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N-doped mesoporous carbon embedded Co nanoparticles for highly efficient and stable H_2 generation from hydrolysis of ammonia borane

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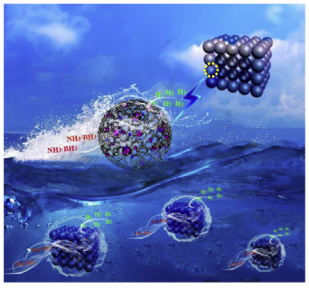
HIGHLIGHTS

- Co@NMC-800-0.5 catalyst with superhigh surface area, pore volume and larger pore size.
- The catalyst possesses a superior catalytic performance for hydrolysis of NH_3BH_3.
- The actual active species should be N-doped carbon embedded Co NPs.
- Apparent activation energy of NH_3BH_3 hydrolysis is as low as 41.6 ± 2 kJ/mol.
- It manifests an excellent recyclability and without any deterioration.

GRAPHICAL ABSTRACT



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ABSTRACT

The highly efficient yet persistent hydrogen generation catalyzed by heterogeneous non-noble metal catalysts is emerging extensive application prospect in energy catalysis and transformation fields. Regrettably, the activity and stability of such catalysts often become the huge stumbling blocks for the catalytic hydrolysis of ammonia borane (NH_3BH_3) to produce hydrogen. Herein, we report a facile and effective in-situ mosaic strategy for preparing non-noble metal and nitrogen co-doped mesoporous carbon catalysts, which feature homogeneously embedded, different sized metal nanoparticles as well as highly tunable nitrogen contents and types. Experimental results indicate that the Co@NMC-800-0.5 catalyst exhibits the highest catalytic activity for the hydrolysis of NH_3BH_3 among all the synthesized catalysts, which can be attributed to the superhigh surface area, pore volume and large pore size (1044 m^2/g, 2.131 cm^3/g, 7.5–13.6 nm) of the support, as well as the modified electronic structure and chemical microenvironment of the metallic Co NPs. More practically, the Co@NMC-800-0.5 catalyst manifests a higher recyclability (up to reuse 10 times without significant loss of its catalytic activity) than those from directly supported Co NPs on N-doped mesoporous carbon, implying a superior recycling stability in the catalytic reaction.

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1. Introduction

Since the ever-increasing consumption of fossil resources and the deterioration of environmental pollution, researchers have to explore a kind of more clean, efficient and conveniently storable alternative energy to eliminate greenhouse gases and pollutants discharges [1–4]. In the current alternative energy sources, hydrogen plays a crucial role in food, medicine, fuel cells and aerospace industry because of its rich source, high energy density and non-pollution advantages, but achieving its efficient storage and transportation still remains challenging [5,6]. According to the U.S. Department of Energy stipulated requirement for on-board hydrogen storage systems, minimum gravimetric and volumetric capacities of hydrogen storage materials should be 7.5 wt% and 70 g/L in the near future. In this case, numerous of researchers have been performed on either physical (compressed/cryo-compressed hydrogen gas and nano-porous hydrogen adsorbents) [7,8] or chemical (metal/organic hydrides, cycloalkanes, N-heterocycles, borane-nitrogen complexes and hydrazine aqueous solution) [9–13] hydrogen storage systems to seek the most appropriate route. Unfortunately, there is still no one hydrogen storage method that is mature enough for industrial applications because of the drawbacks of potential security threat, limited storage capacity, harsh reaction conditions as well as sluggish hydrogen release rate.

For the aforementioned hydrogen storage systems, ammonia borane (NH_3BH_3) is well-known as an ideal chemical hydrogen storage material owing to its excellent stability, ultrahigh hydrogen content (19.6 wt %) and relatively mild H_2 release temperature in aqueous solution under ambient conditions (as depicted in equation (1)) [14,15]. Previous studies have demonstrated that the Pd, Ru, Pt and Rh-based noble metal catalysts possess excellent catalytic activity for the hydrolysis of NH_3BH_3. However, the expensive price and poor stability seriously hinder their further application [16–21]. Thus, it is very urgent and important to develop a highly active, stable and noble-metal-free heterogeneous catalyst towards the hydrolysis of NH_3BH_3 to generate hydrogen.

$$NH_3BH_3+2H_2O \xrightarrow[\text{mild condition}]{\text{Catalyst}} (NH_4)BO_2+3H_2 \quad (1)$$

Over the past decades, the non-noble metals have drawn great attention in the academic and industrial fields because of their abundance and easy availability [22–25]. It is generally known that the main bottleneck of their development is the harsh reaction conditions, low catalytic activity and poor stability in aqueous and ambient atmosphere. To address these issues, a large number of representative studies have been devoted to either enhance the metal-support interactions or encapsulate those metal active sites within various porous supports (such as the hydrophilic TiO_2, SiO_2, hydrophobic carbon and amphiphilic N-doped carbon etc.) [26–32]. Among them, the N-doped nanoporous carbon materials are recognized as the most promising supports for the exploitation of robust and efficient catalytic systems due to their fine-tuning physicochemical, electrical and functional properties [33,34]. More interestingly, some peculiar features, such as synergetic enhancement, spatial confinement as well as Mott-Schottky effect, will emerge once they are hybridized with the non-noble metal units [35–37]. But it is a pity that the currently available strategies prepared noble-metal-free N-doped carbon porous catalysts still exist the defects of precursor skeleton collapse, low specific surface area or pore volume and relatively complicated crystalline phases.

Just recently, our group has successfully prepared a series of N-doped mesoporous carbon embedded Co NPs, which display excellent catalytic activity, selectivity and stability for nitroaromatics hydrogenation under mild conditions [38]. To further grasp the authentic active site and promote the catalytic performance of the heterogeneous non-noble metal catalysts, in this contribution, we report a facile synthesis of highly nitrogen doped and uniformly embedded Co-based mesoporous carbon catalyst through a thermolysis and etching combined strategy, in which the commercial colloidal silica and different non-noble metal organic complexes serve as hard template and precursors, respectively. The influence of different metal types, synthetic precursors, pyrolysis temperature, catalyst dosage and reaction temperature of the as-prepared catalysts for the hydrolysis of NH_3BH_3 has been investigated systematacially. To our delight, the current method prepared Co@NMC-800-0.5 catalyst exhibits superhigh specific surface area, pore volume and large pore size distribution (1044 m^2/g, 2.131 cm^3/g, 7.5–13.6 nm), which shows the highest catalytic activity for the hydrolysis of NH_3BH_3 among all the synthesized catalysts. Furthermore, such catalyst still displays a high recyclability even if it is reused 10 times and without significant loss of its original catalytic activity.

2. Experimental

2.1. Materials and methods

Cobalt phthalocyanine (CoPc, 92%), collodial silica dispersion (Ludox HS-40, 40 wt% suspension in water) and ammonia borane complex (NH_3BH_3, 97%) are provided by J&K Chemical Reagent Co., Ltd. Copper phthalocyanine (CuPc, 99%) and phthalocyanine (Pc, 98%) are obtained from Alfa Aesar. Iron phthalocyanine (FePc, > 95%) is purchased from TCI. Nickel phthalocyanine (NiPc, 95%) is purchased from Meryer. N, N′-Bis(salicylidene)ethylenediamine (Salen), $Co(OAc)_2$ and phenanthroline (Phen) are purchased from Sinopharm Chemical Reagent Co., Ltd. All of other chemicals are used as received without any further purification.

2.2. Synthesis of N-doped mesoporous carbon embedded non-noble metal catalysts

The typical procedure for preparation of Co@NMC-T-0.5 is described as follows: 5.0 g of 40 wt% Ludox HS-40 silica colloid is dispersed in 30 mL of ethanol and chloroform (v/v = 2:1) mixture under ultrasonic oscillation at room temperature. After that, 1.0 g of CoPc is slowly added to the suspension and continues to stir for 1.0 h. After removing the solvent via vacuum-rotary evaporation, the resultant SiO_2@CoPc composite is pyrolyzed at 600-900 °C (heating rate: 5 °C/min) for 2.0 h under flowing Ar gas and cooled naturally to room temperature. The generated black powders are etched two times with 1.0 M NaOH for 24 h to remove the silica template, and then thoroughly washed to pH of 7 with deionized water and dried at 60 °C overnight. The obtained catalyst is denoted as Co@NMC-T-0.5 (NMC refers to the N-doped mesoporous carbon, T represents the carbonization temperature, 0.5 indicates the weight ratio between CoPc and SiO_2).

For comparison, the identical procedure is applied to prepare metal-free, Cu-, Fe- and Ni-based N-doped mesoporous carbon except using Pc, CuPc, FePc and NiPc as starting materials. The Co@NMC-800-0.5 (Phen) and Co@NMC-800-0.5 (Salen) catalysts are prepared by using cobalt phenanthroline and cobalt salen as precursors. For 10 wt% Co/NMC-800-0.5 catalyst, 98 mg of $Co(NO_3)_2{\cdot}6H_2O$ and 200 mg of NMC are dissolved in 10 mL of ethanol. The resulting mixture is stirred at 30 °C for 12 h, and the solvent is removed by vacuum-rotatory evaporation. The produced sample is suffered from thermal reduction under 5 v% H_2/Ar flow at 600 °C for 4 h.

2.3. General procedure for the catalytic hydrolysis of NH_3BH_3

The hydrogen generation rate of NH_3BH_3 catalyzed by various non-noble metal catalysts is measured at different temperatures through a typical water displacement method. Typically, 30 mg of Co@NMC-800-0.5 catalyst (3.0 mol%) is dispersed into 3.0 mL of deionized water in a two-necked round-bottom flask, and then 50 mg of NH_3BH_3 (1.6 mmol) dissolved in 2.0 mL of deionized water is rapidly added into the above catalyst suspension. Start to record the reaction time when the system