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Recent progress in magnesium hydride modified through catalysis and nanoconfinement

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ABSTRACT

Hydrogen is an ideal energy carrier because of its high chemical energy, environmental friendliness and renewability. In order to realize the safe, efficient and compact hydrogen storage, various solid-state hydrogen storage materials based on the physisorption or chemisorption of hydrogen have been developed over the past decades. Among them, magnesium hydride, MgH_2 , is identified as one of the most promising candidates due to its high hydrogen storage density, low cost and abundance of Mg element. However, the sluggish kinetics and high thermodynamic stability of MgH_2 result in its high operation temperature and low hydrogen sorption rate, impeding its practical application. In this article, the recent progress in catalysis and nanoconfinement effects on the hydrogen storage properties of MgH_2 is comprehensively reviewed. In particular, the synergetic roles of catalysis and nanoconfinement in MgH_2 are highlighted. Furthermore, the future challenges and prospects of emerging research for MgH_2 are discussed. It is suggested that the nonmetal-doped porous carbon materials could be a class of ideal additives to enhance the hydrogen storage properties of MgH_2 by the synergetic effects of catalysis and nanoconfinement.

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Contents

Introduction	00
Thermodynamics and kinetics scenarios of Mg/MgH ₂	00
Thermodynamics	00
Kinetics	00
Modifying through catalysis	00
Transition metals catalysts	00
Metal oxides catalysts	00
Metal halides catalysts	00
Metal sulfides/hydrides catalysts	00
Nonmetal catalysts	00
Modifying through nanoconfinement	00
Nanoconfinement by carbon materials	00

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1D carbon materials	00
2D carbon materials	00
3D carbon materials	00
Ordered mesoporous silicas, metal-organic frameworks and nanoporous polymers materials	00
Modifying through synergistic catalysis and nanoconfinement	00
1D nanoconfined materials and catalysts	00
2D nanoconfined materials and catalysts	00
3D nanoconfined materials and catalysts	00
Summary and future prospects	00
Acknowledgments	00
References	00

Introduction

Increasing energy depletion and environmental pollution issues have stimulated the search for alternative and sustainable clean energy. Hydrogen energy is considered as one of the most promising candidates because of its high energy density, environmental friendliness and renewability. Nevertheless, the compact, efficient and safe hydrogen storage is the major challenge for the success of hydrogen economy [1]. Compared with the conventional high pressure gas-state or low temperature liquid-state hydrogen storage systems, the solid-state hydrogen storage systems have the potential to achieve high energy efficiency, good cycle stability, high safety and low cost [2]. Thus, different kinds of solid-state hydrogen storage materials based on physisorption or chemisorption of hydrogen have been developed in the past decades [3,4].

Magnesium hydride, MgH_2 , as a potential solid-state hydrogen storage medium, has attracted great attention due to its high volumetric (110 g/L) and gravimetric (7.6 wt%) hydrogen storage capacities, low cost and abundance of Mg element [5–7]. However, there are still several application bottlenecks for MgH_2 to be solved: (i) the undesirable thermodynamics ($\Delta H = -75 \text{ kJ/mol} \cdot \text{H}_2$) and sluggish kinetics of MgH_2 result in a high temperature ($\sim 573 \text{ K}$) and low rate for hydrogen de/absorption [8]; (ii) the less environmental stability of Mg, which is easily oxidized in the air and forms some by-products like magnesium oxide (MgO) or magnesium hydroxide (Mg(OH)_2); (iii) the agglomeration of Mg/ MgH_2 particles during de/hydrogenation cycles, which results in the poor cycle performance.

So far, lots of attempts, such as catalysts/additives doping [9,10], alloying [11,12], nanosizing [13,14], etc., have been employed to improve the hydrogen storage properties of Mg/ MgH_2 . Among them, the catalysis and nanoconfinement are the two popular modifying strategies. A wide range of metals, especially the transition metals (TMs), and their alternatives have been verified to be effective in enhancing the de/hydrogenation properties when they are ball-milled with Mg/ MgH_2 to form nanocomposites. Besides, nanoconfinement is also proved to be one of the most effective techniques to relieve the kinetic barrier and/or thermodynamics stability of Mg-based hydrides [15,16]. To our knowledge, nanoconfinement can be described regarding two aspects. The first one consists in

decreasing the size (nanosizing) of the particles to 3D dimensions below a few tens of nanometers. The second step (confinement) is mandatory to sterically stabilize and handle such very small particles by embedding them into scaffolds (e.g., nanoporous solids, polymers, stabilizers, etc.) [17]. A theoretical investigation demonstrates that if the particle size decreases below a few nanometers, the total energy becomes more positive (see Fig. 1). Furthermore, the positive change in the total energy for the nanoparticles suggests that there will be modifications in the thermodynamical properties and in particular the hydrogen de/absorption temperature is expected to be reduced in the nanophases compared to the bulk materials [18]. In addition, nanosizing can directly result in a larger surface-to volume ratio of the particles, shorter solid-state diffusion distance for hydrogen, and/or decreased thickness of the H_2 -impermeable layer of MgO [19]. Besides nanosizing, nanoconfinement allows the stabilization of nanoparticles against coalescence and can protect them from reactive environment. Moreover, the scaffold materials may interact with the confined particles due to chemical interactions or mechanical stresses, and this interfacial term may noticeably contribute to the decrease of total energy. The

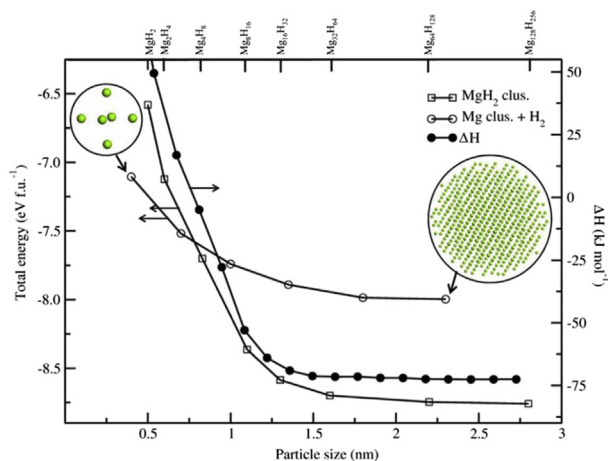


Fig. 1 – Calculated total energy as a function of particle size for the MgH_2 nanoclusters, nanoparticles of Mg together with H_2 molecules, and formation energy as a function of particle size are displayed [18].

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