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DESCRIPTION CN117643888A

A method for preparing doped NiCu-based three-dimensional hierarchical nanocatalysts and its application

[0001]

Technical Field

[n0001]

This invention belongs to the fields of nanomaterials and catalyst preparation technology.

In particular, this invention relates to a method for preparing a doped NiCu-based three-dimensional hierarchical nanocatalyst and its application.

[0003]

Background Technology

[n0002]

Ammonia borane (NHBH, abbreviated as AB) has a high hydrogen energy density (142 MJ/kg) and a high hydrogen content (19.6 wt%), and is considered to be an extremely efficient hydrogen storage material.

It hardly reacts at room temperature, but with the help of a catalyst, 1 mol of AB can release almost 3 mmol of hydrogen through hydrolysis. The hydrogen release rate varies greatly depending on the performance of the catalyst. Therefore, the research and development of new and efficient catalysts for hydrogen production by hydrolysis of ammonia borane is a hot topic in current new energy research.

[n0003]

Three-dimensional hierarchical nanostructures are recognized as a new type of catalytic material with great application prospects. They have the following advantages: (1) They can prevent the aggregation of low-dimensional nanostructures and ensure that the structure and morphology of the nanomaterials themselves are not destroyed; (2) The three-dimensional nanostructures obtained after construction have a large specific surface area and exhibit more active sites; (3) The arrangement and assembly of the building units can produce synergistic and coupling effects.

Although three-dimensional hierarchical nanostructures have received widespread attention in fields such as heterogeneous catalysis, lithium battery electrode materials, and supercapacitor materials.

[n0004]

However, there is no publicly available technology that discloses the application of catalysts with three-dimensional hierarchical nanostructures in the ammonia boron alcoholysis hydrogen production system.

[0007]

Summary of the Invention

[n0005]

The technical problem to be solved by the present invention is to provide a method for preparing a doped NiCu-based three-dimensional hierarchical nanocatalyst. The morphology and microstructure of the product are controlled by a two-phase interface reaction method to obtain a catalyst with a three-dimensional hierarchical structure, which can be used to catalyze the alcoholysis of ammonia and borane to produce hydrogen. Moreover, the doped NiCu-based three-dimensional hierarchical nanocatalyst has the advantages of high activity, high stability and low cost.

[n0006]

This invention provides a method for preparing a doped NiCu-based three-dimensional hierarchical nanocatalyst, comprising the following steps:

[n0007]

S1: Dissolve nickel salt, M metal-doped salt, and copper salt in an organic solvent to prepare a mixed salt solution A;

[n0008]

S2: Dissolve sodium borohydride, the reducing agent, in water, and adjust the alkalinity with sodium hydroxide to obtain solution B;

[n0009]

S3: Solution B is added dropwise to mixed salt solution A. Solution B and mixed salt solution A are immiscible. At the interface between the two phases, metal ions and the strong reducing agent sodium borohydride are present simultaneously. As the reaction proceeds, the concentration of metal ions and sodium borohydride at the interface will decrease. Concentration diffusion will cause metal ions and sodium borohydride in the bulk solution to diffuse continuously to the interface and undergo a reduction reaction, forming a doped NiCu-based three-dimensional hierarchical nanocatalyst.

[n0010]

Furthermore, M metal is one of Co, Mo, Fe, and Mn.

[n0011]

Furthermore, it also includes:

[n0012]

S4: The three-dimensional doped NiCu-based three-dimensional hierarchical nanocatalyst was transferred to a reactor and reacted at 80–180°C for 8–24 h. After filtration and washing, it was dried at 40–80°C to obtain doped NiCu-based three-dimensional hierarchical nanocatalyst particles.

[n0013]

Furthermore, the nickel salt is selected from one or more of nickel chloride hexahydrate, nickel sulfate heptahydrate, nickel nitrate hexahydrate, nickel chloride, nickel sulfate, nickel nitrate, and nickel acetate.

[n0014]

Furthermore, the soluble copper salt is selected from one or more of copper chloride dihydrate, copper sulfate pentahydrate, copper nitrate, and copper acetate.

[n0015]

Furthermore, the M metal doped salt is FeCl_3 or one or more of cobalt acetate tetrahydrate, cobalt chloride, cobalt sulfate, cobalt nitrate, cobalt chloride hexahydrate, cobalt sulfate heptahydrate, cobalt nitrate hexahydrate, and cobalt acetate.

[n0016]

Application of the doped NiCu-based three-dimensional hierarchical nanocatalyst prepared by the method described above in the catalytic hydrolysis of ammonia borane to produce hydrogen.

[n0017]

In summary, the preparation method of the present invention has the following beneficial effects:

[n0018]

This application provides a highly active, highly stable, low-cost, and practically valuable catalyst for hydrogen production from ammonia boron alcoholysis. The doped NiCu-based three-dimensional hierarchical nanocatalyst has the following advantages: (I) It prevents the aggregation of low-dimensional nanostructures and ensures that the structure and morphology of the nanomaterials themselves are not destroyed, thus maintaining the stability of catalytic performance; (II) The three-dimensional nanostructures obtained after construction have a large specific surface area, which is beneficial to providing more active sites for catalytic reactions; (III) The arrangement and assembly of the building units can produce synergistic and coupling effects.

[n0019]

The doped NiCu-based three-dimensional hierarchical nanocatalyst provided in this application has the advantages of preventing the aggregation of low-dimensional nanostructures and ensuring that the structure and morphology of the nanomaterials

themselves are not destroyed. It can effectively maintain the stability of catalytic performance, greatly improve the stability and cycling performance of the catalyst, and achieve a catalytic activity of no less than 85% of the initial value after 5-6 cycles of use.

[0023]

Attached Figure Description

[n0020]

Figure 1 is a SEM image of the doped Co-NiCu three-dimensional hierarchical nanocatalyst in Example 1.

[n0021]

Figure 2 is a TEM image of the doped Co-NiCu three-dimensional hierarchical nanocatalyst in Example 1.

[n0022]

Figure 3 shows the XRD test curves of the doped Co-NiCu three-dimensional hierarchical nanocatalyst in Example 1.

[n0023]

Figure 4 shows the catalytic hydrogen production performance of the doped Co-NiCu three-dimensional hierarchical nanocatalyst in Example 1.

[0028]

Detailed Implementation

[n0024]

The invention will now be described in further detail with reference to specific embodiments.

However, this should not be construed as limiting the scope of the above-described subject matter of the present invention to the following embodiments only.

Without departing from the above-described technical concept of this invention, all substitutions, alterations, and improvements made based on common technical knowledge and conventional methods in the art should be included within the scope of this invention.

[n0025]

This application discloses a method for preparing a doped NiCu-based three-dimensional hierarchical nanocatalyst, comprising the following steps:

[n0026]

S1: Dissolve nickel salt, M metal-doped salt, and copper salt in an organic solvent to prepare a mixed salt solution A; M metal is one of Co, Mo, Fe, and Mn.

When the metal M is Fe, it can be FeCl_3 .

When M is Co, it can be one or more of cobalt acetate tetrahydrate, cobalt chloride, cobalt

sulfate, cobalt nitrate, cobalt chloride hexahydrate, cobalt sulfate heptahydrate, cobalt nitrate hexahydrate, and cobalt acetate.

[n0027]

The nickel salt is selected from one or more of nickel chloride hexahydrate, nickel sulfate heptahydrate, nickel nitrate hexahydrate, nickel chloride, nickel sulfate, nickel nitrate, and nickel acetate.

[n0028]

The soluble copper salt is selected from one or more of copper chloride dihydrate, copper sulfate pentahydrate, copper nitrate, and copper acetate.

[n0029]

S2: Dissolve sodium borohydride, the reducing agent, in water, and adjust the alkalinity with sodium hydroxide to obtain solution B;

[n0030]

S3: Solution B is added dropwise to mixed salt solution A. Solution B and mixed salt solution

A are immiscible. At the interface between the two phases, metal ions and sodium borohydride, a strong reducing agent, coexist. As the reaction proceeds, the concentrations of metal ions and sodium borohydride at the interface decrease. Concentration diffusion causes metal ions and sodium borohydride in the bulk solution to continuously diffuse to the interface and undergo reduction reactions, forming a three-dimensional doped NiCu-based three-dimensional hierarchical nanocatalyst.

[n0031]

The interface is a heterogeneous region with a thickness of about a few nanometers and unique thermodynamic properties such as density and viscosity.

Two-phase interfaces, as a special type of chemical reaction field, can be used in organic synthesis to prepare various nanomaterials such as metals, alloys, oxides, sulfides, and hydroxides.

This synthesis method is simple to operate, generally does not require excessively high reaction temperatures or special reaction equipment, and allows for effective control over the morphology and size of the product.

The two-phase interface reaction method generally involves dissolving an appropriate organometallic precursor in an organic solvent that is completely immiscible with water (such as toluene, chloroform, etc.), and then reacting it with alkali, reducing agent, sulfiding agent, etc. in the aqueous phase under certain temperature conditions. The resulting product is deposited at the two-phase interface.

[n0032]

S4: The three-dimensional doped NiCu-based three-dimensional hierarchical nanocatalyst was transferred to a reactor and reacted at 80–180°C for 8–24 h. After filtration and washing, it was dried at 40–80°C to obtain the doped Co-NiCu three-dimensional hierarchical nanocatalyst.

[n0033]

Example 1

[n0034]

This embodiment discloses a method for preparing a doped NiCu-based three-dimensional hierarchical nanocatalyst, comprising the following steps:

[n0035]

S1: Dissolve cobalt sulfate (2 mmol), nickel sulfate (0.5 mmol), and copper sulfate (0.5 mmol) in 40 mL of chloroform to prepare mixed salt solution A;

[n0036]

S2: Dissolve 2 mmol of sodium borohydride, a reducing agent, in water, and adjust the alkalinity with sodium hydroxide to obtain solution B;

[n0037]

S3: Add solution B dropwise to mixed salt solution A. Since chloroform and water are immiscible, the entire system will separate into layers, with chloroform at the bottom and water at the top.

At the interface between the two phases, metal ions and sodium borohydride, a strong reducing agent, coexist. As the reaction proceeds, the concentrations of metal ions and sodium borohydride at the interface decrease, while concentration diffusion causes metal ions and sodium borohydride in the bulk solution to continuously diffuse to the interface and

undergo reduction reactions, thus forming a three-dimensional doped NiCu-based three-dimensional hierarchical nanocatalyst.

[n0038]

S4: The three-dimensional doped NiCu-based three-dimensional hierarchical nanocatalyst was transferred to a reactor and reacted at 80–180°C for 8–24 h. After filtration and washing, it was dried at 40–80°C to obtain the doped Co-NiCu three-dimensional hierarchical nanocatalyst.

[n0039]

Example 2

[n0040]

This embodiment discloses a method for preparing a doped NiCu-based three-dimensional hierarchical nanocatalyst, comprising the following steps:

[n0041]

S1: Dissolve cobalt chloride (2 mmol), nickel sulfate (0.5 mmol), and copper sulfate (0.5 mmol) in 40 mL of chloroform to prepare mixed salt solution A;

[n0042]

S2: Dissolve 2 mmol of sodium borohydride, a reducing agent, in water, and adjust the alkalinity with sodium hydroxide to obtain solution B;

[n0043]

S3: Add solution B dropwise to mixed salt solution A. Since chloroform and water are immiscible, the entire system will separate into layers, with chloroform at the bottom and water at the top.

At the interface between the two phases, metal ions and sodium borohydride, a strong reducing agent, coexist. As the reaction proceeds, the concentrations of metal ions and sodium borohydride at the interface decrease, while concentration diffusion causes metal ions and sodium borohydride in the bulk solution to continuously diffuse to the interface and undergo reduction reactions, thus forming a three-dimensional doped NiCu-based three-dimensional hierarchical nanocatalyst.

[n0044]

S4: The three-dimensional doped NiCu-based three-dimensional hierarchical nanocatalyst was transferred to a reactor and reacted at 80–180°C for 8–24 h. After filtration and washing, it was dried at 40–80°C to obtain the doped Co-NiCu three-dimensional hierarchical nanocatalyst.

[n0045]

Example 3

[n0046]

This embodiment discloses a method for preparing a doped NiCu-based three-dimensional hierarchical nanocatalyst, comprising the following steps:

[n0047]

S1: Dissolve ferric chloride (2 mmol), nickel sulfate (0.5 mmol), and copper sulfate (0.5 mmol) in 40 mL of chloroform to prepare mixed salt solution A;

[n0048]

S2: Dissolve 2 mmol of sodium borohydride, a reducing agent, in water, and adjust the alkalinity with sodium hydroxide to obtain solution B;

[n0049]

S3: Add solution B dropwise to mixed salt solution A. Since chloroform and water are immiscible, the entire system will separate into layers, with chloroform at the bottom and water at the top.

At the interface between the two phases, metal ions and sodium borohydride, a strong reducing agent, coexist. As the reaction proceeds, the concentrations of metal ions and sodium borohydride at the interface decrease, while concentration diffusion causes metal ions and sodium borohydride in the bulk solution to continuously diffuse to the interface and undergo reduction reactions, thus forming a three-dimensional doped NiCu-based three-dimensional hierarchical nanocatalyst.

[n0050]

S4: The three-dimensional doped NiCu-based three-dimensional hierarchical nanocatalyst was transferred to a reactor and reacted at 80–180°C for 8–24 h. After filtration and washing, it was dried at 40–80°C to obtain the doped Fe-NiCu three-dimensional hierarchical nanocatalyst.

[n0051]

Example 4

[n0052]

This embodiment discloses a method for preparing a doped NiCu-based three-dimensional hierarchical nanocatalyst, comprising the following steps:

[n0053]

S1: Dissolve molybdenum chloride (2 mmol), nickel sulfate (0.5 mmol), and copper sulfate (0.5 mmol) in 40 mL of chloroform to prepare mixed salt solution A;

[n0054]

S2: Dissolve 2 mmol of sodium borohydride, a reducing agent, in water, and adjust the alkalinity with sodium hydroxide to obtain solution B;

[n0055]

S3: Add solution B dropwise to mixed salt solution A. Since chloroform and water are immiscible, the entire system will separate into layers, with chloroform at the bottom and water at the top.

At the interface between the two phases, metal ions and sodium borohydride, a strong reducing agent, coexist. As the reaction proceeds, the concentrations of metal ions and sodium borohydride at the interface decrease, while concentration diffusion causes metal ions and sodium borohydride in the bulk solution to continuously diffuse to the interface and

undergo reduction reactions, thus forming a three-dimensional doped NiCu-based three-dimensional hierarchical nanocatalyst.

[n0056]

S4: The three-dimensional doped NiCu-based three-dimensional hierarchical nanocatalyst was transferred to a reactor and reacted at 80–180°C for 8–24 h. After filtration and washing, it was dried at 40–80°C to obtain the doped Mo-NiCu three-dimensional hierarchical nanocatalyst.

[n0057]

The structure and performance of the Co-NiCu three-dimensional hierarchical nanocatalyst prepared in this invention will be analyzed and tested, taking the doped Co-NiCu three-dimensional hierarchical nanocatalyst in Example 1 as an example.

[n0058]

1. SEM Analysis

[n0059]

Figure 1 is a SEM image of the doped Co-NiCu three-dimensional hierarchical nanocatalyst prepared in Example 1.

As can be seen from the scanning image, the morphology of the doped Co-NiCu three-dimensional hierarchical nanocatalyst is that of particles with a diameter of approximately 50 nm.

[n0060]

2. TEM test

[n0061]

Figure 2 is a TEM image of the doped Co-NiCu three-dimensional hierarchical nanocatalyst prepared in Example 1. The TEM image further confirms that the synthesized doped Co-NiCu three-dimensional hierarchical nanocatalyst consists of uniform nanoparticles.

[n0062]

3. XRD

[n0063]

Figure 3 shows the XRD test of the doped Co-NiCu three-dimensional hierarchical nanocatalyst in Example 1.

The figure shows the characteristic peaks of different crystal planes of the doped Co-NiCu three-dimensional hierarchical nanocatalyst.

[n0064]

4. Testing of catalytic hydrogen production performance

[n0065]

Figure 4 shows the performance test of the doped Co-NiCu three-dimensional hierarchical nanocatalyst as a catalyst for the hydrolysis of ammonia borane to produce hydrogen in Example 1. The amount of NH_3BH_3 was 3 mmol, NaOH was 20 mmol, and the catalyst was 5 mg.

The hydrogen production in the first minute of the doped Co-NiCu three-dimensional hierarchical nanocatalyst at 25°C was measured to be 21 mL.

[n0066]

The doped NiCu-based three-dimensional hierarchical nanocatalyst prepared in this

application has the advantages of preventing the aggregation of low-dimensional nanostructures and ensuring that the structure and morphology of the nanomaterials themselves are not destroyed. It can effectively maintain the stability of catalytic performance, greatly improve the stability and cycling performance of the catalyst, and achieve a catalytic activity of no less than 85% of the initial value after 5-6 cycles of use.

[n0067]

This application provides a highly active, highly stable, low-cost, and practically valuable catalyst for hydrogen production from ammonia boron alcoholysis. The doped NiCu-based three-dimensional hierarchical nanocatalyst has the following advantages: (I) It prevents the aggregation of low-dimensional nanostructures and ensures that the structure and morphology of the nanomaterials themselves are not destroyed, thus maintaining the stability of catalytic performance; (II) The three-dimensional nanostructures obtained after construction have a large specific surface area, which is beneficial to providing more active

sites for catalytic reactions; (III) The arrangement and assembly of the building units can produce synergistic and coupling effects.

[n0068]

The above description represents the preferred embodiments of the present invention. It should be noted that those skilled in the art can make various improvements and modifications without departing from the principles of the present invention, and these improvements and modifications are also considered to be within the scope of protection of the present invention.
