



## **SELECTIVE HYDROGENATION OF 2-CHLORONITROBENZENE OVER SUPPORTED NICKEL CATALYST IN SUPERCRITICAL CARBON DIOXIDE**

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Hydrogenation of chloronitrobenzene (CNB) is commonly used to manufacture chloroaniline (CAN), which are important intermediates in the production of a number of products, including agricultural chemicals, azo dyes, pigments, pharmaceuticals and petroleum solvents. It remains a challenge to hydrogenate the nitro group selectively in green media over non-noble metal heterogeneous catalysts [1-6]. Supercritical carbon dioxide (scCO<sub>2</sub>) is an acceptable replacement for conventional organic solvents, due to its environmentally benign nature, high miscibility with gases, and easy separation from liquid products and solid catalysts [7,8]. In the present work, the performance of supported nickel catalysts, prepared using the incipient wetness impregnation, was studied in the hydrogenation of 2-CNB in compressed CO<sub>2</sub> and in ethanol at a low temperature of 35 °C. The total conversion and selectivity to 2-CAN was significantly enhanced in scCO<sub>2</sub> compared with that in ethanol, and a high selectivity about 99% was attained at a nearly complete conversion. In scCO<sub>2</sub>, with altering CO<sub>2</sub> pressure, a maximum of conversion was obtained, which is strongly related to the phase behavior of the heterogeneous reaction mixture. The superior performance of the nickel catalysts in scCO<sub>2</sub> opens up a cost-effective and eco-friendly route toward the production of chloroanilines. In addition, the ferromagnetic property of nickel catalysts may be useful for performing the reaction as well as separating the catalyst in an applied magnetic field.


 Table 1 Results of hydrogenation of 2-CNB in scCO<sub>2</sub> over different catalysts.

Catalysts	Amounts (mg)	Reaction time (min)	Conversion (%)	Selectivity (%)		
				2-CAN	AN+NB	Others
1% Pt/Fe <sub>2</sub> O <sub>3</sub>	20	140	16.9	86.2	8.5	5.3
5% Pt/C	10	9	98.9	72.9	18.2	8.9
5% Pd/C	10	27	78.0	94.1	5.0	0.9
15% Ni/TiO <sub>2</sub>	150	50	82.0	98.8	0.5	0.7

 Reaction conditions: 35 °C, H<sub>2</sub> 4 MPa, CO<sub>2</sub> 9 MPa, 2-CNB 1.5 g (9.52 mmol), reactor 50 ml.

 Table 2 Results of hydrogenation of 2-CNB in scCO<sub>2</sub> and in ethanol.

Solvents	Reaction time (min)	Concentration (mmol/ml) <sup>a</sup>	Conversion (%)	Selectivity		R <sup>b</sup> (mol/(molNi·h))
				CAN (%)		
EtOH (50 ml) <sup>c</sup>	50	0.19	25.9	70.0		7.72
EtOH (10 ml)	5	0.95	3.6	90.2		-
	50		35.7	69.9		10.64
scCO <sub>2</sub> (10.5 MPa)	5	0.19	9.4	64.6		-
	25		60.7	97.6		-
	50		82.0	98.8		24.43

 Reaction conditions: 35 °C, H<sub>2</sub> 4 MPa, 2-CNB 1.5 g (9.52 mmol), catalyst 150 mg, reactor 50 ml.

<sup>a</sup> The initial concentration of 2-CNB.

<sup>b</sup> Average reaction rate (mol/(molNi·h)), defined as the mole amounts of 2-CNB converted per mol nickel per hour over the first 50 min.

<sup>c</sup> Reactor 100 ml.

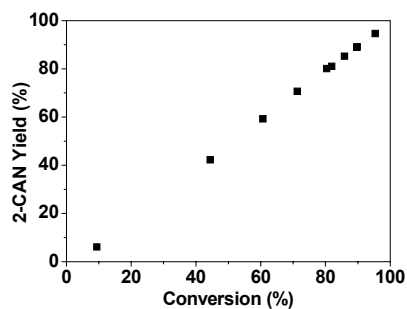


Fig. 1 The yield of 2-CAN versus conversion of 2-CNB in scCO<sub>2</sub> over Ni/TiO<sub>2</sub> at 35 °C.

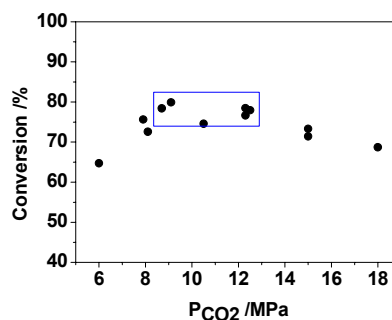


Fig. 2 Influence of CO<sub>2</sub> pressure on the total conversion of 2-CNB at 35 °C.

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