Journal of Catalysis **204,** 230–237 (2001)
doi:10.1006/jcat.2001.3378, available online at http://www.idealibrary.com on

Selective Hydrogenation of Methyl Oleate into Unsaturated Alcohols in the Presence of Cobalt–Tin Supported over Zinc Oxide Catalysts

K. De Oliveira, Y. Pouilloux,[1] and J. Barrault

Laboratoire de Catalyse en Chimie Organique, UMR CNRS 6503, Université de Poitiers, Ecole Supérieure d'Ingénieurs de Poitiers,
40, Avenue du Recteur Pineau, 86022 Poitiers cedex, France

Received May 29, 2001; revised July 30, 2001; accepted July 30, 2001

The hydrogenation of methyl oleate (methyl-9-octadecenoate) into oleyl alcohol (methyl-9-octadecen-1-ol) was studied in the presence of a bimetallic CoSn supported over a zinc oxide catalyst in a stainless steel batch reactor at 270°C and 8.0 MPa. Zinc oxide can activate the carbonyl group and also the hydrogen by a possible heterolytic and homolytic dissociation of dihydrogen. The selectivity to unsaturated alcohol (oleyl alcohol) was significantly enhanced by adding tin to cobalt. The activity and the selectivity to unsaturated alcohols was maximum for an atomic Sn/Co ratio of 1, as for the CoSn alumina sol–gel catalyst. For all CoSn catalysts, the selectivity to unsaturated alcohols goes through a maximum for a surface Sn/Co ratio close to 2, the active species being a mixed Me^0–(SnOx)$_2$, where the oxidation of tin is close to 0. The reduction of CoSn solids with sodium borohydride increased the activity of the catalyst.

Key Words: **hydrogenation; fatty esters; unsaturated alcohols; cobalt–tin catalysts.**

INTRODUCTION

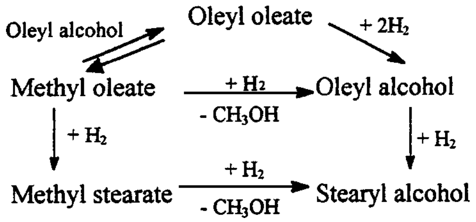
Unsaturated alcohols, such as oleyl alcohol, are important materials for the manufacture of heavy-duty liquid detergents, cosmetics, pharmaceuticals, and toiletries (1). One of the synthesis methods is hydrogenolysis of unsaturated fatty esters, which requires control of the chemioselectivity. Indeed, the formation of unsaturated alcohol involves activation of the carbonyl group without hydrogenation of the C=C bond.

Generally, fatty alcohols (mainly saturated) are obtained from hydrogenolysis of fatty acid methyl esters over zinc chromite catalysts. But the low activity of these materials requires severe reaction conditions (i.e., a temperature of 250°–300°C and a pressure of 20–35 MPa) (2, 3).

More recently, some catalysts containing a noble metal (Rh, Ru, Pd, ...) and an additive (Sn, Zn, ...) were described for the selective reduction of fatty esters to alcohols, especially unsaturated ones (4). In our laboratory, it was demonstrated that $RuSnAl_2O_3$ and $CoSnAl_2O_3$ catalysts were quite comparable, giving the same selectivity to oleyl alcohol, with the first series of catalysts being the more active (5). But besides methyl ester hydrogenation, a side reaction of transesterification between methyl ester and just-formed oleyl alcohol (Scheme 1) took place, especially over CoSn catalysts.

Moreover, it was observed that the transformation of oleyl oleate was much slower over CoSn catalysts than over RuSn catalysts. The hydrogenation rate of methyl oleate or oleyl oleate depends on the nature of the active site at the catalyst surface, the formation of unsaturated alcohols being favored when a metal atom is in interaction with two atoms of the promoting tin species.

From some of our previous work on selectivity enhancement, it was observed that zinc oxide used as support for CoSn active species leads to the same yield of unsaturated alcohols as the one obtained in the presence of a $CoSn/Al_2O_3$ catalyst, so we decided to replace the alumina support with zinc oxide. More recently, Consonni *et al.* (6) claimed that in the presence of Pt/ZnO, a selectivity of 75–80% to crotyl alcohol from crotonaldehyde can be obtained at low hydrogen pressure (1 bar). They suggested that the formation of a Pt–Zn alloy favors preferentially the adsorption of the carbonyl bond of crotonaldehyde and not the adsorption of the olefinic bond. Wehner *et al.* also obtained 50% unsaturated alcohols from methyl oleate over a Pd/ZnO catalyst, resulting in an interaction between reduced zinc and zerovalent Pd species (7, 8). Jacquot and



SCHEME 1. Reaction scheme of the hydrogenation of methyl oleate into oleyl alcohol and other products.

---

[1] To whom correspondence should be addressed. E-mail: yannick.pouilloux@esip.univ-poitiers.fr.

0021-9517/01 $35.00

co-workers (9) have also advanced that ZnO can activate the C=O group, claiming 70% selectivity to aldehyde from the hydrogenation of methyl benzoate over ZnO at a temperature of 370°C and at atmospheric pressure.

In order to explain and to improve the performances of the cobalt catalysts, we investigated and we present in this paper both the preparation and the characterization of cobalt catalysts when supported over ZnO and their catalytic properties in the hydrogenation of methyl oleate (issued from sunflower oil) into oleyl alcohol.

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. Methyl oleate, supplied by Stearinerie Dubois with a purity of 84%, contained other methyl esters: methyl palmitate C16 : 0 (4.5%); linoleic ester C18 : 2 (6%); methyl stearate and methyl elaïdate C18 (4%); others (1.5%).

The reactor was then purged (four times) with nitrogen at 5 MPa, and stirred continuously. The temperature was slowly increased to 270°C at constant pressure (5 MPa), nitrogen was replaced by hydrogen, and the pressure increase to 8 MPa was maintained during the reaction.

Analysis

Liquid samples were mixed with dodecane and analyzed with a CPG equipped with a Flame ionization detector, and a Chrompack Cp sil-5 column (length, 25 m; inner diameter, 0.25 mm; film thickness, 0.11 μm), with the carrier gas being nitrogen. All the methyl esters, alcohols, and heavy esters resulting from transesterification reactions and containing C_{16}–C_{16}, C_{16}–C_{18}, and mainly C_{18}–C_{18} esters were separated.

Using a calibration method, the weight percentage (Xx) of reagents and products were determined as

$$X_x(\%) = \frac{K_x A_x}{\sum_i (K_i A_i)} \times 100,$$

where K_i and A_i represent, respectively, the constant and the surface area of the i compound.

At t time, the conversion is

$$\text{Conversion }(\%) = \frac{\left(\%X^{t^\circ}_{\mathrm{C18:1c}} + \%X^{t^\circ}_{\mathrm{C18:1t}} + \%X^{t^\circ}_{\mathrm{C18:2}}\right) - \left(\%X^{t}_{\mathrm{C18:1c}} + \%X^{t}_{\mathrm{C18:1t}} + \%X^{t}_{\mathrm{C18:2}}\right)}{\left(\%X^{t^\circ}_{\mathrm{C18:1c}} + \%X^{t^\circ}_{\mathrm{C18:1t}} + \%X^{t^\circ}_{\mathrm{C18:2}}\right)} \times 100.$$

where $\%X^{t^\circ}_{\mathrm{C18}}$ is the weight percentage of C18 esters at $t = 0$, and $\%X^{t}_{\mathrm{C18}}$ is the weight percentage of C18 esters at t. The activity of the catalyst is expressed in $\mathrm{mol_{est}\ h^{-1}\ mol_{Co}^{-1}}$.

The selectivity (S_A) to the Y product is calculated according to the expression

$$S_A(\%) = \frac{(\%Y^t - \%Y^{t^\circ})}{\sum_i (\%I^t - \%I^{t^\circ})} \times 100,$$

where $(\%Y^t - \%Y^{t^\circ})$ is the weight percentage of Y formed during t hours of reaction, and $\sum_i (\%I^t - \%I^{t^\circ})$ is the weight percentage of all the detected I products formed during t hours of reaction.

Catalyst Preparation

Coimpregnation. The catalysts were prepared by coimpregnation of ZnO (Union Minière Oxyde–La Ciotat; $S_{\mathrm{BET}} = 44\ \mathrm{m^2/g}$) with an aqueous solution containing $CoCl_2 \cdot 6H_2O$ (Merck), and $SnCl_2 \cdot 2H_2O$ (Fluka). After the impregnation step (24 h), the solids (CoSn/ZnO) were placed in an oven for 12 h at 80°C and dried under a nitrogen flow at 120° C for 4 h.

A series of CoSnB/ZnO catalysts were prepared by reduction of CoSn/ZnO catalysts with sodium borohydride as described by Desphande *et al.* (10). After the impregnation step (24 h), the solids were reduced with an aqueous solution of sodium borohydride in a molar ratio ($NaBH_4$/metal) of 14. The stirring was maintained for 12 h, then the catalysts were filtered and washed with water and ethanol. The resulting CoSnB/ZnO were placed in an oven at 80°C and dried under a flow of nitrogen at 120°C for 4 h.

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

XPS Analysis

X-ray photoelectron spectroscopy (XPS) analysis was performed with an SSI (Surface Science Instruments, Mountain View, CA) model 301 spectrometer with a focused (diameter of 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 samples first reduced and then passivated for 10 min under air. The residual pressure inside the analysis chamber was about 5×10^{-8} Pa. The XPS peaks were decomposed into subcomponents using a Gaussian (80%)–Lorentzian (20%) curve-fitting program with a nonlinear background (11). The quantitative analysis was performed using the sensitivity factors given by Scofield (12) .

Temperature-Programmed Reduction

The temperature-programmed reduction (TPR) analyses were done over catalysts passivated with air at room temperature using a conventional pulse system with a thermal conductivity detector. The catalytic samples were evacuated under an argon flow at 300°C for 2 h and cooled at room temperature. Then, pulses of hydrogen were introduced while heating from 25 to 550°C at a rate of 4°C/min.

RESULTS

Catalytic Properties of Zinc Oxide

To determine the influence of the support, the hydrogenation of methyl oleate was carried out in the presence of zinc oxide under standard conditions. Figure 1 shows that methyl oleate is slowly converted, with the conversion reaching 60% after 60 h of reaction. It must be noted that the conversion variation is very low, between 30 and 70 h.

The formation of heavy esters and their strong adsorption on the surface of zinc oxide can explain the leveling off of the conversion. Indeed, Fig. 2 shows that the major products are heavy esters issued from the transesterification reaction between methyl oleate and oleyl alcohol (Scheme 1). These results show that there is mainly formation of unsaturated alcohols without significant formation of saturated alcohol (no hydrogenation of the olefinic bond). It can be noted that there is a direct relationship between the decrease of the selectivity to heavy esters and the increase of the unsaturated alcohols selectivity, which could indicate that the oleyl alcohol is formed from the hydrogenolysis of heavy esters (Scheme 1). This experiment confirms that zinc oxide activates the carbonyl group and also the hydrogen molecule via hydride species. Such results also confirm the work of Haffad *et al.*, showing that zinc oxide was the more active support for the conversion of benzaldehyde into benzyl alcohol (13). As suggested by Klier and co-workers (14), the more important function of ZnO in methanol synthesis can be the dissociation of hydrogen, and infrared studies of hydrogen adsorption over ZnO suggested a possible heterolytic and homolytic dissociation of dihydrogen (13, 15, 16).

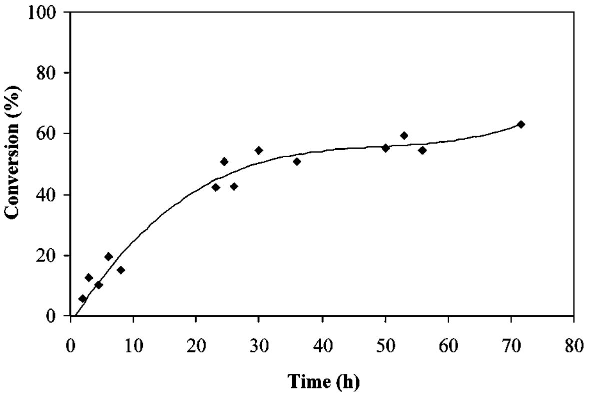


FIG. 1. Hydrogenation of methyl oleate in the presence of zinc oxide.

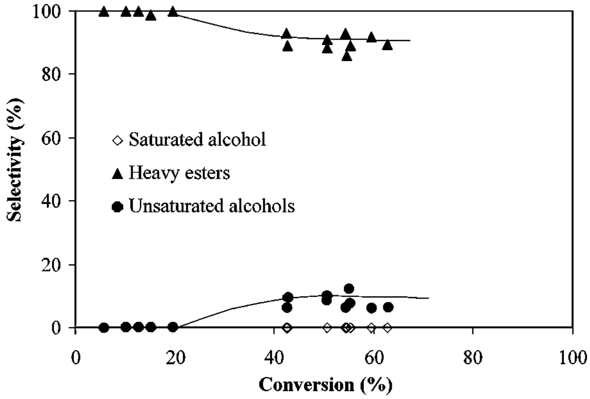


FIG. 2. Hydrogenation of methyl oleate in the presence of zinc oxide. Selectivity (to heavy esters and saturated and unsaturated alcohols) versus conversion.

Modification of Zinc Oxide with Cobalt and/or Tin

The activities of Co/ZnO, Sn/ZnO, and CoSn/ZnO are presented in Fig. 3. It was observed that the Sn/ZnO catalyst is less active than CoSn/ZnO and Co/ZnO catalysts. The absence of zerovalent metal species (see below) can explain this fact, the rate of the hydrogenation of heavy esters being lowered. As was observed on zinc oxide, the methyl oleate conversion varies slowly with time after 30 h of reaction. The strong adsorption of oleyl oleate over the Sn/ZnO catalyst can also inhibit the activation of hydrogen.

On the other hand, even if the activity of CoSn/ZnO and Co/ZnO catalysts are similar, the highest selectivity to unsaturated alcohols (UAs) is obtained in the presence of the CoSn catalyst (Fig. 4). This figure also shows that the Sn/ZnO catalyst favors the formation of UAs, even if the oleyl oleate is the major product of the reaction. In the presence of Co/ZnO, the main reaction, as expected, is the hydrogenation of the olefinic bond since the selectivity to methyl stearate is close to 50%.

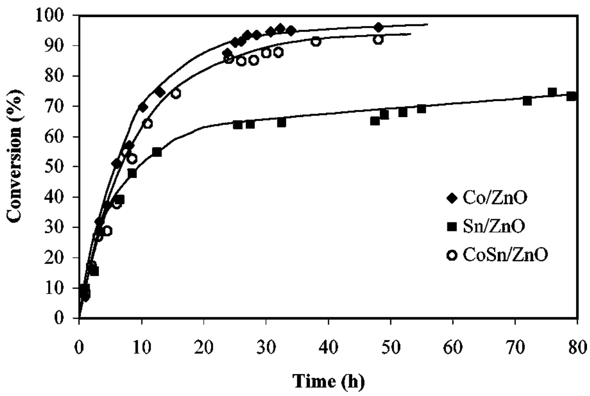


FIG. 3. Activities of Sn/ZnO, C0/ZnO, and CoSn/ZnO catalysts.

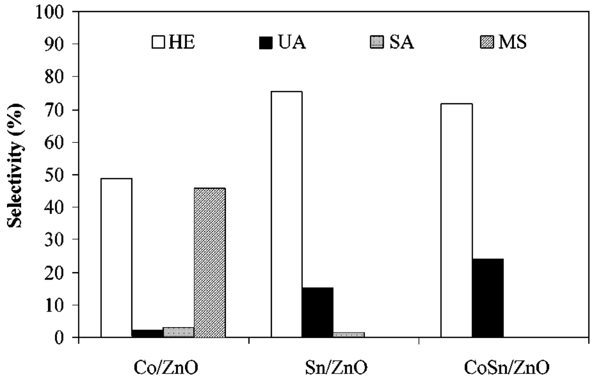


FIG. 4. Selectivity to reaction products at 75% conversion in the presence of Sn/ZnO, Co/ZnO, and CoSn/ZnO. HE, heavy esters; UA, unsaturated alcohols; SA, saturated alcohol; MS, methyl stearate.

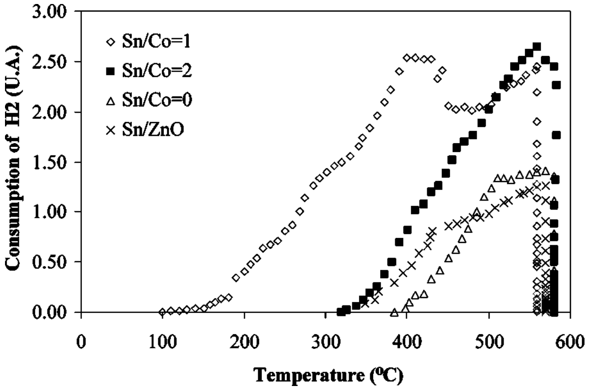


FIG. 6. Temperature-programmed reduction of Co/ZnO, Sn/ZnO, and CoSn/ZnO (Sn/Co = 1 or 2).

Effect of Chlorine on the Activity and Selectivity of CoSn/ZnO Catalysts with an Atomic Ratio Sn/Co of 1

The catalyst CoSn/ZnO without chlorine was prepared by using $Co(NO_3)_2 \cdot 6H_2O$ (Fluka), and $SnC_4H_4O_6$ (Sigma) instead of $CoCl_2 \cdot 6H_2O$ (Merck), and $SnCl_2 \cdot 2H_2O$ (Fluka). It appears that the catalyst without chlorine has a lower activity than the chlorinated CoSn/ZnO catalyst (9.0 $\mathrm{mol_{est}\ h^{-1} mol_{Co}^{-1}}$ instead of 17.8 $\mathrm{mol_{est}\ h^{-1} mol_{Co}^{-1}}$), but the selectivity to oleyl alcohol is slightly increased in the presence of the solid prepared without chlorine salts (Fig. 5). This result shows that if chlorine has an inhibiting effect at low conversion, the selectivity to UAs at higher oleate conversion seems rather similar. The presence of chlorine at the catalyst surface could increase the transesterification reaction rate, compared to the hydrogenation reaction. At the end of the reaction, the methyl oleate conversion is high enough so that the hydrogenation of oleyl oleate can take place.

TPR of CoSn/ZnO: Influence of Tin

Figure 6 shows that tin has an effect on the reducibility of the CoSn/ZnO catalysts. Indeed the Co/ZnO catalyst is reducible at high temperature (>550°C). When tin is added with a bulk atomic Sn/Co ratio of 1, there are two reduction peaks, at 420°C and at a temperature higher than 550°C; the first peak indicates that the catalyst contains more easily reducible species. But when a higher tin content is added, the catalyst becomes less reducible, the reduction profile being quite similar to that of the Sn/ZnO catalyst. This could indicate that the excess of tin species covers the cobalt particles. The hydrogen adsorption over Co/ZnO is rather low owing to strong interactions between cobalt and zinc oxide and a low zerovalent cobalt species content (see below).

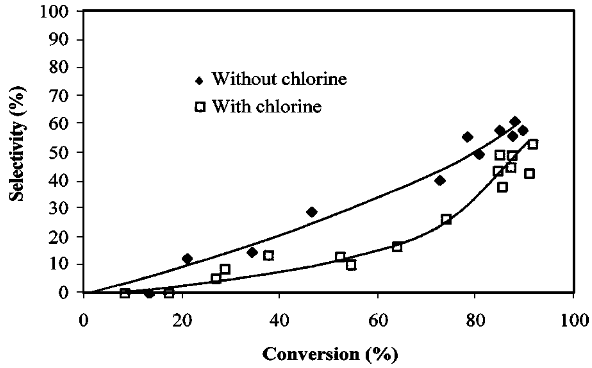


FIG. 5. Hydrogenation of methyl oleate. Selectivity to unsaturated alcohols in the presence of CoSn/ZnO catalyst ($(Sn/Co)_{bulk} = 1$). Effect of chlorine.

XPS Characterization of CoSn/ZnO

Influence of the tin content. The XPS data obtained with the catalysts reported in Table 1 show that the surface cobalt content decreases when the tin content increases. The $(Co/Zn)_{surf.}$ ratio varies from 0.092 to 0.009. On the other hand, the $(Sn/Zn)_{surf.}$ ratio is smaller than the bulk Sn/Zn ratio. These results indicate a surface tin enrichment, with the $(Sn/Co)_{surf.}$ ratio varying from 1 to 8.4 instead of 0.35 to 2.1 for the bulk Sn/Co ratio.

Table 2 shows that the addition of tin favors the reduction of cobalt since the percentage of zerovalent cobalt is maximum for a bulk Sn/Co ratio of 1. If zerovalent tin species were observed, the amount of metallic tin species decreases with the addition of tin and there is an increase in the tin oxide SnOy content. The presence of cobalt particles close to tin oxide particles favors the reduction of both cobalt

TABLE 1

Co and Sn Content (Atomic) at the Surface of CoSn/ZnO Catalysts Determined by XPS Analysis: Influence of Tin Content

Catalysts (CoSn/ZnO)	Bulk analysis			XPS analysis		
	Co/Zn	Sn/Zn	Sn/Co	Co/Zn	Sn/Zn	Sn/Co
$Co_{2.9}$	0.046	0	0	0.092	0	0
$Co_{3.0}Sn_{2.1}$	0.047	0.018	0.35	0.019	0.021	1.1
$Co_{2.7}Sn_{5.3}$	0.046	0.044	0.95	0.015	0.033	2.2
$Co_{2.6}Sn_{10.8}$	0.047	0.100	2.10	0.009	0.076	8.4

TABLE 2

Surface Composition of CoSn/ZnO from XPS analysis: Influence of Tin Content

Catalysts (CoSn/ZnO)	$(Sn/Co)_{bulk}$	Co^0(%)	CoOx (%)	Sn^0(%)	SnOy(%)
$Co_{2.9}$	0	0	100	0	0
$Co_{3.0}Sn_{2.1}$	0.35	10	90	40	60
$Co_{2.7}Sn_{5.3}$	0.95	20	80	35	65
$Co_{2.6}Sn_{10.8}$	2.10	10	90	15	85
BE (eV)		777.5	781.5	484.9	486.7

and tin species (especially when tin and cobalt content are similar at the catalyst surface) (Figs. 7 and 8).

Influence of reduction of CoSn/ZnO catalysts with sodium borohydride. In our previous work, we have shown that the reduction step with sodium borohydride improves the activity of $CoSn/Al_2O_3$ catalysts (17). A series of CoSnB/ZnO catalysts prepared by varying the tin content were reduced with sodium borohydride.

Table 3 shows that the reduction with $NaBH_4$ modifies the surface composition of the CoSnB/ZnO catalyst as follows.

- When the Sn/Co ratio is between 0 and 1, a surface cobalt enrichment is observed owing to a cobalt migration at the surface of the catalyst. As shown in Tables 1 and 3, the reduction step leads to a large excess of cobalt at the catalyst surface contrary to what was observed with the unreduced (with $NaBH_4$) CoSn/ZnO catalyst. The same variations are observed for tin species.
- For a bulk Sn/Co ratio equal to 1, the tin and cobalt contents are rather similar so that the surface Sn/Co ratio is equal to 1.2.
- At higher tin content, there is a large tin enrichment at the catalyst surface and the $(Sn/Co)_{surf.}$ ratio is close to 8 (instead of 2). We can expect a covering of cobalt particles by tin species.

After treatement with sodium borohydride, the reducibility of the cobalt species is more difficult if the $(Sn/Co)_{bulk}$ is below 1 (Table 4). Indeed, only cobalt oxide species are observed when the bulk Sn/Co ratio is between 0 and 1, and it is only when the Sn/Co ratio is above or equal to 1 that cobalt metallic particles appear at the catalyst surface. In the same way, the reduction step with sodium borohydride favors the reduction of tin oxide into metallic tin species.

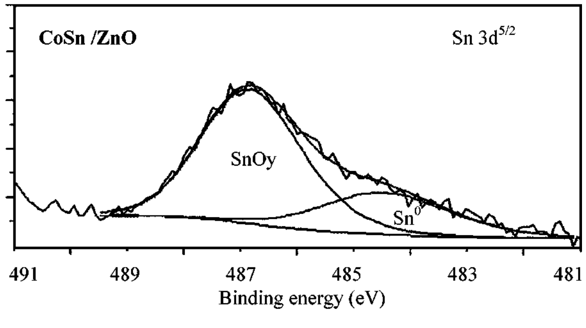


FIG. 7. XPS spectrum of Sn $3d^{5/2}$ of CoSn/ZnO catalyst ($(Sn/Co)_{bulk} = 1$).

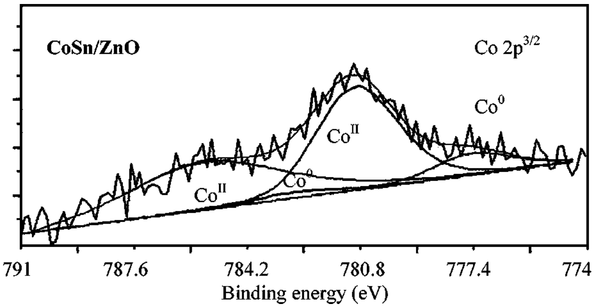


FIG. 8. XPS spectrum of Co $2p^{3/2}$ of CoSn/ZnO catalyst ($(Sn/Co)_{bulk} = 1$).

Activity of CoSn Catalysts

Figure 9 shows that the variation in the activity of the two catalysts with the surface Sn/Co ratio have some similarities, since a minimum and a maximum are observed for a Sn/Co ratio close to 1 and 2, respectively. Moreover, the reduction step with sodium borohydride increases both the amount of surface cobalt species and the activity of CoSn/ZnO catalysts.

This result is similar to that previously obtained in the presence of $CoSnB/Al_2O_3$ catalysts (17). The addition of a small amount of tin inhibits the catalytic activity due to a poisoning effect, while for the highest tin content, the covering of cobalt by tin species strongly decreases the hydrogenation properties of cobalt. It seems that there is formation of new active and selective sites (see below) only for a particular stoechiometry corresponding to a surface Sn/Co ratio around 2.

Selectivity of CoSn/ZnO Catalysts (without $NaBH_4$ Reduction)

Figure 10 shows that the maximum oleyl alcohol formation is obtained for a bulk Sn/Co ratio of 1. As reported

TABLE 3

Co and Sn Content (Atomic) at the Surface of CoSnB/ZnO Catalysts Determined by XPS Analysis: Influence of Tin Content

Catalysts (Co/Sn/ZnO)	Bulk analysis			XPS analysis		
	Co/Zn	Sn/Zn	Sn/Co	Co/Zn	Sn/Zn	Sn/Co
$Co_{3.5}$	0.051	0	0	0.289	0	0
$Co_{3.3}Sn_{3.1}$	0.053	0.026	0.5	0.246	0.189	0.77
$Co_{3.4}Sn_{6.4}$	0.056	0.052	1.0	0.050	0.058	1.2
$Co_{3.2}Sn_{11.5}$	0.061	0.122	2.0	0.024	0.19	7.93

TABLE 4

Surface Composition of CoSn/ZnO Reduced with $NaBH_4$ from XPS Analysis: Influence of Tin Content

Catalysts (CoSn/ZnO)	$(Sn/Co)_{bulk}$	Co^0(%)	CoOx (%)	Sn^0 (%)	SnOy (%)
$Co_{3.5}$	0	0	100	0	0
$Co_{3.3}Sn_{2.1}$	0.5	0	100	8	92
$Co_{3.4}Sn_{6.4}$	1.0	15	85	40	60
$Co_{3.2}Sn_{11.5}$	2.0	50	50	30	70
BE (eV)		777.5	781.5	484.9	486.7

before for $CoSnB/Al_2O_3$ catalysts (17), the rate of the alcohol desorption was faster than the rate of the transesterification reaction for the particular surface ratio Sn/Co of 2. This result confirms that the unsaturated alcohol is favored when active centers Me^0–$(SnOx)_2$ are formed at the catalyst surface (where SnOx means zerovalent or low valent tin species).

For a bulk Sn/Co ratio smaller than 1, the hydrogenation of the olefinic bond is the main reaction, but the formation of heavy esters from the reaction of methyl esters and alcohols over isolated tin oxide species is also observed.

When the Sn/Co ratio is above 1, the covering of cobalt particles with tin oxide species becomes too significant, so that the main reaction is the formation of heavy esters which are further strongly adsorbed over the catalyst, decreasing the hydrogenation rate even if the relative Co^0 content is rather significant. If the experiment is reproduced with the same CoSn/ZnO catalyst (atomic Sn/Co ratio around 1), the same activity and selectivity are observed (Table 5). The catalyst was collected after the experiment and the atomic composition was similar to the unused solid.

Selectivity of CoSnB/ZnO Catalysts

The significant change of selectivity to heavy esters and saturated alcohols are observed for the bulk Sn/Co ratio of 0.5 (Fig. 11) for which the major products are saturated esters, heavy esters, and alcohols. This result can be explained by the large excess of cobalt at the catalyst surface of CoSnB/ZnO, which favors the hydrogenation of the olefinic bond.

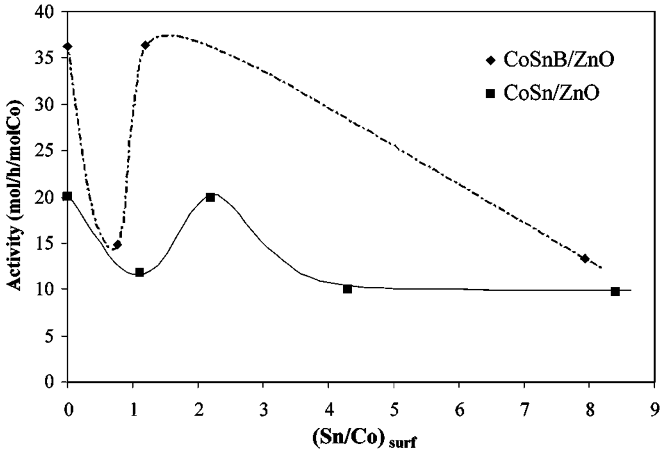


FIG. 9. Activity of CoSnB and CoSn over ZnO catalysts. Influence of tin content.

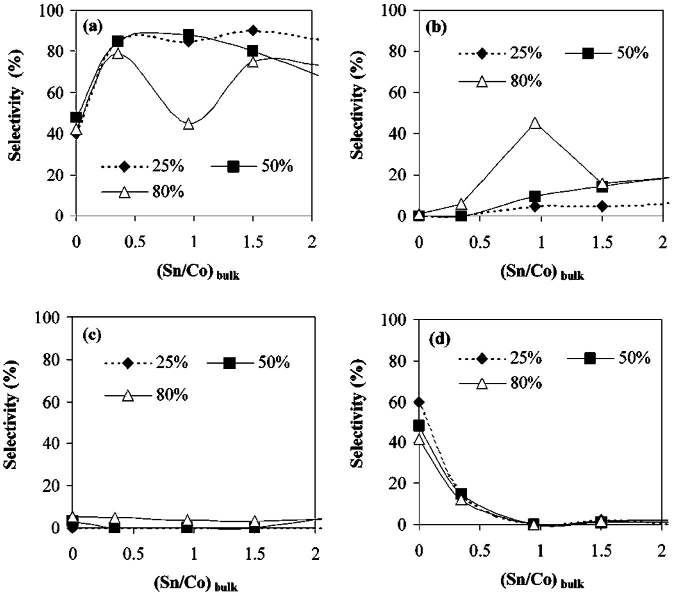


FIG. 10. Hydrogenation of methyl oleate in the presence of CoSn/ZnO catalysts. Influence of tin content at 25, 50, and 80% conversion on selectivity to (a) heavy esters, (b) unsaturated alcohols, (c) saturated alcohols, and (d) saturated esters.

On the other hand, the formation of UAs is lower than that observed in the presence of the unreduced (with $NaBH_4$) CoSn/ZnO catalyst. If we suppose that the active sites are similar for all the catalysts, these results could be due to a lower superficial Sn/Co ratio. Indeed, the $Sn/Co_{surf.}$ ratio (1.2) of the reduced catalyst is two times lower than the one obtained in the presence of the unreduced catalyst (2.2) or of the $CoSnB/Al_2O_3$ (17). For a bulk Sn/Co ratio equal to or higher than 1, the main reaction is the transesterification reaction between alcohols formed and the methyl oleate. As for the unreduced catalyst, the rate of the hydrogenating

TABLE 5

Reproducibility of the CoSn/ZnO Catalyst with an Atomic Sn/Co Ratio of 1: Activity and Selectivity in the Hydrogenation of Methyl Oleate

		Selectivity (%) (40% conversion)				Selectivity (%) (90% conversion)			
Catalysts	Activity (mol h^{-1} mol_{Co}^{-1})	HE	MS	SA	UA	HE	MS	SA	UA
CoSn/ZnO[a]	19.8	86	0	0	13	50	0	0	45
CoSn/ZnO[b]	19.7	94	0	0	6	52	0	0	43

[a] HE, heavy esters; UA, unsaturated alcohols; SA, saturated alcohol; MS, methyl sterate.

[b] Hydrocarbons are formed in all cases.

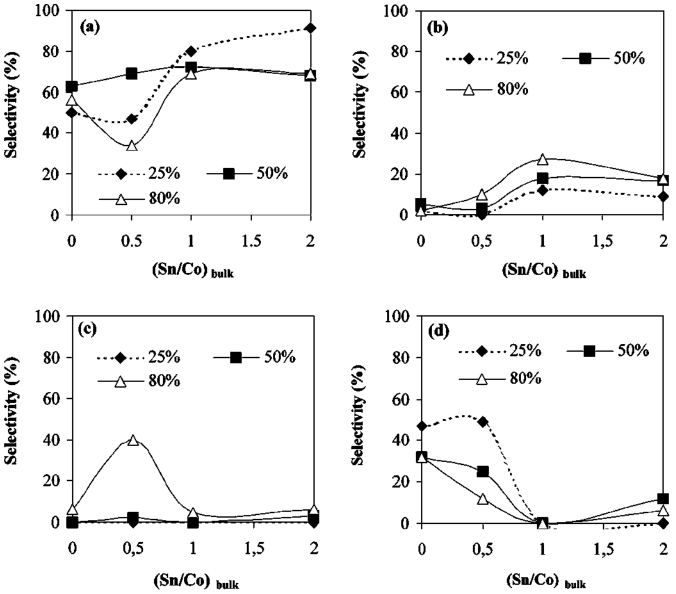


FIG. 11. Hydrogenation of methyl oleate in the presence of CoSnB/ZnO catalysts. Influence of tin content at 25, 50, and 80% conversion on selectivity to (a) heavy esters, (b) unsaturated alcohols, (c) saturated alcohols, and (d) saturated esters.

step is limited by the covering of cobalt particles with a tin oxide species.

DISCUSSION

The results of this paper show that the addition of tin to Co/ZnO catalyst and the prereduction of such catalysts have an effect on their catalytic properties in the hydrogenation reaction of methyl oleate into UAs. Indeed, the nature and the quantity of cobalt and tin species at the catalyst surface influence the following:

- the rate of the methyl oleate transformation,
- the rate of the heavy esters formation, and
- the rate of the heavy esters hydrogenation.

The XPS analysis indicates the following:

(i) The addition of tin to the Co/ZnO catalyst leads to a significant tin enrichement at the catalyst surface. This effect is more marked when the CoSn/ZnO catalyst is reduced with sodium borohydride since there is also an increase in the superficial cobalt amount. However, if the $(Sn/Co)_{surf}$ ratio is modified by the reduction with sodium borohydride (factor of 2 when $(Sn/Co)_{bulk} \leq 1$), there is in both cases a large excess of tin at the catalyst surface when the bulk Sn/Co ratio is above 1 (Fig. 12).

(ii) The addition of tin favors the reduction of both cobalt and tin species when they are in close interaction at the catalyst surface. However, the percentage of metallic species goes through a maximum when the composition of CoSn/ZnO corresponds to a $(Sn/Co)_{bulk}$ ratio around 1.

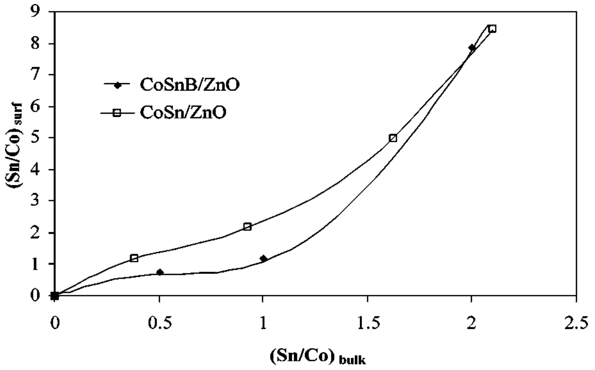


FIG. 12. Effect of the reduction (with $NaBH_4$) of CoSn/ZnO catalysts. Modification of the surface Sn/Co ratio.

On the other hand, the temperature-programmed reduction profiles of CoSn/ZnO catalysts show that there are some species more easily reducible when the bulk Sn/Co ratio is around 1.

For the CoSn/ZnO and CoSnB/ZnO catalysts, a similar variation of activities with $(Sn/Co)_{bulk}$ ratio is observed with a maximum for a bulk Sn/Co ratio around 1, as was already mentioned in the presence of $CoSnB/Al_2O_3$ catalysts (14). However, the reduced catalyst with sodium borohydride is more active than the nonreduced catalyst owing to an increase in the cobalt and tin amount at the catalyst surface.

The main significant results concern the selectivity to UAs. Indeed, the previous results show that the selectivity to UAs strongly depends on the superficial composition of cobalt and tin, since there is a maximum of selectivity to UAs in the presence of CoSn/ZnO and CoSnB/ZnO catalysts when the bulk Sn/Co ratio is around 1 (Figs. 10 and 11). But Fig. 13, presenting the selectivity to UAs obtained in the presence of CoSn/ZnO catalyst versus the atomic $(Sn/Co)_{surf}$ ratio, shows that the selectivity goes through a maximum for an atomic $(Sn/Co)_{surf}$ ratio of 2. The values

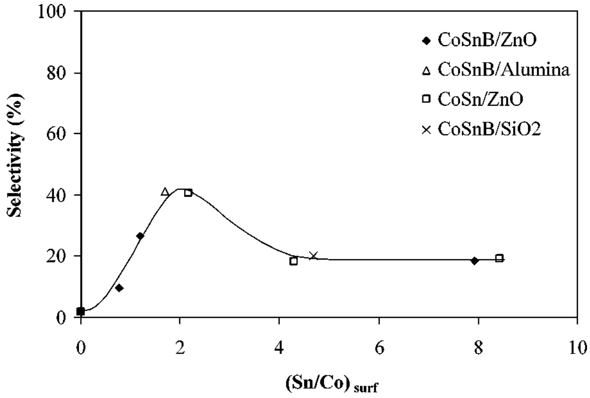


FIG. 13. Selectivity to unsaturated alcohols (at 80% conversion) of CoSn-supported catalysts.

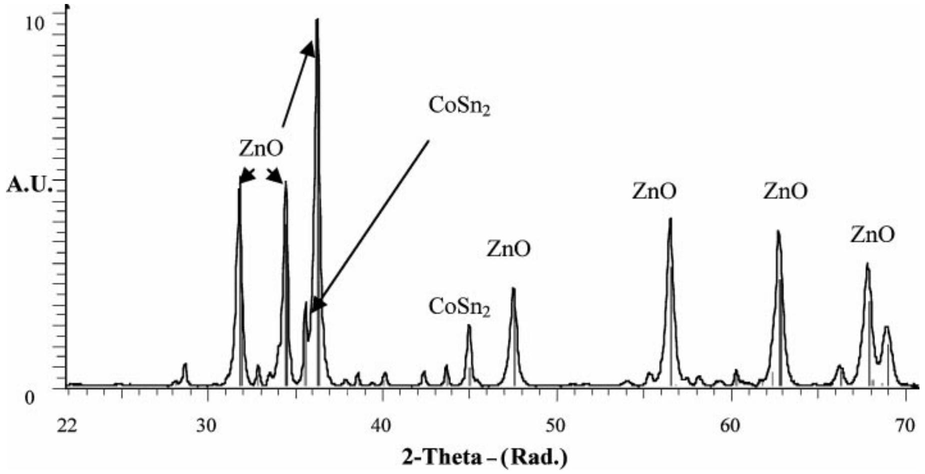


FIG. 14. X-ray diffraction of CoSn/ZnO catalyst ($(Sn/Co)_{bulk} = 1$).

of the selectivity to UAs obtained in the presence of the CoSnB catalysts supported over alumina (17), zinc oxide, and silica (18) reported in Fig. 13 show that they are in good agreement with the data of the CoSn/ZnO catalysts.

It seems that mixed sites (one cobalt atom with two tin atoms) are necessary to selectively form the UAs. These results confirm the previous assumption showing that the mixed sites Me^0–$(SnOx)_2$ of alumina-supported MeSn materials are active centers in the hydrogenation of methyl oleate. Moreover, an X-ray diffraction analysis (with a Brucker D5005 apparatus) done over CoSn/ZnO catalyst ($(Sn/Co)_{bulk}$ ratio of 1) shows that there are $CoSn_2$ species on this catalyst, which confirms the presence of two tin species close to one cobalt particle (Fig. 14). When the surface Sn/Co ratio is above 2, the tin species covered the cobalt particles so that the selectivity to UAs decreased until a leveling off at 20%, that is, similar to the selectivity obtained in the presence of the Sn/ZnO catalyst (Fig. 4), the CoSn catalysts having properties similar to tin supported over zinc oxide.

CONCLUSION

In this work, it has been demonstrated that the hydrogenation of methyl oleate into oleyl alcohol can be performed in the presence of CoSn/ZnO catalysts. The addition of tin increases the selectivity to oleyl alcohol, with a maximum for a bulk Sn/Co ratio of 1. The rate of the transesterification reaction is higher than the rate of the hydrogenation of methyl oleate. The reduction with sodium borohydride increases the activity of CoSn/ZnO catalysts owing to an increase in the zerovalent Co and Sn species. It was shown that the selectivity to UAs has a maximum for a surface Sn/Co ratio close to 2 for CoSn supported over zinc oxide catalysts, the $CoSn_2$ species being suggested as the active sites for the formation of UAs from the hydrogenation of methyl oleate.

ACKNOWLEDGMENTS

This study was carried out within the framework of a (AAIR) European Program. The authors from the University of Poitiers are very grateful to the French Ministry of Education and Research for a grant to K. De Oliveira. The authors also thank Prof. C. Guimon of the University of Pau for XPS analysis.

REFERENCES

1. Kaufmann, A. J., and Ruebush, R. J., *in* "Proceedings of the World Conference on Oleochemicals into the 21st Century" (T. H. Applewhite, Ed.), Vol. 10, p. 25. Am. Oil Chem. Soc., Champaign, IL, 1990.
2. Sauer, J., and Adkins, H., *J. Am. Chem. Soc.* **59**, 1 (1937).
3. Boerma, H., *Stud. Surf. Sci. Catal.* **1**, 105 (1976).
4. Pouilloux, Y., Autin, F., Guimon, C., and Barrault, J., *J. Catal.* **176**, 215 (1998).
5. Pouilloux, Y., Piccirilli, A., and Barrault, J., *J. Mol. Catal. A* **108**, 161 (1995).
6. Consonni, M., Jokic, D., Murzin, D., and Touroude, R., *in* "5th Int. Symp. Heterogeneous Catalysis and Fine Chemicals," Lyon (France), Aug. 30–Sept. 3 1999.
7. Wehner, P. S., Gustafson, B. L., and Tustin, G. C., *J. Catal.* **88**, 246 (1984).
8. WO 89/0086, to Eastman Kodak (1989).
9. Aboulayt, A., Chambellan, A., Martin, M., Saussey, J., Mauge, F., Lavalley, J. C., Mercier, C., and Jacquot, R., *Stud. Surf. Sci. Catal.* **78**, 131 (1993).
10. Desphande, V. M., Patterson, N. R., and Narasimhan, C. S., *J. Catal.* **121**, 165 (1990).
11. Shirley, D. A., *Phys. Rev. B.* **5**, 4709 (1972).
12. Scofield, J. H., *J. Electron Spectrosc. Relat. Phenom.* **8**, 129 (1976).
13. Haffad, D., Kameswari, U., Bettahar, M. M., Chambellen, A., and Lavalley, J. C., *J. Catal.* **175**, 85 (1997).
14. Herman, R. G., Klier, K., Simmons, G. W., Finn, B. P., Bulko, J. B., and Kobylinski, T. P., *J. Catal.* **56**, 407 (1979).
15. Eischens, R. P., Pliskin, W. A., and Low, M. J. D., *J. Catal.* **1**, 180 (1962).
16. Griffin, G. L., and Yates, J. T., *J. Catal.* **73**, 396 (1982).
17. Pouilloux, Y., Piccirilli, A., Autin, F., Guimon, C., and Barrault, J., *Appl. Catal. A* **169**, 65 (1998).
18. Pouilloux, Y., Autin, F. C., and Barrault, J., *Catal. Today* **63**, 87 (2000).