rGO supported PdNi-CeO$_2$ nanocomposite as an efficient catalyst for hydrogen evolution from the hydrolysis of NH$_3$BH$_3$

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ABSTRACT

The hydrogen economy is a proposed system that utilizes hydrogen to deliver energy. For the realization of this concept, how to safely, controllably and reversibly store and release hydrogen are critical problems which must be resolved. Metal alloys combined with suitable support materials are widely applied to various catalytic reactions. Here palladium nickel bimetallic nanoparticles doped with cerium oxide on a reduced graphene oxide (rGO) support were prepared by combining metal ion precursors and graphene oxide in a one-pot co-reduction approach. The as-received catalysts were characterized by XRD, TEM, SEM, XPS and ICP-OES, and the results revealed that PdNi-CeO$_2$ nanoparticles were uniform dispersal on rGO. The as-synthesized PdNi-CeO$_2$/rGO had been adopted as a heterogeneous catalyst for the hydrogen evolution from the hydrolysis of ammonia borane (NH$_3$BH$_3$, AB) at room temperature. Kinetically, the hydrogen-release rate was first-order with the increased concentration of catalysts. The optimized catalyst of Pd$_{0.8}$Ni$_{0.2}$-CeO$_2$/rGO with the CeO$_2$ content of 13.9 mol% exhibited an excellent activity with a turnover frequency value of 30.5 mol H$_2$ (mol catalyst)$^{-1}$ min^{-1} at 298 K, and a low apparent activation energy (E_a) of 37.78 kJ mol^{-1}. The robust catalytic performance of the Pd$_{0.8}$Ni$_{0.2}$-CeO$_2$/rGO is attributed to the uniform controlled nanoparticle size, the synergic effect between the nanoparticles bimetallic properties, and the effective charge transfer interactions between the metal and support.

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Introduction

Hydrogen has been regarded as the energy carrier of the future due to its merits as a zero-carbon emitter which can be readily oxidized in a fuel cell to produce locally generated electricity, eliminating transportation efforts [1,2]. However, efficiently storing hydrogen remains a major challenge for the implementation of the hydrogen economy, since hydrogen has a very low volumetric density under the ambient conditions [3]. Therefore, the development of an effective means of hydrogen storage and controlled release under mild conditions is still critical [4–6]. Among the reported chemical hydrogen storage reagents, ammonia borane (NH_3BH_3, AB) is considered as a perfect candidate in light of its outstanding hydrogen storage content (19.6 wt %), good stability in the aqueous solution and excellent volumetric density (146 g/L) [7,8]. More crucial is attaining a method of how to effectively release hydrogen from AB over a suitable catalyst under a moderate condition, which currently draws a lot of attention in the catalytic field [9,10]. The catalytic hydrolysis reaction can be represented by the following reaction (Eq. (1)) [11].

$$NH_3BH_3 + 2H_2O \xrightarrow{\text{catalyst}} NH_4^+ + BO_2^- + 3H_2 \qquad (1)$$
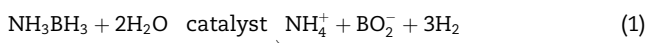
It is well documented that the noble metal Pd is among the most active catalysts for AB dehydrogenation [12,13]. Luo et al. reported ultrafine Pd nanoparticles (NPs) confined in the pores of MIL-101, a Cr(III)-based MOF, to promote the AB hydrolysis with a turnover frequency (TOF) value of 45 mol H_2 (mol Pd)$^{-1}$ min^{-1} [14]. Özkar et al. also demonstrated that Pd NPs supported on polydopamine-coated cobalt ferrite exhibited the good catalytic activity during AB dehydrogenation and high durability after 10 cycles of the catalytic reaction [15]. Although precious metal catalysts can achieve excellent catalytic activity, their practical applications are limited by their earth-scarcity and high cost. To decrease the employment of an expensive noble metal catalyst and maintain their high catalytic activity, an efficient strategy is to combine the expensive metal with an earth-abundant transition metal [16,17]. The strong synergic effects, between noble and transition metals, have been extensively studied for the bimetallic nanocatalysts. Owing to the intrinsic changes of the surface geometric or electronic properties, even a small amount of the bimetallic effect can result in an enhanced catalytic performance and selectivity, compared with the monometallic counterparts [18,19]. Previously, the doping of Pd NPs with Ni has been demonstrated to be feasible for boosting the catalytic efficiency for various reactions, such as Miyaura-Heck coupling [20] and dehydrogenation of AB [21]. However, the synthesis of PdNi alloys with a facile synthetic strategy, a high dispersion and excellent catalytic performance remains a challenge.

On the other hand, the catalytic activity for the hydrogen evolution could be greatly improved by coupling cerium oxide with the functional nanoparticles [22,23]. The interconversion nature of cerium oxide from cerium(III) and cerium(IV) will occur under a catalytic reaction, in which the existence of cerium(III) will induce a stronger coordination of metal nanoparticles, exposing more metal catalyst active sites [24,25]. However, metal-CeO_2 NPs tend to aggregate in the catalytic process. This can be resolved by immobilizing metal NPs on a support material, such as reduced graphene oxide (rGO). The performance of nanocatalysts supported on a suitable support material can be significantly enhanced by restraining the aggregation of nanoparticles, facilitating the electron and mass transport through the strong electronic perturbation of the catalytic sites [26–29]. Therefore, to achieve the enhancement on the catalytic efficiency and stability of the catalyst, we exploit the bimetallic nanocatalysts interacting with CeO_2, anchored on rGO for AB dehydrogenation.

Herein, for AB hydrolysis, PdNi-CeO_2/rGO catalysts had been optimized to be $Pd_{0.8}Ni_{0.2}$-CeO_2/rGO with the CeO_2 content of 13.9 mol%. The catalyst demonstrated a high TOF value of 30.5 mol H_2 (mol catalyst)$^{-1}$ min^{-1} and a low apparent activation energy (37.78 kJ mol^{-1}). In comparison with the controlled component of Pd-CeO_2/rGO, Ni-CeO_2/rGO, PdNi NPs, PdNi-CeO_2 and PdNi/rGO, the nanocomposite of PdNi-CeO_2/rGO exhibited a significant enhancement on the catalytic efficiency. In addition, the detailed kinetics of AB dehydrogenation catalyzed by $Pd_{0.8}Ni_{0.2}$-CeO_2/rGO had been investigated with different metal and substrate loading concentrations, and various reaction temperatures.

Experimental

Materials

Sodium borohydride ($NaBH_4$, 98%), palladium chloride ($PdCl_2$, 98%), nickel(II) chloride hexahydrate ($NiCl_2 \cdot 6H_2O$), hexadecyltrimethyl ammonium bromide (CTAB) and cerium(II) nitrate hexa-hydrate ($Ce(NO_3)_3 \cdot 6H_2O$, 99.5%) were purchased from Aladdin. Graphite powder, potassium permanganate ($KMnO_4$), sulfuric acid (H_2SO_4, 98%), hydrogen peroxide (H_2O_2, 30%), hydrochloric acid (HCl, 30%), and ammonia borane (NH_3BH_3, AB, 97%) were obtained from Sigma Aldrich. All reagents were used without further purification. The reaction solvent used was twice-redistilled water.

Characterization

The power X-ray diffraction (PXRD) patterns of all samples were collected on a Shimadzu X-ray diffractometer-6000 (XRD-6000) using Cu Kα radiation source (λ = 0.1542 nm). Transmission electron microscopic (TEM) images were obtained on a JEOL-2010 microscope with an accelerating voltage of 100 kV, and high-resolution TEM (HRTEM) images were obtained on a JEM-2100 microscope operated at an accelerating voltage of 200 kV. The energy dispersive X-ray (EDX) spectroscopy were recorded on Field Emission Scanning Electron Microscope (FESEM, S-4800) for elemental analysis. Raman spectra were collected with a confocal Raman microscope (LabRAM HR). X-ray photoelectron spectroscopy (XPS) was surveyed by a Thermo Fisher Scientific ESCALAB 250× imaging electron spectrometer. The element contents of Pd, Ni, and Ce were measured by means of Agilent 7700ce inductively coupled plasma-optical emission spectroscopy (ICP-OES) after the samples were completely digested in aqua-regia solution.