

SYNTHESIS OF HIGHLY DISPERSED CNTS SUPPORT NI CATALYSTS FOR HYDROGENATION OF CHLORONITROBENZENE

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Abstract

CNT-supported nickel catalysts with high dispersion and controlled nickel crystalline size have been prepared via a facile deposition-precipitation method using glycerol as solvent. Ni/CNTs catalysts were characterized by TEM, XRD and ICP techniques. It has been found that the precipitation temperature is one of the crucial parameters in determining the crystalline size, the loading of Ni, and the catalytic properties Ni/CNTs catalysts. When the precipitation temperature increased from 80 °C to 160 °C, the Ni particle size of the as-obtained Ni/CNTs catalysts increased from about 7 nm to 12 nm and the Ni content increased from 2.9 wt% to 5.2 wt%. The Ni/CNTs catalyst prepared in glycerol at 160 °C showed the best catalytic activity for hydrogenation of ortho-chloronitrobenzen with a conversion of over 99% and a selectivity of 97.0% at 2.0 MPa and 140 °C. The Ni/CNTs catalysts were also active for the hydrogenation of *p*-chloronitrobenzene and *m*-chloronitrobenzene to make corresponding chloroanilines. The as-synthesized Ni/CNTs catalysts are of great potential as cheap and highly active catalysts for production of chloroanilines.

Introduction

Chloroanilines (CAN) are important intermediates for fine chemicals and are mainly produced by selective hydrogenation of corresponding chloronitrobenzenes (CNBs) over metal catalysts such as Pt, Pd and Ru supported on active carbon, polymers and metal oxides, and Raney-Ni catalysts. However, for most catalysts used right now that have high catalytic activity in the CNB hydrogenation reactions, the selectivity of CAN is unsatisfactory, unless special supports such as SnO₂ and Fe₂O₃ are used or modification of metal catalysts by other metal cations. Due to the high cost of noble metal catalysts and the unsatisfactory selectivity of Raney Ni catalyst, much attention have been paid to develop a much cheaper and more selective catalyst which are also highly active in hydrogenation reactions. Supported Ni catalysts have long been used in steam reforming of hydrocarbons, dehydrogenation, especially in hydrogenation reactions owing to their high catalytic activity and rather low price, but they are less studied in selective hydrogenation of CNBs. Encouraged by this, we focus on the preparation and use of supported Ni catalysts in chloronitrobenzene hydrogenation reactions.

Carbon materials are widely used as metal catalyst support in heterogeneous catalysis, among which, CNTs, a new form of carbon, have attracted great attention due to their intrinsic properties such as high surface area, unique electronic properties and chemical inertness. Some studies have shown that they are promising alternative support materials for many metal catalysts, especially for catalysts used in liquid-phase hydrogenation reactions in which CNTs-support catalysts show high performance. Planeix et al. showed that Ru/CNTs catalysts exhibited higher activity and cinnamyl alcohol selectivity in liquid phase cinimmaldehyde hydrogenation than Ru catalysts supported on active carbon and Al₂O₃. As such, much attention has been paid to the preparation and use of CNTs support metal catalysts, however, the synthesis of highly dispersed and highly active CNTs support metal catalyst is still a challenge due to its chemical inertness. In this paper, we report the synthesis of highly dispersed CNTs support nickel catalysts using the deposition precipitation (DP) method with the mediation of glycerol. The as-synthesized Ni/CNTs catalysts showed excellent catalytic activity and selectivity in chloronitrobenzene hydrogenation reactions.

Experimental

The employed CNTs (the o.d.: 40-60 nm, specific surface area: 67 m²/g) were bought from Shenzhen Nano-Technologies Port Co., Ltd., and the commercially available activated carbon (1037 m²/g) were purchased from Beijing Broad Activated Carbon Co., Ltd.. Before use, the CNTs and AC were first oxidized in mixed acids of HNO₃ and H₂SO₄ at 120 °C for 4 h, and washed with water several times until the pH of the filtrate was 7, then dried at 100 °C over night.

Catalyst preparation

For deposition precipitation, the CNTs supported Ni catalysts were prepared as follows: the oxidized CNTs support was mixed with nickel acetate ($\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$) in glycerol, and the mixture was then stirred to obtain a homogeneous black solution which was heated to a certain temperature (80-160 °C) under stirring, at the meanwhile, a certain amount of 0.2 M Na_2CO_3 aqueous solution was added dropwise to the solution, after that, the mixture was agitated at that temperature for 1 h. Finally, the mixture was filtered and washed thoroughly with deionized water and ethanol, after being dried at 90 °C for 12 h and finally calcined at 400 °C for 4 h, the samples were reduced in a flowing hydrogen-nitrogen mixture at 400 °C for 1 h. The catalysts were labeled as Ni/CNTs-Gy-T (T refers to the precipitation temperature, and Gy is glycerol).

For comparison, Ni/CNTs catalyst was also prepared by precipitation of nickel acetate dissolved in water with sodium carbonate aqueous solution at 80 °C using the same procedure described above. The sample was regarded as Ni/CNTs-H₂O-80.

Catalyst Characterization

The Ni content in catalyst was analyzed using inductively coupled plasma emission spectrometry (ICP-OES) (2000DV). The XRD patterns were recorded with a Rigaku D/MAX-2400 X-ray diffraction diffractometer equipped with a Cu $K\alpha$ X-ray source operating at 40 kV and 50 mA. The mean crystallite sizes of nickel were calculated from the Scherrer equation, where the particle shape factor was taken as 0.9. TEM images of Ni/CNTs catalysts were taken on a philips Tecnai G² 20 transmission electron microscope.

Catalytic activity measurement

The liquid phase hydrogenation of chloronitrobenzene was carried out in a 100 mL Parr 4843 auto clave reactor, which was charged with chloronitrobenzene (0.5 g) and the catalyst (0.1 g) in 50 mL ethanol. Air was flushed out by sweeping the system three times with hydrogen. The reaction mixture was stirred for 150 min at 140 °C. Products were analyzed using a Techcomp GC-7890 equipped with a SE-54 capillary column and a FID detector.

Results and discussion

The Ni/CNTs precursors prepared both in water and glycerol have been characterized by XRD techniques (Fig. 1). Precursors of Ni/CNTs-Gy-80 and Ni/CNTs-Gy-120 exhibit almost the same patterns in which no diffraction peaks of metallic Ni phases were detected. While for Ni/CNTs-Gy-160 precursor, a small and broad peak at around 10° corresponding to nickel hydroxide is revealed. Besides, a weak diffraction peak at 33.3° displayed in all precursors, also indicating the formation of nickel hydroxide.

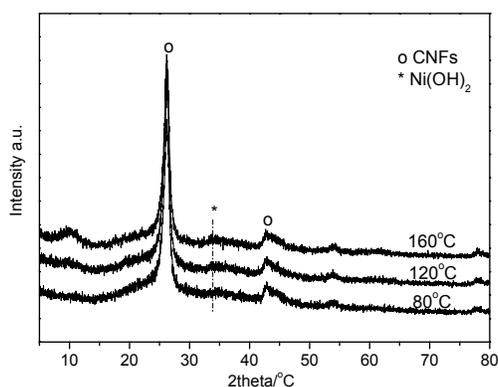


Figure 1. XRD Patterns of Ni/CNTs-Gy-T Precursors

For samples Ni/CNTs after calcination and reduction at 400 °C, XRD results are displayed in Fig. 2. Diffraction peaks at 44.4° are corresponding to Ni (111) face in all cases with the intensities vary considerably. For the catalyst Ni/CNTs-Gy-80, Ni (111) diffraction line is broad indicating rather small Ni particles, about 7 nm according to Scherrer Equation. While precipitation at 120 and 160 °C, Ni nanoparticle sizes of the obtained catalysts are larger, about 12 nm both.

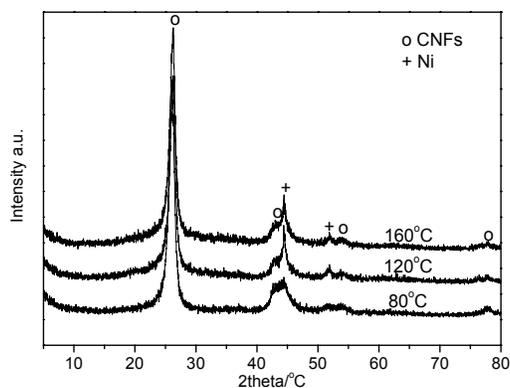


Figure 2. XRD Patterns of Ni/CNTs-Gy-T Catalysts

Fig. 3a shows the TEM image of Ni/CNTs-Gy-80 catalyst. The dispersion is good with particle sizes around 7 nm. Fig. 3b and 3c show the TEM images of Ni/CNTs-Gy-160 catalyst. Ni nanoparticles have an average diameter 8 nm and are highly dispersed on CNTs. However, in some parts of the sample, big Ni nanoparticles are also displayed, which can also be seen from the sharp diffraction line of Ni(111) face in the XRD patterns (Fig. 2). It is quite clear that the precipitation temperature indeed plays an important role in determining the particles size of Ni/CNTs-Gy catalysts.

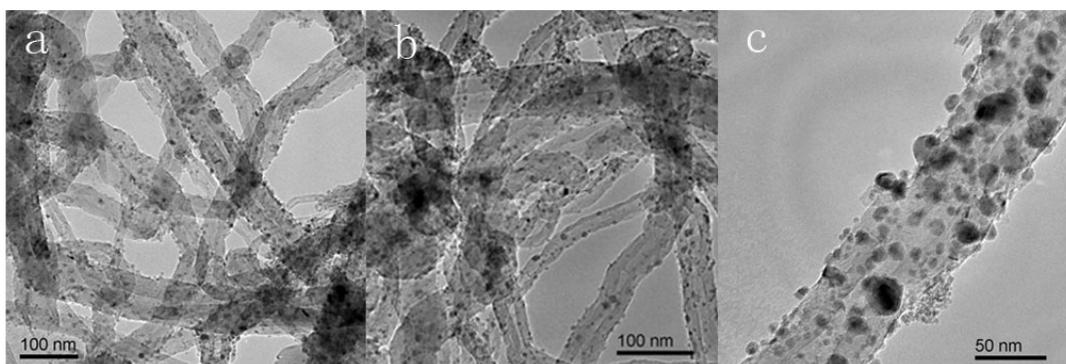


Figure 3. TEM Images of (a) Ni/CNTs-Gy-80 and (b), (c) Ni/CNTs-Gy-160 Catalysts

The hydrogenation of *o*-CNB was selected as the probe reaction to test the activities and selectivities of the Ni/CNTs catalysts and the results are listed in table 1. There was a remarkable difference of specific activity over different catalysts. Ni/CNTs-Gy-80 showed the lowest activity among all the Ni/CNTs-Gy-T catalysts, the conversion of *o*-CNB was 89% in 150 min, with 97% selectivity towards *o*-CAN. When Ni/CNTs-Gy-120 and Ni/CNTs-Gy-160 catalysts were used in the reaction, very high activities were achieved, the conversions of *o*-CNB were 97% and 99% respectively, with selectivity of *o*-CAN over 97%. For comparison, Ni/CNTs-H₂O-80 was also tested in the hydrogenation reaction. The activity was lower than Ni/CNTs-Gy-T catalysts with conversion of *o*-CNB 69%, and the selectivity to *o*-CAN 97%.

Table 1. Catalytic properties of Ni/CNTs catalysts

Catalyst	Ni loading / wt%	Particle size / nm	Conv. / %	Sel. / %
Ni/CNTs-Gy-80	2.9	7	89	97
Ni/CNTs-Gy-120	4.7	12	97	97
Ni/CNTs-Gy-160	5.2	12	99	97

Ni/CNTs-H ₂ O-80	4.4	11	69	97
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Reaction conditions: P=2 MPa, T=140 °C, t=150 min

Ni contents of all the Ni/CNTs catalysts were analyzed using ICP techniques, the results of which were also listed in table 1. Ni loading amounts of Ni/CNTs-Gy-T catalysts increased with the increase of precipitation temperature, which maybe caused by the decrease of glycerol viscosity with temperature favors the deposition of Ni species on CNTs surface. As such, Ni content of Ni/CNTs-H₂O-80 catalyst is higher than that of Ni/CNTs-Gy-80.

Conclusions

We have reported Ni/CNTs catalyst prepared by deposition precipitation in glycerol with good dispersion and controlled particle size of nickel. The catalysts show very good activity and selectivity for hydrogenation of chloronitrobenzenes to the corresponding chloroanilines. Precipitation temperature was found to play an important role in determining the crystalline size of Ni nanoparticles and the catalytic activity of the as-synthesized catalyst. The results show that the as-synthesized Ni/CNFs catalysts are of great potential as cheap and highly active catalysts for production of chloroanilines.

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