Catalysis Letters Vol. 106, Nos. 3–4, February 2006 (© 2006)
DOI: 10.1007/s10562-005-9620-6

Tuning *cis*-decalin selectivity in naphthalene hydrogenation over carbon-supported rhodium catalyst under supercritical carbon dioxide

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Received 8 August 2005; accepted 7 November 2005

Catalytic hydrogenation of naphthalene to decalin was studied over a carbon-supported rhodium catalyst in supercritical carbon dioxide solvent at 333 K, and the results were compared with those in an organic solvent. *cis*-, *trans*-Decalin and tetralin were formed from the beginning of the reaction in supercritical carbon dioxide. Higher concentration of hydrogen in carbon dioxide solvent and on the active site, and also the suppression of desorption of partially hydrogenated tetralin molecules from the active site would be responsible for higher selectivity to *cis*-decalin in supercritical carbon dioxide than that in an organic solvent.

KEY WORDS: supercritical carbon dioxide; hydrogenation; naphthalene; decalin; hydrogen storage; carbon-supported rhodium catalyst.

1. Introduction

Hydrogen storage is a key process for its utilization as a clean energy source being developed recently. Cyclic saturated hydrocarbons such as decahydronaphthalene (decalin), bicyclohexyl, methylcyclohexane etc. are proposed as new mobile hydrogen storage media for proton exchange membrane fuel cells [1–3]. Hydrogen storage system with cyclic saturated hydrocarbons is more stable and inexpensive than with inorganic hydrogen-absorbing alloys. Cyclic saturated hydrocarbons are flammable; however, safer than using hydrogen cylinders, because pure hydrogen gas would detonate with a violent explosion when exposed to a spark accidentally.

Hydrogen can be obtained by catalytic dehydrogenation of the cyclic saturated hydrocarbons to the corresponding aromatic compounds such as naphthalene, biphenyl, toluene etc. [1–3] and stored by the hydrogenation of the aromatic products [4–6]. For hydrogen production from decalin, *cis*-isomer is more preferable, because dehydrogenation rate of *cis*-decalin is faster than that of *trans*-decalin [1(d)]. Also, *cis*-decalin can be used to produce sebacic acid that can be used in the manufacture of Nylon 6, 10 and plasticizer [7]. Hydrogenation of aromatic compounds is also important for the production of a high performance diesel fuel [8]. Selective hydrogenation of naphthalene to *cis*-decalin is an important reaction to study from both fundamental understanding of its adsorption characteristics and industrial application point of view.

Vapor and liquid phase hydrogenation of naphthalene over supported metal catalysts has been investigated by several researchers [9–14]. However, high temperature (>473 K) and acidic nature of catalyst supports used in the dearomatization form hydrocracking byproducts and high molecular weight products that cause the decrease in the yield of cyclic saturated hydrocarbons in vapor phase reaction [9,10,14]. Hence, dearomatization involving liquid phase hydrogenation under mild temperature (<373 K) is highly desirable; however, low reaction rates, low selectivity to decalin and difficulty in the separation of pure products from solvents become the critical issues. These drawbacks can be overcome by carrying out catalytic hydrogenation in supercritical carbon dioxide. Supercritical carbon dioxide ($T_c = 304.2$ K and $P_c = 7.38$ MPa) can be made miscible with light gasses and aromatics by proper choice of pressure and temperature conditions. Higher reaction rates and hence higher productivity, and easy separation of liquid products without using organic solvents can be achieved by conducting catalytic hydrogenations with solid catalysts in supercritical carbon dioxide medium [5,6,15–23]. Especially, this technique is very effective for the hydrogenation of solid substrates to liquid products, which are soluble in supercritical carbon dioxide. Recently, we have reported that a carbon-supported rhodium catalyst was found to be highly active and

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selective for the formation of decalin by the hydrogenation of naphthalene at very low temperature (333 K) in supercritical carbon dioxide [5]. While continuing our efforts to understand the catalysis in supercritical carbon dioxide, we report here a detailed comparative study of hydrogenation of naphthalene in supercritical carbon dioxide and in *n*-heptane solvent over the carbon-supported rhodium catalyst. In this work, a very high selectivity (60%) to decalin was achieved from the beginning of reaction and the direct hydrogenation of naphthalene to *cis*-decalin was found to be a probable pathway under supercritical carbon dioxide conditions.

2. Experimental

A commercially available carbon-supported rhodium catalyst (Rh/C) with metal loading of 5 wt% from Wako Pure Chemical Ind., Ltd., Japan was used without further reduction for the hydrogenation of naphthalene. The metal dispersion value of rhodium particles was found to be 12% determined by hydrogen adsorption method using AUTOSORB-1C (Quantachrome) [20]. The weighed amounts of the catalyst (typically 0.10 g) and naphthalene (typically 0.30 g) (supplied by Wako Pure Chemical Ind., Ltd., ≥99% purity) were placed in a stainless-steel high pressure reactor (50 mL capacity) and the reactor was flushed three times with carbon dioxide. After the required temperature (333 K) was attained with an oil bath, first hydrogen and then carbon dioxide were introduced into the reactor to the desired pressure levels and then the content was magnetically stirred. After the reaction period, the reactor was cooled down rapidly with an ice bath, the pressure was released slowly and the contents were discharged to separate the catalyst by simple filtration. The unreacted naphthalene and products were recovered with acetone, which showed a material balance of more than 90%. The quantitative analysis was conducted using GC-MS (HP-6890 and 5973) and GC-FID (HP-6890) equipped with HP-5 MS and DB-WAX capillary columns, respectively. *n*-Heptane was used as a solvent (Wako Pure Chemical Ind., Ltd.) for studying liquid phase hydrogenation of naphthalene under 0.1 MPa of carbon dioxide.

3. Results and Discussion

3.1. Reaction pathway of naphthalene hydrogenation

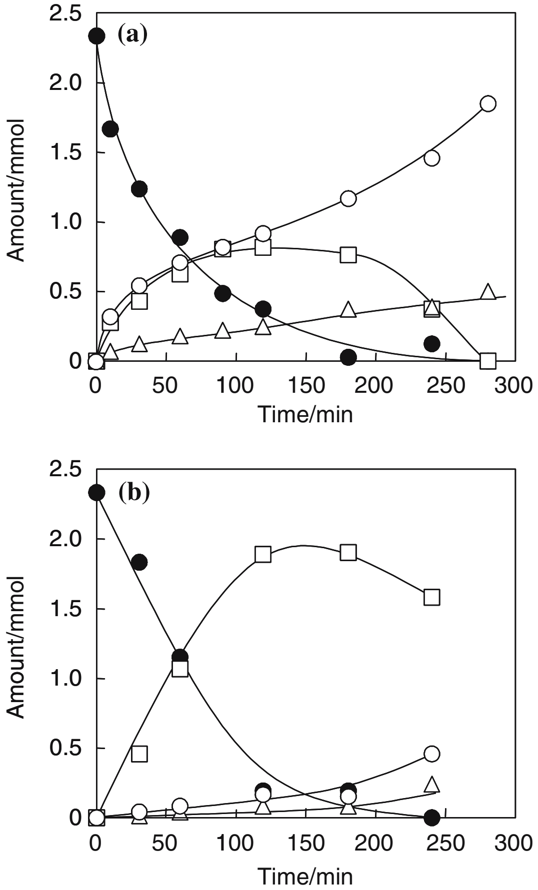

Figure 1. Hydrogenation of naphthalene over Rh/C in 10 MPa of carbon dioxide (a) and in 20 cm^3 of *n*-heptane (b). Naphthalene (●); tetralin (□); *cis*-decalin (○); *trans*-decalin (△). Temperature 333 K; hydrogen pressure 6 MPa; catalyst weight 0.10 g.

Figure 1 (a) shows the reaction profile for the hydrogenation of naphthalene over Rh/C in supercritical carbon dioxide at 333 K. The product distribution in the hydrogenation of naphthalene showed the formation of *cis*-, *trans*-decalin and 1,2,3,4-tetrahydronaphthalene (tetralin) as major products. Small amount of octahydronaphthalene (octalin) (we could not determine the position of carbon-carbon double bond from GC-MS library) was also detected (figure 2) as reported by Weitkamp [24]. The total yield of octalin was less than 0.5%. *cis*-, *trans*-Decalin and tetralin were formed simultaneously from the beginning of the reaction and their concentrations increased with increase in reaction time up to 90 min (80% conversion of naphthalene) in supercritical carbon dioxide at 333 K. The ratio of decalin (ca. 60%) to tetralin (ca. 40%) was almost constant for about 90 min initially beyond which the amount of tetralin decreased gradually and that of decalin increased till all naphthalene was consumed. Thus decalin was formed by both, the direct hydrogenation of naphthalene as well as consecutive hydrogenation via tetralin under supercritical carbon dioxide. It is important to note that *cis*-decalin was the major product in supercritical carbon dioxide medium. The *cis*-decalin selectivity (ratio, *cis*-decalin/(*cis*- + *trans*-decalin)) was constant at 81% from the beginning of the reaction up to 90 min. The naphthalene hydrogenation over Rh/C in *n*-heptane solvent at 333 K was also investigated separately, which exhibited a different product selectivity pattern from that observed in the

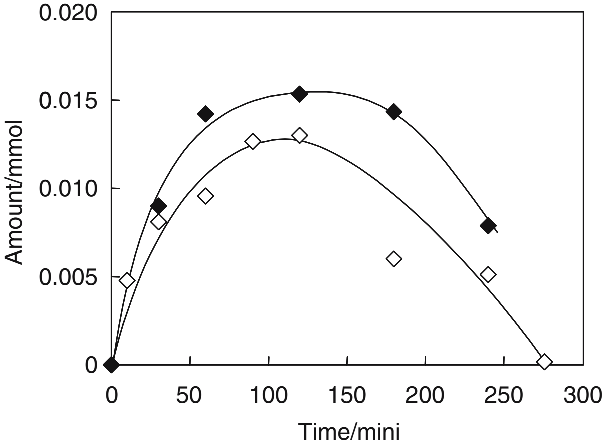

Figure 2. Octalin formation in naphthalene hydrogenation in 10 MPa of carbon dioxide (◇) and 20 cm^3 of *n*-heptane (◆). Temperature 333 K; hydrogen pressure 6 MPa; catalyst weight 0.10 g; initial naphthalene 2.3 mmol.

case of supercritical carbon dioxide solvent. The reaction profile of naphthalene hydrogenation in *n*-heptane solvent at 333 K is shown in figure 1 (b). Both decalin and tetralin were formed in a constant proportion of 1:9 up to 120 min for which naphthalene conversion was 80%. Beyond this conversion level decrease in concentration of tetralin was observed, indicating further hydrogenation of tetralin to decalin. However, initial formation of tetralin was much higher (9 times) than that of decalin and it almost remained constant with a marginal decrease for complete conversion of naphthalene, indicating a lower selectivity to decalin compared with that in supercritical carbon dioxide. In the case of liquid phase naphthalene hydrogenation in *n*-heptane, octalin was also formed more rapidly and its concentration was higher than that in supercritical carbon dioxide solvent (figure 2). *cis*-Decalin was also formed preferably in *n*-heptane; however, the selectivity to *cis*-decalin (in comparison to *trans*-decalin) was constant at 71% from the beginning of the reaction and was lower than that in supercritical carbon dioxide solvent. Thus higher selectivity to total decalin and particularly to *cis*-decalin (61% and 49%) was obtained in supercritical carbon dioxide solvent than those in *n*-heptane solvent (11% decalin and 7.8% *cis*-decalin) because the reaction pathway in supercritical carbon dioxide was different from that reported for gas/liquid phase naphthalene hydrogenation in which first tetralin is formed followed by its slow hydrogenation to decalin [11–13]. We also investigated the hydrogenation of tetralin and the mixture of naphthalene and tetralin separately, in order to confirm the reaction pathway for decalin formation. As seen from Table 1, turnover number of Rh/C catalyst for the hydrogenation of tetralin to decalin was 34 times higher than that for the hydrogenation of naphthalene in supercritical carbon dioxide. The lower activity for naphthalene hydrogenation could be due the fact that about 0.63 mol% benzothiophene was detected in the naphthalene feed. In the case of hydrogenation of a mixture of naphthalene and tetralin (entry 3, Table 1) tetralin was the major product while, decalin was hardly formed. These results suggest that the consecutive hydrogenation of tetralin to decalin proceeded only after most of naphthalene was hydrogenated (figure 1(a)), because naphthalene molecules get adsorbed more strongly than tetralin molecules on the active rhodium surface. The amount of decalin formed was also very small in the hydrogenation of naphthalene carried out in *n*-heptane solvent under 10 MPa of hydrogen pressure (Table 1 run 4). In the case of hydrogenation carried out in organic solvent (tetralin or *n*-heptane), it was visually observed through the view cell that organic phase (naphthalene and tetralin/*n*-heptane) was not miscible with the carbon dioxide solvent. The results in Table 1 show that the naphthalene hydrogenation in organic phase (tetralin/*n*-heptane, entry 3 and 4) preferentially gave tetralin as the major product (figure 1(b)), while decalin was the major product in supercritical carbon dioxide solvent.

3.2. *Effect of hydrogen pressure*

Figure 3(a) shows the dependence of the initial conversion of naphthalene on hydrogen pressure in supercritical carbon dioxide and *n*-heptane solvent. The conversion of naphthalene in supercritical carbon dioxide increased linearly with increase in hydrogen pressure from 2 to 6 MPa, and became constant at 45% over 6 MPa of hydrogen pressure. The increase in the conversion would be caused by increase in concentration

Table 1

Hydrogenation of naphthalene, tetralin, and mixture of naphthalene and tetralin over Rh/C [a]

Run	Reactant (initial amount / mmol)	Weight of Rh/C/g	Recovered product / mmol				TON [b]
			Naphthalene	Tetralin	Decalin	Octalin	
1	Naphthalene (2.34)	0.10	1.23	0.43	0.67	0.01	190
2	Tetralin (2.34)	0.005	–	0.44	1.80	0.10	6500
3	Naphthalene (2.34) + Tetralin (2.34)	0.10	2.03	2.64	0.02	0.01	–
4	Naphthalene (2.34) + *n*-Heptane (2.05)	0.10	1.48	0.70	0.16	0.01	150

[a] Reaction temperature 333 K; reaction time 30 min; hydrogen pressure 6 MPa; carbon dioxide pressure 10 MPa.

[b] TON = (the amount of naphthalene or tetralin reacted / the number of surface rhodium atoms).

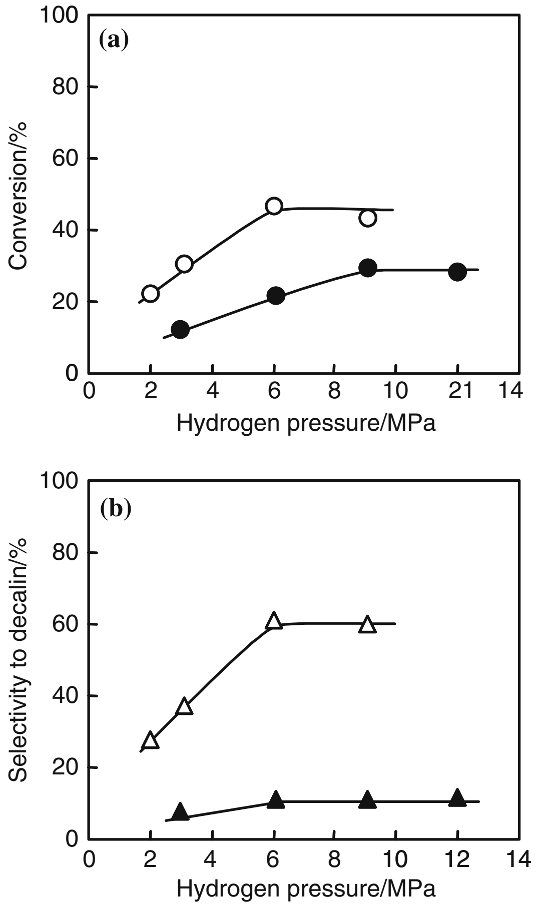

Figure 3. Effect of hydrogen pressure on the conversion of naphthalene (a) and selectivity to decalin (b) in the hydrogenation of naphthalene over Rh/C. In 10 MPa of carbon dioxide (○, △); in 20 cm^3 of *n*-heptane (●,▲). Temperature 333 K; reaction time 30 min; catalyst weight 0.10 g; initial naphthalene 2.3 mmol.

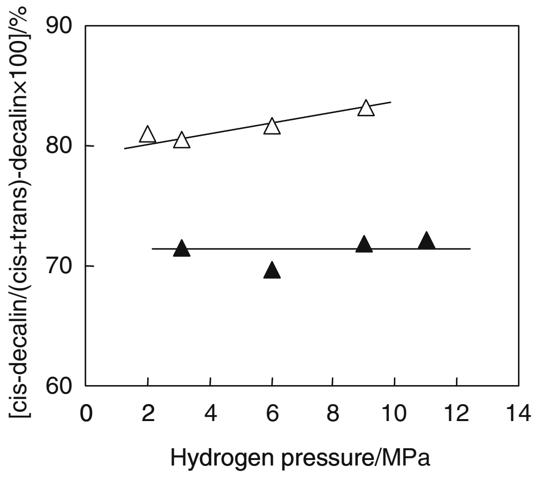

Figure 4. The effect of hydrogen pressure on the ratio of *cis*-decalin in the hydrogenation of naphthalene over Rh/C. In 10 MPa of carbon dioxide (△); in 20 cm^3 of *n*-heptane (▲). Temperature 333 K; reaction time 30 min (10 MPa of carbon dioxide) and 90 min (20 cm^3 of *n*-heptane); catalyst weight 0.10 g; initial naphthalene 2.3 mmol.

of surface hydrogen atoms with increasing hydrogen pressure. Over 6 MPa of hydrogen pressure, catalyst surface would be saturated with hydrogen atoms, thereby the conversion became constant. In the case of naphthalene hydrogenation in *n*-heptane solvent, the conversion increased with increase in hydrogen pressure up to 9 MPa, and became constant beyond 9 MPa of hydrogen pressure, indicating the similar trend observed for supercritical carbon dioxide conditions. However, overall conversion of naphthalene was two times higher in supercritical carbon dioxide than that in *n*-heptane solvent under the same hydrogen pressure. This is due to higher solubility of hydrogen in supercritical carbon dioxide than in *n*-heptane. All of the hydrogen gas introduced in the reactor was completely miscible with supercritical carbon dioxide solvent, whereas only a part of the hydrogen gas introduced was soluble in *n*-heptane solvent. Also, it should be noted that the constant naphthalene conversion observed beyond 6 MPa of hydrogen pressure in supercritical carbon dioxide was higher (45%) than that obtained (24%) beyond 9 MPa of hydrogen pressure in *n*-heptane. This suggests that the high concentration of surface hydrogen, available in supercritical carbon dioxide under 6 MPa of hydrogen pressure, could not be achieved even at higher (9 MPa) hydrogen pressure in *n*-heptane.

Figure 3(b) shows the effect of hydrogen pressure on the selectivity to decalin in supercritical carbon dioxide and *n*-heptane solvent. Similar to the conversion trend the selectivity to decalin in supercritical carbon dioxide also increased linearly up to 60% with increase in hydrogen pressure from 2 to 6 MPa beyond which it remained constant. On the other hand, the selectivity to decalin was much lower (<15%) in *n*-heptane than that in supercritical carbon dioxide and remained almost constant regardless of increase in hydrogen pressure. The higher (60%) selectivity to decalin obtained in supercritical carbon dioxide than that (<15%) in *n*-heptane solvent could be due to (i) the direct hydrogenation of naphthalene to decalin in supercritical carbon dioxide takes place at a faster rate because of higher hydrogen solubility in supercritical carbon dioxide leading to increase in surface hydrogen concentration and/or (ii) other electronic properties of supercritical carbon dioxide leading to different adsorption/desorption characteristics of naphthalene, intermediates and products. For example, although the conversion of naphthalene in supercritical carbon dioxide at 3 MPa of hydrogen pressure was 30% and comparable to 29% in *n*-heptane at 9 MPa of hydrogen pressure (figure 3(a)), the selectivity to decalin in supercritical carbon dioxide at 3 MPa of hydrogen was 3.5 times higher than that in *n*-heptane at 9 MPa of hydrogen (figure 3(b)). This result indicates that not only the concentration of surface hydrogen determines the decalin selectivity but also the rate of tetralin desorption from catalyst surface would play an important role to direct the selectivity to decalin.

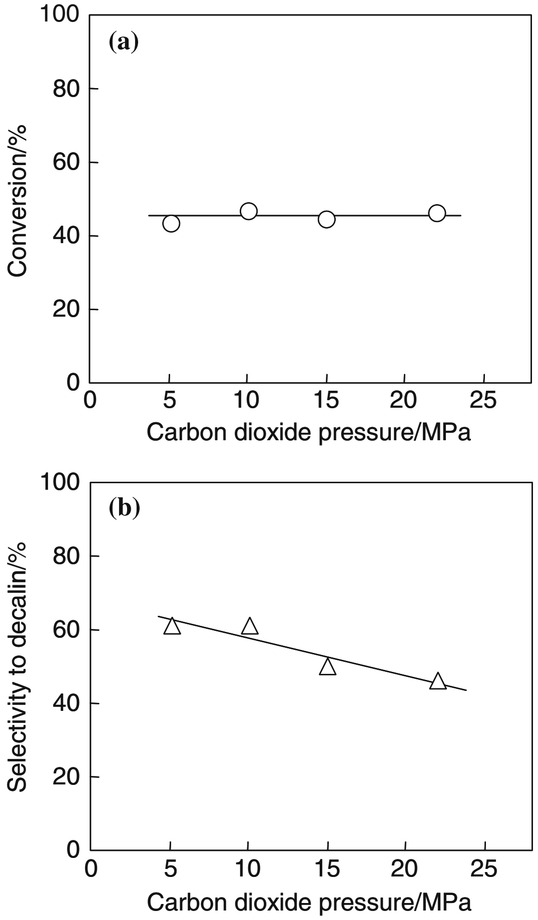

Figure 5. The effect of carbon dioxide pressure on the conversion (a) and selectivity to decalin (b) in the hydrogenation of naphthalene over Rh/C. Temperature 333 K; reaction time 30 min; catalyst weight 0.10 g; hydrogen pressure 6 MPa; initial naphthalene 2.3 mmol.

An interesting observation was made while studying the effect of hydrogen pressure on the ratio of *cis*-decalin to the total (*cis*- + *trans*-) decalin formed in both supercritical carbon dioxide and *n*-heptane solvent and the results are presented in figure 4. This ratio increased from 81 to 83% with increase in hydrogen pressure from 2 to 9 MPa in supercritical carbon dioxide. While the ratio of *cis*-decalin to the total decalin formed was lower (71%) in *n*-heptane than that observed in supercritical carbon dioxide and remained constant regardless of hydrogen pressure. It is reported that only *cis*-isomer is formed via the hydrogenation of tetralin adsorbed on active site (Scheme 1(a)) and the *trans*-isomer is formed via the flipping of 2,3,4,5,6,8,10-octahydronaphthalene ($\Delta^{1,9}$-octalin) intermediate, in which $\Delta^{1,9}$-octalin desorbs from the metal surface and re-adsorbs on its other side, followed by its further hydrogenation to give *trans*-decalin (Scheme 1(b)) [24]. Trace amounts of octalin were detected in our system (supercritical carbon dioxide conditions) by GC and GC-MS analyses; however, we could not determine the position of carbon–carbon double bond in octalin by GC-MS library. We also investigated the isomerization of *cis*- to *trans*-decalin over Rh/C under 6 MPa of hydrogen and 10 MPa of carbon dioxide pressure. Although, *trans*-decalin is the thermodynamically stable isomer, *cis* to *trans* isomerization did not occur under the conditions of our work. The detection of traces of octalin and *trans*-decalin would indicate the possibility of decalin formation via $\Delta^{1,9}$-octalin intermediate pathway in naphthalene hydrogenation under supercritical carbon dioxide system. However, higher selectivity to *cis*-decalin in supercritical carbon dioxide than in *n*-heptane can be explained by the rapid hydrogenation of $\Delta^{1,9}$-octalin intermediate to produce more *cis*-decalin, and/or lower possibility of the desorption of $\Delta^{1,9}$-octalin intermediate in supercritical carbon dioxide. Also, the selectivity to *cis*-decalin increased with increasing hydrogen pressure in supercritical carbon dioxide probably due to higher concentration of hydrogen atoms on surface at higher hydrogen pressure leading to enhance hydrogenation rate of $\Delta^{1,9}$-octalin in supercritical carbon dioxide.

3.3. *Effect of carbon dioxide pressure*

Figure 5 shows the effect of carbon dioxide pressure on the conversion of naphthalene and selectivity to decalin at 6 MPa of hydrogen pressure. The conversion of naphthalene was almost constant in the range of 5–22 MPa of carbon dioxide pressure (figure 5(a)). The naphthalene introduced (2.3 mmol) was found to be completely dissolved under around 10 MPa of carbon dioxide pressure and 6 MPa of hydrogen pressure at 333 K by direct observation with a view cell. A part of naphthalene molecules introduced were not dissolved under 7 MPa of carbon dioxide solvent. On the other hand, the conversion of naphthalene was almost constant in the range of 5–22 MPa of carbon dioxide pressure (figure 5(a)), because only naphthalene molecules dissolved in carbon dioxide were hydrogenated for

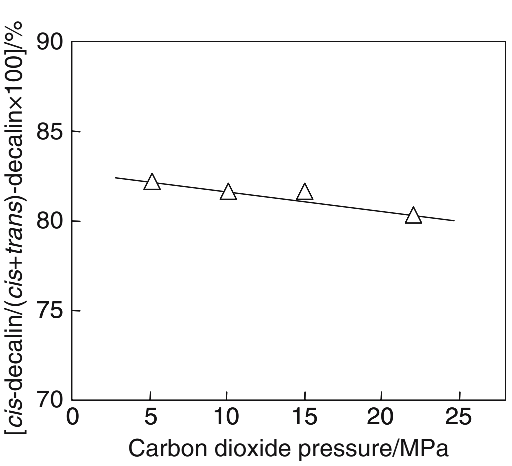

Figure 6. The effect of carbon dioxide pressure on the ratio of *cis*-decalin in the hydrogenation of naphthalene over Rh/C. Temperature 333 K; reaction time 30 min; catalyst weight 0.10 g; hydrogen pressure 6 MPa; initial naphthalene 2.3 mmol.

30 min at 333 K. We have confirmed by the view cell that 6 MPa of hydrogen gas was completely miscible with carbon dioxide solvent in the range of 5–22 MPa of carbon dioxide pressure to produce one phase. At 6 MPa of hydrogen pressure, active sites would be saturated with hydrogen atoms; hence the conversion was not influenced by the ratios of hydrogen to carbon dioxide in fluid phase. On the other hand, the selectivity to decalin and the ratio of *cis*-decalin to the total decalin (*cis*- + *trans*-) decreased with increase in carbon dioxide pressure (figures 5(b) and 6). This result would show that the desorption of tetralin molecules and $\Delta^{1,9}$-octalin intermediates from rhodium active sites was enhanced due to higher solubility of surface species in supercritical carbon dioxide as the carbon dioxide pressure increased.

4. Conclusion

The hydrogenation of naphthalene in supercritical carbon dioxide was compared with that in *n*-heptane solvent over a carbon-supported rhodium catalyst (Rh/C) at 333 K. A high selectivity to *cis*-decalin was achieved due to its direct formation from naphthalene at the beginning of the reaction in supercritical carbon dioxide, whereas the consecutive hydrogenation via tetralin pathway in *n*-heptane was mainly operative to give decalin. Higher rate of naphthalene hydrogenation and higher selectivity to *cis*-decalin in supercritical carbon dioxide than in *n*-heptane was observed due to higher concentration of surface hydrogen arising from higher solubility of hydrogen in supercritical carbon dioxide solvent.

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