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Research Note

Hydrogenation of nitrobenzene with supported platinum catalysts in supercritical carbon dioxide: effects of pressure, solvent, and metal particle size

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Abstract

Hydrogenation of nitrobenzene (NB) has been investigated with Pt/C catalysts in supercritical carbon dioxide ($scCO_2$) and ethanol. The selectivity of aniline (AN) in $scCO_2$ is $\geqslant 80\%$, which is twice as high as that in ethanol, in which comparable amounts of AN and azobenzene (AB) are produced. In $scCO_2$, the overall conversion of NB increases with CO_2 pressure, has a maximum at around 10 MPa, and then decreases at 14 MPa. The product selectivity in $scCO_2$ does not change much with the size of Pt particles while, in ethanol, the selectivity to AN and AB changes slightly with the particle size. The overall hydrogenation of NB is not structure sensitive in $scCO_2$, while it is structure sensitive in ethanol in which turnover frequency tends to decrease with an increase in the degree of Pt dispersion.

Keywords: Nitrobenzene hydrogenation; Supported platinum catalyst; Supercritical carbon dioxide; Particle-size effect; Solvent effect

1. Introduction

Supercritical carbon dioxide ($scCO_2$) is an environmentally acceptable replacement for conventional organic solvents due to its environmentally benign nature. The use of $scCO_2$ has other merits of low cost, tuning ability of solvent properties, miscibility of gaseous reacting species, and easy separation by depressurization [1–4]. In addition, $scCO_2$ has the possibility of modifying the catalytic activity of supported metal particles [5]. The combination of $scCO_2$ and solid catalysts would be a green chemistry reaction system in which no organic solvent is used and separation of the CO_2 solvent after use is easy. Several authors studied chemical transformations with supported metal catalysts in $scCO_2$ [6–12]. For example, Poliakoff and co-workers reported continuous hydrogenation of cyclohexene and acetophenone in $scCO_2$ with a polysiloxane-supported palladium catalyst [6]. The present authors showed a significant enhancement of activity and selectivity for hydrogenation of α,β-unsaturated aldehydes with supported transition metal catalysts [13–15]. Other hydrogenation reactions have been studied in $scCO_2$ and the results obtained are reviewed in the literature [1–4]. In the present work, hydrogenation of nitrobenzene (NB) has been undertaken with Pt/C catalysts in $scCO_2$, with the aim of investigating features of $scCO_2$ solvent and structure sensitivity in this new type of medium. The structure sensitivity is an important issue in catalytic chemistry and has been studied under ordinary conditions [16–21], but so far not examined in $scCO_2$ medium. It is interesting to note here that the selectivity to the formation of AN is even higher ($\geqslant 80\%$) and the overall hydrogenation of NB is not structure sensitive in $scCO_2$.

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 NB 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 [22–26]. Hydrogenation of NB in organic

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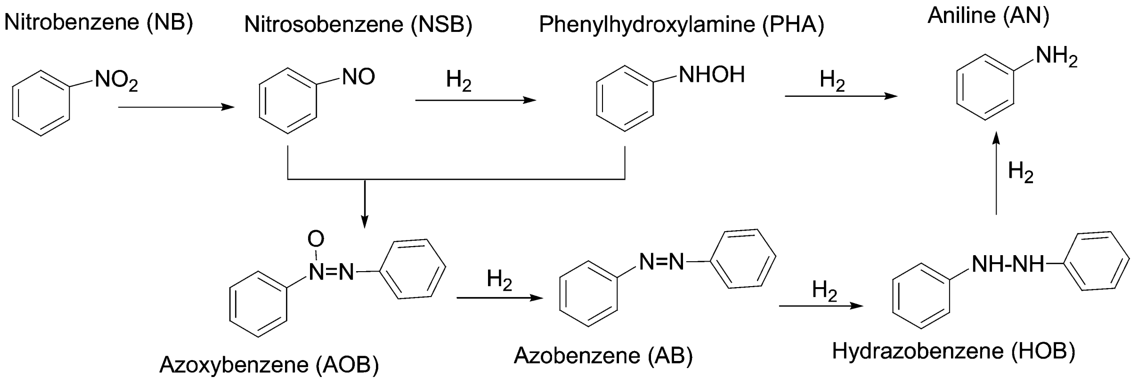


Scheme 1. Possible reaction pathways in hydrogenation of nitrobenzene.

solvents was reported to produce aniline (AN) along with several intermediates and products such as nitrosobenzene (NSB), phenylhydroxylamine (PHA), azoxybenzene (AOB), azobenzene (AB), and hydrazobenzene (HOB), as shown in Scheme 1.

2. Experimental

A 5 wt% Pt/C sample (Wako) was reduced in a flowing H_2 gas under different temperatures and times to prepare several Pt/C catalysts with different size or Pt particles. The catalysts prepared were examined by X-ray diffraction (XRD) on a Rigaku RINT 220VK/PC powder diffractometer using Cu-K_α radiation. The average crystallite sizes of supported Pt were determined from the XRD line broadening using the Scherrer equation. The particle size was also measured by using a transmission electron microscope (TEM, TECNAI-20ST). Those catalysts were used for hydrogenation of NB using a 50 cm^3 high-pressure autoclave. NB 2.0 g (16.2 mmol) and a 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 °C and then H_2 (4 MPa) and compressed liquid CO_2 were introduced up to the desired pressure with a high-pressure liquid pump. The 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) using a flame ionization detector. It is important to see the state of reaction mixture including $scCO_2$ and so the phases present were examined by the naked eye using another reactor attached with sapphire windows. Details of experimental setups and procedures are described elsewhere [27].

3. Results and discussion

3.1. *Influence of CO_2 pressure*

Fig. 1 shows the influence of CO_2 pressure on the total NB conversion and the selectivity to AN with two Pt/C

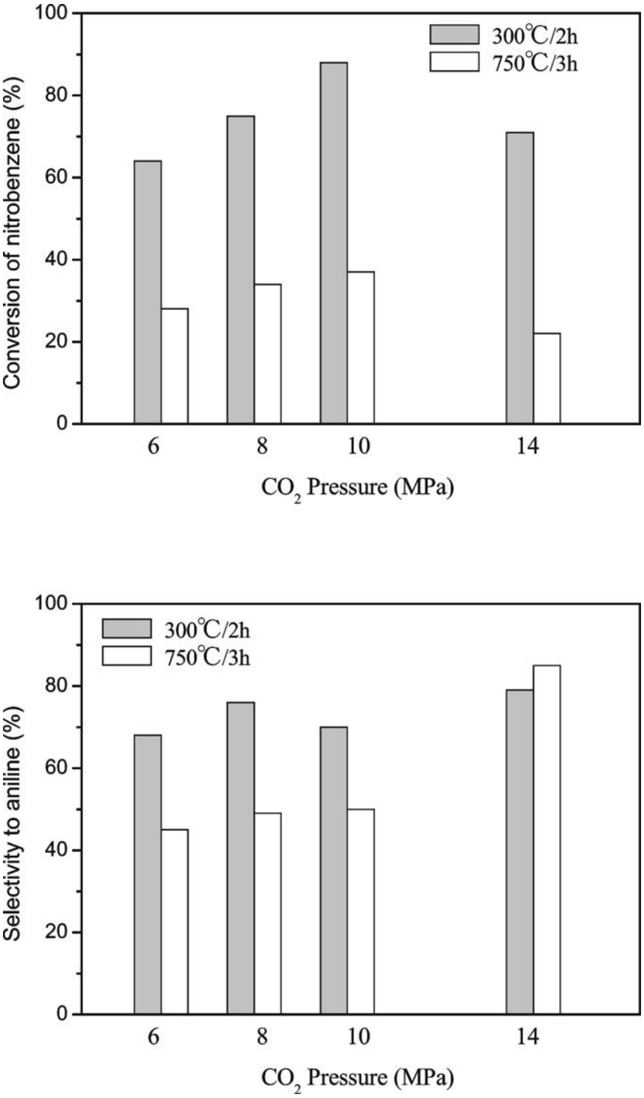


Fig. 1. Influence of CO_2 pressure on the overall conversion of NB and the selectivity to AN for two Pt/C catalysts reduced under different conditions (reduction temperature and time are given above). Reaction conditions: NB 2 g (16.2 mmol, 0.324 mmol/ml in reactor); catalyst 5% Pt/C 0.01g (Pt 2.56 µmol); H_2 4 MPa; time 10 min; temperature 35 °C.

Table 1
Results of nitrobenzene hydrogenation in $scCO_2$ and ethanol with several Pt/C catalysts at 35 °C

Reduction conditions		Pt particle size[a]	Total conversion[b]	Product selectivity (%)[c]				TOF[d]
Temperature (°C)	Time (h)	(nm)	(%)	AN	NSB	AB	AOB	(s^{-1})
(a) In $scCO_2$ at 14 MPa[e]								
200	2	7.2	78	84	2	9	5	66
300	2	8.3	71	79	4	12	5	69
500	2	9.8	70	83	2	8	7	80
600	2	12.4	54	82	2	12	4	78
750	3	19.6	22	85	3	10	3	50
(b) In ethanol[f]								
200	2	7.2	73	56	4	30	10	62
300	2	8.3	63	58	4	26	12	61
500	2	9.8	60	43	7	33	17	69
600	2	12.4	63	44	4	39	13	92
750	3	19.6	61	44	5	38	13	140

[a] Determined by XRD.

[b] Total conversion of NB.

[c] For these abbreviations of products, see Scheme 1.

[d] Turnover frequency, (moles of NB reacted)/((moles of surface exposed Pt atoms) × (reaction time)). The number of surface exposed Pt atoms was calculated from the metal dispersion estimated from an approximate expression, degree of metal dispersion $= 0.9/\text{diameter}$ (in nm) [16], and it was calculated by (the metal dispersion) × (the total number of supported metal atoms).

[e] NB 2 g (16.2 mmol, 0.324 mmol/ml in reactor); catalyst 5% Pt/C 0.01 g (Pt 2.56 µmol); H_2 4 MPa; time 10 min.

[f] NB 2 g (16.2 mmol, 1.62 mmol/ml in ethanol); ethanol 10 ml; catalyst 5% Pt/C 0.01 g (Pt 2.56 µmol); H_2 4 MPa; time 10 min.

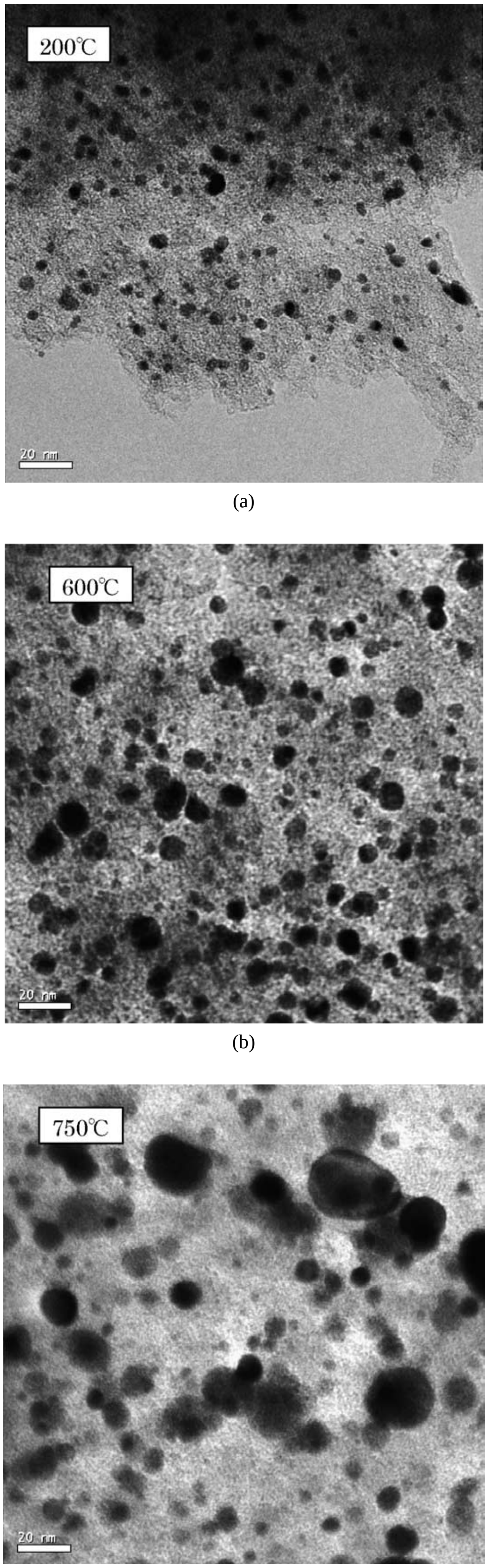
catalysts reduced at 300 and 750 °C, with different size Pt particles as described below (Table 1). The same trends are seen with these catalysts: the total conversion increases with CO_2 pressure up to 10 MPa but decreases at 14 MPa. The AN selectivity does not depend on the pressure so much for the catalyst reduced at 300 °C; but, it increases at 14 MPa for the other catalyst reduced at 750 °C compared with that obtained at 6 MPa. The metal particle size of these two catalysts was quite different and larger metal particles were seen to exist on the catalyst reduced at 750 °C (Table 1). Thus, we can say that larger metal particles benefit the formation of aniline in the supercritical region. It was reported in the literature [28] 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 metal particles and this would be a possible reason for the different pressure effects between the two catalysts.

The phase behavior is important for the present heterogeneous reaction mixture. It was observed that the reaction mixture included three phases, gas (CO_2 rich), liquid (NB rich), and solid (catalyst), at pressures at 10 MPa or below. The volume of the liquid phase decreased with CO_2 pressure and the liquid phase disappeared at 14 MPa. The hydrogenation is possible to occur in the gas and liquid phases since NB and H_2 can be soluble in these phases. With an increase in CO_2 pressure (a) the volume of the liquid phase decreases but (b) probably H_2 (and CO_2) concentration in the liquid phase increases; (c) the NB concentration in the CO_2-rich gas phase increases but (d) the H_2 partial pressure decreases. The influence of CO_2 pressure in the three-phase reaction should be a complicated result of these combined changes (a)–(d). At 14 MPa or higher, the reaction mixture included the gas and solid phases and so the dilution of NB and H_2 in the gas phase by more introduced CO_2 molecules should be responsible for the decreased total conversion.

3.2. *Effects of metal particle size in different solvents*

Hydrogenation reactions were conducted in 14 MPa CO_2, where the reaction mixture was a gas–solid system, as described above, to examine the influence of CO_2 solvent and Pt particle size. Table 1 shows the results obtained in $scCO_2$ and ethanol with several Pt/C catalysts reduced under different conditions. The particle size determined from the XRD line broadening increased with reduction temperature, which is in agreement with the results of TEM as shown in Fig. 2. Table 1 gives several interesting results: the total NB conversion levels are similar but the product distribution is different between $scCO_2$ and ethanol. The AN selectivity in $scCO_2$ is 80% or higher, which is much larger than that in ethanol where a comparable amount of AB is also formed along with AN. The product selectivity in $scCO_2$ does not change so much with the size of Pt particles, while the total conversion decreases from 78 to 22% with a change in the size from 7.2 to 19.6 nm. In ethanol, both the total conversion and AN selectivity decrease with the increase in the Pt particle size while the AB selectivity slightly increases.

Fig. 3 shows turnover frequency (TOF) for the overall NB conversion against the degree of Pt dispersion (the fraction of exposed metal atoms of all the atoms in a metal particle), which is here estimated by such an approximate conversion as the dispersion $= 0.9/\text{diameter}$ (in nm) [16]. In ethanol,



(a)

(b)

(c)

Fig. 2. TEM images for 5% Pt/C catalysts reduced at different temperatures given.

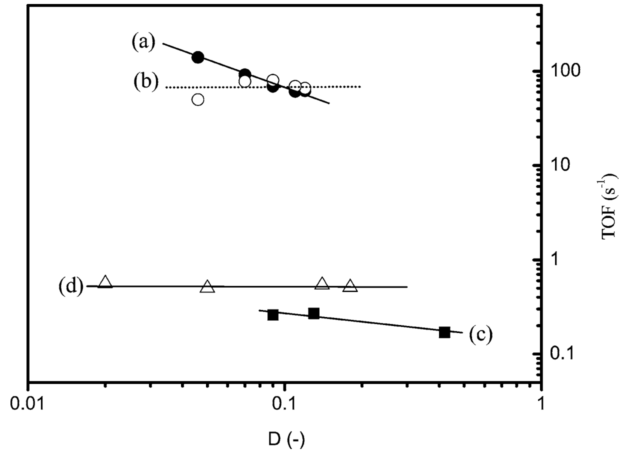


Fig. 3. Plots of TOF against the degree of metal dispersion for liquid-phase hydrogenation of NB using different catalysts and reaction conditions. (a, b) This work. 5 wt% Pt/C catalysts, solvent: (○) $scCO_2$ (14 MPa), (●) ethanol. (c) (■) Ref. [22], 3 wt% Pd/C catalysts, H_2 0.5 MPa, reaction temperature 50 °C, methanol. (d) (△) Ref. [25], Pt/C catalysts, atmospheric H_2 pressure, reaction temperature 0 °C, ethanol.

the TOF decreases with an increase in the Pt dispersion and so the reaction is structure sensitive. In $scCO_2$, however, the TOF does not seem to depend on the Pt dispersion; the reaction is not structure sensitive. Fig. 3 also shows the results of liquid-phase hydrogenation of NB reported by other two groups [22,25], who used different reaction conditions. Gelder et al. applied 3 wt% Pd/C (activated carbon) catalysts for NB hydrogenation in methanol at 50 °C and 0.5 MPa H_2 [22]. In this case, the TOF changes slightly with the metal dispersion, similar to our results in ethanol. Macias Perez et al. used Pt/C (activated carbon cloth) catalysts in ethanol at 0 °C and atmospheric pressure [25], in which the reaction was not structure sensitive. Those results show that the structure sensitivity depends on several reaction variables for the same NB hydrogenation. It is interesting to study further the structure sensitivity of supported metal catalysts for other chemical reactions in $scCO_2$ since the combination of those catalysts and $scCO_2$ may contribute to the design and optimization of a green chemistry reaction and separation processes.

4. Conclusions

The influence of pressure, solvent and metal particle size has been investigated for NB hydrogenation with Pt/C catalysts in $scCO_2$. The total conversion increases with CO_2 pressure up to 10 MPa but decreases at 14 MPa. The reaction mixture includes the gas and solid phases at 14 MPa or higher and so the dilution of NB and H_2 in the gas phase by more introduced CO_2 molecules should be responsible for the decreased total conversion. At lower pressures there are two fluid phases, CO_2-rich gas and organic liquid phases, in the reaction mixture and the reaction is complicated because these two phases can contribute to the overall NB conversion. The product selectivity in $scCO_2$ does not change with the size of Pt particles so much while, in ethanol as a control conventional solvent, the selectivity to AN and AB slightly changes with the particle size. The selectivity of AN in $scCO_2$ is $\geqslant 80\%$, which is much larger than that in ethanol ($\leqslant 58\%$). The hydrogenation in ethanol is structure sensitive; TOF tends to decrease with an increase in the degree of Pt dispersion. In contrast, it is not structure sensitive in $scCO_2$.

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