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Effect of the Acid Treatment of Montmorillonite Clay in the Oleic Acid Esterification Reaction

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Biodiesel is a fuel renewable, biodegradable and environmentally correct fuel, which can be obtained from the esterification reactions, transesterification and pyrolisis. Montmorillonite is a clay mineral of the smectite group and are of great interest for industrial processes such as catalysis and adsorption. Acid activation of clay minerals is one of the most effective methods proposed to produce active materials. In this work, montmorillonite clay was treated with H_2SO_4 in different concentrations (0.2 – 0.8 mol L^{-1}), characterized by X-ray diffraction (XRD), infrared spectroscopy (FT-IR) and applied in the catalytic esterification of oleic acid. The results reveal that the clay treated with aqueous solutions 0.8 mol L^{-1} H_2SO_4 shows promising catalytic activity toward the studied reaction, with maximum conversion of oleic acid of 65% at 30 °C.

Keywords: *montmorillonite clay, acid treatement, esterification, oleic acid, biofuel*

1. Introduction

The searching for biofuels has been object of study in many research centers, due to the incentive from Brazilian Government in increasing 20% the use of biodiesel until 2020[1]. The production and use of biodiesel, in substitution of diesel oil, allow the development of a sustainable energy source under environmental, economic and social aspects, besides the perspective of decreasing diesel oil imports[1]. Biodiesel can be obtained from reactions of esterification, transesterification or pyrolysis. The reaction of esterification happens among carboxylic acids, found in vegetable oils with methanol or ethanol, in presence of a catalyst to form esters and water[2-3], being typically catalysed by acids.

The processing of raw materials rich in fatty acids for biodiesel production can be achieved through the reaction esterification employing traditional acid catalysts. As reported in literature[4-10], several solid catalysts have been studied for the production of biodiesel. In this scenario there are the clays, especially those of the smectite group, because it is a natural raw material, abundant in nature, easy operation and excellent physicochemical properties. These clays in their natural form do not have the appropriate properties acidic esterification process and, therefore, have not been studied for this purpose. However, suitable acid treatments can make these solid potential catalysts for biodiesel production by esterification route. Thus, in the present work, montmorillonite clay was treated with sulfuric acid at different concentrations to obtain a material with higher acidity and applied in the oleic acid esterification reaction. The treatment process with sulfuric acid was used because it is a relatively cheap and simple process.

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The clay minerals from the smectite group, such as montmorillonite, are constituted of stacked unities which comprehend layers of ions coordinated in octahedral shape between two layers of ions coordinated in tetrahedral shape. These materials show high adsorption capacity and absorption for metallic ions, organic molecules, gases and liquids, and also can suffer changes in surface or layers to increase this ability[11-13]. The cation exchange capacity of clays is an important property because the cation exchange can modify them chemically influencing directly on their physicochemical properties and potential technological applications. Acids treatments cause the ion exchange interlayer cations (Na^+or Ca^{2+}) by H^+ ions, and the crystalline layers, as Al^{3+} of the octahedral sheets, are withdrawn from their positions in the crystal structure, leaving groups tetrahedral SiO_4 intact, increasing the acidity. When the solid precursor is activated at temperatures between 100 - 200 °C, bronsted acid sites are formed and under activation above of 200 °C result in a collapse of the structure interlayer of the clay mineral, with this there is a proportionate increase in acidity for Lewis sites. The material, after acid treatment (HCl or H_2SO_4), increases its adsorption ability and is used in bleaching, deodorization and dehydration of vegetable, mineral and animal oils, as also in catalysis[14-20].

The activation force and the number of acidic sites increase with the acid treatment, however, in excess, decreases the catalytic activity of clays because of the impairment of the octahedral layers. According to the literature[21], the acid attack on clay minerals such, as montmorillonite, with a solution of high concentration causes leaching of ions located in sites octahedral responsible for the stability of the clay mineral, collapsing the structure. The chemical attack of the mineral acids on clay is initially by adsorption of the acid on the surface of the solid leading to replacement of exchangeable cations by protons, and then the adsorbed protons diffuse into the lamella, where the chemical reaction occurs. The constituent cations in the octahedral sheet become soluble and are desorbed selectively to the liquid phase. Thus, the intensity of the acid treatment should be chosen according to the application of the material, so that the most important properties are adjusted in the best way.

2. Experimental Procedure

2.1. Materials

Montmorillonite clay used in this study was obtained from the city of Joao Pessoa, Brazilian northeast region. The material was passed through a 200 mesh sieve and after this process was calcined in air at 550 °C for 2 hours.

2.2. Treatment acid and characterization of the materials

The treated samples of montmorillonite clay were obtained through the contact process with addition of aqueous solution sulfuric acid at different concentrations (0.2 - 0.8 mol L^{-1}) in room temperature, agitation constant at 500 rpm for a period of 2 hours. Then made to vacuum filtration on a Büchner funnel, washing to obtain a clear filtrate with pH of approximately 7 (measured with universal indicator paper). After filtration, the material was dried at 100 °C for 2 h. The samples were characterized by X-ray diffraction (XRD), using radiation CuKa, in an equipment Shimadzu, model XRD-7000, where the data were collected over a range of angular variation between 5 and 80°; and infrared spectroscopy (FT-IR), performed in a spectrometer Perkin Elmer obtained in the mid-infrared region (400 - 4000 cm^{-1}) and resolution of 4 cm^{-1}.

2.3. Esterification reaction

The esterification reactions were conducted in a 250 mL batch reactor, with 50 mL of oleic acid, 30 mL of absolute ethanol and 0.25 g of catalyst, previously dried in an oven at 110 °C for 1 hour. The reactions were done using temperatures of 30 °C, 45 °C and 60 °C under vigorous agitation, until the stabilization of the conversion. Aliquots of 1 mL were collected in intervals of 5 minutes to determine the level of conversion using standard solution of NaOH 0.025 mol L^{-1} as titrant and a solution of 1% of phenolphthalein as indicator.

3. Results and Discussion

3.1. Characterization of the materials and catalytic tests

Infrared analyses of the natural and treated samples were performed to evaluate the influence of the acid treatments on the composition and structure of crystalline solid. The Figures 1 and 2 show infrared spectra of montmorillonite clay samples which were submitted to acid treatment with sulfuric acid at different concentrations and the XRD of natural montmorillonite clay and treated montmorillonite clay (0.2 – 0.8 mol L^{-1}), respectively.

For the materials studied, was observed the presence of bands at 3456 cm^{-1} related to internal and external hydroxyl groups interact with water molecules by hydrogen bonds and, in 1644 cm^{-1}, attributed to the angular vibration of water molecules adsorbed on material surface[15]. Can to be observed bands at 3629 cm^{-1} and 920 cm^{-1} related to stretching vibration of Al-OH-Al and deformation vibration Al-OH-Al, respectively. The spectra of the materials showed band at

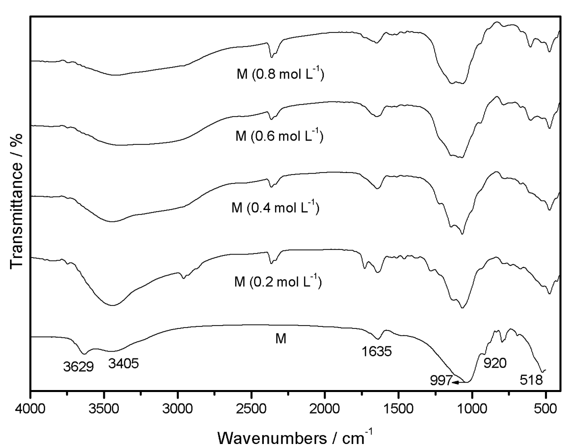

Figure 1. Infrared spectra of treated montmorillonite clay with sulfuric acid at different concentrations.

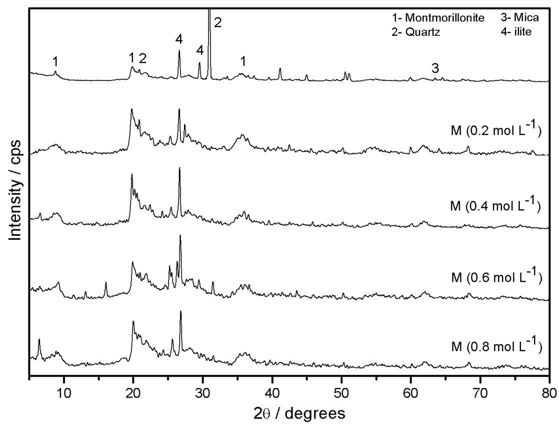

Figure 2. X-ray patterns of natural montmorillonite clay and treated montmorillonite clay (0.2– 0.8 mol L^{-1}).

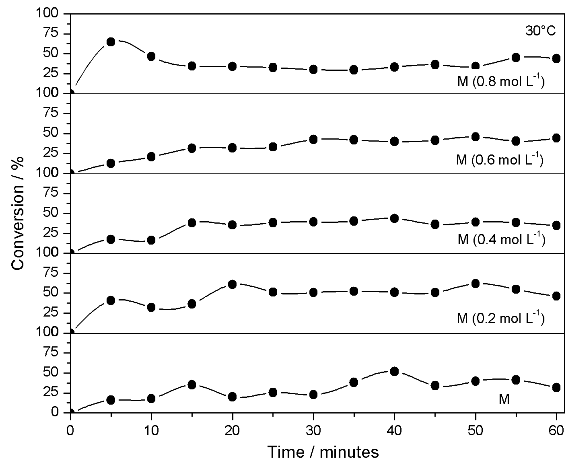

Figure 3. Conversion of oleic acid at 30 °C, using natural montmorillonite clay and treated montmorillonite clay with sulfuric acid at different concentrations (0.2 – 0.8 mol L^{-1}).

997 cm^{-1} related to Si-O-Si stretching and at 518 cm^{-1} band of Si-O deformation[22].

Through the International Center for Diffractional Data (ICDD) library were identified that the materials presented in Figure 2, show peaks associated smectite montmorillonite (02-0009), quartz (86-1560), mica (78-1928) and illite (43-0685). After the acid treatment, the samples were analyzed using XRD. The XRD patterns reported in Figure 2 show the effect of acid treatment on the crystalline phases present in the composition of the natural sample. It can be observed generally that the acid attack caused a decrease of the intensities of the peaks related to quartz and did not negatively affect the crystal structure of montmorillonite, which can perceive maintenance of reflection characteristic of this clay mineral in the region of 2θ between 5 and 7°. This is an important point, since the maintenance of the crystal structure is essential for the material to maintain its thermal stability when applied in catalytic processes. Therefore, one can conclude that the pre-treatment acid was sufficiently promoted to obtain a point of potential clay treated with acidic properties, as required for the esterification reactions of vegetable oils.

The appearance of peaks at 2θ = 5 and also at 2θ = 10 and 20 shown in Figure 2, relative to samples treated with 0.8 mol L^{-1} solution and 0.6 mol L^{-1} of H_2SO_4 respectively can be related to a decrease of peak intensity after the quartz etching, which was previously masked peaks of lesser intensity. This is a very common occurrence in natural materials that exhibit, in its composition, a complex of minerals and clay minerals, such as clays[15,23-26]. The Figures 3, 4, 5 and 6 show the obtained conversions of oleic acid from the esterification reaction versus the time in 30, 45 and 60 °C for natural montmorillonite clay and treated montmorillonite clay (0.2 – 0.8 mol L^{-1}).

It is observed in Figures 3, 4 and 5 that the concentration of the H_2SO_4 acid afforded greater stability for the conversion of oleic acid, as observed by the decrease of the dispersion of points throughout the reaction. Treatment with sulfuric acid solution in varying concentrations resulted in a higher catalytic activity of the material at low temperature. The

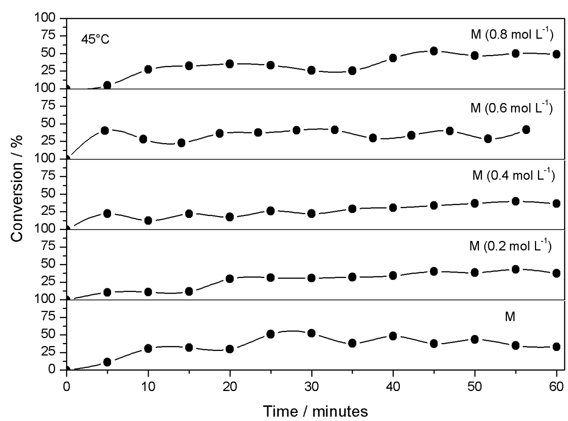

Figure 4. Conversion of oleic acid at 45 °C, using natural montmorillonite clay and treated montmorillonite clay with sulfuric acid at different concentrations (0.2 – 0.8 mol L^{-1}).

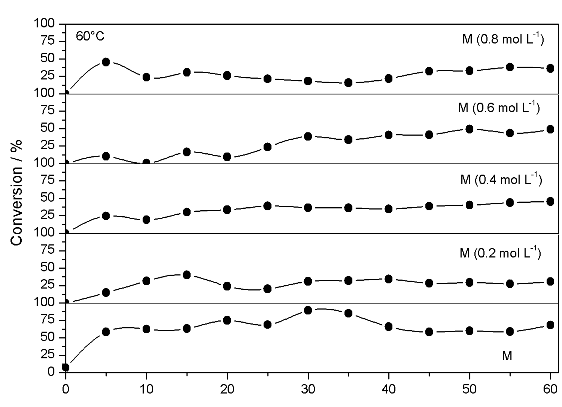

Figure 5. Conversion of oleic acid at 60 °C, using natural montmorillonite clay and treated montmorillonite clay with sulfuric acid at different concentrations (0.2 – 0.8 mol L^{-1}).

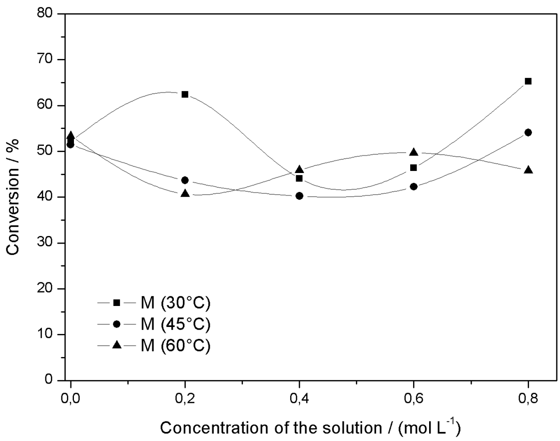

Figure 6. Comparative conversion of oleic acid obtained from reactions in 30 °C, 45 °C and 60 °C using natural montmorillonite clay and treated montmorillonite clay with sulfuric acid at different concentrations (0.2 – 0.8 mol L^{-1}).

greatest conversion of oleic acid for each concentration of H_2SO_4 solution used at temperatures of 30 °C, 45 °C and 60 °C are presented in Figure 6.

According to Figure 6, it is observed that the oleic acid esterification is dependent on the reaction temperature and concentration of sulfuric acid. The best conversion results, using montmorillonite clay, occurred in a temperature of 30 °C. It was observed that the treated material with solution of 0.8 mol L^{-1} showed the highest oleic acid conversion, with approximately 65%, followed by the treated material with solution of 0.2 mol L^{-1}, showing conversion of 62% along the reaction. In a temperature of 45 °C, a conversion of 54% was obtained with solution of 0.8 mol L^{-1}. The montmorillonite clay in 30 °C, 45 °C and 60 °C showed similar conversions in absence of the solution sulfuric acid. After the addition of it, the oleic acid conversion decreased in temperatures of 45 °C and 60 °C, being that, in the solution of concentration 0.8 mol L^{-1} in 45 °C there was increase in the conversion.

In the work accomplished by Nascimento and collaborators[27], MCM-41 was submitted to the acid treatment in the same solutions and concentrations studied and tested in the oleic acid esterification reaction, in the temperatures of the 30 °C, 45 °C and 60 °C. The obtained results showed conversion around 80% in temperature of 45 °C, with concentration solution of 0.8 mol L^{-1}. The lower catalytic activity can be related to lower specific area of microporous clay (about 75-150 m^2g^{-1})[28] compared with that presented by the mesoporous MCM-41 (> 700 m^2g^{-1})[29].

According to the results of the catalytic tests, it can be seen that acid treatment of montmorillonite clay, at room temperature, increases its activity against esterification reaction when it is carried out at ambient temperature and pressure.

4. Conclusions

It can be seen that the natural montmorillonite clay has been activated successfully by treatment with dilute sulfuric acid. XRD and FT-IR analyzes show maintenance of the structure of the material after acid attack. It was verified that its conversion of oleic acid is dependent of the reactional temperature and of the concentration of sulfuric acid utilized, occurring the best conversion in 30 °C with concentration solution of 0.8 mol L^{-1}. Treatment with sulfuric acid increased the montmorillonite clay catalyst activity, showing promise for acid catalysis.

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