Catalyst for the Evolution of Hydrogen from Borohydride Solution

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CATALYSTS FOR THE EVOLUTION OF HYDROGEN FROM BOROHYDRIDE SOLUTION

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ABSTRACT

Organic pigments are capable of catalyzing the decomposition reaction of hydrogen-rich, stabilized, borohydride solutions to generate hydrogen gas on-board an operable hydrogen-consuming device such as a motor vehicle or other combustion engine. The organic pigments are used in hydrogen generating systems and in methods for controlling the generation of hydrogen gas from metal hydride solutions.

4 Claims, 5 Drawing Sheets
Testing parameters:
- 5 ml purified water
- neutral solution
- 1 gram of NaBH₄
- 100 mg catalyst

Fig. 1

Time (min)

Hydrogen Volume - ml

- No catalyst
- 4, Cobalt
- 9
- 5
- 10
- 11
- 13
- 14

Testing parameters:
- 5 ml purified water
- neutral solution
- 1 gram of NaBH₄
- 100 mg catalyst
Fig. 4

- Pyranthrene dione
- Indanthrene Gold Orange
- Perylenetetracarboxylic diimide
- Plain buffer + sodium borohydride
CATALYSTS FOR THE EVOLUTION OF HYDROGEN FROM BOROHYDRIDE SOLUTION

This invention claims the benefit of priority from U.S. Provisional Application Ser. No. 60/535,293 filed Jan. 9, 2004, and was supported in part by the National Aeronautics and Space Administration (NASA), grant #NAG3-2751 and Department of Energy, Office of Energy Efficiency and Renewable Energy (EERE), contract #DEFC3699G010449 to University of Central Florida, Florida Solar Energy Center.

FIELD OF THE INVENTION

This invention relates to the novel use of organic pigments as catalysts, in particular to a catalytically controlled system for the release of hydrogen from a hydrogen-rich borohydride solution.

BACKGROUND AND PRIOR ART

Hydrogen gas is a very desirable fuel because it can be reacted with oxygen in hydrogen-consuming devices, such as a fuel cell, combustion engine or gas turbine, to produce energy and water. The use of hydrogen gas can ameliorate environmental pollution; lessen the world’s dependency on fossil fuels or petroleum; ease fears of depleted energy sources.

Safe and efficient storage of hydrogen is a prerequisite for widespread commercial use as a fuel. U.S. Pat. No. 6,534,033 B1 to Amendola et al., discloses the use of stabilized metal hydride solutions as an example of a safe, hydrogen-rich storage medium. Thus, with an abundant supply of metal hydride solutions, research is focused on the release of hydrogen from the storage medium.

The class of metal hydrides known as borohydrides is known to decompose in water, in the following manner: borohydride plus water yields methanoborate and hydrogen gas. The chemical reaction illustrated with borohydride is:

\[ \text{BH}_4^- + 2\text{H}_2\text{O} \rightarrow \text{BO}_4^{2-} + 4\text{H}_2 \]

Hydrogen-rich borohydrides are also of interest in electroconversion devices where the alkali metal-containing compound, such as borohydride is oxidized to generate electricity (U.S. Pat. No. 5,804,329 to Amendola; U.S. Pat. No. 6,468,694 B1 to Amendola; and U.S. Pat. No. 6,554,877 B2 to Finkelstein et al.). Although oxidation reactions are required to generate electric current, the spontaneous release of hydrogen gas when borohydrides are in contact with water is reported in each of the patents cited above. The borohydride decomposition reaction in water occurs very slowly without a catalyst. Thus, catalysts become the critical component in any hydrogen gas delivery system based on borohydride decomposition.

Catalysts used in hydrogen gas evolution or production of hydrogen compounds have been identified as amines (U.S. Pat. No. 3,923,966 to Vaughan); metal derivative catalysts (U.S. Pat. No. 4,448,951 to Ruptet et al. and U.S. Pat. No. 6,387,843 B1 to Yagi et al.); and transition metal catalysts (U.S. Pat. No. 5,804,329 to Amendola and U.S. Pat. No. 6,534,033 B1 to Amendola et al.).

There is a need for a broader range of catalytic materials, so that there are more choices for use in hydrogen-consuming devices. The present invention provides consumers with a broader choice of catalysts, which, in some cases, catalyze the hydrogen gas evolution reaction at a rate exceeding that of catalysts identified in the prior art.
The present invention provides a novel use of organic pigment catalysts in a hydrogen generation system utilizing stabilized borohydride solutions. Table 1 is a ranking of catalysts from the fastest to the slowest for the decomposition of sodium borohydride (NaBH₄) in a buffered solution of pH 11. Table 1 shows that pyranthreneone is first with a mean evolution rate of 6.5 ml of hydrogen gas per minute.

Further objects and advantages of this invention will be apparent from the following detailed description of a presently preferred embodiment that is illustrated schematically in the accompanying drawings.

BRIEF DESCRIPTION OF THE FIGURES

FIG. 1 shows hydrogen gas evolution from non-buffered 0.1 M NaBH₄ solution in the presence of many catalysts. FIG. 2 shows hydrogen gas evolution from 0.1 M NaBH₄ solution buffered at pH 11 in the presence of many catalysts. FIG. 3 shows pH dependence of catalytic hydrogen gas evolution from 0.1 M NaBH₄ solution using pyranthreneone catalyst. FIG. 4 shows the evolution of hydrogen gas from NaBH₄ solution at pH 11 over immobilized organic pigment catalysts. FIG. 5 is a schematic view of a hydrogen gas generation device using LiBH₄ tablets.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Before explaining the disclosed embodiment of the present invention in detail it is to be understood that the invention is not limited in its application to the details of the particular arrangement shown since the invention is capable of other embodiments. Also, the terminology used herein is for the purpose of description and not of limitation.

The present invention provides a novel use of organic pigments as catalysts in a hydrogen generation system utilizing stabilized borohydride solutions. Table 1 is a ranking of catalysts from the fastest to the slowest for the decomposition of sodium borohydride (NaBH₄) in a buffered solution of pH 11. Table 1 shows that pyranthreneone is first with a mean evolution rate of 6.5 ml of hydrogen gas per minute.

Table 1-continued

<table>
<thead>
<tr>
<th>RANK</th>
<th>CATALYST</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>1,4-Diketo-pyrrrole (3:4 Ciproxone)</td>
</tr>
<tr>
<td>8</td>
<td>Quinacridone</td>
</tr>
<tr>
<td>9</td>
<td>Indanthrene Yellow</td>
</tr>
<tr>
<td>10</td>
<td>Copper Phtalocyanine</td>
</tr>
<tr>
<td>11</td>
<td>3,4,9,10-Perylenetetraoxylic diimide</td>
</tr>
<tr>
<td>12</td>
<td>Isoviolanthrone</td>
</tr>
<tr>
<td>13</td>
<td>Perylene tetraoxylic diimide</td>
</tr>
<tr>
<td>14</td>
<td>Indigo</td>
</tr>
</tbody>
</table>

FIG. 1 shows hydrogen generation from an unbuffered aqueous borohydride solution using organic pigments as catalysts. In FIG. 1, the evolution of hydrogen gas is plotted for many different catalysts, including cobalt, a catalyst known in the prior art. Five milliliters (ml) of purified water is adjusted to have neutral alkalinity (pH 7) prior to the addition of one gram of sodium borohydride (NaBH₄) in the presence of 100 milligrams (mg) of a catalyst, in the form of a loose powder, selected from the catalysts shown in Table 1. The identity of each catalyst in FIG. 1 corresponds to the numerical ranking in Table 1, which ranks catalytic activity in a buffered solution (pH 11).

FIG. 2 shows hydrogen generation from NaBH₄ solution using organic pigments as catalysts in Table 1. FIG. 3 shows pH dependence of catalytic hydrogen gas evolution from NaBH₄ solution at pH 11 over immobilized organic pigment catalysts. FIG. 4 shows hydrogen generation from NaBH₄ solution at pH 11 over immobilized organic pigment catalysts. FIG. 5 shows the evolution of hydrogen gas from NaBH₄ solution buffered at pH 11 in the presence of many catalysts.

An equal amount (100 mg) of metallic cobalt powder was employed to serve as a basis of comparison with the existing art in borohydride decomposition catalysts. FIG. 2 shows the rate of hydrogen production with organic pigment catalysts using sodium borohydride in a buffered solution with pH 11. Each catalyst is identified by the unique legend shown on the left of the graph. When buffered solutions are used for borohydride decomposition, the free hydrogen ion concentration remains constant, and so H₂ evolves at a constant rate. At pH 11, the evolution rate is slow enough that it can be readily monitored. The order of activity is basically the same for all catalysts, except for pyranthreneone (also known as pyranthrone), which is the most active catalyst. When plotting the volume of hydrogen generated over a period of time, the graph reveals that 300 ml of hydrogen are generated in approximately 20 minutes by the organic pigment catalyst, pyranthreneone. The remaining catalysts perform at a slower rate, generating a lower volume of hydrogen, in a range of approximately 250 ml in a time period from...
approximately 30 minutes to approximately 80 minutes. Cobalt powder, a prior art catalyst, generated approximately 350 ml of hydrogen in approximately 40 minutes. Thus, it is seen that a buffered solution gives a different result for each catalyst used for generating hydrogen. A comparison of the results in FIGS. 1 and 2 shows that the rate of hydrogen evolution during the decomposition of alkali metal borohydride solutions is a function of several factors, including the choice of organic pigment catalyst, the pH of the aqueous solution, and concentration of catalyst.

FIG. 3 compares the rates of hydrogen production using sodium borohydride and pyranthrenedione in buffered solutions in a range from pH 9 to pH 12. Using the same catalyst, the hydrogen gas evolution at pH 9 is about 650 ml in less than 5 minutes, at pH 10. 400 ml of hydrogen are evolved in approximately 6 minutes; at pH 11 it takes approximately 30 minutes to generate 250 ml hydrogen and at pH 12 the hydrogen evolved is less than 50 ml in over 40 minutes. FIG. 3 graphically illustrates how changing only the pH can be used with an organic pigment catalyst to control rate of hydrogen evolution. The pH is a measure of free hydrogen ion (hydrogen ion) concentration in the solution. A first order dependence of gas evolution rate with pH is observed. There is an inverse relationship between pH and the free hydrogen ion concentration. Therefore, as pH increases, the H2 evolution rate decreased, as shown in FIG. 3. Each unit increase in pH translates to an order of magnitude decrease in hydrogen ion concentration. Consequently, the slope of the gas evolution curve decreased by nearly an order of magnitude with each unit increase of pH.

FIG. 4 shows the varying rates of hydrogen gas evolution from sodium borohydride (NaBH₄) solution catalyzed by organic pigments immobilized on polycarbonate substrates and buffered to a pH 11. A plain polycarbonate strip and select group of organic pigment catalyst powders, are individually blended with a poly(methyl methacrylate) binder and fixed onto a plastic substrate. The resulting gas evolution curves for the organic pigment catalysts show that the immobilized catalyst powders are still active for hydrogen evolution. After approximately 1 hour immobilized pyranthrenedione generates 250 ml of hydrogen gas; indanthrene gold orange immobilized on a substrate generates approximately 240 ml of hydrogen gas in 75 minutes and immobilized perylenetetracarboxylic diimide 95% catalyzes the evolution of hydrogen at a slightly slower rate, 225 ml in approximately 80 minutes. FIG. 4 provides a further example of how the organic pigment catalysts can be used to control the rate of H₂ evolution. Immobilization of the selected catalysts did not change the activity ranking of the same catalysts in loose powder form.

The importance of the use of an immobilized catalyst is shown in the design of a hydrogen supply system based on lithium borohydride and shown in FIG. 5. A prototype hydrogen supply system is shown in FIG. 5. Tablets of compressed borohydride powder, 10 are loaded into a horizontal canister equipped with a spring-loaded plunger 11. A pH electrode 12, pressure gauge 13, or other sensor detects the state of H₂ evolution. A catalyst strip 14 is immersed in the alkaline solution receiving the lithium borohydride tablets 10 that dissolve in the alkaline solution and in the presence of the catalyst strip 14 decompose into BH₄⁻ ions and BO₂⁻ ions with the release of hydrogen gas (H₂). The equation for the catalyzed reaction is BH₄⁻ + 2H₂O → BO₂⁻ + H₂. Alternatively, the throttle of a hydrogen fueled vehicle could be coupled to the plunger to control the rate of mixing. The pH and temperature of the solution can be controlled so that the background rate of H₂ evolution in the absence of catalyst can be minimized.

As learned from FIG. 4, an immobilized catalyst 14, is fastened onto the end of an armature 15, which is manipulated by a gear wheel 16, or other adjustment mechanism so that the immersion depth of the catalyst 14 into the borohydride solution can be varied at will. During high fuel consumption modes, such as highway driving or acceleration in general, the catalyst strip can be lowered further into the borohydride solution to expand the total area that is performing the gas-evolving borohydride decomposition reaction.

There are many advantages to the present organic pigment catalysts, including, but not limited to, increased utilization of known materials, versatility, reliability, accuracy of hydrogen release and economy in material consumption and fuel production.

While the invention has been described, disclosed, illustrated and shown in various terms of certain embodiments or modifications which it has presumed in practice, the scope of the invention is not intended to be, nor should it be deemed to be, limited thereby and such other modifications or embodiments as may be suggested by the teachings herein are particularly reserved especially as they fall within the breadth and scope of the claims here appended.

We claim:
1. An organic pigment catalyst-controlled hydrogen generation system, comprising: a borohydride solution, consisting of only four components; a hydrogen-rich borohydride selected from the group consisting of sodium borohydride, lithium borohydride, potassium borohydride, ammonium borohydride, tetramethyl ammonium borohydride, and mixtures thereof combined with water and a stabilizing agent selected from at least one of sodium hydroxide, lithium hydroxide, potassium hydroxide, ammonium hydroxide, and mixtures thereof to provide a pH of 9 or greater; and a catalyst strip consisting of an organic pigment selected from the group consisting of pyranthrenedione, indanthrene gold orange dodecyl-3,4,9,10-perylenetetracarboxylic diimide, indanthrene black, dimethoxy violanthrone, 1,4-diketopyrrolo-3,4C pyrrole, quinacridone, indanthrene yellow, 3,4,9,10-perylenetetracarboxylic diaminohydride, isoviolanthrone, and perylenetetracarboxylic diimide, in the form of a solid, loose powder immobilized on a substrate selected from the group consisting of ceramics, cements, glass, zeolites, perovskites, fibers, fibrous material, mesh, polymeric resin and plastic, wherein the catalyst strip is manipulated so that an immersion depth of the catalyst into the borohydride solution is varied to expand the total area that is performing the hydrogen gas-evolving borohydride decomposition reaction represented by the equation, BH₄⁻ + 2H₂O→BO₂⁻ + H₂, where the only four components of the borohydride solution are the hydrogen-rich borohydride, the water, the stabilizing agent, and the organic pigment catalyst strip.
2. The hydrogen generation system of claim 1, wherein the solid, loose catalyst powder is blended with a poly (methyl methacrylate) (PMMA) binder and the blended material is fixed onto the PMMA plastic substrate.
3. The hydrogen generation system of claim 1, wherein a hydrogen-consuming device uses a substantial portion of the hydrogen gas reaction product, said device being operably connected with said system.
4. The hydrogen generation system of claim 3, wherein the hydrogen-consuming device is selected from the group consisting of a fuel cell, a combustion engine, a gas turbine, and combinations thereof.