1. Introduction

Chemoselective reactions convert specific functional groups of a multifunctional compound into other moieties, so are extremely important for the synthesis of value-added chemicals, such as the selective hydrogenation of unsaturated aldehydes to form unsaturated alcohols, which are used for perfume, pharmaceutical, and fine chemical production. In the case of SnPt catalysts, the presence of metallic Sn and the formation of Sn-Pt alloys are believed to be key factors strongly affecting the selectivity of unsaturated alcohol formation. This review describes the relationship between the catalytic crotonaldehyde (CH₃–CH = CH–CHO) hydrogenation performance of supported and non-supported SnPt catalysts and the structure of the component SnPt alloys, which reveal that at the same Sn/Pt atomic ratio, the composition of the produced SnPt alloys depends on the preparation method. The SnPt₃, SnPt₄, and SnPt₅ phases identified in SnPt catalysts exhibited higher crotyl alcohol (CH₃–CH = CH–CH₂OH) formation selectivity than the monometallic Pt phase. Furthermore, the SnPt₁ and SnPt₂ phases showed lower crotonaldehyde conversion than the Pt phase. Formation of Sn oxides over the supported SnPt catalysts was confirmed with excess amount of Sn. The crotyl alcohol selectivity increased with the transition from SnPt₃ to SnPt₁, then decrease with the further transition to the more Sn-rich SnPt₂ phase. Thus, the SnPt₁ alloy phase was concluded to be the most effective bimetallic SnPt structure for the selective formation of crotyl alcohol.

Keywords

Selective hydrogenation, Tin platinum catalyst, Nanoparticle, Unsaturated aldehyde, Unsaturated alcohol

[Review Paper]

Effects of SnₓPtᵧ Alloy Structures on the Performance of SnPt Catalysts for the Selective Hydrogenation of Unsaturated Aldehydes to Unsaturated Alcohols

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The development of next-generation heterogeneous catalysts for the chemoselective hydrogenation of unsaturated aldehydes to unsaturated alcohols requires extensive structural understanding of active catalyst sites. In the case of SnPt catalysts, the presence of metallic Sn and the formation of Sn-Pt alloys are believed to be key factors strongly affecting the selectivity of unsaturated alcohol formation. This review describes the relationship between the catalytic crotonaldehyde (CH₃–CH = CH–CHO) hydrogenation performance of supported and non-supported SnPt catalysts and the structure of the component SnPt alloys, which reveal that at the same Sn/Pt atomic ratio, the composition of the produced SnPt alloys depends on the preparation method. The SnPt₃, SnPt₄, and SnPt₅ phases identified in SnPt catalysts exhibited higher crotyl alcohol (CH₃–CH = CH–CH₂OH) formation selectivity than the monometallic Pt phase. Furthermore, the SnPt₁ and SnPt₂ phases showed lower crotonaldehyde conversion than the Pt phase. Formation of Sn oxides over the supported SnPt catalysts was confirmed with excess amount of Sn. The crotyl alcohol selectivity increased with the transition from SnPt₃ to SnPt₁, then decrease with the further transition to the more Sn-rich SnPt₂ phase. Thus, the SnPt₁ alloy phase was concluded to be the most effective bimetallic SnPt structure for the selective formation of crotyl alcohol.

Keywords

Selective hydrogenation, Tin platinum catalyst, Nanoparticle, Unsaturated aldehyde, Unsaturated alcohol

1. Introduction

Chemoselective reactions convert specific functional groups of a multifunctional compound into other moieties, so are extremely important for the synthesis of value-added chemicals, such as the selective hydrogenation of unsaturated aldehydes to unsaturated alcohols, which are used for perfume, pharmaceutical, and fine chemical production.

The formation of saturated aldehydes preferentially proceeds over conventional (e.g., supported group VIII metal) hydrogenation catalysts. The modification of noble metal catalysts with secondary metals or their oxides is reported to prevent C=C bond hydrogenation and/or promote C=O bond hydrogenation to improve the selectivity for unsaturated alcohol formation. Scheme 1 shows the reaction pathway for the hydrogenation of crotonaldehyde as a model unsaturated aldehyde to form crotyl alcohol (UOL) or butyraldehyde (SAL), both of which can be further hydrogenated to generate 1-butanol (SOL).

Bimetallic SnPt catalysts are widely used for the hydrogenation of unsaturated aldehydes (e.g., supported group VIII metal) hydrogenation catalysts depend on factors such as the Sn/Pt atomic ratio, types of precursors and supports, and preparation procedures/conditions. The function of the Sn component is not yet fully understood, but the improvement in catalytic selectivity achieved by inclusion of Sn has been ascribed to two effects. First, ionic Sn species (Sn²⁺ or Sn⁴⁺) are believed to interact with the carbonyl oxygen of unsaturated aldehydes, resulting in activation of the C=O group and acceleration of the hydrogenation reaction (e.g., supported group VIII metal) hydrogenation catalysts depend on factors such as the Sn/Pt atomic ratio, types of precursors and supports, and preparation procedures/conditions. The function of the Sn component is not yet fully understood, but the improvement in catalytic selectivity achieved by inclusion of Sn has been ascribed to two effects. First, ionic Sn species (Sn²⁺ or Sn⁴⁺) are believed to interact with the carbonyl oxygen of unsaturated aldehydes, resulting in activation of the C=O group and acceleration of the hydrogenation reaction. Second, metallic Sn is thought to dilute the Pt ensembles and form Sn-Pt alloys. Pt ensembles are known to activate the C=C bonds of unsaturated aldehydes, thus catalyzing the undesired formation of saturated compounds, so dilution of Pt ensembles prevents C=C bond hydrogenation in unsaturated aldehydes and alcohols.

The well-characterized Sn-Pt phase diagram describes the formation of five different alloy phases, face-centered cubic (fcc) SnPt₃, hexagonal SnPt₁, hex-
agonal SnPt₅, cubic Sn₂Pt₃, and orthorhombic Sn₄Pt₁₂3). However, the relationships between the properties of Sn₄Pt₁₂ alloys and their catalytic activities are not yet understood, as mono- and bimetallic phases cannot be observed in the very active SnPt bimetallic catalysts because of the presence of highly dispersed metal species11). Therefore, investigation of the catalytic behavior of specific Sn₄Pt₁₂ alloys for unsaturated aldehyde hydrogenation may facilitate the design of SnPt catalysts with high selectivity for unsaturated alcohols.

The present study describes the hydrogenation of crotonaldehyde over SiO₂-supported SnPt catalysts prepared by co-impregnation20 and successive impregnation25, and over SnPt nanoparticles (SnPt-NPs) synthesized by a polyalcohol reduction method26. The bulk structures of SnPt catalysts were analyzed by X-ray diffraction (XRD) to identify the most effective SnPt structure and composition. Furthermore, the relationships between Sn₄Pt₁₂ alloy structures and their catalytic performance for the hydrogenation of crotonaldehyde to UOL are discussed.

2. Effect of Preparation Method and Sn/Pt Atomic Ratio on Crotonaldehyde-to-crotyl-alcohol Hydrogenation Activity of Supported SnPt Catalysts

2.1. Preparation of SiO₂-supported SnPt Catalysts by Different Impregnation Methods

2.1.1. Preparation by Co-impregnation (Sn–Pt/SiO₂)

Silica Q-10 (Fuji Silysia Chemical Ltd.), used as a support to prepare SnPt catalysts, was calcined in a flow of air at 773 K for 5 h and then co-impregnated with an ethanolic solution of H₂PtCl₆·6H₂O (Tanaka Kikinzoku Kogyo Co.) and SnCl₂·2H₂O (Nacalai Tesque, Inc.) at 353 K. The obtained samples were dried overnight at 393 K, calcined in a flow of air at 823 K for 2 h, and reduced in a flow of H₂ at 573 K for 2 h to afford SnPt/SiO₂ catalysts with a Pt loading on SiO₂ of 4 wt% and Sn/Pt atomic ratios of 0.2–2.0.

2.1.2. Preparation by Successive Impregnation (Sn/Pt/SiO₂)

Silica Q-10, used as the support for preparing Sn/Pt/SiO₂ catalysts, was pretreated in the same way as SiO₂ during the preparation of co-impregnated Sn/Pt/SiO₂ catalysts (section 2.1.1). SiO₂-supported Pt catalyst (Pt/SiO₂) was prepared by impregnating SiO₂ with an aqueous solution of H₂PtCl₆·6H₂O (Tanaka Kikinzoku Kogyo Co.) diluted with ethanol at 353 K. The impregnated sample was dried overnight at 393 K, calcined in a flow of air at 823 K for 2 h, and reduced in a flow of H₂ at 573 K for 2 h. The loading of Pt on the SiO₂ support was 4 wt%. Bimetallic Sn/Pt/SiO₂ catalysts were prepared from Pt/SiO₂ as described above, except that the H₂ reduction step was omitted, then the Pt/SiO₂ sample was impregnated with an ethanolic solution of SnCl₂·2H₂O (Nacalai Tesque, Inc.) at 353 K followed by overnight drying at 393 K, calcination for 2 h in a flow of air at 823 K, and reduction for 2 h in a flow of H₂ at 573 K. The Sn/Pt atomic ratio varied from 0.2 to 2.0.

2.2. Chemoselective Hydrogenation of Crotonaldehyde over SiO₂-supported SnPt Catalysts

The effect of the Sn/Pt atomic ratio on the performance of Sn/Pt/SiO₂ and Sn/Pt/SiO₂ catalysts was assessed by performing liquid-phase hydrogenation of crotonaldehyde (0.2 mL) in 2-methyl-2-butanol (4.0 mL) in a stainless-steel autoclave (30 mL) at 373 K under H₂ at 2.0 MPa (gauge). The catalyst weight/reaction time was 25 mg/l and 50 mg/20 h for Sn/Pt/SiO₂ and Sn/Pt/SiO₂, respectively.

2.2.1. Effect of Sn/Pt Atomic Ratio on the Performance of Sn/Pt/SiO₂ Catalysts Prepared by Co-impregnation

Figure 1 shows the conversion and selectivity for crotonaldehyde hydrogenation over co-impregnation-prepared Sn-Pt/SiO₂ catalysts. Crotonaldehyde conversion gradually increased with higher Sn/Pt atomic ratio (Fig. 1(a)), whereas UOL selectivity was maintained at ~15% irrespective of this ratio, and UOL selectivity increased with higher Sn/Pt atomic ratio (Fig. 1(b)). The highest UOL selectivity (~50%) was observed at ~3% conversion and Sn/Pt = 2.0.

The presence of mono- and bimetallic structures containing Sn and/or Pt was investigated by XRD, which revealed peaks attributable to reduced Pt metal26,27 (2θ = 39.5° and 46.5°), Sn₄Pt₁₂ (2θ = 38.8° and 48.6°), Sn₄Pt₁₂ (θ = 25.0, 30.0, 41.5, and 44.0°), and Sn₄Pt₁₂ (2θ = 24.0, 40.0, 47.0, and 57.5°).

Figure 2 presents the XRD patterns of co-impregnation-synthesized Sn/Pt/SiO₂ catalysts, showing that the characteristic peaks of fcc crystalline Pt were observed for Pt/SiO₂ (Sn/Pt = 0) (Fig. 2(a)) and Sn/Pt/SiO₂ (Sn/Pt = 0.2 and 0.5) (Figs. 2(b) and (c), respectively).
For the catalyst with Sn/Pt \(= 1\) (Fig. 2(d)), the peaks of reduced Pt metal were shifted to slightly lower angles. As the Sn\(_{1}\)Pt\(_{3}\) peaks appeared close to the reduced Pt metal peaks, this peak shift was ascribed to the formation of small amounts of Sn\(_{1}\)Pt\(_{3}\) and the resulting overlap of its peaks with those of reduced Pt metal. Additionally, Sn\(_{1}\)Pt\(_{1}\) was observed at Sn/Pt \(= 1.5-2.0\) (Figs. 2(e) and (f)), and the peak intensities of Sn\(_{1}\)Pt\(_{3}\) and Sn\(_{1}\)Pt\(_{1}\) decreased and increased, respectively, with higher Sn content. For Sn/Pt \(= 1.0-2.0\) (Figs. 2(d)-(f)), the peaks of SnO\(_{2}\) appeared at \(2\theta = 27.0, 34.0,\) and \(52.0^\circ\), which suggested that some Sn species did not interact with Pt species in Sn-Pt/SiO\(_{2}\) catalysts.

Formation of Sn\(_{1}\)Pt\(_{3}\) and Sn\(_{1}\)Pt\(_{1}\) alloys over Sn-Pt/ SiO\(_{2}\) catalysts decreased the conversion (Fig. 1(a)) and SAL selectivity (Fig. 1(b)) but increased UOL selectivity (Fig. 1(b)), which suggested that Sn-Pt alloy generation affects the catalytic selectivity for unsaturated aldehyde hydrogenation.

### 2.2. Effect of Sn/Pt Atomic Ratio on Catalytic Performance of Sn/Pt/SiO\(_{2}\) Catalysts Prepared by Successive Impregnation

Figure 3 shows the catalytic activity and selectivity for crotonaldehyde hydrogenation over Sn-Pt/SiO\(_{2}\) catalysts prepared by successive impregnation. At Sn/Pt \(= 0\), the main product was SAL and no UOL was formed (Fig. 3(b)). At \(0 < \text{Sn/Pt} \leq 1.0\), crotonaldehyde conversion was maintained at 100 \%, but significantly decreased at higher Sn/Pt ratios (Fig. 3(a)). UOL selectivity (Fig. 3(b)) increased with higher Sn/Pt ratios up to 0.5 and was maintained at \(\sim 70\%\) at 0.5 \(\leq \text{Sn/Pt} \leq 1.0\), increasing to \(\sim 90\%\) at Sn/Pt \(= 1.2-2.0\). Therefore, Sn-Pt/SiO\(_{2}\) catalysts prepared by successive impregnation provided better UOL selectivity than Sn-Pt/SiO\(_{2}\) catalysts prepared by co-impregnation.

Figure 4 shows the XRD patterns of Sn-Pt/SiO\(_{2}\) catalysts prepared by successive impregnation, revealing that Pt metal peaks were shifted to slightly lower angles at Sn/Pt \(= 0.2\) (Fig. 4(b)) and demonstrating the co-existence of Sn\(_{1}\)Pt\(_{3}\) and Sn\(_{1}\)Pt\(_{1}\) at Sn/Pt \(= 0.5\) (Fig. 4(c)). At Sn/Pt \(> 0.5\), the intensities of the Sn\(_{1}\)Pt\(_{3}\) peaks decreased with higher Sn content (Figs. 4(c)-(g)).
whereas the intensity of the Sn1Pt1 peaks increased up to Sn/Pt = 1.5 (Figs. 2 (c)-(g)), decreasing with higher Sn content at higher Sn/Pt ratios (Fig. 2 (h)). At Sn/Pt = 2.0 (Fig. 2 (h)), Sn2Pt1 peaks appeared.

Although the supported SnPt catalysts were prepared at the same Sn/Pt atomic ratios, their phase composition depended on the impregnation method. For instance, at Sn/Pt = 1.0, Pt metal, Sn1Pt3, and SnO2 were formed in Sn-Pt/SiO2 catalysts (Fig. 2 (d)), whereas Sn1Pt3 and Sn1Pt1 were formed in Sn/Pt/SiO2 catalysts (Fig. 4 (e)). In addition, the composition of the Sn1Pt1 alloy structures formed in Sn/Pt/SiO2 catalysts prepared by successive impregnation was close to that expected from the bulk Sn/Pt atomic ratios, whereas that of Sn/Pt/SiO2 catalysts prepared by co-impregnation was lower than expected. Thus, Sn and Pt species were presumably better mixed in the former case. Further investigation is required to clarify why the preparation methods affect the state of mixing of Sn and Pt.

Sn1Pt1 formation apparently increased UOL formation selectivity in Sn/Pt/SiO2 catalysts. The UOL and SOL selectivities (Fig. 3(b)) were almost constant and independent of the Sn/Pt ratio at 0.5 ≤ Sn/Pt ≤ 1.0, although the intensities of the Sn1Pt3 and Sn1Pt1 peaks decreased and increased, respectively (Figs. 4 (c)-(e)), with higher Sn content. Assuming that the surface area occupied by these alloys varied, the UOL and SOL selectivities were expected to increase and decrease, respectively, with higher Sn/Pt atomic ratio because of the concomitant dilution of Pt ensembles by Sn. Consequently, the formation of Sn1Pt1 presumably proceeded from the surface to the inside of Sn- and Pt-containing particles, so that the surface area occupied by Sn1Pt1 remained constant at Sn/Pt = 0.5-1.0.

Figure 5 displays the Sn/Pt-ratio-dependent H2 and CO chemisorption capacities of Sn/Pt/SiO2 catalysts prepared by successive impregnation, revealing that the addition of a small amount of Sn to Pt/SiO2 (Sn/Pt = 0.2) sharply inhibited irreversible H2 and CO adsorption. At Sn/Pt = 0.2, the CO chemisorption capacity exceeded the H2 chemisorption capacity, presumably because dissociative H2 adsorption requires at least two

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**Fig. 3** Effect of the Sn/Pt Atomic Ratio of Sn/Pt/SiO2 Catalysts Prepared by Successive Impregnation on (a) Conversion and (b) Product Formation Selectivity during Crotonaldehyde Hydrogenation

The diffraction patterns were recorded at a scanning speed of 4.0°/min.

**Fig. 4** XRD Patterns of Sn/Pt/SiO2 Catalysts Prepared by Successive Impregnation with Sn/Pt = 0 (a), 0.2 (b), 0.5 (c), 0.7 (d), 1.0 (e), 1.2 (f), 1.5 (g), and 2.0 (h)
adjacent Pt atoms, whereas effective CO adsorption requires only one vacant Pt atom. Additionally, H₂ and CO cannot be chemisorbed on metallic Sn. These results indicate that successively impregnated Sn species can easily interact with Pt to form SnₓPtᵧ alloys and thus dilute Pt ensembles, consistent with the well-known ensemble effect of bimetallic catalysts 31).

The amount of surface Sn oxides present in Sn/Pt/SiO₂ catalysts was evaluated by benzaldehyde–ammonia titration (BAT), which can determine the surface amount of basic metal cations using a pulse technique 32). First, benzaldehyde is adsorbed until saturation on the basic sites of the metal oxide surface to form benzoate anions, which react with ammonia (supplied in pulses) to form easily desorbed benzonitrile. The amount of produced benzonitrile indicates the amount of surface metal oxides.

Figure 6 shows the effect of the Sn/Pt ratio of Sn/Pt/SiO₂ catalysts on the amount of benzonitrile (i.e., the amount of surface Sn oxides) formed during BAT. For Pt/SiO₂, benzonitrile production reached 5.5 μmol/g-cat., which suggested that benzaldehyde can be adsorbed on the SiO₂ surface 33). The addition of a small amount of Sn (Sn/Pt = 0.2) facilitated benzonitrile formation, and benzonitrile productivity was maintained at Sn/Pt = 0.2-1.0. These results imply that fine Sn oxide particles undetectable by XRD were formed on the Sn/Pt/SiO₂ catalysts. Significantly higher amounts of benzonitrile were formed at Sn/Pt = 1.2-1.5 (Fig. 6). As shown in Figs. 3 and 6, the conversion of crotonaldehyde considerably decreased at Sn/Pt = 1.2 (Fig. 3(a)), presumably because of the concomitant increase in the amount of Sn oxides (Fig. 6). These oxides were presumably located on the surface of SnₓPtᵧ alloy particles and suppressed H₂ activation. Further addition of Sn considerably inhibited benzonitrile formation, presumably due to the sintering of Sn species and/or SnₓPtᵧ formation (Fig. 4 (h)).

Scheme 2 presents the mechanism of crotonaldehyde hydrogenation over Sn/Pt/SiO₂ catalysts with different Sn/Pt atomic ratios prepared by successive impregnation. In the case of Pt/SiO₂ (Sn/Pt = 0), C = C bond activation over the Pt surface leads to the preferential formation of SAL (Scheme 2(a)). Introduction of Sn into Pt/SiO₂ promoted both UOL and SOL formation (Fig. 3(b)), and no SAL formation was observed at Sn/Pt = 0.2-1.0, which indicated preferential crotonaldehyde and SAL C = O bond hydrogenation. At Sn/Pt = 0.5-1.0, the UOL and SOL selectivities were maintained (Fig. 3(b)) despite the concomitant increase of Sn content during the transition from SnₓPtᵧ to SnₓPt₁ (Figs. 4 (c)-(e)). These results suggest that a core-shell structure comprising a Sn₁Pt₃ core and a Sn₁Pt₁ shell is presumably formed in the bimetallic active sites, and the growth of the Sn₁Pt₁ shell with higher Sn/Pt ratio results in a constant surface composition (Scheme 2(b)). At Sn/Pt = 1.2, hydrogenation activity significantly decreased (Fig. 3(a)), presumably due to the suppression of hydrogen activation with the facilitated formation of Sn oxides over SnPt bimetallic active sites, as indicated by the BAT measurements (Fig. 6). In this Sn/Pt ratio range, Pt ensembles are further diluted by the formation of SnₓPt₁ and/or covered with Sn oxides, which further enhances UOL selectivity (Scheme 2(c)).

In the case of SiO₂-supported SnPt catalysts, the impregnation method affected the formation of SnₓPtᵧ at the same Sn/Pt atomic ratio, resulting in different catalytic performance for selective crotonaldehyde hydrogenation. The co-existence of SnₓPt₁ and Sn₁Pt₁, and that of Sn₁Pt₁ and SnO₂, seems to be responsible for the selective formation of UOL.
3. Effect of Sn/Pt Atomic Ratio on Crotonaldehyde-to-crotyl-alcohol Hydrogenation over SnPt–NP Catalysts

As mentioned earlier, several Sn sites including Sn$_x$Pt$_y$ and Sn oxides are concurrently formed over SiO$_2$-supported SnPt catalysts prepared by co-impregnation and successive impregnation, resulting from the strong metal-support interactions. The presence of various Sn sites on SnPt catalysts makes it difficult to elucidate the specific sites responsible for the selective formation of unsaturated alcohols. To exclude the metal-support interaction during catalyst preparation, unsupported SnPt-NP catalysts were prepared using a polyalcohol reduction method.$^{24}$

3.1. Preparation of SnPt–NP Catalysts

SnPt-NP catalysts were prepared by a polyalcohol reduction method described elsewhere$^{37)$–$^{39)}$. A 50 mL three-neck round-bottom flask was charged with 0.197 g of platinum(II) acetylacetonate (Pt(acac)$_2$, Tanaka Kikinzoku Kogyo Co.), 0-0.12 g of tin(II) acetate (Sn(OAc)$_2$, Aldrich), 0.34 mL of oleylamine (Aldrich), 0.32 mL of oleic acid (Nacalai Tesque, Inc.), 0.78 g of 1,2-hexadecanediol (Tokyo Chemical Industry Co., Ltd.), and 20 mL of dioctyl ether (Tokyo Chemical Industry Co., Ltd.). The amount of Sn(OAc)$_2$ was varied to control the Sn/Pt ratio. The Sn/Pt atomic ratio in the starting mixture for polyalcohol reduction was 0, 0.2, 0.5, 0.7, 1.0, 1.2, or 1.5 of the catalyst. The mixture was bubbled with N$_2$, heated to 533 K using a heating mantle, maintained under reflux for 1 h, cooled to room temperature, diluted with ethanol (Nacalai Tesque, Inc.), and centrifuged to separate the nanoparticles. The precipitate was rinsed three times with ethanol and dried in vacuo at room temperature to obtain the SnPt-NP catalysts, and the Sn/Pt ratios were determined by atomic adsorption spectroscopy.

3.2. Structural Properties of SnPt–NP Catalysts

The morphologies of Pt-NP (Sn/Pt = 0) and SnPt-NP (Sn/Pt = 1.40) catalysts observed by transmission electron microscopy (TEM) are shown in Fig. 7. Pt-NP catalysts (Fig. 7(a)) consisted of polyhedral nanoparticles with diameters of 10-20 nm, whereas SnPt-NP catalysts with Sn/Pt = 1.40 (Fig. 7(b)) contained quasi-spherical nanoparticles with diameters of 2-10 nm. Both Pt-NP and SnPt-NP catalysts were synthesized under the same conditions except for the amount of Sn introduced during the polyalcohol reduction, but their nanoparticle sizes were different, probably because of the presence of a second metal. A similar effect of a second metal on nanoparticle size has been reported previously$^{39)}$.

Figure 8 shows the XRD patterns of SnPt-NP catalysts with different Sn/Pt ratios. In the cases of Sn/Pt = 0 (Pt-NP) (Fig. 8 (a)) and 0.48 (Fig. 8 (b)), the observed peaks were characteristic of fcc Pt and fcc Sn$_3$Pt$_3$, respectively. Peaks of Sn$_3$Pt$_3$ and Sn$_1$Pt$_1$ were observed at Sn/Pt = 0.71 and 0.92 (Figs. 8 (c) and (d), respectively). In this ratio range, the intensities of the Sn$_3$Pt$_3$ and Sn$_1$Pt$_1$ peaks decreased and increased, respectively, with higher Sn content. Only Sn$_1$Pt$_1$ peaks were observed at Sn/Pt = 1.40 and 1.51 (Figs. 8 (e) and (f), respectively), and Sn$_3$Pt$_3$ peaks were detected at Sn/Pt = 2.19 (Fig. 8 (g)). Thus, the formation of Sn$_3$Pt$_3$ alloys in SnPt-NP catalysts could be controlled by varying the initial Pt(acac)$_2$ : Sn(OAc)$_2$ ratio.
3.3 Relationship between Sn\textsubscript{x}Pt\textsubscript{y} Alloy Composition and Crotonaldehyde Hydrogenation Performance of SnPt\textsubscript{NP} Catalysts

To investigate the relationship between Sn\textsubscript{x}Pt\textsubscript{y} alloy structures in SnPt\textsubscript{NP} catalysts and catalytic performance, liquid-phase hydrogenation of crotonaldehyde (0.2 mL) in 2-methyl-2-butanol (4.0 mL) was carried out over NP catalysts (10 mg) in a stainless-steel autoclave (30 mL) at 373 K under H\textsubscript{2} at 2.0 MPa (gauge) for 0.5 h (Fig. 9). SAL was predominantly produced over Pt\textsubscript{NP} (Sn/Pt \textsubscript{0}) (Fig. 9(b)). Crotonaldehyde conversion was maximized at Sn/Pt = 0.49, subsequently decreasing with higher Sn content (Fig. 9(a)). SAL selectivity decreased with higher Sn/Pt ratio up to 1.40, subsequently increasing at Sn/Pt ≥ 1.51 (Fig. 9(b)). The highest SOL selectivity was obtained at Sn/Pt = 0.48 and remained almost constant in the range Sn/Pt = 0.71-2.19 (Fig. 9(b)). The maximum UOL selectivity was obtained as 71.5 \% at 37.6 \% conversion over the SnPt\textsubscript{NP} catalyst with Sn/Pt = 1.40 (Fig. 9(b)).

Scheme 3 shows the suggested mechanism of crotonaldehyde hydrogenation over SnPt\textsubscript{NP} catalysts. At Sn/Pt = 0.48, the formation of Sn\textsubscript{Pt}\textsubscript{i} was confirmed by XRD (Fig. 8(b)), and the crotonaldehyde conversion (Fig. 9(a)) and UOL and SOL selectivities (Fig. 9(b)) were improved compared with those for Pt\textsubscript{NP} catalysts, which suggested that the Sn\textsubscript{Pt}\textsubscript{i} alloy can accelerate not only C=O activation but also H\textsubscript{2} and/or C=C activation. At Sn/Pt = 0.71-1.51, the Sn\textsubscript{Pt}\textsubscript{i} to Sn\textsubscript{Pt}\textsubscript{1} transition proceeded with higher Sn content (Figs. 8(c)-(f)). Notably, the catalytic activity decreased (Fig. 9(a)), but the UOL selectivity increased with higher Sn content for Sn\textsubscript{Pt}\textsubscript{1} alloy formation (Fig. 9(b)). This behavior agrees well with the results obtained for SiO\textsubscript{2}-supported SnPt catalysts (Figs. 1-4). These results strongly suggest that Sn\textsubscript{Pt}\textsubscript{1} features higher UOL formation selectivity and lower H\textsubscript{2} activation activity than Sn\textsubscript{Pt}\textsubscript{i}. As shown in Fig. 7, the SnPt\textsubscript{NP} catalyst with Sn/Pt = 1.40 contained smaller particles than Pt\textsubscript{NP}. The size of metal particles in a catalyst is well known to affect catalytic activity. Cinnamaldehyde conversion increased with smaller particle...
size of Pt nanoparticle catalysts\(^{37}\). Despite the smaller particle diameter, crotonaldehyde conversion over the SnPt-NP catalyst with Sn/Pt = 1.40 was almost the same as that over the Pt-NP catalyst, implying that Sn\(_{2}\)Pt\(_{3}\) has a lower \(\text{H}_2\) activation activity than Sn\(_{1}\)Pt\(_{3}\). Sn\(_{2}\)Pt\(_{3}\) alloy is mainly formed in the SnPt-NP catalyst with constant Sn/Pt ratio of 2.19 (Fig. 8(g)), and the UOL and SAL selectivities over this alloy are lower and higher, respectively, than those over Sn\(_{1}\)Pt\(_{1}\) (Fig. 9(b)). The formation of Sn\(_{2}\)Pt\(_{3}\) over Pt/SnO\(_2\) catalysts was reported to decrease UOL selectivity\(^{15}\). As mentioned earlier in Section 2, similar behavior was observed for Sn\(_{2}\)Pt\(_{1}\) on Sn/Pt/SiO\(_2\) catalysts (Sn/Pt = 2.0) (Figs. 3(b) and 4(h)). Thus, Sn\(_{2}\)Pt\(_{3}\) was concluded to be ineffective for UOL formation.

The results of catalytic performance screening for the selective hydrogenation of crotonaldehyde over SnPt-NP catalysts revealed that SnPt (Sn\(_{1}\)Pt\(_{3}\), Sn\(_{1}\)Pt\(_{1}\), and Sn\(_{2}\)Pt\(_{1}\)) alloys had higher selectivity for UOL formation than reduced Pt metal. The highest UOL selectivity was obtained for SnPt-NP (Sn/Pt = 1.40) catalysts with a uniform Sn\(_{1}\)Pt\(_{3}\) alloy structure, which was concluded to be the most effective among the Sn\(_{x}\)Pt\(_{y}\) phases for UOL formation during the hydrogenation of unsaturated aldehydes to the corresponding unsaturated alcohols.

The improvement of UOL selectivity during the Pt \(\rightarrow\) Sn\(_{3}\)Pt\(_{3}\) \(\rightarrow\) Sn\(_{2}\)Pt\(_{3}\) transition is presumably due to the dilution of Pt ensembles by the added Sn species. A previous diffuse-reflectance infrared Fourier transform spectroscopy study showed that strong crotonaldehyde adsorption through the C = C bond (assigned to the di-\(\sigma\)CC adsorption mode over the Pt surface) was observed over Pt/TiO\(_2\) catalysts reduced with \(\text{H}_2\) at 573 K\(^{40}\). The di-\(\sigma\)CC adsorption configuration requires at least two adjacent Pt atoms, forming a Pt ensemble. The number of Pt ensembles decreased with the Pt \(\rightarrow\) Sn\(_{3}\)Pt\(_{3}\) \(\rightarrow\) Sn\(_{2}\)Pt\(_{3}\) transition, which suppressed C = C bond hydrogenation. A previous infrared spectroscopy study showed that Sn is important in the enhancement of the donating-on-top adsorption of propionaldehyde on Sn species through the carbonyl group oxygen\(^{31}\). As the carbonyl group of crotonaldehyde can be adsorbed in the donating-on-top \(\eta^1\) (O) configuration on one Sn atom, the increase of Sn content in Sn\(_{2}\)Pt\(_{3}\) enhances activation of this group. The dilution of Pt ensembles by metallic Sn not only suppresses C = C bond activation, but also enhances C = O bond activation and thus increases the selectivity for UOL formation over Sn\(_{3}\)Pt\(_{3}\) and Sn\(_{2}\)Pt\(_{3}\). The Sn content of Sn\(_{2}\)Pt\(_{3}\) exceeds that of Sn\(_{3}\)Pt\(_{3}\), but the UOL selectivity decreased from Sn\(_{3}\)Pt\(_{3}\) to Sn\(_{2}\)Pt\(_{3}\), which suggests that at least one lattice plane of Sn\(_{2}\)Pt\(_{3}\) contains Pt ensemble sites. Therefore, the mechanism of hydrogenation over Sn\(_{2}\)Pt\(_{1}\) requires further investigation.

4. Conclusion

Selective liquid-phase hydrogenation of crotonaldehyde was investigated over SiO\(_2\)-supported SnPt catalysts and unsupported SnPt nanoparticulate catalysts. The relationship between the Sn\(_{x}\)Pt\(_{y}\) alloy composition of the obtained catalysts and their activity for crotonaldehyde hydrogenation was also studied, with the key findings summarized below.
(1) The maximum UOL selectivity observed over Sn/Pt/SiO\textsubscript{2} catalysts prepared by successive impregnation exceeded that observed over Sn-Pt/SiO\textsubscript{2} catalysts prepared by co-impregnation. At the same Sn/Pt atomic ratio, the impregnation method affected the formation of Sn\textsubscript{Pt} alloys, and thus the catalytic performance for selective crotonaldehyde hydrogenation.

(2) Unsupported SnPt\textsubscript{NP} catalysts with several types of Sn/Pt\textsubscript{y} alloy phases were synthesized by varying the amount of Sn(OAc)\textsubscript{2} introduced during the polyalcohol reduction method. SnPt\textsubscript{NP} catalysts with Sn/Pt = 0.48 and 1.40 contained uniform Sn\textsubscript{1}Pt\textsubscript{3} and Sn\textsubscript{1}Pt\textsubscript{1} alloy phases, respectively.

(3) SnPt\textsubscript{y} species were suggested to affect the performance of both supported and non-supported SnPt catalysts. Sn\textsubscript{Pt}\textsubscript{x}, Sn\textsubscript{Pt}\textsubscript{1}, and Sn\textsubscript{Pt}\textsubscript{2} alloys achieved higher UOL formation selectivities than reduced Pt metal. The Sn/Pt\textsubscript{y} → Sn\textsubscript{Pt}\textsubscript{1} phase transition increased UOL formation selectivity, whereas Sn\textsubscript{Pt}\textsubscript{1} alloy formation decreased it. Sn\textsubscript{Pt}\textsubscript{1} was suggested to carry the most effective sites for the selective production of unsaturated aldehydes from the corresponding alcohols.

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References

1) Ponec, V., *Appl. Catal. A: Gen.*, 149, 27 (1997).
2) Claus, P., *Top. Catal.*, 5, 51 (1998).
3) Maki-Arvela, P., Häjek, J., Salmi, T., Muzin, D. Y., *Appl. Catal. A: Gen.*, 292, 1 (2005).
4) Tamura, M., Nakagawa, Y., Tomishige, K., *J. Jpn. Petrol. Inst.*, 62, 3, (106 (2019).
5) Marinelli, T. B. L. W., Ponec, V., J. Catal., 156, 51 (1995).
6) Englisch, M., Ranade, V. S., Lercher, J. A., *J. Mol. Catal. A: Chem.*, 121, 69 (1997).
7) Coloma, F., Sepúlveda-escobano, A., Fierro, J. L. G., Rodríguez-Reinosa, F., *Appl. Catal. A: Gen.*, 136, 231 (1996).
8) Altmann, L., Wang, X., Borchert, H., Kolny-Olesiak, I., Zielasek, V., Parisi, J., Kunz, S., Bäumer, M., *Phys. Chem. Chem. Phys.*, 17, 28186 (2015).
9) Santori, G. F., Casella, M. L., Siri, G. J., Aduríz, H. R., Ferretti, O. A., *Appl. Catal. A: Gen.*, 197, 141 (2000).
10) Ruiz-Martín, J., Coloma, F., Sepúlveda-escobano, A., Anderson, J. A., Rodríguez-Reinosa, F., *Catal. Today*, 133-135, 35 (2008).
11) Hou, F., Zhao, H., Song, H., Chou, L., Zhao, J., Yang, J., Yan, L., *RSC Adv.*, 7, 48649 (2017).
12) Stassi, J. P., Zgollice, P. D., de Miguel, S. R., Szelza, O. A., J. Catal., 306, 11 (2013).
13) Coloma, F., Llorca, J., Homs, N., Ramírez de la Piscina, P., Rodríguez-Reinosa, F., Sepúlveda-Escobano, A., *Phys. Chem. Chem. Phys.*, 2, 3063 (2000).
14) Zgolice, P. D., Rodríguez, V. I., Vilella, I. M. J., de Miguel, S. R., Szelza, O. A., *Appl. Catal. A: Gen.*, 392, 208 (2011).
15) Liberková, K., Tournoue, R., J. Mol. Catal. A: Chem., 180, 221 (2002).
16) Santori, G. F., Casella, M. L., Siri, G. J., Aduríz, H. R., Ferretti, O. A., *React. Kinet. Catal. Lett.*, 75, 225 (2002).
17) Coloma, F., Sepúlveda-Escobano, A., Fierro, J. L. G., Rodríguez-Reinosa, F., *Appl. Catal. A: Gen.*, 148, 63 (1996).
18) Margitfalvi, J. L., Tompos, A., Kolosova, I., Valyon, J., *J. Catal.*, 174, 246 (1998).
19) Margitfalvi, J. L., Vankó, G., Borbáth, I., Tompos, A., Vértes, A., J. Catal., 190, 474 (2000).
20) Taniya, K., Yu, C. H., Tsang, S. C., Ichihashi, Y., Nishiyama, S., *Catal. Commun.*, 14, 6 (2011).
21) Taniya, K., Jinno, H., Kishida, M., Ichihashi, Y., Nishiyama, S., *J. Catal.*, 258, 84 (2012).
22) Taniya, K., Haru, T., Imai, T., Ichihashi, Y., Nishiyama, S., *J. Chem. Eng. Jpn.*, 47, 130 (2014).
23) Durussel, P., Massara, R., Feschotte, P., *J. Alloys Compd.*, 215, 175 (1994).
24) Taniya, K., Yu, C. H., Takaco, H., Haru, T., Okomoto, A., Horie, T., Ichihashi, Y., Tsang, S. C., Nishiyama, S., *Catal. Today*, 303, 241 (2018).
25) Taniya, K., Ichihashi, Y., Nishiyama, S., *Catal. Lett.*, 55, 110 (2013).
26) Ito, S., Tomishige, K., *Catal. Commun.*, 12, 157 (2010).
27) Hori, K., Matsune, H., Takenaka, S., Kishida, M., *Sci. Technol. Adv. Mater.*, 7, 678 (2006).
28) Kwak, D.-H., Lee, Y.-W., Han, S.-B., Hwang, E.-T., Park, H.-C., Kim, M.-C., Park, K.-W., *J. Power Sources*, 275, 557 (2015).
29) Llorca, J., Homs, N., Fierro, J.-L. G., Sales, J., Ramírez de la Piscina, P., *J. Catal.*, 166, 44 (1997).
30) Colmati, F., Antolini, E., Gonzalez, E. R., *J. Solid State Electrochem.*, 12, 591 (2008).
31) Paál, Z., Wootsch, A., Teschner, D., Lázár, K., Sajó, I. E., Gyorffy, N., Weinberg, G., Knop-Gericke, A., Schlögl, R., *Appl. Catal. A: Gen.*, 391, 377 (2011).
32) Niwa, M., Inagaki, S., Murakami, T., *J. Phys. Chem.*, 89, 2550 (1985).
33) Niwa, M., Inagaki, S., Murakami, Y., *J. Phys. Chem.*, 89, 3869 (1985).
34) Niwa, M., Matsuoka, Y., Murakami, Y., *J. Phys. Chem.*, 91, 4519 (1987).
35) Taniya, K., Izumi, A., Ichihashi, Y., Nishiyama, S., *Mater. Sci. Forum*, 658, 420 (2010).
36) Segawa, A., Taniya, K., Ichihashi, Y., Nishiyama, S., Yoshida, N., Okamoto, M., *Ind. Eng. Chem. Res.*, 57, 70 (2018).
37) Tsang, S. C., Cailuo, N., Oduro, W., Kong, A. T. S., Clifton, L., Yu, K. M. K., Thiebaut, B., Cookson, J., Bishop, P., *ACS Nano*, 2, 2547 (2008).
38) Oduro, W. O., Cailuo, N., Yu, K. M. K., Yang, H., Tsang, S. C., *Phys. Chem. Chem. Phys.*, 13, 2590 (2011).
39) Somodi, F., Peng, Z., Getsoian, A. B., Bell, A. T., *J. Phys. Chem. C*, 115, 19084 (2011).
40) Dandekar, A., Vannice, M. A., *J. Catal.*, 183, 344 (1999).
41) Nishiyama, S., Hara, T., Tsuirtya, S., Masai, M., *J. Phys. Chem. B*, 103, 4431 (1999).
要　旨

SnPt 二元系触媒における Sn, Pt 合金構造が不飽和アルデヒドの選択水素化に及ぼす影響

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不飽和アルデヒドから不飽和アルコールへの選択水素化反応における触媒性能についての向上には、不均一触媒における活性点構造を理解する必要がある。SnPt 二元系触媒では、合金構造を形成する Sn, Pt 金属が選択性に強く影響を及ぼす重要な要因の一つと考えられている。本稿では、Sn/Pt 原子比が異なる担持および非担持の SnPt 二元系触媒上のクロトンアルデヒドの選択水素化反応における Sn, Pt 合金構造と触媒性能の関係について解説する。SnPt 二元系触媒調製時の Sn, Pt 原子比が同じでも、調製方法の違いにより異なる合金相が形成した。本研究では、SnPt, Sn, Pt, および Sn, Pt 合金の形成を確認し、いずれの合金も Pt 金属より高いクロトンアルコール選択性を示した。共含浸および逐次含浸で調製した担持触媒およびポリアリール触媒還元法で調製した非担持触媒のいずれにおいても、Sn, Pt 合金構造から Sn, Pt 合金構造に相変化するに従ってクロトンアルコールの選択率が向上した。また、さらに Sn 含有量が多い Sn, Pt 合金構造が触媒上に形成するとクロトンアルコールの選択率が低下した。不飽和アルデヒドの水素化反応においてSn, Pt 合金構造が不飽和アルコールの形成に最も有効な合金構造であった。