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Short Communication

Preparation of SiO_2-encapsulated SnPt nanoparticle catalysts for selective hydrogenation of unsaturated aldehyde

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ABSTRACT

The SiO_2-encapsulated SnPt catalysts having the core–shell structures were prepared by using the polyol process. Transmission electron microscopy (TEM) and X-ray diffraction (XRD) results indicated the SnPt alloy nanoparticles were covered with a thin silica layer with the porous structures. The SiO_2-encapsulated SnPt catalysts showed the higher selectivity of crotyl alcohol for selective hydrogenation of crotonaldehyde in comparison with the Sn-Pt/SiO_2 catalysts prepared by a conventional co-impregnation. It was considered that the formation of uniform SnPt alloy phases and the pore structures in the silica layers with the steric hindrance would enhance the chemo-selective hydrogenation of crotonaldehyde.

1. Introduction

The selective hydrogenation of unsaturated aldehyde to corresponding unsaturated alcohol (Scheme 1) is an important step in the synthesis of fine chemicals [1]. In this field, many researchers have investigated group VIII metal modified by Sn to suppress the unfavorable hydrogenation of C=C bonds and accelerate the hydrogenation of C=O bonds [2–6]. However, the C=C hydrogenation could not be avoided owing to the existence of Pt domains. In order to further improve selectivity of unsaturated alcohol, it is important that the adsorption through the oxygen atom of C=O functional group [7] occurs when the unsaturated aldehyde is adsorbed over active sites. Namely, the control of adsorption mode by physical modification as well as chemical modification is needed in the Sn–Pt bi-metallic catalyst system.

Recently, the core–shell materials have been extensively investigated in order to stabilize the nanoparticles [8]. The nanoparticles of various metals, metal oxides, or bi-metallic complexes, which are covered with silica layers particularly have been reported [9–15]. In the core–shell materials, sintering each core metal particle is avoided during the pre-treatment and reaction, because the core particles exist in the SiO_2 particles. Few literatures reported that the porous structures of silica including metal nanoparticles were utilized for the improvement of selectivity in the catalytic reactions. Kishida et al. have reported the silica-coated Pt catalysts for the competitive oxidation of methane and other higher hydrocarbons with gaseous oxygen [15]. The silica-coated Pt catalysts oxidized the methane preferentially in the competitive oxidation of iso-butane and methane, even though methane is the most inactive for the oxidation among all the hydrocarbons. They concluded that the porous structure of silica, which wrapped Pt metal particles, controlled selectivity in the catalytic reaction because of controlling the diffusion rate of reactant molecules by the porous structure [15].

In the method reported by Kishida et al., however, the synthesis of uniformed bi-metallic nanoparticles is difficult, because their procedures are one-pot synthesis which the synthesis of core metal nanoparticles and the formation of silica layer are simultaneously carried out and the interaction between the core metal and the silica layer would not be avoided. Therefore, we focused on the polyol process for synthesis of SiO_2-encapsulated SnPt nanoparticles. In the polyol process, the metal or bi-metal nanoparticles are prepared, and then these nanoparticles are covered with silica. There is a possibility to synthesize the bi-metallic core particle with uniform contents.

In this study, we prepared the SiO_2-encapsulated SnPt catalyst in which the shape selectivity was added to SnPt nanoparticles by covering with porous silica in order to improve the selectivity of unsaturated alcohol for hydrogenation of unsaturated aldehyde. To evaluate the catalytic performance, hydrogenation of crotonaldehyde was carried out.

2. Experimental

2.1. Catalyst preparation

The SiO_2-encapsulated SnPt catalysts were prepared by the polyol process [11], which consists of the following two processes; (1) metal

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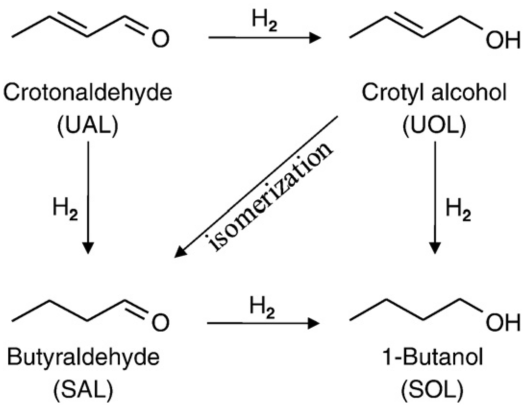


Scheme 1. Reaction pathway of crotonaldehyde hydrogenation.

nanoparticle formation step and (2) SiO_2 coating step. In the first step, 0.197 g (0.5 mmol) of platinum (II) acetylacetonate and 0.118 g (0.5 mmol) of tin (II) acetate were dispersed in 20 mL of dioctylether. Then, 0.32 mL of oleic acid, 0.34 mL of oleyl amine and 0.78 g of 1,2-hexadecanediol were added to the above solution. The solution was heated up to ca. 553 K with bubbling of N_2, and then kept refluxing for 1 h. A color change (from yellow to auburn via orange) was observed during heating up. After cooling to room temperature, the mixture, which had a black color, was centrifuged in order to separate the bi-metal nanoparticles from the solution. The supernatant was discarded, and the obtained precipitates were washed three times by ethanol. The samples after washing by ethanol were dried at room temperature overnight and the SnPt nanoparticle (Sn/Pt = 1.0) was finally obtained. In the second step, to encapsulate the SnPt nanoparticles in silica, 50 mmol of Igepal CO-520 (polyoxyethylene (5) nonylphenyl ether) was added to 450 mL of cyclohexane and the mixture was subjected to an ultrasonic treatment for 10 min. Then, 50 mL of a SnPt solution prepared by redispersion of the SnPt solid in cyclohexane (1 mg/mL) was added to the above solution. After the mixture had been stirred for 2 h, 4.0 mL of ammonia solution (35%) was added. Finally, 3.0 mL of tetraethyl orthosilicate was added, and the mixture was stirred for 48 h to encourage hydrolysis and condensation of the silica precursor. The resulting nanoparticles were collected by using centrifugation, and washed by ethanol. These samples are denoted as the SiO_2-encapsulated SnPt as synthesized. Additionally, these samples were calcined in flowing air at 623 K for 2 h and reduced in flowing H_2 at 573 K for 2 h under atmospheric pressure. The samples after these treatments are referred to SiO_2-encapsulated SnPt. The SiO_2-encapsulated Pt catalysts were prepared by the above method without tin (II) acetate.

To compare the catalytic performance, the supported Pt and Sn–Pt bi-metallic catalyst was prepared by an impregnation method and a co-impregnation method, respectively. Silica support used in this study was Q-10 supplied from FUJI SILYSIA CHEMICAL LTD. It was calcined in a flowing air at 773 K for 5 h prior to catalyst preparation. The Pt/SiO_2 was prepared by an impregnation of SiO_2 support (1.0 g) at 353 K with a solution prepared by diluting an aqueous solution of $H_2PtCl_6 \cdot 6H_2O$ with ethanol (30 mL). The loading of Pt was 4 wt.%. The $Sn\text{-}Pt/SiO_2$ was prepared by impregnation of SiO_2 support (1.0 g) at 353 K with a solution prepared by diluting an aqueous solution of $H_2PtCl_6 \cdot 6H_2O$ and $SnCl_2 \cdot 2H_2O$ with ethanol (30 mL). The loading of Pt was 4 wt.% of the support and the molar ratio of Sn/Pt was 1.0. Then the samples were dried overnight at 393 K, calcined under air flow at 823 K for 2 h and then reduced under H_2 flow for 2 h at 573 K.

2.2. Characterization

Transmission electron microscopy (TEM) images of the $Sn\text{-}Pt/SiO_2$ and the SiO_2-encapsulated SnPt as synthesized were taken with a JEOL JEM-2000FX and a JOEL JEM2011, respectively. Energy dispersive X-ray was performed for the SiO_2-encapsulated SnPt as synthesized by using INCA (Oxford Instruments). X-ray powder diffraction patterns of the catalysts were measured at room temperature on using the Rigaku RINT-2000 with Cu–Kα radiation.

2.3. Catalytic test

Hydrogenation of crotonaldehyde was carried out in a 30 mL autoclave. The reagent grade of crotonaldehyde was purchased by Nacalai Tesque, Kyoto, Japan. Crotonaldehyde (0.2 mL) was diluted with 4 mL of 2-methyl-2-butanol as a solvent and charged in a glass tube with 20–25 mg of catalyst. The glass tube was inserted in autoclave. The reaction solution was not in direct contact with the inner surface of the autoclave, and was vigorously agitated by a magnetic stirrer. Hydrogen was charged and discharged several times in order to substitute the air in the autoclave with hydrogen. The autoclave was heated up to 373 K in an oil bath in which the temperature was controlled by a temperature regulator. The reaction lasted for 20 h. Then, the autoclave was cooled to 273 K, and 0.2 mL of cyclohexane as an internal standard was added to the solution. The solution was centrifuged to separate catalysts, and the products were analyzed by GC (GC-18A, Shimazu) equipped with G-300 column (Chemicals Evaluation and Research Institute, Japan).

3. Results and discussion

The XRD patterns of Pt/SiO_2, $Sn\text{-}Pt/SiO_2$ and SiO_2-encapsulated SnPt as synthesized are shown in Fig. 1. In the Pt/SiO_2, three peaks were observed around 39.5°, 46.5° and 67.5° (open circle) of 2θ, which were assigned to the reduced Pt metal [15–17]. In the $Sn\text{-}Pt/SiO_2$, the peaks ascribed to the SnPt alloy phase, which the molar ratio Sn to Pt is 1:1, appeared around 41.5°, 44.0° and 62.0° (open down triangle) [18,19], and the peaks around 39.0°, 45.5° and 66.0° (open square) were observed. The positions of latter peaks were close to the Pt metal peaks, and these peaks appeared on the Sn containing catalysts. Because these peaks were observed at the lower angles than the Pt metal peaks, it was suggested that the Sn species would be incorporated into the Pt phase, bringing about expanding the lattice structure (of the Pt phase). Therefore, we identified these peaks with the Sn-doped Pt phase. As for the SiO_2-encapsulated SnPt as synthesized, the peaks attributed to the SnPt alloy phase were mainly observed. These results indicated that the uniform SnPt alloy phase could be synthesized by polyol process.

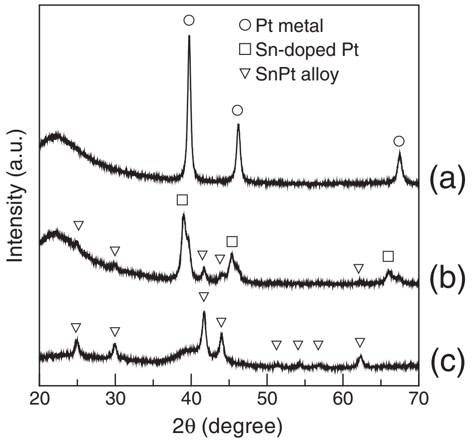


Fig. 1. XRD patterns of each catalyst; (a) Pt/SiO_2, (b) $Sn\text{-}Pt/SiO_2$ and (c) SiO_2-encapsulated SnPt as synthesized.

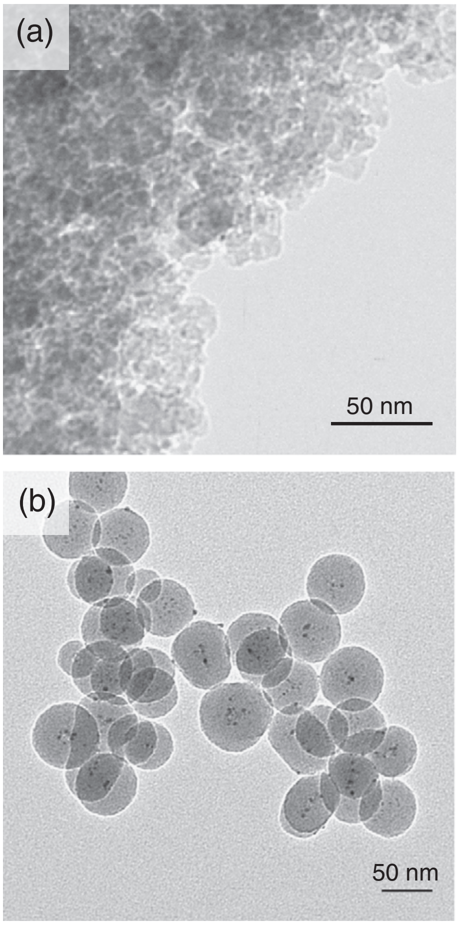


Fig. 2. TEM image of (a) Sn-Pt/SiO_2 and (b) SiO_2-encapsulated SnPt as synthesized.

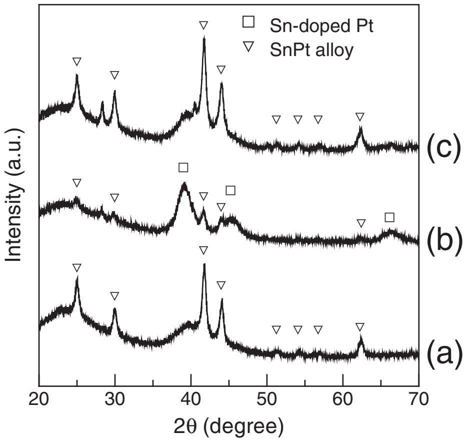


Fig. 3. XRD patterns of SiO_2-encapsulated SnPt; (a) as synthesized, (b) after air calcination and (c) after H_2 reduction.

Fig. 2 shows the TEM images of Sn-Pt/SiO_2 and SiO_2-encapsulated SnPt as synthesized (Sn/Pt = 1). As for the Sn-Pt/SiO_2 (Fig. 2a), there were black spots with 2–3 nm on the SiO_2. It was considered that these black spots were due to the Pt and/or Sn species. These particles seemed to be supported on the surface of SiO_2. In the SiO_2-encapsulated SnPt as synthesized (Fig. 2b), the monodispersed spherical particles were obtained. The small particles with 2–4 nm were located near the center of each spherical particle. The diameter of the spherical particle was ca. 50 nm. As shown in Fig. 1, the peaks ascribed to the SnPt alloy phase were observed in the XRD pattern of the SiO_2-encapsulated SnPt as synthesized with the 1.0 of Sn/Pt molar ratio. These results strongly suggested that the small particles observed by the TEM image as shown in Fig. 2b are composed of the SnPt alloy. Judging from the contrast of the TEM image, the particles were mainly composed of SiO_2. The loadings of Pt and Sn in the SiO_2-encapsulated SnPt as synthesized were estimated by EDX analysis to be 7.3 and 3.5 wt.%, respectively, and the Sn/Pt molar ratio was ca. 0.8. The size of SnPt complex nanoparticles and the spherical particles was very uniform. These results suggest that the same size of each SiO_2-encapsulated SnPt catalyst can be prepared by polyol process.

It has been reported that the particle size of metal components would affect the selectivity of unsaturated alcohol in the hydrogenation of unsaturated aldehyde [17]. As shown in the TEM images, the particle size of SnPt complexes in the SiO_2-encapsulated SnPt is almost the same as that in the Sn-Pt/SiO_2. In this report, therefore, it is considered that the effect of particle size for the selectivity of unsaturated alcohol should not be considered.

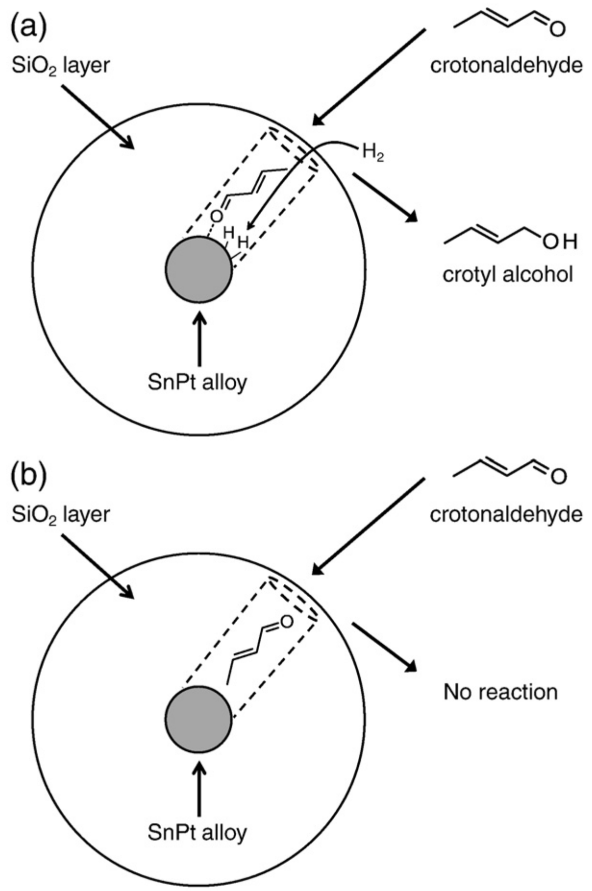
Fig. 3 shows the XRD patterns of the SiO_2-encapsulated SnPt as synthesized and the SiO_2-encapsulated SnPt after each treatment. After the air calcination at 623 K, the intensity of SnPt alloy peaks was markedly decreased and the peaks ascribed to the Sn-doped Pt were appeared. The latter peaks were observed in the case of Sn-Pt/SiO_2. It is considered that the Sn species were segregated from the SnPt alloy phases by the air calcination to form the SnOx species and the metallic Pt species. Since the SnOx species could not be observed in the XRD patterns, the SnOx species would probably be fine particles. The peaks of SnPt alloy phase reappeared and the unidentified peaks were simultaneously appeared after subsequently H_2 reduction at 573 K. It is implied that the Sn-doped Pt phases, which were observed after the air calcination, could be reversibly reduced to form the SnPt alloy by H_2 gases and therefore the SnOx species would be over the nanoparticles. The SnPt structure was changed during the air calcination and the H_2 reduction even though the SnPt nanoparticles were covered with the SiO_2 layer as shown in the TEM image. These results indicated that H_2 and O_2 gases reached the inner core SnPt nanoparticles through the SiO_2 layer and suggested that the SiO_2 layer of SiO_2-encapsulated SnPt possessed a porous structure.

Table 1 shows the results of crotonaldehyde hydrogenation over each catalyst. The butyraldehyde (SAL) is mainly produced over the Pt/SiO_2 catalyst prepared by a conventional impregnation method and over the SiO_2-encapsulated Pt catalyst prepared by polyol process. The Sn modifications to Pt/SiO_2 and SiO_2-encapsulated Pt brought about the enhancement of selectivity of crotyl alcohol (UOL). In particular, as for SiO_2-encapsulated SnPt prepared by the polyol process, the selectivity of crotyl alcohol (UOL) is markedly enhanced from 3.4% to 66.7%.

In case of the core–shell catalysts, SiO_2-encapsulated Pt and SiO_2-encapsulated SnPt, the catalytically active metal components, Pt nanoparticles and SnPt alloy nanoparticles, respectively, were covered with the silica layers with the porous structures. The reactant molecules, crotonaldehyde and hydrogen, are diffused in the silica layers and they can be contacted with core nanoparticles. Because of the diffusion limitation, the conversion of crotonaldehyde over the

Table 1
Hydrogenation of crotonaldehyde over each catalyst.

Catalyst	Sn/Pt ratio [–]	Reaction time [h]	Conversion [%]	Selectivity of UOL [%]	Yield[%]		
					UOL	SAL	SOL
Pt/SiO_2	–	2	93.5	1.4	1.3	79.2	13.0
Sn-Pt/SiO_2	1.0	2	34.1	38.0	13.0	15.1	6.0
SiO_2-encapsulated Pt	–	20	43.3	3.4	1.5	39.1	2.7
SiO_2-encapsulated SnPt	1.0	20	41.1	66.7	27.4	9.5	4.2



Scheme 2. Reaction scheme of unsaturated aldehyde over SiO_2-encapsulated SnPt; (a) C=O group hydrogenation and (b) suppression of C=C hydrogenation.

core–shell catalyst was lower than that over the Pt/SiO_2 and Sn-Pt/SiO_2.

The SiO_2-encapsulated SnPt catalyst showed the higher selectivity of crotyl alcohol than the Sn-Pt/SiO_2 catalyst. This result implied that the Pt domains existed on the surface of the Sn-Pt/SiO_2. The Pt domains preferentially hydrogenated the C=C bond of crotonaldehyde and therefore the unfavorable products would be largely produced. On the other hand, the uniform formation of SnPt alloy phase in the SiO_2-encapsulated SnPt leads to decreasing the Pt domains and therefore the C=C hydrogenation of crotonaldehyde would be suppressed. Additionally, the catalytically active sites, namely SnPt alloy nanoparticles, are covered with the SiO_2 layer in the SiO_2-encapsulated SnPt. The hydrogenation of crotonaldehyde would be controlled by the silica layer with the porous structure. When the terminal methyl group of crotonaldehyde would access to the core SnPt nanoparticles, the hydrogenation itself would not proceed (Scheme 2b). On the other hand, the target molecular, crotyl alcohol, could be mainly produced when the terminal carbonyl group of crotonaldehyde would access to the core SnPt nanoparticles (Scheme 2a). The existence of silica layer would lead to the suppression of the interaction between the C=C bound and the SnPt surface because of the addition of a *direction selectivity* to the SnPt nanoparticles. Therefore, it was considered that the adsorption of crotonaldehyde through the oxygen atom of the C=O group would occur and the reaction as shown in Scheme 2a would proceed.

4. Conclusions

As for the selective hydrogenation of unsaturated aldehyde over the SnPt bi-metallic catalysts, the following were clarified.

(1) The SiO_2-encapsulated SnPt catalysts (the molar ratio of Sn/Pt = 1.0) having the core–shell structures were prepared by using the polyol process. In the SiO_2-encapsulated SnPt catalysts, the SnPt alloy phases were uniformly formed. The size of SnPt complex nanoparticles and the spherical particles was very uniform.
(2) The formation of uniform SnPt alloy phases and the pore structures in the silica layers to add a *direction selectivity* would enhance the chemo-selective hydrogenation of crotonaldehyde.

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