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# Hydrogenation of nitro compounds with supported platinum catalyst in supercritical carbon dioxide

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## Abstract

Hydrogenation of a series of substituted nitro compounds such as 2-,3-,4-nitroanisole, 2-,3-,4-nitrotoluene, 2,4-dinitrobenzene and 2,4-dinitrotoluene has been studied in supercritical carbon dioxide, $scCO_2$ (two phases), and ethanol (three phases) with a 5 wt.% carbon supported platinum catalyst. The solubility of these compounds in $scCO_2$ has also been examined in the presence and absence of hydrogen. The solubility of those nitro compounds increases with increasing $CO_2$ pressure but decreases with the presence of hydrogen. The solubility is in the order of nitrotoluene > nitroanisole > dinitrotoluene, dinitrobenzene. Although the total conversion obtained with hydrogenation in $scCO_2$ is similar to that in ethanol, the selectivity to amino products is higher in the former reaction medium, indicating that $scCO_2$ is an ideal medium for the production of amino compounds with hydrogenation of nitro substrates using conventional supported metal catalysts.

*Keywords:* Nitro compounds; Hydrogenation; Supercritical $CO_2$; Pt/C catalyst; Solubility

## 1. Introduction

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 parameters [1–4]. 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 [5]. In contrast, hydrogen is completely miscible with $scCO_2$, and this is beneficial for enhancement of hydrogenation reactions. 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, Hitzler and Poliakoff 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].

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 [16–19]. 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,

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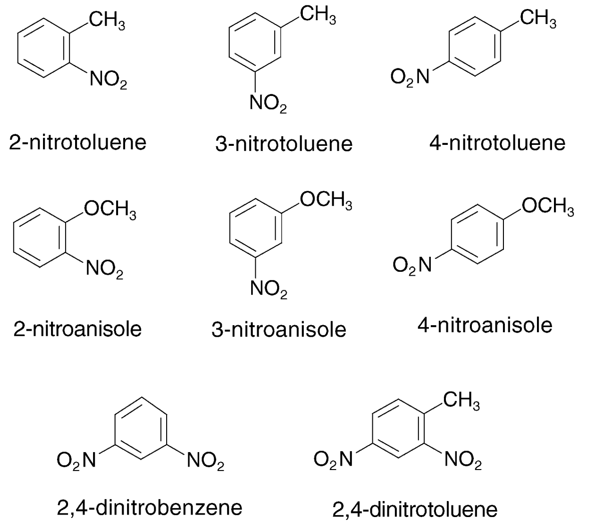


Scheme 1. Nitro compounds used.

the choice of solvent is important and a green solvent should be considered for contemporary chemical processes.

The present authors have investigated the influence of metals (Pt, Pd, Ru, Rh), supports (C, $SiO_2$, $Al_2O_3$), and metal particle size on the catalytic activity and selectivity for nitrobenzene hydrogenation in both $scCO_2$ and ethanol [20,21]. It has been found that Pt/C is the most active catalyst, and in the present work using a 5 wt.% Pt/C catalyst we have studied hydrogenation of various nitro compounds (Scheme 1) in $scCO_2$ and in ethanol at a temperature of 50 °C. The solubility of the nitro compounds in dense $CO_2$ has also been estimated by the visual observations of phase behavior at different pressures. The hydrogenation reactions have been conducted under solid (catalyst)–gas ($CO_2$, $H_2$, and substrate) two-phase conditions, and the influence of substrates and reaction media ($scCO_2$, ethanol) has been studied.

## 2. Experimental

### 2.1. Materials

All the chemicals used were purchased from Wako Pure Chemicals and used without further purification. Eight kinds of nitro compounds were used, as shown in Scheme 1: 2-,3-,4-nitroanisole, 2-,3-,4-nitrotoluene, 2,4-dinitrobenzene, 2,4-dinitrotoluene. 2,4-Dinitroanisole was insoluble in dense $CO_2$ and it was not used. A 5 wt.% Pt/C catalyst purchased was reduced by flowing hydrogen at 300 °C for 2 h before activity measurements. The average size of Pt particles obtained was shown to be 8.3 nm from X-ray diffraction line broadening, in accordance with the size seen by transmission electron microscopy (Fig. 1). Using an approximate expression, degree of metal dispersion = 0.9/diameter (in nm) [22], the degree of Pt dispersion was about 0.15.

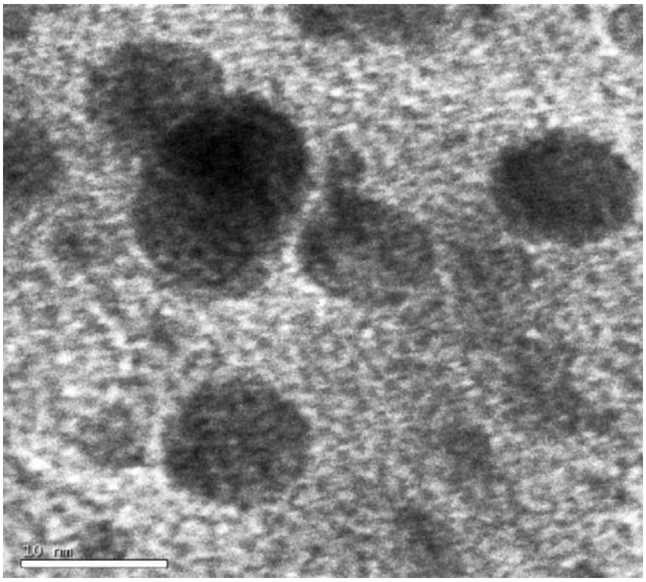


Fig. 1. TEM image for 5 wt.% Pt/C catalyst after reduced with hydrogen at 300 °C for 2 h (scale = 10 nm).

### 2.2. Hydrogenation reactions

The hydrogenation of nitro compounds was carried out at a temperature of 50 °C in a 50 $cm^3$ high-pressure autoclave (JASCO Corporation). The concentrations of nitro substrate and catalyst were 0.1 mmol/$cm^3$ and $2.56 \times 10^{-2}$ mmol (Pt)/$cm^3$, respectively, for reactions in both $scCO_2$ and ethanol. For $scCO_2$, 5 mmol nitro compound and 0.005 g Pt/C catalyst were charged into the reactor and it was flushed with 2.0 MPa $CO_2$ three times. The reactor was then heated up to the desired temperature of 50 °C and then $H_2$ was introduced to 1.0 MPa, followed by introduction of $CO_2$ 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 (Shimadzu 390B, GL Science TC-17 capillary column) using a flame ionization detector. The conversion was determined from the amount of nitro substrate consumed and the selectivity was calculated by the amount of a certain product/the total amount of substrate consumed. When the reaction was carried out in ethanol, 2 mmol nitro compound and 0.002 g Pt/C catalyst were charged into the reactor and 20 $cm^3$ ethanol was added. The following procedures were the same as used for $scCO_2$.

### 2.3. Phase behavior and solubility estimation

It is significant to examine the phase behavior and to know the phases present where reactions take place. A 10 $cm^3$ high-pressure sapphire-windowed view cell was used for this purpose. A certain amount of nitro compound was added into the cell and then the cell was flushed with 0.5 MPa $CO_2$ twice. After the cell was heated up to 50 °C by circulation of pre-heated oil outside the cell, $CO_2$ was introduced into it slowly. The pressure was increased slowly while stirring by a Teflon-coated magnetic stirrer. When the cell pressure reached to a certain value, the stirring was further continued for 3–5 min and stopped; then, the state of mixture including nitro compound and $CO_2$ was visually examined. This examination was made at intervals of 0.2–0.5 MPa to determine the pressure at which the nitro compound was completely dissolved into $CO_2$, forming a single phase. Then, the pressure was decreased in a similar way to determine the pressure at which droplets of nitro compound appeared (dew point), changing into a two-phase mixture. The pressures determined at increasing and decreasing pressures were in a difference less than ±0.5 MPa and the average value of these two pressures determined was used. Those observations were used to estimate the solubility of nitro compounds in $CO_2$ at different pressures.

## 3. Results

### 3.1. Solubility of nitro compounds in $scCO_2$

The solubility of nitro compounds in $scCO_2$ is shown in Fig. 2, in which the solid mark indicates the solubility in pure $CO_2$ and the open mark the solubility in a mixture of $CO_2$ and 1.0 MPa $H_2$. Fig. 2(a) shows that the solubility of nitroanisoles increases with increasing $CO_2$ pressure and it decreases in the presence of $H_2$. The solubility of 3-nitroanisole is larger than that of 2-nitroanisole and 4-nitroanisole. Fig. 2(b) indicates the solubility of nitrotoluenes and similar effects of $CO_2$ and $H_2$ pressures were also observed. These pressure effects are in accordance with our previous results with an unsaturated aldehyde, cinnamaldehyde [5]. The solubility of nitrotoluenes is in the order of 2-nitrotoluene, 3-nitrotoluene > 4-nitotoluene irrespective of the presence and absence of $H_2$, which is much larger than that of nitroanisoles. Fig. 2(c) shows that the solubility of 2,4-dinitrotoluene in pure $CO_2$ is comparable with that of 2,4-dinitrobenzene at pressures below 16 MPa. At higher pressures, however, the former solubility is larger than the latter. The presence of $H_2$ also decreases the solubility of these two compounds and 2,4-dinitrotoluene has a larger solubility at low and high pressures compared with 2,4-dinitrobenzene. Fig. 2 indicates that the solubility of nitro compounds is in the order of nitrotoluene > nitroanisole > dinitrotoluene > dinitrobenzene.

### 3.2. Hydrogenation of nitro compounds in $CO_2$ and ethanol

Hydrogenation of nitro compounds in organic solvents was reported to produce arylaniline along with several intermediates and products such as nitroso-, phenylhydroxylamine (PHA), azoxy- (AOB), azo- (AB), and hydrazo- (HOB), as illustrated in Scheme 2.

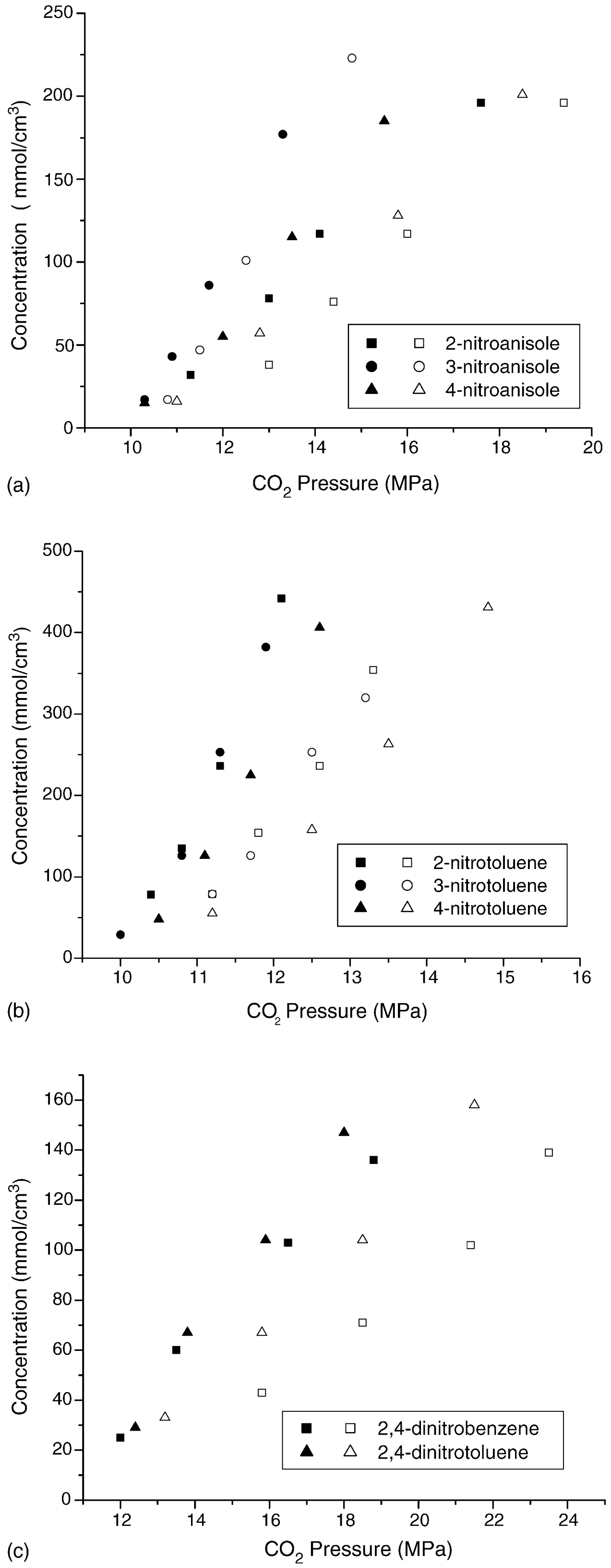
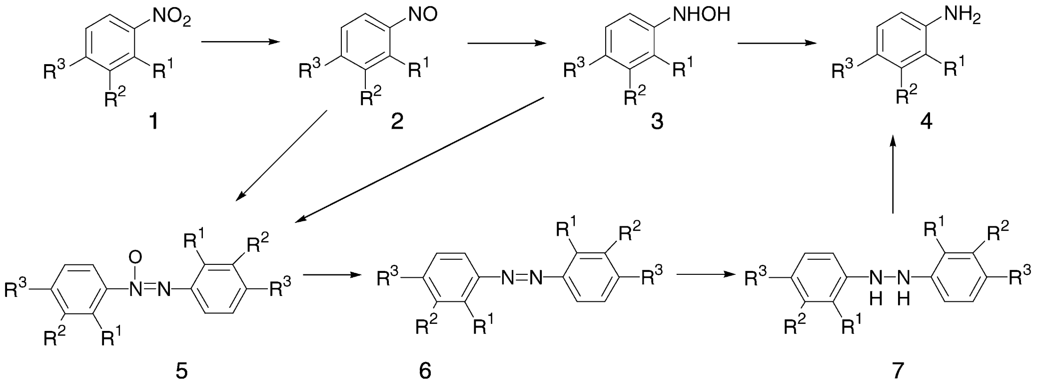


Fig. 2. The solubility of substituted nitro compounds in $CO_2$ at 50 °C: (a) nitroanisole, (b) nitrotoluene, (c) 2,4-dinitrobenzene and 2,4-dinitrotoluene. The solid marks show the solubility in pure $CO_2$; the open marks show the solubility in the presence of 1.0 MPa hydrogen in $CO_2$.



Scheme 2. Reaction products for hydrogenation of substituted nitro compounds.

The concentration of nitro compounds in $CO_2$ used was 0.1 mmol/cm$^3$, much smaller than the solubility (Fig. 2), under which the reaction system was in two phases including gas ($CO_2$, $H_2$, substrate) and solid (catalyst). The reaction conversion and product selectivity in such a two-phase hydrogenation of nitro compounds have been compared with those in a conventional solvent, ethanol, in which the reaction occurs in a three-phase (gas–liquid–solid) system. The results obtained are shown in Table 1. In $scCO_2$ (15 MPa), the conversion of nitroanisole is 2-nitroanisole > 3-nitroanisole > 4-nitroanisole and the selectivity to aminoanisole is 100% for these substrates (entries 1–3). Similar results were also obtained in ethanol (entries 9–11) and the conversion obtained in ethanol was slightly higher than that in $scCO_2$ under the conditions used. For nitrosubstituted toluenes, the same order of conversion, 4-nitrotoluene > 3-nitrotoluene > 2-nitrotoluene, is seen in both $scCO_2$ and ethanol (entries 4–6, 12, 13, 15). The selectivity to aminotoluene with 4-nitrotoluene was 100% in both $scCO_2$ and ethanol (entries 6, 15), while the selectivity to aminotoluene with either 2-nitrotoluene or 3-nitrotoluene in $scCO_2$ is higher than that in ethanol. For 3-nitrotoluene in ethanol, large amounts of by-products were formed, showing a selectivity to aminotoluene of 62% in contrast to a higher selectivity of 96% in $scCO_2$ (entries 4, 5, 12, 13).

Table 1
Results of hydrogenation reactions of various nitro compounds with 5 wt.% Pt/C catalyst in $scCO_2$ and ethanol at 50 °C

| Entry | Substrate | Conversion (%) | Selectivity (%) | | | | |
|---|---|---|---|---|---|---|---|
| | | | 2 | 3 | 4 | 5 | 6 |
| Two-phase (gas–solid) reactions in $scCO_2$ | | | | | | | |
| 1 | 2-Nitroanisole | 73 | – | – | 100 | – | – |
| 2 | 3-Nitroanisole | 60 | – | – | 100 | – | – |
| 3 | 4-Nitroanisole | 35 | – | – | 100 | – | – |
| 4 | 2-Nitrotoluene | 60 | 5 | – | 95 | – | – |
| 5 | 3-Nitrotoluene | 85 | 4 | – | 96 | – | – |
| 6 | 4-Nitrotoluene | 89 | – | – | 100 | – | – |
| 7 | 2,4-Dinitrobenzene | 48 | – | – | 97/3[a] | – | – |
| 8 | 2,4-Dinitrotoluene | 52 | 4 | – | 61/23/4[b] | 1 | 7 |
| Three-phase (gas–liquid–solid) reactions in ethanol | | | | | | | |
| 9 | 2-Nitroanisole | 90 | – | – | 100 | – | – |
| 10 | 3-Nitroanisole | 58 | – | – | 100 | – | – |
| 11 | 4-Nitroanisole | 55 | – | – | 100 | – | – |
| 12 | 2-Nitrotoluene | 73 | 17 | – | 83 | – | – |
| 13 | 3-Nitrotoluene | 76 | 10 | – | 62 | 6 | 19 |
| 14[c] | 3-Nitrotoluene | 69 | 24 | – | 72 | 1 | 3 |
| 15 | 4-Nitrotoluene | 100 | – | – | 100 | – | – |
| 16 | 2,4-Dinitrobenzene | 98 | – | – | 85/10[a] | – | 5 |
| 17 | 2,4-Dinitrotoluene | 100 | – | – | 50/27/10[b] | 6 | 7 |
| 18[c] | 2,4-Dinitrotoluene | 94 | – | – | 51/33/13[b] | 1 | 2 |

Reaction conditions—in $scCO_2$: nitro compounds 5 mmol, Pt/C 0.005 g, $H_2$ 1.0 MPa, $CO_2$ 15 MPa, time 10 min; in ethanol: nitro compounds 2 mmol, Pt/C 0.002 g, $H_2$ 1.0 MPa, ethanol 20 cm$^3$, time 10 min.

[a] 3-Nitroaniline/3-aminoaniline.

[b] 2-Nitro-4-aminotoluene/4-nitro-2-aminotoluene/2,4-diaminotoluene.

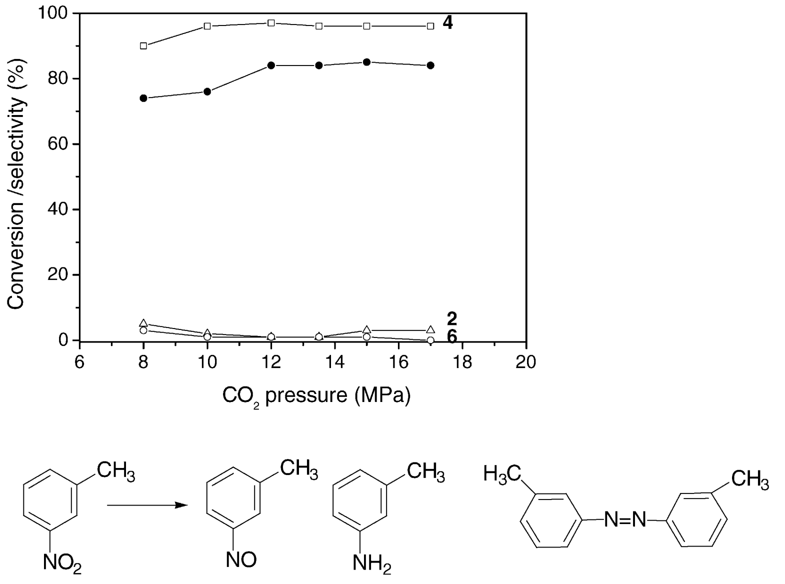
[c] Reactions were carried out in ethanol under $H_2$ (1.0 MPa) and $N_2$ (10 MPa).

For dinitro compounds, 2,4-dinitrobenzene and 2,4-dinitrotoluene, the main products are mono hydrogenation products hydrogenated at 2- or 4- position and double hydrogenation products. These two substrates show similar total conversion levels either in $scCO_2$ or in ethanol and the conversion obtained in $scCO_2$ is smaller (about half) than that in ethanol (entries 7, 8, 16, 17). The product distribution is different between $scCO_2$ and ethanol. In the former medium, the selectivity to mono hydrogenated products is larger and the hydrogenation at 4-position is easier to occur scompared with that at 2-position. In ethanol, more double hydrogenated products are formed along with other by-products.

The influence of high pressure was also checked with hydrogenation reactions of 4-nitrotoluene and 2,4-dinitrotoluene in ethanol under pressurized nitrogen (10 MPa) and hydrogen (1 MPa). The results obtained are given in Table 1, showing that the presence of high-pressure nitrogen decreases the total conversion slightly but increases the selectivity to amino products (entries 14, 18). The compressed nitrogen has a similar effect as does $scCO_2$.

### 3.3. Influence of $CO_2$ pressure

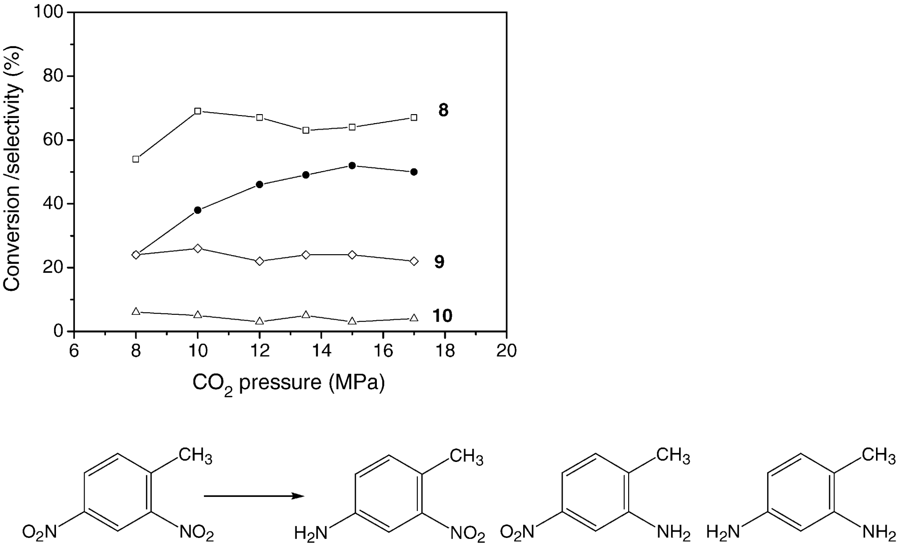
The influence of $CO_2$ pressure on the conversion and selectivity has been examined in hydrogenation of 3-nitrotoluene and 2,4-dinitrotoluene. As shown in Fig. 3, the



**2** **4** **6**

Fig. 3. Influence of pressure on 3-nitrotoluene hydrogenation with 5 wt.% Pt/C catalyst in $scCO_2$. Reaction conditions: 3-nitrotoluene 5 mmol, $H_2$ 1.0 MPa, Pt/C 5 mg, temperature 50 °C, time 10 min. The solid mark shows the total conversion of 3-nitrotoluene; the open mark shows the product selectivity.

total conversion of 3-nitrotoluene increased with increasing $CO_2$ pressure up to 12 MPa and then changed little at higher pressures. The selectivity to 3-aminotoluene (**4**) also showed a similar change with $CO_2$ pressure. Fig. 4 gives the results of 2,4-dinitrotoluene hydrogenation at different $CO_2$ pressures, in which mono-hydrogenation products, 2-nitro-4-aminotoluene (**8**) and 4-nitro-2-aminotoluene (**9**) were mainly formed along with small quantities of double hydrogenation product, 2,4-diaminotoluene (**10**), and others. The total conversion is 24% at 8 MPa and it increases with $CO_2$ pressure but this pressure effect is less marked at higher pressures. The selectivity to 2-nitro-4-aminotoluene is 54% and that to 4-nitro-2-aminotoluene is 24% at 8 MPa. The former selectivity increases to 69% at 10 MPa but it marginally decreases at 12 MPa above which it does not change with the pressure so much. A similar pressure dependence was also observed for the selectivity to 4-nitro-2-aminotoluene.



**8** **9** **10**

Fig. 4. Influence of pressure on 2,4-dinitrotoluene hydrogenation with 5 wt.% Pt/C catalyst in $scCO_2$. Reaction conditions: 2,4-dinitrotoluene 5 mmol, Pt/C 5 mg, $H_2$ 1.0 MPa, temperature 50 °C, time 10 min. The solid mark shows the total conversion of 3-nitrotoluene; the open mark shows the product selectivity.

## 4. Discussion

The solubility of all the nitro compounds examined increases with increasing $CO_2$ pressure, which is in the order of nitrotoluene > nitroanisole > 2,4-dinitrotoluene > 2,4-dinitrobenzene. The presence of hydrogen has a negative effect of decreasing the solubility of all these nitro compounds, in accordance with our previous results with cinnamaldehyde [5]. The differences in the solubility of those nitro compounds in dense $CO_2$ indicate significant effects of the kind and position of functional groups ($NO_2$–, $CH_3$–, $CH_3O$–).

The selectivity to amino products is higher in $scCO_2$ than in ethanol, as shown in Table 1. A similar result was also obtained with nitrobenzene using various supported transition metal catalysts [21]. Two possible factors are considered here. One is that high static pressure is beneficial for the formation of amino products, which can be indicated by a fact that pressurized $N_2$ enhances the formation of amino compounds in ethanol (Table 1). The other one is the properties and functions intrinsic to $scCO_2$, which would affect the substrate. For 2,4-dinitrotoluene, the hydrogenation at 4-position is easier to occur compared with 2-position, which may be explained by electron inductive effects. The hydrogenation is an electrophilic addition and –$CH_3$ is an electron donating group, which activates the 4-position and 3-position but deactivates the 2-position. Thus, N=O at 4-position is more polar and the oxygen atom is more negative, making the electrophilic addition of hydrogen to occur easier at such a position than the –$NO_2$ at the 2-position. $scCO_2$ could be a medium suitable for this hydrogenation due to an increased polarity at higher pressures. However, the results in $scCO_2$ and organic solvents cannot be explained by bulk properties, such as dielectric constant, and so local properties of dense $CO_2$ molecules around substrate molecules should be of significance. Further study is needed to do at molecular level using, for example, high-pressure FTIR.

The total conversion increases with increasing $CO_2$ pressure at low pressures but it changes marginally at higher pressures, as shown in Figs. 3 and 4 for 3-nitrotoluene and 2,4-dinitrotoluen. When $CO_2$ pressure is raised, the concentration of substrates in $CO_2$ is more diluted and this is a negative effect. So, some more positive effects should operate for the change of conversion with $CO_2$ pressure. It was previously suggested that dense $CO_2$ changes the nature of supported metal particles and/or substrates for similar hydrogenation reactions [23,24]. For the present reactions as well, dense $CO_2$ may modify the reactivity of a polar functional group of $NO_2$– and/or the activity of supported Pt particles.

## 5. Conclusions

The solubility of substituted nitro compounds in $scCO_2$ has been estimated by the visual inspection. The solubility order is nitrotoluene > nitroanisole > dinitro compounds and the solubility decreases in the presence of hydrogen. The total conversion in hydrogenation in $scCO_2$ is comparable with that in ethanol. However, the selectivity to the formation of amino products is larger in $scCO_2$ than in ethanol. The reaction mixture in $scCO_2$ is a simple gas ($CO_2$, $H_2$, substrate)–solid (catalyst) two-phase system. It is easy to separate the catalyst (solid phase), the organic phase (the hydrogenated products), the aqueous phase (by-product, water) and the gas phase ($CO_2$, $H_2$) by simple phase separation after reaction. $scCO_2$ is a good replacement for conventional organic solvents in hydrogenation of nitro compounds.

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