Hydrogenation of 9-Octadecenoic Acid by Ru-Sn-Al$_2$O$_3$ Catalysts: Effects of Catalyst Preparation Method

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Evaluation of the method of preparation and the sequence of metal incorporation onto the catalyst showed that they had profound effects on the catalytic behavior of Ru-Sn-Al$_2$O$_3$ catalysts used in the selective hydrogenation of oleic acid to 9-octadecen-1-ol. When Ru was loaded first onto the support and then followed by Sn, the catalyst had lower activity but greater ability to preserve the unsaturated bond. On the other hand, when the sequence of loading was reversed, the behavior of the catalyst changed correspondingly, i.e., the catalyst showed higher activity but poorer ability to protect the unsaturated bond. The metal particles incorporated *via* the sol-gel method were finely and evenly distributed on the support. As such, they were more readily shielded by the second metal particles that were subsequently incorporated *via* the impregnation process. When both metals were loaded *via* the sol-gel process, the best result was obtained with superior performance in activity, as well as selectivity in the preservation of double bond.

KEY WORDS: Catalyst preparation methods, 9-octadecen-1-ol, oleic acid, ruthenium-tin-alumina catalyst, selective hydrogenation.

Hydrogenation of fatty acids and methyl esters derived from vegetable oils is an important industrial process, which is currently carried out under high pressure and temperature (1,2). Several attempts have been made to develop suitable catalysts that can hydrogenate these materials under milder conditions (3–6). Although progress has been made in the hydrogenation of saturated fatty acids (3,7) and saturated and unsaturated methyl esters (4,5) to saturated alcohols, selective hydrogenation of unsaturated fatty acid, such as oleic acid, to the corresponding unsaturated alcohol under mild conditions still remains a challenge. We have developed two supported bimetallic catalysts, Ru-Sn and Re-Sn, that can selectively hydrogenate oleic acid (9-octadecenoic acid) to 9-octadecen-1-ol at a lower pressure of 5.6 MPa and a temperature of 250°C with a conversion of 81.3% and unsaturated and saturated alcohol selectivities of 80.9 and 16.1%, respectively. Detailed investigations on the reaction conditions have been reported earlier (8,9). In that study, we demonstrated that preparation methods, raw materials, activation and reaction conditions have significant effects on the performance of the catalyst. As an extension of our previous work, we have examined further the effects of the catalyst preparation method on the hydrogenation of oleic acid to 9-octadecen-1-ol to elucidate the nature of the active sites that are responsible for the selective hydrogenation. For this purpose, we prepared several ruthenium-tin-alumina catalysts by various methods, namely sol-gel, sequential impregnation and different combinations of impregnation and sol-gel. Hydrogenation of oleic acid with each of the catalysts was carried out under identical conditions to evaluate their performance.

EXPERIMENTAL PROCEDURES

Catalyst raw materials. Chloride-free chemicals were used as our previous studies showed that chloride has a negative effect on the activity of catalyst in the hydrogenation. The precursors for ruthenium, tin and alumina were trisacetylacetonato ruthenium [Ru(acac)$_3$], tin tetrabutoxide [Sn(OC$_4$H$_9$*n*)$_4$] and aluminium isopropoxide [Al(OC$_3$H$_7$*iso*)$_3$], respectively. The solvents used were 2-methyl-2,4-pentanediol (in the sol-gel method) and ethanol (in the impregnation method).

Preparation of alumina by sol-gel method. The alumina was prepared according to the method of Mizukami (10). Al(OC$_3$H$_7$*iso*)$_3$ (40 g) was dissolved in 93 g 2-methyl-2,4-pentanediol by heating at 110°C for 3–4 h until a homogeneous solution was obtained. It was then hydrolyzed by adding a solution of 60 g water in 40 g 2-methyl-2,4-pentanediol and aged for 1 h. After filtration, the gel (filter cake) obtained was dried under vacuum at 170°C, and the dry powder was calcined at 300°C for 1 h, 450°C for 3 h and 600°C for 3 h to yield the sol-gel alumina support.

Preparation of catalysts. Five types of 2 wt% Ru-4.7 wt% Sn-Al$_2$O$_3$ catalysts were prepared by different methods: (i) Catalyst A (RuSn-SG)—complexing agent-assisted sol-gel method:

$$\begin{array}{c} \mathrm{Ru + Sn + [Al(OC_3H_7}\mathit{iso})_3] \\ \downarrow \text{sol-gel} \\ \mathrm{Ru\text{-}Sn\text{-}Al_2O_3} \end{array} \qquad [1]$$

(ii) Catalyst B (RuSn-imp 12)—sequential impregnation of Ru and Sn on alumina in that order:

$$\begin{array}{ccccc} & \mathrm{Ru} & & \mathrm{Sn} & \\ & \downarrow \text{impregnation} & & \downarrow \text{impregnation} & \\ \mathrm{Al_2O_3} & \text{---------}> & \mathrm{Ru\text{-}Al_2O_3} & \text{---------}> & \mathrm{Ru\text{-}Sn\text{-}Al_2O_3} \end{array} \qquad [2]$$

(iii) Catalyst C (RuSn-imp 21)—sequential impregnation of Sn and then Ru on alumina in that order:

$$\begin{array}{ccccc} & \mathrm{Sn} & & \mathrm{Ru} & \\ & \downarrow \text{impregnation} & & \downarrow \text{impregnation} & \\ \mathrm{Al_2O_3} & \text{---------}> & \mathrm{Sn\text{-}Al_2O_3} & \text{---------}> & \mathrm{Ru\text{-}Sn\text{-}Al_2O_3} \end{array} \qquad [3]$$

(iv) Catalyst D (RuSn-SI)—sequential loading of Ru on alumina by sol-gel method first, then Sn by impregnation:

$$\begin{array}{ccc} \mathrm{Ru + [Al(OC_3H_7}\mathit{iso})_3] & \mathrm{Sn} & \\ \downarrow \text{sol-gel} & \downarrow \text{impregnation} & \\ \mathrm{Ru\text{-}Al_2O_3(sol\text{-}gel)} & \text{---------}> & \mathrm{Ru\text{-}Sn\text{-}Al_2O_3} \end{array} \qquad [4]$$

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(v) Catalyst E (RuSn-IS)—sequential loading of Sn on alumina by sol-gel method first, then Ru by impregnation:

$$\begin{array}{ll} \text{Sn} + [\text{Al(OC}_3\text{H}_7\textit{iso})_3] & \text{Ru} \\ \downarrow \text{sol-gel} & \downarrow \text{impregnation} \\ \text{Sn-Al}_2\text{O}_3\text{(sol-gel)} \dashrightarrow & \text{Ru-Sn-Al}_2\text{O}_3 \end{array} \qquad [5]$$

Catalyst A, RuSn-SG—sol-gel method. Concentrated HNO_3 (60 mL) was added to 3 g of $Ru(acac)_3$, and the mixture was heated at 80–90°C until the evolution of nitrogen oxide had completely ceased, resulting in the formation of a clear, red solution. After drying under vacuum at 120°C, 20 mL ethanol was added. Meanwhile, 142 g $[Al(OC_3H_7\textit{iso})_3]$ was dissolved in 163.7 g 2-methyl-2,4-pentanediol at 100°C, and the ethanolic solution of ruthenium nitrate compound and 4.5 g $Sn(OC_4H_9\textit{n})_4$ were added. The whole mixture was stirred for 4 h at 110°C. Water (65 g) was then added, and the gel formed was aged for 2 h at the same temperature before drying at 170°C under vacuum.

Catalyst B, RuSn-imp 12. The ethanolic solution (50 mL) of ruthenium nitrate compound, derived from 2 g of $Ru(acac)_3$, was added to 23.7 g sol-gel alumina, which had been perviously degasified for 2 h at 200°C under vacuum and cooled. The mixture was stirred at room temperature for 3 h and then dried under vacuum at 80°C initially, then at 150°C. The dry powder was then further degasified at 200°C for 2 h and cooled. Ethanolic solution (50 mL) containing 3.02 g of $Sn(OC_4H_9\textit{n})_4$ was then added to the dry powder impregnated with Ru, and the mixture was again stirred for 3 h at room temperature, followed by drying under vacuum as before.

Catalyst C, RuSn-imp21. The procedure for this catalyst was the same as that described for Catalyst B, except that the sequence of impregnation of Ru and Sn was reversed.

Catalysts D (RuSn-SI) and E (RuSn-IS). These catalysts were prepared *via* a combination of sol-gel and impregnation by first incorporating one of the metals onto the alumina by the sol-gel method and then, after drying, the other metal was incorporated to the system by the conventional impregnation.

Simultaneous impregnation of Rn and Sn on alumina was also tried, but it was difficult because a mixture of the above ruthenium nitrate and tin butoxide in ethanol gave a precipitate in the absence of aluminium alkoxide.

Hydrogenation reaction. This was carried out with a 500-mL reactor equipped with a pressure regulator. The reactor was charged with 50 g oleic acid (99.5% purity, Nippon Oils & Fats Co. Ltd., Tokyo, Japan), together with 3 g of catalyst, which had just been activated at 400°C for 4 h under a stream of H_2. The reactor was then purged with hydrogen four times at different pressures (1.0, 1.0, 2.0 and 4.0 MPa) to remove air. The reaction was carried out at a pressure of 5.6 MPa and a temperature of 250°C for about 20 h. Stirring was maintained at about 1000 rpm. Samples were drawn during the course of reaction for analysis.

Analysis of products. The course samples and final products were analyzed by gas chromatography with a 50 m × 0.25 mm fused-silica capillary column ULBON HR-SS-10 (Shinwa-kako Co. Ltd., Kyoto, Japan) operated with temperature programming from 150–200°C at 2°C/min and with helium as the carrier gas. A flame-ionization detector was used. The fatty acids and fatty alcohols in the reaction mixtures were first converted to their methyl esters (by methonolic BF_3) and alkyl acetates (by acetic anhydride in pyridine), respectively, without prior separation. Prior to methylation, the product mixture was first treated with a 0.5 M methanolic NaOH solution. For quantitation, *n*-heptadecanoic acid was used as an internal standard.

Catalyst characterization. X-ray powder diffraction (XRD) was carried out on an MXP 18 machine (MAC Science Co., Hachiohji, Japan) by CuKα radiation with a nickel filter. Pore size distributions were obtained from N_2 absorption measurement in an Omisorp 100 (Omicron Tech. Co., Coulter, FL).

RESULTS

Data in Table 1 show the results of the hydrogenation of oleic acid with the various $Ru\text{-}Sn\text{-}Al_2O_3$ catalysts (catalysts A, B, C, D and E) prepared as described earlier. Figures 1 to 5 show the graphs of the respective time course, whereas Figures 6 and 7 are the combined graphs of the unsaturated (9-octadecen-1-ol) alcohol and saturated (stearyl) alcohol selectivities, respectively.

These graphs show that all the catalysts provided high conversion of more than 80% after 5 h of reaction and more than 95% at the end of the experiment (20 h). The exception was Catalyst D, which gave a poorer conversion of 89.4% after 20 h.

Selectivities. The difference between the selectivities of the five types of catalysts can be best visualized by studying the graphs in Figures 6 and 7. The following observations on the unsaturated alcohol selectivities stand out

TABLE 1

Hydrogenation of Oleic Acid with $Ru\text{-}Sn\text{-}Al_2O_3$ Prepared by Different Methods[a]

Catalyst	Preparation method	Conversion (%)	Selectivities (%)		
			Unsaturated	Saturated	Total
A	RuSn-SG	97.3	82.3	10.9	93.2
B	RuSn-imp12	98.2	69.4	23.0	92.3
C	RuSn-imp21	98.4	52.4	36.1	88.5
D	RuSn-SI	87.2	78.4	10.0	88.4
E	RuSn-IS	98.5	53.4	35.8	89.2

[a] All catalysts were supported on Al_2O_3 and were activated at 400°C for 4 h in a stream of H_2 before use. Atomic ratio of Ru/Sn was 1:2 in all cases. Reaction conditions: temperature, 250°C; pressure, 5.6 MPa; reaction time, 20 h; oleic acid, 50 g; catalyst, 4% by weight.

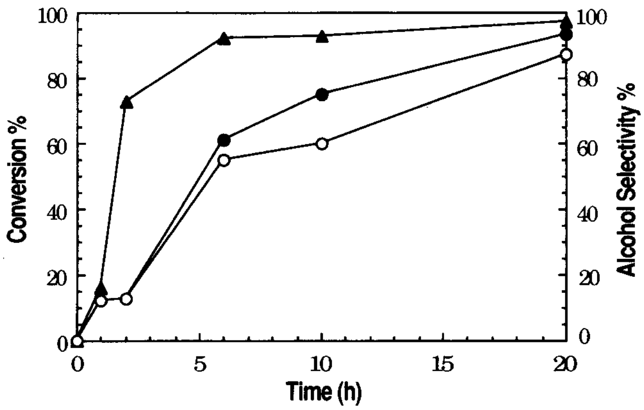

FIG. 1. Time course of hydrogenation of oleic acid with Catalyst A (RuSn-SG). Reaction conditions: temperature, 250°C; pressure, 5.6MPa; oleic acid, 50 g; catalyst, 4% by weight. ▲, Conversion; ●, total alcohol selectivity and ○, unsaturated alcohol selectivity.

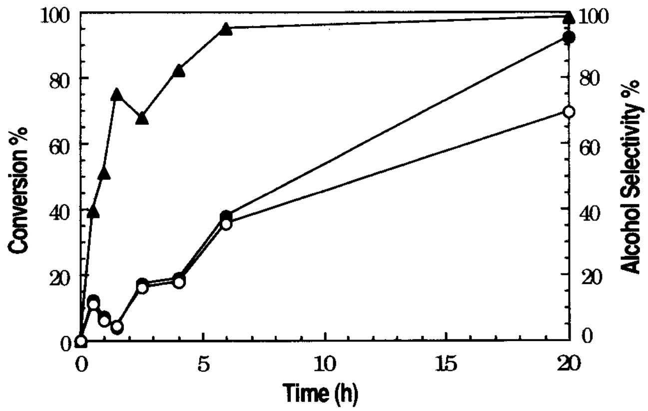

FIG. 2. Time course of hydrogenation of oleic acid with Catalyst B (RuSn-imp12). Reaction conditions: temperature, 250°C; pressure, 5.6MPa; oleic acid, 50 g; catalyst, 4% by weight. ▲, Conversion; ●, total alcohol selectivity and ○, unsaturated alcohol selectivity.

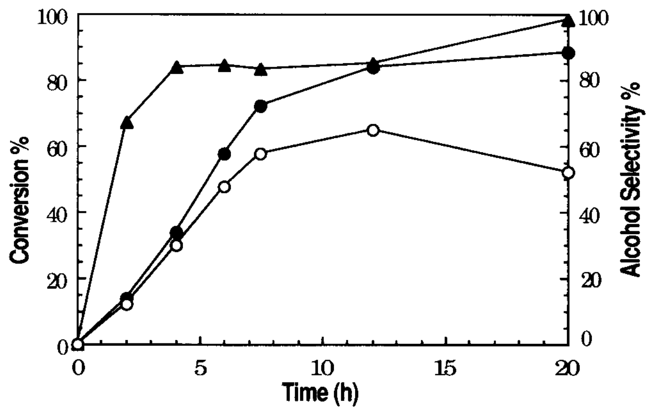

FIG. 3. Time course of hydrogenation of oleic acid with Catalyst C (RuSn-imp21). Reaction conditions: temperature, 250°C, pressure, 5.6MPa; oleic acid, 50 g; catalyst, 4% by weight. ▲, Conversion; ●, total alcohol selectivity and ○, unsaturated alcohol selectivity.

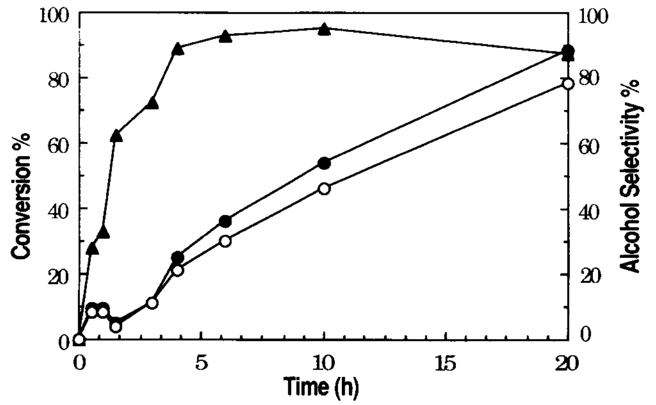

FIG. 4. Time course of hydrogenation of oleic acid with Catalyst D (RuSnk-SI). Reaction conditions: temperature, 250°C; pressure, 5.6 MPa; oleic acid, 50 g; catalyst, 4% by weight. ▲, Conversion; ●, total alcohol selectivity and ○, unsaturated alcohol selectivity.

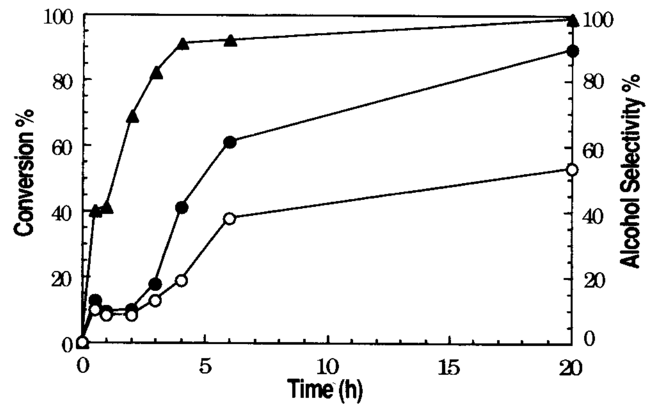

FIG. 5. Time course of hydrogenation of oleic acid with Catalyst E (RuSn-IS). Reaction conditions: temperature, 250°C; pressure, 5.6 MPa; oleic acid, 50 g; catalyst, 4% by weight. ▲, Conversion; ●, total alcohol selectivity and ○, unsaturated alcohol selectivity.

quite clearly: A = C > B = D = E, at about 10 h of reaction time: A > D > B > C = E, at the end of the experiment (20 h). Generally, the unsaturated alcohol selectivities of the catalysts increased with time, albeit at different rates throughout the reaction, with the exception of Catalyst C, which initially behaved like other catalysts, but after 12 h showed poorer unsaturated alcohol selectivity. Likewise, the saturated selectivities of Catalysts B, D and A were considerably lower than those of Catalysts C and E. As a result of the drop in unsaturated alcohol selectivity, the saturated alcohol selectivity of Catalyst C showed a larger increase after 12 h.

DISCUSSION

During the hydrogenation of oleic acid, under the experimental conditions, the reactions result in the formation of a mixture of unsaturated alcohols, saturated alcohol and saturated acid:

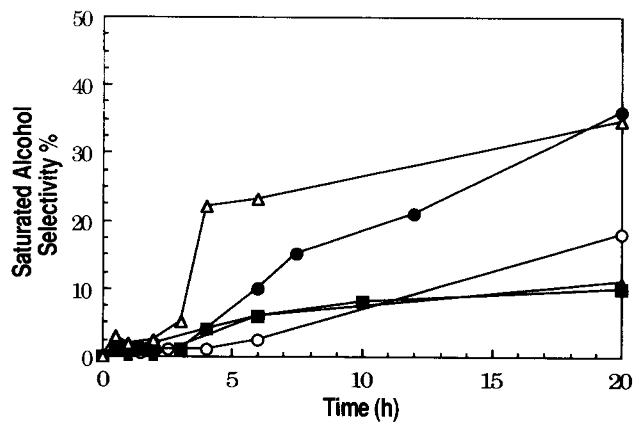

FIG. 6. Unsaturated alcohol selectivities of the various Ru-Sn catalysts. Reaction conditions: temperature, 250°C; pressure, 5.6 MPa; oleic acid, 50 g; catalyst, 4% by weight. ▲, Catalyst A (RuSn-SG); ○, Catalyst B (RuSn-impl2); ●, Catalyst C (RuSn-imp21); ■, Catalyst D (RuSn-SI); △, Catalyst E (RuSn-IS).

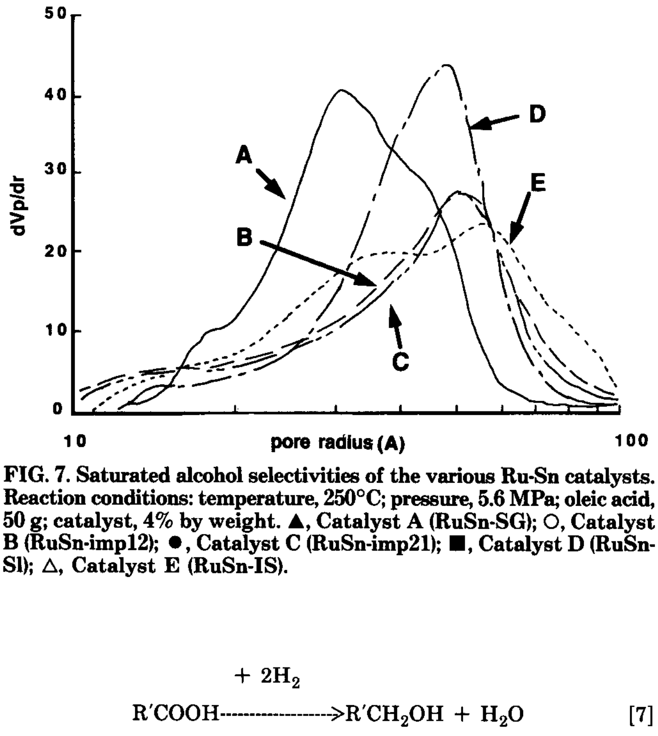

FIG. 7. Saturated alcohol selectivities of the various Ru-Sn catalysts. Reaction conditions: temperature, 250°C; pressure, 5.6 MPa; oleic acid, 50 g; catalyst, 4% by weight. ▲, Catalyst A (RuSn-SG); ○, Catalyst B (RuSn-impl2); ●, Catalyst C (RuSn-imp21); ■, Catalyst D (RuSn-SI); △, Catalyst E (RuSn-IS).

$$\begin{array}{lcl} R'COOH & \xrightarrow{+\ 2H_2} & R'CH_2OH + H_2O \qquad [7] \\ \downarrow + H_2 & & \downarrow + H_2 \\ RCOOH & \xrightarrow{+\ 2H_2} & RCH_2OH + H_2O \end{array}$$

where $R' = CH_3(CH_2)_7CH{=}CH(CH_2)_7$ and $R = CH_3(CH_2)_{16}$.

Conversion. All catalysts could achieve high conversion of more than 80% at almost the same time. This indicates that the oleic acid was reduced quite rapidly in the first 5 h of reaction time and that the rate decreased gradually and approached 90–98% at the end of the experiment. The completeness of the reduction suggests that the oleic acid was adsorbed rapidly on the surface of the catalyst and was subsequently attacked by the adsorbed hydrogen atoms to form either alcohols or stearic acid. Some long-chain esters could also be formed as a result of the reaction between the fatty acids present and the alcohols produced. These esters were then further hydrogenated to the respective alcohols. These side reactions probably explained the slow reaction after the initial 5-h period. Thus, a desirable catalyst for the selective hydrogenation of oleic acid to 9-octadecen-1-ol should possess the following abilities: to preserve the double bonds; to hydrogenate the carboxylic (-COOH) group to hydroxy (-CH_2OH); and to hydrogenate the long-chain esters to their corresponding alcohols.

The behavior of the catalysts in this study could be attributed to the nature of the Ru and Sn on the surface of the catalyst and to the interaction between these two metals on the surface. In our earlier report (8), we demonstrated that Sn could suppress hydrogenation and preserve the unsaturated bond of the oleic acid during the process of hydrogenation with the Ru-Sn-Al_2O_3 catalyst. The role of Sn in suppressing hydrogenation and preserving the double bonds in the hydrogenation of other unsaturated compounds with other supported bimetallic catalysts, such as Ru-Sn-B (4,5), Pt-Sn (11–16) and Rh-Sn (17), has also been observed and reported by other researchers. Ruthenium is well known for the hydrogenolysis of hydrocarbons (18–21). As we examined in greater detail the selectivities and activities of the various Ru-Sn-Al_2O_3 catalysts (A–E) prepared by different methods, we developed a better understanding of the roles played by the Ru and Sn in the catalysts.

Selectivities and activities. Our results revealed that the method of preparation, especially the sequence of the incorporation of the Ru and Sn, has a profound effect on the performance of the catalyst. From the selectivity and activity (based on conversion) profiles, we could categorize the five catalysts into three groups, with each displaying different behavior: (i) Catalyst A (RuSn-SG). This sol-gel catalyst exhibited the highest activity and the greatest unsaturated alcohol selectivity, resulting in preferential conversion of oleic acid to unsaturated alcohol (9-octadecen-1-ol) and low formation of stearyl alcohol. (ii) Catalysts B (RuSn-Imp 12) and D (RuSn-SI). These two catalysts were also active and showed increasing unsaturated alcohol selectivity with time, although at a slower rate. Toward the end of the experiment, however, Catalyst D yielded a higher amount of unsaturated alcohol. This indicated that these two catalysts still could preserve the double bond fairly efficiently. (iii) Catalysts C (RuSn-imp21) and E (RuSn-IS). The unsaturated alcohol selectivity of these two catalysts, although increased with reaction time initially, decreased after reaching a maxima (after 12 h of reaction), as in Catalyst C, or with only a slight increase, as in Catalyst E. As a result, the hydrogenation product contained a relatively higher percentage of stearyl alcohol. Thus, compared with the other three, Catalysts C and E were poorer in terms of their ability to preserve the double bonds.

The above observations showed that all the Ru-Sn-Al_2O_3 catalysts exhibited the property of preserving the double bonds of oleic acid in the course of hydrogenation, although with different degrees of ability. This difference in ability can be explained by considering the manner by which the Ru and Sn metals were incorporated onto the alumina support.

The high activity and unsaturated alcohol selectivity exhibited by Catalyst A reaffirmed our earlier finding on the superior performance of the sol-gel Ru-Sn-Al_2O_3 catalyst in the selective reduction of the carboxylic group of oleic acid (8). This behavior is probably due to the fact that the sol-gel process produces more finely and evenly dispersed particles. The uniform dispersion of the Ru and Sn on the support is evident as indicated by the near-Gaussian mesopore distribution of Catalyst A (Fig. 8). Characterization by XRD also supported this hypothesis because the peaks corresponding to γ-Al_2O_3 in the diffraction pattern of Catalyst A were the least prominent (Fig. 9).

Catalysts B and D, which showed fairly high ability in the preservation of double bonds have Ru compound incorporated first, followed by Sn compound. This order of incorporation likely resulted in the shielding of Ru by Sn particles. Thus, the activity of the catalyst was somewhat reduced, but the ability to preserve the double bonds, however, was maintained. A distinction could also be drawn between Catalysts B and D. Catalyst D showed better unsaturated alcohol selectivity and poorer activity than did Catalyst B. This was due to the difference in the loading of Ru on the support. In Catalyst D, the Ru was introduced first by sol-gel, whereas in Catalyst B it was loaded by the impregnation method. As the sol-gel method yields more finely and evenly distributed particles than the impregnation method, the Ru particles in Catalyst D were located deeper in the alumina than in Catalyst B (22). In this state, the Ru in Catalyst D was more effectively shielded by the Sn particles. This suppressed the activity, as observed in Catalyst D. In contrast, the blocking effect of Sn or Ru in Catalyst B was less prominent because both the Ru and Sn co-existed on the bigger alumina particles.

On the other hand, in Catalysts C and E, the Sn compound was incorporated first onto the alumina, followed by the Ru compound. In such a situation, the shielding effect is reversed, the Sn was blocked by the Ru particles, and a similar line of explanation applies. As Sn particles were partially shielded by Ru particles, the ability of the catalysts to preserve the double bonds was reduced. Thus, these two catalysts produced relatively higher amounts of stearyl alcohol, clearly shown in Figure 6. However, both catalysts showed similar activities and unsaturated alcohol selectivities, which implies that the ability of tin to preserve the double bond was not much affected by the method of incorporation.

The above discussion suggests that the sequence of metal loading and method of preparation have profound effects on the nature of the catalyst site. Characterization of the various catalysts by XRD supported partly the above explanation, i.e., the sol-gel method gives more finely and evenly dispersed particles. This is in agreement with the observations made by Mizukami *et al.* (22) and Gomez *et al.* (23), who showed that the sol-gel method produces finely dispersed particles in the catalyst support. Figure 9 shows the XRD patterns of the five types of catalysts studied. All the patterns essentially showed diffraction peaks corresponding to the γ-Al_2O_3 structure. However, these diffraction patterns changed with the method of preparation. Catalysts prepared by only the impregnation method showed distinct pattern of γ-Al_2O_3 (which was calcined at 600°C prior to use as impregnation support). When one of the loading methods was replaced by sol-gel, the XRD peaks became less prominent, and when sol-gel was the sole preparation method, the XRD peaks became the least prominent. This suggests that the sol-gel method produced fine particles that were evenly dispersed in the Al_2O_3, and thus changed the XRD pattern.

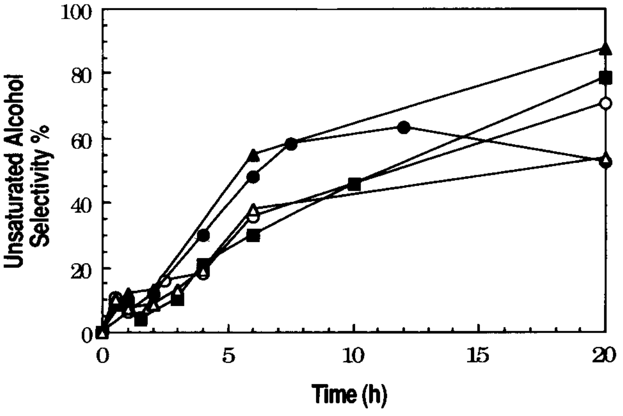

FIG. 8. Meso- and macropore distributions of Ru-Sn-Al_2O_3. A, RuSn-SG; B, RuSn-impl2; C, RuSn-imp2; D, RuSn-Sl; E, RuSn-IS. Vp and r are volume of pores and pore radius.

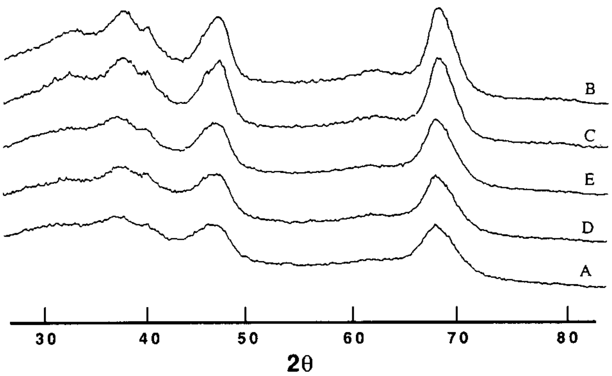

FIG. 9. X-ray powder diffraction patterns of Ru-Sn-Al_2O_3. A, RuSn-SG; B, RuSn-impl2; C, RuSn-imp2; D, RuSn-Sl; E, RuSn-IS.

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