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Liquid phase hydrogenation of phenylacetylene over Pd and PdZn catalysts in toluene: effects of alloying and CO_2 pressurization†

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Liquid-phase hydrogenation of phenylacetylene was investigated with Pd and PdZn alloy catalysts in toluene compressed by CO_2. The influence of alloying and dense phase CO_2 on the rate of conversion and the product selectivity was examined. With either Pd or PdZn the partially hydrogenated product of styrene was produced in high selectivity but the selectivity to styrene obtained with the latter was larger than that with the former when compared at the same conversion level. After the initial substrate was fully consumed, the styrene was fully hydrogenated to ethylbenzene for both catalysts but more slowly with the PdZn alloy catalyst. The presence of a dense phase of CO_2 (1.5 MPa) enhanced the rate of phenylacetylene hydrogenation and the selectivity to styrene for the Pd and PdZn catalysts. Possible reasons for the positive effects of alloying and dense phase CO_2 on the partial hydrogenation of phenylacetylene to styrene are discussed.

1. Introduction

Selective hydrogenation of alkynes to alkenes is one of the important hydrogenation reactions in industry.[1,2] An alkyne is partially hydrogenated to the corresponding alkene and the alkene so formed is also hydrogenated to the fully hydrogenated alkane. It is desirable to suppress the full hydrogenation for the selective production of the alkene at a high conversion level. There is a trend that the adsorption of alkynes is stronger than that of alkenes and the hydrogenation of alkenes is difficult to achieve when the initial alkynes remain unreacted in the reaction mixture; when the alkynes are almost consumed, the alkenes may then be adsorbed and hydrogenated. It is therefore required that the desired catalysts should adsorb alkynes but not alkenes.[3] The selective hydrogenation of alkynes is still a challenging task from industrial and academic points of view. Several previous authors investigated the liquid-phase hydrogenation reactions using different alkynes such as pentyne,[4,5] hexyne,[6] heptyne,[7–11] octyne,[12] phenylacetylene,[13–16] and 1-phenyl-1-pentyne.[17] The most common catalysts used in industry and academia are Pd-based catalysts. Several authors used bimetallic Pd catalysts and examined the impact of alloying on the catalytic performance in the selective hydrogenation of alkynes.[1] For example, Pârvulescu *et al.* prepared SiO_2-embedded Pd, Au, and PdAu colloids and tested their catalytic performance in the liquid phase hydrogenation of 3-hexyn-1-ol at 20 °C.[18] They showed that the alloying of Pd with Au was effective for enhancing the rate of hydrogenation and the selectivity to *cis*-3-hexen-1-ol. Scott *et al.* investigated the hydrogenation of 3-hexyn-1-ol over poly(vinylpyrrolidone)-stabilized PdAu bimetallic particles in 1-butyl-3-methyl-imidazolium hexafluorophosphate and indicated that the catalytic performance depended on the composition.[19] Panpranot *et al.* prepared several PdAu catalysts by the combination of incipient wetness impregnation and deposition-precipitation methods.[20] The authors applied those PdAu catalysts for the hydrogenation of 1-heptyne in toluene at 30 °C and discussed the relationship between the catalytic performance (activity and selectivity) and structural features.

In the present work, Pd and PdZn alloy catalysts supported on ZnO were prepared according to the previous works[21,22] and applied for the liquid phase selective hydrogenation of a model alkyne of phenylacetylene in toluene compressed by CO_2. Earlier Rodriguez made a detail study on the electronic and chemical properties of PdZn surface.[23] It is noted that the electronic perturbations induced by the alloying of Pd with Zn decrease its CO chemisorption ability by weakening the Pd(4d)–CO(2π) bonding interactions. This allows us to expect that the PdZn surface is different from the Pd surface in the adsorption of the substrate of phenylacetylene and its hydrogenated product of styrene and then in the catalytic activity for the hydrogenation of these reacting species. The present authors have investigated the catalytic performance of these Pd and

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PdZn catalysts with respect to the total conversion and the product selectivity for the hydrogenation of phenylacetylene. To our knowledge only a few works were reported so far on the hydrogenation of alkynes using PdZn alloy catalysts in the literature. Engels *et al.* used PdZn alloy catalysts different in the composition for hydrogenation of phenylacetylene in methanol at 50 °C.[24] They showed that the hydrogenated product of styrene was exclusively produced during the course of reaction up to 100% conversion and the further hydrogenation of styrene started to occur after the initial substrate was fully consumed. Tew *et al.* showed the effectiveness of PdZn alloy catalyst for the gas-phase hydrogenation of 1-pentyne to 1-pentene at temperatures of 45–100 °C.[25] The present authors have studied the selective hydrogenation of phenylacetylene in toluene that is compressed by CO_2. It is demonstrated that CO_2 can act as a reaction promoter enhancing the reaction rate and controlling the product selectivity in several reactions.[26,27] These actions are ascribable to interactions of CO_2 molecules with organic substrates, intermediates, and/or catalysts in liquid phases. For example, in liquid-phase hydrogenation of aromatic nitro compounds, the desired aniline products can be obtained in 100% selectivity at any conversion level up to 100% conversion.[28,29] The CO_2 molecules dissolved in the liquid phase interact with nitro group and decrease its reactivity while the interactions with CO_2 increase the reactivity of intermediates such as nitrosobenzene and *N*-phenylhydroxylamine. There is another effect of CO_2 that the dissolution of CO_2 changes the liquid properties from pure organic liquid to dense phase CO_2 fluid, facilitating the dissolution of a gaseous reactant of H_2. As a result, the nitro compounds can be hydrogenated more rapidly and the aniline products can be produced in almost 100% selectivity in the presence of compressed CO_2. These interesting results have motivated us to study the impact of CO_2 pressurization on the selective hydrogenation of phenylacetylene with Pd and PdZn alloy catalysts.

2. Experimental

2.1. Catalyst preparation and characterization

Impregnation and coprecipitation methods were used to prepare Pd/ZnO catalyst samples according to the previous works.[21,22] For the former, a commercial ZnO powder (Kanto Chemical) was impregnated with a $Pd(NO_3)_2$ solution (Tanaka Kikinzoku), dried at 100 °C overnight, heated in air at 5 K min^{-1} to 500 °C, and calcined for 3 h. The loading of Pd was 1, 10, and 30% by weight. For the latter, a mixed 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 and placed in an water bath at 70–80 °C. Then, drops of another solution of Na_2CO_3 (Wako) was added slowly to this solution until pH of the mixture became to 8. The precipitate formed was filtered, washed with distilled water, separated by centrifuge, and dried at 100 °C. The resultant solid materials were calcined in the same manner as mentioned above. The loading of Pd was 30% by weight. Those ZnO-supported Pd samples were reduced in 4% H_2 (in N_2) at ambient temperature for 1 h to prepare Pd catalysts or at ambient temperature for 1 h and increasing temperatures at a rate of 5 K min^{-1} to 500 °C to obtain PdZn alloy catalysts.[21,22]

X-ray diffraction (XRD) patterns of ZnO-supported Pd samples so prepared were measured on JOEL JDX-8020 using Cu Kα radiation through a Ni filter to determine the phases (Pd, PdZn) present therein and estimate the sizes of Pd and PdZn crystallites by Pd (111) ($2\Theta = 40.1°$) and PdZn (111) ($2Q = 41.2°$) diffraction line broadening, respectively, with the Scherrer equation. The surface of Pd and PdZn supported on ZnO was examined by X-ray photoelectron spectroscopy (XPS) measurement. The sample was ground in a mortar, pressed onto a sample holder, and measured by a JEOL JPS-9200 without such a pretreatment as Ar sputtering. The charge-up shift correction of binding energy for Pd was made by setting the C 1s binding energy at 248.5 eV. The amount of exposed Pd species in the catalyst was determined by CO pulse chemisorption at 50 °C using a BEL-METAL-1 system. About 150 mg sample was heated in a quartz cell at 100 °C for 30 min in H_2 and the cell was cooled to 50 °C in He. Then 1 cm^3 CO (1% in He) was pulsed over the sample until the TCD signal for the effluent gas became unchanged.

2.2. Liquid-phase hydrogenation

Liquid-phase hydrogenation of phenylacetylene and styrene (partially hydrogenated product) was conducted according to the previous works.[28–31] A stainless steel reactor (100 cm^3) was loaded with a catalyst sample 10 mg and toluene 5 cm^3, the remaining air was replaced with H_2 by purging a few times, and the mixture was compressed by H_2 at 0.6 MPa. The reactor was heated to 100 °C and maintained for 30 min for *in situ* reduction of catalyst. Then, phenylacetylene 0.5 cm^3 and toluene 25 cm^3 were added to the reactor at ambient temperature, it was cooled to 0 °C in an ice-water bath, 0.6 MPa H_2 was introduced, and the mixture was stirred by a magnetic stirrer. When CO_2 was used, it was added to the reactor with a liquid pump (JASCO SCF-Get) to a partial pressure of 1.5 MPa after the introduction of H_2. After the reaction, the reactor was depressurized slowly to ambient pressure and the liquid mixture was analyzed by a gas chromatograph (GL Science Micro GC CP4900). The total conversion of phenylacetylene was determined from the amounts of the substrate measured before and after reaction. 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.

2.3. High-pressure FTIR and phase behavior measurement

Molecular interactions of phenylacetylene and styrene with CO_2 in the liquid phase were examined by an *in situ* high pressure FTIR (JASCO FTIR-620) in attenuated total reflection (ATR) mode at ambient temperature. The formation and adsorption of CO from H_2 and CO_2 over Pd and PdZn catalysts at high pressures were examined by FTIR in transmittance mode using a different laboratory-made cell. A catalyst (20 mg) and SiO_2 powder (20 mg) were ground in a mortar and the mixture was pressurized at 50 MPa for 1 h to prepare a catalyst pellet. The pelletized catalyst sample was placed in a high-pressure FTIR cell (JASCO). The cell volume was 1.5 cm^3 and the optical pathway was 1 cm. The cell was purged by H_2 gas (99.99%) a few times to remove the air at room temperature. *In situ* FTIR measurements were made at a H_2 pressure of 0.6 MPa and at different CO_2 pressures up to 3 MPa using the JASCO FTIR-620 spectrometer with a resolution of 2 cm^{-1}. The spectra collected in the presence of 0.6 MPa H_2 and CO_2 at different pressures was used as a background. The extent of volume expansion of the reaction liquid phase pressurized by CO_2 was examined with a high pressure view cell equipped with two sapphire windows, through which the liquid mixture was examined by naked eye. The details of those experimental setups and procedures were described elsewhere.[30,32]

3. Results and discussion

The ZnO-supported Pd and PdZn catalysts prepared and used in the present work are listed in Table 1, which includes the metal crystallite sizes determined by XRD and the numbers of exposed Pd species determined by CO chemisorption. XRD patterns obtained are presented in ESI (Fig. S1†). Those catalysts were used to study the liquid phase selective hydrogenation of phenylacetylene.

3.1. Hydrogenation with Pd/ZnO and PdZn/ZnO catalysts prepared by impregnation

Features of the hydrogenation of phenylacetylene in toluene were examined with several Pd/ZnO catalysts different in the reduction temperature and the Pd loading (catalysts # 1–6 of Table 1). The reaction results obtained are given in Fig. 1. The substrate was hydrogenated to styrene and it was further hydrogenated to ethylbenzene. Fig. 1 shows that the rate of phenylacetylene conversion with Pd catalysts is larger than that with PdZn alloy catalysts. For the PdZn catalysts, the selectivity to styrene was high irrespective of the large difference in the PdZn crystallite size (Table 1), which was larger than 90% at almost complete conversion. For the Pd catalysts, in contrast, the selectivity to styrene became lowered as the Pd loading was increased. For the 30 wt% Pd catalyst, the selectivity was smaller than 85% at a higher conversion. It was observed that the styrene was further hydrogenated to ethylbenzene at a longer reaction time for the PdZn and Pd catalysts, similar to the previous result of Engels *et al.*,[24] but more gradually for the former (ESI, Fig. S2†). In addition, styrene was used as a starting substrate instead of phenylacetylene. Table 2 shows the results obtained with either styrene or phenylacetylene. The conversion

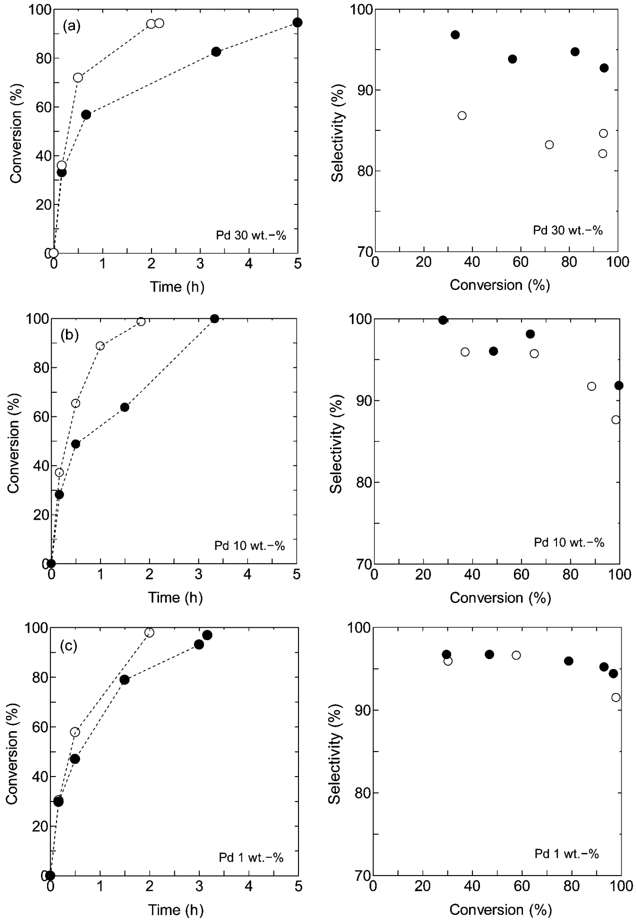

Fig. 1 Conversion – time and styrene selectivity – conversion profiles in hydrogenation of phenylacetylene over Pd (○) and PdZn alloy (●) catalysts including different amounts of Pd on ZnO. Pd loading: (a) 30 wt%, (b) 10 wt%, (c) 1wt%.

Table 1 ZnO-supported Pd catalysts prepared and used in the present work

Catalyst no.	Preparation method	Pd loading (wt%)	Reduction temperature[a] (°C)	Chemical state	Crystallite size[b] (nm)	CO adsorbed[c] (μmol g^{-1})
1	Impregnation	30	Room	Pd	3.8	0.30
2	Impregnation	30	500	PdZn	115	na
3	Impregnation	10	Room	Pd	4.4	0.26
4	Impregnation	10	500	PdZn	42	na
5	Impregnation	1	Room	Pd	4.5	0.10
6	Impregnation	1	500	PdZn	19	na
7	Coprecipitation	30	Room	Pd	4.4	1.0
8	Coprecipitation	30	500	PdZn	28	na

[a] Reduced in a 4% H_2 stream at ambient temperature for 1 h for Pd; at ambient temperature and at increasing temperatures with a rate of 5 K min^{-1} to 500 °C for PdZn. [b] Determined by X-ray diffraction line broadening. [c] Amount of CO chemisorbed per 1 g of Pd/ZnO catalyst. na: not adsorbed.

Table 2 Activity of ZnO-supported Pd catalysts prepared by impregnation for hydrogenation of phenylacetylene and styrene[a]

			Conversion (%)		TOF[b] (s^{-1})	
Catalyst no.	Pd loading (wt%)	Chemical state	Phenylacetylene	Styrene	Phenylacetylene	Styrene
1	30	Pd	35.9	35.2	0.30 (4.5)	0.16 (2.1)
2	30	PdZn	33.1	6.5	9.9	0.94
3	10	Pd	37.1	42.3	1.2 (5.2)	0.67 (2.9)
4	10	PdZn	28.2	21.3	9.2	3.4
5	1	Pd	30.3	26.2	10.0 (11.1)	4.3 (4.6)
6	1	PdZn	29.7	15.8	44.0	11.4

[a] Reaction conditions: reaction time: 10 min for phenylacetylene, 20 min for styrene. [b] The amounts of exposed Pd species were estimated from the results of XRD and CO chemisorption. TOF values determined from CO chemisorption results are given in parenthesis. The estimation of the amounts of exposed Pd species is explained in ESI.

of styrene in 20 min was comparable to that of phenylacetylene in 10 min for the Pd/ZnO catalysts. For the PdZn/ZnO ones, in contrast, the styrene was hydrogenated even more slowly compared to the phenylacetylene. This may explain the higher selectivity to styrene in hydrogenation of phenylacetylene with the PdZn alloy catalysts. In a previous work,[11] it was shown that when Pd was alloyed with Au on a support of TiO_2, the activity to the hydrogenation of 1-heptyne was increased while the selectivity to the partially hydrogenated product of 1-heptene was deceased. The Au species were assumed to act as an electronic promoter for Pd. The influence of Au for Pd/TiO_2 is different from that of Zn for Pd/ZnO observed in the present work.

Table 2 also shows turnover frequency (TOF) values for hydrogenation of phenylacetylene and styrene, in which the amounts of exposed Pd species were determined from the results of XRD and CO chemisorption. Table 2 indicates that the TOF values of the hydrogenation of phenylacetylene and styrene were comparable for the monometallic Pd catalysts. For the PdZn alloy catalysts, these TOF values were enhanced but to a larger extent for the hydrogenation of phenylacetylene. Fig. 2 shows XPS spectra collected, indicating that the binding energy (BE) of Pd $3d_{5/2}$ was 335.2 eV for the Pd catalysts (Fig. 2a) and the BE was shifted to 335.9 eV by the formation of PdZn alloy (Fig. 2b). Namely, the BE of Pd 3d became higher when Pd was allowed with Zn, in accordance with the previous results of Rodriguez;[23] Pd species in the PdZn alloy crystallites was more electron-deficient compared to that in the Pd ones. These electron-deficient Pd sites on the PdZn crystallites are likely to be more beneficial for the adsorption of alkyne (phenylacetylene) and alkene (styrene), which may explain the larger TOF values of the hydrogenation of these substrates over the PdZn alloy catalysts (Table 2). This effect should be more significant for the phenylacetylene than the styrene, in which the former alkyne is more easily adsorbed than the latter alkene.[3] The surface of PdZn alloy on Pd (111) surface may expose both Pd and Zn atoms in ordered structures.[33,34] The authors speculate that the surface of nano-sized PdZn alloy crystallites is a mosaic-like structure exposing Pd and Zn atoms and so the catalytic function of exposed Pd species are unlikely to change with the crystallite size, which is responsible for the higher selectivity to styrene irrespective of the Pd loading. Carturan *et al.* reported that the formation of β Pd–H is facilitated over larger Pd crystallites and this promotes the hydrogenation of styrene to ethylbenzene.[35] In addition, one can speculate that the surface of larger Pd crystallites is less electron-deficient, which decreases the difference in the adsorption between phenylacetylene and styrene; namely, the difference in the specific hydrogenation activity for these alkyne and alkene is decreased, resulting in an increase in the selectivity to the alkene, styrene, for larger Pd crystallites, as observed (Fig. 1).

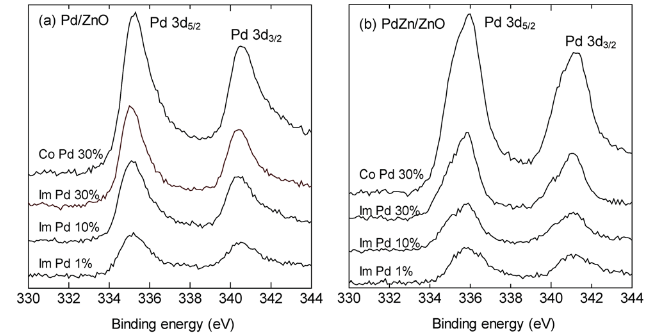

Fig. 2 XPS spectra of (a) Pd on ZnO and (b) PdZn alloy on ZnO samples prepared by impregnation (Im) and coprecipitation (Co) followed by the reduction at ambient temperature and at 500 °C, respectively.

3.2. Hydrogenation with Pd/ZnO and PdZn/ZnO catalysts prepared by coprecipitation

The above results demonstrate that the PdZn alloy catalysts are more selective to the partial hydrogenation of phenylacetylene to styrene as compared to the Pd ones but less active (Fig. 1). To improve the performance of the former catalyst, coprecipitation was used to prepare Pd/ZnO samples, in which Pd loading was 30 wt% (catalyst # 7 and 8 of Table 1). The XRD patterns of these catalysts reduced at ambient temperature and 500 °C are given in ESI (Fig. S1†). Fig. 3 compares the performance between the Pd/ZnO catalysts prepared by coprecipitation and impregnation. The catalyst prepared by coprecipitation was highly active than that by impregnation while keeping the high selectivity to styrene. This may result from its smaller PdZn crystallite size, 28

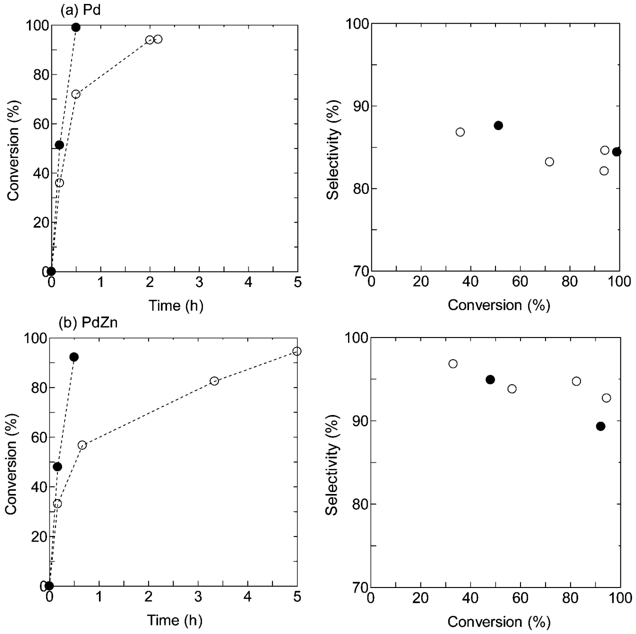

Fig. 3 Conversion – time and styrene selectivity – conversion profile in hydrogenation of phenylacetylene hydrogenation over 30 wt% Pd loaded ZnO catalysts prepared by coprecipitation (●) and impregnation (○) for Pd (a) and PdZn (b) catalysts reduced at ambient temperature and 500 °C.

nm, compared to 115 nm for the corresponding catalyst prepared by impregnation (Table 1).

3.3. Hydrogenation in the presence of dense phase CO_2

To examine the influence of CO_2 pressurization, the hydrogenation of phynylacetylene was further studied in the presence of dense phase CO_2, in which the Pd/ZnO catalysts prepared by coprecipitation were used (catalyst # 7 and 8 of Table 1) because of their better performance compared to those prepared by impregnation. The hydrogenation of phenylacetylene was conducted in toluene pressurized by CO_2 at a pressure of 1.5 MPa. The influence of CO_2 on the catalytic performance is shown in Fig. 4. It is noteworthy that the rate of hydrogenation and the selectivity to styrene can be improved in the presence of 1.5 MPa CO_2 for either Pd or PdZn catalyst. Under the conditions used, the volume of the liquid phase was observed to expand to some small extent in the presence of 1.5 MPa CO_2. Dissolution of a certain amount of CO_2 promotes the dissolution of the gaseous reactant of H_2 and this may cause the increase in the rate of phenylacetylene conversion. The concentration of phenylacetylene in toluene used was 0.13 mol dm^3 and, at such a low substrate concentration, the positive effect of the promoted dissolution of H_2 into the liquid phase should surpass the negative effect of the dissolution of CO_2 as a diluent. It was previously indicated that the presence of dense phase CO_2 causes interactions of CO_2 molecules with certain functional groups such as carbonyl, nitro, and cyano groups of substrates and intermediates and this results in changes in the rate of reaction and the product selectivity for hydrogenation and other reactions.[26,27] For the present cases of phenylacetylene and styrene in toluene, however, no significant interactions of CO_2 with the alkynyl and alkenyl groups were observed as confirmed by ATR-FTIR (ESI Fig. S3 and S4†). Other possible factors are interactions of CO_2 with supported Pd and PdZn crystallites. Previously high-pressure UV/Vis absorption was measured for silver particles dispersed on the surface of a quartz plate in CO_2 at high pressures.[36] The optical absorption was found to change with CO_2 pressure and the properties of the metal particles were probably changed through interactions with CO_2 molecules accumulating on their surface. These interactions could occur for the present supported Pd and/or PdZn crystallites and change their catalytic functions. For the hydrogenation over noble metal catalysts in the presence of dense phase CO_2, CO is often formed through the reverse water gas shift reaction of H_2 + CO_2 → H_2O + CO, which is adsorbed on their surface and changes their catalytic performance.[30,32,37,38] The formation and adsorption of CO on Pd and PdZn catalysts was examined by *in situ* FTIR in transmission mode. Fig. 5 shows FTIR spectra collected in the presence of 0.6 MPa H_2 and CO_2 at high pressures. No CO adsorption was observed for the alloyed PdZn catalyst at 1.5 MPa CO_2 (used in the reaction runs) and a higher CO_2 pressure of 3.0 MPa. For the Pd catalyst, an absorption band appeared at 1900–1800 cm^{-1}, assignable to CO species adsorbed. The absorption band on Pd/ZnO is located at lower frequency compared to a Pd/Al_2O_3 sample under similar pressure conditions.[32] Fig. 5a indicates that the spectra collected at different CO_2 pressures are not so different. For the Pd/ZnO catalyst, the type of CO adsorption (linear, bridge) and the structure of Pd sites for CO adsorption are unclear. However, a possibility is given here; if CO could preferentially be adsorbed

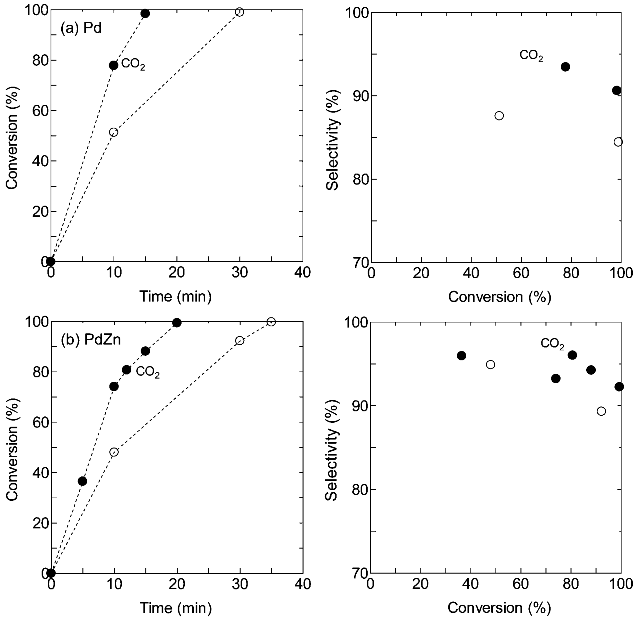

Fig. 4 Influence of the presence of 1.5 MPa CO_2 (●) on the activity and selectivity in phenylacetylene hydrogenation for Pd (a) and PdZn alloy (b) catalysts that were prepared by coprecipitation with a Pd loading of 30 wt% and reduced at ambient temperature and 500 °C.

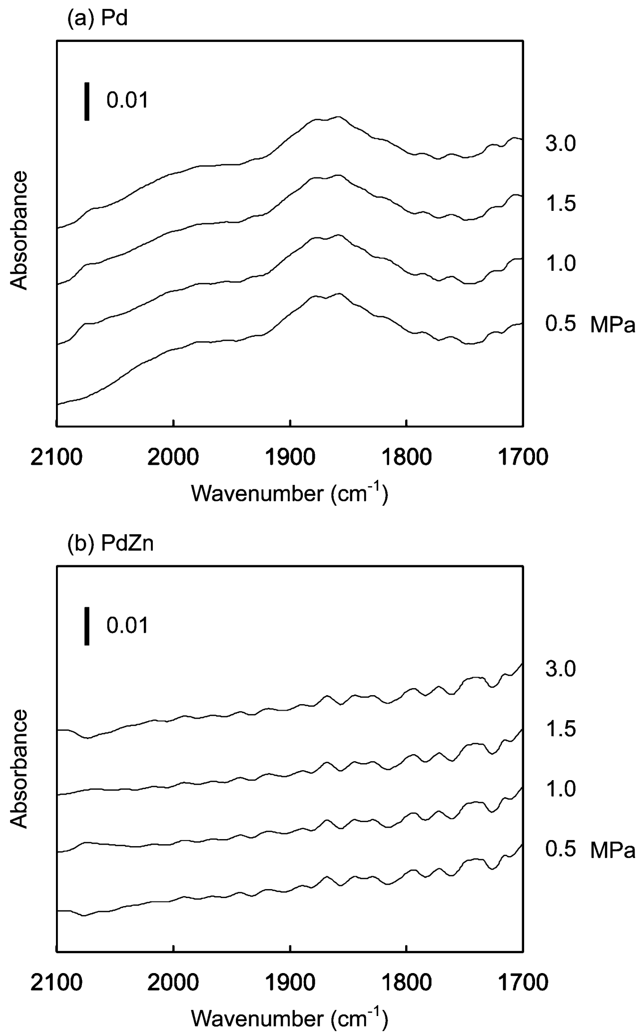

Fig. 5 High-pressure FTIR spectra of CO formed and adsorbed on Pd (a) and PdZn alloy (b) in the presence of 0.6 MPa H_2 and at different CO_2 pressures given.

on highly coordinated Pd sites (less electron-deficient sites) and low coordinated Pd sites (more electron-deficient sites) could be effective for the adsorption and hydrogenation of phenylacetylene and styrene, the relative reactivity of styrene could be lowered and this would enhance the selectivity to styrene, similar to the effect of Pd crystallite size as discussed above. Further physicochemical study is needed to have a deep insight into those possible direct impacts of CO_2 on the Pd and PdZn crystallites.

Another example in which the presence of dense phase CO_2 has positive effects on both the reaction rate and the product selectivity is the hydrogenation of an α,β-unsaturated aldehyde of cinnamaldehyde to the corresponding unsaturated alcohol of cinnamyl alcohol over supported Pt catalysts.[39,40] For this substrate, CO_2 molecules interact with the polar carbonyl group, weaken the C–O bond strength, and increase its reactivity relative to the nonpolar vinyl group, which does not have interactions with the CO_2 molecules. Some possible roles of CO_2 as discussed above would also contribute to the promotional effects of CO_2 in the liquid-phase hydrogenation of cinnamaldehyde.

4. Conclusions

Compared to ZnO-supported Pd catalyst prepared by impregnation and reduced at ambient temperature, alloyed PdZn/ZnO one reduced at 500 °C is less active but more selective to the hydrogenation of phenylacetylene to styrene in toluene. For the latter, the selectivity to styrene does not depend on the amount of Pd loaded (1, 10, 30 wt%) so much but it decreases with increasing Pd loading for the former. The chemical state of active Pd species on the surface of PdZn crystallites is unlikely to change with the Pd loading due to its nature that Pd and Zn species are regularly exposed irrespective of the Pd loading (the size of PdZn crystallites). In contrast, the properties of Pd species on Pd crystallites may depend on their size changing with the Pd loading. The TOF value (per exposed Pd atom) for the PdZn alloy catalysts is significantly higher than that of the Pd ones. The difference between PdZn and Pd catalysts is more significant for the hydrogenation of phenylacetylene than for that of styrene, resulting in a higher selectivity to styrene in the hydrogenation of phenylacetylene over the PdZn catalysts. The enhanced TOF for the PdZn catalysts may result from electronic and/or morphological modification of Pd species by alloying with Zn at a high reduction temperature of 500 °C. The activity of PdZn alloy catalyst can be improved by using coprecipitation instead of impregnation, which decreases the size of PdZn crystallites formed and hence increases the number of exposed Pd species, while keeping its higher selectivity to styrene. The simple pressurization of the reaction mixture by CO_2 (1.5 MPa) enhances the rate of phenylacetylene conversion and the selectivity to styrene for both Pd and PdZn catalysts. The dissolution of H_2 into the liquid phase is promoted by the dissolution of CO_2 and this may be a reason for the enhancement of the rate of phenylacetylene hydrogenation. No interactions of CO_2 with the alkynyl and alkenyl C–C bonds were detected by *in situ* high pressure FTIR. The formation and adsorption of CO from CO_2 and H_2 at high pressures were observed by the FTIR for the Pd catalyst but not for the alloyed PdZn one. Possible reasons for the roles of CO_2 as a reaction promoter were given.

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