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Current situation and prospect of hydrogen storage technology with new organic liquid

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ABSTRACT

This paper starts with the brief introduction to various methods of hydrogen storage, such as pressurized gaseous hydrogen storage, cryogenic liquefaction hydrogen storage, carbonaceous materials hydrogen storage, metal alloy hydrogen storage, complexation hydride hydrogen storage, glass microspheres hydrogen storage, liquid organic hydrogen storage, and so on. The corresponding principles of hydrogen storage were summarized with the analysis on advantages and disadvantages. Additionally, the characteristics of hydrogen storage with N-ethylcarbazole were profoundly discussed. The conditions and catalysts for hydrogenation and dehydrogenation (N-ethylcarbazole) were also analyzed at some length as well. According to the present situation of hydrogen storage with organic liquids, some ideas were put forward to get higher content and speed of absorbing and releasing hydrogen.

Introduction

Among the new energy resources, hydrogen energy has been considered the ideal energy due to its advantages, such as being rich in quantity, pollution-free, renewable, higher energy density and so on. It is widely accepted that hydrogen will become the fuel for most vehicles and portable devices within a few decades of years [1,2]. In recent years, with the shortage of fossil fuels and the pressure from environment and sustainable development, the exploitation and utilization of hydrogen energy seem more urgent. So, hydrogen will become the means of storing and transporting energy in the future [3]. As well known, a complete hydrogen energy system should include the exploitation of hydrogen sources, the production of hydrogen, the hydrogen storage, the transportation and utilization of hydrogen. However, so far, the application of hydrogen has not gone too far in commercial field as a renewable energy source, for the prime reason of hydrogen storage [4,5].

More and more criteria are put forward to weigh the relative advantages of different methods for hydrogen storage, including the hydrogen storage density (gravimetric and volumetric capacity), the cost, the hydrogen recovery speed and the operating safety, etc. As for the technical targets for hydrogen storage from 2010 to 2015 given by the U.S. Department of Energy (DOE), the specific information can be seen in Table 1 [6,7].

Until now, the technologies of hydrogen storage have been mentioned in many literature, such as pressurized gaseous hydrogen storage [8,9], cryogenic liquefaction hydrogen storage [10], carbonaceous materials hydrogen storage [11–13], metal alloy hydrogen storage [14], complexation hydride hydrogen storage [15,16], glass microspheres hydrogen storage [17], liquid organic hydrogen storage [18–26] and so on. Although lots of materials have been developed, many aspects

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Table 1 – U.S. Department of energy (DOE) revised targets for hydrogen storage systems [6,7].

Storage parameter	Target (2010)	Target (2015)
Gravimetric capacity ($kWh\ kg^{-1}$)	1.5	1.8
H_2 (wt%)	4.5	5.5
Volumetric capacity ($kWh\ kg^{-1}$)	0.9	1.3
H_2 ($g\ H_2\ L^{-1}$ system)	28	40
Operating temperature	−30/50 °C	−40/60 °C
Min/max delivery temperature	−40/85 °C	−40/85 °C
Cycle life	1000	1500
System fill time for 5 kg H_2 (min)	4.2	3.3

need to be studied further, such as enhancing the gravimetric density, volumetric density, energy efficiency, safety, etc. Therefore, the great challenge of large-scale application of hydrogen is to develop the new hydrogen storage system with sufficient storage capacity and mild operating condition.

At present, the basic principle and characteristics of liquid organic hydrogen storage are analyzed compared with other common methods. Also, the reaction conditions and catalytic effect are compared with different catalysts used for hydrogenation and dehydrogenation, in order to accelerate the follow-up research in hydrogen storage field. At last, some feasible suggestions are put forward to enhance the catalytic performance in hydrogenation/dehydrogenation.

Classification of hydrogen storage technology

The total hydrogen path from production to on-board vehicle consumption is shown in Fig. 1. Because vehicles cannot storage sufficient hydrogen, so it is needed to compress hydrogen gas, to liquefy hydrogen then transport and store as a liquid phase, or to make it adsorb into a solid material [27]. The hydrogen storage approaches can be divided into two parts, physical and chemical methods. The physical method contains compressed hydrogen, cryogenic and liquid hydrogen, metal hydrides, high surface area sorbents, etc. According to the gas state equation, for a certain amount of gas, the volume will decrease by increasing the pressure at a constant temperature. The compressed hydrogen method is based on this principle. Although the operation process is convenient, the low capacity of hydrogen storage and insecurity restrict the use of compressed hydrogen, so the research needs to develop new compressed hydrogen storage system [8]. Cryogenic and liquid hydrogen can be obtained by decreasing the hydrogen temperature at a constant pressure. Comparing with compressed hydrogen, the volume required for liquid hydrogen is smaller [10]. However, due to the physical properties of hydrogen, the high consumption of cooling energy and cooling equipment are required to prevent hydrogen from being vaporized [10]. In the past few years, the interesting physical properties of carbon nanotubes [11,12] and nanofibers [13] have drawn great attentions from physicists and material researchers. The ultra high content of hydrogen uptake for these materials shows that they might be promising as hydrogen-storage materials for fuel-cell electric vehicles. In 1997, Dillon et al. [11] firstly raised the viewpoint that hydrogen can be compressed into high density inside narrow, single-walled nanotubes (SWNTs). They measured its hydrogen capacity and drew the conclusion that the gravimetric capacity of hydrogen storage in SWNTs can be up to 5–10 wt% under normal temperature and SWNTs might be promising as a hydrogen storage material for fuel-cell electric vehicles as well. Unfortunately, as for nanofibers, according to the latest theoretical and experimental results, it is difficult to realize the target of DOE for vehicle hydrogen storage [13]. About 50 metallic elements of the periodic table can adsorb hydrogen in certain quantity, which provides the possible choices of hydrogen storage materials. However, because of the low hydrogen storage capacity and high specific gravity, metal hydrides have been researched for hydrogen storage and the results show that metal hydrides are not suitable for fuel-cell electric vehicles [14,15]. Another group of materials which have potential for hydrogen storage are chemical hydrides. They have drawn attentions from researchers due to the practicability and high efficiency for hydrogen storage. Complex metal borohydrides with the general formula of $M(BH_4)_n$ are attractive with their high storage hydrogen capacity [16], such as $NaBH_4$, KBH_4, $NaAlH_4$, $NaAlNH_4$, etc. For example, $NaBH_4$ has a theoretical hydrogen capacity of 10.6 wt% [28].

Besides, the hydrogen storage technology based on liquid organic hydrides is indeed a promising candidate for hydrogen storage for the high storage capacity and recyclability, especially the long distance transportation of hydrogen. This technology is considered to be the substitute of conventional methods of compressed hydrogen, cryogenic and liquid hydrogen, so it will possibly play an important role in hydrogen storage industry in the future [29–33]. The advantages and disadvantages of different methods are compared in Table 2.

Liquid organic hydrogen storage

The principle and characteristics of liquid organic hydrogen storage

As for organic liquid hydrides, the process of storage and releasing is achieved through the hydrogenation and dehydrogenation reaction, which is a pair of reversible reaction [34–36]. According to the related study, hydrogenation and dehydrogenation reaction of unsaturated aromatics can take place without the destruction of main body structure of carbon ring, showing the property of insensitive structure. At present, the conversion and selectivity of dehydrogenation have been enhanced further by researchers through all kinds of means, in order to achieve the purpose of utilizing the hydrogen storage medium circularly. The circular process of hydrogen storage between N-ethylcarbazole and dodecahydro-N-ethylcarbazole is shown in Fig. 2.

Comparing with the traditional hydrogen storage materials, hydrogen storage in the form of organic liquids has their own characteristics as follows [35–44,49]:

(1) They have the high gravimetric/volumetric hydrogen storage density, over 5 wt% and 50 $g\ L^{-1}$ respectively.