



## PREPARATION AND CHARACTERIZATION OF CASSITERITE (SnO<sub>2</sub>) AND ITS APPLICATION IN THE HYDROGENATION OF METHYL ESTERS

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### Abstract

Tin oxide (IV) or cassiterite obtained by the controlled precipitation method was characterized by different physical and chemical techniques such as TEM, surface area, XRD and RTP for the determination of the morphology, particle size distribution and reduction temperature of the system and then, a pure catalyst and doped with tin (Sn) and nickel (Ni) is employed in the hydrogenation of methyl esters from palm oil. Monitoring the reaction was carried out by gas chromatography and it was found that the Sn-doped system showed a higher activity towards hydrogenation. The products obtained during and after the reaction were analyzed by FT-IR. We found that the hydrogenation of double bonds of the carbon chain was the main reaction, but there were also products resulting from isomerization and surprisingly a small fraction of fatty alcohols with tin-based catalyst Sn/SnO<sub>2</sub>.

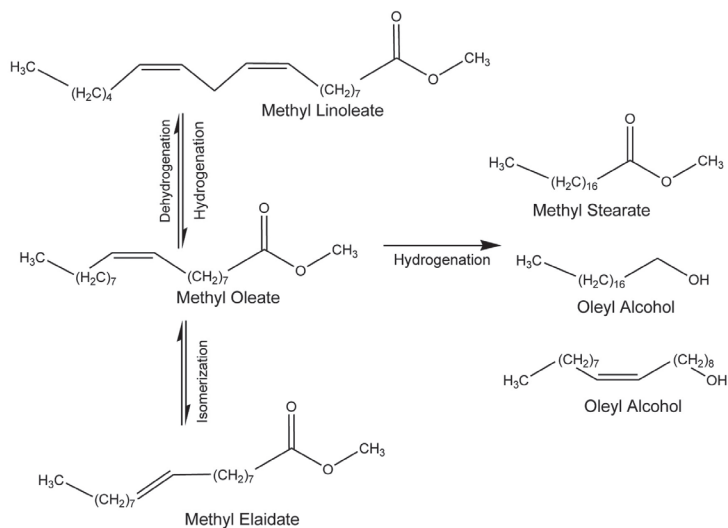
**Keywords:** methyl esters, heterogeneous catalysis, hydrogenation, tin oxide.

## 1 Introduction

In the field of oil-chemistry, the hydrogenation of fatty acids and esters is one of the pathways for the production of compounds such as substitutes and additives for diesel and bio-diesel, lubricants, detergents, and non-ionic surfactants [1, 2], all of which are utilized in the industry.

The bibliographical analysis show that in the hydrogenation of fatty acids and esters, there are substrates with unsaturated bonds of the type C=C and C=O; being the hydrogenation of the double bond C=C in the lineal chain, the most favorable one from the thermodynamic stand point ( $\Delta H_{C=C} = 610 \text{ kJmol}^{-1}$ ) in contrast with the enthalpy of C=O ( $\Delta H_{C=O} = 730 \text{ kJmol}^{-1}$ ). This difference in reactivity is due to the weak polarizable character of the C=O ester bond, but it is also due to the esters own inhibition for that function [3]. To better illustrate this, figure 1 shows the possible products generated by catalytic hydrogenation of a non-saturated ester such as methyl oleate.

To achieve the selective hydrogenation of the function C=O, it is necessary the joint presence of two species: one metallic center and one electro-deficient center. The last one could be obtained from the support as 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 the process of obtaining alcohols by ester hydrogenation, the most frequently found in hydrogenation-favorable metals were: Ru, Rh, Re, and Ni with the addition of a second promoting metal such as Ge, Fe, Ga, or Sn.



**Figure 1:** Possible products obtained from the hydrogenation of methyl oleate.

Barrault and collaborators have demonstrated that when an adequate support is used coupled with a second metal that would interact with nickel (Ni), ruthenium (Ru) or any other hydrogenation-favorable metal, important selections could be achieved towards the formation of alcohol [6]. The metals used as support could be Aluminum Oxide (Al<sub>2</sub>O<sub>3</sub>), Silicon Oxide (SiO<sub>2</sub>), Titanium Oxide (TiO<sub>2</sub>), or Zinc Oxide (ZnO) and the second metal could be one of the following: tin, germanium, gallium, lead, or iron. The same authors have studied bi-metal systems such as Ru-Sn and Rh-Sn supported on Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, or ZnO<sub>2</sub>. These catalyst show a high affinity towards alcohol with a molar reaction between Rh and Sn = 1.0.

In addition, for binary catalyst such as cobalt, ruthenium with tin, studies have been made on the preparation method, the kinetics and the nature of support modifying the solid final composition [5, 14] showing that the use of the later or zinc oxide results in equal yields of unsaturated alcohol whereas, the one made with silicon present many more Co metallic species which causes a low activity towards the enrichment of tin species. It is also demonstrated that the hydrogenation of methyl oleate could be carried out in the presence of CoSn species which could be needed.

It is clear that in order to carry out this reaction on the carbon group to obtain fatty alcohols, the use of one hydrogenation-favorable metal and a promoting one is necessary [8, 9]. The hydrogenation-favorable metal chosen for this study is nickel and the promoting metal is tin.

## 2. Methodology

### 2.1 Obtaining methyl esters and methanolysis of palm oils

Palm oil (67 g), methanolic KOH 0.1M (3 mL), sodium methoxide (0.8 g), methanol (17.5 g), were introduced into a provided three-mouth balloon. This system underwent a reflux process during 4 hours at 65 °C. After that, it is filtered for an hour, the glycerin formed in the process is decanted, and the two obtained phases are poured into a funnel where they are separated. The product is washed several times with distilled water in order to eliminate the excess methoxide until the pH is neutral. Subsequently, the washing water is eliminated in a rotary-evaporator. This way, the methyl esters are obtained to be used in the hydrogenation.

### 2.2 Synthesis of the catalyst systems

Synthesis of Tin Oxide (SnO<sub>2</sub>): It is prepared using the controlled precipitation method (CPM), as it is described by Avila and colleagues [10].

Impregnation of Sn and Ni: To the solid obtained in the previous step, it is added a metallic solution of nickel and/or tin salt. Then the solvent is eliminated through constant agitation at a temperature of approximately 60 °C. Finally, it is dried at 110 °C for 12 hours. After that, the system calcination is carried out at 450 °C in a calcinatory RAC SICO TEMP MOD, with air flow of 10Lh<sup>-1</sup>. For this heating process, the following temperature ramp is considered: 25 °C – 4 °Cmin<sup>-1</sup> – 110 °C1h<sup>-1</sup> – 4 °Cmin<sup>-1</sup> – 450 °C/8 hrs. Solids activation is carried out for 4 hours making a flow of 1 Lh<sup>-1</sup> of hydrogen undergo temperatures of 400 °C. The catalyst systems being studied were: SnO<sub>2</sub>, Sn3%SnO<sub>2</sub>, Ni3%SnO<sub>2</sub>, and Ni2%-Sn0.5%SnO<sub>2</sub>.

### 2.3 Hydrogenation reaction

The hydrogenation reactions were carried out in a micro-pilot reactor type Parr with 250 mL capacity. 50 mL of methane esters, especially that from palmitate (39.1%) and oleate (43.1%), and the reduced catalyst in a mass proportion of 4% were introduced. The reactor is closed and it is purged 4 times with gas hydrogen. Then, hydrogen is introduced at the desired pressure in order to subsequently heat it to reach the working temperature and under the magnetic agitation. The reactions were carried out during 24 hours. Samples were taken every 2 hours from the moment in which the conditions of temperature (190, 230, and 270 °C) and of pressure (50, 65, and 80 bar) are reached and they are analyzed in a Shimadzu GC-14B gas chromatograph with an FID detector.

### 2.4 Catalyst characterization

This characterization was carried out with the aid of different spectroscopic techniques such as infrared, to know the superficial groups in different catalyst. The sample was analyzed through a red spectrometer Nicolet IR-200 with software EzOmic 32. The number of scans was 32 at a resolution of 16cm<sup>-1</sup>/s; X-ray diffraction, to determine whether there is presence of crystalline phases formed during the activation phase through a diffract meter RIGAKU 2200 with radiation CuK $\alpha$  = 1,54056 every 0.02 degrees and at a fixed time of 0,3 seconds in a range of 20 – 80 (2 $\theta$ ); transmission electronic microscopy (TEM), to identify the morphology, distribution, and particle

size in an electronic microscope Jeol 1200 EX; determination of the superficial area to find out the texture of the catalyst through a SE micro meter ASAP 20110; and finally, program temperature reduction (PTR) to know the reduction temperature for each of the metals present in the catalyst. This analysis was carried out in a Micromeritics autochem 2910 with detector TCD.

### 3. Results and discussion

#### 3.1 Characterization of catalyst

Infrared: The infrared spectrum (figure 2) provides evidence of the presence of functional groups and their possible interactions when preparing  $\text{SnO}_2$  as cassiterite.

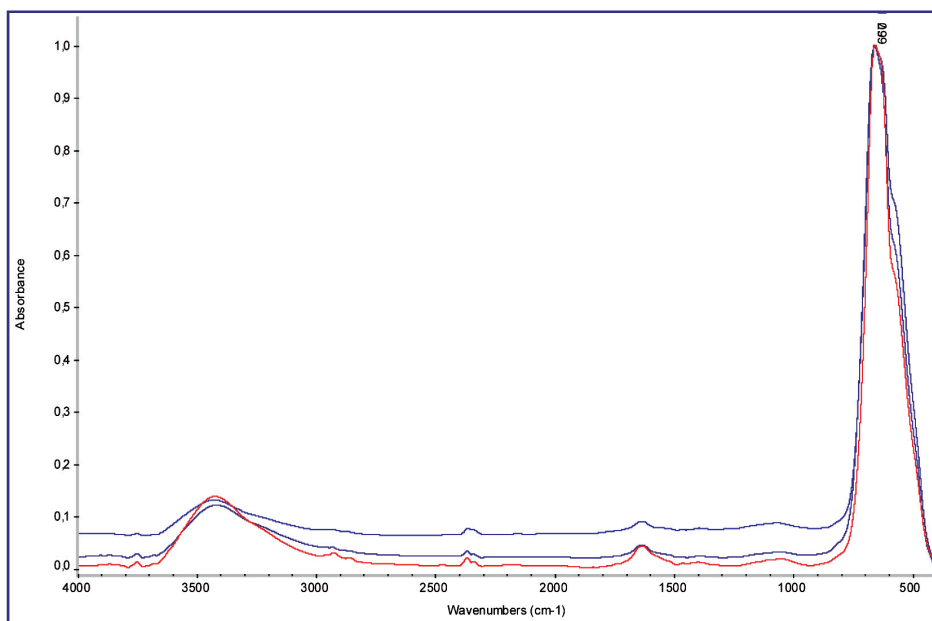
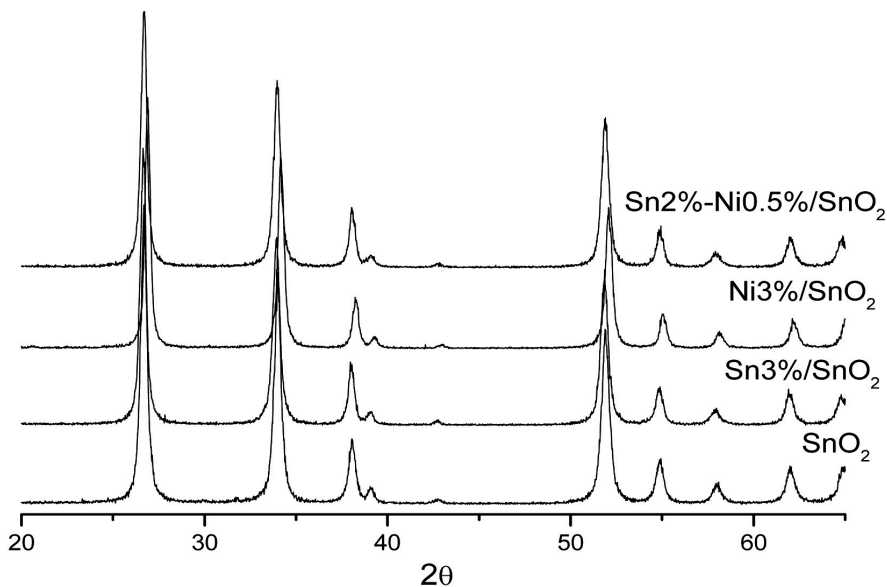


Figure 2. FT-IR spectrum of  $\text{SnO}_2$ .

Figure 2 shows a main band found at 647 cm and which corresponds to the present bonds between tin and oxygen showing that the oxide has been formed. Another noticeable band is the one located at 3425 cm and corresponds to the hydroxyl (-OH) groups, which remain even after the oxide calcination, due to the braking of tin hydroxide after the reaction of ammonium hydroxide with tin dichloride. Other bands present are the following: one, corresponding to the flexion of water ( $\delta$  H-O-H) at 1637.4 cm, a second one which is present in the environment or as impurity in the structure at 2929 cm corresponding to a bond C-H, those are probably impurities of hydrocarbons involved in the washing process as ethylenediamine. The IR for all the supported catalyst is very similar to that of the support since they only differ in the addition of a metal at very low concentrations, which allows a good detection of these systems and their possible interactions.

X-ray Diffraction (XRD): figure 3 shows the diffractograms of the used solids. It is observed that for  $\text{SnO}_2$ , the rutile structure is the main phase. In the case of doped  $\text{SnO}_2$  with Ni and Sn, in any of the diffractograms was observed additional picks that could correspond to the secondary phases of the doped metals. This is due to a small quantity of them, but it is evident that the doped does not result in drastic changes in the  $\text{SnO}_2$  structure. What it is observed, for the particular case of the catalysts modified with nickel, is a displacement in the diffraction picks, being more evident with the increase in mass proportion.

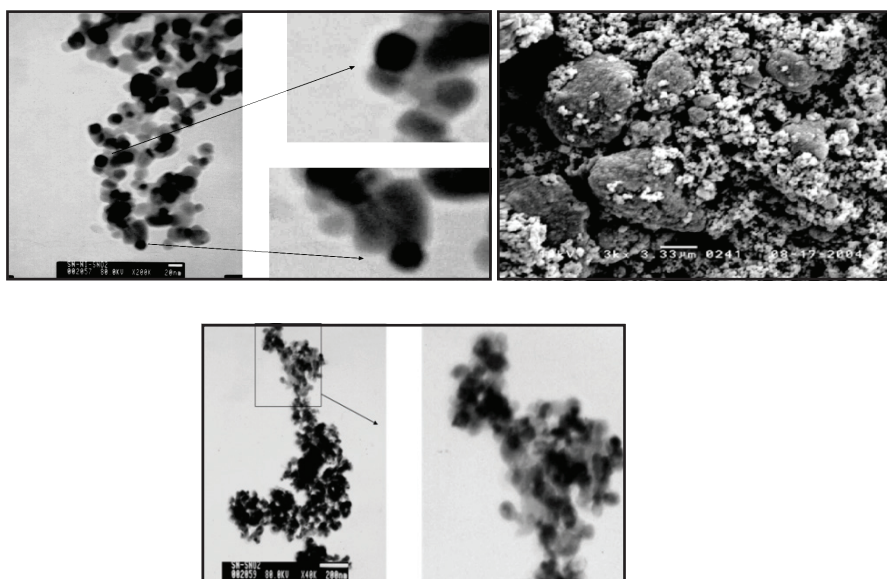


**Figure 3.** XRD of the catalyst supported with  $\text{SnO}_2$  (see original text for this illustration).

Transmission Electronic Microscopy (TEM): in order to determine the particle size and to know how they form clusters among themselves, the micrographs of some solids were taken.

When doping the particles with Sn, for  $\text{Sn3\%SnO}_2$  (Figure 4b), certain amorphous characteristic and clustering is generated. These clusters affect the porosity as well as the superficial area of the solid.

The dispersion of metals over  $\text{SnO}_2$  could also be established, from these micrographs. In the case of the solid  $\text{Sn3\%SnO}_2$ , it is observed that the dispersion is not very good (many dark spots together). For the case of the solid  $\text{Ni/SnO}_2$ , it is observed that the formed crystals of nickel are not distributed uniformly on the oxide surface, but rather in clusters. However, for the system of  $\text{Sn2\%-Ni 0.5\%/SnO}_2$ , it could be observed a mayor distribution of the metals over the support. It could also be stated that when preparing  $\text{SnO}_2$  for the controlled precipitation, nanoparticles are obtained, making possible for the molecules to interact better, and this way it could decrease the dysfunctional limitations regarding the different mass transport phenomenon linked to the support.



**Figure 4.** Micrographs of (a)  $\text{Sn}3\%/\text{SnO}_2$ , (b)  $\text{Ni}3\%/\text{SnO}_2$ , (c)  $\text{Sn}2\%/\text{Ni}0, 5\%/\text{SnO}_2$ .

Superficial Area and Pore Size: table 1 shows the results obtained from the superficial area and the pore size. The tin oxide superficial area was  $15.9 \text{ m}^2\text{g}^{-1}$ , which is a small area even compared with other oxides [11]. The obtained value for the pore size was 18.0 nm.

**Table 1.** Results of the superficial area and porous size.

SYSTEM	AREA BET ( $\text{m}^2\text{g}^{-1}$ )	PORE SIZE ( nm )
$\text{SnO}_2$	15.9	18.0
$\text{Sn}3\%/\text{SnO}_2$	11.8	24.6
$\text{Ni}0.5\%/\text{Sn}2\%/\text{SnO}_2$	14.9	17.8
$\text{Ni}3\%/\text{SnO}_2$	15.1	16.4

When doped  $\text{SnO}_2$ , modifications in porous size and superficial area are observed. These modifications are of different proportions due to the interactions that occur between metals and the support. The decrease in area is due to the increase in size of the particles because of the clustering that was observed through TEM and the increase in porous size, in the case of tin, due to new channels in the metal that has been added to the tin oxide structure, which is produced in the water elimination process during the calcination of the material [12].

Reduction in Programmed Temperature (RPT): the results of the studied systems Sn, Ni, and Sn-Ni/ $\text{SnO}_2$  for programmed temperature reduction are shown in table 2.

**Table 2.** Results of RPT of the studied solids in SnO<sub>2</sub> base.

SYSTEM	TEMPERATURE REDUCTION °C	SPECIES
SnO <sub>2</sub>	900	SnO <sub>2</sub>
Sn3%/SnO <sub>2</sub>	1. 260 2. 450 3. 900	Sn <sup>4+</sup> Sn <sup>2+</sup> SnO <sub>2</sub>
Ni3%/SnO <sub>2</sub>	1. 200 2. 450	Ni <sub>x</sub> Sn <sub>y</sub> SnO <sub>2</sub>
Sn2%-Ni0.5%/SnO <sub>2</sub>	1. 150 2. 195 3. 610	Ni <sub>m</sub> Sn <sub>n</sub> Ni <sub>x</sub> Sn <sub>y</sub> SnO <sub>2</sub>

Different temperature reductions are observed in each case. This results in the generation of different species. In this case, we are looking for a partially reduced tin to act as a Lewis acid that could polarize the carboxyl function. These tin and nickel species are accurate for their oxidation state and for the case of the Ni/SnO<sub>2</sub> and Sn-Ni/SnO<sub>2</sub> catalysts, the reduction of a Ni-Sn species at temperatures ranging between 150 and 200°C, is confirmed. This makes one think that there is formation of nickel and tin species.

### 3.2 Hydrogenation reaction

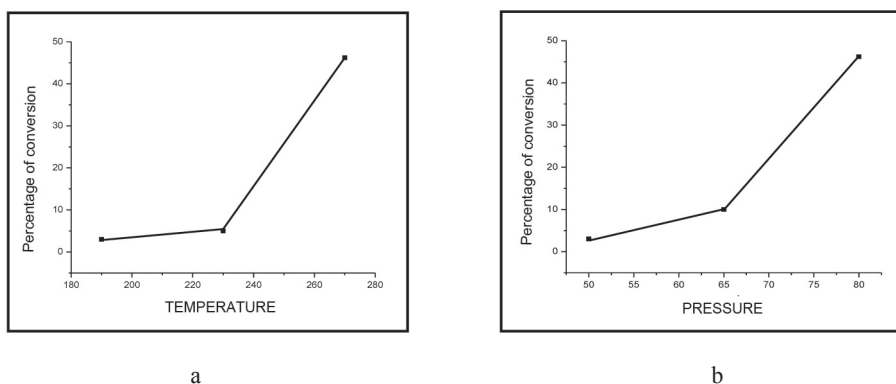
Table 3 shows the composition of palm oil used to obtain esters.

**Table 3.** Palm oil composition to be used as raw material.

FATTY ACIDS	( % )
<i>Saturated</i>	46.3
Lauric	0.25
Myristic	0.75
Palmitic	39.1
Stearic	5.15
Arachidic	1.05
<i>Mono y polyinsaturated</i>	53.6
Oleic	43.1
Linoleic	10.5

The results obtained in the characterization of used solids are directly related with the catalyst behavior in the hydrogenation of methyl esters. To verify the effect of temperature, the reaction is carried out, first of all, in the absence of a catalyst, at 270 °C. After 24 hrs the rate of conversion is zero. This shows that the presence of the catalyst is necessary.

Determining the best conditions for the reaction: effect of temperature and pressure. Due to the hydrogenation-favorable character of nickel, the Ni3%/SnO<sub>2</sub> system is chosen as catalyst to determine the best conditions of the reaction since temperature and pressure, variables associated with the hydrogenation reaction, are high due to the high level of bond energy to be broken (200 kJmol<sup>-1</sup> for C=C and 369 kJmol<sup>-1</sup> for C=O).



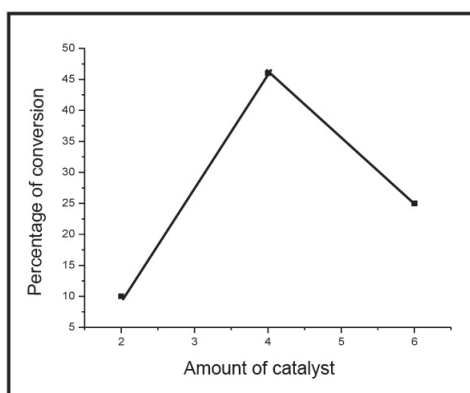
**Figure 5.** Percentage of the Ni3%/SnO<sub>2</sub> system conversion: a) temperature function; b) pressure function. Reaction conditions: catalyst quantity of 2% mass; a reduction temperature of 400 °C for 4h and at agitation speed of 800 rpm.

Figure 5a shows the rate of conversion in function of temperature, keeping the remaining variables constant. It is observed that even at temperatures of 250 °C there is a minimum conversion. At 270 °C, the processes that take place are mainly isomerization, dehydrogenation, and hydrogenation of double bonds. This behavior happens to be an advantage since it does not seem to be an active catalyst in a wide range of temperatures and it doesn't present formation of fatty alcohols.

As far as pressure is concerned, figure 5b shows that 3 values were tried to observe the behavior of the Ni3%/SnO<sub>2</sub> system against this variable and to obtain a half conversion it is necessary to work at pressures of at least 80 bar. Figure 6 shows the different products that could be obtained through the transformation of methyl oleate when it is hydrogenated and / or dehydrogenized.

Effect of the catalyst proportion in the transformation of the methyl ester: this parameter is also associated with transport phenomenon. A great amount of catalyst represents a big inter-phase liquid/solid area, so this would make difficult for hydrogen to penetrate from the gas phase to the solid one and to be absorbed on the catalyst active site. For this reason, the hydrogenation reactions requiring high hydrogen availability need small amounts of catalyst.





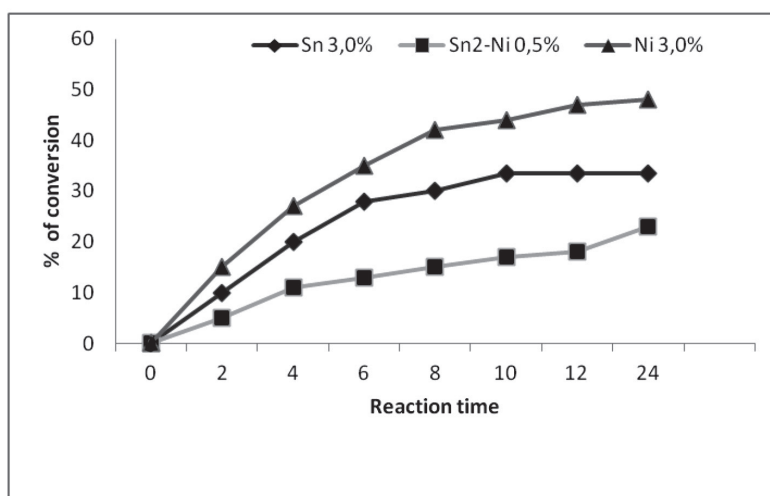
**Figure 6.** Proportion of the Ni3%/SnO<sub>2</sub> system conversion in function of the catalyst amount; reaction conditions: amount of catalyst = 2.6, and 6% mass; temperature of reduction: 400° C for 4h, and speed of agitation: 800 rvp.

Reactions at 2%, 4%, and 6% of catalyst mass were carried out (figure 6) and it is observed how the highest conversion rate is obtained with 4% catalyst. Anything above or below this value makes the conversion decrease and the only reactions being observed are mainly those of hydrogenation of the double bond. This catalyst activity is limited by the quantity present in the reaction medium. When it is low (2%), the activity is minimum due to not having enough quantity of catalyst or active sites to interact with the mixture of methyl esters. At a greater rate (6%), the transport phenomenon plays a role inhibiting an adequate interaction between the three phases, and therefore, the activity decreases. As far as the reactants in the methyl ester mixture, the ones that were most transformed were methyl palmitate and methyl linoleate. The first one possible due to its high concentration and the second one, for having two unsaturated bonds, which could bond with the catalyst active sites as reduced metals or to electro-deficient sites, as in the case of tin +2 or +4. Methyl laureate and methyl myristate did not undergo any modifications due to their low concentration.

It could be concluded, then, that the most adequate conditions for the hydrogenation reaction would be: pressure: 80 bar; temperature: 270 °C; catalyst amount: 4% mass, reduction temperature: 400° C during 4 h; and agitation speed: 800 rpm. In addition to the hydrogenation reaction, two other processes can occur under these conditions: the first one is the isomerization of the most unsaturated substrate (methyl oleate), and the second one is the dehydrogenation of methyl palmitate. The later mentioned agrees with what is published by Grau and colleagues in their study on kinetic modeling for the isomerization of methyl oleate on catalyst of the Ni/Al<sub>2</sub>O<sub>3</sub> type [13]. Under these conditions and using tin oxide as catalyst, the maximum rate of conversion after 24 hours is 5%; a very low value that indicates that SnO<sub>2</sub> is not sufficiently active as a catalyst for the hydrogenation of methyl esters.

### 3.2.1 Effect of tin as a doping substance

Taking into account that what it is wanted is to evaluate the presence of tin as metal or as doping substance among a hydrogenation-favorable metal such as nickel, figure 7 shows the results of the system based on mono and bi-metal  $\text{SnO}_2$ , which finds for the  $\text{Sn}3\%/\text{SnO}_2$  system a rate conversion of 30% after 8 hours of reaction remaining constant the rest of the time. This system is active for obtaining fatty alcohols, with a maximum selectivity of 32%. A rate of conversion of 78% is reached for methyl oleate, being the most transformed substrate. This substrate is the one that can be better absorbed by the catalyst due to possession of two unsaturated bonds. For this reason, it can be stated that methyl oleate undergoes transformations of isomerization forming geometric isomers of the type *cis-trans*, and it is hydrogenated totally becoming methyl stearate and this last one, subsequently, is transformed into stearic alcohol.



**Figure 7.** Rate of conversion of the  $\text{Sn}3\%$ ,  $\text{Ni}3\%$ , and  $\text{Sn}2\%-\text{Ni}0.5\%/\text{SnO}_2$  systems. Pressure: 80 bar; temp. 270 °C; mass of catalyst: 4%; reduction temp. 400 °C for 4 hours; and speed of agitation: 800 rpm.

For the  $\text{Sn}2\%-\text{Ni}0.5\%$  system, it is observed and activity as a result of this reaction achieving a conversion rate of 15% after 8 hours of reaction. In addition, it can be noted that the selectivity towards AG decreases with respect to the  $\text{Sn}3\%/\text{SnO}_2$  system (32 vs. 23%), which is evidence of the effect tin has over the selectivity towards AG.

According to the superficial area results (SAR), it is shown that at temperatures ranging from 260 to 450 °C, tin is mainly found in the form of  $\text{Sn}^{+2}$  and so it can be bonded to a molecule with great electronic density in the unsaturated levels as well as to oxygen. What probably has happened is that at 400 °C certain amount of reduced tin, in its 0 state, is behaving as a hydrogenation metal only to attack the double bond where molecules with unsaturated bonds, such as methyl oleate, are fixed to the metal in the acidic sites, and then, the previously mentioned reactions occur.

The best results at the conversion level are obtained for the  $\text{Ni}3\%/\text{SnO}_2$  system since the hydrogenation capacity of this metal is well known even when the fatty alcohols were not obtained at the pressures used, and only secondary reactions were present. This showed that under these conditions the catalyst is not selective towards the formation of fatty alcohols.

#### 4. Conclusions

First of all, the characterization of solids through different techniques demonstrated that the preparation of tin oxide using the method of controlled precipitation lead to obtaining the cassiterite crystalline structure and according to measures of superficial area, there were found small, but superior areas to those reported for these systems. The catalyst supported by tin (Sn) and nickel (Ni) did not lead to the modification of the structure of the used support.

As far as the hydrogenation reaction, it could be said that the heterogeneous catalyst systems based on nickel at 3% happened to be active in the hydrogenation of methyl esters from palm oil. The best conditions for the catalyst activity were: a pressure of 80 bar; a temperature of 270 °C; and a catalyst amount of 4% mass. At temperatures less than 270 °C, and at pressures less than 80 bar, the catalyst is not capable of reducing the activation energy for the hydrogenation processes involved, and therefore, important activities are not obtained.

The mono metal systems were active mainly for the hydrogenation of the double bonds presenting a low conversion, although fatty alcohols were obtain with Sn 3% and Sn2%-Ni 0.5% systems. Tin behaved as a hydrogenation-favorable metal due to the fact that part of it is in the oxide form and another part is reduced at a reduction temperature of 400° C, making possible the hydrogenation reaction to obtain fatty alcohols.

According to what is observed, any way, it could be stated that the most interesting system, as far as the transformation of the starting ester, is tin supported by tin oxide.

Finally, the tin oxide supported catalysts prepared for the controlled precipitation method showed special properties such as a greater superficial area with respect to commercial tin oxide prepared by conventional methods and a nano-metric particle size, which is important for the catalyst activity.

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