1. Introduction

Stereoselective control in catalytic hydrogenation is extremely important for both development of industrial processes and academic studies. For example, stereoselective hydrogenation of various alkylphenols to the corresponding alkylcyclohexanols is of great commercial interest in the fragrance and perfume industry. The cis form of 4-t-butylocyclohexanol is useful for the manufacture of fragrance intermediates, and is produced industrially by the liquid-phase hydrogenation of 4-t-butylocyclohexane in organic solvents. In the conventional hydrogenation route, the trans isomer is also formed simultaneously because it is thermodynamically more stable than the cis form. In addition, an energy intensive distillation process is required for the separation of products from solvents. Therefore, the development of a highly efficient stereoselective catalytic system that can be operated under mild reaction conditions is desirable.

Hydrogenation using solid catalysts and supercritical carbon dioxide (scCO₂) solvent is an attractive process option because of the high reaction rate as a result of the high miscibility of hydrogen in the scCO₂ phase which reduces the mass transfer resistance, and the easy separation of solid catalysts and products.

2. Experimental

Activated carbon-supported rhodium catalyst (Rh/C) with metal loading of 5 wt% (Wako Pure Chemical Industries, Ltd., Japan) was used without further treat-
Ammonium of 4-t-butylphenol (●), 4-t-butylcyclohexanol (○), cis-4-t-butylcyclohexanol (▲), trans-4-t-butylcyclohexanol (△), and t-butylcyclohexane and ring-opened alcohol (◇).

Temperature: 313 K; reactor volume: 50 cm³; 4-t-butylphenol introduced: 2.00 mmol; catalyst weight: 0.005 g; initial hydrogen pressure: 2 MPa (38 mmol).

Fig. 1 Hydrogenation of 4-t-Butylphenol over Rh/C under 22 MPa Total Pressure

3. Results and Discussion

Figure 1 shows the reaction profile of 4-t-butylphenol hydrogenation over Rh/C in scCO₂ under a total pressure of 22 MPa at 313 K. cis-4-t-Butylcyclohexanol, trans-4-t-butylcyclohexanol, 4-t-butylcyclohexane, and a small amount of t-butylcyclohexane were directly formed from 4-t-butylphenol. Both cis- and trans-4-t-butylcyclohexanol were also subsequently formed from 4-t-butylcyclohexane. Small amounts of ring-opened alcohol were also formed from 4-t-butylcyclohexane. The cis ratio (cis/(cis + trans)) was almost constant at ca. 0.76 from the beginning to the end of the reaction. We previously confirmed that isomerization of cis-4-t-butylcyclohexanol to trans isomer does not occur over Rh/C in scCO₂ at 313 K \(^{15}\). The reaction pathway of 4-t-butylphenol hydrogenation is shown in Scheme 1.

We previously investigated the effect of carbon dioxide pressure on the initial activity for 4-t-butylphenol hydrogenation over Rh/C catalyst with the initial amount of 2.00 mmol of 4-t-butylphenol under hydrogen pressure of 2 MPa (38 mmol) in the carbon dioxide system at 313 K (Fig. 2)\(^{15}\). The conversion of 4-t-butylphenol increased almost 10 fold with an increase in total pressure from 2 to 27 MPa under pressurization with carbon dioxide.

In the present study, we focused on the relationship between the initial consumption of 4-t-butylphenol and pressurization with carbon dioxide based on the solubility of 4-t-butylphenol in scCO₂. Figure 3 shows the phase behavior of the 4-t-butylphenol (2.0 mmol)–hydrogen (2 MPa, 38 mmol)–carbon dioxide system in the same volume (50 cm³) of the view cell at 313 K. 4-t-Butylphenol was solid at 313 K under 2 MPa of hydrogen (Fig. 3(a)). No dissolution of solid 4-t-butylphenol was observed even after increasing the total pressure to 10 MPa by the addition of carbon dioxide (Fig. 3(b)). The amount of solid 4-t-butylphenol was slightly reduced under 12 MPa of total pressure compared to the initial states at 2-10 MPa, indicating that 4-t-butylphenol was partially dissolved under 12 MPa of total pressure (Fig. 3(c)). The amount of solid 4-t-butylphenol decreased with higher pressure >12 MPa and only a small amount of solid 4-t-butylphenol remained under 27 MPa of total pressure (Fig. 3(d)-(h)). The conversion of 4-t-butylphenol substantially increased from 5 to 40 % under 12 MPa of total pressure, at which the start of dissolution of 4-t-butylphenol was observed.

We estimated the amount of 4-t-butylphenol dissolved in the mixture of hydrogen (constant at 2 MPa, 38 mmol) and carbon dioxide in the 50 cm³ reactor (and the view cell) at 313 K as a function of total pressure as follows. First, the amount of carbon dioxide in the binary mixture of hydrogen and carbon dioxide was determined, and then the solubility of 4-t-butylphenol in the mixture was estimated as a function of the total pressure. The amount of carbon dioxide added to the 50 cm³ of hydrogen–carbon dioxide binary mixture containing 2 MPa (38 mmol) of hydrogen as a function...
of the total pressure was calculated using the Peng-Robinson equation of state\(^ {19} \):

\[
P = RT (v - b) - a [v (v + b) + b (v - b)]
\]

where \(P\) is pressure, \(T\) is temperature, \(R\) is the gas constant, and \(v\) is the molar volume. \(a\) and \(b\) are parameters related to the intermolecular attraction force and the size of hard spheres, respectively, and are given for pure substances as follows.

\[
a = a(T_c) [1 + \kappa[1 - (T/T_c)^{1/2}]]^2
\]

\[
\kappa = 0.37464 + 1.54226 \omega + 0.26992 \omega^2
\]

\[
b = 0.0778 \omega
\]

where \(P_c\) is the critical pressure, \(T_c\) is the critical temperature, and \(\omega\) is the acentric factor of pure substance. In this study, the parameters \(a\) and \(b\) of the mixtures were calculated using the van der Waals mixing rule:

\[
a_{x} = \sum x_i a_i
\]

\[
b = \sum b_i
\]

where \(x_i\) is the mole fraction of component \(i\), \(a_i\) and \(b_i\) are the parameters of pure substances, and \(k_{ij}\) is the binary interaction parameter between components \(i\) and \(j\).

The solubility of solid organic substances such as 4-t-butylphenol \((y_i)\) is given by

\[
y_i = (P_{v1}/P)(1/\phi_i) \exp[(V_i/RT)(P - P_{v1})]
\]

where \(P_{v1}\) is the vapor pressure, \(\phi_i\) is the fugacity coefficient, and \(V_i\) is the molar volume of the solid organic substance\(^ {20} \). The fugacity coefficient \(\phi_i\) is expressed as follows\(^ {20} \) based on the Peng-Robinson equation state:

\[
\ln \phi_i = (b_i / b) (Z - 1) - \ln (Z - B) - [A/(2 \sqrt{B})]
\]

\[
[2 \Sigma (1 - k_{ij}) [(a_i a_j)^{1/2} / a_i y_j - b_i / b]]
\]

\[
\ln [(Z + 2.414B)/(Z - 0.414B)]
\]

\[
A = aP/(RT^2)
\]

\[
B = bP/(RT)
\]

\[
Z = Pv/(RT)
\]

The values used for the calculation are summarized in Table 1.
Tables 1 and 2.

Figure 4 shows the amount of carbon dioxide introduced into the 50 cm³ reactor (and the view cell) and the amount of 4-t-butylphenol dissolved in the 50 cm³ reactor (and the view cell). Figure 4(a) shows that the amount of carbon dioxide in the reactor (and the view cell) sharply increased between 10 and 15 MPa of the total pressure, and Fig. 4(b) shows that the increase in the amount of 4-t-butylphenol dissolved was associated with the increase in the amount carbon dioxide added. The amount of 4-t-butylphenol dissolved according to the calculation was increased significantly from a total pressure of 11 MPa, which agreed with the findings of phase observation with the view cell. In addition, this pressure value (11 MPa) was consistent with the pressure at which the conversion of 4-t-butylphenol increased significantly (Fig. 2). These results of both phase observation and solubility calculation clearly show that higher solubility of 4-t-butylphenol can explain the enhanced hydrogenation activity at higher carbon dioxide pressure. The calculated solubility in Fig. 4(b) seemed to be lower than that expected by the observation (Fig. 2) at high pressure, suggesting that adjustment of the binary interaction parameters \( k_{ij} \) is needed to obtain the calculated solubility more accurately, but we believe that our present calculation results are useful for understanding the effect of carbon dioxide pressure on hydrogenation behavior.

4. Conclusion

The effect of carbon dioxide pressure on 4-t-butyl-
phenol hydrogenation over an activated carbon-supported rhodium catalyst in carbon dioxide at 313 K was studied by direct phase observation and solubility calculation using the Peng-Robinson equation of state. The increase in initial hydrogenation rate with higher carbon dioxide pressure could be explained by increased solubility of 4-t-butylphenol at higher carbon dioxide pressure.

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要 旨
担持ロジウム触媒を用いる4-ブチルフェノールの水素化反応の活性に対する二酸化炭素圧効果

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二酸化炭素溶媒と活性担持ロジウム触媒を用いた4-ブチルフェノールの水素化反応における二酸化炭素圧効果について
相関観察と溶解度計算を基に議論した。水素化反応の初速度は二酸化炭素圧とともに増加した。ベンゼンを用いた相関観察
により基質の溶解量が二酸化炭素圧とともに増加することを確認した。Peng-Robinson 状態式を用いた溶解度計算を行い基質
の溶解量が二酸化炭素圧とともに増加する結果を得た。4-ブチルフェノール水素化反応の初速度が二酸化炭素圧とともに増加
するのには、二酸化炭素圧の増加とともに二酸化炭素溶媒中の4-ブチルフェノール濃度が増加するためと結論した。