Co nanoparticles supported 3D structure for catalytic H₂ production

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Abstract

Cobalt nanoparticles supported elastic foam (Co-F) was prepared by coating commercial polyurethane foam with cobalt nanoparticle loaded hybrids (Co/rGO). The Co-F was applied to catalyze hydrolysis reaction of sodium borohydride to produce hydrogen gas. Co-F has large surface area and interconnected pores, so it showed outstanding activity in catalyzing the hydrolysis reaction and achieved a hydrogen production rate of 33.2 mL·min⁻¹. The conditions for Co/rGO and Co-F preparation as well as reaction conditions like the reaction temperature, the concentration of NaBH₄ and pH value all affected the catalytic hydrolysis of NaBH₄. The Co-F could be easily recovered by taking out, pressing and rinsing in distilled water, and it exhibited almost unfaded catalytic activity in the reuse. The unique properties will make Co-F potential applications in catalytically chemical reactions.

Keywords:

A. Coating

A. Nano particles

D. Scanning electron microscopy (SEM)

D. Photoelectron spectroscopy (XPS)

1. Introduction

Materials in nano-size or with nanostructure have unique physical and chemical properties that are different from their bulk materials [1]. In the past decade, various nanomaterials like metal or metal oxide nanoparticles have been developed and applied in areas such as electronic and communicational, optical, biomedical, environmental and areas [2-5]. In particular, nanoparticles have been demonstrated to be efficient electrode materials for electrochemical reactions and active catalysts for various reactions. Metal nanoparticles with different components and architectures have been studied in chemical reactions like Suzuki-Miyaura reactions, aryl and vinyl dithiocarbamates synthesis [6-8]. Metal or metal oxide nanoparticles and their nanocomposites exhibit excellent performance as electrode materials in many kinds of batteries, supercapacitors, methanol oxidation, oxygen reduction and evolution, photocatalytic and photoelectrochemical hydrogen evolution [9-16]. All these applications related to the energies that can be considered green or clean energy resources.

Keeping up with the growing energy requirement owing to increasing population and rising standards of living is considered to be one of the major challenges of this century [17]. For instance, 15 TW-energy was consumed world-wide in 2011, however it expected to escalate to 30 TW by 2050 [17], resulting in rising of greenhouse gas emission, as well as global warming and climate changes. These issues force researchers to develop alternative energies, especially clean and renewable energy sources [18, 19], of which fuel cells are considered powerful environment friendly tool for energy production [20]. However, they require hydrogen as fuel, and its

production, storage and transportation becoming a big challenge [21].

Hydrogen energy is regarded as a promising alternative to fossil fuels, since in principle it can be produced from renewable resources such as water [22]. Nowadays, many hydrogen production approaches based on different primary energy and material sources have been created. Thermal, electrical, photonic (from solar irradiation), and biochemical energy (from organic matter) are the primary energy sources to generate hydrogen. The electrical and thermal energy can be generated from fossil fuels, renewable energies (i.e. solar and wind etc), biomass, or nuclear. They also may be mixed forms of energy like electrical-photonic, electrical-thermal, or biochemical-photonic. At present, the basic industrial approach for hydrogen production is water electrolysis [23]. Other methods include thermochemical water splitting, fossil fuel reforming, plasma arc decomposition, water thermolysis, dark fermentation, photoelectrolysis, biophotolysis and photofermentation, thermochemical conversion of biomass, gasification and biofuel reforming [24-29].

Hydrogen storage is another issue should be considered. Manners of hydrogen storage may be liquefied and compressed hydrogen, or hydrogen storage materials like NH_3 and metal hydrides. Metal hydrides are a family of materials including MgH_2 and NaH ; NaBH_4 , LiBH_4 , and H_3NBH_3 ; NaAlH_4 , and $\text{Mg}(\text{AlH}_4)_2$ etc [30-34]. Of these hydrides, NaBH_4 is regarded as one of the most key hydrogen storage materials, because it displays high hydrogen storage capacity, satisfied stability and safety, and controllable production rate [35]. The hydrolysis reaction of NaBH_4 is as shown below:

This reaction can easily take place in the presence of a catalyst, and it generates much more hydrogen than the amount that NaBH_4 contains. Inspired by the catalytic

activity of nanoparticles applied in some other clean energy resources [9-16], metal nanoparticles are being utilized as catalysts in the hydrolysis reactions of NaBH_4 and ammonia borane, for instance, water dispersible acetate stabilized ruthenium (0) nanoclusters as catalyst for hydrogen generation from the hydrolysis of sodium borohydride [34]. Rakap synthesized intrazeolite cobalt (0) nanoclusters as low-cost and reusable catalyst for hydrogen generation from the hydrolysis of sodium borohydride [31]. Non-noble metal nanoparticles such as Co, NiFePd nanoalloy and Ni-Ru also exhibited high catalytic performance in the hydrolysis reaction of sodium borohydride [19, 36, 37].

Here, Co nanoparticles were loaded on polyurethane foam (Co-F) bridged by reduced graphene oxide (rGO) nanosheets. Graphene nanosheets have large surface area and can provide adaptable support for nanoparticles to prevent agglomeration of nanoparticle [38]. Graphene oxide (GO) or light reduced rGO is amphiphilic, so they can take the action of surfactant to promote compatibility of two phases. Here, it used for easy loading of Co nanoparticles on PU foam. PU foam has three-dimensional structure with interconnected pores and large surface area. It is tough and flexible, so it provides recyclable and stable supporter for Co nanoparticles. The as-prepared Co-F material could catalyze the hydrolysis reaction of sodium borohydride for the production of hydrogen and demonstrated high catalytic activity and excellent recyclability.

2. Experimentals

2.1. Materials

Polyurethane foam was provided by Tianjin Hongfu Foam Plant, and graphite was from Qingdao Graphite Factory. Potassium permanganate, 30% hydrogen peroxide, sodium nitrate, hydrochloric acid, concentrated sulfuric acid, sodium hydroxide,

cobalt dichloride hexahydrate, and sodium borohydride were all purchased from Tianjin Chemical Co. All these chemicals were used as received.

2.2. Preparation of the Co loaded foam

Graphite oxide was manufactured from natural graphite by a modified Hummer's method [39]. A suspension of GO sheets was prepared by sonicating in distilled water for 20 min. GO suspension (10 mL, 10 mg·mL⁻¹) was poured in a 250 mL beaker, diluted to 100 mL with distilled water, and then ultrasonically treated for 25 min. After 1.0 mmol CoCl₂·6H₂O had been added and dissolved in the GO suspension, 10 mL NaBH₄ solution (0.50 mol·L⁻¹) was supplied dropwise under stirring. The mixture was continually stirred for four hours to obtain Co-rGO.

The commercial PU foam was cut to cubes of 0.5×0.5×0.5 cm³, ultrasonically rinsed in ethanol, and then washed with distilled water and dried in a vacuum oven at 60 °C. These cubes were soaked in the above as-prepared Co-rGO suspension for 90 min, and then they were taken out, washed with distilled water, transferred into a vacuum oven and dried at 50 °C for 36 h to get the Co-F.

2.3. Characterization

XRD patterns of the Co-rGO hybrids were recorded using an X-ray diffractometer (D/MAX-2500, Rigaku Corporation, Tokyo, Japan) with a reference target: Co K α radiation ($\lambda = 1.73 \text{ \AA}$), voltage: 45 kV, and current: 30 mA, from 20 to 80° (2 θ) with a step of 0.02°.

The Co-rGO suspension was diluted and then dropped onto a carbon coated copper grid and dried in air before being transferred into the TEM chamber (Tecnai G2 F20, FEI, US). The morphology of the Co-F was also observed with SEM (S-4800, Hitachi, Japan) after it was coated with gold using a sputter coater (Desk-II; Denton Vacuum)

The thermogravimetric curves of the samples were measured at a heating rate of 5

°C·min⁻¹ with a TG-DTA analyzer (Rigaku Corporation, Tokyo, Japan).

The porosity of the Co-F was determined by liquid displacement method. The foam cubes were immersed in a known volume (V_1) of hexane in a graduated cylinder for 5 min. The total volume of hexane and the hexane impregnated foam was recorded as V_2 . The hexane-impregnated cubes were then removed from the cylinder and the residual hexane volume was recorded as V_3 . For each sample, the experiments have carried on in triplicate. The porosity of the Co-F (p) was calculated based on the average by the following equation:

$$p = \frac{V_1 - V_3}{V_2 - V_3} \times 100\% \quad (1)$$

2.4. Catalytic activity of the Co-F in the catalytic hydrogen production

In a typical reaction, Co-F cubes were put under a 500 rpm stirring rate at 20 °C in a 50 mL flask that contains 20 mL NaBH₄ aqueous solution to start the hydrolysis reaction of NaBH₄. The generated hydrogen was measured with the water displacement method [40-42]. The volume of hydrogen gas was recorded by an inverted water-filled graded cylinder. To get rid of the interference of water vapor, the produced H₂ gas need go through a gas washing set up containing 100 mL concentrated sulfuric acid. In the H₂ measurement, the gas collection set-up was kept at 25±2 °C. As the reaction completed, the Co-F cubes were taken out, pressed with fingers, and washed with distilled water before the next round of reaction. The Co-F cubes were applied for five successive runs to inspect its reusability.

3. Results and discussion

3.1 Characterization of Co-rGO hybrids and Co-F

Noble metal nanoparticles play an important role in catalytic chemical reactions and have received much attention in recent years. However, Non-noble metal

nanoparticles are even more attractive because they are abundant and cost-effective. Here, Co nanoparticles are chosen as a catalyst and attached to elastic foam through the “bridge” of rGO nanosheets, because rGO nanosheets are amphiphilic and can take the role. Therefore, for manufacturing Co-F, the Co loaded rGO nanosheets were firstly synthesize and analyzed, and the morphology of the Co nanoparticles was observed with TEM. Figure 1a shows the TEM photo of GO nanosheets. They have several graphitic layers with many surface wrinkles. The thin nanosheets together with numerous hydrophilic functional groups make GO dispersible in water and polar solvents. This is available for GO modification, functionalization and compositing. Figure 1b and 1c are the photos of the Co-rGO hybrids, in which huge number of nanoparticles were clearly observed. They dispersed uniformly on the rGO nanosheets and have diameters of approximately 3-6 nm. The activity of metal nanoparticle catalyst is very sensitive to the size of the nanoparticles [43]. And the small diameter and high dispersion of nanoparticles lead to large amount, easily accessible surfaces to serve as active catalytic sites for various chemical reactions [44]. So these nanoparticles are expected to display high catalytic activity as catalysts.

Figure 1 TEM photos of GO (a) and Co-rGO hybrids (b-c); XRD diagram (d) and TG curve (e) of the Co-rGO hybrids; and SEM photos for Co-F (f, g).

In order to identify the above observed nanoparticles, XRD analysis was conducted and the XRD diagram of the Co-rGO hybrid is shown in Figure 1d. Since rGO itself exhibits no obvious peak in the XRD diagram, the diffraction peaks at the 2θ values of 44.4° , 51.7° and 76.0° correspond to the (111), (200) and (220) planes that prove the formation of cubic crystalline cobalt (JCDPS, card no 15-0806) [45]. The XRD result indicates that the nanoparticles observed on rGO in TEM photos are crystalline Co nanoparticles.

Figure 1e is the TG curve of Co-rGO hybrids conducted in air atmosphere. The mass loss below 410°C is due to the degradation of the rGO, including removal of the oxygen-containing groups followed by skeleton broken of the graphene sheet. Beyond 410°C , Co-rGO undergoes a series of oxidation and finally changed to CoO. Since the final residue is about 63 %, Co accounts for about 29.1 wt% of the Co-rGO hybrid.

The modification of the foam with Co-rGO can be easily identified because it changes from light yellow to black. The density and porosity of the Co-F are $0.0088 \text{ g}\cdot\text{cm}^{-3}$ and 92.29 v % while those of the pristine foam become $0.0085 \text{ g}\cdot\text{cm}^{-3}$ and 92.30 v %, respectively. So it is hard to tell one from another based on porosity and density. However, the changes in microstructure could be observed by SEM. As shown in Figure 1f-g, the Co-F, like the pristine foam, has a plenty of interconnected pores that are about hundreds of micrometers (Figure 1f). This demonstrates that it is a suitable supporter for nanoparticles since it can supply unimpeded passage for reactants and products during chemical reactions. Although the pore structure of the Co-F showed no perceivable altering compared with the pristine foam, some fine changes could be found after carefully observation. The typical wrinkles of rGO nanosheets could be perceived on the skeleton of the Co-F (Figure 1g).

Due to oxidization, there are abundant holes and defects on GO nanosheets. Around these holes, there are many oxygen containing groups such as carboxyl, hydroxyl and carbonyl groups. These electronegative groups can adsorb metal (Co^{2+}) ions, which were reduced to nonvalent metal nanoparticles during the reaction with sodium borohydride and eventually deposit and dispersed near the holes. Meanwhile, the wrinkles on GO nanosheets also offer the support of metal nanoparticles. In a word, there was no chemical force between the metal particles and GO sheets.

On the other hand, the interaction between the GO coating and the foam skeleton is not chemical but physical adhesion [46]. The surface energy of GO sheet is high and thus it is easy to combine tightly with the surface of the foam [47].

3.2 Catalytic performance of Co-F for NaBH_4 hydrolysis

Hydrolysis of NaBH_4 may happen under mild conditions if proper catalysts are

supplied. Co-F is expected to be a good catalyst because it can supply well dispersed metallic nanoparticles and unimpeded passage for reactants and products. Figure 2 shows the relationship between reaction rate and Co precursor amount. It is obvious that the reaction rate increased as the Co precursor amount rose, however, these reactions produced same volume of hydrogen gas when the reaction finished. As the Co precursor was 0.5 mmol, the reaction finished in 40 min, however, the reaction completed in 5 min if the Co precursor was increases to 4 mmol. The reaction is too fast to trace, so the precursor amount of 1mmol will be used in the following discussion.

Figure 2 Effect of Co precursor amount (mmol) on the H₂ production. Reaction conditions: NaBH₄:20 mL (52.87 mmol/L), pH 10, 20 °C

Figure 3 illustrates the effect of coating times on the reaction rate. The hydrolysis reaction obviously became fast as the coating times increased because more catalytic Co nanoparticles were loaded on the foam. For monitoring the reaction more accurately, the Co-F coated for three times will be utilized in the following discussion.

Figure 3 Effect of coating times on the H₂ production. Reaction conditions: NaBH₄:20 mL (52.87 mmol/L), pH 10, 20°C

Besides catalysts, the hydrolysis of NaBH₄ also relies on other reaction conditions, like reaction temperature, reactant concentration, and medium pH etc. The influence of pH on the reaction was investigated in order to find the optimum pH value for the hydrolysis of NaBH₄. As shown in Figure 4, the hydrolysis reaction became fast as the solution acidity increased, but the difference is not significant. The reason of the difference of the peak rate duration is due to the catalytic effect of acid in the reaction [48]:

Thus, in the following studies, pH 10 is chosen in the hydrolysis reaction.

Figure 4 Effect of pH on the H₂ production. Reaction conditions:

NaBH₄: 20 mL (52.87 mmol/L), 20 °C

Next factor, NaBH₄ concentration also influences the catalytic H₂ production. As shown in Figure 5, the hydrolysis reactions of NaBH₄ performed at three different concentrations, 52.87, 39.65 and 26.43 mmol·L⁻¹ (40 mg, 30 and 20 NaBH₄), respectively. When the concentration of NaBH₄ decreased, the reaction rate did not change, indicating that the reaction is zero order for the initial NaBH₄ concentration. However, the volume of the H₂ gas reduced. For instance, 20 mg NaBH₄ created 51 mL H₂ in 10 min, and 40 mg NaBH₄ generated 103 mL H₂ in 18 min. The H₂ volume and reaction time are almost linearly grew.

Figure 5 Effect of NaBH₄ concentrations on the hydrolysis reaction.

Reaction conditions: pH 10, 20 °C

The influence of temperature on the hydrolysis reaction is shown in Figure 6. For all these hydrolyses, nearly the same volume of H₂ gas was generated once the reaction finished (Figure 6a); however, the reaction time was different. The reaction finished in 20 min at 20 °C while it needed only 4 min at 50 °C. The reaction at high temperature is obviously rapid. The rates for hydrogen production are 33.2, 17.43,

7.92, 4.85 mL·min⁻¹ at the temperature of 50, 40, 30 and 20°C (Figure 6b).

(a)

(b)

Figure 6 Influence of reaction temperature on the hydrolysis reaction.

Reaction conditions: NaBH₄:20 mL (52.87 mmol/L), pH 10

In order to compare the present work with others, the activation parameters for the hydrolysis reaction were calculated according to the Arrhenius (Eq 1) and Eyring (Eq 2) equations, respectively:

$$\ln k = \left(-\frac{E_a}{R} \right) \frac{1}{T} + \ln A \quad (1)$$

$$\ln \frac{k}{T} = \left(-\frac{\Delta H}{R} \right) \frac{1}{T} + \ln \left(\frac{k_B}{h} \right) + \frac{\Delta S}{R} \quad (2)$$

where k is the rate constant, E_a represents the activation energy, R and T represent the

gas constant ($8.314 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$) and absolute temperature, ΔS and ΔH are entropy of activation and activation enthalpy, k_B and h are Boltzmann's constant ($1.381\times 10^{-23} \text{ J}\cdot\text{K}^{-1}$) and Planck's constant ($6.626\times 10^{-34} \text{ J}$). The plots of $\ln k\cdot T^{-1}$ and $\ln(k/T)\cdot T^{-1}$ should be straight lines, and from their slopes and intercepts, the E_a , ΔH and ΔS can be calculated. As shown in Figure 7, the hydrolysis of NaBH_4 catalyzed by Co-F agree well with the Arrhenius and Eyring equations. The calculated activation energy, activation enthalpy and entropy were $40.20 \text{ kJ}\cdot\text{mol}^{-1}$, $37.67 \text{ kJ}\cdot\text{mol}^{-1}$ and $-136.3 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, respectively. The activation energy value is lower than those of other NaBH_4 hydrolyses reported in references. Metin et al has synthesized a water-soluble polymer-stabilized Co^0 nanoclusters catalyst for the hydrolysis of NaBH_4 . The activation energy was $63 \text{ kJ}\cdot\text{mol}^{-1}$, activation enthalpy $61 \text{ kJ}\cdot\text{mol}^{-1}$, and activation entropy $-49 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ [49]. The hydrolysis reaction catalyzed by the following catalysts all have activation energy values higher than Co-F: Co/AC ($44 \text{ kJ}\cdot\text{mol}^{-1}$) [50], Co powder ($42 \text{ kJ}\cdot\text{mol}^{-1}$) [51], NiCo-Pt ($45.72 \text{ kJ}\cdot\text{mol}^{-1}$) [52].

(a)

(b)

Figure 7 Plots of $\ln k$ vs. T^{-1} (Arrhenius eq) (a) and $\ln(k/T)$ vs. T^{-1} (Eyring eq) (b).

Catalysts are usually expected to have good reusability except for high catalytic performance, since it is important for the practical application of catalysts. This is especial crucial for cobalt catalysts in hydrolysis of NaBH_4 because most of them rapidly lose activity over cycles [53]. Two reasons may explain the decay of catalytic activity: catalyst morphology may evolve during the reaction (for instance agglomeration of nanoparticles) [54], and catalyst surface may strongly adsorb reaction intermediates or products, leading to poisoning of catalytic sites [51]. Co-F is flexible and can be readily removed from the reaction solution and reused for another round of reaction after being pressed with hands, rinsed with water and dried. Figure 8 gives the rate constant and yield of hydrogen gas for five successive rounds of reactions. Though the constant rate had a little reduction, the yield remained nearly 100 %, indicating good recyclability of Co-F for NaBH_4 hydrolysis. It is superior to some reported catalysts. The catalyst $\text{Co}_{0.9}\text{Ni}_{0.1}/\text{graphene}$ remained only 44% of its initial catalytic activity at 5th use [55], intrazeolite cobalt (0) nanoclusters kept 60 % their initial catalytic activity [31], and the catalytic activity of bulk p(VPA)-Co was even significantly reduced to 15 % [56].

Figure 8 Yield of hydrogen (a) and rate constant (b) for successive five rounds of catalytic reaction. (Reaction conditions: NaBH₄: 20 mL (52.87 mmol/L), pH 10, 20 °C)

Conclusion

Co nanoparticles supported flexible foam Co-F was fabricated by modifying the elastic foam with Co-rGO. The prepared Co-F catalysts are efficient in the hydrolysis reaction of NaBH₄ with ~100% conversion for 5 repetitive usages with a little loss in reaction rate. Hydrogen generation from the hydrolysis of NaBH₄ depended on the catalysts, NaBH₄ concentration, temperature and pH of the medium. A kinetic study shows that the catalytic hydrolysis of NaBH₄ is zero order with respect to NaBH₄

concentration; and the activation energy is $40.20 \text{ kJ}\cdot\text{mol}^{-1}$. The high catalytic activity and stability of Co-F are attributed to the high dispersibility of Co nanoparticles, their strongly attachment through rGO on the skeleton of the elastic foam, the accessibility by the way of the opened pores of the foam, and the convenient recycle process.

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