Hydrogenation of Nitrobenzene with Supported Transition Metal Catalysts in Supercritical Carbon Dioxide

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Abstract: Transition metal catalysts such as Pd, Pt, Ru, and Rh supported on carbon, silica and alumina have been examined for the hydrogenation of nitrobenzene (NB) in supercritical carbon dioxide ($scCO_2$) and in ethanol. The order of hydrogenation activity is Pt > Pd > Ru, Rh in $scCO_2$ and in ethanol. The effectiveness of the support is C > Al_2O_3, SiO_2 for either Pt or Pd in $scCO_2$. For all the catalysts, higher selectivity to aniline has been obtained in $scCO_2$ compared with ethanol. 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 reaction temperature of 35 °C. The product aniline (organic phase) can be easily separated from the side-product water (aqueous phase), solvent ($scCO_2$), and catalyst (solid) by a simple phase separation process. The hydrogenation of NB is a structure-sensitive reaction in ethanol as well as in $scCO_2$ except for a few Pt/C catalysts in which the degree of metal dispersion is small (<0.08).

Keywords: hydrogenation; nitrobenzene; supercritical carbon dioxide; transition metal catalysts

Introduction

The selective hydrogenation of nitro compounds is commonly used to manufacture amines, which are important intermediates for dyes, urethanes, agro-chemicals and pharmaceuticals. The hydrogenation of nitrobenzene is used to produce aniline, which can be carried out in the gas or liquid phase by using supported metal catalysts and organic solvents such as alcohols, acetone, benzene, ethyl acetate, or aqueous acidic solutions.[1–4] 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 the wide tuning range of the solvent's properties.[5–8] Moreover, the rate of catalytic hydrogenation in a gas-liquid system is not so high because of the low solubility of gaseous hydrogen in common solvents.[9] In contrast, hydrogen is completely miscible with $scCO_2$, and this is beneficial for the enhancement of hydrogenation reactions. We have reported a significant enhancement of activity and selectivity for the hydrogenation of unsaturated aldehydes with supported transition metal catalysts in $scCO_2$.[9–12] It was also suggested that a direct interaction existed between transition metal particles and the $scCO_2$ medium, influencing the reaction rate and selectivity.[13]

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 °C using several supported transition metal catalysts. The influence of the 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. 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), the aqueous phase (the only by-product, water), the gas phase (CO_2, H_2), and the solid phase (the catalyst).

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Results

The 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 as shown in Scheme 1.[1,4] It has been observed in the present work that all of the tested catalysts show 100% selectivity towards aniline in $scCO_2$ at 50 °C. 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 °C. At this temperature as well, PHA and HOB were not detected. All the reactions were carried out using the catalysts in the fine powder form with vigorous stirring and so the catalyst powder was shown to be well dispersed in the solvents $scCO_2$ and ethanol. Under the conditions (stirring, catalyst size, and gas pressures) used, the reactions were unlikely to be mass-transfer controlled. Gelder et al. studied the hydrogenation of nitrobenzene in the conventional solvents methanol and isopropanol under similar conditions as used in the present work.[16] They showed the absence of mass-transfer control from reaction runs using a range of stirring speeds. It is known that mass transfer is faster in $scCO_2$ than in normal liquids.[5–8] The product selectivity has been calculated from moles of a certain product/total moles of all the products formed.

Catalyst Characterization

The XRD patterns for all the Pt, Pd, Ru and Rh catalysts used are presented in Figure 1, which show diffraction peaks assigned to their metallic state. The Pd/C and Pt/C catalysts exhibit narrower peaks compared with those on Al_2O_3 and SiO_2, and so the size of the metal particles on C is larger, which is in agreement with the results of TEM as shown in Figure 2. No diffraction peaks were observed with the SiO_2-supported Pd and Pt catalysts, indicating that the metals are highly dispersed on this support. The metal particles of the SiO_2-supported catalysts are smaller than 2 nm from TEM measurements.

Catalytic Activity

Influence of metal, support and solvent

Ethanol was selected as a reference solvent because it is known to be a better, frequently used solvent for the hydrogenation of nitrobenzene in the literature.[1] The influence of metals has been examined using C-supported catalysts (Table 1). In $scCO_2$ after a reaction time of

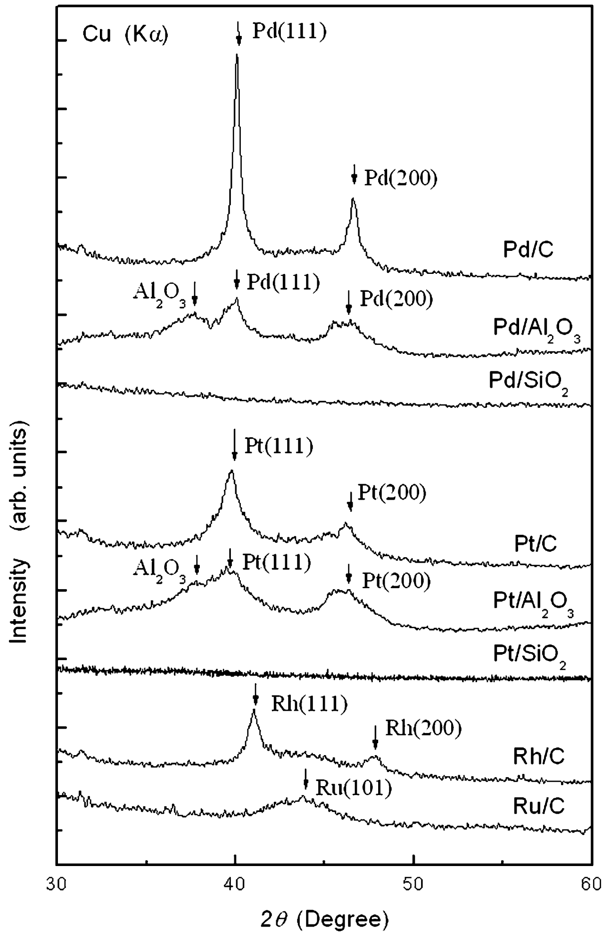
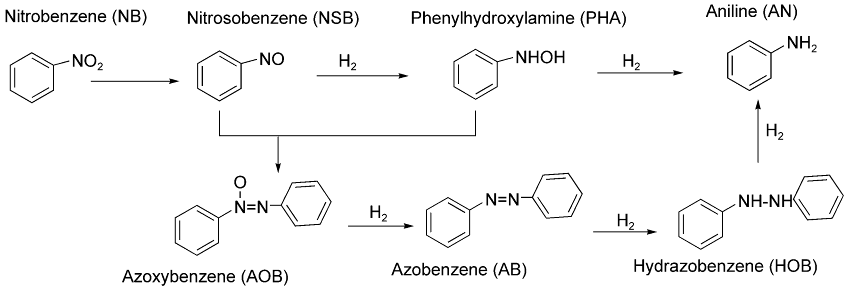


Figure 1. XRD patterns of 5 wt. % Pd, Pt, Rh and Ru supported catalysts after being reduced at 300 °C for 3 h with hydrogen.



Scheme 1. Hydrogenation of nitrobenzene.

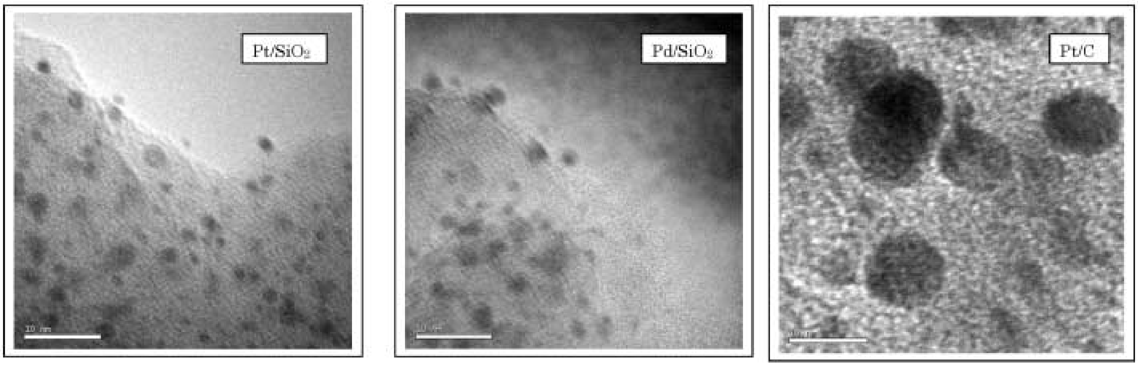


Figure 2. TEM images for Pt/SiO$_2$, Pd/SiO$_2$, Pt/C catalysts after being reduced with hydrogen at 300 °C for 3 h. Scale bar = 10 nm.

10 min, the highest conversion of 71% was obtained with the 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 exhibited 100% selectivity to aniline in scCO$_2$. In the conventional organic solvent ethanol, Pt/C also showed a higher conversion compared with the other catalysts. With Rh/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 those obtained in ethanol. The order of overall 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 the equation of state for ideal gases indicate that the concentration of H$_2$ in CO$_2$ is about 15 times higher than that in ethanol. However, the NB concentration in CO$_2$ is about 1/5 of that in ethanol.

Next, the total conversion and the selectivity to aniline obtained with various supported metal catalysts in scCO$_2$ and ethanol are compared in Figure 3. In scCO$_2$, all the Pd catalysts indicate 100% selectivity to aniline, while the Pt catalysts have lower selectivity to aniline. NSB, AOB, and AB were produced with the Pt catalysts. In ethanol, the same by-products were also detected with all the Pt and Pd catalysts, decreasing the aniline selectivity. Higher aniline selectivity values were obtained in scCO$_2$ than those obtained in ethanol for all the catalysts used. The order of the total conversion with respect to the supports is C > Al$_2$O$_3$, 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$_2$O$_3$ and SiO$_2$ supported Pt and Pd catalysts; for Pd/C and Pt/C catalysts, in the contrast, the conversion in scCO$_2$ is higher than that in ethanol.

Table 1. Results of hydrogenation of nitrobenzene in scCO$_2$ and in ethanol with different carbon supported metal catalysts.

Solvent	Catalyst	Time (min)	Conversion (%)	Selectivity (%)				Concentration of NB (mmol/mL)	Solubility of H$_2$ (mole fraction)
				AN	NSB	AB	AOB		
CO$_2$ (14.0 MPa)	5% Pd/C	10	52	100	–	–	–	0.324	0.25[a]
	5% Pd/C	50	1000	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 (10 mL)	5% Pd/C	10	21	68	16	–	16	1.62	0.020[b] (51 °C, 4.0 MPa)
	5% Pt/C	10	63	58	4	26	12		0.013[b] (26 °C, 4.0 MPa)
	5% Ru/C	10	0	–	–	–	–		
	5% Rh/C	10	0	–	–	–	–		

Reaction conditions: nitrobenzene 2.0 g (16.2 mmol), catalyst 0.01 g, H$_2$ 4.0 MPa, temperature 35 °C.

[a] H$_2$ is completely miscible with scCO$_2$ and the solubility of H$_2$ in scCO$_2$ was estimated from moles of CO$_2$ and H$_2$ calculated by the equation of state for ideal gases.

[b] The solubility of H$_2$ in ethanol was estimated from Henry's constant at 51 °C and 26 °C.[14]

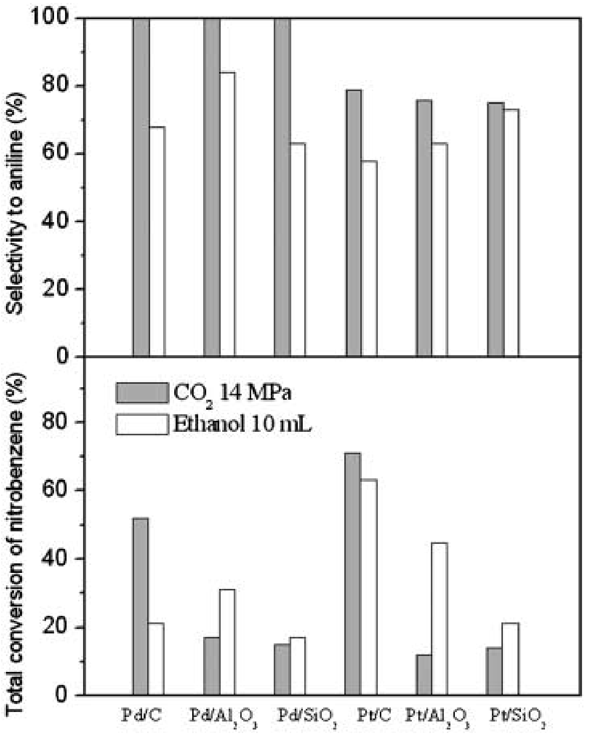


Figure 3. Hydrogenation of nitrobenzene in $scCO_2$ and in ethanol at 35 °C. Reaction conditions: nitrobenzene 2.0 g (16.2 mmol), catalyst 0.01 g, H_2 4.0 MPa, temperature 35 °C, reaction time 10 min.

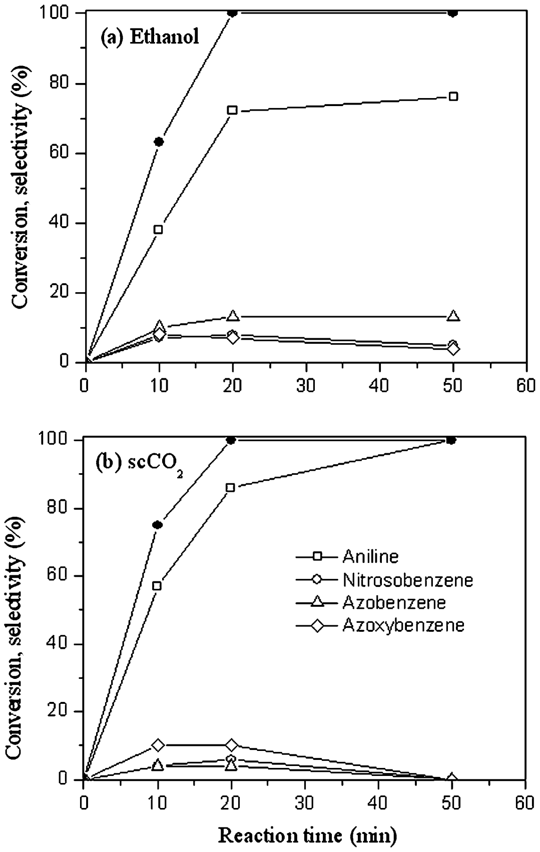


Figure 4. Changes of conversion (closed circles) and product selectivity (open marks) with reaction time during the hydrogenation of nitrobenzene with Pt/C catalyst in $scCO_2$ and in ethanol at 35 °C. (**a**) Reaction in ethanol, NB 16.2 mmol, Pt/C 0.01 g, ethanol 10 mL, H_2 4 MPa. (**b**) Reaction in CO_2, NB 16.2 mmol, Pt/C 0.01 g, CO_2 14 MPa, H_2 4 MPa

Influence of reaction time

Figure 4 shows the influence of reaction time in $scCO_2$ and in ethanol with Pt/C catalyst, indicating that the selectivity of aniline formed increases with reaction time during the first 20 min, after which it increases very slightly in ethanol while it increases gradually in $scCO_2$ and reaches 100% within 50 min. These results could be explained with hydrogen concentration dissolved in the reaction medium and the properties of $scCO_2$, as discussed later.

Influence of CO_2 pressure, total pressure and phase behavior

Table 2 shows the influence of CO_2 pressure on the total conversion and the selectivity to aniline with Pd/C and Pt/C catalysts in $scCO_2$. The conversion increases with CO_2 pressure up to 12 MPa for both Pt/C and Pd/C catalysts, but it decreases thereafter probably due to the dilution effects. With increasing CO_2 pressure, the selectivity to aniline increases and has a higher value at 8.0 MPa near the critical pressure of pure CO_2 (7.3 MPa), which is 100% for Pd/C catalyst. Then, the selectivity decreases slightly at 10 MPa and increases again after 12 MPa for both Pd/C and Pt/C catalysts. These results may be explained with taking into account the phase behavior and the properties of CO_2, as discussed later. When the catalysts Pd/C and Pt/C were used without reduction before reaction, the conversions were shown to be lower than those obtained with the pre-reduced catalyst. However, the selectivity to aniline showed no differences, indicating that the selectivity did not depend on the electronic state of the metals of the catalysts. Both the conversion and selectivity to aniline at 14 MPa are higher than those obtained at 8 MPa for all the catalysts used, suggesting that the two-phase (solid-$scCO_2$ fluid) reaction at 14 MPa is faster than the three-phase (solid-liquid-$scCO_2$ fluid) reaction at 8 MPa. A reason for this is that all the organic substrates are dissolved in $scCO_2$ at 14 MPa and the phase-transfer resistant state (liquid-$scCO_2$ fluid) has disappeared.

The influence of total pressure on the conversion and selectivity has been examined with 5% Pt/C catalyst (Table 3). The reactions were conducted in the presence and absence of a high pressure of N_2 in ethanol and un-

Table 2. Hydrogenation of nitrobenzene with different catalysts in compressed CO_2.

Catalyst	CO_2 Pressure (MPa)	Conversion (%)	Number of phases[a]	Selectivity (%)			
				AN	NSB	AB	AOB
5% Pd/C	6	38	3	88	3	6	3
	7	43	3	96	–	4	–
	8	48	3	100	–	–	–
	8[b]	10	3	100	–	–	–
	10	50	3	91	2	4	3
	12	62	3	94	1	2	3
	14	52	2	100	–	–	–
	16	49	2	100	–	–	–
5% Pt/C	6	64	3	68	7	15	10
	7	67	3	72	6	17	5
	8	75	3	76	6	6	12
	8[b]	12	3	76	9	15	–
	10	88	3	70	6	17	7
	12	93	2	74	5	15	6
	14	71	2	79	4	17	–
	16	58	2	84	4	12	–
5% Pd/SiO_2	8	8	3	100	–	–	–
	14	15	2	100	–	–	–
5% Pd/Al_2O_3	8	12	3	100	–	–	–
	14	17	2	100	–	–	–
5% Pt/SiO_2	8	12	3	65	10	19	6
	14	14	2	75	–	25	–
5% Pt /Al_2O_3	8	9	3	71	12	20	7
	14	12	2	76	1	23	–

Reaction conditions: nitrobenzene 2.0 g (16.2 mmol, 0.324 mmol/mL in the reactor), catalyst 0.01 g, H_2 4.0 MPa, temperature 35 °C, reaction time 10 min.

[a] Two or three phases were observed depending on the conditions used: at low CO_2 pressures there existed a CO_2-rich gas phase, a liquid phase, and a solid phase (catalyst); at high CO_2 pressure there were a CO_2-gas phase and a solid phase (catalyst).

[b] The catalysts were used without prior reduction.

Table 3. Influence of total pressure on the hydrogenation of nitrobenzene.

Entry	Solvent	Gas	Total pressure (MPa)	Time (min)	Conversion (%)	Selectivity (%)			
						AN	NSB	AB	AOB
1	Ethanol	H_2	4.0	10	63	58	4	26	12
2	Ethanol	H_2, N_2	12.0	4	49	48	5	45	2
3	No	H_2	4.0	20	50	86	4	9	1
4	No	H_2, N_2	12.0	15	45	87	3	10	–

Reaction conditions: nitrobenzene 2.0 g (16.2 mmol), catalyst 5% Pt/C 0.01 g, H_2 4.0 MPa, ethanol 10 mL, N_2 8.0 MPa, temperature 35 °C.

der solvent-free conditions. Similar aniline selectivity values were obtained at similar total conversion levels, indicating that the selectivity did not depend on the reaction pressure. Lower selectivity to aniline has been obtained in ethanol compared with those obtained under the solvent-free conditions. However, the reaction rate in ethanol is about two times higher than that under the solvent-free conditions, suggesting that the reaction rate and selectivity depend not only on the substrate concentrations but also on the reaction medium.

The state of the reaction mixture was examined by the naked eye through a transparent window at a reaction temperature of 35 °C. Figure 5 shows the visual observations at an H_2 pressure of 4.0 MPa and CO_2 pressures of 0.5, 8.0, 11.0, and 12.0 MPa. When the CO_2 pressure is as low as ambient pressure, there are two phases, $CO_2 + H_2$ gas phase and a liquid phase. At CO_2 pressures of 8.0 and 11.0 MPa – higher than the critical pressure of CO_2, two phases are still present. In this case the reacting species should be distributed in these two phases and the hydrogenation should occur in the CO_2-rich gas and liquid phases. At 12 MPa or above, the mixture changes into a single phase, in which all the reacting species are dissolved in CO_2 completely, forming a homogeneous phase. Figure 6 shows the phase behavior of NB in a mixture of H_2 (4 MPa) and CO_2, which was also examined with the same viewing cell. In Figure 6, solid and open marks indicate the presence of a single (gas) phase and two (gas-liquid) phases at the CO_2 pressures given. The solubility of NB is between these two marks. It is seen that the solubility is very small at CO_2 pressures lower than 8.0 MPa and increases with increasing CO_2 pressure. When the CO_2 pressure is raised up to 11 MPa, the solubility increases very markedly.

Influence of particle size

The metal crystallite sizes were determined from XRD line broadening with the Scherrer equation as well as from TEM measurements. The degree of metal dispersion was estimated from the approximate equation: metal dispersion = 0.9/particle diameter (in nm).[15] Figure 7 shows the influence of the metal dispersion on turnover frequency (TOF) in $scCO_2$ (14 MPa) and in ethanol for the catalysts of Pt and Pd supported on the different supports. The reaction mixture was a fluid-solid two-phase system for $scCO_2$ and ethanol under the conditions used. For the Pd catalysts in $scCO_2$ and in ethanol, the results are correlated with a single line of negative gradient. This means that the reaction is structure-sensitive in $scCO_2$ and in ethanol, the TOF decreasing with the Pd dispersion, and the influence of support materials may be explained by the difference in Pd dispersion on them. Gelder et al. also reported that the TOF decreased with increasing metal dispersion in the hydrogenation of NB with 3 wt % Pd/C (activated carbon) in methanol at 50 °C and 0.5 MPa H_2.[16] In the present work, a single line approximately correlates the results with the Pt catalysts, except for a few samples of smaller Pt dispersion in $scCO_2$. Its gradient is very similar to that for Pd; namely, the structure sensitivity is similar between the Pd and Pt catalysts and between $scCO_2$ and ethanol. When compared at the same metal dispersion, the TOF value of Pt is about three times larger than that of Pd; Pt is more active than Pd. As mentioned, a few exceptions are Pt/C catalysts of smaller metal dispersion (< 0.08) in $scCO_2$, which seem to have very similar TOF values; the reaction is not structure sensitive. The reason for this is not clear at present.

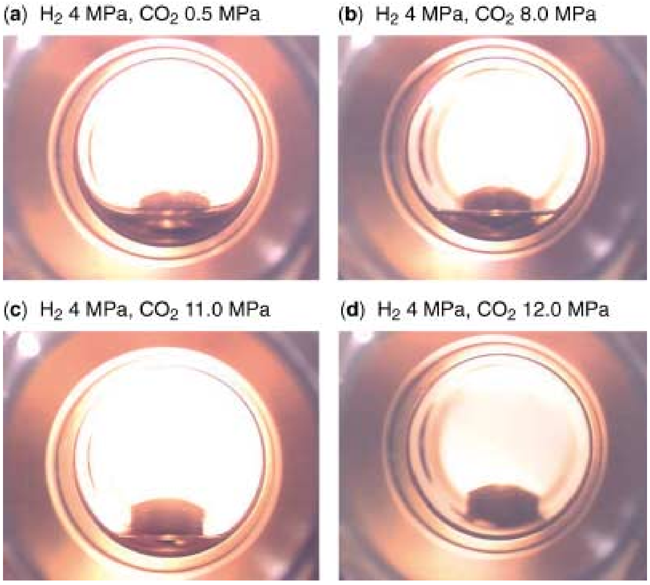


Figure 5. Visual observations of a reaction mixture including nitrobenzene, hydrogen, and CO_2 at 35 °C. Conditions: viewing cell volume 10 mL, temperature, 35 °C, nitrobenzene 0.40 g (3.24 mmol).
(**a**) H_2 4 MPa, CO_2 0.5 MPa
(**b**) H_2 4 MPa, CO_2 8.0 MPa
(**c**) H_2 4 MPa, CO_2 11.0 MPa
(**d**) H_2 4 MPa, CO_2 12.0 MPa

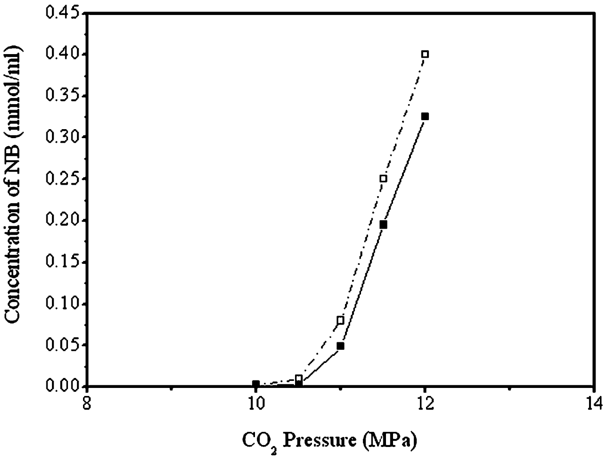


Figure 6. The phase behavior of mixture of nitrobenzene (NB) and H_2 in CO_2 at different CO_2 pressures for estimation of the solubility of nitrobenzene. Conditions: H_2 4.0 MPa, temperature 35 °C. The y-axis is the apparent concentration of NB in the reactor. The solid and open marks indicate the presence of a single phase (gas) and two phases (gas and liquid), respectively.

Discussion

Influence of Pressure and Phase Behavior

The CO_2 pressure exerts a significant effect on the reaction conversion and product selectivity, as shown in Table 2. The conversion increases with CO_2 pressure up to

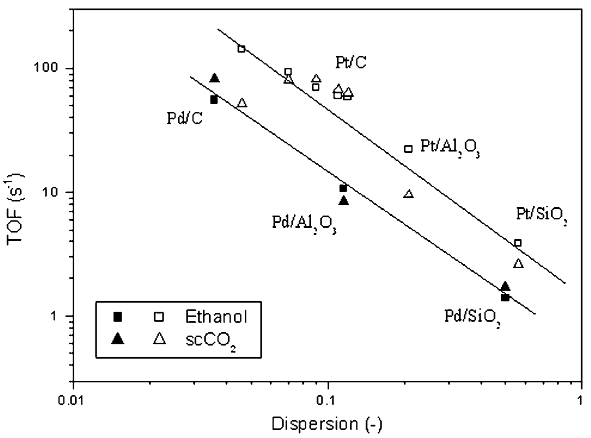


Figure 7. Plots of TOF against the degree of metal dispersion for hydrogenation of nitrobenzene using different catalysts. Reaction conditions: nitrobenzene 2.0 g (16.2 mmol), catalyst 0.01 g, H_2 4.0 MPa, CO_2 14 MPa or ethanol 10 mL, temperature 35 °C, reaction time 10 min. Average turnover frequency (TOF): moles of substrate reacted per mole of exposed surface metal atoms per second.

12 MPa, which can be explained by the phase behavior and the concentration of NB distributed in the liquid and CO_2 phases. The concentration of NB in CO_2 increases with increasing CO_2 pressure; when the CO_2 pressure was raised to 12 MPa, a completely miscible mixture (NB, H_2 and CO_2) was formed (Figure 5). In this case, the mass-transfer resistance between gas (H_2) and liquid (NB) decreased with increasing CO_2 pressure and then disappeared at 12 MPa as a result of the phase change to a homogeneous phase. This is one reason that the conversion increases with increasing CO_2 pressure. The selectivity to aniline increases and has a maximum at 8.0 MPa, and then decreases with increasing CO_2 pressure for both Pd/C and Pt/C catalysts. The similar results of a maximum selectivity at a pressure near the critical point of CO_2 were also found in the hydrogenation of unsaturated aldehydes[11] as well as in the Diels–Alder reaction.[17] It was supposed that density variations around the critical point would cause a change in chemical or physical properties and affect the rate and selectivity of reactions. The density of $scCO_2$ is highly pressure-dependent; for instance, when the CO_2 pressure changes from 6.0 MPa to 8.0 MPa, the density changes from 160.0 to 520.8 kg m^{-3}.[13] It was also postulated that in a network of parallel or competing reactions as in the present NB hydrogenation, the thermodynamic pressure effect on each of the individual rate constants may be different due to different activation volumes; increasing the CO_2 pressure may favor one of the reactions over the others and one could enhance the selectivity to the desired product by operating at the appropriate pressure and temperature.[6]

Influence of Solvent and Metal Particle Size

Next, we will discuss the influence of solvent and metal particle size on the catalytic activity and product selectivity, using the reaction data at high CO_2 pressure (14 MPa) under which the reaction system is gas-solid biphasic. For Al_2O_3 and SiO_2 supported Pt and Pd catalysts, higher activities were obtained in ethanol than in $scCO_2$ and, on the contrary, for C supported catalysts, higher activities were shown in $scCO_2$. For all the catalysts used, higher selectivity to aniline was obtained in $scCO_2$ than in ethanol. These results could be explained with metal particle size and interaction between reaction medium and metal particle. The metal particle size on the supports was quite different and larger metal particles were seen to exist in the C-supported Pd and Pt catalysts (Figures 1 and 2). Thus, we can say that larger metal particles are more active in $scCO_2$ than in ethanol. It was reported in the literature [13] that a direct interaction existed between transition metal particles and $scCO_2$ medium, which was suggested to influence the reaction rate and selectivity. Such an interaction may depend on the size of the metal particles and this would be a possible reason for the different effects of the two solvents, $scCO_2$ and ethanol, on the overall activity between larger metal particles on C and smaller ones on Al_2O_3 and SiO_2. The possibility is not denied that the effects of solvents depend on differences in the surface properties between the C support and the oxide ones. In the present cases, however, the influence of the supports is simple, which affects the size of metal particles on them, and the supports does not directly influence the reactions, judging from the simple correlation as shown in Figure 7.

The TOF of NB hydrogenation decreased with metal dispersion for all the Pt and Pd catalysts in ethanol and in $scCO_2$ except for a few Pt/C catalysts with smaller metal dispersion (<0.08) in $scCO_2$, This means that the reaction is structure-sensitive in $scCO_2$ (metal dispersion >0.08) as well as in ethanol. These results are consistent with the literature.[16,18] A higher TOF was reported with larger metal particle in the liquid-phase NB hydrogenation with activated carbon supported palladium catalysts in methanol at 50 °C;[16] in addition, a higher activity was observed for larger metal particles in the hydrogenation of nitrosobenzene, an intermediate product of NB hydrogenation.[18]

Conclusions

The following significant conclusions are drawn from the present work on the hydrogenation of nitrobenzene (NB) with supported transition metal catalysts in $scCO_2$ and in ethanol. The order of catalytic activity of metals in these solvents is Pt > Pd > Ru, Rh and the latter two metals are much less active. The activity of both Pd and Pt catalysts was observed to depend on the support used in $scCO_2$ and the effectiveness of the supports is $C > Al_2O_3$, SiO_2. The hydrogenation of NB is a structure-sensitive reaction in ethanol as well as in $scCO_2$, except for a few Pt/C catalysts with smaller degrees of metal dispersion (< 0.08). The TOF value of Pt catalysts is about three times larger than that of Pd catalysts when compared at the same metal dispersion levels. Higher selectivity to aniline was obtained in $scCO_2$ than in ethanol for all the catalysts used. $scCO_2$ is a suitable replacement for organic solvent in the hydrogenation of NB 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), the aqueous phase (the only by-product, water), and the gas phase (CO_2, H_2).

Experimental Section

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 an ion-exchange method as described previously.[10] All the catalysts were reduced by hydrogen at 300 °C for 2 h before activity measurements.

Activity Measurement

The activity of these 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 three times. The reactor was heated up to the desired temperature of 35 °C and then H_2 and compressed liquid CO_2 were introduced up to the desired pressures 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 a Rigaku RINT 220VK/PC powder diffractometer operating at 40 kV and 20 mA, using CuKα monochromatized radiation ($\lambda = 0.154178$ nm). The crystallite size, D, 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. The particle size was also measured using a transmission electron microscope (TEM, TECNAI-20ST).

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