

Selective hydrogenation of fatty acids and methyl esters of fatty acids to obtain fatty alcohols – a review

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Abstract

In this paper, a review is presented of the evolution of different catalytic systems and operating conditions used in the selective hydrogenation of acids and esters of fatty acids to obtain fatty alcohols, which have broad industrial applications in the oleochemical industry. In addition, the current status of the different technologies used industrially (Lurgi, Davy and Henkel) for obtaining fatty alcohols, as well as major global sources of raw materials for the oleochemical industry are put forward. Finally, the reaction mechanisms of the selective hydrogenation process of oleic acid and methyl oleate to obtain the corresponding unsaturated alcohol as well as the new catalysts proposed by researchers are described.

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Keywords: selective hydrogenation; fatty alcohols; methyl esters; catalysts

INTRODUCTION

Because several reviews have been dedicated to selective hydrogenation reactions,^{1–6} this review will focus on the hydrogenation of unsaturated fatty acids and esters of fatty acids over supported metal catalysts, specifically on the hydrogenation of oleic acid (*cis*-9-octadecenoic acid) and methyl oleate (methyl-9-octadecenoate) to obtain oleyl alcohol (9-octadecen-1-ol). The homogenous catalysts are very briefly treated too.

From the environmental point of view, vegetable oils can be considered as promising renewable raw materials with high biodegradability and low eco-toxicity.^{7,8} Alcohols with six and seven carbon atoms are used primarily as plasticizers while heavier alcohols are used as detergents. Unsaturated fatty alcohols are used in the production of detergents (due to their excellent cleaning properties and superior biodegradability), solvents, defoamers, super-fating agents, oily components and as esters in lubricants, liquid oily soaps, shampoos, hair conditioners, skin emollients, emulsifiers, thickeners, lotions and cosmetic creams, as plasticizers and antifoaming agents and in the textile and hide industries.^{9–14}

Oleyl alcohol provides several advantages over saturated alcohols with the same chain length, for example, a lower melting point, greater solubility in water and the possibility of introducing functional groups. For this reason, oleyl alcohol is particularly used as an additive for petroleum oils and lubricants.¹⁵ In agriculture, it is used as an additive in insecticide formulations and animal fodder; in polymer processing, it is used in rubber, PVC and PU-molding; regarding metal working processes, it is used in drilling, milling, cutting and rolling and as an additive in lubricants, anticorrosive agents, polishing agents and cleaner emulsifier; in the printing industry, it is used in color pastes, inks and stencils as softener, solubilizer and dispersing aid. Figure 1 shows the total fatty alcohol market by application (from Brackmann and Hager).¹⁶

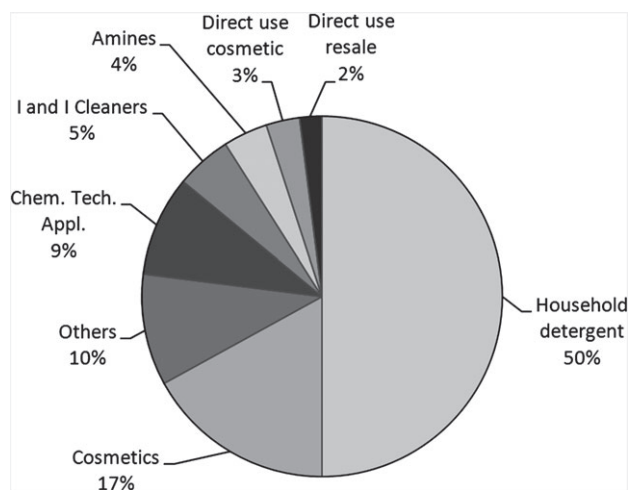


Figure 1. Total fatty alcohol market by application.¹⁶

Currently, large-scale fatty alcohols production is carried out mainly in the petrochemical industry based on non-renewable resources.^{17–19} Natural vegetable oil is an ideal substitute feedstock since it contains mainly fatty acids with 12 to 20 carbon atoms and up to 3 double bonds. Vegetable oil is a commodity with relatively low prices and represents an inexhaustible renewable resource that can be obtained from a wide variety of plants.^{20–22}

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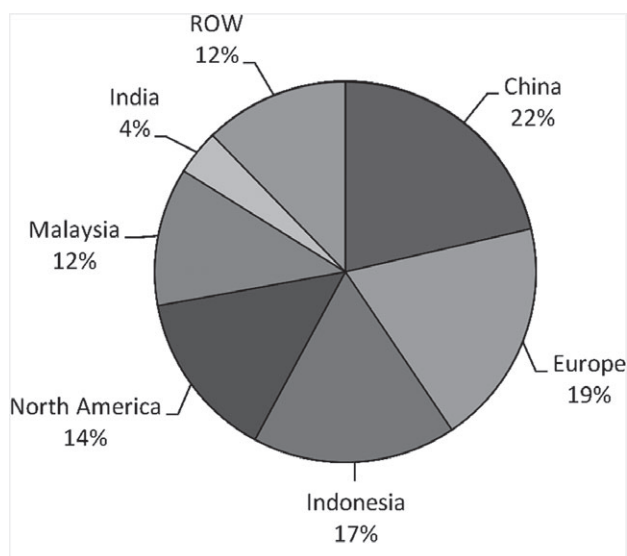


Figure 2. The global fatty alcohol capacity distribution by region.²⁶

For these reasons, at present, about 20% of the surfactants produced worldwide are oleochemicals (i.e. chemicals derived from plant and animal fats) with a market share expected to grow since these biosourced products will eventually substitute their petrochemical competence due to:

- the great availability of vegetable oils, which allows part of this production to be used for the elaboration of oleochemical products;
- the diminution of the known world petroleum reserves, the main feedstock for the production of synthetic surfactants;
- the marked fluctuation in the available commodities prices (including petroleum, fats and oils).

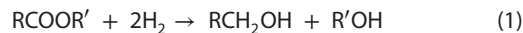
The principal sources of fatty alcohols in the C_{12} – C_{14} range are coconut and palm kernel oil; while tallow, soybean oil and palm oil are used to produce most of the C_{16} – C_{18} alcohols. Rapeseed oil and fish oil can be used to obtain C_{20} – C_{22} alcohols. Also, some special alcohols are readily available in great variety from selected starting oils. Rapeseed oil can be used to produce behenyl and erucyl alcohol while castor oil can give hydroxy-stearyl alcohol. Another big set of unsaturated alcohols can be synthesized from linseed oil.²³ Erucic acid can be found in high concentration in rapeseed oil. Castor oil is a source of hydroxy acids for producing diols.²⁴

The economical importance of fatty alcohols is reflected in the global production increase from 2.5 million tons in 2005²⁵ to an estimated production of 3.1 million tons in 2015²⁶ with an estimated global demand growth (2012–2017) of 3.2% per year.²⁷ The global fatty alcohol production capacity was about 4.8 Mt in 2015, and their distribution by region can be seen in Fig. 2.²⁶

INDUSTRIAL PRODUCTION OF FATTY ALCOHOLS

Fatty alcohols are produced in large-scale by hydrogenation of fatty acid methyl esters (FAME), which is a process that has remained practically unchanged for decades.²⁸ However, current processes have little to offer in terms of variety of the alcohols produced.

Fatty alcohols are obtained by catalytic hydrogenation at high pressure and temperatures from the corresponding fatty acids or esters. The overall reaction is:



where R' corresponds to a methyl group or hydrogen atom if the process uses methyl esters or acids as a feedstock, respectively. Most of the processes start from esters since fatty acids are corrosive at high temperatures. In some cases, fatty acids can also attack the catalysts. Hence, the contact equipment is subject to deterioration while the catalysts are inactivated which increases production downtimes. On the other hand, the use of esters as feedstock implies additional esterification and separation operations.

The commercial processes use Cu–Cr-based catalysts under severe reaction conditions (250–350 °C and 10–20 MPa).^{18,29–35} The hydrogen solubility in the feed is relatively limited and the catalyst is solid. Therefore, the reaction takes place in a triphasic reactor, particularly in the solid–liquid interphase. Depending on the catalyst's morphology, the process uses either a slurry reactor or a fixed bed reactor.²⁵

These Cu–Cr-based catalysts present good selectivity towards alcohols but induce environmental risks given the use of Cr, the drastic reaction conditions and the high energy consumption. Moreover, the catalyst suffers deactivation and, as a consequence, conversion levels are maintained by continuously adding a small amount of fresh catalyst in the recycle stream, and withdrawing spent catalyst.^{29,36,37} For these reasons, chromium replacement by other promoters like manganese and zinc is being pursued.^{38–41} Other industrial catalysts like Cu/Zn are poisoned by fatty acid esters with chlorinated compounds and water as impurities.^{42,43} Furthermore, the reaction conditions favor the undesired hydrogenation of the oil unsaturations along with the carbonyl group, particularly in the case of fatty chains with multiple double bonds.

Commercial catalysts include promoters such as ZnO, Al_2O_3 , Cr_2O_3 , Fe_2O_3 and others.^{44–46} Additional literature on the traditional catalysts used until the 1970s is available.^{47–49} Recent patents show great interest in catalysts with higher selectivity but to the best of our knowledge they have not seen commercial implementation yet.^{50–55}

From an industrial point of view it is important to achieve high activity and selectivity at lower pressures and/or lower H_2 /oil ratios, since the major drawback of current processes is the high hydrogen compression costs (Lurgi, Henkel).

Currently, there are industrial processes for the production of oleyl alcohol by selective hydrogenation either from oleic acid or methyl oleate. In general, it could be said that Cu-based catalysts have reached their maximum possible efficiency and no further modifications are expected on currently used processes (cf. Table 1).

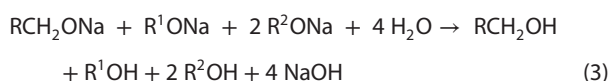
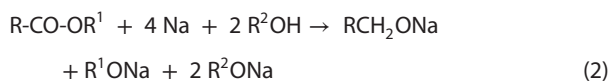
A deprecated industrial process for the production of unsaturated fatty alcohols is the reduction of esters with sodium, which was mainly used for the production of oleyl alcohol but has been in disuse since the 1950s.^{56,57} Sodium reduction specifically targets the ester group without affecting unsaturations except in the case of α,β -unsaturated esters.⁵⁸ In summary, reduction with sodium involves mixing a solution of the dry and neutralized ester, the reducing alcohol, and a dispersion of metallic sodium in an inert solvent, then reacting at atmospheric pressure in a stirred carbon steel reactor. The reaction is fast and exothermic. Upon completion, the resulting mixture is quenched or hydrolyzed by

Table 1. Processes for the production of fatty alcohols from fatty acid methyl esters (FAME) or fatty acids (FA)

Process	Precursor	Oil Phase	Catalyst	P, MPa	T, °C	Ref.
Lurgi	FAME	Liquid	Cu–Cr	25.3–30.4	210	46
Lurgi	FAWE	Liquid	Cu–Cr	25.3–30.4	----	46
Davy	FAME	Vapor	Cu	4.1	220	47
Henkel	FAME	Liquid	Cr–Cu	5.1–10.1	200	48–49

FAWE: fatty acid wax esters

water addition.⁵⁷ The overall reaction can be summarized by the Equations (2) and (3)^{56,57}



In the case of hydrogenation using homogeneous catalysts the problem of the separation and recovery of the catalyst must be addressed. Nonetheless, there are several scientific works and patents in which the hydrogenation is carried out in a homogeneous media. Selective hydrogenation can also be carried out in a homogeneous phase using metallic soaps as catalysts. Copper and cadmium oxides react with a fatty acid to create a homogeneous soap solution. Either Cu and Cd, or Pb and Cd soaps of unsaturated fatty acids react to give unsaturated fatty alcohols. Cu and Sn soaps produce saturated alcohols.⁵⁹ The presence of Cd-soap seems to be of fundamental importance if a selective hydrogenation to unsaturated alcohols is desired.^{50,60} The homogeneous catalyzed reaction proceeds via a CuH-acid complex, Cd probably acting as a stabilizer⁵⁹ and as an intermediate for the hydrogenation.⁶⁰ According to some patents, Cr-, Cd-, Pb- and Zn-soaps, or combinations of Cr–Cd and Pb–Sn, can catalyze the selective hydrogenation of oleic acid to oleyl alcohol.^{61–63}

Although, to the best of our knowledge, the hydrogenation of esters and fatty acids using homogeneous catalysts has not been implemented yet on an industrial process, it is important to point out that the homogeneously catalyzed hydrogenation of other carboxylic acids to alcohols using Co, Fe or Ru complexes has been implemented recently. However, no information has been published on the effect of this process on the C=C bonds of unsaturated fatty acids.^{64–67}

In the last decade, the interest of researchers has turned toward catalysts based on Group VIII metals, since they are very active towards hydrogenation reactions and their selectivity could be improved by the use of promoters. For this reason, it could be possible to achieve yields comparable with Cu-based catalysts but under milder conditions and in liquid phase.

Industrial processes with slurry-type reactors

A simplified flow diagram for the hydrogenation process in a slurry-type reactor is shown in Fig. 3. The fatty ester and hydrogen are pre-heated and fed to the reactor at the bottom. The catalyst, a suspension with at least 2% of powdered copper chromite in methyl oleate, is added with a dosing pump. The reactor is a vertical tube with no packing. The reaction occurs at 25.3–30.4 MPa and 250–300 °C.

The reactor output is cooled and the gas and liquid are separated. The gas, mostly composed of hydrogen, is recycled. The fatty alcohol/methanol mixture is distilled in the methanol separation unit. After removing the methanol, the catalyst is recovered by filtration. The crude fatty alcohol still contains 2–5% of esters that can be eliminated by adding a base to form a soap that will decant to the bottom during the distillation stages.^{23,68,69}

Industrial process with a fixed bed reactor

It is possible to distinguish two different alternatives to conduct fixed-bed hydrogenation, either it is carried out in the liquid phase (trickle hydrogenation) or in the vapor phase (vapor phase hydrogenation). However, this is hardly a clear-cut distinction, since the aggregation state of the feed depends on a great variety of factors. Moreover, some processes employ a largely (but not completely) vaporized feed, a case in which it is impossible to determine if the reaction is carried out in the liquid or vapor phase. It is simpler to differentiate between processes using compacted pellets or a supported catalyst.

Independent of the catalyst morphology, the process follows the scheme shown in Fig. 4.²³ First, the methyl ester is mixed with hydrogen at high pressure and is preheated using the reactor output and then adjusted with a peak heater. A part of the organic solution is vaporized in the excess hydrogen. Hydrogenation is carried at 20.3–30.4 MPa and at a temperature of 200–300 °C. After cooling, the output gases and liquids are separated. The gas, mostly composed of hydrogen, is recycled. The liquid phase is flashed to recover the methanol and the resulting fatty alcohol does not require further refinement. If a specific composition is required, either a specific methyl ester mixture can be used as feedstock or the output fatty alcohols can be rectified.

The vapor phase process is carried out with a similar setup. During the 1990s, Davy Technologies Ltd presented a new process based in the vapor phase hydrogenation of methyl esters at 4.05 MPa and lower temperatures thanks to the use of new higher activity catalysts. A hot hydrogen current is used to vaporize the feed which is then introduced into a downward co-current single-phase fixed bed reactor. The process uses a chrome-free Cu-based catalyst. Nonetheless, the Davy process still suffers from high recycle flowrates and high H₂/oil ratios required to vaporize the feed. Methanol is added to increase the volatilities of esters but methanol decomposition produces carbon monoxide, water and dimethyl ether.^{23,69}

Other processes

The conversion of fatty acids into fatty alcohols by catalytic hydrogenation without previous esterification requires corrosion-resistant materials of construction and acid-resistant catalysts. Required reaction temperatures are higher, resulting in higher hydrocarbon contents.²³ However, Lurgi developed a

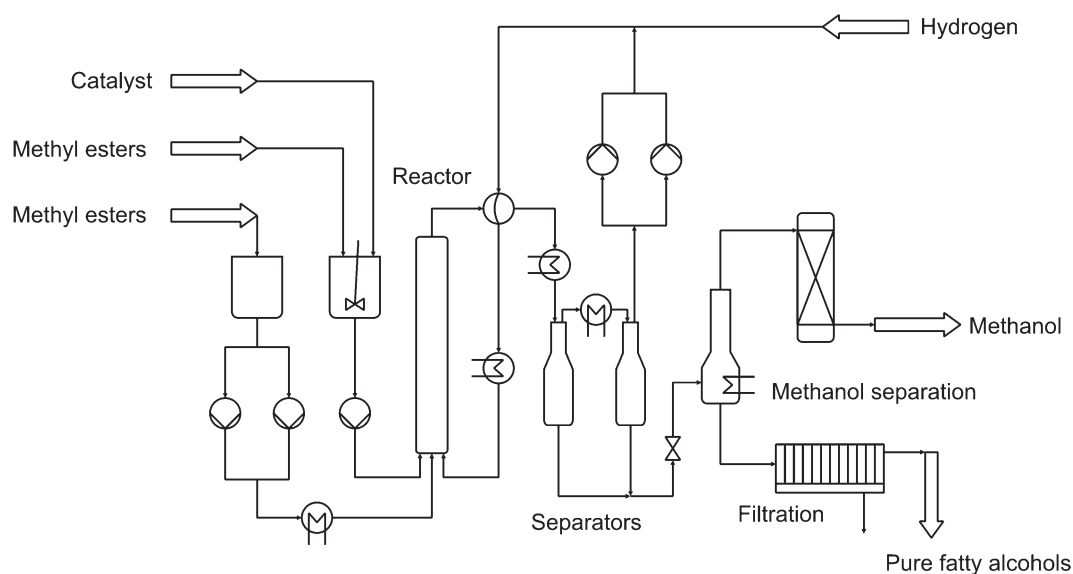


Figure 3. Flowsheet for the industrial process using a slurry-type reactor.²³

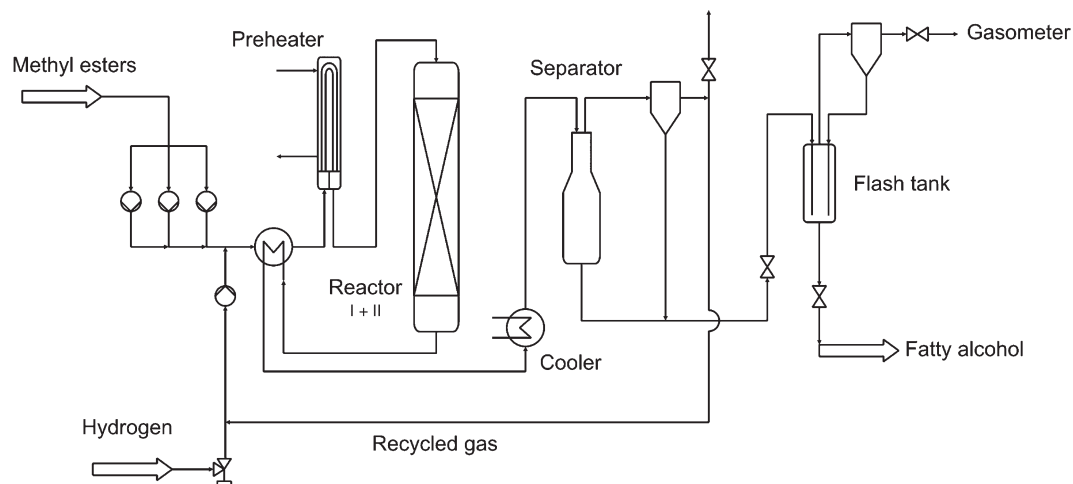


Figure 4. Flowsheet for the industrial process using a fixed bed reactor.²³

process to convert fatty acids directly to fatty alcohols by hydrogenation using a slurry-type reactor and a copper–chromite catalyst.⁷⁰ This technology has been replaced by a more conventional process using methyl esters as intermediates since the 1990s. The methyl ester route reduces investment and operating costs. Since 2004, a new process has been commercialized at Lurgi. The scheme for this process is presented in Fig. 5. It uses wax esters as an intermediate and fatty acids as a feedstock. These wax esters are spontaneously produced by mixing fatty acids with fatty alcohols at high temperature and atmospheric pressure. Then, the wax esters are mixed with hydrogen and fed into a downflowing trickle bed reactor with a commercial catalyst, producing two molecules of fatty alcohols for each wax ester molecule. After cooling and fractionation, part of the fatty alcohols is recycled to produce the intermediate esters. Glycerin and the required fatty acids are produced from fatty oil by splitting. Hence, the overall process is insensitive to the acid content of the oil feed, contrary to other processes relying on converting the oils to methyl esters. Furthermore, the process requires no methanol handling, reducing environmental hazard and costs.

CATALYSTS

It has already been mentioned that current industrial processes are subject to chemical deactivation, low energetic efficiency and low selectivity. Also, the presence of chromium presents an environmental hazard and future catalysts are required to be Cr-free. Hence, the three principal research lines being studied are:

- increasing the activity, to work under milder conditions;
- increasing the selectivity, to improve the alcohol yield;
- increasing the stability of the catalyst in acid environments to synthesize alcohols directly from fatty acids.^{32,60,68,71}

From a chemical viewpoint, the production of fatty alcohols from methyl esters is accomplished through the selective hydrogenation of the carbonyl group and later hydrogenolysis of the C—O bond of the methoxyl group. In particular, the selective hydrogenation of the methyl oleate or oleic acid (and other unsaturated fatty acids) requires to be carried out without affecting the C=C bonds. In recent decades, competitive hydrogenation of the carbonyl group in the presence of C=C bonds has been the subject

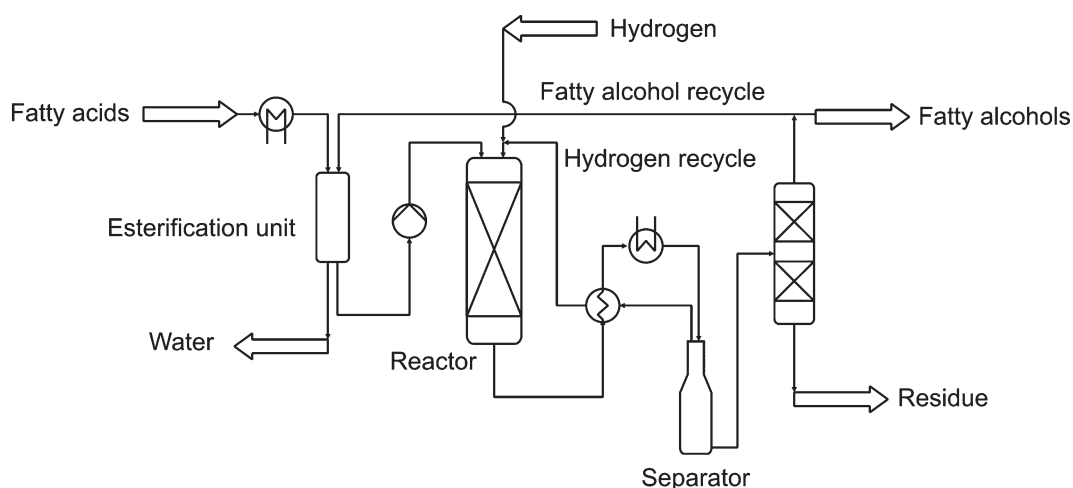


Figure 5. Flowsheet for the wax ester route using the Lurgi process.⁷⁰

of many scientific articles and is considered a difficult task since the hydrogenation of C=C bonds using metallic catalysts is usually faster than reduction of the C=O bond.^{3,72–74}

There have been also some studies in order to replace Cu-based catalysts with others based on noble metals in order to reduce the reaction temperature and pressure. These catalysts present higher activity but show little selectivity without additives. Monometallic catalysts, such as Raney Nickel or Pt(Pd)/Al₂O₃, used for the hydrogenation of olefins, are useless for selective hydrogenation since they present great affinity towards the reduction of the C=C bond.^{1,75} Moreover, hydrogenation of the C=C double bond in the linear chain is favored from the thermodynamic point of view ($\Delta H_{C=C} = -120 \text{ kJ mol}^{-1}$) versus C=O ($\Delta H_{C=O} = -50 \text{ kJ mol}^{-1}$). This reactivity difference seems to be due to the weak polarization of the C=O bond, but also from the steric hindrance characteristic of this function.⁷⁶

Cu-based catalysts are adequate for this process since they allow the selective hydrogenation of C=O bonds while remaining relatively inactive towards C=C. Bulk copper is usually inactive, does not resist sinterization and does not present enough mechanical stability for industrial operation. Consequently, promoters are added in order to achieve the mechanical and chemical requirements needed. A commonly used additive is chromium. As early as 1931, Adkins described the use of a Cu–Cr catalyst for the hydrogenation of esters.⁷⁷ Similar catalysts are frequently still in use.^{30,68,78–80} The addition of ZnO to Cu/SiO₂ catalysts increases the activity with higher selectivity. Moreover, it has been proved that Cu/ZnO/SiO₂ catalysts are competitive against industrial Cu–Cr.^{80,81} It has been suggested that the anionic vacancies in ZnO are able to increase the electronic density of copper⁸² or that ZnO allows for the activation and storage of H₂ by spillover.³⁵ Besides Cr and Zn, other promoters for Cu-based catalysts have been mentioned in patents and the open literature. The addition of Mn on Cu/ZnO/Al₂O₃,⁸² Cu–Cr^{83,84} and unsupported copper catalysts with multiple promoters^{85,86} has been reported to increase the activity of the catalysts and/or the selectivity towards hydrogenolysis and hydrogenation. Manganese,^{83,84} iron,⁸² magnesium, zinc, silica-supported copper and cobalt⁸² have also been tested as additives. Despite the positive effect of promoters on the hydrogenation and hydrogenolysis activity, increase in the formation of byproducts is equally important. In the industrial process, alkanes and wax esters are the main byproducts. It is hard to

remove alkanes from the product and hence, they are undesirable products.

Catalysts based on Group VIII metals (Pt, Rh, Ru, etc.)^{3,87,88} can be improved through various means:

- the use of reducible oxide supports (TiO₂, WO₃, MoO₃, etc.);^{88–91}
- the use of mesoporous silica as support;^{92–95}
- the addition of promoters such as Sn, Ge, Fe, Cd, etc.;^{5,23,53,96–105}
- the preparation method of the catalyst.^{106–108}

The activity increase caused by reducible oxide supports is attributed to oxygen interaction with metallic ions of the support and/or oxygen vacancies on the metal–support interface. These electrophilic groups promote hydrogenation of the carboxylic acid by interacting with the carbonyl oxygen and weakening the C=O bond.^{109,110} They are created during the reduction stages by hydrogen spillover activated by the metal.^{111–114} Promoters such as Sn, Ge, Fe, etc. also interact with the oxygen free electron pairs, activating the C=O bond.³ The oxidation state of the promoters after the reduction stage has received a lot of attention, given the possibility of alloying and metal–support and metal–promoter interactions.³ Physicochemical characterization and test reaction studies have been used to study the kinetic effect of these promoters, including the selective hydrogenation of α,β -unsaturated aldehydes. Extrapolation based on results from hydrogenation of α,β -unsaturated aldehydes should be avoided given that the reduction of fatty acid or esters of fatty acids is not directly affected by the C=C bond, as opposed to the case of those conjugated aldehydes. There is still a certain degree of uncertainty about these aspects that can be attributed to the preparation methods and pretreatments.

The most promising catalysts are based on Ru–Sn^{21,115–119} and Co–Sn.^{118,120–123} The literature also describes catalytic systems composed of a noble metal (Rh, Ru, Pd, Pt) and an additive (Sn, Zn, Cd) that are very active towards the reduction of esters towards alcohols.^{5,124–128} The selective hydrogenation of unsaturated compounds requires a more complex system.

Therefore, a second transition metal is added (bimetallic catalysts) and/or a promoter is added to favor C=O hydrogenation.

In the following section, the reaction schemes for oleic acid or methyl oleate to oleyl alcohol as proposed by several research groups are detailed along with some of the most outstanding results.

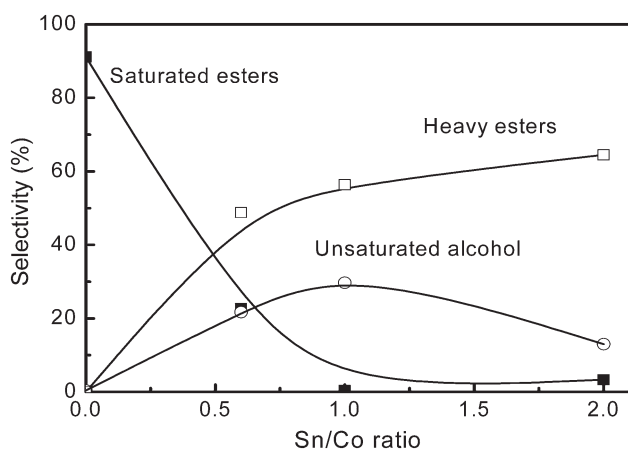


Figure 6. Selectivity to unsaturated alcohol, heavy esters and saturated esters on Co-Sn/Al₂O₃ catalyst as a function of Sn/Co ratio at 40% conversion.¹¹⁷

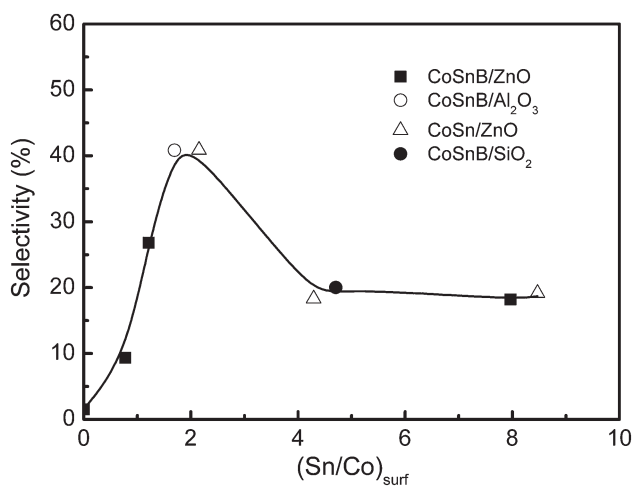


Figure 7. Selectivity to unsaturated alcohols (at 80% conversion) of CoSn-supported on ZnO, Al₂O₃ and SiO₂.¹²²

Co-based catalysts

It has also been reported that Co-Sn/Al₂O₃ and Co-Sn/ZnO catalysts are active toward the hydrogenation of methyl oleate^{117,120–123} while Co/SiO₂ catalyst can selectively reduce the C=O group of α,β -unsaturated aldehydes.¹²⁹ The addition of tin increases the activity and selectivity towards oleyl alcohol, reaching a maximum at a bulk composition with a Sn/Co ratio of unity as can be seen in Fig. 6.¹¹⁷ However, the selectivity to the unsaturated alcohols has been found to be strongly affected by the superficial Sn/Co ratio and the maximum selectivity to the unsaturated alcohol was found at a (Sn/Co)_{surf} ratio of 2 (Fig. 7).¹²²

Pouilloux *et al.*¹¹⁷ also reported that the selectivity of the Co-Sn catalyst to oleyl alcohol is comparable with that of the Ru-Sn catalyst but with higher activity.

The secondary transesterification reaction between the methyl oleate and oleyl alcohol is more marked with the Co-Sn catalysts than with the Ru-Sn catalyst¹¹⁷ and can occur over acid and/or basic sites of the catalyst as SnO_y species and/or the support.¹²¹ On the other hand, the preparation method seems to be important for the activity and selectivity given that the catalyst reduced with sodium borohydride is more active than those produced by the sol-gel or incipient wetting methods. The reduction step by

sodium borohydride improves the reduction efficiency of cobalt and tin species. XPS analysis confirmed the presence of Co⁰ species in the surface of Co-Sn-B/Al₂O₃ catalysts while the surface content of Co remains unmodified. In spite of this, the Sn/Co surface ratio decreases after the reduction step, increasing the activity. XPS analysis also shows two distinct tin oxide peaks after reduction, one of them being responsible for the transesterification reaction.¹¹⁷

Pouilloux *et al.*¹²¹ reported the product distribution as a function of the methyl oleate conversion for Co-Sn-B catalysts on different supports, as reproduced in Table 2. An important effect of the support was noted: at low conversion (b) the methyl oleate is converted to the unsaturated alcohol (by hydrogenation of the C=O bond) and to saturated esters such as methyl stearate (by hydrogenation of the olefinic bond) especially over catalysts containing alumina and active carbon as supports. 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. Poiulloux *et al.*¹²¹ reported that in silica, the cobalt-support interactions are weaker than in alumina, leading to an increase of the Co⁰ surface content but with a low hydrogenation activity, given the great surface tin enrichment. They determined that, depending on the relative amounts of Co⁰, SnO_x, SnO_y, as measured by XPS, the methyl ester is transformed in a saturated ester (Co⁰), an unsaturated alcohol (Co⁰-(SnO_x)₂) or heavy esters (Co⁰-(SnO_x)₂+SnO_y).¹²¹ It was also proven that Ru-Sn/Al₂O₃ and Co-Sn/Al₂O₃ catalysts are fairly comparable, presenting the same selectivity towards oleyl alcohol and higher activities than first-generation catalysts.¹¹⁷ The hydrogenation of methyl oleate depends on the nature of the active site on the surface of the catalyst, the formation of unsaturated alcohols is favored when the metal is interacting with two atoms of one of the tin species.¹³⁰

Hydrogenation of methyl oleate into oleyl alcohol using CoSn/ZnO catalysts showed that the carbonyl group is activated by zinc oxide while tin addition increases the selectivity towards unsaturated alcohols according to De Oliveira *et al.*¹²² Furthermore, selectivity to unsaturated alcohols goes through a maximum for a surface Sn/Co ratio close to 2. The active species are mixed Me⁰-(SnO_x)₂, where the oxidation state of tin is close to 0.

If NaBH₄ is used for the reduction of the CoSn catalyst, an increase in the activity is noted.

From XPS analysis, Co⁰ and two tin-oxide species were identified at the surface of the Co-Sn-B/Al₂O₃ catalyst after reduction with sodium borohydride. The addition of tin species does not modify the surface cobalt content. The reduction with sodium borohydride increased the reducibility of the metal oxide species.

Ru-Sn catalysts

Catalysts of the type Ru-Sn-B, present a good selectivity for the conversion of fatty esters to the correspondent unsaturated fatty acids.^{118,131–141} The hydrogenation of methyl oleate over 2%Ru/TiO₂, 4.7%Sn/TiO₂ and 2%Ru-4.7%Sn/TiO₂ catalysts was studied by Corradini *et al.*¹⁴² These studies revealed that addition of ruthenium negatively affects the activity of the catalyst in the hydrogenation of methyl oleate. However, the activity decrease is accompanied by a considerable increase of alcohols yield, in particular of unsaturated alcohols, probably due to the formation of Ru₃Sn₇ species.

Table 2. Selectivity (%) to different reaction products of the hydrogenation of methyl oleate over CoSnB/support catalysts (from Ref. 121)

Support	Unsaturated alcohol	Saturated alcohol	Saturated esters	Heavy esters	Others
Al₂O₃					
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
SiO₂					
b	0	0	8	86	6
c	15	5.5	11.5	56.5	11.5
d	21	5	5	58.5	10.5
Active carbon					
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

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%.

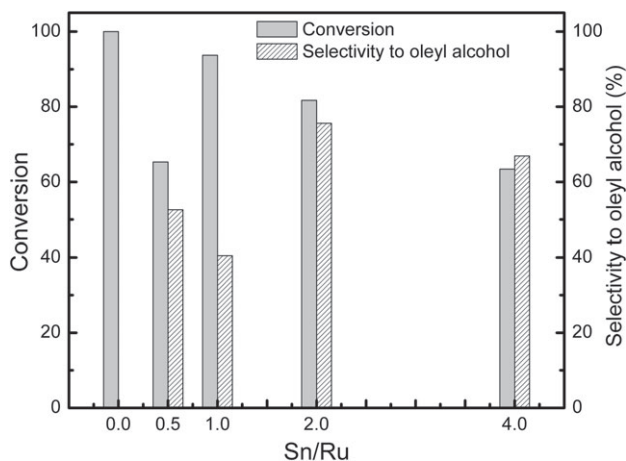


Figure 8. Conversion of methyl oleate and selectivity to oleyl alcohol as a function of Sn/Ru ratio. Reaction conditions: T: 270 °C, P: 4.4 MPa, Catalyst weight/reactive = 0.025, reaction time: 7 h.¹¹⁸

Deshpande *et al.*¹¹⁸ found that the Ru–Sn–B catalyst system shows maximum activity and selectivity for hydrogenation of methyl oleate to oleyl alcohol at a Ru/Sn ratio of 1/2 as can be seen in Fig. 8. The highest activity and selectivity were attributed to Ru^o sites interacting with Sn²⁺ or Sn⁴⁺ Lewis acid sites via oxygen, wherein the Lewis acid preferentially activates the C=O bond of the ester, facilitating hydrogen transfer from adjacent Ru–H sites. The role of boron probably lies in increasing the electronic charge density around Ru, thereby facilitating activation of H₂ as a hydride. The nonselective sites are the monometallic Ru^o sites which contribute mainly to the hydrogenation of C=C.

The influence of the kind of support (Al₂O₃, SiO₂, and TiO₂) on the catalytic activity and selectivity of Ru–Sn–B catalysts for the hydrogenation of methyl oleate to oleyl alcohol was studied by

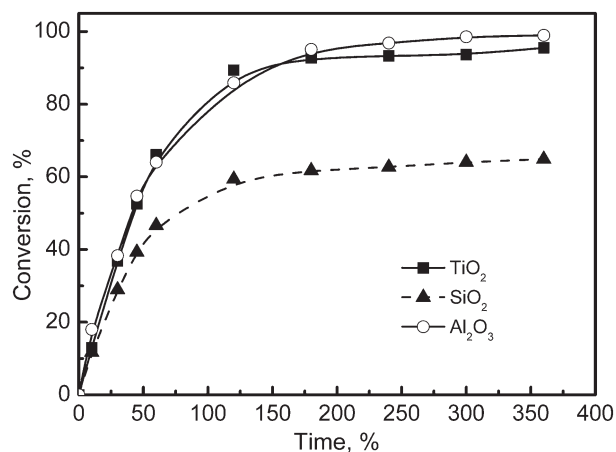


Figure 9. Methyl oleate conversion as a function of time of Ru–Sn–B supported catalysts. Reaction conditions: temperature = 290 °C, hydrogen pressure = 50 atm, mass of catalyst = 1 g, methyl oleate = 3.5 g, n-dodecane = 60 cm³, stirring speed = 800 rpm.¹³²

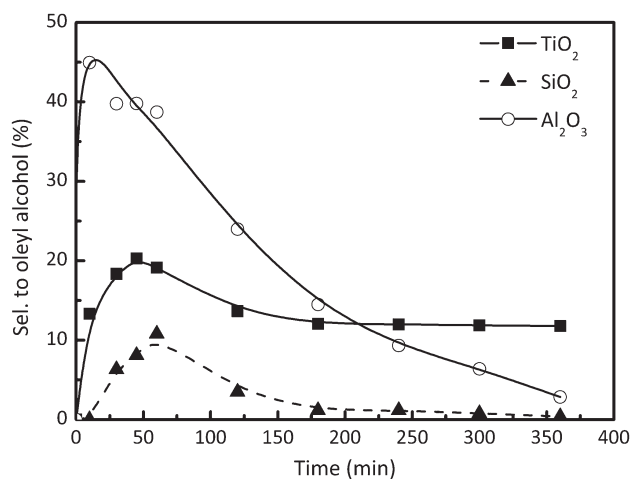


Figure 10. Selectivity to oleyl alcohol as a function of time of Ru–Sn–B supported catalysts. Reaction conditions: temperature = 290 °C, hydrogen pressure = 50 atm, mass of catalyst = 1 g, methyl oleate = 3.5 g, n-dodecane = 60 cm³, stirring speed = 800 rpm.¹³²

Sánchez *et al.*¹³² They found that the most active and selective catalyst for producing oleyl alcohol was Ru(1%)–Sn(2%)–B/Al₂O₃, as can be seen in Figs 9 and 10. This was attributed to the catalyst having a favorable surface Sn/Ru ratio (~2). A SiO₂-supported Ru–Sn–B catalyst presented good activity but hydrogenated both C=C double bonds and the C=O group, thus producing stearyl alcohol with a high yield. It was also strongly affected by deactivation problems, its final conversion being lower than with catalysts supported on Al₂O₃ and TiO₂. Furthermore, a TiO₂-supported catalyst hydrogenated C=C double bonds but had little activity for the hydrogenation of the C=O group, yielding methyl stearate instead of the desired alcohols. The adequacy of Al₂O₃ as a support for Ru–Sn compared with zirconia, silica and titania for the selective hydrogenation of oleic acid was also reported by Cheah *et al.*¹²⁴

Echeverri *et al.*¹¹⁵ studied the hydrogenation of methyl oleate to oleyl alcohol over Ru–Sn/Al₂O₃ catalysts, prepared from different precursors, at 270 °C and 5.0 MPa. They used two kinds of metal precursors: chlorine-free precursors and inorganic chlorides. Selectivity toward unsaturated alcohols was higher with the

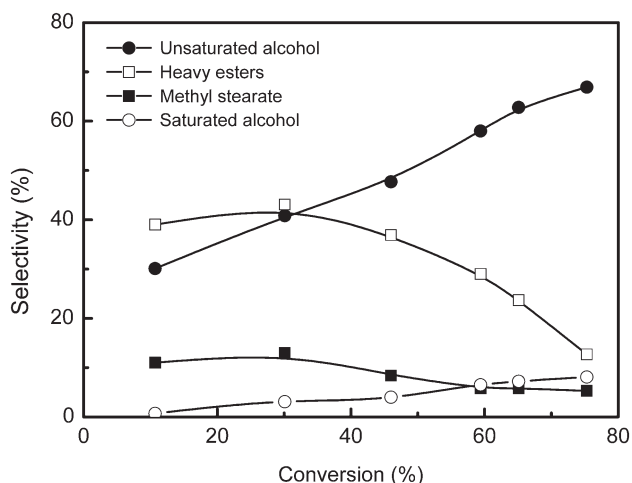


Figure 11. Selectivity as a function of conversion of methyl oleate for RuSn/Al₂O₃ without Cl.¹¹⁵

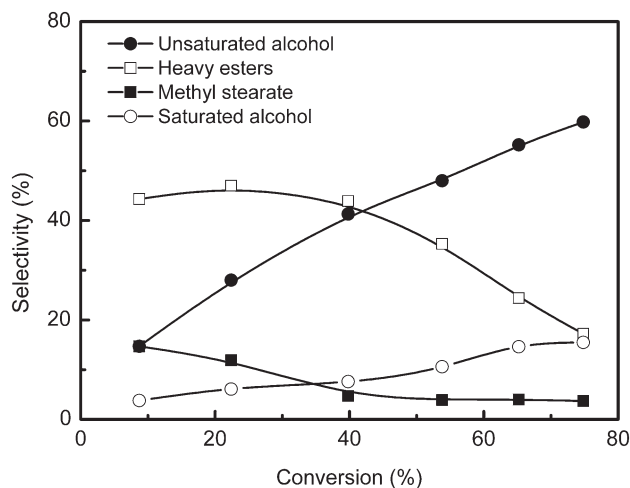


Figure 12. Selectivity as a function of conversion of methyl oleate for RuSn/Al₂O₃ with Cl.¹¹⁵

bimetallic catalyst based on chlorine-free precursors than with the catalyst based on metal chlorides, because chlorine prevents, to a certain extent, effective interaction between ruthenium and tin species. However, the most selective catalyst was the bimetallic one based on chloride precursors and reduced with NaBH₄, due to elimination of residual chlorine and the higher dispersion of Ru–Sn species. The catalyst based on chlorine-free precursors (Fig. 11) had higher selectivity to oleyl alcohol and lower formation of heavy esters than the metal-chloride-based catalyst. This indicates that residual chlorine has a negative effect on the selectivity to oleyl alcohol, and increases the rate of the transesterification reaction. This is explained by the fact that chlorine lowers the formation of Ru–Sn species, as suggested by TPR analysis, rendering isolated ruthenium and tin species. According to Pouilloux *et al.*,¹³³ the formation of heavy esters is catalyzed by tin oxides without interaction with ruthenium particles. As a consequence, metal-chloride-based catalyst (Fig. 12) showed a rapid formation of heavy esters at reaction start. At conversions above 30% the formation of heavy esters decreases, while there is a sudden increase in the formation of unsaturated alcohols, possibly due to the hydrogenolysis reaction which produces two molecules of alcohol. Methyl stearate is formed at the beginning of the reaction but is consumed possibly by hydrogenolysis to produce stearyl alcohol, which increases slowly with conversion. In comparison with the other catalysts, the bimetallic catalyst reduced with NaBH₄ (Fig. 12) presents remarkably higher suppression of transesterification reactions, i.e. reduced wax esters formation, and a higher selectivity to oleyl alcohol (about 74%). It seems that the reduction step eliminates residual chlorine from the catalyst, favoring the formation of Ru–Sn species.

The activation methods applied to the catalysts have a marked influence on the electronic state of Ru and its interaction with Sn, so that its metallic activity is strongly modified, as can be seen in Fig. 13.¹⁰⁷ TPR, FTIR-CO and XPS results clearly show that the incorporation of sodium borohydride in the preparation leads to higher Ru–Sn interaction compared with catalysts prepared by co-impregnation without B. On the other hand, the activation of Ru–Sn catalysts without B (either by direct reduction or calcinations-reduction) does not produce a strong interaction between these two components. The degree of interaction between Ru and Sn strongly affects the selectivity for the hydrogenation of methyl oleate. With a strong interaction the catalyst is

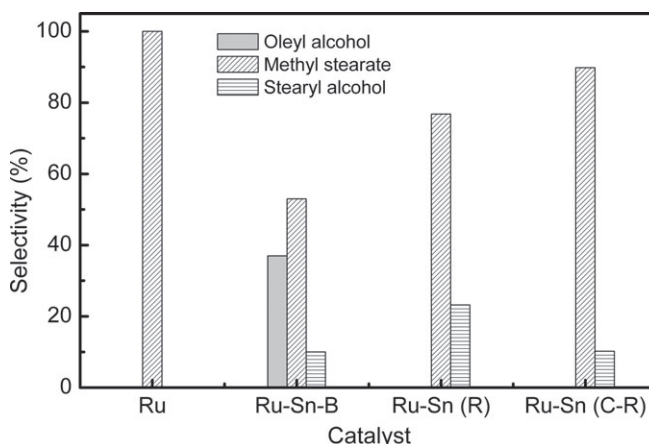


Figure 13. Selectivity to oleyl alcohol, methyl stearate and stearyl alcohol obtained at 360 min reaction time. The products not identified (<5%) were not included in the calculation of selectivity. R: activated by direct reduction, C–R: activated by calcination-reduction.¹³⁶

selective for oleyl alcohol formation. In contrast, for catalysts with a weak Ru–Sn interaction, the unsaturated alcohol is not produced in any significant amount. Tang *et al.*¹³⁴ reported a similar negative effect of calcination on the yield of unsaturated alcohol using Re–Sn catalysts supported on Al₂O₃ and SiO₂ for oleic acid hydrogenation. They proposed that Sn interacting with either Ru or Re can activate the more polar carbonyl group while remaining tin decreases the relative number of metals on the surface of the catalyst, affecting the reactivity.¹³⁴ Tang *et al.*¹⁴¹ found that catalysts prepared by the sol–gel method are more active and selective to unsaturated alcohol since the sol–gel process leads to the formation of finely dispersed metal particles.

Piccirilli *et al.*¹³⁵ and Pouilloux *et al.*¹³⁷ found a selectivity of 80% towards oleyl alcohol using Ru–Sn–B/Al₂O₃ catalysts (prepared by impregnation and reduction with sodium borohydride) or Ru–Sn/Al₂O₃ prepared by a sol–gel method. They also found a transesterification reaction between methyl oleate and the oleyl alcohol initially formed. This ester was then transformed into oleyl alcohol at a higher conversion of methyl oleate (Fig. 14). The results showed that the formation of oleyl oleate that occurred on tin species decreased the selectivity to unsaturated alcohol. When the

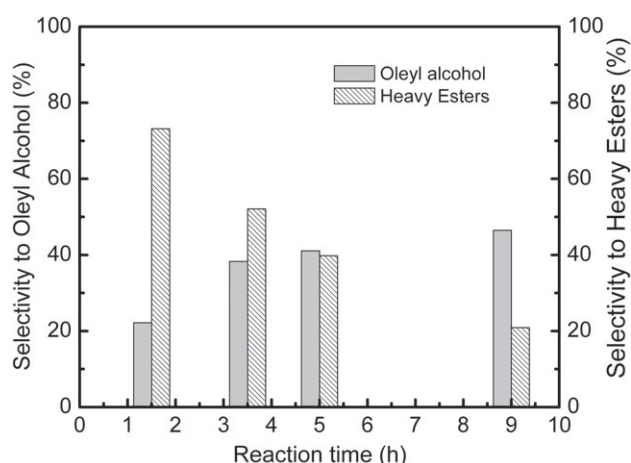


Figure 14. Selectivity to heavy esters and unsaturated alcohol with reaction time in the presence of a Ru–Sn–alumina catalyst (Sn/Ru = 3.7). Reaction conditions: T = 270 °C, P = 8 MPa, catalyst weight = 2.2 g, molar ratio $H_2/ester = 1.5$.¹³⁷

atomic ratio Ru/Sn is between 1/4 and 1/2, a selectivity of about 50% to oleyl alcohol (at quite a complete conversion) is obtained. Nevertheless the unsaturated alcohol yield is lower because of the formation of wax esters (oleyl oleate). This ester is formed rapidly from methyl oleate and oleyl alcohol and then retransformed into oleyl alcohol at a higher conversion of methyl oleate.

Moreover, it was found that catalysts prepared by incipient wetness are more active and selective than those prepared by coimpregnation.¹³⁸ This better performance is possibly due to a lower level of residual chlorine.

Cheah *et al.*¹²⁴ developed a Ru–Sn/Al₂O₃ catalyst prepared by different methods such as sol–gel, successive impregnations, and a combination of both methods in the selective hydrogenation of oleic acid at low pressures (5.6 MPa) and 250 °C. They found excellent yields of 9-octadecen-1-ol as can be seen in Table 3. Moreover, catalysts prepared by an improved sol–gel method showed higher selectivity than catalysts prepared by impregnation and coprecipitation methods. Chloride was found to have a negative effect on catalytic activity in agreement with Echeverri *et al.*¹¹⁵ The best catalyst was prepared from chloride-free ruthenium and tin raw materials. Under the optimum reaction conditions of 250 °C and 5.6 MPa, the selectivities to 9-octadecen-1-ol and total alcohol (9-octadecen-1-ol + stearyl alcohol) formation are 80.9% and 97%, respectively, at a conversion of 81.3%. In accordance with these results, Tahara *et al.*¹³⁹ reported that chlorine avoids reduction of Sn lowering the alcohol yield. The influence of the Ru/Sn ratio on the catalyst activity and selectivity in the hydrogenation of oleic

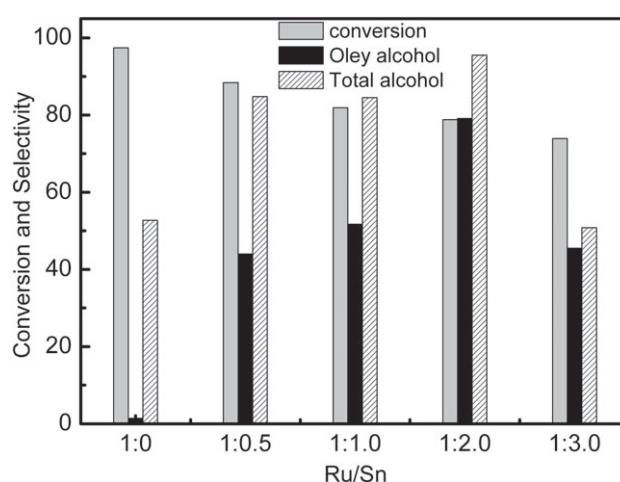


Figure 15. Effect of the Ru/Sn atomic ratio on the catalyst activity and selectivity in the hydrogenation of oleic acid. T = 250 °C, P = 5.6 MPa, reaction time = 17 h, oleic acid = 50 g, and catalyst 6% by weight.¹²⁴

acid to oleyl alcohol was studied by Cheah *et al.*¹²⁴ Their results are reproduced in Fig. 15. Clearly, it can be seen that there is an optimum in the selectivity to oleyl alcohol at a Ru/Sn atomic ratio of 1/2.

The reported optimal Sn/Ru ratio to oleyl alcohol was 2 for several research groups.^{117,124,131,143} However, Pouillieux *et al.*¹³³ found this optimum at Ru/Sn = 4 and reported that the active center in this catalyst could be a cluster composed of a Ru atom in close interaction with two Sn oxidized species (Ru^o–(SnOx)₂). In agreement with this latter hypothesis, Sánchez *et al.*¹⁴³ found that a Ru–Sn (2.0) catalyst showed the highest amount of SnOx species and the highest selectivity to oleyl alcohol. The difference may be linked to the different catalyst preparation methods and metal precursors used by these different research groups.

Rizea *et al.*¹⁴⁴ reported that a higher concentration of weak acid sites on Ru–Sn/γ–Al₂O₃ compared to Ru–Sn–Ba/γ–Al₂O₃ is probably responsible for the adsorption of functional groups, favoring the yield of saturated and even unsaturated fatty alcohols. On the other hand, they proposed that the strong acid and medium acid sites promote side reactions (e.g. hydrocracking, isomerization). However, only the influence of Ba on the acid function was studied, leaving the possible interactions between Ba and Ru–Sn metallic species unconsidered.

Other Ru-based catalysts

The influence of Ge content on the activity and selectivity of Ru–Ge–B/Al₂O₃ catalysts for the hydrogenation of methyl oleate

Table 3. Effect of catalyst preparation method on the hydrogenation of oleic acid. Catalysts with 2% Ru and Sn/Ru ratio = 2 (from Ref. 124)

Catalyst	Method of preparation	Reaction time (h)	Conversion (%)	Alcohol selectivity (%)	
				9-octadecen-1-ol	Total
Ru–Sn/Al ₂ O ₃	Impregnation	16.5	62.4	67.0	84.3
Ru–Sn/Al ₂ O ₃	Coprecipitation	17.0	82.2	52.1	84.2
Ru–Sn/Al ₂ O ₃	Sol–gel	17.0	78.8	79.1	95.5
Ru–Sn/ZrO ₂	Impregnation	21.5	65.1	22.4	44.5
Ru–Sn/ZrO ₂	Sol–gel	20.0	70.3	13.1	33.4

Reaction conditions: T = 250 °C, P = 5.6 MPa, oleic acid: 50 g and catalyst, 6% by weight.

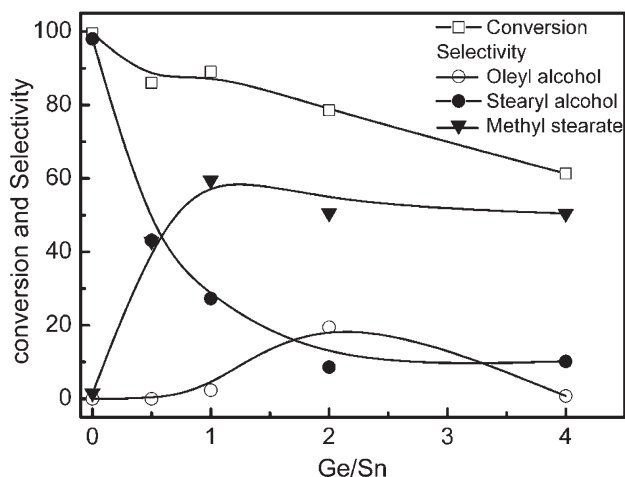


Figure 16. Percentage values of conversion and yield to different products at 120 min reaction time. Ru(1%)–Ge(x)–B/Al₂O₃ catalysts. Influence of Ge content.¹³⁰

to oleyl alcohol was also studied by Sánchez *et al.*¹³⁰ The results of catalyst characterization by TPR and XPS show that Ge is deposited both on the metal function aggregates and on the support surface. The fraction of Ge deposited on the metal function is in strong interaction with Ru, so that its metallic activity is significantly modified. Both dehydrogenating and hydrogenolytic activities of Ru are strongly diminished by Ge addition. The ratio Ge/Ru = 2 is the optimum for oleyl alcohol production, as can be seen in Fig. 16.

Other catalysts

Simonetti *et al.*¹⁴⁵ proposed that a bimetallic catalyst with a monolayer of Pt on Ni (1 1 1) on the surface could be adequate for the industrial oil hydrogenation. Their theoretical studies based on density functional theory estimates that the Pt/Ni (1 1 1) catalyst is more active on the preservation of the double carbon-carbon bond of the original organic acid than the Ni(1 1 1) catalyst. However, experimental hydrogenation results were not reported.

The hydrogenation of oleic acid to unsaturated oleyl alcohol was also studied using Re–Sn supported on Al₂O₃, SiO₂, ZrO₂ and TiO₂ by Tang *et al.*¹³⁴ They found that the optimum Re/Sn ratio was 2. The catalyst only with Re produces stearyl alcohol with high activity, while higher amounts of Sn rendered the catalyst more selective to unsaturated alcohol but less active. They also reported that the yield to oleyl alcohol decreases in the order Al₂O₃ > TiO₂ > SiO₂ > ZrO₂, showing the great influence of the support on catalyst performance.

INFLUENCE OF OPERATING CONDITIONS ON THE CONVERSION OF METHYL OLEATE TO OLEYL ALCOHOL

Figure 17 presents the reaction scheme proposed by Pouilloux *et al.* for the hydrogenation of the methyl oleate.^{117,133}

The experiments in hydrogenation of methyl oleate showed that activity increases as the reaction temperature increases while the selectivity to oleyl alcohol goes through a maximum.¹³⁸ This could be due to the higher activation energies for hydrogenolysis of carboxymethyl groups compared with the simpler hydrogenation of C=C double bonds. The increase in operating pressure has a similar positive effect on activity but it influences selectivity time patterns in a complex way. Experiments carried out using methyl oleate/n-dodecane mixtures with different ester/alkane ratios show that the selectivity and conversion does not depend on this parameter, implying that only first-order reaction rates are involved.

In the interesting review of Singh and Vannice² the influence of the solvent was analyzed. They concluded that solvent effects can influence the kinetics of competitive hydrogenation reactions of both polar and non-polar substrates. The polar solvent enhances adsorption of the non-polar reactant. Conversely, a non-polar solvent enhances the adsorption of a polar reactant. A thermodynamic analysis of the system indicates that solvent effects can increase the adsorption of hydrogen on the catalyst surface at constant H₂ partial pressure and that in the absence of solvent effects, surface coverage should be independent of the concentration of hydrogen in the liquid phase.² Richter proposed that the solvent should be inert and the solubility of hydrogen in the solvent must be such that the available amount will exceed the hydrogenation requirements.⁷² Moreover, the vapor pressure at reaction temperature must be low. Saturated normal paraffins would meet these requirements, especially those of medium molecular weight, because of their relatively low vapor pressure.⁷² However, no more attention was dedicated in the open literature to the influence of the solvent, probably because the industrial process does not use solvents.

The use of supercritical operation conditions were studied by Van den Hark *et al.*¹⁴⁶ They found that an extremely rapid hydrogenation of fatty acid methyl esters to fatty alcohols occurs when the reaction is conducted in a substantially homogeneous supercritical phase, using propane as a solvent, over a solid catalyst (chromium-free, copper-based catalyst, Davy Process Technology, Cleveland, England). In these conditions, the limitations of hydrogen transport are eliminated.¹⁴⁷ At temperatures above 240 °C, complete conversion of the starting material was reached at residence times of 2 to 3 s, which is several orders of magnitude shorter than the values reported in the literature

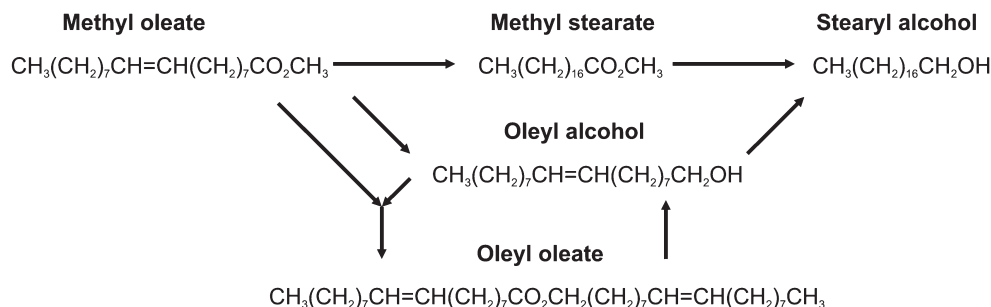


Figure 17. Reaction scheme for methyl oleate.

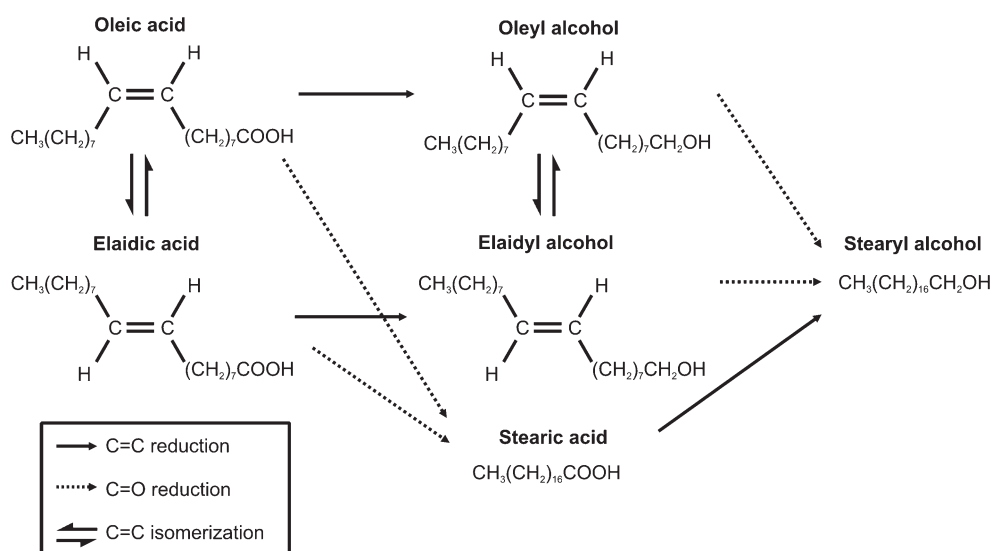


Figure 18. Reaction scheme for oleic acid.

in non-supercritical media. Unfortunately, the hydrogenation of the C=C double bond is much faster than the hydrogenation of the carboxyl group and occurs readily at temperatures below 200 °C. As a consequence, only saturated alcohols are obtained. It was found that the product concentration and the minimum pressure in the reactor are decisive factors to guarantee that the reaction mixture remains in a single phase in the reactor.¹⁴⁸ On the other hand, Andersson *et al.*¹⁴⁹ studied the reduction of fatty methyl esters to fatty alcohols in two different supercritical media (H₂/CO₂ and H₂/propane) at 250 °C using a copper chromite and a chromium-free catalyst. They obtained a high yield to saturated fatty alcohol. However, significant amounts of n-alkanes (C₁₆ and C₁₈) were formed using propane as supercritical media.

INFLUENCE OF OPERATING CONDITIONS ON THE REACTION OF OLEIC ACID TO OLEYL ALCOHOL

Despite the numerous kinetic models developed for fats and oils hydrogenation and the existence of reasonable reaction pathways for the selective hydrogenation of carbonyl groups, no such studies are easily found in the literature. A very simple pseudo-first-order kinetic model was proposed by Sánchez *et al.*¹⁵⁰ based on the reaction scheme proposed by Mendes *et al.*¹⁰⁹ for the selective hydrogenation of oleic acid, which is presented in Fig. 18.

The primary reactions concerned are the following:^{109,119,124}

- hydrogenation of the C=C bond to form stearic acid;
- isomerization of the C=C bond to form an unsaturated elaidic acid;
- hydrogenation of the carbonyl group to form the oleic unsaturated alcohol.

The scheme of reaction proposed by Sánchez *et al.*¹⁵⁰ was very simple with only four components (oleic acid, oleyl alcohol, stearic acid and stearyl alcohol). The cis-trans isomerization reactions were not considered because both isomers have the same reactivity. Hence, elaidic acid and oleic acid were lumped under the term 'oleic acid' while the elaidyl and stearyl alcohols are named 'stearyl alcohol'. The kinetics for each model step are supposed

Table 4. Conversion and selectivity to oleyl alcohol at 1 and 2 h reaction time (from Ref. 150)

Pressure (atm)	Conversion		Yield to oleyl alcohol	
	1 h	2 h	1 h	2 h
20.5	44.8	56.2	0.05	0.09
35.0	50.6	75.8	0.13	0.16
50.0	78.6	90.7	0.13	0.07

Operating conditions: temperature: 250 °C; mass of catalyst: 1 g; reactant (oleic acid) volume: 4 mL; solvent (n-dodecane) volume: 60 mL and stirring speed: 800 rpm.

Table 5. Hydrogenation of oleic acid with Ru-Sn/Al₂O₃ and Ru-Sn/TiO₂ catalysts at 15 h reaction. Influence of the support (from Ref. 109)

Distribution of products (%)	Ru-Sn/Al ₂ O ₃	Ru-Sn/TiO ₂
Unsaturated acid	64.7	19.7
Unsaturated alcohol	23.6	74.6
Stearic acid	7.3	1.5
Stearyl alcohol	4.4	4.2

to be first-order and irreversible, and the effect of hydrogen is not taken into account explicitly and is indirectly considered in the rate constants. Another reasonable simplification would come from the chemical similarity of oleic acid/stearic acid and oleyl alcohol/stearyl alcohol molecules. Therefore, the proposed model has only two rate constants: one for the selective hydrogenation of carbonyl groups ($k_{C=O}$) and the other for the C=C double bond hydrogenation ($k_{C=C}$).

It was reported that the reaction rate increases with H₂ pressure indicating that the reaction depends on the amount of H₂ dissolved in the reactant medium. However, given the high hydrogen excess used, the hydrogen concentration can be considered to depend solely on the temperature and its partial pressure (which is generally about the overall pressure). Hence, a pseudo-rate

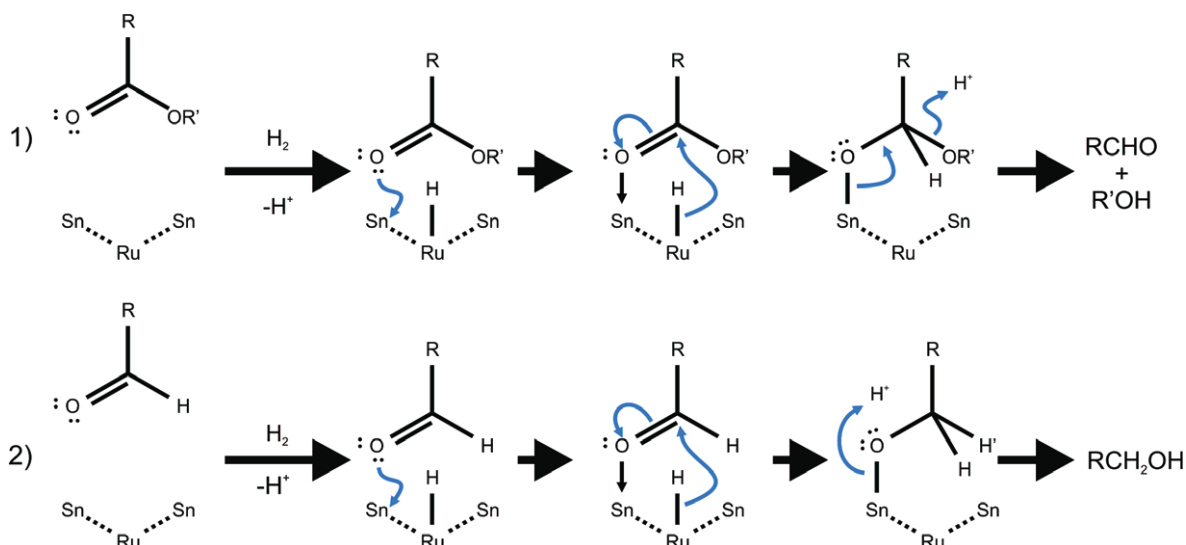


Figure 19. Mechanism of the hydrogenation of methyl oleate into oleyl alcohol via the formation of aldehyde.¹³³

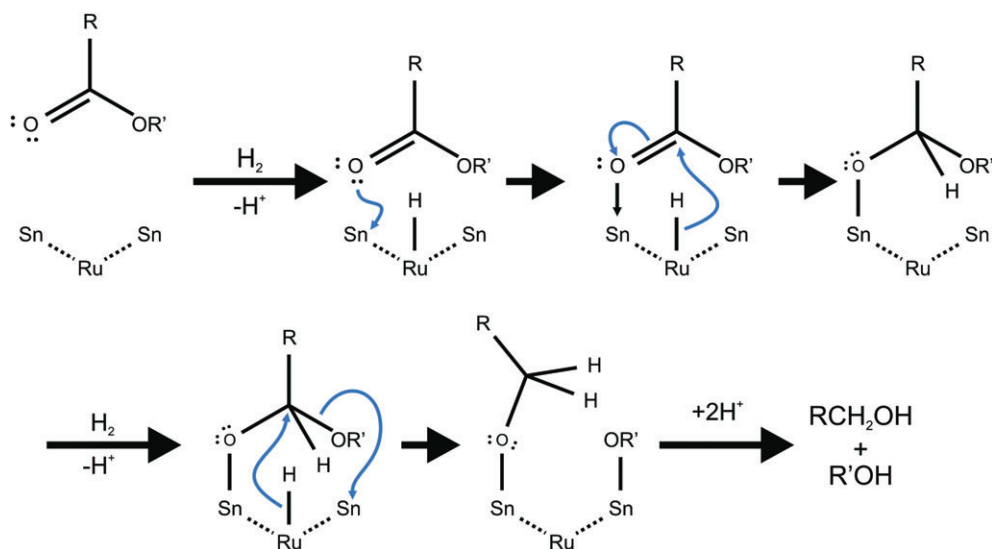


Figure 20. Mechanism of the direct hydrogenation of methyl oleate into unsaturated alcohol RuSnB/Al₂O₃ catalyst.

constant can be proposed to exclude an explicit hydrogen concentration term in the kinetic expressions used. A positive effect of pressure on these pseudo-rate constants is expected. Nonetheless, this pseudo-rate constant can be used to determine the corresponding activation energies for the hydrogenation of C=O and C=C bonds, and gives values of 116 kJ mol⁻¹ and 56 kJ mol⁻¹, respectively.¹³⁸ It is important to point out that these constants were obtained considering the reaction as pseudo-first-order, hydrogen concentration was assumed included in the constants. But hydrogen concentration decreases as the temperature increases; as a consequence, the real constants are higher and the activation energies are higher too. Coenen *et al.*⁵¹ gives a close value of 103 kJ mol⁻¹ for the formation of unsaturated fatty alcohols.

The influence of the operating conditions on the selectivity and activity of Ru-Sn-B/Al₂O₃ catalysts for the hydrogenation of oleic acid to oleyl alcohol was also studied.¹⁵⁰ Oleic acid hydrogenation experiments showed that an increase in reaction temperature leads to an increase in activity while the selectivity to oleyl alcohol

goes through a maximum. This is because the reactions of hydrogenation of C=C double bonds have lower activation energies than hydrogenolytic reactions. It can be seen in Table 4 that the increase in the operating pressure had a positive effect on conversion, but the yield to oleyl alcohol passes through a maximum due to the formation of the final reaction product (stearyl alcohol).

The hydrogenation of oleic acid to oleyl alcohol over Ru-alumina and Ru-Sn-alumina sol-gel catalysts has been studied by Costa *et al.*¹⁵¹ They found that, besides its hydrogenation activity, the Ru-Sn-alumina catalyst promotes the cis-trans isomerization of the unsaturated acid. This effect was used to explain some kinetic features of the system, like the high induction time observed in the formation of alcohols, and to re-examine the role of tin. The influence of the support (titania and alumina) on the hydrogenation of oleic acid over ruthenium catalysts was reported by Mendes *et al.*¹⁰⁹ They found that hydrogenation over the monometallic ruthenium catalysts leads primarily to the saturated stearic acid, which is then consecutively hydrogenated to the saturated stearyl alcohol.

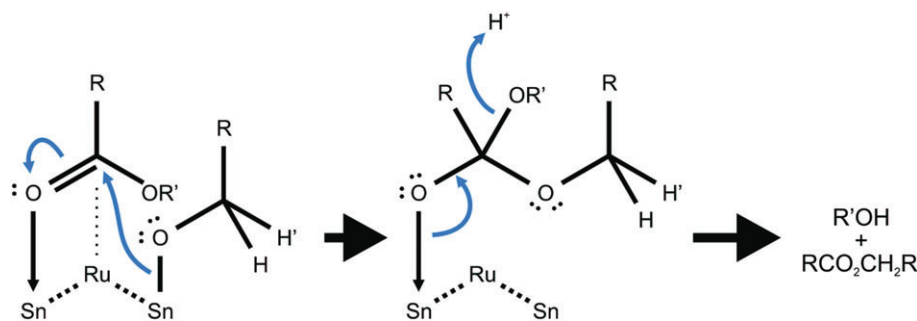


Figure 21. Mechanism of formation of heavy esters over RuSnB/Al₂O₃ catalyst.

The titania-supported monometallic ruthenium catalyst shows greater activity than the alumina-supported sol-gel one for the hydrogenation of oleic acid to the saturated stearyl alcohol. The hydrogenation over the bimetallic ruthenium-tin catalysts is characterized by near total suppression of the hydrogenation of C=C bond in favor of the activation of the hydrogenation of the carboxylic bond, thus leading to the selective formation of unsaturated alcohols. The impregnated titania-supported ruthenium-tin catalyst shows a better performance than the alumina-supported sol-gel ruthenium-tin catalyst for the selective hydrogenation of oleic acid to unsaturated alcohols (Table 5).

REACTION MECHANISMS

There is very little information in the open literature regarding the mechanism of hydrogenation of esters using heterogeneous catalysts.

Deshpande *et al.*¹¹⁸ proposed a reaction mechanism through an aldehyde intermediate. According to this representation, Ru⁰ is present as an electron-rich species due to the presence of boride and sodium. Such Ru⁰ species are likely to be responsible for activating the H₂ molecule in a more hydridic form, which could be the attacking species in the first step of the mechanism. In this mechanism Sn²⁺ or Sn⁴⁺ Lewis acid sites polarize the carbonyl of the ester, facilitating hydrogen transfer from an adjacent Ru-H site. This is the first step in the formation of an unstable hemiacetal which, as already suggested, forms the aldehyde by spontaneous and non-catalytic elimination of OR'. The aldehyde could again rapidly form the fatty alcohol by catalytic hydrogenation. The eliminated species OR' would form the alcohol R'OH, picking up a dissociated hydrogen. Their kinetic studies were unable to detect the intermediate aldehyde presumably because the hydrogenation of the aldehyde is quite fast at the high H₂ pressures of the reaction (4.4 MPa).

Pouilloux *et al.*¹³³ proposed a more detailed mechanism in which the reaction proceeds via the hemiacetal, which subsequently forms the fatty alcohol. In this case, metallic ruthenium activates hydrogen into a 'hydride form' while tin oxides (SnO_x) 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 a tin acetal. This hemiacetal is either converted to an aldehyde which is rapidly hydrogenated into an alcohol form under high hydrogen pressure (Fig. 19), or the alcohol is directly formed via a hemiacetal adsorbed at the catalyst surface (Fig. 20). This mechanism is in accordance with the one proposed by Rieke *et al.*¹⁵²

Another transesterification mechanism that justifies the increase in the transesterification rate at higher tin contents in the catalyst

was also proposed. They propose that the hydrogenation step is faster than the alcohol desorption and that the alcoholate adsorbed on the tin surface reacts with an ester molecule adsorbed on an adjacent SnO_y species (Fig. 21). The wax esters produced can be reduced to two moles of oleyl alcohol by hydrogenation.

CONCLUSION

In general, it can be concluded that great interest has been shown in the development of alternative catalysts, more active towards the selective hydrogenation of fatty acids and unsaturated esters with great emphasis on the preservation of C=C double bonds on the original acid or ester for the production of unsaturated fatty alcohols.

To achieve this goal, Ru-Sn-B and Co-Sn catalysts are presented as the best alternative to current commercial copper-based catalysts. The support, preparation of the catalyst, reduction procedure and Ru/Sn and Ru/Co ratio have been put forward as the most important variables to achieve an effective catalyst.

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