

Hydrogenation of phenol in scCO₂ over carbon nanofiber supported Rh catalyst

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Abstract

A catalyst of Rh nanoparticles supported on a carbon nanofiber, 5 wt.% Rh/CNF, with an average size of 2–3 nm has been prepared by a method of incipient wetness impregnation. The catalyst presented a high activity in the ring hydrogenation of phenol in a medium of supercritical CO₂ (scCO₂) at a low temperature of 323 K. The presence of compressed CO₂ retards hydrogenation of cyclohexanone to cyclohexanol under the reaction conditions used, and this is beneficial for the formation of cyclohexanone, increasing the selectivity to cyclohexanone. But the selectivity to cyclohexanone is very low at the completion of reaction in the absence of CO₂, at low CO₂ pressures, and in the presence of pressurized N₂ instead of CO₂. That is, high selectivity to cyclohexanone can be achieved with CO₂ species at higher pressures but not with the application of an inert hydrostatic pressure on the liquid substrate phase.

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1. Introduction

Carbon nanofibers (CNF) and carbon nanotubes (CNT) receive growing attention as support materials for heterogeneous catalysts because of their purity, high mechanical strength, tunable surface properties, high surface area, and so forth [1,2]. CNT is usually synthesized by arc discharge techniques and CNF is obtained by catalytic decomposition of carbon-containing gases on supported metal particles. CNF, as a promising alternative support material, may be easier to produce on a commercial scale as compared with CNT. Hoogenraad and co-workers [3–6] investigated the hydrogenation of nitrobenzene to aniline with a Pd/CNF catalyst and they obtained higher activity with this Pd/CNF catalyst compared to a conventional activated carbon supported palladium catalyst (Pd/

AC with a higher metal loading). Baker and co-workers [7–9] compared the activities of several metals on CNFs in the hydrogenation of 1-butene and 1,3-butadiene. They observed that both the activity and selectivity were dramatically altered when nickel crystallites were dispersed on graphite nanofibers, compared to conventional support materials such as active carbon and γ -alumina [7]. A similar result was reported for the hydrogenation of cinnamaldehyde over Pd/CNF catalysts that the product selectivity over Pd/CNF was largely different from that over Pd/AC [10]. Toebe et al. [11,12] discussed the influence of oxygen-containing surface groups on CNF and the characteristics of the CNF support in the liquid phase hydrogenation of cinnamaldehyde over Ru/CNF. In the present work, we will report the catalytic performance of Rh/CNF catalysts in the ring hydrogenation of phenol under pressurization with CO₂. Previous works show interesting effects of the presence of compressed CO₂ in chemical reactions although it is not a reactant [13–17].

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The ring hydrogenation of phenol to cyclohexanol and cyclohexanone is a key step for preparing adipic acid, which is an important intermediate of the manufacture of Nylon-6,6. The catalytic ring hydrogenation is usually difficult under moderate reaction conditions and so the development of a catalyst for this process is currently of great significance. Generally, the hydrogenation of phenol is carried out in vapor phase over supported palladium catalysts [18–25]. However, the vapor phase hydrogenation needs high reaction temperature, which usually causes catalyst deactivation by coking during reaction. Recently, Rode et al. [26] reported that charcoal-supported rhodium catalyst was highly active for the ring hydrogenation of phenol and cresols in supercritical carbon dioxide (scCO₂) and the complete conversion of phenol to cyclohexanol was achieved over Rh/C catalyst under such conditions as 353 K, 10 MPa H₂ and 12 MPa CO₂. The present paper will report an active catalyst of Rh supported CNF for the ring hydrogenation of phenol in scCO₂ at a low temperature of 323 K and at a low hydrogen pressure of 4 MPa. It has been shown that the total conversion does not depend on CO₂ pressure so much but the product selectivity significantly changes with the pressure. The use of dense CO₂ is effective in retarding the hydrogenation of cyclohexanone to cyclohexanol, thus increasing the selectivity to cyclohexanone.

2. Experimental

2.1. Catalyst synthesis and characterization

The CNFs used in the present work were supplied by Tianjin University, China, which was of fishbone type and prepared by methane decomposition on Ni–Cu/Al₂O₃ catalyst in an autoclave with Teflon liner. The CNFs samples were first surface oxidized with a mixture of concentrated sulfuric and nitric acids before use. The supported Rh catalysts were prepared by an incipient wetness impregnation method. The total pore volume of the pre-oxidized CNFs was determined by adding demineralized water to degassed CNFs with a syringe until the fibers had a sticky appearance [27]. Next, degassed CNFs were impregnated with an aqueous solution of RhCl₃ with a concentration of about 0.24 mol/l in order to get a rhodium metal loading of 5 wt%. Degassing of the fibers was performed by evacuation at room temperature for several hours. The Rh-impregnated fibers were dried at room temperature for 48 h and subsequently dried at 393 K for 16 h. Then the Rh-impregnated fibers were heated at 653 K for 4 h under nitrogen and reduced at 573 K for 4 h with hydrogen before use for hydrogenation runs. The catalysts prepared were characterized by XRD (Rigaku SLX-2000) and TEM (JEM-3010, JEOL) methods.

2.2. Hydrogenation

The hydrogenation reactions were carried out in a 50 ml stainless steel autoclave. A certain amount of the catalyst

of Rh supported on carbon nanofiber (Rh/CNF) and phenol were charged into the reactor and the reactor was flushed with 2.0 MPa N₂ or CO₂ three times to remove the air. The reactor was then heated up to the desired temperature and H₂ and compressed liquid CO₂ were introduced with a high-pressure liquid pump. The reaction runs were conducted while stirring with a magnetic stirrer. At the end of reaction, the autoclave was cooled down to room temperature and then depressurized carefully by a backpressure regulator. The composition of reaction mixture was analyzed by a gas chromatograph using a flame ionization detector.

2.3. Phase behavior and FTIR

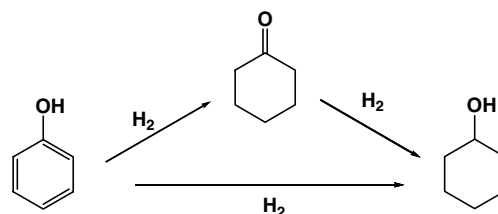
The phase behavior of reaction mixture was examined at different CO₂ pressures to see what phases existed and where hydrogenation occurred. High-pressure FTIR was used to examine interactions of CO₂ molecules with reacting species involved in hydrogenation. The experimental setup and procedures for these measurements are described elsewhere [16,17].

3. Results and discussion

The hydrogenation of phenol is a successive reaction in which phenol is first hydrogenated to cyclohexanone, followed by its hydrogenation to cyclohexanol; at the same time, cyclohexanol could also be directly produced from phenol, as shown in Scheme 1 [26]. The hydrogenation of phenol was tested in a temperature range from 308 to 393 K and it was found that the selectivity to cyclohexanone is smaller at a higher temperature and at a larger total conversion. In the following reaction runs, a moderate temperature of 323 K was used for the present purpose of examining the influence of dense CO₂ on the total conversion and the product selectivity.

3.1. Catalyst characterization

The Rh/CNF catalysts were prepared by the incipient wetness impregnation method as described above and reduced before reaction runs. The reduction temperature may be an important factor determining the metal particle size and the catalytic activity and, therefore, the influence of the reduction temperature was examined. The samples were reduced at 573, 673 and 773 K with a hydrogen



Scheme 1. Reaction paths in phenol hydrogenation.

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