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Carbon dispersed copper-cobalt alloy nanoparticles: A cost-effective heterogeneous catalyst with exceptional performance in the hydrolytic dehydrogenation of ammonia-borane

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ABSTRACT

Herein, we report the development of a new and cost-effective nanocatalyst for the hydrolytic dehydrogenation of ammonia-borane (NH_3BH_3), which is considered to be one of the most promising solid hydrogen carriers due to its high gravimetric hydrogen storage capacity (19.6 wt%) and low molecular weight. The new catalyst system consisting of bimetallic copper-cobalt alloy nanoparticles supported on activated carbon was simply and reproducibly prepared by surfactant-free deposition-reduction technique at room temperature. The characterization of this new catalytic material was done by the combination of multi-pronged techniques including ICP-MS, XRD, XPS, BFTEM, HR-TEM, STEM and HAADF-STEM-line analysis. The sum of their results revealed that the formation of copper-cobalt alloy nanoparticles ($d_{mean} = 1.8$ nm) on the surface of activated carbon (CuCo/C). These new carbon supported copper-cobalt alloy nanoparticles act as highly active catalyst in the hydrolytic dehydrogenation of ammonia-borane, providing an *initial* turnover frequency of TOF = 2700 h^{-1} at 298 K, which is not only higher than all the non-noble metal catalysts but also higher than the majority of the noble metal based homogeneous and heterogeneous catalysts employed in the same reaction. More importantly, easy recovery and high durability of these supported CuCo nanoparticles make CuCo/C recyclable heterogeneous catalyst for the hydrolytic dehydrogenation of ammonia-borane. They retain almost their inherent activity even at 10th catalytic reuse in the hydrolytic dehydrogenation of ammonia-borane at 298 K.

1. Introduction

Hydrogen has been considered as a promising and clean energy carrier [1,2] for our future society as it has a high energy density (142 MJ/kg) almost three times higher than that of natural gas (55 MJ/kg) and only water plus small amounts of heat are the byproducts when it is utilized in proton exchange membrane fuel cells (PEMFC) [3,4]. Although there has been enormous efforts to develop suitable hydrogen storage and releasing materials in the last few decades, the efficient storage and production of hydrogen are still two key problems in the "Hydrogen Economy" [5]. Among the new hydrogen storage materials [6,7], ammonia-borane (H_3NBH_3, AB) appears to be the most promising material for this purpose [8] because of its low molecular weight (30.9 g/mol), high stability under possible fuel cell applications, nontoxicity, and high hydrogen density (19.6 wt%), which is greater than the 2015 target of U.S. Department of Energy (5.5 wt% H_2) [9]. To date thermal decomposition [10], alcoholysis [11] or dehydrocoupling [12] have been demonstrated to provoke the hydrogen release from AB. Although, difficulties in the regeneration of hydrolysis products due to the strong B—O bonds, there is much interest in the transition-metal-catalyzed hydrolytic dehydrogenation of AB (**1**) due to favorable kinetics and mild reaction conditions [13].

$$H_3NBH_3 + 2H_2O \rightarrow NH_4BO_2 + 3H_2 \quad (1)$$

The literature survey shows that various homogeneous [8] and heterogeneous [13–16] catalysts have already been tested in the hydrolytic dehydrogenation of AB. Although, some of homogeneous catalysts provide high activities and selectivities in the

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hydrolytic dehydrogenation of AB, the difficulties met during their isolation-recovery steps hinder their practical application for onboard systems. At this concern, because of the advantages of nanocatalysis [17], the current research has been concentrated on the development of metal nanoparticles (NPs) possessing high activity and reusability in the hydrolytic dehydrogenation of AB. Among tested heterogeneous catalysts precious metals (such as Rh [18–21], Pt [18,19] and Au [22–24]) based systems provide remarkable activities in the hydrolytic dehydrogenation of AB. However, the concerns over the practical use of these high cost metals have motivated the research for the development of low cost catalyst systems in the hydrolytic dehydrogenation of AB. In this context, the recent studies have revealed that heterogeneous catalysts of low-cost 3d metals such as Fe [25–27], Co [28–37], Ni [38–44] and Cu [45–48] can catalyze the hydrolytic dehydrogenation of AB. Unfortunately, most of these low-cost catalytic systems suffer from low activity and reusability performance. Hereof, the development of highly active and reusable heterogeneous catalysts based on low-cost 3d metals is clearly a desired goal for this important reaction.

In this study, we report a facile synthesis of bimetallic copper-cobalt alloy NPs supported on activated carbon, hereafter referred to as CuCo/C, and their excellent catalysis in the hydrolytic dehydrogenation of AB. CuCo/C catalyst was simply and reproducibly prepared through surfactant-free deposition-reduction technique [49] at room temperature, and characterized by inductively coupled plasma-optical emission spectroscopy (ICP-OES), powder X-ray diffraction (PXRD), high resolution X-ray photoelectron spectroscopy (HRXPS), bright field transmission electron microscopy (BFTEM), high resolution transmission electron microscopy (HRTEM), scanning transmission electron microscopy (STEM) and high angle annular dark field-scanning transmission electron microscopy (HAADF-STEM). The sum of their results revealed that the formation of well-dispersed 1.8 ± 0.4 nm CuCo alloy NPs on the surface of activated carbon. These new CuCo alloy NPs provide exceptional activity (TOF = 2700 h^{-1}) and reusability (>95% activity and >90% conversion at 10th reuse) performance in the hydrolytic dehydrogenation of AB at room temperature. Moreover, the excellent durability of supported CuCo alloy NPs against to sintering and leaching make CuCo/C reusable catalyst for the hydrolytic dehydrogenation of AB.

2. Experimental

2.1. Materials

Copper(II) chloride dihydrate ($CuCl_2{\cdot}2H_2O$), cobalt(II) sulfate heptahydrate ($CoSO_4{\cdot}7H_2O$), ammonia-borane ($NH_3BH_3 \sim 90\%$), sodium borohydride ($NaBH_4$), boron trifluoride diethyl etherate ($BF_3{\cdot}(C_2H_5)_2O$) and activated carbon were purchased from Sigma–Aldrich®. Deionized water was distilled by water purification system (Milli-Q Water Purification System). All glassware and Teflon-coated magnetic stir bars were washed with acetone and copiously rinsed with distilled water before drying in an oven at 323 K.

2.2. Characterization

Cu and Co contents of the samples were determined by ICP-OES (Leeman, Direct Reading Echelle) after each sample was completely dissolved in a mixture of HNO_3/HCl (1/3 ratio). PXRD patterns were recorded with a MAC Science MXP 3TZ diffractometer using Cu-Kα radiation (wavelength 1.54 Å, 40 kV, 55 mA). BFTEM, HRTEM, STEM, and HAADF-STEM samples were pre-pared by dropping one drop of dilute suspension on copper coated carbon TEM grid and the solvent was then dried. BFTEM was carried out on a JEOL JEM-200CX transmission electron microscopes operating at 120 kV. HRTEM, STEM, and HAADF-STEM were run on a JEOL JEM-2010F transmission electron microscope operating at 200 kV. Oxford EDXS system and Inca software were used to collect and process STEM-EDX data. HRXPS analyses were performed on a Physical Electronics 5800 spectrometer equipped with a hemispherical analyzer and using monochromatic Al-Kα radiation (1486.6 eV, the X-ray tube working at 15 kV and 350 W, and pass energy of 23.5 eV). ^{11}B NMR spectra were recorded on a Bruker Avance DPX 400 with an operating frequency of 128.15 MHz. D_2O and $BF_3{\cdot}(C_2H_5)_2O$ were used as a lock and an external reference, respectively. At the end of the catalytic reaction, the resulting solutions were filtered and the filtrates were collected for taking the ^{11}B NMR spectra.

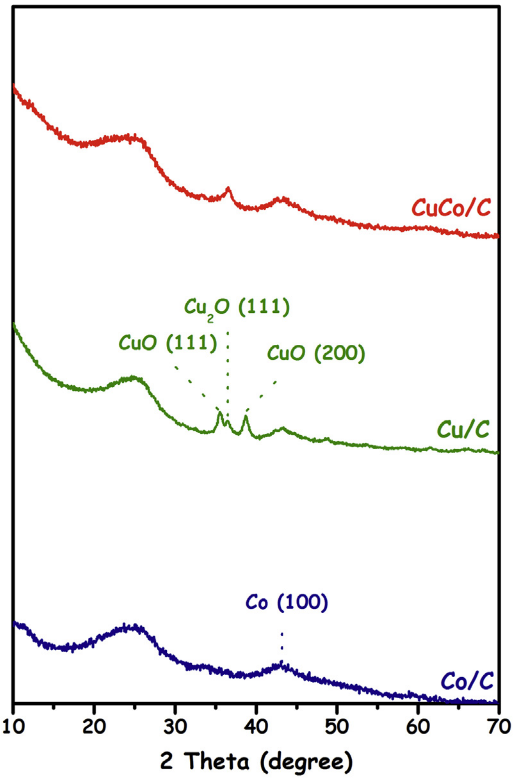

Fig. 1. The powder X-ray diffraction (P-XRD) patterns of Co/C, Cu/C and CuCo/C samples in the range of $2\theta = 10–70°$.

2.3. Preparation of CuCo/C catalyst

In a typical experiment, 5.0 mL of aqueous solution containing 24.0 μmol copper (4,09 mg $CuCl_2.2H_2O$) and 24.2 μmol cobalt (6,8 mg $CoSO_4.7H_2O$) is mixed with activated carbon (140 mg) at 400 rpm for 2 h. Then, 1.0 mL aqueous solution of $NaBH_4$ (27.8 mg, 0.60 mmol) was added to this mixture and the resulting solution was stirred for half an hour under air at room temperature. After centrifugation (6000 rpm, 5 min.), copious washing with water (3 × 20 mL), filtration, and drying in vacuum oven at 323 K under 10^{-2} Torr, CuCo/C catalyst was obtained as powder and stored under argon atmosphere in the glovebox.

2.4. Determination of the catalytic activity of CuCo/C Catalyst in the hydrolytic dehydrogenation of ammonia-borane

The catalytic activity of CuCo/C catalyst in the hydrolytic dehydrogenation of AB was determined by measuring the rate of hydrogen generation. The volume of released gas during the reac-