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Stereoselective hydrogenation of *tert*-butylphenols over charcoal-supported rhodium catalyst in supercritical carbon dioxide solvent

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Abstract

Hydrogenation of 2-, 3-, and 4-*tert*-butylphenols was studied over a charcoal-supported rhodium catalyst in supercritical carbon dioxide (scCO_2) solvent, and the results were compared with those in organic solvents. In the hydrogenation of 4-*tert*-butylphenol, a higher cis ratio for 4-*tert*-butylcyclohexanol (0.79) was obtained in scCO_2 (10 MPa) than in 2-propanol (0.70) and cyclohexane (0.64) under similar conditions of hydrogen pressure (2 MPa) and temperature (313 K). In the case of 2-*tert*-butylphenol, the cis ratio for 2-*tert*-butylcyclohexanol was as high as 0.95 in both scCO_2 and 2-propanol (hydrogen pressure, 2 MPa; reaction temperature, 313 K). In the case of hydrogenation of 3-*tert*-butylphenol, the cis ratio decreased with the progression of consecutive hydrogenation of 3-*tert*-butylcyclohexanone intermediate. In addition, the stereoselectivity to *cis*-*tert*-butylcyclohexanols in scCO_2 was improved in the presence of hydrochloric acid. It was found that the protons of hydrochloric acid accelerated the hydrogenation of the intermediates, *tert*-butylcyclohexanones, to the corresponding *cis*-*tert*-butylcyclohexanols. The hydrogenation mechanism of *tert*-butylphenols, particularly the enhanced selectivity to *cis*-*tert*-butylcyclohexanols in scCO_2, is postulated based on the observed reaction profiles.

Keywords: Supercritical carbon dioxide solvent; Stereoselective hydrogenation; *tert*-Butylcyclohexanol; Charcoal-supported rhodium catalyst

1. Introduction

The stereoselective hydrogenation of various *tert*-butylphenols to the corresponding *tert*-butylcyclohexanols is of commercial interest because the cis forms of 4-*tert*-butylcyclohexanol [1] and 2-*tert*-butylcyclohexanol [2], and the trans form of 3-*tert*-butylcyclohexanol [3] are useful intermediates for the fragrance and perfumery industry. *cis*-4-*tert*-Butylcyclohexanol is usually synthesized by the liquid-phase hydrogenation of 4-*tert*-butylphenol over supported metal catalysts in organic solvents [1,4–9]; however, trans isomer is also formed simultaneously as a byproduct. In addition, an energy-intensive distillation process is mandatory for the separation of products from solvents. Kalantar et al. reported the vapor-phase hydrogenation of 4-*tert*-butylphenol over silica-supported platinum catalysts; however, the cis ratio [*cis*-4-*tert*-butylcyclohexanol/(*cis*- + *trans*-4-*tert*-butylcyclohexanol)] obtained was as low as 0.47, and the catalysts were deactivated rapidly at reaction temperatures above 400 K [10]. *cis*-2-*tert*-Butylcyclohexanol is usually synthesized by the hydrogenation of 2-*tert*-butylphenol over metal catalysts in organic solvents or under neat conditions at temperatures above 393 K [6,11–15]; however, a lower reaction temperature is desired for preventing catalyst deactivation and obtaining a high cis ratio. Liquid-phase hydrogenation of 3-*tert*-butylphenol in 2-propanol has been reported [3] with a selectivity to *trans*-3-*tert*-butylcyclohexanol as 0.75. In this case, improved selectivity to *trans*-3-*tert*-butylcyclohexanol also is desired.

The addition of protonic acids to the catalyst systems is known to be effective in controlling the stereoselectivity of 3- and 4-*tert*-butylphenol hydrogenation in organic solvents [1,3,7,8]. The cis ratio has been found to increase by the addition of a protonic acid in 4-*tert*-butylphenol hydrogenation [1,7,8]

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whereas the cis ratio is known to decrease in 3-*tert*-butylphenol hydrogenation [3]. However, the roles of such acid additives have not yet been addressed in detail.

It is well known that organic synthesis using solid catalysts and supercritical carbon dioxide ($scCO_2$) solvent have several advantages, including (i) a high reaction rate due to increased solubility of reactant gases in supercritical fluids, thereby eliminating mass transfer resistance; (ii) elimination of reactions with solvents, such as alcoholysis; and (iii) easy separation of solid catalysts and products [16–20]. Moreover, we have already reported that the $scCO_2$ solvent is very effective for the stereoselective ring hydrogenation of naphthalene and tetralin to *cis*-decalin [21–24] and that of 4-*tert*-butylphenol to *cis*-4-*tert*-butylcyclohexanol [25]. In continuation of our earlier work, here we report a detailed study of the hydrogenation of 2-, 3-, and 4-*tert*-butylphenols over a charcoal-supported rhodium catalyst in $scCO_2$. We also explore the hydrogenation mechanism of *tert*-butylphenols and the enhanced stereoselectivity to the corresponding *cis*-*tert*-butylcyclohexanols in $scCO_2$, along with the enhanced cis-selectivity achieved by the addition of hydrochloric acid.

2. Experimental

A charcoal-supported rhodium catalyst (Rh/C) with metal loading of 5 wt% (Wako Pure Chemical Ind. Ltd., Japan) was used without further treatment. The dispersion value of rhodium metal particles on charcoal, determined by a hydrogen adsorption method using a Quantachrome Autosorb-1C device, was 12% [26]. Charcoal-supported rhodium catalysts containing hydrochloric acid (HCl–Rh/C) were prepared by mixing 36% hydrochloric acid aqueous solution and Rh/C in a sealed vial (0.0066–0.132 g of 36% hydrochloric acid per 1 g of Rh/C). XPS (Ulvac PHI, 5601ci) analysis was applied to determine the amount of chloride species present on the HCl–Rh/C catalysts. 4-*tert*-Butylphenol (Aldrich, 99%), 4-*tert*-butylcyclohexanone (Aldrich, 99%), 2-*tert*-butylphenol (Aldrich, 99%) and 3-*tert*-butylphenol (Tokyo Kasei, 99%) were used as received. The weighed amounts of catalyst and substrate (typically 2.0 mmol) were placed in a stainless steel high-pressure reactor (50 mL capacity), and the reactor was flushed three times with carbon dioxide. Once the desired temperature was attained in an oil bath, hydrogen and then carbon dioxide were introduced into the reactor to the desired pressure levels and the contents were stirred magnetically. After the reaction was completed, the reactor was rapidly cooled in an ice bath, the pressure was slowly released, and the contents were discharged to separate the catalyst by simple filtration. The unreacted substrate and the products were recovered with acetone, which showed a material balance of >95%. 2-Propanol (Wako Pure Chemical Ind. Ltd., Japan) was used as a solvent for studying liquid-phase hydrogenation under 2 MPa of hydrogen and 0.1 MPa of carbon dioxide. The quantitative analysis was conducted by GC-FID (HP-6890) and GC-MS (HP-6890 and 5973) equipped with a DB-WAX capillary column. Conversion, selectivity, and cis ratio were defined as follows:

$$\text{conversion (\%)} = \frac{\text{sum of products (mol)}}{\text{sum of products (mol)} + \text{unreacted substrate (mol)}} \times 100,$$

$$\text{selectivity (\%)} = \frac{\text{each product (mol)}}{\text{sum of products (mol)}} \times 100,$$

$$\text{cis ratio} = \frac{\textit{cis-tert}\text{-butylcyclohexanol (mol)}}{\textit{cis-tert}\text{-butylcyclohexanol (mol)} + \textit{trans-tert}\text{-butylcyclohexanol (mol)}} \times 100.$$

3. Results and discussion

3.1. Hydrogenation of 4-tert-butylphenol over Rh/C

Table 1 gives the results of the hydrogenation of 4-*tert*-butylphenol in $scCO_2$ (10 MPa), 2-propanol, and cyclohexane over 0.02 g of Rh/C at 313 K. Higher selectivity to *cis*-4-*tert*-butylcyclohexanol and a higher cis ratio were obtained in $scCO_2$ compared with those in 2-propanol and cyclohexane. The selectivity to *tert*-butylcyclohexane in $scCO_2$ was six times lower than that in 2-propanol and three times lower than that in cyclohexane, indicating suppressed dehydroxylation in $scCO_2$. However, small amounts of other byproducts (ring-opened alcohol compounds, based on the retention time detected by GC analysis) were formed in $scCO_2$. We studied the reactions of 4-*tert*-butylphenol and 4-*tert*-cyclohexanone in 2-propanol over 0.02 g of Rh/C at 313 K without hydrogen and found that the hydrogenation did not proceed, indicating that hydrogen transfer from 2-propanol did not occur.

Fig. 1a shows the reaction profile for the hydrogenation of 4-*tert*-butylphenol over 0.005 g of Rh/C in 15 MPa of carbon dioxide at 313 K. From the beginning of the reaction, *cis*-, *trans*-4-*tert*-butylcyclohexanol, 4-*tert*-butylcyclohexanone, and small amounts of other products (*tert*-butylcyclohexane and ring-opened alcohol) were formed with selectivities of 35, 10,

Table 1
Hydrogenation of 4-*tert*-butylphenol over Rh/C[a]

Solvent	Conversion (%)	Selectivity (%)					Cis ratio
		cis-4-*tert*-Butylcyclohexanol	*trans*-4-*tert*-Butylcyclohexanol	4-*tert*-Butylcyclohexanone	*tert*-Butylcyclohexane	Ring-opened alcohols	
Carbon dioxide (10 MPa)	99.9	75.0	20.0	2.7	0.6	1.7	0.79
2-Propanol (10 mL)	99.2	66.4	28.5	1.2	3.8	0.1	0.70
Cyclohexane (10 mL)	99.9	62.9	35.0	0.7	1.4	0.0	0.64

[a] Substrate 2.00 mmol; partial hydrogen pressure 2 MPa; catalyst weight 0.02 g; temperature 313 K; reaction time 60 min.

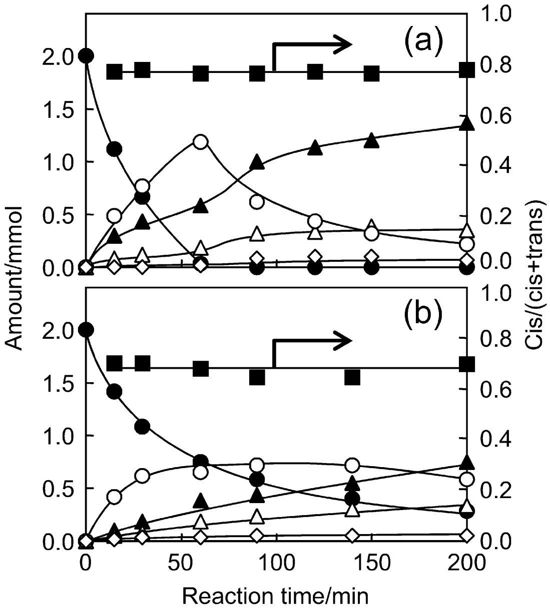


Fig. 1. Hydrogenation of 4-*tert*-butylphenol over Rh/C in 15 MPa of carbon dioxide (a) and 10 mL of 2-propanol (b). Amounts of 4-*tert*-butylphenol (●), 4-*tert*-butylcyclohexanone (○), *cis*-4-*tert*-butylcyclohexanol (▲), *trans*-4-*tert*-butylcyclohexanol (△), others (◇), and cis ratio of 4-*tert*-butylcyclohexanol (■). Catalyst weight, 0.005 g; partial hydrogen pressure, 2 MPa; reaction temperature, 313 K.

55, and 0.5%, respectively. The selectivity pattern was almost constant up to 60 min, indicating that 4-*tert*-butylcyclohexanols and 4-*tert*-butylcyclohexanone were formed directly from 4-*tert*-butylphenol up to 60 min. Once most of 4-*tert*-butylphenol was hydrogenated (within 60 min), the amount of 4-*tert*-butylcyclohexanone decreased and the amounts of *cis*- and *trans*-4-*tert*-butylcyclohexanol increased, indicating consecutive hydrogenation of 4-*tert*-butylcyclohexanone to *cis*- and *trans*-4-*tert*-butylcyclohexanol. Small amounts of ring-opened alcohol also were formed after 60 min. The cis ratio was almost constant at 0.77 from the beginning of reaction up to 200 min. It was confirmed separately that the isomerization of *cis*-4-*tert*-butylcyclohexanol to trans isomer did not occur under hydrogen and carbon dioxide pressures of 2 and 15 MPa, respectively, at 313 K.

We also studied the hydrogenation profile in 2-propanol solvent (Fig. 1b), and found that the initial rate of 4-*tert*-butylphenol hydrogenation was half of that in $scCO_2$ (15 MPa). *cis*-, *trans*-4-*tert*-Butylcyclohexanol, 4-*tert*-butylcyclohexanone, and other products (*tert*-butylcyclohexane and ring-opened alcohol) also were formed from the beginning of the reaction in 2-propanol with selectivities of 19, 8, 70, and 3%, respectively. The parallel hydrogenation of 4-*tert*-butylphenol proceeded in 2-propanol; however, the initial selectivity to 4-*tert*-butylcyclohexanone (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-*tert*-butylcyclohexanone decreased and that to *cis*- and *trans*-4-*tert*-butylcyclohexanol increased, indicating that the consecutive hydrogenation of 4-*tert*-butylcyclohexanone to *cis*- and *trans*-4-*tert*-butylcyclohexanol proceeded simultaneously in the presence of 4-*tert*-butylphenol. The cis ratio of *tert*-butylcyclohexanol in 2-propanol was as low as 0.70, comparable to that reported by Konuspaev et al. [4] in the hydrogenation of 4-*tert*-butylphenol over a charcoal-supported rhodium catalyst in 2-propanol. Another experiment confirmed that the isomerization of *cis*-4-*tert*-butylcyclohexanol to trans isomer did not occur in 2-propanol under 2 MPa of hydrogen at 313 K over Rh/C.

We also examined the hydrogenation of the intermediate, 4-*tert*-butylcyclohexanone, over Rh/C in $scCO_2$ (10 MPa) as well as in 2-propanol under 2 MPa of hydrogen pressure at 313 K (Table 2). The cis ratios obtained in $scCO_2$ (0.77) and 2-propanol (0.70) at 10 MPa were similar to those values obtained for the hydrogenation of 4-*tert*-butyphenol in $scCO_2$ and 2-propanol (Table 1).

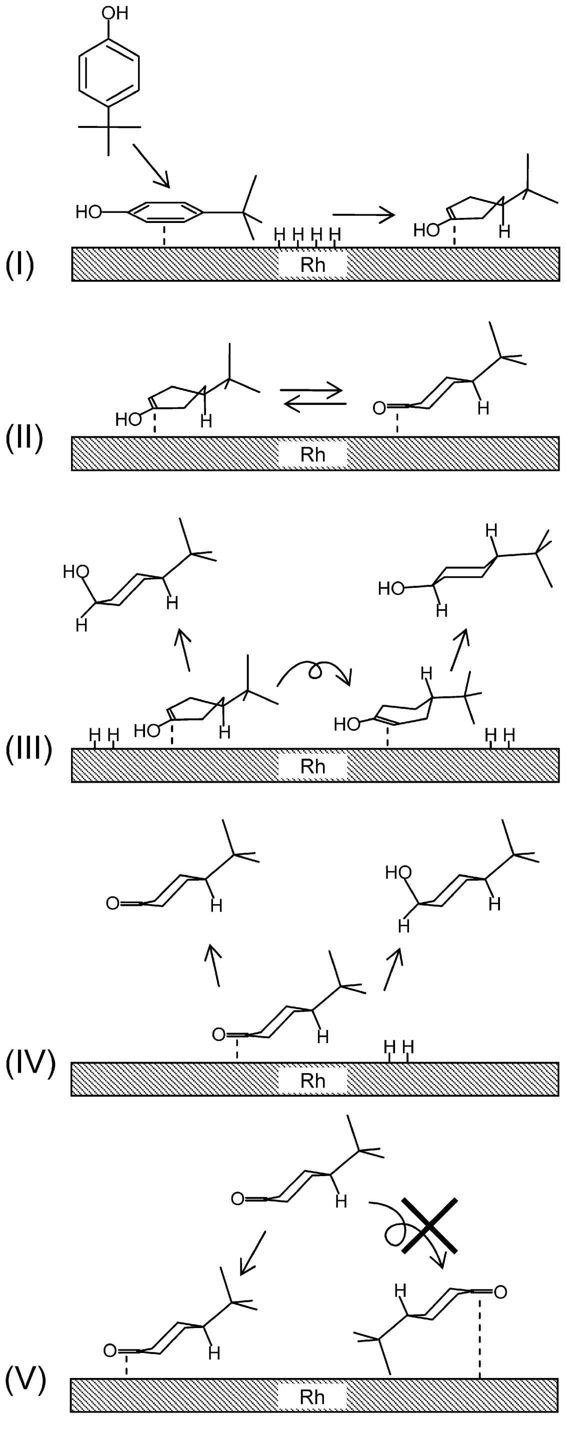
It has been reported that cyclohexenols (enol forms) are formed by the partial hydrogenation of benzene rings and interconvert rapidly (tautomerization) with the corresponding cyclohexanones in the hydrogenation of phenols [27,28]. It also has been reported that the trans isomer of hydrogenated products is formed by the cis addition of hydrogen and the flipping of intermediate cyclohexene species in the hydrogenation of aromatic hydrocarbons [29,30]. On the basis of these previous reports, we propose 4-*tert*-butylphenol hydrogenation steps on active sites as Scheme 1. 4-*tert*-Butylphenol molecules adsorbed on rhodium surface are partially hydrogenated to 4-*tert*-butylcyclohexene-1-ol (enol) by the cis addition of four hydrogen atoms (step I). 4-*tert*-Butylcyclohexene-1-ol adsorbed species are in equilibrium with 4-*tert*-butylcyclohexanone (tautomerization) (step II). 4-*tert*-Butylcyclohexene-1-ol adsorbed species are hydrogenated to *cis*-4-*tert*-butylcyclohexanol by the cis addition of hydrogen atoms, or, alternatively, is flipped over and hydrogenated to *trans*-4-*tert*-butylcyclohexanol (step III). 4-*tert*-Butylcyclohexanone also is either hydrogenated to *cis*-4-*tert*-butylcyclohexanol or desorbed from the surface (step IV).

The final cis ratio values for the hydrogenation of 4-*tert*-butylphenol and 4-*tert*-butylcyclohexanone were almost the same, indicating that reaction steps in the hydrogenation of 4-*tert*-butylcyclohexanone are the same as those of 4-*tert*-butylcyclohexanone formed by the tautomerization from 4-*tert*-

Table 2
Hydrogenation of 4-*tert*-butylcyclohexanone over Rh/C[a]

Solvent	Conversion (%)	Selectivity (%)				Cis ratio
		cis-4-*tert*-Butylcyclohexanol	*trans*-4-*tert*-Butylcyclohexanol	*tert*-Butylcyclohexane	Ring-opened alcohols	
Carbon dioxide (10 MPa)	85.4	74.8	22.8	0.2	2.2	0.77
2-Propanol (10 mL)	99.8	68.8	29.5	1.6	0.1	0.70

[a] Substrate 2.00 mmol; partial hydrogen pressure 2 MPa; catalyst weight 0.02 g; temperature 313 K; reaction time 60 min.



Scheme 1. Hydrogenation of 4-*tert*-butylphenol over Rh/C.

butylcyclohexene-1-ol in the hydrogenation of 4-*tert*-butylphenol. 4-*tert*-Butylcyclohexanone would adsorb on active sites in its chair form with the *tert*-butyl group in an equatorial position and would not readsorb after flipping over, due to the steric hindrance of the *tert*-butyl group (step V).

For the hydrogenation of 4-*tert*-butylphenol, the cis ratio of 4-*tert*-butylcyclohexanol in $scCO_2$ was higher than in 2-propanol. We previously reported that the concentration of hydrogen atoms on active sites in $scCO_2$ is higher than that in organic solvent under the same hydrogen pressure, due to the greater solubility of hydrogen in $scCO_2$ [21]. Moreover, in the hydrogenation of 4-*tert*-butylphenol, the hydrogenation of adsorbed 4-*tert*-butylcyclohexene-1-ol and 4-*tert*-butylcyclohexanone to *cis*-4-*tert*-butylcyclohexanol is enhanced by the greater surface concentration of hydrogen atoms; however, the flipping of adsorbed 4-*tert*-butylcyclohexene-1-ol is not enhanced, and thus a greater cis ratio is obtained in $scCO_2$. In our previous work, we found that the selectivity to *cis*-decalin in the hydrogenation of naphthalene and tetralin in $scCO_2$ was higher than that in *n*-heptane, due to the lower likelihood of flipping of the $\Delta^{1,9}$-octalin, which is a partially hydrogenated intermediate because of the lower solubility of $\Delta^{1,9}$-octalin in $scCO_2$ than in *n*-heptane [21–23]. Similarly, the flipping of adsorbed 4-*tert*-butylcyclohexene-1-ol was likely to be more suppressed in $scCO_2$ than in 2-propanol, due to the lower solubility of adsorbed 4-*tert*-butylcyclohexene-1-ol species in $scCO_2$ compared with that in 2-propanol. The lower solubility of the intermediate alcohol in $scCO_2$ also would be supported by the fact that the initial selectivity to 4-*tert*-butylcyclohexanone was lower in $scCO_2$ than in 2-propanol.

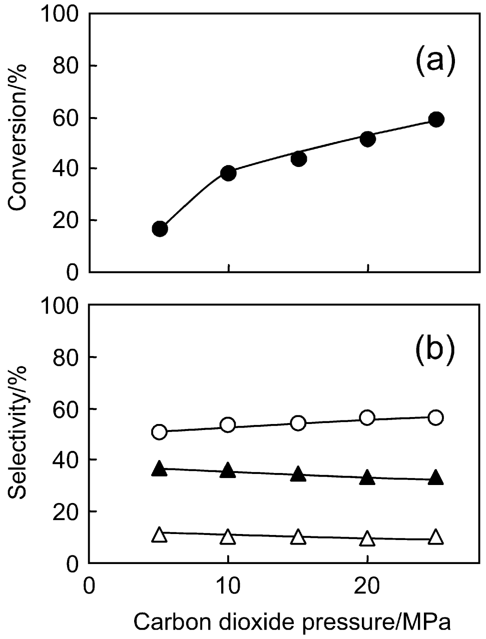


Fig. 2. Effect of carbon dioxide pressure on conversion (a) and product distribution (b) for the hydrogenation of 4-*tert*-butylphenol over Rh/C. Conversion of 4-*tert*-butylphenol (●), selectivity to 4-*tert*-butylcyclohexanone (○), *cis*-4-*tert*-butylcyclohexanol (▲), and *trans*-4-*tert*-butylcyclohexanol (△). Catalyst weight, 0.005 g; reaction time, 15 min; partial hydrogen pressure, 2 MPa; initial 4-*tert*-butylphenol, 2.00 mmol; reaction temperature, 313 K.

3.2. *Effect of carbon dioxide pressure on 4-tert-butylphenol hydrogenation over Rh/C*

Fig. 2 shows the effect of carbon dioxide pressure on the hydrogenation of 4-*tert*-butylphenol. The conversion of 4-*tert*-butylphenol was increased almost threefold with an increase in carbon dioxide pressure from 5 to 25 MPa. Another experiment using a view cell showed that some of 4-*tert*-butylphenol was dissolved in 10 MPa of carbon dioxide and 2 MPa of hy-

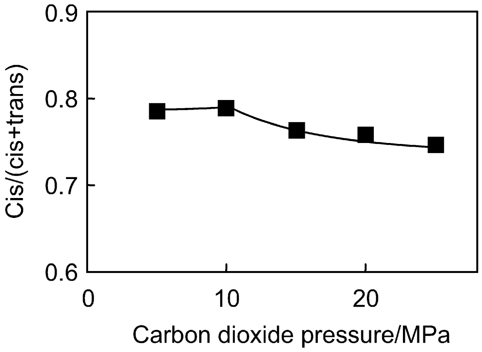


Fig. 3. Effect of carbon dioxide pressure on final cis ratio in 4-*tert*-butylphenol hydrogenation. Catalyst weight, 0.02 g; reaction time, 60 min; partial hydrogen pressure, 2 MPa; initial 4-*tert*-butylphenol, 2.00 mmol; reaction temperature, 313 K.

drogen at 313 K, and most of it was dissolved in 25 MPa of carbon dioxide and 2 MPa of hydrogen pressure. The higher solubility of 4-*tert*-butylphenol at higher carbon dioxide pressures led to enhanced hydrogenation activities. This is in accordance with our earlier report demonstrating that the initial activities in the hydrogenation of biphenyl, naphthalene, and tetralin increased with increasing carbon dioxide pressure [20,22–24]. It is also noteworthy that as the carbon dioxide pressure increased, the selectivities to *cis*- and *trans*-4-*tert*-butylcyclohexanol decreased, whereas the selectivity to 4-*tert*-butylcyclohexanone increased. In addition, the final cis ratio decreased with an increase in carbon dioxide pressure from 10 to 25 MPa in the hydrogenation of 4-*tert*-butylphenol at 313 K (Fig. 3). We found similar results in our previous work on the hydrogenation of naphthalene and tetralin in $scCO_2$, that the selectivity to *cis*-decalin decreased with increasing carbon dioxide pressure, due to the increased likelihood of the flipping of $\Delta^{1,9}$-octalin because of the greater solubility of $\Delta^{1,9}$-octalin in $scCO_2$ at higher carbon dioxide pressures [21–23]. According to the same analogy, the decrease in the cis ratio at higher carbon dioxide pressures would be caused by the enhanced flipping of 4-*tert*-butylcyclohexene-1-ol due to higher solubility of 4-*tert*-butylcyclohexene-1-ol at higher carbon dioxide pressures. Increased interaction between adsorbed intermediate and carbon dioxide at higher pressure also can be supported by the fact that the initial selectivity to 4-*tert*-butylcyclohexanone increased with increasing carbon dioxide pressure (Fig. 2b).

3.3. Hydrogenation of 4-tert-butylphenol over HCl–Rh/C

The reaction pathway over HCl–Rh/C for the hydrogenation of 4-*tert*-butylphenol in $scCO_2$ (10 MPa + 2 MPa of H_2) obtained from the reaction profile was similar to that observed for the Rh/C catalyst. The hydrogenation of 4-*tert*-butylphenol in 2-propanol also proceeded over HCl–Rh/C; however, the initial rate of 4-*tert*-butylphenol hydrogenation was half of that in 10 MPa of $scCO_2$ solvent.

Fig. 4 shows the effect of adding hydrochloric acid to the Rh/C catalyst on initial conversion and selectivity for the hydrogenation of 4-*tert*-butylphenol. The conversion values decreased substantially (from 40 to 12%) with increasing amounts of hydrochloric acid added. This was due to the blocking of active rhodium sites by chloride atoms, thus reducing the extent of adsorption of 4-*tert*-butylphenol and/or hydrogen. As the amount of hydrochloric acid added to Rh/C was increased, the selectivity to *cis*-4-*tert*-butylcyclohexanol also increased, whereas that to 4-*tert*-butylcyclohexanone decreased. The cis ratio increased with an increase in the amount of hydrochloric acid and remained constant at 0.88 beyond 1.9 μmol of hydrochloric acid added to 0.005 g of Rh/C.

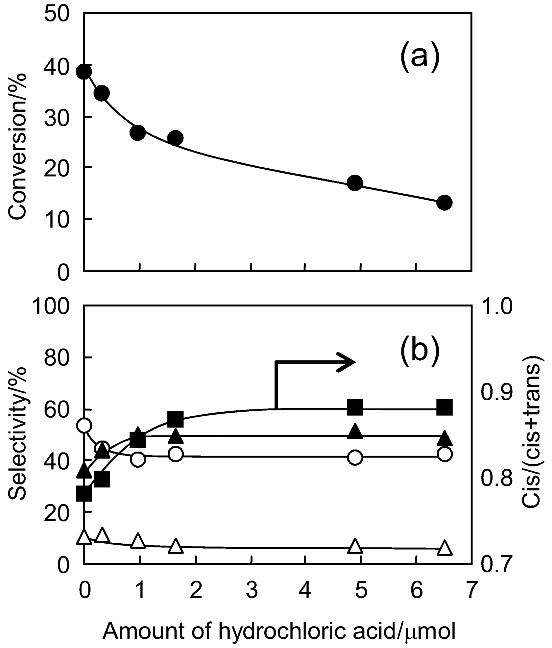


Fig. 4. Effect of addition of hydrochloric acid to Rh/C on conversion (a) and product distribution (b) for the hydrogenation of 4-*tert*-butylphenol in $scCO_2$. Conversion of 4-*tert*-butylphenol (●), selectivity to 4-*tert*-butylcyclohexanone (○), *cis*-4-*tert*-butylcyclohexanol (▲), *trans*-4-*tert*-butylcyclohexanol (△), and cis ratio of 4-*tert*-butylcyclohexanol (■). Catalyst weight, 0.005 g; reaction time, 15 min; partial carbon dioxide pressure, 10 MPa; partial hydrogen pressure, 2 MPa; initial 4-*tert*-butylphenol, 2 mmol; temperature, 313 K.

Fig. 5 shows the final cis ratio obtained over HCl–Rh/C for the hydrogenation of 4-*tert*-butylphenol. The addition of hydrochloric acid was very effective in improving the cis ratio for 4-*tert*-butylphenol hydrogenation in both $scCO_2$ and 2-propanol; however, the final cis ratio in $scCO_2$ (0.88) was higher than that in 2-propanol (0.82). We also studied the hydrogenation profile of the system with Rh/C in 2-propanol with hydrogen chloride and found similar cis ratio values to those for HCl–Rh/C in 2-propanol.

Fig. 6 shows the effect of addition of hydrochloric acid on conversion, yield, and cis ratio for the hydrogenation of 4-*tert*-butylcyclohexanone over Rh/C in $scCO_2$ solvent. Conversion of 4-*tert*-butylcyclohexanone as well as the yield of *cis*-4-*tert*-butylcyclohexanol first increased with increasing amounts of hydrochloric acid up to 2.6 μmol, then decreased. The yield of *trans*-4-*tert*-butylcyclohexanol decreased monotonously with an increase in the concentration of hydrochloric acid. As shown in Fig. 6b, the cis ratio increased from 0.77 to 0.88 with an increase in hydrochloric acid concentration from 0 to 3.9 μmol,

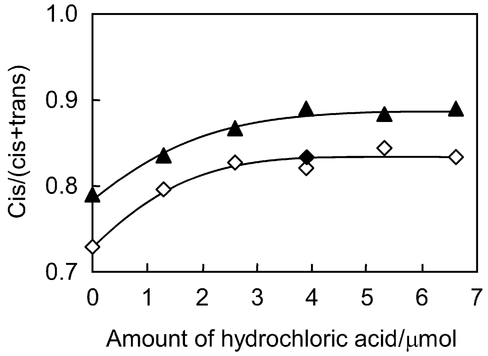


Fig. 5. Effect of addition of hydrochloric acid to the Rh/C catalyst on final cis ratio of 4-*tert*-butylcyclohexanol for the hydrogenation of 4-*tert*-butylphenol in $scCO_2$ (10 MPa) (▲) and in 2-propanol (10 mL) (◇) and in 2-propanol containing hydrochloric acid (◆). Catalyst weight, 0.02 g; reaction time, 60 min; partial hydrogen pressure, 2 MPa; initial 4-*tert*-butylphenol, 2 mmol; reaction temperature, 313 K.

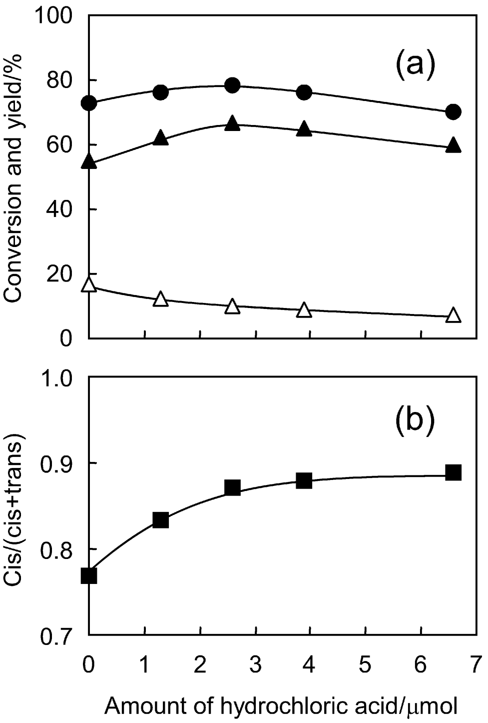


Fig. 6. Effect of addition of hydrochloric acid to Rh/C on conversion and yield (a), and cis ratio (b) for hydrogenation of 4-*tert*-butylcyclohexanone. Conversion of 4-*tert*-butylcyclohexanone (●), yield of *cis*-4-*tert*-butylcyclohexanol (▲), yield of *trans*-4-*tert*-butylcyclohexanol (△), and cis ratio of 4-*tert*-butylcyclohexanol (■). Catalyst weight, 0.02 g; reaction time, 30 min; partial carbon dioxide pressure, 10 MPa; partial hydrogen pressure, 2 MPa; initial 4-*tert*-butylcyclohexanone, 2 mmol; temperature, 313 K.

beyond which it remained constant. The effect of hydrochloric acid concentration on cis ratio for the hydrogenation of 4-*tert*-butylcyclohexanone was quantitatively almost the same as that observed for the hydrogenation of 4-*tert*-butyphenol (Fig. 5). The foregoing results demonstrate that the hydrogenation of 4-*tert*-butylcyclohexanone to *cis*-4-*tert*-butylcyclohexanol was enhanced by the addition of hydrochloric acid to the system.

Table 3
XPS analysis of HCl–Rh/C

Treatment	Atomic concentration (%)			Cl/Rh
	C_{1s}	Cl_{2p}	Rh_{3d}	
None[a]	98.13	0.53	1.34	0.40
$scCO_2$[b]	98.30	0.45	1.25	0.36
2-Propanol[c]	98.47	0.35	1.18	0.30

[a] HCl–Rh/C containing 3.91 μmol of HCl per 0.02 g of Rh/C.

[b] The sample a (0.02 g) was treated with 10 MPa of carbon dioxide in 50 mL of reactor at 313 K for 60 min.

[c] The sample a (0.02 g) was treated with 10 mL of 2-propanol at 313 K for 60 min.

We also found that the final cis ratio was increased up to 0.85 by the addition of 6.6 μmol of phosphoric acid to 0.02 g of Rh/C compared with that of an acid-free system (0.79) for the hydrogenation of 4-*tert*-butylphenol in $scCO_2$. Although phosphoric acid had a lesser effect than hydrochloric acid, it is likely that the cis ratio was improved substantially by protons. It has been reported that partial hydrogenation of α,β-unsaturated ketones to α,β-unsaturated alcohol was enhanced by the addition of protons to supported metal catalysts [31]. This supports the notion that the interaction between the protons adsorbed on the catalyst and carbonyl oxygen atom of 4-*tert*-butylcyclohexanone (forming an intermediate cationic species) gives the hydrogenation product, *cis*-4-*tert*-butylcyclohexanol preferentially. In addition, it is likely that the equilibrium between 4-*tert*-butylcyclohexanone and 4-*tert*-butylcyclohexene-1-ol on the active sites shifted to 4-*tert*-butylcyclohexanone by the interaction with protons, forming *cis*-4-*tert*-butylcyclohexanol.

Higher cis ratio values also were obtained over HCl–Rh/C in $scCO_2$ compared with 2-propanol for the same concentration of hydrochloric acid because of a higher hydrogenation rate in $scCO_2$ and lower solubility of the adsorbed species in $scCO_2$, resulting in a lower probability of flipping of the enol form. Another probable explanation is the higher solubility of hydrochloric acid in 2-propanol than in $scCO_2$. XPS characterization of the HCl–Rh/C catalyst before and after treatment with solvents revealed a Cl/Rh ratio value of 0.40 before the treatment, decreasing to 0.36 after $scCO_2$ treatment and to 0.30 after 2-propanol treatment (Table 3). A major part of hydrochloric acid is dissolved in 2-propanol; on the other hand, the solubility of hydrochloric acid is very low in $scCO_2$, and thus most of the protons remain on the catalyst surface in $scCO_2$.

3.4. Hydrogenation of 2-tert-butylphenol over Rh/C

Fig. 7a shows the reaction profile for the hydrogenation of 2-*tert*-butylphenol over Rh/C (0.020 g) in $scCO_2$ at 313 K. From the beginning of the reaction up to 120 min, *cis*-, *trans*-2-*tert*-butylcyclohexanol, 2-*tert*-butylcyclohexanone, and small amounts of *tert*-butylcyclohexane were formed with almost constant selectivity (37, 1.5, 62, and 0.1%, respectively), indicating that all of these products are formed from 2-*tert*-butylphenol in a parallel reaction. Once most of 2-*tert*-butylphenol was hydrogenated after 120 min, 2-*tert*-butylcyclohexanone decreased slightly with a simultaneous increase

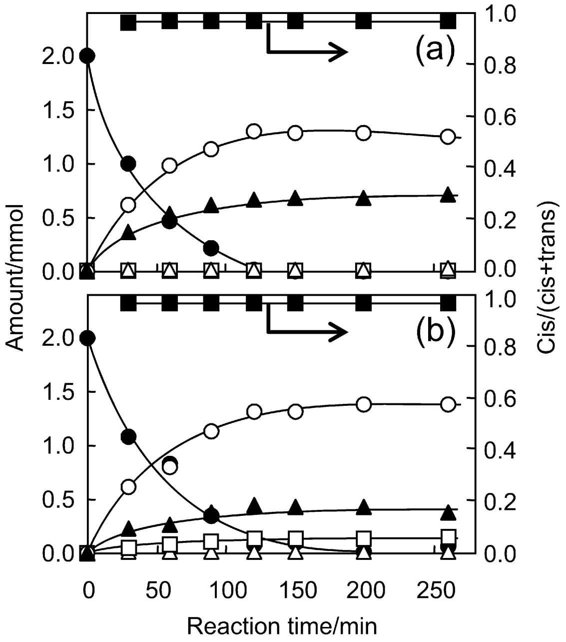
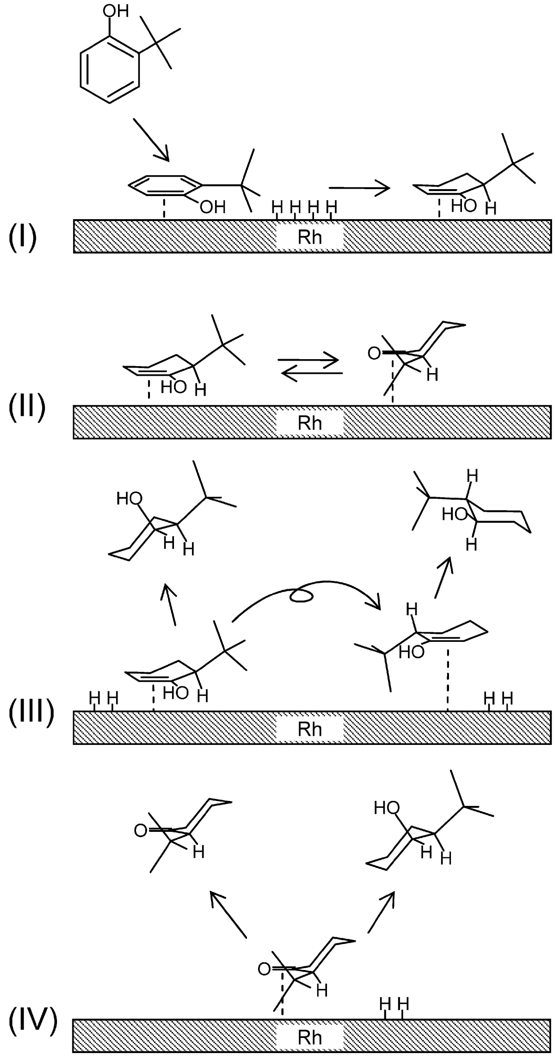


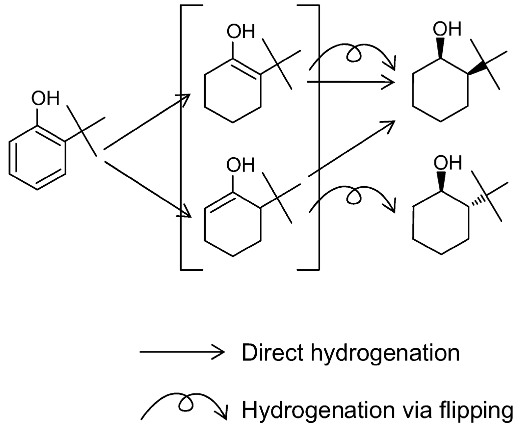
Fig. 7. Hydrogenation of 2-*tert*-butylphenol over Rh/C in 10 MPa of carbon dioxide (a) and 10 mL of 2-propanol (b). Amounts of 2-*tert*-butylphenol (●), 2-*tert*-butylcyclohexanone (○), *cis*-2-*tert*-butylcyclohexanol (▲), *trans*-2-*tert*-butylcyclohexanol (△), *tert*-butylcyclohexane (□), and cis ratio of 2-*tert*-butylcyclohexanol (■). Catalyst weight, 0.02 g; partial hydrogen pressure, 2 MPa; reaction temperature, 313 K.

in *cis*-2-*tert*-butylcyclohexanol, indicating slow hydrogenation of 2-*tert*-butylcyclohexanone to *cis*- and *trans*-2-*tert*-butylcyclohexanol compared with that of 2-*tert*-butylphenol. This is in contrast to the hydrogenation of 4-*tert*-butylphenol, where consecutive hydrogenation of 4-*tert*-butylcylcohexanone was faster with the simultaneous formation of 4-*tert*-butylcyclohexanol in $scCO_2$ (Fig. 1a). The cis ratio was almost constant at 0.96 from the beginning of the reaction up to 260 min.

The hydrogenation of 2-*tert*-butylphenol proceeded with slightly slower rate in 2-propanol than that in $scCO_2$, with *cis*-, *trans*-2-*tert*-butylcyclohexanol, 2-*tert*-butylcyclohexanone, and *tert*-butylcyclohexane formed simultaneously (Fig. 7b). The selectivity to 2-*tert*-butylcyclohexanone was higher in 2-propanol (68%) than in $scCO_2$ (62%). The cis ratio in 2-propanol (0.96) was comparable to that in $scCO_2$ (0.96). It is noteworthy that dehydroxylation was strongly suppressed in $scCO_2$.



Scheme 2. Hydrogenation of 2-*tert*-butylphenol over Rh/C.



Scheme 3. Formation of 2-*tert*-butylcyclohexanol via *tert*-butylcyclohexenol intermediate.

The hydrogenation of 2-*tert*-butylphenol and 4-*tert*-butylphenol exhibited similar reaction profiles, indicating that the mechanism of 2-*tert*-butylphenol hydrogenation is similar to that of 4-*tert*-butylphenol hydrogenation, in which partial hydrogenation, tautomerization, and complete hydrogenation occurred (Scheme 2). However, the hydrogenation of 2-*tert*-butylphenol has two distinctive characteristics: (1) high cis ratios in both $scCO_2$ and 2-propanol and (2) a lower hydrogenation rate of the intermediate *tert*-butylcyclohexanone. The high cis ratio values can be explained in terms of the structures of the partially hydrogenated enol species. Two isomers of the intermediate enol can be formed in 2-*tert*-butylphenol hydrogenation: 2-*tert*-butylcyclohexene-1-ol and 6-*tert*-buthylcyclohexene-1-ol. 2-*tert*-Butylcyclohexene-1-ol cannot lead to *trans*-2-*tert*-butylcyclohexanol (Scheme 3). Thus, *cis*-2-*tert*-butylcyclohexanol has more reaction pathways than *trans*-2-*tert*-butylcyclohexanol in the hydrogenation of 2-*tert*-butylphenol. Furthermore, the flipping of 6-*tert*-butylcyclohex-

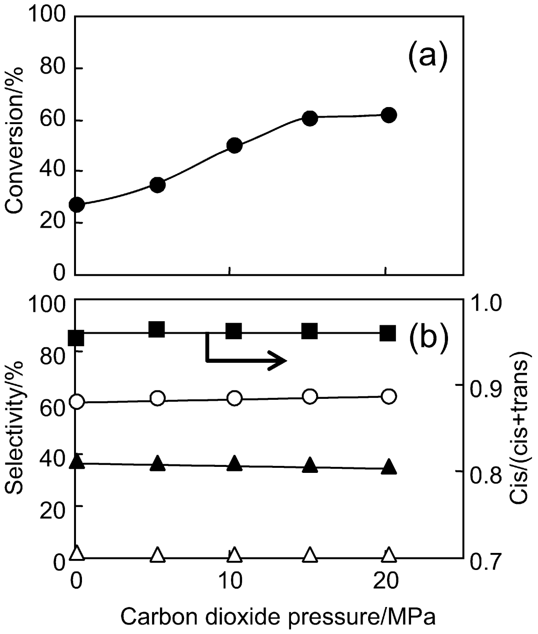


Fig. 8. Effect of carbon dioxide pressure on conversion (a) and product distribution (b) for hydrogenation of 2-*tert*-butylphenol over Rh/C. Conversion of 2-*tert*-butylphenol (●), selectivity to 2-*tert*-butylcyclohexanone (○), *cis*-2-*tert*-butylcyclohexanol (▲), *trans*-2-*tert*-butylcyclohexanol (△), and cis ratio of 2-*tert*-butylcyclohexanol (■). Catalyst weight, 0.02 g; reaction time, 30 min; partial hydrogen pressure, 2 MPa; initial 2-*tert*-butylphenol, 2.00 mmol; reaction temperature, 313 K.

ene-1-ol, a precursor of *trans*-2-*tert*-butylcyclohexanol, is difficult, because the *tert*-butyl group hinders the adsorption of 6-*tert*-buthylcyclohexene-1-ol from another side (step III in Scheme 2). Thus the similar high cis ratio was obtained in the hydrogenation of 2-*tert*-butylphenol regardless of the type of solvent. The lower reactivity of *tert*-butylcyclohexanone than that of 2-*tert*-butylphenol also can be explained in terms of steric hindrance due to *tert*-butyl groups of 2-*tert*-butylcyclohexanone.

In the hydrogenation of 2-*tert*-butylphenol, using $scCO_2$ solvent conferred no advantage over organic solvent for increasing the cis ratio. However, the selectivity to *cis*-2-*tert*-butylcyclohexanol in the initial stage of the reaction was higher in $scCO_2$ than in 2-propanol, indicating suppressed desorption of 2-*tert*-butylcyclohexanone intermediate due to the lower solubility of the intermediate in $scCO_2$ than in 2-propanol.

3.5. Effect of carbon dioxide pressure on 2-tert-butylphenol hydrogenation over Rh/C

Fig. 8 shows the effect of carbon dioxide pressure on the hydrogenation of 2-*tert*-butylphenol over Rh/C at 313 K. The initial conversion of 2-*tert*-butylphenol at 30 min increased from 27 to 61% with an increase in carbon dioxide pressure from 0.1 to 15 MPa, beyond which it remained constant. The initial conversion would depend on the amount of 2-*tert*-butylphenol dissolved in $scCO_2$. The phase behavior observed through a view cell revealed that the solubility of 2 mmol of 2-*tert*-butylphenol increased with increasing carbon dioxide pressure up to 15 MPa, and that all of 2-*tert*-butylphenol was dissolved in $scCO_2$ at 15 MPa carbon dioxide pressure. The increase in the conversion of 2-*tert*-butylphenol with increasing carbon dioxide pressure is due to the increased amount of 2-*tert*-butylphenol dissolved in the carbon dioxide phase. As the carbon dioxide pressure was increased from 0.1 to 15 MPa, the selectivity to 2-*tert*-butylcyclohexanone increased slightly, from 60 to 63%, and that of *cis*-2-*tert*-butylcyclohexanol decreased slightly, from 38 to 36%. The cis ratio remained almost constant at 0.96 regardless of the carbon dioxide pressure.

Low-temperature hydrogenation of 2-*tert*-butylphenol under neat conditions is possible because its melting point is as low as 267 K. However, our results indicate that higher reaction rates can be obtained at higher carbon dioxide pressure, demonstrating the usefulness of the $scCO_2$ solvent. It has been reported that the hydrogenation rates of liquid substrates, such as phenylacetylene, in $scCO_2$ over supported metal catalysts are higher than those under neat conditions, due to the elimination of mass transfer resistance of hydrogen [32,33]. The dissolution of 2-*tert*-butylphenol into $scCO_2$ would enhance the hydrogenation rate due to an increased mass transfer of hydrogen.

3.6. Hydrogenation of 2-tert-butylphenol over HCl–Rh/C

Figs. 9a and 9b show the reaction profiles for the hydrogenation of 2-*tert*-butylphenol over HCl–Rh/C at 313 K in $scCO_2$ (10 MPa) and 2-propanol, respectively. The addition of hydrochloric acid to Rh/C increased the initial selectivity to *cis*-2-*tert*-butylcyclohexanol (from 37 to 43%) in $scCO_2$ and increased the initial selectivity to *tert*-butylcyclohexane (from 5.9 to 10%) in 2-propanol. The cis ratio was as high as 0.96 regardless of the solvent used and the addition or nonaddition of hydrochloric acid.

It should be noted that the consecutive hydrogenation of 2-*tert*-butylcyclohexanone to *cis*-2-*tert*-butylcyclohexanol was clearly observed over HCl–Rh/C in $scCO_2$ at 313 K after most of 2-*tert*-butylphenol was hydrogenated (Fig. 9a), whereas this was not observed in 2-propanol (Fig. 9b). The consecutive hydrogenation of 2-*tert*-butylcyclohexanone by the addition of hydrochloric acid to the Rh/C catalyst was observed in $scCO_2$. The interaction between the protons adsorbed on the catalyst surface (from hydrochloric acid) and carbonyl oxygen of 2-*tert*-butylcyclohexanone was likely to enhance the consecutive hydrogenation of 2-*tert*-butylcyclohexanone in $scCO_2$. The fact that this effect of hydrochloric acid was observed only in $scCO_2$ and not in 2-propanol suggests that more hydrochloric acid was adsorbed on the catalyst surface in $scCO_2$ than in 2-propanol, due to the greater solubility of hydrochloric acid in 2-propanol.

As shown in Fig. 9c, the consecutive hydrogenation of 2-*tert*-butylcyclohexanone to 2-*tert*-butylcyclohexanol proceeded rapidly over HCl–Rh/C in 15 MPa of carbon dioxide at 353 K, whereas it was very slow in 2-propanol at 353 K (Fig. 9d). The cis ratio of 2-*tert*-butylcyclohexanol was also constant (0.94) in 15 MPa of carbon dioxide at 353 K, indicating similar cis ratios for the direct hydrogenation of 2-*tert*-butylphenol to 2-*tert*-butylcyclohexanol and the consecutive hydrogenation of 2-*tert*-butylcyclohexanone to 2-*tert*-butylcyclohexanol. This means that the desorption, flipping, and readsorption of 2-*tert*-

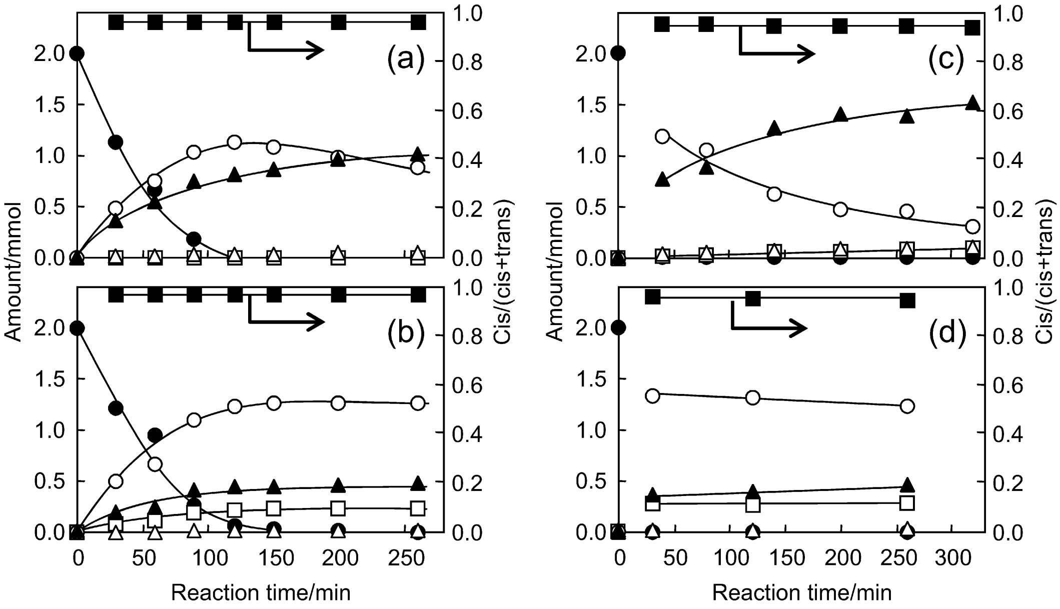


Fig. 9. Hydrogenation of 2-*tert*-butylphenol over HCl–Rh/C in $scCO_2$ (10 MPa) at 313 K (a), in 2-propanol (10 mL) at 313 K (b), in $scCO_2$ (15 MPa) at 353 K (c), and in 2-propanol (10 mL) at 353 K (d). 2-*tert*-Butylphenol (●), 2-*tert*-butylcyclohexanone (○), *cis*-2-*tert*-butylcyclohexanol (▲), *trans*-2-*tert*-butylcyclohexanol (△), *tert*-butylcyclohexane (□), and cis ratio of 2-*tert*-butylcyclohexanol (■). Catalyst weight, 0.02 g; hydrochloric acid, 3.9 µmol; partial hydrogen pressure, 2 MPa.

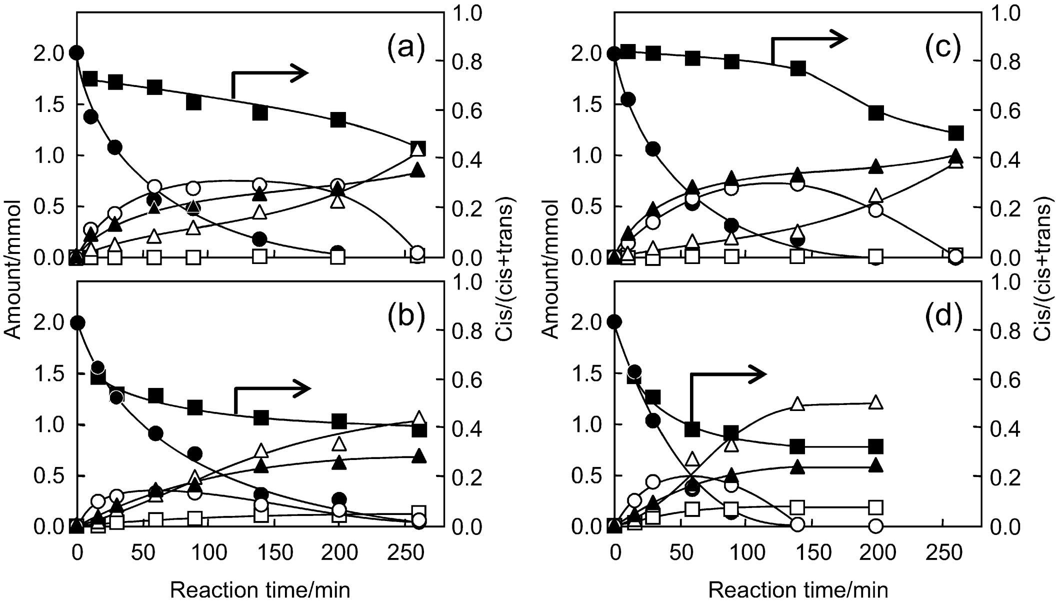


Fig. 10. Hydrogenation of 3-*tert*-butylphenol over Rh/C in 10 MPa of carbon dioxide (a) and in 10 mL of 2-propanol (b), over HCl–Rh/C in 10 MPa of carbon dioxide (c) and in 10 mL of 2-propanol (d). Amounts of 3-*tert*-butylphenol (●), 3-*tert*-butylcyclohexanone (○), *cis*-3-*tert*-butylcyclohexanol (▲), *trans*-3-*tert*-butylcyclohexanol (△), *tert*-butylcyclohexane (□), and cis ratio of 3-*tert*-butylcyclohexanol (■). Catalyst weight, 0.02 g; partial hydrogen pressure, 2 MPa; reaction temperature 313 K.

butylcyclohexanone on the other side did not occur in the hydrogenation of 2-*tert*-butylphenol.

3.7. Hydrogenation of 3-tert-butylphenol over Rh/C and HCl–Rh/C

Fig. 10 shows the reaction profile of the hydrogenation of 3-*tert*-butylphenol over Rh/C and HCl–Rh/C in $scCO_2$ and in 2-propanol. In both solvents, the amounts of *cis*-, *trans*-3-*tert*-butylcyclohexanol, 3-*tert*-butylcyclohexanone, and *tert*-butylcyclohexane increased from the beginning of the reaction, indicating that these products were formed in parallel. The amount of 3-*tert*-butylcyclohexanone decreased and the amounts of *cis*- and *trans*-3-*tert*-butylcyclohexanol increased, indicating that 3-*tert*-butylcyclohexanone was consecutively hydrogenated to 3-*tert*-butylcyclohexanol. More *tert*-butylcyclohexane, a dehydroxylation product, was formed in 2-propanol (0.13 mmol for Rh/C and 0.18 mmol for HCl–Rh/C)

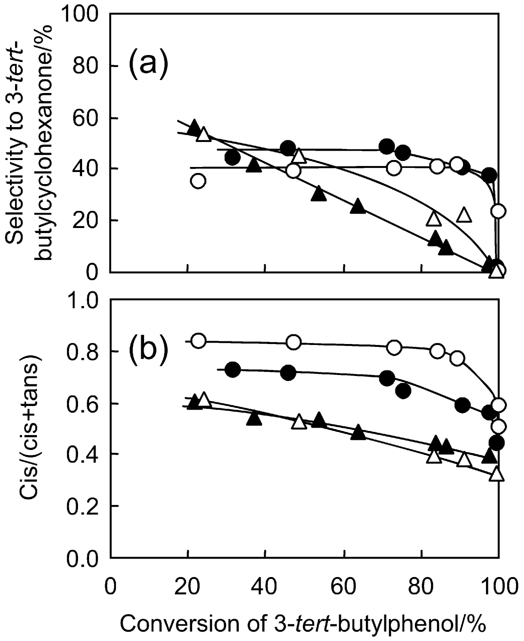


Fig. 11. Selectivity to 3-*tert*-butylcyclohexanone (a) and cis ratio (b) as a function of conversion of 3-*tert*-butylphenol in $scCO_2$ (10 MPa) over Rh/C (●), in $scCO_2$ (10 MPa) over HCl–Rh/C (○), in 2-propanol (10 mL) over Rh/C (▲), and in 2-propanol (10 mL) over HCl–Rh/C (△). Catalyst weight, 0.02 g; hydrochloric acid, 3.9 µmol; partial hydrogen pressure, 2 MPa; catalyst weight, 0.02 g; temperature, 313 K.

than in $scCO_2$ (0.014 mmol for Rh/C and 0.029 mmol for HCl–Rh/C). Note that the cis ratio decreased with increasing reaction time in both cases, in contrast to the hydrogenation of 2- and 4-*tert*-butylphenol. The final cis ratio was greater in $scCO_2$ than in 2-propanol.

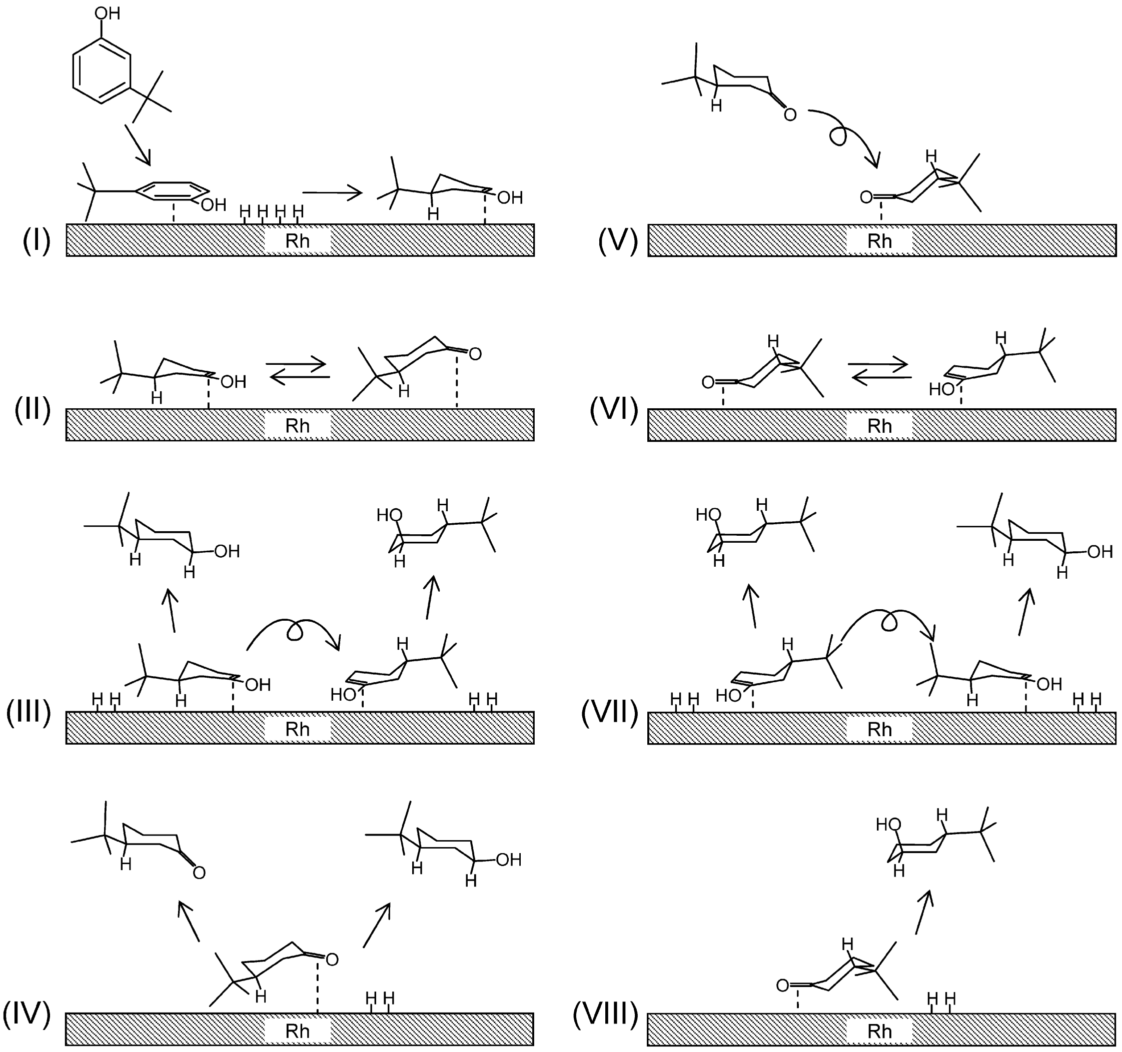
Fig. 11 shows the changes in the selectivity to 3-*tert*-butylcyclohexanone and cis ratio as a function of conversion of 3-*tert*-butylphenol. In $scCO_2$, the selectivity to 3-*tert*-butylcyclohexanone remained constant up to 70% conversion and began to decrease once most of 3-*tert*-butylphenol was converted, indicating that the consecutive hydrogenation of 3-*tert*-butylcyclohexanone to 3-*tert*-butylcyclohexanol occurred after most of 3-*tert*-butylphenol was hydrogenated. In contrast, the selectivity to 3-*tert*-butylcyclohexanone in 2-propanol decreased linearly from the beginning of the reaction, indicating that the consecutive hydrogenation of ketone occurred in the presence of 3-*tert*-butylphenol. In both the cases, a decreased cis ratio accompanied the decreased selectivity to 3-*tert*-butylcyclohexanone. This suggests a lower cis ratio of 3-*tert*-butylcyclohexanol in the hydrogenation of 3-*tert*-butylcyclohexanone compared with that in the hydrogenation of 3-*tert*-butylphenol.

It is interesting to note that at up to 80% conversion of 3-*tert*-butylphenol, the selectivity to 3-*tert*-butylcyclohexanone for HCl–Rh/C was lower than that for Rh/C in $scCO_2$, indicating that the extent of direct hydrogenation of 3-*tert*-butylphenol to 3-*tert*-butylcyclohexanol was increased by the addition of hydrochloric acid in $scCO_2$. Also, at up to 80% conversion of 3-*tert*-butylphenol, the cis ratio for HCl–Rh/C was higher than that for Rh/C in $scCO_2$ and was almost the same for both catalysts in 2-propanol, indicating that hydrochloric acid enhanced the direct hydrogenation of 3-*tert*-butylphenol to *cis*-3-*tert*-butylcyclohexanol in $scCO_2$.

The initial cis ratio in $scCO_2$ was higher than that in 2-propanol for both HCl–Rh/C and Rh/C. However, in all the cases, the cis ratio decreased with the progress of the subsequent hydrogenation of 3-*tert*-butylcyclohexanone, and the final cis ratio was in the following order: HCl–Rh/C in $scCO_2$ > Rh/C in $scCO_2$ > Rh/C in 2-propanol > HCl–Rh/C in 2-propanol. Interestingly, the final cis ratio was decreased by the addition of hydrochloric acid in 2-propanol, whereas it was increased in $scCO_2$.

A characteristic of 3-*tert*-butylphenol hydrogenation is the decreased cis ratio with the progress of consecutive hydrogenation of 3-*tert*-butylcyclohexanone, which indicates that the hydrogenation mechanism of 3-*tert*-butylphenol differs from those of 2- and 4-*tert*-butylphenol. Scheme 4 shows the mechanism of 3-*tert*-butylphenol hydrogenation based on partial hydrogenation to enol, followed by tautomerization and then complete hydrogenation. In the hydrogenation of 3-*tert*-butylphenol, 3-*tert*-butylcyclohexanone formed on the active sites by tautomerization of enol had a large steric hindrance due to the *tert*-butyl group and cyclohexane ring (step II in Scheme 4); thus, desorbed 3-*tert*-butylcyclohexanone was readsorbed on the active sites from another side (step V in Scheme 4). Consequently, in the initial stage of hydrogenation, *cis*-3-*tert*-butylcyclohexanol was formed by the direct hydrogenation of enol or 3-*tert*-butylcyclohexanone (steps III and IV in Scheme 4), and trans isomer was formed by the hydrogenation of enol after the flipping of enol (step III in Scheme 4); however, in the consecutive hydrogenation of 3-*tert*-butylcyclohexanone, trans isomer was formed by the hydrogenation of enol or 3-*tert*-butylcyclohexanone (steps VII and VIII in Scheme 4), and cis isomer was formed by the hydrogenation of enol after the flipping of enol (step VII in Scheme 4). In addition, direct hydrogenation without flipping would be kinetically more favorable than that through the flipping of enol. Thus, the cis ratio would decrease with the progression of consecutive hydrogenation of 3-*tert*-butylcyclohexanone.

In the direct hydrogenation of 3-*tert*-butylphenol to 3-*tert*-butylcyclohexanol, the enhanced cis ratio by the addition of hydrochloric acid to Rh/C in $scCO_2$ could be explained by the enhanced hydrogenation of the adsorbed 3-*tert*-butylcyclohexanone intermediate to *cis*-3-*tert*-butylcyclohexanol. However, the cis ratio of 3-*tert*-butylcyclohexanol formed in the consecutive hydrogenation of 3-*tert*-butylcyclohexanone would be decreased by the addition of hydrochloric acid, because the hydrogenation of readsorbed 3-*tert*-butylcyclohexanone to *trans*-3-*tert*-butylcyclohexanol would be enhanced. With the combination of $scCO_2$ and HCl–Rh/C, a greater amount of 3-*tert*-butylcyclohexanol was formed directly from 3-*tert*-butylphenol than from 3-*tert*-butylcyclohexanone consecutively, and thus the final cis ratio was higher. In the combination of 2-propanol and HCl–Rh/C, the amount of *trans*-3-*tert*-butylcyclohexanol from 3-*tert*-butylcyclohexanone was greater, leading to a lower final cis ratio.



Scheme 4. Hydrogenation of 3-*tert*-butylphenol over Rh/C.

4. Conclusion

The stereoselective hydrogenation of various *tert*-butylphenols to the corresponding cyclohexanols was investigated over Rh/C in $scCO_2$ as well as in organic solvents. In the hydrogenation of 4-*tert*-butylphenol, a higher cis ratio (0.79) was obtained in $scCO_2$ compared with that in 2-propanol and cyclohexane, due to suppressed flipping of the enol intermediate. In the case of 2-*tert*-butylphenol, the cis ratio was as high as 0.96 in both $scCO_2$ and 2-propanol, because more pathways were available for the formation of cis isomer from the enol intermediate, and also because the flipping of enol was inhibited by steric hindrance of the *tert*-butyl group at the 2-position. In the hydrogenation of 3-*tert*-butylphenol, desorbed 3-*tert*-butylcyclohexanone intermediate was readsorbed on the active sites from another side; thus, the cis ratio decreased with the progression of consecutive hydrogenation of 3-*tert*-butylcyclohexanone.

We investigated the role of hydrochloric acid in directing the stereoselectivity in the hydrogenation of *tert*-butylphenols over Rh/C in $scCO_2$ and 2-propanol and found that (i) in the hydrogenation of 4-*tert*-butylphenol, a cis ratio as high as 0.9 could be achieved for 4-*tert*-butylcyclohexanol in $scCO_2$ at 313 K by adding hydrochloric acid to Rh/C; (ii) in the hydrogenation of 2-*tert*-butylphenol, a cis ratio as high as 0.95 was obtained in both $scCO_2$ and 2-propanol over the HCl–Rh/C catalyst, and the consecutive hydrogenation of the intermediate, 2-*tert*-butylcyclohexanone to *cis*-2-*tert*-butylcyclohexanol was enhanced by the addition of hydrochloric acid to Rh/C in $scCO_2$; (iii) in the hydrogenation of 3-*tert*-butylphenol, selectivity to *trans*-3-*tert*-butylcyclohexanol (the preferred product) was greater in 2-propanol than in $scCO_2$.

Supplementary data

The online version of this article contains additional supplementary material.

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