

# Selective hydrogenation of *m*-dinitrobenzene to *m*-nitroaniline catalyzed by PVP-Ru/Al<sub>2</sub>O<sub>3</sub>

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## Abstract

Selective hydrogenation of *m*-dinitrobenzene to *m*-nitroaniline (*m*-NA) catalyzed by polyvinylpyrrolidone stabilized Ru/Al<sub>2</sub>O<sub>3</sub> (PVP-Ru/Al<sub>2</sub>O<sub>3</sub>) was studied experimentally. The effects of solvents, metal cation additives and reaction conditions were examined. The highest total yield of *m*-NA was obtained with 97.9% selectivity at 100% conversion when Sn<sup>4+</sup> used as modifier (the molar ratio of *m*-DNB to catalyst was 477:1, the molar ratio of Sn<sup>4+</sup> to ruthenium was 1:4) under suitable conditions.

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**Keywords:** Selective hydrogenation; *m*-Dinitrobenzene; *m*-Nitroaniline; Ruthenium; Metal cations

## 1. Introduction

*m*-Nitroaniline (*m*-NA) is an important intermediate for the preparation of dyestuffs, mechanical and electronic corrosion inhibitor. The traditional routes for the chemical were done through: (1) Partial reduction of *m*-dinitrobenzene (*m*-DNB) with sodium disulfide or a metal system. (2) From aniline by nitration after acetylation, with subsequent removal of acetyl group by hydrolysis. These methods are hazardous to the environment and required high cost for the waste of disposal, and work-up of the reaction mixture is cumbersome. The catalytic hydrogenation of *m*-DNB to *m*-NA should be the method of choice for the preparation of *m*-NA from *m*-DNB, provided a high selectivity with respect to *m*-NA could be realized [1].

The catalytic hydrogenation of *m*-DNB (shown in Scheme 1) has been reported using catalysts based on both base transition metals such as nickel, copper [2–6] and noble metals such as palladium and platinum [1,7], but which generally leading to the formation of *m*-phenylenediamine

(*m*-PDA) [2–9], hence development of a catalytic system to achieve a high selectivity to *m*-NA is highly desirable.

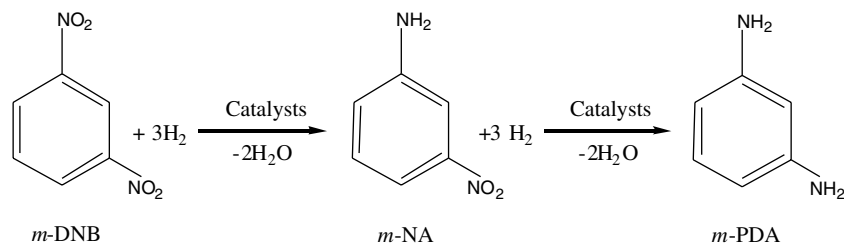
As an important member of the platinum group metals, ruthenium is well known as a novel catalyst for selective hydrogenation of aromatic ring to cycloalkenes, halonitroaromatics to aromatic haloamines, carbonyl group in the vicinity of conjugated or isolated double bonds to corresponding unsaturated alcohol [10]. However, to our knowledge, catalysts based on ruthenium have scarcely been used in selective hydrogenation of *m*-DNB to *m*-NA. Herein, an attempt was made to use polyvinylpyrrolidone stabilized Ru/Al<sub>2</sub>O<sub>3</sub> (designated as PVP-Ru/Al<sub>2</sub>O<sub>3</sub>) as catalyst in the reaction experimentally. The effects of solvents, metallic cation additives and experimental parameters, such as reaction time, reaction temperature and hydrogen pressure were examined.

## 2. Experimental

### 2.1. Materials

PVP (average molecular weight 40,000) was supplied by BASF. Ruthenium chloride (RuCl<sub>3</sub>) was purchased from

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E-mail address: [zhaosonglin@tzc.edu.cn](mailto:zhaosonglin@tzc.edu.cn) (S. Zhao).

Scheme 1. Pathway of the hydrogenation of *m*-dinitrobenzene.

Kunming Institute of Precious Metals. The carrier  $\gamma$ -alumina, 160–180 mesh, surface area 200 m<sup>2</sup> g<sup>-1</sup>, was supplied by Shanxi Branch of China Aluminium Co., Ltd. Anhydrous metallic chlorides were prepared according to the literature [11]. Hydrogen (H<sub>2</sub>) with a purity of 99.99% was used for the catalytic experiments (supplied by Sichuan Tianyi Science & Technology Co., Ltd). *m*-Dinitrobenzene, methanol, ethanol, *i*-propanol, THF, toluene and ethyl acetate (Beijing Chemicals, analytical grade) were used without further purification.

## 2.2. Catalyst preparation

The catalyst PVP-Ru/Al<sub>2</sub>O<sub>3</sub> was prepared by the reported method [12]: The carrier  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was impregnated in aqueous solution of RuCl<sub>3</sub> in the presence of PVP-40000 overnight. Thereafter, the sample was reduced by refluxed mixed alcohol (ethanol and isopropanol in presence of KOH) for 2.5 h, filtered and washed with distilled water for several times until the final filtrate was free from Cl<sup>-</sup> by AgNO<sub>3</sub> test, subsequently vacuum dried at 333 K for 24 h. The content of ruthenium is 2.1 wt.% (detected by IRIS Advantage ICP).

## 2.3. Catalyst characterization

X-ray diffraction (XRD) studies were performed with a D/max-TTR instrument equipped with a Cu K $\alpha$  source ( $\lambda = 0.1542$  nm) and in the range of 10–75° 2 $\theta$ .

The X-ray photoelectron spectrums (XPS) were recorded using a KRATOS CO XSAM800 spectrometer (Mg K $\alpha$  X-ray radiation (1215 eV), operated at 10 mA and 12 kV). The vacuum of the chamber was 2  $\times$  10<sup>-8</sup> Pa during data acquisition. All binding energy values were referenced to carbon (C 1s 284.9 eV).

## 2.4. Catalytic tests

Catalytic hydrogenation of *m*-DNB was conducted in a 60 mL stainless autoclave equipped with magnetic stirrer. The typical hydrogenation procedure was conducted as follows: The catalyst, *m*-DNB and solvent were added to the reactor. It was purged with H<sub>2</sub> for three times and then H<sub>2</sub> was introduced to the desired pressure. The reaction temperature was maintained by a thermostat. The reaction was started by switching the stirrer on. The speed of agita-

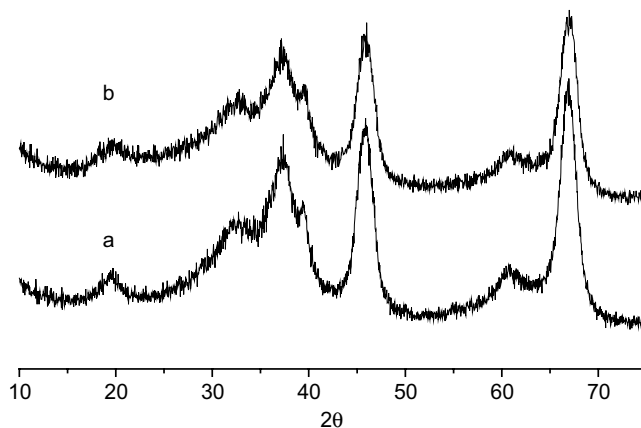
tion was set at 1000 rpm. *m*-DNB conversion and product selectivity were determined by GC-1890-II (Agilent), coupled with FID detector and quartz capillary column (Supelco, SE-30 capillary column, 30 m length  $\times$  0.53 mm i.d.), carrier gas, nitrogen. Reactants and products were identified by comparison with samples, and GC-MS coupling.

## 3. Results and discussion

### 3.1. The results of XRD and XPS study

The XRD pattern of the support (Al<sub>2</sub>O<sub>3</sub>, Fig. 1a) was very broad and diffuse. The diffraction peaks at 2 $\theta = 31.78$ , 37.80, 45.35 and 66.81° due to  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> were observed. The corresponding diffraction peaks of Al<sub>2</sub>O<sub>3</sub> on PVP-Ru/Al<sub>2</sub>O<sub>3</sub> catalyst XRD pattern (Fig. 1b) were broadened. The result could be explained in terms of strength of the metal-support interactions. Furthermore, a high and homogeneously dispersion of Ru species in catalyst did not allow the detection of the ruthenium or ruthenium oxide phases.

Since the binding energy of Ru (around 281 eV) overlapped with that of C 1s (around 284 eV), it was difficult to resolve the tiny Ru peak out from the large peak of C 1s. Two Ru species were detected after a careful deconvolution: Ru<sup>0</sup> at 280.3 eV and another corresponding to electron-deficient Ru specie (Ru <sup>$\delta$ +</sup>) at 281.4 eV. This indicates the incomplete reduction of Ru<sup>3+</sup> to Ru<sup>0</sup>.

Fig. 1. XRD patterns of Al<sub>2</sub>O<sub>3</sub> (a) and PVP-Ru/Al<sub>2</sub>O<sub>3</sub> catalyst (b).

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