Infrared Spectroscopy Study of Aldehydes Adsorbed on Rh–Sn Bimetallic Systems: Selective Activation of Aldehydes by Tin

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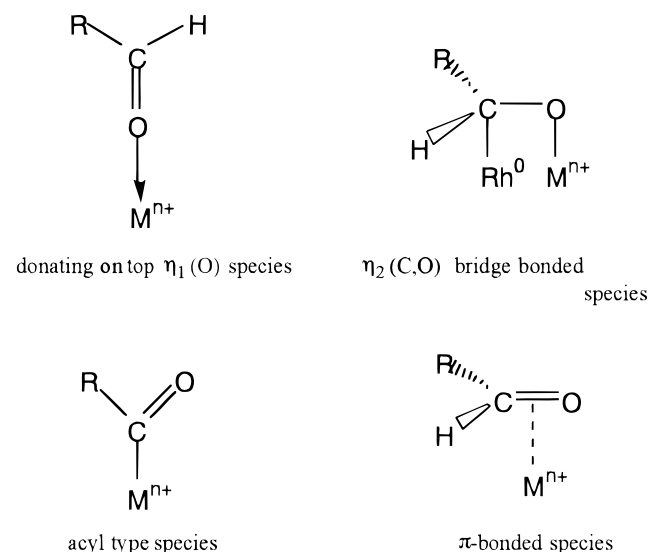
Infrared spectra of propionaldehyde was studied over silica-supported Rh–Sn bimetallic catalysts. Two absorption bands of the carbonyl group were observed at 1670 and 1720 cm^{-1}, and the aldehyde hydrogen ($-CH=O$) was also observed at 2748 and 2848 cm^{-1} over the $Sn/Rh/SiO_2$ catalysts on which propionaldehyde was preadsorbed. One of the absorption bands of carbonyl groups at 1670 cm^{-1} readily disappeared by contact with H_2, whereas the other band at 1720 cm^{-1} remained. The band of the aldehyde hydrogen also disappeared by the contact with H_2. The absorption band at 1670 cm^{-1} was assigned to a donating-on-top η^1 adsorbed species that were bound to tin atoms with oxygen atoms of carbonyl groups. The band observed at 1720 cm^{-1} was assigned to a species weakly adsorbed on the catalyst surface. The intensity of the band at 1670 cm^{-1} was increased with an Sn/Rh ratio up to unity and then was gradually decreased with the Sn/Rh ratio of the catalysts. The reduction temperature at 573 K yielded a maximum intensity ratio of I_{1670}/I_{1720}. The activity for selective hydrogenation of unsaturated aldehydes to unsaturated alcohols indicated a maximum at 573 K of reduction temperature. These results clearly indicate that the adsorbed species observed at 1670 cm^{-1} in the infrared spectra is one of the most effective surface adsorption states in the selective hydrogenation reaction of carbonyl groups in unsaturated compounds. Adsorption experiments indicated that the tin addition increased the O_2-adsorption capacity of the catalysts. Tin showed a high affinity for oxygen. These results can conclude that one of the roles of tin is selective activation of carbonyl groups by binding to the Sn atoms with oxygen atoms of carbonyl groups in unsaturated carbonyl compounds, which can be reduced to unsaturated alcohol by hydrogen atoms spilt over from Rh sites, in the hydrogenation of unsaturated aldehydes.

Introduction

Group VIII–Sn bimetallic catalysts were studied extensively in the field of reforming catalysts. Tin in the catalysts plays an important role in selectivity and catalyst life during the reforming reaction.[1] The Sn is considered to weaken C–H and C–C bond breaking activity of the metallic catalysts for the reforming reaction. The mild hydrogenolysis activity of the group VIII–Sn catalysts brought about slower catalyst deactivation. For oxidation reactions in addition to hydrogenation and/or hydrogenolysis reactions, Sn is one of the effective additives to the metallic catalysts. Oxygen isotope exchange ($^{16}O_2-^{18}O_2$ exchange) and carbon monoxide oxidation reaction over Rh/SiO_2 indicated that the addition of Sn enhanced the catalytic activities.[2-5] The decrease of activation energy for the oxygen isotope exchange reaction and the remarkable lowering of the ignition temperature for the CO oxidation reaction were observed over the tin-added Rh/SiO_2 catalysts. These reports suggest Sn is also effective for reactions of oxygenated compounds. Recently, selective hydrogenation reactions over Sn-containing noble metallic catalysts have been reported. Candy et al.[6,7] have reported that hydrogenation of ethyl acetate over Rh/SiO_2 catalyst was enhanced by the addition of Sn. Ponec has reviewed the selective hydrogenation reaction of unsaturated aldehyde over the promoted Pt/SiO_2 catalysts.[8] The unsaturated aldehydes were reduced to the corresponding unsaturated alcohols with high selectivity over the tin-modified Pt/SiO_2.[8] We have reported that addition of Sn brought about a high selectivity of crotyl alcohol in hydrogenation of crotonaldehyde

over Rh/SiO_2 catalysts.[9-12] We considered that the role of Sn in the selective hydrogenation reaction was selective activation of the carbonyl group in crotonaldehyde over the bimetallic catalysts. Selective activation of the carbonyl group in ethyl acetate on the *Rh–Sn pair sites* over the Rh–Sn/SiO_2 catalysts has also been suggested.[6,7] An adsorption state of di-σ η^2 type was considered for the selective hydrogenation to unsaturated alcohols. It was considered that carbon and oxygen atoms in an unsaturated aldehyde were attached to Rh and Sn atoms in the catalyst, respectively.[6,7] Margitfalvi et al. have also reported that Sn improved the selectivity of crotyl alcohol from crotonaldehyde hydrogenation over Sn–Pt/SiO_2 catalysts.[13] Our previous reports[12] have indicated that the supported tin catalysts without any active components such as Rh was able to activate crotonaldehyde in the selective liquid-phase reduction. These results indicate that Sn itself is important for a selective reduction of unsaturated aldehyde. It is, however, difficult to obtain evidence for the intimate interaction between Sn sites and carbonyl group in the unsaturated compounds. For this purpose, vibrational spectroscopy is a powerful tool to study the reaction mechanism of heterogeneous catalysis. Infrared and electron energy loss spectroscopy of adsorbed species on the catalysts are available to elucidate active intermediates during the reaction.

A number of vibrational spectra of adsorbed carbonyl compounds were reported on metal catalysts. Several absorption bands were observed, and four types of chemisorbed aldehyde have been proposed.[8,14-22] Those are di-σ η^2 (C, O) type bridge-

SCHEME 1: Postulated Surface Adsorption Species of Aldehydes

donating on top η_1 (O) species

η_2 (C,O) bridge bonded species

acyl type species

π-bonded species

Figure 1. Adsorption capacity of Sn/Rh/SiO$_2$ catalysts: (closed circle) H$_2$; (square) C$_2$H$_4$; (triangle) CO; (open circle) O$_2$. Adsorption temperature: room temperature. Adsorption pressure: 1.3 kPa.

bonded carbonyl, acyl type, side-on type π-complex, and donating-on-top type species (η^1 (O) type), as shown in Scheme 1. It is significantly expected that the reactivities of these species are markedly different from each other. In this paper, IR spectra of aldehyde adsorbed on Rh—Sn/SiO$_2$ are reported. The dependence of the reduction temperature of the catalysts should be discussed because the reduction temperature strongly affects the catalytic activity for the selective hydrogenation of unsaturated aldehyde. Furthermore, the reactivity of the adsorbed aldehyde with H$_2$ is also investigated. These results will shed light on not only an active surface species but also a reaction mechanism for selective hydrogenation of unsaturated aldehydes.

Experimental Section

Catalyst Preparation. The Sn/Rh/SiO$_2$ catalysts were prepared by the successive impregnation method described in the previous paper in detail.[4] The support, silica gel SIO-8, was obtained from The Catalysis Society of Japan. The silica was impregnated with an aqueous solution of Rh(NO$_3$)$_3$. The chemicals used here were obtained from Nakarai Tesque Inc., Kyoto, Japan. The loading of Rh was 5 wt % with respect to the support. Tin was supported on Rh/SiO$_2$ by impregnating with an ethanolic solution of SnCl$_2$·2H$_2$O. The catalysts were calcined in flowing air at 773 K for 5 h followed by reduction in flowing hydrogen at 573, 673, 773, or 873 K for 5 h.

Adsorption Capacity. The adsorption capacity of the catalysts was evaluated in a conventional static system for H$_2$, O$_2$, CO, and ethylene. The catalyst was reduced in the adsorption cell at the prescribed temperature. The adsorption was carried out in 1.3 kPa of each gas at room temperature. The adsorption capacity, amount of irreversible adsorption, was calculated from the difference of the total amount of adsorption and reversible adsorption.

XPS Measurement. XPS spectra were measured with a spectrometer of Kratos XSAM800 (Manchester, U.K.) at The Center for Instrumental Analysis, Kobe University. The magnesium Kα ray (1253.6 eV) was used for excitation, and the X-ray tube was operated at 300 W. The binding energy of each peak (Rh3d and Sn3d) was calibrated with the Si2p peak position of the silica support at 103.8 eV. The data processing was carried out by the data system of DS800 supplied from Kratos Co.
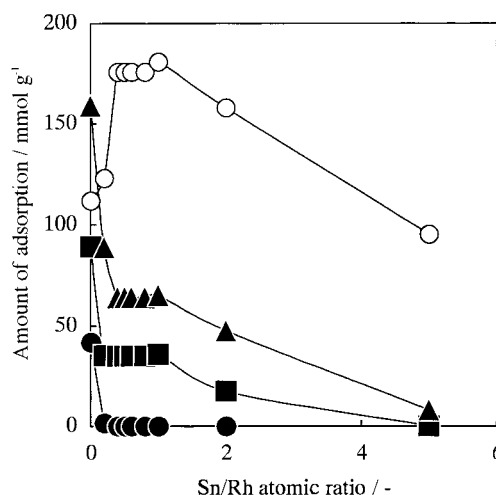
IR Spectroscopy. Infrared spectra were obtained by a FT-IR spectrometer, JASCO VALOR III, with a MCT highly sensitive detector. A diffuse reflectance unit and a catalyst reaction cell, which were purchased from Spectratech Co., were equipped in the spectrometer. The spectra were accumulated by 1500 times, and the resolution of the spectrometer was 4 cm^{-1}. The catalyst sample was prereduced in the in-situ cell by flowing H$_2$, then purged by flowing He, and then cooled to room temperature. The adsorption was carried out by introducing 25 μL of propionaldehyde in the He stream with a microsyringe. The reactivity of adsorbed aldehyde was also studied by flowing H$_2$ after the adsorption of propionaldehyde. Infrared spectra of propionaldehyde in an ethanolic solution of SnCl$_2$·2H$_2$O were also obtained with a liquid solution cell in order to identify adsorbed species on the Sn/Rh/SiO$_2$ catalysts.

Hydrogenation of Crotonaldehyde. Liquid-phase hydrogenation of crotonaldehyde was carried out in a stainless steel autoclave. One-fifth milliliter of crotonaldehyde obtained from Aldrich Chemicals was charged in a glass tube with 4 mL of 2-butanol as a solvent. The catalyst weight charged was 20 mg. The glass tube including the reactant, the solvent, and the catalyst was inserted into the autoclave. Hydrogen gas was charged several times to substitute air in the autoclave and pressurized up to 1.0 MPa. The autoclave was heated to 383 K. The reaction lasted for 20 h. The products were analyzed by GC (4 m of PEG20M packed column).

Results and Discussion

Adsorption Capacity. The adsorption capacity of the Sn/Rh/SiO$_2$ catalysts for H$_2$, CO, CH$_2$=CH$_2$, and O$_2$ was shown in Figure 1. Only small amount of Sn addition (Sn/Rh = 0.2) sharply decreased the adsorption capacity for H$_2$, and the capacity indicated ca. zero. The amount of CO and CH$_2$=CH$_2$ adsorption was decreased by the Sn addition, but the capacity for CO and CH$_2$=CH$_2$ did not reach zero. On the other hand, The amount of O$_2$ adsorption was increased with Sn content up to unity of Sn/Rh ratio. These results were identical to the data obtained over the coimpregnated Rh—Sn/SiO$_2$ catalysts previously reported.[3,5] The sharp decrease of H$_2$ adsorption indicates that the dissociative adsorption of hydrogen molecules was strongly suppressed by the addition of Sn. The gradual decrease of CO and CH$_2$=CH$_2$ adsorption shows that CO and CH$_2$=CH$_2$ molecules were adsorbed associatively and that the surface Sn concentration was not so seriously enriched. The
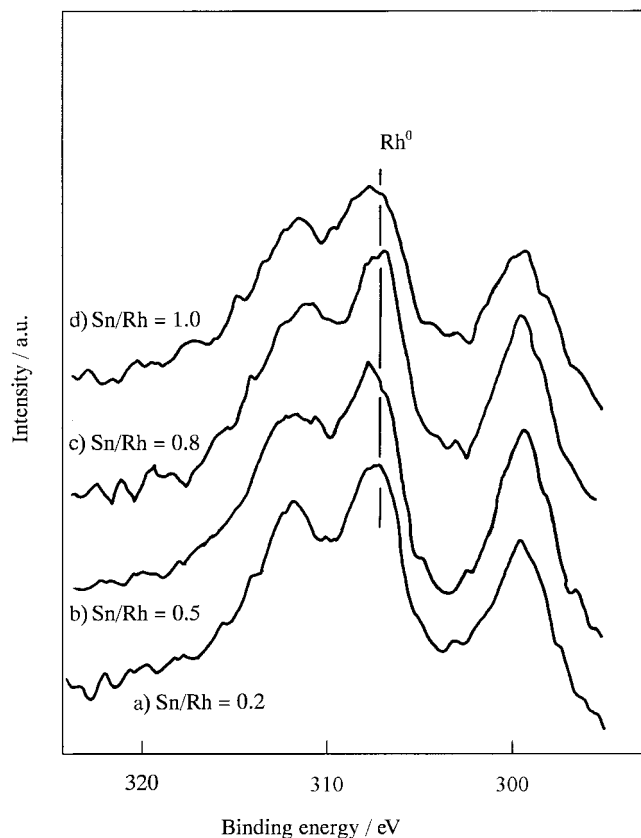
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Figure 2. Rh 3d XPS spectra of Sn/Rh/SiO$_2$ catalysts. Reduction temperature: 573 K.

increase of O$_2$ adsorption suggests that Sn sites played an important role for dissociative adsorption of oxygen molecules, as proposed in the previous paper.[3,5]

   XPS Analysis. X-ray photoelectron spectra of the Rh 3d region and the Sn 3d region of the Sn/Rh/SiO$_2$ catalysts are shown in Figures 2 and 3, respectively. The spectra were obtained without a further pretreatment in the spectrometer. Rhodium 3d spectra show that the electronic state of Rh was in a metallic state and was not modified by the addition of Sn, as shown in Figure 2. Tin 3d spectra indicate that most Sn was in an oxidized state, but unfortunately, the exact valence, +2 or +4 was not distinguished by a conventional X-ray photoelectron spectrometer. The broad Sn 3d$_{5/2}$ peak also suggests that the Sn^0 component was included. As the oxidized catalysts indicated the sharp Sn 3d peaks at 486.6 eV, the Sn in the reduced Sn/Rh/SiO$_2$ catalysts was considered to be a partly reduced Sn species, like Sn^{2+}. Although the surface of the catalysts was reoxidized by exposure to the atmosphere before XPS measurement, the presence of a lower binding energy component in the Sn 3d$_{5/2}$ spectra suggests that some amount of Sn^{4+} in the catalysts was reduced to a species with lower valence. Our previous TPR study of Rh−Sn/SiO$_2$ catalysts prepared by the coimpregnation method also indicates the partly reduced Sn species.[23] The surface concentration of Sn and Rh with respect to Si of the SiO$_2$ support was shown in Figure 4a. The concentration of Rh (Rh/Si atomic ratio) was kept constant because the loading of Rh was constant in the catalysts used here (5 wt % except Sn/SiO$_2$). On the other hand, the concentration of Sn (Sn/Si atomic ratio) was almost linearly increased with the Sn/Rh bulk ratio. The surface Sn/Rh ratio was slightly larger than the balk value, as also shown in Figure 4b. These results indicate that Sn and Rh were well dispersed on SiO$_2$ and the slight Sn enrichment was observed because of
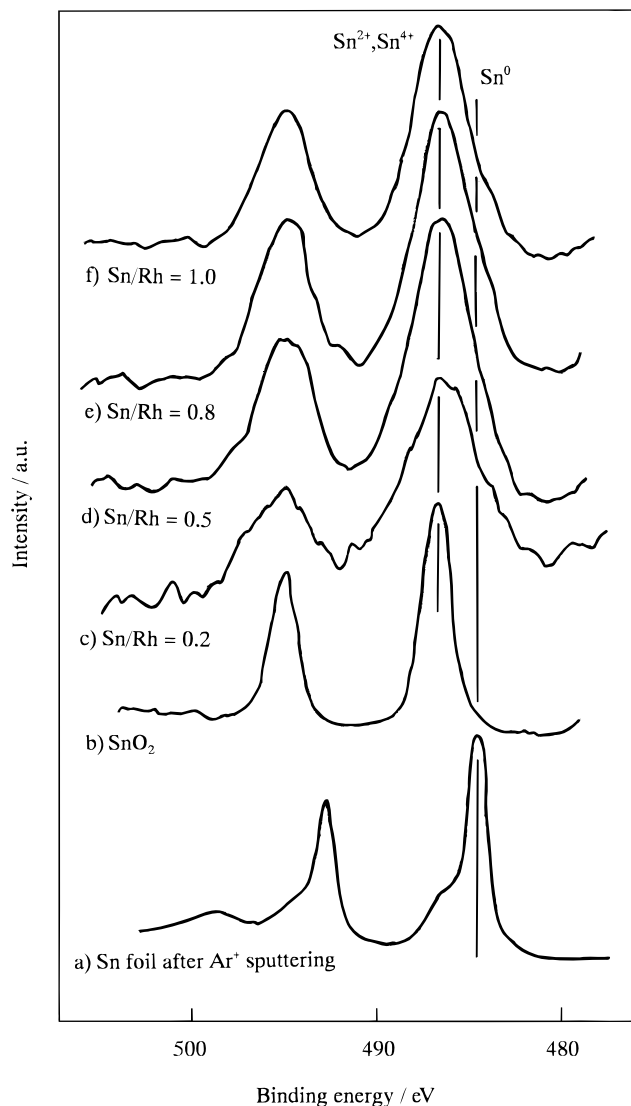

Figure 3. Sn 3d XPS spectra of Sn/Rh/SiO$_2$ catalysts. Reduction temperature: 573 K.

the successive impregnation preparation method. Although there was no indication of a strong perturbation of the electronic structure of Rh in the alloy, the strong effect on the adsorption capacity noted in the previous section suggests an intimate contact of Sn and Rh.

   IR Spectra of Adsorbed Aldehydes. *Effect of Sn/Rh Ratio.* Figures 5 and 6 show IR spectra of propionaldehyde adsorbed on Sn/Rh/SiO$_2$ catalysts at 300 K in the C=O and C−H stretching regions, respectively. The physisorbed or condensed phase of propionaldehyde on the silica was also shown in the figures. The propionaldehyde without interaction with surfaces showed a C=O stretching vibration band at 1747 and 1762 cm^{-1}, as shown in spectrum a in Figure 5. On the Rh/SiO$_2$ catalysts, a major peak was observed at 1720 cm^{-1} accompanied by a shoulder at 1670 cm^{-1}, as shown in spectrum b. The shoulder peak at 1670 cm^{-1} was gradually developed with increasing Sn/Rh ratio. The relative intensity of the peak observed at 1670 and 1720 cm^{-1} was increased with an Sn/Rh ratio up to unity and then slightly decreased at an Sn/Rh ratio of 2, as shown Figure 7. The C−H stretching band of the aldehyde hydrogen of the condensed phase on the silica was observed at 2719 and 2805 cm^{-1}, as shown in Figure 6. Over the Sn/Rh/SiO$_2$, the peak assigned to the C−H stretching of the aldehyde hydrogen was observed at higher wavenumbers
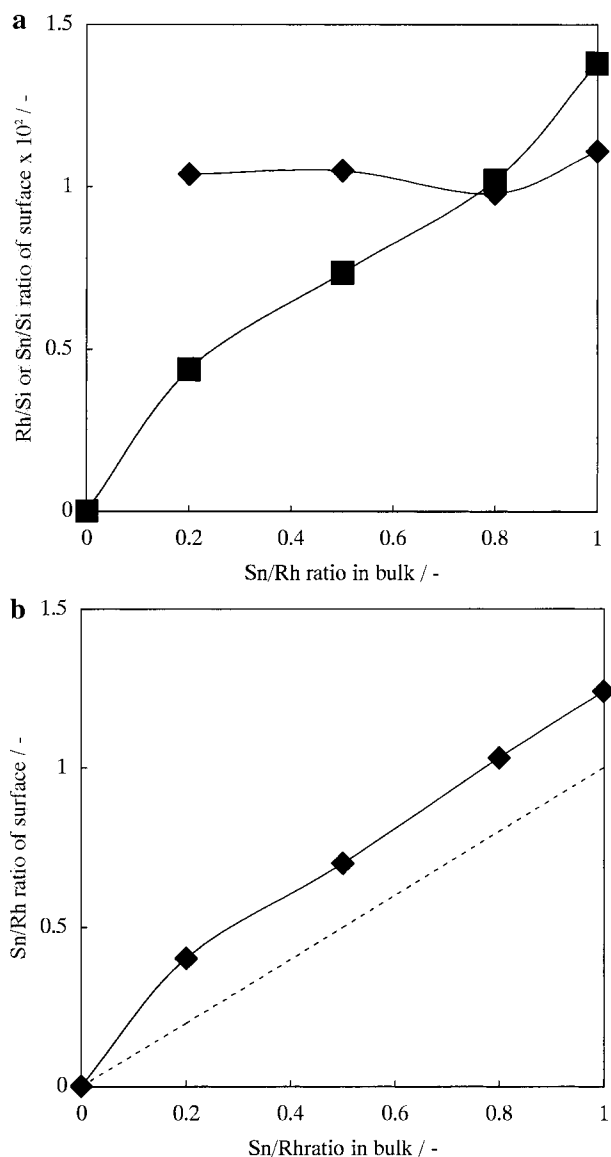
Figure 4. (a) Surface concentration of Rh and Sn: (circle) Rh/Si atomic ratio; (square) Sn/Si atomic ratio. (b) Surface Sn/Rh ratio. The dashed line indicates surface and bulk compositions are identical.

and became significantly sharp, as shown in spectra b–f. The observed absorption bands are summarized in Table 1.

Dependence of Adsorption Temperature. IR spectra of adsorbed propionaldehyde were obtained at an adsorption temperature of 383 K, as shown in Figure 8. The spectra were acquired after a He purge for 2 h at 373 K. The intensity of the peak observed at 1670 cm^{-1} was significantly enhanced by the increasing adsorption temperature, as shown in Figures 5 and 8. The change of the relative intensity at an adsorption temperature of 373 K was also shown in Figure 7. The relative intensity of the peak at 1670 cm^{-1} was strongly enhanced. The behavior was identical to that observed at an adsorption temperature of 300 K as shown in Figure 7. The enhancement of the relative intensity of the peak at 1670 cm^{-1} strongly suggests that the adsorption corresponding to the peak at 1670 cm^{-1} is an activated adsorption that requires a higher temperature for adsorption. The slight decrease of the relative intensity of the peak at 1670 cm^{-1} with increasing Sn/Rh ratio over unity suggests a decrease of sites for the activated adsorption. At a high Sn/Rh ratio over unity, the amount of Sn that cannot contact with Rh directly was decreased. The Rh atoms in the Rh–Sn bimetallic system were considered to be an active center of
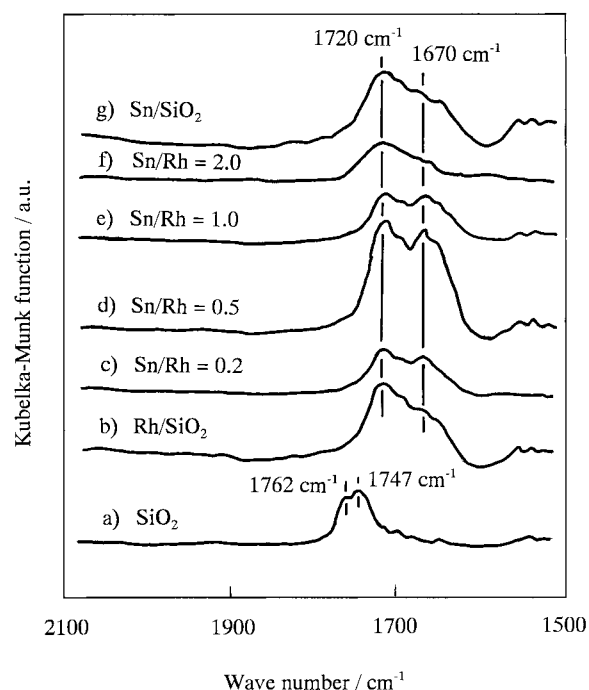

Figure 5. IR spectra of propionaldehyde on Sn/Rh/SiO$_2$ catalysts (C–O stretching band). Adsorption temperature: room temperature.
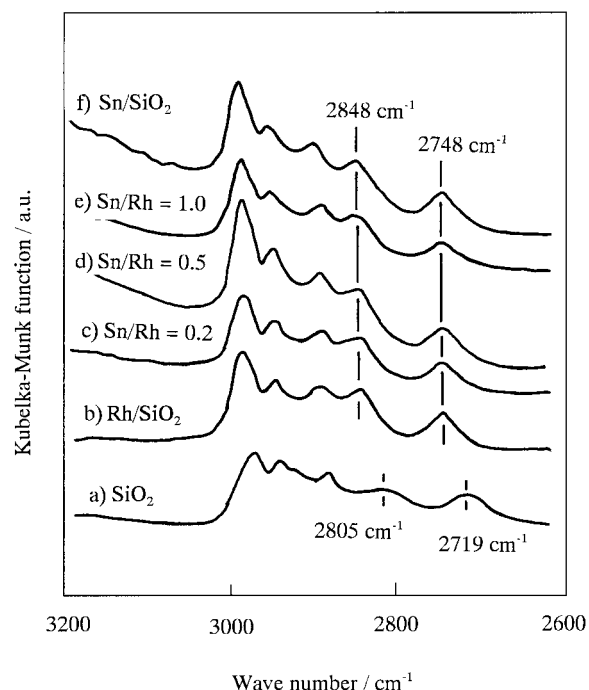

Figure 6. IR spectra of propionaldehyde on Sn/Rh/SiO$_2$ catalysts (C–H stretching band). Adsorption temperature: room temperature.

spillover of hydrogen atoms that are effective for reduction of Sn oxide during the pretreatment by H$_2$. The prereduction of the catalysts was essential for the selective hydrogenation reaction of unsaturated aldehydes. The reduced Sn sites (Sn^{2+}) seemed to be important for activation of the carbonyl group in aldehydes.[12]

Reactivity of Adsorbed Aldehydes with Hydrogen. The reactivity of the adsorbed species was investigated by contacting with H$_2$ at room temperature for 1 h. Figures 9 and 10 show the change of the IR spectra of adsorbed species in both C=O and C–H stretching regions, respectively. Over Rh/SiO$_2$, the contact with H$_2$ brought about a complicated change. The peak

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TABLE 1: IR Absorption Bands on Rh/SiO_2, $Sn/Rh/SiO_2$, and Sn/SiO_2 Catalysts[a]

	adsorption of propionaldehyde		contact with H_2	
	(C=O)str/cm^{-1}	(CO−H)str/cm^{-1}	(C=O)str/cm^{-1}	(CO−H)str/cm^{-1}
Rh/SiO_2	1670 (w), 1720 (m)	2748, 2848	1720 (m) 1829 (m), 2035 (s)	disappear
$Sn/Rh/SiO_2$	1670 (m), 1720 (m)	2748, 2848	1720 (w) 2008 (w)[c]	disappear
Sn/SiO_2	1670 (w), 1720 (m)	2748, 2848	1670, 1720 (no change)	2748, 2848 (no change)
SiO_2[b]	1747 (w), 1762 (w)	2719, 2805	not measured	

[a] Key: s, strong; m, medium; w, weak. [b] Liquid propionaldehyde was directly sorbed on the SiO_2. [c] The peak at ca. 2000 cm^{-1} was observed on the low-Sn containing $Sn/Rh/SiO_2$.
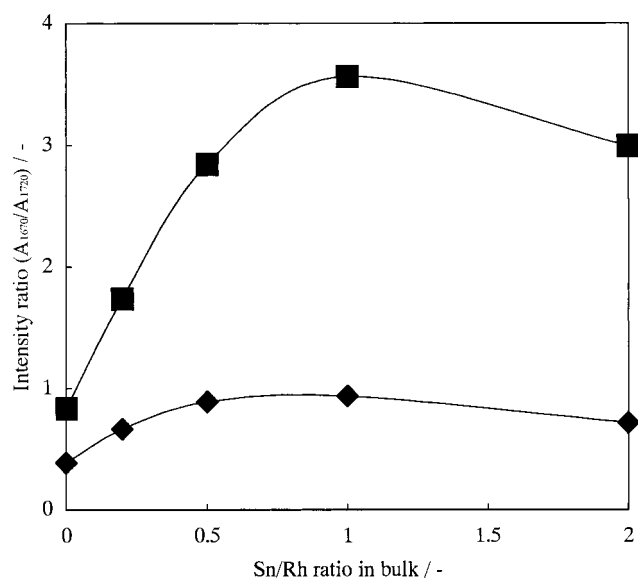
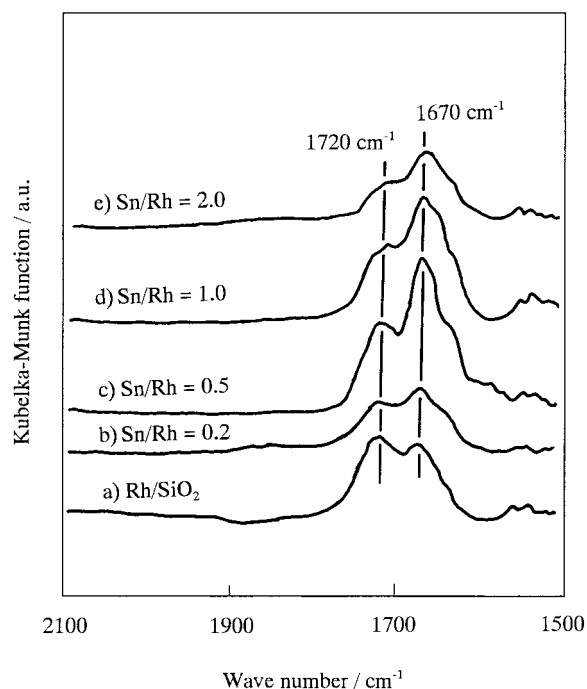**Figure 7.** Intensity ratio of the carbonyl stretching peaks: (circle) adsorbed at 300 K; (diamond) adsorbed at 373 K.

Figure 8. IR spectra of propionaldehyde on $Sn/Rh/SiO_2$ catalysts (C−O stretching band). Adsorption temperature: 373 K.

at 1670 cm^{-1} disappeared, and new bands at 1829 and 2035 cm^{-1} were observed accompanied by no change of the intensity of the peak at 1720 cm^{-1}, as shown in Figure 9a. On the low Sn content $Sn/Rh/SiO_2$ catalysts, a peak appears at 2008 cm^{-1}

and a significant decrease of the intensity of the peak at 1670 cm^{-1} occurs, as shown in Figure 9b. The bands at 1829, 2008, and 2035 cm^{-1} can be assigned to adsorbed carbon monoxide, which was produced mainly on Rh metals. The 1829 cm^{-1} band should be a bridge-bonded CO and the 2008 and 2035 cm^{-1} band can be assigned to linearly bonded CO on Rh metallic particles. The higher Sn content $Sn/Rh/SiO_2$ and Sn/SiO_2 did not indicate a significant adsorbed CO band, as shown in Figures 9c,d. On the $Sn/Rh/SiO_2$ (Sn/Rh = 1.0), the absorption bands at 1670 and 1720 cm^{-1} were strongly decreased by the contact with H_2, accompanied by a slight residual peak at 1720 cm^{-1}. No change of the intensity of the adsorption bands was observed over Sn/SiO_2 samples. Figure 10 shows the change in the IR spectra in the C−H stretching region. Over Rh/SiO_2 and $Sn/Rh/SiO_2$ catalysts, the aldehyde hydrogen disappeared by the contact with H_2. No change was observed on Sn/SiO_2. These results indicate that hydrogen, dissociatively adsorbed on Rh, can react with the adsorbed species observed at 1670 cm^{-1}. It should be noted that the adsorbed species observed at 1720 cm^{-1} did not indicate the C−H stretching band of the aldehyde hydrogen. The infrared absorption data were summarized in Table 1.

Assignment of the Adsorbed Species. Two different adsorption species of aldehyde should be considered because of the difference of the reactivity for hydrogen. One species was markedly reactive and easily converted by the contact with hydrogen observed at 1670 cm^{-1}. It was also accompanied by the absorption band of the aldehyde hydrogen (−CH=O). The wavenumber of its C=O stretching band indicated a red shift of 50 cm^{-1}. These results indicate that the active species was not the di-σ η^2 (C, O) type adsorbate but an adsorbed molecule of aldehyde because the bond between carbon and still remained in a double bond. And it is also suggested that the carbonyl group of the adsorbed aldehyde, which was observed at 1670 cm^{-1}, was not parallel to the catalyst surface because of the presence of the absorption band of the aldehyde hydrogen (−CH=O). If the aldehyde were adsorbed by a parallel form like a π-complex with the surface, a C−H stretching absorption would be significantly weakened by the surface selection rule.[24−26] The surface selection rule of the adsorbed species suggests a very weak infrared absorption of the C−H bond parallel to an electric field of the metal surfaces. The adsorption sites for active adsorbed aldehydes is considered to be Rh^0 and/or Sn^{2+} because the appropriate reduction temperature was required for the activation of the catalysts, as discussed below (Figure 12). The TPR study of Rh−Sn/SiO_2 catalysts indicated that the reduction of Sn oxide in the catalyst precursor of Rh−Sn/SiO_2 proceeded at higher than 473 K in flowing hydrogen.[23] This result indicates that Sn^{4+} is not effective for the activation of aldehydes. It is considered that the lone pair of oxygen atoms of carbonyl groups prefers Sn atoms to Rh atoms because of the Lewis acidity of Sn^{2+}. The inactive adsorption species
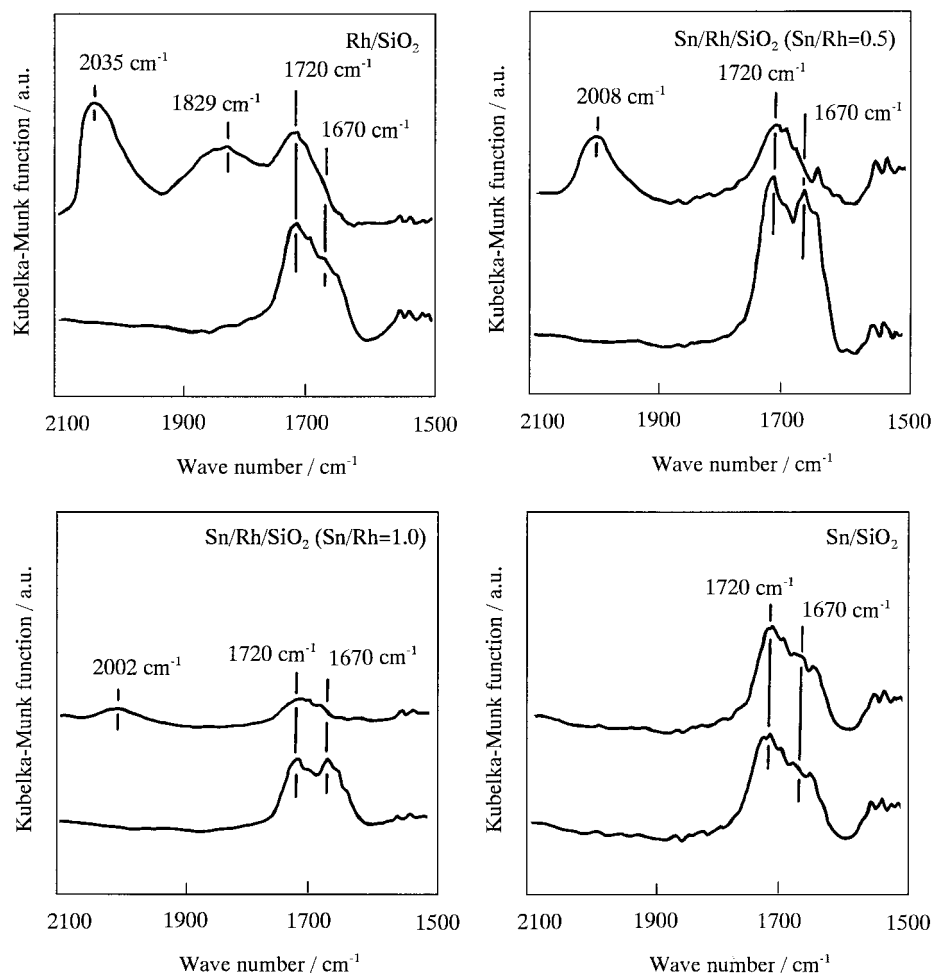
Figure 9. Change of IR spectra of propionaldehyde adsorbed on Sn/Rh/SiO₂ catalysts (C—O stretching band) by H₂ treatment: (top spectra) after H₂ treatment; (bottom spectra) before H₂ treatment.

observed at 1720 cm^{-1} should be assigned as weakly adsorbed parallel on the surface, because the aldehyde hydrogen band was not observed. It was not, however, a species in a condensed phase because the absorption band was significantly different from the species on the SiO₂ support, which was observed at 1747 and 1762 cm^{-1}. The acetoaldehyde in the gas phase also indicated the C═O stretching band at 1743 cm^{-1}.[17] The acyl type species would indicate the absence of the band of aldehyde hydrogen, but the C═O stretching band should be observed near 1600 cm^{-1}. Davis et al.[20] have reported formation of the acyl type of species on Pd (111) observed at 1595 cm^{-1} in energy loss spectra. Therefore, the absorption peak observed at 1720 cm^{-1} can be assigned not to the acyl type species but to a species weakly adsorbed parallel to the surface.

To confirm the interaction between the catalyst surface, maybe Sn atoms, and aldehydes, IR spectra of propionaldehyde in ethanolic solution in the presence of SnCl₂ were measured. The mixed solution was very clear and homogeneous. The obtained spectra are shown in Figure 11. The IR spectra of propionaldehyde in ethanol in the absence of SnCl₂ indicated peaks at 1695 and 1730 cm^{-1} in the C═O stretching region. The peak at 1695 cm^{-1} was assigned to aldehyde coordinated by the solvent ethanol molecules because the hydrogen bonds might weaken the C═O stretching vibrations.[27] The peak observed at 1730 cm^{-1} suggests free aldehyde molecules. The presence of SnCl₂ in the solution brought about a new absorption band at 1665 cm^{-1}, as shown in Figure 11. It is expected that the hydrogen bonding to the carbonyl group lowers the absorption band of the C═O stretching and that the shift is in

the range 30−40 cm^{-1}. The interaction between carbonyl groups and Lewis acids brings about the large shift of the CO stretching vibration band to lower frequencies.[27] The interaction with BF₃ or AlF₃ caused the shift of the order of 70−150 cm^{-1}.[27] The Lewis acids cordinate to oxygen atoms of the carbonyl groups.[27] The peak observed at 1665 cm^{-1} in the ethanolic solution can be assigned to the carbonyl group coordinated to Sn^{2+}. Henderson et al.[21] have reported a red shift of the energy loss peak of acetoaldehyde adsorbed on Ru (001). The red shift was observed to be 50 cm^{-1}. They assigned the peak to the donating-on-top η^1 (O) species. The similar shift in the presence of SnCl₂ (65 cm^{-1} of red shift) suggests that Sn^{2+} interacts with oxygen atoms of carbonyl groups.

As a result, the absorption peak observed at 1670 cm^{-1} over Sn/Rh/SiO₂ catalysts can be assigned to the donating-on-top η^1 (O) species and the peak at 1720 cm^{-1} was also assigned to the species weakly adsorbed parallel to the surface. The assignments were summarized in Table 2.

Role of Sn in Aldehyde Adsorption and Selective Reduction of Unsaturated Aldehydes. The effects of reduction temperature on the intensity of IR spectra of adsorbed aldehyde were shown in Figure 12. The reduction temperature significantly affects the relative intensity of I_{1670}/I_{1720}, as shown in Figure 12. The relative intensity showed a maximum at 573 K of the reduction temperature. It is important to discuss the relationship between the catalytic activity and the intensity of absorption band for elucidating the active sites on Rh−Sn/SiO₂ catalysts for selective reduction of unsaturated aldehyde. Figure 13 shows the effect of reduction temperature on yield of crotyl
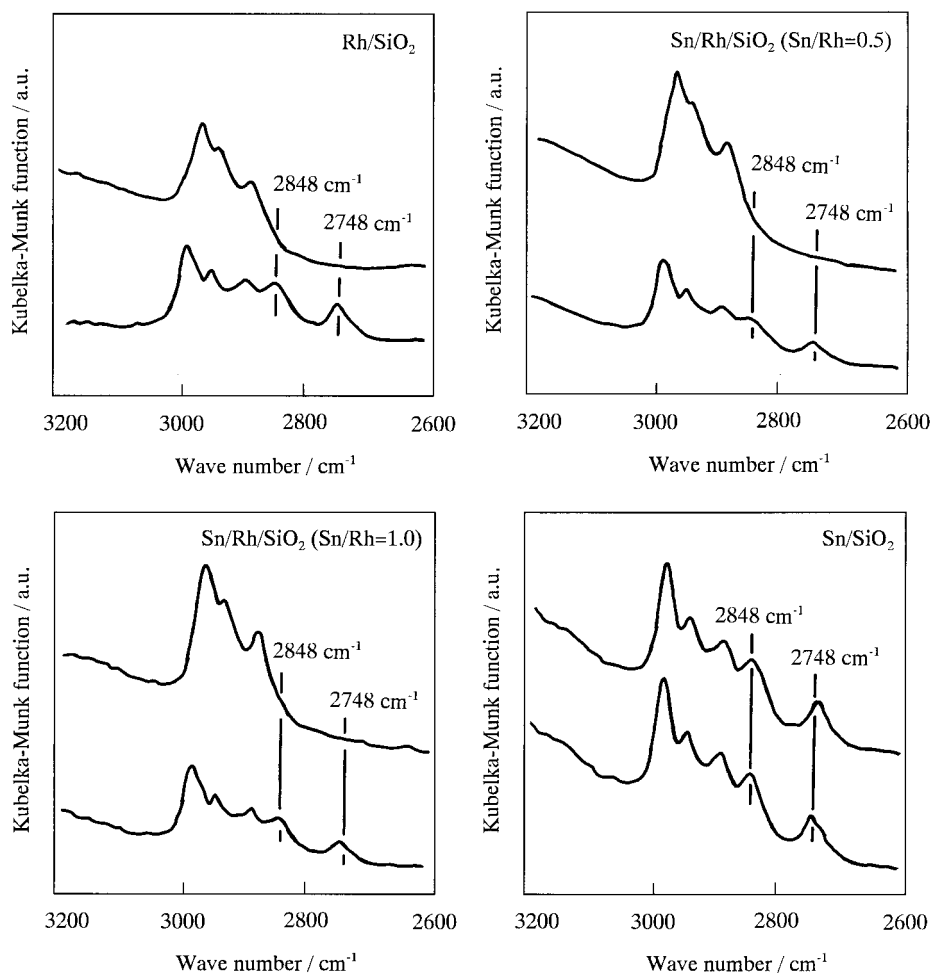
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Figure 10. Change of IR spectra of propionaldehyde adsorbed on Sn/Rh/SiO$_2$ catalysts (C—H stretching band) by H$_2$ treatment: (top spectra) after H$_2$ treatment; (bottom spectra) before H$_2$ treatment.
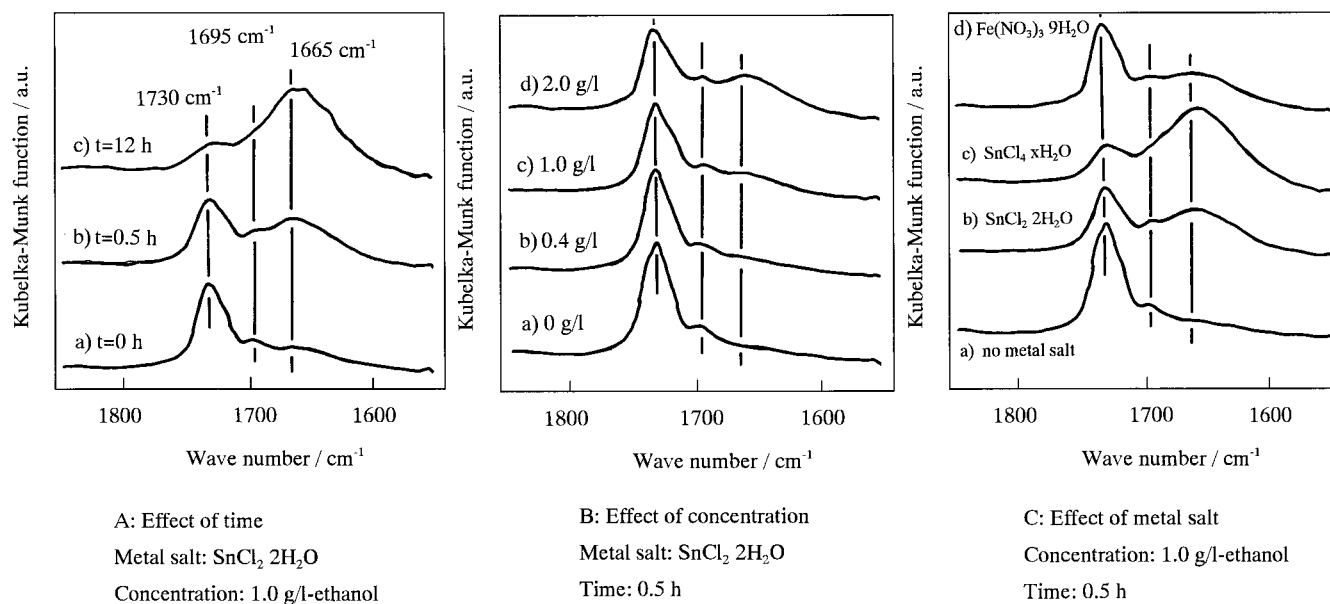

A: Effect of time

Metal salt: SnCl$_2$ 2H$_2$O

Concentration: 1.0 g/l-ethanol

B: Effect of concentration

Metal salt: SnCl$_2$ 2H$_2$O

Time: 0.5 h

C: Effect of metal salt

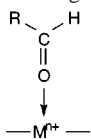Concentration: 1.0 g/l-ethanol

Time: 0.5 h

Figure 11. IR spectra of mixed solutions of metal salt and propionaldehyde (C—O stretching band). Mixed solution: metal salt + ethanol (0.1 mL) + propionaldehyde.

alcohol in the selective reduction of crotonaldehyde. The yield of crotyl alcohol increased with temperature up to 573 K and then decreased gradually with reduction temperature. The optimum reduction temperature was 573 K. The behavior of the formation of crotyl alcohol over the catalysts reduced at

various temperatures was almost identical to the relative intensity of the IR band at 1670 cm^{-1}, which was considered to be the active species, as shown Figures 12 and 13. The optimum reduction temperature of 573 K for the formation of crotyl alcohol and the relative intensity of the band at 1670 cm^{-1} was

TABLE 2: Assignment of the Species and Their Reactivity

assignment	(C=O)str/cm^{-1}	(CO—H)str/cm^{-1}	reactivity with hydrogen
donating-on-top η^1 (O) species	1670	2748, 2848	very high
weakly adsorbed species parallel to the surface	1720	not observed	almost no (but some part of species was converted to the η^1 species)
condensed aldehyde on SiO$_2$	1747, 1762	2719, 2805	
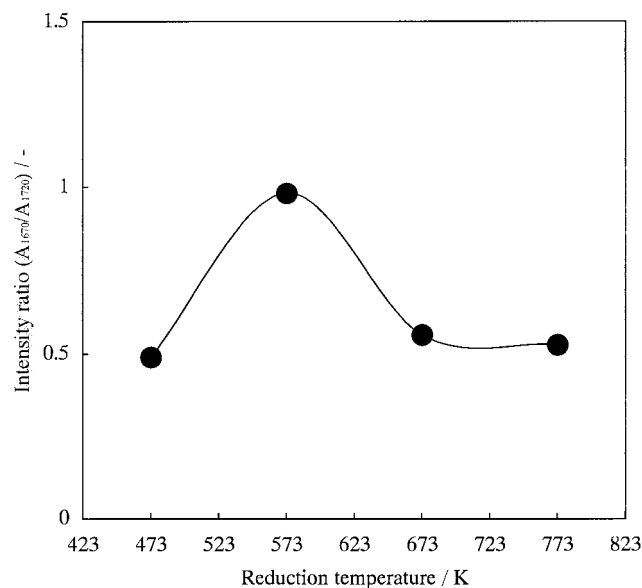
Figure 12. Intensity ratio of the carbonyl stretching peaks as a function of reduction temperature. Adsorption temperature: room temperature.
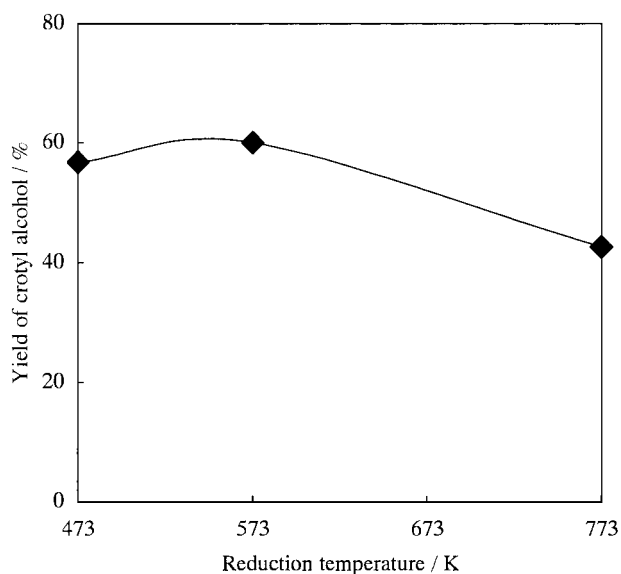
Figure 13. Effect of reduction temperature on the activity of selective hydrogenation of crotonaldehyde. Catalyst: Rh—Sn/SiO$_2$, 20 mg (Rh: 5 wt %, Sn/Rh = 1). Reaction temperature: 423 K. H$_2$ pressure: 1.0 MPa. Reaction time: 20 h.

similar to the temperature at which the reduction of tin oxide in the catalyst precursor of Rh—Sn/SiO$_2$ started, as discussed in the previous TPR study.[23] These results indicate that the
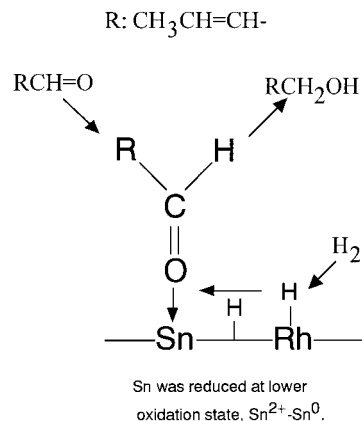
Figure 14. Reduction mechanism of selective hydrogenation of unsaturated aldehydes.

effective Sn species on the Rh—Sn/SiO$_2$ catalysts for the reduction of aldehyde is in a lower oxidation state, like Sn^{2+}. In the group VIII—Sn bimetallic catalysts, tin plays a role of suppression of high activity of the group VIII metal components and decreases catalyst deactivation by carbon deposition.[28] These reports suggest that tin is not a catalysts but a modifier to control the selectivity. But we have already found the hydrogenation activity of Rh/SiO$_2$ for hydrogenation of benzaldehyde to benzyl alcohol was strongly enhanced by the addition of tin.[9] The effect of tin addition on the hydrogenation reaction of benzaldehyde could not be explained by only a role of suppressor. It should be considered that tin participates in the catalytic cycle of the hydrogenation reaction. The IR spectra of adsorbed aldehyde strongly support this hypothesis. An aldehyde is adsorbed on Sn through the oxygen atom of the carbonyl group and reacted with the activated hydrogen atoms diffused from metallic Rh sites. The postulated scheme is shown in Figure 14. The important step is the adsorption of aldehydes to the Sn sites for the selective hydrogenation of unsaturated aldehydes. The adsorption state of aldehyde on the Sn sites significantly decreases the chance of hydrogenation of the C=C double bond in unsaturated aldehydes. This is the reason the Rh—Sn bimetallic catalysts indicate the high activity for the selective reduction of unsaturated catalysts. Englisch et al.[29] have recently reported that TiO$_x$ suboxide in Pt/TiO$_2$ catalysts plays an important role for the selective hydrogenation of crotonaldehyde, because an appropriate reduction of the catalyst (maybe the support TiO$_2$) was required. They proposed a scheme like a di-σ η^2 (C, O) type adsorbed species over Pt/TiO$_2$.[29] Their infrared spectroscopy study also showed the weakly adsorbed species of crotonaldehyde on Pt/SiO$_2$ near 1720 cm^{-1} and adsorbed carbon monoxide at 2030 cm^{-1}, which caused the catalyst deactivation.[29] However, the activated adsorption of

crotonaldehyde observed here at 1670 cm^{-1} was not noted, and the presence of the di-σ η^2 (C, O) type adsorbed species over Pt/TiO$_2$ was not confirmed neither.[29] They expected the interaction of oxygen atoms of carbonyl groups and the Lewis acid sites on the TiO$_x$ suboxide.[29] Margifalvi et al. have reported an organic carbonyl group stretching band at 1690 cm^{-1} over only Pt/SiO$_2$ in crotonaldehyde adsorption in addition to adsorbed CO at ca. 2060 cm^{-1}, which was caused from the decarbonylation reaction.[13] Our IR spectra of the liquid-phase mixture of propionaldehyde and tin salt in ethanol (1665 cm^{-1}) clearly indicate that cationic tin can interact with a carbonyl group in aldehydes and strongly suggest that oxygen in the carbonyl group is coordinated with a tin cation. It should be noted that the absorption band at 1670 cm^{-1} and its reactivity with H$_2$ show one of the active intermediates for the selective hydrogenation of unsaturated aldehydes, that is, the on-top η^1 (O) species.

Conclusions

(1) Two adsorbed species of aldehyde were observed on the Sn/Rh/SiO$_2$ catalysts, corresponding to the IR absorption bands at 1670 and 1720 cm^{-1}. One observed at 1670 cm^{-1} was assigned to the donating-on-top η^1 adsorbed aldehyde bound to Sn atoms with oxygen atoms of carbonyl groups (η^1 (O) species). The others observed at 1720 cm^{-1} species were weakly adsorbed parallel on the catalyst surface.

(2) The presence of Sn enhanced the formation of the donating-on-top η^1 (O) species.

(3) The donating-on-top η^1 (O) species was easily reacted with H$_2$ at room temperature, whereas the weakly adsorbed species at 1720 cm^{-1} was not changed after the contact with H$_2$. The donating-on-top η^1 species was one of the active intermediates of hydrogenation of aldehydes.

(4) The presence of Sn strongly suppressed the adsorption with C=C double bonds. This indicates that the hydrogenation of C=C double bonds would be suppressed.

(5) The roles of Sn in the Sn/Rh/SiO$_2$ catalysts are the enhancement of the formation of active species, the donating-on-top η^1 (O) species, and the suppression of hydrogenation of C=C double bonds in the selective hydrogenation of unsaturated aldehydes.

(6) Sn^{2+} is an important species on the Sn/Rh/SiO$_2$ catalysts for the activation of the carbonyl group in the selective hydrogenation of unsaturated carbonyl compounds.

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