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Synthesis of Bimetallic SnPt-Nanoparticle Catalysts for Chemoselective Hydrogenation of Crotonaldehyde: Relationship between Sn_xPt_y Alloy Phase and Catalytic Performance

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Graphical abstract



Highlight

- Effect of Sn_xPt_y alloy phase for <u>crotonaldehyde</u> hydrogenation is investigated.
- <u>SnPt-NP catalysts can be prepared by a polyalcohol reduction process.</u>
- Sn₁Pt₃, Sn₁Pt₁ and Sn₂Pt₁ alloy phases were formed by changing Sn/Pt atomic ratio.
- <u>Sn₁Pt₁ alloy is the most effective for selective formation of unsaturated alcohols.</u>

Abstract

Bimetallic SnPt-nanoparticle (SnPt-NP) catalysts with several types of Sn_xPt_y alloy structures were prepared using a polyalcohol reduction process; the catalytic behavior of each Sn_xPt_y alloy phase toward the selective hydrogenation of unsaturated aldehydes to the corresponding unsaturated alcohols was elucidated. Atomic absorption spectroscopy (AAS) and transmission electron microscopy (TEM) indicate that SnPt-NP catalysts with various Sn/Pt atomic ratios can be successfully prepared by a polyalcohol reduction process using $Pt(acac)_2$ and $Sn(AcO)_2$ as the metal precursors. X-ray diffraction (XRD) results reveal that the Sn₁Pt₃, Sn₁Pt₁, and Sn₂Pt₁ alloy phases are formed through control of the Sn/Pt atomic ratio of the starting mixture during preparation. The Sn₁Pt₃ alloy phase enhanced the hydrogenation of both the C=C and C=O bonds during the selective hydrogenation of crotonaldehyde. When only Sn₁Pt₁ alloy phases (Sn/Pt = 1.40), accompanying with separated Sn phase, were formed in the SnPt-NP catalysts, the highest unsaturated alcohol (UOL) selectivity (71.5% at 37.6% conversion) was observed. The formation of the Sn₂Pt₁ alloy phase led to decreased UOL selectivity. We suggest that the Sn₁Pt₁ alloy phase is an effective bimetallic SnPt hydrogenation catalyst for the selective formation of unsaturated alcohols.

Keywords: SnPt bimetallic catalysts, Nano particles, Polyalcohol reduction process, Selective hydrogenation, Unsaturated aldehyde

1. Introduction

Addition of Sn to Pt catalysts has been investigated in several different catalytic reaction systems [1-18]. These include the dehydrogenation of light alkanes [1-3], reforming of hydrocarbons [4-6], oxidation of carbon monoxide [7, 8], and selective hydrogenation of unsaturated carbonyl compounds [9-22].

During the selective hydrogenation of unsaturated carbonyl compounds, the addition of Sn to the hydrogenation catalyst has been reported to improve selectivity toward the corresponding unsaturated alcohols [9-22]. We have also investigated the selective hydrogenation of unsaturated aldehydes over bimetallic Sn-Pt and Sn-Rh catalysts [21-24].

The catalytic performance of bimetallic catalysts has been reported to depend on the Sn/Pt atomic ratio, precursors employed, and preparation procedures [9-22]. Even though the role of Sn is not yet completely understood, two effects have been proposed to explain the observed enhancement of catalytic selectivity by adding Sn. The carbonyl group is activated by an ionic Sn species (Sn²⁺ or Sn⁴⁺) through interactions with the oxygen atom of the carbonyl group; consequently, the hydrogenation of the C=O bond is facilitated [9-12]. Based on IR studies, we proposed that Sn plays an important role not only in the suppression of interactions between the C=C bond and the group 14 metal, but also in the selective activation of the carbonyl group [24]. The Pt ensembles are diluted by metallic Sn and are accompanied by the formation of Sn_xPt_y alloys. Pt ensembles preferentially activate the C=C bonds of unsaturated aldehydes, catalyzing the formation of the undesired saturated aldehydes and alcohols. Dilution of the Pt

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ensemble with metallic Sn sites hinders the hydrogenation of the C=C bond and inhibits the readsorption of the unsaturated alcohol; this suppressed further hydrogenation of the unsaturated alcohol to the corresponding saturated alcohol [9-11, 14]. Several researchers have investigated supported bimetallic SnPt catalysts using inert supports such as carbon or silica in order to remove any possible strong interactions involving the metal support [9, 10, 16]. Tin species on SnPt catalyst systems have been reported to be present in oxidized states, which include SnO_x species, and/or metallic states that form Sn_xPt_y alloy particles on the supported bimetallic SnPt catalysts. Claus [19] and Marinelli et al. [20] independently reported that C=O bonds are more easily activated over oxidized Sn species than the SnPt alloy phase formed in Sn-Pt/SiO₂. Coloma et al. [9, 10] suggested that the Sn₁Pt₁ alloy phase also suppresses the hydrogenation of the C=C double bond.

When supported bimetallic SnPt catalysts are prepared by conventional methods, such as the co-impregnation method, several Sn_xPt_y-alloy and Sn-oxide compositions are formed concurrently. The presence of several Sn sites of differing composition on these bimetallic SnPt catalysts makes it difficult to clarify which Sn sites determines the catalytic performance for the formation of unsaturated alcohols. Therefore, it is important to prepare bimetallic nanoparticles with "uniform composition and structure." Recently, methods for the preparation of unsupported monometallic and bimetallic nanoparticle (NP) have been investigated. For example, NPs composed of Co [25], Pt [26], CoPt [26-28], FePt [29, 30], and SnPt [31-34] have been successfully prepared by several procedures. If bimetallic SnPt NPs with various Sn/Pt atomic ratios can be

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prepared, then these unsupported catalysts can be applied in studies aimed at solving the above-mentioned problems, namely the interference by interactions involving the metal support.

In order to remove the effect of the metal support, the preparation of unsupported bimetallic SnPt-nanoparticle (SnPt-NP) catalysts was attempted using a polyalcohol reduction process. The Sn/Pt atomic ratios introduced in the prepared SnPt-NP catalysts during the polyalcohol reduction process were varied to form the several types of Sn_xPt_y alloys. To find an effective bimetallic SnPt structure and composition, the bulk structures of the SnPt-NP catalysts obtained in this study were examined by XRD measurements. We show that these NPs not only catalyze the reduction of unsaturated aldehydes, but also selectively produce crotyl alcohol during the hydrogenation of crotonaldehyde.

2. Experimental

2.1. Catalyst preparation

2.1.1. Pt-NP and SnPt-NP catalysts

Unsupported Pt-NP and SnPt-NP catalysts were prepared by the polyalcohol reduction process in the liquid phase [26, 27, 32]. A three-neck round bottom flask was charged with a mixture of platinum(II) acetylacetonate (0.197 g), tin(II) acetate (0-0.177 g), oleic acid (0.32 mL), oleyl amine (0.34 mL), and 1,2-hexadecanediol (0.78 g) in dioctyl ether (20 mL). The Sn/Pt atomic ratio was controlled to be between 0 and 1.5 by varying the amount of introduced tin(II) acetate. N₂ was bubbled through the mixture while it was

heated to ~553 K using a heating mantle, followed by heating at reflux for 1 h. After cooling to room temperature, the mixture, which was originally yellow (without Sn precursor) or auburn (with Sn precursor) in color and had changed to black during heating, was centrifuged to separate the bimetallic nanoparticles. The supernatant was discarded, and the obtained precipitate was washed three times with ethanol (the total amount = 60 mL). The sample was dried at room temperature for 2 h in a vacuum desiccator to finally obtain Pt nanoparticle (Pt-NP) or SnPt nanoparticle (SnPt-NP) catalysts.

2.1.2. SiO₂-supported bimetallic Sn-Pt catalysts (Sn-Pt/SiO₂) prepared by the coimpregnation method

The Sn-Pt/SiO₂ catalysts were prepared by co-impregnating 1-2 g of a SiO₂ support at 353 K with an ethanolic solution (30 mL) of $H_2PtCl_6 \cdot 6H_2O$ and $SnCl_2 \cdot 2H_2O$. The Pt loading on the support was 4 wt% and the atomic ratio of Sn/Pt was between 0 and 2.0. The samples were dried overnight at 393 K in a static oven, then calcined at 823 K for 2 h under a flow of air, followed by reduction at 573 K for 2 h under a flow H₂.

2.2. Characterization

2.2.1. Atomic Absorption Spectroscopy (AAS)

The compositions of Pt and Sn in the Pt-NP and the SnPt-NP catalysts were determined by Atomic Absorption Spectroscopy (HITACHI, Z-2000). Prior to each measurement, 10 mg of the sample was dissolved in 10 mL of aqua regia at 353 K.

2.2.2. High Resolution Transmission Electron Microscopy (HR-TEM)HR-TEM images of the Pt-NP and the SnPt-NP (Sn/Pt = 1.40) were acquired on a JOELJEM2011 instrument operating at 200 kV.

2.2.3. X-ray diffraction (XRD)

X-ray powder diffraction patterns of the catalysts were acquired at room temperature using a Rigaku RINT-2000 instrument equipped with a Cu-K α radiation source. The X-ray tube operated at 40 kV and 40 mA. The diffraction patterns were recorded over the 20-60° 20 range at a rate of 0.5 °/min.

2.3. Chemoselective hydrogenation

The hydrogenation of crotonaldehyde was carried out in a stainless steel autoclave (30 mL). A glass tube was charged with crotonaldehyde (0.2 mL) in 2-methyl-2-butanol (4 mL) and 10 mg of NP catalysts was added. The glass tube was inserted into an autoclave such that the reactant solution was not in direct contact with the inner surface of the autoclave. The autoclave was charged and discharged with hydrogen several times in order to replace the air in the autoclave with hydrogen, after which it was charged with 2.0 MPa (gauge) of H₂. The autoclave was heated to 373 K in an oil bath in which the temperature was controlled by a temperature regulator, and the solution was vigorously agitated using a magnetic stirrer for 0.5 h. The autoclave was then cooled to 273 K to quench the reaction, and cyclohexane (0.2 mL) was added as an internal standard. The mixture was centrifuged to separate the catalyst, and the products were analyzed by gas

chromatography (GC) (GC-18A, Shimazu) with a G-300 column (Chemicals Evaluation and Research Institute, Japan; column dimensions: 40 m, 1.2 mm i.d., 1.0 μ m film thickness).

As for the hydrogenation of crotonaldehyde over the Sn-Pt/SiO₂ catalysts prepared by the co-impregnation method, the reaction was carried out at 373 K under 2.0 MPa (gauge) of H_2 for 1 h with 25 mg of catalysts.

3. Results and discussion

3.1. The Sn and Pt content of the SnPt-NP catalysts

The Pt nanoparticles and Pt-based bimetallic nanoparticles were previously prepared using a polyalcohol reduction process [26, 27, 32], and we applied this method to the preparation of the SnPt nanoparticles in this study. Table 1 lists the Pt and Sn compositions, and the Sn/Pt atomic ratios in each NP as determined by AAS. The amounts of Sn in the SnPt-NP catalysts increased, while the levels of Pt decreased with increasing amounts of Sn introduced during preparation. Each nanoparticle (Pt-NP and SnPt-NP) included ~30 wt% of unidentified compounds that could not be observed by AAS. These probably arise from the capping agents (oleyl amine and oleic acid) that stabilize the NPs, and the ethanol used for NP washing during preparation. The Sn/Pt atomic ratio in the various SnPt-NP catalysts as a function of the Sn/Pt atomic ratio of the starting mixture is shown in Fig. 1. As shown in Fig. 1, the Sn/Pt atomic ratios introduced during preparation. In the following sections, the Sn/Pt atomic ratios of the NP catalysts

are assumed to be those determined by AAS, as shown in Table 1.

3.2. Morphologies of the SnPt-NP catalysts

HR-TEM images of the Pt-NP and SnPt-NP (Sn/Pt = 1.40) prepared by polyalcohol reduction are displayed in Fig. 2. Nanoparticles with polyhedral structures are observed for the Pt-NP catalysts in Fig. 2a, and the diameters of these nanoparticles were in the 10-20 nm range. As for the SnPt-NP catalysts (Sn/Pt = 1.40) (Fig. 2b), smaller particles with diameters of 2-10 nm were obtained. The addition of Sn brought about a decrease in particle size compared to the Pt-NP catalysts, although the same amounts of Pt precursor, oleyl amine, oleic acid, and 1,2-hexadecanediol were employed during The initial Sn content has been reported to affect the particle size preparation. distribution of SnPt-NP; one is synthesized by a polyalcohol reduction method similar to our procedure except for Sn precursor using $Sn(acac)_2$ [32], and another is fabricated by contacting $Pt(dba)_2$ (dba = dibenzylidene acetone) and (n-Bu)₃SnH in THF under H₂ at room temperature without the use of stabilizing ligands [34]. A similar observation was observed during the synthesis of CoPt₃ nanoparticles, prepared by a polyalcohol reduction method via simultaneous reduction of Pt(acac)₂ and thermodecomposition of Co₂(CO)₈ in the presence of 1-adamantanecarboxylic acid and hexadecylamine as stabilizing agents [28]. This behavior was attributed to the apparent presence of a second metal species. Nevertheless, the effect of second metals on the size of bimetallic NPs is currently under investigation.

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3.3. Composition of the Sn_xPt_y alloys in various SnPt-NP catalysts of differing Sn/Pt atomic ratios

Figure 3 displays the XRD patterns of the Pt-NP, and SnPt-NP catalysts of varying Sn/Pt atomic ratios. The peaks at 20 values of around 39.5 and 46.5° are assigned to reduced Pt metal [27, 35, 36]. The peaks ascribed to the Sn₁Pt₁ alloy phase, in which the molar ratio of Sn to Pt is 1:1, appeared at 20 values of around 25.0, 30.0, 41.5, and 44.0° [37, 38], and the peaks attributed to the Sn₂Pt₁ alloy phase, in which the molar ratio of Sn to Pt is 2:1, can be observed at 20 values of around 24.0, 40.0, 47.0, and 57.5° [39].

In case of the Pt-NP catalysts, the observed peaks are characteristic of face-centeredcubic (fcc) crystalline Pt. Upon the addition of a small amount of Sn (Sn/Pt = 0.48), these diffraction peaks were observed to shift to slightly lower 20 diffraction angles than the corresponding Pt-NP peaks. The peaks at 20 values of 38.8 and 44.6° are assigned to the Sn₁Pt₃ alloy phase [40]. This result suggests that the lattice has undergone expansion resulting from the insertion of the larger Sn atoms into the fcc Pt unit structure in order to form the Sn₁Pt₃ alloy phase. The Sn₁Pt₁ alloy phase appeared at Sn/Pt atomic ratios between 0.71 and 0.92. In this ratio range, the Sn₁Pt₃ and Sn₁Pt₁ alloy phases were observed to coexist. The intensities of the peaks corresponding to the Sn₁Pt₃ phase were observed to decrease, while those of the Sn₁Pt₁ phase increased with increasing Sn content. The Sn₁Pt₁ alloy phase was the only phase observed at Sn/Pt atomic ratios between 1.40 and 1.51. The addition of further Sn (Sn/Pt = 2.19) brought about the formation of the Sn₂Pt₁ alloy phase.

The SnPt-NP catalysts with 1.51 and 2.19 of Sn/Pt atomic ratios showed Sn₁Pt₁ and

 Sn_2Pt_1 alloy phases, respectively. They are higher than 1 and 2 of stoichiometric Sn/Pt atomic ratios of Sn_1Pt_1 and Sn_2Pt_1 alloy phases, respectively. The excess amount of Sn would exist as Sn metal and/or Sn oxides nanoparticles which are separated from SnPt bimetallic nanoparticles.

3.4. Relationship between the Sn_xPt_y alloy composition and the catalytic performance of the SnPt-NP catalysts for selective hydrogenation of crotonaldehyde

The reaction pathway for the hydrogenation of crotonaldehyde is shown in Scheme 1. The hydrogenation of the C=O bond in crotonaldehyde gives crotyl alcohol (UOL, target The hydrogenation of the C=C bond in crotonaldehyde results in the molecule). production of butyraldehyde (SAL), while the sequential hydrogenation of UOL and SAL gives 1-butanol (SOL). These molecules were the only detected products in this study. Figure 5 depicts the catalytic activity and products distribution for hydrogenation of crotonaldehyde over the Pt-NP and SnPt-NP catalysts depend on the Sn/Pt atomic ratio of the various NPs. SAL was mainly formed over the monometallic Pt-NP catalyst. The conversion was significantly enhanced by the addition of a small amount of Sn (Sn/Pt = 0.48), after which it gradually decreased with increasing Sn content. The SAL selectivity gradually decreased until the Sn/Pt ratio reached 1.40, after which it gradually increased between Sn/Pt atomic ratios of 1.51 and 2.19. The maximum SOL selectivity was 28.2%, which was observed at a Sn/Pt ratio of 0.48, and this selectivity was almost constant over the 0.71-2.19 Sn/Pt ratio range. The selectivity for UOL gradually improved as the Sn/Pt ratio reached 1.40; the addition of further Sn decreased the UOL

selectivity. The highest UOL selectivity obtained was 71.5% at 37.6% conversion over the SnPt-NP (Sn/Pt = 1.40) catalyst.

It is well known that the conversion level also affects the selectivity of UOL, because the hydrogenation of crotonaldehyde is the successive reaction. Figure 6 shows the selectivity of UOL as a function of crotonaldehyde conversion for hydrogenation of crotonaldehyde over the SnPt-NP catalysts of varying Sn/Pt atomic ratios. The clear correlation between the conversion and the UOL selectivity, higher selectivity at only lower conversions, was not observed. These results strongly suggest that the UOL selectivity depends on the Sn_xPt_y alloy species in the SnPt-NPs catalysts.

Figure 7 shows the relationship between C=C and C=O bond hydrogenation and the Sn/Pt atomic ratio. The total amount of hydrogenated crotonaldehyde increased through the addition of a small amount of Sn (Sn/Pt = 0.48). Further addition of Sn resulted in a gradual decrease in the total amount of hydrogenation. As for the amounts of C=C hydrogenation products (SAL and SOL), their maximum conversions were at Sn/Pt = 0.48. On the other hand, the amount of C=O hydrogenation gradually increased as the Sn/Pt atomic ratio approached 0.92. These results indicate that increases in UOL selectivity are not only due to inhibition of the C=C hydrogenation reaction, but are also due to the acceleration of the C=O hydrogenation reaction over the bimetallic SnPt-NP catalysts. It should be noted that the addition of a small amount of Sn enhances the hydrogenation of both C=C bonds and carbonyl groups.

The reaction model for the hydrogenation of crotonaldehyde over the bimetallic SnPt NPs is shown in Scheme 2. With respect to the SnPt-NP catalysts with a Sn/Pt atomic

ratio of 0.48, the Sn₁Pt₃ alloy phase was the only observed phase by XRD (Fig. 4) and the total amount of crotonaldehyde hydrogenation was enhanced (Fig. 7). At this atomic ratio, the Sn₁Pt₃ phase facilitates hydrogenation on its own, presumably because of enhanced H₂ activation and/or enhanced C=C and/or C=O adsorption. At Sn/Pt atomic ratios between 0.71 and 1.50, the intensities of the XRD peaks corresponding to the Sn₁Pt₃ alloy gradually decrease and those of the Sn_1Pt_1 alloy phase gradually increase (Fig. 4). The phase transfer from Sn_1Pt_3 to Sn_1Pt_1 appears to correlate with catalytic performance; crotonaldehyde conversion gradually decreases but the selectivity for the formation of crotyl alcohol gradually increases as the intensities of the Sn₁Pt₁-alloy phase XRD peaks increase (Fig. 5). We suggest that the Sn₁Pt₁ alloy phase possesses higher UOL formation selectivity and lower catalytic H₂-activation activity in comparison with the Sn_1Pt_3 alloy phase. When Sn/Pt = 2.19, the XRD pattern indicates that the Sn_2Pt_1 alloy phase is mainly formed (Fig. 4). SAL is mainly formed during crotonaldehyde hydrogenation over the Sn₂Pt₁ alloy phase. Liberková et al. [39] also reported that UOL selectivity decreased upon formation of the Sn₂Pt₁ alloy phase. We reported that the isomerization of crotyl alcohol to butyraldehyde proceeds over Rh-Sn/SiO₂ catalysts [23]. In order to determine whether the decrease in UOL selectivity in the presence of the Sn₂Pt₁ alloy phase is due to the isomerization of UOL to SAL, or hydrogenation of the C=C bond, the hydrogenation of UOL was carried out for 2 h under 2.0 MPa of H₂ in the presence of SnPt-NP (Sn/Pt = 2.19) catalysts at 373 K; no formation of SAL was observed under these conditions, and a 6.8% yield of SOL was obtained. These results confirm that UOL does not isomerize to SAL, and that C=C bond hydrogenation takes place over

the Sn_2Pt_1 alloy phase. As for the structure of the Sn_2Pt_1 alloy phase, Pt ensembles are unlikely to exist because the amount of Sn present in this alloy is higher than that in the Sn_1Pt_1 alloy. The crystal structure of the Sn_2Pt_1 alloy phase has been ascribed as cubic [41]. Even though the arrangements of Sn and Pt in the Sn_2Pt_1 alloy are not yet understood, at least one of the lattice planes in the Sn_2Pt_1 alloy phase probably contains Pt ensemble sites that can activate hydrogen and C=C bonds. We suggest that the Sn_2Pt_1 alloy structure clearly causes UOL selectivity to decrease, although the reaction mechanism of hydrogenation (the C=C activation and the H₂ activation) over the Sn_2Pt_1 alloy phase is not well understood.

The SnPt-NP catalysts (Sn/Pt = 1.51) exhibited mainly Sn_1Pt_1 alloy phases, but the UOL selectivity was lower in comparison with the material produced when Sn/Pt = 1.40, implying that a small amount of the Sn_2Pt_1 alloy phase formed on these SnPt-NP catalysts. These results indicate that the intrinsic ability of the Sn_1Pt_1 alloy phase to form UOLs during the hydrogenation of unsaturated aldehydes is higher than other bimetallic SnPt alloy phases.

In order to compare the catalytic performance of the SnPt-NP catalysts with those of the Sn-Pt/SiO₂ catalysts prepared using the co-impregnation method, the dependence of Sn/Pt atomic ratios in the Sn-Pt/SiO₂ on the catalytic activity and the products distribution for crotonaldehyde hydrogenation in Fig. 8. The conversion decreased with increasing Sn content. The selectivity for UOL gradually improved with increasing Sn/Pt atomic ratios. The SOL selectivity was almost constant independent of Sn/Pt atomic ratios. The highest UOL selectivity obtained was 48.8% at 2.7% conversion over the Sn-Pt/SiO₂

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(Sn/Pt = 2.0) catalyst. As shown in Fig. 4, the Sn₁Pt₃ and Sn₁Pt₁ alloy phases were formed at the Sn/Pt atomic ratio between 1.5 and 2.0. The increase of UOL selectivity is suggested to be due to the formation of these alloy species over the Sn-Pt/SiO₂ catalysts. Figure 9 shows the selectivity of UOL as a function of crotonaldehyde conversion for hydrogenation of crotonaldehyde over the Sn-Pt/SiO₂ catalysts of varying Sn/Pt atomic ratios. Notably, the UOL selectivity markedly decreased from 33.7% (Sn/Pt = 1.0) to 9.5% (Sn/Pt = 0.5), even though the conversion only increased from 30.9% to 37.4%, respectively. The selectivity of UOL is considered to monotonically vary in accordance with the conversion level when the reaction proceeds over the same catalytic active species. This result also suggests that the selectivity of UOL is strongly affected by the surface species. It is implied that the Sn_xPt_y (probably Sn₁Pt₃) alloy phases are formed as small particles and/or thin layers on the surface of Sn-Pt/SiO₂ catalysts with 1.0 of Sn/Pt atomic ratio although the peaks attributed to these alloy species cannot be confirmed in XRD measurement (Fig. 4).

Figure 10 shows the relationship between C=C and C=O bond hydrogenation and the Sn/Pt atomic ratio over the Sn-Pt/SiO₂ catalysts. The total amount of hydrogenation and the amounts of C=C hydrogenation products decreased with increasing Sn content. The amount of C=O hydrogenation decreased until the Sn/Pt atomic ratio approached 0.5, increased at the Sn/Pt atomic ratio between 0.5 and 1.0, and then decreased over the 1.0-2.0 Sn/Pt ratio range. At the Sn/Pt atomic ratios higher than 1.0 on the Sn-Pt/SiO₂ catalysts, the Sn₁Pt₃ and Sn₁Pt₁ alloy phases were observed in XRD measurement (Fig. 4). These results strongly suggest that the catalytic selectivity over the Sn-Pt/SiO₂

catalysts prepared using the conventional co-impregnation catalysts also depends on the formed Sn_xPt_y alloy species.

The liquid phase hydrogenation of crotonaldehyde over the SnPt bimetallic catalysts was summarized in Table 2. The selectivity of UOL over the SnPt/SiO₂ catalysts prepared by the successive modification with Sn to Pt/SiO₂ catalysts (Entries 1 and 2) was higher than that prepared by the co-impregnation method (Entries 4 and 5). The XRD measurements of these catalysts have not been carried out in these papers. The preparation methods would affect the formation of Sn_xPt_y alloy phases in the SnPt bimetallic catalysts, bringing about the difference of catalytic performance for the hydrogenation of crotonaldehyde.

Catalytic activity (i.e. conversion of crotonaldehyde) was different between the SnPt-NP catalysts and the Sn-Pt/SiO₂ catalysts, which was due to the amount of surface Pt. The presence of capping agents (oleyl amine and oleic acid) in the SnPt-NP catalysts makes it difficult to estimate the amount of surface Pt by means of a conventional H₂ and CO chemisorption procedure, because the capping agents themselves probably affects the adsorption of H₂ and CO, and they are decomposed during the H₂ pretreatment at 573 K to sinter the nanoparticles. Therefore, we have not obtained the accurate data on the amount of surface Pt in this study yet. Further investigation must be necessary.

4. Conclusions

The selective hydrogenation of crotonaldehyde over SnPt nanoparticles prepared using a polyalcohol reduction process in the liquid phase was investigated. Key observations

are provided below.

1. SnPt NPs with various Sn/Pt atomic ratios can be successfully prepared by a polyalcohol reduction process using $Pt(acac)_2$ and $Sn(AcO)_2$ as precursors. Sn_1Pt_3 , Sn_1Pt_1 , and Sn_2Pt_1 alloy phases were formed by changing the atomic ratio of Sn to Pt introduced during preparation.

2. The relationship between catalytic behavior for selective hydrogenation of crotonaldehyde and the alloy structure was also investigated. The Sn_1Pt_3 alloy phase was observed to bring about a significant enhancement in conversion and C=O hydrogenation. When only the Sn_1Pt_1 alloy phase was formed in the SnPt NPs (Sn/Pt = 1.40), the highest UOL selectivity (71.5% at a conversion of 37.6%) was obtained. The formation of the Sn_2Pt_1 alloy phase led to a decrease in UOL selectivity. We strongly suggest that the Sn_1Pt_1 alloy is the most effective Sn_xPt_y phase for the selective formation of unsaturated alcohols.

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Fig. 1 Sn/Pt atomic ratio in the nanoparticles determined by AAS as a function of Sn/Pt atomic ratio in starting mixture during preparation. The dashed line of unit slope indicates where the Sn/Pt atomic ratio of the NP is equal to the Sn/Pt atomic ratio in the starting mixture.



Fig. 2 TEM images of (a) Pt-NP and (b) SnPt-NP (Sn/Pt=1.40) catalysts



Fig. 3 XRD patterns of Pt-NP and SnPt-NP catalysts: Sn/Pt= 0 (a), 0.48 (b), 0.71 (c), 0.92 (d), 1.40 (e), 1.51 (f) and 2.19 (g).



Fig. 4 XRD patterns of Pt/SiO_2 and $Sn-Pt/SiO_2$ prepared by the conventional coimpregnation method: Sn/Pt=0 (a), 0.2 (b), 0.5 (c), 1.0 (d), 1.5 (e), and 2.0 (f).



Fig. 5 Dependence of Sn/Pt atomic ratio for crotonaldehyde hydrogenation over the SnPt-NP catalysts: (a) conversion and (b) selectivity of products.



Fig. 6 Relationship between the conversion of crotonaldehyde and the selectivity of crotylalcohol for the hydrogenation of crotonaldehyde over the SnPt-NP catalysts. The number described near each plot indicates the Sn/Pt atomic ratio in the SnPt-NP catalysts.



Fig. 7 Dependence of Sn/Pt atomic ratio on the amount of hydrogenation of the C=C bond and C=O bond.



Fig. 8 Dependence of Sn/Pt atomic ratio in the Sn-Pt/SiO₂ catalysts for crotonaldehyde hydrogenation over the Sn-Pt/SiO₂ catalysts prepared by the co-impregnation method: (a) conversion and (b) selectivity of products.



Fig. 9 Relationship between the conversion of crotonaldehyde and the selectivity of crotylalcohol for the hydrogenation of crotonaldehyde over the $Sn-Pt/SiO_2$ catalysts. The number described near each plot indicates the Sn/Pt atomic ratio in the $Sn-Pt/SiO_2$ catalysts.



Fig. 10 Dependence of Sn/Pt atomic ratio in the Sn-Pt/SiO₂ catalysts on the amount of hydrogenation of the C=C bond and C=O bond.



Scheme 1 Reaction pathway of crotonaldehyde hydrogenation

Scheme 2 Reaction model of crotonaldehyde hydrogenation over SnPt-NP (Sn/Pt=0-2.19) catalysts.

						Sn/Pt atomic
Entry	Catalst	Sn/Pt atomic ratio	Pt	Sn	Others*	ratio
		in starting mixture				
		(-)	(g/g-cat.)	(g/g-cat.)	(g/g-cat.)	in particle (-)
	Pt					
1	NPs	0	0.69	0	0.31	0
	SnPt					
2	NPs	0.2	0.55	0.16	0.29	0.48
3		0.5	0.51	0.22	0.27	0.71
4		0.7	0.44	0.24	0.32	0.92
5		1.0	0.35	0.30	0.34	1.40
6		1.2	0.40	0.37	0.23	1.51
7		1.5	0.30	0.40	0.30	2.19

Table 1Composition of Pt and Sn estimated by AAS in each nanoparticle.Table 1

* Others included oleyl amine, oleic acid and ethanol.

Reaction condition				Conv.	UOL	Ref.
<u> </u>	Temp.	Pressure	Time	(%)	sel.	
Solvent	(K)		(h)		(%)	
E thanol + H_2O	297	25 bar	16	65 ^{<i>a</i>}	51	[15]
2 Propagol	298 0.	0.1 MPa	-	5	80	[16]
2-r 10pail01				90	60	
2. Propanol	313	313 1.0 MPa	-	20	24	[17]
2-110panoi				80	18	
2 Mothyl 2 hutanol	373	73 2.0 MPa	2	37	9	This
2-memyi-2-outanoi						work
2 Mothyl 2 hutanol	373	373 2.0 MPa	2	7	44	This
2-memyi-2-outanoi						work
2 Mothyl 2 hutanol	373	2.0 MDo	0.5	38	72	This
2-ivietityi-2-outanoi		2.0 MPa	0.3			work

Table 2Liquid phase hydrogenation of crotonaldehyde over SnPt bimetallic catalysts.