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Catalytic ring hydrogenation of phenol under supercritical carbon dioxide

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A charcoal-supported rhodium catalyst was highly active for the ring hydrogenation of phenol and cresols under supercritical carbon dioxide.

Adipic acid is an important chemical intermediate, for the manufacture of nylon-6,6. The worldwide industrial processes of adipic acid production are up to 2.2 million tons per year.[1,2] Most industrial adipic acid production processes use nitric acid oxidation of cyclohexanol, cyclohexanone, or both. Also, cyclohexanol and cyclohexanone are produced by the ring hydrogenation of phenol in industry. Generally, the hydrogenation of phenol is carried out in the vapour phase and supported palladium catalysts have been reported as the best catalysts for this reaction.[2–9] There has been hardly any work reported for liquid phase hydrogenation of phenol except that by Velasco *et al.*[10] Supported metal catalysts are useful for hydrogenation processes in industry. However, in the case of vapor phase hydrogenation, high temperatures are needed and coking during reaction causes catalyst deactivation. Hydrogenation reactions in the liquid phase using supported metal catalysts have wide ranging applications in pharmaceutical and 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.[11] Organic gas–liquid reactions with solid catalysts under supercritical carbon dioxide have several other advantages: i) high reaction rates due to increased solubility of reactant gases in supercritical fluids, thereby eliminating mass transfer resistance; ii) easy separation of catalysts and products.[12,13] Here we report the catalytic ring hydrogenation of phenol and its derivatives with supported metal catalysts under supercritical carbon dioxide.

Commercially available catalysts were used in this work, *viz.* 5 wt% carbon supported palladium (5% Pd/C), rhodium (5% Rh/C), platinum (5% Pt/C), and ruthenium (5% Ru/C), from Wako Chemicals, Japan. The dispersion values of metal particles on charcoal were determined by a hydrogen adsorption method. Before hydrogen adsorption all catalysts were treated with flowing hydrogen at 573 K for 10 min. The adsorption temperature was 323 K. Hydrogenation reactions were carried out in stainless-steel reactors (50 ml capacity). The weighed amount of catalyst and reactants were placed in a reactor and flushed twice with carbon dioxide. After the required temperature was attained with a hot air circulating oven, hydrogen and carbon dioxide were introduced into the reactor. After reactions, the pressure was released slowly and the contents were discharged to separate the catalyst by simple filtration. The reaction mixture was diluted with methanol and a sample was analyzed with GC-FID and GC-MS.

The catalyst screening results for phenol hydrogenation are shown in Table 1. Charcoal-supported rhodium, ruthenium and palladium catalysts were active for the ring hydrogenation of phenol to cyclohexanone and cyclohexanol at 328 K under supercritical carbon dioxide conditions and the turnover numbers for different catalysts were in the following order: rhodium > ruthenium > palladium > platinum. Hitzler *et al.* have reported ring hydrogenation of cresols over a commercial Pd catalyst under supercritical carbon dioxide at very high temperature (523 K). However, maximum selectivity to the corresponding cyclohexanol derivative was only 70%, with formation of several other side products.[14] In our work, at very low temperature (328 K) rhodium was found to be the most active for the ring hydrogenation of phenol, while for gas and liquid phase reactions at >453 K palladium is reported to be a suitable catalyst for this hydrogenation.[2–9] We used commercial supported metal catalysts and did not add any promoter to, or perform any special treatment on, the catalysts. The catalyst performances observed for two systems (*i.e.* under gas/liquid phase and supercritical carbon dioxide conditions) can not be compared directly because the reaction conditions such as temperature range and solvent system are totally different. However, it is expected that the reaction mechanism under supercritical carbon dioxide is totally different from that under gas and liquid phase conditions. Not only does the enhancement of hydrogen solubility in supercritical carbon dioxide contribute to the higher catalyst activity but also there is an additional role played by the supercritical carbon dioxide suggesting i) the adsorption characteristics of phenol on active sites on metal particles and/or ii) the electronic structures of the metal particles are different under supercritical carbon dioxide from non-supercritical conditions. Bhanage *et al.* reported that the activities and selectivities for hydrogenation of α,β-unsaturated aldehydes over a supported platinum catalyst under supercritical carbon dioxide were higher than those in ethanol solvent.[15] They explained the enhancement not only by the activation of reactants and but also by a change in electronic state of the supported metal particles in supercritical carbon dioxide which has a large dielectric constant. Arai *et al.* also reported that the electron density of gold particles decreased in supercritical carbon dioxide.[16] The catalytic activities of metals under supercritical carbon dioxide conditions could be different due to modification by electron transfer to carbon dioxide which would affect the adsorption characteristics of phenol as compared with gas and liquid phase conditions. The lower electron density of rhodium under supercritical carbon dioxide would cause strong adsorption of phenol leading to the highest catalyst activity. The apparent activation energy of ring

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

Catalyst	Dispersion (%)[b]	Catalyst amount/g	Conversion (%)	Selectivity (%) Cyclohexanone	Selectivity (%) Cyclohexanol	TON[c]
5% Rh/C	12	0.0228	53	17	83	8244
5% Ru/C	25	0.0639	30	5	95	759
5% Pd/C	3	0.1400	3	54	46	304
5% Pt/C	8	0.0780	0	—	—	—
5% Pt/C[d]	8	0.0780	1	97	3	125

[a] Reaction temperature 328 K; reaction time 2 h; hydrogen pressure 10 MPa; carbon dioxide pressure 10 MPa; initial phenol 0.02 mol. [b] The dispersion was determined by a hydrogen adsorption method. [c] TON = (moles of phenol reacted)/(moles of surface metal atoms). [d] Reaction temperature 353 K.

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hydrogenation over the 5% Rh/C catalyst under supercritical carbon dioxide conditions evaluated in our work was 32 kJ mol^{-1}. In order to compare the performance under the same conditions but without supercritical carbon dioxide (*i.e.* 328 K) a separate experiment was conducted which showed no hydrogenation. This indicates the reaction mechanism is different in the two cases. The apparent activation energies previously reported for liquid and gas phase phenol hydrogenation (Pd/Al_2O_3 and Pd/MgO catalysts) were 57 and 65 kJ mol^{-1}, respectively.[2,17] The low apparent activation energy under mild temperature in supercritical carbon dioxide suggests the different adsorption characteristic of phenol and/or the electronic interactions of metal particles with carbon dioxide under supercritical conditions. We do not have any direct evidence about the electronic state of the metal particles, however, there is a strong possibility that carbon dioxide molecules are more strongly adsorbed on the surface of palladium metal than on other metal particles, making the palladium surface inaccessible so that it exhibits lower activities than rhodium and ruthenium in supercritical carbon dioxide. Further study such as *in-situ* investigations of the structure and electronic state of metal particles under supercritical carbon dioxide and determination of the surface concentrations of hydrogen and phenol adsorbed are needed.

The conversion over the Rh/C catalyst increased with increasing reaction temperature and time. For example, complete conversion of phenol to cyclohexanol was achieved at 353 K in 2 h over Rh/C. The reuse of the Rh/C catalyst was also studied. No deactivation was observed after use 3 times. 100% conversion (10% selectivity for cyclohexanone and 90% for cyclohexanol) was obtained over the Rh/C catalyst at 328 K after 4 h for each run.

In addition, we also examined the influence of the pressures of both hydrogen and supercritical carbon dioxide on the catalyst activity and selectivity and these results are presented in Table 2. It was found that both hydrogenation activity and selectivity to cyclohexanol increased with increasing hydrogen pressure at 10 MPa carbon dioxide, caused by an increase in the concentration of surface hydrogen with increasing hydrogen pressure. Phenol hydrogenation is a successive reaction in which first phenol is hydrogenated to cyclohexanone followed by its hydrogenation to cyclohexanol. However, cyclohexanol was observed at low phenol conversion under high hydrogen pressure, indicating that cyclohexanol would be formed not only *via* the cyclohexanone intermediate but also directly from phenol. At high concentration of surface hydrogen, the hydrogenation of phenol to cyclohexanol would easily occur, resulting in higher selectivity to cyclohexanol (Table 2).

Table 2 Effect of hydrogen and carbon dioxide pressures on the hydrogenation of phenol over 5% Rh/C[a]

			Selectivity (%)	
H_2 pressure/ MPa	CO_2 pressure/ MPa	Conversion (%)	Cyclo-hexanone	Cyclo-hexanol
6	10	39	40	60
7.5	10	42	31	69
10	10	53	17	83
10	14	72	22	77
10	20	87	34	65

[a] Reaction temperature 328 K; reaction time 2 h; initial phenol 0.02 mol.

Table 3 Hydrogenation of cresol over 5% Rh/C[a]

		Selectivity (%)	
Reactant	Conversion (%)	Methycyclo-hexanone	Methycyclo-hexanol
m-Cresol	99	83	17
o-Cresol	88	31	69
p-Cresol	47	55	45

[a] Reaction temp. 328 K; hydrogen pressure 9 MPa; carbon dioxide pressure 11 MPa; reaction time 2 h; initial cresol 0.0185 mol; weight of catalyst 0.0455 g.

The hydrogenation activity also increased with increasing carbon dioxide pressure. Bhanage *et al.* also observed higher conversions with increasing carbon dioxide pressure in the case of cinnamaldehyde hydrogenation under supercritical carbon dioxide.[15] Enhanced mass transfer may contribute to the increased activity at higher carbon dioxide concentration. On the other hand, the selectivity to cyclohexanol did not increase with increasing carbon dioxide pressure. The surface hydrogen concentration would decrease at higher carbon dioxide pressure because of the dilution of carbon dioxide, reducing the possibility of direct transformation from phenol to cyclohexanol, thus the selectivity to cyclohexanol did not increase.

The hydrogenation activities for cresols, derivatives of phenol, were also investigated over 5% Rh/C (Table 3). The 5% Rh/C catalyst also showed high activities for ring hydrogenation of cresols and corresponding methylcyclohexanone and methylcyclohexanol were formed. Among cresols, the catalysts showed the lowest activity for *p*-cresol hydrogenation, which may be due to the position of the methyl group with respect to the hydroxy group. The position of the substituent has also affected the selectivity pattern substantially.

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