



# Effect of Co-B supporting methods on the hydrogenation of *m*-chloronitrobenzene over Co-B/CNTs amorphous alloy catalysts

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## ABSTRACT

Carbon nanotubes (CNTs)-supported Co-B amorphous alloy catalysts, with selective deposition of Co-B particles inside or outside of CNTs (labeled as Co-B-in/CNTs and Co-B-out/CNTs), were prepared based on the difference in the interface energies of organic and aqueous solutions with the CNTs surface. The catalysts were tested for the liquid-phase hydrogenation of *m*-chloronitrobenzene (*m*-CNB) to *m*-chloroaniline. Compared with Co-B-out/CNTs, Co-B-in/CNTs shows smaller, homogeneous size, and greatly improved thermal stability. The hydrogenation of *m*-CNB over Co-B-out/CNTs occurs on the outside of CNTs, while the hydrogenation of *m*-CNB over Co-B-in/CNTs occurs in the nanospace inside of CNTs. Co-B-in/CNTs exhibits a much higher activity than Co-B-out/CNTs.

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## 1. Introduction

Selective hydrogenation of chloronitrobenzenes (CNBs) to the corresponding chloroanilines (CANs) is a major reaction in the synthesis of various fine chemicals [1,2]. Ni-B and Ni-P, as two representatives of metal-metalloid amorphous alloy catalysts used in the hydrogenation of CNBs, have been studied in detail [3–5]. In contrast, cobalt salt, an example of a Co-B amorphous alloy catalyst, has been seldom investigated for the hydrogenation of CNBs. Cobalt-based catalysts are important in catalytic fields and are widely used in Fischer–Tropsch synthesis [6,7] and selective hydrogenation [8,9]. As reported, Co/SiO<sub>2</sub> catalysts show exceptionally high activity and selectivity for the hydrogenation of nitro-substituted aromatics, such as nitrobenzene, 3-nitrophenol, and 3-nitro-*o*-cresol [10]. A facile solvothermal method for preparation of Co/C catalysts has shown high activity and selectivity for CNBs hydrogenation and could be used for magnetic separable catalysts [11].

Amorphous alloys are long-range disordered, but have short-range ordered structures, which are responsible for excellent catalytic properties compared with their crystalline counterparts. However, the amorphous structures are thermodynamically metastable and crystallization can occur spontaneously during

reactions, even at very low temperatures, resulting in an abrupt decrease in activity. Therefore, it is very important to improve the thermal stability to slow down crystallization. Supported amorphous alloy catalysts have been proven to be promising in industrial applications, owing to the great improvement of the surface active area and thermal stability caused by the high dispersion of amorphous alloy particles on the support and the strong metal-support interaction [12].

Recently, carbon nanotubes (CNTs) have received considerable attention in heterogeneous catalysis due to their high mechanical strength, large surface area, hollow geometry, and unique physical morphology [13–15]. As reported, CNTs used as cobalt-based catalyst supports allow for better metal dispersion control and minimization of the metal phase interaction (formation of mixed compounds) with the support [16]. Therefore, it is of great importance to study the application of CNTs-supported Co-B amorphous alloy catalysts for CNBs hydrogenation. In this work, with CNTs as the support, we selectively deposited Co-B amorphous alloy particles, inside or outside of CNTs, to prepare Co-B/CNTs catalysts (labeled as Co-B-in/CNTs and Co-B-out/CNTs) and studied the selective hydrogenation of *m*-CNB to *m*-CAN. Compared with Co-B-out/CNTs, the particle aggregation of Co-B in Co-B-in/CNTs was limited by the geometric space of CNTs, which improved the thermal stability of amorphous alloy particles, while the internal space of CNTs can be regarded as a special nanoreactor, helpful for improving the hydrogenation activity of *m*-CNB.

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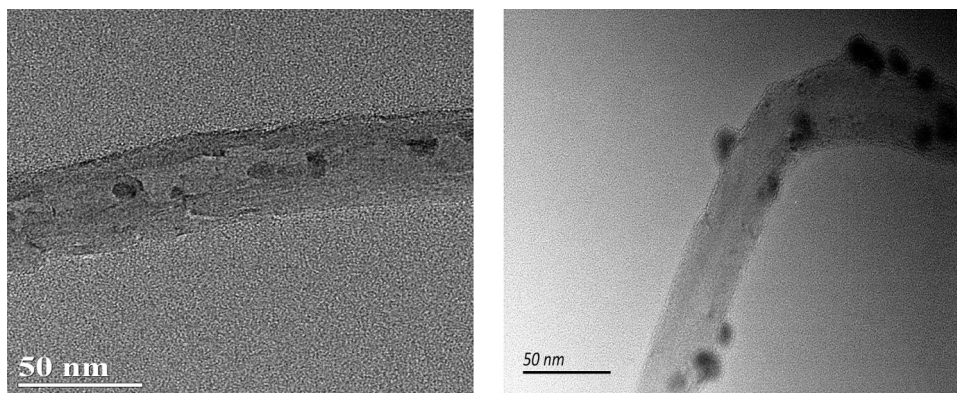


Fig. 1. TEM micrographs of (a) Co-B-in/CNTs; (b) Co-B-out/CNTs.

## 2. Experimental

### 2.1. Catalyst preparation

Based on the research of Tessonier et al. [17], we selectively deposited Co-B amorphous alloy particles inside or outside of CNTs. CNTs were placed into concentrated  $\text{HNO}_3$  with reflux for 6 h, followed by suction filtration, washing, and drying to get purified CNTs. The saturated water absorption rate of the purified CNTs was measured to be 5.23 ml/g. Based on the difference in the interface energies of ethanol and water with the CNTs surface,  $\text{CoCl}_2$  can be selectively deposited inside or outside of the CNTs. For the Co-B-in/CNTs catalyst, 1.0 g of CNTs was impregnated with 3.5 ml of  $\text{CoCl}_2$  ethanol solution (about 2/3 of CNTs saturated water absorption rate). Then 2.6 ml of  $\text{H}_2\text{O}$  was added (about 1/2 of CNTs saturated water absorption rate). After being dried, the  $\text{CoCl}_2$ -in/CNTs precursor was reduced by adding  $\text{KBH}_4$  solution ( $\text{Co}^{2+}:\text{BH}_4^-$  molar ratio 1:3) dropwise with vigorous stirring in an ice-water bath. The resulting Co-B-in/CNTs sample was first washed thoroughly with distilled water until pH 7 was reached, and then washed with absolute ethanol. Finally, the obtained catalyst was kept in absolute ethanol for future use. The Co theoretical loading was 10 wt%. For the Co-B-out/CNTs catalyst, 1.0 g of CNTs was impregnated with 5.2 ml of ethanol. Then, 3.5 ml of  $\text{CoCl}_2$  aqueous solution was added. After being dried, the other steps were performed the same as for the Co-B-in/CNTs catalyst.

### 2.2. Catalyst characterization

The shape and morphology of the catalysts were observed through transmission electron microscopy (TEM, JEOL JEM-4000EX). The structures of the as-prepared catalysts, before and after heat treatment, were determined by X-ray powder diffraction (XRD, Rigaku, D/max-2200). Thermal stability was analyzed

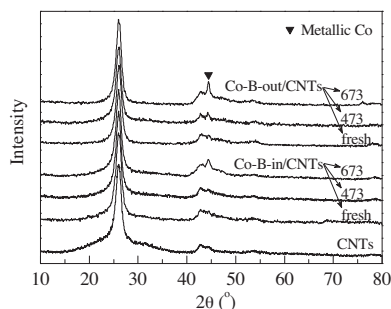


Fig. 2. XRD patterns of CNTs, Co-B-in/CNTs and Co-B-out/CNTs treated at different temperature in  $\text{N}_2$  flow for 2 h.

using a differential scanning calorimeter (DSC, Nezhsc Corp, 200 F3) under  $\text{N}_2$  atmosphere at a heating rate of 10 K/min. Temperature programmed desorption with hydrogen ( $\text{H}_2$ -TPD) analyses were performed on a CHEMBET 3000 (Quantachrome Instrument Corp.) coupled with a thermal conductivity detector. The Co loading (wt%) and the Co-B alloy composition (at%) were analyzed by means of an inductively coupled plasma spectrometer (ICPS-7510, Shimadzu) and X-ray photoelectron spectrometer (XPS, ThermoFisher Scientific, K-Alpha). The specific surface areas of the catalysts were determined by  $\text{N}_2$  adsorption with a TristarII3020 surface area and porosity analyzer (Micromeritics Instrument Corp.).

### 2.3. Catalytic hydrogenation activity test

Catalytic hydrogenation of *m*-CNB was conducted in a 100 ml high pressure reactor with a magnetic stirrer. Before the reaction, 0.05 g of catalyst and 20 ml of  $5 \times 10^{-2}$  mol/L *m*-CNB ethanol solution were added to the reactor. The air in the reactor was replaced with  $\text{H}_2$  6 times to ensure that there is no air was present. The pressure in the reactor was regulated at 2 MPa, and the high pressure reactor was put into an oil bath with gradual heating to 413 K. Then, the stirrer was turned on at a stirring speed of 1000 rpm, when the pressure in the reactor was balanced to eliminate the effect of diffusion on dynamics. This action was performed at constant temperature for 3 h. After centrifugal separation, the liquid-phase products were analyzed with a gas chromatograph (GC, Shimadzu GC-14C, FID, SE-30 capillary column), and were identified by gas chromatography/mass spectrometry (GC/MS, Agilent 5890).

## 3. Results and discussion

The TEM image of Co-B-in/CNTs catalyst (Fig. 1(a)) clearly shows that the Co-B amorphous alloy particles are well confined within the channels of CNTs. While the Co-B amorphous alloy particles of Co-B-out/CNTs catalyst are clearly dispersed on the outer surface of CNTs (Fig. 1(b)). The sizes of Co-B amorphous alloy particles in Co-B-in/CNT catalyst are uniform (about 11 nm), while those in Co-B-out/CNTs catalyst are non-uniform and range from 13 to 24 nm.

The XRD patterns (Fig. 2) revealed that the purified CNTs exhibited three distinct characteristic diffraction peaks at  $2\theta = 26.1^\circ$ ,  $43.1^\circ$  and  $53.5^\circ$ , which correspond to the diffraction of three crystal faces (002), (100) and (004) of the graphited carbon tube wall [18,19], respectively. For the fresh Co-B-in/CNTs catalyst, except for the diffraction peaks of CNTs, no other crystalline peak in the sample is observed, indicating that the Co-B is present as an amorphous [20,21]. The Co-B alloy, when in the amorphous structure, shows a weak and broad characteristic diffraction peak at  $2\theta = 44^\circ$  [22–24]. In the Co-B-in/CNTs catalyst, CNTs show a strong diffrac-

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