

# Selective Hydrogenation of *m*-Dinitrobenzene to *m*-Nitroaniline over the Supported-Iridium Catalyst

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The mono-reduction of *m*-dinitrobenzene (*m*-DNB) to *m*-Nitroaniline (*m*-NA) is of industrially immense importance as it is widely used as intermediates for dyes, pharmaceuticals and agrochemicals. The traditional methods of reduction based on the use of sulphides or metal acid are hazardous to the environment and require high cost for waste disposal. Therefore, catalytic hydrogenation has attracted increasing attention<sup>[1~4]</sup>.

Studies of various of catalyst systems have mainly focused on the hydrogenation of *m*-DNB to *m*-phenylenediamine (*m*-PD) rather than *m*-NA<sup>[5,6]</sup>. Although both skeletal nickel<sup>[7]</sup> and carbon supported palladium<sup>[8]</sup> as catalysts for selective hydrogenation of *m*-DNB to *m*-NA have also been studied extensively, the crucial problem appears to be not only the worse yield of *m*-NA but also the short lifetime of the catalysts. Hence developing high selective catalyst system for *m*-NA from *m*-DNB is desirable. Liu Xiaozhi<sup>[9]</sup> firstly reported the selenium-catalyzed reduction of *m*-DNB with CO/H<sub>2</sub>O as a hydrogenation source to *m*-NA, the *m*-DNB conversion was up to 100% with *m*-NA selectivity and *m*-NA yield of 95.7%. However, iridium-based catalysts have less been used in selective hydrogenation of aromatic nitro-compound to corresponding amine in

comparison with other platinum group metals. A example of supported-iridium catalyst for the selective hydrogenation of substituted *m*-DNB (e. g. dinitrotoluene) was found, but which exhibited outstanding selectivity to completely hydrogenated product toluenediamine<sup>[10]</sup>. To the best of our knowledge, this paper reported the first example of iridium-catalyzed hydrogenation of *m*-DNB to *m*-NA.

The supported-iridium catalyst was prepared through the conventional impregnation method with hexachloroiridium(VI) acid as the precursor and aluminum oxide as the carrier, and activated by hydrogen. The content of Ir was 1.0% by weight as determined by IRIS Advantage ICP. Diffraction signal of the Ir particle couldn't be observed in X-ray diffraction (XRD, D/max-TTR) pattern due to the low concentration and small particle size of Ir in the catalyst. The binding energy of Ir 4f<sub>7/2</sub> level in the catalyst, measured from its X-ray photoelectron spectrums (XPS, KRATOS CO XSAM800), had a value of 60.55 eV, revealing that Ir<sup>6+</sup> had been well reduced to Ir<sup>0</sup> (the binding energy of Ir<sup>0</sup> 4f<sub>7/2</sub> 60.6 eV).

Catalytic hydrogenation of *m*-DNB was performed in a 60 ml stainless steel autoclave with magnetic stirrer as a batch process. The catalyst, *m*-DNB and sol-

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vent were placed in the autoclave. The autoclave was sealed and purged with H<sub>2</sub> five times and then H<sub>2</sub> was charged to the desired pressure. After the reaction finishing, the catalyst was filtrated and the products were analyzed by GC-1890- II through temperature programming. The conditions for determination were as follows: FID detector, SE-30 capillary column (30 m × 0.53 mm), the temperature program starting at 100℃ (holding 10 min) and ending at 260 ℃ (holding 15 min), the programming rate 15℃/min, the injector temperature 280℃ and detector temperature 280℃. The relative content of each component was determined by area normalization method. Reactants and products were identified by comparison with authentic samples, and GC-MS coupling.

The effect of reaction temperature on hydrogenation of *m*-DNB was investigated and the results were showed in Fig. 1. The catalytic activity increased line-

ded stepwise by the sequential hydrogenation of both nitrogroups, and increasing temperature was favorable for the hydrogenation of the second step nitrogroup to produce *m*-PD. On the contrary, the results( Fig. 1. ) seemly indicated the formation of *m*-NA could occur rapidly in the presence of the supported iridium catalyst, whereas the hydrogenation of second step nitrogroup had nothing to do with increasing reaction temperature. The supported-iridium catalyst even thoroughly avoided the formation of *m*-PD under the reaction conditions employed. Obviously, increase of selectivity for *m*-NA was ascribed to Phenylhydroxylamine intermediate gradual transformation. Emphatically, only at temperature 120℃ did an extremely low amount of azo- and azoxy-compounds accompany.

Table1 Recycle of the supported-iridium catalyst in selective hydrogenation of *m*-dinitrobenzene

Cycle	Conversion ( % )	Selectivity ( % )		
		<i>m</i> -NA	<i>m</i> -PD	Side products <sup>b</sup>
1	100	96.3	2.7	1.0
2	100	97.0	–	3.0
3	92.2	99.0	–	<1.0
4	67.0	99.1	–	<0.9
5	50.0	99.3	–	<0.7
6	37.6	99.5	–	0.5
6 *	100	100	–	–

Reaction conditions: temperature, 90 ℃; pressure of H<sub>2</sub>, 0.8 MPa; time, 1 h; the weight of *m*-DNB, 0.34 g; the mole ratio of *m*-DNB to Ir, 5 000; 5 mL methanol as solvent. \* t = 2.5 h.

<sup>b</sup>Side products only including phenylhydroxylamine intermediate.

All further experiments to investigate reaction conditions showed that the best yield of *m*-NA (96.3%) could be obtained under the following conditions: 90 ℃, 0.8 MPa, 1 h, the mole ratio of *m*-DNB to Ir 5 000 and methanol as solvent. Therefore, the testing of the catalyst recycle was carried out under the above conditions. Before each recycle operation, the previous batch product and solvent were removed completely with sucker and the catalyst still remained in the reactor. Results of recycle in table 1 showed the activity of catalyst still kept an high level after the third recycle, and then decreased considerably. Moreover, the selec-

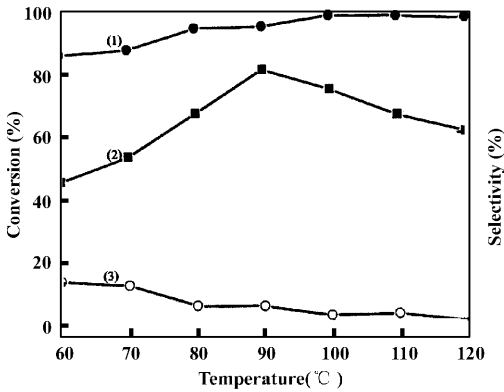


Fig. 1 Effect of temperature on selective hydrogenation of *m*-dinitrobenzene over the supported-iridium catalyst  
(1) Selectivity of *m*-NA; (2) Conversion of *m*-DNB;  
(3) Selectivity of Side products <sup>a</sup>

Reaction condition: pressure of H<sub>2</sub>, 0.5 MPa; time, 1 h; the weight of *m*-DNB, 0.34 g; the mole ratio of *m*-DNB to Ir, 5 000; 5 mL methanol as solvent. <sup>a</sup>Side products including azo- and azoxy-compounds, or phenylhydroxylamine intermediate, but no *m*-phenylenediamine

arly with the rise of reaction temperature under 90 ℃, and then began to decrease gradually when the temperature above 90 ℃. Maximum conversion of *m*-DNB was obtained at 90 ℃. As known from the literature<sup>[11]</sup>, the hydrogenation of *m*-DNB to *m*-NA procee-

tivity of *m*-NA kept higher than 96.3% all the time. Conversion of *m*-DNB and selectivity of *m*-NA increased from 37.6% and 99.5% to 100%, respectively, when the reaction period was prolonged from 1 h to 2.5 h in the sixth recycle. The supported Iridium catalyst had rather longer lifetime as compared with palladium catalyst supported on carbon, which obtained only 13.5% overall conversion of *m*-DNB in the case of the second reusability of the catalyst<sup>[8]</sup>.

In summary, the supported Iridium catalyst had an excellent performance in the selective hydrogenation of *m*-DNB to form *m*-NA. The research of the mechanism for the high yield and long lifetime is in process.

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# 负载铱催化剂选择性催化间二硝基苯制间硝基苯胺

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**摘要:** 用浸渍法制备的负载铱催化剂催化间二硝基苯部分加氢制间硝基苯胺, 考察了温度对反应的影响和催化剂循环实验, 结果表明, 催化剂活性在 90 ℃ 最佳; 间硝基苯胺选择性随温度升高而增加. 以甲醇作溶剂, 在  $n(\text{substrate})/n(\text{Ir}) = 5\ 000$ , 90 ℃, 0.8 MPa 条件下, 反应 1 h, 间二硝基苯转化率 100%, 间硝基苯胺选择性 96.3%, 全部加氢产物间苯二胺很少生成. 催化剂经 3 次循环, 活性下降不明显, 在第 6 次循环时延长反应时间至 2.5 h, 间二硝基苯转化率和间硝基苯胺选择性均能达到 100%. 催化机理有待进一步研究.

**关键词:** 选择性加氢; 负载铱催化剂; 间二硝基苯; 间硝基苯胺