

## Partial Ring Hydrogenation of Naphthols over Supported Metal Catalysts in Supercritical Carbon Dioxide Solvent

Eiichi Mine,<sup>†</sup> Eiji Haryu,<sup>††</sup> Kunio Arai,<sup>†,††</sup> Takafumi Sato,<sup>†</sup> Osamu Sato,<sup>†</sup> Akiyoshi Sasaki,<sup>†</sup>  
Chandrashekhar V. Rode,<sup>†††</sup> and Masayuki Shirai<sup>\*†</sup>

<sup>†</sup>*Supercritical Fluid Research Center, National Institute of Advanced Industrial Science and Technology,  
4-2-1, Nigatake, Miyagino, Sendai 983-8551*

<sup>††</sup>*Graduate School of Environmental Studies, Tohoku University, 6-6-07 Aoba, Aramaki, Aoba, Sendai 980-8579*

<sup>†††</sup>*Homogeneous Catalysis Division, National Chemical Laboratory, Dr. Homi Bhabha Road, Pune 411008, India*

(Received February 10, 2005; CL-050189)

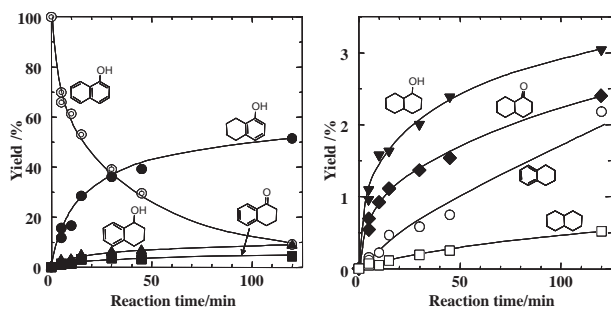
Selective ring hydrogenation of naphthols to tetrahydronaphthols and tetralones proceeded at 323 K over a charcoal supported rhodium catalyst in supercritical carbon dioxide.

Tetrahydronaphthols and tetralones are important intermediates for synthesizing drugs, and agricultural chemicals. Ionic hydrogenation of naphthols with excess of aluminium halides is reported in the literature;<sup>1</sup> however, generation of large amounts of inorganic salts in these processes is a serious problem for disposal. Supported solid catalysts have also been reported for the naphthol hydrogenation in conventional hydrotreating processes. Such catalysts include supported nickel–molybdenum and cobalt–molybdenum catalysts; however, these are active only at a very high reaction temperature of 600 K and above.<sup>2</sup> Shao and Song reported that a titania supported platinum–palladium bimetal catalyst was active for the hydrogenation at 423 K in *n*-tridecane solvent;<sup>3</sup> however, large amounts of dehydroxylated compounds such as decalin and tetralin were formed even at 423 K. Catalytic reactions of solid substrates in organic solvents using supported metal catalysts have wide ranging applications in fine chemical processes; however, reaction velocities are not so high and the separation of pure products from solvents is critical. Moreover, eliminating the use of organic solvents is highly desirable for environmentally benign processing. Organic transformations involving gas-liquid systems with solid catalysts under supercritical carbon dioxide have several other advantages; i) high reaction rates due to increased gas solubility in supercritical carbon dioxide, thereby eliminating mass transfer resistances, ii) easy separation of catalysts and products, iii) maintaining clean solid surfaces by washing with supercritical carbon dioxide solvent.<sup>4</sup> Especially, higher solubility of hydrogen in supercritical carbon dioxide, is advantageous for controlling the product selectivity and catalyst activity in catalytic hydrogenation reactions involving consecutive and parallel reaction pathways. In this paper, we report the partial ring hydrogenation of naphthols with supported metal catalysts under supercritical carbon dioxide.

Catalysts used in this work, viz. 5 wt % carbon and  $\gamma$ -alumina supported rhodium (Rh/C (12%) and Rh/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (34)), palladium (Pd/C (3) and Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (18)), platinum (Pt/C (8) and Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (18)), and ruthenium (Ru/C (25) and Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (32)) were commercially available from Wako Chemicals, Japan. The values in parentheses are the dispersion values of metal particles on the supports determined by a hydrogen adsorption method.<sup>5</sup> Hydrogenation reactions were carried out in

stainless-steel reactors (50 mL capacity). The weighed amount of catalyst and reactant were placed in a reactor and flushed twice with carbon dioxide. After the desired temperature was attained using an oil bath, hydrogen and carbon dioxide were introduced into the reactor. At the end of the reaction, contents were discharged to separate the catalyst by simple filtration and analyzed with GC-FID and GC-MS that showed the material balance >90%.

The activities of various catalysts for the ring hydrogenation of 1-naphthol were examined at 323 K under 3 MPa of hydrogen and 10 MPa of carbon dioxide. We observed that the most of the 1-naphthol was dissolved under this condition. The activities expressed as turnover numbers (TON) (in parentheses)<sup>6</sup> were found to be in the following order: Rh/C (544) > Pd/C (139) > Rh/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (96) > Pt/C (66) > Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (33) > Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (10) > Ru/C (9) > Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (1), indicating that Rh/C was the most active catalyst. While, supported palladium catalysts were found to be highly active for the ring hydrogenation of both 1-naphthol and phenol at 423 K in organic solvents,<sup>3,7,8</sup> our results showed that a different metal function (rhodium) was active for 1-naphthol hydrogenation in supercritical carbon dioxide. It is expected that the reaction mechanism under supercritical carbon dioxide is totally different from liquid-phase conditions. Not only the enhancement of hydrogen solubility in supercritical carbon dioxide contributes to the higher catalyst activity, but also there is an additional role played by supercritical carbon dioxide; i) the adsorption characteristics of 1-naphthol on active sites of rhodium-metal particles and/or ii) the electronic structure of metal particles are different under supercritical carbon dioxide from that in non-supercritical media. This is also supported by the fact that in spite of higher dispersions of metals than those of the same metals on  $\gamma$ -alumina, they showed lower hydrogenation activities than on carbon support. Hence, usual criteria like higher metal dispersion, may not be directly applicable for the catalyst activity in supercritical carbon dioxide medium. Arai et al. reported that the electron density of gold particles decreased in supercritical carbon dioxide.<sup>9</sup> The catalytic activities of metals under supercritical carbon dioxide conditions could be different owing to modification by electron transfer to carbon dioxide which would affect the adsorption characteristic of naphthol as compared with those under gas- and liquid-phase conditions. The lower electron density of rhodium under supercritical carbon dioxide would cause strong adsorption of 1-naphthol leading to the highest catalyst activity. Further in situ investigation of the structure and electronic state of metal particles under supercritical carbon dioxide and deter-



**Figure 1.** The hydrogenation of 1-naphthol under hydrogen pressure 3.0 MPa, carbon dioxide pressure 10 MPa over a Rh/C catalyst. Initial 1-naphthol 0.20 g, reaction temperature 323 K.

mination of the surface concentration of hydrogen and 1-naphthol adsorbed are needed.

The reaction profile of naphthol hydrogenation under supercritical carbon dioxide over the Rh/C catalyst is shown in Figure 1. The conversion of naphthol obtained was 90% after 2 hours. 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 1-naphthol hydrogenation over supported metal catalysts is a parallel reaction similar to phenol hydrogenation to cyclohexanone and cyclohexanol in supercritical carbon dioxide.<sup>10</sup>

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 while naphthalene formation was not observed even at 95% of conversion. Dehydroxylation was considerably suppressed under our reaction conditions owing to the low reaction temperature unlike the hydrogenation in organic solvents. We also studied separately, the hydrogenation of **2**, **4**, and **3** and it was found that **2** was hardly hydrogenated, while **7** and **8** were easily formed in the hydrogenation of **4**. **4** was also formed by the hydrogenation of **3**. Based on the product distribution observed, the proposed reaction pathway for naphthol hydrogenation in supercritical carbon dioxide medium is shown in Graphical abstract.

In addition, we have also examined the influence of pressure of both hydrogen and carbon dioxide on the catalyst activity and selectivity. These results are presented in Table 1. It was found that hydrogenation activity increased with increase in hydrogen pressure from 1 to 6 MPa at 10 MPa carbon dioxide, caused by increase in the concentration of surface hydrogen with increase in hydrogen pressure. 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 from 8 to 18 MPa at constant hydrogen pressure of 3 MPa. We observed that the most of the 1-naphthol was dissolved under 10 MPa of carbon dioxide. Enhanced mass transfer can contribute to the increase the activity. On the other hand, the selectivity to partial hydrogenation product **2**, was almost constant regard-

**Table 1.** Effect of hydrogen and carbon dioxide pressures on the hydrogenation of 1-naphthol over a 5 wt % Rh/C catalyst<sup>a</sup>

Pressure/MPa		Conversion/%	Selectivity/%				
H <sub>2</sub>	CO <sub>2</sub>		2	3	4	5 + 6	7 + 8
1	10	24	65	18	11	4	2
3	10	56	72	7	12	7	2
6	10	80	72	3	11	12	1
3	8	49	74	6	13	9	1
3	14	57	72	6	13	8	1
3	18	73	74	5	12	8	1

<sup>a</sup>Reaction temperature 323 K; reaction time 15 min.; Rh/C 0.02 g; initial 1-naphthol 0.20 g.

less of increase in carbon dioxide pressure.

The hydrogenation of 2-naphthol was also investigated over the 5% Rh/C catalyst. 2-naphthol conversion was substantially lower (4 to 13 times) than that of 1-naphthol in supercritical carbon dioxide; however, the same (5 wt % Rh/C) catalyst as in case of 1-naphthol hydrogenation showed high selectivity (~85% total) to the partial ring hydrogenation products. In contrast to this, 2-naphthol hydrogenation in methanol solvent showed a very low conversion (<1%) and high selectivity (66%) to the dehydroxylated products. From the beginning of the reaction, the ring of 2-naphthol was partially hydrogenated to 5,6,7,8-tetrahydro-2-naphthol, 1,2,3,4-tetrahydro-2-naphthol, and 2-tetralone. The total selectivity to the partial hydrogenated compounds was 98%. The selectivity of each partial hydrogenated product was constant until most of 2-naphthol was hydrogenated. In addition to the formation of tetralin and decalin, naphthalene was also observed in the hydrogenation of 2-naphthol. However, the selectivity to the dehydroxylated products was too low in supercritical carbon dioxide medium compared with that observed in methanol.

## References and Notes

- K. Y. Koltunov, G. K. S. Prakash, G. Rasul, and G. A. Olah, *Tetrahedron*, **58**, 5423 (2002).
- C.-L. Li, Z.-R. Xu, Z.-A. Cao, and B. C. Gates, *AIChE J.*, **31**, 170 (1985).
- J. Shao and C. Song, *Catal. Today*, **65**, 59 (2001).
- P. G. Jessop and W. Leitner, "Chemical Synthesis Using Supercritical Fluids," Wiley (1999).
- T. Sato, C. V. Rode, O. Sato, and M. Shirai, *Appl. Catal., B*, **49**, 181 (2004).
- TON values were determined by (moles of 1-naphthol reacted for 15 min at 323 K under 3 MPa of hydrogen and 10 MPa of carbon dioxide)/(moles of surface metal atoms). Initial 1-naphthol was 0.20 g and the ratio of [initial 1-naphthol (mol)]/[surface metal atoms (mol)] was 1250.
- S. Scire, S. Minico, and C. Crisafulli, *Appl. Catal., A*, **235**, 21 (2002).
- S. G. Shore, E. Ding, C. Park, and M. A. Keane, *Catal. Commun.*, **3**, 77 (2002).
- M. Arai, Y. Nishiyama, and Y. Ikushima, *J. Supercrit. Fluids*, **13**, 149 (1998).
- C. V. Rode, U. D. Joshi, O. Sato, and M. Shirai, *Chem. Commun.*, **2003**, 1960.