



# PREPARATION AND CHARACTERIZATION OF CATALYSTS BASED ON CASSITERITE ( $\text{SnO}_2$ ) AND ITS APPLICATION IN HYDROGENATION OF METHYL ESTERS.

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## Abstract

Tin oxide (IV) or cassiterite obtained by controlled precipitation method was characterized by different physical and chemical techniques like Transmission Electronic Microscopy (TEM), surface area, X-ray Powder Diffraction (XRD), Infrared spectroscopy (FTIR) and Temperature Programmed Reduction (TPR) to determine the morphology, particle size distribution, crystalline

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phases, functional groups and reduction temperature of the system and then employed pure and/or doped with Sn and Ni as catalyst in the hydrogenation of methyl esters obtained from palm oil. The Sn-doped system showed higher activity towards hydrogenation. We found that a small fraction of fatty alcohols is achieved with Sn/SnO<sub>2</sub> catalyst as well as others products by hydrogenation of olefin bonds and isomerization reactions.

**Key words:** methyl esters; heterogeneous catalysis; hydrogenation; tin oxide

### Resumen

El óxido de estaño (IV) o casiterita obtenido por el método de precipitación controlada fue caracterizado por diferentes técnicas físicas y químicas, tales como Microscopía electrónica de transmisión (MET), área superficial, Difracción de rayos X (DRX), Infrarrojo con transformada de Fourier (IR-TF) y Reducción a Temperatura Programada (RTP) para la determinación de la morfología, la distribución y tamaño de partícula, las fases cristalinas, los grupos funcionales y la temperatura de reducción del sistema, y posteriormente este sistema se emplea como catalizador puro y dopado con Sn y Ni en la hidrogenación de metil esterres provenientes del aceite de palma. El sistema dopado con Sn mostró mayor actividad hacia la hidrogenación, encontrándose una pequeña fracción de alcoholes grasos, así como también productos de la hidrogenación de los enlaces olefinicos y de las reacciones de isomerización.

**Palabras clave:** ésteres metílicos; catálisis heterogénea; hidrogenación; óxido de estaño

## Introduction

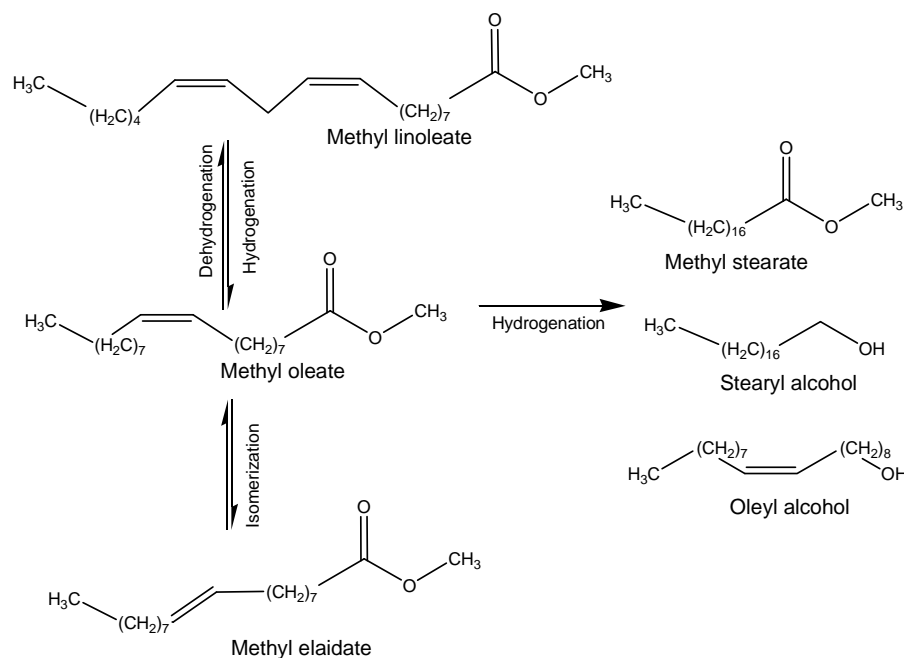
In the oleochemical field, hydrogenation of acids and fatty esters is one of the ways of obtaining compounds for industrial use, such as substitutes and additives for diesel and biodiesel, lubricants, detergents, and non-ionic surfactants [1, 2].

Fatty acids and esters contains unsaturated linkages like C=C and C=O. Hydrogenation of the C=C double bond in the linear chain is the most favored from the thermodynamic point of view ( $\Delta H_{C=C} = 120$  kJ/mol) *versus* C=O ( $\Delta H_{C=O} = -50$  kJ/mol). This reactivity difference seems due to weakly polarized bond C=O, but also from the steric hindrance characteristic of this function [3]. Figure 1 shows the possible products generated by the catalytic hydrogenation of unsaturated ester, like methyl oleate.

Selective hydrogenation of C=O function needs presence of two species, a metallic center and an electron-poor center like SnO<sub>2</sub> [3], TiO<sub>2</sub> [4], ZnO [5], Al<sub>2</sub>O<sub>3</sub> [6], or MgO [7]. Specifically in alcohols obtaining by ester hydrogenation, the most frequently hydrogenating metals are Ru, Rh, Re, and Ni and sometimes is necessary a second metal as promoter like Ge, Fe, Ga, or Sn.

Previously, Barrault *et al.* have shown that by employing an adequate support, as well as a second metal to interact with the hydrogenating metal (Ni, Ru, or another) important selectivity can be achieved toward the formation of the alcohol [6]. The support can be Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, TiO<sub>2</sub>, or ZnO and the second metal can be tin, germanium, gallium, lead, or iron. They have also studied bi-metallic systems like Ru-Sn and Rh-Sn supported on Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, or ZrO<sub>2</sub>. These catalysts shown a high selectivity toward alcohol, with a molar ratio close to Rh/Sn = 1.0.

With regard to cobalt or ruthenium bimetallic catalysts doped with tin, the preparation method and the nature of the support have been studied [5]. It is shown that the use of aluminum oxide and zinc to support leads to increased efficiency to the unsaturated alcohols, while the use of silica as support leads to obtain metallic cobalt species, which causes low activity due to enrichment of tin species. It is also shown that hydrogenation of methyl oleate can be carried out because of the presence of Co-Sn species, which would be necessary.



**Figure 1.** Possible products of methyl oleate hydrogenation.

It is clear that to carry out this reaction on the carbonyl group and obtain fatty alcohols, we need to use a hydrogenating metal and a promoter [8, 9]. The hydrogenating metal chosen for this study was nickel and tin as promoter.

## Experimental procedure

### *Obtaining methyl esters. Methanolysis of palm oil.*

In a flask of 100 mL palm oil (67 g), KOH 0.1 N in methanol (3 mL), sodium methoxide (0.8 g), and methanol (17.5 g) are introduced; the system is left at reflux during 4 h at 65 °C. The system is then cooled for 1 h, the glycerin formed during the process is decanted and the two phases obtained are brought to a funnel where they are separated. The product is washed several times with distilled water to eliminate remnant methoxide until neutral pH. Thereafter, the water from the washing is eliminated in a rotary evaporator; thus, obtaining the methyl esters for the hydrogenation reaction.

### *Synthesis of catalytic systems*

*SnO<sub>2</sub> synthesis.* Tin oxide is prepared by the controlled precipitation method (CPM), as described by Ávila *et al.*, [10].

*Impregnation of Sn and Ni.* A 0.1-M solution of the Ni nitrate and/or Sn chloride is added to the solid obtained in the previous step. Then, with constant agitation and temperature around 60 °C, the solvent is eliminated and finally dried at 110 °C for 12 h. Then calcination is conducted at 450 °C of the system obtained in a calcinator RACK SICO TEMP MOD, with air flow of 10 L/h. In this heating, the following temperature ramp is considered: 25 °C – 4 °C/min – 110 °C/1 h – 4 °C/min – 450 °C/8 h. Activation of solids is performed for 4 h, passing a 1 L /h hydrogen flow at 400°C. The catalytic systems studied were SnO<sub>2</sub>, Sn 3%/SnO<sub>2</sub>, Ni 3%/SnO<sub>2</sub>, and Ni 2%-Sn 0.5%/SnO<sub>2</sub>.

### **Hydrogenation reaction**

Hydrogenation reactions were carried out in a stainless steel batch reactor (type Parr, 250-mL); 50 mL of the methyl esters and the reduced catalyst are introduced in a 4% mass proportion. The reactor is closed and four times purged with gaseous hydrogen. Thereafter, hydrogen is introduced at the desired pressure, and then heated until reaching working temperature and under magnetic agitation. The reactions were followed for 24 h. Samples were taken every two hours, from the moment that temperature and pressure conditions were reached (190, 230, and 270 °C) and (50, 65, and 80 bar); each was analyzed by gas chromatography.

### **Characterization of catalysts**

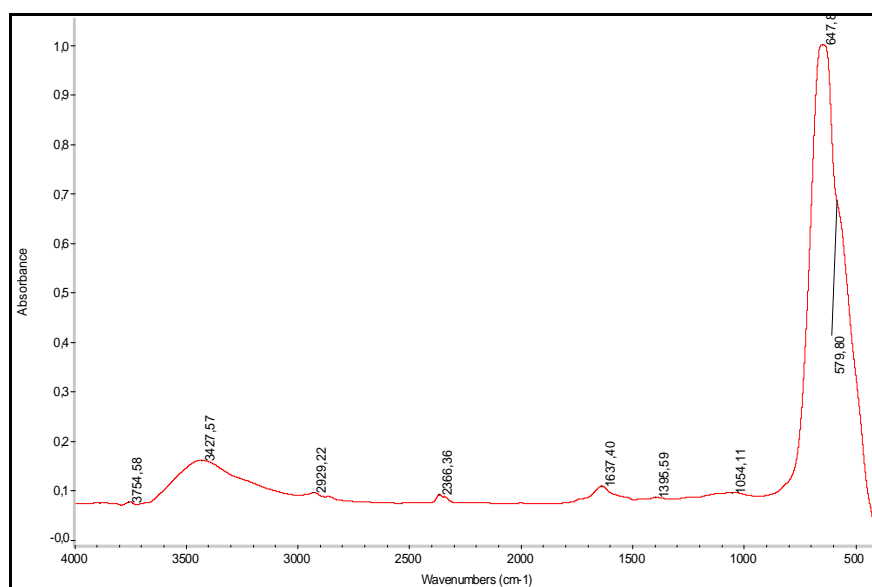
This characterization is carried out with the aid of different spectroscopic techniques, such as: Fourier Transformer Infrared (FT-IR), to know the functional groups in the surface of different catalysts, the sample is analyzed in a Nicolet IR-200 infrared spectrophotometer with EzOmic 32 software – 32 scans were performed at a resolution of 16 cm<sup>-1</sup>/s; X-ray Diffraction (XRD), to determine the presence or lack of crystalline phases formed during the activation stage, in a RIGAKU 2200 Diffractometer with CuK $\alpha$  = 1.54056 Å radiation at a step every 0.02 degrees and a fixed time of 0.3 seconds in a range of 20 – 80 (2 $\theta$ ); Transmission electron microscopy (TEM) to identify the morphology, distribution, and particle size, in a Jeol 1200 EX electron microscope; Determination of the surface area, to learn about the texture of the catalyst, by using a Micromeritics ASAP 2010; and finally Temperature Programmed Reduction (TPR) to obtain the temperature at which each of the metals present in the catalyst is reduced, the analysis was done in a Micromeritics Autochem 2910 with TCD detector.

## **Results and discussion**

### **Catalysts characterization**

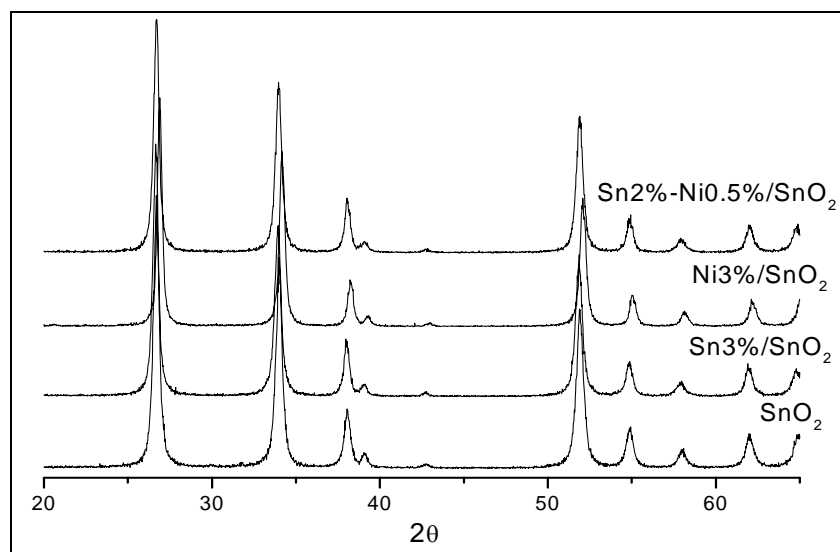
*Fourier Transformer Infrared (FT-IR).* The infrared spectrum reveals the existence of the functional groups and their possible interactions, when preparing SnO<sub>2</sub> as cassiterite. Figure 2 shows a main band at 647 cm<sup>-1</sup>, corresponding to the bond Sn-O; thus, revealing that the oxide has been formed.

Another outstanding band is found at 3425 cm<sup>-1</sup> and corresponds to the hydroxyl groups (-OH), which still remain after calcination in the oxide because it breaks from tin hydroxide after the reaction between ammonium hydroxide and tin dichloride. Other bands present are H-O-H stretching of water at 1637.4 cm<sup>-1</sup>, which is present in the environment or as impurity in the structure and at 2929 cm<sup>-1</sup>, corresponding to a C-H bond, possibly impurities of organic compounds involved in the washing process like ethylenediamine. The IR for all supported catalysts is very similar to that of the support, given that they only differ in the addition of a metal and at very low concentrations, which does not permit good detection of these systems and their possible interactions.



**Figure 2.** FT-IR spectrum of SnO<sub>2</sub>

**X-ray diffraction (XRD).** Figure 3 shows diffractograms of the solids used. Note that for SnO<sub>2</sub> the rutile structure is the main phase. For SnO<sub>2</sub> doped with Ni and Sn, none of the diffractograms show additional peaks that can correspond to secondary phases of the doping metals, this is because of the small amount of these; but it is evident that the doping does not lead to drastic changes in the SnO<sub>2</sub> structure.

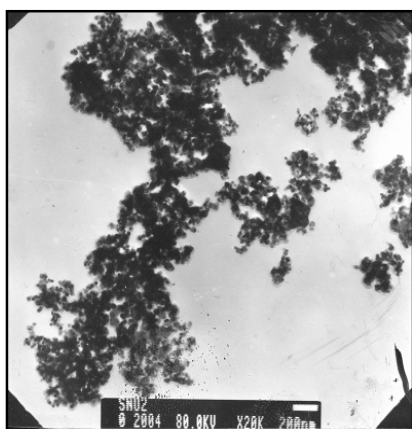


**Figure 3.** XRD of catalysts supported based on SnO<sub>2</sub>.

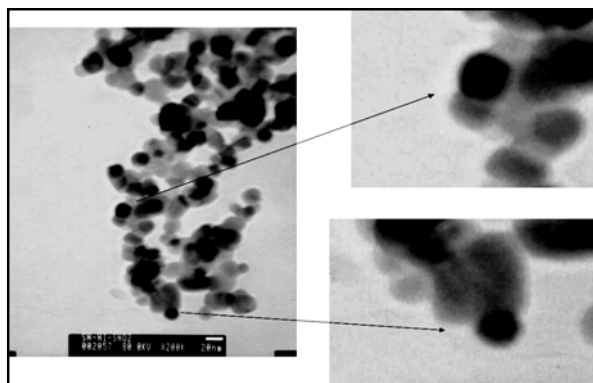
What is observed, specifically for nickel-modified catalysts, is a displacement in the diffraction peaks; this behavior is more evident in the solid with greater mass percentage. This phenomenon is due to solid solutions formation, where the Ni is introduced into  $\text{SnO}_2$  structure by substitution of  $\text{Sn}^{+4}$ .

**Transmission electron microscopy (TEM).** To determine the size of the particles and know how these are grouped, micrographs were taken of some solids.

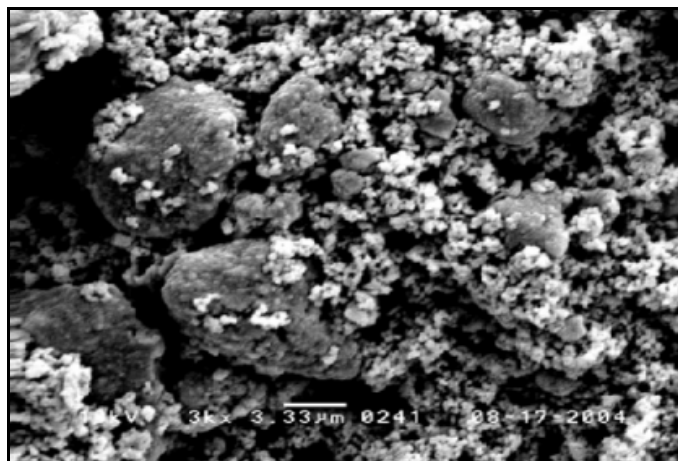
For the  $\text{Ni}/\text{SnO}_2$  solid (Figure 4(c)), note that the nickel crystallites formed are not uniformly distributed on the oxide surface; rather, they are agglomerated. Conversely, for the  $\text{Sn } 2\%-\text{Ni } 0.5\% /\text{SnO}_2$  system (Figure 4(b)), we can observe a better distribution of the metal in the the support. By doping with Sn at 3%,  $\text{SnO}_2$  catalyst (Figure 4 (d)) generates some amorphicity and agglomeration. These clusters have their effect on both the porosity and surface area of the solid. Dispersion of metals on  $\text{SnO}_2$  can also be established from these micrographs, for the  $\text{Sn } 3\%/\text{SnO}_2$  solid (Figure 4(d)), it is observed a loss of dispersion (significant Sn agglomerate). We can also say that when preparing  $\text{SnO}_2$  by the controlled precipitation method, nanoparticles are obtained permitting the molecules a better interaction and; thus, diminishing the diffusion limitations related with the diverse mass transport phenomena linked to the support.



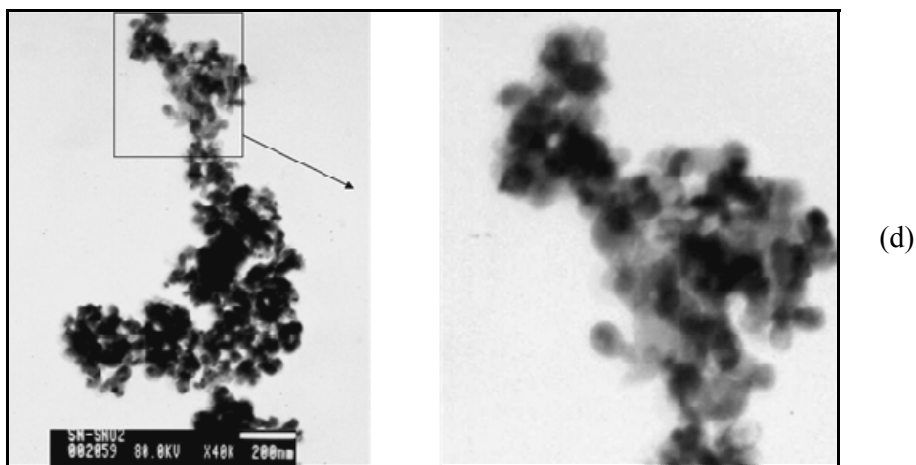
(a)



(b)



(c)



**Figure 4.** TEM of (a) SnO<sub>2</sub>, (b) Sn 2%Ni<sub>0</sub>, 5%/SnO<sub>2</sub>, (c) Ni 3%/SnO<sub>2</sub> and (d) Sn 3%/SnO<sub>2</sub>.

**Surface area and pore size.** Table 1 presents surface area and pore size results obtained. The surface area of the tin oxide was 15.9 m<sup>2</sup>/g, which is a small area even when compared with other oxides [11]. For the pore size, we obtained a value of 18.0 nm.

When doping SnO<sub>2</sub>, modifications are observed in pore size and surface area in diverse proportions due to the interactions present between the metals and support. The decrease of the area is because of the size increase of the particles due to the agglomeration present observed by TEM and the increase in pore size, given the formation of new channels of the metal added on the tin oxide structure.

**Table 1.** Results of surface area and pore size.

SYSTEM	Surface BET (m <sup>2</sup> /g)	PORE SIZE (nm)
SnO <sub>2</sub>	15.9	18.0
Sn 3% / SnO <sub>2</sub>	11.8	24.6
Ni 0.5% Sn 2% / SnO <sub>2</sub>	14.9	17.8
Ni 3 % / SnO <sub>2</sub>	15.1	16.4

**Temperature-programmed reduction (TPR).** Results of temperature-programmed reduction studies of Sn, Ni, and Sn-Ni/SnO<sub>2</sub> systems are shown in Table 2.

**Table 2.** TPR results of the solids studied based on SnO<sub>2</sub>.

SYSTEM	TEMPERATURE REDUCTION °C	SPECIES
SnO <sub>2</sub>	900	SnO <sub>2</sub>
Sn 3% / SnO <sub>2</sub>	1. 260	Sn <sup>4+</sup>
	2. 450	Sn <sup>2+</sup>
	3. 900	SnO <sub>2</sub>
Ni 3% / SnO <sub>2</sub>	1. 200	Ni <sub>x</sub> Sn <sub>y</sub>
	2. 450	SnO <sub>2</sub>
Sn 2%-Ni 0.5%/SnO <sub>2</sub>	1. 150	Ni <sub>m</sub> Sn <sub>n</sub>
	2. 195	Ni <sub>x</sub> Sn <sub>y</sub>
	3. 610	SnO <sub>2</sub>

Different reduction temperatures are observed in each of the cases, this leads to the generation of different species. In this instance, we seek partially hydrogenated tin to act as a Lewis acid that can polarize the carboxyl function. These nickel and tin species are in agree with oxidation state for Ni/SnO<sub>2</sub> and Sn-Ni/SnO<sub>2</sub> catalysts, there is the reduction of an Ni-Sn species between 150 and 200 °C, which may indicate the formation of nickel tin species.

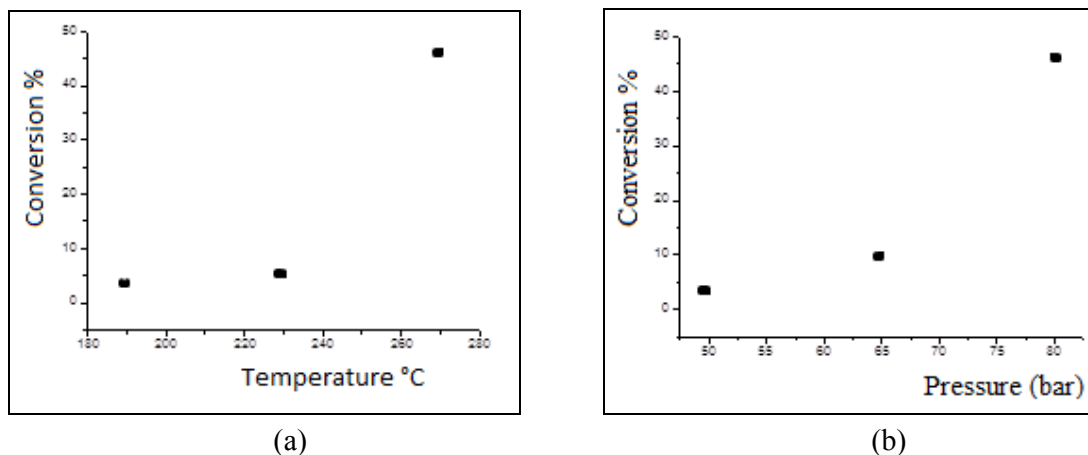
### **Hydrogenation reaction**

The results obtained in the characterization of the solids used are directly related to the behavior of the catalyst in the hydrogenation of methyl esters. To verify the temperature effect, the reaction is first carried out in the absence of the catalyst at 270 °C, after 24 h the conversion is zero, which shows that the presence of the catalyst is necessary.

*Effect of temperature and pressure in the hydrogenation reaction.* Because of the hydrogenating character of nickel, the system Ni3% / SnO<sub>2</sub> is chosen as a catalyst to determine the best reaction conditions. The temperature and pressure variables associated with the process of hydrogenation is high due to high binding energy to break (200 kJ/mol for C=C and 369 kJ/mol for C=O). Figure 5a shows the conversion percentages as a function of temperature, keeping the other variables constant. It is noted that at temperatures up to 250 °C there is minimal conversion. At 270 °C, the processes presented are mainly isomerization, dehydrogenation, and olefinic-bond hydrogenation. This behavior turns out to be disadvantageous; given that it demonstrates that it is not an active catalyst in a broad temperature range and does not present formation of fatty alcohols.

Regarding pressure, Figure 5b shows that three values were tested to observe the behavior of the Ni 3% / SnO<sub>2</sub> system against this variable and to obtain a mean conversion it is necessary to work at pressures under 80 bar.

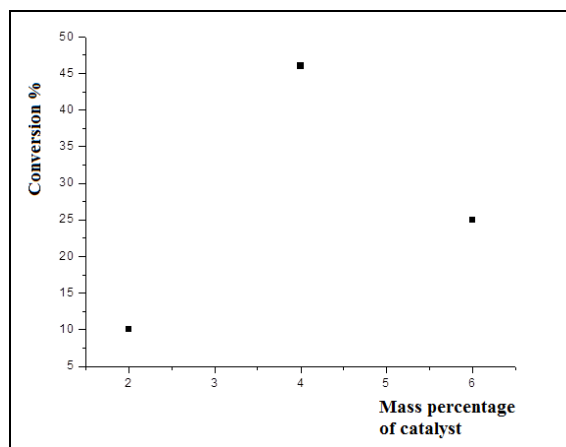




**Figure 5.** Conversion percentage of the Ni 3%/SnO<sub>2</sub> system as a function of temperature. Reaction Conditions: Catalyst quantity of 2% mass; reduction temperature at 400 °C for 4 h, and agitation rate of 800 rpm.

*Effect of the catalyst percentage in the transformation of methyl ester.* This parameter is also related with transport phenomena. A large amount of catalyst represents a large liquid/solid interface area; thereby, making it difficult for hydrogen to penetrate from the gaseous phase to the solid and be adsorbed on the active sites of the catalyst. For this reason, the hydrogenation reaction requiring high availability of hydrogen needs small quantities of the catalyst.

Reactions were carried out at 2%, 4%, and 6% catalyst mass (Figure 7) and it can be seen how the highest conversion percentage is obtained by catalyst percentage at 4%. Above and below this value, the conversion diminishes and only hydrogenation reactions of the olefinic-bond are mainly observed. The activity of this catalyst is limited by the amount present in the reaction medium; when it is low (2%), the activity is minimal because of the insufficient amount of catalyst and of active sites to interact with the mixture of methyl esters. At a greater percentage (6%) other transport phenomena come into play, which impede an appropriate reaction among the three phases; hence, the activity diminishes.



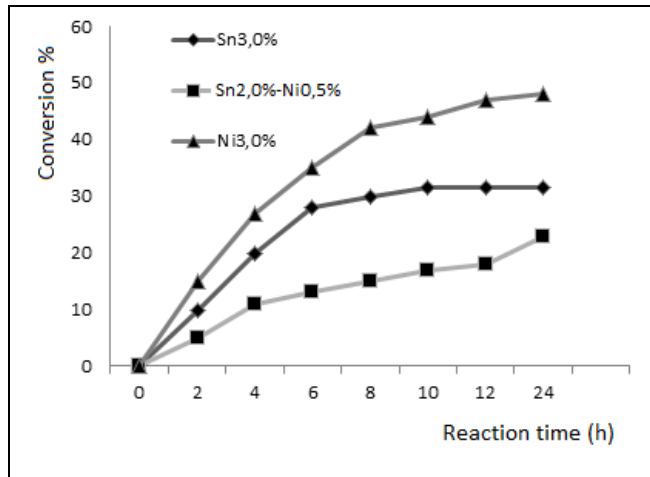
**Figure 6.** Conversion percentage of the Ni 3%/SnO<sub>2</sub> system as a function of the quantity of catalyst. Reaction Conditions: Quantity of catalyst of 2, 4, and 6% mass; reduction temperature at 400 °C for 4 h, and agitation rate of 800 rpm.

It may then, be concluded that the most adequate conditions for the hydrogenation reaction would be: pressure at 80 bar, temperature at 270 °C, quantity of catalyst of 4% mass, reduction temperature at 400 °C for 4 h, and agitation rate of 800 rpm. At these conditions, in addition to the hydrogenation reaction, two more processes also take place: isomerization of the most unsaturated substrate (methyl linoleate) and methyl palmitate dehydrogenation. This agrees with that published by Grau *et al.*, in their study of kinetic modeling in methyl oleate isomerization on Ni/Al<sub>2</sub>O<sub>3</sub>- type catalysts [12].

Under these conditions and using the tin oxide as catalyst, the maximum conversion percentage at 24 h is of 5%, a very low value; thus, indicating that SnO<sub>2</sub> as catalyst in the hydrogenation of methyl esters is not sufficiently active.

#### *Effect of tin as doping agent.*

Now, given that what is to be evaluated is the presence of tin as a metal or doping agent in a medium of a hydrogenating metal like nickel, Figure 7 shows the results with the system based on mono- and bi-metallic SnO<sub>2</sub>, finding 31.5% conversion for the Sn3%/SnO<sub>2</sub> system at 7 h of reaction and remaining constant during the rest of the time. This system is active and selective to fatty alcohols, with a maximum of 31%. For methyl linoleate, 78% conversion percentage is reached, this being the most transformed substrate. Because it has two insaturations, methyl linoleate becomes a substrate that can be better adsorbed on the catalyst. According to the afore mentioned, it may be stated that methyl linoleate undergoes isomerization transformations forming *cis-trans* geometric isomers and it hydrogenates completely becoming methyl stearate, and this last one consequently becomes stearic alcohol.



**Figure 7.** Conversion percentage of the Sn3%, Ni3%, and Sn2%-Ni 0.5%/SnO<sub>2</sub> systems. Pressure at 80 bar, Temp 270 °C, catalyst 4% mass, reduction temperature at 400 °C for 4 h, and rate of agitation at 800 rpm.

For the Sn2%-Ni0,5%/SnO<sub>2</sub> system, we also observe increased conversion with relation to the support and selectivity for fatty alcohols (FT) diminishes with regards to the Sn3%/SnO<sub>2</sub> system (32 *versus* 23%), which evidences the effect of Sn on the selectivity to fatty alcohols.

**Table 3.** Conversion of the methyl ester in presence of solids.

SYSTEM	% CONVERSION	% SELECTIVITY
SnO <sub>2</sub>	5	0
Sn 3%/SnO <sub>2</sub>	31.5	32
Sn2% Ni0.5% /SnO <sub>2</sub>	21	23
Ni 3%/SnO <sub>2</sub>	45	0

According to temperature reduction results, it is shown that at temperatures between 260°C and 450°C, Sn is mainly found in Sn<sup>2+</sup> form, and thus can bond to a molecule, where there is much electronic density in the unsaturations, as well as oxygen. What has probably occurred is that at 400 °C there is presence of zerovalent metal species and under these conditions it has behaved as a hydrogenating metal, exclusively to attack the double bond. Because of the great amount of acid sites, the molecules with many insaturations like methyl linoleate have been fixed to the metal and the previously mentioned reactions have occurred.

For the Ni3%/SnO<sub>2</sub> system, we obtained the best conversion results, given the well-known hydrogenating capacity of this metal, and although fatty alcohols were not obtained at those pressures and only secondary reactions were present, revealing that under these conditions, the catalyst is not selective for the formation of fatty alcohols.

## Conclusions

First, the characterization of solids through the different techniques employed showed that the preparation of tin oxide by controlled precipitation method lead to obtaining the cassiterite crystal structure and according to surface area measurements, we found small areas, but bigger than those reported for these systems. Catalysts based on tin oxide, Sn and Ni, did not lead to substantial modification of the support structure used.

The catalysts supported in tin oxide, prepared by the controlled precipitation method, showed special properties like greater surface area with respect to commercial tin oxide prepared via conventional methods, along with nanometric particle size, which is important for the catalytic activity.

Regarding the hydrogenation reaction, it may be stated that heterogeneous catalytic systems based on nickel at 3% resulted active in the hydrogenation of methyl esters from palm oil. The best conditions for catalytic activity were 80 bar, 270 °C, and 4% catalyst mass. At temperatures below 270 °C and under 80 bars, the catalyst is not able to reduce the activation energy of the hydrogenation processes involved; hence, important activities are not obtained.

Finally, monometallic systems were mainly active for the hydrogenation of the double bonds, presenting low conversion, although with the Sn 3% and Sn 2%-Ni 0.5% systems fatty acids were obtained. The behavior of tin as a hydrogenating metal may be due to a percentage of tin is in reduced form another part in oxidized form as the reduction temperature is 400 ° C, being not sufficient to achieve a total reduction and permitting the hydrogenation reaction to obtain fatty alcohols.

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