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Catalytic properties of bimetallic NiCoB nanoalloy catalysts for hydrogenation of *p*-chloronitrobenzene

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Abstract

Nanosized NiCoB amorphous alloy catalysts with Co/Ni ratios varying from 0 to 3 were prepared by chemical reduction of nickel acetate and cobalt acetate with sodium borohydride in methanolic solution at room temperature under N_2 gas with vigorous stirring. The catalysts were characterized by nitrogen sorption, X-ray diffraction (XRD), transmission electron microscopy (TEM), differential scanning calorimetry (DSC), and X-ray photoelectron spectroscopy (XPS). NiCoB catalysts were tested for liquid-phase hydrogenation of *p*-chloronitrobenzene (*p*-CNB). The liquid-phase hydrogenation of *p*-CNB was carried out at 1.2 MPa hydrogen pressure, 373 K reaction temperature, methanol as reaction medium, 500 rpm stirring speed, 0.2 M *p*-CNB and 2 mmol Ni catalysts. The molar ratios of Co/Ni in the starting materials affected the concentrations of boron bounded to the nickel and cobalt metals, resulting in the change of surface area, electronic structures of the metals and catalytic activities of the catalysts. Nickel is enriched on the surface. Doping Co in NiB decreased the particle size and increased the stability of the NiCoB amorphous alloys. Doping Co in NiB increased the boron content, which in turn increased the electron density of Ni. The sample NiCoB(1:0.1) (the value in the bracket is the Ni:Co ratio in bulk) had the highest surface area of 23.5 m^2/g and the smallest particle size. TEM micrographs show that Co can reduce the particle size of NiB catalyst. DSC patterns demonstrated that the addition of cobalt suppressed the growth of crystalline structure of NiB. Adding small amount of cobalt to the NiB catalyst increased the surface area and reaction activity, but decreased the selectivity for the desired product, *p*-chloroaniline (*p*-CAN). However, overdosed cobalt had an opposite effect on Ni catalyst, i.e., reduced the reaction activity and increased the selectivity for *p*-CAN. The Co-dopant could weaken the extent of electron donation from the Ni atoms to the aromatic ring in *p*-CAN, which would further suppress the hydrodechlorination of *p*-CAN. The selectivity for *p*-CAN was also a function of conversion of *p*-CNB. Based on the electron transfer between elemental nickel and boron, NiCoB(1:0.1) had the most d-band electrons and the highest activities in hydrogenation of nitro group and dechlorination. The results can be interpreted by the electronegativity of the functional groups.

Keywords: NiCoB amorphous alloy; Nanometal; Nickel boride; *p*-Chloronitrobenzene; Liquid-phase hydrogenation

1. Introduction

Hydrogenation of halo-nitroaromatics to the corresponding halo-anilines was at one time a formidable problem, which has now found satisfactory solutions practiced industrially on a large scale. Aromatic halo-amines are used extensively in industrial applications in the production of fine chemicals, i.e., dyes, herbicides, pesticides, etc. The main route for their production is the selective hydrogenation of the corresponding nitro compounds over heterogeneous metal catalysts. Dehalogenation has been found to occur with palladium [1–3], platinum [1–3], rhodium [4], nickel [5], and copper chromite [6] catalysts. Among these, palladium, platinum, and rhodium are noble metals, which limit their implementation to industrial applications because of cost-effectiveness.

Depending on the halogen and its position relative to the nitro group in the aromatic system, dehalogenation can vary from negligible to 100%. In order to achieve high yields of halo-anilines, many approaches have been developed either by controlled preparation of the catalysts (alloying [7], controlling the metal particle dispersion and metal–support interaction [8], etc.) or the use of specific additives (promoters or inhibitors) [9–11].

In the reaction of *p*-chloronitrobenzene (*p*-CNB), its nitro group may be hydrogenated or it may be dehalogenated (see Fig. 1). Yu and Liu [12] have reported the selective hydrogena-

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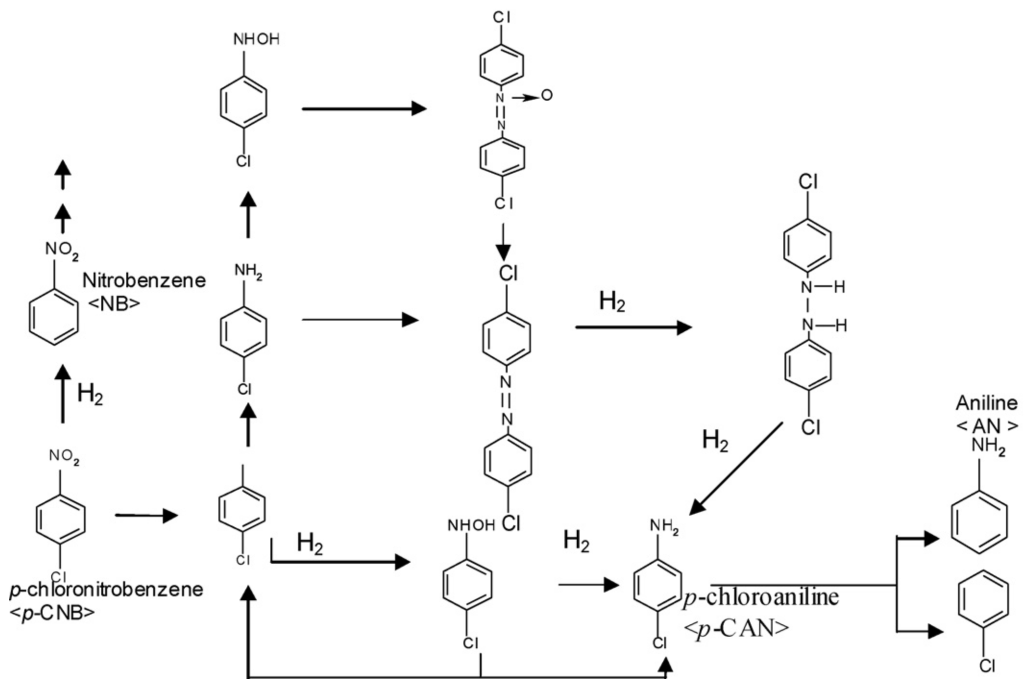

Fig. 1. Reaction scheme of hydrogenation of *p*-CNB.

tion of *o*-chloronitrobenzene to *o*-chloroaniline on Pt catalysts. Besides the desired product *o*-chloroaniline, many byproducts such as aniline, nitrobenzene, *o*-chlorophenylhydroxylamine, *o*-chloronitrosobenzene, azo- and azoxy-dichlorobenzenes, and chlorobenzene were formed at the same time.

Hydrogenation of *p*-CNB has been known to be an industrially important process. It is usually catalyzed by two classes of solids: noble metals, such as platinum, palladium, ruthenium, rhodium, and Raney nickel [13–15].

Nanoparticles exhibit unique and excellent properties from a fundamental and technological viewpoint. Recently, more and more researchers realized that ultrafine amorphous alloy particles could be new catalytic materials that exhibit attractive selectivity and activity for some reactions [16–19]. The nanocatalysts have more surface atoms and a higher concentration of highly coordinated unsaturated sites. Studies on ultrafine amorphous alloy particles have attracted much attention because of their interesting intrinsic properties, e.g., short-range order, long-range disorder, and high dispersion, as well as their potential applications, e.g., in powder metallurgy, magnetic materials, catalysts, and ferrofluids. The powder samples obtained by chemical reduction are highly dispersed and can be compacted to serve for different purposes. The ultrafine amorphous alloy powders combine the features of amorphous and ultrafine powder and have properties that are of interest in catalysis: (1) the presence of a large number of coordinatively unsaturated surface sites, (2) the lack of crystal defects, and (3) the isotropic, single phase nature of the materials. Nanosized Ni catalyst modified with boron has been reported to be a good catalyst for the hydrogenation of nitrobenzene and furfural [15,20–23]. In order to implement amorphous metal alloys as catalysts, some problems need to be solved. One problem among them is to find a method for increasing the surface area of the amorphous alloy and stabilizing the amorphous state during the reaction process. In other words, to produce smaller particles at nano scale and to enhance the thermal stability of catalysts are the focus of many researches on amorphous catalysts. The catalytic properties are highly dependent upon the preparation method [24,25]. Many systematic studies have been made on catalytic properties for NiB catalysts [26–33].

Bimetallic catalysts have been studied to discover the relationship between catalytic activity and the metal structure [34]. Many types of stable bimetallic particles have been reported, such as platinum–copper [35], platinum–rhodium [36], rhodium–gold [36], palladium–copper [37], palladium–gold [38], palladium–nickel [39], platinum–cobalt [40], etc. However, very few on NiCo catalysts have been reported [41–45]. Nitta et al. [41] investigated the formation of α, β-unsaturated alcohols from α, β-unsaturated aldehydes, finding that CoB catalysts has higher selectivity than NiB catalyst but that CoB catalyst has lower activity for the formation of olefins from acetylenes. The differences in the adsorption strength of reactants on Co and Ni metal resulted in the differences between the two catalysts. In 1997, Shen et al. [42] studied the structure of ultrafine NiCoB amorphous alloy by analysis of the extended X-ray absorption fine structure (EXAFS) spectra, and concluded that the catalytic activity of the ternary amorphous alloy NiCoB for the hydrogenation of benzene is related to both the 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 may have caused a structural change or electronic effect on the amorphous NiB. In the previous studies [25,46–49], the authors have reported the application of NiB catalysts in hydrogenation of *p*-CNB. They showed that the different preparation conditions affect the morphology, particle size, and surface area of the catalyst. The NiB catalyst