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Selective hydrogenation of acetophenone with supported Pd and Rh catalysts
in water, organic solvents, and CO₂-dissolved expanded liquids

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(Abstract)

Solvent effects were investigated for selective hydrogenation of acetophenone (AP) with commercial 5% Pd/Al₂O₃ and 5% Pd/C catalysts using polar and nonpolar solvents. The rate of AP hydrogenation varied with the solvents used in different manners depending on the catalysts used. The highest AP conversion was achieved with water for the two catalysts and the AP conversion was correlated to hydrogen-bond-acceptance (HBA) capability (β) for Pd/Al₂O₃ while hydrogen-bond-donation (HBD) capability (α) for Pd/C. These trends were the same as the corresponding solvent effects obtained previously with Rh/Al₂O₃ and Rh/C catalysts, respectively (*Green Chem.* 2015, **17**, 1877-1883). The **influence of solvents** on the rate of AP hydrogenation depends on the support materials but not on the metal species. Furthermore, the AP hydrogenation was conducted with the four supported noble metal catalysts in different solvents pressurized by CO₂ (CO₂-dissolved expanded solvents). The influence of CO₂ pressurization on the rate of reaction, the product selectivity, and the catalyst life was investigated to know **whether or not** CO₂ molecules could function as a reaction promoter in the heterogeneous AP hydrogenation reactions with supported Pd and Rh catalysts in different solvents.

Key words: hydrogenation; acetophenone; solvent effects; water; carbon dioxide

Introduction

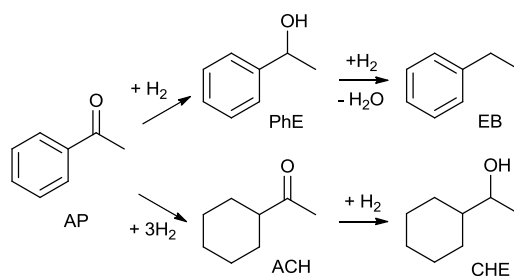
Solvent effects are an important issue in choosing a suitable solvent for organic synthetic reactions using either homogeneous molecular catalysts or heterogeneous solid catalysts.¹ The physicochemical properties of solvents would have an impact on reaction rate, product selectivity, and/or catalyst stability depending on the type/nature of reactions and reaction conditions used. The selection of suitable solvents is also important in post-reaction processes such as separation and purification of desired products. Although supported metal catalysts are used for liquid-phase reactions,² solvent effects have not sufficiently been investigated so far. The present authors recently investigated the solvent effects in a model reaction of selective hydrogenation of acetophenone with conventional C- and Al₂O₃-supported Rh catalysts.³ Some previous workers studied the solvent effects in the same hydrogenation using a few different organic solvents.⁴ In our previous work, 13 different kinds of protic, aprotic, and nonpolar liquids were used, in which water was also included because it was reported to act as a reaction promoter/controller in organic synthetic reactions.⁵ Important results obtained in the previous work³ are: (1) the rate of hydrogenation of acetophenone is largest in water with either C- or Al₂O₃-supported Rh catalyst; (2) the rate of hydrogenation is larger for a solvent having a larger hydrogen-bond-donation (HBD) capability (α)^{1,6} for the former catalyst but for a solvent having a smaller hydrogen-bond-acceptance (HBA) capability (β)^{1,6} for the latter one. In other words, interactions between the solvents and the supports (not Rh metal) are significant in determining the rate of hydrogenation and larger α and smaller β values of water are responsible for the largest rate of hydrogenation observed with both Rh catalysts. It is also important to note that water is useful for the heterogeneous hydrogenation of acetophenone with supported Rh catalysts in accordance with the result of Shirai et al. using Pd/C.^{4h} It is interesting and significant to examine whether the same correlations could be obtained or not and whether water would also be most effective or not

with other supported metal catalysts.

The properties of a solvent is changed when it is pressurized by CO₂ and a certain amount of CO₂ molecules is dissolved. This will cause an increase in the solvent volume and the resulting solvent is referred to as CO₂-dissolved expanded liquid.^{1,7} The dissolved CO₂ molecules may act as a reaction promoter/controller via interactions with substrates, intermediates, and/or solid catalysts in CO₂-dissolved liquid phases.⁸ One of CO₂-promoted reactions is selective hydrogenation of nitrobenzene to aniline with a Ni/Al₂O₃ catalyst.⁹ In the liquid reaction mixture, CO₂ interacts with nitro group of the substrate and retards the first step of nitrobenzene to nitrosobenzene while the subsequent steps are promoted. The dissolution of CO₂ changes the nature of the liquid phase, which assists the dissolution of a gaseous reactant of H₂. These effects of CO₂ can result in the perfect selective of hydrogenation of nitrobenzene to the desired product of aniline under CO₂ pressurization conditions. The occurrence of CO₂ promotional effects should depend on the nature of reactions and reaction conditions used, including the nature of solvents. For selective hydrogenation of 3-nitrostyrene with a Pt/TiO₂ catalyst, CO₂ pressurization (10 MPa) changed the product selectivity for the reaction in toluene but not in ethanol.¹⁰

Those results indicate that further works are required to investigate the solvent effects for synthetic reactions with heterogeneous catalysts under conventional and CO₂ pressurization conditions. Thus, the present work has been undertaken to study the **influence of solvents** in the same model reaction of acetophenone hydrogenation (Scheme 1) with different metal catalysts of Pd on the same supports of C and Al₂O₃ as used for Rh in the previous work.³ In addition, the effects of CO₂ pressurization on the same hydrogenation in different solvents with supported Pd and Rh catalysts have been examined. The **influence of solvents** on the rate of hydrogenation have been observed to depend on the support materials (C, Al₂O₃) but not on the metal species (Rh, Pd). It has also been observed that the

effectiveness of CO₂ pressurization on the rate of hydrogenation and the durability of catalyst is different depending on the catalysts and solvents. Possible factors responsible for the effects of solvents and CO₂ pressurization observed have been discussed.



Scheme 1. Hydrogenation of acetophenone (AP). PhE: 1-phenylethanol, ACH: acetylcyclohexane, EB: ethylbenzene, CHE: 1-cyclohexylethanol

Results and discussion

Hydrogenation with supported Pd catalysts in water and organic solvents

The authors recently investigated the influence of solvents in selective hydrogenation of acetophenone (AP) with Rh/C and Rh/Al₂O₃ catalysts using 13 different solvents.³ The solvent effects have further been examined with different supported metal catalysts of Pd/Al₂O₃ and Pd/C using selected solvents in the present work. Table 1 presents the degree of metal dispersion measured by CO chemisorption and transmission electron microscopy for these catalysts used. Fig. 1 shows the total conversion of AP obtained in different solvents and the highest conversion was obtained in H₂O for the two catalysts in common. In addition, the conversion was larger in the order of H₂O > apolar > aprotic > protic solvent for Pd/Al₂O₃ and of H₂O > protic > aprotic > apolar solvent for Pd/C. The largest AP conversion was observed in water, in accordance with the result of Shirai et al. using Pd/C.^{4h}

Table 1 Al₂O₃ and C supported metal catalysts used in this work

Catalyst	Metal dispersion ^a (%)	Metal particle size ^b (nm)
5% Pd/Al ₂ O ₃	44	3.6
5% Pd/C	34	– ^c
5% Rh/Al ₂ O ₃	38	3.4
5% Rh/C	73	– ^c

^a. CO chemisorption. CO/Pd = 1/2, CO/Rh = 1/1. ^b. TEM. ^c. Not measured.

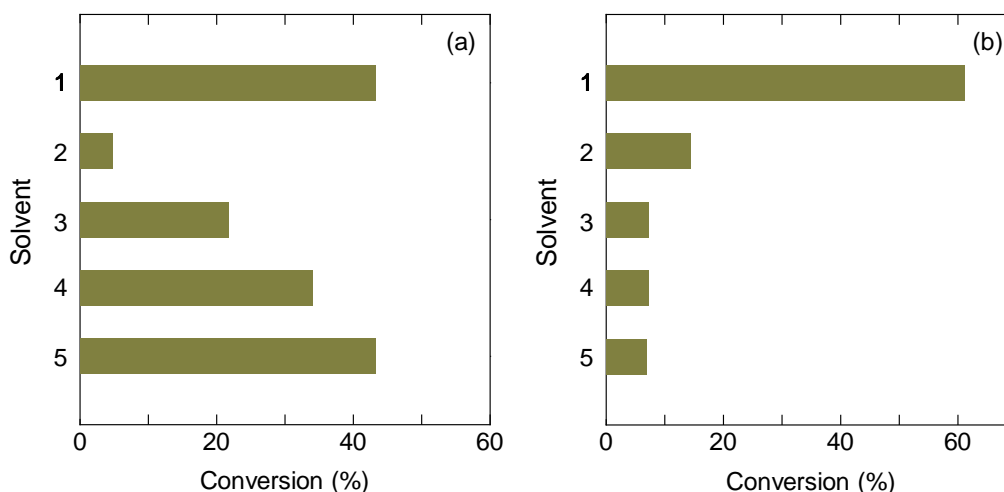


Fig. 1. Results of AP hydrogenation obtained with (a) Pd/Al₂O₃ and (b) Pd/C in different solvents. 1: water, 2: methanol, 3: ethanol, 4: diethyl ether, 5: *n*-hexane. Reaction conditions: AP 2 cm³, solvent 5 cm³, catalyst 20 mg (Pd/Al₂O₃), 10 mg (Pd/C), reaction temperature 353 K, time 60 min, H₂ 4 MPa.

The impact of different solvents on the heterogeneous AP hydrogenation was examined using the Kamlet-Taft solvatochromic parameters α and β , measuring empirically the solvent's HBD acidity and HBA basicity, respectively. Fig. 2 presents the plots of AP conversion against β and α values for Pd/Al₂O₃ and Pd/C, respectively. These relationships are the same trends as observed for the same reactions with corresponding Rh/Al₂O₃ and

Rh/C catalysts.³ That is, the **influence of solvents** in heterogeneous AP hydrogenation **does** not depend on the metal species (Pd, Rh) but on the support materials (C, Al₂O₃) under the conditions used. It is assumed that the interactions between the substrate and solvent molecules are important for Pd/C and Rh/C catalysts. The solvent molecule interacts with the carbonyl group of AP and modifies its reactivity. This modification is more significant for a solvent having a larger α value. The interactions between the substrate and solvent molecules were confirmed by FTIR spectroscopy measurements.³ For Pd/Al₂O₃ and Rh/Al₂O₃ catalysts, in contrast, the interactions between the solvent molecules and the Al₂O₃ support should be important. A solvent having a larger β value is more likely to interact with surface hydroxyl groups of the support and so the access of the substrate to the catalyst surface should be hindered.³

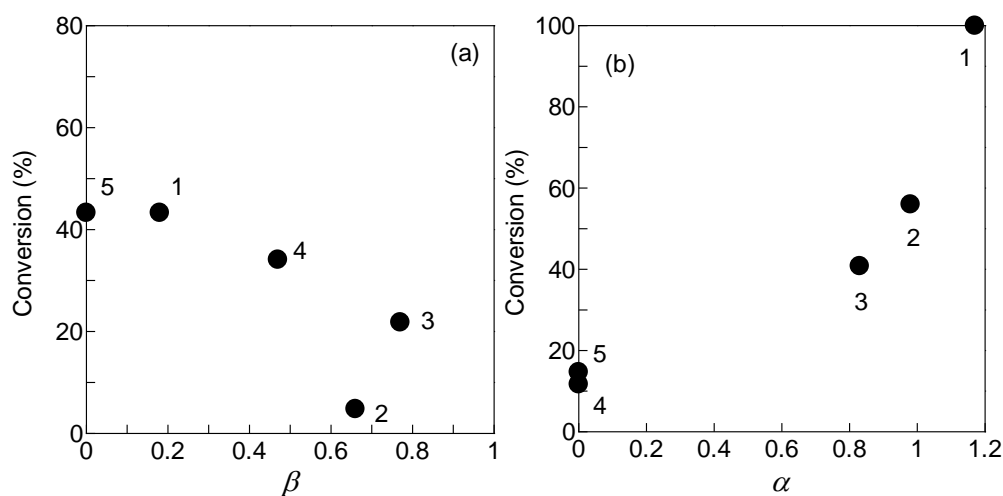


Fig. 2. Plots of the conversion values obtained with Pd/Al₂O₃ (a) and Pd/C (b) against the β and α values of solvents used, respectively. 1: water, 2: methanol, 3: ethanol, 4: diethyl ether, 5: n-hexane. Reaction conditions: AP 2 cm³, solvent 5 cm³, temperature 353 K, H₂ 4 MPa, (a) catalyst 20 mg, time 60 min, (b) catalyst 10 mg, time 240 min.

In AP hydrogenation with either Pd/C or Pd/Al₂O₃ catalyst, PhE was the main product in a selectivity > 95% at conversion levels of $\leq 90\%$. The ring hydrogenation

reactions of AP to ACH and of a product of PhE to CHE were difficult to occur under the conditions used. That is, the product selectivity did not depend on the support materials used for the Pd catalysts, and the nature of catalytic Pd species should be important in determining the product selectivity. This is different from the previous results with Rh/Al₂O₃ and Rh/C catalysts. In the previous AP hydrogenation with supported Rh catalysts, PhE was also the main product in a selectivity of 70 - 80% for Rh/Al₂O₃ and of 60 - 70% for Rh/C depending on solvents used and the byproduct was ACH for the former catalyst but EB for the latter.³ The parallel reactions from AP to PhE and ACH occurred for the former and the successive reactions from AP through PhE to EB for the latter (Scheme 1). This may be due to a difference in the surface properties between the two supports; PhE may be adsorbed on Al₂O₃ through interactions with the surface hydroxyl group of the support, which suppresses its further hydrogenation/dehydration to EB. In contrast, such a significant adsorption of PhE does not occur on the surface of C and so it can be further hydrogenated to EB.

Hydrogenation with supported Pd and Rh catalysts in CO₂-dissolved expanded liquids

Next, the selective hydrogenation of AP has been studied in different solvents pressurized by CO₂ using supported Pd and Rh catalysts to examine the influence of CO₂ pressurization on reaction rate, product selectivity, and catalyst life. It was found that the product selectivity was little affected by CO₂ pressurization and so the effects of CO₂ on AP conversion and catalyst life will be described in the following. Fig. 3 compares the AP conversion values obtained in different solvents in the absence and presence of CO₂ (1 MPa). For Pd catalysts (Fig. 3a, b), the pressurization of CO₂ increased the conversion except for the case of Pd/C in diethyl ether, for which comparable conversion values were obtained in the absence and presence of CO₂. The relative extent of enhancement in the conversion was not so large,

being < 2.0 , for most solvents but it was 5 for methanol with Pd/Al₂O₃. For Rh catalysts (Fig. 3c, d), in contrast, pressurized CO₂ had no or negative impact on the AP conversion.

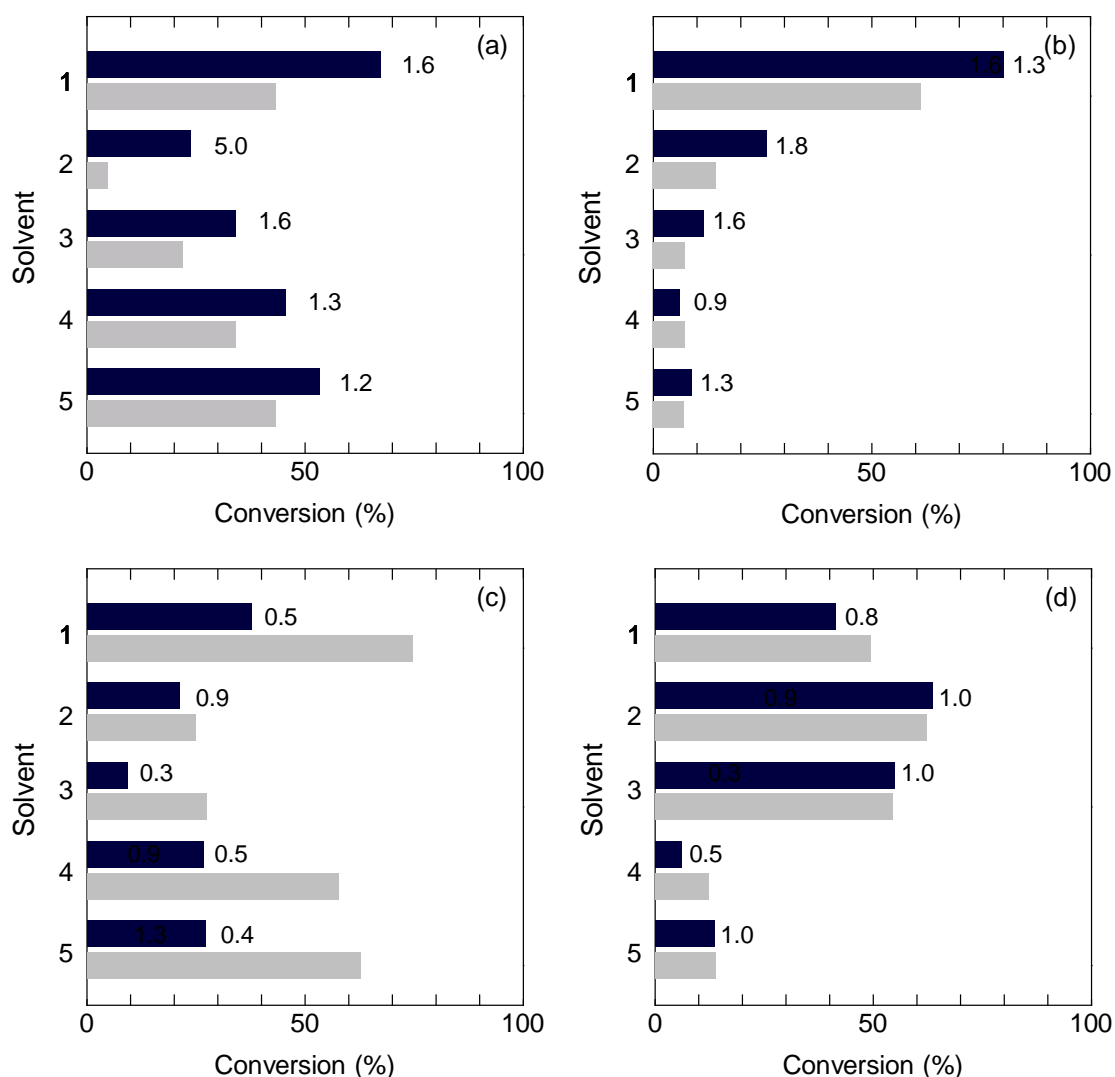


Fig. 3. Results of AP hydrogenation obtained with (a) Pd/Al₂O₃, (b) Pd/C, (c) Rh/Al₂O₃, and (d) Rh/C in different solvents in the absence (gray) and presence (black) of dense phase CO₂. 1: water, 2: methanol, 3: ethanol, 4: diethyl ether, 5: *n*-hexane. Figures given indicate the relative extent of enhancement in the conversion by the presence of CO₂. Reaction conditions: AP 2 cm³, solvent 5 cm³, temperature 353 K, CO₂ 1 MPa, (a, b) catalyst 20 mg (a), 10 mg (b), H₂ 4 MPa, time 60 min, (c, d) catalyst 20 mg (c), 10 mg (d), H₂ 2 MPa, time 120 min (c), 30 min (d).

When the liquid reaction mixture is pressurized by CO₂, CO₂ is dissolved and this

may assist the dissolution of a gaseous reactant of H₂ in the liquid phase. The extent of promotion of H₂ dissolution may depend on the solvents but it may be not so significant in the present case because CO₂ pressure used was only 1 MPa. Then other factors should be considered for explaining the effects of CO₂ pressurization observed (Fig. 3). An important factor is interaction between the CO₂ and solvent molecules. Shirai et al. pointed out the importance of H⁺ species in AP hydrogenation with a Pd/C catalyst, which was formed by the dissolution of CO₂ into water and acted to accelerate the reaction.^{4h} Here, three solvents, water, methanol, and ethanol are compared, which react with CO₂ forming **carbonic acid and carbonic acid monoalkyl esters**. Table 2 shows that the solubility of CO₂ is methanol > ethanol > water and the pK_a values of corresponding acid and carbonates are not so different. The amount of H⁺ species is thus expected to be the largest for methanol, which may explain the largest promotional effect of CO₂ on the AP hydrogenation in methanol for Pd/Al₂O₃ and Pd/C catalysts (Fig. 3a, b). Another important factor is molecular interaction of CO₂ with the carbonyl group of AP. As demonstrated in several reactions, CO₂ molecules interact with polar functional groups of organic substrates and modify their reactivity.⁸ Such interactions between CO₂ and AP molecules in different solvents were examined by FTIR - ATR spectroscopy.¹⁰ FTIR spectra of AP in different solvents in the absence and presence of 1 MPa CO₂ collected are given in Fig. S1 of Supporting Information. The wavenumber of absorption band assignable to the carbonyl group of AP in each solvent was not found to change on the pressurization with CO₂ and so its reactivity was not affected by the presence of CO₂ in the solvents examined. The interactions of CO₂ with the substrate is therefore insignificant for the present AP hydrogenation. The HBA and HBD capacities of CO₂ are less significant according to its α value and B_{MeOD} (one of Lewis basicity parameters) value, which are comparable to those of *n*-hexane.¹²

Table 2. Comparison of the solubility of CO₂ in water, methanol, and ethanol and the pK_a values of carbonic acid and its corresponding monoalkyl esters.

Entry	Solvent	<i>b</i> ^a	Carbonate	pK _a ^b
1	H ₂ O	0.828	H ₂ CO ₃	4.36 ± 0.41
2	CH ₃ OH	3.837	CH ₃ CO ₂ OH	4.02 ± 0.41
3	C ₂ H ₅ OH	2.706	C ₂ H ₅ CO ₂ OH	4.15 ± 0.41

a. Ostwald solubility coefficient of CO₂ at 298 K^{11a}.

b. Predicted pK_a value of carbonate at 298 K^{11b}.

For the reactions with Rh/C catalyst (Fig. 3d), the conversion of AP was little affected by the CO₂ pressurization. The above-mentioned positive effect of CO₂ via the formation of H⁺ species in the liquid phase can also be expected and so there should be some negative effects. A possible negative effect is the dilution of reacting species (substrate, H₂, catalyst) in the liquid phase by the dissolution of CO₂. Another one is the formation and adsorption of CO from CO₂ and H₂ on the surface of Rh/C catalyst. No catalyst deactivation was observed to occur with the Rh/C catalyst as described later and so the surface of supported Rh particles would be partially poisoned by CO molecules. There are two different adsorption sites for CO on the surface of Rh/Al₂O₃ sample as confirmed by *in situ* high-pressure FTIR spectroscopy, on which linear and hydride types of CO can be adsorbed.¹³ It may be assumed that there exist different CO adsorption sites on the surface of the Rh/C sample as well and a certain type of CO adsorption sites become inactive for the AP hydrogenation in the presence of CO₂. Those positive and negative effects should result in no/little impact of CO₂ pressurization as observed with Rh/C catalyst (Fig. 3d). The effect of CO₂ with Rh/Al₂O₃ catalyst will be discussed in the following, for which severe catalyst deactivation was

observed to occur, in contrast to the other three catalysts.

In some hydrogenation reactions using supported metal catalysts in the presence of dense phase CO₂, the catalysts lose their activity due to the formation and adsorption of CO from H₂ and CO₂ over the surface of supported metal particles.¹⁴ The possibility of such a catalyst deactivation has been examined for the present heterogeneous AP hydrogenation. Fig. 4 shows the time - conversion profiles of hydrogenation reactions with Pd and Rh catalysts in different solvents pressurized by CO₂ at 1 MPa. For the reactions with Rh/Al₂O₃ (Fig. 4c), the conversion did not increase after 50 min and so the catalyst became deactivated during the reactions irrespective of the solvents used. In contrast, such a catalyst deactivation was not observed with Pd/Al₂O₃, Pd/C, and Rh/C catalysts (Fig. 4a, b, d). Previously, the authors studied the adsorption of CO on the surface of Al₂O₃-supported Pd and Rh particles in the absence and presence of H₂ and/or water vapor by *in situ* FTIR measurements.¹³ It was observed that CO was adsorbed on Pd in bridge-type species while on Rh in linear and hydride species on low-coordinated (unsaturated, rough surface) and high-coordinated (saturated, smooth surface) Rh sites, respectively. When water vapor was present, bridge-type CO species adsorbed on low-coordinated Pd sites and linear-type CO species adsorbed on low-coordinated Rh sites were replaced by water molecules. It is suggested from the results of the previous FTIR and the present AP hydrogenation that the high-coordinated metal sites (on supported Pd and Rh particles) should be catalytically active for the hydrogenation of AP and the hydride-type CO species formed from H₂ and CO₂ on Rh/Al₂O₃ should cause its deactivation. In contrast to Rh/Al₂O₃, Rh/C did not become deactivated (Fig. 4b), probably due to its higher metal dispersion (Table 1); the hydride-type CO species were difficult to form and it was unlikely to lose its activity by the adsorption of water molecules on low-coordinated Rh sites. On the other hand, no hydride-type CO species were formed on supported Pd catalysts and so no catalyst deactivation occurred.

In the above discussion, the interactions of CO₂ with the surface of supported noble metal particles via CO forming from CO₂ and H₂, as evidenced by *in situ* high-pressure FTIR measurements, are considered.^{13, 14} In addition, the surface of support materials (Al₂O₃, C in the present work) might be modified by CO₂, CO, and/or other species that are formed from CO₂ and H₂. This possibility may be worth examining by FTIR spectroscopy and other techniques in the future.

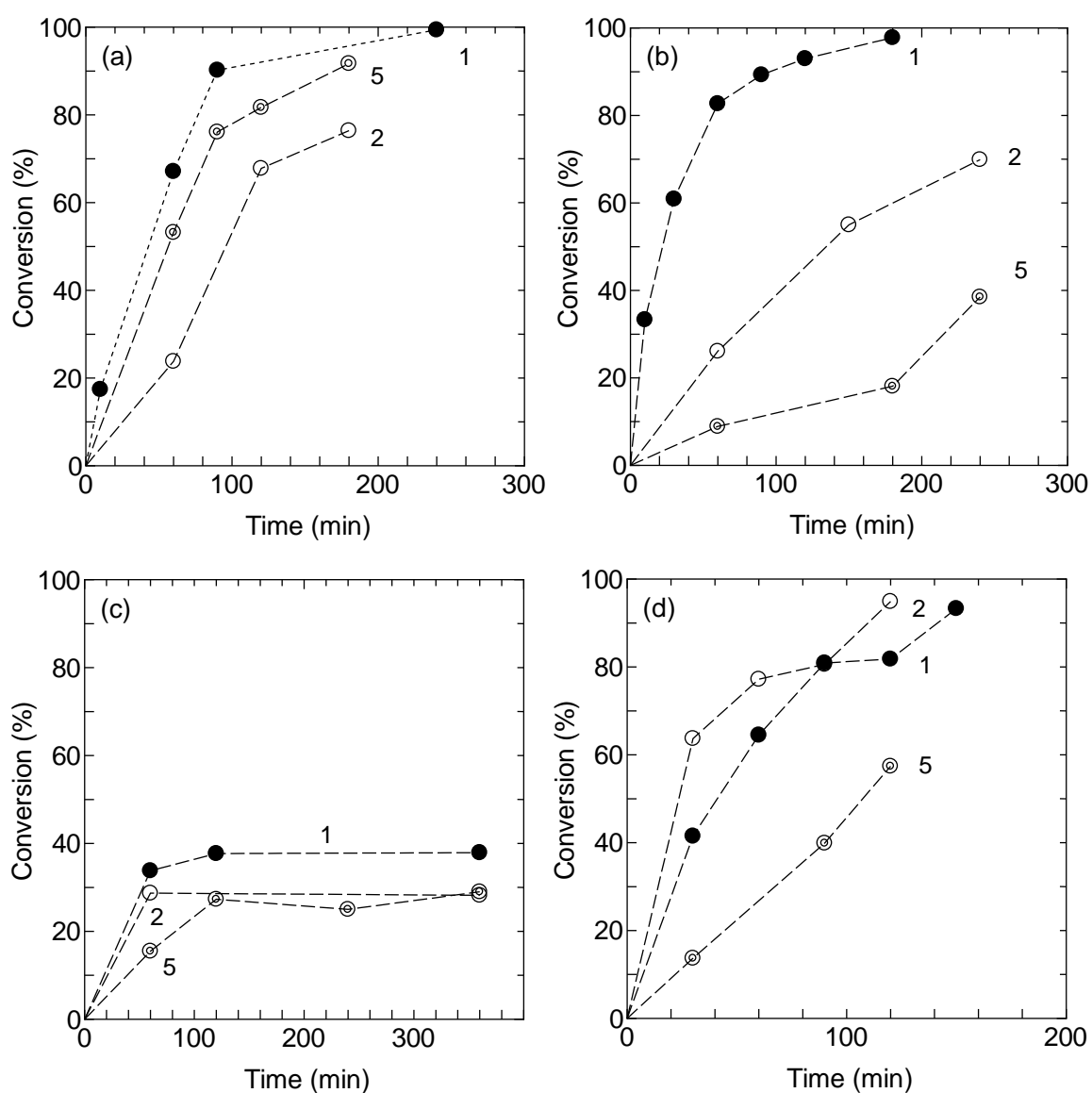


Fig. 4. Time - conversion profiles of AP hydrogenation with (a) Pd/Al₂O₃, (b) Pd/C, (c) Rh/Al₂O₃, and (d) Rh/C in different solvents given in the presence of CO₂. 1: water, 2:

methanol, 5: *n*-hexane. Reaction conditions: AP 2 cm³, solvent 5 cm³, temperature 353 K, CO₂ 1 MPa, (a, b) catalyst 20 mg (a), 10 mg (b), H₂ 4 MPa, (c, d) catalyst 20 mg (c), 10 mg (d), H₂ 2 MPa.

It is interesting to note that water is useful in the AP hydrogenation. The conversion of AP with Al₂O₃ and C supported Pd catalysts is the highest in water compared to the other organic solvents examined and it is enhanced by CO₂ pressurization with no catalyst deactivation. Water is a better solvent for the AP hydrogenation with Rh/C catalyst in the absence and presence of CO₂, in which the effect of CO₂ pressurization is less significant. Unfortunately, severe catalyst deactivation occurs in the AP hydrogenation with Rh/Al₂O₃ catalyst in water as well as in the other organic solvents.

Conclusions

The solvent effects on the conversion of heterogeneous acetophenone (AP) hydrogenation with Pd/Al₂O₃ and Pd/C may be correlated to hydrogen-bond-acceptance (HBA) capability (β) for Pd/Al₂O₃ while hydrogen-bond-donation (HBD) capability (α) for Pd/C. The highest AP conversion can be achieved when using water as solvent for the two catalysts in common. These results are the same as obtained previously with Rh/Al₂O₃ and Rh/C catalysts; that is, the **influence of solvents depends** on the support materials (Al₂O₃, C) but not on the metal species (Pd, Rh). The pressurization with CO₂ (1 MPa) improves the conversion of AP hydrogenation with Pd/Al₂O₃, in particular, in methanol, due to the action of H⁺ species formed. There are no interactions between CO₂ and AP molecules modifying the reactivity of its carbonyl group. No significant promotional effects of CO₂ appear for the reactions with Pd/C and Rh/C catalysts, probably due to offset of positive (H⁺) and negative (dilution, CO formation) effects. Serious catalyst deactivation occurs with Rh/Al₂O₃ catalyst via poisoning with CO formed from CO₂ and H₂. The nature of supported metal catalysts is significant for

the occurrence of positive and negative effects of CO₂ pressurization in the liquid phase AP hydrogenation.

Experimental

Four supported metal catalysts of 5 wt% Rh/C and 5 wt% Rh/Al₂O₃ (Aldrich) and 5 wt% Pd/C and 5 wt% Pd/Al₂O₃ (Wako) were used. Water and a few organic solvents (Wako) were used as received for reaction runs. The hydrogenation of AP (Wako) was carried out in a 50 cm³ stainless steel autoclave.³ The reactor was flushed with H₂ (99.99%) three times to remove the air and heated up to 353 K and then H₂ was introduced to the desired pressure (2 MPa for Rh catalysts, 4 MPa for Pd ones). For reaction runs in the CO₂-dissolved solvents, CO₂ (99.99%) was then introduced to 1 MPa. The reaction runs were conducted while stirring the reaction mixture with a magnetic stirrer. At the end of reaction, the autoclave was cooled to room temperature and slowly depressurized. The composition of reaction mixture was analyzed by a gas chromatograph (GL Science GC-4000) using a flame ionization detector. Decane was used as an internal standard for the analysis.

In situ FTIR measurements were made in attenuated total reflection (ATR) mode for AP dissolved in solvents in the absence and presence of 1 MPa CO₂ using a JASCO FTIR-620 spectrometer with a triglycine sulfate detector at a wavenumber resolution of 2 cm⁻¹.^{10, 13} A liquid mixture of AP and a solvent with a volume ratio of 2:5 was loaded into a home-designed ATR cell of 1.18 cm³ attached with a ZnSe rod. The cell was purged with N₂ three times while stirring and then the FTIR spectra were collected at ambient temperature.

The size of supported metal particles was measured by CO pulse chemisorption (BEL Japan BEL-METAL) at 323 K using a pulse of 1% CO in He.¹³ Prior to the measurement, the sample was reduced in a stream of 100% H₂ at 373 K for 30 min and heated up to 383 K in He for 10 min to remove hydrogen species adsorbed on the surface. The metal

dispersion was calculated using a stoichiometry of either CO/Rh = 1/1 or CO/Pd = 1/2. Selected samples were also examined by transmission electron microscopy (TEM, JEOL JEM-2000ES).¹³ The sample was ground in a mortar and dispersed in ethanol; a few drops of the suspension were put on a carbon-coated collodion film on a TEM grid and dried under ambient conditions.

Acknowledgements

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References

- 1 C. Reichardt, T. Welton, *Solvents and Solvent Effects in Organic Chemistry*, Wiley-VCH, Weinheim, 4th edn, 2010.
- 2 (a) G. V. Smith, F. Notheisz, *Heterogeneous Catalysis in Organic Chemistry*, Academic, London, 1995. (b) R. A. van Santen, P. W. N. M. van Leeuwen, J. A. Moulijn, B. A. Averill (eds.), *Catalysis: An Integrated Approach*, Elsevier, Amsterdam, 2nd edn, 1999. (c) R. A. Sheldon, H. van Bekkum, *Fine Chemicals through Heterogeneous Catalysis*, Wiley-VCH, Weinheim, 2001.
- 3 H. Yoshida, Y. Onodera, S. Fujita, H. Kawamori, M. Arai, *Green Chem.* 2015, **17**, 1877-1883.
- 4 (a) M. A. Aramendía, V. Borau, J. F. Gómez, A. Herrera, C. Jiménez, J. M. Marinas, *J. Catal.* 1993, **140**, 335-343. (b) R.V. Malyala, C. V. Rode, M. Arai, S. G. Hegde, R. V. Chaudhari, *Appl. Catal. A Gen.* 2000, **193**, 71-86. (c) M. Bejblová, P. Zamostny, L. Cervený, J. Cejka, *Collect. Czech. Chem. Commun.* 2003, **68**, 1969-1984. (d) A. Drelinkiewicz, A. Waksmundzka, W. Makowski, J.W. Sobczak, A. Król, A. Zięba,

- Catal. Lett.* 2004, **94**, 143-156. (e) H. Cheng, J. Hao, H. Wang, C. Xi, X. Meng, S. Cai, F. Zhao, *J. Mol. Catal. A Chem.* 2007, **278**, 6-11. (f) N. M. Bertero, A. F. Trasarti, C. R. Apesteguía, A. J. Marchi, *Appl. Catal. A Gen.* 2011, **394**, 228-238. (g) A. F. Trasarti, N. M. Bertero, C. R. Apesteguía, A. J. Marchi, *Appl. Catal. A Gen.* 2014, **475**, 282-291. (h) N. Hiyoshi, O. Sato, A. Yamaguchi, M. Shirai, *Chem. Commun.* 2011, **47**, 11546-11548.
- 5 (a) C. I. Herrerias, X. Yao, Z. Li, C. Li, *Chem. Rev.* 2007, **107**, 2546–2562. (b) A. Chanda, V. V. Fokin, *Chem. Rev.* 2009, **109**, 725–748. (c) R. Butler, A. G. Coyne, *Chem. Rev.* 2010, **110**, 6302–6337.
- 6 M. J. Kamlet, J.-L. M. Abboud, M. A. Abraham, R. W. Taft, *J. Org. Chem.* 1983, **48**, 2877-2887.
- 7 (a) P. G. Jessop, B. Subramaniam, *Chem. Rev.* 2007, **107**, 2666-2694. (b) G. R. Akien, M. Poliakoff, *Green Chem.* 2009, **11**, 1083-1100. (c) M. Arai, S. Fujita, M. Shirai, *J. Supercrit. Fluids* 2009, **47**, 351-356.
- 8 (a) H. Yoshida, S. Fujita, M. Arai, B. M. Bhanage, in B. M. Bhanage, M. Arai (eds.), *Transformation and Utilization of Carbon Dioxide*, Springer, New York, 2014, pp. 369-388. (b) R. Liu, H. Yoshida, S. Fujita, M. Arai, in S. L. Suib (ed.), *New and Future Developments in Catalysis: Activation of Carbon Dioxide*, Elsevier, Amsterdam, 2013, pp. 357-377.
- 9 (a) X. Meng, H. Cheng, Y. Akiyama, Y. Hao, W. Qiao, Y. Yu, F. Zhao, S. Fujita, M. Arai, *J. Catal.* 2009, **264**, 1-10. (b) X. Meng, H. Cheng, S. Fujita, Y. Hao, Y. Shang, Y. Yu, S. Cai, F. Zhao, M. Arai, *J. Catal.* 2010, **269**, 131-139. (c) F. Zhao, Y. Ikushima, M. Arai, *J. Catal.* 2004, **224**, 479-483.
- 10 H. Yoshida, K. Kato, J. Wang, X. Meng, S. Narisawa, S. Fujita, Z. Wu, F. Zhao, M. Arai, *J. Phys. Chem. C* 2011, **115**, 2257-2267.
- 11 (a) Kagaku Binran, Vol. II, Chem. Soc. Jpn., Maruzen, Tokyo, 1984, 3rd edn., pp.158-

165. (b) SciFinder, Calculated using Advanced Chemistry Department (ACD/Labs) Software V11.01 (©1994-2016 ACS).
- 12 Y. Ikushima, N. Saito, M. Arai, K. Arai., *Bull. Chem. Soc. Jpn.* 1991, **64**, 2224-2229.
- 13 H. Yoshida, S. Narisawa, S. Fujita, R. Liu, M. Arai, *Phys. Chem. Chem. Phys.* 2012, **14**, 4724-4733.
- 14 (a) D. Ferri, T. Bürgi, A. Baiker, *Phys. Chem. Chem. Phys.* 2002, **4**, 2667-2672. (b) B. Minder, T. Mallat, K. H. Pickel, K. Steiner, A. Baiker, *Catal. Lett.* 1995, **34**, 1-9. (c) S. Ichikawa, M. Tada, Y. Iwasawa, T. Ikariya, *Chem. Commun.* 2005, 924-926. (d) M. Burgener, D. Ferri, J.-D. Grunwaldt, T. Mallat, A. Baiker, *J. Phys. Chem. B* 2005, **109**, 16794-16800. (e) V. Arunajatesan, B. Subramaniam, K. W. Hutchenson, F. E. Herkes, *Chem. Eng. Sci.*, 2007, **62**, 5062-5069. (f) C. D. Zeinalipour-Yazdi, A. L. Cooksy, A. M. Efstathiou, *J. Phys. Chem. C* 2007, **111**, 13872-13878. (g) S. Fujita, T. Yamada, T. Akiyama, H. Cheng, F. Zhao, M. Arai, *J. Supercrit. Fluids* 2010, **54**, 190-201.