

Assessing the Activity of Solid-Supported SnCl_2 Catalysts on the Oleic Acid Esterification for Biodiesel Production

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Abstract

The search for cleaner methodologies has forcing the chemical industry to seek environmentally benign acid catalysts. $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ is an affordable commercially Lewis acid, water tolerant and easy to handling, cheaper, and less corrosive. Recently, we have demonstrated that it is an efficient catalyst to produce biodiesel in homogeneous catalysis conditions. In this work, we have supported $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ over different solid matrix (i.e., such as SiO_2 , Nb_2O_5 and ZrO_2) and evaluated its catalytic activity in FFA esterification reactions. In this case, the reaction occurs in heterogeneous phase bringing with itself all the pertinent advantages to this rational system as the best separation of products and reuse of the catalyst. It was appraised reaction parameters such as thermal treatment temperature nature of the support; leaching test was also accomplished.

Keywords: Esterification; Tin chloride; Free fatty acids; Heterogeneous catalysis

Introduction

The exhaustion of the fossil petrol reserves, in combination with the environmental impact generated by the green-house effect gas emission has stimulated the search by alternative and renewable feedstock for energy production [1]. Besides this crescent demand, the industry chemistry and academy in all parts of world are developing environment friendly technologies for the production of alternative fuels [2]. Nowadays, the biodiesel is a “green” alternative fuel that has arisen as an attractive option, mainly because it’s less pollutant than fossil diesel and can be obtained from renewable sources. Currently, the biodiesel is manufactured from alkaline transesterification of edible or non-edible vegetable oils via a well-established industrial process [3,4]. However, there are serious drawbacks related to its conventional production process, such as a greater generation of effluents and salts from neutralization steps of the products and wastes, the use of non-recyclable catalysts and the incompatibility with acid raw material with high amount of FFA [4,5]. These important features have hardly affected the final cost to biodiesel production [6].

An interesting alternative for lower biodiesel price is produce it directly from low cost lipidic raw materials are normally rich in FFA [7]. It should be mentioned that even though traditional mineral acids are an inexpensive catalysts able to those processes, they are equally corrosive, are not reusable and results in a large generation of acid effluents which should be neutralized at the end of the reaction, leaving greater amount of salts to be disposed of into environment [7,8]. Therefore, to develop recyclable alternative catalysts for FFA esterification reactions presents in low cost feedstokes and food industry rejects can be an option strategically important, and undoubtedly can produce biodiesel at more competitive cost via a cleaner technology [9]. Recently, several works have been described the development of heterogeneous catalysts based on acids solids that appear to offer a good perspective to make the biodiesel production more environment friendly [10,11]. Nevertheless, serious technological drawbacks such as drastic conditions reaction, the rigorous control of raw material quality in relation to water content, beyond of the leaching catalyst provoked by presence of alcohol seems suggest that those process yet are hard to control.

Alternatively, to develop catalysts for the direct conversion into biodiesel of lipid wastes basically constituted of FFA, or yet for the pre-esterification of raw materials that have high acidity seem be also a challenge to be overcome [12]. Nowadays, the majority of the catalysts conventionally used in the FFA esterification reactions are Brønsted acids. However, features such the higher corrosive character besides greater generation of residues and salts compromises the use of these traditional catalysts [13]. Lewis acids can be interesting alternative catalysts for biodiesel production. However, their high cost, the manipulation difficult and the intolerance to water of compounds traditionally used such as BF_3 and others common reagents of organic synthesis, also does not favor the use of these latter in FFA esterification at industrial scale [14].

Particularly, we have concentrating efforts in developing an alternative esterification processes based on tin chloride, an simple, easily handling, water tolerant and inexpensive Lewis acid [15,16]. On the other hand, the SnCl_2 is also most attractive, because it is commercially available and easy to handle [17]. Moreover, its display remarkably low toxicity, is tolerant to water, economically cost effective, and can be used in recyclable processes [18]. Although Sn(II) catalysts have been used in homogeneous phase, they are though less corrosive than mineral acids [19]. In this work, the application of solid supported SnCl_2 catalysts on FFA esterification is described. Our intention was assess if supported tin(II) catalysts can be potentially used on direct conversion of FFA into biodiesel via ethanol esterification reactions. The reusability, the less corrosion, the mild condition reactions and the compatibility with ethanol, which is also a renewable raw material, comprise positive aspects of this process. Moreover, the stability and possibility of reuse of supported Sn(II) catalysts were investigate.

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Materials and Methods

Chemicals

All chemicals were purchased from commercial sources and used as received unless otherwise stated. Ethanol was acquired from Sigma-Aldrich (99.9% wt.). The tin(II) chloride dihydrate (SnCl₂·2H₂O; 99.5% wt.), niobium(V) oxide (Nb₂O₅), silicon(IV) oxide (SiO₂) and zirconium(IV) oxychloride octahydrate (ZrOCl₂·8H₂O) were purchased from Sigma Aldrich. Oleic acid (99% wt.) was obtained from Modern Chemistry (São Paulo, SP, Brazil).

Synthesis of supported tin(II) catalysts

The supported tin catalysts were prepared by impregnation method. SnCl₂·2H₂O alcoholic solutions were prepared using 10 ml of solution per gram of supported catalyst to obtain a concentration of SnCl₂ 10, 30 and 50% w/w. The support (SiO₂, Nb₂O₅ or ZrO₂) was added to the solution resulting in a suspension. The suspension was kept under constant stirring and evaporated at 80 degrees until complete dryness. Then the solid obtained was pulverized and dried at 100 degrees in an oven for 3 hours. The supported tin samples were divided into two portions and each was thermally treated at 200 or 300 degrees for 4 h.

Catalytic runs

Catalytic tests were conducted in a 50 mL three-necked glass flask, equipped with sampling system, a reflux condenser, in thermostatic bath and under magnetic stirrer. In all runs, ethanol was used in large excess for to shift the equilibrium towards the esters formation. In a typical experiment, oleic acid (ca. 1.00 mmol) was dissolved in 7 ml (ca.155.0 mmol) of ethanol, which were heated to the reflux temperature. After the addition of catalyst (ca. 50.0 mg) the reaction was started.

Reaction monitoring and identification of products reaction

The reaction progress was continuously monitored taking aliquots at regular intervals of 30 min and analyzing them via gas chromatography. The temperature program was as follows: 150°C for 1 min, 10°C/min up to 240°C, hold time of 5 min. Both injector and FID detector were kept at 250 and 280°C, respectively. The GC was fitted with a DB5 capillary column (0.25 μm × 0.25 mm × 30 m) and reaction yields were calculated by matching the areas of the esters GC peaks into the corresponding calibration curves. Analyses were carried out in a Shimadzu GC gas chromatograph coupled with a MS-QP 2010A mass spectrometer (Tokyo, Japan), fitted with a DB5 capillary column (0.25 μm × 0.25 mm × 30 m), with helium as the carrier gas at 2 mL/min. The temperature program was as follows: 150°C for 1 min, 10°C/min up to 250°C, hold time of 5 min. The GC injector and MS ion source temperatures were kept at 250 and 260°C, respectively. The MS detector was operated in the EI mode at 70 eV, with a scanning range of *m/z* 50-400.

Recovery and reuse of heterogeneous catalysts

After reaction end, the solid catalyst was filtered, washed and dried in oven. Immediately, it was reused in another run without any previous activation.

Determination of the Sn content

The acid digestion and measurements of tin content was done in according with literature [18]. Typically, a mix of HNO₃/H₂O₂ solutions was added to 0.1 gram of sample drop by drop. Afterward, the sample was gently swirled for a complete homogenization. After transfer to a tube, the digestion was performed at microwave oven. The digestion parameters as following: 1000 Watt; 80°C/ 5 min; 10°C min⁻¹ to 200°C; time hold by 20 min. After cooling the rotor until the solution

reaches room temperature, open the vessel and transfer the solution to a volumetric flask. The concentration of tin was determined by AAS analysis (Varian Spectra A- 200 model), in a spectrophotometer equipped with broker-absorbing substance. The samples were pumped into flame: acetylene-nitrous oxide. The parameters used were λ (235.5 nm), flame (C₂H₂/N₂O) and detection limit (1 ppm). A calibration curve was built based on a stock standard solution of Tin (Merck, Germany).

Results and Discussion

General aspects

Initially, the catalytic activity of the stannous chloride was compared with the activity of others typical tin catalysts. It can be seen (Figure 1) that although a large excess of ethanol has been used, the reactions achieved poor conversions when the catalysts with low activity were present. Indeed, the insoluble oxide catalysts (i.e., SnO, SnO₂) were the less active. These commercial oxides have low surface area and consequently are few active. For this reason, they are generally used supported on the matrix with higher surface area [20].

However, it should be noted the significant activity of tin(II) sulfate, which was almost insoluble; literature suggests that sulfate ion exert an electron withdrawing effect on the tin increasing its Lewis acidity [21]. Conversely, although totally soluble, the tin(II) acetate was almost inactive. Probably, the presence of bidentate ligand on tin(II) hampered the activation of oleic acid carbonyl group, making difficult its attack by the hydroxyl group of ethyl alcohol. Notably, the SnCl₂ was the most active catalyst. This result is in agreement with literature [22]. This support the choice of SnCl₂ as dopant to synthesizes heterogeneous catalysts. In next sections, the results of oleic acid esterification with ethyl alcohol over different supports (i.e., ZrO₂, Nb₂O₅ and SiO₂) treated thermally at temperatures of 100, 220 and 300 degrees are displayed. In each case are also presented the results of the reaction without catalyst, only in the presence and support catalyzed by SnCl₂ in homogeneous phase.

Esterification of oleic acid over SnCl₂/ ZrO₂: Effect of the thermal treatment

The temperature of thermal treatment was the parameter selected for an adequate comparison between the catalytic activities of different tin(II) composites. Temperatures higher than 300°C may reduce the surface area of support. For this reason, and because this parameter will not discuss herein, the temperatures selected were 100, 200 and 300°C. The kinetic curves are displayed in Figure 2. Even being carried

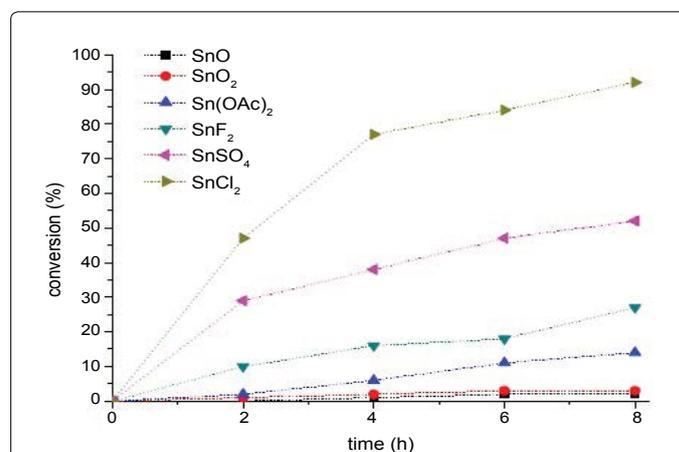
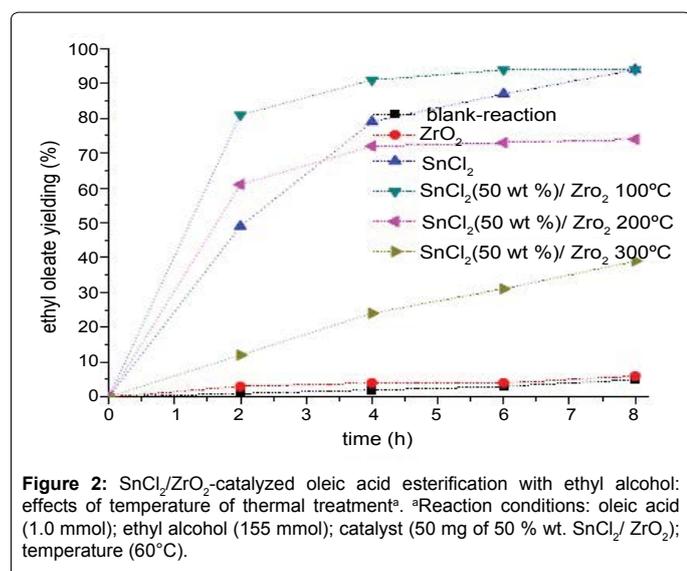


Figure 1: Tin(II)-catalyzed oleic acid esterification with ethyl alcohol^a. ^aReaction conditions: oleic acid (1.0 mmol); ethanol (155 mmol); tin catalyst (0.1 mmol) 60°C.



out with a large excess of ethyl alcohol, the reaction-blank achieved only a poor yielding (ca. 5%). In the presence of ZrO₂ support, the esterification of oleic acid reached <10% of conversion. It can be attributed to the presence of the weak Brønsted acid sites present in the zirconia [23]. The results obtained in SnCl₂ (50 wt.)/ZrO₂-catalyzed reactions (Figure 2) showed that the thermal treatment temperature was an extremely important factor for the activity of tin composites. The catalyst treated to 100C temperatures gave best results followed by the one treatment at 200°C. Indeed, the SnCl₂ (50 wt.)/ZrO₂ 100°C solid catalyst was more active than soluble SnCl₂. Conversely, for the composite treated to 300°C, the lowest conversion was achieved (ca. 43%). The literature describes that at temperatures higher than 80°C the SnCl₂·2H₂O loses its 2 water molecules [24]. Therefore, as water has negative contribution in esterification reaction (i.e., it is a by-product and can shift equilibrium toward reactants) the catalysts treated to 100°C was thus more active than hydrate tin chloride, even being this latter a homogeneous catalyst. The catalyst treated to 200 C displayed a high initial reaction rate, however, at reaction end, the conversion reached was lower than one obtained by the SnCl₂. Probably, at this temperature, the catalyst comprises of mixture of SnCl₂ and SnO, as may be inferred if we comparing the color of samples of these composites (Figure 3).

Figure 3 shows that the composite SnCl₂ (50 wt.)/ZrO₂-100°C has white coloration, while the composite treated to 200°C darkens, possibly suggesting that there is the formation of SnO, which has brown color. When the sample is heated to 300°C the composite to turn white, suggesting that prevails such as SnO₂ species (Figure 3). However, when highest treatment temperatures was used (i.e., 300°C), a drastic drop on yielding happened; only 44% was reached. This fact could be triggered by the transformation of tin(II) chloride to tin(IV) oxide, which has low catalytic activity (see Figure 3). Therefore, it can be seen that the performance of zirconium-supported SnCl₂ undergoes a strong influence of the thermal treatment, and the best and worst results were observed for the catalysts treated to 100 and 300°C, respectively.

Esterification of oleic acid over SnCl₂/Nb₂O₅: Effect of the thermal treatment

When we analyzing the reactions carried over tin/ niobia catalysts, we can realize that thermal treatment temperature plays a

crucial role on activity of these composites. The following increasing trend of activity was observed: SnCl₂/Nb₂O₅ (100°C)>SnCl₂/Nb₂O₅ (200°C)>SnCl₂/SnCl₂/Nb₂O₅ (300°C) (Figure 4). The tendency observed was similar to that verified in reactions with zirconia supported catalysts. The alone support had negligible activity and once more, the treatment temperature drastically affected the activity of supported catalysts.

Esterification of oleic acid over SnCl₂/SiO₂: Effect of the thermal treatment

The tendency to low conversions for the composites treated to 300°C temperature continues, therefore, low conversions were obtained as confirming the results shown in Figure 5. It is suggestive that part of the tin chloride is truly becoming tin(IV) oxide. As observed for the other supports, the reaction catalyzed by the composite treated to 100°C achieved the highest ethyl oleate yielding (i.e., SnCl₂ (50 wt.)/SiO₂ 100°C).

Assessment the stability of solid supported tin(II) catalysts

The catalysts treated to 100 and 300 degrees were selected to investigate the leaching. Figures 6-8 displays the main results. To do it, the reactions were carried by 30 minutes and afterward, the catalysts were filtered and the reaction monitored during 8 hours without the presence of catalyst. The Figure 6a and 6b shows that Sn(II) cations are leaching to the reaction solution, because even after the catalyst was removed, the reaction had its progress continued, mainly for the SnCl₂/Nb₂O₅ catalyst treated to 100°C. The stability of tin/zirconia supported



Figure 3: Samples of commercial and synthesized SnCl₂/ZrO₂ supported catalysts^a. ^aFrom left to right: tin(II) chloride dihydrate, tin(II) oxide, tin(IV) oxide, zirconium oxide, and composites SnCl₂ (50 wt. %)/ZrO₂-100°C, SnCl₂ (50 wt. %)/ZrO₂-200°C and SnCl₂ (50 wt. %)/ZrO₂-300°C, respectivamente.

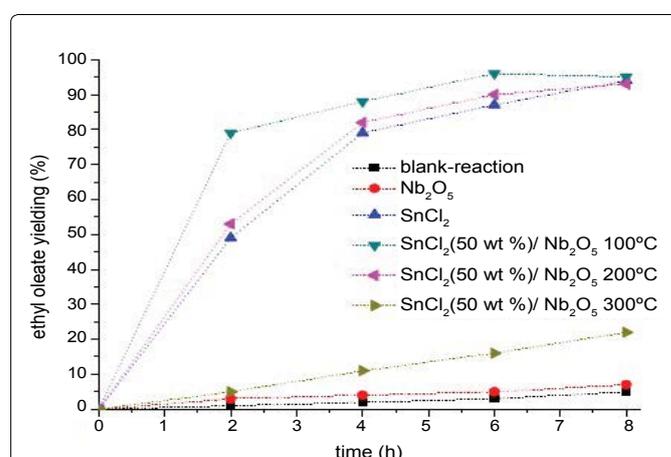


Figure 4: SnCl₂/Nb₂O₅-catalyzed oleic acid esterification with ethyl alcohol: effects of temperature of thermal treatment^a. ^aReaction conditions: oleic acid (1.0 mmol); ethyl alcohol (155 mmol); catalyst (50 mg of 50% wt. SnCl₂/Nb₂O₅); temperature (60°C).

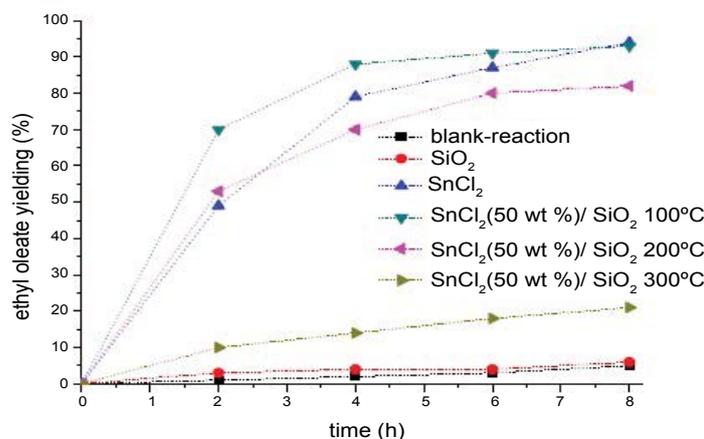
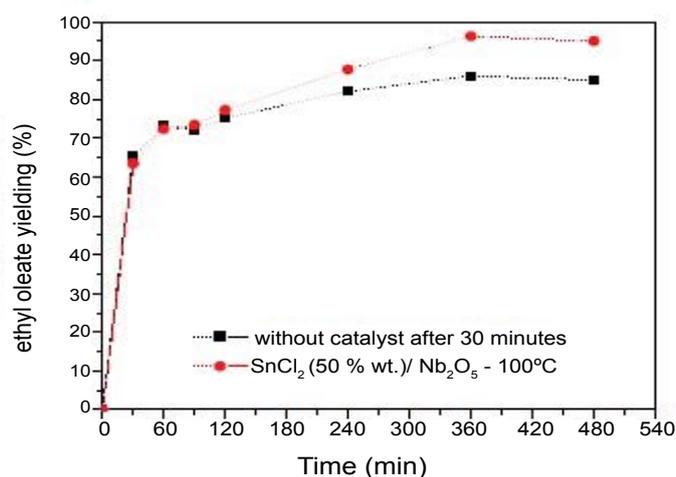
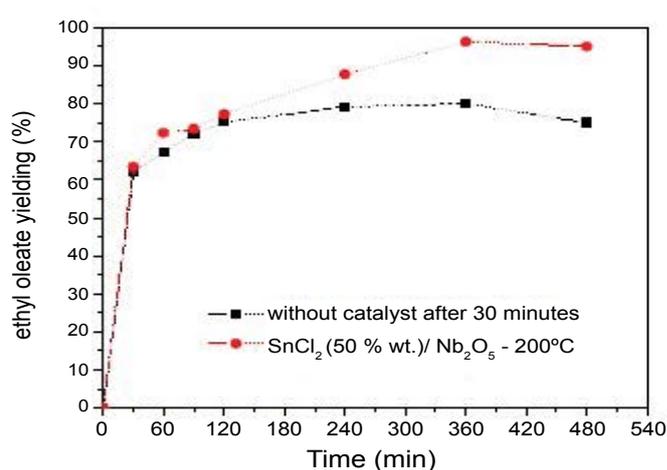


Figure 5: SnCl₂/SiO₂-catalyzed oleic acid esterification with ethyl alcohol: effects of temperature of thermal treatment^a. ^aReaction conditions: oleic acid (1.0 mmol); ethyl alcohol (155 mmol); catalyst (50 mg of 50% wt. SnCl₂/SiO₂); temperature (60°C).



(a)



(b)

Figure 6: SnCl₂/Nb₂O₅-catalyzed oleic acid esterification with ethyl alcohol: assessment of catalyst leaching^a. ^aReaction conditions: oleic acid (1.0 mmol); ethyl alcohol (155 mmol); catalyst (50 mg of 50% wt. SnCl₂/ Nb₂O₅); temperature (60°C).

solid catalysts in the reaction medium was also low as to that verified for the tin/ niobium catalysts (Figure 7). Conversely, an auspicious result was obtained for the silica supported catalyst treated to 200°C; almost no conversion was observed in the reaction after the removing of solid catalyst (Figure 8). Therefore, this catalyst was selected to be recovered and reused in consecutive catalytic tests (Figure 9).

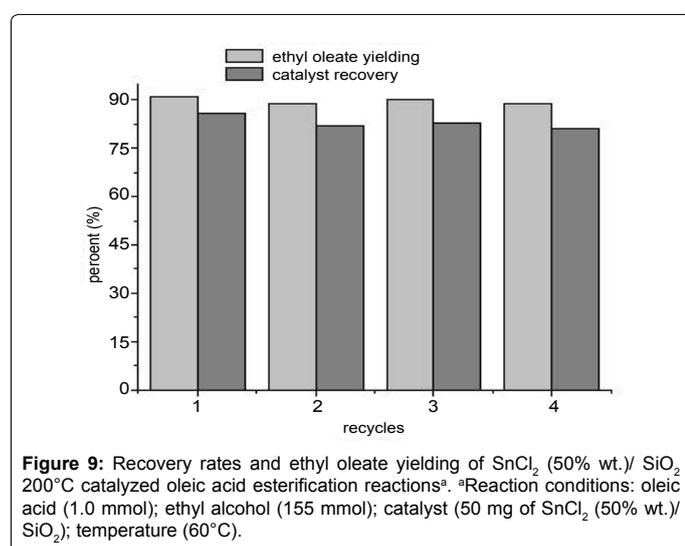
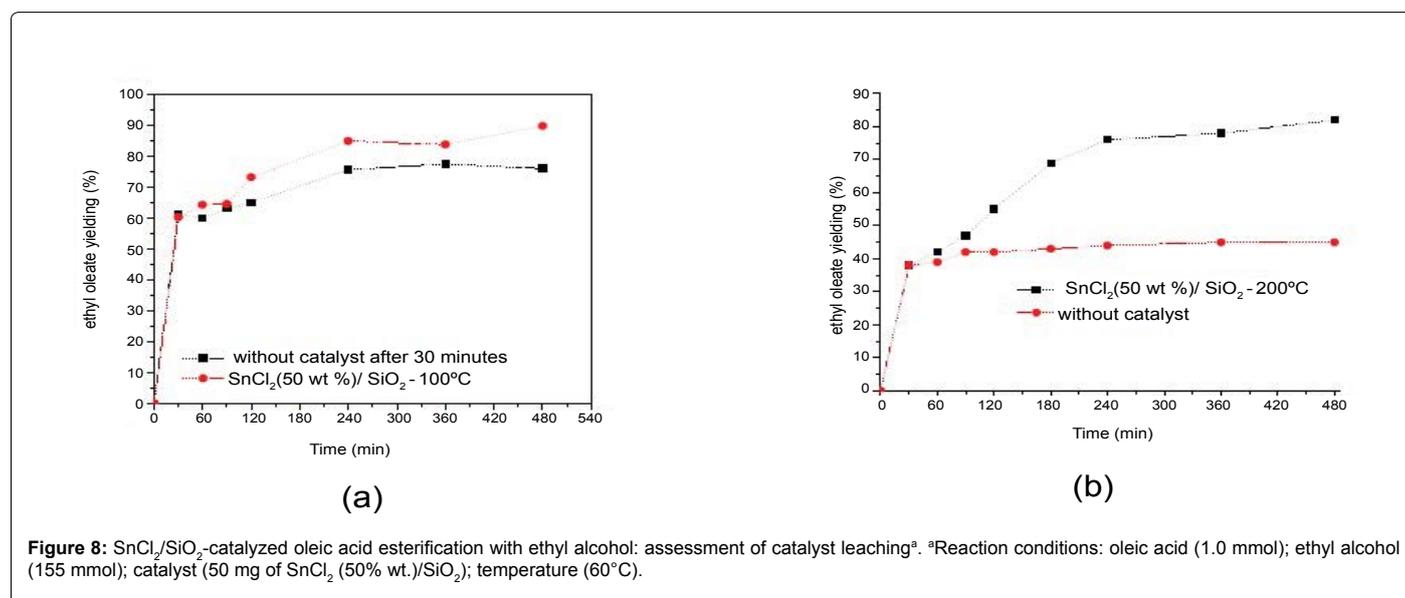
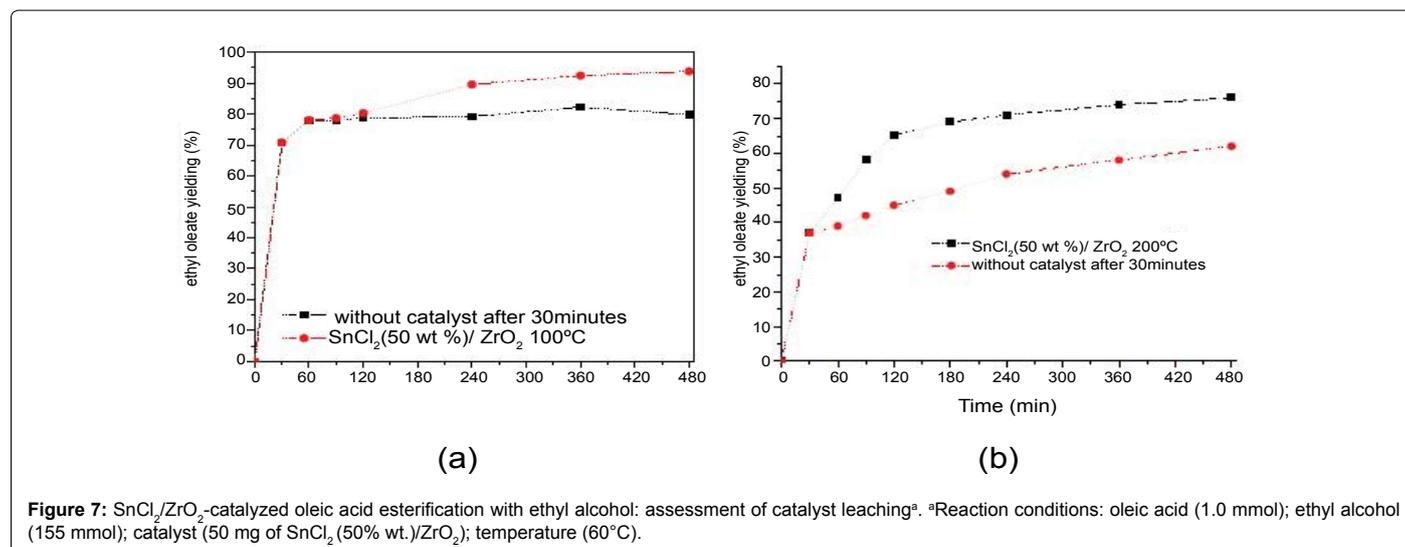
Heterogeneous catalysts have the main advantage over homogeneous catalysts the possibility of recovery and reuse. However, the leaching of the active component of the catalyst can cause its deactivation and contaminate the products. So, recovery and reuse tests should be performed only for catalysts that do not leach easily. The results show that the catalytic activity of SnCl₂ (50% wt.)/ SiO₂ 200°C) suffered a decrease after three cycles of recovery/reuse (Figure 9).

The catalyst recovery rate varied between 86 and 82%, but, as we have seen, the SnCl₂ (50% wt.)/ SiO₂-200°C does not suffer a significant

leaching process (Figure 8b). Thus is possible that some catalyst have been lost in steps of centrifugation, filtration or washing of catalyst.

FTIR spectra of the solid-supported tin(II) catalysts: SnCl₂/ZrO₂, SnCl₂/Nb₂O₅ and SnCl₂/SiO₂: Effect of thermal treatment

The supported tin(II) composites were analyzed by FT-IR aims to assess if the presence of tin(II) when the support were thermally treated had provoke any significant change. FT-IR spectra were obtained from all samples with different content of Sn(II) (ca. 30 and 50% w/w). The FT-IR spectra of solid supported catalysts were measured in the wavenumber range between 500- 4000 cm⁻¹ (Figure 10). In general, all bands were overlapping by support bands. No significant changes could be observed after thermal treatment to 300 degrees temperature. At the same time, the characteristic bands of Sn-O or Sn-Cl were absent. Indeed, literature describes that stretching frequencies of Sn-



Cl bond are commonly observed between 325 and 384 cm⁻¹ [25]. The characteristic bands of vibration of Sn-O are typically found at 500-523 cm⁻¹ or 509 to 581 cm⁻¹ wavenumbers [26,27]. However, these regions were overlapped by the support bands.

Determination of tin load in the solid supported catalysts

AAS analyses confirmed that the tin content in all samples synthesized, regardless support employed (Table 1).

Composite	Theoretical amount (wt. %)	Measured amount (wt. %)
SnCl ₂ /SiO ₂	30.0	29.3
SnCl ₂ /ZrO ₂	30.0	30.2
SnCl ₂ /Nb ₂ O ₅	30.0	29.4

^aAnalysis conditions: See Materials and Methods (Determination of the Sn content)

Table 1: AAS analyses of samples of solid supported tin catalysts^a.

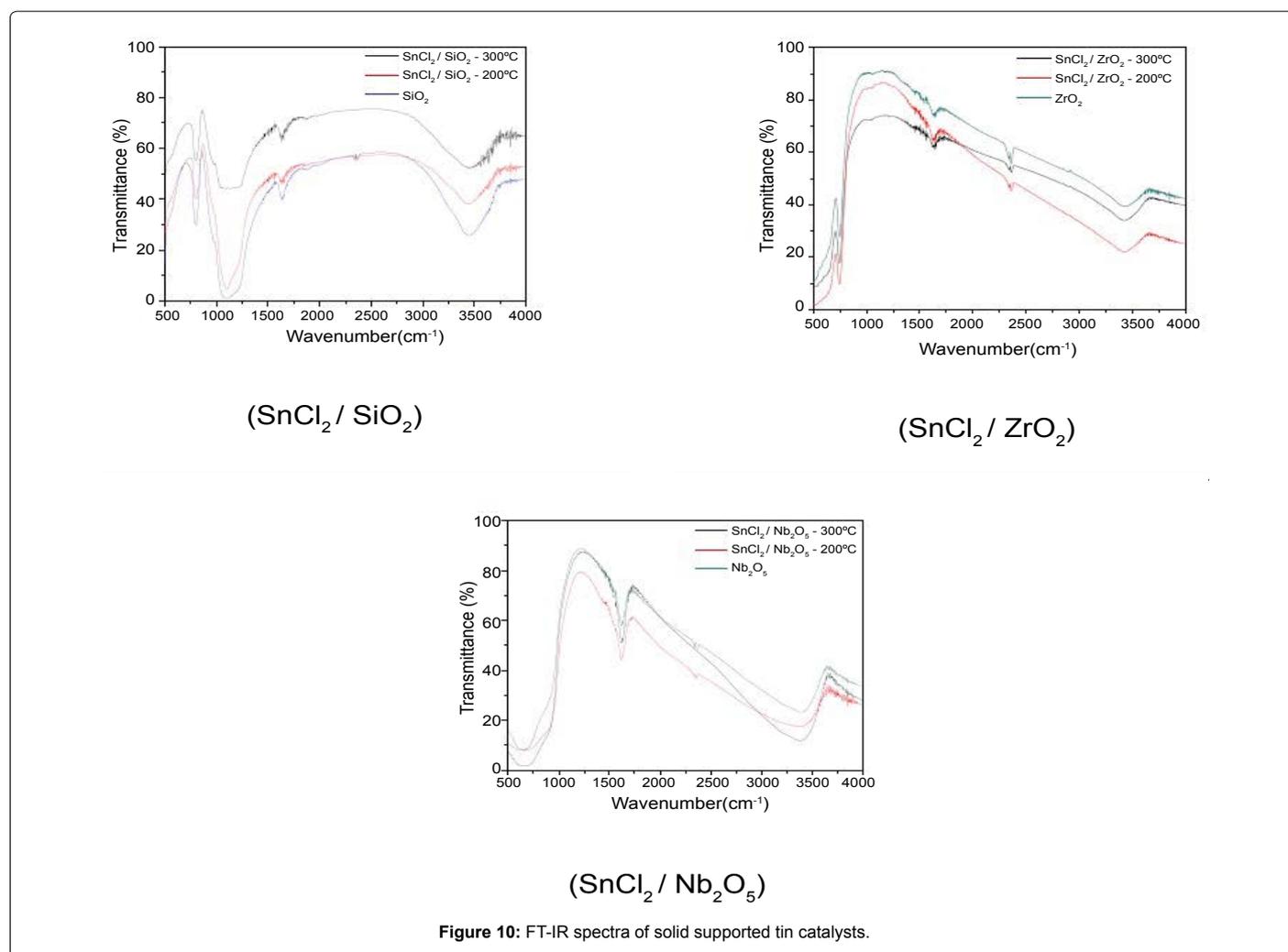


Figure 10: FT-IR spectra of solid supported tin catalysts.

Conclusion

The method used was efficient for the impregnation of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in different support. The thermal treatment had a crucial role on catalytic activity of supported tin composites. In general, high yielding were achieved when the catalyst was treated to 100°C or 200°C . However, in these cases, a leaching of active phase was responsible by the activity, regardless support employed. When the temperature of treatment was 300°C , the change on the coloring of support indicated that the tin was converted to SnO_2 or SnO . Previous tests had supported that the SnO and SnO_2 pure solids were less active catalysts in these reactions. Nonetheless, the results obtained in esterification reactions in heterogeneous phase were highly promising; in the case of $\text{SnCl}_2/\text{SiO}_2$ - 200°C ; this was the most efficient and stable catalyst, and was recovered and reused without loss activity.

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References

1. Santacesaria E, Martinez-Vicente G, Di Serio M, Tessera R (2012) Main technologies in biodiesel production: State of the art and future challenges. *Catal Today* 195: 2-13.
2. Leung DY, Wu X, Leung MKH (2010) A review on biodiesel production using catalyzed transesterification. *Appl Energy* 87: 1083-1095.
3. Singh AP, Chouhan AKS (2011) Modern heterogeneous catalysts for biodiesel production: A comprehensive review. *Renew Sust Energ Rev* 15: 4378-4399.
4. Lopez DE, Goodwin JG, Bruce DA, Lotero E (2005) Transesterification of triacetin with methanol on solid acid and base catalysts. *Appl Catal A* 295: 97-105.
5. Semwal S, Arora AK, Badoni RP, Tuli DK (2011) Biodiesel production using heterogeneous catalysts. *Bioresour Technol* 102: 2151-2161.
6. Su F, Guo Y (2014) Advancements in solid acid catalysts for biodiesel production. *Green Chem* 16: 2934-2957.
7. Zheng S, Kates M, Dub MA, McLean DD (2006) Acid-catalyzed production of biodiesel from waste frying oil. *Biomass Bioenergy* 30: 267-272.
8. Di Serio M, Tesser R, Dimiccoli M, Cammarota F, Nastasi M, et al. (2005) Synthesis of biodiesel via homogeneous Lewis acid catalyst. *J Mol Catal A* 239: 111-115.
9. Yunuskhani TM, Atabani AE, Badruddin IA, Badarudin MSA, Khayoon M, et al. (2014) Recent scenario and technologies to utilize non-edible oils for biodiesel production. *Renew Sust Energ Rev* 37: 840-851.
10. Endalew AK, Kiros Y, Zanzi R (2011) Inorganic heterogeneous catalysts for biodiesel production from vegetable oils. *Biomass Bioenergy* 35: 3787-3809.
11. Yan S, Di Maggio C, Mohan S, Kim M, Salley SO, et al. (2010) Advancements in Heterogeneous Catalysis for Biodiesel Synthesis. *Topic Catal* 53: 721-736.
12. Shahid EM, Jamal Y (2011) Production of biodiesel: a technical review. *Renew Sustain Energy Rev* 15: 4732-4745.
13. Di Serio M, Tesser R, Casale L, D'Angelo A, Trifuoggi M, et al. (2010) *Top Catal* 53: 811.

14. Lee AF, Wilson K (2015) Recent developments in heterogeneous catalysis for the sustainable production of biodiesel. *Catal Today* 242: 3-18.
15. Silva MJ, Cardoso AL, Neves SCG (2009) Kinetic Study of Alcoholysis of the Fatty Acids Catalyzed by Tin Chloride(II): An Alternative Catalyst for Biodiesel Production. *Energ Fuels* 23: 1718-1722.
16. Da Silva ML, Figueiredo AP, Cardoso AL, Natalino R, da Silva MJ (2011) Effect of Water on the Ethanolysis of Waste Cooking Soybean Oil Using a Tin(II) Chloride Catalyst. *J Am Oil Chem Soc* 88: 1431-1437.
17. Silva MJ, Cardoso AL, Neves SCG (2008) Esterification of Oleic Acid for Biodiesel Production Catalyzed by SnCl₂: A Kinetic Investigation. *Energies* 1: 79-92.
18. Silva MJ, Cardoso AL, Natalino R (2010) *I J Chem React Eng* 8: 1.
19. Goncalves CE, Laier LO, da Silva MJ (2011) Novel Esterification of Glycerol Catalysed by Tin Chloride (II): A Recyclable and Less Corrosive Process for Production of Bio-Additives. *Catal Lett* 141: 1111-1117.
20. Xie W, Wang H, Li H (2012) Silica-Supported Tin Oxides as Heterogeneous Acid Catalysts for Transesterification of Soybean Oil with Methanol. *Ind Eng Chem Res* 51: 225-231.
21. Pereira CO, Portilho MF, Henriques CA, Zotin FMZ (2014) *J Braz Chem Soc* 25: 2123.
22. Cardoso AL, da Silva MJ (2013) Novel and Highly Efficient SnBr₂-Catalyzed Esterification Reactions of Fatty Acids: The Notable Anion Ligand Effect. *Catal Lett* 143: 1240-1246.
23. Peng G, Wang X, Chen X, Jiang Y, Mu X (2014) Zirconia-supported niobia catalyzed formation of propanol from 1, 2-propanediol via dehydration and consecutive hydrogen transfer. *J Ind Eng Chem* 20: 2641-2645.
24. Al-Gaashani R, Radimana S, Tabet N, Dauda AR (2012) *Mat Science Engin B* 177: 462.
25. Taimsalu P, Wood JL (1984) *Spectrochimica Acta* 20: 1043.
26. Abu-Samn RH (1983) *J Chem Soc Pak* 5: 23.
27. Nath M, Pokharia S, Song X, Eng G, Gielen M, et al. (2003) *Appl Organomet Chem* 17: 305.