

Full Research Paper

## Catalytic Ring Hydrogenation of Benzoic Acid with Supported Transition Metal Catalysts in $scCO_2$

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**Abstract:** The ring hydrogenation of benzoic acid to cyclohexanecarboxylic acid over charcoal-supported transition metal catalysts in supercritical  $CO_2$  medium has been studied in the present work. The cyclohexanecarboxylic acid can be produced efficiently in supercritical  $CO_2$  at the low reaction temperature of 323 K. The presence of  $CO_2$  increases the reaction rate and several parameters have been discussed.

**Keywords:** Hydrogenation; benzoic acid; cyclohexanecarboxylic acid;  $scCO_2$

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### 1. Introduction

Hydrogenation of benzoic acid (BA) is an important industrial reaction as its product cyclohexanecarboxylic acid (CCA) is a very important and excellent chemical or pharmaceutical intermediate, which have been used in the synthesis of 1-hydroxy cyclohexyl phenyl ketone and praziquantel, and its derivatives, such as trans-4-isopropylcyclohexyl acid and cyclohexylmethyl carbamate, N-(cyclohexylcarbonyl)-D-phenylalanine are important intermediates for organic synthesis in fine chemical industries [1,2]. The production of cyclohexanecarboxylic acid by catalytic hydrogenation of benzoic acid is well known, but it endures some disadvantages in both technical and economic aspects, which inhibit their application on a commercial scale. Cyclohexanecarboxylic acid can be produced from hydrogenation of molten benzoic acid without any solvent, but the reaction

temperature and pressure are relatively high [3]. Practically, Pd/C catalyst was used to produce cyclohexanecarboxylic acid from the hydrogenation of benzoic acid at high temperature of 423 K and high H<sub>2</sub> pressure of 15 MPa [4-6]. Furthermore, organic solvents used in the process usually bring some drawbacks. For example, when methanol was used as solvent in the hydrogenation of benzoic acid, ester was usually formed and which should be removed carefully from the desired product; The higher alcoholic solvents are not only relatively difficult to separate from product but also expensive [7]; Acidic solvents, such as acetic acid, bring a serious waste disposal problem for it is difficult to recover; Basic solvents, like aqueous alkali, cause decarboxylation and thus give relatively low yield to the desired product [8,9]. Recently, much effort has been paid to avoid using organic solvents, and supercritical fluids are used as a replacement in various chemical reactions [10-13]. Especially, supercritical carbon dioxide (scCO<sub>2</sub>) as an environmentally benign solvent for organic synthetic reactions is currently receiving much attention. For its physicochemical properties may be manipulated by changing the pressure and temperature slightly, scCO<sub>2</sub> has been widely used as a green reaction medium in hydrogenation reactions [14-19]. It was reported that the hydrogenation of unsaturated aldehydes could be performed successfully in scCO<sub>2</sub> with a significant improvements in activity and product selectivity [15-19]. The hydrogenation of butynediol in scCO<sub>2</sub> was reported to be promoted by a steel-stainless reactor wall in the absence of any catalyst [20,21]. Rode et al. [22] reported that Rh/C was highly active for the ring hydrogenation of phenol and cresols in scCO<sub>2</sub>.

The present paper reports the ring hydrogenation of benzoic acid with transition metals supported on carbon under low reaction temperature in scCO<sub>2</sub>. The solubility of benzoic acid in scCO<sub>2</sub> and phase behavior was inspected, and several reaction parameters were discussed.

## 2. Experimental

### 2.1 Hydrogenation studies

The transition metal catalysts were purchased from Wako Pure Chemical Industries, Ltd., which were reduced at 573 K for 2 h with hydrogen gas before reaction. The hydrogenation reactions were carried out in a 50 mL stainless steel autoclave. A certain amount of catalyst and the reactant, benzoic acid was charged into the reactor and the reactor was flushed with N<sub>2</sub> or 2.0 MPa CO<sub>2</sub> three times to remove the air. The reactor was then heated up to the desired temperature and H<sub>2</sub> and compressed liquid CO<sub>2</sub> were introduced with a high-pressure liquid pump. The reaction runs were conducted while stirring with a magnetic stirrer. At the end of the reaction, the autoclave was cooled to room temperature then depressurized carefully by backpressure regulator. The composition of reaction mixture was analyzed by a gas chromatograph using a flame ionization detector.

### 2.2 Phase behavior observation

A viewing cell (internal volume 80 ml) was used to observe the phase behavior of reactants in scCO<sub>2</sub>, it is equipped with windows and connected to a temperature-controlled system. A certain amount of substrate was added into the cell, and then the cell was flushed with 0.5 MPa CO<sub>2</sub> twice. After the cell was heated to 323 K (reaction temperature), CO<sub>2</sub> was introduced into it and the stirring was started. When the pressure reached a certain value, the stirring was continued for 3-5 min and then

stopped; the state of the mixture including the substrate and CO<sub>2</sub> was visually inspected. This examination was made at intervals of 0.2-0.5 MPa to determine the pressure at which the substrate was completely dissolved into CO<sub>2</sub>, forming a single phase. Then, the pressure was decreased in a similar way to determine the pressure at which droplets appeared (dew point), changing into a two-phase mixture. The pressures determined at increasing and decreasing pressures were less than 0.3 MPa different, and the average value of the two pressures determined was used. Those observations were used to estimate the solubility of BA, CCA and the mixture of them in CO<sub>2</sub> at different pressures.

### 3. Results and discussion

#### 3.1 Hydrogenations in scCO<sub>2</sub> with different catalysts

The catalytic performance of several transition metal catalysts for hydrogenation of benzoic acid in scCO<sub>2</sub> are compared in Table 1, Carbon-supported transition metal catalysts such as Pd/C, Rh/C, Ru/C and Pt/C, were active for hydrogenation of benzoic acid to cyclohexanecarboxylic acid at the lower temperature of 353 K in scCO<sub>2</sub>. Under the reaction conditions used, benzoic acid was almost completely converted with Rh/C catalyst to produce cyclohexanecarboxylic acid as an isolated product with 100 % selectivity. The activity order of these transition metal catalysts is Rh/C > Ru/C > Pt/C > Pd/C. While, it was reported in the literature that Pd/C is a suitable catalyst for benzoic acid hydrogenation in three-phases of gas (H<sub>2</sub>)-liquid (molten benzoic acid)-solid (catalyst) at temperature above 453 K [6].

**Table 1.** Results of benzoic acid hydrogenation with supported transition metal catalysts in scCO<sub>2</sub>.

Catalysts	Product Yield (%)
Pd/C	3.3
Pt/C	3.4
Ru/C	68.3
Rh/C	99.1

Reaction conditions: H<sub>2</sub> pressure, 10 MPa; CO<sub>2</sub> pressure, 10 MPa; reaction temperature, 323 K; reaction time, 3 h.

#### 3.2 Effects of CO<sub>2</sub> and H<sub>2</sub> pressures

Table 2 shows that the yield of CCA is dependent on CO<sub>2</sub> pressure. The hydrogenations were carried out in the presence of 2 MPa H<sub>2</sub> at 323 K for 3 h, as can be seen from the data in the Table 2 the yield of CCA increases with increasing CO<sub>2</sub> pressure from 0 to 10 MPa, indicating that the presence of CO<sub>2</sub> can improve the reaction rate. Usually, a dilution effect (negative) should exist by introducing large amount of CO<sub>2</sub>, while the reaction conversion did not decrease but increased slightly with increasing CO<sub>2</sub> pressure, suggesting that the positive effect should exist and which is dominant and retards the dilution effects of introducing large amount of CO<sub>2</sub>. This may be attribute to several

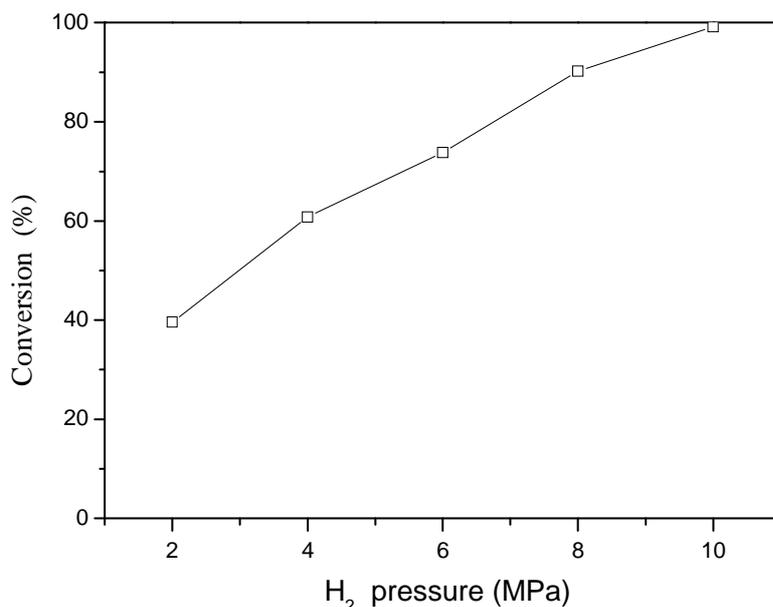
positive factors (1) enhancing hydrogen concentration; (2) phase behavior; (3) the molecule interaction among substrate, catalyst and CO<sub>2</sub> molecules [12-14].

**Table 2.** Influence of CO<sub>2</sub> pressure on the hydrogenation of benzoic acid over 5 % Rh/C catalyst in scCO<sub>2</sub>.

H <sub>2</sub> pressure (MPa)	CO <sub>2</sub> pressure (MPa)	Yield of CCA (%)
2	0	24.6
2	4	28.4
2	8	32.9
2	10	39.6

Reaction conditions: temperature, 323 K; reaction time, 3 h; benzoic acid, 8.2 mmol.

The influence of hydrogen pressure has been studied for benzoic acid hydrogenation in the presence of 10 MPa CO<sub>2</sub> as shown in Figure 1. The conversion increased linearly with increasing H<sub>2</sub> pressure from 2 to 10 MPa and a high conversion of 99.1 % was achieved at H<sub>2</sub> pressure of 10 MPa, while it is about 39.6 % at 2 MPa, suggesting the reaction rate depends on the concentration of hydrogen largely in scCO<sub>2</sub>.

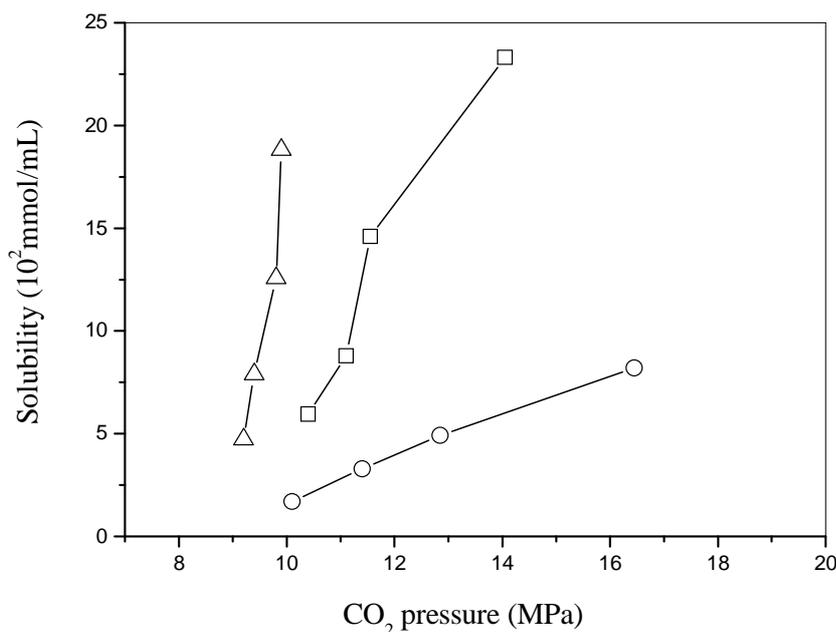


**Figure 1.** Influence of H<sub>2</sub> pressure on hydrogenation of benzoic acid over Rh/C catalyst in the presence of 10 MPa CO<sub>2</sub>. Reaction conditions: benzoic acid, 8.2 mmol; catalyst, Rh/C 0.05 g; temperature, 323 K; reaction time, 3 h.

### 3.3 Solubility and phase behavior in scCO<sub>2</sub>

For confirming whether the reaction in scCO<sub>2</sub> is taking place homogeneously in a single phase or heterogeneously in two or more phases, phase behavior observation and solubility estimation have been carried out with a high-pressure view-cell. Figure 2 shows the solubilities of benzoic acid, cyclohexanecarboxylic acid and the mixture of them at 50 °C. The results indicate that the solubilities

of these solid substrates increase with increasing CO<sub>2</sub> pressure, namely, the higher CO<sub>2</sub> pressure, the more solid substrate dissolved. The order of the solubility is cyclohexanecarboxylic acid > the mixture of benzoic acid and cyclohexanecarboxylic acid > benzoic acid. The state of the reaction mixture under different CO<sub>2</sub> pressures was observed in the absence of catalyst. At the CO<sub>2</sub> pressure below 7 MPa, two phases presented as gas (CO<sub>2</sub> riched gas phase) and solid (benzoic acid) phases for its melting point is 395 K higher than the reaction temperature of 323 K, the reaction should occur on the interface of the solid (benzoic acid)- solid (catalyst) -gas (H<sub>2</sub>). With increasing CO<sub>2</sub> pressure, a part of benzoic acid could dissolve into supercritical CO<sub>2</sub> phase. Furthermore, in the presence of catalyst with the formation of cyclohexanecarboxylic acid (liquid state under the reaction conditions), a part of reactions performed on the interface of liquid-solid. When CO<sub>2</sub> was raised up to an assured pressure or with the reaction process deeply, a homogeneous and uniform phase was formed in which all the substrate dissolved into CO<sub>2</sub> gas phase. Since the reaction system is not simple, the overall rate of reaction should depend on several factors including the volume of the phases present, the concentration of the reacting species, the activity of catalytic active species and the reaction kinetics in these phases. Further study is needed to explain the results and several chemical and physical factors should be considered.



**Figure 2.** Solubility estimation of benzoic acid, cyclohexanecarboxylic acid and mixture of them in CO<sub>2</sub> at 323 K. △ cyclohexanecarboxylic acid; □ the mixture of benzoic acid and cyclohexanecarboxylic acid; ○ benzoic acid.

### 3.4 Hydrogenations of several substrates

The catalytic activity of the Rh/C catalysts have been examined for the hydrogenation of phenol, benzoic acid, p-toluic acid and 4-ethylbenzoic acid in scCO<sub>2</sub>, the results are shown in Table 3. The catalysts are active for hydrogenation of benzene ring at the lower temperature of 323 K in scCO<sub>2</sub>. At the pressures of CO<sub>2</sub> 10 MPa and H<sub>2</sub> 4 MPa, benzoic acid and phenol were quite reactive and converted to its ring hydrogenation products with a conversion of 95.8 % and 91.8 %, respectively; the conversion of 4-ethylbenzoic acid is 56.6 % and p-toluic acid is 20.8 % under the same reaction

conditions. These results indicated the substituent group attached the benzene ring has a significant effect on the reactivity of the ring hydrogenation.

**Table 3.** Hydrogenation of aromatic compounds over 5 % Rh/C at 323 K.

Reactant	Conversion (%)
Benzoic acid	95.8
Phenol	91.8
4-Ethylbenzoic acid	56.6
p-Toluic acid	20.8

Reaction conditions: H<sub>2</sub> pressure 4 MPa; CO<sub>2</sub> pressure 10 MPa; reactant 8.2 mmol; reaction time 6 h.

#### 4. Conclusions

Hydrogenation of benzoic acid to cyclohexanecarboxylic acid over several transition metal catalysts under supercritical CO<sub>2</sub> medium has been studied. This study demonstrates that ring hydrogenation of benzoic acid can be successfully carried out in scCO<sub>2</sub> medium with Rh/C catalyst at the low reaction temperature of 323 K, in which without any waste was produced and the catalyst separation from product can be handled easily by simple phase separation. Use of scCO<sub>2</sub> as alternative media for hydrogenations promises to overcome some of drawbacks described associated with conventional organic solvents and offers both process and environmental advantages.

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