

Synthesis of Co/N-HNTs composites and investigation on its catalytic activity for H₂ generation



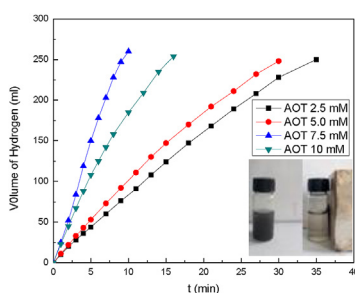
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HIGHLIGHTS

- Co/N-HNTs composites are synthesized.
- The dispersibility and morphology of the Co particles anchored at the N-HNTs are modified by AOT.
- The composite shows higher catalytic activity for production H₂ gas.

GRAPHICAL ABSTRACT



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ABSTRACT

Co/N-HNTs composites were synthesized via a one-pot solvothermal method, where amine functional halloysite nanotubes (N-HNTs) were used as support materials. Effects of sulfosuccinate sodium salt (AOT), an anionic surfactant, on morphology and dispersibility of Co particles anchored at the N-HNTs were studied. The dispersibility of the Co particles was promoted with the increase of the AOT concentration. The as-obtained composite was used as a catalyst to generate H₂ gas by hydrolysis of NaBH₄ solution. The catalytic activity of the composite was significantly enhanced than the pure Co and Co/graphene composite at the same experimental conditions reported by our laboratory, and the catalyst was conveniently separated from the solution by a magnet. The catalytic activity was enhanced when the dispersibility of the Co particles was improved at the surface of the N-HNTs and the Co content contained in the composite was lowered. At the same time, the Co particles anchored at the inner surface of the N-HNTs resulted in higher catalytic activity, where the Co particles may bond with nitrogen atoms. The activation energy for the hydrolysis of NaBH₄ was calculated to be about 15.42 kJ mol⁻¹. The catalyst can be continuously used for four times with about the same catalytic activity.

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1. Introduction

Hydrogen (H₂) has many attractive features such as that can be produced from different sources and used as a renewable energy

carrier combined with its high power density (142 MJ/kg) [1–3]. NaBH₄ is always employed to produce H₂ through a hydrolysis reaction with a suitable catalyst in alkaline medium at room temperature [4–6]. Precious metals exhibit always better catalytic performance than non-noble metals. However, the high price of these metals limits their large scale application. From the reactivity and cost point of view, cobalt-based (Co) catalysts are very efficient and have been demonstrated to be a potential alternative to noble

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metals [7]. However, aggregation can be found for this kind of materials because of effects of magnetic force and smaller particle [8,9], which decreases the dispersion of the catalyst in water. In order to reduce aggregation of the catalyst particles and further improve the catalytic activity, different materials have been chosen as supports [10–18]. Among different kinds of supports, nanotubes are always regarded as a potential candidate for catalyst supports.

Halloysite nanotubes (HNTs) show inherent hollow nanotubular structure, different outside and inside chemistry essence, which potentially allows a selective loading of different molecules of interest [19,20]. Siloxane chemistry can be used for subsequent grafting and deposition of nanoparticles on the external and internal surfaces. In order to improve depositing and dispersibility of catalysts on the HNTs, chemical functionalization is a convenient and widely used way to modify HNTs for its relatively chemically inert [21–23].

Precious metals decorated on functional HNTs were reported as catalysts in reduction of 4-nitrophenol and photocatalysts in degradation of methyl orange [24,25]. However, Co/functional HNTs composites as catalysts in hydrolysis of NaBH_4 aqueous solutions for formation H_2 have not been reported as far as we know.

In this paper, Co/functional HNTs composites were prepared by using a one-step solvothermal method. The composite showed high catalytic activity for the hydrolysis of NaBH_4 than those reported, can be conveniently separated from the aqueous solution by an external magnetic field, and reused for several times with high activity.

2. Experimental

$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, hydrazine monohydrate, ethylenediamine (EDA), ethylene glycol (EG), and bis (2-ethylhexyl) sulfosuccinate sodium salt (AOT), 3-aminopropyl-triethoxysilane (APTES) and absolute ethanol were of analytical grade, which were obtained from Sinopharm Chemical Reagent Company, and used as-received without further purification. Halloysite nanotubes (HNTs) were obtained from Tianjin Linruide Science and Technology Co., Ltd., China.

The surface of the HNTs was initially functionalized with amine groups by using APTES as a silanization agent, which the amination process has been described elsewhere [26]. Briefly, 0.4000 g of the HNTs was suspended into 10 mL of absolute ethanol. 50 μL of APTES was added into the ethanol solution and vigorously stirred for 24 h at room temperature, where the molar ratio of the APTES to the HNTs was 1/7. In order to enhance the covalent bonding between the APTES and the HNTs surface, the mixture was subsequently refluxed for two hours at 84.0 °C. After cooling down to the room temperature, the APTES grafted HNTs were centrifuged at 8000 rpm for 10 min. The cleaning process was repeated three times by using the absolute ethanol. The obtained sample was named as N-HNTs.

10.0 mL of EG solution contained different concentrations of AOT was heated to approximately 462 K. 50.0 mL of hydrazine monohydrate was added dropwise to the solution. 100.0 mg of the obtained N-HNTs was mixed into the solution. Then 10.0 mL of EDA solution in EG, 10.0 mL of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution in EG (0.5 mol/L), and 10.0 mL of hydrazine monohydrate solution in EG (0.5 mol/L) were added rapidly to the above solution by turns under magnetic stirring. The EDA concentration was 4.5 mM, and the AOT concentrations were controlled as 2.5, 5.0, 7.5, and 10.0 mM, respectively. After refluxing for approximately 60 min, the final product was obtained by magnetic separation. The sample was rinsed repeatedly with absolute ethanol for several times, dried at 333 K for more than 24 h in vacuum, and afterwards stored in a desiccator for further characterization. The obtained samples were named as Co/

N-HNTs025, Co/N-HNTs050, Co/N-HNTs075, and Co/N-HNTs100, corresponding to the AOT concentrations 2.5, 5.0, 7.5, and 10.0 mM, respectively.

Hydrolysis of a NaBH_4 solution occurred with 50 mL of 50 mM NaBH_4 (0.0965 g) solution (containing 5 wt% NaOH) at 303 K in a 100 mL flask, where 100.0 mg of the obtained Co/N-HNTs sample was used as a catalyst. The reaction was kept stirring at 1000 rpm. The volume of the generated H_2 gas was measured via an inverted volumetric cylinder, based on the principle substitution (filled water replaced by H_2 gas).

Five different temperatures with an increment of 10 K in the range from 303 to 343 K were selected to study the effects of experimental temperature on the hydrolysis.

To assess the reusable ability of the catalyst, the as-synthesized Co/N-HNTs075 was continuously used four times as the catalyst at 303 K. After each use, the catalyst was washed by distilled water for several times.

A Bruker D8 Advanced X-ray powder diffraction (XRD) diffractometer with Cu K α radiation at a scanning rate of 0.04 °s⁻¹ ($\lambda = 1.5405 \text{ \AA}$) was used to record XRD patterns. A JEOL-2010 transmission electron microscopy (TEM) was used to measure TEM images at an acceleration voltage of 200 kV. N_2 adsorption/desorption isotherms was measured at 77 K by using a model NOVA 3200e automated gas sorption system (Quantachrome, USA). Prior to measurement, each sample was degassed for 6 h at 120 °C. The specific surface area was calculated by using the Brunauer–Emmett–Teller (BET) equation. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was used to measure the Co content on an Optima7300 DV (Perkin Elmer). The as-prepared sample was dissolved in 5 mL of HCl aqueous solution (28 wt%) for several minutes, and the suspension was centrifuged for about 60 min. The homogeneous solution was diluted with water to 100 mL, and 2 mL of the dilute solution were obtained and diluted to 100 mL again.

3. Results and discussion

3.1. Catalyst characterization

The TEM images of the HNTs and the amine functional HNTs (N-HNTs) are shown in Fig. 1, in which tubes can be clearly found with average lengths about 200–500 nm, inner diameters about 20–25 nm for the HNTs and 15–25 nm for the N-HNTs. These results demonstrated that the HNTs and the N-HNTs shown similar morphology and length, the inner diameter became smaller after the amine function. APTES was mostly anchored at the internal surface of HNTs through covalent grafting, forming a functionalized surface covered by aminopropyl groups [27], which was proved by the following FTIR result. These anchored APTES resulted in the decrease of the inner diameter of the N-HNTs. This result was further demonstrated by the determination of the surface area, the pore volume, and the pore size of the HNTs and N-HNTs as shown in the Supporting information as Fig. S1 and Table S1.

Fig. 2 shows FTIR analysis of the HNTs and N-HNTs, in which positions and assignments of the IR vibration bands were given based on Refs. [28]. Such as the characteristic peaks of HNTs occurred at 3691, 3622, and 1647 cm⁻¹ are attributed to O–H stretching of inner-surface hydroxyl groups, O–H stretching of inner hydroxyl groups, and deformation of water, respectively. Another two characteristic peaks at 1087 and 1038 cm⁻¹ correspond to in-plane stretching of Si–O in HNTs. For the curve of N-HNTs, most of the peaks for the HNTs were maintained, which indicates that the main crystal structures of HNTs are preserved in the N-HNTs. The newly emerged peaks at 3360 and 2930 cm⁻¹ for the N-HNTs were attributed to asymmetric stretching –NH₂ and

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