



# 1,5-Dinitronaphthalene hydrogenation to 1,5-diaminonaphthalene over carbon nanotube supported non-noble metal catalysts under mild conditions

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## ABSTRACT

Carbon nanotubes (CNTs) were firstly thermal treated and then acid treated in HNO<sub>3</sub> or mixture of HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>. The treated carbon nanotubes were used as support to load nickel to prepare non-noble metal hydrogenation catalysts. These catalysts were characterized and applied in 1,5-dinitronaphthalene hydrogenation. The characterization results indicate that acid modified carbon nanotubes not only possess a more hydrophilic surface by introducing a variety of oxygen-containing functional groups, but also improve the nickel dispersion, hydrogen uptake quantity and metallic surface area. The Ni/CNTs catalysts show good catalytic activity in 1,5-dinitronaphthalene hydrogenation under mild reaction conditions, and the Ni/CNTs-4 gives the best result of 100% conversion of 1,5-dinitronaphthalene and 92.04% selectivity to 1,5-diaminonaphthalene under 0.6 MPa and 393 K. The influences of reaction conditions and metal loading amount are discussed, and a possible reaction routes of 1,5-dinitronaphthalene hydrogenation is proposed. Such non-noble metal hydrogenation catalysts are expected to replace the present supported palladium or platinum noble catalysts in industry.

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## 1. Introduction

Active carbon supported palladium or platinum noble metal catalysts are widely used in hydrogenation, especially in fine chemicals hydrogenation process. 1,5-diaminonaphthalene can be used in the manufacture of dyestuff, pesticide, rubber chemicals, resin and photographic materials [1]. Particularly, it is the critical material to produce 1,5-diisocyanatonaphthalene, which is an advanced polyurethane for large machinery production, the shock absorption and noise reduction of railway transportation equipments, the composite materials of wind power equipment vane, new membrane materials of solar cell module and so on [2–5]. The traditional technology of 1,5-diaminonaphthalene production suffers from many disadvantages such as the complex routes, the generation of large quantities of organic wastes and lower yield [5–8]. Hence, many researchers have tried to develop novel methods for the production of 1,5-diaminonaphthalene. In industry, the higher cost of

1,5-dinitronaphthalene hydrogenation to 1,5-diaminonaphthalene lies in the use of noble metal catalysts such as Pt/C or Pd/C [9,10]. Therefore, non-noble metal catalysts have obtained more and more attention in the hydrogenation processes [11–14]. Carbon nanotubes (CNTs) have been reported to be excellent catalyst supports based on their intrinsic properties such as high surface area, unique electronic properties and chemical inertness, thermal stability and high mechanical strength [15–20]. And carbon nanotubes supported metal catalysts exhibited high activity in hydrogenation processes [21–23], it has been assumed that the phenomenon of Hydrogen Spillover on the catalysts plays an important role. Quite a few literature are concerned with the using of modified carbon nanotubes as catalyst support [24–32].

In this paper, carbon nanotubes supported non-noble nickel catalysts were prepared and applied in 1,5-dinitronaphthalene hydrogenation to 1,5-diaminonaphthalene. It has been found that modified carbon nanotubes supported non-noble metal catalysts show good catalytic activity and selectivity to 1,5-diaminonaphthalene under mild conditions.

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## 2. Experimental

### 2.1. Materials

The CNTs with a diameter of 10–20 nm were purchased from Shenzhen Nanotech Port Co., Ltd., China. 1,5-dinitronaphthalene was purchased from Shanghai Jingchun Reagent Co., Ltd. Nickel nitrate ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) was purchased from Shanghai Aibi Chemistry Reagent Co., Ltd. And all the other reagents were analytical grade. The 1,5-diaminonaphthalene (97 wt.%) standard sample was purchased from Alfa Aesar-A Johnson Matthey Company.

### 2.2. Catalyst preparation

The raw CNTs material were denoted as CNTs-1. The raw CNTs underwent acid treatment in 65 wt.%  $\text{HNO}_3$  at 303 K for 12 h, 50 wt.%  $\text{HNO}_3$  at 373 K for 4 h, a mixture of  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  ( $v/v=3:1$ ) at 373 K for 4 h, respectively. And then the solids were washed with deionized water and dried in vacuum at 383 K overnight, the corresponding materials were denoted as CNTs-2 (65 wt.%  $\text{HNO}_3$ ), CNTs-3 (50 wt.%  $\text{HNO}_3$ ) and CNTs-4 ( $\text{HNO}_3 + \text{H}_2\text{SO}_4$ ,  $v/v=3:1$ ), respectively.

The CNTs supported Ni catalysts were prepared by impregnation method. The CNTs-1, CNTs-2, CNTs-3 and CNTs-4 were mixed with an aqueous solution of 0.1 M  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , stirred at 313 K for 12 h and dried at 373 K overnight. Finally, the catalysts were calcinated at 673 K for 4 h in flowing nitrogen and reduced under hydrogen at 673 K for 2 h. The corresponding catalysts were denoted as Ni/CNTs-1, Ni/CNTs-2, Ni/CNTs-3 and Ni/CNTs-4, respectively. The metal loading content of these catalysts was 20 wt.%.

### 2.3. Catalyst characterizations

The surface oxygen-containing functional groups on the CNTs supports were determined according to Boehm titration [33,34].

Fourier transform infrared (FT-IR) spectra of the CNTs were recorded on a Nicolet 380 spectrometer. The spectra of the samples were acquired in the wavenumber range of 400–4000  $\text{cm}^{-1}$ .

Temperature programmed desorption (TPD) analyses of the CNTs were carried out on a CHEMBET-3000 instrument. The samples were pretreated at 373 K for 18 h under a flow of helium at the flow rate of 18 mL/min.

X-ray diffraction (XRD) data of the Ni/CNTs catalysts were collected on a Japan Rigaku D/Max 2550 VB<sup>+</sup> 18 kw X-ray diffractometer under the following conditions: 40 kV, 30 mA, Cu K $\alpha$  radiation, with a scanning rate of 10°  $\text{min}^{-1}$  in the range of  $2\theta = 10\text{--}90^\circ$ .

The morphology of the samples were examined using scanning electron microscopy (SEM) on a JSM-6610LV spectrometer and the microstructure of the catalysts were observed by transmission electron microscopy (TEM) on a TecnaiG2 20 STwin electron microscope working at less than 200 kV.

Hydrogen chemisorption was measured on CHEMBET 3000. The sample was previously reduced at 393 K for 3 h in hydrogen stream, and the adsorbed hydrogen on the nickel surface was removed under flowing nitrogen stream. The sample was subsequently cooled to ambient temperature under the nitrogen stream. The hydrogen pulses were injected until the eluted areas of consecutive pulses became constant. The amount of nickel atoms were calculated by assuming the stoichiometric adsorption of hydrogen. Nickel surface area was calculated from the nickel atomic cross-sectional area.

Specific surface area, pore volume and pore size distribution of the samples were obtained by the Nitrogen adsorption–desorption on a NOVA-2200e automated gas sorption system. Specific

surface areas and pore size distributions were calculated by Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods.

The atomic absorption spectrometry (AAS) was tested on a AA-7000 spectrophotometer. The samples were calcinated at 873 K for 12 h, added into 5 mL formic acid and 8 mL nitrohydrochloric acid successively and dried at 358 K for 2 h. The treated samples were dissolved in 20 mL concentrated hydrochloric acid at 353 K and diluted by appropriate amount of distilled water. The nickel content of the sample was tested at  $\lambda = 232$  nm by AAS and the loading content was obtained by the standard curve method.

### 2.4. Procedures for the catalytic test

The liquid phase hydrogenation of 1,5-dinitronaphthalene was carried out in a 50 mL Teflon-lined stainless-steel autoclave reactor under magnetic stirring, with 2.0 g 1,5-dinitronaphthalene and 0.1 g catalyst in 20 mL *N,N*-dimethylformamide (DMF). The autoclave was sealed and flushed with hydrogen for three times, and then heated to the required temperature and pressurized with  $\text{H}_2$ . After the reaction, the catalysts were removed by filtration. And the products were analyzed by a high performance liquid chromatography method. The turnover frequency is the number of product molecules formed per active site per second. In addition, for the test of reusability, the catalysts were removed from the reaction mixture by filtration and used for the next run without any other treatment.

## 3. Results and discussions

### 3.1. Characterization of catalysts

Boehm titration results of the supports are presented in Table 1. The results indicate that there are a small quantity of carboxylic and phenolic groups on the surface of CNTs-1. Surface modification with various oxidants leads to the increment of acidic groups [34,35]. Hence, the modified samples show significant difference in their chemical nature. CNTs-2 oxidized with 65 wt.%  $\text{HNO}_3$  at 303 K exhibits the presence of the lactonic groups and a small quantity of carboxylic groups, and the number of phenolic groups increases apparently. And CNTs-3 treated with 50 wt.%  $\text{HNO}_3$  at 373 K shows more carboxylic groups and lactonic groups than CNTs-2. Among these samples, CNTs-4 oxidized with a mixture of  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  at 373 K exhibits a significant increase of the carboxylic groups and shows the largest acidic sites on the surface. From this we can know that the pretreatment methods introduce a variety of oxygen-containing functional groups on the surface, which change the physicochemical properties of the CNTs.

Fig. 1 presents the FT-IR spectra of the samples. The peaks of 3440  $\text{cm}^{-1}$  and 1640  $\text{cm}^{-1}$  are attributed to O–H bond stretching and bending vibrations of water. The peak around 3750  $\text{cm}^{-1}$  is attributed to free hydroxyl group [36], which is not obvious in CNTs-1. It may result from the residual acid through the pretreatment process. Compared with CNTs-1, other samples appear five obvious peak regions of 2800–3000  $\text{cm}^{-1}$ , 1680–1750  $\text{cm}^{-1}$ , 1385–1560  $\text{cm}^{-1}$ , 1100–1170  $\text{cm}^{-1}$  and  $\sim 1000$   $\text{cm}^{-1}$ . The peaks around 1680–1750  $\text{cm}^{-1}$  are assigned to C=O stretching mode in lactones and carboxylic acids [37–39]. The peak around 1560  $\text{cm}^{-1}$  is related to the  $-\text{COO}^-$  asymmetric stretching vibration of carboxylic acids, while the peak around 1457  $\text{cm}^{-1}$  is due to the  $-\text{COO}^-$  symmetric stretching vibration, which is normally weaker than the peak of asymmetric stretching vibration [40]. And the peaks of  $\sim 1385$   $\text{cm}^{-1}$  and  $\sim 1000$   $\text{cm}^{-1}$ , as well as the wide and scattered peaks around 2800–3000  $\text{cm}^{-1}$  are also attributed to the existence of the carboxylic acids. The peaks around 1100–1170 are

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