Selective Hydrogenation of Naphthols to Tetralones over Supported Palladium Catalysts in Supercritical Carbon Dioxide Solvent

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Naphthols were selectively hydrogenated to the corresponding tetralones over supported palladium metal catalysts in supercritical carbon dioxide solvent.

Tetralones, which are important intermediates for synthesizing drugs and agrochemicals, can be obtained by the oxidation of tetralin,[1] alkylation–acylation of aromatics with γ-butyrolactone,[2] ionic hydrogenation of naphthols,[3] and intermolecular Friedel–Craft reaction of 4-arylbutyric acids.[4] 1-Tetralone can be also obtained by the hydrogenation of 1-naphthol with supported metal catalysts in organic solvents; however, large amount of dehydroxylated products were also obtained leading to low yield of 1-tetralone.[5,6] These methods have serious environmental problems due to use of hazardous reagents in stoichiometric quantities and organic solvents and tedious procedure of separation of products from the solvents. Hydrogenation with supported metal catalysts under supercritical carbon dioxide have several advantages; i) higher solubility of hydrogen in supercritical carbon dioxide giving enhanced activity and controlling the product selectivity, and ii) easy separation of catalysts and products. Recently, we have found that a hydrogenation system with a carbon-supported rhodium catalyst and supercritical carbon dioxide was very effective for the partial hydrogenation of 1-naphthol to 1,2,3,4-tetrahydro-1-naphthol, 5,6,7,8-tetrahydro-1-naphthol, and 1-tetralone.[7] In continuation of our studies, we now report the selective hydrogenation of naphthols to tetralones with a carbon-supported palladium catalyst in supercritical carbon dioxide solvents.

Carbon- or γ-alumina-supported metal (rhodium, palladium, platinum, and ruthenium) catalysts were examined. All catalyst used in this work were commercially available from Wako Pure Chemical Ind., Ltd., Japan and used without further reduction for the hydrogenation. The detailed reaction procedure are given in our previous paper.[7]

The conversion (in parentheses) of 1-naphthol (**1**) over supported metal catalysts for 15 min at 323 K under 3 MPa of hydrogen and 10 MPa of carbon dioxide were in the following order: Rh/C (42.6) > Rh/γ-Al_2O_3 (24.1) > Pd/C (11.2) > Pt/C (5.4) > Pd/γ-Al_2O_3 (2.7) > Ru/C (0.8) > Pt/γ-Al_2O_3 (0.8) > Ru/γ-Al_2O_3 (0.1) as we reported in our earlier communication.[7] Supported rhodium catalysts were highly active; however, supported palladium catalysts showed higher selectivity to 1-tetralone (**2**) than rhodium catalysts. The order of catalysts for the selectivity of **2** was as follows: Pd/γ-Al_2O_3 (38.0) > Pd/C (36.1) > Rh/C (7.8) > Rh/γ-Al_2O_3 (6.4). Considering the metal dispersion of Pd/γ-Al_2O_3 and Pd/C as 18 and 3%, respectively,[8] the turnover number ((1-naphthol molecules reacted)/(surface palladium atoms of a catalyst)) of Pd/C was four times higher than that of Pd/γ-Al_2O_3. Thus, these results showed that the Pd/C catalyst was the most active catalyst to give the highest yield of **2**. Similar to other aromatic hydrogenation in supercritical carbon dioxide,[7,9] the carbon-supported metal catalysts showed higher TON values than the γ-alumina-supported ones for the hydrogenation of **1** to **2**. Hydrogen atoms spilled over the support would take part in the hydrogenation of aromatic rings; however, further in situ characterization is needed. Baiker et al. reported that carbon monoxide was formed over γ-alumina-supported noble metal catalysts during hydrogenation in supercritical carbon dioxide;[10] however, carbon monoxide was not detected in the systems over both Pd/C and Pd/γ-Al_2O_3 catalysts under our reaction conditions.

For the Pd/C catalyst, the conversion of **1** was found to increase with an increase in reaction temperature; however, the yield of dehydroxylated compounds also increased for the temperature > 383 K. Figure 1 shows the best results obtained at 383 K for the hydrogenation of **1** over the Pd/C catalyst under 0.5 MPa of hydrogen and 16 MPa of carbon dioxide pressure. The highest conversion of **1** achieved was 98% within 60 min while from the beginning of the reaction, **1** was partially hydrogenated to **2**, 1,2,3,4-tetrahydro-1-naphthol (**3**) and 5,6,7,8-tetrahydro-1-naphthol (**4**) with their respective selectivities as 86, 3, and 11% at the conversion of 40%, indicating that the hydrogenation of **1** was a parallel reaction. The yield of **2** as high as 71% was obtained and almost constant after 60 min, beyond which a part of **2** was hydrogenated to **3**. Strong adsorption of carbon dioxide to the active site may prohibit the adsorption of **2** to form **3**. Fully ring-hydrogenated products, 1-decalone (**5**) and decahydro-1-naphthol (**6**), were not obtained even after 100 min. The amounts of dehydroxylated compounds (tetralin (**7**) and naphthalene (**8**)) were almost negligible (<1%). The hydrogenation

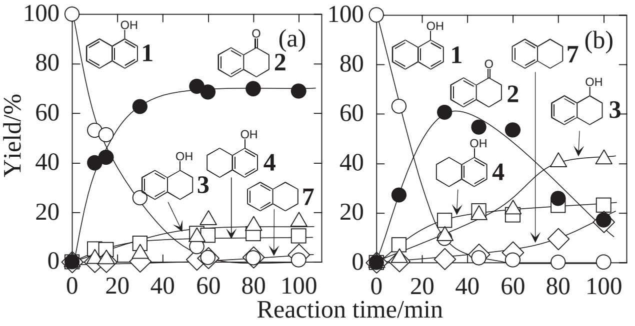

Figure 1. The hydrogenation of 1-naphthol under hydrogen pressure 0.5 MPa over 5 wt % Pd/C (0.075 g). Initial 1-naphthol 1.4 mmol; reaction temperature 383 K; carbon dioxide pressure 16 MPa (a); *n*-heptane 10 mL (b).

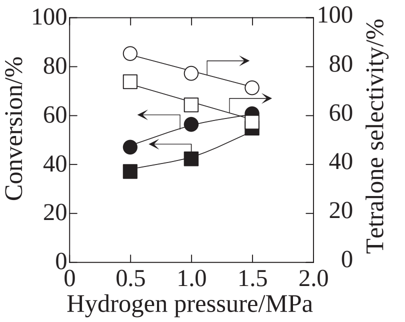

Figure 2. Effect of hydrogen pressure on the hydrogenation of 1-naphthol over 5 wt % Pd/C (0.075 g) at 383 K for 10 min. Initial 1-naphthol 1.4 mmol; carbon dioxide pressure 16 MPa (○, ●); 10 mL of *n*-heptane (□, ■).

of **1** was also examined over the Pd/C catalyst at 383 K under 0.5 MPa of hydrogen in *n*-heptane (10 mL) and methanol (10 mL) solvents. The hydrogenation did not proceed in methanol as indicated by <1% conversion of **1** even after 60 min of the reaction time. As against this, almost complete conversion of **1** was obtained in about 40 min in *n*-heptane, indicating that the rate of hydrogenation in *n*-heptane was faster than that in carbon dioxide solvent (Figure 1). From the beginning of the reaction, **2**, **3**, and **4** were also formed simultaneously in *n*-heptane. The product selectivities to these partial ring-hydrogenated compounds viz. **2**, **3**, and **4** were 75, 5, and 20% in *n*-heptane at the conversion of 40%. The maximum yield of **2** was 61% and the selectivity to **2** decreased after 30 min because of further hydrogenation of **2** to **3** and dehydroxylation to **7**. The yield of **7** was as high as 18%, indicating higher extent of dehydroxylation taking place in *n*-heptane solvent. Fully ring-hydrogenated products, **5** and **6** were also obtained in *n*-heptane. The above results indicate that dehydroxylation was considerably suppressed under supercritical carbon dioxide solvent unlike the hydrogenation in organic solvents even at the same reaction temperature.

We have also examined the influence of carbon dioxide pressures on the catalyst activity and selectivity for Pd/C-catalysed hydrogenation of **1**. The activity and selectivity to partial hydrogenated products for **2**, **3**, and **4** were almost constant regardless of carbon dioxide pressure from 16 to 22 MPa at 1 MPa of hydrogen. The density of supercritical carbon dioxide and solubility of **1** in supercritical carbon dioxide solvent increase with increasing pressure; however, the hydrogenation rates were not affected by carbon dioxide pressure, indicating that the diffusion of the reactant and products was not a rate-determining step. In addition, we also examined the hydrogen pressure effect (Figure 2) at a constant carbon dioxide pressure of 16 MPa and in *n*-hentane solvent. The conversion of **1** increased with an increase in the hydrogen pressure from 0.5 to 1.5 MPa of hydrogen in both carbon dioxide and *n*-heptane solvents, indicating that surface hydrogen concentration increased with increase in hydrogen pressure. On the other hand, the initial selectivities to **2** decreased with an increase in the hydrogen pressure from 0.5 to 1.5 MPa in both carbon dioxide and *n*-heptane solvent. It is noteworthy that the selectivity to **2** in carbon dioxide was higher than that in *n*-heptane under the similar conversion of **1**.

The hydrogenations of 2-naphthol and 2-methyl-1-naphthol in supercritical carbon dioxide and *n*-heptane solvents were also investigated over the Pd/C catalyst (Figure 3). From the beginning of the hydrogenation, tetralones, 1,2,3,4-tetrahydronaphthols, and 5,6,7,8-tetrahydronaphthols were parallely formed in the four systems. Among them, tetralones were highly obtained and their yields were almost constant even though most of naphthols were hydrogenated in carbon dioxide. The yields of tetralones were also high in *n*-heptane; however, decreased after the maximum at 50 and 60 min, respectively because of further hydrogenation of tetralones to the corresponding 1,2,3,4-tetrahydronaphthols.

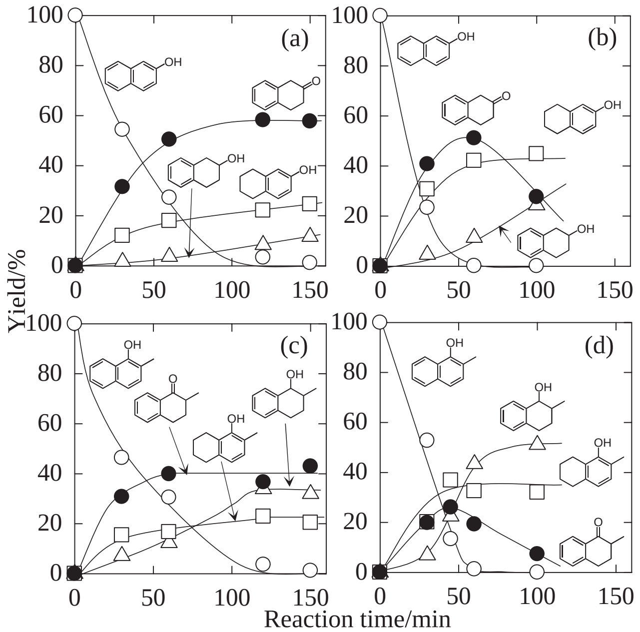

Figure 3. The hydrogenation of 2-naphthol and 2-methyl-1-naphthol under hydrogen pressure 0.5 MPa over a Pd/C catalyst. Initial 2-naphthol and 2-methyl-1-naphthol 1.4 mmols; carbon dioxide pressure 16 MPa ((a) and (c)); *n*-heptane 10 mL ((b) and (d)).

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