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Hydrogenation of *o*-chloronitrobenzene to *o*-chloroaniline over Pd/C in supercritical carbon dioxide

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Abstract

Hydrogenation of *o*-chloronitrobenzene (*o*-CNB) to *o*-chloroaniline (*o*-CAN) with Pd/C has been investigated in supercritical carbon dioxide ($scCO_2$) at 308 K. The influences of several parameters such as CO_2, H_2 pressures, Pd metal particle size and reaction time have been discussed. CO_2 pressure presented markedly effects on the reaction rate and product selectivity under the reaction conditions used, the selectivity to *o*-CAN at CO_2 pressure from 8 to 13 MPa (supercritical region) was larger than that at CO_2 pressure below 6 MPa (subcritical region). Moreover, the larger selectivity to *o*-CAN was obtained in $scCO_2$ compared with that in ethanol.

Keywords: Hydrogenation; *o*-Chloronitrobenzene; Supercritical carbon dioxide; Pd/C

1. Introduction

Chloroaniline (CAN) as an important chemical intermediate is widely applied in the manufacture of polyurethanes, rubber, pesticides and drugs. It is generally prepared from the hydrogenation of chloronitrobenzene (CNB) (Scheme 1), but in this process the dechlorination usually occurs and results in the formation of aniline. Thus, the hydrogenation of CNB to CAN with high selectivity is still a challenge up to now. Recently, many studies have been devoted to prevent the hydrodechlorination of CAN, such as introducing suitable modifier (promoters, inhibitors), adjusting the properties of the catalyst (alloying, controlling the metal particle dispersion and metal-support interaction) and selecting appropriate reaction conditions (temperature, solvent, etc.) [1–11]. It was reported that Pt/γ-Fe_2O_3 was effective for hydrogenation of chloronitrobenzene and bromonitrobenzene with high selectivity to the chloroaniline and bromoaniline [10,11]. Supercritical carbon dioxide ($scCO_2$) is an environmentally acceptable replacement to the harmful conventional organic solvents for chemical reactions due to its non-toxic, non-flammable, moderate critical parameter and potentially easy separation [12–14]. Furthermore, $scCO_2$ affords some potential advantages: the complete miscibility with hydrogen, high diffusivity, good mass and thermal transport properties. Thus, it has been attracting much attention in the selective hydrogenations [15–18]. In the present work, the hydrogenation of *o*-CNB to *o*-CAN in $scCO_2$ has been studied at a low temperature of 308 K over Pd/C catalyst due to it is cheaper compared to Pt catalysts. The influence of several parameters such as CO_2 pressure, phase behavior, reaction time and H_2 pressure have been discussed and the performance of the hydrogenation in $scCO_2$ has been compared with that in the conventional organic solvent of ethanol.

2. Experimental

2.1. Hydrogenation of *o*-chloronitrobenzene

The hydrogenation of *o*-CNB was carried out in a 50 ml Teflon-lined high-pressure stainless steel batch reactor. A certain amount of 5 wt% Pd/C (0.01 g) and *o*-CNB (0.254 mmol/ml) were loaded into the reactor. Then the reactor was sealed and flushed three times with 2 MPa CO_2 to remove the air. After flushing, the reactor was heated up to 308 K. A prescribed amount of H_2 was introduced and then liquid CO_2

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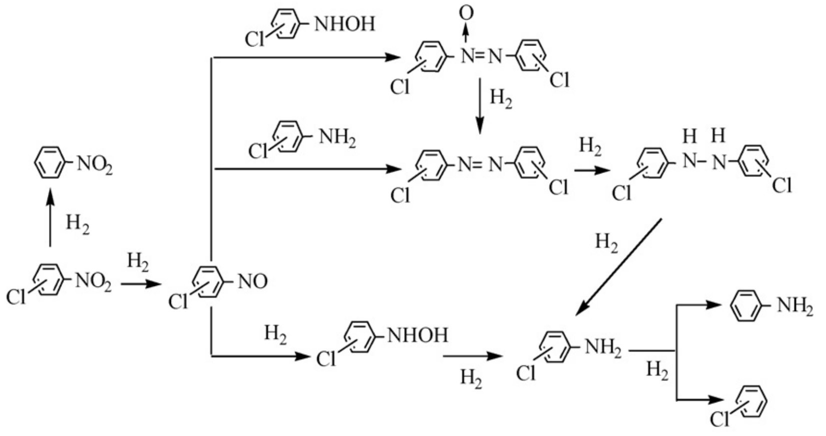

Scheme 1. Reaction pathways of the hydrogenation of chloronitrobenzene.

was compressed into the reactor using a high-pressure liquid pump to the desired pressure. The reaction mixture was stirred continuously with a magnetic stirrer for a certain time. After reaction, the liquid product was separated from the catalyst through filtration and analyzed with a gas chromatograph (GC-Shimadzu-14C, FID, Capillary column, Rtx-Wax 30 m × 0.53 mm × 0.25 m) and identified by gas chromatography/mass spectrometry (GC/MS, Agilent 5890).

2.2. *Catalyst characterization*

The 5 wt% Pd/C catalyst (Wako) was used without or with heat treatment at different temperatures for 4 h under H_2 gas atmosphere before used. The palladium crystalline grain was estimated by XRD pattern recorded on Rigaku SLX-2000. The average size of the Pd crystalline grain was calculated by the Debye–Scherer formula $t = 0.89\lambda/(\beta\cos\theta)$, where t is the average diameter of the particles, λ is the X-ray wavelength (1.5418 Å), θ is the Bragg diffraction angle (half of the measured diffraction angle) and β is the peak width in radians at half-height.

2.3. *Phase behavior and high pressure*

The observation of the phase state of *o*-CNB in CO_2 was carried out in an 85 ml high-pressure view cell. The operating procedure is as same as our previous work described [19]. A certain amount of *o*-CNB (0.254 mmol/ml) was added and the reactor was heated up to 308 K, then H_2 (4 MPa) and CO_2 were introduced into the reactor to the required pressure. At each pressure the mixture was stirred for several minutes, and then the stirring was stopped and the phase behavior was observed by the naked eye from the windows.

3. Results and discussion

3.1. *Influence of CO_2 and H_2 pressures*

Table 1 shows the results of the product distribution of hydrogenation of *o*-CNB at different pressures of CO_2. Under the reaction conditions used, all the reactions were run until *o*-CNB was converted completely according to the hydrogen consumption. The results indicate that the yield of *o*-CAN reached 94% in the presence of 10 MPa CO_2, it was 10% higher than that in ethanol under the reaction conditions. The variation of the CO_2 pressure exhibited a large impact on the reaction rate and product distribution, the yield to *o*-CAN was 82% in the absence of solvent or at a lower CO_2 pressure of 6 MPa (subcritical region), while it increased up to 93% at CO_2 pressures above 8 MPa (supercritical region). The yield to *o*-CAN changed very slightly at a pressure range of 8–13 MPa. When CO_2 pressure was raised up to 14 MPa or higher, both the yield to *o*-CAN and reaction rate decreased. These results may be explained with the phase behavior and the properties of CO_2, as discussed below.

Fig. 1 shows the influence of CO_2 pressure on the yield of *o*-CAN at the different H_2 pressures. The yield of *o*-CAN increased with increasing of CO_2 pressure at the complete conversion of *o*-CNB, and it increased largely at CO_2 pressure above 8 MPa irrespective to the H_2 pressures checked. The yield to *o*-CAN was low at the higher H_2 pressure, suggesting that high H_2 pressure was favorable to the dehalogenation of *o*-CAN to AN.

The phase behavior is important for understanding whether the reaction occurs homogeneously or heterogeneously, and it

Table 1
Results of *o*-CNB hydrogenation over Pd/C catalyst at 308 K

Solvent	Time (min)	Yield[a] (%)			Phase state
		CAN	AN	Others	
6 MPa CO_2	120	82	17	1	3
8 MPa CO_2	90	93	6	1	3
10 MPa CO_2	90	94	5	1	3
12 MPa CO_2	90	92	7	1	3
13 Mpa CO_2	90	93	5	2	2
14 MPa CO_2	120	87	10	3	2
16 MPa CO_2	180	83	13	4	2
–	150	82	17	1	3
Ethanol	75	84	12	4	3

Reaction conditions: *o*-CNB 12.7 mmol; catalyst 5% Pd/C (without heat treatment) 0.01 g; H_2 4 MPa; temperature 308 K; in the case of organic solvent, ethanol 5 ml.

[a] At the conversion of *o*-CNB just reaching 100%.

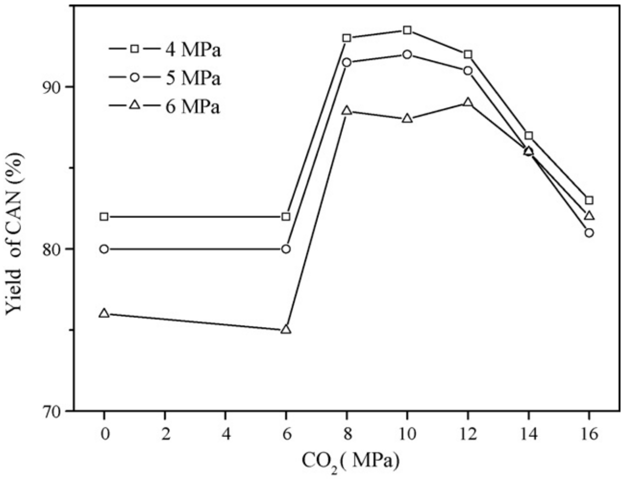

Fig. 1. Influence of CO_2 pressure on the yield of *o*-CAN at the different H_2 pressures at 308 K. Reaction conditions: *o*-CNB12.7 mmol; catalyst 5%Pd/C 0.01 g (without heat treatment). All the values of *o*-CAN yield were at 100% conversion of *o*-CNB.

was observed with visual inspection at 308 K under a CO_2 pressure range of 0–16 MPa and 4 MPa H_2.The results are given in Table 1. At CO_2 pressures lower than 6 MPa, three phases of gas ($CO_2 + H_2$), liquid (*o*-CNB) and solid (catalyst) presented in the reaction mixture. A certain amount of *o*-CNB dissolved into the CO_2 phase with increasing of CO_2 pressure, and the reaction mixture changed to CO_2 fluid (CO_2, H_2, dissolved *o*-CNB), liquid (*o*-CNB, dissolved CO_2 and H_2) and solid (catalyst) phases at a range of CO_2 pressures from 8 to 12 MPa. When CO_2 pressure was raised up to 13 MPa, the liquid phase *o*-CNB disappeared and the reaction system contained two phases of CO_2-riched fluid phase (CO_2, H_2, dissolved *o*-CNB) and solid phase (catalyst). When a larger amount of CO_2 was introduced (at 14 MPa CO_2 or above), the mole ratio of *o*-CNB in reaction mixture decreased and led to decrease in reaction rate and the yield of *o*-CAN, which is in agreement with the literature that the higher concentration of *o*-CNB is favorable to the selective hydrogenation of *o*-CNB to CAN [5].

It was suggested that molecular interaction existed between the reactant and CO_2 molecules and which affected the reaction rate and product distribution in the hydrogenations [20–23]. Chen et al. reported that the hydrogenation of *p*-CNB was favorable in CO_2-expanded methanol due to the enhancement in hydrogen solubility and mass transfer [24]. Ichikawa et al. suggested that CO generated from CO_2 hydrogenation could act as a modifier for Pt/C catalyst to block the active sites for dechlorination in scCO_2 [25]. However, in the present work CO was not detected with GC–MS using either TCD or FID detector. Therefore, besides the influence of CO, some other factors should be considered such as molecular interactions among the substrate, catalyst and CO_2 molecules, this will be discussed in our further works.

3.2. *Influence of reaction time*

The total conversion and selectivity to *o*-CAN at different reaction time are listed in Table 2. The results showed that the

Table 2
Changes of conversion and selectivity to *o*-CAN with reaction time

Solvent	Time (min)	Conversion (%)	Selectivity (%)		
			CAN	AN	Others
Ethanol	40	56	89	9	2
	50	68	88	10	2
	60	90	86	10	4
	75	100	84	12	4
	90	100	79	16	5
6 MPa CO_2	80	58	97	2	1
	90	78	94	5	1
	105	88	88	11	1
	120	100	82	17	1
	135	100	78	19	3
8 MPa CO_2	65	60	96	3	1
	70	80	94	5	1
	75	84	94	5	1
	90	100	93	6	1
	105	100	91	8	1
10 MPa CO_2	65	64	97	2	1
	70	78	96	3	1
	75	88	95	4	1
	90	100	94	5	1
	105	100	92	7	1
12 MPa CO_2	65	61	96	3	1
	70	76	95	4	1
	75	86	95	4	1
	90	100	92	7	1
	105	100	91	8	1
14 MPa CO_2	75	63	96	1	2
	90	82	93	5	2
	105	93	89	8	3
	120	100	87	10	3
	135	100	84	12	4

Reaction conditions: *o*-CNB 12.7 mmol; catalyst 5% Pd/C (without heat treatment) 0.01 g; H_2 4 MPa; temperature 308 K; in the case of organic solvent, ethanol 5 ml.

conversion of *o*-CNB increased with extending reaction time, and it increased faster in ethanol than those in scCO_2. When *o*-CNB was just converted completely, the selectivity to *o*-CAN was 89% and 97% in ethanol and in 10 MPa CO_2, respectively. However, it decreased slightly with further extending the reaction time. In ethanol, the selectivity to *o*-CAN decreased 5% with extending the reaction time for extra 15 min after 100% conversion of CNB, but it decreased only about 1–2% in supercritical region with CO_2 pressures of 8–12 MPa. Fig. 2 shows the changes in selectivity to *o*-CAN along with the conversion in ethanol and in 10 MPa CO_2, the results showed that the selectivity to *o*-CAN decreased with the proceeding of reaction, and it was irrespective to the reaction medium used.

3.3. *Effect of metal particle size in scCO$_2$*

To investigate the effect of palladium particle size, 5 wt% Pd/C catalysts were heat-treated under hydrogen atmosphere at different temperatures for 4 h. The XRD patterns of the catalysts are shown in Fig. 3, in which the diffraction peaks

Table 3
The results of hydrogenation of *o*-chloronitrobenzene with Pd/C catalysts

Treating temperature (K)	Pd crystalline grain size[a] (nm)	Pd dispersion[b]	Reaction time	Conversion (%)	Selectivity (%)		
					CAN	AN	Others
–	17	0.053	75 min	88	94	5	1
537[c]	19	0.047	3 h	81	97	2	1
937[c]	28	0.032	24 h	85	98	1	1

Reaction conditions: *o*-CNB 12.7 mmol; catalyst 5% Pd/C 0.01 g; H_2 4 MPa; CO_2 10 MPa; temperature 308 K.

[a] Determined by Debye–Scherer formula.

[b] Metal dispersion = 0.9/particle diameter (in nm) [21].

[c] The duration for the heat treatment is 4 h.

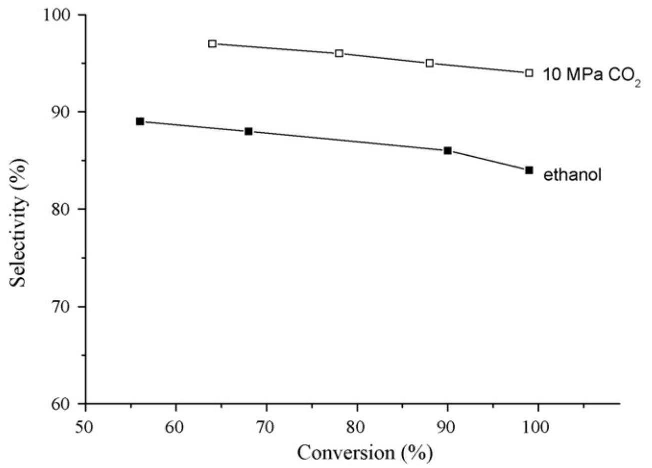

Fig. 2. Changes of the selectivity to *o*-CAN with conversion at 308 K. Reaction conditions: *o*-CNB 12.7 mmol; catalyst 5%Pd/C 0.01 g (without heat treatment); H_2 4 MPa; in the case of organic solvent; ethanol 5 ml.

of Pd(1 1 1) and Pd(2 0 0) became to narrow and sharp with increasing heat-treating temperature, indicating that the particle size grew to larger at high temperature. The average size of Pd crystalline grain was estimated by Debye–Scherer formula and the results of the *o*-CNB hydrogenation in 10 MPa CO_2 over these Pd/C catalysts with different crystalline grain size are listed in Table 3. It showed that the selectivity to *o*-CAN depended on Pd particle size and it was higher at larger dimension of Pd particle. Coq et al. [5] suggested that the adsorption of CAN was weak compared to the adsorption of CNB on the larger Pt particles, which retarded the dechlorination of CAN to AN, it is in agreement with our present results. Fig. 4 shows the diagram of average turnover frequency (TOF) against the degree of Pd dispersion at 100% conversion of CNB. The result suggests that the TOF depended on the Pd dispersion, it increased with an increase in the Pd dispersion, namely the reaction rate is larger for the catalyst with smaller Pd crystalline grain. The TOF depending on metal dispersion was also reported for the hydrogenation of nitrobenzene with Pd/C [26,27].

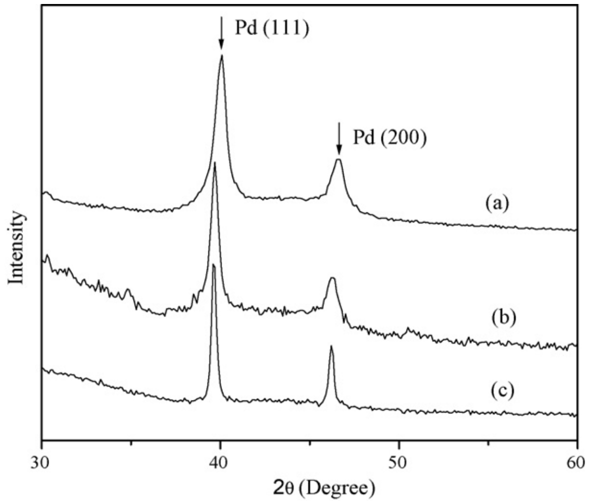

Fig. 3. X-ray diffraction patterns of Pd/C catalysts (a) without heat treatment, (b) heat-treated at 573 K and (c) at 973 K with H_2 gas for 4 h.

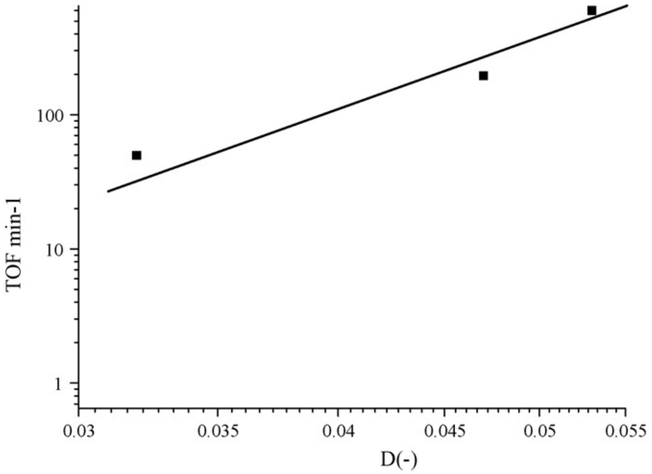

Fig. 4. Plots of TOF against the degree of metal dispersion. Reaction conditions: *o*-CNB 12.7 mmol; catalyst 5% Pd/C 0.01 g; H_2 4 MPa; CO_2 10 MPa; temperature 308 K.

4. Conclusions

The hydrogenation of *o*-CNB over Pd/C catalyst in $scCO_2$ has been studied and the results showed that the introduction of $scCO_2$ with the proper pressure could improve the selectivity to *o*-CAN and the reaction rate. The selectivity to *o*-CAN changed very slightly with increasing CO_2 pressure at a range from 8 to 13 MPa. At CO_2 pressure higher than 12 MPa, the selectivity to *o*-CAN and the reaction rate decreased because of the dilution effects. Furthermore, the reaction rate and product selectivity of *o*-CNB hydrogenation depended on the crystalline grain size of Pd metal dispersed on the catalyst surface.

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