

Hydrogenation of Fatty Esters over Ruthenium–Tin Catalysts; Characterization and Identification of Active Centers

Y. Pouilloux,* F. Autin,* C. Guimon,† and J. Barrault*¹

*Laboratoire de Catalyse, UMR 6503, ESIP, 40, Avenue du Recteur Pineau, 86022 Poitiers, France; and †Laboratoire de Physicochimie moléculaire, UMR 5624, 64000 Pau, France

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The selective hydrogenation of methyl oleate into oleyl alcohol was performed over RuSn/alumina catalysts. A maximum yield of unsaturated alcohol was obtained for a bulk atomic ratio to Sn/Ru = 4. The side reaction of the transesterification between methyl oleate and oleyl alcohol leading to oleyl oleate was strongly decreased. The ruthenium–tin catalysts prerduced with NaBH₄ have been characterized by TPR and XPS analysis. The addition of tin increased the content of Ru^o on the catalyst surface without modification of the total Ru content. When the catalysts were reduced with NaBH₄, a decrease of the tin and ruthenium contents on the surface was observed. On the catalyst surface were found two separate tin oxide species which differed in the oxidation state of tin. The proportion and the repartition of each species was a function of the total tin content. Over such catalysts, the reaction scheme involved three steps: (1) the hydrogenation of the methyl oleate into the oleyl alcohol, (2) the transesterification reaction between the methyl oleate and the oleyl alcohol with the formation of the heavy oleyl oleate ester, (3) the hydrogenation of this heavy ester into oleyl alcohol. The first and the third step could involve mixed ruthenium–tin sites while the second step could require tin species without an interaction with ruthenium. If it is assumed that the rate determining step is the oleyl oleate hydrogenation, the results of this study show that active centers corresponding to a stoichiometry Ru/SnOx = 2 could be involved in this reaction. The activation of esters (methyl oleate and oleyl oleate) would occur via a hemiacetal intermediate over these mixed sites where the more reduced tin species could be close to the ruthenium. © 1998 Academic Press

Key Words: hydrogenation; fatty esters; unsaturated alcohols synthesis; ruthenium–tin catalysts.

INTRODUCTION

The selective formation of unsaturated alcohols from the hydrogenation of α,β unsaturated carbonyl compounds, particularly α,β unsaturated aldehydes, in the presence of solid catalysts has been previously reported (1–4).

This reaction requires the control of the chemoselectivity since the formation of unsaturated alcohol involves

the activation of the (C=O) carbonyl groups without the reduction of the C=C bond. On the other hand, the hydrogenation of esters is more difficult to achieve since the carbonyl group of ester is less active than the hydrogenation of a ketone and a aldehyde group.

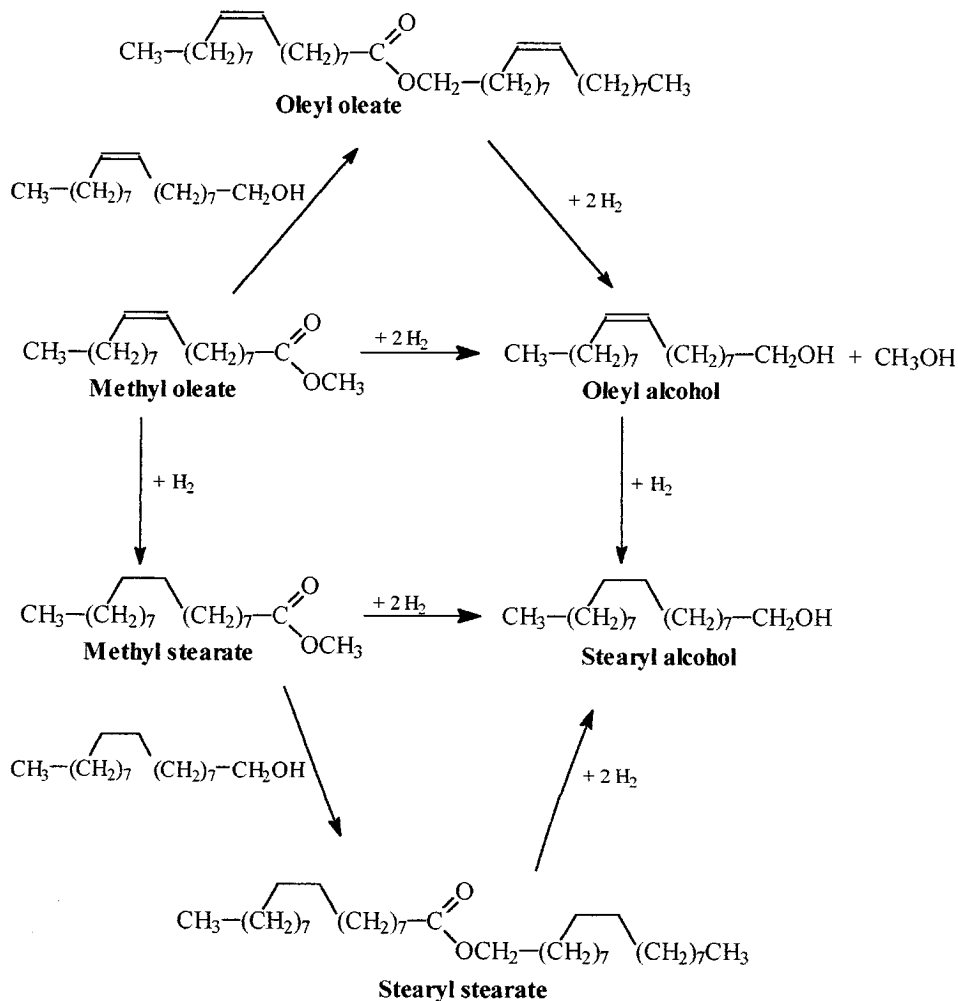
Generally, these works concerned the hydrogenation of light esters (5, 6). When using similar catalysts (noble metal with promoter) for the hydrogenation of more complex unsaturated esters, it was observed that the selectivity to unsaturated alcohols could also be improved, i.e., oleyl alcohol (9-octadecen-1-ol) from methyl oleate (methyl-9-octadecenoate). But we also demonstrated that the reaction scheme of the methyl oleate hydrogenation over RuSnB/Al₂O₃ (7) catalyst is more complex than the one proposed by Narasimhan *et al.* (8). We have observed the formation of heavy esters (i.e., oleyl oleate) and an unsaturated alcohol yield lower than the one obtained in previous works (9). Indeed, Scheme 1 shows that oleyl alcohol can react with methyl oleate to form oleyl oleate which decreases the alcohol yield at least at the beginning of the reaction. It seems that tin species dispersed on alumina favor the side reaction of transesterification and that the hydrogenation of heavy esters (giving two moles of unsaturated alcohol) is the rate-limiting step of the whole process.

In order to get further informations on the reaction mechanism (including the nature of active sites) we investigate detailed characterization of RuSn catalysts. In the present paper, the surface and bulk characteristics of samples differing in their ruthenium or tin content and the prerduction process are established and discussed in relation with the catalytic properties.

EXPERIMENTAL

Catalytic test. The hydrogenation reaction was carried out in a stainless steel batch reactor (300 ml). The reagent (100 ml of methyl oleate) 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:

¹ Corresponding author. E-mail: joel.barrault@esip.univ-poitiers.fr.



SCHEME 1. Reaction scheme of the hydrogenation of methyl oleate in the presence of RuSn/Al₂O₃ catalyst.

C₁₄ = 1.5%, C₁₆ = 15%, C₁₈ = 80%. The reactor was then purged (4 times) with nitrogen at 5 MPa and stirred continuously. The temperature was slowly increased up to 270°C at constant pressure (5 MPa), nitrogen was substituted for hydrogen and the pressure increased up to (8 MPa) was maintained during the reaction.

Analysis. Liquid samples were mixed with dodecane and analyzed by a GPC equipped with FID and a Chrompack Cp Sil-5 column (L, 25 m; ID, 0.25 mm; thickness of film, 0.11 μm). The carrier gas was nitrogen.

Catalyst Preparation

Coimpregnation and reduction with sodium borohydride. The catalysts were prepared by coimpregnation of the support (Al₂O₃ GFSC from Rhône Poulenc, area 200 m² · g⁻¹) with RuCl₃ and/or SnCl₂, according to the method described by Narasimhan *et al.* (10). 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 120°C under nitrogen for 4 h.

Before use the catalysts were reduced with hydrogen at 400°C and passivated with air at room temperature.

XPS characterization. (α) X-ray photoelectron spectroscopy (XPS) analyses were performed with an SSI (Surface Science Instruments, Mountain View, CA) model 301 spectrometer with focused (diameter of the irradiated area (600 μm)) monochromatic Alk α 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 Al₂O₃ support.

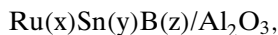
The XPS peaks were decomposed into subcomponents using a Gaussian (80%)–Lorentzian (20%) curve fitting program with a nonlinear background (11). The quantitative

analyses were performed with the sensitivity factors given by Scofield (12).

Temperature-programmed reduction. TPR experiments were performed in a conventional flow system using a thermal conductivity detector (TCD). The catalytic sample was swept by Argon at 300°C for 2 h. After cooling, it was heated under hydrogen at a heating rate of 4°C/min from 25°C to 450°C.

H₂ or CO chemisorption. Chemisorption of H₂ or CO has been performed using a conventional pulse system operating at room temperature. After reduction with H₂ at 400°C (12 h), a He stream was passed over the sample at the same temperature and the catalyst was cooled down to room temperature. A fixed amount of gas was then periodically injected into the He stream over the sample and hydrogen or carbon monoxide not adsorbed on the catalyst was analyzed with a TC cell.

Nomenclature. All catalysts are referenced as



where x, y, and z are the weight content (%) of each element.

RESULTS

Effect of the Addition of Tin

In order to examine the effect of the tin content on bimetallic RuSn/Al₂O₃ catalysts, we have prepared a series by varying the tin content.

Temperature-programmed reduction of RuSn/Al₂O₃ catalysts. In Fig. 1, the effect of the tin content on TPR profiles of RuSn–alumina is presented. First, we can see, since there is only one reduction peak, that ruthenium and tin are in strong interaction. Furthermore, the addition of tin decreases the hydrogen consumption and the maximum temp-

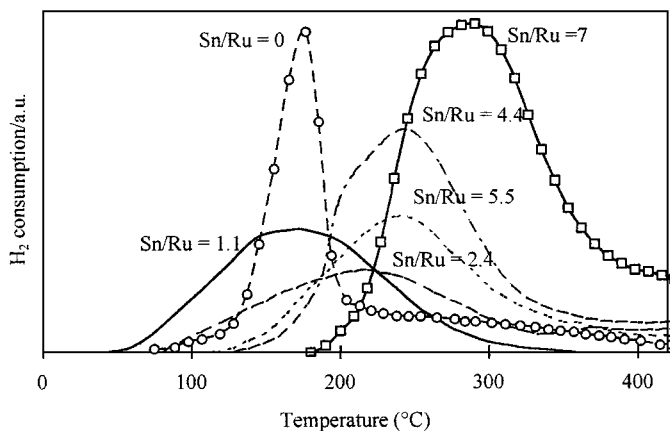


FIG. 1. TPR profiles of RuSnB/Al₂O₃ catalysts and effect of the tin content.

TABLE 1

XPS Analysis of the RuSnB/Al₂O₃ Catalysts: Effects of the Tin Content

RuSnB/Al ₂ O ₃	Ru (at%)	Sn (at%)	Sn/Ru ^a	Ru/Al	Sn/Al	Sn/Ru
Ru(2)B(0.7)	0.53	—	0	0.014	—	—
Ru(1.5)Sn(4.1)B(1.1)	0.60	1.8	2.4	0.016	0.048	3.0
Ru(1.6)Sn(8.5)B(1.1)	0.48	3.0	4.4	0.014	0.087	6.2
Ru(1.5)Sn(10)B(1.3)	0.43	3.0	5.5	0.012	0.082	6.9

^a Atomic ratio determined by elementary analysis.

erature of the reduction step increases with the Sn/Ru ratio. The H₂ and CO chemisorption values confirm that tin inhibits totally the adsorption both of hydrogen and of CO (7).

According to the TPR results, we can say that there are three kinds of catalysts, depending on the Sn/Ru ratio:

(i) the RuSn systems ($0 \leq \text{Sn/Ru} \leq 1$) which are easily reducible ($T_{\text{max}} \cong 175^\circ\text{C}$).

(ii) the RuSn systems ($2 \leq \text{Sn/Ru} \leq 5$) for which only one reduction peak ($200^\circ\text{C} < T < 250^\circ\text{C}$) is detected.

(iii) the RuSn system ($\text{Sn/Ru} > 7$) for which a reduction at higher temperature is observed. From these results a modification of the accessibility and of the electronic properties of ruthenium can be expected.

XPS analysis of the RuSn/Al₂O₃ catalysts. The addition of tin has no effect on the surface ruthenium content since the Ru/Al is more or less constant (0.014 ± 0.002) (Table 1). On the other hand, a surface tin enrichment can be observed, the surface Sn/Ru ratio varies from 3 to 7 instead of 2.4 to 5.5 for the bulk Sn/Ru ratio (Table 1). This result could indicate the presence of isolated tin oxides without any interaction with ruthenium. The percentage of all the species detected on the solid surface (Fig. 2) reported in Table 2 shows that, in the presence of tin, there is only zerovalent Ru⁰ species varying by binding energy. Under

TABLE 2

XPS Analysis of RuSnB/Al₂O₃: Influence of the Tin Content

RuSnB/Al ₂ O ₃	Ru 3d _{5/2}		Sn 3d _{5/2}	
	Ru ⁰ (%)		SnO _x (%)	SnO _y (%)
Ru(2)B(0.7) ^a	—	100	—	—
Ru(1.5)Sn(4.1)B(1.1) ^a	100	—	20	80
Ru(1.6)Sn(8.5)B(1.1) ^a	100	—	30	70
Ru(1.5)Sn(10)B(1.3) ^a	100	—	25	75
Ru(1.5)Sn(4.1)B(1.1) ^b	100	—	35	65
BE (eV)	279.3	280.1	484.9	486.7

^a Reduced under H₂ at 400°C and passivated 10 min.

^b Reduced under H₂ at 400°C.

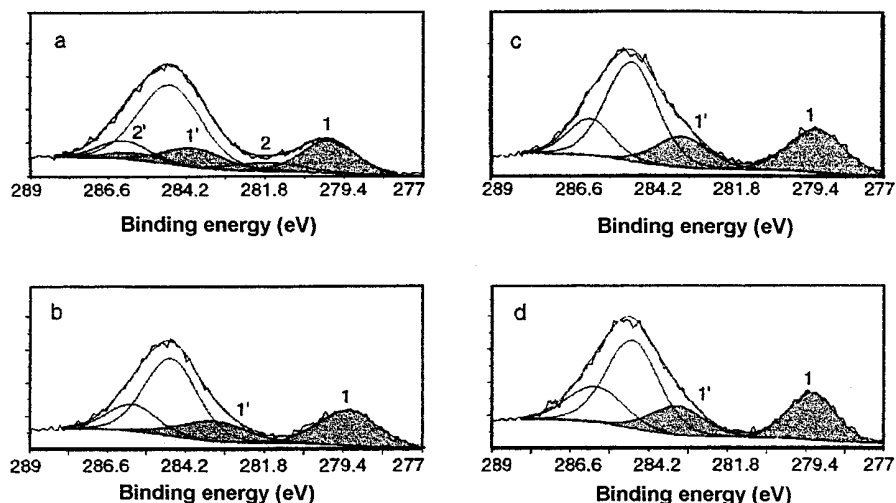


FIG. 2. XPS spectra of the Ru 3d of the RuSn/Al₂O₃ catalysts. Influence of the Sn/Ru ratio: (a) Sn/Ru = 0; (b) Sn/Ru = 2.4; (c) Sn/Ru = 4.4; (d) Sn/Ru = 5.5.

these conditions, the hydrogenating character of metal particles should not be modified. It can also be noticed that two kinds of tin oxides (SnO_x and SnO_y with $0 < x < y$) are formed and that the relative amount of these oxides varies with the tin content (Fig. 3). Indeed, a maximum of SnO_x (30%) is obtained for a Sn/Ru ratio of 4 (Table 2). Contrary to Narasimhan's previous propositions (10), we did not detect any zerovalent tin (Sn⁰) at the surface of these solids nor any alloys or intermetallics (Ru_xSn_y) that Narasimhan (10) or Ferretti (13) assumed to be present. But we can observe that for SnO_x the binding energy of Sn 3d is not very different of the binding energy of Sn⁰ (BE = 484, 5 eV). Some experiments have been done with samples pre-reduced *in situ* with hydrogen (Fig. 3d); so that we can com-

pare the results with that observed over passivated samples (Table 2).

Over reduced RuSn catalyst, the content of SnO_x species is more significant than over passivated materials, showing that they could have a role during the passivation.

Hydrogenation of the methyl oleate. Figure 4 shows that the addition of tin leads to a modification of the hydrogenating properties of ruthenium. But the increase of the tin content does not change significantly the catalyst activity. However, Figs. 5 and 6 show that the selectivity is strongly modified by the addition of tin. Figure 5 presents the variation, at different methyl oleate conversions, of the unsaturated alcohol selectivity with the Sn/Ru atomic

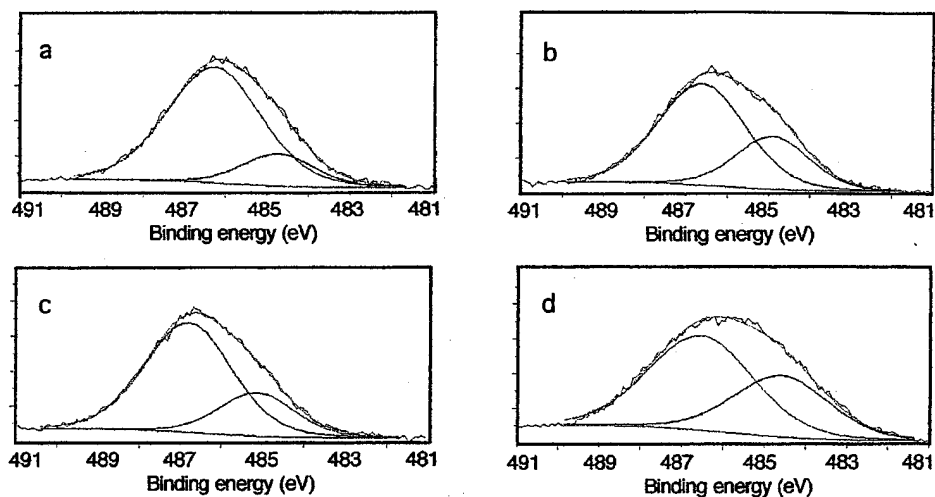


FIG. 3. XPS spectra of the Sn 3d of the RuSn/Al₂O₃ catalysts reduced with H₂ and passivated 10 min under air. Influence of the Sn/Ru ratio: (a) Sn/Ru = 2.4; (b) Sn/Ru = 4.4; (c) Sn/Ru = 5.5; (d) Sn/Ru = 2.4 reduced *in situ* and not passivated.

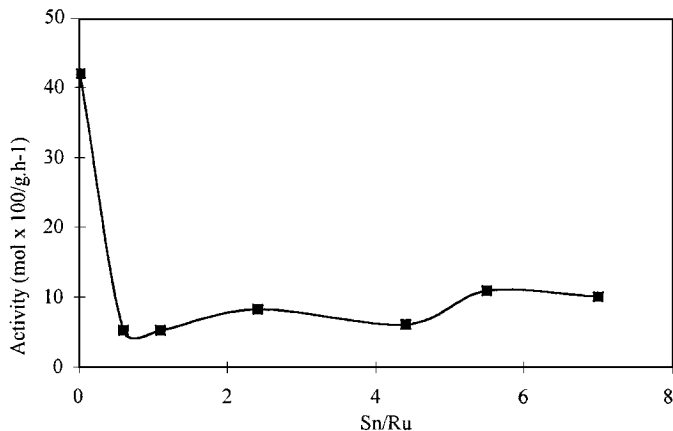


FIG. 4. Hydrogenation of methyl oleate in the presence of RuSnB/Al₂O₃ catalysts. Variation of the activity with Sn/Ru ratio.

ratio. The selectivity to oleyl alcohol is maximum for a Sn/Ru ratio of 4 and in these conditions a yield of 75% of unsaturated alcohol is obtained for a conversion of about 90%, the formation of heavy esters being very low (Fig. 6). These facts clearly show that there is: (i) an increase of the hydrogenation rate of the oleyl oleate which seems to be the limiting step; (ii) a limitation of the side reaction of transesterification; (iii) the selectivity to the saturated alcohol (stearyl alcohol) is even low whatever the tin content.

Effect of the NaBH₄ Prereduction

In order to study the effect of the reducing agent on the activity and the selectivity of the RuSnB/Al₂O₃ catalysts and the effect of boron, the amount of sodium borohydride used during the reduction step was varied.

Table 4 shows that the increase of NaBH₄ involves a decrease of the ruthenium content. This could be due to a par-

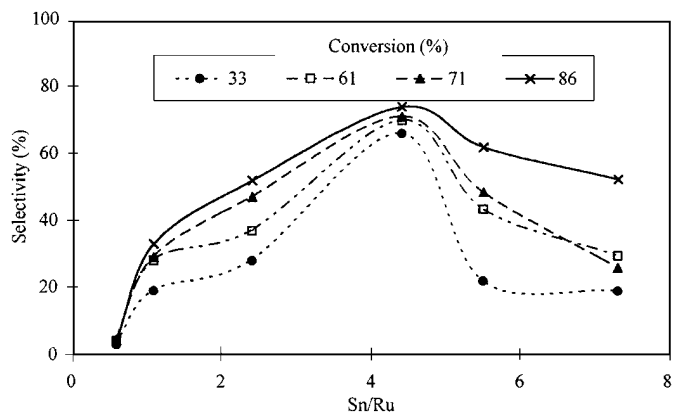


FIG. 5. Hydrogenation of methyl oleate in the presence of RuSnB/Al₂O₃ catalysts. Variation of the selectivity to unsaturated alcohol with the Sn/Ru ratio at different conversions.

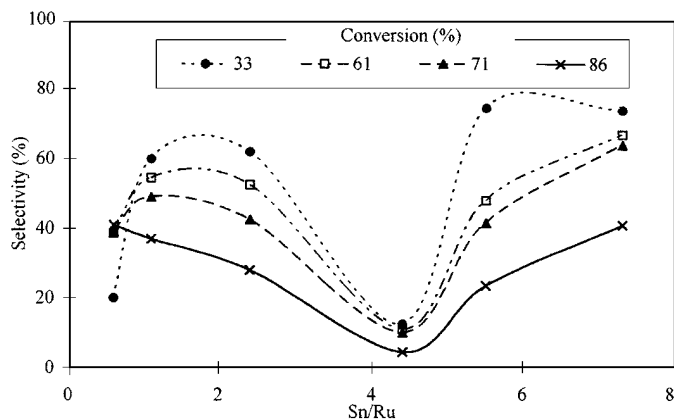


FIG. 6. Hydrogenation of methyl oleate in the presence of RuSnB/Al₂O₃ catalysts. Variation of the selectivity to heavy esters with the Sn/Ru ratio at different conversions.

tial leaching of the catalyst with the removal of ruthenium during the reduction step and an increase of the Sn/Ru ratio. On the other hand, the boron content increases to about 1% with the addition of sodium borohydride.

Temperature-programmed reduction of RuSnB systems.

Figure 7 presents the TPR profiles of RuSnB solids after a prereduction with a progressive increase of the amount of sodium borohydride (NaBH₄/Ru). We can see that the increase of the NaBH₄ content modifies the hydrogen consumption.

First, we observed a decrease of the H₂ consumption which could indicate that the species formed during the reduction with NaBH₄ are either less reducible or not reoxidized during the passivation step. Indeed, once the ruthenium and tin are totally oxidized after the passivation with air, the H/Ru ratio corresponding to the reduction of (Ru⁺⁴ to Ru⁰) and two (Sn⁺⁴ to Sn⁺²) is equal to 8 (Table 3). After a prereduction with a small amount of NaBH₄, the H/Ru ratio first increases and then drops to a value close to

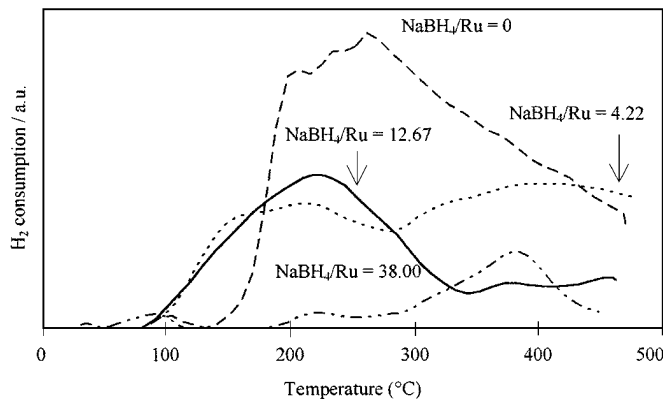


FIG. 7. TPR profiles of RuSnB/Al₂O₃ systems. Influence of the prereduction with increasing amount of NaBH₄.

TABLE 3
Influence of NaBH₄ Amount on the H₂ Consumption on the Formation Rate of Unsaturated Alcohol and the Selectivity to Unsaturated Alcohol over RuSnB/Al₂O₃ Catalysts

RuSnB/Al ₂ O ₃	Sn/Ru ^a	NaBH ₄ /Ru	H/Ru	r _{unsat. alcohol} (mol/h · g _{Ru} ⁻¹)	Selectivity ^b to unsat. alcohol (%)
Ru(1.9)Sn(4.3)	—	0	9.8	0.26	27
Ru(1.6)Sn(4.2)B(0.3)	2.2	4.2	10.4	0.32	28
Ru(1.5)Sn(4.1)B(1.1)	2.4	12.7	5.1	0.37	45
Ru(1.2)Sn(4.6)B(1.1)	3.3	38.0	3.2	0.49	34

^a Atomic ratio.

^b Calculated at 70%; PH₂ = 8 MPa, temperature = 270°C, m_{cata} = 2.2 g.

3. These results could indicate that after the prereduction with a large amount of sodium borohydride, new species like alloys (Ru_nSn_p) are formed at the surface of the catalyst. Indeed, tin and ruthenium, which are practically not miscible, can give different kinds of alloys such as RuSn₃, RuSn₂, Ru₃Sn₇ (14).

XPS analysis of RuSnB catalysts. Although on the solid surface the tin content is always larger than the amount of ruthenium, the reduction with NaBH₄ leads to a relative ruthenium surface enrichment. The Ru/Al ratio is doubled which means that the (Sn/Ru)_{surf} ratio decreases after the NaBH₄ reduction from 3.7 to 3.0. Moreover, the XPS analysis also showed that besides the formation of metallic ruthenium particles (Ru⁰), two kinds of tin oxides (SnOx and SnOy) were also formed in the same proportion 20/80 (Table 4).

Catalyst activity. The rate of formation of oleyl alcohol rises with the sodium borohydride content (Table 3) without significant change of the total activity. We can notice that the unsaturated alcohol selectivity is higher when the NaBH₄/Ru ratio is equal to 12 (Table 3). Then the variations of catalytic properties could be due to the change of the Sn/Ru ratio after the NaBH₄ reduction.

Effect of the Ruthenium Content

When the ruthenium content is increased (× 2), there is no modification of the activity of the catalyst nor of the spe-

cific surface area since the initial activities are comparable (Table 5). However, the selectivity to unsaturated alcohol and to heavy esters (Table 5) are significantly changed. Indeed, the oleyl oleate formation is more significant when the ruthenium and tin contents are increased. It has been suggested that the distribution of active species is modified when the ruthenium and tin contents are increased. Tin species without interaction with ruthenium or covering ruthenium particles are more numerous at the surface thus leading to an increase of the transesterification reaction and the formation of heavy esters.

DISCUSSION

In this work, we have studied the selective hydrogenation of methyl oleate into oleyl alcohol in the presence of bimetallic RuSn catalysts supported on alumina. The selective hydrogenation of fatty unsaturated esters (or acids), via the reaction scheme proposed in this paper, is not fully understood but apparently both the basic and the hydrogen adsorption properties of the catalyst are involved in a multistep process.

With regard to the overall activity (Fig. 4), Narasimhan in previous works (8) shows that the addition of tin leads to a decrease of activity. Ferretti (13) proposed, on one hand, that tin acts as a poisoning agent by decreasing the hydrogenating and the hydrogenolysis activity of rhodium and on the other that tin participates to the activation of carbonyl bond (increasing the overall activity). Furthermore, to justify the change of the C=O bond polarization the change of the electronic properties of the metal particles close to tin species has been suggested by numerous authors (15, 16). However, the percentage of oleyl alcohol is maximum for a Sn/Ru ratio of 4 at which the heavy esters issued from the transesterification reaction are strongly decreased (Fig. 8). The other products are the saturated alcohol and the methyl stearate.

According to these results, one can assume that the tin species located at the solid surface change (Scheme 2):

- (i) the rate of the direct formation of oleyl alcohol (k₁)

TABLE 4
XPS Analysis of RuSnB/Al₂O₃: Effect of the Reduction with NaBH₄

RuSnB/Al ₂ O ₃	Sn/Ru		Ru 3d _{5/2}		Sn 3d _{5/2}		
	Bulk	XPS	Ru/Al	Sn/Al	Ru ⁰	SnOx	SnOy
Ru(1.9)Sn(4.3)	1.9	3.7	0.008	0.030	100	20	80
Ru(1.5)Sn(4.1)B(1.1)	2.4	3.0	0.016	0.050	100	20	80
BE (eV)					279.3	485	486.7

TABLE 5
Effect of the Ruthenium Content; Characteristics of the RuSnB/Al₂O₃ Catalysts

RuSnB/Al ₂ O ₃	Sn/Ru	Activity ^a (mol · h ⁻¹ · g _{Ru} ⁻¹)	BET area (m ² · g ⁻¹)	Selectivity ^b (%)	
				Unsat. Al.	Heavy esters
Ru(1.6)Sn(8.5)B(1.1)	4.5	6.10 ⁻²	134	73	10
Ru(2.9)Sn(14.9)B(1.6)	4.4	7.10 ⁻²	129	27	72

^a Calculated at isoconversion.

^b Calculated at 70% conversion, PH₂ = 8 MPa, temperature = 270°C, m_{cata} = 2.2 g.

- (ii) the rate of the heavy esters formation (k_2 or k'_2)
- (iii) the rate of the heavy esters hydrogenation (k_3 or k'_3)

Identification of Active Sites

At low tin content, Fig. 8 shows that there is mainly (i) formation of saturated ester (methyl stearate) issued from the hydrogenation of the C=C bond and (ii) formation of heavy esters (SS) due to the transesterification between stearyl alcohol and methyl stearate. The hydrogenation of the C=C bond (k_4) is much faster than the reduction of the C=O bond (k_1). This means that the hydrogenating properties of ruthenium are only slightly modified and that the hydrogenation rate of heavy ester (k'_3) is still low. Indeed, there remains 40% of oleyl oleate at total ester conversion. Several hypotheses can be proposed: (i) the addition of tin inhibits the hydrogen adsorption and the tin content is not enough for the C=O bond activation; (ii) tin species could be on the ruthenium particles or/and dispersed on the support with or without interaction with ruthenium particles. Depending on the localization of the tin species, the oxidation state of Sn varies and associations between tin and ruthenium particles could or could not occur.

Over RuSnB/Al₂O₃ catalyst (Sn/Ru ratio = 7), the transesterification step (k_2) is apparently very fast. In this case, the hydrogenation of heavy esters (k_3) may be the limiting

step which could be due to a significant coverage of ruthenium by tin oxides SnO_y in agreement with the TPR profiles (Fig. 1). But as stated by Mizukami *et al.*, it could be that the carbonyl groups of esters are more strongly adsorbed over the catalyst, thus leading to an inhibition of the hydrogen adsorption and of the hydrogenation steps (17).

Over RuSnB/Al₂O₃ catalyst (Sn/Ru = 4), the maximum of selectivity to oleyl alcohol can be explained if the variation of the unsaturated alcohol selectivity and the proportion of SnOx over the solid surface versus the Sn/Ru ratio are considered (Fig. 9). Indeed, this figure shows clearly that (i) there is a synergetic effect between Ru⁰ and tin species for the formation of SnOx and (ii) the selectivity to unsaturated alcohol changes like the SnOx content. According to surface ruthenium and tin content (XPS analysis), there are six tin atoms in the oxide form for one ruthenium atom in the RuSnB/Al₂O₃ (Sn/Ru = 4) catalyst (Table 6). As the proportion of SnOx is around 30% there are two SnOx sites which could be very close to Ru particles (this assumption could explain the binding energy shift recorded by XPS). This result suggests that reactive centers such as Ru⁰—(SnOx)₂ are formed in which Ru⁰ could be associated with two SnOx species.

In Fig. 9, we also report the data of oleyl alcohol selectivity obtained over RuSnB/Al₂O₃ with Sn/Ru ratios of 0.6, 1.1, and 7 (represented by Δ). We can see that these values

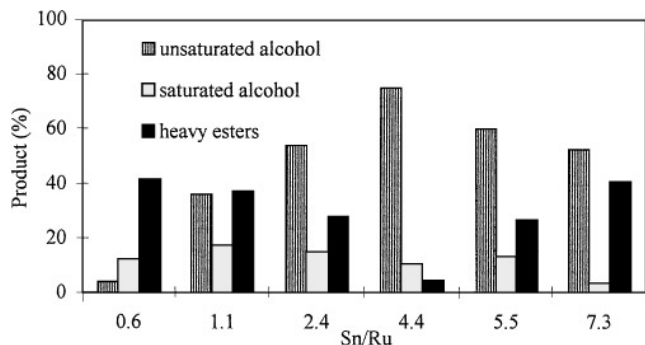
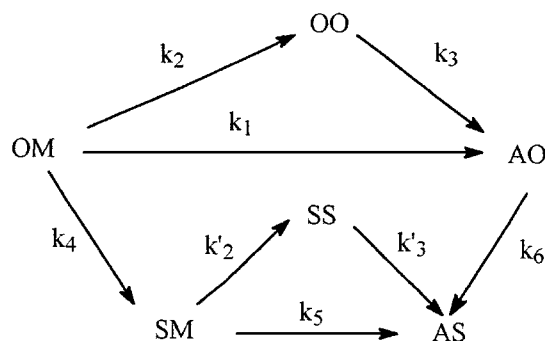


FIG. 8. Hydrogenation of methyl oleate in the presence of RuSnB/Al₂O₃ catalysts. Selectivity to unsaturated alcohol, to saturated alcohol, and to heavy esters with the Sn/Ru ratio (compared at isoconversion of methyl oleate, 80%).



SCHEME 2. Kinetic scheme of the hydrogenation of methyl oleate (OM): OO, oleyl oleate; OA, oleyl alcohol; MS, methyl stearate; SS, stearyl stearate; SA, stearyl alcohol.

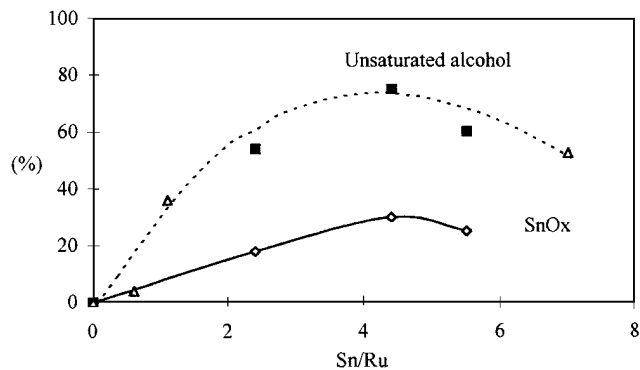


FIG. 9. Hydrogenation of methyl oleate in the presence of RuSnB/Al₂O₃ catalysts. Relationship between selectivity to unsaturated alcohol and SnOx species with Sn/Ru ratio.

are in good agreement with the other results. The discrepancy observed for the lowest Sn/Ru ratio (i.e., 0.6) proves that (i) the surface SnOx content could be very small and (ii) the formation of SnOx is quite dependent of the Sn content as already suggested. The transesterification is favored over SnOy sites. The high reducibility of this catalyst (TPR profile) is in agreement with the presence of ruthenium species in weak interactions with tin.

According to these results, we propose a schematic representation of the catalyst surface (Scheme 3):

(1) when the tin content is low, ruthenium and tin species are dispersed without interaction, tin being in a high oxidation state.

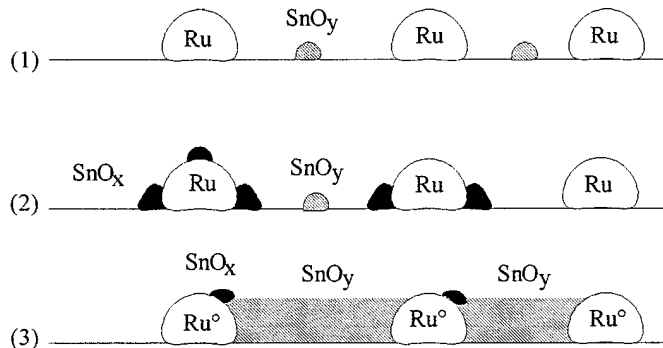
(2) when the tin content increases, some tin species are near the ruthenium particles, mixed species (SnO-Ru) being formed at the surface of ruthenium particles and alumina (type I) or by "decoration" of ruthenium particles with tin oxides (type II). As in the first case, tin oxides dispersed on alumina having the same nature than the one described in (1) remain.

(3) after increasing the relative amount of tin, there would be a rather complete covering of alumina and a "decoration" or an "encapsulation" of ruthenium particles by tin oxides and a decrease of mixed sites (active for the formation of unsaturated alcohol).

TABLE 6

Relative Composition to Ruthenium, Tin, and SnOx of the Catalyst RuSnB/Al₂O₃

RuSnB/Al ₂ O ₃	Ru (atom.)	Sn (atom.)	SnOx (%)	SnOx/Ru
Ru(1.5)Sn(4.1)B(1.1)	1	3	20	0.5
Ru(1.6)Sn(8.5)B(1.1)	1	6	30	1.9
Ru(1.5)Sn(10)B(1.3)	1	7	25	1.8



SCHEME 3. Model representing the RuSnB centers with different tin contents: (1) Sn/Ru < 4; (2) 4 < Sn/Ru < 5.5; (3) Sn/Ru > 5.5.

Reaction Mechanism

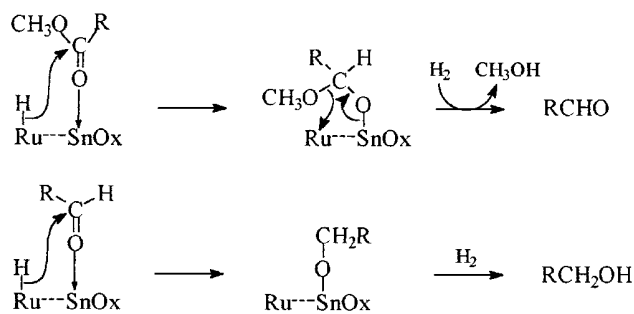
Concerning the elementary chemical steps occurring over these different sites, metallic ruthenium activates hydrogen into a "hydride form". Tin oxides (SnOx) which are in interaction with Ru favor the O adsorption of the C=O bond of the ester. The activated hydrogen on ruthenium attacks the carbon atom of carbonyl groups to obtain an acetal of tin. This acetal is converted to an aldehyde which is rapidly hydrogenated into an alcohol form under high hydrogen pressure (Scheme 4).

In our case, we suggest that the alcohol is directly formed via a hemiacetal adsorbed at the catalyst surface (Scheme 5). This mechanism is in accordance with the one proposed by Rieke *et al.* (18).

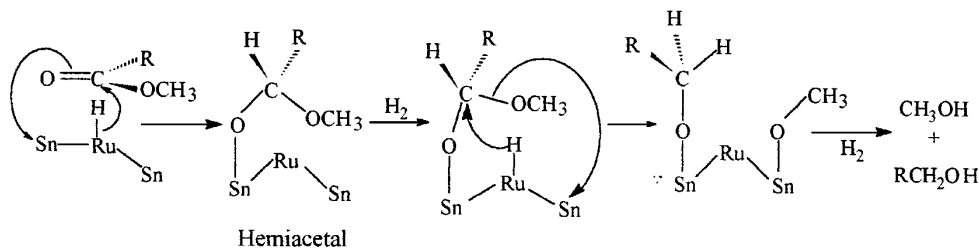
When the tin content is more significant, the rate of the transesterification is greater than the one of the alcohol desorption and the alcoholate adsorbed on the tin surface reacts with an ester molecule adsorbed on adjacent SnOy species (Scheme 6). Then the heavy esters can lead to two moles of oleyl alcohol by hydrogenation (Scheme 7).

Influence of NaBH₄ Reduction

The prerduction of monometallic catalysts with NaBH₄ modifies the reducibility of the metal particles as well as



SCHEME 4. Mechanism of the hydrogenation of methyl oleate into oleyl alcohol via the formation of aldehyde.



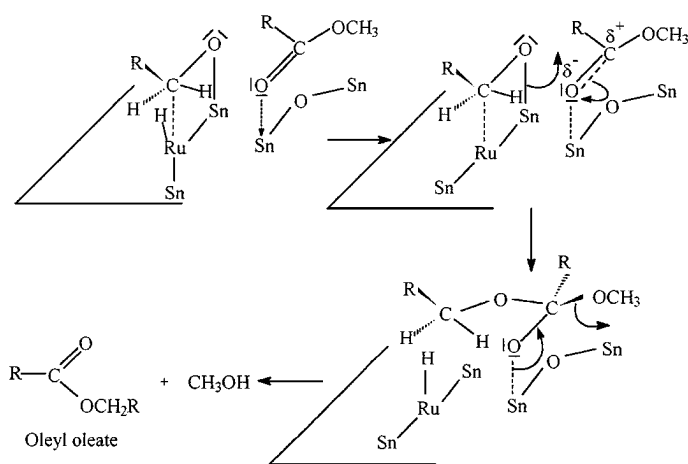
SCHEME 5. Mechanism of the direct hydrogenation of methyl oleate into unsaturated alcohol over RuSnB/Al₂O₃ catalyst.

the surface composition and similar results are obtained with bimetallic systems. Indeed, TPR results show that the prereluction step lead to:

- ruthenium species easily reoxidized
- a similar surface distribution of SnO_x and SnO_y
- the possible formation of a Ru_xSn_y alloy.

From XPS analysis, a surface enrichment of ruthenium and especially of tin was observed. The (Sn/Ru)_{surf.} ratio is greater than the bulk Sn/Ru ratio but the (Sn/Ru)_{surf.} ratio of the unreduced and reduced catalysts are comparable. Such a ruthenium surface enrichment can easily explain the enhancement of the RuSnB activity (Table 3). Nevertheless, there is no significant change of the selectivity (Fig. 10) because the relative contents of SnO_x and SnO_y are quite identical (Table 4).

Furthermore, these experiments prove that the introduction of boron during the prereluction step with NaBH₄ has no effect on the catalytic properties of these catalysts. These results are in agreement with our previous works (19), where we showed that the activity of the catalyst prepared via a sol-gel method (without boron) was the same as that of a solid prepared in accordance with the Narasimhan method.



SCHEME 6. Mechanism of formation of heavy esters over RuSnB/Al₂O₃ catalyst.

CONCLUSION

The hydrogenation of methyl oleate over bimetallic RuSnB/Al₂O₃ catalysts is selective to unsaturated alcohol while saturated esters are formed over Ru monometallic catalysts. Indeed, a yield to oleyl alcohol of 75% for a conversion of 90% was obtained over a RuSnB/Al₂O₃ for a bulk atomic ratio Sn/Ru of 4. Owing to the side reaction of the transesterification between methyl oleate and oleyl alcohol the tin content strongly affects the selectivity to unsaturated alcohol. This side reaction is catalyzed by tin oxides without interaction with ruthenium particles. The characterizations of RuSnB/Al₂O₃ by TPR and XPS analysis have shown that:

- (i) Ru⁰ particles are formed at the catalyst surface in the presence of tin species
- (ii) the addition of tin does not modify the surface ruthenium content
- (iii) there are two tin oxides species (SnO_x and SnO_y) whose surface content varies with the tin content
- (iv) the SnO_x species (x < y) would be in interaction with ruthenium (without significant formation of alloy Ru_nSn_p).

All these results indicate that there is a correlation between the selectivity to oleyl alcohol and such SnO_x species. The active center could be constituted by a ruthenium atom in interaction with two SnO_x species.

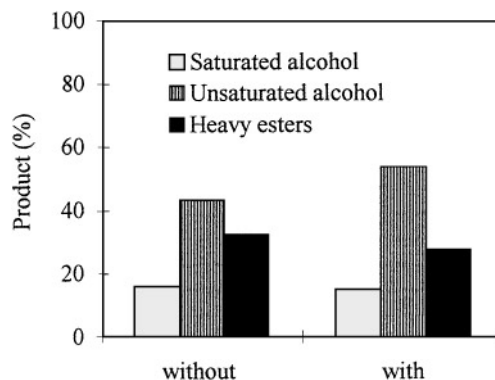
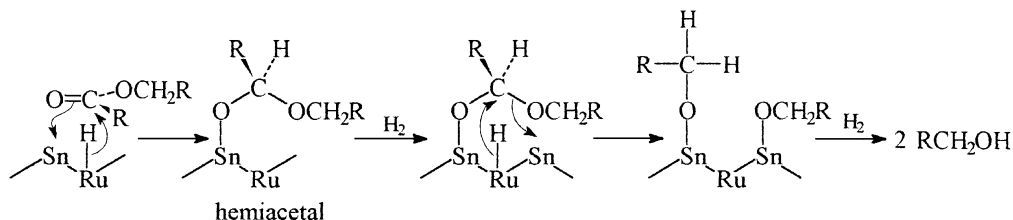


FIG. 10. Hydrogenation of methyl oleate in the presence of RuSnB/Al₂O₃ catalysts. Effect of the prereluction step with NaBH₄.



SCHEME 7. Mechanism of the hydrogenation of oleyl oleate into oleyl alcohol over RuSnB/Al₂O₃ catalyst.

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