Preparation of Ru–Sn/C Catalysts and Their Performance in Hydrogenation of Lactic Acid

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Ru–Sn/C catalysts were prepared by the conventional impregnation method and characterized by XRD, H2-TPR, visible light absorption, EDX and XPS. The combination of metal sources, RuCl3, Ru(NO)(NO3)3, Ru(NO3)3, SnCl2, SnCl4 and Sn(OOCCH3)2, significantly influenced the metal structure of the catalysts. Using RuCl3 and SnCl4 as the metal sources, no XRD peaks for metals were observed and high dispersion of metals was estimated. On the other hand, use of RuCl3 and SnCl2 or Ru(NO3)3 and Sn(OOCCH3)2 resulted in a distinct XRD pattern determined to be a RuSn intermetallic compound of body-centered cubic structure. Presumably a type of complex formed between RuCl3 and SnCl2 or Ru(NO3)3 and Sn(OOCCH3)2 during the impregnation procedure. Hydrogenation of lactic acid to 1,2-propanediol was investigated with a 200 mL autoclave between 150 °C and 200 °C under 2-6 MPa of hydrogen (initial pressure at room temperature). The catalyst prepared from RuCl3 and SnCl4 had superior activity compared to reported catalysts under the following reaction conditions: 0.55 M lactic acid, 150 °C, 5.7 MPa of hydrogen and 4 h with 0.80 g of 5 % Ru–5 % Sn/C catalyst. The yield and productivity of this catalyst were 99.0 % and 0.51 g g-cat–1 h–1 (6.7 mmol g-cat–1 h–1), respectively. The high yield was achieved because no substantial consecutive hydrogenation of 1,2-propanediol occurred on the binary catalyst.

Keywords
Ruthenium–Tin intermetallic compound, Hydrogenation, Lactic acid, Catalyst preparation, 1,2-Propanediol

1. Introduction

Diols are important raw materials for the manufacture of polyesters and polyurethane, and consequently demand for diols has increased for decades. 1,2-Propanediol (1,2-PDO) is an industrially important commodity chemical with uses not only as an antifreeze agent but also as a precursor for drugs, cosmetics and food additives. 1,2-PDO is synthesized on the industrial scale by hydration of propylene oxide, which is produced from propylene obtained by the cracking of naphtha by the chlorohydrin process using chlorine or the Halcon process using hydroperoxide. However, the recent high crude oil price has increased interest in other processes to produce 1,2-PDO based on renewable resources. Lactic acid is obtained by fermentation of glucose, so 1,2-PDO synthesis from this biomass-based compound will be a renewable and environmentally benign process. Hydrogenation of lactic acid or its ester has been studied in the liquid phase and in the vapor phase.

Hydrogenation of lactic acid in the liquid phase was studied with Ru/C catalyst at high hydrogen pressure of 14.5 MPa. Study of the kinetics of the reaction concluded that a Langmuir-Hinshelwood type reaction was proceeding: the rate determining step is the reaction between adsorbed lactic acid and adsorbed hydrogen. Hydrogenation of ethyl lactate to 1,2-PDO was investigated with Ru/B/γ-Al2O3 catalyst in n-hexane. Investigation of combinations of Ru and Sn catalyst showed that Sn in the oxidized state was favorable but metallic Sn had no promotional effect. Study of hydrogenation of lactic acid to 1,2-PDO on Ru/TiO2 found that TiO2 was superior to carbon as a support because TiO2 might adsorb and activate lactic acid. Hydrogenation of lactic acid in the vapor phase was investigated over Cu/SiO2 catalyst and showed that dissociative adsorption of lactic acid and hydrogenation of the resulting acyl species were kinetically significant elementary steps. Study of the hydrogenation of ethyl lactate over Cu/SiO2 catalysts prepared by the precipitation-deposition, sol-gel and impregnation methods con-
cluded that catalyst prepared by the precipitation-deposition method was superior because the Cu particle size was smallest and SiO2 nanoparticles blocked aggregation of Cu species9). Under the optimized reaction conditions at 453 K and 1.5 MPa, productivity of 1,2-PDO of 3.1 mmol g-cat−1 h−1 was obtained. Close to quantitative yields of 1,2-PDO were reported in both the liquid phase and vapor phase, although the yield was highly dependent on the reaction conditions such as the concentration or partial pressure of lactic acid.

Recently, hydrogenation of carboxylic acids or alkyl esters has been investigated using binary catalysts such as Ru-Sn10),11), Ru-Co12) and Rh-Sn13). Tin has been widely studied as an additive (second component)10),11),13)∼18). Although Sn has no or little hydrogenation activity, Sn modifies the properties of single-component noble metal catalysts, resulting in drastic improvements in the catalytic performance14). In the case of hydrogenation of esters with Ru–Sn catalyst, Ru is believed to activate hydrogen and Sn is considered to activate the substrate by adsorbing the carboxyl group11),19),20).

The present study investigated the preparation of carbon-supported Ru–Sn binary catalysts and the hydrogenation of lactic acid using the obtained catalysts. We report that the preparation method of catalysts, especially the combination of the metal components, significantly influenced the metal structure and particle size, and that high productivity of 1,2-PDO could be attained using the catalyst with fine intermetallic RuSn supported on carbon.

2. Experimental

2.1. Preparation of Catalysts

Two types of active catalysts kindly supplied by Kuraray Co., Ltd., Japan were used as supports; GGS 1000 m2 g−1 (hereafter, denoted as C) and AC 200 m2 g−1. The active carbon samples were crushed and sieved to pass a 100 mesh screen. Catalysts were prepared by the conventional impregnation method. Typically, 0.23 g of RuCl3·2H2O (Furuya Metal Co., Ltd., Japan) and 0.190 g of SnCl2·2H2O (Wako Pure Chemicals Industries, Ltd., Japan) were placed into a glass flask, and 20 cm3 of distilled water was added to dissolve the salts. Then, 0.995 g of the active carbon support was added, and the mixture was stirred at 80 °C using a rotary evaporator at 200 hPa. The obtained catalyst precursor was reduced at 350 °C for 1 h under pure hydrogen stream of 150 cm3 min−1. The loading of Ru and Sn were 5.0 wt% and 5.9 wt%, respectively. The other Ru and Sn sources were Ru(NO)(NO3)3, Ru(NO3)3, and SnCl2, Sn(OCOCH3)2, respectively.

2.2. Characterization of Catalysts

The crystalline structure was analyzed by X-ray diffraction (XRD, Rigaku Corp., RINT 2000) using CuKα radiation (λ = 1.5418 Å) at 40 kV and 20 mA. Temperature-programmed reduction in hydrogen (H2-TPR) was carried out with a thermal gravimetric analyzer (TG-DTA; Shimadzu Corp., DTG-60H) under a gas flow consisting of 10 cm3 min−1 of H2 and 90 cm3 min−1 of Ar at a ramp rate of 10 °C min−1 from 25 to 1000 °C. Visible light absorption was measured with a V-650 (JASCO Corp.) X-ray photoelectron spectra (XPS) were measured with a JPS-9000 MX (JEOL Ltd.) using MgKα radiation at 10 kV and 10 mA. Peak position was calibrated for Cls at 284.2 eV. Energy dispersive X-ray absorption (EDX) was measured with an EMAX ENERGY (HORIBA Ltd.) attached to an FE-SEM (Hitachi High-Technologies Corp., S-4800) at 20 kV and magnification of 2500 times.

2.3. Hydrogenation of Lactic Acid and Analysis of Products

Typically, 1.23 g (13.7 mmol) of lactic acid and 37.7 g of distilled water as a solvent were introduced into a 200 cm3 stainless steel autoclave (Taitatsu Techno Corp., Japan), and 0.80 g of the catalyst was added. After purging the autoclave three times with nitrogen, the autoclave was pressurized with hydrogen to 4.0 MPa (gauge pressure). The temperature was then increased to 190 °C and maintained at this temperature for 4 h without supply of hydrogen. The stirring rate was adjusted to 1000 rpm to circumvent the diffusional limitation of hydrogen. The initial hydrogen pressure was 6.15 ± 0.10 MPa at 190 °C. After the reaction, the heater was removed and the temperature was lowered rapidly.

Gaseous products, methane, ethane, propane, CO and CO2, were collected into a gas reservoir and analyzed with a gas chromatograph (Shimadzu Corp., GC-8A) equipped with a thermal conductivity detector. Porapak Type Q and Molecular Sieve 13X packed in glass columns (i.d. 3.2 mm and length 2.0 m) were used. For analysis of the liquid products, the catalyst was removed by centrifugation. A 4.0 g portion of the solution was mixed with 0.50 g of ethylene glycol as an internal standard, and the products were analyzed with a gas chromatograph (Shimadzu Corp., GC-18A) equipped with a flame ionization detector. A capillary column (BP21 (polar), SGE Corp., length 25 m, internal diameter 0.22 mm and film thickness 0.25 μm) was used to analyze 1,2-PDO, 1-propanol and lactic acid. The material balance based on carbon (C3 unit) was 100 ± 5 %. Identification of products was conducted with a GC-MS (Shimadzu Corp., GC-MS-QP2010 Plus). Hydrogenation of 1,2-PDO used similar reaction conditions with 1.66 g (20.0 mmol) of 1,2-PDO instead of lactic acid.
### 3. Results and Discussion

#### 3.1. Catalyst Screening

The hydrogenation of carboxylic acids and their esters has been extensively investigated using many catalysts\(^{10}~^{13}\). Binary catalysts are preferably used for their high selectivity for the target alcohols. Ru or Rh is the main choices for precious metal catalysts. Some of the present authors have also studied the hydrogenation of fatty acid methyl esters\(^ {13}\) and dimethyl adipate\(^ {21}\) using Ru and Rh based catalysts. In the present study, we chose Ru as the main component because of its high activity for the hydrogenation of carboxylic acids.

| Catalyst | Conv. [%] | Selectivity [%] |
|----------|-----------|-----------------|
| Ru [%]   | M\(^a\)   | 1,2-PDO | CH\(_4\) | C\(_2\)H\(_6\) | C\(_3\)H\(_8\) | CO\(_x\) |
| 0.50     | -         | 3.9    | 96.3 | 0.5 | 0.0 | 0.0 | 3.2 |
| 1.0      | -         | 7.1    | 89.1 | 8.0 | 0.2 | 5.7 | 4.2 |
| 2.0      | -         | 11.9   | 82.4 | 3.1 | 0.4 | 8.5 | 12.8 |
| 5.0      | -         | 31.7   | 80.3 | 1.8 | 0.5 | 10.2 | 7.1 |
| 7.0      | -         | 41.3   | 77.8 | 2.2 | 0.7 | 13.7 | 6.2 |
| 5.0 Sn(Cl\(_2\))\(^b\) | 11.0     | 99.8   | 0.0 | 0.1 | 0.0 | 0.1 |
| 5.0 Cu   | 8.2       | 79.7   | 4.5 | 0.5 | 9.2 | 6.1 |
| 5.0 Zn   | 14.1      | 78.2   | 5.4 | 0.4 | 9.5 | 6.5 |
| 5.0 Co   | 8.6       | 72.4   | 5.6 | 0.8 | 15.7 | 5.6 |
| 5.0 Fe   | 36.5      | 67.8   | 8.7 | 0.5 | 21.2 | 1.8 |

| Catalyst | Conv. [%] | Selectivity [%] |
|----------|-----------|-----------------|
| Sn source | Sn/Ru [-] | 1,2-PDO | 1-Propanol | CH\(_4\) | C\(_2\)H\(_6\) | C\(_3\)H\(_8\) | CO\(_x\) |
| -        | 0         | 31.7 | 80.3 | - | 1.8 | 0.5 | 10.2 | 7.1 |
| Sn(Cl\(_2\))\(^a\) | 0.25     | 9.2 | 93.1 | - | 2.5 | 0.1 | 2.7 | 1.5 |
|          | 0.50      | 6.3 | 98.5 | - | 0.0 | 0.1 | 0.1 | 1.3 |
|          | 1.0       | 11.0 | 99.8 | - | 0.0 | 0.1 | 0.0 | 0.1 |
|          | 2.0       | 3.0 | 96.1 | - | 0.0 | 3.2 | 0.0 | 0.7 |
| Sn(Cl\(_4\))\(^b\) | 0.50     | 14.8 | 97.4 | 2.6 | - | - | - | - |
|          | 1.0       | 33.2 | 97.1 | 2.9 | - | - | - | - |
|          | 2.3       | 8.4 | 94.6 | 5.4 | - | - | - | - |

a) Catalysts (0.5-7.0 % Ru/C and 5.0 % Ru-M/C (1000 m\(^2\) g\(^{-1}\)): 0.800 g, lactic acid: 12.3 g, water: 27.7 g, initial \(P_{H_2}\): 6.0 MPa-G (r. t.), 150 °C, 1000 rpm, 4 h.  
\(b\) M/Ru (molar ratio) = 1.  
c) Prepared with SnCl\(_2\) \(2\)H\(_2\)O.

#### 3.2. Detailed Studies on the Formation of Catalysts

Firstly, the XRD patterns of monometallic catalysts were investigated (Fig. 1). No peaks were observed for Ru/C and Ru was highly dispersed on the carbon support. The broad peak around \(2\theta = 43.5°\) was

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**Table 1** Effects of Ru Loading and Combination with Secondary Metal (M) on Hydrogenation of Lactic Acid\(^a\)

| Catalyst | Conv. [%] | Selectivity [%] |
|----------|-----------|-----------------|
| Ru [%]   | M\(^a\)   | 1,2-PDO | CH\(_4\) | C\(_2\)H\(_6\) | C\(_3\)H\(_8\) | CO\(_x\) |
| 0.50     | -         | 3.9    | 96.3 | 0.5 | 0.0 | 0.0 | 3.2 |
| 1.0      | -         | 7.1    | 89.1 | 8.0 | 0.2 | 5.7 | 4.2 |
| 2.0      | -         | 11.9   | 82.4 | 3.1 | 0.4 | 8.5 | 12.8 |
| 5.0      | -         | 31.7   | 80.3 | 1.8 | 0.5 | 10.2 | 7.1 |
| 7.0      | -         | 41.3   | 77.8 | 2.2 | 0.7 | 13.7 | 6.2 |
| 5.0 Sn(Cl\(_2\))\(^b\) | 11.0     | 99.8   | 0.0 | 0.1 | 0.0 | 0.1 |
| 5.0 Cu   | 8.2       | 79.7   | 4.5 | 0.5 | 9.2 | 6.1 |
| 5.0 Zn   | 14.1      | 78.2   | 5.4 | 0.4 | 9.5 | 6.5 |
| 5.0 Co   | 8.6       | 72.4   | 5.6 | 0.8 | 15.7 | 5.6 |
| 5.0 Fe   | 36.5      | 67.8   | 8.7 | 0.5 | 21.2 | 1.8 |

**Table 2** Effects of Molar Ratio of Sn to Ru and Sn Sources on Hydrogenation of Lactic Acid

| Sn source | Sn/Ru [-] | Conv. [%] | Selectivity [%] |
|-----------|-----------|-----------|-----------------|
| -         | 0         | 31.7      | 80.3 | - | 1.8 | 0.5 | 10.2 | 7.1 |
| Sn(Cl\(_2\))\(^a\) | 0.25     | 9.2 | 93.1 | - | 2.5 | 0.1 | 2.7 | 1.5 |
|          | 0.50      | 6.3 | 98.5 | - | 0.0 | 0.1 | 0.1 | 1.3 |
|          | 1.0       | 11.0 | 99.8 | - | 0.0 | 0.1 | 0.0 | 0.1 |
|          | 2.0       | 3.0 | 96.1 | - | 0.0 | 3.2 | 0.0 | 0.7 |
| Sn(Cl\(_4\))\(^b\) | 0.50     | 14.8 | 97.4 | 2.6 | - | - | - | - |
|          | 1.0       | 33.2 | 97.1 | 2.9 | - | - | - | - |
|          | 2.3       | 8.4 | 94.6 | 5.4 | - | - | - | - |

a) Catalyst (5.0 % Ru-Sn/C (1000 m\(^2\) g\(^{-1}\)): 0.800 g, lactic acid: 12.3 g, water: 27.7 g, initial \(P_{H_2}\): 6.0 MPa-G (r. t.), 150 °C, 1000 rpm, 4 h.  
b) Catalyst (5.0 % Ru-Sn/C (1000 m\(^2\) g\(^{-1}\)): 0.800 g, lactic acid: 1.96 g, water: 37.7 g, initial \(P_{H_2}\): 4.0 MPa-G (r. t.), 150 °C, 1000 rpm, 1 h.
assigned to the carbon support. For Sn/C prepared with SnCl₂ or SnCl₄, sharp peaks ascribed to metallic Sn were observed, especially at 2θ = 31, 32 and 45°. However, combination of Ru and Sn species showed greatly different findings as follows.

Figure 2 shows the XRD patterns of Ru–Sn/C catalysts prepared by co-impregnation with various metal sources. The catalysts prepared using RuCl₃ and SnCl₂ showed a distinct pattern with peaks at 2θ = 40, 58 and 73°. Similar XRD pattern was observed for the catalyst prepared with Ru(NO₃)₃ and Sn(OCOCH₃)₂. Use of Ru(NO)(NO₃)₃ in combination with SnCl₂ resulted in peaks ascribed to Sn metal but no peaks for Ru metal. Using RuCl₃ with SnCl₄, no distinct peaks were observed. These results suggest that use of RuCl₃ and SnCl₄ resulted in good dispersion of the metals on the carbon support, whereas use of Ru(NO)(NO₃)₃ and SnCl₂ resulted in good dispersion of Ru but formation of large particles of Sn, probably on the external surface of the carbon support. Using RuCl₃ and SnCl₂ or Ru(NO₃)₃ and Sn(OCOCH₃)₂ resulted in formation of large particles of Ru and Sn with Sn/Ru = 1. Detailed analysis of this compound will be given later. Comparison with the results in Fig. 1 suggests that some phenomenon occurred in the impregnation solution involving the Ru and Sn sources.

To investigate the phenomenon occurring during the impregnation procedure, sequential impregnation of Ru on Sn/C or Sn on Ru/C was studied using RuCl₃, SnCl₂ and SnCl₄ as metal sources. After impregnation of the first metal source, the dried precursor was once reduced at 350 °C, and then the second metal source was impregnated, dried and the product was reduced again. As shown in Fig. 3, XRD of Sn impregnated on Ru/C using SnCl₂ (Fig. 3 a)) or Sn/C prepared using SnCl₂ impregnated with RuCl₃ (Fig. 3 b)) did not demonstrate the distinct pattern observed for the catalyst prepared by the co-impregnation of RuCl₃ and SnCl₂. In particular, the sharp peaks observed for Sn/C were completely absent, which suggests that at least part of the large metallic Sn particles dissolved during the impregnation of RuCl₃. However, XRD of Sn/C prepared using SnCl₄ then impregnated with RuCl₃ (Fig. 3 d)) did show the distinct pattern although the intensities of the peaks were very low compared to those of the co-impregnation product. Again, the sharp peaks observed for Sn/C were completely absent. XRD of Ru/C impregnated with SnCl₄ (Fig. 3 c)) detected other peaks ascribed to Ru₃Sn₇. However, when SnCl₂ was impregnated on Ru/C, this pattern was not detected (vide supra) possibly because of the difference in the number of Cl atoms.

The formation of the distinct XRD pattern presumably depends on the co-existence of Ru and Sn species in the solution, suggesting that Ru species and Sn species interact in the solution and this interaction depends on the amount of Cl present. Therefore, we added the required amount of Cl⁻ using 0.02 M (1 M = 1 mol L⁻¹) of HCl solution to the impregnation solution containing

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*Fig. 1 XRD Patterns of Monometallic Catalysts*

*Fig. 2 XRD Patterns of Ru–Sn/C Catalysts Prepared by Co-impregnation Method with Various Ru and Sn Sources*

*Fig. 3 XRD Patterns of Catalysts Prepared by Sequential Impregnation*
RuCl₃ and SnCl₂ so that the amount of Cl in the solution became equal to that of the solution made from RuCl₃ and SnCl₄. As is shown in Fig. 4, the distinct pattern was not observed. Doubling of the amount of added Cl⁻ (Fig. 4 c)) again resulted in no distinct XRD pattern. These findings suggest that the interaction between RuCl₃ and SnCl₂ was prevented by the presence of added Cl⁻. The pH was measured to be 1.40, 1.72 or 1.60 for the impregnation solutions of RuCl₃-SnCl₄, RuCl₃-SnCl₂ or RuCl₃-SnCl₂ with 0.02 mol L⁻¹ HCl, respectively. Compared to the significant differences in metal structures for the catalysts prepared from RuCl₃-SnCl₂ (Fig. 4 a) and RuCl₃-SnCl₂ with 0.02 mol L⁻¹ HCl (Fig. 4 b), differences in pH were not large.

RuCl₃ and SnCl₂ may form a complex during the impregnation, so that the time for standing the prepared impregnation solution may be important. Therefore, the time before impregnation after mixing the two metal sources was varied and the XRD patterns of obtained catalysts are given in Fig. 5. With very short times, namely immediate impregnation after dissolving the two metal sources, the distinct peaks were small. To directly observe the interaction between RuCl₃ and SnCl₂ or RuCl₃ and SnCl₄, the visible light absorption of the impregnation solution was measured and the preliminary results are given in Fig. 6. At present, we cannot provide a detailed description of the mechanisms, but clearly the absorption spectra differed between the two combinations and were affected by heating to 70 °C. Therefore, the interaction between RuCl₃ and SnCl₂ in the impregnation solution is one of the key factors for the metal structure of the final catalysts.

The above findings indicate that the interaction between metal sources in the impregnation solution have significant influences on the metal structure of the final catalyst. Here, we have to confirm if the same species are actually formed from the combinations of RuCl₃ and SnCl₂ and RuCl₃ and SnCl₄. To confirm this point, two solutions of the same composition as used for the co-impregnation were prepared. These solutions were dried and the remaining powders were reduced under the same conditions used for the catalysts. The XRD patterns obtained for these reduced powders are given in Fig. 7. Clearly, the same XRD pattern as that observed for 5 % Ru-5.9 % Sn/C catalyst prepared with RuCl₃ and SnCl₂ was observed irrespective of the Sn sources (Fig. 7 c) and d)). These findings suggest that even though no peaks were observed for the catalyst prepared from RuCl₃ and SnCl₄, the same RuSn species was formed on the support but the particle size was too small to be detected by XRD.

To further confirm the formation of these very small particles from RuCl₃ and SnCl₂, the hydrogen reduction temperature was varied and the obtained XRD patterns are shown in Fig. 8. No distinct peaks were observed for the catalyst prepared from RuCl₃ and SnCl₂ and reduced at 350 °C (standard condition). However, the distinct pattern appeared when the reduction temperature was raised to 450 °C or 550 °C. This observation indicates that even though Ru–Sn particles were not observed at the lower reduction temperature, the same

Fig. 4 Effect of Addition of Cl⁻ during Impregnation Using RuCl₃ and SnCl₂

Fig. 5 Effect of Aging Time of Impregnation Solution on XRD Patterns of Obtained Catalysts Prepared Using RuCl₃ and SnCl₄

Fig. 6 Changes in Visible Light Absorption of Impregnation Solution at Room Temperature and 70 °C
kind of very small particles not detectable by XRD were present on the support. Further, we adopted a carbon support with a lower surface area of 200 m² g⁻¹, and prepared a catalyst using RuCl₃ and SnCl₄. The catalyst obtained showed the same distinct XRD pattern as observed for the catalyst prepared from RuCl₃ and SnCl₂ (Fig. 9). This observation also supports our idea that very small but the same kind of intermetallic particles are formed for catalysts prepared from RuCl₃ and SnCl₄ even though the distinct XRD pattern is not observed.

The reduction behavior of catalyst precursors after impregnation and drying was studied by H₂-TPR as shown in Fig. 10. RuCl₃ was reduced at 250 °C, and SnCl₂ and SnCl₄ were reduced at higher temperatures than 250 °C. Combination of SnCl₂ or SnCl₄ with RuCl₃ promoted the reduction of SnCl₂, which suggests that RuCl₃ and SnCl₂ or SnCl₄ were closely located in the dried catalyst precursor. The same phenomenon was observed for the combination of Ru(NO₃)₃ and Sn(OCOCH₃)₂. Here, we mention that XPS results (data not shown) have suggested that both Ru and Sn were present as metals in accordance with the weight loss observed by H₂-TPR.

The interaction between Ru species and Sn species was examined by calculating the metal particle sizes using Scherrer’s equation (Table 3). The sizes of the Sn particles were calculated to be 590 Å and 520 Å for monometallic Sn/C catalysts prepared using SnCl₂ and SnCl₄, respectively. On the other hand, irrespective of the presence of the carbon support, the combination of Ru and Sn resulted in smaller particle sizes, suggesting some type of interaction between Ru species and Sn species. This finding supports the discussion above for the interaction of the two species in the impregnation solution.

3.3. Crystalline Structure

Up to now, we have suggested that a compound with a distinct XRD pattern with Sn/Ru ratio of unity was formed for the catalyst prepared from RuCl₃ and SnCl₂, Ru(NO₃)₃, and Sn(OCOCH₃)₂, and even from RuCl₃ and SnCl₄. Here, we would like to show that the species is a RuSn intermetallic compound with a body-centered cubic structure. Figure 11 compares the distinct XRD pattern observed for the material prepared from the solution of RuCl₃ and SnCl₂ with that of (Co₀.₈Ni₀.₂)Zr reported as PDF(ICDD) 01-071-7889, with a crystal structure reported as body-centered cubic (bcc). Clearly, the patterns match very well, suggesting the same bcc structure for RuSn. The Rietveld analysis in Fig. 12 reveals that the pattern shows excellent matching and that the discrepancy is due to the presence of a small amount of another intermetallic compound of Ru₃Sn₇. Elemental analysis by EDX (Table 4) indicated that the molar ratio Ru to Sn of the catalyst was close to unity, confirming again the formation of the RuSn intermetallic compound.
3. Optimization of the Reaction Conditions and Comparison of Yield with Literature

At first, the concentration of lactic acid was varied and the results are shown in Table 5. Decreased concentration of lactic acid increased the conversion of lactic acid to complete conversion at 0.55 M with 97.3% selectivity to 1,2-PDO. Further decrease in the concentration of lactic acid caused a significant loss of 1,2-PDO selectivity with the formation of propane due to consecutive hydrogenolysis. Using a hydrogen pressure higher than 4.0 MPa (initial), complete conversion of lactic acid was obtained. Using a hydrogen pressure of 6.0 MPa (initial), the formation of propane and other paraffins was increased. Investigation of the reaction time revealed that even for 1 h, the conversion of lactic acid was 100.0% with 97.5% selectivity of 1,2-PDO. Longer reaction time did not decrease 1,2-PDO selectivity, probably because the hydrogen pressure was lowered to 4.0 MPa and hydrogenolysis of 1,2-PDO was suppressed. These dependences on the concentration of lactic acid, hydrogen pressure and reaction time are mostly consistent with those previously reported for liquid phase hydrogenation3),4) and for vapor phase hydrogenation of lactic acid8).

Table 3  Crystallite Size of Sn or RuSn Calculated from XRD

| Catalyst Crystal | \(d^\circ [\text{Å}]\) |
|------------------|---------------------|
| Sn(Cl\(_2\))/C   | 590                 |
| Sn(Cl\(_4\))/C   | 520                 |
| Ru(NO)(NO\(_3\))\(_3\)-SnCl\(_2\)/C | 660 |
| RuSn(Cl\(_2\)) without C | 270 |
| RuSn(Cl\(_3\))/C | 230                 |
| RuSn(Cl\(_3\))/C-500 | 240 |
| RuSn(Cl\(_4\))/C-550 | 230 |
| RuSn(Cl\(_4\))/C (200 m\(^2\) g\(^{-1}\)) | 190 |

a) Crystallite size \(d = 0.9 \times 1.5418/(b \cdot \cos \theta)\), b) From (200) at \(2\theta = 30.56^\circ \pm 0.03^\circ\), c) From (110) at \(2\theta = 39.78^\circ \pm 0.06^\circ\).
parison with the literature data, the reaction temperature was decreased to 150°C with 0.55 M of lactic acid and 5.7 MPa of hydrogen (Table 6). As shown, 99% yield of 1,2-PDO was attained which was superior to the reported value of 92%3).

Finally, to understand the reason for the excellent selectivity for 1,2-PDO, hydrogenolysis of 1,2-PDO was studied using 5% Ru-5.9% Sn/C catalyst under the same reaction conditions in Table 6 except for the use of 1.66 g of 1,2-PDO in 37.7 g of water and reaction time between 1 to 5 h (data not shown). No substantial hydrogenolysis of 1,2-PDO was observed, which suggests that the reaction conditions adopted for the hydrogenation of lactic acid were adequate to maintain the high selectivity of 1,2-PDO by suppressing hydrogenolysis of the target product.

4. Conclusions

Preparation of carbon-supported bimetallic Ru-Sn catalysts was extensively studied and the obtained catalysts were used for the hydrogenation of lactic acid to synthesize 1,2-propanediol.

The sources of Ru and Sn significantly influenced the structure of the resultant catalysts. Using RuCl₃ and SnCl₂ as the sources of Ru and Sn, respectively, a distinct XRD pattern was observed which was confirmed as a RuSn intermetallic compound with a body-centered cubic structure. Using SnCl₄ instead of SnCl₂, no XRD pattern was observed, but the formation of very small particles of RuSn intermetallic compound was suggested. Visible light absorption indicated an interaction between Ru and Sn species in the impregnation solution, suggesting that this complex significantly influenced the final structure of the metals.

Reaction conditions for the hydrogenation of lactic acid were investigated and optimized. Consecutive hydrogenolysis of 1,2-propanediol was suppressed on Ru catalyst combined with Sn, so an almost quantitative yield of 1,2-propanediol was attained under the following reaction conditions: 0.80 g portion of 5% Ru-5.9% Sn/C catalyst prepared using RuCl₃ and SnCl₂ as metal sources, 0.55 M of lactic acid, 150°C, H₂ pressure of 5.7 MPa, 4 h reaction time and stirring rate of 1000 rpm. The yield and productivity are excellent compared to reported results adopting similar reaction conditions.

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Table 6 Comparison of Catalytic Performances

| Catalyst                  | Conv. [%] | 1,2-PDO sel. [%] | Conditions                                      |
|----------------------------|-----------|-----------------|------------------------------------------------|
| This work                  | 5 % Ru-5.9 % Sn/C | 100             | Catalyst: 0.80 g, lactic acid: 0.55 mol L⁻¹, P_{H₂}: 5.7 MPa-G, 150 °C, 4 h |
| Zhang et al.⁵⁶           | 5 % Ru/C  | 96              | Catalyst: 0.50 g, lactic acid: 0.55 mol L⁻¹, P_{H₂}: 14.5 MPa-G, 150 °C, 4 h |

a) Prepared by co-impregnation with RuCl₃ and SnCl₂.
b) Reference 3).

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要 旨
Ru-Sn/C触媒の調製とその乳酸水素化における性能
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活性炭担持Ru-Sn触媒を通常の浸没法で調製し、XRD、H₂-TPR、可視光吸収、EDXおよびXPSで特性を評価した。RuCl₃、Ru(NO)(NO₃)₂、SnCl₂、SnCl₆、あるいはSn(OCCOCH₃)₂の金属塩の組み合わせが得られる触媒の金属の状態に大きな影響を及ぼした。RuCl₃とSnCl₂を原料とした場合にはXRDでピークが見られず、金属は高分散していると推定された。一方、RuCl₃とSnCl₂またはSn(NO₃)₂、あるいはSn(OCCOCH₃)₂、あるいはRu(NO)(NO₃)₂とSn(OCCOCH₃)₂の組み合わせでは特徴的な回折パターンが認められ、これは体心立方構造の金属間化合物RuSnであることが分かった。RuCl₃とSnCl₂、あるいはRu(NO)(NO₃)₂とSn(OCCOCH₃)₂の組み合わせでは浸没作中にある種の錯体が生成していることが示唆された。乳酸の水素化を200 mLのオートクレープ内で、150 ～ 200 ºC、2 ～ 6 MPaの水素圧下（室温における初圧）で検討した。RuCl₃とSnCl₂から調製した触媒は、乳酸濃度0.55 M, 150 °C, 5.7 MPa, 4時間, 0.80 gの5 % Ru-5.9 % Sn/C触媒の酸化条件で、公知の触媒よりも優れた性能を示した。この触媒での1,2-プロパンジオールの収率と生産性は、それぞれ99.0 %, 0.51 g-cat⁻¹ h⁻¹ (6.7 mmol g-cat⁻¹ h⁻¹)であり、この高収率は本触媒で生成物の選移水素化が進行しないためと分かった。