Effect of reduction method on the activity of Pt-Sn/SiO₂ for dehydrogenation of
propane

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Abstract

The effect of reduction method (direct reduction (*DR*), decomposition in inert gas (*DI*) and calcination-reduction (*CR*)) on the catalytic performances of Pt-Sn/SiO₂ catalyst in the dehydrogenation of propane was investigated. The Pt-Sn/SiO₂ (*DR*) showed the highest activity among the catalysts tested. The order of activities of Pt/SiO₂ and Pt-Sn/SiO₂ catalysts was Pt/SiO₂ (*DR*) $\leq$ Pt-Sn/SiO₂ (*CR*) < Pt-Sn/SiO₂ (*DI*) < Pt-Sn/SiO₂ (*DR*). The results of structural characterization by X-ray diffraction (XRD), CO pulse, transmission electron microscopy (TEM), and Pt L_{III} and Sn K-edges X-ray absorption fine structure (XAFS) spectroscopy indicated that Pt₃Sn alloy nanoparticle was mainly formed on the Pt-Sn/SiO₂ (*DR*). In the case of the Pt-Sn/SiO₂ (*CR*) catalyst, PtSn alloy particle was mainly dispersed on SiO₂. On the other hand, Pt metal particles and highly dispersed SnO₂ were present on the Pt-Sn/SiO₂ (*DI*). The relationship between activity and structure of platinum-tin catalysts suggested that Pt₃Sn alloy acts as active site for dehydrogenation of propane, whereas PtSn alloy shows low or no activity.

Keywords

Platinum-tin alloy; Dehydrogenation; Propane; Direct reduction; XAFS

1. Introduction

The catalytic dehydrogenation of light alkanes such as propane and butane is of great interest due to growing demands of alkenes as an important raw chemical intermediate to produce rubber, plastics and many other products [1, 2]. The conventional way of light alkenes in the petrochemical industry is steam cracking of alkanes, naphtha, and gas oil. The steam cracking is typically carried out above 1000 K. Thus, this reaction is energetically-unfavorable and shows low selectivity to alkenes. For example, in the case of steam cracking of naphtha, the yields of ethane and propylene are ca. 30 and 20 %, with substantial amounts of by-products including methane and coke. On the other hand, catalytic dehydrogenation of light alkanes provides an alternative for producing light alkenes as well as hydrogen.

Supported platinum-tin alloy catalysts have been widely studied in catalytic dehydrogenation of propane (DHP) [3-6]. The addition of Sn to Pt/support catalyst system has been found to favor selective lower alkane dehydrogenation, suppress the coke formation and increase the lifetime of the catalyst. These positive effects of Sn on the catalytic performance of supported Pt catalysts have been interpreted from both a geometrical (ensemble) and an electronic point of view [3-12]. Despite extensive studies, the role of Sn in a Pt-Sn catalyst remains elusive and the accurate nature of Pt-Sn system is complicated for many years. It has been well known that the properties of Pt-Sn alloy catalyst have been found to depend on the several factors such as support, metallic precursor, and preparation procedure [8, 13, 14]. Moreover, the active alloy phases often collapse into each metal oxide under ambient oxygen, resulting in deactivation of catalyst. Uemura et al. reported the reductive formation and oxidative phase separation of Pt₃Sn alloy nanoparticle in the reduction and oxidation

processes by the *in situ* time resolved XAFS techniques [15, 16]. This indicates that the stability of supported alloy catalyst is affected by the reaction and regeneration conditions [6, 15, 16]. As a consequence, there has been considerable interest in developing means to control the interactions between platinum and tin by appropriate catalyst preparation, pretreatment, and regeneration procedure.

In the present study, three different reduction procedures (direct reduction (*DR*), decomposition in inert gas (*DI*) and calcination-reduction (*CR*)) were applied to prepare a series of Pt-Sn/SiO₂ catalysts with different interactions between platinum and tin. The structure of platinum and tin was investigated by using X-ray absorption fine structure (XAFS) at Pt L_{III}- and Sn K-edges, TEM, CO-pulse, XRD techniques, and the catalytic test in propane dehydrogenation. The effect of reduction procedures on the nature of the Pt-Sn systems was investigated. The relationship between the structure of Pt-Sn nanoparticles and activity for propane dehydrogenation was discussed.

2. Experimental

2.1. Preparation

A silica (JRC-SIO-9, 334 m² g⁻¹) was used as support to prepare Pt and Pt-Sn catalysts. Prior to impregnation, the SiO₂ support was treated at 773 K for 3h in air. Silica-supported Pt catalyst (Pt/SiO₂) was prepared by impregnation of SiO₂ with the adequate volume of an aqueous solution of H₂PtCl₆·6H₂O (Wako, 99.9%), followed by the stirring at 353 K for 3h and dried at 353 K for 20h. A bimetallic Pt-Sn/SiO₂ was prepared by sequential impregnation method. The SiO₂ support was firstly impregnated with an aqueous solution of H₂PtCl₆·6H₂O, and then stirred at 353K for 3h, and dried at 353 K for 20h. Then the precipitate was added to

an acetone solution of SnCl₂·2H₂O (Wako, 97%), stirred at 353 K for 3h and dried at 353 K for 20h to yield the catalyst precursor. The Pt content was 3wt.%. The molar ration of Pt to Sn was 1.0. Prior to the reaction, the catalyst precursor was reduced by following three methods (Scheme 1): 1) Direct reduction (*DR*) The catalyst precursor was *in situ* reduced in 20 vol% H₂ diluted with N₂ (total flow rate 50ml min⁻¹) at 1073 K for 1h, and then cooled to 773 K in N₂ (100ml min⁻¹). 2) Decomposition in inert gas (*DI*) The catalyst precursor was treated with N₂ (total flow rate 50ml min⁻¹) at 1073 K for 1h, and then cooled to 773 K in N₂ (100ml min⁻¹). 3) Calcination-Reduction (*CR*) The catalyst precursor was firstly calcined in 20vol % O₂ diluted with N₂ (total flow rate 50ml min⁻¹) at 773 K for 1 h, and then reduced in 20 vol% H₂ diluted with N₂ (total flow rate 50ml min⁻¹) at 1073 K for 1h. Finally, the catalyst was cooled to 773 K in N₂ (100ml min⁻¹).

2.2. Propane dehydrogenation

Propane dehydrogenation was carried out by using a quartz reactor at atmospheric pressure with C₃H₈/N₂ (20/80) mixed gas at 773 K. Total flow rate was 100 ml min⁻¹. The catalyst precursor (50 mg) was placed between glass-wool. The gas composition was analyzed with an on-line gas chromatographs (Shimadzu GC-8A, Japan) equipped with a TCD (Molecular Sives-5A column) and a methanizer FID (Porapak-Q column) detectors.

2.3. Characterization

The Brunauer—Emmett—Teller (BET) specific surface area was estimated from N₂ isotherm at 77 K. The N₂ adsorption isotherm measurements were carried out by using a BELSORP 28SA (BEL Japan, Osaka, Japan) at 77 K. Prior to the measurement, each sample

was evacuated at 573 K for 3 h. The amount of adsorbed CO was determined by CO pulse method with an Okura BP-2 instrument (Okura Riken, Japan) interfaced with a TCD. X-ray diffraction (XRD) patterns were obtained by means of a MultiFlex DR powder X-ray diffractometer (Rigaku, Tokyo, Japan) with Cu K α radiation ($\lambda = 1.5405 \text{ \AA}$). The samples were scanned from $2\theta=38^\circ$ to 46° at the scanning rate of 0.067 s^{-1} and the resolution of 0.01° . TEM images were obtained by a JEOL JEM-2100F transmission electron microscope operating at an accelerating voltage of 200 kV. TEM samples were prepared by depositing drops of a methanol suspension containing small amounts of the powders onto a carbon-coated copper grid (Okensoji Co. Ltd.) following the evaporation of methanol in air. X-ray absorption experiments were carried out at the BL01B1 at SPring-8 (Hyogo, Japan). The ring energy was 8 GeV, and the stored current was 99.5 mA. The Pt L_{III}-edge (11.56 keV) X-ray absorption spectra were recorded by using a Si(111) monochromator in transmission mode in air at room temperature. The Sn K-edge (29.19 keV) X-ray absorption spectra were recorded by using a Si (311) monochromator in transmission mode in air at room temperature. The data [reduction](#) was performed by using the REX2000 Ver.2.5.9 (Rigaku) and FEFF8.40 programs [17].

3. Results

3.1 Propane dehydrogenation

Figure 1 shows the time course of propane conversion on Pt/SiO₂ and Pt-Sn/SiO₂ catalysts. The propane conversion on Pt/SiO₂ (*DR*) was quite low (ca. 5 %) and sharply declined, indicating that monometallic Pt catalyst showed a low activity and stability. The Pt-Sn/SiO₂ (*DR*) catalyst showed the highest activity and selectivity towards propylene (>

99%). A trace amount of methane and ethane were detected as by-products. Up to now, many researchers have reported the positive effect of Sn on the catalytic property of supported Pt catalyst for dehydrogenation of propane [6, 12, 18, 19], butane [7, 20], isobutane [4, 21], and hexane [8]. Generally, the selectivity to alkene improved by the addition of Sn because of the suppression of hydrogeolysis property, but the activity decreased. In contrast, in the case of the Pt-Sn/SiO₂ (*DR*) catalyst, the addition of Sn improved not only the catalytic performance (activity and selectivity to propylene) but also the stability. On the other hand, the Pt-Sn/SiO₂ (*CR*) catalyst showed a low activity and the selectivity to propylene on Pt-Sn/SiO₂ (*CR*) was slightly lower (ca. 95 %) than Pt-Sn/SiO₂ (*DR*), regardless of the coexistence of Sn with Pt. The conversion of propane on Pt-Sn/SiO₂ (*DI*) was higher than Pt-Sn/SiO₂ (*CR*), but lower than Pt-Sn/SiO₂ (*DR*). The selectivity to propylene on Pt-Sn/SiO₂ (*DI*) was about 99%. The activity gradually decreased with time on stream.

3.2 Physical and chemical properties of Pt/SiO₂ and Pt-Sn/SiO₂

Table 1 summarizes the BET specific surface area and the amount of adsorbed CO. Figure 2 shows TEM images of Pt/SiO₂ and Pt-Sn/SiO₂, and the particle size histograms of black spot observed in TEM images. Black spots were assigned to Pt or Pt-Sn alloy particle on SiO₂. The BET surface area of Pt/SiO₂ (*DR*) was slightly larger than bare SiO₂. On the Pt/SiO₂ (*DR*), small Pt particles whose mean particle size was about 2.0 nm were observed. When Sn was added into monometallic Pt catalyst system, the BET surface area slightly decreased compared with that of Pt/SiO₂ (*DR*). The particle size on Pt-Sn/SiO₂ catalysts (2.2–3.3 nm) was slightly larger than that on Pt/SiO₂ catalyst regardless of the reduction method. However, the amount of adsorbed CO remarkably decreased by the addition of Sn. These

results suggest the formation of Pt-Sn alloy and/or the deposition of Sn species on the surface of Pt metal particle. Meriaudeau et al. reported that the addition of Sn to Pt reduced the strength of Pt-CO bond by the preferential blocking of higher binding sites of Pt by Sn [19]. The reduction of strength of Pt-CO bond was interpreted as this geometric effect. Recently, Wang et al. synthesized Pt-Sn intermetallic, core/shell, and alloy nanoparticles by using colloidal technique, and investigated the CO adsorption properties of prepared Pt-Sn compounds [22]. The intensity of linearly adsorbed CO clearly decreased with increasing the surface Sn/Pt ratio, that is, the increasing of Sn surface coverage. On the other hand, Liu et al reported that the PtSn@Pt core-shell nanoparticle electrocatalysts prepared by potential cycling of PtSn intermetallic nanoparticles in CO-saturated H₂SO₄ solutions exhibited a substantially higher CO-tolerance property to Pt, PtRu alloy, and PtSn alloy catalysts [23]. They proposed that the superior CO-tolerance of the PtSn@Pt catalyst was mainly due to the electronic effect of the PtSn core on the Pt shell. In our cases, the catalysts prepared by the different reduction methods exhibited different catalytic activities, which were not proportional to the amount of adsorbed CO, in other words, the number of accessible Pt sites on Pt-Sn/SiO₂ catalyst. Therefore, the change in local structure and electronic state of Pt and Sn should be considered.

3.3 XRD patterns of Pt/SiO₂ and Pt-Sn/SiO₂

Figure 3 shows the XRD patterns of Pt/SiO₂ and Pt-Sn/SiO₂ catalysts. The XRD patterns of Pt/SiO₂ (*DR*) and Pt-Sn/SiO₂ (*DI*) exhibit a peak at $2\theta=39.8^\circ$, which is assigned to Pt (111). The full-width at half maximum (FWHM) of this diffraction line of Pt-Sn/SiO₂ (*DI*) was slightly narrower than that of Pt/SiO₂ (*DR*), indicating that the crystalline size of Pt metal

on Pt-Sn/SiO₂ (*DI*) was slightly larger than that on Pt/SiO₂ (*DR*). This result was consistent with TEM observation. However, as mentioned above, the amount of adsorbed CO on Pt-Sn/SiO₂ (*DI*) was much smaller than that on Pt/SiO₂ (*DR*). Moreover, no diffraction line due to Sn compounds including SnO and SnO₂ appeared in XRD patterns of Pt-Sn/SiO₂ catalysts regardless of reduction method. This indicates that Sn species was separated from Pt metal, and was highly dispersed on the Pt-Sn/SiO₂ (*DI*) catalyst. Considering a small amount of adsorbed CO, it is likely that the surface of Pt metal on Pt-Sn/SiO₂ (*DI*) was partially covered with highly dispersed SnO and/or SnO₂. The XRD pattern of Pt-Sn/SiO₂ (*DR*) shows two diffraction lines around $2\theta=39^\circ$ and 45° for the Pt₃Sn alloy phase (ICSD 105796) together with diffraction lines around 42° and 44° for the PtSn alloy phase (ICSD 42593). These lines are assignable to Pt₃Sn (111) ($2\theta=38.93^\circ$), Pt₃Sn (200) ($2\theta=45.26^\circ$), PtSn(102) ($2\theta=41.81^\circ$), and PtSn(110) ($2\theta=44.10^\circ$), respectively. The intensities of diffraction lines for Pt₃Sn alloy phase are much stronger than those for PtSn alloy phase, suggesting that the major part of Pt-Sn/SiO₂ (*DR*) catalyst possesses the Pt₃Sn alloy structure in the fcc arrangement. In the case of Pt-Sn/SiO₂ (*CR*), diffraction lines for the PtSn alloy phase was mainly observed in addition to weak diffraction lines for the Pt₃Sn alloy phase. This suggests that PtSn alloy, which is the same structure as NiAs, is mainly formed on Pt-Sn/SiO₂ (*CR*).

3.4 XAFS analysis of Pt/SiO₂ and Pt-Sn/SiO₂

3.4.1 Pt L_{III}-edge XAFS

Figure 4 shows Pt L_{III}-edge XANES spectra of Pt/SiO₂, Pt-Sn/SiO₂ catalysts, and reference samples (Pt foil, PtCl₂, and PtO₂). XANES spectrum of Pt-Sn/SiO₂ catalyst precursor exhibited essentially the same features as that of PtCl₂. This suggests that Pt²⁺

species having Pt-Cl bond such as $[\text{PtCl}_4]^{2-}$ adsorbed on SiO₂ surface. After reduction, platinum in all catalysts possessed the similar feature as that of Pt [metal](#). The white line intensities of Pt/SiO₂ (*DR*) and Pt-Sn/SiO₂ (*DI*) were similar each other, and slightly higher than that of Pt foil. As for [Pt-Sn/SiO₂](#) (*DR*) and Pt-Sn/SiO₂ (*CR*), their spectra were close and the white line intensities were slightly less than that of Pt foil. Since the intensity of the white line reflects the vacancy population of the 5d orbital of Pt [24, 25], the intensity of white line decreases when Pt receives electrons from the surrounding atoms. From this viewpoint, the decrease of white lines of Pt-Sn/SiO₂ (*DR*) and Pt-Sn/SiO₂ (*CR*) strongly suggests an electron donation from Sn to Pt and alloy formation between Pt and Sn. A similar result has previously observed in Pt-Sn bimetallic catalysts by Uemura et al. [15, 16]. They assigned this small decrease in the white line intensity to the formation of a Pt-Sn alloy since the [d](#)-electron density of platinum atoms will increase with alloying with Sn that shows lower electronegativity than Pt.

Figure 5(A) shows k^3 -weighted EXAFS oscillation at Pt L_{III}-edge. The EXAFS oscillation of Pt-Sn/SiO₂ catalyst [precursor](#) exhibited essentially the same features as that of PtCl₂. In the radial structure function (RSF) of Pt-Sn/SiO₂ catalyst [precursor](#) shown in Figure 5(B), the peak around 0.19 nm assigned to Pt-Cl linkage appeared. This peak disappeared after the reduction. Combined with the XANES spectrum of Pt-Sn/SiO₂ catalyst [precursor](#), these results suggest that [during impregnation and dryness](#), $[\text{PtCl}_6]^{2-}$ species in H₂PtCl₆·6H₂O precursor was transformed to $[\text{PtCl}_4]^{2-}$ and adsorbed on SiO₂. After the following reduction treatment, $[\text{PtCl}_4]^{2-}$ was decomposed and reduced to Pt metal or Pt-Sn alloy. The EXAFS oscillation of Pt-Sn/SiO₂ (*DI*) catalyst is similar to that of Pt foil, although the intensity of oscillation is weaker than that of Pt foil. The peak around 0.25 nm in the RSF of Pt-Sn/SiO₂

(*DI*) catalyst is assignable to Pt–Pt linkage. A smaller Pt–Pt contribution than that in Pt foil indicates that small Pt nanoparticle (ca. 2.2 nm) was formed on Pt-Sn/SiO₂ (*DI*).

In contrast, the EXAFS oscillation of Pt-Sn/SiO₂ (*DR*) is significantly different from and much weaker than that of Pt foil. This suggests the interference of scattered electrons by Sn and Pt, in other words, the contribution of Pt–Sn linkage in addition to Pt–Pt linkage in the Pt-Sn alloy phase as reported by Uemura et al.. Table 2 and Figure S1 show the curve-fitting analysis of Pt-Sn/SiO₂ (*DR*) catalyst. The EXAFS data for Pt-Sn/SiO₂ (*DR*) catalyst were well fitted by assuming two shells (Pt–Pt and Pt–Sn linkages). No Pt–O linkage was observed, indicating that the all of supported Pt species was completely reduced to metallic state after the treatment with H₂ diluted with N₂ at 1073 K. The bond distances of Pt–Pt and Pt–Sn of Pt-Sn/SiO₂ (*DR*) catalyst were shorter than the crystallographic values (Pt–Pt = 0.283 nm and Pt–Sn = 0.283 nm) in the Pt₃Sn crystal [26]. The ratio of the coordination numbers, $N_{\text{Pt-Sn}}/N_{\text{Pt-Pt}}$, was 0.49 which is compatible with 0.50 expected for Pt₃Sn. The coexistence of a small fraction of PtSn phase (Figure 2) and the interference of Pt and Sn scattering in the Pt-Sn/SiO₂ (*DR*) catalyst result in relatively larger *R*-factors. In the case of Pt-Sn/SiO₂ (*CR*), the EXAFS oscillation is different from that of Pt-Sn/SiO₂ (*DR*). Moreover, the oscillation period was slightly different from that of Pt foil. These results and XRD pattern suggest the formation of PtSn alloy phase on Pt-Sn/SiO₂ (*CR*).

3.4.2 Sn K-edge XAFS

Figure 6 shows Sn K-edge XANES spectra of Pt-Sn/SiO₂ catalysts, and reference samples (Sn(II)O and Sn(IV)O₂). The white line intensity of Pt-Sn/SiO₂ catalyst precursor was much higher than that of SnO, and slightly lower than that of SnO₂. This suggests that

Sn²⁺ was oxidized to Sn⁴⁺ during the impregnation in air. In the case of Pt-Sn/SiO₂ (*DI*), the white line intensity was slightly lower than that of SnO₂, and the peak assignable to Sn–O linkage around 0.16 nm was observed in the RSF (Figure 7). Moreover, no X-ray diffraction peaks due to SnO₂ appeared (Figure 2) and the amount of adsorbed CO was much smaller than that on Pt/SiO₂ (*DR*). Based on these results, we proposed that highly dispersed SnO₂ was formed and a part of Pt surface on Pt-Sn/SiO₂ (*DI*) was covered with SnO₂ (SnO₂ decorated the surface of Pt metal).

The white line intensity of Pt-Sn/SiO₂ (*DR*) was slightly higher than that of SnO, whereas much lower than that of SnO₂. The intensity of peak assignable to Sn–O linkage around 0.16 nm was less than that of Pt-Sn/SiO₂ (*DI*). Appreciable oscillation appeared around 0.75 nm⁻¹ (Figure 7(A)). These results suggest that the EXAFS oscillation includes the contribution of Sn–Pt linkage as a result of the formation of Pt-Sn alloy phase. Table 3 and Figure S2 show the curve-fitting analysis of Pt-Sn/SiO₂ (*DR*) catalyst. The EXAFS data for Pt-Sn/SiO₂ (*DR*) catalyst were well fitted by assuming two shells (Sn–Pt and Sn–O linkages). The RSF of the Pt-Sn/SiO₂ (*DR*) catalyst gave three weak peaks, at 0.15, 0.21, and 0.26 nm (Figure 7(B)). The first peak corresponds to a Sn–O linkage. The second and third peaks correspond to Sn–Pt linkage. The bond distances of Sn–Pt (0.274 nm) agrees with that of Pt–Sn (0.273 nm) shown in Table 2. In the Pt₃Sn phase, a Pt atom is surrounded by 4 Sn atoms and 8 Pt atoms, while a Sn atom is surrounded by 6 Pt atoms (Figure S3). Thus, the ratio of the coordination numbers, $N_{\text{Pt-Sn}}/N_{\text{Sn-Pt}}$ is estimated to be 0.67 for Pt₃Sn. This value is almost compatible with 0.46 for Pt-Sn/SiO₂ (*DR*), considering a large uncertainty in the coordination number due to the coexistence of small fraction of PtSn alloy and the interference of Pt and Sn scattering (Tables 2 and 3). The coordination number of O

surrounding Sn atoms in Pt-Sn/SiO₂ (*DR*) was ca. 4, which is smaller than that for bulk SnO₂. This is probably due to the formation of amorphous SnO₂ phase and small SnO₂ nanoparticles. Based on these results, we concluded that Pt₃Sn alloy particles were present together with highly dispersed SnO₂ on Pt-Sn/SiO₂ (*DR*).

Similarly, the white line intensity of Pt-Sn/SiO₂ (*CR*) was slightly higher than that of SnO, whereas much lower than that of SnO₂. Moreover, appreciable oscillation was also observed, however the position is slightly different from that of Pt-Sn/SiO₂ (*DR*). The RSF of the Pt-Sn/SiO₂ (*CR*) catalyst gave three weak peaks, at 0.15, 0.22, and 0.27 nm. The first peak corresponds to a Sn–O linkage similar with Pt-Sn/SiO₂ (*DR*). Although the positions of second and third peaks are slightly different from those of Pt-Sn/SiO₂ (*DR*), these peaks seem to correspond to Sn–Pt linkage. All of these structural analyses strongly suggest the coexistence of highly dispersed SnO₂ and Pt-Sn alloy whose local structure is different from that of Pt₃Sn alloy phase. Considering XRD pattern, we concluded that PtSn alloy particle was regarded as the main species on Pt-Sn/SiO₂ (*CR*) catalyst.

4. Discussion

The results of propane dehydrogenation over Pt/SiO₂ and Pt-Sn/SiO₂ catalysts show that the addition of tin to platinum improves the catalytic performance. Structural analyses by XRD, TEM, and XAFS techniques clearly indicate that the geometric and electronic states of platinum remarkably changed with the addition of tin followed by different reduction method. It appears that the activity for propane dehydrogenation strongly depends on the structure and electronic state of platinum and tin.

The Pt/SiO₂ (*DR*) catalyst showed a low activity and stability. This clearly indicates

that monometallic platinum is not active and is unstable. On the other hand, the Pt-Sn/SiO₂ (*DR*) catalyst, on which small Pt₃Sn alloy nanoparticles were present as the main phase, showed much higher activity than that of Pt/SiO₂ (*DR*). These results strongly suggest that Pt₃Sn alloy acts as active site for dehydrogenation of propane. Among the Pt-Sn alloy phases (PtSn₄, PtSn₂, Pt₂Sn₃, PtSn, and Pt₃Sn [27, 28]), a superior catalytic performance was often assigned to Pt₃Sn alloy phase [7, 29-31]. The present work also showed that PtSn alloy was mainly formed on the Pt-Sn/SiO₂ (*CR*) catalyst, which showed a low activity, although the conversion of propane was stable. Thus, it would appear that PtSn alloy is not active for propane dehydrogenation despite the coexistence of platinum and tin. Likewise, Llorca et al reported that PtSn alloy showed high stability and selectivity in *n*-hexane dehydrogenation while the selectivity to benzene and hydrogenolysis products were low [8]. Recently, Yang et al. investigated the effect of Sn on the activity and selectivity of Pt catalyst in propane dehydrogenation by using density functional calculation (DFT) method [32]. They reported that the introduction of Sn lowers the energy barrier for propylene desorption and simultaneously increases the activation energy for propylene dehydrogenation, which has a positive effect on the selectivity toward propylene production, and proposed that the Pt₃Sn bulk alloy is the most suitable for propane dehydrogenation by considering the compromise between the catalytic activity and selectivity.

In the case of the Pt-Sn/SiO₂ (*DI*) catalyst, XRD, CO pulse, TEM, and XAFS results implied that monometallic platinum particle decorated with small SnO₂. When Sn was absent (Pt /SiO₂ (*DI*) catalyst), the dispersion of Pt was quite low (data not shown), indicating that the introduction of Sn suppressed the aggregation of Pt. This implies the intimate contact of Sn with Pt. Although Pt₃Sn alloy phase was not detected by XRD and XAFS techniques, the

conversion of propane on the Pt-Sn/SiO₂ (*DI*) catalyst was ca. 60 % of that on the Pt-Sn/SiO₂ (*DR*) catalyst having Pt₃Sn alloy phase. This relatively high activity is probably caused by the strong interaction between the platinum metal particle and highly dispersed SnO₂ such as electron transfer between SnO₂ and Pt, or the formation of Pt₃Sn alloy phase at the interface of platinum metal particle and highly dispersed SnO₂. The low ratio of surface to bulk would make the detection of formation of Pt₃Sn alloy at the interface of platinum metal particle and highly dispersed SnO₂ by XAFS difficult, since XAFS analysis yields the average information of surface and bulk. Therefore, further investigation is necessary to verify these hypotheses.

Conclusion

The Pt-Sn/SiO₂ catalysts were reduced by three methods (direct reduction (*DR*), decomposition in inert gas (*DI*) and calcination-reduction (*CR*)), and were examined for propane dehydrogenation. The activities of the Pt-Sn/SiO₂ catalysts were strongly influenced by the reduction method. Decomposition in inert gas (*DI*) method resulted in the coexistence of Pt metal and highly dispersed SnO₂ on SiO₂, which showed the medium activity among the catalysts tested. Direct reduction (*DR*) caused that Pt₃Sn alloy nanoparticle was mainly formed on Pt-Sn/SiO₂ (*DR*) catalyst, which showed the highest activity. Calcination-reduction (*CR*) method also led to PtSn alloy formation. PtSn alloy nanoparticles were present as the main phase. However, this catalyst was not active in propane dehydrogenation. The relationship between activity and structure of platinum-tin alloy suggested that Pt₃Sn alloy acts as active site for dehydrogenation of propane, whereas PtSn alloy shows low or no activity.

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Figure captions

Figure 1 Time course of conversion of propane.

(●) Pt-Sn/SiO₂ (*DR*), (■) Pt-Sn/SiO₂ (*DI*), (◆) Pt-Sn/SiO₂ (*CR*)
(▲) Pt/SiO₂ (*DR*) (773 K)

Figure 2 TEM images and particle size distributions of (a) Pt/SiO₂ (*DR*) (773_K), (b) Pt-Sn/SiO₂ (*DI*), (c) Pt-Sn/SiO₂ (*DR*), and (d) Pt-Sn/SiO₂ (*CR*).

Figure 3 XRD patterns of (a) Pt/SiO₂ (*DR*) (773_K), (b) Pt-Sn/SiO₂ catalyst precursor, (c) Pt-Sn/SiO₂ (*DI*), (d) Pt-Sn/SiO₂ (*DR*), and (e) Pt-Sn/SiO₂ (*CR*).
(●) Pt₃Sn, (○) PtSn, (▼) Pt

Figure 4 Pt L_{III}-edge XANES spectra of Pt/SiO₂, Pt-Sn/SiO₂ and references: (a) Pt/SiO₂ (*DR*) (773_K), (b) Pt-Sn/SiO₂ catalyst precursor,, (c) Pt-Sn/SiO₂ (*DI*), (d) Pt-Sn/SiO₂ (*DR*), (e) Pt-Sn/SiO₂ (*CR*), (f) Pt foil, (g) PtCl₂, (h) PtO₂.

Figure 5 (A) *k*³-weighted EXAFS oscillation at Pt L_{III}-edge and (B) their Fourier transforms: (a) Pt/SiO₂ (*DR*) (773_K), (b) Pt-Sn/SiO₂ catalyst precursor, (c) Pt-Sn/SiO₂ (*DI*), (d) Pt-Sn/SiO₂ (*DR*), (e) Pt-Sn/SiO₂ (*CR*), (f) Pt foil, (g) PtCl₂, (h) PtO₂.

Figure 6 Sn K-edge XANES spectra of Pt-Sn/SiO₂ and references: (a) Pt-Sn/SiO₂ catalyst precursor, (b) Pt-Sn/SiO₂ (*DI*), (c) Pt-Sn/SiO₂ (*DR*), (d) Pt-Sn/SiO₂ (*CR*), (e) SnO,

(f) SnO₂.

Figure 7 (A) k^3 -weighted EXAFS oscillation at Sn K-edge and (B) their Fourier transforms: (a) Pt-Sn/SiO₂ catalyst precursor, (b) Pt-Sn/SiO₂ (DI), (c) Pt-Sn/SiO₂ (DR), (d) Pt-Sn/SiO₂ (CR), (e) SnO, (f) SnO₂.

Scheme 1 Scheme of catalyst preparation and reduction.

Figure S1 Fourier transform of the Pt L_{III}-edge EXAFS spectrum of Pt-Sn/SiO₂ (DR) catalyst.

Figure S2 Fourier transform of the Sn K-edge EXAFS spectrum of Pt-Sn/SiO₂ (DR) catalyst.

Figure S3 Crystal structure of Pt₃Sn.

Table 1 Physical and chemical properties of Pt/SiO₂ and Pt-Sn/SiO₂.

Catalysts	Pt content (wt%)	Sn content ^a (wt%)	BET surface area ^b /m ² g ⁻¹	CO <u>adsorption</u> ^c /μmol g ⁻¹
Pt/SiO ₂ (<i>DR</i>)	3.0	-	334	54.9
Pt-Sn/SiO ₂ <u>precursor</u>	3.0	1.8	242	-
Pt-Sn/SiO ₂ (<i>DI</i>)	3.0	1.8	326	10.6
Pt-Sn/SiO ₂ (<i>DR</i>)	3.0	1.8	296	6.5
Pt-Sn/SiO ₂ (<i>CR</i>)	3.0	1.8	290	7.3

a: The molar ratio of Pt to Sn was fixed as 1:1.

b: The surface area of SiO₂ (*JRC-SIO-9*) is 325 m² g⁻¹.

c: The amount of CO adsorption was estimated from the CO-pulse experiments.

Table 2 The curve-fitting results of the Pt L_{III}-edge EXAFS data for Pt-Sn/SiO₂ (DR)

	N	$r/10^{-1} \text{ nm}$	$\Delta E/\text{eV}$	$\sigma^2/10^{-2} \text{ nm}^2$
Pt-Sn	1.8(5)	2.73(1)	3(2)	0.006(4)
Pt-Pt	3.7(6)	2.78(1)	7(2)	0.006(1)
Pt-Sn*	4	2.83		*(Pt ₃ Sn ₁)
Pt-Pt*	8	2.83		*(Pt ₃ Sn ₁)

N : Coordination number; ΔE : threshold energy difference; r : bond distance; σ : Debye-Waller factor, k range / 10 nm^{-1} $3.5 < k < 13.0$, r range / 10^{-1} nm $0.18 < r < 0.32$, R -factor: 4.4 %

* Crystallographic data

Table 3 The curve-fitting results of the Sn K-edge EXAFS data for Pt-Sn/SiO₂ (DR)

	N	$r/10^{-1} \text{ nm}$	$\Delta E/\text{eV}$	$\sigma^2/10^{-2} \text{ nm}^2$
Sn-Pt	3.9(6)	2.74(1)	-1(2)	0.008(1)
Sn-O	4.1(9)	2.03(1)	-1(3)	0.009(1)
Sn-Pt*	6	2.83		*(Pt ₃ Sn ₁)
Sn-O*	6	2.05		*(SnO ₂)

N : Coordination number; ΔE : threshold energy difference; r : bond distance; σ : Debye-Waller factor, k range / 10 nm^{-1} $3.5 \text{ nm} < k < 13.0$, r range / 10^{-1} nm $1.8 < r < 3.2$, R -factor: 3.6 %

* Crystallographic data

Figure 1

En

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Scheme 1

Supporting Information

Effect of reduction method on the activity of Pt-Sn/SiO₂ for dehydrogenation of propane

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Figure S1

Figure S2

Figure S3