Synthesis and Performance of Sulfated Zirconia Catalyst in Esterification of Oleic Acid

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Abstract: *In this work, the performance of sulfated zirconia catalyst used in the synthesis of biodiesel by esterification of oleic acid was studied. For catalyst preparation the zirconium dioxide (ZrO) by Aldrich was used as precursor. The sulfated zirconia obtained was calcined for 3 hours at different temperatures (200, 400, 600 and 700 °C) in an oxygen atmosphere. Each of the calcination conditions generated a sample of catalyst, which was used in the esterification reaction. The esterification reaction was carried out using reagents such as oleic acid and methanol at a molar ratio 1:20. The sulfated zirconia catalyst was used in the reaction in various proportions by weight relative to the weight of oleic acid (0.5, 1.0, 3.0 and 5%). The analysis of methyl ester conversion was performed by gas chromatography and mass spectrometry (CGMS) and the percentage area of the characteristic peaks as methyl oleate was quantified. A characterization of sulfated zirconia was also performed using scanning electron microscopy (SEM) and X-ray diffraction (XRD). Finally, the catalyst performance was studied in the reduction of the acid index (AI) and the conversion of free fatty acids of oleic acid and compared to other commonly used catalyst for this purpose, which is concentrated sulfuric acid (H_2SO_4).*

1. INTRODUCTION

Biodiesel is a liquid fuel which is obtained from vegetable oil and animal fats from reaction with an alcohol of low molecular weight by transesterification and esterification reactions, which in both cases can be catalyzed or un-catalyzed [1-6]. The catalysis can be basic, acidic or enzymatic [7-10] and in turn can be carried out in a homogeneous or heterogeneous medium [11]. Non-catalytic methods involve high temperature and pressure and are known as supercritical methods [12-15].

Currently, there are different ways for obtaining biodiesel, today the most commercially used method is based on the transesterification of vegetable oils and animal fats, using methanol by homogeneous catalysis, with the application of catalysts such as KOH and NaOH [16]. This method is carried out under relatively normal conditions (atmospheric pressure, temperature of 50-60 °C).

The homogeneous catalysts used are inexpensive and the reaction times are short (30-50 min) and high yields > 90%. Among

the disadvantages of this method is that it should use high purity raw materials or refined, which increases the pretreatment, and with low content of free fatty acids (FFA) <1-5% [17-19]. The biofuel purification steps become expensive for the removal of excess methanol, the catalyst residue and soaps formed by saponification due to water wash stage of biodiesel purification. This has led to recent research focus on heterogeneous catalysis, which decreases the problems of purification of raw materials and finished product. On the subject of heterogeneous catalysis it has been studied synthesis and performance of the solid catalyst with application in the production of biodiesel by transesterification of triglycerides and esterification of fatty acids. The solid catalyst was recovered after the reaction and can be used again. They are easily separated from the product and can be used in esterification and transesterification reactions with less pure reagents and in the presence of water without the risk of the formation of soaps. One of the disadvantages of heterogeneous catalysts is the low yield, to increase their effectiveness it requires high temperature and pressure and more alcohol in the reaction [11, 16, 20]. In heterogeneous catalysts, we can mention the sulfated zirconia which has been

studied for its properties of super acid [21, 22] and which is capable of using in esterification and transesterification simultaneously [23-26]. The sulfated zirconia has been synthesized, characterized and subjected to different calcination temperatures and evaluated in the transesterification of palm oil and cerbera oil. It was found that the best calcination temperature was 400 °C and the conversion of fatty acid methyl esters (FAMEs) were closer to 75%, when the sulfated zirconia was supported with Al_2O_3 [27, 28]. In other work, sulfated zirconia was used as a catalyst in transesterification reactions of palm kernel oil and coconut oil and it was compared in performance with other catalysts including the following: ZrO_2, ZnO, SO_4^{2-}/SnO_2, KNO_3/KL (zeolite) and KNO_3/ZrO_2. It was found that sulfated zirconia had better performance with respect to other catalysts, reaching a conversion of methyl ester of 90.3 and 86.3, in the case of palm oil and coconut oil respectively, using only 1% of the catalyst [29]. In this context, different types of zirconia-based catalysts, such as zirconium oxide catalyst (ZrO_2), mixed zirconium oxide catalyst doped with titanium (ZrO_2/TiO_2), sulfated zirconia catalyst and zirconia catalyst doped with 5 % cerium sulphate (ZrO_2Ce) were evaluated. The result of this study showed that the sulfated zirconia catalyst ($ZrO_2SO_4^{-2}$) had higher catalytic activity compared with other catalysts in the transesterification reaction of cottonseed oil. In this experiment, the reaction conditions were 200 °C for 2 hours with only 1% of catalyst. By using computational methods, sulfated zirconium catalyst $Zr(SO_4)_2$ was evaluated as a potential catalyst for transesterification reactions and observed that only small amounts of energy (about 0.006275095 Kcal/mol) was required for a chemical reaction occurring between a theoretical structure of $Zr(SO_4)_2$ and triacetin $(CHCO_2CH_2)_2CH(O_2CCH_3)$, which corresponds to the theoretical model to the fatty acid.

In this work, characterization and performance of sulfated zirconia catalyst synthesized from commercial ZrO_2, which was impregnated with H_2SO_4 0.5 M, was studied. The sulfated zirconia catalyst obtained by sulfating of ZrO_2, was calcined at different temperatures to evaluate the effect of the calcination temperature and percentage of catalyst used in the esterification of oleic acid reacting at 55 °C for 50 minutes. Subsequently, the performance of the catalyst in the reduction of the acid Index (AI) and the conversion of FFA to 5% by weight of catalyst relative to the weight of oleic acid was assessed. During this stage the reaction times were 2 to 54 hours. All esterification reactions were carried out in a molar ratio of 1:20 of oleic acid and alcohol respectively. Finally, sulfated zirconia catalyst was compared with a homogeneous acid catalyst, H_2SO_4, which is commonly used in processes of esterification of FFA. With this catalyst, alkyl esters conversions were higher than 80% in short reaction times (30 minutes) and at low temperatures (50 °C).

2. MATERIALS AND METHODS

2.1. Materials

As catalyst precursor, analytical grade 99% zirconium oxide (ZrO_2) (powder of 5 microns) by Aldrich Chemistry was used. As catalyst and to prepare standard solutions and sulfation solutions, concentrated sulfuric acid (ACS grade 96.4%) by Fermont, was used. As esterification reagents, technical grade Meyer brand oleic acid and industrial grade (99.95%) Abamil Chemistry brand methyl alcohol were used. For measurement of acid index standard solution prepared with potassium hydroxide (KOH) ACS grade
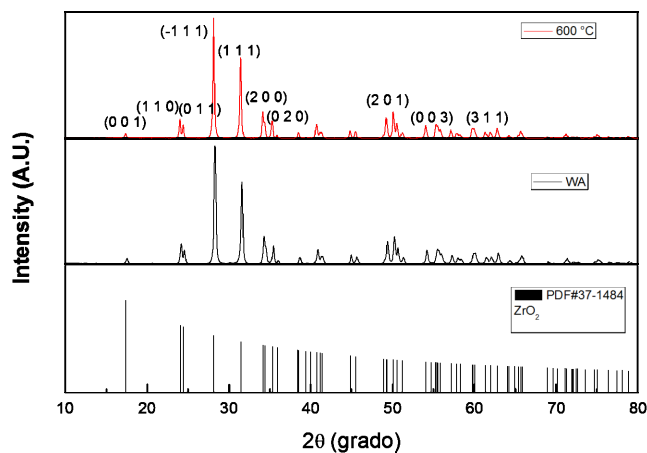

Figure 1. XRD patterns of the sulfated zirconia catalysts prepared without annealing and calcined at 600 °C

(87.6%) Fermont brand and ethyl alcohol (96%) was used.

2.2. Synthesis of the Catalyst

For preparation of the zirconium sulfate catalyst, 99 % zirconium dioxide (ZrO_2) powder was used. The ZrO_2 was introduced into a 0.5 M solution prepared with H_2SO_4. Solution and ZrO_2 were mixed in a ratio of 10 ml of solution per gram of solid for a period of 3 hours. After the sulfation process, sulfated zirconia catalyst was separated into an Eppendorf Centrifuge Model 5804 R at 2500 rpm and 20 minutes at room temperature. The liquid was decanted and the catalyst was dried for 12 hours at 100 °C and then calcined at different temperatures (200, 400, 600 and 700 °C) in an oxygen atmosphere for 3 hours with the help of a Tube furnace 21100 Barnstead Thermolyne.

2.3. Catalyst Characterization

The x-ray diffraction (XRD) analysis was performed with a Rigaku equipment DMAX model 2200, with copper anode (Cu Ká = 1.54 Å) with a measurement range of 2è of 5 to 80 °.

The morphological characterization of sulfated zirconia catalyst was performed by means of scanning electron microscopy (SEM) in a Topcon microscope model SM-510.

2.4. Chromatography Analysis (GCMS)

To measure the effect of the calcination temperature and the performance of the catalyst, the oleic acid was esterified with methanol in a glass reactor of 500 ml with stirring. Sulfated zirconia catalyst un-calcined and calcined at different temperatures (200, 400, 600 and 700 °C) was added to each reaction in proportions of 0.5, 1.0, 3.0 and 5% by weight relative to the weight of oleic acid. The conditions of each reaction were 55 ° C for 50 minutes.

After the reaction, the catalyst was separated from the reaction by centrifugation in an Eppendorf Centrifuge Model 5804 R at 2500 rpm for 20 minutes at 4 °C in order to quench the reaction. The separation of excess methanol by distillation was carried out in a water bath at a temperature not above 80 °C to ensure the integrity of the sample and prevent the damage from overheating. Samples for performance evaluation were taken from each esterification

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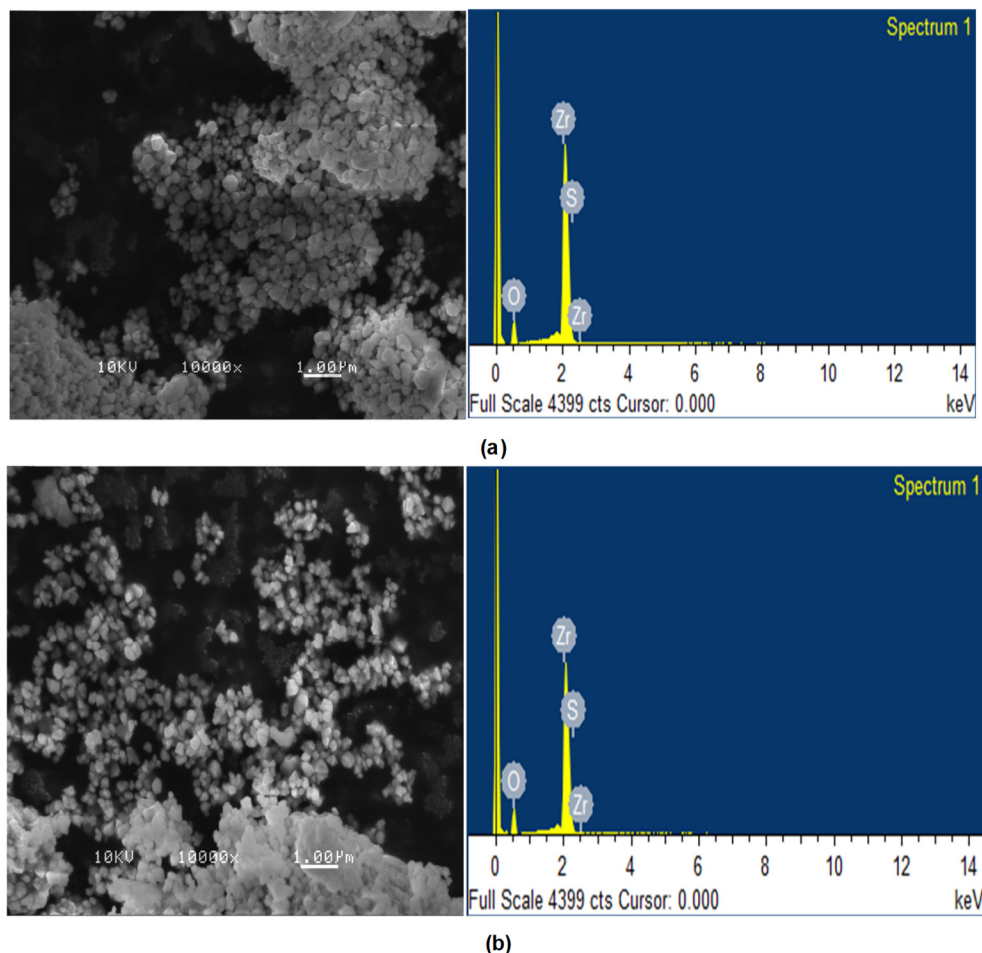*/ J. New Mat. Electrochem. Systems*

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Figure 2. EDS patterns of the sulfated zirconia catalysts prepared (a) untreated and (b) calcined at 600 °C.

reaction with different prescribed conditions. Conversion analysis was performed on a gas chromatograph coupled to a mass spectrometer (Agilent Technologies) with a DB-Waxter (J & W) column with a helium flow of 1 mL min^{-1}. The furnace conditions were programmed to start at 150 °C and increasing 30 °C min^{-1} up to 210 °C, then the increase was 1 °C min^{-1} up to 213 °C, finally the temperature increased 20 °C min^{-1} to 225 °C, which was maintained for 20 min. The injection port temperature was maintained at 250 °C. Helium was used as carrier gas at a flow rate of 1 mL min^{-1}. The HP ChemStation Nist software was used.

2.5. Esterification

The esterification reaction was conducted in a glass reactor of 500 ml with stirring and temperature controlled by thermostatic bath at 50-55 °C and reaction times were 30 and 54 hours. The molar ratio of methanol and oleic acid was 20:1. A percentage of 5% catalyst was used by weight relative to the weight of oleic acid. During the reaction, samples were taken at different time intervals to determine the acid index. Esterification reactions were performed in triplicate.

2.6. Acid Index and Conversion of FFA

For the determination of the acid index (AI) and the content of free fatty acids (FFA) the methodology proposed by the NMX-F-101-1987 standard and the AOCS Ca 5a-40 standard were used. The percentage conversion of free fatty acid methyl esters was calculated by the equation (1);

$$Conversion\ (\%) = \left(1 - \frac{AI_m}{AI_{oleic}}\right) \times 100 \tag{1}$$

where, AI_m and AI_{oleic} represent acid index of the sample at time t and the acid index of oleic acid at the beginning of the reaction, respectively [30, 31]. This methodology was also used to evaluate the performance of the sulfated zirconia catalyst in comparison with H_2SO_4 acid, which is another type of homogeneous catalyst used in esterification reactions of free fatty acids.
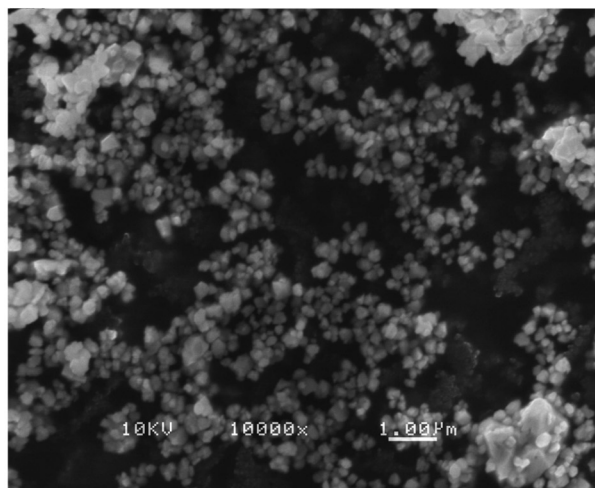
3. RESULTS AND DISCUSSION

3.1. Catalyst Characterization

XRD patterns in Figure 1, the main peaks of zirconia was observed in the diffracted angles 2θ = 17.419, 24.047, and 28.17,
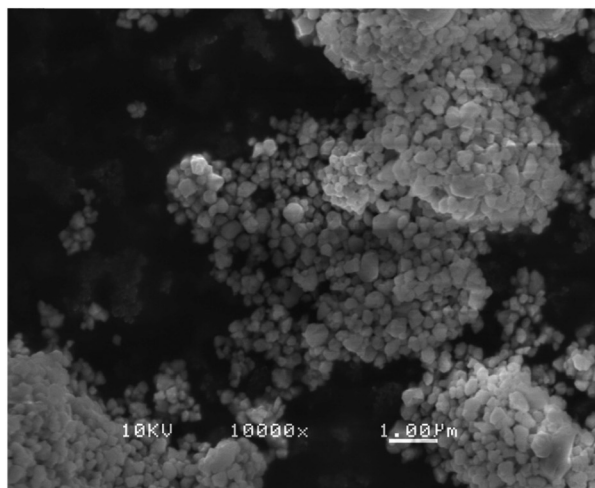
(a)

(b)

Figure 3. SEM micrographs of selected calcined samples of sulfated zirconia particles: (a) untreated and (b) treated at 600 °C.

Figure 4. Effect of different calcination temperatures and amounts of catalyst: (■) 0.5%, (●) 1%, (▲) 3% and (▼) 5% w/w

which are confirmed by the PDF#37-1484 card, which indicates the predominant presence of this material. However, it also can be seen in sulfur component as zirconium sulfate in the diffracted angles 2θ = 13.633, 20.542, y 30.785, which are confirmed by the PDF#08-0495 card. By applying heat treatment, the recrystallization of material was carried out, which is confirmed by the intensity of the peaks of the XRD patterns.

In related work, Keat Teong Lee *et al* found similar patterns for XRD as sulfated zirconia when it was calcined at various temperatures [28]. An additional confirmatory test to identify the presence of sulfate in the calcined samples was performed by energy dispersive spectroscopy (EDS). The results of these tests are shown in figure 2, where (a) and (b) correspond to samples un-calcined and calcined at 600 °C respectively. In both cases there is the presence of sulfur.

Images taken by SEM of the sample without calcination treatment and sample calcined at 600 ° C are shown in Figure 3 (a) and
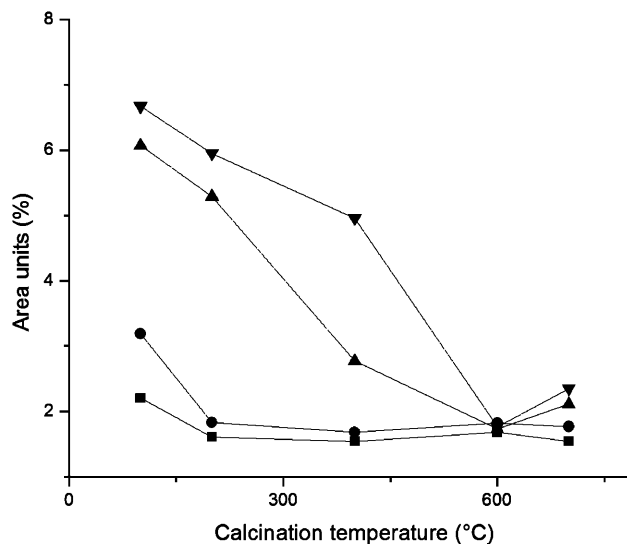
(b) maintaining a uniform spherical structure and good dispersion. Moreover, the difference between (a) and (b) is the form of nanometric particles. In (b), the particles are better defined.

3.2. Effect of the Calcination Temperature and Catalyst Content

The results of chromatography were the basis for the conversion rate of oleic acid based on the peak area of methyl oleate component, obtained in the mean retention time of 13.15 min. In Figure 4 it can be seen that increasing calcination temperature, diminishes the ability of conversion of oleic acid and therefore the potential of the catalyst in the esterification. This may be due to a decrease of sulfate present in the catalyst due to heating. Lee *et al* found this downward trend in the efficiency of the catalyst with increasing temperature after 400 °C of calcination [28], unlike this work, where the fall of the conversion is from the calcination temperature of 200 °C. This helped to establish that the catalyst was used after the sulfation without calcination.

At the same time it was observed that a greater amount of catalyst added to each reaction of esterification increased the conversion of oleic acid. This effect is similar to that found by Srinophakun *et al* [25] during the esterification of myristic acid using a sulfated zirconia. Increased catalyst concentrations from 1 to 3% significantly improved the conversion of FFA, but at temperatures above 120 °C.

3.3. Acid Index and Conversion of FFA

The results from the esterification of oleic acid, measured as the decrease of the acid and the conversion of FFA can be seen in Figure 5. For a total time of 30 hours AI decreased from 193.28 to 45.04 and a maximum conversion of 76.76% of FFA was reached. The most significant conversions were achieved during the first 8 hours. However, as shown in Figure 6, to achieve better performance in the reaction 54 hours were necessary to decrease the val-
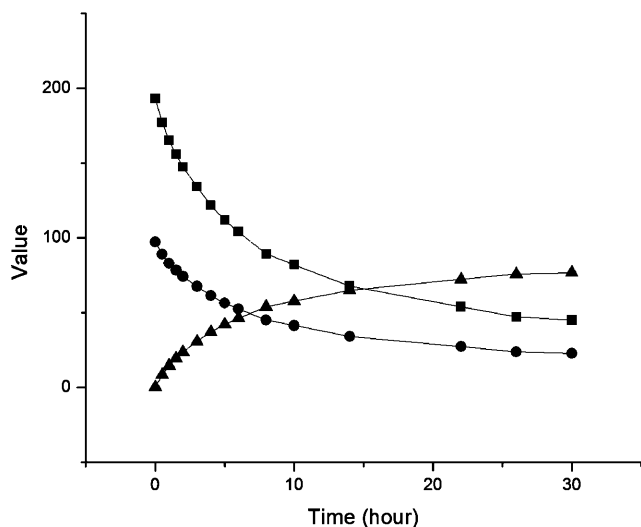
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Figure 5. Sulfated zirconia catalyst performance with 5% w/w. (■) acid index, (●) FFA %, (▲) conversion of FFA (%)

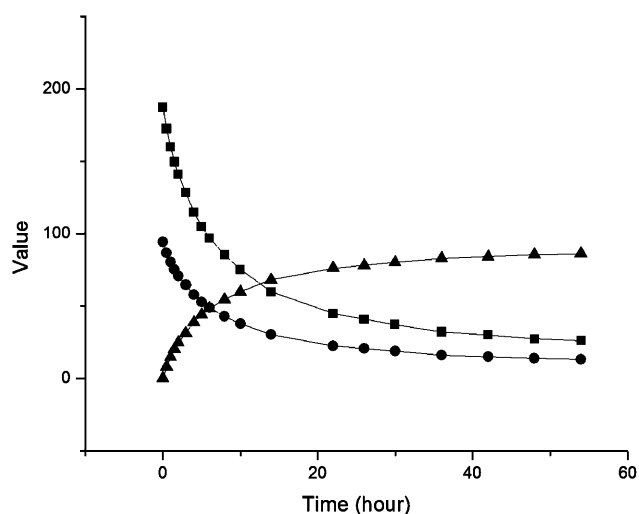Figure 7. Comparative FFA variation using the two catalysts: (■) H_2SO_4, (●) sulfated zirconia; amount of both catalysts - 5% w/w

Figure 6. Extended time line from sulfated zirconia catalyst performance with 5% w/w. (■) acid index, (●) FFA %, (▲) conversion of FFA (%)

Figure 8. Comparative conversion of FFA using the two catalyst. (■) H_2SO_4, (●) sulfated zirconia

ue of IA to 26.01 and increase the conversion of FFA to 86.10%. After 22 hours of reaction, increased conversion is not significant and the curve shows a constant tendency. This behavior differs from that found by Amin *et al* [32] in which the methyl ester conversion reached about 75% in 180 minutes, although the reactions were carried out at temperatures above 120 ° C.

The performance of the catalyst of sulfated zirconia was compared with a homogeneous acid catalyst, H_2SO_4, from esterification of oleic acid in which the value of the FFA and the conversion of this was measured. The esterification was carried out between 50-55 °C for 120 minutes. Both catalysts were added in a proportion of 5.1% by weight relative to the weight of oleic acid. Figure 7 shows that the H_2SO_4 content of free fatty acids decreased from 99.7 to
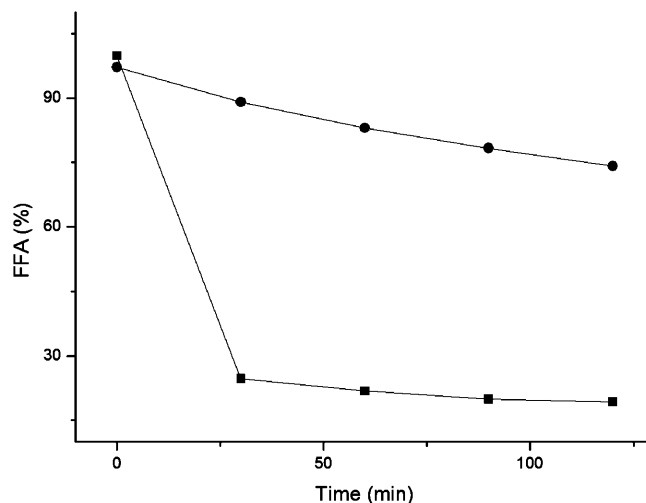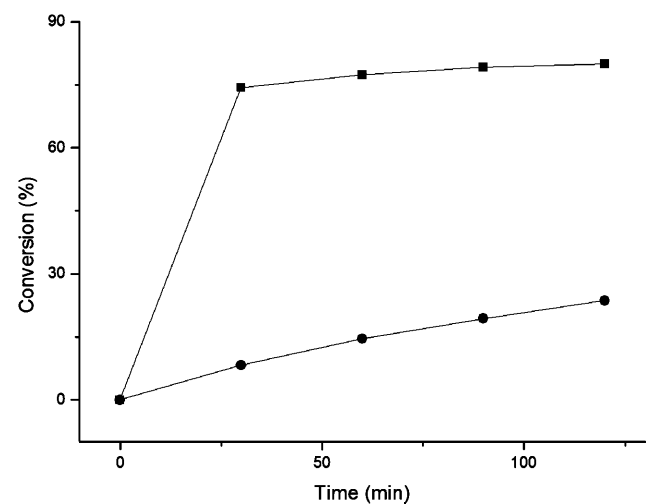
19.26% while the sulfated zirconia only decreased to 74.17%. This is mainly because the H_2SO_4 is maintained in a homogeneous phase in the reaction medium, in contrast to the heterogeneous phase in that sulfated zirconia is maintained. Similarly, with respect to conversion of FFA with H_2SO_4 catalyst 79.97% conversion is reached, while with the sulfated zirconia a conversion of only 23.67% is reached. Figure 8 shows the comparative data conversion of FFA for both catalysts.

4. CONCLUSIONS

The calcination of the catalyst, after having been sulfated, did not improve the production efficiency of methyl esters. This is attributed to a possible loss of sulfur in the high temperature calcination. Higher conversions of methyl esters were obtained with the uncalcined catalyst, which means lower energy consumption in the

synthesis of the catalyst. The heterogeneous catalyst of sulfated zirconia requires long times of over 50 hours to achieve conversions of 86% FFA. Furthermore, it was observed that the efficiency of sulfated zirconia is very low compared with that observed for the homogeneous catalyst H_2SO_4 as this achieved a conversion of FFA to 77% only in the first 30 minutes of reaction, while sulfated zirconia only reached a conversion to 13% of FFA. However, these preliminary results can be used in further studies to optimize catalyst efficiency.

5. ACKNOWLEDGEMENT

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