

Studies on Ruthenium–Tin Boride Catalysts

II. Hydrogenation of Fatty Acid Esters to Fatty Alcohols

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Hydrogenation of methyl hexadecanoate, methyl-9-octadecenoate, and dimethyl succinate was studied as a function of catalyst composition as well as various reaction parameters. It was found that an atomic ratio of Ru to Sn of 1 : 1 gave maximum activity and selectivity for alcohol formation from methyl hexadecanoate and dimethyl succinate. Methyl-9-octadecenoate gave the best yield of 9-octadecen-1-ol (the unsaturated alcohol) at an atomic ratio of Ru to Sn of 1 : 2. The hydrogenation of dimethyl succinate was found to depend delicately on the temperature of the reaction, with the diol yields reaching a maximum at 200°C. Based on the characterization of the catalysts and the catalytic activity data, the nature of the active species responsible for the selective hydrogenation and the mode of activation of the ester are discussed. © 1990 Academic Press, Inc.

INTRODUCTION

There are numerous studies in the literature on the catalytic activity of metal boride catalysts for hydrogenation reactions (1–6). Paul *et al.* (7) were the first to report the use of NiB prepared from nickel salt and NaBH₄ as hydrogenation catalysts. Unpromoted NiB was found to be almost as active as Raney nickel in the hydrogenation of safrole, furfural, and other compounds, but exhibited better catalyst life. Alkenes in the presence of ketones, alcohols and ethers could be selectively hydrogenated by nickel boride without any hydrogenolysis. Nickel boride promoted with Cr, Mo, W, V, or Mn was found to be more active than Raney nickel (8). NiB was also reported to selectively reduce dienes and alkynes to monoenes (9). Co(II) in the presence of NiBH₄ was found to effect selective monohydrogenation of limonene. In addition, there are many other reports of the reduction of aromatic ring systems, nitriles, and nitroaromatic compounds to useful products using various transition metal ions in conjunction with NaBH₄ (10, 11).

In our laboratory, studies on metal borides were undertaken to design novel catalysts for selective hydrogenation reactions. During the course of our investigations, we found that the catalytic activity and selectivity of ruthenium boride could be altered in a rather dramatic manner by the introduction of a second metal, tin. For instance, it was found that the mixed metal boride, Ru–Sn–B, could selectively hydrogenate (i) α,β -unsaturated aldehydes to unsaturated alcohols (12), (ii) saturated fatty acid esters like methyl hexadecanoate to the corresponding alcohol, and (iii) methyl-9-octadecenoate to 9-octadecen-1-ol. In this paper, we present a detailed account of the catalytic activity of the above new mixed metal boride system for the hydrogenation of fatty acid esters to fatty alcohols. We further discuss the nature of the active species and the mode of activation of the organic reactant in the light of the characterization studies presented in Part I (13).

EXPERIMENTAL

Preparation of the Catalysts

The metal boride catalysts were prepared from the corresponding metal salts by re-

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duction with sodium borohydride (NaBH_4) as described in detail in Part I (13). The catalysts, reduced by NaBH_4 , were used directly for the reactions without pretreatment. Some catalysts were also prepared by the conventional impregnation method by the incipient wetness technique. The supports were impregnated with the mixed aqueous salt solutions of the metals, dried at 100°C , and reduced in H_2 flow at 300°C .

Reagents

$\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (Fluka, Switzerland), $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, GeCl_4 , and $\text{Pb}(\text{NO}_3)_2$ (BDH, India) were of 99% purity. The supports $\gamma\text{-Al}_2\text{O}_3$ (surface area $200 \text{ m}^2/\text{g}$) and $\alpha\text{-Al}_2\text{O}_3$ (surface area $4 \text{ m}^2/\text{g}$) were procured from Harshaw-Chemie B.V. (Netherlands), while TiO_2 of surface area $100 \text{ m}^2/\text{g}$ was supplied by Ketjen. SiO_2 support of surface area $400 \text{ m}^2/\text{g}$ was obtained from Alpha Products Inc. (USA).

Methyl hexadecanoate and methyl-9-octadecenoate of 99% purity were supplied by ACME Chemicals Limited, Bombay, India. Cinnamaldehyde and dimethyl succinate of 99% purity were procured from Fluka, Switzerland. H_2 used was of 99% purity and was supplied by Indian Oxygen Limited, Bombay.

Reaction Procedure

The hydrogenation reactions were carried out in a 300-ml-capacity Parr autoclave (Model 4561). The autoclave was charged with the organic reactant and the catalyst, purged with H_2 six times, and finally pressurized to the required pressure. The temperature was then gradually raised to the reaction temperature, while the contents were stirred. At the end of the specified duration, the autoclave was cooled to room temperature.

All the catalytic measurements were made at a catalyst concentration of 2.5% by weight with respect to the reactant to enable direct comparison of the activities of the catalysts.

The activity and selectivity data refer to

steady-state conditions, which were attained in 7 h for most of the catalysts. It was also found that the selectivities did not vary significantly with time ($\pm 3\%$) on the catalysts studied. Selectivity for alcohol is defined as $(\% \text{ alcohol}/\% \text{ conversion}) \times 100$.

Analysis of Products

The products of the hydrogenation of methyl hexadecanoate and cinnamaldehyde were analyzed by GC using Carbowax 400M on Chromosorb as the column. The column was operated at 200°C . The products of the hydrogenation of methyl-9-octadecenoate were analyzed using a 10-ft-long EG SS-X column operated at a temperature of 210°C . A flame ionization detector was used in all cases.

RESULTS

Table 1 lists the type of hydrogenation reactions catalyzed by the mixed metal boride system, ruthenium-tin boride. The salient points to be noted in the table are as follows. (i) The catalyst distinguishes between $\text{C}=\text{O}$ and $\text{C}=\text{C}$ and preferentially attacks the former in α,β -unsaturated aldehyde (see entry 1 of Table 1). (ii) The fatty acid esters are hydrogenated to alcohols in high yields. (iii) More significantly, the unsaturated ester, methyl-9-octadecenoate, is converted to the unsaturated alcohol, 9-octadecen-1-ol, to the extent of 61.8%. (iv) Dimethyl succinate can be converted to 1,4-butanediol.

While many catalyst systems have been reported for the selective hydrogenation of fatty acid esters to fatty alcohols (14-17), very few catalyst systems are described for the selective formation of unsaturated alcohol from unsaturated esters (18, 19), apart from our example shown in entry 3 of Table 1.

In the following paragraphs, we focus our attention only on the reactions of esters to alcohols.

The influence of catalyst parameters like Ru/Sn atomic ratio, nature of support, choice of group IVA metal and noble metal,

TABLE I
 Ru-Sn-B-Catalyzed Hydrogenation Reactions^a

| Reactant | Conditions | Conversion (%) | Major product distribution (%) | |
|---------------------------|---|----------------|-----------------------------------|------|
| 1. Cinnamaldehyde | $T = 100^{\circ}\text{C}$ $H_2 = 0.69 \text{ MPa}$ | 73.0 | Cinnamyl alcohol | 47.0 |
| | | | 3-Phenyl propanal | 5.3 |
| | | | 3-Phenyl-1-propanol | 14.4 |
| 2. Methyl hexadecanoate | $T = 270^{\circ}\text{C}$ $H_2 = 4.4 \text{ MPa}$ | 86.4 | 1-Hexadecanol | 71.9 |
| 3. Methyl-9-octadecenoate | $T = 270^{\circ}\text{C}$ $H_2 = 4.4 \text{ MPa}$ | 80.0 | 9-Octadecen-1-ol | 61.8 |
| | | | 1-Octadecanol | 12.5 |
| 4. Dimethyl succinate | $T = 200^{\circ}\text{C}$ $H_2 = 8.8 \text{ MPa}$ | 98.0 | 1,4-Butanediol | 76.0 |
| | | | Tetrahydrofuran | 8.9 |
| | | | Methyl- γ -hydroxybutyrate | 11.2 |

^a The catalyst used for entry 1 is unsupported Ru-Sn-B (Ru:Sn = 1:1); Ru-Sn-B/ γ -Al₂O₃ (Ru:Sn = 1:1) for entries 2 and 4; and Ru-Sn-B/ γ -Al₂O₃ (Ru:Sn = 1:2) for entry 3. On the supported catalyst, ruthenium loading was 1.1% (w/w). The duration of reaction was 7 h.

quantity of catalyst, and method of preparation of the catalyst on the activity and selectivity for hydrogenation are considered first, followed by a study of reaction parameters like temperature, pressure, and organic reactant-to-H₂ ratio.

Effect of Ru/Sn Ratio

Figure 1 shows the effect of Ru/Sn atomic ratio on the activity and selectivity for alcohol formation for the conversion of methyl hexadecanoate to 1-hexadecanol. It may be seen that while Ru-B is highly active, showing 100% conversion, it is highly nonselective for alcohol formation. Introduction of a small amount of tin (Ru:Sn = 1:0.25) dramatically increases the selectivity for 1-hexadecanol to 86.8%.

However, the conversion of the ester falls to 65.6%. There is very little change in selectivity beyond a Ru:Sn ratio of 1:0.25. However, conversion increases gradually to 86.4% at a Ru:Sn ratio of 1:1. Thus, the yield of the fatty alcohol also attains a peak of 71.9% at the ratio of 1:1 (the yield of alcohol may be obtained by multiplying conversion by selectivity).

Figure 2 shows the effect of the ruthenium-to-tin ratio on the hydrogenation of methyl-9-octadecenoate. In this case also,

tin increases the selectivity of 9-octadecen-1-ol as for hydrogenation of methyl hexadecanoate, with the difference that the peak for 9-octadecen-1-ol formation occurs at a ratio of ruthenium to tin of 1:2.

Effect of Nature of Support

The effect of support on the hydrogenation of methyl hexadecanoate is presented in Table 2. Among the supports studied (γ -Al₂O₃, α -Al₂O₃, TiO₂, and SiO₂), γ -Al₂O₃

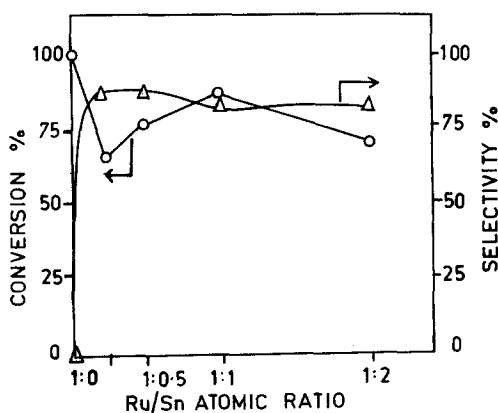


FIG. 1. Effect of atomic ratio of ruthenium to tin on activity and selectivity for the hydrogenation of methyl hexadecanoate. (○) Conversion and (△) selectivity for 1-hexadecanol. Reaction conditions are given in Table 2.

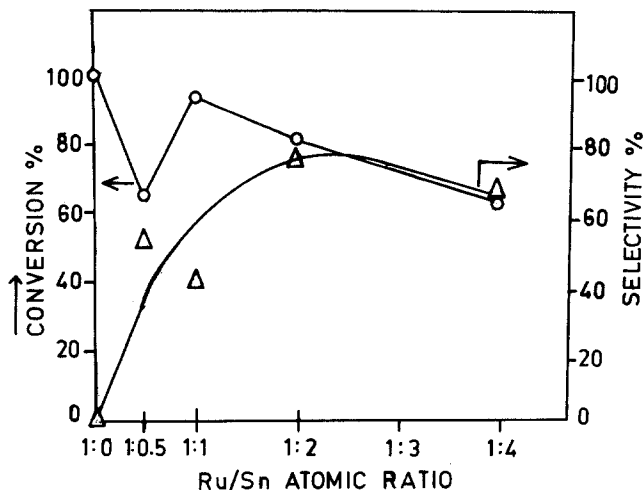


FIG. 2. Effect of atomic ratio of ruthenium to tin on activity and selectivity for the hydrogenation of methyl-9-octadecenoate. (○) Conversion and (△) selectivity for 9-octadecen-1-ol. Conditions of reaction are given in Table 2.

showed the best activity. The selectivity for alcohol formation at the steady state, however, is not affected much by variation of the support. Activity varied in the order $\gamma\text{-Al}_2\text{O}_3 > \alpha\text{-Al}_2\text{O}_3 > \text{TiO}_2 \sim \text{SiO}_2$. A more or less similar trend was observed for the other reactants as well. The changes in conversion with support may simply be a result of changes in dispersion of ruthenium.

Effect of Group IVA Metal and the Other Noble Metal Combinations

Table 3 shows the effect of tin, ger-

manium, and lead on the activity for hydrogenation of methyl hexadecanoate. Tin, as an additive to ruthenium, exhibits the highest activity and selectivity for 1-hexadecanol formation. Germanium shows considerably less conversion (54%) and selectivity (54.4%) for fatty alcohol formation compared to the ruthenium-tin system. Interestingly, lead seems to completely poison the catalyst.

Catalysts comprising group IVA metals along with the noble metals Pt and Pd were also studied for hydrogenation. It was again found that only ruthenium showed the high-

TABLE 2

Effect of Support^a on Hydrogenation of Methyl Hexadecanoate to 1-Hexadecanol^b

| Support | Conversion (%) | Yield of hexadecanol ^c (%) | Selectivity for alcohol (%) |
|-----------------------------------|----------------|---------------------------------------|-----------------------------|
| 1. $\gamma\text{-Al}_2\text{O}_3$ | 86.4 | 71.9 | 83.2 |
| 2. $\alpha\text{-Al}_2\text{O}_3$ | 68.3 | 60.8 | 89.0 |
| 3. SiO_2 | 30.0 | 26.5 | 88.3 |
| 4. TiO_2 | 25.5 | 23.5 | 86.2 |

^a Ruthenium metal loading was 1.1% and the atomic ratio of ruthenium to tin was ~1:1.

^b Conditions: $T = 270^\circ\text{C}$, H_2 pressure = 4.4 MPa, catalyst = 2.5% by weight, duration of reaction = 7 h, and H_2 : ester (molar) ratio = 1:23.

^c Unidentified lower esters constitute the rest of the products.

TABLE 3

Effect of Group IVA Metal^a on the Hydrogenation of Methyl Hexadecanoate to 1-Hexadecanol^b

| Group IVA metal | Conversion (%) | Yield of 1-hexadecanol ^c (%) | Selectivity for alcohol (%) |
|-----------------|----------------|---|-----------------------------|
| 1. Tin | 86.4 | 71.9 | 83.2 |
| 2. Germanium | 54.0 | 29.6 | 54.8 |
| 3. Lead | 1.0 | 0.8 | — |

^a The catalyst had 1.1% Ru loading with an atomic ratio of Ru to group IVA metal of ~1 : 1. The support was γ -Al₂O₃.

^b Conditions: as in Table 2.

^c Unidentified lower esters constitute the rest of the products.

est activity and selectivity for alcohol formation.

Effect of Method of Preparation of the Catalyst

Ru–Sn catalyst prepared by the conventional method was also studied for the hydrogenation of methyl hexadecanoate. It may be seen from Table 4 that the Ru–Sn–B/Al₂O₃ catalyst shows significantly higher selectivity for alcohol than the Ru–Sn/Al₂O₃. Conventional catalysts do not exhibit a synergistic effect on addition of Sn to Ru with respect to selectivity for alcohol whereas the NaBH₄-reduced catalysts do show synergism, as already seen earlier. We do not wish to compare the activities of the catalysts since data on

metal dispersion for Ru/Al₂O₃ and Ru–Sn/Al₂O₃ are not available.

Effect of Catalyst Quantity

Hydrogenation of methyl hexadecanoate. Under a given set of conditions, the amount of catalyst used was varied and its effect is shown in Fig. 3 for the hydrogenation of methyl hexadecanoate. The percentage conversion is not much affected by variation of the catalyst charge. However, the selectivity for 1-hexadecanol formation decreases significantly when the quantity of catalyst used is doubled from 2.5 to 5% of methyl hexadecanoate charged. The non-selective reaction products were essentially low-molecular-weight hydrocarbon fragments and esters. This clearly indicates that

TABLE 4

Effect of Method of Preparation on the Hydrogenation of Methyl Hexadecanoate^a

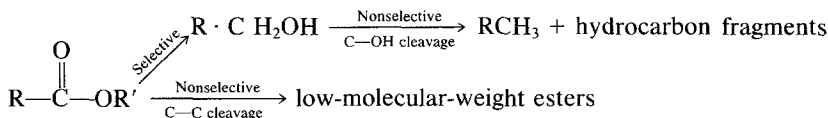
| Catalyst | Conversion (%) | Yield of 1-hexadecanol (%) | Selectivity for alcohol (%) |
|---|----------------|----------------------------|-----------------------------|
| 1. Ru–B/Al ₂ O ₃ | 88.2 | 1.3 ^b | 0 |
| 2. Ru–Sn–B/Al ₂ O ₃ | 86.4 | 71.9 | 83.2 |
| 3. Ru/Al ₂ O ₃ | 50.9 | 27.7 | 54.4 |
| 4. Ru–Sn/Al ₂ O ₃ | 30.0 | 17.2 | 57.3 |

^a Conditions: as in Table 2. The metal loading was 1.1% and the atomic ratio of Ru to Sn was ~1 : 1.

^b Other products are mostly unidentified low-molecular-weight fragments. About 60% was methyl myristate, as found by GC.

the catalyst contains both selective and nonselective sites. Beyond a catalyst charge of 2.5% (w/w), the population of

nonselective sites seems to become large enough to give rise to a significantly competitive nonselective reaction pathway:



The nature of such selective and nonselective sites is discussed later.

Hydrogenation of dimethyl succinate. A similar dependence of selectivity for alcohol formation on catalyst quantity was observed, except that the optimum quantity of catalyst required for diol formation was higher (10%) than that for the hydrogenation of methyl hexadecanoate to 1-hexadecanol.

Effect of Temperature

For methyl hexadecanoate hydrogenation, lowering of temperature leads to decreased rates of reaction as well as lower yields of the fatty alcohol, as expected. However, the temperature of the reaction affects the hydrogenation of dimethyl succinate in a rather interesting way. There is

an optimum temperature (200°C) at which a maximum yield of 1,4-butanediol is obtained (75%). At a lower temperature (180°C), methyl- γ -hydroxybutyrate was the main product (47%), while at a higher temperature (220°C), tetrahydrofuran was the main product (45%). Quite clearly, 180°C is not sufficient to hydrogenate both ester groups, whereas at a temperature of 220°C, 1,4-butanediol dehydrates on acidic alumina support to yield tetrahydrofuran.

DISCUSSION

The results presented above raise many interesting questions as to the nature of the active species present on the catalysts, the mode of preferential activation of the carbonyl of the ester instead of the indiscriminate hydrogenolytic cleavage of C-C bonds or C-OH bonds, and the specific role of tin and boron. In the following discussion we attempt to provide answers to some of these questions, based on the catalyst characterization data [presented in Part I (13)] and the results of catalytic activity.

Nature of Active Species and the Reaction Mechanism

It was suggested in Part I (13) that the mixed metal boride catalysts essentially contain two types of sites, Ru-Sn bimetallic alloy sites and ruthenium metal interacting with Sn^{2+} ions through oxygen. It was also suggested that the former are present in minor quantities while the latter are the predominant species. Let us examine a possible mechanism in the light of the nature of the surface species suggested.

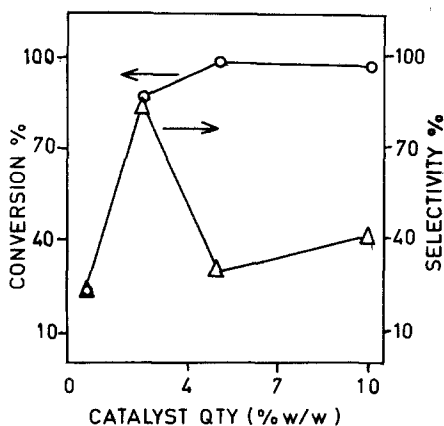
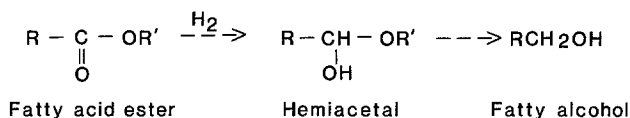


FIG. 3. Effect of catalyst quantity on activity and selectivity for hydrogenation of methyl hexadecanoate. (○) Conversion and (△) selectivity for 1-hexadecanol. Conditions of reaction are given in Table 2.

As far as we know, there is very little information in the open literature regarding the mechanism of hydrogenation of esters using heterogeneous catalysts. Most of the literature concerning copper chromite-

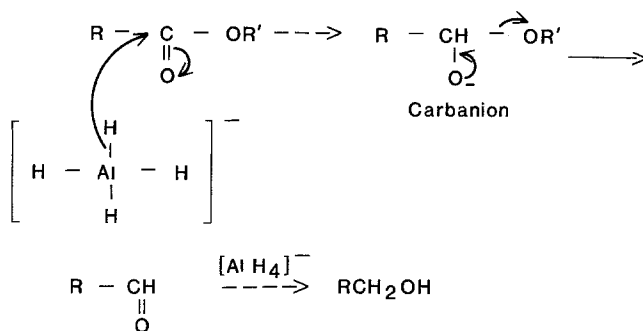
catalyzed hydrogenation of esters is in patents. There are, however, two possible schemes. The reaction might proceed via the hemiacetal, which subsequently forms the fatty alcohol:



In our case we did not observe any hemiacetal formation at any stage of the hydrogenation. While it is possible that the hemiacetal is a fleeting intermediate, it is hard to imagine hydrogenolytic cleavage of the C-OR' bond on the Ru-Sn boride catalysts, which, as we have seen, are not

capable of C-C or C-OH hydrogenolysis.

The second mechanism that has been suggested in the literature is related to the use of lithium aluminum hydride as a reagent for the reduction of esters to alcohols:

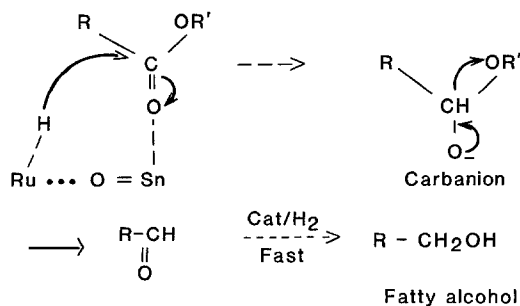


In this mechanism, initial hydride attack results in the formation of a highly unstable carbanion, which gives rise to the aldehyde and then the alcohol. A somewhat similar scheme was also suggested by Evans *et al.* (17) for the hydrogenation of ethyl acetate on Raney copper catalysts. We believe that a similar mechanism operates on our catalyst system Ru-Sn-B. We have two compelling reasons to propose this mechanism:

1. Ru⁰, in our catalyst, is present as an electron-rich species due to the presence of boride and sodium [see the XPS data on Ru-Sn-B in Part I (13)]. 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 shown below.

2. It was suggested in Part I (13) that the catalyst Ru-Sn-B contains, predominantly Ru⁰ interacting with Sn²⁺ or Sn⁴⁺ Lewis acid sites via the oxygen. Such sites could have a role to play in activating the otherwise inert C=O of the ester.

Thus, the mechanism involving the major surface species may be depicted as



In this mechanism Sn^{2+} or Sn^{4+} Lewis acid sites polarize the carbonyl of the ester, facilitating hydrogen transfer from an adjacent Ru-H site. This is the first step in formation of the unstable carbanion which, as already suggested, forms the aldehyde by spontaneous and noncatalytic elimination of OR' . The aldehyde could again rapidly form the alcohol (RCH_2OH) by catalytic hydrogenation. The eliminated species OR' will form the alcohol $\text{R}'\text{OH}$, picking up a dissociated hydrogen. Our kinetic studies did not detect the aldehyde $\text{R} \cdot \text{CHO}$ presumably because the hydrogenation of the aldehyde is quite fast at the high H_2 pressures of the reaction (4.4 MPa).

We do not envisage any specific role for Ru-Sn (alloy type) sites [type 2 sites in Part (13)]. Thus, the selective sites referred to in Part I are the $\text{Ru} \dots \text{O}=\text{Sn}$ sites as described above, while the nonselective sites are the monometallic Ru^0 sites. This explains why the monometallic catalyst RuB is highly nonselective, forming only C-C or C-OH cleavage products.

Interestingly, in the case of hydrogenation of methyl-9-octadecenoate, a maximum yield of 9-octadecen-1-ol is achieved at an atomic ratio of ruthenium to tin of 1:2 rather than 1:1, which was the case with the hydrogenation of methyl hexadecanoate. This fact fits in with the observation that the catalyst with the atomic ratio of ruthenium to tin of 1:1 still contains a certain number of nonselective Ru-B sites (see the results on the effect of catalyst quantity). As the ruthenium-to-tin ratio is increased to 1:2, the relative ratio of selective to nonselective sites increases further, which results in higher yields of unsaturated alcohol. Thus, it appears that the selective sites, which interact with ester groups to produce alcohol, are incapable of interacting with $\text{C}=\text{C}$ of the ester.

Role of Boron

It is difficult to rationalize the role of boron in the catalysts. Boron is present as borate as well as boride associated with

ruthenium (as suggested in Part I). Then, by analogy with NiB and CoB systems (20), we speculate that boron increases the electron density around ruthenium, thereby increasing its intrinsic ability to activate H_2 in a hydride form.

CONCLUSIONS

1. The Ru-Sn-B catalyst system shows maximum activity and selectivity for hydrogenation of fatty acid esters to alcohols at a Ru-to-Sn ratio of 1:1. The corresponding Ru-to-Sn ratio for maximum yield of the 9-octadecen-1-ol was found to be 1:2.

2. The highest activity and selectivity are attributed to Ru^0 sites interacting with Sn^{2+} or Sn^{4+} Lewis acid sites via oxygen, wherein the Lewis acid preferentially activates $\text{C}=\text{O}$ of the ester, facilitating hydrogen transfer from adjacent Ru-H sites.

3. The role of boron probably lies in increasing the electronic charge density around Ru, thereby facilitating activation of H_2 as a hydride.

4. Among the various combinations of group IVA metal and noble metals studied, only the Ru-Sn-B system shows maximum activity and selectivity for alcohol formation.

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