

Review Article

Heterogeneous Tin Catalysts Applied to the Esterification and Transesterification Reactions

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The interest in the development of efficient and environmentally benign catalysts for esters synthesis has increased exponentially, mainly due to the demand for biodiesel. In general, fatty esters are used as bioadditive, cosmetic ingredients, polymers, and, more recently, biofuel. Nevertheless, most of the production processes use nonrecyclable and homogenous alkaline catalysts, which results in the reactors corrosion, large generation of effluents, and residues on the steps of separation and catalyst neutralization. Heterogeneous acid catalysts can answer these demands and are an environmentally benign alternative extensively explored. Remarkably, solid acid catalysts based on tin have been shown highly attractive for the biodiesel production, mainly via FFA esterification reactions. This review describes important features related to be the synthesis, stability to, and activity of heterogeneous tin catalysts in biodiesel production reactions.

1. Introduction

The recent demand by alternative energy sources has made the biodiesel production a concern worldwide. Biodiesel is a renewable, biodegradable, and less polluting fuel than mineral diesel. It consists of ethyl (FAEE) or methyl esters of fatty acids (FAME), which are obtained from the triglycerides (TG) transesterification reactions present in vegetal oil (Figure 1), such as showed in Figure 1 [1].

Currently, most of the processes used for biodiesel production from the vegetable oils transesterification operating under homogeneous alkaline catalysis conditions (i.e., NaOH, KOH, or NaOCH₃) [1]. However, if a high content of FFA is present, homogeneous acid catalysts (i.e., H₂SO₄) are commonly applied on the steps of preesterification [1]. Both processes result in a large generation of wastewaters, residues, and salts formed during the catalyst neutralization and products recovery.

Currently, the greater part of the biodiesel consumed is produced by transesterification of expensive edible vegetable oils, which are responsible for 65% of the final price [2]. Alternative routes for the production of biodiesel where inexpensive feedstock such as animal fats, waste frying, and highly acid vegetable oil are an attractive option [3].

Nevertheless, these low cost raw materials are incompatible with alkaline catalysts due the formation of soaps, which hinders the separation of the FAME or FAEE from the glycerol, reducing consequently the biodiesel yields [4]. For these reasons, developing active catalysts for the FFA esterification reactions can contribute to making biodiesels more competitive regarding their cost and to making production more benign environmentally. In general, esterification reactions are faster than transesterification. This fact allows the replacement of the methyl alcohol, generally obtained from the fossil resources, by ethyl alcohol, a renewable raw material, on the FFA esterification reactions present in the low cost lipid feedstock (Figure 2).

Heterogeneous solid acid catalysts based technologies are a viable alternative to the traditional homogeneous acid-catalyzed processes and are attractive economically and friendly environmentally [5]. Actually, several reviews have reported the use of numerous solid acid catalysts based on resins, metal oxides, or supported transition metal compounds, on the biodiesel production processes [6–8].

Herein, we wish to describe the main advances obtained in the development of heterogeneous tin catalysts. The use of tin catalysts (i.e., metal oxides, anchored or supported metal-compounds) has assumed highlight position on biodiesel

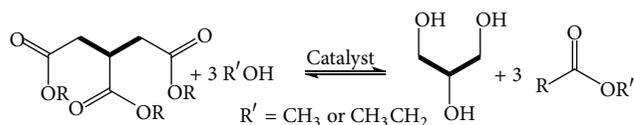


FIGURE 1: Transesterification of triglycerides with methyl or ethyl alcohol.

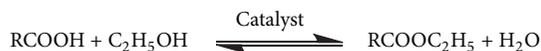


FIGURE 2: Esterification reaction of fatty acids with ethyl alcohol.

production, because they are cheaper than zirconium catalysts and equally active in FFA esterification or TG transesterification reactions [6–8].

2. Heterogeneous Solid Acid Catalysts Applied on the Biodiesel Production: A Brief Introduction

Various solid acid catalysts such as resins, sulfated tungsten and zirconium oxides, heteropolyacids, sulfated polyaniline, metal complexes, and zeolites have been employed as heterogeneous catalysts on the biodiesel production reactions [9]. In general, they are preferred over homogenous catalysts mainly because they can be easily isolated from reaction medium by filtration and easily reused. However, there are negative aspects that compromise the use of heterogeneous catalysts at the industrial scale [10]. A comparison between the heterogeneous solid acid catalysts and conventional homogeneous acid based on literature is summarized in Table 1 [11, 12].

Heterogeneous acid catalysts are synthesized as insoluble salts or solid matrices of high surface area containing an active dopant, in most times via sol-gel processes, precipitation or impregnation methods [12]. Currently, biodiesel production processes employing heterogeneous catalysis require more severe working conditions than those used in the homogeneous ones (i.e., higher temperature and pressure) [13]. Unfortunately, due to the presence of water or glycerol generated throughout the reaction, the leaching possibility is often present, which might contaminate the biodiesel and reduce the lifetime of the catalyst [14]. In conclusion, toward to be used on the biodiesel production at industrial scale, the heterogeneous catalyst should be active, stable throughout the reaction, easily recoverable, and reusable without activity loss [15].

Actually, the driving force to develop heterogeneous catalysts aims at the biodiesel production being cost saving and lowering the generation of environmentally undesirable wastes. These aspects can minimize the environmental impact of the processes and decrease the production costs, widening the scope of raw materials, a pivotal factor for biodiesel manufacturing [16].

3. Tin Catalyzed-Transesterification Reactions

Tin(IV) oxides loaded on the different oxides and activated at same temperature can result in solid acid catalysts with

different activities. For instance, over $\text{SnO}_2/\gamma\text{-Al}_2\text{O}_3$, a reasonable conversion of soybean oil into FAMES (ca. 68.5%) was obtained, whilst a conversion of 64.3% was reached using $\text{SnO}_2\text{-TiO}_2/\text{SiO}_2$ catalyst [17]. On the other hand, $\text{SnO}_2/\text{SiO}_2$ solid exhibited higher catalytic activity, giving a conversion of 81.6%.

Alternatively, the literature reports two strategies frequently employed toward the improvement of the performance of tin catalysts:

- (i) a treatment of tin oxides with sulfuric acid;
- (ii) incorporation of Lewis acid metals (i.e., Zn(II), Al(III), or Fe(III)) to the tin oxides.

Guo and coworkers studied the incorporation of aluminum in $\text{SO}_4^{2-}/\text{SnO}_2\text{-Al}_2\text{O}_3$, resulting into super acid catalyst, via co-condensation method [18]. They found that catalysts with Sn/Al ratio molar equal to 9:1 and calcined to 500°C temperature gave a highest activity than that of $\text{SO}_4^{2-}/\text{ZrO}_2\text{-Al}_2\text{O}_3$ and $\text{SO}_4^{2-}/\text{TiO}_2\text{-Al}_2\text{O}_3$ super acids [18]. Those authors, based on the FT-IR results, suggested that the active sites were due to the tin atoms chelated with sulfate groups; on the other hand, using thermogravimetric analyses, they also showed that by, introducing aluminum, the number of the sulfate groups attached on the surface increased, strengthening the activity of catalysts.

Lam and coworkers assessed the catalytic activity of $\text{SO}_4^{2-}/\text{SnO}_2\text{-SiO}_2$ in vegetal oil transesterification; after 3 hours, they achieved 92.3% of FAMES yield, performing reactions under the temperature of 150°C, 3 wt% of catalyst, and 15:1 methyl alcohol:oil molar ratio [19]. Those authors concluded that catalyst calcinations temperature was an essential aspect for those reactions: at low calcination temperatures (i.e., 200°C), the catalyst was not crystallized and remained in gel form, whereas, at high temperature (i.e., 500°C), the catalyst collapsed due to loss of sulfate group. The optimum calcination temperature was 300°C [19].

In this same study, BET surface area and crystal size of sulfated tin oxide catalysts were determined. In addition, the activation energy of the NH_3 desorption super acid sulfated tin oxide catalyst (Table 2) was determined.

The activation energy of the NH_3 desorption gives a measurement of acid strength of catalyst. Expectedly, it was found that $\text{SO}_4^{2-}/\text{SnO}_2\text{-SiO}_2$ (300°C) catalyst with the highest surface area and NH_3 desorption activation energy was the most active. Whereas the lower values for activation energy and surface area were shown by the least active catalyst (i.e., SnO_2).

In 2010, Lam and Lee investigated the cosolvent effect in transesterification reactions catalyzed by $\text{SO}_4^{2-}/\text{SnO}_2\text{-SiO}_2$ super acids [20]. They verified that the employment of THF as cosolvent improved the FAME yield; the reaction conditions were temperature of 150°C, 15:1 methyl alcohol:oil molar ratio, and catalyst loading of 6% wt. Those authors assessed the catalytic activity of $\text{SO}_4^{2-}/\text{SnO}_2\text{-SiO}_2$ super acid tin oxide in the presence of ethyl alcohol; the best result was achieved using an ethyl alcohol:oil ratio molar on the range of 9–6:1, with 6% wt. catalyst and temperature of 150°C (i.e., 81.4% FAME after 1 h reaction) [21].

TABLE 1: Comparison between homogeneous and heterogeneous catalysts employed in the transesterification reactions [11, 12]^a.

Factors	Heterogeneous catalysis	Homogeneous catalysis
Reusability	Easy	Non reusable
Operation	Continuous fix bed	Limited used of continuous methodology
Recovery	Easy	Brønsted acids are not recoverable
Reaction temperature	In general, high temperature can be used because the reactions occur under high pressure	Normally limited by boiling point of the alcohol
Corrosiveness	In general, are few or noncorrosive	Brønsted acids are highly corrosive,
Environmental problems	Fewer problems of effluents disposal	Larger generation of effluent and neutralization residues
Water sensibility	The catalyst is leached	More water tolerant

^aThese data were adapted from references [11, 12].

TABLE 2: Activation energy for NH₃ desorption, BET surface, and crystal size for super acid sulfated tin oxide catalysts [19]^a.

Catalyst activation	Activation energy (kJ/mol)	Correlation factor (R^2)	BET (surface area)	Crystal size (nm)
SnO ₂	5.69	0.9540	8.32	60.7
SO ₄ ²⁻ /SnO ₂ , 300°C	7.25	0.9687	6.77	42.9
SO ₄ ²⁻ /SnO ₂ , 400°C	7.18	0.9715	—	59.6
SO ₄ ²⁻ /SnO ₂ , 500°C	6.01	0.9877	—	62.0
SO ₄ ²⁻ /SnO ₂ -SiO ₂ , 300°C	9.40	0.9991	13.90	47.7
SO ₄ ²⁻ /SnO ₂ -Al ₂ O ₃ , 300°C	7.51	0.9925	14.04	45.4

^aNH₃-TPD patterns for different samples of catalyst at a ramping rate of 10°C min⁻¹ which allowed calculating the NH₃ desorption activation energy (adapted from [19]).

Jitputti and coworkers investigated the catalytic activity of acid and basic solids catalysts (i.e., ZrO₂, ZnO, SO₄²⁻/SnO₂, SO₄²⁻/ZrO₂, KNO₃/KL zeolite, and KNO₃/ZrO₂) for transesterification of crude palm oil and crude coconut oil with methyl alcohol [22]. The reactions were heated to 200°C and carried out with 1 wt.% catalyst content, 50 bar pressure, and 6:1 of methanol/oil ratio in a high pressure reactor. After 1 h reaction time, activity of solid catalysts for crude palm oil transesterification was in the order of SO₄²⁻/ZrO₂ > SO₄²⁻/SnO₂ > ZnO > KNO₃/ZrO₂ > KNO₃/KL zeolite > ZrO₂. In the case of crude coconut oil, the catalysts activity was in the order of SO₄²⁻/ZrO₂ > SO₄²⁻/SnO₂ > ZnO > KNO₃/KL zeolite > KNO₃/ZrO₂ > ZrO₂.

The use of tin(II) oxide as heterogeneous catalyst on the soybean oil methanolysis was investigated by Abreu and coworkers; were obtained high conversion yields (up to 93% in 3 h), and was also possible to catalyst recycle without any activity loss (Table 3) [23].

Conversely, the use of mixed tin oxides with other Lewis acid metals has been rather described in the literature. Macedo and coworkers reported that composites oxides such as (Al₂O₃)_x(SnO)_y(ZnO) efficiently catalyzed the soybean oil transesterification reactions [24]. Those authors verified that (Al₂O₃)₃(SnO) and (Al₂O₃)₄(ZnO) catalyzed reactions reached conversions of 80%, after 4 hours of reaction at 60°C. Moreover, both catalysts showed high stability up to four cycles of reaction. However, they were active only on the transesterification reactions with methanol.

Zhai and coworkers studied the esterification and transesterification reactions over Fe₂O₃-doped sulfated tin oxide

catalysts [25]. Those authors assessed the recovery and reuse of the catalyst of Fe₂O₃-doped sulfated tin oxide. The addition of catalytic amounts of Fe₂O₃ to the sulfated tin oxide resulted in an augment on both the amount and acid sites strength, which makes the Fe₂O₃-doped catalysts more active than the undoped catalysts. As model reactions, the lauric acid esterification and the triacetin transesterification, were used both with methyl alcohol. The sulfated tin oxide catalyst containing 1.0% Fe₂O₃ exhibits the highest activity for biodiesel production reactions (Figure 3).

4. Tin Catalyzed-Esterification Reactions

The literature has reported several methods for sulfated metal oxides synthesis [26, 27]. Consequently, several techniques have been also used to characterize these acid solids. In particular, Furuta and coworkers using SnCl₄ and SnO₂ as precursors synthesized sulfated catalysts, after treatment with sulfuric acid, and assessed their catalytic activity on the esterification and etherification reactions [28]. Sulfated tin obtained by the route SnCl₄ was termed as STO-1 and by route SnO₂ as STO-2. Additionally, the sulfated zirconium catalyst (named SZ) was also synthesized. The main properties of these catalysts are shown in Table 4.

All catalysts were characterized by displayed tetragonal crystalline structure (Table 4). Tin catalysts obtained from the different precursors resulted in colors different solids (i.e., tin(IV) chloride and tin(IV) oxide resulted into yellow and white crystals, resp.). Finally, sulfated zirconium oxide catalysts have higher surface area and size of crystallite.

TABLE 3: SnO-catalysed soybean oil methanolysis [23].

Entry	Time (h)	Reaction yield (%)			
		First substrate charge	Second substrate charge	Third substrate charge	Fourth substrate charge
1	1	56.5	56.5	57.9	55.3
2	2	92.6			
3	3	94.7			

^aReaction conditions: CH₃OH : oil : catalyst molar ratio = 400 : 100 : 1; 80°C; 1000 rpm.

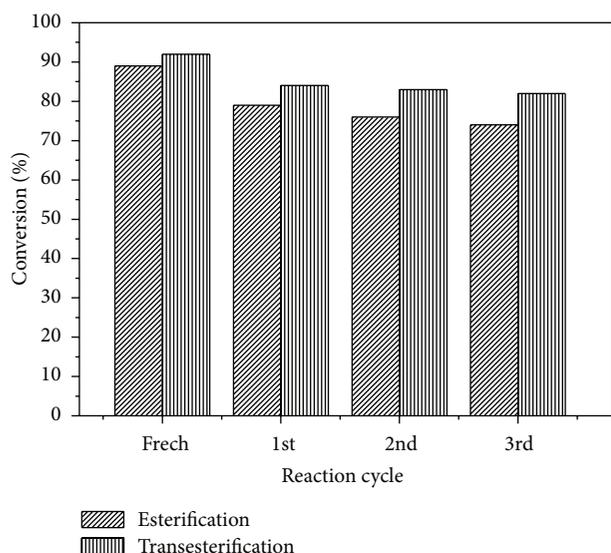


FIGURE 3: Reusability of the Fe₂O₃-doped sulfated tin oxide catalyst for the lauric acid esterification and triacetin transesterification reactions after 8 hours reaction per cycle [25]. (Reaction conditions: transesterification (0.25 g of catalyst, 5.675 g of triacetin, and 7.5 g of methanol, 8 h); esterification (0.16 g of catalyst, 4.167 g of lauric acid, and 10 g of methanol, 6 h); 60°C temperature in both reactions.)

Kinetic curves obtained from the octanoic acid esterification with methyl alcohol over sulfated tin and zirconium oxides catalysts, in the range of temperatures of 333 to 473 K, after 20 hours reaction are shown in Figure 4 [28].

The tin catalysts STO-1 and STO-2 were highly effective achieving high conversion values at lower temperatures. Those authors highlighted that the ability of sulfated tin oxide catalysts remains stable even in the presence of water generated throughout reaction. They emphasize that catalysts action mechanism consists probably in the interaction of carboxyl anion generated after the release of a carboxylic acid proton with metal oxide surface, favoring then ester formation [27, 28].

Khder and coworkers published a study where the effects of sulfate content and calcinations temperature on acidity, structure, and catalytic activity of sulfated tin oxides were assessed [29]. The model reaction selected was acetic acid esterification with amyl alcohol in the vapor phase (*ca.* 150 to 250°C). They synthesized numerous catalysts with different sulfate content using different thermal treatment temperatures (Table 5).

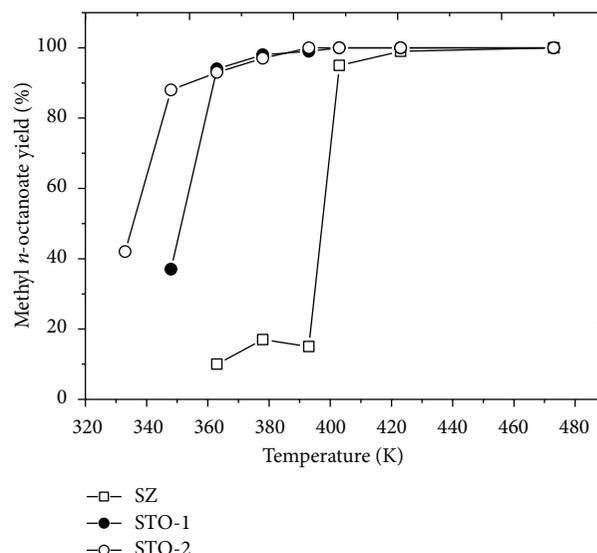


FIGURE 4: Octanoic acid esterification with methyl alcohol over STO-1 (●), STO-2 (○), and SZ (□) for 20 h [28]. (Reaction conditions: 4.0 g of catalyst, methanol : octanoic acid molar ratio 4.5 : 1.)

Regardless of the calcinations temperature, an increase in SO₄²⁻ ions load resulted in consequent increase in SnO₂ surface area. Conversely, an increase in the calcination temperature results in the decrease in the surface area of both catalysts SO₄²⁻/SnO₂ as well as SnO₂. Those authors suggested that the presence of sulfate ions in the surface of tin oxide prevents a higher reduction in surface area provoked by an increase in the calcinations temperature (Table 5).

Another important characteristic of solid catalysts is the nature and the amount of acidic sites. Several methods allow obtaining information about the nature, amount, and strength of acid sites on the solid catalyst surface. Potentiometric titration with n-butylamine allows estimating the total number of acidic sites (NAS) and their relative strength. On the other hand, via the FT-IR analysis of pyridine adsorption, it becomes possible to identify the Lewis and Brønsted acid sites. The acid properties of SO₄²⁻/SnO₂ catalysts synthesized at 400, 550, and 750°C were reported by Khder and coworkers and are displayed in Table 6 [29].

Table 6 reveals a notable effect provoked by both increase in the sulfate content and increase in the calcination temperature; these main effects are summarized as follows:

TABLE 4: Physical properties of sulfated metal oxides catalysts [28].

	S (wt.%)	BET surface area (m ² /g)	Crystalline (%)	Crystallite (nm)	Crystal Structure	Color
STO-1 (SnCl ₄)	2.0	142	88.2 (Sn)	3.2	Tetragonal	Yellow
STO-2 (SnO ₂)	2.6	151	88.2 (Sn)	3.5	Tetragonal	White
SZ	3.0	165	89.4 (Zr)	11.5	Tetragonal	White

TABLE 5: BET surface area measurements obtained from SO₄²⁻/SnO₂ catalysts synthesized at temperatures of 400, 550, and 750 °C [29].

SO ₄ ²⁻ content on SnO ₂ catalyst (wt.%)	surface area (m ² /g)		
	400 °C	550 °C	750 °C
0	61.2	46.3	20.4
1	69.9	52.3	28.5
5	76.2	64.7	36.5
15	90.2	80.8	57.2
20	101.3	87.3	62.5
30	129.5	100.8	70.1

- (i) an increase in the sulfate ions load resulted in the increase of the NAS (number of acid sites); nevertheless, this effect was noticed only in the temperature range of 400 to 550 °C; at higher temperature (i.e., 750 °C), a remarkable reduction in the sites of acid concentration (NAS) occurred, attributed by the authors to decomposition of these sulfate anions [29];
- (ii) in addition, this same increase in the sulfate ions load resulted in the increase of the strength of acid sites, comprised by increase verified in the potential measurements; on the other hand, once more these effects were not observed at the highest temperature [29];
- (iii) an increase in the calcinations temperature of 440 to 550 °C also increases the acidic sites strength, which again was not observed at the temperature of 750 °C [29].

The presence of Lewis and Brønsted acids sites was confirmed by two pyridine adsorption characteristics bands measured via FT-IR (i.e., 1445 and 1541 cm⁻¹, resp.). In compounds with a higher amount of SO₄²⁻ ions, it was observed that the band correspondent to Lewis acid sites had higher intensity, due to electron withdrawing effect of sulfate group, which thus increases the Lewis acidity of the Sn cations (Figure 5) [28].

Kdher and coworkers showed that the highest conversions obtained on acetic acid esterification with amyl alcohol occurred when the catalyst contained the highest NAS and the highest amount of sulfate ions (Figure 6) [29].

The reuse of the SO₄²⁻/SnO₂ catalyst test was also carried out by successive reactions at 250 °C, keeping the reaction

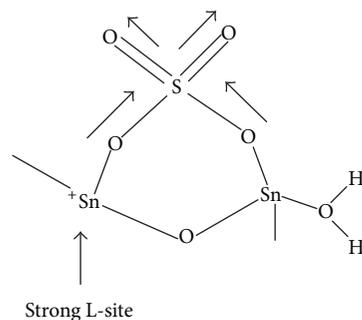


FIGURE 5: Electron withdrawing effect of sulfate group on sulfated tin oxide [28, 29].

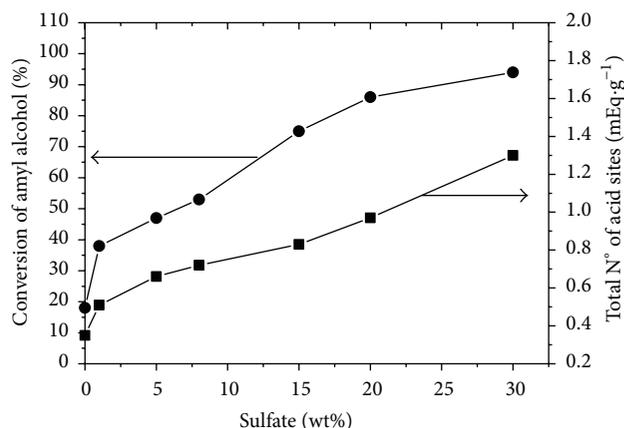


FIGURE 6: Effect of sulfate ions load and of NAS (number of acid sites) on acetic acid esterification reaction with amyl alcohol [29]. (Reaction conditions: runs were carried out in a pulse fixed-bed, vertical-flow type microreactor attached online with gas chromatography; amyl alcohol:HOAc molar ratio is equal to 2:1, 250 °C temperature.)

conditions constant. However, a step of reactivation with N₂ at temperature of 400 °C during 4 h was performed.

After recovery/reuse of successive cycles, there was a gradual deactivation of catalyst, provoked by leaching sulfate anions, which made the active acid sites weaker (Figure 7). A similar deactivation was also described in the literature for other sulfated metal oxides catalysts [28].

Furuta and coworkers measured the sulfated oxides acidity by means of desorption of ammonia temperature programmed (TPD). The measurements were made at temperatures of 373, 473, 573, 673, and 873 K. The nitrogen

TABLE 6: Acidic properties of the $\text{SO}_4^{2-}/\text{SnO}_2$ catalysts synthesized at temperatures of 400, 550, and 750 °C^a [29].

Calcination temperature (°C)	400		550		750		Pyridine loss (wt.%)	<i>t</i> (°C)
SO_4^{2-} content on SnO_2 catalyst (wt.%)	NAS (meq g ⁻¹)	E_i (mV)	NAS (meq g ⁻¹)	E_i (mV)	NAS (meq g ⁻¹)	E_i (mV)		
0	0.20	-84	0.35	+27	0.14	-127	0.210	424.5
1	0.31	-70	0.51	+194	0.24	-109	0.448	460.8
5	0.38	-61	0.66	+316	0.30	-97	0.667	468.4
15	0.50	-27	0.83	+479	0.42	-54	1.430	479.4
20	0.56	+9	0.97	+510	0.51	-41	1.841	482.0
30	0.68	+25	1.30	+555	0.60	-23	2.440	482.5

^aNAS: acid sites number; E_i : initial electrode potential indicates the maximum acid strength of the sites; *t*: pyridine loss temperature.

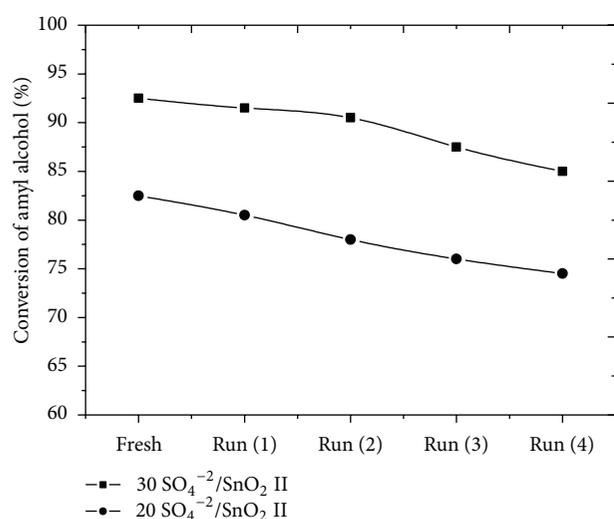


FIGURE 7: Reusability of $\text{SO}_4^{2-}/\text{SnO}_2$ catalysts at acetic acid esterification with amyl alcohol at 250 °C and 2 : 1 alcohol : acid molar ratio [29]. (Reaction conditions are similar to those in Figure 6.)

content that remained on the catalyst surface was determined by elementary analysis of nitrogen (Figure 8) [28].

Figure 8 shows that in, the range of 373–673 K, the amount of nitrogen adsorbed at the surface of the sulfated tin oxide catalysts remains constant, unlike what occurs with sulfated zirconium oxide catalysts. This means that tin catalysts present a much higher acidity in a wide temperature range [28]. Those authors described that tests with pyridine show noticeable difference between the surface acidity of the tin-based compounds and zirconium and that the same fact was also observed using ammonia as probe molecule. They concluded that (i) the sulfated tin oxides have high acidity and evenly distributed on its surface and (ii) the strength of the sulfated tin oxide acid sites is greater than that of sulfated zirconium oxide acid sites.

Sarkar and coworkers investigate the use of mesoporous catalysts based on SnO_2/WO_3 and used the oleic acid esterification with ethyl alcohol as model reaction [30]. A comparison with sulfuric acid was performed which showed that SnO_2/WO_3 catalyst was equally efficient in the reaction

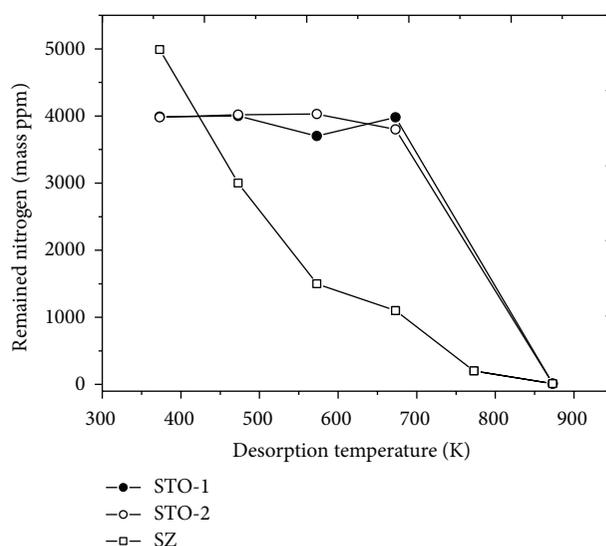


FIGURE 8: Ammonia-TPD profiles of STO-1 (●), STO-2 (○), and SZ (□) catalysts [28].

conditions studied (Figure 9) [30]. However, when the catalyst was used at lower concentration (i.e., 0.05 and 0.01% wt.), conversions obtained do not exceed 70%. The remarkable result of this work is that although solid catalyst, the SnO_2/WO_3 heterogeneous catalyst was as active as sulfuric acid, becomes thus an attractive option.

Recently, Moreno and coworkers also assessed the sulfated tin oxides catalytic activity on the FFA esterification reactions [31]. The synthesis of $\text{SO}_4^{2-}/\text{SnO}_2$ solid catalyst was made via precipitation of $\text{Sn}(\text{OH})_2 \cdot \text{H}_2\text{O}$, starting of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ with NH_4OH , filtration, and the solid impregnation with H_2SO_4 , which was thermally treated. Thermogravimetric analysis (TGA) and BET surface area data are summarized in Table 7 [31].

It was verified that the thermal treatment at higher temperatures results in the lowering of surface area. Those authors concluded that sulfate groups increase the specific surface area, stabilizing the mesostructured walls and increasing its thermal stability [31].

TABLE 7: Textural properties of the SnO₂ and SO₄²⁻/SnO₂ catalysts [31].

Entry	Catalyst-sulfate (% wt.) Temperature (K)	Specific surface area [m ² /g]	Pore volume [cm ³ /g]	Pore diameter [Å]	[TGA] mmol SO ₃ /g catalyst
1	SnO ₂ 0 773	62	0.051	70	
2	SO ₄ ²⁻ /SnO ₂ 0.45 773	99	0.054	25	0.201
3	SO ₄ ²⁻ /SnO ₂ 0.45 873	88	0.052	28	0.137
4	SO ₄ ²⁻ /SnO ₂ 0.30 773	87	0.050	28	0.194
5	SO ₄ ²⁻ /SnO ₂ 0.15 773	85	0.060	28	0.129
6	SO ₄ ²⁻ /SnO ₂ 0.45 673	92	0.060	26	0.194

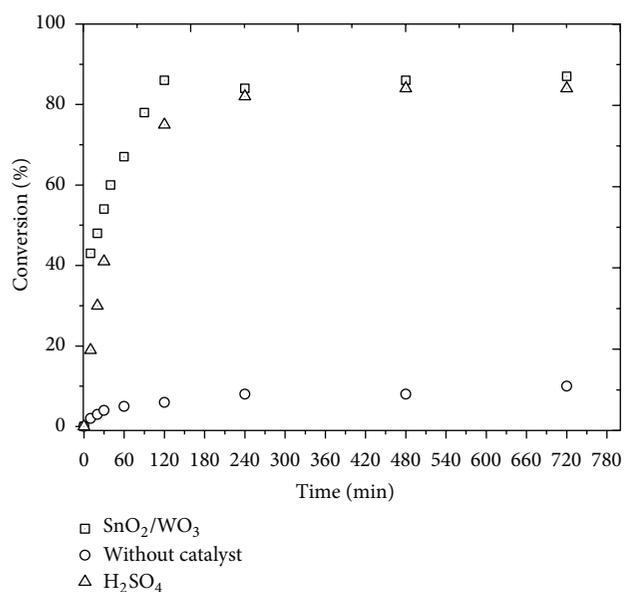


FIGURE 9: Oleic acid esterification in presence of 0.1g mesoporous calcined SnO₂/WO₃, in absence of catalyst and H₂SO₄ [30]. (Reaction conditions: oleic acid : ethyl alcohol molar ratio (1:120), temperature (80°C), 12-hour reaction.)

An important factor considered by the authors in that work is the relationship between the acidity (determined by titration method with n-butylamine using Hammett Indicators) and the solid catalyst activity. The results obtained from the oleic acid esterification with ethyl alcohol displayed in Figure 10 are useful for understanding this relation.

The catalyst with the highest NAS was more active; however, it does not have the highest surface area (Table 7);

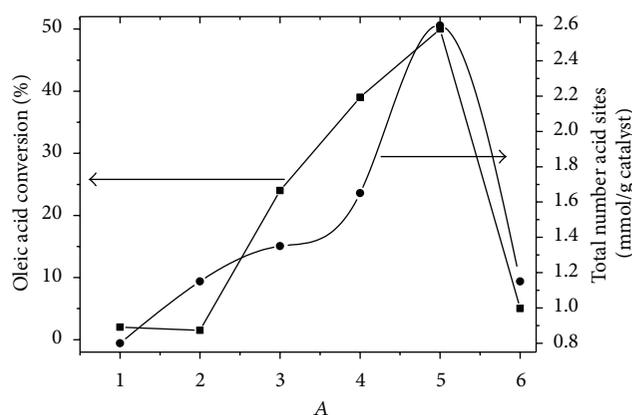


FIGURE 10: Effect of sulfated tin oxides NAS on the oleic acid conversion into ethyl oleate after esterification with ethyl alcohol; catalysts: (1) SnO₂—773 K, (2) SO₄²⁻/SnO₂—0.45—673 K, (3) SO₄²⁻/SnO₂—0.45—773 K, (4) SO₄²⁻/SnO₂—0.45—873 K, (5) SO₄²⁻/SnO₂—0.3—773 K and (6) SO₄²⁻/SnO₂—0.15—773 K [31]. (Reaction conditions: oleic acid : ethyl alcohol molar ratio (1:10); load catalyst (3% wt.); stirring (250 rpm); reaction temperature (353 K) time (4 hours) of reaction.)

this fact reinforces that the acid sites are also essential in the acid solid-catalysed esterification reactions.

The literature reported that the worst drawback of sulfated catalysts is the leaching undergone by these compounds, which is generally provoked by highly polar medium and by the water generated throughout esterification reactions [28, 29].

Nevertheless, in spite of the leaching problem, it was demonstrated that, at moderate conversions, this problem was minimized (Figure 11) [31]. Those authors reinforced that the oleic acid conversion was of 50% in the fresh and used

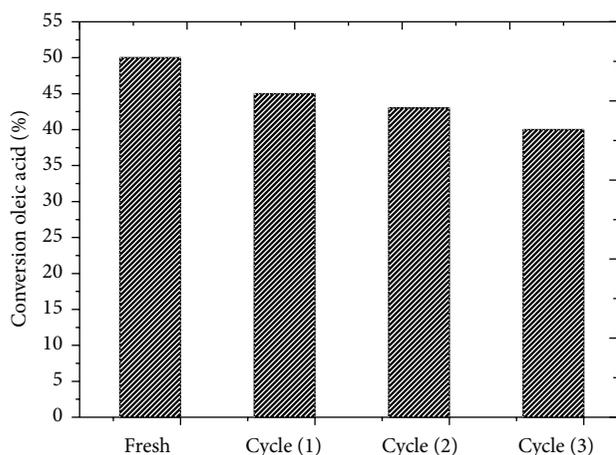


FIGURE 11: Conversion of oleic acid obtained with the fresh and used $\text{SO}_4^{2-}/\text{SnO}_2$ -0.3-773 K catalyst during the esterification reaction with ethanol [31]. (Reaction conditions: ethanol:oleic acid molar ratio is equal to 1:10, 353 K, 4 h.)

catalysts after 4 h. This result indicates that a heterogeneous catalytic process is happening. The leaching of the sulfates species produces homogeneous catalytic reactions with 100% oleic acid conversion in 2 h of reaction [32].

Similar to the work of Furuta and coworkers [28], the group of Nuithitikul at the same year conducted a study about the iron oxides catalytic activity and tin sulfate, in the FFA esterification reactions presents in the palm oil [33]. Particularly, those authors focused their study on the influence of the iron and sulfate concentrations on the activity of $\text{SO}_4^{2-}/\text{Fe}_2\text{O}_3$ - SnO_2 catalysts. The effect of different sources of Fe(III) cations was investigated in the esterification reactions: were used as start material the iron salts FeCl_3 (1), $\text{Fe}(\text{NO}_3)_3$ (2) and $\text{Fe}_2(\text{SO}_4)_3$ (3).

Table 8 shows the results of BET surface area, pore volume, acid sites strength, NAS, and conversion obtained on FFA esterification reactions in presence of $\text{SO}_4^{2-}/\text{Fe}_2\text{O}_3$ - SnO_2 catalysts calcined at 500°C temperature.

The catalyst with the highest surface area, with strongest acid sites and highest NAS, was the most active: 30% wt. $\text{SO}_4^{2-}/\text{Fe}_2\text{O}_3$ - SnO_2 catalyst was synthesized from the $\text{Fe}_2(\text{SO}_4)_3$. Those authors attributed this result to interaction of sulfate ion with Sn(II) which favors the formation of two acid sites (Figure 12) [33]. However, we would like to highlight that this effect was more pronounceable when iron nitrate precursor, probably because nitrate ions also can act as electron withdrawing increasing consequently the Lewis acid of tin catalysts.

A comparison between the activity and stability of 30% wt. $\text{SO}_4^{2-}/\text{Fe}_2\text{O}_3$ - SnO_2 catalysts and 30% wt. $\text{SO}_4^{2-}/\text{SnO}_2$ catalysts was performed (Figure 13) [33].

The results evidenced that sulfated tin oxide catalysts containing iron(III) oxide were more active and more stable in the FFA esterification reactions of palm oil. Probably the Fe(III) cations should be increasing the Lewis acidity of Sn(II)

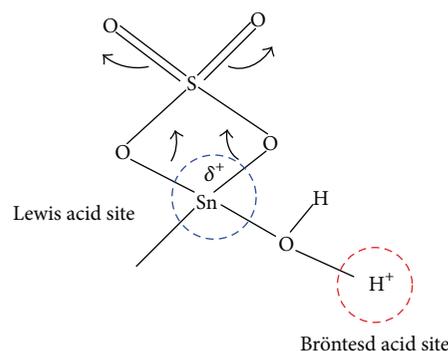


FIGURE 12: Lewis and Brønsted acid sites [33].

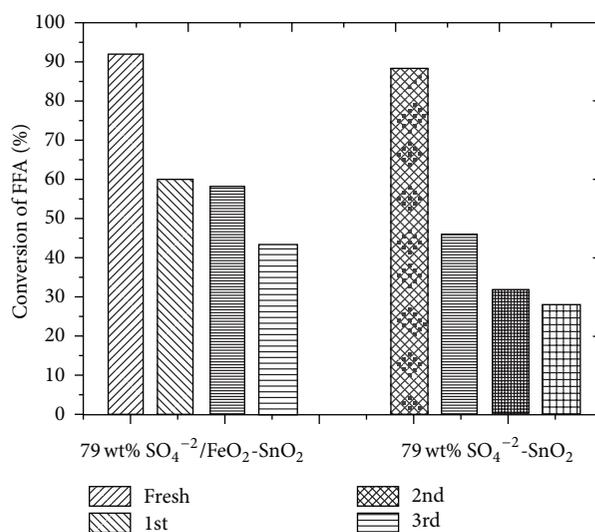


FIGURE 13: Reusability of 79 wt% $\text{SO}_4^{2-}/\text{Fe}_2\text{O}_3$ - SnO_2 and 79 wt% $\text{SO}_4^{2-}/\text{SnO}_2$ calcined at 450°C in the crude palm oil esterification reactions containing FFA [33]. (Reaction conditions: runs performed in a stirred-tank reactor are equipped with a reflux condenser; crude palm oil containing 10.2% wt FFA (25 mL); methanol (45 mL); catalyst (1 g); 80°C.)

cations that resulted in higher activity as well as stability of sulfated catalysts.

The precipitation method has been used to prepare mixed tin oxide catalysts [34]. Mello and coworkers produced mixtures of oxides with catalytic activity in FFA esterification present in vegetal oil. The $(\text{Al}_2\text{O}_3)_8(\text{SnO})_2$, $(\text{Al}_2\text{O}_3)_8(\text{SnO})$, and $(\text{SnO})\text{Al}_2\text{O}_3$ oxides were used as catalysts in FFA esterification with methyl alcohol (Table 9).

Comparative to conversions obtained in the reactions catalyzed by sulfated tin oxide, the conversions reached herein were lower; however, they remained constant even after successive cycles of recovery and reuse of catalyst (Table 10).

The trends observed in relation to catalytic activity were: $\text{Al}_2\text{O}_3 > \text{SnO} > (\text{Al}_2\text{O}_3)_8(\text{SnO}) > (\text{Al}_2\text{O}_3)_8(\text{SnO})_2 > (\text{ZnO})_2$. The authors suggested that the explanation for this may lie in the surface texture of the different catalysts, in addition to other aspects such as surface area and characteristic acidity.

TABLE 8: Properties of 30% wt. $\text{SO}_4^{2-}/\text{Fe}_2\text{O}_3\text{-SnO}_2$ catalysts obtained from iron(III) different precursors FeCl_3 (1), $\text{Fe}(\text{NO}_3)_3$ (2), and $\text{Fe}_2(\text{SO}_4)_3$ (3) calcined at 500°C and conversion of FFA esterification^{a,b} [33].

30% wt. $\text{SO}_4^{2-}/\text{Fe}_2\text{O}_3\text{-SnO}_2$ catalyst	BET surface area (m^2/g)	Pore volume (cm^3/g)	E_i (mV)	NAS (meq./g)	FFA Conversion (%) ^b
Precursor (1)	84.9	0.17	+394	1.18	70.3
Precursor (2)	67.4	0.11	+380	0.96	64.0
Precursor (3)	86.0	0.18	+402	1.20	72.1

^a E_i : initial electrode potential indicates the maximum acid strength of the sites; NAS: acid site numbers.

^bReaction conditions: 250 rpm, 25 mL of methanol 25 mL of crude palm oil (10.2 wt.% of FFA) was added, followed by methanol (45 mL), 1 g of catalyst, 3 hours, 80°C .

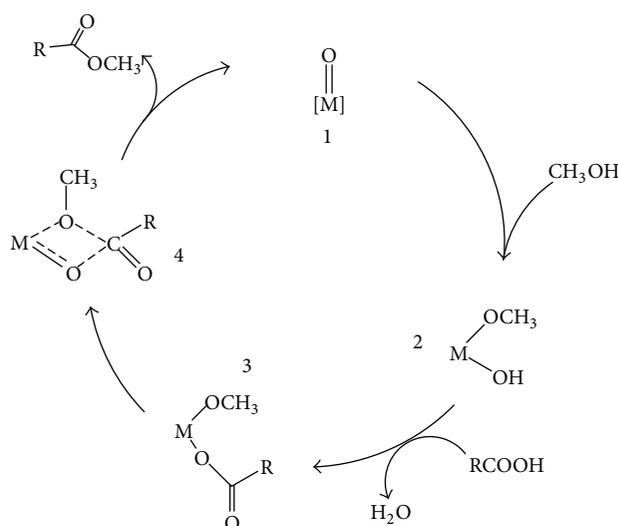


FIGURE 14: Proposed mechanism for the esterification of fatty acids catalyzed by Lewis acid metal oxides [34].

TABLE 9: FFA esterification with methyl alcohol catalyzed by metal oxides^a [34].

Entry	Catalyst	Yield (%)
1	—	32
2	Al_2O_3	74
3	SnO	69
4	$(\text{Al}_2\text{O}_3)_8(\text{SnO})$	61
5	$(\text{Al}_2\text{O}_3)_8(\text{SnO})_2$	60

^aReaction conditions: methyl alcohol (4 g); fatty acid (10 g), catalyst (0.1 g), temperature (160°C); reaction time (1 hour).

The feasible procedure for recovery and reuse besides the high yields suggest that these catalyst are potentially useful for biodiesel production. Those authors proposed a mechanism of the catalytic action as described in Figure 14 [34].

The solid catalysts action mechanism has been described by several authors, as is pictured in Figure 15 [35, 36].

The authors suggested that fatty acid molecules should be adsorbed on the catalyst surface, due to Lewis acid-base interaction between the nonligand electrons of the carbonyl

TABLE 10: SnO recycling study reaction conditions [34]^a.

Cycle	1	2	3	4	5	6	7	8	9	10
Yield (%)	69	68	67	66	65	65	64	64	62	62

^aReaction conditions: methyl alcohol (4 g); fatty acid (10 g), catalyst (0.1 g), temperature (160°C); reaction time (1 hour).

group oxygen atom and the metal cation present in the catalyst oxide. This interaction triggered an increase in the positive charge density over carbonyl carbon, favoring its nucleophilic attack by electrons pair of the alcohol hydroxyl, resulting then in the coordination of alcohol to catalyst surface. This intermediate eliminates a water molecule and furthermore the monoester. Afterward, the catalyst surface is free to participate in the next catalytic cycles.

5. Final Thoughts

Several classes of tin-based compounds have been assessed as potential heterogeneous catalysts for biodiesel production. The action of these catalysts depends on the catalytic sites nature (i.e., type Lewis or Brønsted acid) nearby in the

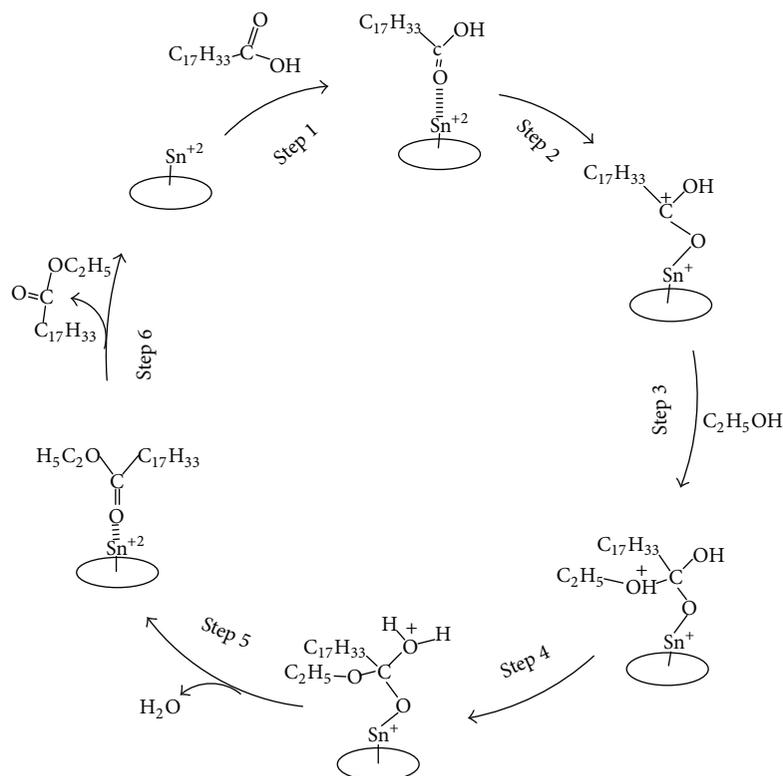


FIGURE 15: Proposal of a mechanism for the ester formation catalyzed by $SnCl_2/M_xO_y$ ($M = Zr$ or Nb ; $x = 1$ or 2 ; $y = 2$ or 5) in the oleic acid esterification into ethyl oleate [35, 36].

solids structure. In general, Lewis acidity is associated with systems without protons, and the resulting catalytic activity is often attributed to interaction with catalyst metal. For these reactions, Lewis acid sites must have the ability to interact with the carbonyl of triglycerides or fatty acids so as to favor the nucleophilic attack on the carbonyl carbon and then start the catalytic cycle.

Several strategies have been employed to increase the efficiency of solid acid catalysts based on tin; the treatment with sulfuric acid resulting in super acid sulfated tin oxide has been explored and resulted in active catalysts. However, the leaching of sulfate groups is yet a challenge to be overcome. On the other hand, the introduction of other metals such as iron and alumina into catalyst structure was also shown as being an efficient alternative. The understanding of main structural characteristics and physical properties of solid tin catalysts can contribute significantly to the advance in the biodiesel production field production as well as other important industrial esters. Moreover, the development of solid catalysts has occupied a highlighted position due to the demand for benign environmentally industrial processes. We hope that the advances summarized herein can contribute to the improvement and progress in heterogeneous catalysis field.

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