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Multiphase reaction media including dense phase carbon dioxide and/or water: A case study for hydrogenation of phenol with a Pd/Al₂O₃ catalyst

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Abstract

Multiphase reaction media including dense phase CO₂ and/or water were applied for a test reaction of hydrogenation of phenol with a Pd/Al₂O₃ catalyst. The features of these reaction media were clarified and the actions of dense phase CO₂ and water were discussed. Different characterization methods (XPS, *in situ* high pressure FTIR, ICP) were used to study (i) the surface of supported Pd particles that varied during the reaction, (ii) the competitive adsorption of phenol, water, and CO that was formed from H₂ and CO₂ under pressurized conditions, and (iii) the leaching of active Pd species. Dense phase CO₂ caused the deactivation of catalyst and it

occurred more rapidly in the presence of both dense phase CO₂ and water. In the system including water alone, the catalyst deactivation also happened but gradually. At the latter stage of reaction in this system, phenol was not consumed but cyclohexanone did transform to cyclohexanol. Those results may be explained by the leaching of Pd species and a structural change of supported Pd particles, resulting in a change in their adsorption behavior. The Pd leaching is more significant in acidic aqueous phase dissolving CO₂ at high pressure.

Keywords

Carbon dioxide; water; hydrogenation; catalyst deactivation; CO formation

1. Introduction

Dense phase CO₂ and water are interesting components for the design of green multiphase reaction media/systems for organic synthetic reactions. So-called CO₂ dissolved expanded liquid phases (CXLs) are an interesting reaction medium for several synthetic reactions including gaseous reactants like H₂, O₂, and CO [1-5] and those including no gaseous reactants such as Heck coupling and Diels-Alder reactions [6-8]. The dissolution of CO₂ into an organic phase (solvent, substrate) changes its solvent properties from its intrinsic organic liquid to dense phase CO₂ and assists the dissolution of gaseous reactants. This would result in acceleration of chemical reactions involving gaseous reactants in CXLs. In addition, the CO₂ molecules dissolved in a CXL may interact with some functional groups of a substrate and/or an intermediate and change their reactivity, influencing the product selectivity as well as the total reaction rate. The interactions of CO₂ molecules with organic compounds were studied and

proved by *in situ* high pressure Fourier transform infrared (FTIR) spectroscopy. The significance of these molecular interactions was demonstrated for several reactions in CXLs. One of noteworthy examples is selective hydrogenation of aromatic nitro compounds with a Ni/TiO₂ catalyst [9]. When a reaction mixture (H₂, liquid substrate, solid catalyst) was pressurized by CO₂, the total rate of conversion increased and the selectivity to the desired aniline products was almost 100% at any conversion level. These results are due to the above-mentioned actions of CO₂ molecules in the CXLs. The dissolved CO₂ molecules decrease the reactivity of NO₂ group of the nitro substrates but increase the rates of transformation of such intermediates as nitrosobenzene and *N*-phenylhydroxylamine into the final aniline products. It is interesting to note that when another component of water was also added to the reaction mixture, the positive impact of CO₂ on the selective hydrogenation of nitrobenzene to aniline appeared at a low CO₂ pressure of 1 MPa [10]. Water is not miscible with nitrobenzene and so the reaction mixture is a multiphase system including gas (H₂, CO₂), organic, aqueous, and solid (catalyst) phases. The existence of interface between the organic and aqueous phases might be important. It is known that water is an interesting promoter for organic synthetic reactions and an explanation for the promotional effects observed is hydrogen bonding that could occur at the organic (substrate) - aqueous interface but not in the bulk. Such promoted reactions are referred to as on-water reactions [11, 12]. Most of on-water reactions reported are homogeneous synthetic reactions including molecular catalysts and no gaseous reactants.

Those results indicate that it is interesting to use the two green components of CO₂ and water to design an effective multiphase reaction medium. The present work has been undertaken as a case study, using hydrogenation of phenol over a Pd/Al₂O₃ heterogeneous catalyst. The reaction was conducted in four different reaction systems in the presence and absence of dense phase CO₂

and/or water (Fig. 1). The features of these reaction media were examined and actions of dense phase CO₂ and water were discussed. For this discussion, the surface of supported Pd particles was characterized by X-ray photoelectron spectroscopy (XPS), CO chemisorption, and FTIR using CO as a probe molecule. The FTIR was also used to study the competitive adsorption on the catalyst among CO, water, and organic substrate (phenol or cyclohexanone). Carbon monoxide can be formed over supported noble metal catalysts from H₂ and CO₂ under pressurized conditions. In addition, the leaching of active Pd species during the reaction was also studied. Recently Zhao *et al.* studied the effect of water on the hydrogenation of *o*-chloronitrobenzene in organic solvents (ethanol, *n*-heptane) and compressed CO₂ using Pd/C and Pt/C catalysts [13].

2. Experimental

2.1. Hydrogenation

A 5 wt% Pd/Al₂O₃ sample was purchased from Wako and used as a catalyst for hydrogenation reactions without further treatment. The hydrogenation of phenol was conducted in a stainless steel autoclave of 50 cm³. The reactions were run in four different multiphase reaction media in the presence and absence of dense phase CO₂ and/or water, as illustrated in Fig. 1 (below). The reactor was charged with 1.0 g phenol (Aldrich), 1 cm³ water (Wako) and 100 mg Pd/Al₂O₃ catalyst. The reactor was purged by pure H₂ for three times and it was heated to a reaction temperature of 323 K in a water bath. Then, 4 MPa H₂ was introduced to the reactor, followed by the introduction of CO₂ (99.99 %) to the desired pressure with a high-pressure liquid pump

(JASCO SCF-Get). The reaction was conducted while stirring the reaction mixture with a magnetic stirrer. After the reaction, the reactor was cooled in an ice-water bath and depressurized carefully. The reaction mixture was analyzed by a gas chromatograph (GL Sciences GC-390B) using a capillary column (Phenomenex ZB-WAX) and a flame ionization detector. The total conversion was determined from the initial and final amounts of phenol and the selectivity to a product (cyclohexanone and cyclohexanol) was determined from the amount of the product formed divided by the total amount of all the products formed. In some runs, cyclohexanone was hydrogenated in the same reactor and procedures as used for phenol. For the present reaction runs, the stirring speed was set in a range where it little affected the overall rate of reaction, which was confirmed by a few preliminary runs conducted at different stirring speeds.

To study the influence of water on the surface properties of catalyst, a certain amount of Pd/Al₂O₃ sample was treated by immersing in water at a reaction temperature of 323 K while stirring with a magnetic stirrer under ambient atmosphere and pressurized CO₂ conditions for 2 and 15 h. Then, the catalyst sample was separated by filtration, dried in oven at 323 K, and then characterized.

2.2. Characterization

The surface of Pd particles on Al₂O₃ 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.

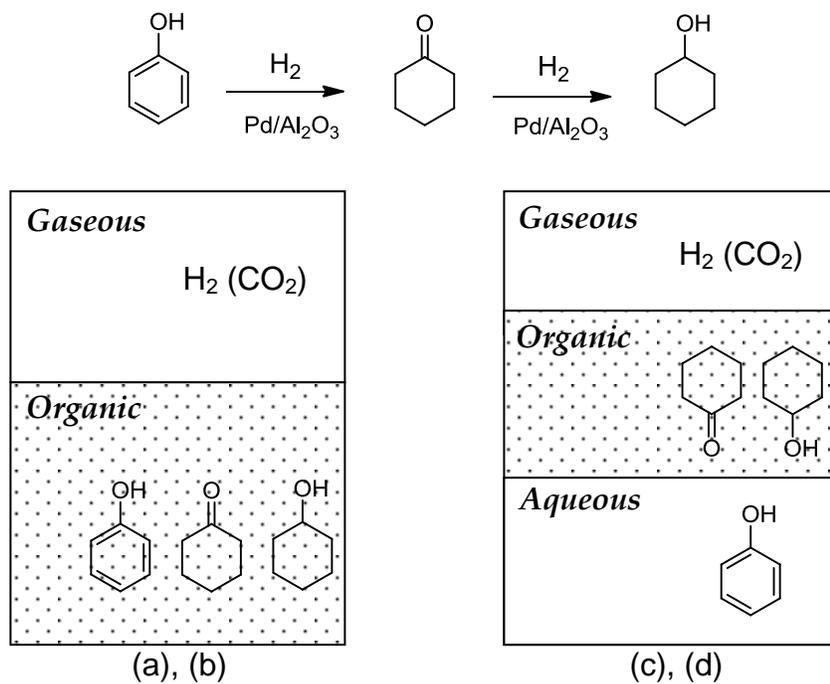
The amount of exposed Pd species in the catalyst was determined by CO pulse chemisorption at 323 K using a BEL-METAL-1 system. Approximately 150 mg of catalyst was heated in a quartz cell at 353 K for 1 h in H₂ and the cell was cooled to 323 K in He. Then 1 cm³ of CO (5% in He) was pulsed over the catalyst until the TCD signal for the effluent gas became unchanged. The amount of Pd present in the catalyst was measured by inductively coupled plasma (ICP). The sample was dissolved in a mixture of chloric and nitric acid, and the solution was measured by a Shimadzu ICPE-9000.

The surface of supported Pd particles was also examined by FTIR with CO as a probe adsorbate molecule using a JASCO FTIR 620 spectrometer and a laboratory designed cell. The FTIR measurements were made in the presence of water and/or organic substrate (phenol, cyclohexanone) to examine the competitive adsorption of CO, water vapor, and organic substrate vapor on the catalyst. A 30 mg of catalyst sample was ground in a mortar and the resulting catalyst powder was pressurized at 50 MPa for 1 h to prepare a catalyst pellet. After the sample was loaded into the cell, it was purged by H₂ gas for a few times to remove the air and heated to 343 K; H₂ was further introduced to 4 MPa and maintained at this temperature for 1 h to reduce the catalyst. The cell was cooled to 323 K and purged with atmospheric N₂ for a few times, and the FTIR spectra were collected as background. A certain amount of phenol and/or water was introduced into the bottom of the cell with a syringe through a small hole where N₂ was flowing out. Then CO (1% in He) was introduced at ambient pressure for 15min, and the FTIR spectra were collected after which the cell was purged with N₂ to remove phenol and/or water vapor from the atmosphere.

The phase behavior of our gas - liquid (organic) - liquid (water) - solid (catalyst) multiphase reaction systems was examined under similar conditions as used for hydrogenation reaction runs. The organic substrate (1 cm^3) was put into a 10 cm^3 sapphire-windowed view cell and it was purged with H_2 for three times. The cell was heated up to 323 K (reaction temperature) by circulation of preheated water outside the cell and introduced with 4 MPa H_2 . Then, CO_2 was slowly introduced into the cell to the desired pressure while stirring the mixture by a magnetic stirrer. The phase behavior was visually examined by naked eyes at different CO_2 pressures. In addition, the state of dispersion of $\text{Pd/Al}_2\text{O}_3$ granules in the present reaction systems was examined at atmospheric pressure.

3. Results and discussion

In the present work using a commercial $5 \text{ wt}\%$ $\text{Pd/Al}_2\text{O}_3$ catalyst, which had a BET surface area of $98.0 \text{ m}^2 \text{ g}^{-1}$ and a degree of Pd dispersion of 0.60 , the hydrogenation of phenol was studied in four different multiphase reaction systems as illustrated in Fig. 1. From the observation of phase behavior at atmospheric pressure, the catalyst was mainly dispersed in the organic phase even in the presence of aqueous phase.



| System | (a) | (b) | (c) | (d) |
|-----------------------------|-----|-----|-----|-----|
| Dense phase CO ₂ | × | ○ | × | ○ |
| Water | × | × | ○ | ○ |

Fig. 1. Multiphase reaction systems (a) - (d) studied for phenol hydrogenation in the absence and presence of dense phase CO₂ and/or water. × : not included; ○ : included.

3.1. Hydrogenation

The hydrogenation of phenol was tested in four different multiphase systems (a) - (d) in the absence and presence of dense phase CO₂ and/or water (Fig. 1). Fig. 2 shows the time profiles of total conversion and product (cyclohexanone and cyclohexanol) selectivity. The reaction went forward smoothly in the system (a) including neither CO₂ nor water, in which the selectivity to cyclohexanone decreased during the reaction while that to cyclohexanol increased. The conversion of phenol leveled off in the systems of (b) and (d) including dense phase CO₂, more rapidly in the latter in which water was also included. For the system (c) including water alone, the conversion of phenol also leveled off but gradually. It is interesting to note that cyclohexanone was transformed to cyclohexanol during the latter stage of reaction in which phenol was little converted. The volume of liquid organic phase can be changed by the dissolution of CO₂, which may affect the reaction rate and/or product selectivity [14]. Phase behavior of phenol in the presence of dense phase CO₂ was observed and the volume of phenol hardly changed from atmospheric pressure to 8 MPa CO₂, indicating that the reaction media was not so significantly diluted by compressed CO₂ (Fig. 3). At higher pressure, the volume of phenol slightly decreased with increasing CO₂ pressure, meaning that phenol became dissolved into supercritical CO₂ phase.

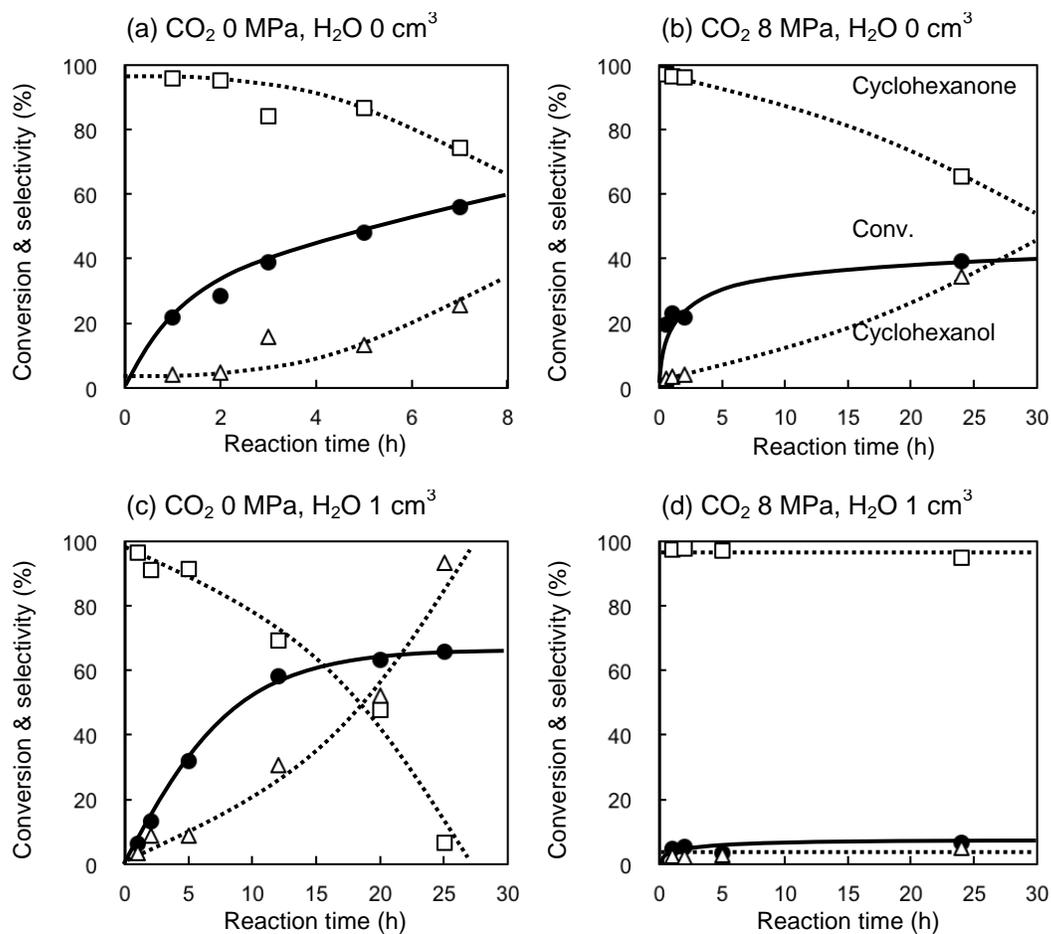


Fig. 2. Time profiles of total conversion of phenol (●) and the selectivity to cyclohexanone (□) and cyclohexanol (△) in four different reaction systems of (a) - (d) as illustrated in Fig. 1. CO₂ 0 or 8 MPa; H₂O 0 or 1 cm³.

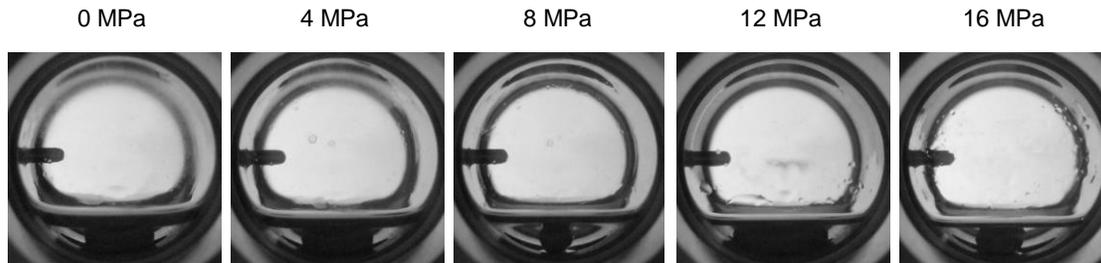


Fig. 3. Phase behavior observations of phenol at a reaction temperature of 323 K and at different CO₂ pressures given.

The leaching of Pd was examined as will be discussed later; the catalyst, Pd/Al₂O₃, was immersed in water at a reaction temperature of 323 K for 15 h, the catalyst was separated by filtration, and the filtrate was used for hydrogenation of either phenol or cyclohexanone with no Pd/Al₂O₃ catalyst. It was found that the hydrogenation of either phenol or cyclohexanone did not occur, indicating that all the reactions of the present work were heterogeneous with supported Pd particles and the dissolved Pd species did not work as a homogeneous catalyst.

In our recent work, the effects of CO₂ and/or water have been investigated on selective hydrogenation of benzonitrile with Pd/Al₂O₃ catalyst [15]. The selectivity to primary amine increased from 85% to more than 96% by the presence of CO₂ and water with no catalyst deactivation. Such synergistic effect was well explained by the formation of carbamate species from primary amine and CO₂ and by the dissolution of the carbamate species into aqueous phase. Cheng *et al.* have also investigated similar reaction media including CO₂ and water on

hydrogenation of *o*-chloronitrobenzene in ethanol and *n*-heptane over Pt/C and Pd/C catalysts [13]. They mentioned that the formation of hydrogen bonds between organic substrate and water might change the reactivity of functional groups, resulting in an increase of reaction rate. They also suggested that the solubility of hydrogen decreased with increasing the amount of water in ethanol and it was significant for controlling the reaction rate. However, the solubility of phenol into water is so small (9.7 g/100 cm³, 313 K) that there are two (phenol-water) liquid phases under the present reaction conditions and the influence of hydrogen solubility is different from that in ethanol-water single liquid phases.

3.2. Catalyst characterization

The surface of Pd/Al₂O₃ catalysts was characterized by FTIR measurements using CO as a probe molecule. The FTIR of CO adsorbed on the catalysts was made in the presence of organic substrate (phenol or cyclohexanone) and/or water to examine the competitive adsorption of substrate vapor, water vapor, and CO on the catalysts. Generally, CO could be formed in hydrogenation reactions in the presence of dense phase CO₂ and H₂ at high pressures and would affect the outcome of these reactions [16-18]. Fig. 4 shows the FTIR spectra collected for CO adsorbed on Pd/Al₂O₃ (untreated) in the absence and presence of phenol or cyclohexanone and/or water. Two absorption bands appeared in the absence of phenol and water at 1968 cm⁻¹ and 1909 cm⁻¹, which were assigned to bridge type CO molecules adsorbed on edge sites and multi-bond type CO on terrace sites of the surface of supported Pd particles [19-24], respectively. The absorption band, assignable to linear type CO, also appeared at 2070 cm⁻¹ in Fig. 4a but it was quite small and it could not be seen in the presence of water (Fig. 4b). A very similar spectrum

was also seen when gaseous phenol existed (Fig. 4c), indicating that the CO adsorption was not affected by phenol; in other words, CO was preferentially adsorbed on Pd than phenol. When water vapor was present, the absorption of the CO species on edge sites became weakened (Fig. 4b). These CO species might be removed by or replaced with water molecules as mentioned in our previous work [25]. Ebbesen *et al.* also investigated the FTIR spectra of CO adsorption on Pd/Al₂O₃ catalyst in the absence and presence of water [26], and they proposed that water adsorbed on the catalyst increased π back-donation from noble metal particle to CO. Therefore, one can say that the state of CO species changes from bridge type to multi-bond type due to stronger π back-donation from Pd particle in the presence of water. When both phenol and water were present, a broad absorption band existed with a peak maximum at 1946 cm⁻¹ (Fig. 4d). This broad band is different from the spectra collected in the presence of either phenol (Fig. 4c) or water (Fig. 4b). The same FTIR measurements were also made with cyclohexanone instead of phenol. Fig. 4e also shows that a broad absorption band appeared at about 1942 cm⁻¹ in the presence of cyclohexanone alone, indicating that cyclohexanone is preferentially adsorbed on Pd than CO, which is different from the case of phenol. A similar broad but a little weaker absorption band was also seen when both cyclohexanone and water coexisted (Fig. 4f). These results imply that the CO adsorption is influenced by either water or cyclohexanone and the influence of cyclohexanone is stronger compared to water.

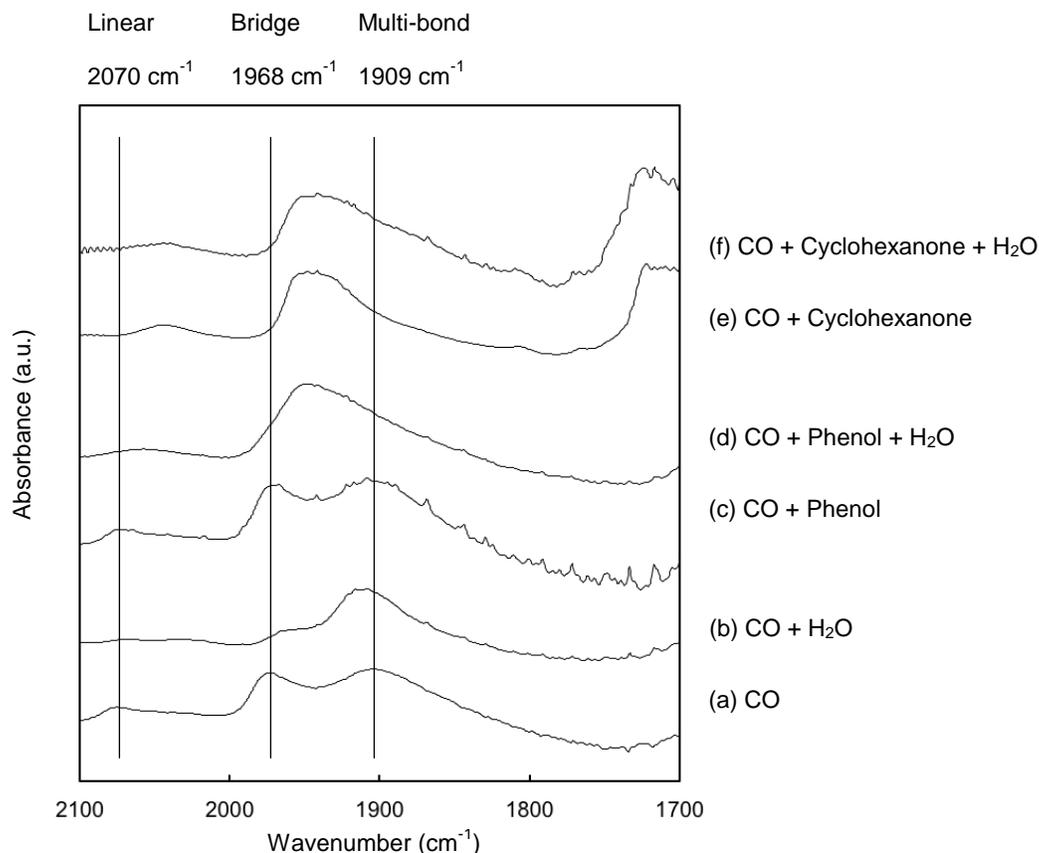


Fig. 4. FTIR spectra of CO adsorbed on Pd/Al₂O₃ in the absence and presence of water vapor and/or organic substrate vapor (phenol, cyclohexanone).

To find a factor responsible for the level-off of conversion at the latter stage of hydrogenation in the presence of water (Fig. 2c), the surface of Al₂O₃-supported Pd particles treated in water was also examined by the same FTIR measurement. Fig. 5 gives FTIR spectra collected, showing that the absorption band assigned to multi-bond CO adsorbed on terrace sites becomes significantly weaker by the treatment with water at 323 K. Thus, the water treatment changed the surface of supported Pd particles.

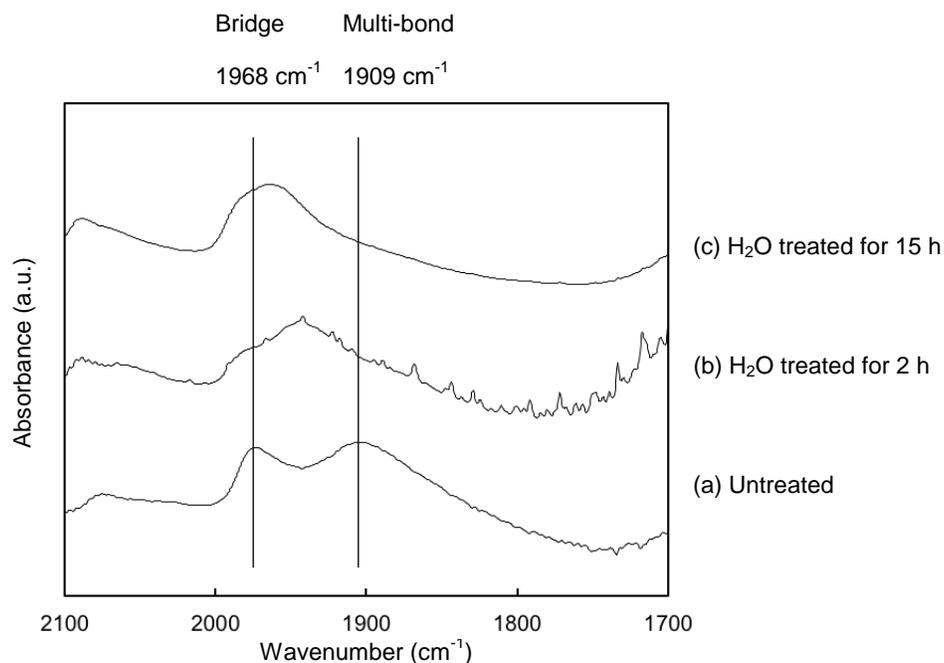


Fig. 5. FTIR spectra of CO adsorbed on Pd/Al₂O₃ catalyst samples untreated (a) and treated with H₂O at a reaction temperature of 323 K for 2 h (b) and 15 h (c).

Furthermore, the untreated and water-treated Pd/Al₂O₃ catalysts were characterized by different methods. Fig. 6 shows XPS spectra of Pd 3d for the three samples untreated and treated with water at 323 K for 2 h and 15 h. No difference was observed in the binding energy among these samples and so the chemical state of surface Pd species remained unchanged by the treatment. However, the ratio of Pd/Al was found to decrease by the water treatment (Table 1), in accordance with the results of CO chemisorption that the amounts of CO adsorbed on the treated catalysts were smaller than that of the untreated one. The amounts of Pd species in the same water-treated catalysts were examined by ICP. Table 1 shows that the amount of Pd on the

catalyst decreased by 30% after the treatment for 15 h. Those results demonstrate that some supported Pd species are leaching from the catalyst to the aqueous phase by the water treatment but this does not change the properties of exposed Pd species remaining on the supported particles. The leaching of Pd was shown to occur more extensively in the presence of dense phase CO₂; the amount of Pd on the catalyst decreased by 40% after the treatment with water at a CO₂ pressure of 8 MPa in 2 h. A possible form of Pd species dissolved in the aqueous phase is Pd(H₂O)₄²⁺ [27] and it is unlikely to be active for hydrogenation of phenol and cyclohexanone. It is important to note that, generally speaking, one should consider the possibility of leaching of active metal components into water as well as organic solvents/substrates when one uses multiphase media including water for organic synthetic reactions. [11, 12]

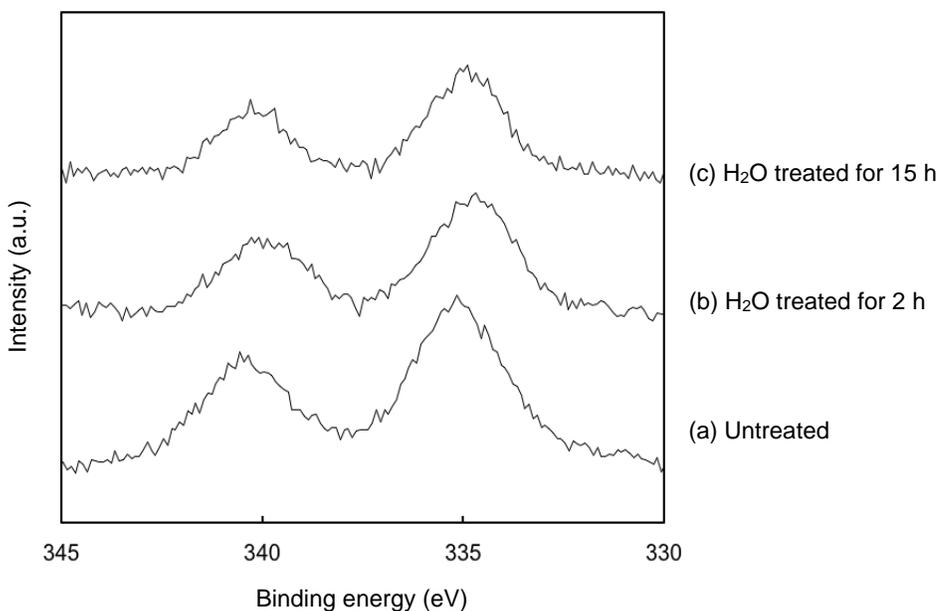


Fig. 6. XPS spectra of Pd/Al₂O₃ catalyst samples untreated (a) and treated with H₂O at a reaction temperature of 323 K for 2 h (b) and 15 h (c).

Table 1. The relative changes of supported Pd particles by water treatment as measured by XPS, CO chemisorption and ICP.

| | XPS (Pd/Al ratio) | CO chemisorption (Pd surface area) | ICP (Pd amount) |
|---------------------------|----------------------|---------------------------------------|--------------------|
| Untreated | 1.00 | 1.00 | 1.00 |
| H ₂ O for 2 h | 0.45 | 0.61 | 0.77 |
| H ₂ O for 15 h | 0.31 | 0.36 | 0.70 |

3.3. Features of the multiphase hydrogenation reactions

A Pd/Al₂O₃ catalyst was used for the hydrogenation of phenol in the present work. The FTIR results show that there are edge and terrace sites exposed on the surface of supported Pd particles, and both these sites can be occupied by CO formed from CO₂ and H₂ at high pressures. Phenol is mainly adsorbed on the terrace sites of metal particle as side-on type and the strength of phenol adsorption is weaker than CO adsorption, resulting in the retardation of phenol hydrogenation in the presence of dense phase CO₂. In contrast, adsorption of cyclohexanone on Pd particles as end-on type is stronger than CO adsorption and the hydrogenation of cyclohexanone can take place even in the presence of dense phase CO₂. Coexisting water in a reaction system influences the surface of supported Pd particles as shown from FTIR results with untreated and water-treated Pd/Al₂O₃ catalysts. The strength of π back-donation from Pd surface to adsorbate species is weakened by the action of water during the reaction, resulting in the catalyst deactivation for hydrogenation of phenol but not for hydrogenation of cyclohexanone. The relative strength of

adsorption among CO, water, and organic substrate is responsible for the difference in the hydrogenation behavior between phenol and cyclohexanone.

The effects of dense phase CO₂ and water on the hydrogenation reactions are summarized: the Pd/Al₂O₃ catalyst loses its activity during the reaction in the presence of dense phase CO₂, more rapidly in the presence of water as well. The catalytic activity also decreases but gradually during the latter stage of reaction in the presence of water alone. As mentioned above, the activity loss caused by the presence of CO₂ may be explained by the formation and adsorption of CO from CO₂ and H₂ on the surface of supported Pd particles. The adsorption of CO is stronger than that of phenol and so the substrate cannot be adsorbed on the catalyst, resulting in the catalyst deactivation as observed. The influence of the strength of CO adsorption on hydrogenation of phenol was investigated in our previous work using Rh/Al₂O₃ and Rh/C catalysts [28]. The strong CO adsorption retards the adsorption of phenol on Rh/Al₂O₃ catalyst and this causes the catalyst deactivation, but the reaction occurs with no catalyst deactivation for Rh/C catalyst because of very weak CO adsorption. The coexistence of water affects the potential of supported Pd particles and weakens π back-donation from Pd to adsorbate species, which prevents the phenol from adsorption and reaction. The rapid catalyst deactivation observed in the presence of both CO₂ and water may be ascribed to the acidic nature of the aqueous phase [29-31]. This causes the leaching of Pd in a larger amount and a more significant structural change in the surface of Pd particles. No catalyst deactivation was observed on the reaction in the absence of CO₂ and water, indicating that the leaching of Pd into organic phase was unlikely to occur in the present reaction systems.

The multiphase reaction media including dense phase CO₂, water, and Pd/Al₂O₃ are not good for the selective and partial hydrogenation of phenol to cyclohexanone because of the catalyst deactivation caused by CO formation and Pd leaching and the over hydrogenation of cyclohexanone to cyclohexanol. It is interesting that the gradual catalyst deactivation occurs in the medium including water alone but cyclohexanone can still be hydrogenated during the latter stage of reaction on the surface of Pd particles on which the hydrogenation of phenol does not take place. It should be noted that the importance of Pd leaching into aqueous phase is less mentioned so far compared to that into organic phases; however, one should consider the former Pd leaching when one apply a multiphase reaction medium including CO₂ and water.

4. Conclusions

The selectivity to cyclohexanone does not depend so much on the reaction media used. The conversion of phenol levels off at the early stage of reaction in the presence of CO₂. The formation and adsorption of CO from H₂ and CO₂ is responsible for the catalyst deactivation. More acidic nature of water compressed by CO₂ causes the leaching of Pd and this would change the structural properties of supported Pd particles, which might cause the catalyst deactivation for phenol hydrogenation. Unexpectedly the catalyst deactivation also happens in the presence of water alone but gradually compared to that in the presence of CO₂. Probably this gradual deactivation may be ascribed to the leaching of Pd species and the resulting structural change of supported Pd particles. Interestingly, cyclohexanone can still be hydrogenated on the Pd surface on which phenol is hardly reacted. The Pd species dissolved in aqueous phase is unlikely to be active for the hydrogenation of phenol and cyclohexanone as a homogeneous catalyst. Less

attention is given to the leaching into aqueous phase but this phenomenon is an important factor in determining the outcome of multiphase reactions in the presence of CO₂ and water.

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Figure captions

Fig. 1. Multiphase reaction systems (a) - (d) studied for phenol hydrogenation in the absence and presence of dense phase CO₂ and/or water. × : not included; ○ : included.

Fig. 2. Time profiles of total conversion of phenol (●) and the selectivity to cyclohexanone (□) and cyclohexanol (△) in four different reaction systems of (a) - (d) as illustrated in Fig. 1. CO₂ 0 or 8 MPa; H₂O 0 or 1 cm³.

Fig. 3. Phase behavior observations of phenol at a reaction temperature of 323 K and at different CO₂ pressures given.

Fig. 4. FTIR spectra of CO adsorbed on Pd/Al₂O₃ in the absence and presence of water vapor and/or organic substrate vapor (phenol, cyclohexanone).

Fig. 5. FTIR spectra of CO adsorbed on Pd/Al₂O₃ catalyst samples untreated (a) and treated with H₂O at a reaction temperature of 323 K for 2 h (b) and 15 h (c).

Fig. 6. XPS spectra of Pd/Al₂O₃ catalyst samples untreated (a) and treated with H₂O at a reaction temperature of 323 K for 2 h (b) and 15 h (c).

Table 1. The relative changes of supported Pd particles by water treatment as measured by XPS, CO chemisorption and ICP.