Phase Behavior of Hydrogenation of 2-*tert*-Butylphenol over a Charcoal-Supported Rhodium Catalyst in Carbon Dioxide Solvent[†]

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Catalytic hydrogenation of 2-*tert*-butylphenol over a charcoal-supported rhodium catalyst in carbon dioxide solvent at 313 K was studied in a batch reactor. To elucidate the effect of carbon dioxide pressure on the initial rate of reaction, the phase behavior of the ternary (2-*tert*-butylphenol−carbon dioxide−hydrogen) system was separately observed with a view cell, and the calculations of vapor−liquid equilibrium and compositions in the vapor and liquid phases inside the reactor were carried out using the Peng−Robinson equation of state. The hydrogenation behavior in the carbon dioxide solvent is discussed based on the phase behavior of the ternary system.

Introduction

Catalytic hydrogenations in organic solvents using supported metal catalysts have wide ranging application in chemical processes; however, the development of safer and more energy-saving systems is desirable. Supercritical carbon dioxide is a prominent candidate as an alternative solvent because of its nontoxic and nonflammable properties.[1] Organic transformations using hydrogen gas with supported metal catalysts in supercritical carbon dioxide solvent have several other advantages: (1) higher solubility of hydrogen in supercritical carbon dioxide, thereby controlling activities, (2) easy separation of products and catalysts, and (3) maintaining clean active sites of metal surfaces by rinsing with supercritical carbon dioxide solvent.[2,3] For the development of industrial applications, information about the phase state of the reaction system is very important. The solubility of organic compounds in supercritical carbon dioxide solvent is relatively well studied;[4] however, there are few reports on states of phases for ternary (unsaturated compound−hydrogen−carbon dioxide) systems.[5,6]

In this manuscript, we discuss the hydrogenation behavior of 2-*tert*-butylphenol over a charcoal-supported rhodium catalyst in supercritical carbon dioxide based on the ternary phase states estimated by direct observation and simulation.

Experimental

Carbon dioxide (> 99.995 %) and hydrogen (> 99.95 %) were purchased from Nippon Tansan Co., Ltd. and Taiyo Nippon Sanso Co., respectively. 2-*tert*-Butylphenol (Aldrich, 99 %) was used as received. A commercially available 5 % charcoal-supported rhodium (Rh/C) catalyst from Wako Pure Chemical Ind., Ltd., Japan, was used without further reduction.

The hydrogenation activity was studied in a batch system.[7] The weighed amounts of the solid catalyst (0.020 g) and liquid 2-*tert*-butylphenol (2.00 mmol) were placed in a stainless steel high-pressure reactor (50 cm^3 capacity), and the reactor was flushed three times with carbon dioxide. After the required temperature was attained with an oil bath, first hydrogen (2 MPa) and then carbon dioxide were introduced into the reactor to the desired pressure levels, and then the content was magnetically stirred. In this paper, we used the total pressure values for describing reaction pressure. After the reaction period, the reactor was cooled rapidly with an ice bath; the pressure was released slowly; and the contents were discharged to separate the catalyst by simple filtration. The unreacted 2-*tert*-butylphenol and the products formed were recovered with acetone, which showed a material balance of more than 95 %. The quantitative analysis was conducted with GC-MS (HP-6890 and 5973) and GC-FID (HP-6890).

The phase behavior of the 2-*tert*-butylphenol−carbon dioxide−hydrogen system was observed with a view cell (50 cm^3 capacity) with two Pyrex windows. The view cell containing 2-*tert*-butylphenol (2.00 mmol) was heated to 313 K, and hydrogen was introduced into the view cell to the desired pressure level (2 MPa). Then carbon dioxide was introduced step by step with magnetic stirring, and the phase behavior was recorded with a CCD camera.

The vapor−liquid equilibrium of the 2-*tert*-butylphenol−hydrogen−carbon dioxide mixture was calculated with VMGSim software (version 4.0, Virtual Materials Group Inc.), which was based on the Peng−Robinson equation of state (eq 1)[8]

$$P = \frac{RT}{v - b} - \frac{a}{v(v + b) + b(v - b)} \qquad (1)$$

where P is pressure; T is temperature; R is the gas constant; and v is molar volume. To extend this equation to mixtures, the van der Waals mixing rule was used. The parameters a and b were calculated from the pure substance parameters.

Results and Discussion

Figure 1 shows the effect of total pressure on the initial activity for the 2-*tert*-butylphenol hydrogenation over the Rh/C

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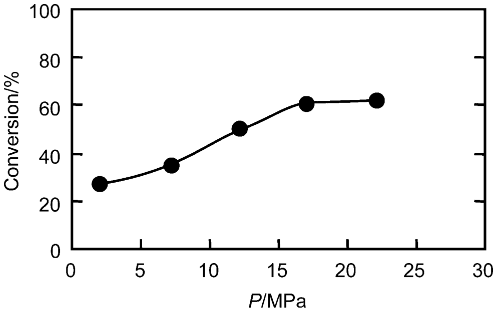

Figure 1. Effect of pressure on the initial conversion at 30 min in the hydrogenation of 2-*tert*-butylphenol (2.00 mmol) over 0.020 g of Rh/C in 2 MPa of hydrogen pressure at 313 K. Data from ref 9.

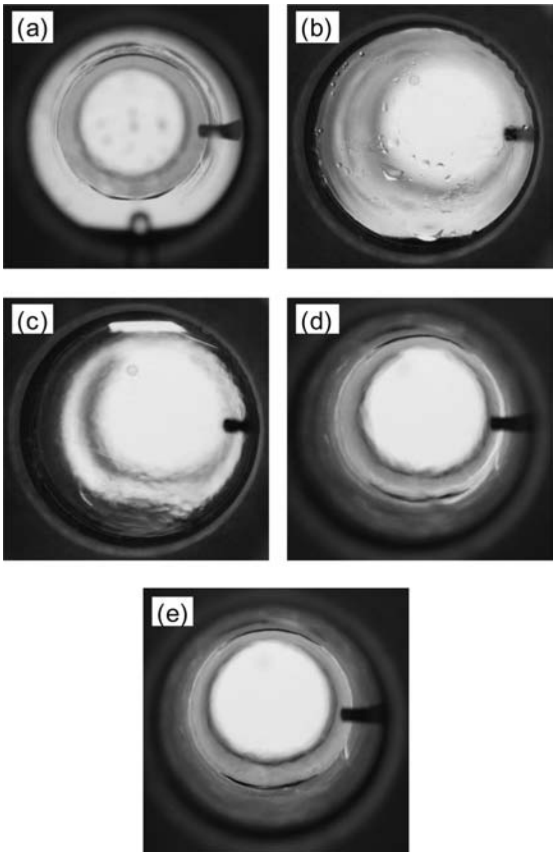

Figure 2. Phase behavior of the 2-*tert*-butylphenol−hydrogen−carbon dioxide system. Temperature, 313 K; view cell volume, 50 cm^3; 2-*tert*-butylphenol, 2.00 mmol; initial hydrogen pressure, 2 MPa; total pressure, 2 MPa (a), 8 MPa (b), 12 MPa (c), 17 MPa (d), and 22 MPa (e).

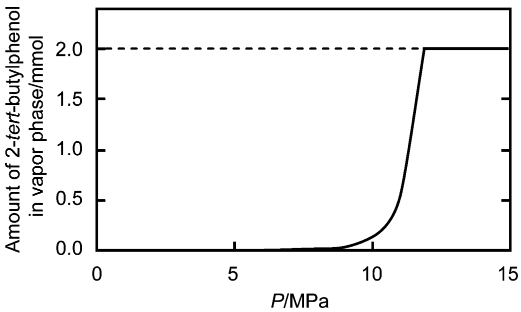

Figure 3. Estimated amount of dissolved 2-*tert*-butylphenol in the vapor phase. Temperature, 313 K; volume, 50 cm^3; introduced 2-*tert*-butylphenol, 2.00 mmol; initial hydrogen pressure, 2 MPa.

catalyst at 313 K. The initial conversion of 2-*tert*-butylphenol in 30 min increased from (27 to 61) % with an increase in the total pressure from (2 to 17) MPa, beyond which it became constant. The products of 2-*tert*-butylphenol hydrogenation were 2-*tert*-butylcyclohexanone (with the selectivity of (60 to 63) %), *cis*-2-*tert*-butylcyclohexanol [(38 to 36) %], and a small amount of *trans*-2-*tert*-butylcyclohexanol.[9] The ratios of 2-*tert*-butylcyclohexanone/2-*tert*-butylcyclohexanols and *cis*-2-*tert*-butylcyclohexanol/*trans*-2-*tert*-butylcyclohexanol were almost constant independent of the total pressure, indicating that the consecutive hydrogenation of 2-*tert*-butylcyclohexanone to 2-*tert*-butylcyclohexanol did not proceed in 30 min of the reaction in supercritical carbon dioxide.[9]

Figure 2 shows the images of the 2-*tert*-butylphenol−hydrogen−carbon dioxide system at 313 K. After introducing 2 MPa of hydrogen to the view cell containing 2.00 mmol of liquid 2-*tert*-butylphenol (Figure 2a), carbon dioxide was introduced. A gaseous phase, in which mainly hydrogen and carbon dioxide would exist, and a liquid phase of 2-*tert*-butylphenol were observed. Although, it was difficult to observe the extent of change of the liquid phase with an increase of total pressure to 8 MPa, the liquid phase of 2-*tert*-butylphenol was clearly visible at 8 MPa of total pressure (Figure 2b). With a further increase of the total pressure to 12 MPa, the extent of the liquid phase became smaller with an unclear phase boundary; however, the phases seemed to still be heterogeneous (Figure 2c). This state can be called a cloud point. We could clearly see a homogeneous phase beyond 17 MPa of total pressure (Figure 2d). It should be noted that at total pressure of 17 MPa, complete dissolution of 2.00 mmol 2-*tert*-butylphenol was observed, and this was almost the same as the total pressure beyond which the conversion of 2-*tert*-butylphenol hydrogenation became constant (Figure 1).

Figure 3 shows the amount of 2-*tert*-butylphenol dissolved in the vapor phase obtained by the Peng−Robinson equation of state. The amount of 2-*tert*-butylphenol in the vapor phase was low (< 0.044 mmol in 50 cm^3) below a total pressure of 9 MPa. It drastically increased with increasing pressure from 9 MPa, and 2-*tert*-butylphenol introduced (2.00 mmol) was completely dissolved in the vapor phase at 12 MPa of total pressure. The composition of the liquid phase was also examined (Figure 4). The mole fraction of hydrogen in the liquid phase increased with increasing amount of carbon dioxide in the system, which would be caused by an increase in mole fraction of carbon dioxide in the liquid phase. A similar increase in solubility of hydrogen to the liquid phase by adding carbon dioxide has been pointed out by Devetta et al.[10] The mole fraction of hydrogen in the liquid phase was calculated to be 0.0088 under a hydrogen pressure of 2 MPa without carbon dioxide, and it increased to 0.0135 by adding carbon dioxide to the total pressure of 9 MPa.

The results of 2-*tert*-butylphenol hydrogenation can be explained from the results of observation of phase behavior and calculation of vapor−liquid equilibrium. Below a total pressure of 9 MPa, hydrogenation would proceed mainly in the liquid phase because the amount of 2-*tert*-butylphenol in the vapor phase is very small. The increase in the hydrogenation rate below 9 MPa would be caused by the increase in the concentration of hydrogen in the liquid phase. Between (9 and 12) MPa, where the amount of 2-*tert*-butylphenol in the vapor phase increased, the reaction would proceed in both the liquid phase and the vapor phase. The increase in the conversion in this range could be explained by both the increase in hydrogen concentration in the liquid phase and the proceeding of the reaction in the hydrogen-rich vapor phase. At 12 MPa, the liquid phase was calculated to disappear, and the phase boundary became

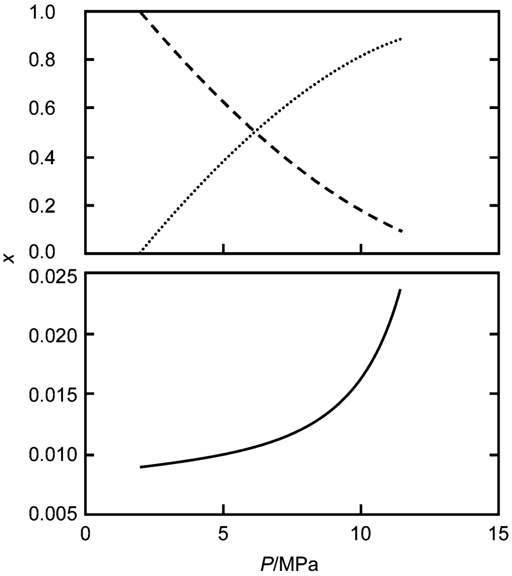

Figure 4. Relation between total pressure and mole fraction in the liquid phase (*x*). Temperature, 313 K; volume, 50 cm^3; introduced 2-*tert*-butylphenol, 2.00 mmol; initial hydrogen pressure, 2 MPa. ---, 2-*tert*-butylphenol; ····, carbon dioxide; —, hydrogen.

unclear in the phase observation; however, the fluid seemed to still be inhomogeneous in the visible observation. The density of the fluid would fluctuate between the transient region and a single phase. Hence, at 12 MPa total pressure, the conversion increased only around 50 %. As total pressure increased to 17 MPa, the inhomogeneity of the fluid almost disappeared leading to the enhanced rate of hydrogenation of 2-*tert*-butylphenol. Beyond 17 MPa, the hydrogenation proceeded in the vapor phase with a higher rate than in the liquid because of the higher concentration of hydrogen.

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