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Stereoselective Aromatic Ring Hydrogenation over Supported Rhodium Catalysts in Supercritical Carbon Dioxide Solvent

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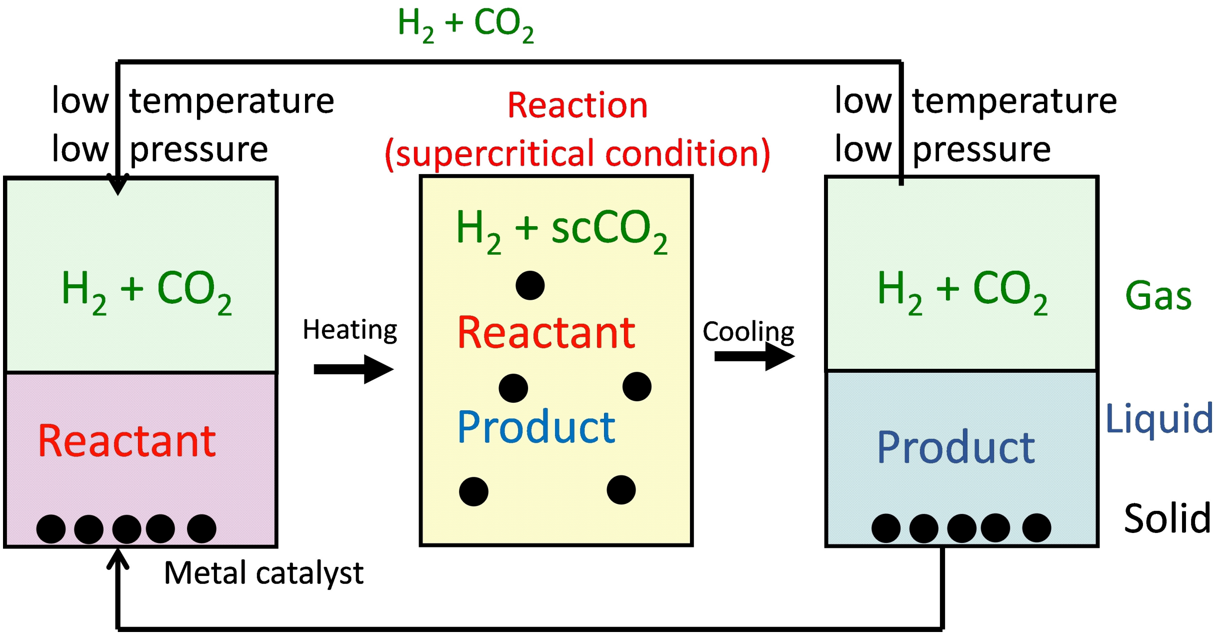

Abstract: The combination of supported rhodium metal catalysts and supercritical carbon dioxide solvent was effective for the stereoselective ring hydrogenations of aromatic compounds at low temperature. Higher solubility of hydrogen in supercritical carbon dioxide provides higher concentration of hydrogen on the rhodium surface, but lower that of the intermediate on rhodium surface, which suppresses the flipping of surface intermediate, leading to higher catalyst activities and cis selectivities to the corresponding ring-hydrogenated products as compared with those in organic solvents.

Keywords: hydrogenation, supercritical carbon dioxide, stereoselectivity, rhodium catalyst

1. Introduction

Catalytic hydrogenation is an important core unit process in chemical industry.[1] The stereoselective hydrogenation of aromatic compounds to the corresponding saturated compounds is also important for chemical industry. For example, *cis*-alkylcyclohexanols are important intermediates for the production of fragrance and perfume industry, which could be obtained by the hydrogenation of corresponding alkylphenols. *cis*-Decalin, obtained by the hydrogenation of tetralin and/or naphthalene, is a starting chemical for production of sebacic acid that is used in the manufacture of 6, 10-nylone and plasticizer and proposed as hydrogen storage media.

Vapor and liquid phase hydrogenation of aromatic compounds having high boiling points, over supported metal catalysts were commercially operated. Higher activities could be obtained for vapor phase hydrogenation; however, the yields and selectivities are low because coking of metal catalysts occurred on acidic supports and the formation of byproducts. Higher selectivities could be obtained for liquid phase hydrogenation with organic solvents; however, reaction rates are low and the separation of products from solvents is critical. Moreover, eliminating the use of organic solvents is highly desirable for environmentally benign processing.

Supercritical carbon dioxide ($scCO_2$ having, critical temperature of 304.2 K and critical pressure of 7.38 MPa) is a prominent candidate as an alternative solvent because of its non-toxic and non-flammable properties. Also, higher reaction rates and simple separation of products from the system without distillation are possible using $scCO_2$ solvent.[2,3] Organic transformations using hydrogen gas with solid catalysts in $scCO_2$ solvent (multi-phase hydrogenation with supported metal catalysts and $scCO_2$) has several other advantages: (1) higher solubility of hydrogen in $scCO_2$, thereby controlling the product selectivity and activity, (2) easy separation of products and catalysts and (3) maintaining clean active sites of solid surfaces by their rinsing with $scCO_2$ solvent.[4] Conceptual representation of the hydrogenation with supported metal catalysts in $scCO_2$ is shown in Figure 1. Several groups have succeeded in demonstrating the application of the multiphase hydrogenation over supported metal catalysts in $scCO_2$ solvent for enhancing the activities and chemoselectivities for unsaturated compounds.[2–8] In this account, we focus on the stereoselective ring hydrogenation of aromatic compounds with the multiphase hydrogenation over supported metal catalysts in supercritical carbon dioxide solvent.

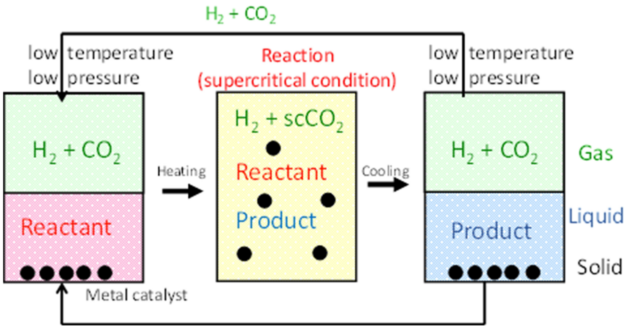

Figure 1. Multiphase hydrogenation with supported metal catalysts and supercritical carbon dioxide solvent.

2. Experimental

The catalytic hydrogenation over supported metal catalysts in $scCO_2$ was studied in a batch reaction system (Figure 2). The system was composed of hydrogen and carbon dioxide cylinders, carbon dioxide feed pump, stainless steel reactor (50 ml), oil bath with jacket, and back-pressure valve.

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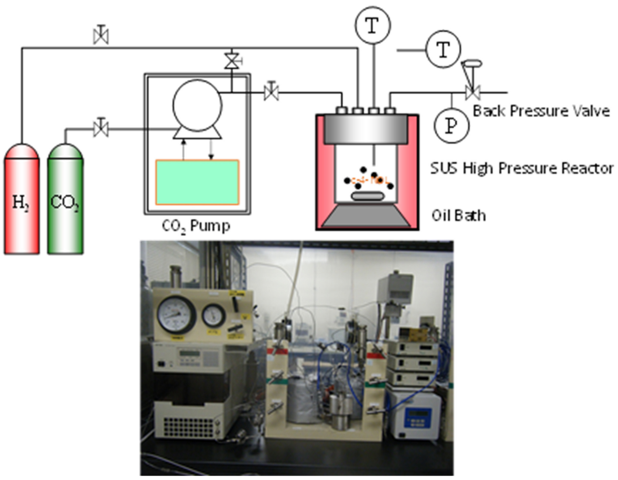

Figure 2. Apparatus for multiphase hydrogenation with supported metal catalyst and supercritical carbon dioxide.

The hydrogenation procedure with $scCO_2$ solvent was as follows. After the weighed amounts of catalyst, substrate and a magnetic bar were placed in the reactor, the reactor was purged with carbon dioxide to remove air and heated in an oil bath to the desired temperature. Hydrogen and then carbon dioxide were introduced into the reactor to the desired pressure levels and contents were stirred magnetically. We designated the reaction start time as the completion of the hydrogen introduction. The carbon dioxide pressure was determined from the difference of the total pressure and hydrogen pressure introduced. After the desired time, the reactor was rapidly cooled in an ice bath, the pressure was slowly released, and the contents were discharged to separate the catalysts by simple filtration with organic solvent.

For the catalytic hydrogenation in organic solvents, the same stainless reactor was used. After the weighed amounts of catalyst, substrate, and organic solvent were placed in the reactor, the reactor was purged with nitrogen to remove air and heated in an oil bath to the desired temperature. Hydrogen was introduced into the reactor to the desired pressure levels and the contents were stirred magnetically. After the desired time, the reactor was rapidly cooled in an ice bath, the pressure was slowly released, and the contents were discharged to separate the catalysts by simple filtration with the organic solvent.

Commercially available 5 wt% charcoal-supported metal catalysts (rhodium (Rh/C), metal dispersion 12 %[9]), ruthenium (Ru/C, 25 %[9]), palladium (Pd/C, 3 %[9]), and platinum (Pt/C, 8 %[9])) from Wako Chemicals, were used in this study.

3. Hydrogenation of Aromatic Ring

3.1. Phenol Hydrogenation

Adipic acid, which is an intermediate for nylon 6, 6, is manufactured by the oxidation of cyclohexanone (None), cyclohexanol (Nol) or both. None and Nol are industrially produced by vapor phase ring hydrogenation of phenol over Pd catalysts for which high temperature is employed causing catalyst deactivation due to coke formation. Liquid phase

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hydrogenation under mild conditions is therefore, more desirable. Hence, the ring hydrogenation of phenol was studied over commercially available supported noble metal catalysts in $scCO_2$. The catalyst screening results for phenol hydrogenation with commercially available charcoal-supported metal catalysts at 328 K under 10 MPa of $scCO_2$ are shown in Table 1.[10,11] Rh/C, Ru/C and Pd/C catalysts were active for the ring hydrogenation of phenol to None and Nol. On the other hand, Pt/C, which is an active catalyst for hydrogenation, was inactive in $scCO_2$. It is probable that carbon monoxide, which was formed by the water gas shift reaction during hydrogenation in $scCO_2$, deactivate the platinum sites. Table 1 shows that rhodium is the most active metal for the benzene ring hydrogenation in $scCO_2$ while, Pd was found to be the most active catalyst under non-supercritical conditions. Under the $scCO_2$ conditions, higher hydrogen solubility in $scCO_2$ does contribute to the higher catalyst activity but additionally, the adsorption characteristics of phenol on active metal sites and the electronic structures of metal particles also influence the activity and selectivity behavior in supercritical CO_2 solvent.[10]

Table 1. Catalyst screening for phenol hydrogenation.[a]

Catalyst	Conversion (%)	Selectivity (%) None	Nol	TON
Rh/C	53	17	83	8244
Ru/C	30	5	95	759
Pd/C	3	54	46	304
Pt/C[b]	1	97	3	125

[a] Reaction temperature 328 K, reaction time 2 h, H_2 pressure 10 MPa, CO_2 pressure 10 MPa, [b] Reaction temperature 353 K.

3.2. Alkylphenol Hydrogenation

Stereoselective hydrogenation of 4-*tert*-butylphenol (4-*t*-BP) produces *cis*-4-*tert*-butylcyclohexanol (*c*-4-*t*-BNol), which is an important raw material for the production of perfume and fragrance intermediates.[12] The multiphase hydrogenation of 4-*t*-BP was studied using Rh/C catalyst in $scCO_2$. Table 2 gives the results of the hydrogenation of 4-*t*-BP under 10 MPa of $scCO_2$ and in 2-propanol solvents over 0.02 g of Rh/C at 313 K.[13,14] Hydrogenation of aromatic rings of 4-*t*-BP proceeded and *c*-4-*t*-BNol, *trans*-4-*tert*-butylcyclohexanol (*t*-4-*t*-BNol), 4-*tert*-butylcyclohexanone (4-*t*-BNone) were formed for both the solvent systems. It is noteworthy that higher selectivity to *c*-4-*t*-BNol and higher cis ratio (*c*-4-*t*-BNol/(*c*-4-*t*-BNol + *t*-4-*t*-BNol)*100) were obtained in $scCO_2$ compared with those in 2-propanol. The amounts of undesirable byproduct due to dehydroxylation (*tert*-butylcyclohexane (4-*t*-BH)) and ring-opening reactions in 10 MPa of carbon dioxide was six times lower than those in 2-propanol, indicating that the dehydroxylation could be successfully suppressed in $scCO_2$ solvent.

The hydrogenation of 4-*t*-BNone, which is a partial hydrogenation product from 4-*t*-BP, was also studied over Rh/C under the same reaction conditions (Table 2). The cis ratio obtained for *t*-BNone hydrogenation in $scCO_2$ and in 2-propanol was almost the same as those for 4-*t*-BP hydrogenation. It was confirmed that the hydrogenation of 4-*t*-BP and 4-*t*-None in 2-propanol without hydrogen did not proceed, indicating that hydrogen transfer from 2-propanol did not occur and hydrogen atoms from hydrogen gas reacted with 4-*t*-BP molecules under the reaction conditions.

Figure 3(a) shows the reaction profile for the hydrogenation of 4-*t*-BP in 15 MPa of $scCO_2$ solvent. The ring hydrogenation reaction, *c*-4-*t*-BNol, *t*-4-*t*-BNol, 4-*t*-BNone, and small amounts of other side products (4-*t*-BH and ring-opened alcohol) were formed. The selectivity pattern and cis ratio were almost constant up to 60 min, indicating that 4-*t*-BNols and 4-*t*-BNone were formed directly from 4-*t*-BP. Once most of 4-*t*-BP was hydrogenated (within 60 min), the amount of 4-*t*-BNone decreased and the amounts of *c*-4-*t*-BNol, *t*-4-*t*-BNol increased, indicating that consecutive hydrogenation of 4-*t*-BNon to 4-*t*-BNols proceeded. Small amounts of ring-opened alcohol also were formed after 60 min. It was confirmed separately that the isomerization of *c*-4-*t*-BNol to trans isomer *t*-4-*t*-BNol did not occur under the reaction conditions.

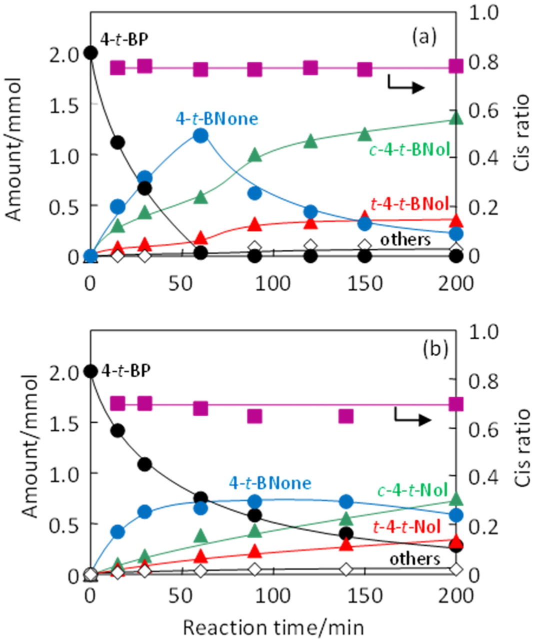


Figure 3. Hydrogenation of 4-*t*-BP over Rh/C in carbon dioxide (15 MPa) (a) and 10 mL of 2-propanol (10 mL) (b) [14]. Catalyst weight, 0.005 g, hydrogen pressure 2 MPa, reaction temperature 313 K.

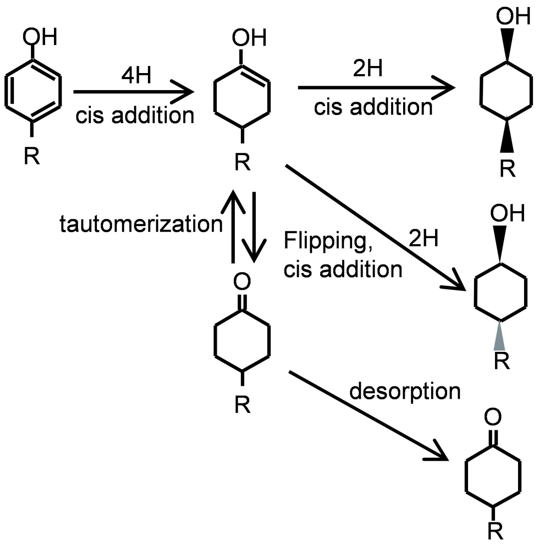
Table 2. Hydrogenation of 4-*tert*-butylphenol (4-*t*-BP) and 4-*tert*-butylcyclohexanone (4-*t*-BPNone) over supproted rhodium catalyst.[a]

Substrate	Solvent	Catalyst [a]	Conversion (%)	Selectivity(%)					cis ratio
				c-4-*t*-BNol	*t*-4-*t*-BNol	*t*-BNone	*t*-BH	Ring-opened alcohol	
4-*t*-BP	CO_2 (10 MPa)	Rh/C	99.9	75.0	20.0	2.7	0.6	1.7	0.79
	2-propanol (10 mL)	Rh/C	99.2	66.4	28.5	1.2	3.8	0.1	0.70
4-*t*-BNone	CO_2 (10 MPa)	Rh/C	85.4	74.8	22.8	-	0.2	2.2	0.77
	2-propanol (10 mL)	Rh/C	99.8	68.8	29.5	-	1.6	0.1	0.70
4-*t*-BP	CO2 (10 MPa)	HCl-Rh/C	99.9	83.5	10.4	2.8	1.1	2.2	0.89
	2-propanol (10 mL)	HCl-Rh/C	99.2	76.2	16.8	1.3	5.7	0.0	0.82

[a] substrate 0.02 g. hydrigen pressure 2 MPa, carbon dioxide pressure 10 MPa, 2-propanol 10 mL, catalyst weight 0.02 g. temperature 313 K, reaction time 60 min.

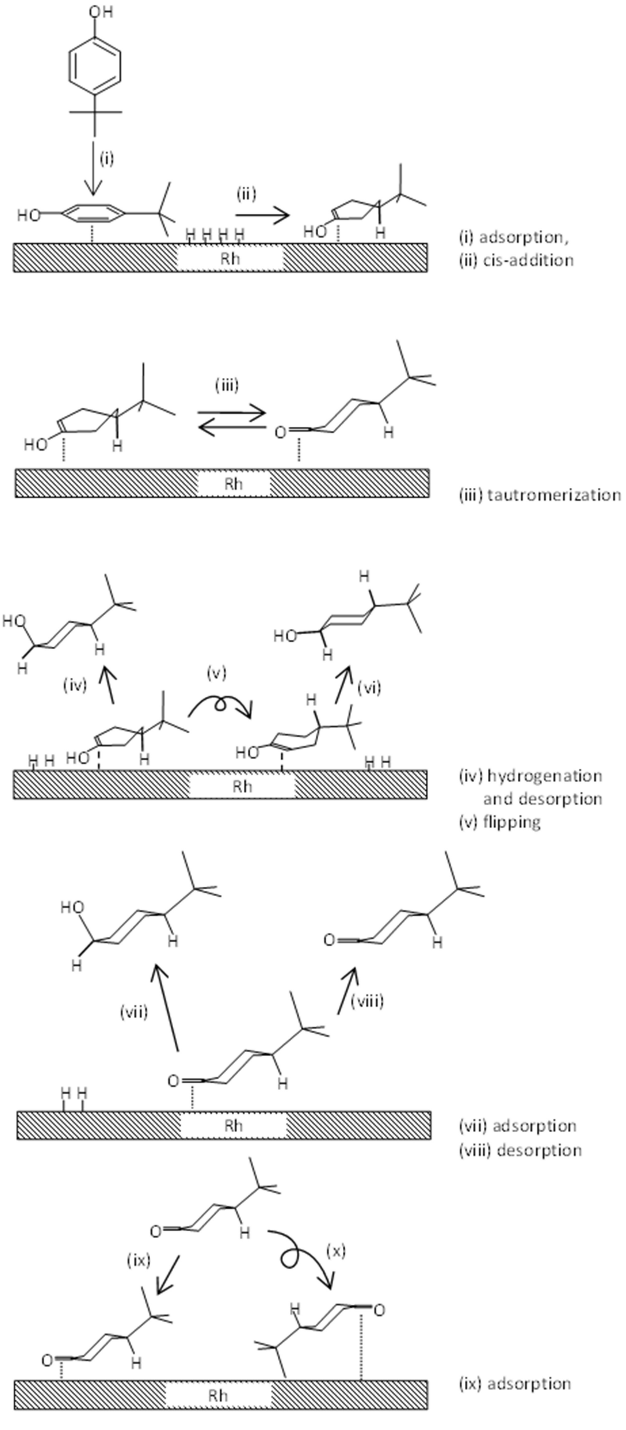
The hydrogenation profile in 10 mL of 2-propanol solvent is shown in Figure 3(b). The initial hydrogenation rate of 4-*t*-BP hydrogenation was half of that in 15 MPa of CO_2. *c*-4-*t*-BNol, *t*-4-*t*-BNol, 4-*t*-BNon, 4-*t*-BH, and ring-opened alcohol also were formed from the beginning of the reaction in 2-propanol. For the parallel hydrogenation of 4-*t*-BP proceeded in 2-propanol; however, the initial selectivity to 4-*t*-BNone (70 %) in 2-propanol was higher than that in the $scCO_2$ (55 %) at the beginning of the reaction. After 40 min, the selectivity to 4-*t*-BNone decreased and that to *c*-4-*t*-BNol and *t*-4-*t*-BNol increased, indicating that the consecutive hydrogenation of 4-*t*-BNone to *c*-4-*t*-BNol and *t*-4-*t*-BNol proceeded simultaneously in the presence of 4-*t*-BP. The cis ratio in 2-propanol was as low as 0.70. It was also confirmed that the isomerization of *c*-4-*t*-BNol to trans isomer did not occur in 2-propanol over Rh/C.

It is reported that partially hydrogenated enol species are formed and they are interconverted rapidly to the corresponding cyclohexanone species[15–17] and cis form of cyclohexanol was formed from the enol species by the cis addition of hydrogen atoms and trans form of cyclohexanol was formed by the flipping of the enol species and the following cis addition of hydrogen atoms for ring hydrogenation of phenols (Scheme 1).



Scheme 1. Hydrogenation of aromatic compounds over metal catalyst.

The reaction pathway of 4-*t*-BP hydrogenation over active rhodium sites is shown in Scheme 2. 4-*t*-BP molecules adsorbed on rhodium surface (i) are partially hydrogenated to 4-*tert*-butylcyclohexene-1-ol (4-*t*-BEnol) by the cis addition of four hydrogen atoms (ii). 4-*t*-BEnol adsorbed species are in equilibrium with 4-*t*-BNone (tautomerization) (ii). 4-*t*-BEnol adsorbed species are hydrogenated to *c*-4-*t*-BNnol by the cis addition of hydrogen atoms (iv), or alternatively, is flipped over (v) and hydrogenated to *t*-4-*t*-Bnol (vi). 4-*t*-BNone also is either hydrogenated to *c*-4-*t*-BCNol or desorbed from the surface (viii). The final cis ratio values for the hydrogenation of 4-*t*-BP and 4-*t*-BNone were almost the same, indicating that reaction steps in the hydrogenation of 4-*t*-BNone are the same as those of 4-*t*-BNone formed by the tautomerization from 4-*t*-BEnol in the hydrogenation of 4-*t*-BP. 4-*t*-BNone would adsorb on active sites in its chair form



Scheme 2. Proposed mechanism for of 4-*tert*-butylphenol hydrogenation over charcoal-supported rhodium catalyst.

with the *tert*-butyl group in an equatorial position (ix) and would not readsorb after flipping over, due to the steric hindrance of the *tert*-butyl group (x). This reaction scheme shows that the adsorption of the intermediate of 4-*t*-BEnol species is critical for the cis selectivity. For the hydrogenation of 4-*t*-BP, the cis ratio of 4-*t*-BNol in $scCO_2$ was higher than those in 2-propanol. The high selectivity in $scCO_2$ is because of (1) the higher concentration of hydrogen atoms on rhodium sites in $scCO_2$ than in 2-propanol solvent under the same hydrogen pressure, because of the greater solubility of hydrogen in $scCO_2$ and (2) the suppression of the flipping of adsorbed 4-*t*-BEnol in $scCO_2$ because of the lower solubility of adsorbed 4-*t*-BEnol species compared with that in 2-propanol.

It is a unique feature of $scCO_2$ solvent that the solubility of reactants can be enhanced by the increase of carbon dioxide densities. Figure 4 shows the carbon dioxide pressure on 4-*t*-BP hydrogenation over Rh/C. The conversion of 4-*t*-BP increased; however, cis ratio decreased with an increase in carbon dioxide pressure. Direct observation using a view cell showed that 4-*t*-BP was dissolved in 10 MPa of $scCO_2$ and 2 MPa of hydrogen at 313 K, and most of 4-*t*-BP was dissolved in 25 MPa of carbon dioxide and 2 MPa of hydrogen pressure. The higher solubility of 4-*t*-BP at higher carbon dioxide pressures enhanced hydrogenation activities and decreased the cis ratio.

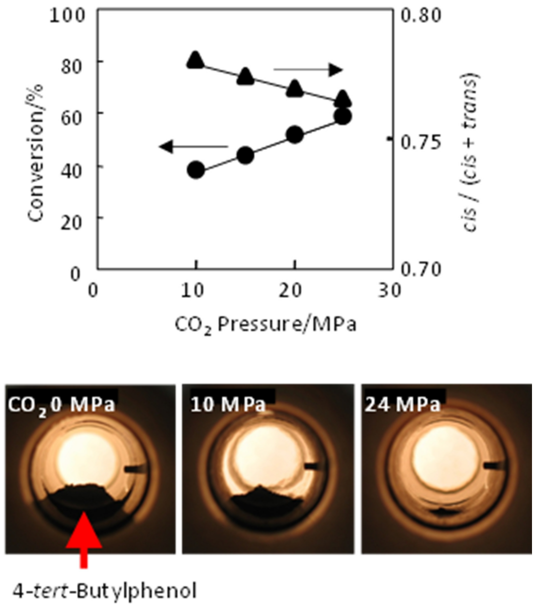


Figure 4. Carbon dioxide pressure effect on 4-*tert*-butylphenol hydrogenation over charcoal-supported rhodium catalyst and phase of 4-*tert*-butylphenol under 2 MPa of hydrogen at 313 K in carbon dioxide.

The decrease in the cis ratio at higher carbon dioxide pressures would be caused by the enhanced flipping of 4-*t*-BEnol because of the higher solubility of 4-*t*-BEnol at higher carbon dioxide pressures. This higher cis selectivity over Rh/C in $scCO_2$ than in 2-propanol was also observed for

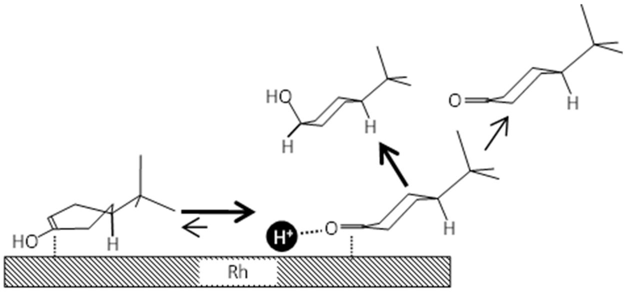
Table 3. Hydrogenation of 4-alkylphenol over Rh/C.[a]

Alkyl group	Solvent	Conversion (%)	Selectivity				cis ratio
			c-4-RNol	*t*-4-RNol	t-RNone	4-RXne	
Cyclohexyl	CO_2 (15 MPa)	99.9	74.5	21.5	1.3	2.1	0.77
	2-propanol (10 mL)	99.8	58.7	28.6	0.2	12.5	0.67
tert-Butyl	CO_2 (15 MPa)	99.9	75.0	20.0	2.7	0.6	0.79
	2-propanol (10 mL)	99.2	66.4	28.5	1.2	3.8	0.70
sec-Butyl	CO2 (10 MPa)	99.9	77.5	20.0	0.8	1.3	0.80
	2-propanol (10 mL)	99.9	65.3	23.6	0.2	10.8	0.73
n-Butyl	CO_2 (10 MPa)	99.9	75.3	22.3	1.3	2.3	0.77
	2-propanol (10 mL)	99.9	59.2	26.8	0.2	13.5	0.69
iso-Propyl	CO_2 (10 MPa)	100	76.6	21.2	0.5	1.0	0.78
	2-propanol (10 mL)	99.9	66.6	24.4	0.1	8.7	0.73
n-Propyl	CO_2 (10 MPa)	99.9	76.0	21.4	0.7	1.4	0.78
	2-propanol (10 mL)	99.9	59.3	26.8	0.2	13.6	0.69
Ethyl	CO_2 (10 MPa)	100	73.7	23.1	0.5	1.3	0.76
	2-propanol (10 mL)	99.8	60.1	26.1	0.1	12.6	0.70
Methyl	CO_2 (10 MPa)	100	72.7	22.3	3.0	1.5	0.77
	2-propanol (10 mL)	99.9	63.5	24.5	0.1	11.7	0.72

[a] substrate 0.02 mmol; initial H_2 pressure 2 MPa, temperature 313 K, reaction time 60 min.

hydrogenation for several types of alkylphenol. Table 3 shows the hydrogenation of several 4-alkylphenols (4-RP) in $scCO_2$ and in 2-propanol. Higher selectivity to *cis*-4-alkylcyclohexanol (*c*-4-RNol) was obtained in $scCO_2$ than in 2-propanol for the hydrogenation of all 4-RP substrates tested.[18,19] The selectivity to alkylcyclohexane (4-RX) in $scCO_2$ was much lower than that in 2-propanol, indicating that dehydroxylation was suppressed in $scCO_2$. The cis ratios for various 4-RP hydrogenations obtained in $scCO_2$ were in the range of 0.76–0.80, while those in 2-propanol were in the range of 0.67–0.73. Hydrogenation of 4-RP having branched alkyl groups showed slightly higher cis ratio than those having normal alkyl groups in both $scCO_2$ and 2-propanol.

The addition of protonic acids to the catalyst systems is known to be effective to enhance the cis-selectivity of the 4-RP hydrogenation.[8] Table 4 also shows the hydrogenation of 4-RP over hydrochloric acid modified Rh/C (HCl–Rh/C) catalyst in $scCO_2$ and 2-propanol.[18] It should also be noted that higher cis ratio values were obtained in $scCO_2$ than in 2-propanol with HCl–Rh/C. The XPS analysis of the HCl–Rh/C catalyst before and after the treatment with $scCO_2$ and 2-propanol showed that most of hydrochloric acid remained on the catalyst surface after $scCO_2$ treatment, whereas a major part of hydrochloric acid was leached in 2-propanol because of the lower solubility of HCl into $scCO_2$.[13] The cis ratio with HCl–Rh/C did not change during the direct hydrogenation and the consecutive hydrogenation, and it was higher than that with Rh/C. The higher cis ratio obtained by adding hydrochloric acid can be explained by (1) the strong adsorption of 4-*t*-BNone, which is hydrogenated to only the cis isomer and/or (2) the promotion of hydrogenation of adsorbed 4-*t*-BNone to the cis isomer. These effects are caused by the interaction of protons with oxygen atoms of 4-*t*-BNone (Scheme 3).



Scheme 3. Proposed mechanism for of 4-*tert*-butylphenol hydrogenation over HCl-modified charcoal-supported rhodium catalyst.

3.3. Naphthalene Hydrogenation

Catalyst screening results showed that Rh/C was the most active for the naphthalene (Naph) hydrogenation in $scCO_2$.[16] In the hydrogenating of naphthalene in $scCO_2$ solvent, tetrahydronaphthalene (Tetra), octahydronaphthalene (Octa), *cis*-decahydronaphthalene (*c*-Deca) and *trans*-decahydronaphthalene (*t*-Deca) were obtained as hydrogenated products. We could not determine the position of carbon-carbon double bond in Octa. Among all the catalysts screened in this work, the Rh/C was also the most active for the ring hydrogenation of Naph in $scCO_2$ solvent.

Figure 5(a) shows the reaction profile of hydrogenation of Naph over the Rh/C catalyst under 10 MPa of $scCO_2$ solvent.

Table 4. Hydrogenation of 4-alkylphenol over HCl–Rh/C.[a]

Alkyl group	Solvent	Conversion (%)	Selectivity				cis ratio
			c-4-RNol	*t*-4-RNol	*t*-RNone	4-REne	
tert-Butyl	CO_2 (15 MPa)	99.9	83.5	10.4	2.8	1.1	0.89
	2-propanol (10 mL)	99.2	76.2	16.8	1.3	5.7	0.82
sec-Butyl	CO_2 (10 MPa)	99.9	85.8	10.5	0.2	3.0	0.89
	2-propanol (10 mL)	99.8	71.2	14.6	0.1	14.0	0.83
n-Butyl	CO_2 (10 MPa)	99.9	73.7	15.0	2.2	8.5	0.83
	2-propanol (10 mL)	99.9	62.3	17.9	0.2	19.3	0.78
iso-Propyl	CO_2 (10 MPa)	99.9	84.4	11.7	0.2	3.0	0.88
	2-propanol (10 mL)	99.9	73.1	15.3	0.1	11.4	0.83
n-Propyl	CO_2 (10 MPa)	97.6	72.9	12.8	8.0	5.9	0.85
	2-propanol (10 mL)	99.8	63.2	17.7	0.2	18.8	0.78

[a] substrate 0.02 mmol; initial H_2 pressure 2 MPa, temperature 313 K, reaction time 60 min.

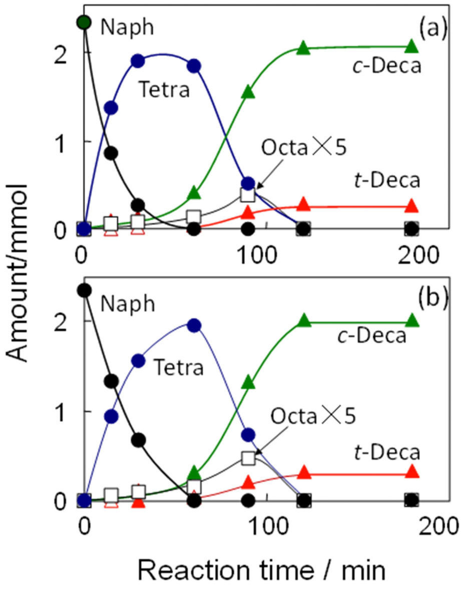


Figure 5. Naphthalene hydrogenation over Rh/C (0.010 g) under 3 MPa of hydrogen in 10 MPa of $scCO_2$ (a) and in 10 mL of *n*-heptane at 313 K.

As the amount of Naph decreasing, Tetra, which is a partially ring hydrogenated compound, was formed simultaneously from the beginning of the reaction. After most of Naph was consumed, the amount of Tetra decreased, and those of Octa, *c*-Deca and *t*-Deca increased, indicating that the hydrogenation of Naph to Deca proceeded consecutively through the hydrogenation of Tetra and Octa. After most of Tetra and Octa were hydrogenated, the amounts of *c*-Deca and *t*-Deca did not change and the final cis ratio (*c*-Deca/*c*-Deca + *t*-Deca) was as high as 0.88.[20] It was confirmed that the isomerization of *c*-Deca did not proceed over Rh/C under these reaction condition.[21]

The hydrogenation of Naph over the Rh/C catalyst in *n*-heptane is also shown in Figure 5(b). Naph was also completely converted to Deca over the Rh/C catalyst in *n*-heptane and the final cis ratio in *n*-heptane was 0.86, which is slightly lower than that obtained in $scCO_2$.

The hydrogenation of Tetra was also studied in $scCO_2$. Figure 6 shows the Tetra hydrogenation profile over Rh/C under 3 MPa of hydrogen in 10 MPa of scCO2 solvent.[22] The initial Tetra hydrogenation rate was almost the same as the Tetra hydrogenation in Naph hydrogenation. The final cis ratio was 0.88, was the same as that obtained in Naph hydrogenation. Similar Tetra hydrogenation rates and final cis ratio in Figures 5 and 6 indicate that hydrogenation of Naph is a consecutive reaction via Tetra in $scCO_2$ solvent

It has been reported that *c*-Deca is formed by the hydrogenation of Tetra adsorbed on metal sites while, *t*-Deca

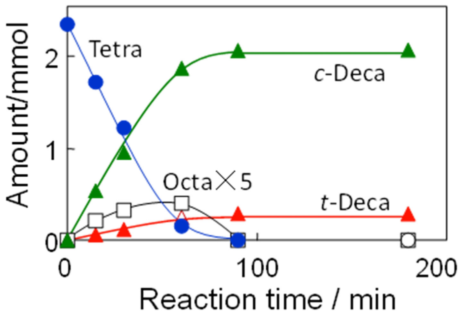
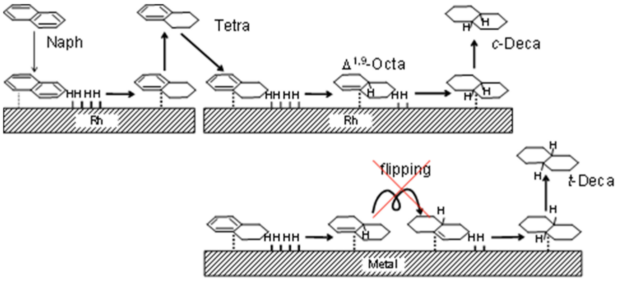


Figure 6. Tetralin hydrogenation over Rh/C (0.010 g) under 3 MPa of hydrogen and 10 MPa of carbon dioxide at 313 K in 10 MPa of $scCO_2$ (a) and in 10 mL of *n*-heptane.

is formed via flipping of the intermediate 2,3,4,5,6,8,10-octahydronaphthalene ($\Delta^{1,9}$-Octa), in which it desorbs from the metal surface and immediately readsorbs on its other side, followed by its further hydrogenation to give *t*-Deca.[23] Scheme 4 shows the reaction mechanism of Naph hydrogenation on Rh/C. Similar to the ring hydrogenation of 4-*t*-BP at low temperature described in section 3.2, higher cis ratio was obtained for hydrogenations of Naph and Tetra in $scCO_2$ solvent than organic solvents. Higher hydrogen atom concentration on rhodium sites could enhance the cis addition of hydrogen atom to the surface intermediate and lower solubility of surface intermediate would retard the flipping of the intermediate.



Scheme 4. Formation of *c*-Deca (a) and *t*-Deca via $\Delta^{1,9}$-Octa in Naph hydrogenation.

4. Summary

Multi-phase hydrogenation with supported rhodium catalysts and supercritical carbon dioxide solvent was effective to give higher reaction rates and higher cis ratio for ring hydrogenation of aromatic compounds.

References

[1] Paul N. Rylander, "Hydrogenation and Dehydrogenation" in *Ullmann's Encyclopedia of Industrial* Chemistry, Wiley-VCH, Weinheim, **2005**. doi:10.1002/14356007.a13_487.

[2] P. G. Jessop, W. Leitner in *Chemical Synthesis Using Supercritical Fluids* (Eds.: P. G. Jessop, W. Leitner), Wiley, New York, **1999**.

[3] A. Baiker, *Chem. Rev.* **1999**, *99*, 453–474.

[4] M. Arai, S. Fujita, M. Shirai, *J. Supercrit. Fluids* **2009**, *47(3)*, 351–356.

[5] B. Subramanian, C. J. Cyon, V. Avunajatesun, *Appl. Catal. B* **2002**, *37*, 279–292.

[6] P. Licence, J. Ke, M. Sokolave, S. K. Ross, M. Poliakoff, *Green Chem.* **2003**, *5*, 99–104.

[7] M. Burgener, D. Ferri, J. D. Grunwaldt, T. Mallat, A. Baiker, *J. Catal.* **2005**, *109*, 16794–16800.

[8] J. Kobayashi, Y. Mori, S. Kobayashi, *Chem. Commun.* **2005**, 2567–2568.

[9] T. Sato, C. V. Rode, O. Sato, M. Shirai, *Appl. Catal. B* **2004**, *49(3)*, 181–185.

[10] C. V. Rode, U. D. Joshi, O. Sato, M. Shirai, *Chem. Commun.* **2003**, 1960–1961.

[11] C. V. Rode, U. D. Joshi, T. Sato, O. Sato, M. Shirai, *Stud. Surf. Sci. Catal.* **2004**, *153*, 385–388.

[12] M. Sekiguchi, S.Tanaka, Jpn. Patent 3528519, 2004.

[13] N. Hiyoshi, E. Mine, C. V. Rode, O. Sato, T. Ebina, M. Shirai, *Chem. Lett.* **2006**, *35(9)*, 1060–1061.

[14] N. Hiyoshi, C. V. Rode, O. Sato, H. Tetsuka, M. Shirai, *J. Catal.* **2007**, *252(1)*, 57–68.

[15] H. A. Smith, B. L. Stump, *J. Am. Chem. Soc.* **1961**, *83*, 2739–2743.

[16] S. R. Konuspaev, K. N. Zhanbekov, N. V. Kul'kova, D. Y. Murzin, *Chem. Eng. Technol.* **1997**, *20*, 144–148.

[17] S. Siegel, G. V. Smith, B. Dmuchovsky, D. Dubbell, W. Halpern, *J. Am. Chem. Soc.* **1962**, *84*, 3136–3139.

[18] N. Hiyoshi, K. K. Bando, O. Sato, A. Yamaguchi, C. V. Rode, M. Shirai, *Catal. Commun.* **2009**, *10(13)*, 1702–1705.

[19] N. Hiyoshi, O. Sato, A. Yamaguchi, C. V. Rode, M. Shirai, *Green Chem.* **2012**, *14*, 638–633.

[20] N. Hiyoshi, M. Osada, C. V. Rode, O. Sato, M. Shirai, *Appl. Catal. A* **2007**, *331*, 1–7.

[21] N. Hiyoshi, E. Mine, C. V. Rode, O. Sato, M. Shirai, *Chem. Lett.* **2006**, *35*, 188–189.

[22] N. Hiyoshi, E. Mine, C. V. Rode, O. Sato, M. Shirai, *Appl. Catal. A* **2006**, *310*, 194–98.

[23] W. Weitkamp, *Adv. Catal.* **1968**, *18*, 1–110.

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PERSONAL ACCOUNT

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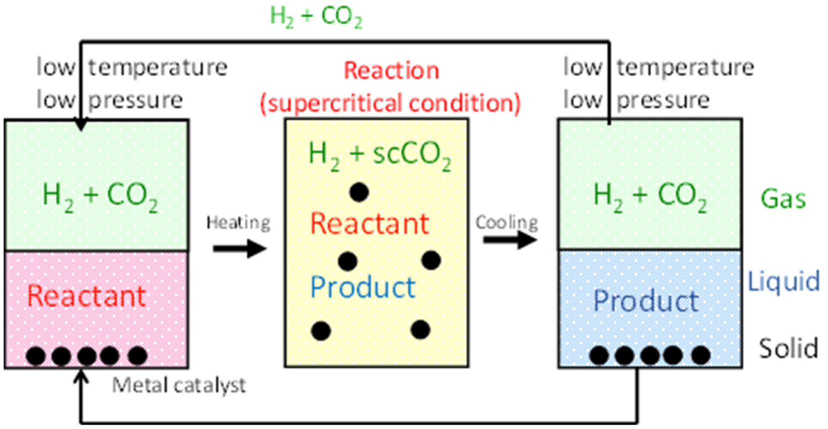
Stereoselective Aromatic Ring Hydrogenation over Supported Rhodium Catalysts in Supercritical Carbon Dioxide Solvent



In this account, show stereoselective ring hydrogenations of aromatic compounds over supported rhodium metal catalysts in supercritical carbon dioxide. Higher solubility of hydrogen in supercritical carbon dioxide provides higher hydrogen concentration on rhodium surface, but lower that of the intermediate on rhodium surface, which suppresses the flipping of surface intermediate, gave higher catalyst activities and cis selectivities to the corresponding ring-hydrogenated products as compared with those in organic solvents.