# Preparation, Characterization, and Catalytic Properties of Bimetallic NiCoB Nanoalloy Catalysts for Hydrogenation of *p*-chloronitrobenzene

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## Introduction

Aromatic halo-amines are important materials in the chemistry of dyes, pharmaceuticals, pesticides, etc. They are mainly produced by the selective hydrogenation of the corresponding nitro compounds over heterogeneous metal catalysts. Dehalogenation has been studied to occur with palladium and platinum, rhodium, nickel and copper chromite catalysts. Depending on the halogen and its position relative to nitro group in the aromatic system, dehalogenation can vary from negligible to 100%. In order to achieve high yields of haloanilines, several approaches have been developed either by controlled preparation of catalysts or the use of specific additives.

Hydrogenation of *p*-chloronitrobenzene (*p*-CNB) has been known to be an important industrial process. It is usually catalyzed by two classes of solids: noble metals such as platinum, palladium, ruthenium, rhodium; and Raney nickel [1–3]. Recently, several researchers realized that ultrafine amorphous alloy particles could be new catalytic materials that exhibit attractive selectivity and activity for some reactions. The nanocatalysts have more surface atoms and a higher concentration of highly coordinated unsaturated sites. Bimetallic catalysts have been studied to discover the relationship between catalytic activity and the metal structure. Many types of stable bilmetallic particles have been reported, such as platinum–copper, platinum–rhodium, palladium–nickel, platinum–cobalt, etc. However, very few on nickel–cobalt catalysts have been reported. In 1997, Shen et al. [4] reported the structure of ultrafine Ni–Co–B amorphous alloy by analysis of the extended X-ray absorption fine structure spectra and concluded that the catalytic activity for hydrogenation of benzene of the ternary amorphous alloy Ni–Co–B is related to both nickel content and the structural disorder, the latter is mainly adjusted by the cobalt content. They also pointed out that cobalt acted as a chemical modifier and it may have caused a structural change or electronic effect on Ni–B amorphous.

The aim of the present study is to prepare a series of nanosized NiCoB amorphous alloy catalysts by chemical reduction method with various compositions of starting materials. The materials were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), differential scanning calorimetry (DSC), and X-ray photoelectron spectroscopy (XPS). The catalytic activity of the materials was investigated for liquid phase dehydrogenation of *p*-CNB.

## Materials and Methods

*p*-CNB (99%), nickel acetate tetrahydrate (>98%) and cobalt acetate tetrahydrate (>98%), sodium borohydride (>99%) and methanol (>99.9%) were used. High purity hydrogen gas (>99%) was used without further purification. Double distilled water was used for the synthesis of catalysts. XRD measurements were recorded over the range $2\theta = 5$–$60°$ to identify amorphous structure. TEM was operated at 160 kV to determine the morphologies of the materials. DSC was conducted under a nitrogen atmosphere. XPS spectra were recorded at 23.5 eV pass energy using Al Kα radiation.

## Results and Discussion

The composition of the starting materials significantly influenced the morphology and particle size of the NiCoB amorphous catalysts, subsequently affecting the surface areas of the catalysts. The presence of smaller particles in NiCoB catalyst indicates that cobalt can reduce the particle size of nickel catalyst and improve the metal dispersion. The addition of cobalt facilitates the precipitation of boron in the catalysts. Moreover, it would suppress the growth of the crystalline structure of NiB and helps to retain its amorphous nature. The content of elemental nickel increased with an increase in cobalt loading. However, it tends to decrease at higher loading. An electron transfer between neighboring elemental nickel and elemental boron in NiB catalyst can be observed as boron donates electrons to the alloying nickel. Addition of small amount of cobalt increased the conversion of *p*-CNB, but decreased the selectivity of *p*-CAN.

**Table 1. The effect of various cobalt content on the hydrogenation of *p*-CNB over NiB and NiCoB catalyst**

| Sample | Reaction Time (min) | *p*-CNB conversion [a] (%) | Selectivity [b] (%) | | |
|---|---|---|---|---|---|
| | | | AN | NB | *p*-CAN |
| NiB | 70 | 100 % | 9.94 % | 0 % | 90.06 % |
| NiCoB(1:0.1) | 40 | 100 % | 15.01 % | 0.68 % | 84.30 % |
| NiCoB(1:0.3) | 30 | 85.22 % | 4.79 % | 1.60 % | 78.82 % |
| NiCoB(1:1) | 100 | 100 % | 5.45 % | 0 % | 94.55 % |
| NiCoB(1:3) | 170 | 100 % | 3.63 % | 0.22 % | 96.15 % |

[a] Reaction condition: 1.2 MPa hydrogen pressure, 373 K reaction temperature, absolute methanol was medium, 500 rpm stirring speed, 0.2M p-CNB and 2 mmol Ni catalyst
[b] AN: aniline; NB: nitrobenzene; *p*-CAN: *p*-chloroaniline

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