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Pd and PdZn supported on ZnO as catalysts for the hydrogenation of cinnamaldehyde to hydrocinnamyl alcohol

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Abstract: Liquid phase selective hydrogenation of cinnamaldehyde (CAL) was investigated over ZnO-supported Pd and PdZn catalysts different in the Pd loading. The former monometallic catalyst was less selective to the formation of cinnamyl alcohol (COL) irrespective of the Pd loading (5 and 30 wt.-% Pd). When the Pd loading was small (5 wt.-%), PdZn catalyst (PdZn-5) indicated similar catalytic actions. However, PdZn catalyst containing Pd in a larger content of 30 wt.-% (PdZn-30) showed different results: the COL selectivity was about 20% at low conversion but it increased with CAL conversion, reaching to > 50% at a conversion of 60%. The COL selectivity was likely to change depending on the concentration of a product of hydrocinnamaldehyde (HCAL). The coadsorption of HCAL should control the orientation of CAL molecules adsorbed on the PdZn-30 catalyst. This may assist the adsorption of CAL via its aldehyde group on the surface of catalyst, resulting in an increase in the COL selectivity. Unique catalysis of PdZn-30 may result from structural features of the surface of its large PdZn particles, which are different from those of PdZn-5 having smaller PdZn particles.

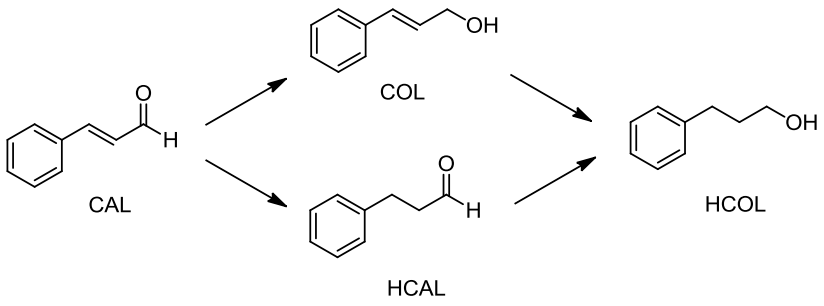
Keywords: PdZn alloy; hydrogenation; α, β-unsaturated aldehyde; selectivity control; substrate-product interaction

1. Introduction

Hydrogenation of various unsaturated substrates is of great industrial importance [1-3]. A class of these reactions is the selective hydrogenation of α, β-unsaturated aldehydes to unsaturated alcohols, which has also been used as a test reaction to characterize the performance of various metal catalysts [4-6]. Ordinary metal catalysts are likely to hydrogenate C=C bond of α, β-unsaturated aldehyde more preferentially than C=O bond and produce saturated aldehyde in high selectivity. Some modification of metal catalysts is therefore required to improve the selective hydrogenation of C=O bond and several modification methods have been reported, one of which is to modify an active metal (I) with another one (II). When metal II is more electropositive than metal I, the selectivity to unsaturated alcohol may be enhanced as compared to that with the metal I alone [4]. For active platinum group metals, Fe, Co, Ge, or Sn may be used as an effective modifier. Generally, alloys are demonstrated to show interesting and useful catalytic features for hydrogenation and other reactions [1].

The present authors investigated the catalysis over PdZn alloys for a few hydrogenation reactions [7-9], steam reforming [10-13], and selective CO oxidation [14, 15]. It was recently shown that PdZn alloy was active for liquid phase hydrogenation of phenylacetylene in toluene, similar to monometallic Pd, but the selectivity to the semi-hydrogenated product of styrene was larger with PdZn than Pd [7]. That is, the activity of Pd to hydrogenate C=C bond is suppressed by alloying with Zn. The partial hydrogenation of alkynes to alkenes with Pd-based catalysts is practically important as reviewed in the literature [3, 16, 17]. Very recently Zhang et al. reported a similar catalysis of PdZn for partial hydrogenation of acetylene to ethylene [18]. The results of phenylacetylene hydrogenation over PdZn [7] have then motivated us to apply such a catalytic feature of PdZn for the selective hydrogenation of α, β-unsaturated aldehyde to unsaturated alcohol, for which the reactivity of C=C bond should be lowered. The present authors have investigated liquid phase hydrogenation of cinnamaldehyde (CAL) with ZnO-supported PdZn and Pd catalysts containing Pd in 30 and 5 wt.-% (Scheme 1). It was found that the selectivity to cinnamyl alcohol (COL) was < 5% at any conversion level for the Pd catalysts and the PdZn one containing Pd in 5 wt.-% while it was about 20% at low conversion level for the PdZn catalyst containing Pd in a larger amount of 30 wt.-%. For the latter, interestingly, the COL selectivity increased with CAL conversion, being > 50% at a conversion of 60%. It is assumed that the

COL selectivity changes depending on the concentration of a product (hydrocinnamaldehyde, HCAL) and the adsorption of the CAL substrate on the surface of PdZn particles is influenced by the coadsorption of HCAL. Previously, Kapteijn et al. pointed out the effect of CAL concentration on the adsorption of the substrate of CAL itself and the selectivity to COL over Pt/C catalyst [19]. The present work will report the unusual change in the product selectivity during the CAL hydrogenation over PdZn/ZnO catalyst in detail. The influence of foreign aldehydes on the product selectivity has been examined using HCAL and other aromatic and aliphatic aldehydes that are different in the size and structure as compared to the CAL substrate. Interactions between the substrate and foreign aldehyde molecules have been inspected by Fourier transform infrared (FTIR) spectroscopy and the surface properties of Pd and PdZn catalysts were examined by X-ray photoelectron spectroscopy (XPS). On the basis of those reaction and characterization results, possible reasons for the unique catalysis of ZnO-supported PdZn catalyst containing a large amount of Pd have been discussed.



Scheme 1. Hydrogenation of cinnamaldehyde (CAL) to cinnamyl alcohol (COL), hydrocinnamaldehyde (HCAL), and hydrocinnamyl alcohol (HCOL)

2. Experimental

2.1. Catalyst Preparation Coprecipitation method was used to prepare Pd and PdZn samples in similar manners as used previously [7-9]. A mixed aqueous solution of $Pd(NO_3)_2$ and $Zn(NO_3)\cdot 6H_2O$ (Wako Pure Chemical), in which Pd : Zn = 1 : 3 in mole, was prepared in a beaker and it was placed in an water bath at 70 – 80 ºC. Drops of an aqueous solution of Na_2CO_3 (Wako) were added to the mixed solution at a rate of 2.5 cm^3 min^{-1} until pH of the mixture became to 8. The mixture was further mixed in the water bath for 1 h and precipitate formed was then separated by decompression filtration. The precipitate was washed several

times by distilled water at room temperature and at about 80 ºC. It was dried in air at 110 ºC overnight, heated at a rate of 5 ºC min^{-1} up to 450 ºC and then at a rate of 2 ºC min^{-1} up to 500 ºC, and further calcined at 500 ºC for 3 h. The ZnO-supported Pd sample so obtained was reduced by 4% H_2 (in N_2) at ambient temperature for 1 h to prepare Pd/ZnO sample or at ambient temperature for 1 h and increasing temperatures at a rate of 5 ºC min^{-1} to 500 ºC to prepare PdZn/ZnO sample. These samples contained Pd in 30 wt.-% (Pd / (Pd + ZnO)). Other samples containing Pd in 10 and 5 wt.-% were also prepared in similar manners by using different mixed precursor solutions. The formation of Pd and PdZn in these samples prepared was confirmed by X-ray diffraction measurements [7-9].

2.2. Liquid-phase Hydrogenation Liquid-phase hydrogenation of CAL was conducted in a stainless steel reactor (100 cm^3) in similar manners as used previously [7]. The reactor was placed on a magnetic stirrer hot plate and heated with an oil bath to the desired temperature of either 80 ºC (hydrogenation) or 100 ºC (reduction). The reactor was loaded with a catalyst sample 50 mg and toluene 5 cm^3, the remaining air was replaced by 0.3 MPa H_2 a few times, H_2 was introduced up to 3 MPa, and the catalyst was reduced at a temperature of 100 ºC for 1 h while stirring with a Teflon-coated magnetic stirrer. After the reactor was cooled to room temperature, CAL 0.5 cm^3 was added and heated again up to 80 ºC. Then, 4 MPa H_2 was introduced to the reactor and the reaction mixture was mixed with the magnetic stirrer at an agitation speed of 400 rpm to start the reaction. After the reaction, the reactor was cooled and depressurized slowly to ambient pressure and the liquid mixture was analyzed by a gas chromatograph (GL Science GC 4000) with flame ionization detector. The total conversion of CAL was determined from the amounts of the substrate measured before and after reaction. The yield of a product was calculated from the amount of the product divided by the amount of the substrate charged. The selectivity to a product was determined from the amount (mole) of the product formed divided by the total amount (mole) of all the products detected. Under the reaction and GC analysis conditions used, carbon mass balance of the total amount (moles) of unreacted substrate and products divided by the initial amount (moles) of substrate was > 90%. The CAL hydrogenation reactions were conducted with the ZnO-supported Pd and PdZn catalysts prepared and also with a commercial Pd black powder (Wako) for comparison. The inertness of the reactor wall was confirmed by a blank reaction experiment.

2.3. Characterization of Catalysts and Substrate - Aldehyde Interactions The phases (Pd, PdZn) present in ZnO-supported Pd and PdZn samples so prepared were examined by X-ray diffraction (XRD) on JOEL JDX-8020 using Cu Kα radiation through a Ni filter. The sizes of Pd and PdZn crystallites were determined by Pd (111) ($2\theta = 40.1^{o}$) and PdZn (111) ($2\theta = 41.2^{o}$) diffraction line broadening, respectively, with the Scherrer equation [20]. The surface layer of supported Pd and PdZn particles was examined by X-ray photoelectron spectroscopy (XPS) on VG Microtech 3000 Multilab. The binding energy of all XPS spectra was corrected to the C 1s peak at 284.6 eV. Interactions between the CAL substrate and the foreign aldehyde (HCAL, for example) were examined by FTIR spectroscopy (JASCO FTIR-620 spectrometer), in which mixture of the two aldehydes in cyclohexane in the form of thin film between two quartz plates was examined at ambient temperatures.

3. Results and Discussion

3.1. Samples Prepared Four Pd/ZnO and PdZn/ZnO samples different in the loading of Pd, 30 and 5 wt.-%, were prepared. These samples will be abbreviated as, for example, Pd-30 and PdZn-5, for Pd and PdZn samples containing Pd in 30 wt.-% and 5 wt.-%, respectively. Fig. 1 presents XRD patterns of these samples, from which the sizes of PdZn crystallites were 60 nm and 13 nm for PdZn-30 and PdZn-5, respectively; that of Pd crystallites was 7 nm for Pd-30 sample. Pd was likely to be dispersed in the form of smaller crystallites in Pd-5 sample, which were therefore not detected by XRD. The liquid-phase hydrogenation of CAL was conducted with these Pd and PdZn samples to examine their catalytic activity and product selectivity.

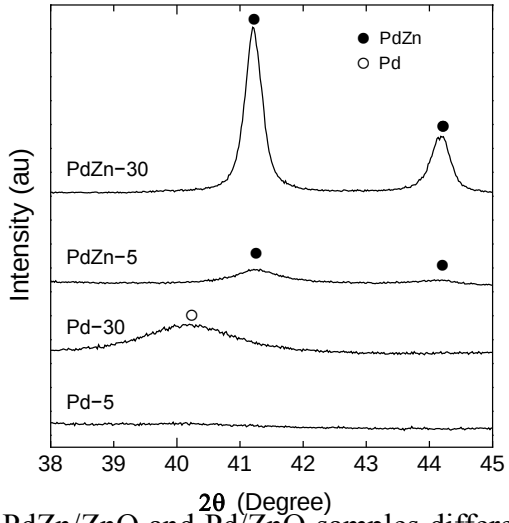


Fig. 1. XRD patterns of PdZn/ZnO and Pd/ZnO samples different in Pd loading (30 wt.-% and 5 wt.-%) prepared.

3.2. CAL Hydrogenation The hydrogenation of CAL was conducted with either PdZn-30 or Pd-30 for different periods of reaction time at 80 ºC. Fig. 2a shows the change of product selectivity and yield with total CAL conversion with the latter Pd catalyst. The selectivity to COL was < 5% at any conversion level while HCAL was more selectively produced and its selectivity decreased slightly from 85% to 70% with conversion. The selectivity to the final hydrogenated product, HCOL, was about 20% at the initial stage of reaction and increased gradually with conversion. Fig. 2b shows the product selectivity and yield as a function of conversion with PdZn-30 catalyst. The HCAL, COL, and HCOL selectivity values were 70%, 20%, and 10%, respectively, at a conversion of 20%. The COL selectivity obtained with PdZn catalyst was even larger compared to that with Pd one. Furthermore, it is interesting to note that the selectivity to HCAL and COL significantly changes with conversion, in contrast to the results with Pd (Fig. 2a). The yield of HCAL did not change so much with conversion but those of COL and HCOL increased. Therefore, the HCAL selectivity decreased with conversion while the COL selectivity increased.

Fig. 3 gives the time profiles of CAL hydrogenation with Pd-30 and PdZn-30 catalysts. Plot of $-\ln(1-\text{conversion})$ against reaction time for the former catalyst shows a linear relationship and, therefore, the hydrogenation is a pseudo first order reaction [21] under the conditions used as expected. For the latter, however, such a linear relationship was

not seen and the reaction rate decreased with time, being smaller than expected from a pseudo first order reaction kinetics. This indicates that some product (HCAL as discussed later) is likely to retard the reaction and change the product selectivity during the reaction (Fig. 2b). The non-linear result was not due to catalyst deactivation because the reaction was completed for a longer reaction time (100% conversion was obtained).

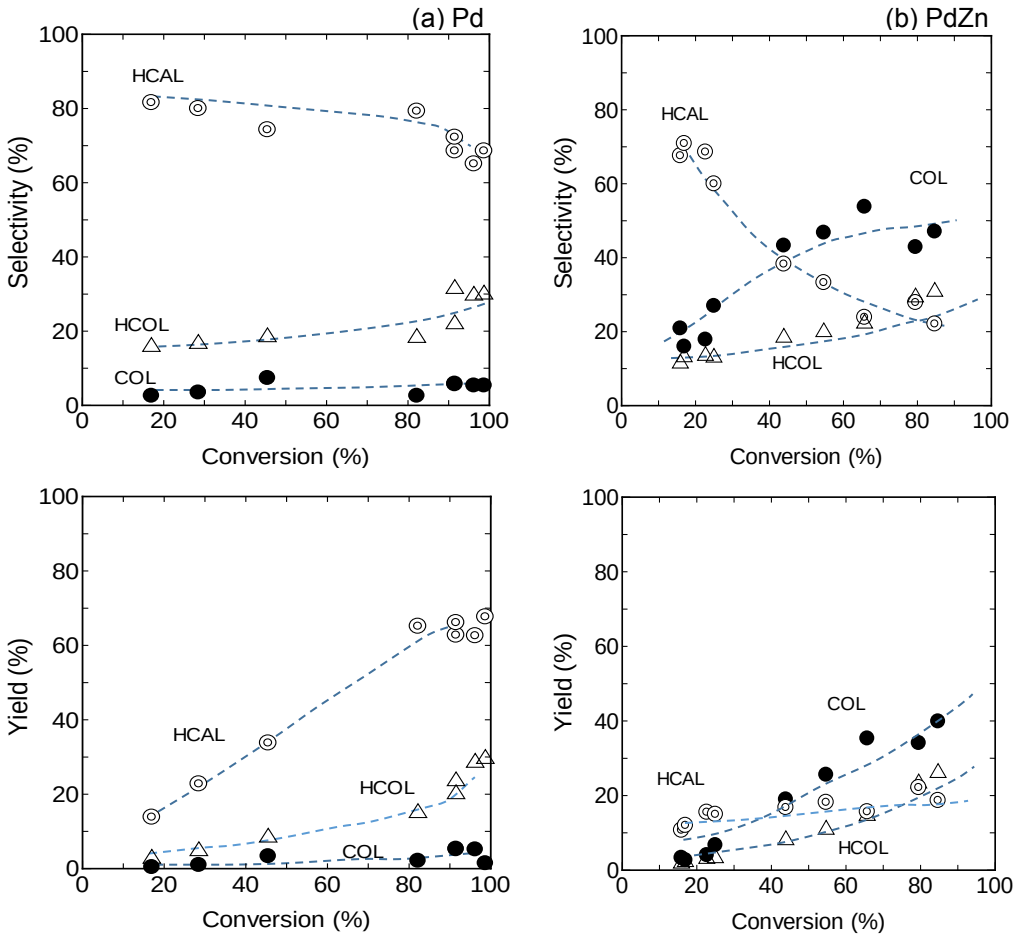


Fig. 2. Selectivity and yield as a function of conversion for the hydrogenation of CAL with Pd-30 (a) and PdZn-30 (b) catalysts. Reaction conditions: CAL 3.97 mmol, catalyst 50 mg, temperature 80 ^{o}C, toluene 5 cm^3, H_2 4.0 MPa.

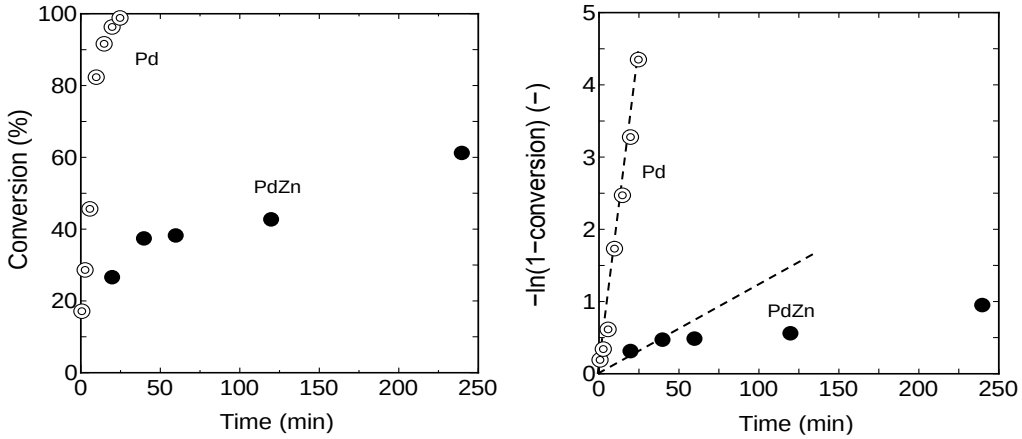


Fig. 3. Time-conversion profiles for CAL hydrogenation obtained with Pd-30 and PdZn-30 catalysts. Reaction conditions: CAL 3.97 mmol, catalyst 50 mg, temperature 80 ^{o}C, toluene 5 cm^3, H_2 4.0 MPa.

In addition, the reactivity of the partially hydrogenated products, COL and HCAL, was examined using the same Pd-30 and PdZn-30 catalysts. The results obtained are given in Table 1. COL was hydrogenated over the two catalysts but at a larger rate on Pd than on PdZn. In contrast to COL, the hydrogenation of HCAL occurred at an even smaller rate on either Pd or PdZn catalyst. The strength of carbonyl group in CAL (α, β-unsaturated molecule) is weaker than that in HCAL, as confirmed by FTIR (shown later in Fig. 5): ν C=O appears at 1679 cm^{-1} and 1727 cm^{-1} for the CAL and HCAL molecules, respectively. This may be a reason for the difference in the reactivity between CAL and HCAL molecules observed. Either COL or HCAL was found to transform exclusively to the fully hydrogenated product, HCOL, and so the isomerization of COL to HCAL (and of HCAL to COL) did not occur over the Pd and PdZn catalysts under the conditions used. In the CAL hydrogenation (Scheme 1), therefore, the fully hydrogenated product of HCOL was mainly produced from COL but not HCAL.

Table 1. Hydrogenation of COL and HCAL over Pd-30 and PdZn-30 catalysts [a]

Catalyst	Substrate	Conversion (%)	
		20 min	60 min
Pd	COL	97	99
	HCAL	9	19
PdZn	COL	34	77
	HCAL	8	21

Reaction conditions: substrate 0.5 cm^3, catalyst 50 mg, toluene 5 cm^3, H_2 4 MPa.

[a] In either COL or HCAL hydrogenation, the selectivity to HCOL was 100%.

As described above, PdZn-30 sample indicates unique catalytic actions in the hydrogenation of CAL, which are the selective formation of COL and the increase in its selectivity with conversion (Fig. 2b). For comparison, PdZn-10 and PdZn-5 samples were also tested, in which the sizes of PdZn crystallites were 46 and 13 nm, respectively. With PdZn-10 catalyst, the selectivity to COL was slightly lower than PdZn-30, but the increase in its selectivity was also observed (Fig. S1). The product distribution obtained with PdZn-5 catalyst was significantly different from those with PdZn-30 and PdZn-10 catalyst. Fig. 4 shows the change of product selectivity and yield with conversion over PdZn-5 catalyst. It is interesting that the results are similar to those obtained with monometallic Pd-30 catalyst rather than alloyed PdZn-30 one. That is, the hydrogenation of C=C bond of CAL occurred preferentially giving HCAL in a high selectivity of about 80%, comparable to that with Pd-30, and the selectivity did not change with conversion so much. For comparison, the catalysis of larger metallic Pd particles was examined; large Pd particles in size similar to PdZn of PdZn-30 sample were unable to prepare by the preparation procedures (coprecipitation) employed and so Pd black was used instead. The CAL hydrogenation was conducted to examine the product selectivity at a few different conversion levels. It was observed that HCAL was produced in the largest selectivity of 71% and 68% at CAL conversion values of 27% and 90%, respectively. At a conversion of 90%, the COL and HCOL selectivity values were 3% and 29%, respectively. The catalysis of Pd black was observed to resemble that of the Pd-30 and Pd-5 catalysts with respect to the high HCAL selectivity and the almost unchangeable product selectivity with conversion. Hence, the present liquid-phase CAL hydrogenation over Pd catalysts is not structure-sensitive under the conditions used. There

are no universal trends of the structure sensitivity in CAL hydrogenation in the literature [4, 22]. Zhu and Zaera have reported that, for Pt/SiO_2 catalysts, the product selectivity is independent of the size of Pt particles and the CAL conversion [22], similar to the present results.

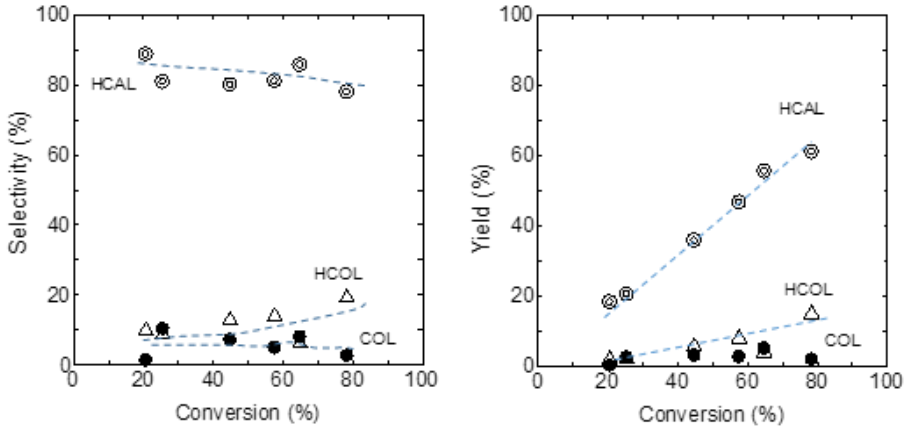
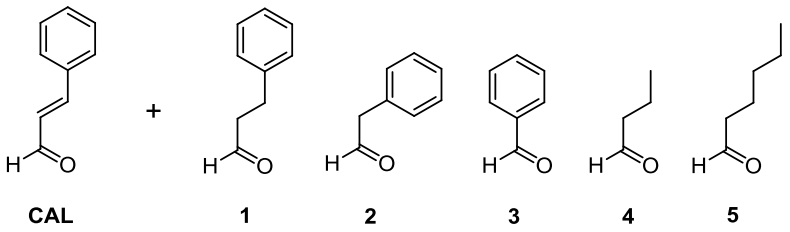


Fig. 4. Selectivity and yield as a function of conversion for the hydrogenation of CAL with PdZn-5 sample. Reaction conditions: CAL 3.97 mmol, catalyst 50 mg, temperature 80 ^{o}C, toluene 5 cm^3, H_2 4.0 MPa.

Note again that Pd catalysts are selective to the hydrogenation of C=C bond of CAL, giving HCAL in the largest selectivity. COL is also produced but at a smaller rate as compared to HCAL and it is hydrogenated to the final product HCOL, the selectivity to COL being smaller than that to HCOL. The product distribution does not change with conversion except for the later stage of reaction of > 80% conversion. The activity of PdZn catalysts depends on the size of PdZn crystallites, and the results with small ones (13 nm) in PdZn-5 are similar to Pd catalysts while larger PdZn crystallites (60 nm) in PdZn-30 show significantly different catalytic actions. The PdZn-30 catalyst is also selective to the hydrogenation of C=C bond of CAL at a small conversion level, HCAL being obtained in the largest selectivity. When conversion further increases, however, COL is produced more selectively than HCAL and the COL selectivity goes over the HCAL selectivity at a conversion of 40%. At a larger conversion level, COL produced is hydrogenated to HCOL and the HCOL selectivity increases. For the case of PdZn-30 catalyst, a partially hydrogenated product, HCAL, is assumed to be responsible for the significant variation in the product selectivity during the

CAL hydrogenation under the conditions used. This unusual phenomenon observed with the PdZn-30 catalyst has further been investigated.

3.3. CAL hydrogenation in the Presence of Other Aldehyde Additives In the hydrogenation of CAL with PdZn-30 catalyst, the product selectivity varied with conversion in an unusual way, as above-mentioned (Fig. 2b). This indicates a possibility that the reaction is influenced by a product of HCAL because it is little produced after a certain period of reaction (Fig. 2b). The possibility was examined by reaction runs with a certain amount of an aldehyde additive added to the reaction mixture of CAL in toluene, in which the concentration of CAL was fixed by changing the volume of solvent used. Five different aldehyde additives, as given in Scheme 2, were used for these reaction runs. Table 2 summarizes the reaction results of CAL hydrogenation in the presence of different additives in the starting reaction mixture. The addition of **1**, HCAL, little changed the total CAL conversion but it increased the COL selectivity (entry 2); that is, HCAL molecules influenced the product selectivity in CAL hydrogenation. It is likely that the adsorption of CAL substrate on the surface of PdZn catalyst is controlled by HCAL molecules coexisting in the reaction mixture, which can control the orientation of CAL adsorption on the catalyst and promote the hydrogenation of its C=O bond rather than C=C bond. Table 2 also indicates that the other additives have the same effect, as observed with HCAL, that the formation of COL is promoted while that of HCAL is suppressed. The extent of the promotional effect was different from one aldehyde to another; it was the largest with **1** (HCAL) and the smallest with **3**. Namely, an aldehyde molecule similar to the substrate CAL in the structure can have the largest effect. Aliphatic aldehydes, **4** and **5**, also appeared to indicate the same effect and the latter larger molecule was more effective. For comparison, similar reaction runs were also conducted with Pd-30 catalyst. The addition of aldehyde additives was not observed to influence the product selectivity for this monometallic catalyst (entries 7-10), in contrast to PdZn-30 alloy one. Those results indicate that the substrate CAL is likely to interact with the aldehyde additive on the surface of PdZn-30 catalyst but neither on Pd catalyst nor in the solvent (bulk liquid phase).



Scheme 2. Aldehydes **1** - **5** added to CAL hydrogenation (Table 2). **1**: Hydrocinnamaldehyde, **2**: Phenylacetaldehyde, **3**: Benzaldehyde, **4**: Butyraldehyde, **5**: 1-Heptaldehyde

Table 2. Influence of the addition of different aldehydes on the hydrogenation of CAL over PdZn-30 and Pd-30 catalysts

Entry	Catalyst	Aldehyde added		CAL conversion	Selectivity (%)		
		#[a]	(mmol)	(%)	COL	HCAL[b]	HCOL
1	PdZn	−	−	25	27	60	13
2		**1**	0.38	25	45	39	16
3		**2**	0.43	33	28	60	12
4		**3**	0.49	36	22	65	13
5		**4**	0.55	40	28	58	14
6		**5**	0.36	34	27	59	14
7	Pd	−	−	84	13	58	29
8		**1**	0.38	85	11	56	33
9		**2**	0.43	79	14	60	26
10		**3**	0.49	79	12	61	27

Reaction conditions: CAL 3.97 mmol, catalyst 50 mg, temperature 80 ºC, H_2 4 MPa, time 20 min. Total volume of mixture was fixed to 5 cm^3 by changing the volume of solvent (toluene) used.

a. See Scheme 2. b. Determined from the amount of HCAL detected - the initial amount of HCAL added.

3.4. Molecular Interactions of CAL with Aldehyde Additives Interactions of CAL and a selected aldehyde additive of **1**, **3**, or **5** (Scheme 2) were examined by FTIR at room temperature. Fig. 5 gives the FTIR spectra obtained with CAL, **1**, **3**, **5**, and mixtures of CAL with **1**, **3**, or **5** (1:1 in volume) in cyclohexane. The absorption band of ν C=O was located at 1679 cm^{-1} for CAL and 1727 cm^{-1} for **1** [23]. When CAL was mixed with **1**, no significant changes were observed for ν C=O, ν C=C (1627 cm^{-1}), and absorption bands due to its phenyl ring (1495 cm^{-1}, 1575 cm^{-1}, 1595 - 1965 cm^{-1}) [23]. Thus there is no significant interactions between free CAL and HCAL (**1**) molecules in the solution. This was also the case for the other aldehydes of **3** and **5**. These results imply that interactions of CAL with **1**, **3**, or **5** occurs when these aldehyde molecules coexist on the surface of PdZn-30 catalyst, which will be discussed later.

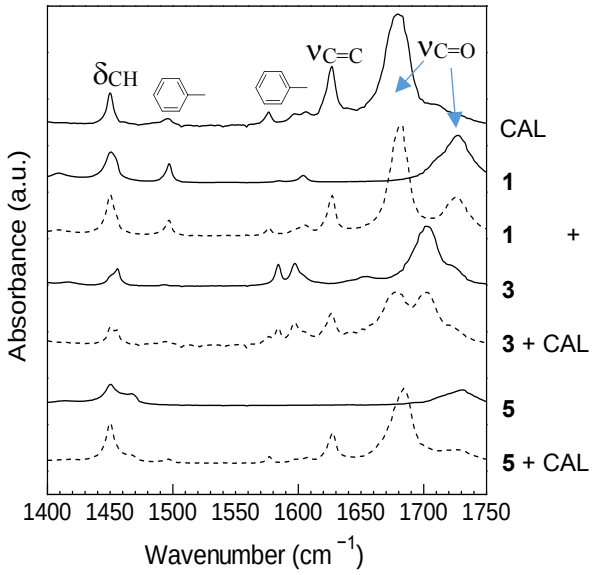


Figure 5. FTIR spectra of CAL, **1**, **3**, and **5** and mixtures of CAL and **1**, **3**, or **5** (1:1 in volume) in cyclohexane measured at room temperature. **1**: Hydrocinnamaldehyde, **3**: Benzaldehyde, **5**: 1-Heptaldehyde. Absorption band at 1450 cm^{-1} is δCH_2 of cyclohexane.

3.5. Surface Properties of PdZn and Pd Catalysts The surface of PdZn and Pd catalysts were examined by XPS measurements. The spectra obtained for Pd 3d are given in Fig. 6 and the values of binding energy (BE) and full width at half maximum (FWHM) are compared in Table 3. The BE value of Pd-5 was a little higher than that of Pd-30, which

would be ascribable to the smaller Pd crystallite size in the former sample [24-27]. For the PdZn samples, the BE value was observed to be independent of the PdZn crystallite size. The BE values were not so significantly different between Pd and PdZn catalysts. Note, however, that the FWHM value of PdZn-30 was even smaller than that of PdZn-5, the latter having a FWHM value comparable to those of Pd samples. Fig. 7 shows the Zn LMM spectra for the Pd and PdZn catalysts and shoulder peaks (marked by arrow) appear at a BE value of around 495 eV in the PdZn catalysts. These are indicative of the presence of alloyed PdZn on the surface of the PdZn-30 and PdZn-5 catalysts [28], which are markedly different in the product selectivity in the CAL hydrogenation as above-mentioned. The FWHM should be a measure of structural order/disorder of the surface layer of dispersed particles. The present ZnO-supported PdZn catalysts were prepared through calcination in air at 500 ºC and subsequent reduction in H_2 at 500 ºC. These thermal treatments and the amount of Pd loaded should be determinant for the resulting surface structure of PdZn particles dispersed on ZnO. When the Pd loading is 5 wt.-%, the size of PdZn crystallites is small (13 nm) and the surface layer of these alloy crystallites might not be of well-ordered structure; Pd and Zn atoms might be exposed in less ordered arrangement. The Pd atoms exposed on PdZn-5 catalyst should be diverse in the chemical state. For the PdZn-30 catalyst, in contrast, ordered PdZn alloy structure might be formed on the surface of its larger PdZn crystallites. This structural feature is likely to result in its unique catalytic actions. Another factor may be the surface geometry (curvature) of PdZn crystallites and the adsorption of HCAL should be more likely to occur with its aldehyde group on the surface of large PdZn crystallites (PdZn-30) than on smaller crystallites (PdZn-5) having a larger curvature. The metallic Pd-30 and Pd-5 catalysts were prepared through calcination in air at 500 ºC and subsequent reduction in H_2 at ambient temperature. Due to this low-temperature reduction, the surface layer of their small Pd particles should be in less ordered structure, similar to the small PdZn particles of PdZn-5 catalyst.

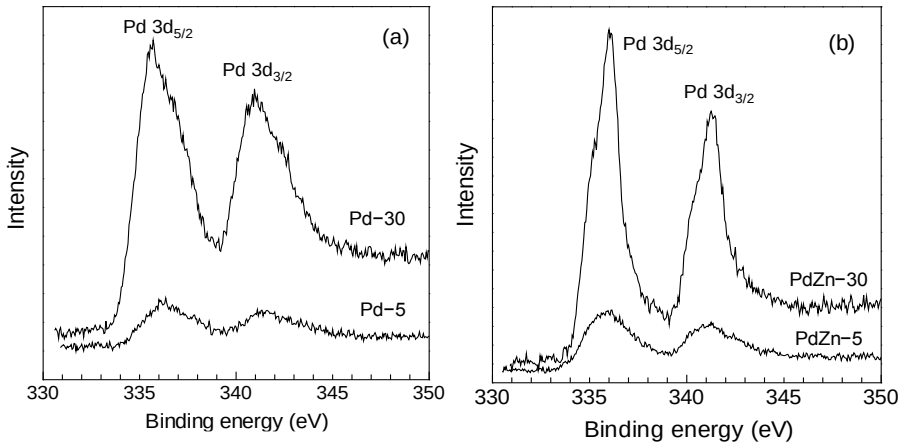


Fig. 6. Pd 3d spectra of Pd (a) and PdZn (b) samples different in the Pd loading

Table 3. Results of XPS for Pd and PdZn samples different in the Pd loading

Sample	Crystallite size [a] (nm)	BE (Pd $3d_{5/2}$) (eV)	FWHM [c] (eV)
Pd-30	7	335.7	2.9
Pd-5	– [b]	336.3	2.7
PdZn-30	60	336.0	1.1
PdZn-5	13	336.0	2.7

a. Determined by XRD. b. Pd crystallites are small. c. Half width at half maximum.

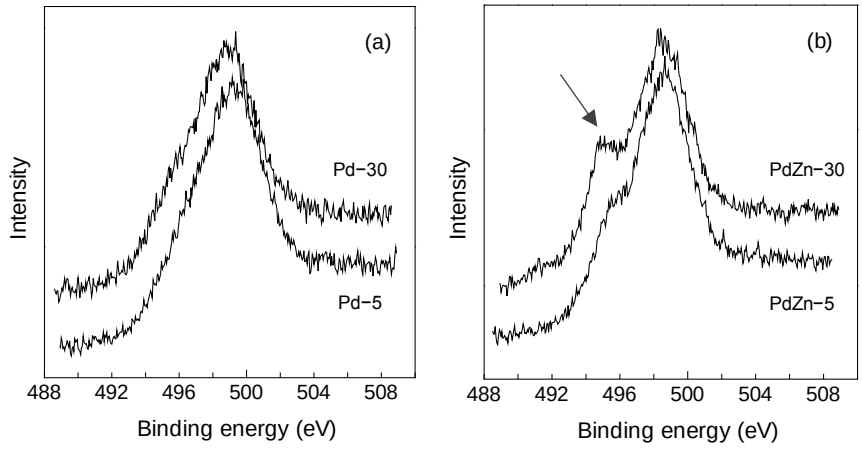


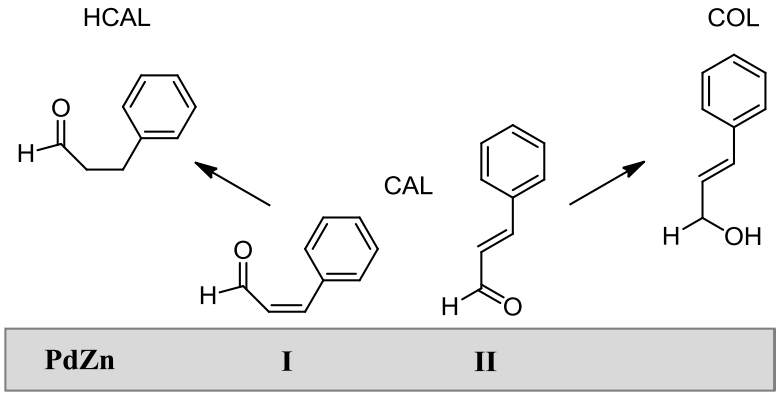
Fig. 7. Zn LMM spectra of Pd (a) and PdZn (b) samples different in the Pd loading

The PdZn catalysts are effective for H_2 production via steam reforming reactions and their structural changes during the reactions have been studied in detail [29-31]. Föttinger et al. indicate that metallic Pd particles dispersed on ZnO change in their structure on methanol steam reforming at 350 ºC, producing PdZn/Pd particles of core-shell structure that PdZn alloy layer covers the surface of Pd particles. It is further noted that the structural and electronic features of the outer PdZn layer resemble the tetragonal Pd:Zn intermetallic compound in the compositional range of around 50 atom %.[31] It is also reported that the surface of PdZn alloy formed on Pd (111) surface contains Pd and Zn atoms in ordered structure [32, 33]. These results support the above-mentioned surface structure of large PdZn particles in the PdZn-30 catalyst, which may be responsible for its unique catalytic actions in CAL hydrogenation as observed. The surface of the PdZn catalyst would expose Pd and Zn atoms in a mosaic-like structure. Such a surface containing two different atoms may assist the adsorption of HCAL via its polar aldehyde group, in which O and H atoms interact with Pd and Zn species, respectively. This should result in the stable adsorption of HCAL on the PdZn catalyst. For Pd catalysts, however, those interactions are unlikely to occur.

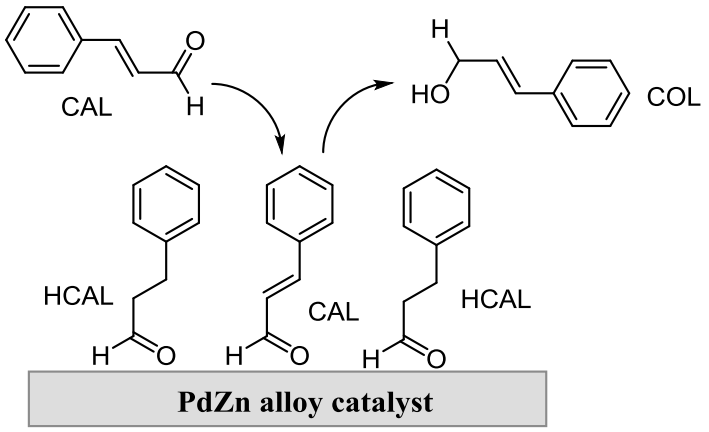
3.6. CAL Hydrogenation on PdZn-30 Controlled by HCAL There are two different modes of adsorption of CAL on the surface of PdZn (Scheme 3), which is adsorbed via either C=C bond (type **I** side-on) or aldehyde group (type **II** end-on). The CAL molecules adsorbed in type **I** may be hydrogenated to HCAL while that in type **II** COL. At the initial stage of hydrogenation, the selectivity to HCAL is the largest compared to COL and HCOL and, therefore, CAL molecules are likely to be mainly adsorbed in type **I** and transform to HCAL. When a certain amount of HCAL is formed, the adsorption of CAL is influenced by the coadsorption of HCAL that should be adsorbed via aldehyde group but its hydrogenation is difficult to occur. The accumulation of HCAL molecules may increase the density of molecules adsorbed on the surface of PdZn and change the mode of CAL adsorption from type **I** to type **II** (Scheme 4). The change in the type of CAL adsorption should also be promoted by interactions between CAL and HCAL molecules through π - π stacking interactions of their benzene rings [34, 35]. The extent of π–π stacking interactions should depend on the structure of two interacting molecules. This may explain that the maximum effect of aldehyde addition on the CAL hydrogenation appears with HCAL, which is similar in the structure and size to the substrate (Table 2). The CAL molecule adsorbed in type **II** yields COL, resulting in the enhanced selectivity to COL as observed (Fig. 1). In addition,

the adsorption of less reactive HCAL molecules on PdZn decreases the total rate of CAL conversion during the reaction. Indeed, the time - conversion data cannot be simulated with a pseudo first order reaction kinetics, which can simulate the results with Pd (Fig. 2).

Recently, Liu et al. reported the influence of Pd particle size on the selective hydrogenation of α, β-unsaturated aldehydes. Their density functional theory calculations indicate the change of CAL adsorption with the size of Pd particles. The adsorption of CAL on a small Pd particle (Pd_4 cluster) may occur more significantly with C=C bond rather than C=O bond; on a large Pd particle (Pd(111) surface), however, the CAL adsorption with C=O bond is more significant than that with C=C bond. This may be related to the present result that the influence of HCAL (and other aldehydes) additive on the COL selectivity appears only for PdZn-30 catalyst including larger PdZn crystallites compared to PdZn-5 one.



Scheme 3. Adsorption of CAL molecule in two different orientations **I** (side-on type) and **II** (end-on type) yielding HCAL and COL, respectively, on the surface of PdZn particles dispersed on ZnO



Scheme 4. Adsorption of CAL and HCAL molecules on the surface of *large* PdZn alloy particles dispersed on ZnO at the middle stage of reaction, producing COL selectively.

Medlin et al. reported an interesting result that the product selectivity in hydrogenation of α, β-unsaturated aldehydes like CAL over a Pt/Al_2O_3 catalyst was controlled by thiolate modifiers introduced on its surface [37, 38]. The modifiers can control the orientation of aldehydes adsorbed and promote the hydrogenation of their carbonyl groups, enhancing the selectivity to the corresponding unsaturated alcohols. The enhancement in the selectivity is explained by interactions between the modifiers and the substrates on the surface of supported Pt particles, similar to our case in which interactions between CAL and a product of HCAL on the surface of PdZn catalyst are responsible for the increase in the COL selectivity during the reaction. Recently, the present authors reported a similar phenomenon for the reduction of nitrobenzene and phenylacetylene with hydrazine over a nitrogen- and oxygen-doped metal-free activated carbon (AC) catalyst [39]. Phenylacetylene alone was not reduced but its reduction was promoted by the coexistence of nitrobenzene that could be reduced alone. Nitrobenzene is adsorbed on the surface of nitrogen- and oxygen-doped AC catalyst through interactions of its nitro group with the surface nitrogen and oxygen species; the adsorption of nitrobenzene may assist the adsorption of phenylacetylene as well, for which interactions among the two substrates and the catalyst surface are likely to occur.; as a result, phenylacetylene can also be reduced in the presence of nitrobenzene and surface-modified AC catalyst. In the present and previous catalytic reactions over PdZn, Al_2O_3-supported supported Pt [37, 38], and nitrogen- and oxygen-doped AC catalysts [39], the product selectivity can be controlled by interactions of substrates and

modifiers on the surface of catalysts. Those results may open interesting catalysis of heterogeneous catalysts.

4. Conclusions

Among ZnO-supported Pd and PdZn catalysts loaded with Pd in 30 and 5 wt.-%, the PdZn catalyst containing Pd in 30 wt.-% (PdZn-30) showed unique catalytic actions in the liquid phase CAL hydrogenation, which were different from those of Pd catalysts and PdZn one having a smaller Pd content of 5 wt.-%. The PdZn-30 catalyst was more selective for the production of COL compared to the other Pd and PdZn ones. For the latter catalysts, COL was produced in a selectivity of < 5% at any total CAL conversion up to 90%, HCAL being formed in a larger selectivity of 70%. For the PdZn-30 catalyst, the product selectivity at a conversion of 20% was similar to that obtained with the others; it was interesting, however, that the COL selectivity increased significantly with conversion while the HCAL selectivity decreased. The unexpected increase in the COL selectivity results from interactions between the substrate, CAL, and a partially hydrogenated product of HCAL on the surface of PdZn crystallites of the catalyst. At the early stage of reaction, CAL is adsorbed on the catalyst via the C=C bond and it is hydrogenated, producing HCAL in a large selectivity. When the reaction proceeds, HCAL molecules formed are then adsorbed on the catalyst via the aldehyde group but it is little hydrogenated. The accumulation of HCAL molecules on the surface of PdZn crystallites controls the orientation of adsorption of CAL thereon, CAL being likely to be adsorbed via the aldehyde group rather than the C=C group. The π–π interactions between the benzene rings of HCAL and CAL that are of similar structure/size are important for these interactions to occur. This promotes the preferential hydrogenation of the aldehyde group and produces COL more selectively. Compared to the size of PdZn crystallites of ZnO-supported PdZn catalyst containing Pd in 5 wt.-% (13 nm), the PdZn-30 catalyst has larger PdZn crystallites (60 nm) and the constituents (Pd, Zn) are likely to be well-ordered on their surface. These structural features may be responsible for the unique catalytic actions of PdZn-30 catalyst in the selective hydrogenation of CAL to COL.

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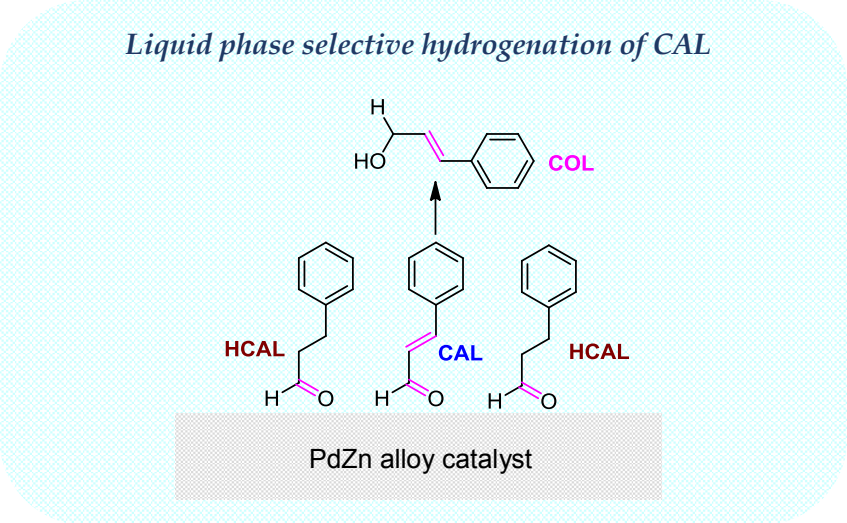
Graphical Abstract



Adsorbed HCAL molecules control the adsorption of CAL and enhance the selective hydrogenation to COL over PdZn catalyst