## Stereoselective Hydrogenation of Tetralin to *cis*-Decalin over a Carbon-supported Rhodium Catalyst in Supercritical Carbon Dioxide Solvent

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*cis*-Decalin was selectively obtained with high *cis/trans* ratio (83%) over a carbon-supported rhodium catalyst at 333 K under 6 MPa of hydrogen and 15 MPa of carbon dioxide.

Cyclic saturated hydrocarbons such as decahydronaphthalene (decalin), bicyclohexane, methylcyclohexane, etc. are proposed as new mobile hydrogen storage media for proton exchange membrane fuel cells.<sup>1</sup> Hydrogen can be obtained by catalvtic dehydrogenation of the cyclic saturated hydrocarbons to the corresponding aromatic compounds and stored by the hydrogenation of the aromatic products. For hydrogen production from decalin. cis-isomer is more preferable, because dehvdrogenation rate of *cis*-decalin is faster than that of *trans*-decalin.<sup>1b</sup> Also, cis-decalin can be used to produce sebatic acid that is used in the manufacture of 6,10-Nylon and softeners. Thus, the stereoselective hydrogenation of tetrahydronapnthalene (tetralin) to cis-decalin is an industrially important reaction. The hydrogenation of tetralin is also important for the production of a high performance diesel fuel.<sup>2</sup> The hydrogenation of tetralin is usually performed at high temperature (>390 K), and coking during reaction causes the catalyst deactivation.<sup>3</sup> As against this, hydrogenation with supported metal catalysts in supercritical carbon dioxide solvent has several advantages; 1) higher solubility of hydrogen in supercritical carbon dioxide, thereby controlling the product selectivity and activity, 2) easy separation of products and catalysts, and 3) maintaining clean active site in solid surfaces by washing with supercritical carbon dioxide solvent.<sup>4,5</sup> We have reported that carbon-supported metal catalysts are effective for the hydrogenation of aromatic compounds at lower temperature in supercritical carbon dioxide.<sup>6-11</sup> In this paper, we report that cis-decalin is obtained by stereoselective hydrogenation of tetralin in supercritical carbon dioxide over a carbonsupported rhodium catalyst at low temperature.

Catalysts used in this work, viz. carbon-supported, 5 wt % rhodium (Rh/C), palladium (Pd/C), platinum (Pt/C), and ruthenium (Ru/C) were commercially available from Wako Pure Chemical Ind., Ltd., Japan. The dispersion values of metal particles on charcoal were determined by a hydrogen adsorption method.<sup>6</sup> All catalysts were used without further reduction for the hydrogenation of tetralin. The hydrogenation of tetralin (2.3 mmol) was carried out in high-pressure stainless-steel reactors (50 mL capacity). After the reaction was over, the unreacted tetralin and products were recovered with acetone, which showed a material balance of more than 95%. The quantitative analysis was conducted with GC-MS and GC-FID.

The activities of various catalysts for the hydrogenation of tetralin were examined after 30 min of reaction at 333 K under 6 MPa of hydrogen and 10 MPa of carbon dioxide. The activities

of carbon-supported catalysts expressed as turnover number (TON, in parentheses) based on the number of surface metal atoms were found to be in the following order: Rh/C (6500) > Pd/C (400) > Pt/C (320) > Ru/C (120), indicating that Rh/C was the most active catalyst among the carbon-supported catalysts. This result was similar to the hydrogenation of naphthalene in supercritical carbon dioxide.<sup>8</sup> Martins et al. reported that an alumina-supported platinum catalyst was active for the hydrogenation of tetralin in supercritical carbon dioxide at 493 K.<sup>12</sup> We also checked the activity of an alumina-supported platinum catalyst, but it showed much lower activity (TON = 120) than Rh/C in supercritical carbon dioxide at 333 K.

Figure 1a shows the reaction profile for the hydrogenation of tetralin over Rh/C under 6 MPa of hydrogen and 15 MPa of carbon dioxide at 333 K. From the beginning of the reaction, cis- and trans-decalin were formed in almost constant cis/trans ratio (cis/(cis + trans) = 0.83), and small amount of octahydronaphthalene (octalin) (we could not determine the position of carbon-carbon double bond from GC-MS analysis) was also detected. Beyond 100 min of reaction, the amount of octalin decreased gradually, and all tetralin was hydrogenated to cis- and trans-decalin after 150 min. The yield of cis-decalin reached 82% after 150 min. The cis/trans ratio did not vary even after longer reaction time (>150 min), indicating that isomerization of cis- to trans-decalin did not occur. We also carried out some hydrogenation experiments in an organic solvent (n-heptane) to investigate the solvent effect on the tetralin hydrogenation over Rh/C (Figure 1b). The initial hydrogenation activity was found to be much higher in supercritical carbon dioxide (r = 12mmol·g<sup>-1</sup>·mim<sup>-1</sup>) than that in *n*-heptane ( $r = 5.9 \text{ mmol·g}^{-1}$ ·  $mim^{-1}$ ). Also, the selectivity to *cis*-decalin (= *cis*-decalin/  $(cis-decalin + trans-decalin + octalin) \times 100)$  in supercritical carbon dioxide (78% at 70% conversion) was higher than that



**Figure 1.** The hydrogenation of tetralin over Rh/C (0.002 g) under hydrogen pressure 6 MPa at 333 K. (a) Carbon dioxide 15 MPa (0.69 mol); (b) *n*-heptane 20 mL (0.14 mol). ( $\bullet$ ) Tetralin; ( $\triangle$ ) *cis*-decalin; ( $\Box$ ) *trans*-decalin; ( $\diamond$ ) octalin.

in *n*-heptane (74% at 70% conversion). It is reported that, in liquid-phase hydrogenation of tetralin, *cis*-isomer is directly formed via the hydrogenation of octalin intermediate adsorbed on an active site and the *trans*-isomer is formed via flipping of 2,3,4,5,6,7,8,10-octahydronaphthalene ( $\Delta^{1,9}$ -octalin) intermediate, in which  $\Delta^{1,9}$ -octalin desorbs from the active site and re-adsorbs on its other side, followed by its further hydrogenation to give *trans*-decalin.<sup>13</sup> We also investigated the isomerization<sup>14</sup> of *cis*- to *trans*-decalin over Rh/C in carbon dioxide solvent. Although *trans*-decalin is the thermodynamically stable isomer, *cis* to *trans* isomerization did not occur under 6 MPa of hydrogen and 15 MPa of carbon dioxide from 313 to 343 K.

Figure 2 shows the effect of reaction temperature on the hydrogenation of tetralin over Rh/C under 6 MPa of hydrogen and 15 MPa of carbon dioxide. As the reaction temperature increased from 313 to 343 K, the conversion of tetralin increased from 12 to 50%, but the selectivity to cis-decalin decreased from 78 to 75%. The cis/trans ratio decreased from 0.87 to 0.82. The cis/ trans ratio was almost constant regardless of the conversion at the same temperature. The density of carbon dioxide decreases from 0.78 to  $0.51 \,\mathrm{g \cdot cm^{-3}}$  with increasing temperature from 313 to 343 K at 15 MPa of carbon dioxide pressure. In a separate experiment at 25 MPa of carbon dioxide pressure, it was found that the selectivity to cis-decalin slightly increased (form 76.3 to 76.5%) with decrease in the density of carbon dioxide from 0.79 (25 MPa of carbon dioxide) to  $0.61 \text{ g} \cdot \text{cm}^{-3}$  (15 MPa) at 333 K. Thus, the decrease in the selectivity to cis-decalin with increasing temperature shown in Figure 2 was mainly due to the thermal effect, inducing activation of the flipping of  $\Delta^{1,9}$ octalin intermediate at higher reaction temperature.

Figure 3a shows the effect of hydrogen pressure on conversion of tetralin after 30 min of the reaction in supercritical carbon dioxide and *n*-heptane solvent. All tetralin was converted to decalin after longer reaction time under the reaction conditions. The conversion of tetralin increased linearly with increase in hydrogen pressure for both supercritical carbon dioxide and *n*-heptane solvents. The increase in the conversion would be caused by increase in the concentration of surface hydrogen atoms with increasing hydrogen pressure. However, it is noteworthy that the conversion of tetralin was two times higher in supercritical carbon dioxide than in *n*-heptane under the same hydrogen pressure. This would be due to higher solubility of hydrogen in supercritical carbon dioxide than in *n*-heptane. Figure 3b shows the effect of hydrogen pressure on selectivity to *cis*-decalin. The selectiv-



**Figure 2.** Effect of reaction temperature on the hydrogenation of tetralin over Rh/C (0.002 g) under carbon dioxide pressure 15 MPa and hydrogen pressure 6 MPa. Initial tetralin 2.3 mmol; reaction time 30 min.



**Figure 3.** Effect of hydrogen pressure on the hydrogenation of tetralin over Rh/C (0.002 g) at 333 K. Initial tetralin 2.3 mmol; reaction time 30 min. ( $\bullet$ ) Carbon dioxide pressure 15 MPa; ( $\triangle$ ) *n*-heptane 20 mL.

ity to *cis*-decalin increased from 76 to 79% with increase in hydrogen pressure from 6 to 12 MPa in supercritical carbon dioxide. On the other hand, the selectivity to *cis*-decalin was lower (73%) in *n*-heptane and almost constant regardless of hydrogen pressure. Higher selectivity to *cis*-decalin in supercritical carbon dioxide than in *n*-heptane could be explained by the rapid direct hydrogenation of  $\Delta^{1,9}$ -octalin intermediate to produce more *cis*decalin, and/or lower possibility of the desorption of  $\Delta^{1,9}$ -octallin intermediate to solvent due to lower solubility of  $\Delta^{1,9}$ -octallin in carbon dioxide solvent. Also, the increase in the selectivity to *cis*-decalin with increasing hydrogen pressure in supercritical carbon dioxide is probably due to higher concentration of hydrogen atoms on surface at higher hydrogen pressure leading to enhance hydrogenation rate of  $\Delta^{1,9}$ -octalin intermediate.<sup>8</sup>

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