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Ring hydrogenation of naphthalene and 1-naphthol over supported metal catalysts in supercritical carbon dioxide solvent

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Abstract

Catalytic ring hydrogenations of naphthalene and 1-naphthol were studied over several supported metal catalysts in supercritical carbon dioxide solvent at low temperature. Higher concentration of hydrogen in supercritical carbon dioxide and lower reaction temperature were responsible for higher catalyst activity and selectivities to the desired partial ring hydrogenated products as compared with those observed in organic solvent for the same catalyst.

Keywords: Supercritical carbon dioxide; Hydrogenation; Naphthalene; 1-Naphthol; Supported metal catalyst

1. Introduction

Catalytic hydrogenations of solid substrates having high melting points such as aromatic compounds, in organic solvents using supported metal catalysts have wide ranging applications in chemical processes; however, the separation of pure products from solvents is critical. Moreover, eliminating the use of organic solvents is highly desirable for environmentally benign processing. Supercritical carbon dioxide ($T_c = 304.2$ K and $P_c = 7.38$ MPa) is a prominent candidate as an alternative solvent because of its non-toxic and non-flammable properties [1]. Also, higher reaction rates and improved selectivity are obtained in supercritical carbon dioxide solvents. Organic transformations using hydrogen gas with solid catalysts in supercritical carbon dioxide solvent has several other 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 sites of solid surfaces by washing with supercritical carbon dioxide solvent [2–13].

Decahydronaphthalene (decalin) is proposed as a new mobile hydrogen storage medium for proton exchange membrane fuel cells [14,15]. Hydrogen can be obtained by catalytic dehydrogenation of the cyclic hydrocarbons to aromatic compounds and be stored by the hydrogenation of binuclear aromatics. Hence, efficient hydrogenation of naphthalene is an important reaction for producing decalin as a hydrogen storage material. The ring hydrogenation of aromatics is also useful for the production of a high performance diesel fuel [16]. Several researchers have investigated vapor and liquid phase hydrogenation of naphthalene over supported metal catalysts [17–22]; however, high temperature (>473 K) and acidic nature of catalyst supports used in the existing dearomatization processes form high molecular weight by products that cause the catalyst deactivation.

Ring hydrogenation of naphthalene derivatives is also important. For example, tetrahydronaphthols and tetralone, obtained by partial hydrogenation of naphthols, are intermediates for synthesizing drugs and agricultural chemicals [23]. Supported solid catalysts such as nickel-molybdenum and cobalt-molybdenum reported for the naphthol hydrogenation in conventional hydrotreating processes are active only at a very high reaction temperature of 600 K and above [24]. Shao and Song reported that a titania supported platinum-palladium

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bimetallic catalyst was active for the hydrogenation at 423 K in *n*-tridecane solvent; however, large amounts of dehydroxylated compounds such as decalin and tetralin were formed even at 423 K [23].

In this paper we demonstrated the application of supercritical carbon dioxide as an environmentally benign and versatile solvent for enhancing the activity and tailoring the selectivity pattern for the hydrogenation of naphthalene and 1-naphthol over solid catalysts.

2. Experimental

Catalysts used in this work, viz. charcoal and γ-alumina-supported, 5 wt.% rhodium (Rh/C and Rh/Al_2O_3), palladium (Pd/C and Pd/Al_2O_3), platinum (Pt/C and Pt/Al_2O_3) and ruthenium (Ru/C and Ru/Al_2O_3) were commercially available from Wako Pure Chemical Ind., Ltd., Japan [7]. All catalysts were used without further reduction for the hydrogenation reactions. Naphthalene and 1-naphthol were purchased from Wako Chemicals, Japan and used without further purification. 0.63 mol% of benzothiophene was present as an impurity in naphthalene used. Hydrogenation reactions were carried out in high-pressure stainless-steel reactors (50 ml capacity). The weighed amount of catalyst and reactant were placed in a reactor and flushed three times with carbon dioxide. After the required temperature was attained with an oil bath, first hydrogen and then carbon dioxide were introduced into the reactor. After the reaction was over, 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 (or 1-naphthol) and products were recovered with acetone. The recoveries were more than 90%. The quantitative analysis was conducted with GC-MS and GC-FID.

3. Results and discussion

3.1. Naphthalene hydrogenation

With a view cell, we confirmed that all naphthalene molecules were dissolved in carbon dioxide solvent under all reaction conditions reported in this paper. The catalyst screening results for naphthalene hydrogenation are shown in Table 1. A charcoal-supported rhodium catalyst was found to be the most active catalyst for the ring hydrogenation at 333 K in supercritical carbon dioxide solvent. γ-Alumina-supported catalysts have higher metal dispersion values; however, the turnover numbers and selectivity to decalin were lower than those of charcoal-supported catalysts. Turnover numbers for different metal particles in a series of charcoal-supported catalysts were in the following order: rhodium > palladium > platinum > ruthenium. Several other supported metal catalysts like nickel, platinum, palladium, and bimetallic palladium-platinum were reported for naphthalene hydrogenation under non-supercritical carbon dioxide conditions; however, the optimum temperature was always >473 K leading to ring opening/cracking reactions [17–22].

Table 1
Catalyst screening for the hydrogenation of naphthalene[a]

Catalyst	Dispersion (%)[b]	Conversion (%)	Selectivity (%)		TON[c]
			Tetralin	Decalin	
10 MPa of carbon dioxide					
5 wt.% Rh/C	12	46.9	38.8	61.2	190
5 wt.% Ru/C	25	9.6	49.0	51.0	18
5 wt.% Pd/C	3	7.6	95.9	4.1	130
5 wt.% Pt/C	8	2.6	95.1	4.9	30
5 wt.% Rh/Al_2O_3	34	15.2	56.9	43.1	22
5 wt.% Ru/Al_2O_3	32	0.9	47.1	52.9	1
5 wt.% Pd/Al_2O_3	18	8.2	100.0	0.0	23
5 wt.% Pt/Al_2O_3	18	0.0	0.0	0.0	0
20 mL of *n*-heptane					
5 wt.% Rh/C	12	21.9	88.7	11.3	88

[a] Reaction temperature, 333 K; reaction time, 30 min; catalyst, 0.10 g; hydrogen pressure, 6 MPa; carbon dioxide pressure, 10 MPa; initial naphthalene, 0.3 g (2.3 mmol).

[b] The dispersion was determined by a hydrogen adsorption method [8].

[c] TON = moles of naphthalene reacted/moles of surface metal atoms.

Fig. 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 decalin and 1,2,3,4-tetrahydronaphthalene (tetralin) as major products. Small amount of octahydronaphthalene (octalin) was also detected [25]. The total yield of octalin was less than 0.5%. Decalin is a

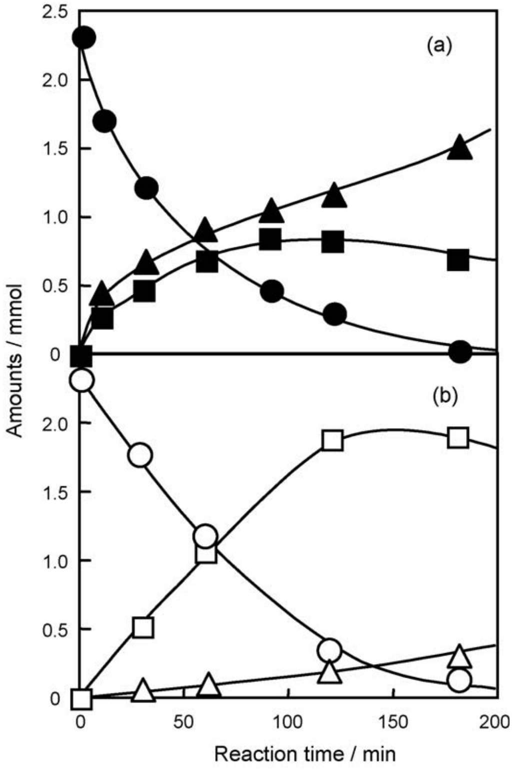


Fig. 1. Hydrogenation of naphthalene over the Rh/C catalyst in 10 MPa of carbon dioxide (a) and in 20 cm^3 of *n*-heptane (b). Naphthalene (●, ○); tetralin (■, □); decalin (▲, △). Temperature, 333 K; hydrogen pressure, 6 MPa, and catalyst weight, 0.10 g.

preferable cyclohydrocarbon having larger hydrogen storage capacity (7.3 wt.%) than tetralin (3.0 wt.%) for hydrogen storage materials. Both 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 and finally all naphthalene was converted to decalin after 280 min (not shown). Thus, decalin was formed by both the direct hydrogenation of naphthalene as well as the consecutive hydrogenation via tetralin under supercritical carbon dioxide. The naphthalene hydrogenation over the 5% Rh/C catalyst in *n*-heptane solvent at 333 K was also investigated separately, which exhibited a different product selectivity pattern from that observed in the case of supercritical carbon dioxide solvent. The reaction profile of naphthalene hydrogenation in *n*-heptane solvent at 333 K is shown in Fig. 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, the decrease in concentration of tetralin was observed, indicating further hydrogenation of tetralin to decalin. However, initial formation of tetralin was much higher (nine 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. Thus higher yield of decalin was obtained in supercritical carbon dioxide solvent than in *n*-heptane solvent because the reaction pathway in supercritical carbon dioxide was different from the pathway reported for gas/liquid phase naphthalene hydrogenation in which first tetralin is formed followed by its slow hydrogenation to decalin [25].

Fig. 2 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 of surface hydrogen atoms with increasing hydrogen pressure. Beyond 6 MPa of hydrogen pressure, catalyst surface would be saturated with hydrogen atoms, therefore, 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 (∼24%) 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 the hydrogen gas introduced into the reactor was completely miscible with supercritical carbon dioxide solvent, whereas only a part of the hydrogen gas introduced could be dissolved in *n*-heptane solvent. Also, it should be noted that the constant conversion of naphthalene observed in supercritical carbon dioxide solvent was 45% beyond 6 MPa of hydrogen pressure, which was higher than that in *n*-heptane (24%). This suggests that the high concentration of surface hydrogen, available in supercritical carbon dioxide under 6 MPa of hydrogen pressure, could not be achieved in *n*-heptane even at higher (9 MPa) hydrogen pressure.

Fig. 2 also 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 solvent than that in supercritical carbon dioxide and remained almost constant regardless of hydrogen pressure. The higher (60%) selectivity to decalin obtained in supercritical carbon dioxide than that (<15%) in *n*-heptane solvent could be due to the direct hydrogenation of naphthalene to decalin at a faster rate in supercritical carbon dioxide. This indicates higher hydrogen solubility in supercritical carbon dioxide leading to increase in surface hydrogen concentration. Although, the conversion of naphthalene in supercritical carbon dioxide at 3 MPa of hydrogen pressure was 30% and comparable to that in *n*-heptane (29%) at 9 MPa of hydrogen pressure, 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. This result indicates that the concentration of surface hydrogen determines the decalin selectivity. However, we cannot deny the possibility of the lower solubility of surface intermediate tetralin into supercritical carbon dioxide compared to heptane leading to accumulation of tetralin on the surface.

Fig. 3 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 10–22 MPa of carbon dioxide pressure. For 6 MPa of hydrogen pressure, active sites of the catalyst

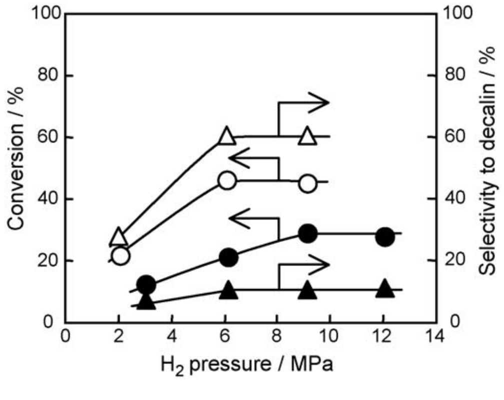


Fig. 2. Effect of hydrogen pressure on the conversion of naphthalene and selectivity to decalin in the hydrogenation of naphthalene over the Rh/C catalyst in 10 MPa of carbon dioxide (○, △) and in 20 cm^3 of *n*-heptane (●, ▲). Temperature, 333 K; reaction time, 30 min; catalyst weight, 0.10 g and initial naphthalene, 0.3 g (2.3 mmol).

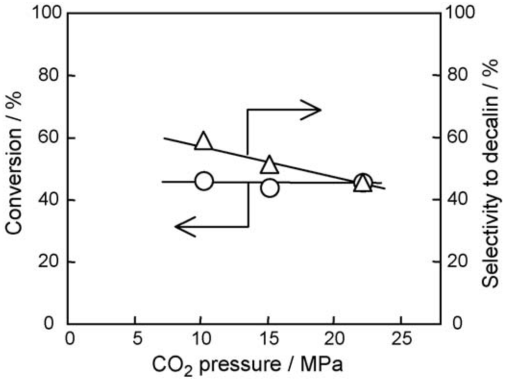


Fig. 3. The effect of carbon dioxide pressure on the conversion and selectivity to decalin in the hydrogenation of naphthalene over Rh/C. Temperature, 333 K; reaction time, 30 min; catalyst weight, 0.10 g; hydrogen pressure, 6 MPa and initial naphthalene, 0.3 g (2.3 mmol).

would be saturated with hydrogen atoms, hence the conversion is independent of carbon dioxide pressure. On the other hand, the selectivity to decalin decreased with increase in carbon dioxide pressure. This suggests that the desorption of the intermediate, tetralin was enhanced due to its higher solubility from the catalyst surface in supercritical carbon dioxide as carbon dioxide pressure was increased.

Fig. 4 shows the reaction profiles of naphthalene hydrogenation over Rh/C, Pt/C, and the mixture of Rh/C and Pt/C catalysts. The Pt/C catalyst showed little activity for the naphthalene hydrogenation under 3 MPa of hydrogen and 10 MPa of carbon dioxide. On the other hand, it is noteworthy that the mixture of Rh/C and Pt/C catalysts showed higher activity and selectivity to decalin than those observed for Rh/C catalyst alone. The enhancement of naphthalene conversion and selectivity to decalin, observed for a mixture of Rh/C and Pt/C catalysts, would be explained by the enrichment of hydrogen atoms on the Rh/C catalyst surface. The enhancement of hydrogen atoms present on rhodium metal surface could be due to spillover hydrogen from platinum surface of the Pt/C catalyst. The hydrogen atom concentration available for naphthalene hydrogenation was found to be important from the fact that charcoal-supported metal particles showed higher turnover numbers than those on γ-alumina (see Table 1).

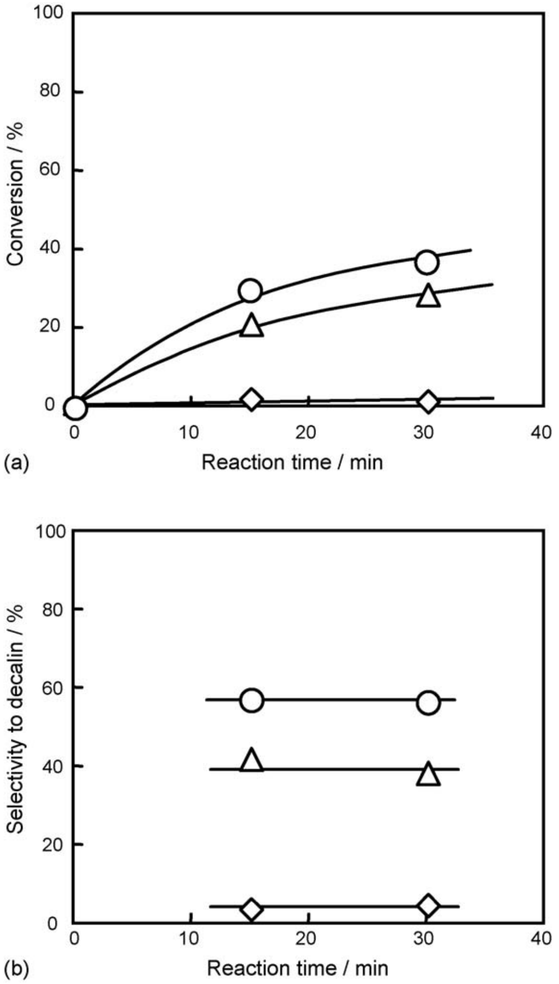


Fig. 4. (a and b) Hydrogenation of naphthalene over Rh/C (0.1 g) (△), Pt/C (0.1 g) (□), and the mixture of Rh/C (0.1 g) and Pt/C (0.1 g) (○) in 3 MPa of hydrogen and 10 MPa of carbon dioxide.

3.2. 1-Naphthol hydrogenation

With the view cell, we confirmed that all 1-naphthol molecules were dissolved in carbon dioxide solvent under all reaction conditions reported in this paper. The catalyst screening results for hydrogenation of 1-naphthol (**1**) are shown in Table 2.

Table 2
Catalyst screening for the hydrogenation of 1-naphthol[a]

Catalyst	Conversion (%)	Selectivity (%)					TON[b]
		2	**3**	**4**	**5 + 6**	**7 + 8**	
5 wt.% Rh/C	42.6	71.6	7.8	11.8	6.9	1.5	544
5 wt.% Ru/C	0.8	59.4	19.9	7.0	8.6	5.0	9
5 wt.% Pd/C	11.2	56.2	36.1	7.0	0.1	0.6	139
5 wt.% Pt/C	5.4	79.6	10.6	3.3	3.1	1.4	66
5 wt.% Rh/Al_2O_3	24.1	75.9	6.4	12.1	4.4	0.8	96
5 wt.% Ru/Al_2O_3	0.1	53.3	46.7	0.0	0.0	0.0	1
5 wt.% Pd/Al_2O_3	2.7	53.6	38.0	8.4	0.0	0.0	33
5 wt.% Pt/Al_2O_3	0.8	76.9	9.9	10.2	2.9	0.0	10

2: 5,6,7,8-tetrahydro-1-naphthol; **3**: 1-tetralone; **4**: 1,2,3,4-tetrahydro-1-naphthol; **5**: 1-decalone; **6**: decahydro-1-naphthol; **7**: tetraline; **8**: decaline.

[a] Reaction temperature, 323 K; reaction time, 15 min; hydrogen pressure, 3 MPa; carbon dioxide pressure, 10 MPa; initial 1-naphthol, 0.2 g (1.4 mmol). Moles of initial 1-naphthol/moles of metal atoms = 1250.

[b] TON = moles of 1-naphthol reacted/moles of surface metal atoms.

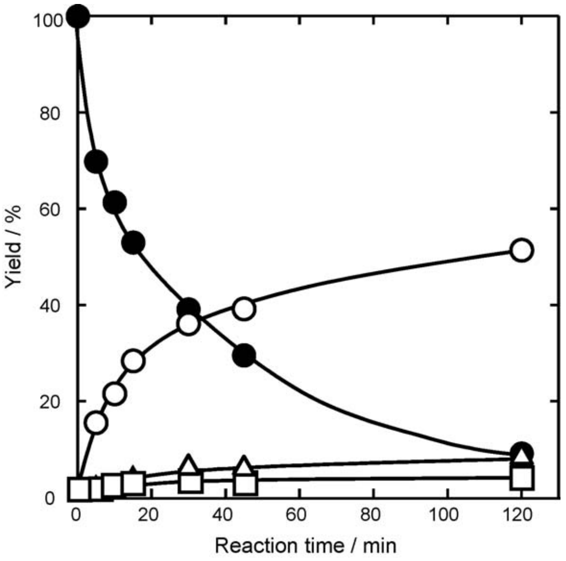


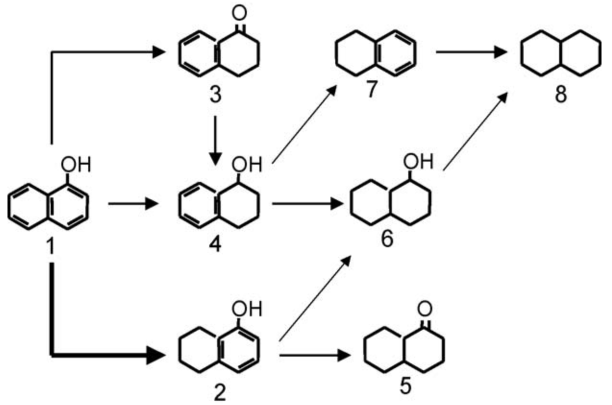
Fig. 5. Hydrogenation of 1-naphthol over the Rh/C catalyst in 3 MPa of hydrogen and 10 MPa of carbon dioxide at 323 K, initial 1-naphthol 0.20 g (1.4 mmol), catalyst weight 0.02 g. 1-Naphthol (●); 5,6,7,8-tetrahydro-1-naphthol (○); 1,2,3,4-tetrahydro-1-naphthol (△); 1-tetralone (□).

It was found that the charcoal-supported rhodium catalyst was also active for the ring hydrogenation of 1-naphthol. The main products formed were: 5,6,7,8-tetrahydronaphthol (**2**), 1-tetralone (**3**), and 1,2,3,4-tetrahydronaphthol (**4**). The minor ones were 1-decalone (**5**), decahydro-1-naphthol (**6**), tetralin (**7**) and decalin (**8**). Tetralin (**7**) and decalin (**8**) were formed through dehydroxylation; however, naphthalene was not observed under these reaction conditions.

The reaction profile of 1-naphthol hydrogenation under supercritical carbon dioxide over the Rh/C catalyst is shown in Fig. 5. The conversion of 1-naphthol was 90% after 2 h. From the beginning of the reaction, 1-naphthol was partially hydrogenated to 5,6,7,8-tetrahydro-1-naphthol (**2**), 1,2,3,4-tetrahydro-1-naphthol (**4**), and 1-tetralone (**3**). The product selectivities were constant until most of 1-naphthol was hydrogenated, indicating that 1-naphthol hydrogenation over supported metal catalysts is a parallel reaction similar to phenol hydrogenation to cyclohexanone and cyclohexanol in supercritical carbon dioxide [7].

Fully ring hydrogenated products, 1-decalone (**5**) and decahydro-1-naphthol (**6**), were also obtained; however, the total selectivity of such products was about 6–7%. Small amounts (<2%) of tetralin (**7**) and decalin (**8**), dehydroxylated compounds were also obtained even at 95% of conversion. Dehydroxylation was considerably suppressed under the supercritical carbon dioxide conditions owing to the low reaction temperature (323 K) unlike the hydrogenation in organic solvents at high temperature (423–600 K).

We also studied separately, the hydrogenation of partially hydrogenated compounds (**2**, **3** and **4**) and it was found that 5,6,7,8-tetrahydro-1-naphthol (**2**) was hardly hydrogenated, while dehydroxylated compounds (**7** and **8**) were easily formed in the hydrogenation of 1,2,3,4-tetrahydro-1-naphthol (**4**). 1,2,3,4-Tetrahydro-1-naphthol (**4**) was also formed by the hydrogenation of 1-tetralone (**3**). Based on the product distribution observed, the proposed reaction pathway for naphthol hydrogenation in supercritical carbon dioxide medium over Rh/C at 323 K is shown in Scheme 1.



Scheme 1. Reaction scheme of 1-naphthol hydrogenation over Rh/C in supercritical carbon dioxide.

We also examined the influence of pressure of hydrogen on the catalyst activity and selectivity (Fig. 6). It was found that hydrogenation activity increased with increase in hydrogen pressure from 1 to 6 MPa at 10 MPa of carbon dioxide, due to increase in the concentration of surface hydrogen with increase in hydrogen pressure similar to naphthalene hydrogenation described above. Higher selectivity to partially hydrogenated compounds (**2**, **3** and **4**) were obtained while, selectivity to dehydroxylated compounds (**7** and **8**) was too low (1–2%) and was not affected by hydrogen pressure.

The hydrogenation activity also increased with increase in carbon dioxide pressure of 3 MPa of hydrogen (Fig. 7). We observed that 1-naphthol was dissolved under 10 MPa of carbon dioxide with the view cell. Due to higher solubility of hydrogen in supercritical carbon dioxide, enhanced mass transfer contributed to the increased catalyst activity. On the

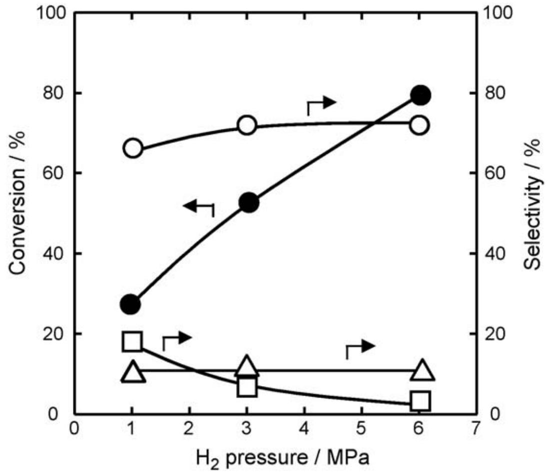


Fig. 6. Effect of hydrogen pressure on the conversion and selectivity in the hydrogenation of 1-naphthol over the Rh/C catalyst in 10 MPa of carbon dioxide. Temperature, 323 K; reaction time, 15 min; catalyst weight, 0.02 g and initial 1-naphthol, 0.20 g (1.4 mmol). 1-Naphthol (●); 5,6,7,8-tetrahydro-1-naphthol (○); 1,2,3,4-tetrahydro-1-naphthol (△); 1-tetralone (□).

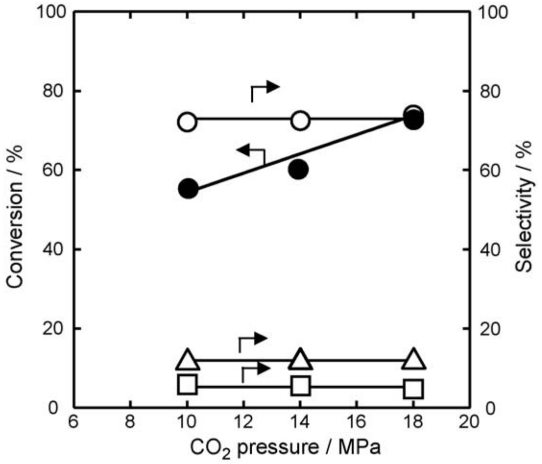


Fig. 7. Effect of carbon dioxide pressure on the conversion and selectivity in the hydrogenation of 1-naphthol over Rh/C. Temperature, 323 K; reaction time, 15 min; catalyst weight, 0.20 g; hydrogen pressure, 3 MPa and initial 1-naphthol, 0.2 g (1.4 mmol). 1-Naphthol (●); 5,6,7,8-tetrahydro-1-naphthol (○); 1,2,3,4-tetrahydro-1-naphthol (△); 1-tetralone (□).

other hand, the selectivity to partial hydrogenation products was almost constant regardless of increase in carbon dioxide pressure.

4. Summary

The hydrogenation of naphthalene in supercritical carbon dioxide was compared with that in *n*-heptane solvent over a charcoal-supported rhodium catalyst (Rh/C) at 333 K. A high selectivity to the desired product, decalin was achieved at the beginning of the reaction in supercritical carbon dioxide, whereas the consecutive hydrogenation via tetralin was observed in *n*-heptane.

The hydrogenation of 1-naphthol also proceeded over Rh/C in supercritical carbon dioxide at 323 K and a high selectivity to partial ring hydrogenated compounds was achieved.

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