Acid-activated montmorillonites as heterogeneous catalysts for the esterification of lauric acid acid with methanol

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ABSTRACT

A standard clay mineral was systematically subjected to activation with phosphoric acid under different concentrations and activation times. The materials were evaluated with regard to their structure, presence of functional groups, textural properties and the presence of Brönsted and Lewis acid sites. After characterization, the best catalyst was evaluated in the esterification of lauric acid with methanol. High conversions were observed in short times (between 91.63 and 96.67%) and relatively mild reaction temperatures, revealing the potential of acid-activated clays as esterification catalysts for industrial applications such as biodiesel production. For comparison purposes, some experiments were also carried out with a standard solid acid catalyst (montmorillonite K10) and conversions of 95.03% were obtained in comparison to the best catalyst obtained in the present study (96.67%).

1. Introduction

In general, biodiesel is produced by transesterification of vegetable oils or animal fats or by esterification of fatty acids with short chain alcohols, in the presence of homogeneous or heterogeneous catalysts (Cho et al., 2012). Homogeneous catalysts are effective and viable but show technical complications such as an extensive contamination of the final product, which increases in production cost by requiring additional procedures for separation and purification (Di Serio et al., 2008).

The esterification enables the use of fatty materials with high acid numbers for biodiesel production, such as unrefined and used frying oils, rendered materials, soybeans and palm oil fatty acid distillates, among others (Cho et al., 2012). The use of mineral acids such as sulfuric acid in the homogeneous catalytic conversion of fatty acids to alkyl esters presents some technical difficulties in the recovery process, as well as equipment maintenance (corrosion) and waste management. In this context, the use of heterogeneous catalysis in esterification reactions is advantageous since it provides an easy catalyst recovery and reuse, reduced effluent generation, and better process sustainability (Park et al., 2010; Shanmugam et al., 2004).

Heterogeneous catalysts based on clays have received considerable attention in different chemical processes due to their environmental compatibility, low cost, selectivity, thermal stability and recyclability (Reddy et al., 2005). Acid activated clays are among the most widely studied solid catalysts as they have been applied in different organic reactions such as alkylation, condensation, dimerization among others, but these are rarely reported as catalyst in esterification reactions of fatty acids (Bouguerra-Neji et al., 2009; Zatta et al., 2012a). The montmorillonite is classified as a 2:1 mineral clay that is widely used due to its large availability, low cost and both adsorbent and catalytic properties that result from their high acidity and surface area. The acid properties of the montmorillonite can be enhanced by acid activation, which increases the catalyst surface area and modifies the structure of the clay mineral (He et al., 2002). The surface area available for adsorption and the presence of hydroxyls on the surface of unmodified clay minerals contributes to the acidity; consequently, studies regarding the increase and improvement of their surface acidity have been developed by many research groups (Narayanan and Deshpande, 1998). The acid treatment of clay minerals, besides leaching cations preferably from the octahedral sheets, also dissolves impurities and replaces exchangeable cations present in the interlayer space by hydrated protons.

The acid treatment causes several changes in the crystal structure of the clay mineral. These include: the edges of the crystals are opened and Al^{3+} and Mg^{2+} cations of the octahedral sheet are exposed to acid and become soluble, causing an increase in both surface area and pore diameter; observing the first basal peak, the intensity is reduced and width is increased, showing a loss in the solids degree of crystallinity; and the surface area is increased up to a maximum, when it is reduced by prolonged acid treatments (Díaz and Santos, 2001).

There are many reports in the literature citing properties acquired due to acid activation of clays but systematic studies are rarely described (Wang et al., 2010). In this work, montmorillonite was activated with phosphoric acid in many different ways and the resulting materials, obtained with different acid concentrations and reaction times were analyzed with regard to changes in their structural and

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textural properties. After this, freshly synthesized acid-activated clays were applied as solid catalysts in the esterification of lauric acid with methanol with the aim of identifying which sample acquired the best catalytic performance. Studies were also performed to characterize the best solid catalyst after use in at least one reaction cycle.

2. Experimental

Sample of montmorillonite STx-1, with a chemical formula $(Ca_{0.27}Na_{0.04} K_{0.01})[Al_{2.41}Fe^{(III)}_{0.09} Mg_{0.71}Ti_{0.03}] [Si_{8.00}] O_{20}(OH)_4$, were obtained from Gonzales County, Texas – USA.

For acid activation, the montmorillonite (STx-1) was mixed with aqueous phosphoric acid (Nuclear – 85%) solutions in a flat-bottomed flask connected to a reflux condenser. The reactions were carried out under vigorous stirring at 100 °C. STx-1 and the acid solution were mixed in a 1:4 ratio (weight per volume) using acid concentrations of 0.5, 1, 2 and 4 mol L^{-1}. After the activation process for 1, 2, 3 and 4 hours, the samples were washed until pH close to 7, dried first at 110 °C for 24 h and then at 250 °C for 2 h.

As the objective of the acid activation was to remove just part of the octahedral coordinated metals from the montmorillonite structure, improve porosity and consequently create acid sites, phosphoric acid which has an intermediary acid character has been chosen (Wang et al., 2010).

For comparison purposes, some experiments were also performed with a standard solid acid catalyst, the montmorillonite K10 supplied by Sigma Aldrich. This catalyst is also obtained by acid activation of montmorillonite and, according to the supplier, has the following chemical composition: SiO_2 (43.77%), Al_2O_3 (18.57%), CaO (1.02%), Na_2O (1.03%), and H_2O (35.61%), with a cation exchange capacity (CEC) from 80 to 120 meq/100 g and the surface area of 220–270 m^2/g.

All esterification reactions were conducted in a steel Cyclone Büchiglasuster reactor, miniclave drive model. The pressure inside the reaction vessel corresponded to the vapor pressure of the most volatile component of the mixture which, in this case, is the methanol. The time was counted from the moment when the desired temperature was reached in the reactor, which was about 25 min after initiation of heating. The catalyst used was separated from the reaction medium by centrifugation after reaction completion. The excess of methanol was recovered by rotatory evaporation and the solid material was washed three times with 15 mL of ethanol:hexane 1:1 (vol/vol), centrifuged and dried in a drying oven at 90 °C for 12 h. Other conditions included a reaction time of 2 h and agitation of 500 rpm, these values being obtained in previous optimization experiments.

The esterification reactions were performed with methanol (QEEL – Química Especializada Erich Ltda., 99.8%) and lauric acid ($C_{12}H_{24}O_2$ – Vetec, 98%).

A test was performed in methanol to investigate the possible occurrence of leaching of the catalytically active species. This test was restricted to the catalyst that showed the highest catalytic activity in previous tests. Approximately 0.89 g of untreated catalyst was added to 18 mL of methanol to mimic the normal conditions used for esterification. No fatty acids were added in this experiment but if 7.40 g of lauric acid had been added, these values would correspond to a molar ratio of 12:1 and 12% of catalysts. After 2 h, the solids were removed from the reactor and washed with approximately 20 mL of methanol. The material was centrifuged, the liquid phase was separated and the solid was transferred to a flask with addition of more 15 mL of methanol. The new mixture was subjected to evaporation at 100 °C in a rotary evaporator. After drying, the solids were applied as catalyst for esterification.

3. Characterization of solid catalysts

Measurements of powder X-ray diffraction (XRD) were obtained by depositing the material in the glass sample holder and analyzing it in a Shimadzu diffractometer model XRD-6000 with Cu Kα (40 kV, 30 mA, λ = 1.5418 Å) at a speed of 2° min^{-1} and step of 0.02°.

The infrared spectra (FTIR) were obtained in the transmission mode using a Bio-Rad, model FTS 3500GX. KBr pellets were prepared from sample specimens and analyzed in the range of 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1} and accumulation of 32 scans.

Nitrogen adsorption isotherms were obtained in a Quantachrome gas sorption analyzer, model NOVA 2000e. The samples were degassed at 250 °C under vacuum for 3 h and the analyses were carried out under liquid nitrogen (− 196 °C). The sample specific surface areas were calculated using the multi-point Brunauer–Emmet–Teller (BET) method. Pore volume and average pore size were calculated by adsorption curve analysis using the Barrett–Joyner–Halenda model (BJH).

The identification of acid sites was performed by calcination of about 100 mg of sample at 300 °C for 90 min and cooling to 120 °C, which was maintained throughout the remaining of the process. The sample was saturated with gaseous diluted pyridine under N_2 for 60 min. After sorption, the sample was kept at 120 °C under N_2 flow for 60 min in order to remove the physically adsorbed pyridine and the sites quantified by thermogravimetric analysis (TGA) (Nascimento et al., 2011).

The FTIR spectrum was acquired from KBr pellets in the range of 1650–1350 cm^{-1} (Nascimento et al., 2011; Reddy et al., 2009). Lewis and Brönsted acids sites were identified by FTIR analysis of their corresponding pyridine adsorbed species, which generate vibration frequencies that are correlated to the chemical properties of these sites.

Scanning electron microscopy (SEM) of the solid catalysts was carried out at 15 kv using a Jeol scanning electron microscope, model JSM-630LV. Each sample specimen was deposited on an aluminum stub and gold sputtered prior to analysis by SEM.

The conversion of lauric acid to fatty esters was quantified by changes in their acid number during a reaction course, which was measured by the American Oil Chemist's Society (AOCS) official method — Ca-5a-40 (Brühl, 1997). This method was found to have a good correlation with other analytical methods such as high performance liquid chromatography and nuclear magnetic resonance (Zatta et al., 2012b).

The conversion of commercial oleic acid and tall oil fatty acids was determined by titration with a standard solution of 0.1 mol.L^{-1} sodium hydroxide. The calculation was based on Eq. 1 (Park et al., 2008).

$$Acid\ value = \frac{M \times A \times F \times N}{S} \tag{1}$$

where M is the molar mass of NaOH, A is the amount of standard NaOH solution used in the titration, F is the concentration factor of the NaOH standard solution, N the molar concentration of the NaOH standard solution, and S is the sample mass.

4. Results and Discussion

Fig. 1 shows the X-ray diffraction patterns of the raw STx-1, before and after activation with phosphoric acid under different conditions.

The peaks (001, 003 and 020) are indexed in the X-ray diffraction patterns of STx-1 (Fig. 1a), according to data obtained from the literature (Viani et al., 2002). For all samples shown in Fig. 1, there are two peaks in the 18–24° region (in 2θ). The first was assigned to the (020) plane of montmorillonite structure and the second at 21.8° (in 2θ) was related to the presence of opal-CT impurities (minerals such as cristobalite and tridymite) (Chipera and Bish, 2001). The presence of the (020) plane shows that the STx-1 retained part of its structure even under severe conditions of acid activation (longer time and higher acid concentrations).

Based on the peak intensity of the (001) plane, acid activation under different conditions led to materials with low crystallinity as