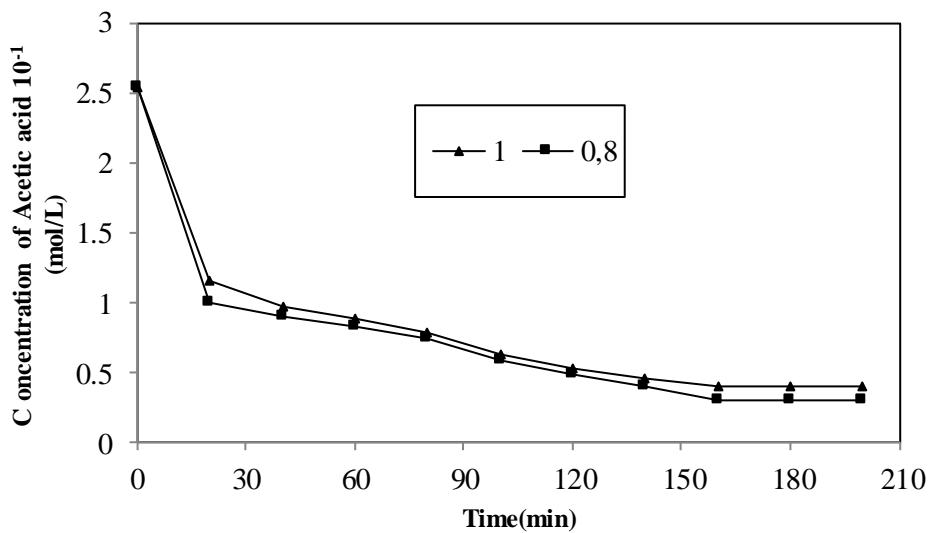


Fig.14. Effect of molar ratio of reagents on the acetic acid esterification with tert-butanol, using Mont-HS3M70

#### 5.4.3. Influence of the catalyst quantity

The effect of catalyst quantity on the acetic acid esterification with tert-butanol is shown in Fig.15.

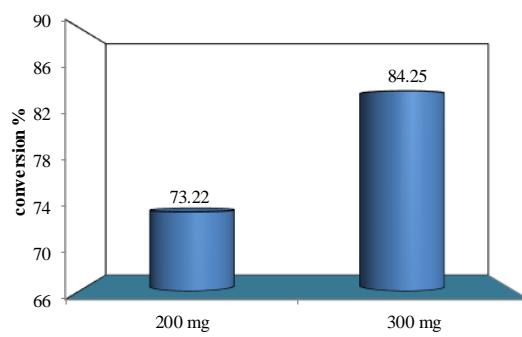


Fig.15. Effect of the Mont-HS3M70 catalyst quantity on the conversion rate of acetic acid

The diminution of the catalyst quantity decreases the acid conversion, which is probably reflected to the diminution of the contact surface between the

catalyst and the reagents [33, 34]. It is well-known that the reactivity at the montmorillonite surface starts by adsorption, then diffusion through the pores and the inter-foliar space [35, 36], and thus the regression of site numbers leads to a very low adsorption and reagent conversion.

## 6. Conclusions

An acidic catalyst having a catalytic activity could be produced through the activation of Algerian bentonite (Maghnia), using  $H_2SO_4$ ,  $HNO_3$  and  $HClO_4$  solutions along with concentrations varying from 1 to 3 M. The best acid retention on clay is that obtained with 3 M sulphuric acid, under temperature of 70 °C and for an activation time of 6 hours. This result proves an interesting modification and thermal stability of the clay. The thermogram of a sample prepared by activation with 3 M  $H_2SO_4$  at 70 °C (Mont-HS3M70) confirms this hypothesis, and the XRD pattern of catalyst concords with it. The acetic acid esterification with four different alcohols, namely ethanol, methanol, 1-propanol and 1-butanol has evidenced the catalytic ability of synthesized catalysts. The highly important conversion rate of acetic acid is that obtained in presence of Mont-HS3M70, which found to be about 81.88%. Therefore, this catalyst becomes an interesting candidate for the acetic acid esterification with tert-butanol. By considering a ratio acid/alcohol equals 0.8, the conversion rate of the acid could reach to 84.25%. This result confirms the efficiency of the synthesized catalyst, as well as its capacity in improving the conversion rate of the acetic acid, even in presence of tertiary alcohol. The optimal quantity of Mont-HS3M70 is about of 300 mg.

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