

Selective Hydrogenation of Oleic Acid to 9-Octadecen-1-ol: Catalyst Preparation and Optimum Reaction Conditions

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A new catalyst, ruthenium-tin-alumina is found to selectively hydrogenate oleic acid to 9-octadecen-1-ol (oleyl + elaidyl alcohol) at low pressure with high yield. Catalyst preparation methods, catalyst raw materials and activation conditions have a significant effect on the activity of the catalyst. The optimum atomic ratio of ruthenium to tin is about 1:2. Catalyst prepared by an improved sol-gel method shows higher activity and selectivity than catalysts prepared by impregnation and coprecipitation methods. Chloride is found to have a negative effect on catalytic activity. The best catalyst is prepared from chloride-free ruthenium and tin raw materials. Under the optimum reaction conditions of 250°C and 5.6 MPa, the selectivities for 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%.

KEY WORDS: 9-Octadecen-1-ol, oleic acid, ruthenium-tin-alumina catalyst, selective hydrogenation, sol-gel method.

Hydrogenation of fatty acids or their methyl esters to fatty alcohols is an important industrial process. Currently, fatty alcohols are produced by the hydrogenation of fatty acids or their methyl esters by means of copper chromite-based catalysts under high pressure (25.3–30.4 MPa) and high temperatures (250–300°C) (1). Apart from copper chromite, there are a number of other catalysts that are known for the hydrogenation of fatty acids or their methyl esters, but most of them produce saturated fatty alcohols under severe reaction conditions (pressure > 15.2 MPa and temperature > 200°C) (2). Recently, Yoshino *et al.* (3) showed that saturated fatty alcohols could be produced with rhenium-osmium bimetallic catalyst and thiophene as additive under mild conditions (pressure, 2.5–10.1 MPa; and temperature, 100–120°C).

There are a few catalyst systems reported in the literature (pertaining to the production of oleyl alcohol by catalytic hydrogenation of oleic acid or methyl oleate) that can preserve the double bond of the oleic acid or methyl oleate during the process of hydrogenation, but all of these processes also are carried out under high pressure (>15.2 MPa) and high temperature (250°C) (4,5). Recently, Narasimhan *et al.* (6–8) showed that methyl oleate could be selectively hydrogenated to oleyl alcohol by using a mixed ruthenium-tin boride catalyst system under relatively low pressure (4.5 MPa) and a temperature of 270°C. They claimed that boride is essential in their process, but they have yet to clarify its role. Furthermore, most catalysts which are used in such a hydrogenation often behave differently depending on whether the substrate is ester or acid. It is also well known that the properties of catalysts sometimes vary dramatically with their preparation procedures.

Some authors have developed a ruthenium-copper sup-

ported catalyst system that can selectively reduce benzene to cyclohexene by the complexing agent-assisted sol-gel (chemical mixing) method. Such catalysts show specific behavior different from the corresponding impregnation catalyst (9). Also, tin has been reported to have the ability to preserve the double bond of methyl oleate during hydrogenation (6–8). Based on these findings we investigated the behavior of ruthenium-tin supported catalyst, prepared by the complexing agent-assisted sol-gel method, on the selective hydrogenation of oleic acid to 9-octadecen-1-ol. Our objective was to overcome the drawbacks in the above-mentioned processes and to develop a new and practical method of producing 9-octadecen-1-ol from oleic acid under mild conditions.

EXPERIMENTAL PROCEDURES

Complexing agent-assisted sol-gel (chemical mixing) method. The ruthenium-tin supported catalysts were prepared by the complexing agent-assisted sol-gel (chemical mixing) method as described in detail by Mizukami *et al.* (10). Basically, the method involves dissolving the raw materials of the ruthenium-tin supported catalysts in an organic solvent, with heating if necessary, until a homogeneous solution is obtained. Water is then added to the organic solution, with heating if necessary. The product of hydrolysis is then coagulated and a gel is formed. After removing the excess water and organic solvent, the dry gel is ground to a fine powder. The final catalyst is obtained after activation in hydrogen atmosphere with or without calcination.

Ruthenium chloride hydrate ($\text{RuCl}_3 \cdot n\text{H}_2\text{O}$) and ruthenium acetylacetonate [$\text{Ru}(\text{acac})_3$] were used as the sources of ruthenium. Sources of tin were from stannous chloride hydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$), stannic chloride hydrate ($\text{SnCl}_4 \cdot n\text{H}_2\text{O}$) and tin ethoxide [$\text{Sn}(\text{OC}_2\text{H}_5)_4$]. Raw materials for support of the catalyst were aluminum iso-propoxide [$\text{Al}(\text{Oiso-C}_3\text{H}_7)_3$], tetraethoxysilane [$\text{Si}(\text{OC}_2\text{H}_5)_4$], zirconium n-propoxide [$\text{Zr}(\text{On-C}_3\text{H}_7)_4$] and titanium iso-propoxide [$\text{Ti}(\text{Oiso-C}_3\text{H}_7)_4$]. In the preparation of ruthenium-tin-silica catalyst, ethylene glycol was used as the solvent. In all other cases hexylene glycol was used as the solvent. $\text{Ru}(\text{acac})_3$ was converted into the corresponding nitrate by treating it at ca. 80°C with nitric acid before use in the catalyst preparation. The typical procedures are as follows.

Ruthenium-tin-alumina catalyst from chloride source. Solutions of 1.5 g $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ and 2.55 g $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in 10 mL and 30 mL ethanol, respectively, were added to 123.5 g of hexylene glycol. Then 106.5 g of $\text{Al}(\text{Oiso-C}_3\text{H}_7)_3$ was added to this solution, and the mixture was stirred for 4 hr at 80–90°C. A homogeneous solution was obtained. Water (42 g) was then added to the solution, and the resultant mixture was aged for 3 hr at the same temperature. The gel obtained was dried at 170°C under vacuum.

Ruthenium-tin-alumina catalyst from chloride-free source. Thirty grams of concentrated nitric acid was added

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to 30 mL of suspended solution of ethanol containing 3 g of $\text{Ru}(\text{acac})_3$, and the mixture was stirred for 2 hr at 80–90°C. An additional 23 g of concentrated nitric acid was then added, and the complex adhering to the wall of the vessel was washed out (with as small an amount of acetic acid as possible) into the solution. After heating for another 3–4 hr at 90–100°C, the solution became red and clear. Nitrogen oxide was generated during heating. After the solution was evaporated, 163.7 g of hexylene glycol and 142 g of $\text{Al}(\text{Oiso-C}_3\text{H}_7)_3$ were added to the residue, and the mixture was stirred for 4 hr at 80–90°C. Then 4.5 g of $\text{Sn}(\text{OC}_2\text{H}_5)_4$ was added, and the mixture was stirred for another hour at the same temperature. Water (65 g) was then added, and the gel obtained was aged for 2 hr at the same temperature before being dried at 160°C under vacuum.

Ruthenium-alumina catalyst. $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ and $\text{Al}(\text{Oiso-C}_3\text{H}_7)_3$ were used as the raw materials, and hexylene glycol was used as the solvent. The catalyst was prepared in a similar way to that described above, except a tin compound was not used.

Conventional impregnation method. The alumina and zirconia supports of the impregnation catalysts were prepared in a similar way as described above, by using only $\text{Al}(\text{Oiso-C}_3\text{H}_7)_3$ and $\text{Zr}(\text{On-C}_3\text{H}_7)_4$ as raw materials and hexylene glycol as the solvent. The impregnation of the ruthenium and tin onto the supports was carried out in the conventional way with ethanol as solvent.

Coprecipitation method. $\text{Al}(\text{Oiso-C}_3\text{H}_7)_3$ (72.3 g) was dissolved in 300 mL of dioxane at 80°C. Twenty mL of 2-propanol solution containing 1 g of $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ and 2.7 g of $\text{SnCl}_4 \cdot n\text{H}_2\text{O}$ was added to the solution. The mixture was a homogeneous solution. Ammonia solution (86 mL, 28%) was then added dropwise and a precipitate was obtained. After filtration, the solid was washed with ethanol and dried under vacuum.

Hydrogenation reaction. The hydrogenation reaction was carried out in a 500-mL reactor equipped with a pressure regulator. The reactor was charged with oleic acid together with the catalyst and purged with hydrogen four times at different pressures (1.0, 1.0, 2.1 and 4.0 MPa) to remove air. The reactor was then heated to the required temperature and pressurized with hydrogen to the reaction pressure, which was maintained throughout the reaction. Stirring was maintained at about 1000 rpm. At the

end of the specified time, the reactor was cooled and the reaction mixture was recovered for analysis.

Analysis of products. The reaction products were analyzed by gas chromatography with a 50 m \times 0.25 mm ULBON HR-55-10 column (Shinwa-kako Co. Ltd., Kyoto) operated with temperature programming from 150°C to 200°C at 2°C/min. A flame ionization detector was used, the carrier gas was helium. The fatty acids and fatty alcohols in the reaction mixture were derivatized to methyl esters and alkyl acetates, respectively, without prior separation. Prior to the normal methylation step with $\text{BF}_3/\text{methanol}$, the reaction mixture was saponified with a 0.5 N $\text{NaOH}/\text{methanol}$ solution. The by-products from the hydrogenation reaction were mainly hydrocarbons.

RESULTS

Effect of atomic ratio of ruthenium to tin. Table 1 shows the effect of atomic ratio of ruthenium to tin on the catalytic activity and selectivity for alcohol formation in the hydrogenation of oleic acid. The $\text{Ru-Al}_2\text{O}_3$ catalyst ($\text{Ru}:\text{Sn} = 1:0$) is highly active, showing about 97% conversion. It also has demonstrated its ability to convert oleic acid to the corresponding saturated alcohol, showing about 53% total alcohol (stearyl alcohol + 9-octadecen-1-ol) selectivity, but is highly nonselective for 9-octadecen-1-ol formation. Other products obtained are mainly hydrocarbons. The incorporation of tin increases the selectivities of total alcohol and 9-octadecen-1-ol formation. However, the activity of the catalyst decreases as the tin content increases. The $\text{Ru}:\text{Sn}$ atomic ratio of 1:2 seems to be quite optimum for the selective hydrogenation of oleic acid to 9-octadecen-1-ol, showing about 95.5% and 79.1% of total alcohol and 9-octadecen-1-ol selectivities, respectively, with a conversion of about 78.8%. Beyond this ratio, the selectivities for the total alcohol and 9-octadecen-1-ol formation decrease.

Effect of catalyst preparation method. Table 2 shows the effect of catalyst preparation method on the activity and selectivity of the Ru-Sn catalyst for the hydrogenation of oleic acid. Catalysts with the same composition were prepared from the same raw materials. For the alumina-supported catalysts, the activity in terms of conversion is affected by the method of preparation and decreases in the order of coprecipitation \approx sol-gel $>$ im-

TABLE 1

Effect of Atomic Ratio of Ruthenium to Tin on the Catalytic Activity and Selectivity in the Hydrogenation of Oleic Acid^a

Atomic ratio of Ru:Sn	Conversion (%)	Alcohol selectivity	
		9-Octadecen-1-ol (%)	Total (%)
1:0	97.4	1.4	52.7
1:0.5	88.4	44.0	84.8
1:1.0	81.9	51.7	84.5
1:2.0	78.8	79.1	95.5
1:3.0	73.9	45.5	50.8

^aExperimental conditions were as follows: The catalysts were prepared from $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ and $\text{Al}(\text{OC}_3\text{H}_7)_3$ with hexylene glycol as solvent with the sol-gel method. Ruthenium metal loading was 2 wt%. The catalysts were calcined at 400°C for 2 hr prior to activation in a hydrogen stream at 400°C for 4 hr. Reaction conditions: temp., 250°C; pressure, 5.6 MPa; reaction time, 17 hr, oleic acid, 50 g, and catalyst, 6% by weight. Total alcohol, 9-octadecen-1-ol + stearyl alcohol; other products obtained were mainly hydrocarbons (similar for the rest of the Tables).

TABLE 2

Effect of Catalyst Preparation Method on the Hydrogenation of Oleic Acid^a

Catalyst	Method of preparation	Reaction time (hr)	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

^aThe experimental conditions were as follows: The sol-gel catalysts were prepared with RuCl₃·nH₂O, SnCl₄·nH₂O, Al(OC₃H₇)₃ and Zr(OC₃H₇)₄ as the raw materials and hexylene glycol as the solvent. The alumina and zirconia used as the supports for the impregnation catalyst also were prepared from the same raw materials in a similar manner with the same solvent. The impregnation of RuCl₃·H₂O and SnCl₄·nH₂O onto the support was carried out in the conventional way with ethanol as solvent. The coprecipitation catalyst was prepared as mentioned in the text. Ruthenium metal loading was 2 wt% and the atomic ratio of Ru:Sn was about 1:2 in all cases. Catalyst activation conditions are the same as Table 1. Reaction conditions: temp., 250°C; pressure, 5.6 MPa; oleic acid, 50 g; and catalyst, 6% by weight.

TABLE 3

Effect of Support of Ru-Sn Catalyst on the Hydrogenation of Oleic Acid^a

Supports	Reaction time (hr)	Conversion (%)	Alcohol selectivity (%)	
			9-Octadecen-1-ol	Total
Al ₂ O ₃	17.0	78.8	79.1	95.5
SiO ₂	20.0	66.6	40.5	53.2
TiO ₂	19.0	54.2	18.4	36.7
ZrO ₂	20.0	70.3	13.1	33.4

^aExperimental conditions were as follows: Method of preparation of catalysts is the same as described in Table 2. For titania-based catalyst the raw material was Ti(*iso*-C₃H₇)₄. Ruthenium metal loading was 2 wt% and the atomic ratio of Ru:Sn was 1:2. Catalyst activation conditions are the same as in Table 1, and the reaction conditions are as in Table 2.

pregnation. When it comes to the selectivity for total alcohol and 9-octadecen-1-ol formation, the catalyst prepared by the sol-gel method performs much better. For the zirconia-supported catalyst the effect of catalyst preparation method on the activity and selectivity is small.

Effect of support of the Ru-Sn catalyst. The effect of support of the sol-gel Ru-Sn catalysts on the hydrogenation of oleic acid is presented in Table 3. The activity of the catalysts depends on the support of the catalyst and decreases in the order of alumina > zirconia > silica > titania. The selectivity for the 9-octadecen-1-ol formation decreases in the order of alumina > silica > zirconia ≈ titania. Alumina is the best support for the Ru-Sn catalyst prepared by the sol-gel method for the selective hydrogenation of oleic acid.

Effect of catalyst raw material. Table 4 shows the effect of catalyst raw material on the hydrogenation of oleic acid with the sol-gel Ru-Sn-Al₂O₃ catalyst. The effect of tin source (Sn^{II} and Sn^{IV}) on the 9-octadecen-1-ol selectivity is small. The effect of the ruthenium source on catalytic activity and selectivity varies with the activation conditions of the catalysts. When the catalysts were calcined prior to activation, catalysts prepared from RuCl₃·nH₂O and Ru(acac)₃ show comparable conversion but different selectivity. RuCl₃ source catalysts show higher selectivity for 9-octadecen-1-ol formation. When the catalysts were only activated in a hydrogen stream

without calcination, Ru(acac)₃ source catalyst shows a much higher activity and slightly better selectivity for 9-octadecen-1-ol formation than the RuCl₃ source catalyst. The effect is quite significant. The best results were obtained with the catalyst prepared from Ru(acac)₃ and used without calcination.

Effect of activation conditions of the sol-gel Ru-Sn-Al₂O₃ catalysts. As mentioned above, catalyst activation conditions effect the catalytic activity and selectivity (see Table 5). For Ru-Sn-Al₂O₃ catalysts prepared from Ru(acac)₃ by the sol-gel method, activating the catalyst in a hydrogen stream at 400°C for 4 hr seems to be the optimum. At an activation temperature of 300°C, the selectivities of 9-octadecen-1-ol and total alcohol formation are much lower, and at 500°C the resultant catalyst was found to promote a sluggish reaction. Calcination of the catalyst prior to activation produced poorer results in terms of activity and selectivity. On the other hand, for catalysts prepared from RuCl₃·nH₂O by the sol-gel method, calcination prior to activation of the catalyst had no significant effect on the performance of the catalyst.

Effect of temperature on the hydrogenation of oleic acid. The activity of Ru-Sn-Al₂O₃ catalysts prepared from different ruthenium sources, i.e., RuCl₃·nH₂O and Ru(acac)₃, increases with temperature as expected (see Table 6). The 9-octadecen-1-ol selectivity remains high at temperatures above 200°C, but temperatures higher than 250°C decrease the 9-octadecen-1-ol and total alcohol selectivities.

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TABLE 4

Effect of Catalyst Raw Material on the Hydrogenation of Oleic Acid^a

Metal source		Reaction time (hr)	Conversion (%)	Alcohol selectivity (%)	
Ru	Sn			9-Octadecen-1-ol	Total
RuCl ₃ ·nH ₂ O	SnCl ₂ ·2H ₂ O	19.2	71.5	82.0	96.9
RuCl ₃ ·nH ₂ O	SnCl ₄ ·nH ₂ O	17.0	78.8	79.1	95.5
Ru(acac) ₃	Sn(OC ₂ H ₅) ₄	20.5	78.0	67.1	91.4
RuCl ₃ ·nH ₂ O	SnCl ₄ ·nH ₂ O	19.25	78.6	75.0	95.3
Ru(acac) ₃	Sn(OC ₂ H ₅) ₄	7.0	78.1	83.9	97.0
		18.5	91.9	61.7	95.7

^aExperimental conditions were as follows: Ru(acac)₃ was converted into the corresponding nitrate by treating it at ca. 80°C with nitric acid prior to the sol-gel catalyst preparation. Ruthenium metal loading was 2 wt% and the atomic ratio of Ru:Sn was 1:2. The catalysts were activated in a hydrogen stream at 400°C for 4 hr after being calcined at 400°C for 2 hr. The catalysts were activated in a hydrogen stream at 400°C for 4 hr without calcination. Reaction conditions: temp., 250°C; pressure, 5.6 MPa; oleic acid, 50 g; and catalyst, 6% by weight.

TABLE 5

Effect of Activation Condition of the Sol-Gel Ru-Sn-Al₂O₃ Catalysts on the Hydrogenation of Oleic Acid^a

Activation conditions	Reaction time (hr)	Conversion (%)	Alcohol selectivity (%)	
			9-Octadecen-1-ol	Total
Ruthenium source: Ru(acac) ₃				
300°C 4h Hydrogen	21.75	94.2	33.1	70.4
400°C 4h Hydrogen	9.0	81.3	80.9	97.0
	18.5	91.9	61.7	95.7
500°C 4h Hydrogen	20.0	88.2	73.4	97.0
400°C 2h Air &				
400°C 4h Hydrogen	20.5	78.0	67.1	91.4
Ruthenium source: RuCl ₃ ·nH ₂ O				
400°C 4h Hydrogen	19.25	78.6	75.0	95.3
400°C 2h Air &				
400°C 4h Hydrogen	17.2	78.8	79.1	95.5

^aRuthenium metal loading was 2 wt% and the atomic ratio of Ru:Sn was 1:2. The reaction conditions were as in Table 4.

TABLE 6

Effect of Temperature on the Hydrogenation of Oleic Acid with the Sol-Gel Ru-Sn-Al₂O₃ Catalysts^a

Temperature (°C)	Time (hr)	Conversion (%)	Alcohol selectivity (%)	
			9-Octadecen-1-ol	Total
Ruthenium source: RuCl ₃ ·nH ₂ O				
150	21.4	8.9	38.4	40.8
200	19.7	57.5	88.5	97.0
250	19.2	71.5	82.0	96.9
275	20.0	94.5	25.8	70.0
Ruthenium source: Ru(acac) ₃				
250	9.0	81.3	80.9	97.0
	18.5	91.9	61.7	95.7
275	20.0	97.4	8.8	21.2

^aRuthenium metal loading was 2 wt% and the atomic ratio of Ru:Sn was 1:2. The catalysts were activated in hydrogen stream at 400°C for 4 hr without calcination. Reaction conditions: pressure, 5.6 MPa; oleic acid, 50 g; and catalyst, 6% by weight.

TABLE 7

Effect of Pressure on the Hydrogenation of Oleic Acid with the Sol-Gel Ru-Sn-Al₂O₃ Catalysts^a

Reaction		Conversion (%)	Alcohol selectivity (%)	
Pressure (MPa)	Time (hr)		9-Octadecen-1-ol	Total
Ruthenium source: RuCl ₃ ·H ₂ O				
4.1	20.0	69.5	71.1	84.4
5.6	19.25	78.6	75.0	95.3
8.1	20.85	68.2	73.8	92.9
10.1	20.0	81.1	64.5	92.1
Ruthenium source: Ru(acac) ₃				
4.1	20.0	87.5	49.2	74.9
5.6	7.0	78.1	83.9	97.0
	18.5	91.9	61.7	95.7
8.1	4.5	76.5	81.2	96.5
	20.0	97.7	29.2	94.7
10.1	20.0	99.0	16.1	85.3

^aRuthenium metal loading was 2 wt% and the atomic ratio of Ru:Sn was 1:2. The catalysts were activated in a hydrogen stream at 400°C for 4 hr without calcination. Reaction conditions: temp., 250°C; oleic acid, 50 g; and catalyst, 6% by weight.

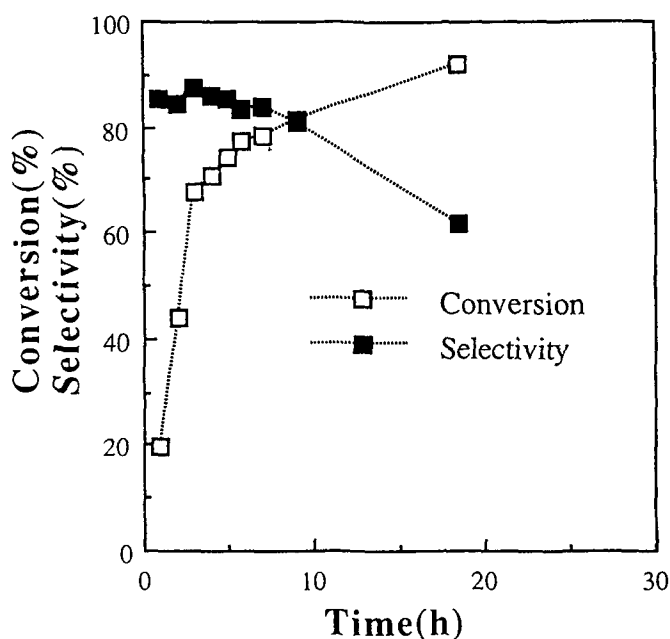


FIG. 1. Time course of hydrogenation of oleic acid with 2 wt% Ru and 4.7 wt% Sn-Al₂O₃ catalyst at 5.6 MPa. Reaction conditions: oleic acid, 50 g; catalyst, 3 g; temp., 250°C. The catalyst was the same as the chloride-free catalyst in Table 7.

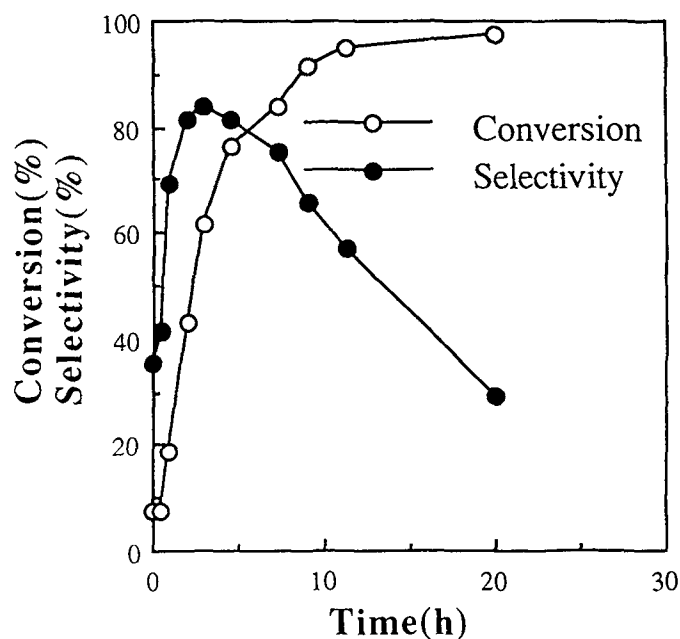


FIG. 2. Time course of hydrogenation of oleic acid with 2 wt% Ru and 4.7 wt% Sn-Al₂O₃ catalyst at 8.1 MPa. Reaction conditions: oleic acid, 50 g; catalyst, 3 g; temp., 250°C. The catalyst was the same as the chloride-free catalyst in Table 7.

Accordingly, the optimum reaction temperature seems to be 250°C, which gives 80% and 97% of 9-octadecen-1-ol and total alcohol selectivities, respectively, as well as a high reaction rate.

Effect of pressure on the hydrogenation of oleic acid. Table 7 shows the effect of pressure on the hydrogenation of oleic acid with the sol-gel Ru-Sn-Al₂O₃ catalysts. For Ru-Sn-Al₂O₃ prepared from RuCl₃·nH₂O, the activity and selectivity do not vary much with reaction pressure. At a reaction pressure in the range from 4.1 to 10.1 MPa, 5.6 MPa seems to be optimal for this type of catalyst. On the

other hand, for Ru-Sn-Al₂O₃ catalyst prepared from Ru(acac)₃, the activity of the catalyst increased with pressure and it is able to maintain the 9-octadecen-1-ol and total alcohol selectivities at higher pressures. Under reaction pressures of 5.6 to 10.1 MPa, the reaction time of 20 hr is too long, and the reaction has proceeded beyond the desired stage. For this type of catalyst, a higher reaction pressure of 8.1 MPa could speed up the reaction while retaining the desired 9-octadecen-1-ol selectivity (see Figs. 1 and 2). However, pressures higher than 8.1 MPa may reduce the selectivity for 9-octadecen-1-ol formation. The

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TABLE 8

Effect of Catalyst Amount on the Hydrogenation of Oleic Acid with the Sol-Gel Ru-Sn-Al₂O₃ Catalysts^a

Amount	Reaction time (hr)	Conversion (%)	Alcohol selectivity (%)	
			9-Octadecen-1-ol	Total
3.0	10.8	70.3	87.6	95.6
6.0	4.5	76.5	81.2	96.5

^aRu(acac)₃ was used as the raw material. Ruthenium metal loading was 2 wt% and the atomic ratio of Ru:Sn was 1:2. The catalysts were activated in a hydrogen stream at 400°C for 4 hr without calcination. Reaction conditions: temp., 250°C; pressure, 8.1 MPa; and oleic acid, 50 g.

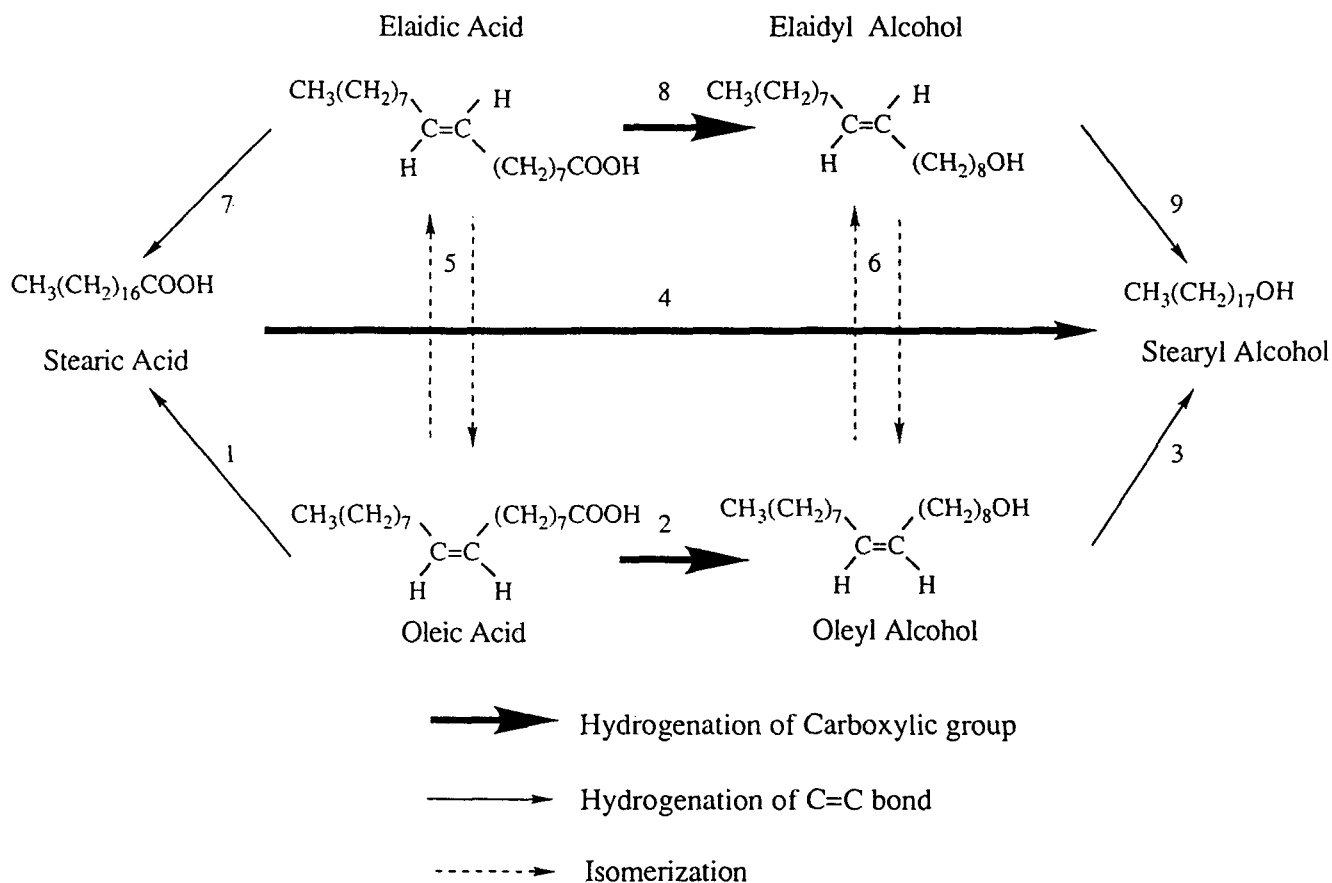


FIG. 3. Hydrogenation of oleic acid.

optimum reaction pressure is 5.6 MPa, because at this pressure the selectivity can be maintained over a wider range of conversion. Again, the ruthenium source affects the hydrogenation of oleic acid.

Effect of catalyst amount. The effect of the amount of catalyst on the hydrogenation is shown in Table 8. The rate of reaction increased significantly when the catalyst amount was doubled. The selectivities of 9-octadecen-1-ol and total alcohol formation were not affected by variations of the catalyst charge.

DISCUSSION

The possible reactions that can occur during the hydrogenation of oleic acids are shown in Figure 3. Parallel reactions 1 and 2 are the first step of the hydrogenation of oleic acid. The reaction products from reactions 1 and 2 can be further hydrogenated to stearyl alcohol *via* reactions 3 and 4. Incorporation of tin into the ruthenium-alumina catalyst promotes reaction 2, the hydrogenation of the carboxylic group, and suppresses reaction 1, the

hydrogenation of the C=C bond. Isomerization reactions 5 and 6 also occur during the hydrogenation of oleic acid. The hydrogenation of the *trans* isomer of oleic acid, *i.e.*, elaidic acid, follows similar pathways, as described above. Reactions 7 and 8 are the hydrogenation of the C=C bond and the carboxylic group, respectively. Elaidyl alcohol can be further hydrogenated to stearyl alcohol *via* reaction 9. Over-hydrogenation can lead to the formation of hydrocarbons.

The detailed understanding of our results requires knowledge about the state of ruthenium and tin on the catalyst surface. We have tried to characterize the Ru-Sn-Al₂O₃ catalyst by X-ray diffraction (XRD), hydrogen adsorption, electron microscopy (EM) and X-ray photoelectron spectroscopy (XPS), but we could not obtain conclusive data about the nature of the catalytic site, probably due to the low metal concentration. We will carry out more characterization work on catalysts of higher metal concentration at a later date. Hence, at this juncture, we could not provide a full explanation for the behavior of the Ru-Sn-Al₂O₃ catalyst. At best we could only speculate on the role of tin in the selective hydrogenation of oleic acid to 9-octadecen-1-ol by Ru-Sn-Al₂O₃ catalyst.

The role of tin in the bimetallic catalyst, especially platinum-tin catalyst, has been postulated by many workers. Burch *et al.* (11,12) suggested that tin modifies the electronic properties of the small Pt particles either by interaction, with the Sn(II) ion donating electrons to the deficient Pt atom, or by incorporation of a few percent metallic Sn as a solid solution in Pt to give electron-rich Pt. This modifies the catalytic properties of the Pt-Sn catalyst, mainly by reducing the activity in cracking and coking reactions. Poltarzewski and Galvagno *et al.* (13,14) have studied the hydrogenation of α,β -unsaturated aldehydes, hydrocinnamaldehyde and phenylacetylene in the presence of a Pt-Sn-nylon catalyst. They concluded that the addition of tin has a double effect. First, the acidic properties of tin ions activate the carbonyl group which becomes more active than the C=C double bond. The second effect of tin is related to its electronic interaction with platinum, which poisons the active metal sites responsible for hydrogen activation. The role of tin in the hydrogenation of fatty acid esters to fatty alcohols on ruthenium-tin catalyst has been studied by Deshpande *et al.* (8). They suggested that the tin ion interacts with ruthenium *via* oxygen to produce the selective site, and the tin ion preferentially activates the C=O bond of the ester. Recently, Galvagno *et al.* (15) also investigated the hydrogenation of C=C and C=O groups on ruthenium-tin catalysts. They concluded that the role played by tin on the catalytic activity of ruthenium depends strongly on the organic substrate that is being hydrogenated. In the case of C=C double bonds, the main effect of tin is that of decreasing the number of ruthenium surface atoms. In the case of the C=O group, tin that is present mainly as tin ions enhances the reactivity of the C=O group.

We agree that the above hypotheses, advanced by various investigators to explain the enhancement effect of tin on the reactivity of the C=O group also can adequately explain the high selectivity of our catalyst. However, these hypotheses do not satisfactorily explain the role of tin in suppressing the reactivity of the

ruthenium-tin-alumina catalyst toward the C=C bond of oleic acid. Hence, we suggest the following explanation. The behavior of the ruthenium-tin-alumina catalyst can be attributed to the selective adsorption of the C=C bond or the carboxylic group of the oleic acid on the catalyst surface under different catalyst compositions and reaction conditions. When the affinity of the catalyst system is stronger for the C=C bond, hydrogenation of the double bond will be predominant with the resultant formation of saturated products. On the other hand, when the affinity of the catalyst system is stronger for the carboxylic group, there are two possible outcomes depending on the degree of adsorption. In the case of very strong adsorption of the carboxylic group, most of the catalyst surface may be covered by the carboxylic group. In this case, no hydrogenation of the carboxylic group will occur because hydrogen cannot be attached to the surface. In the case of moderate adsorption of the carboxylic group, which permits access of hydrogen and its binding to the catalyst surface, selective hydrogenation of the carboxylic group to alcohol will take place.

Tin increases the affinity of the ruthenium-alumina catalyst for the carboxylic group. Ruthenium-alumina catalyst without tin does not possess the ability of preserving the C=C bond because the oleic acid molecule is preferentially adsorbed at its C=C bond to the ruthenium-alumina catalyst. The incorporation of tin into the ruthenium-alumina catalyst changes the adsorption behavior of the catalyst system. As the tin content increases, the adsorption of the carboxylic group gets stronger. This will decrease the catalytic activity of the catalyst system because the carboxylic group will be strongly adsorbed on the active site of the catalyst, which will prevent hydrogen from reaching the catalyst surface.

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