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Facile synthesis of Cu@CoNi core-shell nanoparticles composites for the catalytic hydrolysis of ammonia borane

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ABSTRACT

In this paper, the novel Cu@CoNi tri-metallic core-shell NPs have been synthesized by a facile and efficient in situ method at room temperature. It exhibits superior catalytic activity towards the hydrolysis dehydrogenation of ammonia borane (NH_3BH_3, AB). In these series nanoparticles, the $Cu_{0.4}@Co_{0.5}Ni_{0.1}$ core-shell NPs showed the best catalytic performance that the maximum hydrogen generation rate is 7340.80 mL $min^{-1}g^{-1}$ at 298 K. The hydrolysis reaction towards AB was proved to the first order by the $Cu_{0.4}@Co_{0.5}Ni_{0.1}$ NPs via kinetic studies. The activation energy was 36.08 kJ mol^{-1}. Even after five recycle experiment, the catalysts also showed a good recycle stability in aqueous solution owing to the synergistic effect of Cu, Co and Ni in the tri-metallic core-shell NPs. The core-shell NPs/carbon composites also showed the better catalytic performance for hydrolysis to ammonia borane and rGO is proved to be the best support to catalyst.

Introduction

It must be further dangerous with increasing requirement of fossil fuels and atmospheric contamination for global environment as we can see. So it is a matter of urgent concern to develop clean and renewable energy source for all over the world [1]. Hydrogen is considered as an ideal energy carrier instead of the traditional fossil fuels because of its higher efficiency of energy utilization, more broad application mode and environmentally friendly with no carbon dioxide and exhaust gas emission [2–4]. Thus, abundant efforts have been made to research safe and efficient materials for hydrogen storage and recycling releasing [5–11]. Among many hydrogen storage materials, ammonia borane (NH_3BH_3, AB) is considered as a remarkable candidate owing to its high hydrogen storage capacity (19.6%), excellent stability in aqueous solution and nontoxic for humanity [12,13]. Nevertheless, the hydrogen generation rate of AB is very slow without catalyst. Thus it's really crucial to choose appropriate materials to catalyze the hydrolysis reaction of AB [14,15]. Generally, catalysts for hydrolysis of AB are noble-metal such as Ru [16], Rh [17,18], Pd [17,19] and Pt [17] due to their prominent catalytic performance. However, the high cost extremely limits their development in social demand practical application.

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Table 1 – The activation energy values for the hydrolysis of AB catalyzed by different catalysts at 298 K.

Catalyst	Ea (kJ mol^{-1})	Ref.
Ru	76 ± 0.1	[36]
Ni	70.31	[25]
Co/γ – Al_2O_3	62	[37]
$Ni_{0.97}Pt_{0.03}$ hollow spheres	57	[25]
Intrazeolite Co nanoclusters	56 ± 2	[38]
Pd-PVB-TiO_2	55.9	[20]
Zeolite confined Cu	51.8 ± 1.8	[39]
p(AMPS)-Cu	48.8	[35]
Ni@Ru core-shell	43.99	[40]
$Cu_{0.33}Fe_{0.67}$ alloys	43.22	[41]
Cu@CoNi core-shell	36.08	This study
Cu@CoNi core-shell/rGO composite	35.65	This study
Ru/C	34.89 ± 0.12	[42]
Pt/γ – $A1_2O_3$	21	[43]

Therefore, it's necessary to seek suitable non-noble metals to reduce the cost with the same properties as noble metals materials meanwhile [20,21]. Recently, the compound system formed by two and more kinds of materials have plenty of new function than that consist of monometallic elements, and for this reason core-shell architecture nanoparticles (NPs) have come into our notice because of their novel morphology and outstanding catalytic properties with distinct synergetic effect [22,23]. Till now, Pt–Ni [24,25], Au–Co [12], Fe–Co [26], Au–Ni [27], Fe–Ni [28] have been reported as bimetallic catalysts for hydrolysis reaction of AB. In view of the influence of synergetic interaction among multi-metals in the catalytic activities, some tri-metallic core-shell NPs have been made to synthesis to improve their catalytic property [29,30]. Compared to bimetallic catalysts, tri-metallic core-shells show the excellent performance with high hydrogen generation rate because of their extraordinary structure strengthening the synergetic interaction among the different components. Nevertheless, the reported tri-metallic core-shell structures consist of noble metals almost which severely restrain their practical application in the future [31]. For this reason, it's imperative to synthesis novel tri-metallic core-shell catalysts with non-noble metals and high catalytic performance in the meantime [29,32].

Hence, we successfully synthesize Cu@CoNi tri-metallic core-shell NPs in situ method by a facile and efficient at room temperature in just a few minutes. Moreover, the size of $Cu_{0.4}@Co_{0.5}Ni_{0.1}$ core-shell NPs is less than 10 nm with more active-site, so it makes the excellent catalytic performance towards hydrogen generation from the hydrolysis of AB. For a higher activity of catalyst, different carbon materials are used to improve its dispersity and decrease aggregation of magnetic NPs. The core-shell NPs/carbon composite is also a kind of remarkable catalyst that has lower activation energy to improve hydrogen generation rate. This low-cost and high-efficient series of catalysts can be used as a potential hydrogen-storage material toward the application of AB.

Experimental details

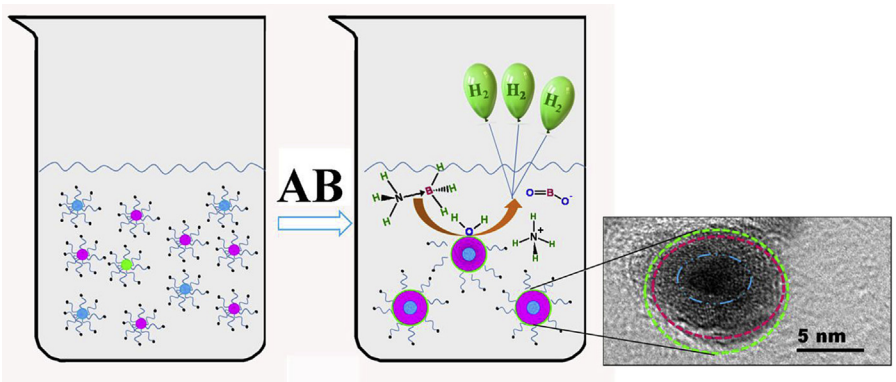
Chemicals

Ammonia borane (NH_3BH_3, Sigma–Aldrich, 90%), nickel (II) chloride hexahydrate ($NiCl_2·6H_2O$, Alfa Aesar, 99$_+$%), copper (II) chloride dihydrate ($CuCl_2·2H_2O$, Alfa Aesar, 99$_+$%), cobalt (II) chloride hexahydrate ($CoCl_2·6H_2O$, Alfa Aesar, 99$_+$%), polyvinylpyrrolidone (PVP, $(C_6H_9NO)_n$, M,W.55000, Alfa Aesar), sodium borohydride ($NaBH_4$, Alfa Aesar, 97%), rGO was synthesized according to a previous method [33,34], Multi-Wall Carbon Nanotubes (MWCNTs, NTP, ≥95%), mesoporous CMK-3 carbon and activated carbon were used as received without any further purification.

Synthesis and characterization

Synthesis of Cu@CoNi core-shell NPs and their catalytic activities for the hydrolysis of AB

In a typical experiment, the Cu@CoNi core-shell NPs were prepared by a facile in situ chemical reductive method. $CuCl_2·2H_2O$, $NiCl_2·6H_2O$, $CoCl_2·6H_2O$ and PVP (100 mg) were dissolved in 10.0 mL distilled water (with conductivity of 1 μS cm^{-1}). The molar ratio of Co^{2+} to Ni^{2+} was controlled as a constant quantity of 1. Contemporaneously, the molar ratio of Cu^{2+} to the entire number of moles in the metal salts was adjusted from 0 to 1 to acquire $Cu_x@(Co_{0.5}Ni_{0.5})_{1-x}$ NPs. When the molar ratio of Cu^{2+} to the entire number of moles in the metal salts was ascertained as 0.4, the molar ratio of Co^{2+} to Ni^{2+} varied from 0 to 1. Thus, $Cu_{0.4}@(Co_yNi_{1-y})_{0.6}$ NPs can be received. After 5 min ultrasonication for scattering, the above



Scheme 1 – The process of the $Cu_{0.4}@Co_{0.5}Ni_{0.1}$ core-shell NPs synthesized.

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