HYDROGENATION OF NITROBENZENE WITH SUPPORTED TRANSITION METAL CATALYSTS IN SUPERCRITICAL CARBON DIOXIDE

Fengyu. Zhao[a,b,c], Rong Zhang[b], Maya Chatterjee[b], Yutaka Ikushima[b,c], and Masahiko Arai[c,d]

a, Japan Society for the Promotion of Science, Domestic Research Fellow. b, Supercritical Fluid Research Center, National Institute of Advanced Industrial Science and Technology, Sendai 983-8551, Japan. c, CREST, Japan Science and Technology Corporation (JST), Japan. d, Division of Materials Science and Engineering, Graduate School of Engineering, Hokkaido University, Sapporo 060-8628, Japan.

Introduction

The selective hydrogenation of nitro-compounds is commonly used to manufacture amines, which are important intermediates for dyes, urethanes, agro-chemicals and pharmaceuticals. Hydrogenation of nitrobenzene is used to produce aniline, which can be carried out in gas or liquid phase by using supported metal catalysts and organic solvents such as alcohols, acetone, benzene, ethyl acetate, or aqueous acidic solutions.[1,2] The use of these solvents has some drawbacks owing to their toxicity, flammability, or environmental hazards. In addition, the solvent may play a crucial role in the stabilization of reactive intermediates and have a decisive influence on chemical reactions. Therefore, the choice of solvent is important and a green solvent should be considered for contemporary chemical processes. Supercritical carbon dioxide ($scCO_2$) is an environmentally acceptable replacement for conventional organic solvents, due to its environmentally benign, non-toxic, and non-flammable nature, low cost, and wide tuning ability of solvent properties.[3,4] Moreover, the rate of catalytic hydrogenation in a gas-liquid system is not so high because of a low solubility of gaseous hydrogen in common solvents. In contrast, hydrogen is completely miscible with $scCO_2$, and this is beneficial for enhancement of hydrogenation reactions. [5]

The present work has been undertaken to study the catalytic hydrogenation of nitrobenzene in $scCO_2$ and in ethanol at a low temperature of 35 ℃ using several supported transition metal catalysts. The influence of metals (Pt, Pd, Ru, and Rh), supports (C, SiO_2, and Al_2O_3), and solvents ($scCO_2$ and ethanol) on the catalytic activity and selectivity has been investigated.

Experimental

Materials. All the chemicals were purchased from Wako Pure Chemicals Industries and used without further purification. Carbon- and alumina-supported Pd, Rh, Pt and Ru catalysts were also purchased from Wako. Silica-supported Pd and Pt catalysts were prepared using ion-exchange method. All the catalysts were reduced by hydrogen at 300℃ for 2 h before activity measurements.

Activity measurement. The activity of those catalysts was tested for the hydrogenation of nitrobenzene, which was carried out in a 50 mL high-pressure autoclave. Nitrobenzene (2.0 g (16.2 mmol)) and catalyst (0.01 g) were charged into the reactor and the reactor was flushed with 2.0 MPa CO_2 for three times. The reactor was then heated up to the desired temperature of 35℃ and then H_2 and compressed liquid CO_2 were introduced up to the desired pressure with a high-pressure liquid pump. The hydrogenation reaction was conducted while stirring with a magnetic stirrer. After the reaction, the reactor was cooled to room temperature and the reaction mixture was analyzed with a gas chromatograph (HP 5890, HP5 capillary column with 0.53 mm in diameter, 0.25 μm in film, and 15 m in length) using a flame ionization detector.

Catalyst characterization. X-ray diffraction (XRD) patterns of catalysts were measured on Rigaku RINT 220VK/PC powder diffractometer operated at 40 kV and 20 mA, using CuKα monochromatized radiation (λ = 0.154178 nm). The crystallite size of supported metals was calculated using the Scherrer equation, $D = K\lambda/(\beta\cos\theta)$, where K is a constant taken as 0.9, λ is the wavelength of the X-ray radiation, β is the peak width at half maximum.

Results and Discussion

Hydrogenation of nitrobenzene in organic solvents was reported to produce aniline along with several intermediate products such as nitrosobenzene (NSB), phenylhydroxylamine (PHA), azoxybenzene (AOB), azobenzene (AB) and hydrazobenzene (HOB), which are formed in several parallel and consecutive reactions. It has been observed in the present work that all the catalysts show 100% selectivity towards aniline in $scCO_2$ at 50℃. In order to compare the influence of metal and support on both activity and selectivity, the reaction has been carried out at a lower temperature of 35℃. At this temperature as well, PHA and HOB were not detected to form.

The influence of metals has been examined using C-supported catalysts (Table 1). In $scCO_2$, the highest conversion of 71% was obtained with Pt/C catalyst; however, the selectivity to aniline was lower compared to these obtained with the other catalysts. The Pd/C, Ru/C, and Rh/C catalysts exhibit 100% selectivity to aniline in $scCO_2$. In a conventional organic solvent of ethanol, Pt/C also shows a higher conversion compared with the other catalysts. With Ph/C and Ru/C catalysts, no products were detected in ethanol. For all the catalysts used, both the conversion and selectivity to aniline obtained in $scCO_2$ are higher than these obtained in ethanol. The order of activity is Pt > Pd > Rh, Ru in $scCO_2$ as well as in ethanol. The solubility of H_2 in ethanol and CO_2 calculated according to Henry's law and equation state for ideal gases, indicated that the concentration of H_2 in CO_2 is 15 times higher than that in ethanol.

Table 1 Results of hydrogenation of nitrobenzene in $scCO_2$ and in ethanol with different carbon supported metal catalysts at 35℃

Solvent	Catalyst	Time (min)	Conversion (%)	Selectivity (%)			
				AN	NSB	AB	AOB
CO_2 14.0 MPa	5% Pd/C	10	52	100	--	--	--
	5% Pd/C	50	100	100	--	--	--
	5% Pt/C	10	71	79	4	12	5
	5% Pt/C	50	100	100	--	--	--
	5% Ru/C	10	4	100	--	--	--
	5% Rh/C	10	12	100	--	--	--
Ethanol	5% Pd/C	10	21	68	16	--	16
	5% Pt/C	10	63	58	4	26	12
	5% Ru/C	10	0	--	--	--	--
	5% Rh/C	10	0	--	--	--	--

Next, the total conversion and the selectivity to aniline obtained with various supported metal catalysts in $scCO_2$ and ethanol were shown in figure 1. In $scCO_2$, all the Pd catalysts indicate 100%

selectivity to aniline, while the Pt catalysts have lower selectivity to aniline. With the Pt catalysts, some amounts of NSB, AOB, and AB were produced. In ethanol, the same byproducts were also detected with all the Pt and Pd catalysts. Higher aniline selectivity values were obtained in $scCO_2$ than these obtained in ethanol for all the catalysts used. The order of the total conversion with respect to the supports is C > Al_2O_3, SiO_2 in $scCO_2$ for both Pt and Pd. It is interesting to see that the total conversion in ethanol is higher than that obtained in $scCO_2$ for Al_2O_3 and SiO_2 supported Pt and Pd catalysts; on the contrary, the conversion in $scCO_2$ is higher than that in ethanol for Pd/C and Pt/C catalysts.

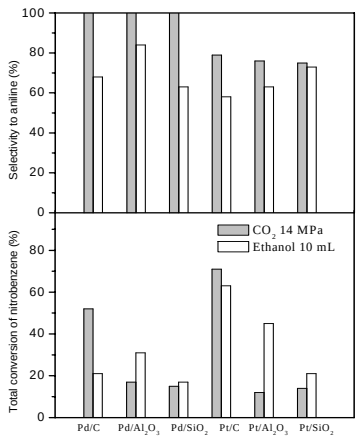

Figure 1. Nitrobenzene hydrogenation in $scCO_2$ and in ethanol at 35℃. Reaction conditions: nitrobenzene 2.0 g (16.2 mmol), catalyst 0.01g, H_2 4.0 MPa, temperature 35℃, reaction time 10 min.

These results can be explained with metal particle size and the interaction between reaction medium and metal particle. The metal particle size on the supports were quite different and a larger metal particle presented on the C-supported Pd and Pt catalysts as calculated by Scherrer equation. The nitrobenzene hydrogenation proceeded on the surface of metal particles, the higher activity presented in $scCO_2$ for Pd/C and Pt/C catalysts indicates a significant interaction existed between $scCO_2$ molecular and the larger Pt and Pd metal particle, which benefits the formation of aniline, thus, the higher selectivities to aniline have been obtained in $scCO_2$ than these obtained in ethanol for all the catalysts used.

The CO_2 pressure presents a significant effect on the reaction conversion and product selectivity in Figure 2. The conversion increases with increasing CO_2 pressure up to 12 MPa , which can be explained by the phase behavior and the concentration of nitrobenzene distributed in liquid and CO_2 phases. The concentration of nitrobenzene in CO_2 increases with increasing CO_2 pressure; when CO_2 pressure was raised to 12 MPa, a completely miscible mixture (NB, H_2 and CO_2) was formed. In this case the mass transfer resistance between gas (H_2) and liquid (NB) was decreased with increasing CO_2 pressure and then it disappeared at 12 MPa as a result of the phase changes to a homogeneous phase. This is a reason for that the conversion increases with increasing CO_2 pressure. The selectivity to aniline increases and has a maximum at 8.0 MPa, and then it decreases with increasing CO_2 pressure for both Pd/C and Pt/C catalysts. It was supposed that density variation around the critical point would cause a change in chemical or physical properties and affects the activity and selectivity of a reaction. The density of $scCO_2$ is highly pressure dependent, for instance, to change CO_2 pressure from 6.0 MPa to 8.0 MPa, the density changes from 160.0 to 520.8 kg/m^3 [6].

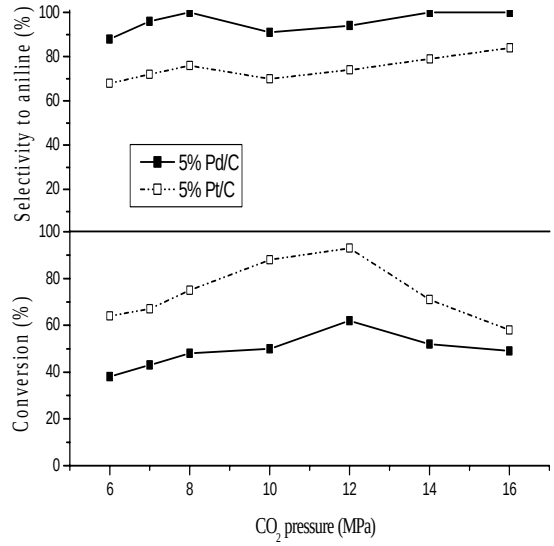

Figure 2 Influence of CO_2 pressure on the total conversion and selectivity to aniline. Reaction conditions: nitrobenzene 2.0 g (16.2 mmol, 0.324 mmol/ml in the reactor), catalyst 0.01g, H_2 4.0 MPa, temperature 35℃, reaction time 10 min.

The transition metal catalysts of Pd, Pt, Ru, and Rh supported on carbon presented a similar active order of Pt > Pd > Ru, Rh in $scCO_2$ as well as in ethanol. An active order of supports is C >Al_2O_3, SiO_2 in $scCO_2$ for both Pd and Pt catalysts. Higher selectivity to aniline has been obtained in $scCO_2$ compared with that in ethanol. the hydrogenation of nitrobenzene catalyzed with Pd/C and Pt/C catalysts was successfully conducted in $scCO_2$ with a 100% yield to aniline at a lower temperature of 35℃ for 50 min. Clearly, $scCO_2$ is a suitable replacement for organic solvent in the hydrogenation of nitrobenzene and the present hydrogenation is an environmentally benign and "green" process as it is free of harmful organic solvents. In addition, it is easy to separate the organic phase (the desired product, aniline), aqueous phase (the only byproduct, water), gas phase (CO_2, H_2).

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