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(54) Title: A CATALYST FOR PREPARING HYDROGEN BY HYDROLYSIS OF METAL HYDROGEN COMPLEXES, PROCESSES FOR PREPARING AND USING THE SAME

(57) Abstract: A catalyst for preparing hydrogen by the hydrolysis of metal hydrogen complexes comprising a powdery metal, wherein it further comprising a binder and a support with the powdery metal and binder being distributed on the support, the contents of said powdery metal, said binder, said support are 5-85%, 1-80% and 2-50% by weight respectively based on the total amount of the catalyst; and said metal is one or more selected from the metals having hydrogenation activity. The catalyst for preparing hydrogen by the hydrolysis of metal hydrogen complexes provided by the present invention is easy to recovery and convenient to use.



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A Catalyst for Preparing Hydrogen by Hydrolysis of Metal Hydrogen Complexes, Processes for Preparing and Using the Same

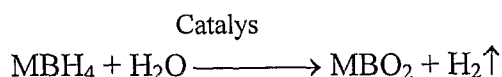
Field of Invention

5 The present invention relates to a catalyst for preparing hydrogen, a process for preparing the catalyst, and a process for preparing hydrogen using the catalyst. In particular, the present invention relates to a catalyst for preparing hydrogen by hydrolysis of metal hydrogen complexes, a process for preparing the catalyst, and a process for preparing hydrogen using the catalyst.

Background

10 Being an ideal portable electric source or the power for electric automobiles, fuel cells have the characters of high specific capacity, cleanness, and no pollution, and generally use hydrogen as a feed stock to generate electric energy. Many methods have been presented to store hydrogen in fuel cells such as high pressure gaseous hydrogen-storage, liquid hydrogen-storage, hydrogen-storage in carbon nanotube, hydrogen-storage in hydrogen-storage alloy. However, these methods have some shortcomings. For example, the high pressure gaseous hydrogen-storage is not safe such as for its high pressure; the liquefaction cost on the liquid hydrogen-storage is high; the hydrogen absorption-desorption rate and capacity stability of the carbon nanotube are low; and the hydrogen-storage capacity of the hydrogen-storage alloy is low.

25 The process for preparing hydrogen by the hydrolysis of borohydrides is presented in recent years, which has the advantages of high hydrogen-storage capacity (taking NaBH_4 as example, its hydrogen-storage capacity attains 10.9% by weight), high hydrogen purity (the generated gas contains no other gases affecting the catalyst of the cell), safety, no pollution, and etc. The principle of this process is shown by the following reaction equation:



30 Wherein M may be any alkali metals such as potassium, sodium or lithium.

 US 6,358,488 discloses a process for preparing hydrogen, which comprises the following steps: (a) dissolving a metal hydrogen complex in an basic aqueous solution to form a reaction medium; (b) contacting said reaction medium with a fluorized or

unfluorized metal or hydrogen-absorption alloy as the catalyst. Wherein said fluorized or unfluorized metal is selected from the group consisting of nickel, cobalt, zirconium, rhodium, platinum, palladium, silver, and gold. Step (b) is carried out by adding said catalyst to the reaction medium or passing the reaction medium through the fixed bed of the catalyst.

For the above reaction, it is necessary to recover and reuse the catalyst when the reaction is complete. Because the catalyst used in the above process is powdered and dispersed in the reaction medium, it needs filtering and drying for recovery. Therefore, the above process possesses the disadvantages of difficulty to recover and inconvenience to reuse the catalyst. Besides, the powdery metal catalyst is easy to be scattered and adsorbed on the reaction container, whereby causes the loss of the catalyst. It is well known that the above powdery metals used as the catalyst are mostly noble metals with high price and should be recovered as much as possible for reuse to save the cost.

Summary of the Invention

An object of the present invention is to provide a catalyst for preparing hydrogen by hydrolysis of metal hydrogen complexes with easiness to recover and convenience to use.

Another object of the present invention is to provide a process for preparing said catalyst.

Another object of the present invention is to provide a process for preparing hydrogen by using said catalyst.

The catalyst for preparing hydrogen by the hydrolysis of metal hydrogen complexes provided by the present invention comprises a powdery metal, wherein it further comprises a binder and a support with the powdery metal and binder being distributed on, and the contents of said powdery metal, said binder and said support are 1-80%, 2-50% and 5-85% by weight respectively based on the total amount of the catalyst; said metal is one or more selected from the metals with hydrogenation activity.

The process for preparing the catalyst for hydrogen preparation by the hydrolysis of metal hydrogen complexes provided by the present invention comprises preparing a viscous fluid or paste by adding and uniformly dispersing a powdery metal and a binder into a solvent, and supporting the obtained viscous fluid or paste on the support, wherein the contents of said powdery metal, said binder and said support are 1-80%, 2-50% and

5-85% by weight respectively based on the total amount of the catalyst; and said metal is one or more selected from the metals with hydrogenation activity.

The process for preparing hydrogen by the hydrolysis of metal hydrogen complexes provided by the present invention comprises preparing a reaction medium by
5 dissolving a metal hydrogen complex in a basic aqueous solution and contacting said reaction medium with a catalyst comprising a powdery metal, wherein the catalyst further comprises a binder and a support with the powdery metal and binder being distributed on the support. Based on the total amount of the catalyst, the contents of said powdery metal, said binder and said support are 1-80%, 2-50% and 5-85% by weight respectively; and said
10 metal is one or more selected from the metals with hydrogenation activity.

The catalyst provided by the present invention provides a hydrogen production rate of over 40% (the ratio of the practical hydrogen output to the theoretical hydrogen output), which is equivalent to or slightly higher than provided by the prior art, and does not obviously deactivate after 50 times of continuous reaction without any treatment.
15 Therefore, the catalyst provided by the present invention possesses relatively high activity and long service life. Additionally, the catalyst provided by the present invention possesses the advantages of easiness to fully recover and convenience to use since the powdery metal is fixed on the support by the binder.

20 Detailed Description of the Preferred Embodiments

The catalyst for preparing hydrogen by the hydrolysis of metal hydrogen complexes provided by the present invention comprises a powdery metal, wherein it further comprises a binder and a support with the powdery metal and binder being distributed on, and the contents of said powdery metal, said binder and said support are
25 1-80%, 2-50%, and 5-85% by weight based on the total amount of the catalyst; said metal is one or more selected from the metals having hydrogenation activity.

According to the present invention, various metals with hydrogenation activity can be used. For example, said metal may be one or more selected from iron, cobalt, nickel, zirconium, rhodium, platinum, and palladium, preferably be cobalt, nickel, or the mixture
30 of both. The content of said powdery metal is preferably 15-70% by weight. There is no special restriction on the average particle diameter of said powdery metal, which may be the conventional size of the powdery metal used as a catalyst. For example, in order to enhance the catalytic performance of the powdery metal, the average particle diameter of

said powdery metal is preferably 0.1-10 μm , more preferably 0.5-5 μm .

According to the present invention, said binder may be one or more selected from polytetrafluoroethylene resin (PTFE), sodium carboxymethylcellulose (CMC), phenol-formaldehyde resin, urea-formaldehyde resin, and epoxide resin. All said binders are commercially available, e.g. 2103 phenol-formaldehyde resin produced by Shanghai Daowang Binding Science & Technology Co. Ltd., urea-formaldehyde resin series products produced by Jilin Tongxin Science & Trade Co. Ltd., and PTFE provided by Hebei Dacheng Changcheng Polytetrafluoro Product Plant. The content of said binder is preferably 2-20% by weight based on the total amount of the catalyst. Said binder may be in the form of solid or aqueous solution, of which the maximum concentration may be the saturation concentration of the same.

According to the catalyst provided by the present invention, said support may be any support for catalyst, such as various porous materials or non-porous materials. For example, porous materials include silk screen, ceramic honeycomb, foam nickel, and foam copper, and non-porous materials include various engineering plastics such as polycarbonate resins, polyformaldehyde resins, polyester resins, polyamide resins, polyphenyl ether resins, acrylonitrile-butadiene-styrene (ABS) resins, and epoxy plastics. There is no special restriction on the shape and size of the support, which may be any shape and size. The content of said support is preferably 20-75% by weight based on the total amount of the catalyst. The powdery metal and binder are distributed on the support, and preferably, in the form of their mixture.

In order to more uniformly mix the powdery metal and the binder, said catalyst can further comprise a dispersant. Said dispersant can be any conventional dispersant known to the skilled in the art and is preferably one or more selected from carbon powder, alumina powder, acetylene black. The content of the dispersant may be 0-5% by weight, preferably 0.5-2% by weight based on the total amount of the catalyst. The average particle diameter of the dispersant is preferably 0.01-5 μm , more preferably 0.1-2 μm .

Said solvent, wherein a powdery metal and a binder are dispersed uniformly, may be one or more of various organic or inorganic solvents which allows the binder to dissolve or disperse in but does not react with the binder and powdery metal. Such organic solvent may be one or more of liquid alcohols, petroleum ether, tetrahydrofuran (THF), acetone, and N,N-dimethyl formamide, wherein said liquid alcohol may be various C_1 - C_{10} alkyl alcohols, and such inorganic solvent may be water. Comprehensively considering the cost

of the solvent, environmental protection, and the volatility of the solvent, the present invention prefers that said solvent is water. There is no special restriction on the amount of the solvent, as long as the binder and powdery metal can be effectively mixed with each other. Generally, the amount of the solvent is 50-300% by weight, preferably 80-260%
5 based on the weight of the powdery metal. It should be mentioned that if the used binder is in the form of aqueous solution, the amount of said solvent should include that included in the aqueous solution of the binder.

Any known method such as stirring with a stirrer and/or oscillation with ultrasonic wave may be used to uniformly disperse the powdery metal and the binder into said
10 solvent to prepare viscous fluid or paste on the support. According to the present invention, the method of a combination of stirring and oscillation with ultrasonic wave is preferable.

Various methods may be used to support the obtained viscous fluid or paste on the support. For example, the support may be impregnated in said viscous fluid or paste, or said viscous fluid or paste may be coated on the support. In the embodiment of the present
15 invention, it is preferred that said viscous fluid or paste be coated on the support using the coating method.

Preferably, a solidification step is further comprised after the viscous fluid or paste is supported on the support. Said solidification step can be carried out at 50-800°C for 10-90 min under the condition of vacuum (the vacuum degree is preferably 10^{-3} - 10^{-4} MPa)
20 or inert gas protection. Said inert gas can be one or more selected from nitrogen, helium, neon, argon, xenon, and krypton, with nitrogen being preferred.

Said metal hydrogen complex can be any metal hydrogen complex conventionally used to prepare hydrogen by the skilled in the art. For example, said metal hydrogen complex can be represented by the general formula of MQH_4 or $M'(QH_4)_2$, wherein M is
25 an alkali metal element, M' is an alkali earth metal element, Q is one or more elements selected from boron, aluminum, and gallium. Preferably, said metal hydrogen complex in the present invention is sodium borohydride or potassium borohydride, or a mixture thereof, and more preferably sodium borohydride.

The examples of said basic aqueous solution include sodium hydroxide solution, potassium hydroxide solution, and ammonia water, and said basic aqueous solution prefers
30 sodium hydroxide solution or potassium hydroxide solution. There is no special restriction on the concentration of the basic aqueous solution, and 5-30% by weight is the preferable.

The concentration of said metal hydrogen complex in said reaction medium is

preferably 2-50% by weight, more preferably 5-30% by weight.

There is no special restriction on the temperature for the contact of said reaction medium with the catalyst, and the temperature of 10-60°C is preferable and 20-40°C is more preferable in order that the catalytic hydrogen generation reaction can be better carried out. Various ways can be used to bring the reaction medium into contact with the catalyst, and the preferable one is to dip the catalyst in said reaction medium.

The present invention will be described in more detail by the following examples.

Example 1

1.5 g cobalt powder, 1.5 g nickel powder (average particle diameter is 5.0 μm), and 3 g 10% by weight of PTFE aqueous solution were mixed, and 3.60 g deionized water was added thereto. The resulted mixture was oscillated by ultrasonic wave while being stirred for about 10 min to yield a uniform viscous fluid. A piece of 0.2 g foam nickel was impregnated in the viscous fluid for 60 min, and then solidified at 350°C for 15 min under the protection of nitrogen to yield 0.4 g catalyst. The contents of the cobalt powder, nickel powder, PTFE, and the support (foam nickel) in the obtained catalyst were 22.75%, 22.75%, 4.5%, and 50% by weight respectively.

1 g sodium borohydride was added to 19 g 10% by weight of solution of sodium hydroxide and uniformly mixed to form a reaction medium, and the concentration of sodium borohydride in the obtained reaction medium was 5% by weight.

The hydrogen generation reaction was started at 30°C by putting the previously obtained catalyst in the reaction medium. The reaction basically stopped after 30 min and 0.073 g hydrogen was obtained. It can be derived according to $\text{NaBH}_4 + 2\text{H}_2\text{O} \rightarrow 4\text{H}_2 + \text{NaBO}_2$ that the theoretical hydrogen output from 1g NaBH_4 is 0.21 g, so the hydrogen production rate (the ratio of the practical hydrogen output to the theoretical hydrogen output) of the catalyst in the reaction was 34.7%.

The catalyst was taken out from the above reaction medium and put in an equal amount of an identical new reaction medium without any treatment to carry out repeated reaction. The catalyst did not obviously deactivate after 50 times of reaction.

Example 2

1 g nickel powder (average particle diameter is 1.0 μm) was mixed with 10 g 3% by weight of CMC aqueous solution. The material was oscillated by ultrasonic wave while

being stirred for about 15 min to yield a uniform viscous fluid. Said viscous fluid was coated onto the two sides of 0.20 g screen. The coated screen was solidified at 200°C for 60 min under vacuum (the vacuum degree was 5×10^{-4} MPa) to yield 0.44 g catalyst. The contents of the nickel powder, CMC, and support (screen) in the obtained catalyst were
5 42%, 12.5%, and 45.5% by weight respectively.

2 g sodium borohydride was added to 18 g 20% by weight of solution of sodium hydroxide and uniformly mixed to form a reaction medium, and the concentration of sodium borohydride in the obtained reaction medium was 10% by weight.

The hydrogen preparation reaction was started at 40°C by putting the previously
10 obtained catalyst in the reaction medium. The reaction basically stopped after 30 min and 0.32 g hydrogen was obtained. The hydrogen production rate (the ratio of the practical hydrogen output to the theoretical hydrogen output) of the catalyst in the reaction was 38%.

The catalyst was taken out from the above reaction medium and put in an equal
15 amount of an identical new reaction medium without any treatment to carry out repeated reaction. The catalyst did not obviously deactivate after 50 times of reaction.

Example 3

3 g cobalt powder (average particle diameter was 3 μm) was mixed with 4.5 g
20 10% by weight of an aqueous solution of phenol-formaldehyde resin, 2.40 g deionized water and 0.03 g alumina powder (average particle diameter was 0.2 μm) were also added. The resulted mixture was oscillated by ultrasonic wave while being stirred for about 10 min to yield a uniform viscous fluid. A piece of 1.7464 g ceramic honeycomb was impregnated in the viscous fluid for 120 min, and then solidified at 220°C for 30 min under
25 the protection of nitrogen to yield 2.4538 g catalyst. The contents of the cobalt powder, phenol-formaldehyde resin, support (ceramic honeycomb), and alumina in the obtained catalyst were 24.8%, 3.7%, 71.2%, and 0.3% by weight respectively.

4 g sodium borohydride was added to 16 g 10% by weight of solution of sodium hydroxide and uniformly mixed to form a reaction medium, and the concentration of
30 sodium borohydride in the obtained reaction medium was 20% by weight.

The hydrogen preparation reaction was started at 30°C by putting the previously obtained catalyst in the reaction medium. The reaction basically stopped after 30 min and 0.34 g hydrogen was obtained. The hydrogen production rate (the ratio of the practical

hydrogen output to the theoretical hydrogen output) of the catalyst in the reaction of this time was 40.7%.

The catalyst was taken out from the above reaction medium and put in an equal amount of an identical new reaction medium without any treatment to carry out repeated
5 reaction. The catalyst did not obviously deactivate after 50 times of reaction.

Claims

We claim:

- 5 1. A catalyst for preparing hydrogen by the hydrolysis of metal hydrogen complexes comprising a powdery metal, characterized in that it further comprises a binder and a support with the powdery metal and binder being distributed on; the contents of said powdery metal, said binder and said support are 1-80%, 2-50% and 5-85% by weight respectively based on the total amount of the catalyst; and said metal is one or more
10 selected from the metals having hydrogenation activity.
2. The catalyst according to claim 1, wherein the powdery metal and binder are distributed on the support in the form of a mixture of both.
3. The catalyst according to claim 1, wherein the contents of said powdery metal, said binder and said support are 15-70%, 2-20%, and 20-75% by weight respectively based
15 on the total amount of the catalyst.
4. The catalyst according to claim 1, wherein said metal is one or more selected from iron, cobalt, nickel, zirconium, rhodium, platinum, and palladium.
5. The catalyst according to claim 1, wherein the average particle diameter of said powdery metal is 0.1-10 μm .
- 20 6. The catalyst according to claim 1, wherein said binder is one or more selected from polytetrafluoroethylene resin, sodium carboxymethylcellulose, phenol-formaldehyde resin, urea-formaldehyde resin, and epoxide resin.
7. The catalyst according to claim 1, wherein said support is silk screen, ceramic honeycomb, foam nickel, foam copper, or engineering plastics.
- 25 8. The catalyst according to claim 1, wherein it further comprises a dispersant, the content of which is 0-5% by weight based on the total weight of the catalyst.
9. A process for preparing the catalyst for preparing hydrogen by the hydrolysis of metal hydrogen complexes of claim 1, which comprises preparing a viscous fluid or paste by adding and uniformly dispersing the powdery metal and binder into a solvent and

supporting the obtained viscous fluid or paste on the support, wherein said metal is one or more selected from the metals having hydrogenation activity.

10. The process according to claim 9, wherein said solvent is one or more selected from water and liquid alcohols, and the amount of which is 50-300% by weight based on
5 the weight of the powdery metal.

11. The process according to claim 9, which further comprises a solidification step under conditions of vacuum or inert gas and 50-800°C for 10-90 min after the viscous fluid or paste being supported on the support.

12. A process for preparing hydrogen by the hydrolysis of metal hydrogen complexes,
10 which comprises dissolving a metal hydrogen complex in a basic aqueous solution to form a reaction medium and contacting said reaction medium with a catalyst, characterized in that said catalyst is a catalyst of claims 1-7.

13. The process according to claim 12, wherein said contact is carried out under the temperature of 10-60°C.

15 14. The process according to claim 12, wherein said metal hydrogen complex is sodium borohydride.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2006/000512

A. CLASSIFICATION OF SUBJECT MATTER

See extra sheet

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 8 C01B B01J C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI EPODOC PAJ CNKI CPRS catalyst, hydrolysis, metal hydrogen complex, borohydride, metal, hydrogenation, iron, Fe, cobalt, Co, nickel, Ni, zirconium, Zr, rhodium, Rh, platinum, Pt, palladium, Pd, binder, resin, support, carrier

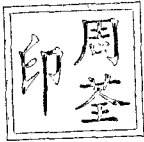
C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US6358488B1(Seijirau Suda, Mar. 19, 2002), see column 1 line 41 ~ column 8 line 55, and claims 1~ 10.	1-14
A	CN1440925A(WUHAN UNIVERSITY, Sep. 10, 2003), see page 1 ~ 2, and claims 1 ~ 9.	1-14
A	CN1458059A(TIANJIN UNIVERSITY, Nov. 26, 2003), see page 1 ~ 4, and claims 1 ~ 3.	12-14
A	US6790416B2(Hewlett-Packard Development Company, Sep. 14, 2004), see columns 2 ~3.	1-14

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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"L" document which may throw doubts on priority claim (S) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

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INTERNATIONAL SEARCH REPORT
Information on patent family members

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Patent Documents referred in the Report	Publication Date	Patent Family	Publication Date
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CN1440925A	2003-09-10	NONE	

INTERNATIONAL SEARCH REPORT

International application No.

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Continuation of : second sheet

A. CLASSIFICATION OF SUBJECT MATTER

B01J 23/74 (2006.01) i

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C01B 3/08 (2006.01) i

According to International Patent Classification (IPC) or to both national classification and IPC