

The role of carbon dioxide in chemoselective hydrogenation of halonitroaromatics over supported noble metal catalysts in supercritical carbon dioxide

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Chemoselective hydrogenation of halogenated nitrobenzenes over Pt/C catalysts proceeds effectively in supercritical carbon dioxide (scCO₂) to produce halogenated anilines with excellent selectivity; the rate of the hydrogenation of nitro groups is markedly enhanced in scCO₂ compared to the neat reaction, and the dehalogenation reaction is significantly suppressed.

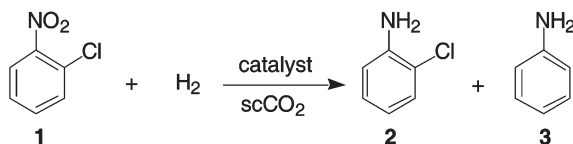
Supercritical fluids are now recognized to be promising reaction media for rapid and selective hydrogenations promoted by both homogeneous and heterogeneous catalysts¹ with significant advantages, particularly because of the high miscibility of reacting hydrogen gas and high diffusivity. In particular, a fine-tuned heterogeneous catalyst in environmentally benign scCO₂ has attracted considerable attention for the achievement of chemoselective hydrogenation over heterogeneous catalysts.² We now describe a chemoselective hydrogenation of halonitroaromatics over conventional Pt/C catalysts in scCO₂, selectively giving the desired halo aromatic amines, which are now industrially produced by hydrogenation of halogenated nitroaromatic compounds over

modified Pt/C or iridium/charcoal (Ir/C) catalysts.³ Since the traditional catalyst systems often need a trade-off between activity and selectivity because of an undesired dehalogenation side-reaction, catalyst-modifiers or additives are required to attain the best catalyst performance from a practical point of view. The utilization of scCO₂ causes a marked increase in the rate of the reaction and product selectivity compared to those attained under conventional reaction conditions. CO₂ works as a reaction medium that is nonflammable, nontoxic and an effective promoter of selective hydrogenation.

We first examined the catalytic performance of some commercially available noble metal solid catalysts for hydrogenation of 2-chloronitrobenzene (**1**) to 2-chloroaniline (**2**) at 40 °C in a mixture of 1.1 MPa of H₂ and 10 MPa of scCO₂.† Hydrogenation over 1% Pt/C catalyst proceeded smoothly to give the desired product **2** in 99.7% yield, while the reaction over Pd/C, Rh/C, and Ru/C catalysts gave unsatisfactory results, although the Ir/C provided reasonably high reactivity and selectivity, as summarized in Table 1. It should be noted that the reaction without scCO₂ under otherwise identical conditions gave lower yield and lower selectivity. These results clearly show that the use of scCO₂

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Table 1 Selective hydrogenation of **1** over supported noble catalysts in scCO₂^a



Catalyst, wt/mg	Medium, pressure/MPa	T/°C	Time/min	Conversion (%)	Selectivity (%)	
					2	3
1% Pt/C, 2	scCO ₂ , 10	40	150	100	99.7	0.3
1% Pt/C, 2	Neat, 0	40	300	100	95.6	2.1
5% Pd/C, 2	scCO ₂ , 10	40	150	100	82.1	16.2
5% Ir/C, 2	scCO ₂ , 10	40	580	100	97.9	nd ^e
5% Rh/C, 2	scCO ₂ , 10	40	60	6	28.0	nd
5% Ru/C, 2	scCO ₂ , 10	40	60	3	16.3	nd
1% Pt/C, 2	scCO ₂ , 10	90	60	100	99.1	0.6
1% Pt/C, 2	Neat, 0	90	90	100	93.4	5.8
2% Pt/Al ₂ O ₃ , 10	scCO ₂ , 10	40	150	72	90.3	0.1
1% Pt/SiO ₂ , 20	scCO ₂ , 10	40	150	69	92.8	0.2
5% Ir/Cu/Fe/C ^b , 2	scCO ₂ , 10	40	150	11	8.6	nd
5% Ir/Cu/Fe/C ^c	Toluene	90	40	100	99.3	<0.1
5% Pt/C/amine, 20 ^d	Neat, 0	100	120	100	98.9	0.5

^a Reaction conditions: 50 mL stainless steel autoclave, [1] = 5 mmol, P_{H₂} = 1.1 MPa. ^b Ir 5%/Cu 0.15%/Fe 0.3%/C. ^c Data cited in ref. 3b.

^d Data cited in ref. 3d. ^e Not detected.

strongly suppresses the dechlorination during the hydrogenation, resulting in a marked improvement in the selectivity compared with the neat reaction. At a higher temperature, 90 °C, the reaction quickly proceeded with a slight loss of the product selectivity. Charcoal is the best choice of supporting material for the present hydrogenation. However, Pt/Al₂O₃ or Pt/SiO₂ can be used for the reaction although there is low activity, as shown in Table 1. Pt catalysts on these supports with high Pt loadings were required to attain comparable reactivity.

The CO₂ pressure was found to influence the outcome of the reaction. When the pressure was increased at 40 °C, the yield of **2** at the initial stage of the reaction increased to reach a maximum at around 10 MPa as shown in Fig. 1. Visual inspection of the phase behavior of the substrate **1** and product **2** revealed that these compounds are all miscible with CO₂ at over 10 MPa at 40 °C.⁴ These results strongly indicate that the supercritical single phase, including the substrate, H₂ and the products, is a crucial factor in attaining the best catalyst performance in terms of activity and selectivity. It should be noted that the H₂O formed during the reaction did not significantly affect the outcome of the reaction since the addition of one equivalent of H₂O, which is not completely miscible in scCO₂, to **1** caused no retardation effect on the reaction under the same reaction conditions.

Notably, a separate experiment of the dechlorination of the hydrogenated product **2** showed that hydrogenolysis of **2** to aniline over 1% Pt/C catalyst at 90 °C was markedly suppressed under

supercritical CO₂ conditions, while the dechlorination in the absence of CO₂ under otherwise identical conditions proceeded to give 30% conversion of **2** after 45 min.⁵ Similarly, the dehalogenation of chlorobenzene bearing no amino group was also strongly suppressed under supercritical CO₂ conditions. These results suggest that CO₂ acts as a modifier of the catalyst surface to block the active sites for dechlorination.

In order to gain further insight into the role of the CO₂ for selective hydrogenation, we examined the effect of Pt loading in the Pt/C catalyst on the hydrogenolysis of 2-chloroaniline **2** in the absence of CO₂ at 90 °C. On increasing the Pt loading from 1 to 5 wt%, which corresponds to a change in the Pt surface area⁶ from 340 to 263 m² per gram of Pt, the dehalogenation product, aniline, markedly decreased from a 30% to a 12% conversion of **2** under the hydrogenation conditions, indicating that the dehalogenation of **2** with H₂ on the Pt surface was the structure-sensitive reaction⁷ as shown in Fig. 2. Since the number of atoms with kinked and stepped surfaces are known to increase on the Pt metal surface when the Pt particle size decreases,⁸ the present structure-sensitive dechlorination in the absence of CO₂ may take place on kinked or stepped sites of the Pt surface. Contrary to the neat reaction without CO₂, the dechlorination of **2** in scCO₂ did not appreciably proceed regardless of the Pt particle size, suggesting that the active site for the dechlorination might be blocked by the addition of CO₂, leading to a marked improvement in the product selectivity in the hydrogenation of **1**.

Recently, Baiker and co-workers reported that the hydrogenation of carbonyl compounds over the Pt/C catalyst in scCO₂ provided CO as a side product, which might strongly bind to the Pt metal on the catalyst surface, resulting in serious catalyst deactivation for the hydrogenation of unsaturated compounds.⁹ In addition, electrochemical reduction of CO₂ to CO was reported to preferentially proceed on stepped or kinked sites on the Pt single crystal surface¹⁰ and the reduced product CO selectively binds to the stepped sites in preference to the terrace sites.¹¹ These reported results as well as the present experimental results suggest that CO generated from CO₂ during the hydrogenation of **1** in the presence of CO₂ might preferentially cover the active sites for dehalogenation of **1** or **2** on the Pt surface, resulting in a significant increase in product selectivity. In fact, the addition of a small amount of CO (0.05 mL) into the neat reaction system containing 1% Pt/C (10 mg) without CO₂ caused a marked suppression of the dehalogenation of **2**, whereas the hydrogenation of nitro group of **1** proceeded.

The *in situ* diffuse reflectance FT-IR spectra of the Pt/C catalyst for the reaction of CO₂ with H₂ (10 : 1) under atmospheric conditions as shown in Fig. 3 clearly indicate that a broad peak due to terminal CO on Pt metal at 2046 cm⁻¹ as observed by Weaber *et al.*¹² in addition to a broad peak around 1780 cm⁻¹ possibly due to bridged CO.¹³ When the fresh CO gas was added to the system, the peaks around 2046 cm⁻¹ increased with the appearance of peaks due to free CO (2177 and 2109 cm⁻¹), indicating that the formation of terminal CO on the Pt is preferable under the tested conditions described in Fig. 3. It should be noted that the concentration of CO generated may not be accumulated under the present reaction conditions because the reversible water–gas shift reaction with aid of the H₂O generated during the hydrogenation of **1** shifted CO back to CO₂ and H₂.

The chemoselective hydrogenation of **1** can be applied to the other chlorinated nitrobenzenes. In particular, the selective

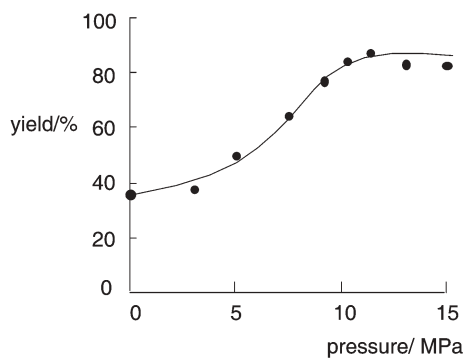


Fig. 1 The effect of CO₂ pressure on the yield of 2-chloroaniline **2** at the initial stage of the hydrogenation of 2-chloronitrobenzene **1**. Conditions: 50 mL stainless steel autoclave, 1% Pt/C 2 mg, [1] = 5 mmol, P_{H_2} = 1.1 MPa, 40 °C, 60 min.

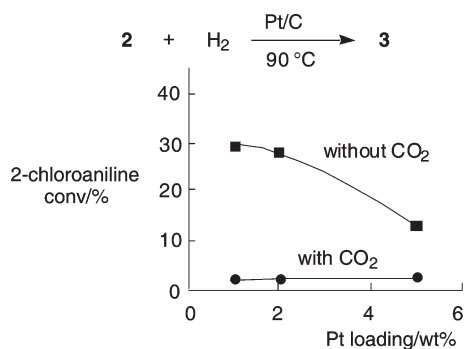


Fig. 2 The effect of CO₂ on the reaction of 2-chloroaniline **2** with H₂. Conditions: 50 mL stainless steel autoclave, [2] = 10 mmol, 90 °C, 45 min, Pt surface area 0.26 m², P_{H_2} = 2.2 MPa.

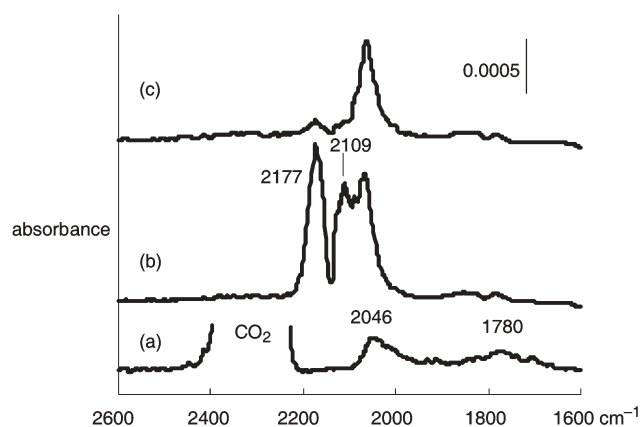


Fig. 3 *In situ* diffuse reflectance FT-IR spectra of CO adsorbed on 5% Pt/C catalyst (a) after treatment with a mixture of CO₂ and H₂ (10 : 1) under atmospheric pressure at 40 °C, (b) purged with He for 5 min after introduction of fresh CO gas into the sample (a), (c) purged with He for 15 min at 40 °C.

hydrogenation of solid nitro compounds in scCO₂ exhibited technical advantages over the reaction in solution phase as observed by Jessop *et al.*¹⁴ For example, the reaction of 3-chloro (mp 46 °C) and 4-chloronitrobenzene (mp 82 °C) proceeded equally well under similar conditions to give the desired products in 100% conversion and with over 99% selectivity. Since the reaction of 2,5-dichloronitrobenzene (mp 55 °C) was slow compared with the reaction of **1**, a higher temperature, 60 °C is required. In general, the rate of the reaction was accelerated by the use of scCO₂ as the reaction medium as observed in the reaction of **1**. The use of scCO₂ caused a marked increase in the product selectivity as well as the rate of the reaction, possibly due to modification of the catalyst surface with CO generated from CO₂ hydrogenation, leading to a significant decrease in formation of the undesired by-product, HCl. In large scale production, the formation of HCl is a problem that cannot be neglected.

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Notes and references

† Experimental details. **Safety warning:** Operators of high-pressure equipment should take proper precautions to minimize the risk of personal injury.

The H₂ gas used was 99.99% purity (Showa Denko). The purity of CO₂ used was 99.999% (Showa Tansan). The catalysts used except for Ir/Cu/Fe catalyst (Degussa) were supplied by N. E. Chemcat corporation.

Standard procedure for the hydrogenation: A 50 mL stainless steel autoclave was filled with N₂ and then charged with the catalyst and reactants. The reactor was evaporated and refilled with N₂ and then placed in the oven at 40 °C. Subsequently, H₂ (1–2 MPa) was introduced, and then CO₂ (0.1–15 MPa) was added with an HPLC pump. After stirring for the desired time, the reactor was cooled in a cold bath with dry ice. The mixture of H₂ and CO₂ was vented, and the reactor was slowly warmed to room temperature. The chemical yield and selectivity of products were determined by GC analyses.

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