Enhanced Selectivity to Decalin in Naphthalene Hydrogenation under Supercritical Carbon Dioxide

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A charcoal-supported rhodium catalyst was highly active and selective to decalin for the hydrogenation of naphthalene at very low temperature (333 K) under supercritical carbon dioxide.

Hydrogen is promised to be one of the clean energy sources without any emission of greenhouse gases. Cyclic saturated hydrocarbons such as decalin, methylcyclohexane, and cyclohexane are proposed as new mobile hydrogen storage media for proton exchange membrane (PEM) fuel cells.[1] Hydrogen can be obtained by catalytic dehydrogenation of the cyclic hydrocarbons to aromatic compounds and be stored by the hydrogenation of aromatic products. Hydrogenation of aromatic compounds is important not only for storing hydrogen by producing cyclic saturated hydrocarbon, but also for the production of a high performance diesel fuel.[2] Vapor and liquid phase hydrogenation of naphthalene over supported metal catalysts has been investigated by several researchers.[3–8] However, high temperature (>473 K) and acidic nature of catalyst supports used in the existing dearomatization processes form high molecular weight byproducts that cause the catalyst deactivation.[3,4,8] Hence, dearomatization involving liquid phase hydrogenation under mild temperature (<373 K) is highly desirable, however, low reaction rates and difficulty in the separation of pure products from solvents become the critical issues. Higher reaction rates and hence higher productivity, and easy separation of catalysts and products without using organic solvents can be achieved by conducting catalytic hydrogenations under supercritical carbon dioxide medium.[9] This technique is very effective for the hydrogenation of substrates, which are solid but soluble in supercritical carbon dioxide. In this paper, we report selective hydrogenation of naphthalene with metal catalysts on a neutral support (carbon) at very low temperature (333 K) in supercritical carbon dioxide.

Commercially available catalysts were used in this study, viz. 5 wt % carbon-supported rhodium (5 wt % Rh/C), platinum (5 wt % Pt/C), palladium (5 wt % Pd/C), ruthenium (5 wt % Ru/C), from Wako Chemicals, Japan. The dispersion values of metal particles on charcoal were determined by a hydrogen adsorption method.[10] All catalysts were used without further reduction for the hydrogenation of naphthalene. Also, a 5 wt % charcoal-supported nickel catalyst (5 wt % Ni/C) prepared with an impregnation method using nickel chloride and charcoal (Wako Pure Chemical Ind., Ltd., Japan), following reduction at 573 K for 2 h was examined. The weighed amounts of catalyst and naphthalene were placed in a stainless-steel reactor (50-mL capacity). The reactor was flushed three times with carbon dioxide. After the required temperature was attained with a hot air circulating oven, hydrogen and carbon dioxide were introduced into the re-

actor. 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 and products were recovered with acetone, which showed a material balance more than 90%. The quantitative analysis was conducted with GC-FID (HP-6890).

The catalyst screening results for naphthalene hydrogenation are shown in Table 1. A charcoal-supported rhodium catalyst was found to be highly active (TON = 190) for the ring hydrogenation at 333 K under supercritical carbon dioxide and the turnover numbers for different catalysts were in the following order: rhodium > palladium > platinum > ruthenium. The 5 wt % Ni/C catalyst did not show any hydrogenation activity for naphthalene under supercritical carbon dioxide conditions. Several supported nickel,[4] platinum,[3,5–7] palladium,[3,7] and bimetallic palladium–platinum[8] catalysts were reported for naphthalene hydrogenation under non supercritical carbon dioxide conditions, however, the optimum temperature was always > 473 K associated with ring opening/cracking reactions. The product distribution in hydrogenation of naphthalene over charcoal-supported metal catalysts under supercritical carbon dioxide showed the formation of *cis*-, *trans*-decalin and tetralin. Decalin is a preferable cyclohydrocarbon having larger hydrogen content (7.3 wt %) than that of tetralin (3.0 wt %). Interestingly, the highest selectivity (61%) to decalin was attained over the 5 wt % Rh/C catalyst under supercritical carbon dioxide. In or-

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

Catalyst	Conversion / %	Selectivity / %		TON[b]
		Tetralin	Decalin	
in 10 MPa of carbon dioxide				
5 wt % Rh/C	46.9	38.8	61.2	190
5 wt % Ru/C	9.6	49.0	51.0	18
5 wt % Pd/C	7.6	95.9	4.1	130
5 wt % Pt/C	2.6	95.1	4.9	30
in 20 mL of *n*-heptane				
5 wt % Rh/C	21.9	88.7	11.3	88
5 wt % Ru/C	1.7	69.7	30.3	3
5 wt % Pd/C	1.2	100	0.0	20
5 wt % Pt/C	0.4	86.8	13.2	5

[a]Temperature 333 K; reaction time 30 min; catalyst 0.10 g; hydrogen pressure 6 MPa; initial naphthalene 2.3 mmol. [b]TON = (moles of naphthalene reacted)/(moles of surface metal atoms). The metal dispersion was determined by a hydrogen adsorption method.
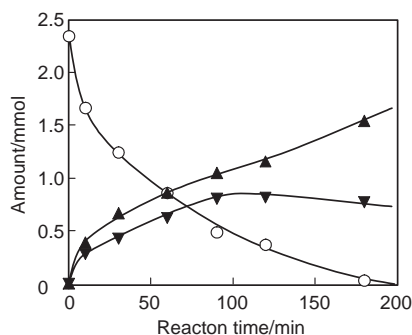
Figure 1. The hydrogenation of naphthalene under hydrogen pressure 6 MPa carbon dioxide pressure 10 MPa, and initial naphthalene 2.3 mmol at 333 K for 0.10 g of 5 wt % Rh/C. (○) Naphthalene; (▼) tetralin; (▲) decalin.

der to compare the catalyst activity for naphthalene hydrogenation under non supercritical conditions, several experiments were separately carried out in *n*-heptane solvent at 333 K and the results are given in Table 1. Under non supercritical conditions also, the 5 wt % Rh/C catalyst was the most active catalyst, however, the activity was about one half times lower than that under the supercritical conditions. Also, it is important to note that the selectivity to decalin was only 11.3% over the 5 wt % Rh/C catalyst under non-supercritical conditions. The maximum selectivity to decalin achieved was only 30% (for 1.7% conversion of naphthalene) over the 5 wt % Ru/C catalyst in liquid phase conditions (Table 1). When the amount of *n*-heptane solvent in the reactor was changed from 20 to 10 mL under 6 MPa of hydrogen, the rate of hydrogenation and selectivity to decalin were not changed over the 5 wt % Rh/C and 5 wt % Ru/C catalysts. The higher naphthalene conversion and higher decalin selectivity in supercritical carbon dioxide than that in *n*-heptane is mainly due to the enhanced solubility and diffusivity of hydrogen in supercritical carbon dioxide.

The hydrogenation profile under supercritical carbon dioxide at 333 K over 5 wt % Rh/C was also examined (Figure 1). Decalin formation was observed along with tetralin without any induction period and its formation increased with increase in reaction time, and the ratio of decalin (60%) to tetralin (40%) was almost constant for about 90 min initially, indicating that both tetralin and decalin are the primary products in naphthalene hydrogenation. After 80% of naphthalene was hydrogenated, the hydrogenation of tetralin to decalin proceeded. Finally almost all naphthalene was hydrogenated to decalin. This pattern is dramatically different from that reported in gas/liquid phase hydrogenation of naphthalene at high temperature, in which first tetralin is formed followed by its hydrogenation to decalin indicating these to be consecutive reactions.[5–7] Also, it is reported that residual naphthalene inhibits the hydrogenation of tetralin to decalin.[11] Thus, in the hydrogenation at high temperature, decalin is not formed at low naphthalene conversion. It is important to note that the formation of decalin becomes a parallel reaction in hydrogenation of naphthalene under supercritical carbon dioxide over supported rhodium catalyst at very low temperature (333 K).

Figure 2 shows the dependence of conversion and selectivity on hydrogen pressure over 5 wt % Rh/C under 10 MPa of supercritical carbon dioxide solvent. The ratio of decalin to tetralin
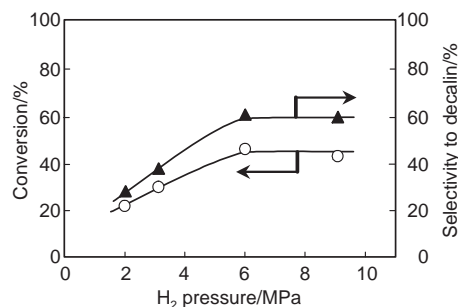

Figure 2. Effect of hydrogen pressure on the hydrogenation of naphthalene over 5 wt % Rh/C (0.10 g) under carbon dioxide pressure 10 MPa and initial naphthalene 2.3 mmol at 333 K for 30 min. (○) Conversion of naphthalene; (▲) selectivity to decalin.

was almost constant in each case. The conversion of naphthalene and decalin selectivity increased linearly with increase in hydrogen pressure (2 to 6 MPa) and both remained constant beyond 6 MPa hydrogen pressure. The increase in activity and decalin selectivity would be caused by increase in concentration of surface hydrogen with increasing hydrogen pressure. Over 6 MPa of hydrogen pressure, catalyst surface would be saturated with hydrogen, then the conversion and decalin selectivity were constant regardless of the increase in hydrogen pressure.

Naphthalene was hydrogenated over 5 wt % Rh/C catalyst under supercritical carbon dioxide solvent at very low temperature (333 K) to give high selectivity to decalin in a shorter reaction time. The formation of tetralin and decalin were parallel reactions unlike the consecutive reactions in the case of hydrogenation at high temperature. In this study, we used commercial supported metal catalysts and did not add any promoter, or did not perform any special treatment on the catalysts. Optimizations of catalyst preparation method and of catalyst components are currently under investigation.

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