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Solvent effects in heterogeneous selective hydrogenation of acetophenone: Difference between Rh/C and Rh/Al_2O_3 catalysts and superiority of water as a green functional solvent

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(Abstract)

Selective hydrogenation of acetophenone (AP) to 1-phenylethanol (PhE) was investigated over Rh/Al_2O_3 and Rh/C catalysts in 13 solvents including water and conventional organic solvents. Strong solvent effects on the overall rate of AP conversion were observed in different manners depending on the catalysts used. The conversion obtained is correlated with hydrogen-bond-donation (HBD) capability for Rh/C but with hydrogen-bond-acceptance (HBA) capacity for Rh/Al_2O_3. The solvent effects should result from interactions between the carbonyl group of AP and the solvent molecules through hydrogen bonding for Rh/C and from those between the solvent molecules and the catalyst surface for Rh/Al_2O_3 having HBD hydroxyl groups on its surface. Water is the most effective functional solvent in the selective hydrogenation of AP for C and Al_2O_3-supported Rh catalysts due to its high HBD capability (α) and low HBA capability (β), respectively. For the hydrogenation with Rh/Al_2O_3 in water, its large polarity/polarizability index (π^*) may contribute to the high selectivity to PhE.

Keywords: hydrogenation; acetophenone; solvent effects; water

Introduction

Solvent effects have been an important issue for liquid phase organic synthetic reactions.[1] The solvent properties/features are characterized by several conventional and solvatochromic parameters. Compared to a number of organic solvents, water is an interesting solvent, which may serve as a green solvent and a reaction promoter for organic synthetic reactions. The usefulness of water for those using homogeneous catalysts is reviewed in the literature. [2-4] The importance of interface between aqueous and organic phases is noted for promotional effects caused by the presence of water, which is believed to interact with organic substrates through hydrogen bonding at the interface and accordingly modify their reactivity. Solvent effects have not been investigated in detail so far for heterogeneous catalytic reactions, which include solid (catalyst) – liquid interfaces that are absent in homogeneous catalytic reactions.

The present work has been undertaken to study solvent effects using various organic solvents and water for a model reaction of selective hydrogenation of acetophenone (AP) over supported Rh catalysts. The selective hydrogenation of aromatic ketones, such as AP, into the corresponding alcohols is of great importance in chemical, pharmaceutical, food, and cosmetic industry.[5,6] The hydrogenation of AP is carried out using supported metal catalysts in organic solvents. Several authors report for this reaction that the rate of AP conversion depends on the properties of organic solvents used.[7-11] The group of Marchi et al. investigated the selective hydrogenation of AP with a Ni/SiO_2 catalyst in 10 organic solvents including protic polar, aprotic polar, and aprotic apolar ones.[12,13] They found that the rate of AP hydrogenation was even larger in cyclohexane than in aprotic polar solvents; the latter solvents were suggested to have strong interactions with the catalyst, as indicated by adsorption enthalpies, blocking its active sites. It is also indicated that the extent of solvent effects depends on supported

metals used, being Ni > Co > Cu (all on SiO_2).[12, 13] In their work, the group of Marchi et al. reviewed previous results on solvent effects in the heterogeneous AP hydrogenation.[12, 13] Shirai et al. reported the superiority of water for the hydrogenation of AP with a Pd/C catalyst, which showed a higher activity in water as compared to the reactions in methanol, ethanol, and heptane.[14] Recently, Subramaniam et al. reported solvent effects on hydrogenation of different oxygenates in 10 solvents including water over a Ru/C catalyst and also indicated the superiority of water.[15]

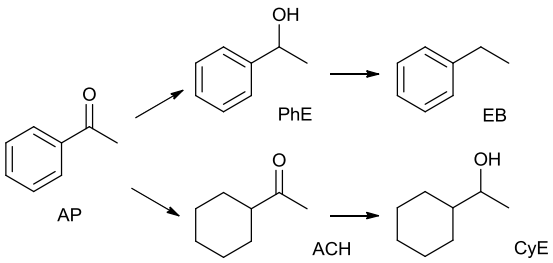
In the present work, the selective hydrogenation of AP has been investigated in water and 12 organic solvents including protic (ethylene glycol, methanol, ethanol, 2-propanol, 1-butanol, *t*-butanol), aprotic polar (*N*,*N*'-dimethylformamide, dioxane, diethyl ether), and aprotic apolar (toluene, cyclohexane, hexane) ones over two different catalysts, Rh/C and Rh/Al_2O_3, which are different in the hydrophilic/hydrophobic (lipophilic/ lipophobic) properties. The two Rh catalysts have been employed because the catalyst – liquid interface should be important, [12, 13] and thus the solvent effects would be different depending on the surface properties of heterogeneous catalysts to be used. Attempts have been made to explain the solvent effects observed on the total conversion and the product selectivity by considering such solvatochromic solvent parameters[1] as hydrogen-bond-donation (HBD) capability (α), hydrogen-bond- acceptance (HBA) capability (β), and the polarity/polarizability index (π^*). It has been found that strong solvents effects appears in different manners for the Rh/C and Rh/Al_2O_3 catalysts and their activity to the selective hydrogenation of AP to 1-phenylenethanol (PhE) is the highest in the presence of water, demonstrating its superiority as a green functional solvent. It is worth noting that different solvent properties of water are responsible for the improvement in the rate of AP hydrogenation with the two Rh catalysts. The function of water may be explained by its large α and small β values for the selective hydrogenation with Rh/C and Rh/Al_2O_3

catalysts, respectively. In addition, for the latter catalyst, large π* value of water may contribute to the high selectivity to the formation of PhE.

Results and discussion

Solvent effects for Rh/C and Rh/Al_2O_3 catalysts

In the hydrogenation of AP, PhE is the desired product, which is important in the synthesis of pharmaceuticals, fragrances, and others.[3] Under the conditions used, in addition to PhE, ethylbenzene (EB) and acetylcyclohexane (ACH) were formed as byproducts over Rh/C and Rh/Al_2O_3, respectively (Scheme 1). The formation of acetylcyclohexene, cyclohexylethanol (CyE), and ethylcyclohexane was also detected but in smaller amounts.



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

The hydrogenation of AP was investigated with Rh/C and Rh/Al_2O_3 catalysts, for which the BET surface area was 834 m^2 g^{-1} and 35 m^2 g^{-1} and the degree of metal dispersion measured by CO chemisorption was 73% and 38%, respectively. Fig. 1 shows the results of AP conversion (left) in various solvents over Rh/C and Rh/Al_2O_3 catalysts and those of product selectivity (right) obtained at similar conversion levels of 25 – 50%. On one hand, the conversion obtained is significantly different among the solvents examined. Note that the solvent effects depend on the catalysts used. Over Rh/C, the

conversion was in an order of protic organic solvent ≥ water > aprotic polar one ≥ aprotic apolar one. Although the conversion obtained with water was lower than those in methanol and ethanol, the yield of PhE with water (36%) was comparable to those in those alcohols (39 and 33 %) because of the highest selectivity to PhE with water. Similar solvent effects were previously obtained with Pd/C [9, 14] for AP hydrogenation and Ru/C [15] for 2-butanone hydrogenation. The superiority of water was also shown by Shirai et al.[6] for Pd/C and by Subramaniam et al.[15] for Ru/C. For Rh/Al_2O_3, in contrast, a different order was observed, water > apolar organic solvent > aprotic polar one ≥ protic one (Fig. 1). This order is in agreement with the previous results; Marchi et al. [12, 13] reported that the activity of Ni/SiO_2 was higher in the order of alcohols > cyclohexane > toluene > methanol and Červeny et al. [9] showed that the activity of Pd on zeolite-β in *n*-hexane was larger than in methanol. Both research groups note that the competitive adsorption of the AP and solvent molecules on the catalysts should be an important factor determining the solvent effects. Methanol is preferentially adsorbed on the acidic surface of Pd/zeolite-β than AP, which hinders the adsorption of the substrate. On the other hand, it was observed that the selectivity to PhE did not change so much with the solvents used, which was in the range of 56-75% for Rh/C and 73-88% for Rh/Al_2O_3, as shown in Fig. 1. Marchi et al. also reported less significant solvent effects on the selectivity with Ni/SiO_2. [12, 13] It should be noted that the highest PhE yield can be achieved in water for both the Rh catalysts using different support materials of C and Al_2O_3.

In liquid phase hydrogenation reactions, H_2 solubility in the solvent is generally an important factor determining the overall reaction rate. However, H_2 solubility cannot explain the present solvent effects. The solubility of H_2 in water is lower than those in the organic solvents (Table S1 in Supporting Information (SI)), which cannot explain the higher AP conversion (and PhE yield) in water observed. The relationship between the

H_2 solubility and the AP conversion observed was examined (Fig. S1 in SI). The AP conversion was not found to be correlated to the H_2 solubility, which is not significant in determining the solvent effects observed (Fig. 1). Then, the relationship between the conversion values and the solvatochromic parameters of the solvents (Table S1) was examined. As shown in Fig. 2, the conversion obtained with Rh/C can be correlated with HBD capability (α). The conversion tends to increase with the α value of the solvent used. In contrast, the conversion obtained with Rh/Al_2O_3 was not correlated with the α value, but a relatively good correlation is seen with HBA capability (β) as shown in Fig. 3. The plots of AP conversion against β and α for Rh/C and Rh/Al_2O_3 catalysts are given, respectively, in Fig. S2 and Fig. S3 in SI. There is a trend for Rh/Al_2O_3 in Fig. 3 that the conversion decreases with the β value. Thus, the significant solvent polarity parameters for determining the rate of AP hydrogenation are different depending on the catalysts used.

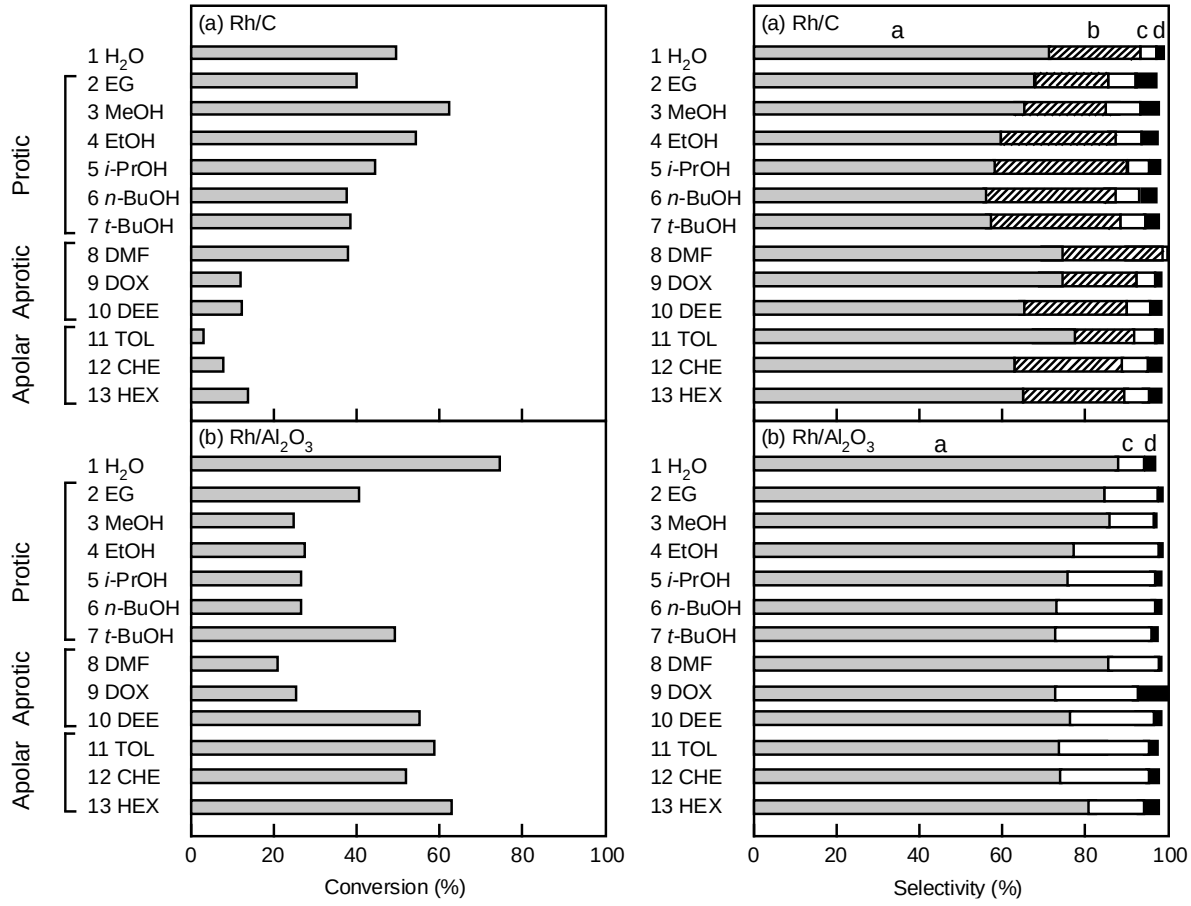


Fig. 1. Conversion and selectivity to PhE obtained in various solvents (a) over Rh/C and (b) over Rh/Al_2O_3. Reaction conditions: AP, 17 mmol; catalyst, 10 mg (Rh/C) or 20 mg (Rh/Al_2O_3); solvent, 5 cm^3; H_2, 2 MPa; temperature, 353 K; time, 30 min for Rh/C and 2 h for Rh/Al_2O_3. EG: ethylene glycol; MeOH: methanol; EtOH: ethanol; i-PrOH: 2-propanol; n-BtOH: 1-butanol; t-BuOH: *t*-butanol; DMF: *N,N'*-dimethylformamide; DOX: dioxane; DEE: diethyl ether; TOL: toluene; CHE; cyclohexane; HEX: *n*-hexane. In the right figure for the selectivity, gray (a), hatched (b), white (c), and black (d) bars represent the selectivities to PhE, EB, ACH, and CyE, respectively.

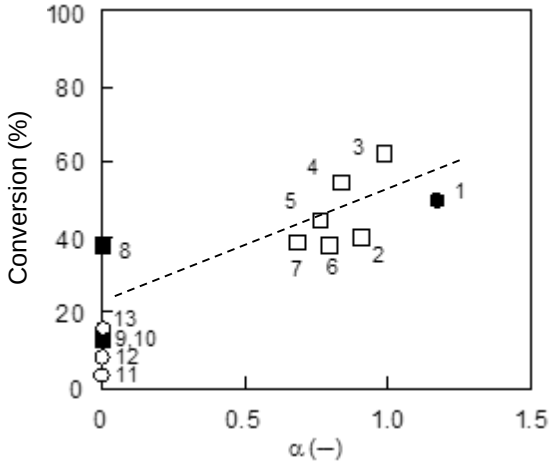


Fig. 2. The conversion over Rh/C vs. the α value of the solvents. Numbers given correspond to the different solvents in Fig. 1.

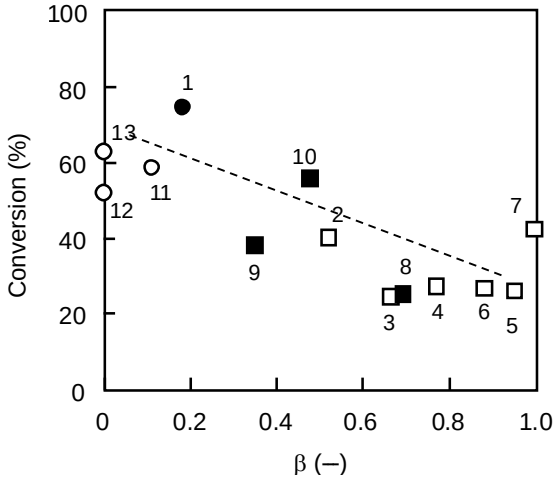


Fig. 3. The conversion over Rh/Al_2O_3 vs. the β value of the solvents. Numbers given correspond to the different solvents in Fig. 1.

FTIR-ATR spectra of AP were measured in a few selected solvents under ambient conditions to examine interactions between the carbonyl group of AP and the solvent molecules. Fig. 4 gives FTIR spectra in the range of ν(CO) frequency. The peak of ν(CO) absorption band is located at a different frequency depending on the solvent used. For AP

in alcohols, two absorption bands are seen at about 1690 cm^{-1} and 1680 cm^{-1}. The former frequency is similar to that of AP in non-polar solvents of *n*-hexane and cyclohexane, in which no interactions exist between the AP and solvent molecules. When the concentration of AP was decreased, the relative strength of the absorption band at 1680 cm^{-1} was increased compared to that at 1690 cm^{-1}, indicating that the absorption at 1680 cm^{-1} should be due to the carbonyl group interacting strongly with the alcohol molecules. The peak frequency of ν(CO) absorption band is in the order of *n*-hexane ≈ cyclohexane (1689 cm^{-1}) > diethyl ether (1688 cm^{-1}) > 1,4-dioxan ≈ toluene (1685 cm^{-1}) > water (1683 cm^{-1}). These results reveal that the strength of the carbonyl bond decreases in the same order and it is most reactive in the presence of water, in accordance with the correlation with the α value. The molecular interactions of the carbonyl group with the solvent molecules, which cannot be evaluated by the α value, may explain the differences in the total conversion among the solvents of $\alpha = 0$ (Fig. 2). Wan et al. reported that the carbonyl stretching absorption band of 2-butanone was shifted to a lower frequency in the presence of such a protic solvent as water and methanol and the extent of the shift was larger in water having larger α value.[15] On the basis of those observations, it is believed that the trend of the conversion increasing with the α value over Rh/C is explained by the interactions between the carbonyl group of AP and solvent molecules through hydrogen bonding, which would be stronger with the solvent having larger α value (HBD capability), resulting in higher reactivity of the carbonyl group. On the other hand, the trend of the conversion decreasing with the β value (HBA capability) over Rh/Al_2O_3 could be due to interactions of the solvent molecules with the surface of Rh/Al_2O_3 catalyst on which HBD hydroxyl groups are present in a larger amount compared to the Rh/C. The FTIR spectra measured for these two catalysts are given in Fig. S4 in SI, in a range of 3800 – 3000 cm^{-1} assignable to surface hydroxyl groups. Those hydroxyl groups are likely

to interact with HBA molecules and the β value of AP (β = 0.49) is smaller than protic and aprotic polar solvents (Table S1 in SI). So, those polar solvents should preferentially be adsorbed on the catalyst surface and, hence, suppress the adsorption of AP on the catalyst. This should also influence the adsorption of AP on the surface of supported Rh particles, decreasing the rate of AP hydrogenation. Such negative solvent effects would be weaker over Rh/C because the catalyst has few hydroxyl groups on its surface (Fig. S2). For the AP hydrogenation with Ni/SiO_2, the group of Marchi et al. pointed out that the competitive adsorption of the substrate and solvents on the catalyst was an important factor for the solvent effects.[12, 13]

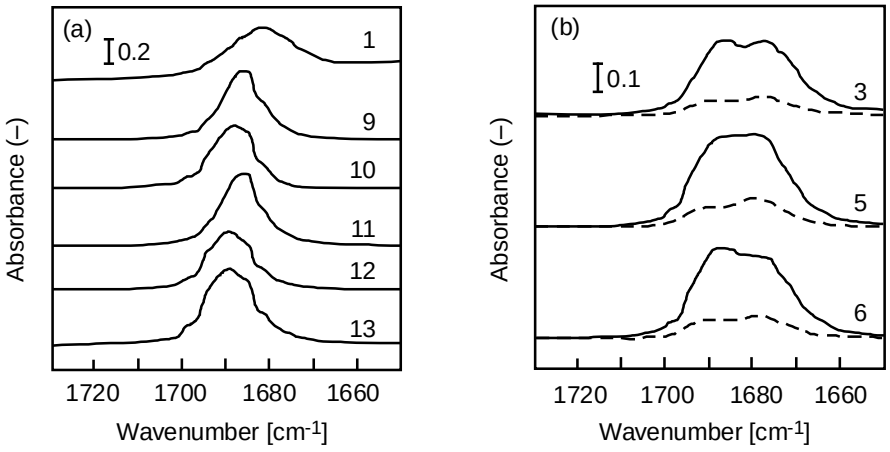


Fig. 4. ATR-FTIR spectra of AP in different solvents measured under ambient conditions. For (a) AP/solvent = 2/5 (volume); (b) AP/solvent = 2/5 (solid lines), 1/15 (broken lines). Numbers given correspond to those solvents in Fig. 1.

As above-mentioned, water can give the higher conversion values to both the catalysts. When water was used, the reaction system consisted of solid-water-AP-gas four phases and the catalysts were dispersed in the organic AP phase, which was confirmed by visual observation. The reaction was further carried out in the absence of any solvent while using the same amount of AP (17 mmol). Under such conditions, the Rh/C and Rh/Al_2O_3 catalysts were observed to give the conversion values of 17% and 61%,

respectively. The conversion over Rh/C obtained in the absence of any solvent was much lower than that (50%) in the presence of water, in accordance with the results with Pd/C.[14] Thus, the higher conversion with water over Rh/C is simply ascribable to its high HBD capability, i.e. the ability to promote the reaction through the interactions with AP molecules at the water – AP interface. Shirai et al. mentioned the importance of increased acidity of aqueous phase compressed by CO_2 for a larger AP conversion compared to ambient water. [14] For the other Rh/Al_2O_3 catalyst, such AP – water interactions at the interface would also be an important factor for the highest conversion observed in water. The conversion values obtained in the absence and presence of water with Rh/Al_2O_3 were 61% and 75%, respectively. However, the difference was not so large as compared to the case of Rh/C (17% and 50%). There should be above-mentioned negative effects of such polar solvents as water that is adsorbed on the catalyst and then hinders the adsorption of AP. Thus, those positive (activation of the carbonyl group) and negative (covering the catalyst surface) effects of water may be responsible for the similar conversion levels observed in the absence and presence of water for the hydrophilic Rh/Al_2O_3 catalyst. It should be noted that the β value of water is lower than those of the polar organic solvents used (Table S1). Hence, the effectiveness of water can be ascribed to its larger α and smaller β values for the Rh/C and Rh/Al_2O_3 catalysts, respectively.

The solvent effects on the selectivity to PhE observed were less significant (Fig. 1), in agreement with the results of Marchi et al. with supported Ni catalysts. [12, 13] The main byproducts observed over Rh/C and Rh/Al_2O_3 were EB and ACH, respectively. The relationship between the PhE selectivity and the solvent polarity parameters was examined but no good correlation was observed with any solvatochromic parameter for the results with Rh/C. At present, the solvent effects on the selectivity over Rh/C is difficult to explain. On the other hand, the selectivity to PhE over Rh/Al_2O_3 is correlated

with the solvent polarity/polarizability index (π*) (Fig. 5). The formation of ACH is parallel with that of PhE. So, the selectivity to PhE would be determined by the relative reactivity between the carbonyl group and the phenyl ring of AP. Probably, the relative reactivity of the carbonyl group would be enhanced by solvation and polarization, resulting in the increase in the PhE selectivity with the π* value.

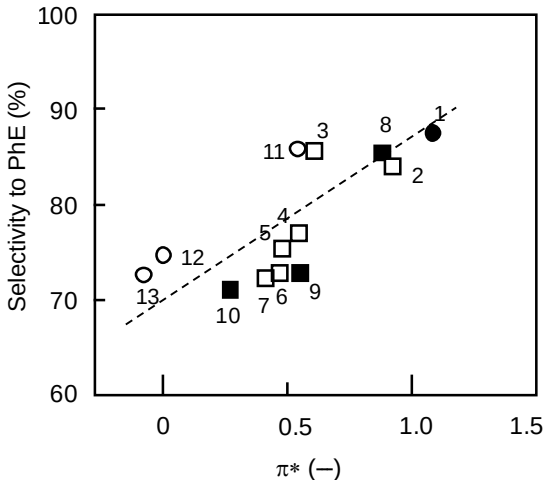


Fig. 5. The selectivity to PhE over Rh/Al_2O_3 vs. the π* value of the solvent. Numbers given correspond to the different solvents in Fig. 1.

Reaction pathways for Rh/C and Rh/Al_2O_3 catalysts

Under the present conditions, the main product is PhE with either Rh/C or Rh/Al_2O_3 catalyst. It is interesting, however, that the main byproduct was EB for the former but ACH for the latter (Scheme 1). The selectivity to EB for the latter catalyst was smaller than 1% irrespective of the solvents used. For Rh/C, AP is hydrogenated to PhE and the PhE formed is further hydrogenated to EB (consecutive reactions) while, for Rh/Al_2O_3, AP is hydrogenated to PhE and ACH (parallel reactions). Possible reasons for the difference in the reaction pathways between the two Rh catalysts will be discussed hereinafter. The degree of metal dispersion measured by CO chemisorption was 73% and 38% for Rh/C and Rh/Al_2O_3 catalysts used, respectively. To examine the influence of

metal dispersion, the former catalyst was treated in an inert atmosphere of N_2 at 773 K for 1 h to cause metal sintering, which decreased the metal dispersion from 73% to 43%, comparable to that of Rh/Al_2O_3. Table 1 compares the results of AP hydrogenation in water or *n*-butanol with untreated and heat-treated Rh/C catalysts. The heat treatment was observed to decrease the rate of AP conversion, increase the selectivity to PhE, and decrease the selectivity to EB. In all these reactions, ACH was formed but in the selectivity of < 5%. Therefore, the difference in the byproduct formation observed between Rh/C and Rh/Al_2O_3 catalysts cannot be explained by the difference in the degree of metal dispersion (the size of metal particles).

Table 1 Results of AP hydrogenation in water and *n*-butanol with untreated and heat-treated Rh/C catalysts

Entry	Treatment	Solvent	Time (min)	Conversion (%)	Selectivity (%)		
					PhE	EB	ACH
1	Untreated	H_2O	30	50	72	22	3
2	HT 500 ºC	H_2O	60	48	78	15	3
3	Untreated	*n*-BuOH	30	38	56	31	6
4	HT 500 ºC	*n*-BuOH	60	43	71	22	3

Reaction temperature: 80 ºC.
AP: acetophenone, PhE: phenylethanol, EB: ethylbenzene, ACH: acetylcyclohexane.
Heat treatment: the catalyst sample was thermally treated in N_2 at 500 ºC for 1 h.

The surface of supported Rh particles were examined by XPS and the results obtained are displayed in Fig. 6. The comparison of Rh $3d_{5/2}$ and $3d_{3/2}$ binding energy (BE) between Rh/C and Rh/Al_2O_3 catalysts indicated no significant difference in the electronic properties of their dispersed Rh particles. The Rh/C catalyst treated at 773 K showed a smaller BE by more than 2 eV compared to the untreated one, which is probably

ascribable to the difference in the degree of metal dispersion (compare 73% and 43%).[16]

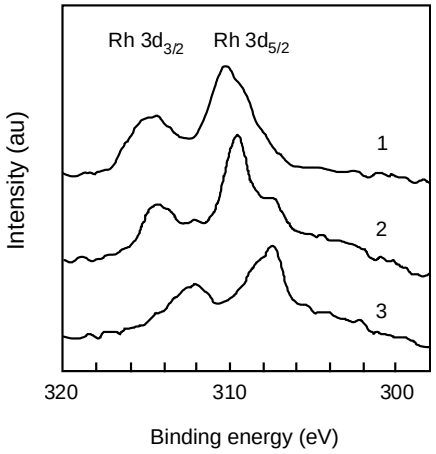


Fig. 6 XPS spectra of Rh 3d region for Rh/Al_2O_3 (1), untreated Rh/C (2), and heat-treated Rh/C catalyst samples

According to a recent work of Chen et al., [17] AP is adsorbed on the surface of Pt particles on Al_2O_3, mainly in the $\eta^1(O)$ configuration, which is beneficial for the hydrogenation of the carbonyl group producing PhE. A small amount of AP may also be adsorbed on Pt through π-bonding, which causes the hydrogenation of the aromatic ring to ACH. On one hand, for our Rh/Al_2O_3 catalyst, the adsorption of AP on Rh particles is suggested to occur mainly in the $\eta^1(O)$ configuration and via π-bonding to some extent, resulting in the formation of PhE as the main product along with the byproduct of ACH. Chen et al. also indicate that PhE is more strongly adsorbed on Al_2O_3 than on Pt and the AP molecules adsorbed on the support are replaced by the PhE ones formed. [17] It is also suggested for our Rh/Al_2O_3 catalyst that PhE molecules formed on the Rh particles are likely to move to the support and this hinders its further hydrogenation to EB. On the other hand, for Rh/C catalyst, the adsorption of AP should occur on the surface of

supported Rh particles in the η^1(O) configuration. The PhE molecules formed may be further hydrogenated to EB over the Rh particles, on which PhE may be adsorbed via its hydroxyl group, similar to the carbonyl group of AP. Table 1 shows that the hydrogenation of PhE to EB is more difficult on the heat-treated Rh/C catalyst than on the untreated one. Probably, the adsorption of PhE should be more difficult on the surface of larger Rh particles, on which the PhE molecules formed are more likely to desorb into the liquid phase. This may be ascribable to the difference in electronic properties of exposed Rh atoms between the two Rh/C catalysts (Fig. 6) but not to the difference in the size of Rh particles after considering the results with the Rh/C and Rh/Al_2O_3 catalyst samples having similar degrees of metal dispersion. The surface of larger Rh particles is more electron-rich (electronegative) than that of small ones, [16] which would not be beneficial for the adsorption of PhE through oxygen of its hydroxyl group.

Conclusions

Strong solvent effects appeared on the rate of reaction in the heterogeneous selective hydrogenation of AP using Rh/C and Rh/Al_2O_3 catalysts. The solvent effects significantly depend on the catalysts used. The interactions between the substrate and solvent molecules may be important for the former while those of the catalyst with the substrate and solvent molecules may also be important for the latter. Solvent effects were less significant for the product selectivity as compared to the total rate of AP hydrogenation. It should be noted that water is a promising green solvent/promoter for the selective hydrogenation of AP to PhE for both the catalysts irrespective of their difference in the hydrophilic/hydrophobic nature, which is ascribable to its high HBD capability α for Rh/C and low HBA capability β for Rh/Al_2O_3. For the hydrogenation with Rh/Al_2O_3 in water, its large polarity/polarizability index π^* may be responsible for

the high selectivity to the formation of PhE.

Experimental

Two supported metal catalysts of 5 wt% Rh/C and 5 wt% Rh/Al_2O_3 (Aldrich), 13 kinds of solvents (Wako), and AP (Wako) were used for reaction runs as received. Polarity parameters and H_2 solubility values of those solvents are listed in Table S1. The hydrogenation of AP was carried out in a 50 cm^3 stainless steel autoclave using 10 mg Rh/C or 20 mg Rh/Al_2O_3, 17 mmol AP, and 5 cm^3 solvent. The reactor was flushed with H_2 three times to remove the air and heated up to 353 K and then 2 MPa H_2 was introduced. The reaction runs were conducted for 30 min and 2 h for Rh/C and Rh/Al_2O_3, respectively, while stirring 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 using a flame ionization detector. Decane was used as an internal standard for the analysis.

FTIR measurements were made in attenuated total reflection (ATR) mode for AP dissolved in a few selected organic solvents using a JASCO FTIR-620 spectrometer with a triglycine sulfate detector at a wavenumber resolution of 2 cm^{-1} under ambient conditions.[18, 19] A liquid mixture of AP and a solvent with a volume ratio of 2:5 or 1:15 was loaded into a home-designed ATR cell of 1.18 cm^3 attached with a ZnSe rod. The cell was purged with N_2 for three times while stirring and then the FTIR spectra were collected at ambient temperature.

The degree of Rh dispersion was measured by CO pulse chemisorption (BEL Japan BEL-METAL) at 323 K using a pulse of 1% CO in He.[18] Prior to the measurement, the sample was reduced in a stream of 100% H_2 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 Rh

dispersion was calculated using a stoichiometry of one CO molecule adsorbed on one exposed Rh atom.

The surface of supported Rh particles was examined by X-ray photoelectron spectroscopy on JEOL JPS-9200 with monochromatic Al-Kα radiation. The charge-up shift correction of Rh 3d binding energy (BE) was made by using C1s BE at 284.5 eV and O1s (for γ-Al_2O_3) BE at 531.6 eV as a reference for Rh/C and Rh/Al_2O_3 catalysts, respectively. [20]

The BET surface area of the two supported Rh catalysts was measured by N_2 adsorption using Quantachrome NOVA 1000.

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Supporting Information

Table S1 Solvatochromic parameters and H_2 solubility of various solvents[1-6]

#	Solvent	α (-)[a]	β (-)[b]	π* (-)[c]	X_{H2} x 10^4 (-)[d]
1	Water	1.17	0.18	1.09	0.14[2]
2	Ethyleneglycol	0.90	0.52	0.92	0.38[3]
3	Methanol	0.98	0.66	0.60	1.61[2]
4	Ethanol	0.83	0.77	0.54	2.06[2]
5	2-Propanol	0.76	0.95	0.48	4.61[4]
6	1-Butanol	0.79	0.88	0.47	2.63[2]
7	*t*-butanol	0.68	1.01	0.41	3.28[5]
8	*N*,*N*''-dimethylformamide	0.00	0.69	0.88	1.47[6]
9	1,4-Dioxane	0.00	0.37	0.55	1.84[6]
10	Diethyl ether	0.00	0.47	0.27	3.46[2]
11	Toluene	0.00	0.11	0.54	3.15[2]
12	Cyclohexane	0.00	0.00	0.00	4.14[2]
13	*n*-Hexane	0.00	0.00	-0.08	6.63[2]

a. Hydrogen-bond-donation ability.[1]

b. Hydrogen-bond-acceptance ability.[1]

c. Polarity/polarizability index.[1]

d. H_2 solubility in mole fraction at 298 K and 1 atm.[2-5]

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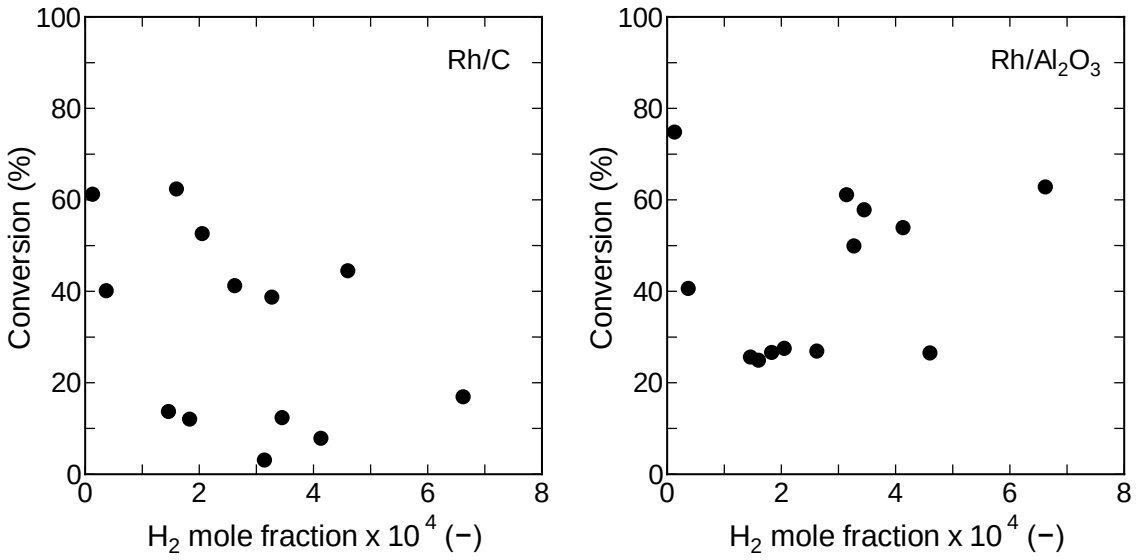

Fig. S1. Plots of total conversion observed in hydrogenation of acetophenone with Rh/C and Rh/Al_2O_3 catalysts (Fig. 1) against the mole fraction of H_2 in solvents used (Table S1)

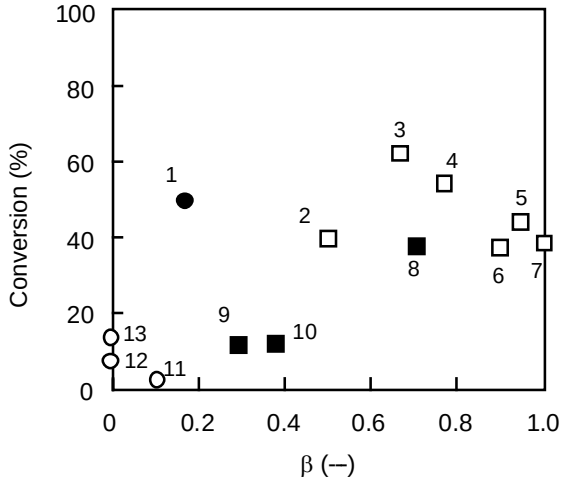

Fig. S2. The conversion over Rh/C vs. the β value of the solvents. Numbers given correspond to the different solvents in Fig. 1.

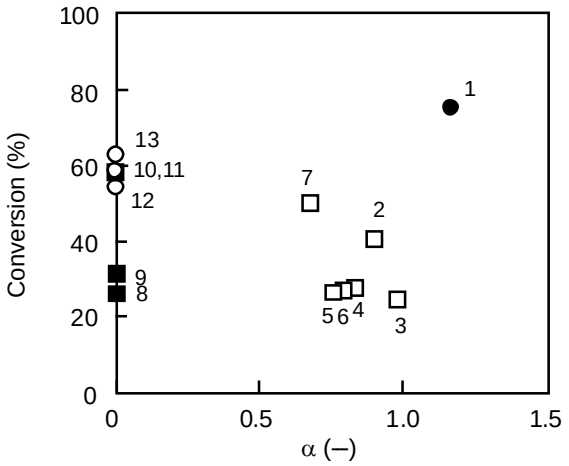

Fig. S3. The conversion over Rh/Al_2O_3 vs. the α value of the solvents. Numbers given correspond to the different solvents in Fig. 1.

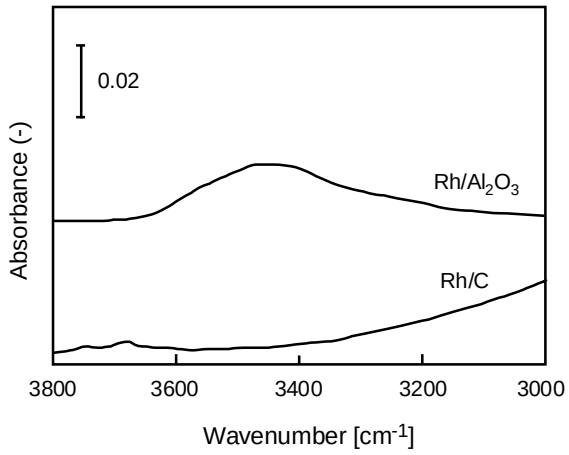

Fig. S4. Diffuse reflectance FTIR spectra of Rh/Al_2O_3 and Rh/C in the range of surface OH vibration. For the measurements, the catalyst samples were diluted with KBr in a 1/200 weight ratio.