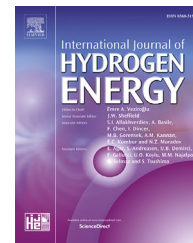




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RuCo bimetallic alloy nanoparticles immobilized on multi-porous MIL-53(Al) as a highly efficient catalyst for the hydrolytic reaction of ammonia borane

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ABSTRACT

Well-dispersed bimetallic RuCo alloy nanoparticles (NPs) were successfully immobilized on the multi-porous, water-tolerant metal organic frameworks MIL-53(Al) by a facile solvent impregnation method. Among the RuCo@MIL-53(Al) with different Ru/Co molar ratios, the Ru₁Co₁@MIL-53(Al) performed better and was superior to Ru@MIL-53(Al) and single RuCo NPs for the hydrolysis of ammonia borane (AB, NH₂BH₃), owing to the synergistic effect caused by the electronic and geometric interactions between Ru and Co atoms and bi-functional effect generated between the RuCo NPs and the MIL-53(Al) support. Compared with bimetallic Ru₁Ni₁ and Ru₁Cu₁ counterparts loadings, the Ru₁Co₁@MIL-53(Al) also showed better catalytic activity for the hydrolysis of AB. Moreover, the Ru₁Co₁@MIL-53(Al) presented good durability and reusability in the catalytic reaction, and the activation energy (E_a) and turnover frequency values (TOF) were 34.32 kJ mol⁻¹ and 87.24 mol H₂ min⁻¹ (mol Ru)⁻¹, respectively.

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Introduction

Hydrogen is a clean energy carrier, which is an ideal choice to replace traditional fossil resources [1]. But an efficient hydrogen storage is still the key to the hydrogen economy [2]. In recent years, there has been a growing interest in investigating chemical hydrogen storage materials [3–6]. Among these materials, ammonia borane (AB) is considered as an important candidate for chemical hydrogen storage materials.

It has a high hydrogen content (19.6%), good stability at room temperature and environmental benignity [7]. The release of hydrogen from AB could be achieved via hydrolysis [8], thermolysis [9] and catalytic dehydrogenations in a non-aqueous solvent [10]. With a suitable catalyst, the hydrolysis of 1 mol AB can release as much as 3 mol H₂ under ambient condition [11,12].

So far, various metal nanoparticles (NPs) catalysts have been tested in the hydrolysis of AB, in which noble metals such as Pt, Pd, Ru and Rh can obtain an excellent activity for

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catalyzing hydrogen generation from AB [13–18]. However, the high cost and the limited resources of these noble metals restrict their practical utilisation. So, it is necessary to design high activity and low cost metal-based catalysts [19]. Bimetallic nanoparticles have recently drawn enough attentions as an efficient series of nanomaterials because of their usage of non-noble metal and better catalytic properties in the dehydrogenation of AB at room temperature [20–22]. It has been proved that bimetallic nanoparticles are more effective than their monometallic counterparts due to the interplay of electronic and lattice effects of the neighbouring metals [23]. However, during the reaction process, these support-free nanoparticles are easy to agglomerate in solution and oxide in air. All these will decrease the activity of catalysts in the hydrolysis of AB. To gain excellent bimetallic catalysts for the dehydrogenation of AB, it is very important to find a suitable support.

Metal Organic Frameworks (MOFs) constructed by metal ions connected with organic ligands have been regarded as new functional materials due to their high thermal and chemical stability, large surface area and high porosity [24], applied to gas sorption [25], storage [26,27], drug delivery [28], luminescence [29], sensor technology [30], proton conduction [31] and heterogeneous catalysis [32]. Especially, their tunable pore size, shape and dimensional structure make them be potential catalysts or supports. In order to get a better catalytic activity and stability, metal nanoparticles can be dispersed by MOFs. The matrix of MOFs can effectively prevent the overgrowth and agglomeration of metal nanoparticles through the well-confined size of its regular pores. Recently, metal nanoparticles supported on MOFs have been reported as more efficient heterogeneous catalysts for the dehydrogenation of AB compared to their bulk metal nanoparticles [33]. In this study, we focus on MIL-53(Al) which was first synthesized by Férey's group in 2003 [34]. It is made up of infinite trans-corner sharing octahedral $\text{AlO}_4(\text{OH})_2$ chains linked to each other through the 1,4-benzenedicarboxylic acid (BDC) molecules which form a three-dimensional framework with one-dimensional diamond shaped tunnels. Due to its high thermal stability and good tolerance in neutral and acidic aqueous solutions, MIL-53(Al) was selected as an excellent support [35]. Also, its large surface area and narrow pore size distribution can make metallic nanoparticles well-dispersed [36]. Among noble transition metals, Ru NPs have a lower cost with good catalytic activity for the hydrolysis of AB. Therefore, it is worth immobilizing Ru-based bimetallic nanoparticles on the MIL-53(Al) as a catalyst.

Herein, we report the RuCo alloy nanoparticles supported MIL-53(Al) catalyst synthesized by a solvent impregnation method under ambient condition and its highly efficient activity for the hydrolysis of AB. The XRD, XPS, TEM, IR, BET and ICP-AES measurements were used to reveal the details of the Ru_1Co_1 @MIL-53(Al) in its structural, morphological and component aspects. In order to highlight the superiority of Ru_1Co_1 @MIL-53(Al) in the catalytic activity, durability and reusability for the AB hydrolysis, the monometallic Ru, Co and bimetallic Ru_1Ni_1 , Ru_1Cu_1 @MIL-53(Al) loading catalysts were also synthesized and discussed. Additionally, the activation energy of the Ru_1Co_1 @MIL-53(Al) was obtained through the hydrolytic experiments of AB at different temperatures.

Experimental

Chemicals

Ammonia borane (NH_3BH_3 , AB, Energy Chemical, 97%), sodium borohydride (NaBH_4 , Sinopharm Chemical Reagent Co. Ltd, 98%), aluminum(III) nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Sinopharm Chemical Reagent Co. Ltd, 99%), cobalt(II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Sinopharm Chemical Reagent Co. Ltd, 99%), copper(II) nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, Sinopharm Chemical Reagent Co. Ltd, 99%), nickel(II) nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Sinopharm Chemical Reagent Co. Ltd, 99%), ruthenium(III) chloride hydrate ($\text{RuCl}_3 \cdot n\text{H}_2\text{O}$, Shanghai Macklin Biochemical Co. Ltd), 1,4-benzenedicarboxylic acid ($\text{C}_8\text{H}_6\text{O}_4$, H_2BDC , Aladin Industrial Corporation, 99%), ethanol absolute ($\text{C}_2\text{H}_6\text{O}$, Sinopharm Chemical Reagent Co. Ltd, 99.7%). All chemicals were used as received. We used deionized water and ethanol as the reaction solvent.

Synthesis of MIL-53(Al)

MIL-53(Al) was synthesized using a hydrothermal method reported in the literature [36]. $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (2.60g), 1,4-benzenedicarboxylic acid (0.576g) and deionized water (10 mL) were placed in a 50 mL Teflon-lined steel autoclave and heated at 210 °C for 3 days. After the end of the reaction, a resulting white powder was filtered, washed with deionized water and ethanol several times. The product was dried in air at 60 °C overnight, defined as MIL-53(Al)_{as}. In order to remove unreacted benzene dicarboxylic acid molecules in the tunnels, the MIL-53(Al)_{as} was calcined in air at 330 °C for 3 days and the calcined one was defined as MIL-53(Al)_{ht}.

Synthesis of Ru@MIL-53(Al) and RuCo@MIL-53(Al) catalysts

Typically, 50 mg of MIL-53(Al)_{ht} well dispersed in 10 mL of ethanol was kept in a round bottom flask. 10 mL of 0.01 M RuCl_3 aqueous solution, 1 mL of 0.1 M $\text{Co}(\text{NO}_3)_2$ aqueous solution and 9 mL deionized water were added into the flask. The mixture solution was dispersed by ultrasonication for 15 min and kept magnetic stirring for 4 h. Then 37.8 mg of NaBH_4 (1 mmol) dissolved in 10 mL deionized water were added dropwise into the flask. After 5 h stirring, the product was obtained through filtration, then washed with deionized water, ethanol and dried under vacuum at 80 °C overnight (see Scheme 1).

In order to find the most efficient catalyst for dehydrogenation of AB aqueous solution, a series of compositions were synthesized with different Ru/Co molar ratios (1:1, 1:2 and 1:3), which can be designated as Ru_1Co_1 @MIL-53(Al), Ru_1Co_2 @MIL-53(Al) and Ru_1Co_3 @MIL-53(Al), respectively. The molar value of Ru was kept as a constant of 0.1 mmol. For comparison, RuCo NPs without MIL-53(Al), Ru@MIL-53(Al), Co@MIL-53(Al) were also prepared by the similar method.

Synthesis of RuM@MIL-53(Al) (M = Ni, Cu)

These RuM@MIL-53(Al) (M = Ni, Cu) catalysts were synthesized by the same method as described above. But we used the

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