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Selective hydrogenation of methyl oleate into unsaturated alcohols Relationships between catalytic properties and composition of cobalt–tin catalysts

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Abstract

The selective hydrogenation of methyl oleate into oleyl alcohol, intermediate in the formulation of surfactant agents, is carried out over bimetallic catalysts containing cobalt and tin. However the tin content modifies the rates of the hydrogenation of the esters (methyl oleate and oleyl oleate) and of the side reaction of the transesterification between the methyl oleate and the alcohol formed. Indeed, the maximum of the unsaturated alcohol yield depends on the Sn/metal ratio.

The analyses of the catalyst surface by XPS have shown that there are coexistence of metallic particles (Co^0) and/or oxides (CoO) with two different tin oxides (SnO_x, SnO_y), the SnO_x species being close to zerovalent metallic particles. It is suggested that (1) $[Co^0 \cdots (SnO_x)_2]$ should be the active sites for the selective hydrogenation of ester, (2) the SnO_y species favor the reaction of transesterification and (3) the free metallic particles favor the hydrogenation of ethylenic bonds. On the other hand, the preparation method of the catalyst and the nature of the support modify the surface composition of the solid. The use of alumina or zinc oxide lead to the same yield of unsaturated alcohol whereas silica which has much more metallic Co^0 species gives a low activity due to a large tin enrichment. Over CoSn catalysts reduced with $NaBH_4$, owing to the formation of cobalt aluminate, a small content of metallic cobalt is observed. The preparation of CoSn catalyst via a sol–gel method improves the homogeneity and the dispersion of the active sites. But the strong interactions between cobalt and the support do not allow the formation of both metallic cobalt and mixed active centers (Co^0, SnO_x). Furthermore, some kinetic studies obtained with cobalt catalysts show that (1) the transesterification reaction is faster than the hydrogenation of esters, (2) the presence of methanol issued from the hydrogenation and from the transesterification strongly modifies the oleyl oleate hydrogenation.

Keywords: Selective hydrogenation; Methyl oleate; Oleyl oleate; Active sites

1. Introduction

Since 1930, a lot of processes have been described regarding the hydrogenation of organic carboxylic acids or organic carboxylic esters to produce aliphatic alcohols. In industrially available processes, hydrogenation is carried out at high temperature and high pressure such as 200–300°C and 20–30 MPa, usually using copper chromium catalysts [1–6]. On the contrary, few proposals exist for the selective hydrogenation of organic substrates containing different unsaturated functional groups. Recently there has been a special emphasis on the preservation of the carbon–carbon double bond especially of fatty

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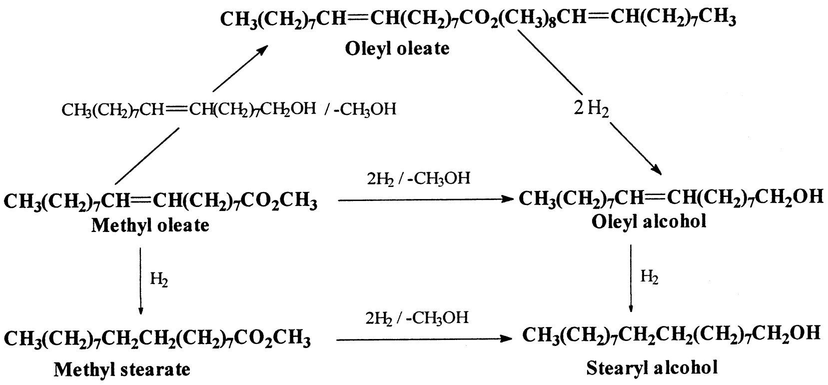
acid/ester molecules in order to obtain fatty unsaturated alcohols. Indeed, these compounds, such as oleyl alcohol, are important materials for the manufacture of heavy duty detergents, cosmetics, pharmaceuticals, toiletries, antifoaming agents, etc. Zinc chromite catalysts [7–9] were used for the hydrogenation of unsaturated fatty methyl esters into the unsaturated corresponding alcohols. But the low activity of these catalysts also requires that these reactions should be carried out under severe conditions of temperature (250–300°C) and pressure (20–35 MPa). Several attempts have been made to develop suitable catalytic systems operating in less severe conditions. Among these studies, we noted a number of works done with “light” esters or aldehydes (cinnamaldehyde and/or citral) and several works starting from unsaturated fatty methyl esters.

In the literature, there are some reviews reporting previous works done on selective hydrogenation [10–12]. But, in this paper, we will present only some trends concerning the intrinsic properties of group VIII metals and the modification of some of these metals in order to increase the selectivity of C=O versus C=C group hydrogenation. Some of our recent results in the field will be considered with a particular emphasis on the nature of active sites in bimetallic [Co–Sn] catalysts. Furthermore we have used some of these catalysts in the transformation of unsaturated compounds.

Besides copper catalysts, palladium, ruthenium, rhodium, rhenium and nickel were mainly studied for selective hydrogenation of esters into alcohols. Palladium supported over alumina was quite inactive for this reaction but when dispersed over zinc oxide, methyl oleate was transformed to oleyl alcohol with a selectivity of 50% [13]. The XPS data revealed that a “palladium–zinc” intermetallic could be formed [14,15], leading to new and specific sites for the selective adsorption and hydrogenation of the C=O bond. More recently, Touroude and co-workers [16] also suggested that the formation of a Pt–Zn alloy when a Pt/ZnO catalyst was reduced at a temperature above 473 K. They also concluded that Pt sites, when alloying to Zn, formed $Pt^{\delta-}$–$Zn^{\delta+}$ entities. These species would not adsorb the crotonaldehyde molecule by binding to olefinic bond but rather by binding to carbonyl bond giving crotyl alcohol.

The addition of a second element to a metal–support catalyst was one of the earliest attempts to improve the selectivity [11,17]. Furthermore the addition of tin to different metals could also give a strong improvement of the alcohol selectivity depending on the method of adding tin modifiers. Rh–Sn/SiO_2 prepared from the controlled reaction of tetrabutyl tin with metal particles can give very selective catalysts for the hydrogenation of citral to geraniol/nerol [18]. The reasons for such selectivity is still open, Basset and co-workers [18,19] suggesting the formation of $Rh[Sn–(nC_4H_8)_x]_y/SiO_2$ (with $x = 2, y = 1$). It was also suggested that bimetallic particles Rh–Sn dispersed over Al_2O_3 or SiO_2 in which Sn^0 was alloyed with the metal were formed and gave a high selectivity to crotyl alcohol [20] Such a result is in agreement with the above assumption concerning the formation of a Pt–Sn alloy on the Pt–ZnO catalyst [16]. None of these catalysts was used for the hydrogenation of an unsaturated fatty ester. Nevertheless, Narasimhan and co-workers [21–23] showed that methyl oleate could be selectively hydrogenated into oleyl alcohol in the presence of a mixed ruthenium–tin–boron supported on alumina catalyst under relatively low pressure (4.5 MPa) and at a temperature of 270°C. They reported a selectivity of about 80% for a conversion of 80% when a $RuSnB/Al_2O_3$ (with $Sn/Ru = 2$) was prepared by impregnation of chlorides over the support followed by reduction with sodium borohydride. Mizukami and co-workers [24] also claimed a selective Ru–Sn catalyst prepared via a sol–gel method without boron for the formation of oleyl alcohol. In our previous works, with RuSn catalysts, we failed at the beginning to obtain oleyl alcohol in similar conditions to those claimed by the above authors. Indeed, we have demonstrated that the reaction scheme of the methyl oleate hydrogenation could be more complex than the one generally proposed [25,26]. Scheme 1 shows that a transesterification step between methyl oleate (the reagent) and oleyl alcohol (one of the primary products) occurs with the formation of oleyl oleate as heavy ester [27]. Such esters are also adsorbed on the catalyst surface and their hydrogenolysis rate (giving oleyl alcohol) compared to the rate of the other reactions is one of the determining steps of the process. The characterization of the surface of the $RuSnB/Al_2O_3$ catalysts used in the reaction showed that zerovalent ruthenium metal particles are formed whereas ionic tin species (Sn^{IV} and Sn^{II}) with a minor content of



Scheme 1. Reaction scheme of the hydrogenation of methyl oleate.

zerovalent tin are formed in the reduced catalysts [26]. This result was quite similar to that observed for the Pt–Sn catalyst [20]. Nevertheless, if tin species close to group VIII metals are tin ions or positively charged tin species as in alloys, a surface polarity was created which favored the interaction of the oxygen atom of the C=O bond of the ester with the catalyst surface.

Recently, it was also demonstrated in our laboratory that cobalt catalysts, well-known catalysts in Fisher–Tropsch synthesis, could also be effective for the selective hydrogenation of methyl oleate, when tin was added to cobalt [28]. Indeed, the first results obtained demonstrated that promoted cobalt catalysts have more or less catalytic properties (activity and selectivity) similar to that of the ruthenium–tin catalysts. We present in this paper the latest results concerning cobalt–tin supported catalysts especially the influence of the support, the tin content, the preparation procedure together with the surface characteristics and the catalytic properties in the hydrogenation of methyl oleate.

2. Experimental

2.1. Catalytic test

The hydrogenation was carried out in a stainless steel batch reactor (300 ml). The reagent (100 ml of methyl oleate, 0.3 mol) and the catalyst (2.2 g) were introduced into the reactor under ambient conditions. The methyl oleate, supplied by Stearinerie Dubois with a purity of 80%, also contained other methyl esters: $C_{14} = 1.5\%, C_{16} = 15\%, C_{18} = 80\%$. The reactor was then purged (four times) with nitrogen at 5 MPa and continuously stirred. The temperature was slowly increased up to 270°C at constant pressure (5 MPa), nitrogen was replaced by hydrogen and the pressure, increased up to 8 MPa, was maintained during the reaction.

The oleyl alcohol supplied by CRODA and the oleyl oleate (heavy esters) supplied by Stearinerie Dubois have a purity of 89 and 70%, respectively.

2.2. Analysis

Liquid samples were mixed with dodecane and analyzed by GPC equipped with FID and a Chrompack Cp Sil-5 column (L: 25 m, ID: 0.25 mm, film thickness: 0.11 μm) flowed with nitrogen. All the methyl esters, alcohols and heavy esters were separated. The heavy esters resulted from transesterification reactions and contained C_{16}–C_{16}, C_{16}–C_{18} and mainly C_{18}–C_{18} esters.

By a calibration method, the weight percentages (X) of reagents and products were determined as

$$\%X_x = \frac{k_x A_x}{\sum_i k_i A_i}$$

where k_i and A_i represent the content and the surface area of the ith compound, respectively.

The conversion was expressed with regard to the total methyl esters transformation as

$$\text{Conversion (\%)} = \frac{(\%^{t^0}_{\text{C18:1c}}+\%^{t^0}_{\text{C18:1t}}+\%^{t^0}_{\text{C18:2}})-(\%^{t}_{\text{C18:1c}}+\%^{t}_{\text{C18:1t}}+\%^{t}_{\text{C18:2}})}{(\%^{t^0}_{\text{C18:1c}}+\%^{t^0}_{\text{C18:1t}}+\%^{t^0}_{\text{C18:2}})} \times 100$$

where $\%^{t^0}_{\text{C18}}$ is the weight percentage of C18 esters at zero time and $\%^{t}_{\text{C18}}$ the weight percentage of C18 esters at t time. The initial activity is expressed in $\text{mol}_{\text{ester}}\,\text{h}^{-1}\,\text{mol}_{\text{Me}}{}^{-1}$(Me). The selectivity to product was calculated as follows:

$$\text{SA (\%)} = \frac{\%^{t}_{\text{A}}-\%^{t^0}_{\text{A}}}{\sum_i (\%^{t}_{i}-\%^{t^0}_{i})} \times 100$$

where $(\%^{t}_{\text{A}}-\%^{t^0}_{\text{A}})$ is the weight percentage of product A.

2.3. Catalyst preparation

2.3.1. Coimpregnation and reduction with sodium borohydride

The catalysts were prepared by coimpregnation of the support (Al_2O_3 GFSC, area 200 m^2/g, SiO_2 DBM250, area 250 m^2/g both from Rhône Poulenc, Active carbon L2S, area 1200 m^2/g from CECA and ZnO, area 50 m^2/g, formed from calcination of $ZnCO_3$ (Union Minière) at 350°C; with $CoCl_2$ or/and $SnCl_2$ according to the method described by Narasimhan et al. [22]. After the impregnation step (12 h), the metallic precursors were reduced with an aqueous solution of sodium borohydride. The solids were then filtered, washed with water and dried at 80°C under nitrogen for 4 h.

2.4. Sol–gel method [24]

The metallic salts ($CoCl_2$, 1 g; $SnCl_2$, 1 g) dissolved in ethanol (20 ml) and hexyleneglycol (42 g) were heated at 90°C before the introduction of the aluminum isopropoxide (36.5 g). The mixture was refluxed at 90°C for 4 h and gelation, started with a small quantity of water, was finally obtained after 3 h of continuous stirring. The gel was dried in vacuum at 120°C for 2 h before being slowly reduced with hydrogen at a temperature of 300°C.

Before use, all the catalysts were reduced with hydrogen at 300°C and passivated with air at room temperature.

The catalysts are referenced as following: Co_xSn_y/support, where x and y are the weight percentages of the corresponding elements.

2.5. Catalyst characterization

2.5.1. X-ray photoelectron spectroscopy analyses

X-ray photoelectron spectroscopy (XPS) analyses were carried out with an SSI (Surface Science Instruments, Mountain View, CA) model 301 spectrometer with focused (diameter of the irradiated area (600 μm)) monochromatic Al Kα radiation (10 kV, 10 mA) and coupled with a glove-box which was used for the transfer of the samples reduced with hydrogen and passivated for 10 min under air. The residual pressure inside the analysis chamber was about 5×10^{-8} Pa. The calibration of the spectra was performed with the Al 2p line (74.4 eV) from an Al_2O_3 support.

The XPS peaks were decomposed into subcomponents using a Gaussian (80%)–Lorentzian (20%) curve fitting program with a non-linear background [29]. The quantitative analyses were performed with the sensitivity factors given by Scofield [30].

2.5.2. Temperature-programmed reduction

The temperature-programmed reduction (TPR) experiments were performed in a conventional pulse system using a thermal conductivity detector (TCD). The catalytic sample was evacuated under an argon flow at 300°C during 2 h. After cooling, pulses of hydrogen were introduced while heating from 25 to 450°C at a rate of 4°C/min.

3. Results

In the following paragraphs, the effect of the support will be presented first, the catalysts being prepared by the impregnation method (followed by a reduction with $NaBH_4$) or via a sol–gel method.

3.1. Influence of the support

Different types of materials were used as a support; they are different in their specific surface area, but also in their acidity or basicity as well as in their hydrophilic properties.

Table 1
XPS analysis of CoSn and CoSnB supported catalysts (influence of the support on the nature of cobalt or tin species)

Support	Bulk			XPS ($Sn\ 3d_{5/2}$, $Co\ 2p_{3/2}$)						Main species
	Co (wt.%)	Sn/Co (mol%)	B (wt.%)	Sn^0	SnO_x	SnO_y	Co^0	Oxide	I_p/I_s	
Al_2O_3	1.9	1.2	–	–	–	100	0	100	1.9	$\mathbf{Co^{II}}$
	2.3[a]	1.1	1.5	–	30	70	15	85	2.4	$\mathbf{Co^{II}}$, Co_3O_4
ZnO	3.0	1.0	–	25	–	75	10	90		$\mathbf{Co^{II}}$
	3.4[a]	0.9	0.3	40	–	60	15	85		$\mathbf{Co^{II}}$
SiO_2	5.3	0.5	–	30	–	70	30	70	3.2	$\mathbf{Co_3O_4}$
	2.6[a]	1.2	5.0	30	–	70	60	40	7	Co_3O_4, $\mathbf{Co^{III}}$
B.E. (eV)				485.0	484.8	486.8	778	781.6		

[a] Reduced with $NaBH_4$.

3.1.1. *Superficial composition of CoSn supported catalysts (XPS)*

The XPS data showing the nature of the species detected at the surface of all catalysts studied are reported in Table 1.

In all cases the content of metallic cobalt (Co^0) is more important when the catalyst is prereduced with $NaBH_4$. Moreover over silica the Co^0 content is more significant than over the other supports which is in agreement with previous results [31–33]. Furthermore, Martin-Luego et al. [33] showed that the second reduction step of Co^{II} to Co^0 occurred at 350°C over SiO_2, i.e. at a temperature much lower than over ZnO while it was the inverse for the first step ($Co^{III} \rightarrow Co^{II}$). Over alumina, Boskovic et al. [34] reported that the two reduction steps occurred at 410 and 550°C, respectively. The unreduced cobalt species are mainly Co^{II} over Al_2O_3 and ZnO and Co^{III} over silica which could indicate the presence of metallic cobalt and less reducible cobalt species over that support. One may suggest that small cobalt particles are formed in strong interaction with the support [35].

Concerning tin XPS characterization, a fraction of tin species is totally reduced over ZnO and SiO_2 while only tin oxides (mainly SnO_y (Sn^{IV})) are formed when alumina is used as a support.

The results reported in Table 2 show that the surface cobalt and tin contents are low (with respect to the bulk composition) before the $NaBH_4$ reduction especially over silica and that in all cases, there is a significant tin enrichment. After the reduction step, the cobalt and tin contents increase except over alumina. However, the Sn/Co ratio increases from 1.1 to 1.7, over Al_2O_3 and from 0.9 to 1.2 over ZnO whereas over SiO_2 the same ratio is four times greater than the bulk Sn/Co ratio.

These results mean that over silica, cobalt when reduced is close to Sn^0 and SnO_y species while over alumina Co^{II} and (SnO_x, SnO_y) are the main surface components (it could be that a part of the cobalt formed an aluminate compound).

Table 2
XPS analysis of CoSn and CoSnB supported catalysts (influence of the support on the surface content of cobalt or tin)

Support	Bulk			Surface area (m^2/g)	XPS		
	Co (wt.%)	Sn/Co (mol%)	B (wt.%)		Co/S	Sn/S	Sn/Co
Al_2O_3	1.9	1.2	–	140	0.021	0.068	3.2
	2.3[a]	1.1	1.5	125	0.013	0.022	1.7
ZnO	3.0	1.0	–	10	0.020	0.041	2.1
	3.4[a]	0.9	0.3	37	0.050	0.058	1.2
SiO_2	5.3	0.5	–	115	0.006	0.025	4.2
	2.6[a]	1.2	5.0	39	0.030	0.140	4.7

[a] Reduced with $NaBH_4$.

Table 3
Hydrogenation of methyl oleate over CoSnB/support catalysts (influence of the support on the reaction rate)[a]

CoSnB/support	Co (wt.%)	Sn/Co (bulk)	BET surface area (m^2/g)	Activity[b]
Al_2O_3	2.3	1.1	125	19.7
ZnO	3.4	0.9	37	24.3
SiO_2	2.6	1.2	39	3.9
C L2S	9.8	0.7	450	8.1

[a] Temperature = 270°C, P_{H_2} = 8.0 MPa, catalyst weight = 2.2 g, V_{ester} = 100 ml, H_2/ester = 1.5.

[b] Activity ($mol_{ester}\ h^{-1}\ mol_{Co}^{-1}$) calculated at 10% ester conversion.

3.1.2. *Catalytic properties*

Table 3 shows that the cobalt–tin supported on alumina or zinc oxide are more active than the other catalysts especially with silica.

It is rather surprising that the Co–Sn/SiO_2 catalyst containing the higher content of Co^0 is the less active solid. In fact the decrease of the activity could be due to the large excess of tin and to the partial covering of cobalt particles by tin species. Indeed the Sn/Co ratio as well as the nature of the tin species are the main determining variables which could influence the rate of the hydrogenation reaction as well as of side reactions (see later).

The product distribution presented for different values of the methyl oleate conversion in Table 4 also shows the important effect of the support. At low conversion (b) the methyl oleate is converted to the unsaturated alcohol (hydrogenation of the C=O bond) and to methyl stearate such as saturated ester (hydrogenation of the olefinic bond) especially over catalysts containing alumina and active carbon as supports (see Scheme 1). Then, particularly with zinc oxide and silica, the alcohols react with methyl oleate to form oleyl oleate and stearyl stearate (heavy esters). At high conversion (d) when the surface coverage of methyl oleate decreases, the heavy ester (i.e. oleyl oleate) is preferentially adsorbed and converted to oleyl alcohol (see Scheme 1).

If the catalysts are ranked according to the rate of the production of the unsaturated alcohol, we observed that

$$Al_2O_3 > \text{active carbon} > ZnO > SiO_2$$

The CoSnB/Al_2O_3 catalyst is the most active and selective catalyst. On the contrary SiO_2 and ZnO

Table 4
Hydrogenation of methyl oleate over CoSnB/support catalysts (influence of the support on the selectivity)[a]

CoSnB/support	Selectivity (%)				
	Unsaturated alcohol	Saturated alcohol	Saturated esters	Heavy esters	Others
Al_2O_3					
b	12	12.5	25.5	49.5	0.5
c	32	12	11.5	41.5	3
d	41	19	4	31	5
ZnO					
b	9	0	4	87	0
c	11	0	0	89	0
d	14	2.5	0	83.5	0
SiO_2					
b	0	0	8	86	6
c	15	5.5	11.5	56.5	11.5
d	21	5	5	58.5	10.5
C L2S					
b	29.5	3.5	26	26	15
c	25	4.5	7.5	62.5	0.5
d	46	13.5	4.5	35.5	0.5

[a] Temperature = 270°C, P_{H_2} = 8.0 MPa, catalyst weight = 2.2 g, V_{ester} = 100 ml, H_2/ester = 1.5; b–d represent the selectivity for a conversion of 15, 60 and 80%.

Table 5
XPS analysis of sol–gel CoSn catalysts (influence of the Sn/Co on the surface content of cobalt or tin)

Catalysts, $CoSnAl_2O_3$	Elementary analysis[a]			XPS[a]			Dispersion[b]	
	Co/Al	Sn/Al	Sn/Co	Co/Al	Sn/Al	Sn/Co	Co	Sn
$Co_{3.5}$	0.041	0	0	0.018	–	–	44	–
$Co_{3.5}Sn_{3.3}$	0.044	0.021	0.5	0.018	0.021	1.1	41	100
$Co_{3.8}Sn_{7.9}$	0.049	0.051	1.0	0.019	0.040	2.1	39	78
$Co_{3.7}Sn_{14.4}$	0.053	0.103	2.0	0.018	0.070	3.8	34	68
$Sn_{4.1}$	–	0.019	–	–	0.022	–	–	100

[a] Molar ratio.
[b] % $(M/Al_{XPS})/(M/Al_{elementaryanalysis})\times100$.

supported catalysts produce mainly heavy esters. These results are quite different of those previously mentioned in the literature which were obtained in the presence of catalysts prepared from different precursors, via other procedures and having different Sn/metal ratio (the metal being a noble one).

From the XPS characterizations and the catalytic properties, it is rather difficult to give a more precise conclusion as to the surface species responsible for the selectivity. In order to obtain more information, we examined the influence of the preparation method and of the Sn/Co ratio.

Table 6
XPS analysis of sol–gel CoSn catalysts (influence of the Sn/Co on the nature of cobalt or tin species)

Catalysts		$Co\ 2p_{3/2}$		$Sn\ 3d_{5/2}$	
$CoSn–Al_2O_3$	Sn/Co[a]	Co oxide (%)	I_p/I_s	SnO_x (%)	SnO_y (%)
$Co_{3.5}$	0	100	1.8	–	–
$Co_{3.5}Sn_{3.3}$	0.5	100	2.0	0	100
$Co_{3.8}Sn_{7.9}$	1.0	100	1.4	0	100
$Co_{3.7}Sn_{14.4}$	2.0	100	1.6	0	100
$Sn_{4.1}$	–	–	–	–	100[b]
B.E. (eV)		781.5		484.9	486.7

[a] Molar ratio.
[b] Binding energy: 487.1 eV.

3.2. Properties of the sol–gel CoSn/alumina catalyst

3.2.1. XPS analysis

The Sn/Co ratio effect on the nature of the surface species of the sol–gel CoSn catalyst was studied by XPS analysis (Table 5). There is a decrease of the tin dispersion when the Sn/Co ratio increases, but the dispersion still stays high (over 60%). This result is in agreement with the observations of Gomez et al. [36] about the Pt–Sn/alumina catalyst prepared via a sol–gel method. On the contrary the Co/Al ratio is two or three times smaller than the bulk Co/Al ratio. The addition of tin leads to a decrease of the cobalt dispersion and the (Sn/Co)s is two times greater than the bulk Sn/Co ratio.

Table 6 shows that only tin oxide species (SnO_y) are observed whatever be the tin content. Moreover Co^0 particles are not observed and only oxide species (B.E.: 781.5 eV), especially CoO, are formed on the catalyst surface. However, the increase of the tin content seems to slightly modify the Co^{II} percentage on the surface. Indeed, the I_{mp}/I_{sat} goes through a minimum when the tin content increases. As the shake-up peak of the Co^{II} is more significant than that of Co^{III}, these previous results indicate that for the Sn/Co ratio of 1, the proportion of Co^{II} is more significant (Fig. 1).

3.2.2. Catalytic properties

Fig. 2 presents the conversion of the methyl oleate for different Sn/Co ratio versus the reaction time. We can see that the conversion is maximum when the Sn/Co ratio is equal to 1. Above this value, the tin seems to inhibit the reaction, the same phenomena was observed in the presence of supported catalysts [37].

The variation of the activity of CoSn catalysts with the Sn/Co ratio confirms that there is a maximum for a Sn/Co ratio of 1 (Fig. 3). Moreover, we can note that the activity of the monometallic catalyst is lower than the one observed in the presence of the bimetallic. This result is in opposition to that obtained with the supported catalysts. Fig. 3 also shows that the selectivity varies with the Sn/Co ratio:

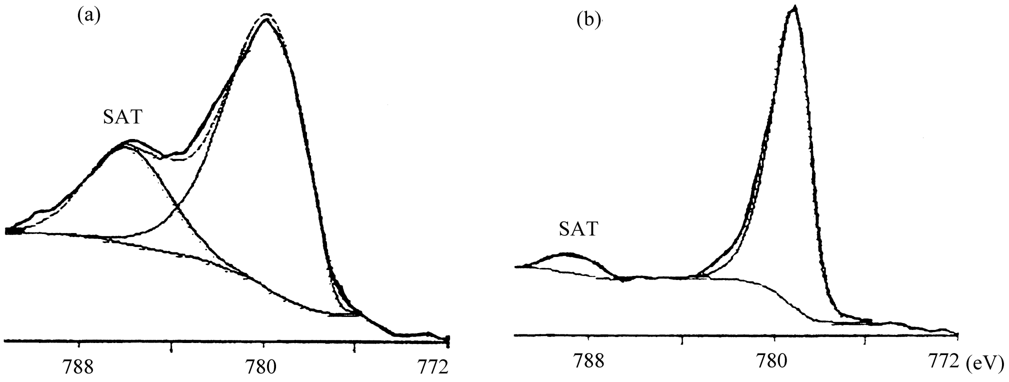


Fig. 1. XPS spectra of the Co $2p_{3/2}$ of: (a) Co^{II} in CoO and (b) Co^{III} in $LiCoO_2$.

- For a Sn/Co ratio smaller than 1, the catalyst is very selective to the saturated ester (70%). The main reaction is the hydrogenation of the olefinic bond.
- For a ratio equal or higher than 1, the main product is the heavy esters (80%). The main reactions are (i) the hydrogenation of the methyl ester following immediately by (ii) the transesterification reaction between the alcohol formed and the reactant.

When the conversion of the methyl oleate increases, the hydrogenation of the heavy esters is favored due to the decrease of the methyl oleate covering of the catalyst surface. This result indicates that the hydrogenation of the heavy esters is slower than the hydrogenation of the methyl oleate. This can be due to a lower reactivity of the heavy esters or to diffusion phenomena.

However, as mentioned by Mizukami and coworkers [24], the olefinic bond is preferentially adsorbed on the metallic particles and the tin increases the catalyst affinity for the carboxylic function. It could be also possible that the carbonyl groups of esters are more strongly adsorbed over the catalyst, leading to an inhibition of the hydrogen adsorption and of the hydrogenation steps.

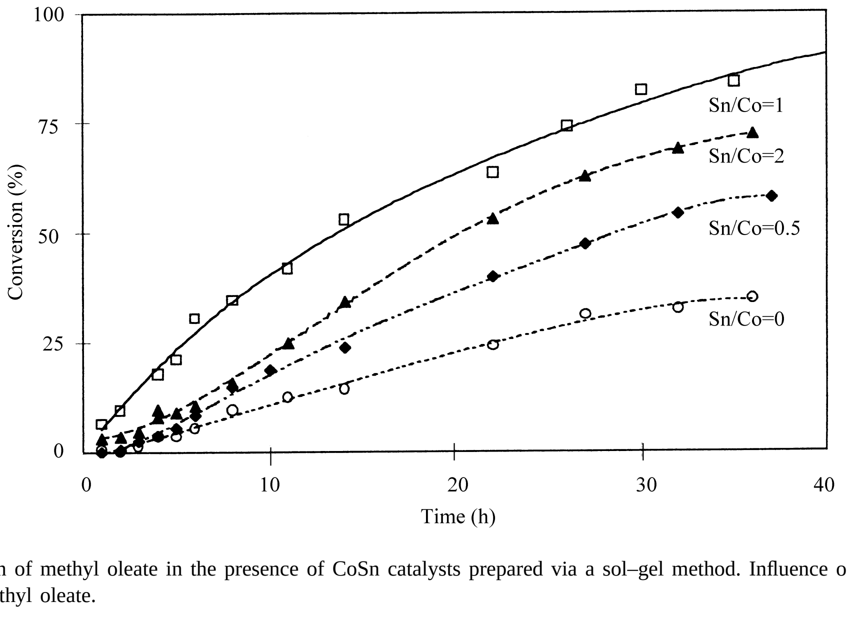


Fig. 2. Hydrogenation of methyl oleate in the presence of CoSn catalysts prepared via a sol–gel method. Influence of the Sn/Co ratio on the conversion of methyl oleate.

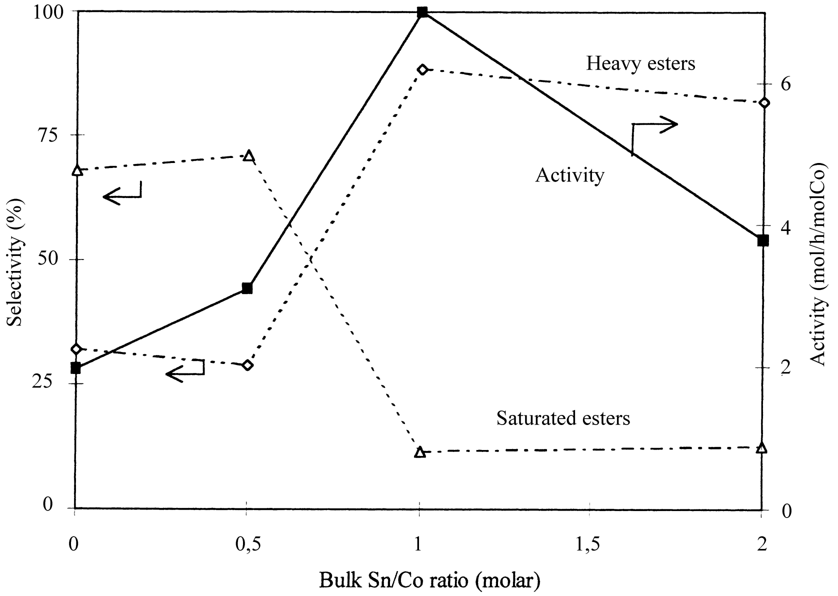


Fig. 3. Hydrogenation of methyl oleate in the presence of CoSn catalysts prepared via a sol–gel method. Influence of the Sn/Co ratio on the activity and selectivity compared at isoconversion (20%).

Table 7
Influence of the tin content on the specific surface area

	Sn/Co (molar)			
	0	0.5	1	2
BET surface area (m^2/g)	477	454	440	309

On the other hand, the decrease of the activity can be due to the addition of tin which decreases the specific area of the catalyst (Table 7).

3.3. *Reactivity of methyl oleate and oleyl oleate*

To confirm the assumptions concerning the different hydrogenation rates of the methyl oleate, we have studied in the presence of the CoSn catalysts (Table 8):

1. the methyl oleate hydrogenation,
2. the transesterification reaction,
3. the oleyl oleate hydrogenation.

3.3.1. *Methyl oleate hydrogenation*

Fig. 4 shows that the conversion of the methyl oleate is more significant in the presence of the CoSnB supported catalyst. Indeed, the activity of the supported catalyst ($39.4\,\mathrm{mol_{ester}\,h^{-1}\,mol_{Co}}^{-1}$) is eight times greater than that the sol–gel catalyst ($4.6\,\mathrm{mol_{ester}\,h^{-1}\,mol_{Co}}^{-1}$). The difference is yet much more important if the activities are calculated in moles of ester transformed per unit time and unit surface area, i.e. 1.13×10^{-2} and $0.36\times10^{-3}\,\mathrm{mol\,h^{-1}\,m^{-2}}$, respectively, for supported and sol–gel catalysts. Such difference comes from the very low Co^0 content as

Table 8
Composition of the CoSn catalysts

Catalysts	Preparation method	Weight content (%)			Sn/Co (mol)	BET surface area (m^2/g)
		Co	Sn	Al		
CoSnB/alumina	Narasimhan	2.1	4.3	40.9	1.02	124
CoSn–alumina	Sol–gel	2.3	4.6	37.1	1.00	497
Sn–alumina	Sol–gel	–	4.1			450

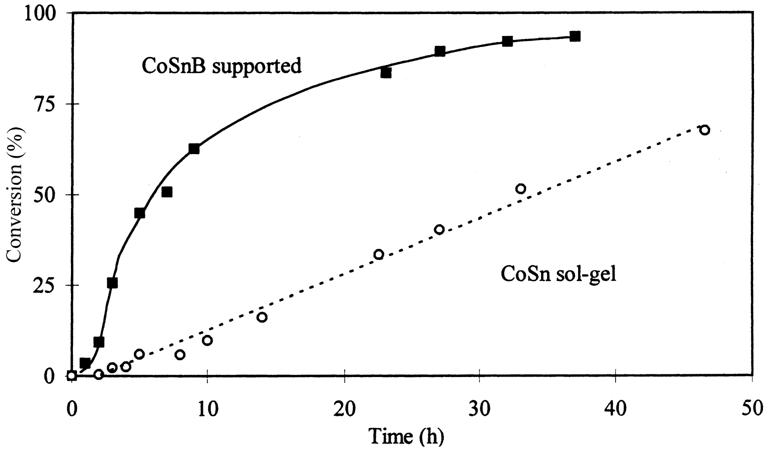


Fig. 4. Hydrogenation of methyl oleate in the presence of CoSn catalysts. Influence of the preparation method (supported or sol–gel) on the conversion of the methyl oleate.

previously reported in Table 10 and discussed in Section 3.2.1.

On the other hand, the selectivity of the two catalysts is rather similar (Fig. 5). The main product of the reaction is the oleyl oleate. The selectivity to the unsaturated alcohol increases when the methyl oleate conversion is higher than 75%. This indicates that the transesterification reaction is much faster than the methyl oleate hydrogenation whatever be the preparation method of the catalyst. Moreover, there is a competitive adsorption between the methyl oleate and the oleyl oleate on the catalyst surface. Owing to a preferential adsorption of the methyl oleate on the catalyst surface, the adsorption of the heavy ester

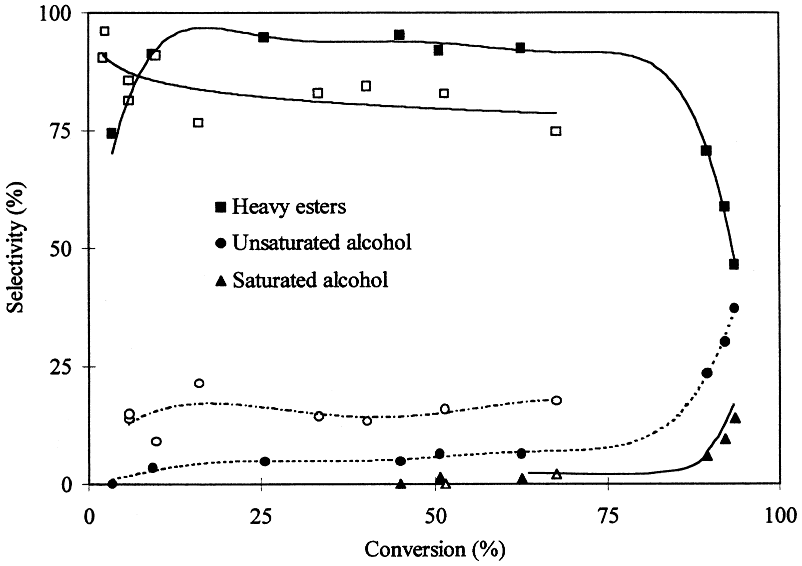


Fig. 5. Hydrogenation of methyl oleate in the presence of CoSn catalysts. Influence of the preparation method (supported or sol–gel) on the selectivity. Open signs: sol–gel catalyst, black signs: supported catalyst.

Table 9
Transesterification rate of methyl oleate with oleyl alcohol obtained in the presence of Sn and CoSn catalysts[a]

Catalysts	Preparation method	Transesterification rate ($mol_{alc.}\ h^{-1}\ mol_{Sn}{}^{-1}$)
CoSn–alumina	Sol–gel	147.3
CoSnB/alumina	Supported	48.4
Sn–alumina	Sol–gel	139.8

[a] Temperature = 270°C, $P_{N_2} = 8.0$ MPa, catalyst weight = 2.2 g, methyl oleate (0.165 mol) and oleyl alcohol (0.135 mol).

Table 10
XPS analysis of CoSn catalysts (influence of the preparation method on the surface content and on the nature of cobalt or tin catalysts species)

Catalysts Sn/Co (bulk)	$Co_{2.3}Sn_{4.9}B$ supported 1.0	$Co_{3.8}Sn_{7.9}$ sol–gel 1.0
XPS		
Co/Al	0.013	0.019
Sn/Al	0.022	0.040
Sn/Co	1.7	2.1
Co^0/Co^{II}	15/85	0/100
SnO_x/SnO_y	30/70	0/100

and its reaction with hydrogen becomes significant when the methyl oleate conversion is more than 80%.

In order to examine the influence of the preparation method of the catalyst on the transesterification rate, we studied the transesterification reaction between the oleyl alcohol and the methyl oleate.

3.3.2. The transesterification reaction between the methyl oleate and the oleyl alcohol

To identify the species involved in the transesterification step, the reaction between the methyl oleate (0.165 mol) and the oleyl alcohol (0.135 mol) was carried out at 270°C under nitrogen pressure (8 MPa) in the presence of CoSn catalysts (supported and sol–gel) and of the Sn/Al_2O_3 catalyst (prepared via a sol–gel method).

The Sn and CoSn catalysts prepared by a sol–gel method have similar activities (Table 9). This result indicates that the cobalt has no influence on the transesterification reaction. Moreover, as previous works showed that alumina was not active in the transesterification reaction [27], tin species act as active sites in the transesterification. However, the preparation method also influences the activity of the solid since the supported catalyst is less active than the catalyst prepared via a sol–gel method. The XPS analyses (Table 10) show that there are only SnO_y species on the surface of the sol–gel catalyst whereas there are two tin oxides (SnO_x and SnO_y) on the supported catalysts. It seems that the SnO_x species ($x \leq 1$) are less active in the transesterification reaction than SnO_y species ($y \approx 2$).

3.3.3. Hydrogenation of the oleyl oleate

The last step of the process is the hydrogenation of the heavy ester; i.e. the oleyl oleate. In order to determine the rate of the oleyl oleate hydrogenation, two experiments were carried out in the presence of two CoSn catalysts:

1. From the heavy esters formed in situ by reaction between the methyl oleate and the oleyl alcohol under nitrogen pressure (see Section 3.3.2). At a methyl oleate conversion of 90%, the nitrogen is replaced by hydrogen (zero time of the heavy esters hydrogenation).
2. From a commercial oleyl oleate (0.15 mol).

Table 11 shows that the activity of the two catalysts is different, the hydrogenation of the heavy esters being much faster over the supported catalyst than over sol–gel catalyst. Furthermore, the rate of the hydrogenation of the commercial product is lower than the one obtained with the heavy ester formed in situ. In this case, during the transesterification reaction, there is the simultaneous formation of methanol which could modify the reaction rate.

Tables 12 and 13 show that the repartition of the products depends on both the nature of the starting methyl oleate and of the catalyst:

Table 11
Activity of the (CoSnB supported) and (CoSn sol–gel) catalysts in the hydrogenation of oleyl oleate (influence of the origin of reactants)[a]

Origin of oleyl oleate	Catalysts	Activity ($mol_{ester}\ h^{-1}\ mol_{Co}{}^{-1}$)
Commercial[b]	Sol–gel	0.5
	Supported	1.1
Formed in situ[c]	Sol–gel	3.6
	Supported	3.7

[a] Temperature = 270°C, $P_{H_2} = 8.0$ MPa, catalyst weight = 2.2 g, H_2/ester = 1.5.

[b] 0.15 mol.

[c] See Table 9.

Table 12
Weight distribution of products issued from the hydrogenation of the oleyl oleate formed in situ in the presence of the (CoSnB supported) and (CoSn sol–gel) catalysts[a]

Catalysts	Time (h)	Conversion (%)	Hydrocarbons[b] (%)	Alcohols (%)	Esters (%)	
					Methyl	Heavy
Sol–gel	t_0		1	3	4	92
	24	26.5	9	9	7.5	71.5
Supported	t_0		1	3.5	6.5	89
	21	26	2.5	22.5	9	65.5

[a] Temperature = 270°C, $P_{H_2} = 8.0$ MPa, catalyst weight = 2.2 g, $V_{ester} = 100$ ml, H_2/ester = 1.5.
[b] Hydrocarbons: octadecadiene, octadecene, octadecane.

From the methyl oleate formed in situ.

1. In the presence of the sol–gel catalyst, there are the formations of alcohols, of methyl esters from the reaction between the oleyl oleate and the methanol, of hydrocarbons from the dehydration of alcohols.
2. In the presence of the supported catalyst, there is mainly formation of the saturated products (alcohols and esters).

From the commercial methyl oleate.

1. Owing to the absence of methanol, there is no formation of methyl esters. In the presence of the sol–gel catalysts, the products are mainly the hydrocarbons obtained from the dehydration of alcohols. But it is only over the supported catalyst that the hydrogenation of the heavy esters into alcohols takes place at the highest rate.

These results show that the methanol seems to strongly influence the reaction via different ways:

- The methanol acts as a reducing agent increasing the number of reduced sites and the hydrogenating properties of the catalyst.
- The methanol favors the dissolution of hydrogen in liquid phase which also induces an increase of the reaction rate.
- The methanol reacts with the oleyl oleate to form the methyl oleate and the oleyl alcohol.

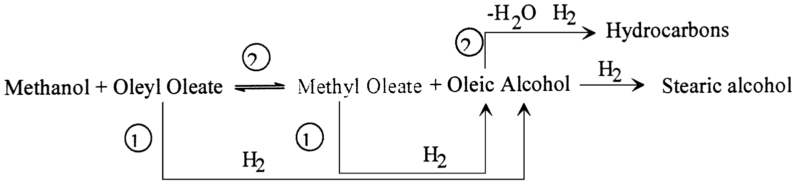
To sum up this work, the reaction scheme of the hydrogenation of the oleyl oleate could be the following (Scheme 2). In this scheme, two kinds of reactions are observed: (i) the reactions ❶ (hydrogenation of methyl oleate or of oleyl oleate) could be catalyzed by the hydrogenating sites (Co^0–$(SnO_x)_2$). (ii) The reactions ❷ (transesterification between methyl oleate and oleyl alcohol or alcohol dehydration) generally known to occur over the acid or/and basic sites of the catalyst that is in the present case over SnO_y species or/and the support.

It could be also suggested that some impurities of the commercial oleyl alcohol or of the oleyl oleate modified the catalytic properties of the solids used in the oleyl oleate hydrogenation. But up to now the analysis of both samples did not showed signif-

Table 13
Weight distribution of products issued from the hydrogenation of the commercial oleyl oleate in the presence of the (CoSnB supported) and (CoSn sol–gel) catalysts[a]

Catalysts	Time (h)	Conversion (%)	Hydrocarbons[b] (%)	Alcohols (%)	(%) Esters	
					Methyl	Heavy
Sol–gel	t_0	0	1	2.5	0	95.5
	52	12.5	10.5	4	0.5	83.5
Supported	t_0	0	1	1	0	97.5
	27	12	2.5	11.5	0	85.5

[a] Temperature = 270°C, $P_{H_2} = 8.0$ MPa, catalyst weight = 2.2 g, $V_{ester} = 100$ ml, H_2/ester = 1.5.
[b] Hydrocarbons: octadecadiene, octadecene, octadecane.



Scheme 2. Reaction scheme of the hydrogenation of oleyl oleate.

icant differences in the composition of both oleyl oleates.

4. Conclusion

In this work, we have showed that the hydrogenation of methyl oleate can be carried out in the presence of CoSn catalysts.

First of all, the nature of the support influences the activity and the selectivity of the reaction. Over silica, the cobalt–support interactions, less significant than on alumina, lead to a increase of the Co^0 content but the hydrogenating activity is low, due to a large tin surface enrichment. Furthermore, a ZnO supported catalyst also activates the ester leading to a similar activity to that observed on alumina.

A series of $CoSnAl_2O_3$ catalysts prepared via a sol–gel method was studied. The XPS analyses showed that the surface cobalt content is more or less half that of the bulk which induced a relative surface tin enrichment, the surface Sn/Co ratio being twice that of the bulk. Moreover the XPS also indicated that cobalt oxides (Co^{II} and Co^{III}) were the major cobalt species at the catalyst surface and that only one type of tin species was formed without significant interaction with cobalt oxides.

Over sol–gel catalysts, the number of specific sites involved in the hydrogenation of methyl oleate to oleyl alcohol is low so that the reaction rate is also low. If the Co^0 content was increased as for $CoSnB/Al_2O_3$ catalysts, both the activity and the selectivity to unsaturated alcohol increase. The SnO_x species were also more numerous at the catalyst surface, and the atomic ratio $(SnO_x)/Co^0$ of the selective centers is around 2.

Finally this study showed that active sites containing zerovalent cobalt and tin oxides SnO_x (where $x \leq 1$) with an atomic ratio $SnO_x/Co^0 \approx 2$ favor the selective hydrogenolysis of methyl esters to unsaturated alcohols. Depending on the relative amount of Co^0, SnO_x, SnO_y, the methyl ester is transformed to saturated ester (Co^0), to unsaturated alcohol (Co^0–$(SnO_x)_2$) or to heavy esters ($\varepsilon Co^0 - (SnO_x)_2 + SnO_y$). A complementary study of the reactivity of oleyl alcohol and oleyl oleate over the same catalysts confirmed these assumptions.

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