

Advances in modification approaches for Mg-based hydrogen storage materials

CHENG Shuang^{1,2,3}, LI Fei^{1,2,3}, WANG Yuqi^{1,2,3,*}, WANG Xiangyi^{1,2,3}, GUAN Sinan^{1,2,3}, WANG Yi^{1,2,3}, WANG Yue^{1,2,3}, OU Guancheng^{1,2,3}, XU Ming^{4,5}

¹ School of Chemical Engineering, Northwest University, Xi'an 710127, China;

² Xi'an Key Laboratory of Green Hydrogen Energy Production, Storage & Application Integration Technology, Xi'an 710127, China;

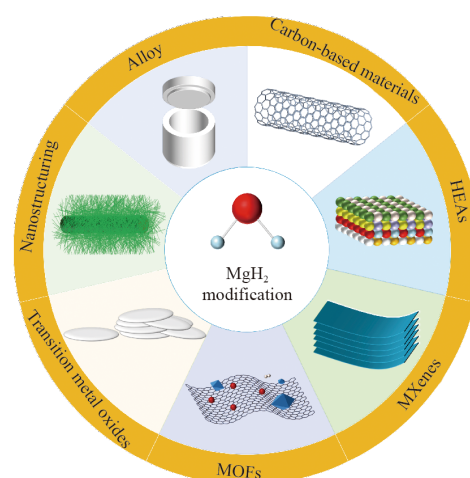
³ Shaanxi Key Laboratory of Carbon Neutral Technology, Xi'an 710127, China;

⁴ Xi'an K-Well New Material Co., Ltd., Xi'an 710086, China;

⁵ Shaanxi Yefang New Material Co., Ltd., Xi'an 712021, China

Abstract: As one of the most promising new energy sources, hydrogen energy is expected to usher in a full-fledged “hydrogen economy” in the 21st century. Compared with traditional high-pressure gaseous and cryogenic liquid hydrogen storage methods, solid-state chemical hydrogen storage shows significant advantages in safety, high efficiency, and cost-effectiveness. Magnesium-based lightweight hydrogen storage materials have attracted widespread attention due to their high gravimetric hydrogen storage density (7.6%) and favorable reversibility. However, their sluggish reaction kinetics and stringent operating conditions (with H₂ release temperatures exceeding 350 °C and H₂ absorption pressures above 4 MPa) pose major challenges for practical applications. Domestic and international researchers have conducted in-depth studies to address these issues, achieving substantial progress in the modification of magnesium-based hydrogen storage alloys. This paper systematically elaborates on major modification techniques such as alloying, nanostructuring, and catalytic material doping, providing a comprehensive analysis of the strengths and limitations of each approach. Furthermore, it offers prospects for the future development of magnesium-based hydrogen storage materials by integrating current theoretical and experimental research findings.

Key words: magnesium hydride; solid-state hydrogen storage; modification; kinetics; thermodynamics



The fossil fuels have propelled the essential progress of human society, but at the same time constrain the further improvement of living standards^[1–3]. Under the increasing global demand for primary energy sources such as coal, oil, and natural gas, environmental issues like smog, greenhouse gas emissions, and global warming have consequently emerged. Currently, it is imperative to vigorously develop renewable energy sources such as solar, wind, biomass, and hydrogen energy^[4–7]. Driven by the global energy transition and carbon neutrality goals, hydrogen energy acts as a clean, high-calorific, and abundant new energy source,

which offers distinctive advantages and provides an effective solution to current energy and environmental challenges. Both academia and industry have conducted extensive research on the large-scale application of hydrogen energy, which is expected to contribute to sustainable industrial and social development worldwide in the future^[8–10]. However, the extremely low density (STP: 0.0899 kg/m³) and flammable, explosive nature of hydrogen makes efficient storage a major bottleneck for its large-scale safe application, posing serious challenges to the joint development of the hydrogen energy chain, including

Received: 2025-06-24; Revised: 2025-08-07

Foundation items: Supported by Design and Performance Study of High-flux Metal Hydride Reactor Based on the Bionic Optimization (2078262) and the ‘Four-Chain’ Integration Project at the Qinchuangyuan Chief Platform (S2025-YF-ZDXM).

* Corresponding author. Tel: 029-88302632, E-mail: wangyuqi@nwu.edu.cn.

DOI: 10.1016/S1872-5813(25)60596-2 CSTR: 32157.14.2097-213X.2025.JFCT.0149

本文的英文电子版由 Elsevier 出版社在 ScienceDirect 上出版 (<http://www.sciencedirect.com/science/journal/18725813>)

production, storage, and utilization^[11]. Hydrogen storage methods can be categorized into gaseous^[3], liquid^[12] and solid-state storage^[13]. Conventional high-pressure gaseous storage (35–70 MPa) is limited by low gravimetric H₂ density and safety concerns, while cryogenic liquid H₂ storage requires cooling temperatures below −253 °C (20 K), which faces severe insulation requirements for storage tanks and high energy consumption during operation. In contrast, solid-state chemical hydrogen storage technology features high volumetric H₂ density, moderate storage/release conditions, and superior safety and economy, making it a prominent research hotspot in the H₂ energy industry chain.

Solid-state chemical hydrogen storage materials can be classified into metal hydrides (e.g., MgH₂, TiFeH₂, LaNi₅H₆), light metal complex hydrides (e.g., LiAlH₄, NaAlH₄, NaBH₄, LiBH₄) and chemical hydrides (e.g., NH₃BH₃)^[14]. Meanwhile, MgH₂ exhibits the notable advantages as follows: (1) a prominent volumetric hydrogen storage density of 110 kg/m³, over 1000 times than that of traditional gaseous under ambient conditions, significantly exceeding the cryogenic liquid H₂ storage of 70.8 kg/m³^[15]; (2) a high gravimetric hydrogen storage density of up to 7.6%, far exceeding the 1.0%–2.0% of high-pressure gaseous storage and 1.5 times that of cryogenic liquid hydrogen storage (5.5%)^[16], which outnumbers five times that of rare-earth-based hydrogen storage alloys like LaNi₅ (1.4%)^[17]; (3) eminent cycling reversibility and vast potential for modification^[9]; (4) abundant reserves (Mg accounts for 2.3% of the Earth's crust, ranking 8th among elements, over 85% of the global supply produced in China) and low cost (approximately 20 ¥/kg), causing it one of the most promising candidates for solid-state hydrogen storage materials^[18].

Nevertheless, Mg-based H₂ storage materials still face several challenges in practical applications that need to be addressed:

(1) The kinetic rate during hydrogenation/dehydrogenation is extremely slow due to the low diffusion coefficients of H atoms in MgH₂ and Mg, which are only 4×10^{-13} and 1.58×10^{-16} m²/s, respectively.

(2) The operating temperatures for H₂ absorption and desorption of MgH₂ are relatively high (above 300 °C), which is mainly due to the strong stability of the Mg–H bond, requiring an adsorption energy barrier of 1–10 kJ/mol to be overcome during the hydriding process and a corresponding dissociation energy barrier as high as 432 kJ/mol during the dehydriding process.

(3) Metallic Mg is highly active and easily forms an oxide layer in air, which hinders further surface hydrogenation and may pose fire risks, while maintaining an oxygen-free environment is particularly difficult and costly.

Due to these unfavorable factors, the large-scale application of MgH₂ has been suspended, and how to rationally modify MgH₂ to overcome these shortcomings has become a major research focus for enhancing its H₂ storage performance. Currently, the major modification

methods for MgH₂ include alloying, nanostructuring^[11,19–21], and catalytic doping with various materials^[9,22–23], including transition metals and their oxides, carbon-based materials, and metal-organic frameworks^[24]. This article summarizes the recent research progress on Mg-based H₂ storage materials and discusses the primary modification methods and relevant reaction mechanisms, while offering a prospective outlook for their future development.

1 Alloying method

Many scholars regard alloying as a traditional modification method, which involves adding metallic elements (such as transition metals Ni, Co and Mn) into Mg-based materials in designated proportions to produce multielement alloys. The successful introduction of metals can create new solid-solution phases and reduce their thermal stability as expected. A large number of transition-metal-centered active sites provide additional reaction pathways for hydrogen absorption and release, thereby effectively enhancing the H₂ storage performance of the prepared materials^[25].

Related studies on the alloying modification of Mg-based H₂ storage materials can be traced back to the pioneering work of Reilly et al.^[26] in 1968. They discovered that the intermetallic compound Mg₂Ni, synthesized by alloying Ni with Mg, could significantly decrease the hydrogenation temperature to 300 °C (2 MPa), highlighting the pivotal role of transition metal elements in manipulating the H₂ storage properties of Mg-based materials. Further investigations by Selvam et al.^[27] and Stucki et al.^[28] found that the Ni content in the alloy had a dominant influence on material performance, and the material almost lost its hydrogenation capability when excess Ni formed the MgNi₂ phase, owing to the enhanced metallic bonding and metastable structural stability. In contrast, a proper amount of Ni doping could produce Mg₂Ni, which effectively weakened the Mg–H bond and reduced the reaction activation energy, thereby facilitating the hydriding/dehydriding process of Mg₂NiH₄. Based on this mechanism, Yang et al.^[29] introduced eight transition metals (Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn) into Mg₂Ni *via* planetary ball milling. The results showed that Cr, Co and Mn markedly reduced the reaction plateau pressure, while Ti and Cu significantly lowered the H₂ absorption temperature, increasing the hydriding capacity of the modified material to 3.0%–3.5% and accelerating its kinetics. Shao et al.^[30] reported that Mg₂Cu (formed by Cu alloying) underwent disproportionation during H₂ absorption, producing MgH₂ and MgCu₂, which resulted in poor cycling reversibility. Zlotea et al.^[31] compared the H₂ absorption behaviors of Mg₅Ga₂ and Mg₆Pd, and revealed that both samples experienced partial disproportionation reactions but exhibited different microstructural evolutions: Mg₅Ga₂ formed elongated polycrystalline particles, while Mg₆Pd generated pyramid-shaped particles. Yajima et al.^[32], Polanski et al.^[33], Gennari et al.^[34], Kyoi et al.^[35] investigated element doping including Fe, Ti and La, and

their work demonstrated clear improvements in the H_2 storage properties of Mg-based alloys. Ding et al.^[25] prepared Mg-2Ni alloy *via* casting and compared it with a sample after ultrasonication (Mg-2Ni UST). The experimental results confirmed that the latter showed a remarkable enhancement in hydriding capacity and kinetic performance. Moreover, the DSC curve of Mg-2Ni UST showed that its decomposition peak temperature decreased from 392.99 to 345.6 °C, and the activation energy dropped from 101.93 to 88.65 kJ/mol. These improvements were attributed to the increase in grain boundary density and crystal refinement induced by ultrasonic treatment, which alleviated the hysteresis effect of the Mg-Mg₂Ni structure and accelerated the formation and decomposition kinetics of metal hydrides. Liu et al.^[36] synthesized MgH₂-15% LaNi_{4.5}X_{0.5} ($X = \text{Ni, Fe, Co, Al}$) through melting, wet ball milling, and dry ball milling. Among them, LaNi_{4.5}X_{0.5} showed the most effective modification, reducing the dehydrogenation temperature of MgH₂ from 380 to 214 °C and lowering the hydrogenation pressure from 3 to 1 MPa. This improvement was attributed to the weakening of the Mg-H bond strength induced by LaNi_{4.5}X_{0.5}, thereby reducing the activation energy of the samples. Liu et al.^[37] prepared a combined LiBH₄/Mg₁₁CeNi hydride system by ball milling a mixture of LiBH₄ and Mg₁₁CeNi hydride at a molar ratio of 17:2.5. This system could release 6.6% H_2 within 280–425 °C. Specifically, 4.0% H_2 was released from the decomposition of MgH₂ and Mg₂NiH₄ at 280–350 °C, while the remaining H_2 was obtained from the decomposition of LiBH₄ catalyzed by Mg₂Ni, CeH₂ and newly formed Mg at 350–425 °C. Moreover, the dehydrogenated sample could be partially regenerated at 400 °C and 9 MPa, achieving a reversible H_2 storage capacity of 4.9%, indicating that hydrogenated Mg-RE-Ni ternary alloys may effectively lower the dehydrogenation temperature of LiBH₄ and improve its reversibility. Yang et al.^[38] produced a three-phase composite of MgH₂-Bi₂Ti₂O₇-Bi₂Mg₃ by ball milling hollow spherical Bi₂Ti₂O₇ with MgH₂. During ball milling, the novel Bi₂Mg₃ alloy appeared, showing a clear promotive effect on hydriding performance. The dehydrogenation onset temperature was only 194.3 °C, much lower than that of pure MgH₂ (335 °C), and the rapid hydrogen absorption capability was demonstrated by absorbing 5.4% H_2 within 60 s at 200 °C. After 50 cycles, the capacity of MgH₂-Bi₂Ti₂O₇-Bi₂Mg₃ remained at 5.2% with a retention rate of 98.1%. Further density functional theory (DFT) calculations indicated that the appearance of Bi₂Mg₃ caused the Mg-H bond length to expand from 1.71 to 1.792, and also reduced the dissociation energy barrier from 1.21 to 0.47 eV. Yoon et al.^[39] employed DFT calculations to reveal the multiscale effects of various elements (e.g., P, As, Sb, Bi, S, Se) on the H_2 storage performance of Mg-Mg₂Ni alloys. The results indicated that Ba, Ca, Y and La preferentially occupy Mg sites, while Ag, Cu and P tend to occupy Ni sites in Mg-rich alloys. Meanwhile, the volume change (ΔV) during hydrogenation of pure Mg to α -MgH₂ and γ -MgH₂ resulted in volume expansions of 31.8% and 29.4%, respectively,

which agreed with experimental data of 31.4% and 29.1%. Alkali metals (K, Rb, Cs) and alkaline earth metals (Ba, Ca, Sr) markedly reduced ΔV , while transition metals (Co, Ni, etc.) significantly increased it. Further electronic structure analysis showed that Mg₂NiH₄ is a semiconductor with a DOS bandgap of 1.53 eV, where the *d*-orbital of Ni strongly hybridized with the *s*-orbital of H, dominating the density of states near the Fermi level. Notably, the introduction of elements such as Sb and P depleted the bandgap and weakened the metal-H bond, whereas Ba and Ru enhanced electron localization and bond strength.

As a result, alloying modification has been proven to be an effective strategy for enhancing the H_2 storage/release performance of MgH₂, and its mechanism primarily involves introducing multi-metal components to generate more active sites, thereby improving the related thermodynamic and kinetic properties. Simultaneously, the adsorption and dissociation of H atoms are promoted through electronic interactions between hydrogen and metal atoms. However, this method has two distinct limitations: (1) irreversible metal bond breakage during metal doping, leading to structural instability and cycling degradation after multiple H_2 absorption/desorption cycles; (2) the use of high-atomic-weight metals inevitably reduces the theoretical gravimetric H_2 storage density of the prepared materials. Due to these constraints, pure alloying modification usually fails to meet practical application requirements. A more promising strategy is to integrate alloying with other modification approaches, particularly catalytic material combination, which can retain the benefits of alloy-derived active sites, further lower reaction energy barriers, and avoid excessive capacity loss. For example, combining nanocatalytic materials with alloying can not only maintain high H_2 storage capacity but also significantly improve cycling stability, enabling comprehensive optimization of the H_2 storage performance of the prepared materials.

2 Nanostructuring method

The nanostructuring approach involves physical or chemical treatments applied to the prepared material or the reduction of its internal particle size to the nanoscale (below 100 nm)^[40]. This strategy can significantly weaken the strength of Mg-H bonds by introducing defects and altering reaction pathways^[41], thereby requiring an in-depth understanding of the rate-determining steps during H_2 absorption/desorption to improve material performance. Meanwhile, the hydrogenation process of Mg (to MgH₂) can be summarized in four steps: (1) physical adsorption of H_2 on the surface of the metal hydrides; (2) dissociation of hydrogen into H atoms; (3) surface penetration and bulk diffusion of H atoms; (4) nucleation and growth of MgH₂. Correspondingly, the dehydrogenation of MgH₂ consists of three stages: (1) dissociation of H atoms from the MgH₂ lattice; (2) diffusion of H atoms to the particle surface (through the MgH₂/Mg phase interface); (3) recombination

of H atoms into H₂ followed by the desorption process^[42–44].

During dehydrogenation, the molar volume of MgH₂ and nano-MgH₂ follows a quantitative relationship with the corresponding partial pressure, as shown in Equation (1):

$$n \frac{p_{\text{nano}}^{\text{eq}}}{p_{\text{bulk}}^{\text{eq}}} = \frac{1}{RT} \left(3 \frac{V_{\text{Mg}} \gamma_{\text{Mg}}}{r_{\text{Mg}}} - 3 \frac{V_{\text{MgH}_2} \gamma_{\text{MgH}_2}}{r_{\text{MgH}_2}} \right) \quad (1)$$

where p represents the equilibrium partial pressure during dehydrogenation, V denotes the molar volume (m³/mol) of the particle, r is the particle radius (m), and γ represents the surface energy (J/m²)^[45–46].

This expression demonstrates that when the particle size decreases to the nanoscale, the noticeable increase in specific surface area exerts a dual effect on the reaction process. On the one hand, the larger specific surface area and shorter interparticle distance can enhance reactant contact and accelerate the diffusion of H atoms, thereby significantly improving kinetic rates. On the other hand, the accumulated free energy at particle surfaces and interfaces can reduce the reaction activation energy barrier, thus endowing the material with higher chemical activity^[47–48].

In 2005, Wagemans et al.^[49] investigated the impact of MgH₂ grain size on its thermodynamic properties through theoretical calculations, and the resulting geometric structure is shown in Figure 1. The authors concluded that the dehydrogenation temperature of the material dropped markedly when the particle size fell below 1.3 nm (each cluster containing fewer than 19 Mg atoms), highlighting the crucial role of nanoscale effects in regulating the H₂ storage performance of the designed materials.

Cheung et al.^[50] conducted a related simulation study and found that the thermodynamic properties were notably improved during the dehydrogenation process when the MgH₂ particle size reached 2 nm, which may provide theoretical evidence for the application of nanoscale technology. Dong et al.^[51] further explored the dehydrogenation process of MgH₂ and discovered a unique “burst effect”. Theoretical calculations showed that both the reaction energy barrier and Mg–H bond strength gradually decreased as the dehydriding reaction progressed, resulting in an accelerated dehydrogenation rate and indicating that precise control of nanoparticle size is of vital importance for promoting both the kinetic rate and thermodynamic stability of MgH₂ materials.

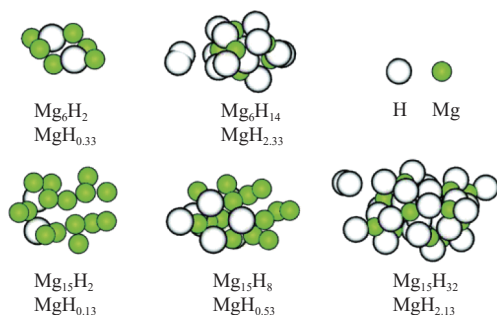


Fig. 1 Selected geometries of Mg₆H_x and Mg₁₅H_x clusters^[49] (with permission from ACS Publication)

Nevertheless, two key issues still need to be addressed: (1) developing preparation methods capable of precisely controlling nanoscale dimensions, and (2) designing effective surface modification strategies to inhibit nanoparticle agglomeration.

In recent years, nanoscale technology has achieved significant progress in improving the H₂ storage and release performance of MgH₂, which can be essentially classified into three preparation methods: mechanical alloying (ball milling), nanoconfinement, and electrochemical reduction. Among them, mechanical ball milling is a conventional method for producing nano-MgH₂ due to its operational convenience and low cost. This method can introduce numerous defects into the samples and reduce particle size through strong metal-metal interactions generated by mechanical energy, thereby effectively shortening the H₂ diffusion distance and accelerating reaction kinetics. Zhang et al.^[52] prepared solid-state H₂ storage materials MgH₂+fl-TiO₂@C and MgH₂+fl-TiO₂ via ball milling. The catalytic precursors were first obtained as white titanium glycerolate powder by hydrothermal synthesis, followed by annealing at 450 °C in air and Ar atmospheres to produce black fl-TiO₂@C and white fl-TiO₂, respectively. As shown in the DSC curves (Figure 2), the initial dehydrogenation temperatures for MgH₂, MgH₂+fl-TiO₂, and MgH₂+fl-TiO₂@C were 294.6, 199.2 and 180.3 °C, respectively, and the corresponding peak temperatures appeared at 362.6, 245.4 and 233.0 °C, respectively. Notably, MgH₂+fl-TiO₂ absorbed 6.0% H₂ in 40 min at 150 °C and 8 min at 250 °C, with a dehydrogenation reaction activation energy of 77.72 kJ/mol.

Chen et al.^[53] used Co(NO₃)₂·6H₂O, Ti(OC₄H₉)₄, C₆H₈O₇·H₂O, and ethanol to carry out a solvothermal reaction in a Teflon-lined autoclave at 190 °C, followed by calcination at 700 °C under Ar atmosphere to obtain the catalytic material Co/TiO₂. The final ball-milled products MgH₂-Co/TiO₂, MgH₂-TiO₂ and MgH₂-Co exhibited dehydrogenation peak temperatures of 235.2, 288.4 and 329.4 °C, respectively, in DSC tests, which were all significantly lower than 367.4 °C for ball-milled MgH₂, confirming the excellent effect of metallic Co and TiO₂ in reducing dehydrogenation temperature. Importantly, MgH₂-Co/TiO₂ started its dehydriding process at 190 °C and released 6.2% H₂ within 15 min at 250 °C.

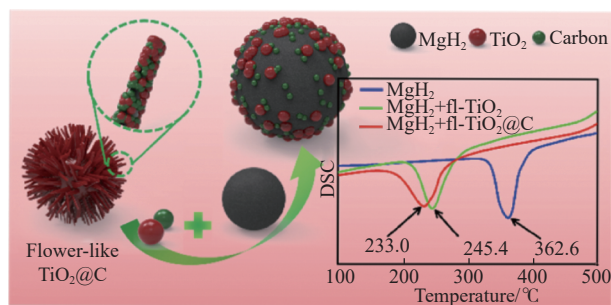


Fig. 2 DSC curves of the prepared MgH₂+fl(3-D flower-like)-TiO₂, MgH₂+fl-TiO₂@C and MgH₂^[52] (Hydrogenation: 5 MPa, dehydrogenation: 1 kPa) (with permission from Elsevier)

Under a 6 MPa H_2 supply pressure, MgH_2 -Co/TiO₂ absorbed 6.07%, 5.56% and 4.24% H_2 within 10 min at 165, 130 and 100 °C, respectively, and 4.0% H_2 after 10 h at 50 °C.

For nanoconfinement research, Nielsen et al.^[54] employed chemical impregnation to load magnesium dibutyl ($MgBu_2$) precursor into aerogel nanochannels, and then prepared confined MgH_2 nanoparticles after the hydrogenation process. The obtained nanoconfined structure reduced the dehydrogenation temperature to below 200 °C, which increased the dehydrogenation rate by a factor of five compared with pure MgH_2 , further confirming the effectiveness of nanoconfinement. Li et al.^[55] successfully prepared diameter-regulable Mg nanowires by precisely manipulating Ar flow during vapor deposition, and found that the nanowire diameter decreased with lower Ar flow, resulting in a clear improvement in hydrogen storage performance. The prepared sample released 3.28% H_2 in 30 min at 200 °C and achieved a maximum capacity of 6.77% at 300 °C, while maintaining excellent capacity stability after 50 absorption-desorption cycles. Compared with traditional bulk materials, the outstanding performance of the as-prepared nanowires likely originated from their high specific surface area, which significantly increased active sites and provided more efficient H_2 diffusion channels. Xia et al.^[56] investigated the combined nanoconfinement effect with graphene (GR) addition on MgH_2 . As shown in Figure 3 (a)–(d), DFT calculations revealed that $(C_4H_9)_2Mg$ had the

lowest adsorption energy among $(C_4H_9)_2Mg$, C_6H_{12} , Mg and MgH_2 during the assembly of $MgBu_2$ on graphene. By precisely regulating the $MgBu_2$ /GR ratio, a series of H_2 storage materials including MHGH-20, MHGH-40, MHGH-60, MHGH-70 and MHGH-75 were synthesized with different MgH_2 loading amounts, and MHGH-75 showed the best H_2 absorption/desorption performance (Figure 4(a)–(d)).

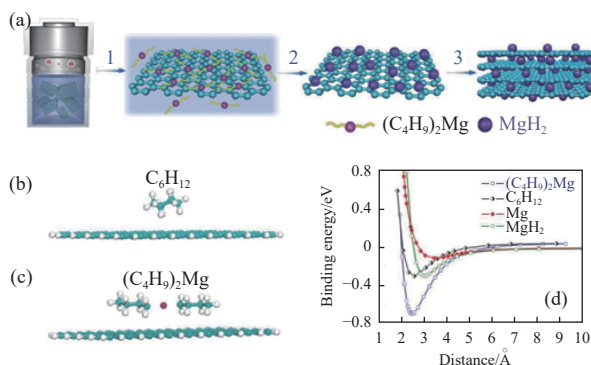


Fig. 3 (a) Schematic illustration of the self-assembly of MgH_2 nanoparticles (NPs) on GR, atomic structures (side views) of the adsorption of (b) C_6H_{12} and (c) $(C_4H_9)_2Mg$ on a GR sheet in their most stable configurations, (d) Binding energy curves for the adsorption of $(C_4H_9)_2Mg$, C_6H_{12} , Mg, and MgH_2 on a GR sheet obtained from DFT calculations^[56] (with permission from John Wiley and Sons)

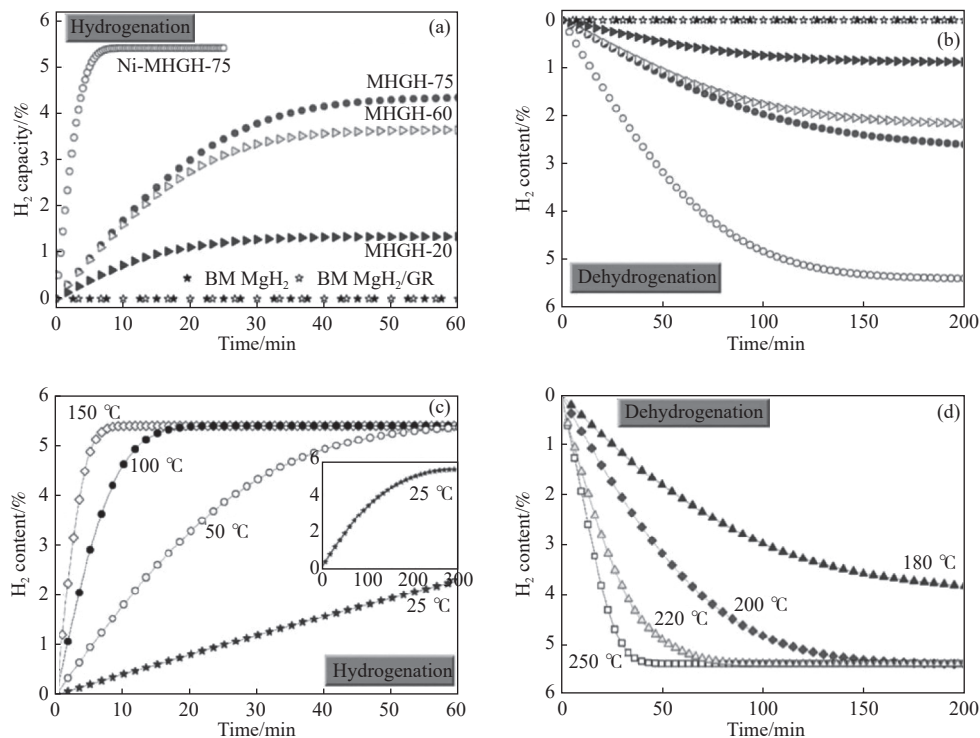


Fig. 4 (a) Hydriding and (b) dehydriding curves of the as-prepared MHGH samples at 200 °C, including ball-milled MgH_2 (BM MgH_2) and ball-milled MgH_2 /GR composite (BM MgH_2 /GR), (c) Hydriding and (d) dehydriding curves of Ni-MHGH-75 at various temperatures, the inset in (c) shows the performance at 25 °C over a longer period Conditions: hydriding at 3 MPa, dehydriding at 1 kPa^[56] (with permission from Elsevier)

Subsequently, Ni nanoparticles were self-assembled on MgH_2 nanoparticle surfaces *via* a solvothermal method, and the resulting Ni-MHGH-75 displayed superior H_2 storage properties, absorbing 2.3% H_2 within 60 min at 50 °C under 3 MPa and releasing 5.4% H_2 in 30 min at 250 °C, with 99.2% capacity retention after 100 cycles.

In electrochemical reduction for nanostructuring, Aguey-Zinsou et al.^[57] obtained nano-sized Mg particles by reducing magnesium salts (Mg^{2+}) in tetrahydrofuran (THF), followed by hydrogenation at 60 °C under 2 MPa to synthesize MgH_2 . The resulting product achieved complete dehydrogenation at just 85 °C, a remarkable decrease compared with conventional bulk MgH_2 (> 350 °C for dehydriding).

It can be concluded from the above investigations that nanostructuring technology plays a vital role in modifying Mg-based H_2 storage materials, as it can overcome the limitations of traditional approaches and balance the thermodynamic stability and kinetic performance of nanomaterials. However, the preparation process introduces additional excess energy that may reduce the stability of MgH_2 and cause unexpected agglomeration and grain growth. As a result, the existing synthesis routes remain relatively complex, and continuous efforts are still required to enable large-scale practical applications in three aspects: fundamental research, engineering implementation, and commercialization. Future research should focus on precise nanostructure control and scalable preparation to advance practical applications.

3 Catalyst doping method

Catalytic material modification is a crucial strategy for effectively improving the performance of Mg-based H_2 storage materials. It essentially involves combining MgH_2 with designated functional materials in adjustable proportions to promote the desired H_2 storage characteristics. The conventional catalytic materials include transition metals, transition metal oxides, and carbon-based materials, while recent research hotspots have also explored novel catalysts such as MOFs and MXenes. The corresponding reaction mechanisms can generally be divided into four categories:

(1) Hydrogen pump effect: Theoretically, doping with transition metals (e.g., Nb, Ni) may destabilize the material and favor dehydrogenation. In this process, H atoms tend to form hydride clusters with the surrounding transition metals, which facilitates rapid hydrogen transfer during reversible hydrogenation/dehydrogenation and thus enhances absorption/desorption kinetics.

(2) Spillover effect: Hydrogen molecules first dissociate into H atoms at the active sites on the catalyst surface, and these atoms then migrate to the MgH_2 interface *via* surface diffusion.

(3) Electron transfer: Catalytic materials (e.g., transition metal oxides, MXenes) can alter the electron cloud distribution of Mg–H bonds through electronic interactions.

When electrons transfer from the catalytic material to MgH_2 , the Mg–H bonds may be weakened and the hydrogen dissociation energy barrier reduced.

(4) Channeling effect: Catalysts with well-defined pore structures or unique interfacial properties (e.g., porous MOFs) can serve as diffusion pathways for H atoms, enabling efficient hydrogen transfer between the catalyst and MgH_2 .

3.1 Transition metals

Transition metals, located in the *d*-block (Groups IIIB to IIB) of the periodic table, display a strong affinity for H atoms. During hydrogen dissociation, the *d*-orbital electrons of transition metals can transfer to the antibonding σ^* orbital of H_2 , thereby strengthening the interaction between the transition metal and H_2 . This process reduces the electron density of the Mg–H bond and subsequently weakens its strength. Consequently, transition metals are regarded as essential catalytic doping materials for MgH_2 .

Owing to its excellent catalytic properties, Ni is considered one of the most extensively studied transition metals. Ölmez et al.^[58] mixed MgNi_2 , Ni and Mg in appropriate proportions through hot pressing, forging, and sintering, ultimately identifying MgNi_2 as an effective H_2 storage component. Mao et al.^[59] used ball milling to mix MgH_2 with $\text{NiCl}_2/\text{CoCl}_2$, effectively lowering the dehydrogenation temperature and improving the hydriding kinetics of MgH_2 . Notably, $\text{MgH}_2/\text{NiCl}_2$ showed outstanding performance, absorbing 5.17% H_2 within 60 s at 300 °C, compared with only 3.51% absorbed by pure MgH_2 within 400 s under the same conditions. Yao et al.^[60] reported that *in situ*-formed Mg_2NiH_2 released hydrogen more readily than MgH_2 , with its “hydrogen pump effect” accelerating dehydrogenation kinetics. Dan et al.^[61] also observed this effect in MgH_2 composites, largely attributed to the improvement in H_2 dissociation, diffusion, and recombination in $\text{Mg}_2\text{NiH}_{0.3}$. Duan et al.^[62] developed a composite material by ball milling MgH_2 with Ni-loaded carbon nanotubes, exhibiting excellent H_2 storage performance due to efficient electron transport facilitated by Ni nanoparticles. Liu et al.^[63] synthesized a Ni/ CeO_2 composite catalyst *via* coprecipitation and reduction, reducing the dehydrogenation peak temperature of MgH_2 from 384.5 to 268.2 °C. This improvement was attributed to interfacial coupling between Ni and CeO_2 , which promoted electron transfer and facilitated oxygen vacancy formation, further enhancing H_2 storage performance. Ma et al.^[64] proposed a template consumption method to construct a CoS framework with specific pore structures and confined MgH_2 nanoparticles inside its cavities *via* impregnation. The active sites provided by *in situ*-formed MgS were shown to remarkably enhance H_2 storage performance. Wang et al.^[65] prepared a core-shell Co@C catalyst *via* solvothermal and annealing methods, which exhibited excellent thermal conductivity. The MgH_2 -10%Co@C sample desorbed H_2 at an onset temperature of 168 °C

(101 °C lower than MgH_2), with maximum dehydrogenation occurring at 300 °C and activation energy reduced to 84.5 kJ/mol. Yin et al.^[66] synthesized a 3D hollow $\text{Ti}^{3+}/\text{TiO}_2$ nanobox by hydrothermal method and compounded it with MgH_2 , where TiO_2 transformed into MgTi_2O_4 during hydrogenation. The multivalent Ti species promoted electron transport during H_2 absorption/desorption. The prepared samples released 6.1% H_2 within 20 min at 325 °C, with dehydrogenation activation energy reduced to 57.2 kJ/mol. Cui et al.^[67] coated Mg powder with catalytic materials such as TiH_2 , TiCl_3 , and TiO_2 , and synthesized a Mg-Ti multivalent composite that acted as an electron transfer mediator. This promoted the reduction of high-valence $\text{Ti}^{3+}/\text{Ti}^{4+}$ to low-valence Ti^{2+} , facilitating electron transfer between Mg^{2+} and H^+ and weakening the Mg–H bond strength. Similarly, Ti^{2+} could lose electrons and convert to $\text{Ti}^{3+}/\text{Ti}^{4+}$, thereby strengthening the hydrogenation process and enhancing dehydrogenation performance.

3.2 Transition metal oxides

Transition metal oxides have emerged as promising materials for modifying the H_2 storage properties of MgH_2 , demonstrating unique advantages. They exhibit greater brittleness than transition metals, which facilitates more uniform dispersion on MgH_2 surfaces during ball milling and effectively reduces MgH_2 particle size through mechanical friction. The pioneering work on transition metal oxides can be traced to Terzieva et al.^[68], who first proposed and validated the catalytic mechanism of metal oxides in H_2 absorption/desorption. Metal oxides can be reduced to metallic species with higher catalytic activity, thereby significantly improving both the thermodynamic and kinetic properties of MgH_2 .

Representative studies include Shi et al.^[69], who developed a fluorinated $\text{TiO}_2(\text{F})$ nanosheet catalyst system. Through precursor reduction in an Ar/H_2 atmosphere, they prepared TiO_{2-x} nanosheets rich in oxygen vacancies. When compounded with MgH_2 at 5%, the material showed exceptional performance: an onset dehydriding temperature of 189 °C with a storage capacity of 6.79%. It released 6.0% H_2 in just 6 min at 250 °C, and even under milder conditions (100 °C), it released 3.62% H_2 within 10 min. After 10 cycles, the sample maintained 92.6% and 93.3% capacity retention for absorption and desorption, respectively, illustrating excellent cycling stability. Mechanistic studies revealed multiple synergistic effects: (1) formation of active catalytic centers from MgF_2 and low-valence $\text{Ti}^0/\text{Ti}^{2+}$; (2) additional H_2 storage sites provided by $\text{MgF}_{2-x}\text{H}_x$ solid solutions during rehydrogenation; (3) significant reduction of the reaction barrier through the cooperative effect of F and oxygen vacancies. These findings not only confirm the effectiveness of TiO_2 -based catalysts in enhancing MgH_2 performance but also provide theoretical guidance for designing high-efficiency H_2 storage materials.

Ren et al.^[70] synthesized 2D- TiO_2 nanosheets rich in oxygen vacancies *via* a surfactant-assisted method. Using nanoconfinement, they grew MgH_2 nanocrystals *in situ* on the nanosheet surfaces, constructing a $\text{TiO}_2/\text{MgH}_2$ heterostructure. This composite showed excellent properties: the initial dehydriding temperature decreased to 180 °C (115 °C lower than pure MgH_2); the hydriding rate at 300 °C reached 2.116% (35 times that of pure MgH_2); and after 100 cycles, it maintained 98.5% capacity retention, indicating remarkable cycling stability. The same team further developed nanosheet $\text{H-V}_2\text{O}_5$ catalysts^[71]. In this work, a “hydrogen pump effect” was achieved through the synergy between *in situ*-formed VH_2/V and abundant oxygen vacancies on V_2O_5 surfaces. This mechanism enabled the material to adsorb 2.38% H_2 at 30 °C within 60 min, release 6% H_2 in 6 min at 275 °C, and maintain 99% capacity retention after 100 cycles.

Zhang et al.^[72] precisely tuned the ratio of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ to TiO_2 to prepare single-atom catalytic materials ($\text{Ni}_x/\text{TiO}_{2-x}/\text{MgH}_2$) with different Ni loadings. Among them, $\text{Ni}_{0.034}/\text{TiO}_2\text{-MgH}_2$ exhibited optimal performance in non-isothermal dehydrogenation curves (Figure 5(a)). Comparative temperature-programmed curves (Figure 5(b)) of MgH_2 , $\text{TiO}_2\text{-MgH}_2$, and $\text{Ni}_{0.034}/\text{TiO}_2\text{-MgH}_2$ showed that both Ni and TiO_2 promote H_2 storage properties. As shown in Figure 5(c), (d), 15% $\text{Ni}_{0.034}/\text{TiO}_2\text{-MgH}_2$ displayed extraordinary kinetics: absorbing 6.53% H_2 within 10 s at 300 °C, 4.6% in 5 min, and nearly 3% within 60 min even at 225 °C. Theoretical calculations (Figure 5(e)) indicated that activation energies for dehydrogenation and hydrogenation decreased from 160 and 87.3 to 64.35 and 35.17 kJ/mol, respectively. After 100 cycles (Figure 5(f)), the material maintained 97.26% capacity, fully illustrating the effectiveness of the single-atom catalytic strategy.

Zhu et al.^[73] constructed novel TiO_2 -based catalytic materials using a metal-organic framework (MOF) templating method. The synthesized copper tetracarboxylphenylporphyrin (TCPP(Cu)) was coordinated with Zn clusters to form a two-dimensional ZnTCuM framework, and TiO_2 nanoparticles grew *in situ* on its surface, enabling precise control of TiO_2 catalysts and offering new insights into the development of MOF-based H_2 storage materials. Oelerich et al.^[74] systematically concluded that multivalent metal oxides (e.g., V_2O_3 , Mn_2O_3 , Fe_3O_4) exhibit superior catalytic performance compared with monovalent metal oxides, as multivalent metals act as electron transfer mediators during H_2 absorption/desorption, thereby promoting the entire process of hydrogen atom adsorption, dissociation, and diffusion, which provides important theoretical guidance for designing efficient catalysts. In single-oxide catalyst systems, Hanada et al.^[75] developed $\text{Nb}_2\text{O}_5/\text{MgH}_2$ composites showing exceptional kinetics, absorbing 4.5% H_2 in just 15 s at 200 °C with a final capacity exceeding 5%, while the hydrogenated material released 6% H_2 at 160 °C, demonstrating the significant role of Nb_2O_5 in MgH_2 hydrogen storage kinetics.

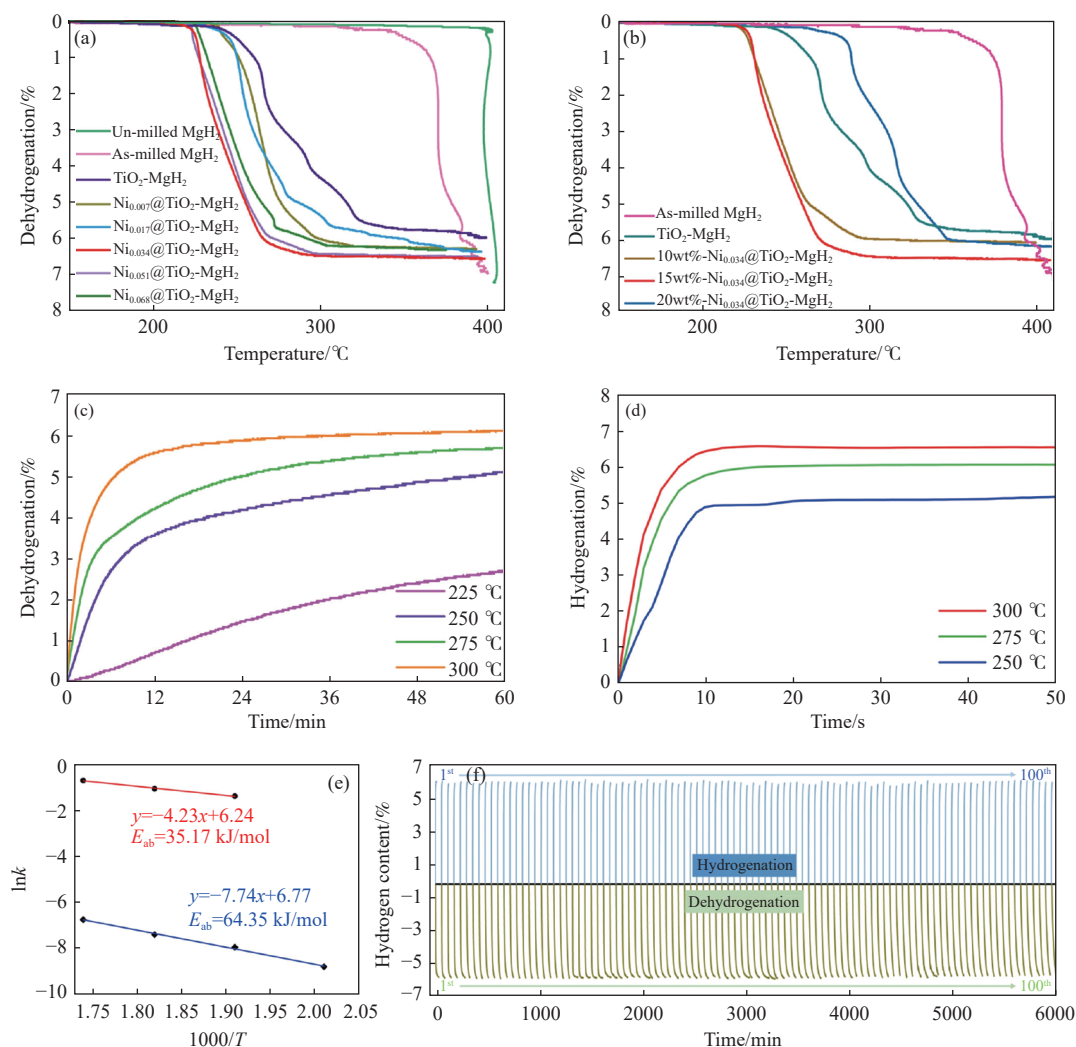


Fig. 5 (a) Temperature-programmed desorption curves of Ni_x@TiO₂-MgH₂ (x = 0.007, 0.017, 0.034, 0.051, 0.068); (b) temperature-programmed desorption curves of x%-Ni_{0.034}@TiO₂-MgH₂ (x = 10, 15, 20); (c) dehydrogenating and (d) hydriding curves of 15%-Ni_{0.034}@TiO₂-MgH₂ at different temperatures; (e) calculated activation energies for dehydrogenating (blue) and hydriding (red) and (f) 100-cycle performance at 300 °C for 15%-Ni_{0.034}@TiO₂-MgH₂^[72] (with permission from American Chemical Society)

Wang et al.^[76] introduced the high-entropy alloy concept into layered metal oxides, successfully preparing anion-regulated Cr-Mn-Fe-Co-Ni-based high-entropy layered metal oxides (HELMO). Comparative studies of NO₃⁻ and Cl⁻ intercalated HELMO revealed the decisive influence of anion type on catalytic performance, with HELMO-NO₃⁻ showing optimal activity by decreasing the onset dehydrogenation temperature from 340.6 to 184.1 °C. At 250 °C, MgH₂+10% HELMO-NO₃⁻ released 6.68% H₂ in 8 min while maintaining 97.8% of its capacity (6.52%) after 50 cycles, and these excellent properties were attributed to high-entropy effects and anion synergy, in which the cooperative action of five transition metals provided abundant active sites, while NO₃⁻ intercalation facilitated oxygen vacancy formation, thereby reducing reaction barriers.

These studies confirmed the benefits of multivalent metal oxides in MgH₂ modification and offered new directions for developing advanced H₂ storage catalysts through

innovative strategies such as high-entropy design and anion regulation. In particular, the concept of high-entropy layered metal oxides successfully achieved synergistic optimization of multiple active components, highlighting their broad application potential. Future research could further investigate other anion types (e.g., F⁻, SO₄²⁻) and advance scale-up production processes to promote the practical application of these materials.

3.3 Carbon-based materials

The research on carbon-based materials (e.g., carbon nanotubes, graphene, activated carbon, and carbon fibers) for H₂ storage can be traced back to Kidnay et al.^[77], whose report on their physical H₂ storage performance was conducted at cryogenic temperatures (76 K). This early insight stimulated extensive research into morphology control and performance optimization of carbon-based

materials for H_2 storage. In 2007, Su et al.^[78] further clarified the H_2 storage mechanism of activated carbon, establishing a positive correlation between H_2 storage capacity and specific surface area, with optimal adsorption occurring when micropore sizes were below 1 nm. Nevertheless, the room-temperature H_2 storage performance of carbon materials remains insufficient for practical applications due to weak van der Waals interactions between carbon and H molecules. To address this limitation, researchers have developed novel metal/carbon composite systems: transition metals (e.g., Fe, Ni), through their $3d$ electrons, can effectively modulate the electronic structure of MgH_2 and reduce reaction energy barriers, while carbon nanotubes and graphene not only inhibit nanoparticle aggregation but also form conductive networks to facilitate charge transfer, thereby enhancing both the kinetic and thermodynamic performance of the designed materials.

Wang et al.^[79] prepared a VTiFe alloy *via* mechanochemical methods and then obtained the final nanocatalytic materials through mechanical alloying with carbon nanotubes. Although CNT incorporation decreased absorption/desorption rates by 15%, cycling stability was greatly improved, achieving 97.3% capacity retention after 31 cycles compared with 80.1% for CNT-free systems under the same conditions. Lu et al.^[80] synthesized TiFe-CNTs/ MgH_2 composites through sintering, mechanical milling, and wet-chemical ball milling, which exhibited exceptional pressure stability (<2% capacity deviation under 0.1–3.0 MPa H_2 fluctuations) and zero capacity decay after 10 cycles, attributed to the dispersive and stabilizing effects of CNTs. Jia et al.^[81] prepared Ni-VO_x/AC- MgH_2 systems that achieved rapid absorption of 6.2% min⁻¹ at 150 °C and 6.5% H_2 release within 10 min at 300 °C, while the dehydrogenation activation energy was halved to 60 kJ/mol compared with MgH_2 . This enhancement was ascribed to the activated porous structure of carbon and uniformly dispersed Ni-VO_x sites. Lu et al.^[82] developed MgH_2 +10% TiO₂-ZnTiO₃@CNTs composites (catalytic mechanism shown in Figure 6(a)), which reduced the initial dehydrogenation temperature to 197 °C and the onset absorption temperature to 50 °C, while enabling 6.1% H_2

release in 10 min at 300 °C with 97% retention over 20 cycles. These improvements were attributed to the buffering effect of CNTs on the 30% volume strain and their promotion of electron conduction.

Graphene oxide (GO), an oxidized derivative of graphene containing abundant oxygen functional groups (–OH, –O–, –COOH), can effectively anchor metal nanoparticles and create oxygen vacancies to enhance performance. Wang et al.^[83] fabricated Ni-Ov-C@GO- MgH_2 *via* electrostatic assembly and calcination, achieving exceptional properties: the dehydrogenation activation energy decreased to 40.78 kJ/mol (20% of that of pure MgH_2), with 97.3% capacity retention (6.32%) after 30 cycles, attributed to the synergistic catalysis between Ni nanoparticles and Co₃O₄ on GO. For graphene-based composites, Singh et al.^[84] developed Ni@GA- MgH_2 , reducing the onset dehydrogenation temperature from 358 to 221 °C while maintaining stable capacity over 27 cycles. Yan et al.^[85] prepared rGO-BTB/ MgH_2 *via* a soft-template method (synthesis flowchart shown in Figure 6(b)), achieving a capacity of 6.6% with dehydrogenation onset at 50 °C, though the performance requires further optimization due to side reactions between silanol and Mg.

Bu et al.^[86] constructed MgH_2 -20 nm TiO₂@Gra composites using atomic deposition, achieving a dehydrogenation onset temperature of 199 °C and 95.5% capacity retention after 50 cycles, attributed to the synergistic effects of internal TiO₂ nanochannels and external graphene coating. Liu et al.^[87] developed a bimetallic Co/Pd@B-CNTs catalyst that demonstrated superior performance: MgH_2 -Co/Pd@B-CNTs absorbed 6.49% H_2 in just 20 s at 200 °C under 8 MPa, with the dehydrogenation activation energy reduced dramatically from 178 to 76.66 kJ/mol. Comparative experiments revealed that Pd exhibited greater catalytic performance than Co, likely due to its stronger hydrogen spillover effect.

These findings fully demonstrate the significant potential of carbon-based composite materials in hydrogen storage, indicating that precise design of metal-carbon interfacial structures and multi-scale morphological control can synergistically enhance both thermodynamic and kinetic properties.

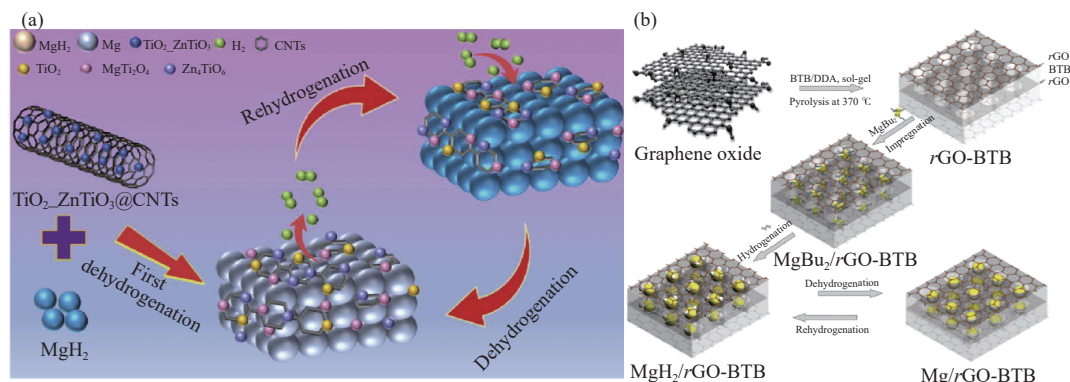


Fig. 6 (a) Catalytic mechanism of MgH_2 +10% TiO₂-ZnTiO₃@CNTs^[82]; (b) Schematic illustration of the preparation process for MgH_2 /rGO-BTB and Mg/rGO-BTB^[85]

(with permission from Elsevier and Royal Society of Chemistry)

Carbon materials not only act as structural stabilizers to prevent active particle aggregation but also facilitate charge transfer through conductive networks, while transition metals effectively reduce reaction barriers. This multifunctional synergy provides valuable insights for developing next-generation high-efficiency H_2 storage materials. Future research should focus on: (1) precise control of interfacial interactions; (2) effective suppression of side reactions; (3) development of scalable preparation processes; and (4) long-term stability evaluation under practical conditions. Breakthroughs in these areas will help advance carbon-based hydrogen storage materials toward real-world applications.

3.4 Metal-organic frameworks (MOFs)

Metal-organic frameworks (MOFs) are crystalline porous materials synthesized through the self-assembly of inorganic metal centers (metal ions or clusters) interconnected with organic ligands, thereby forming periodic network structures. Characterized by large surface areas and tunable micropore sizes, MOFs can be engineered into specific topological configurations to regulate H_2 storage performance. As illustrated by representative MOF structures in Figure 7^[88], their key features include: (1) Synthetic flexibility: MOFs are obtained by self-assembly of metal salts and organic ligands, often containing coordinatively unsaturated metal sites with acidic or basic properties; (2) Porosity: the inherently porous frameworks provide high specific surface areas and abundant adsorption sites; (3) Structural diversity: a wide range of metal-ligand combinations enables diverse spatial architectures, offering multiple synthetic pathways for tailored material design.

The research history of MOF materials can be traced back to 1995, when Hailian et al.^[89] first synthesized the three-dimensional MOF-5. In recent years, significant breakthroughs have been achieved in MOF-derived material studies. Naveen et al.^[90] employed a Co/Zn bimetallic MOF precursor and successfully prepared a single-atom dispersed Co-Zn bimetallic carbon material by precisely regulating the pyrolysis process (Figure 8 illustrates its assembly and synthesis procedure). This material exhibited excellent H_2 storage performance, which was attributed to the synergistic effects between atomically dispersed Co/Zn active sites and

the porous carbon matrix.

Lan et al.^[91] prepared a $(Ni,TiO_2)CN/MgH_2$ composite system (synthesis route shown in Figure 9(a)) that achieved multiple performance enhancements through refined structural design: (1) The Ni-induced $MgNi_2$ phase generated a distinctive “hydrogen pump” effect, markedly promoting hydrogen adsorption and dissociation; (2) Multivalent Ti species (Ti^{3+}/Ti^{4+}) effectively accelerated electron transfer; (3) A stable carbon-nitrogen protective layer successfully inhibited MgH_2 nanoparticle agglomeration during cycling. Performance tests demonstrated remarkable outcomes: 5.85% H_2 release in 10 min at 275 °C, 5.94% release within 5 min at 300 °C, 6.17% absorption within 10 min at 125 °C, and even 5.08% storage capacity after 100 min at near-ambient temperature (40 °C). Zheng et al.^[92] synthesized NiFe MOFs *via* a solvothermal method, followed by 2.5 h hydrogen reduction at 400 °C to obtain flower-like $FeNi_3$ -S catalyst (synthesis and mechanism shown in Figure 9(b)). This catalyst lowered the H_2 absorption peak temperature of MgH_2 from 325 to 202 °C, enabling 3.04% release in 1000 s at 250 °C and complete 6.57% dehydrogenation at 325 °C. After 20 cycles, MgH_2 - $FeNi_3$ -S maintained excellent capacity retention owing to H_2 diffusion channels provided by Fe/MgS phases.

In the field of bimetallic catalysts, Li et al.^[93] developed a $CoFe@C/MgH_2$ composite nanoparticle that demonstrated excellent H_2 storage/release performance (the preparation process and catalytic mechanism are shown in Figure 10). The MgH_2 - $CoFe@C$ -800 exhibited remarkable H_2 storage properties: its onset dehydrogenation temperature was 175.9 °C, with a DSC peak temperature as low as 263 °C. At 250 °C, it could desorb more than 3.6% H_2 within 3600 s, while absorbing over 4.0% H_2 in 3000 s at 150 °C.

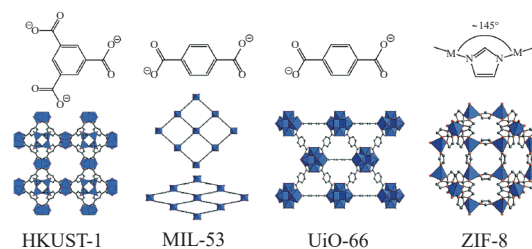


Fig. 7 Schematic diagrams of typical MOF structures^[88]
(with permission from Royal Society of Chemistry)

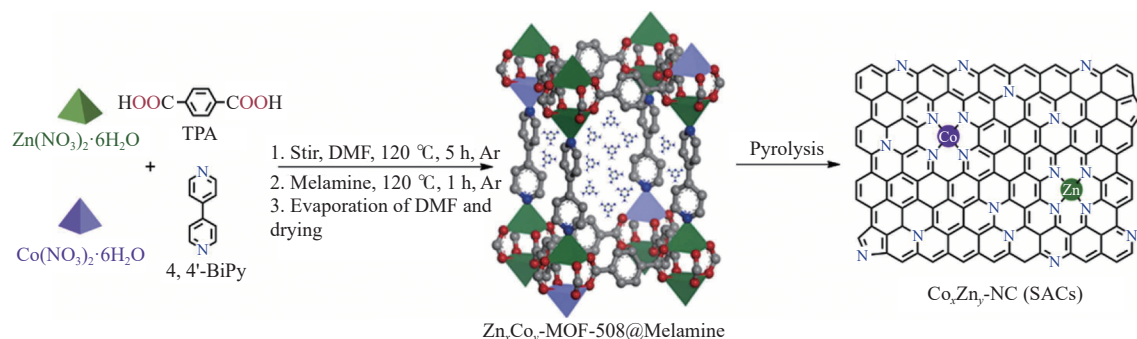


Fig. 8 Schematic diagram of the synthesis of Co_xZn_y -NC^[90]
(with permission from Elsevier)

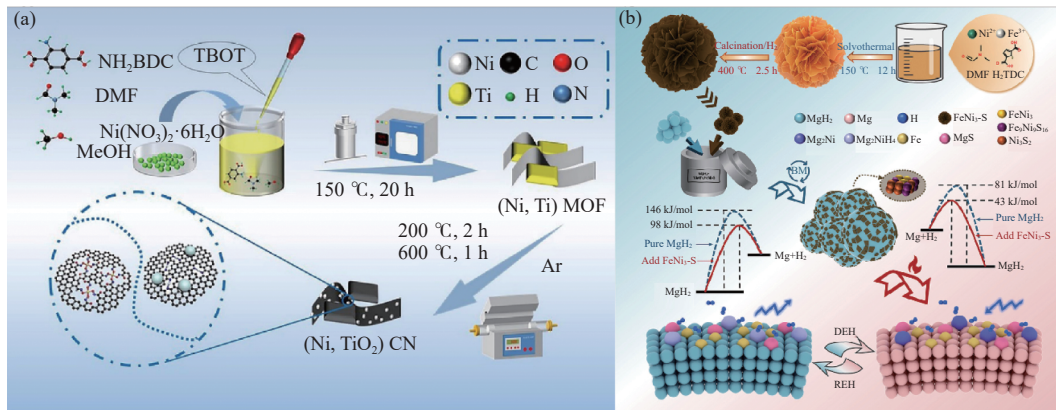


Fig. 9 (a) Schematic synthesis route of (Ni,TiO₂)CN^[91]; (b) Schematic illustration of the synthesis process and multiphase synergistic catalytic mechanism of the MgH₂+10% FeNi₃-S composite^[92] (with permission from Elsevier)

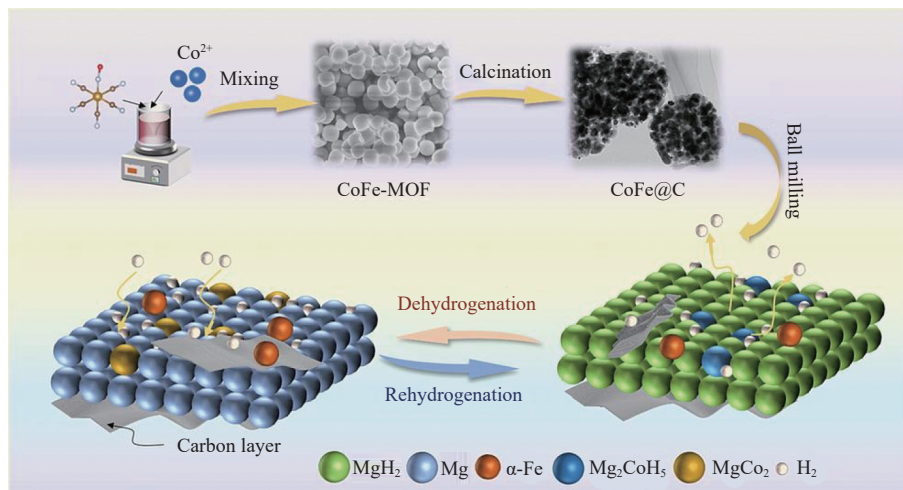


Fig. 10 Schematic illustration of the catalytic mechanism for MgH₂-CoFe@C composite^[93] (with permission from Elsevier)

After 10 cycles, the sample showed negligible capacity attenuation, suggesting that the MOF framework effectively inhibited MgH₂ nucleation. Notably, after 20 cycles, the H₂ absorption rate even improved. These enhancements may be attributed to Co providing hydrogen pump channels through the reversible conversion between Mg₂Co and Mg₂CoH₅, while α-Fe catalyzed the decomposition of MgH₂, and the carbon matrix effectively prevented nanoparticle agglomeration, thereby improving overall cycling performance.

Hu et al.^[94] further revealed the bimetallic synergistic catalytic mechanism through comparative studies, synthesizing MgH₂+Fe/C, MgH₂+Ni/C and MgH₂+TM/C via calcination and ball milling. The tests showed that the dehydrogenation temperatures of these samples were reduced by 103, 73 and 106 °C respectively compared with pure MgH₂. After 10 cycles at 325 °C, the capacity retention rates were 99.8%, 99.7% and 99.8% respectively, with cycling stability attributed to the ability of carbon to prevent MgH₂ particle agglomeration. Comparative analysis of isothermal absorption/desorption and non-isothermal dehydrogenation curves revealed that MgH₂+TM/C

exhibited the best kinetic performance.

Yang et al.^[95] developed a NiCo-MOF/V-O catalyst that reduced the onset dehydrogenation temperature of MgH₂ to 155 °C through vanadium-oxygen species induction. Highly crystalline NiCo layered double hydroxide (LDH) was synthesized through stirring and aging, and then treated in (NH₄)VO₃ aqueous solution at 150 °C for 3 h to produce the final catalytic material, with XRD and XPS confirming its structure. Among the H₂ storage alloys prepared by ball milling MgH₂ with NiCoLDH and NiCo-MOF/V-O, the latter showed superior performance due to the inducing effect of (NH₄)VO₃. MgH₂-7% NiCo-MOF/V-O began dehydrogenation at 155 °C (125 °C lower than pure MgH₂) and achieved complete dehydrogenation (6.5%) within 5 min at 300 °C. After 30 cycles at 325 °C, the absorption/desorption capacities decreased slightly from 6.494%/7.597% to 6.451%/7.239%, demonstrating stable cycling performance.

Chen et al.^[96] systematically investigated the effect of calcination temperature on Ni/Fe-MOF-derived catalysts. Using solvothermal and ultrasonic methods, they prepared Ni/Fe-MOF precursors, which were calcined at 700, 800

and 900 °C to obtain the final catalysts. The hydrogen storage alloys MgH_2 -10NiFe-700, MgH_2 -10NiFe-800 and MgH_2 -10NiFe-900 showed DSC peak temperatures of 305.5, 289.7 and 298.8 °C respectively, remarkably lower than the 395 °C of MgH_2 . The 800 °C-calcined MgH_2 -10NiFe-800 could release 3.70% and 5.95% H_2 within 10 min at 275 and 300 °C respectively, and 6.16% within 5 min at 325 °C. These outstanding results primarily stemmed from synergistic effects between Ni_3Fe , Ni and NiFe_2O_4 during dehydrogenation.

MOF materials demonstrate both advantages and challenges in H_2 storage applications. The main advantage lies in their highly designable crystal structures, which can provide abundant active sites for H_2 adsorption through the selection of suitable metal nodes and organic linkers. Unsaturated metal sites in MOFs can also generate acid-base catalytic activity, while functional groups (e.g., $-\text{COOH}$, $-\text{NH}_2$) allow further surface modification. In addition, MOF-derived materials can form highly dispersed single-atom catalysts through pyrolysis, which can significantly improve H_2 storage performance. However, several challenges remain for practical applications. Most MOFs have poor thermal stability and tend to collapse at high temperatures. Although high-performance MOF-based H_2 storage materials can be prepared at the laboratory scale, large-scale production is still costly and has low yields. Moreover, while microporous structures help increase hydrogen storage density, they may also hinder rapid H_2 diffusion.

3.5 MXenes

MXenes, as a novel class of two-dimensional materials, mainly include transition metal carbides (Ti_3AlC_2 , Ta_4AlC_3 , V_2AlC)^[97], transition metal nitrides (Ti_4AlN_3 , Ti_2AlN)^[98], and transition metal carbonitrides (Ti_3AlCN)^[99]. Their MAX phase precursors are layered ternary carbides or nitrides with the general formula “ $\text{M}_{n+1}\text{AX}_n$ ”, where M, A, and X represent transition metals (e.g., Ti, V, Zr, Nb, Ta), A-group elements (typically Al or Si), and carbon or nitrogen, respectively^[100].

Zhu et al.^[101] synthesized a $\text{Ni}@\text{Ti}_3\text{C}_2$ composite material that exhibited excellent hydriding/dehydriding kinetics. Using liquid-phase reduction, Ni was assembled onto the surface of two-dimensional Ti_3C_2 to obtain Ti_3C_2 MXene-based catalytic materials, with the synthesis strategy illustrated in Figure 11. Under 3 MPa at 125 °C, the material absorbed 5.4% H_2 within 25 s (93% of its maximum capacity), stored over 4.0% H_2 within 60 min at 75 °C, and even absorbed more than 4.0% H_2 within 5 h at room temperature. At 250 °C, the sample released approximately 5.0% H_2 within 10 min, in sharp contrast to only 0.2% for pristine MgH_2 under the same conditions. After 10 absorption/desorption cycles at 275 °C, the composite maintained a storage capacity of 5.2%, further demonstrating the significant enhancement effect of $\text{Ni}@\text{Ti}$ -

MX catalytic materials on the H_2 storage performance of MgH_2 . Researchers including Kim et al.^[102] and Lu et al.^[98] focused on the development of Cl-terminated MXene materials, and the Cl- Ti_2C prepared through Lewis acidic molten salt etching displayed surface chemical properties and a 2D layered structure that offered abundant active sites for H_2 adsorption/dissociation. Lan et al.^[103] designed a MgH_2 +Ni@Nb₂C composite that showed more competitive performance compared with pure MgH_2 , MgH_2 +Ni, and MgH_2 +Nb₂C: absorbing 4.45% H_2 within 5 h at 30 °C and reaching 6.15% at 100 °C; showing a H_2 release rate of 4.26% in 100 min at 225 °C and achieving complete dehydrogenation within 4.3 min at 300 °C. After 100 cycles at 325 °C, the sample maintained a H_2 storage capacity of 5.91% with a retention rate of 93.4%.

These research findings indicate that the two-dimensional layered structure of MXene materials, with their high surface area and excellent mechanical processing and thermal conductivity, can provide abundant active sites for the hydrogenation/dehydrogenation processes of MgH_2 , thereby significantly enhancing its H_2 storage performance. In addition, through metal nanoparticle modification and surface functional group regulation, the H_2 storage properties and cycling stability of the materials can be further optimized synergistically. Future research should focus on addressing key challenges such as large-scale preparation of MXene materials, long-term cycling stability, and performance degradation under practical operating conditions, in order to accelerate the industrial application of MXene-based materials.

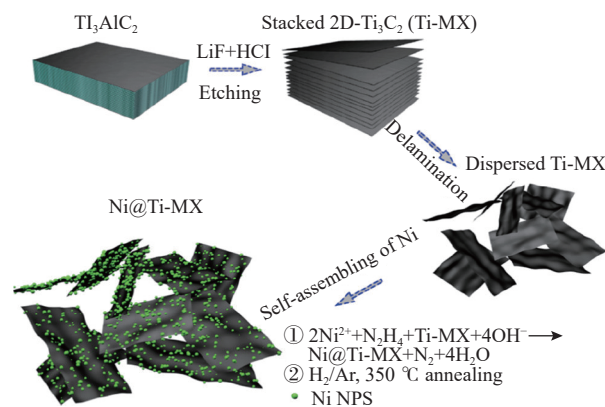


Fig. 11 Schematic illustrations of the synthetic strategy applied for the $\text{Ni}@\text{Ti}$ -MX catalyst^[101] (with permission from American Chemical Society)

3.6 High-entropy alloys (HEAs)

High-entropy alloys (HEAs) are advanced materials composed of five or more principal metallic elements in near-equiatomic ratios. In recent years, HEAs have shown unique advantages in modifying magnesium-based H_2 storage materials, as their high configurational entropy endows them with distinctive features such as lattice

distortion and sluggish diffusion effects.

Wang et al.^[104] innovatively prepared an equimolar (V:Mn:Fe:Co:Ni = 1:1:1:1:1) VMnFeCoNi high-entropy alloy solid solution through mechanical ball milling-compression-sintering processes, and the research results showed that adding 5% of this alloy decreased the hydriding temperature of MgH₂ to 223 °C while increasing the absorption kinetics by 70-fold, which was attributed to the synergistic catalytic effects of transition metal multi-active sites and the lattice distortion effect of the high-entropy solid solution. Deng et al.^[105] synthesized TiCrVM (*M* = Fe, FeCo, FeZr) HEAs *via* vacuum arc melting and prepared Mg/TiCrVM composites by reactive ball milling of HEAs with Mg powder (5 MPa). TiCrVFeCo could reduce the dehydrogenation activation energy of MgH₂ from 183.4 to 81.1 kJ/mol, which may have been due to γ -MgH₂ formation and grain refinement, and it lowered the enthalpy change (ΔH) from 81.76 (pure Mg) to 62.45 kJ/mol (Mg/TiCrVFeCo). At 260 °C, Mg/TiCrVFeCo released 5.27% H₂ in 20 min, significantly outperforming pure Mg (0.20%). Moreover, the onset dehydrogenation temperature decreased from 324 to 205 °C, with only 8.6% capacity decay after 20 cycles. Liu et al.^[106] designed a carbon-supported NiCoFeCuMg HEA catalyst, and the ball-milled MgH₂+NiCoFeCuMg@C sample exhibited extraordinary H₂ storage performance through the “hydrogen pump” effect of Mg₂Ni(Cu)/Mg₂Ni(Cu)H₄, the “hydrogen channel” role of Co₃Fe₇, and the dispersive function of the carbon carrier. The composite lowered the initial dehydrogenation temperature to 167.2 °C (vs. 331 °C for pure MgH₂), with a peak temperature of 302.96 °C (vs. 371.25 °C). In addition, it released 6.01% H₂ in 5 min at 325 °C and completed hydrogenation within 30 s at 275 °C. Furthermore, the dehydrogenation activation energy decreased from 157.9 (pure MgH₂) to 112.4 kJ/mol, with 97% capacity retention after 20 cycles. Wei et al.^[107] designed and synthesized (TiVZrNb)₈₃Cr₁₇ HEA *via* arc melting, ensuring compositional homogeneity through multiple melting cycles. The final MgH₂-6% (TiVZrNb)₈₃Cr₁₇ composite exhibited excellent hydrogen storage performance, absorbing 5.3% H₂ in 5 min at 573 K, with the dehydrogenation activation energy as low as 90.5 kJ/mol and 98.5% capacity retention after 10 cycles. The outstanding results could be attributed to the multi-component characteristics of HEAs (high-entropy effects, lattice distortion, etc.), which suppressed intermetallic compound formation, enhanced catalytic efficiency, and demonstrated specific hydrogen storage capabilities (e.g., rapid room-temperature absorption), thereby promoting the H₂ absorption/desorption kinetics of MgH₂. Wang et al.^[108] chose two HEAs, CrFeCoNi (HEA-1) and CrMnFeCoNi (HEA-2), and prepared them as nanosheets (HEA-3 and HEA-4) *via* wet-chemical ball milling. CrMnFeCoNi nanosheets (HEA-4) showed the best catalytic performance, reducing the onset dehydrogenation temperature from 350 (pure MgH₂) to 198 °C. At 300 °C, the MgH₂-10% HEA-4 composite released 6.5% H₂ in 10 min, with hydrogen

absorption initiating at 40 °C. In terms of kinetics, HEA-4 reduced the dehydrogenation activation energy from 219.23 to 75.81 kJ/mol and the hydrogenation activation energy from 83.79 to 50.25 kJ/mol. The rate-limiting step shifted from a permeation model to diffusion control, significantly enhancing reaction rates. The MgH₂-HEA-4 composite showed only 0.2% capacity loss after 20 cycles, demonstrating excellent cycling stability, and this method triggered H₂ release pathways through multi-element synergy and surface active sites.

Through their unique compositional and structural properties, HEAs provide a threefold solution for magnesium-based H₂ storage materials: kinetic acceleration, thermodynamic modulation, and long-term stability. However, challenges remain regarding cost, mechanistic understanding, and scalability. Future research should therefore focus on rational design, deeper mechanistic exploration, and engineering-oriented applications to promote practical implementation.

4 Conclusions

Although MgH₂ has attracted worldwide attention due to its high hydrogen storage density, strong modification potential, and inherent safety, its thermodynamic and kinetic properties still require significant improvement. In recent years, many scholars have made substantial contributions to enhancing the hydrogen storage performance of MgH₂, and the major research outcomes can be summarized as follows:

Alloying method: Manipulating the composition and ratio of metals can effectively improve the thermodynamic and kinetic properties of Mg-based materials. However, the introduction of metals usually reduces their hydrogen storage capacity, and the breaking of metal bonds during hydrogenation/dehydrogenation may compromise cycling stability. Thus, selecting suitable alloying elements to balance high storage capacity with stable cycling performance remains a major challenge.

Nanostructuring method: Nanostructured materials, with their high surface areas, porosity, and abundant defects, can significantly accelerate hydrogen absorption/desorption kinetics and lower the activation energy of MgH₂. Nanoconfinement, which restricts materials within frameworks with fixed cavities, can effectively suppress nanoparticle growth while preserving desirable thermodynamic and kinetic properties. Nevertheless, several challenges persist: ball milling often induces agglomeration and deteriorates storage performance; chemical synthesis lacks controllability and may produce unwanted oxidized products; other synthetic methods are too complex for large-scale application. Therefore, developing robust nanostructuring strategies is essential to maintain high performance and prevent particle coarsening.

Catalytic material doping: Introducing catalysts can trigger mechanisms such as spillover, hydrogen pump,

channeling, and electron transfer, thereby enhancing hydrogenation/dehydrogenation activity. The synergistic use of carbon-based materials and transition metals has shown impressive improvements in kinetics, activation energy reduction, and cycling stability. This demonstrates that catalytic doping can effectively accelerate reaction kinetics while maintaining hydrogen storage density and retention. However, many existing catalysts still fall short of the comprehensive performance requirements, highlighting the need for novel catalysts with abundant active sites and superior thermal/kinetic characteristics.

Although each of these strategies can independently enhance the hydrogen storage performance of MgH_2 , a single approach is insufficient to achieve the ideal effect. Recent studies have revealed more pronounced benefits from synergistic strategies, such as alloying combined with nanostructuring or catalytic doping coupled with nanoconfinement.

For large-scale application and development of Mg-based hydrogen storage materials, future efforts should focus on the following directions:

Systematic design of novel materials: Leveraging AI-driven big data for catalyst design and exploring emerging modifiers such as MXenes and MOFs, which can provide both catalytic activity and nanoconfinement to enhance cycling stability.

In-depth mechanistic study: Integrating theoretical models (e.g., finite element analysis, kinetics, DFT) with experiments to understand hydrogen adsorption, diffusion, and reaction mechanisms. Kinetic rate-limiting models can guide the rational design of efficient multi-component systems (e.g., HEAs), with experimental validation used to refine theoretical frameworks.

Improvement of preparation techniques: Applying ultrasonic treatment for uniform dispersion of metal/catalyst mixtures, adopting solvothermal methods or aging processes to facilitate lattice incorporation, and combining solvothermal synthesis with ball milling for synergistic modification.

In summary, these strategies can bridge the gap between laboratory research and industrial application, ultimately accelerating the deployment of high-performance Mg-based hydrogen storage materials.

Declaration of Competing Interest

The authors declare no conflict of interest.

References

- [1] QI Y, ZHANG Z, TANG Q, et al. Synergistic effect of the hydrogen pump and heterostructure enables superior hydrogen storage performance of MgH_2 [J]. Chem Mater, 2024, 36(12): 6288–6298.
- [2] TOMINAKA S. Topotactic reduction yielding black titanium oxide nanostructures as metallic electronic conductors[J]. Inorg Chem, 2012, 51(19): 10136–10140.
- [3] ZENG L, SANDER R, CHEN Y, et al. Hydrogen storage performance during underground hydrogen storage in depleted gas reservoirs: A review[J]. Engineering, 2024, 40: 211–225.
- [4] HIRSCHER M, YARTYS V A, BARICCO M, et al. Materials for hydrogen-based energy storage-past, recent progress and future outlook[J]. J Alloys Compd, 2020, 827: 153548.
- [5] LU J, CHOI Y J, FANG Z Z, et al. Hydrogenation of nanocrystalline Mg at room temperature in the presence of TiH_2 [J]. J Am Chem Soc, 2010, 132(19): 6616–6617.
- [6] YARTYS V A, LOTOTSKYY M V, AKIBA E, et al. Magnesium based materials for hydrogen based energy storage: Past, present and future[J]. Int J Hydrogen Energy, 2019, 44(15): 7809–7859.
- [7] ZHANG X, SUN Y, JU S, et al. Solar-driven reversible hydrogen storage[J]. Adv Mater, 2023, 35(2): 2206946.
- [8] SCHLAPBACH L, ZTTEL A. Hydrogen-storage materials for mobile applications[J]. Nature, 2001, 414(6861): 353–358.
- [9] REN L, ZHU W, ZHANG Q, et al. MgH_2 confinement in MOF-derived N-doped porous carbon nanofibers for enhanced hydrogen storage[J]. Chem Eng J, 2022, 434: 134701.
- [10] YAN S, WEI L, GONG Y, et al. Enhanced hydrogen storage properties of magnesium hydride by multifunctional carbon-based materials: A review[J]. Int J Hydrogen Energy, 2024, 55: 521–541.
- [11] ZHU W, REN L, LU C, et al. Nanoconfined and in situ catalyzed MgH_2 self-assembled on 3D Ti_3C_2 MXene folded nanosheets with enhanced hydrogen sorption performances[J]. ACS Nano, 2021, 15(11): 18494–18504.
- [12] LANG C, JIA Y, YAO X. Recent advances in liquid-phase chemical hydrogen storage[J]. Energy Storage Mater, 2020, 26: 290–312.
- [13] LIU J, MA Y, YANG J, et al. Recent advance of metal borohydrides for hydrogen storage[J]. Front Chem, 2022, 10: 945208.
- [14] DU H. Preparation of Ti-based catalysts and effects on hydrogen storage properties of MgH_2 and NaAlH_4 [D]. Hangzhou: Zhejiang University, 2016.
- [15] LIANG C, WANG Z, ZHANG M, et al. Research progress on magnesium-based solid hydrogen storage nanomaterials[J]. Energy Storage Sci Technol, 2024, 13(3): 788–824.
- [16] YANG J. Study on modification and mechanism of magnesium-based composite hydrogen storage materials[D]. Zhengzhou: Zhengzhou University, 2022.
- [17] WANG Z. Preparation of V and Nb-based transition metal catalysts and their effects on hydrogen storage properties of MgH_2 [D]. Hangzhou: Zhejiang University, 2019.
- [18] YUAN Q, WANG L, LÜ Y, et al. Progress of magnesium-based materials toward hydrogen storage[J]. Chem Ind Eng, 2025, 42(3): 57–72.
- [19] DING Z, LI Y, YANG H, et al. Tailoring MgH_2 for hydrogen storage through nanoengineering and catalysis[J]. J Magnesium Alloys, 2022, 10(11): 2946–2967.

- [20] SADHASIVAM T, KIM H T, JUNG S, et al. Dimensional effects of nanostructured Mg/MgH₂ for hydrogen storage applications: A review[J]. Renewable Sustainable Energy Rev, 2017, 72: 523–534.
- [21] ZHANG T, LIU M, WANG L, et al. Research progress in nanomodification of MgH₂[J]. New Chem Mater, 2025, 53(6): 15–21.
- [22] BARKHORDARIAN G, KLASSEN T, BORMANN R. Catalytic mechanism of transition-metal compounds on Mg hydrogen sorption reaction[J]. J Phys Chem B, 2006, 110(22): 11020–11024.
- [23] XU N, WANG K, ZHU Y, et al. PdNi biatomic clusters from metallene unlock record-low onset dehydrogenation temperature for bulk-MgH₂[J]. Adv Mater, 2023, 35(38): 2303173.
- [24] YANG Y, ZHANG X, ZHANG L, et al. Recent advances in catalyst-modified Mg-based hydrogen storage materials[J]. J Mater Sci Technol, 2023, 163: 182–211.
- [25] DING X, CHEN R R, CHEN X Y, et al. A novel method towards improving the hydrogen storage properties of hypoeutectic Mg-Ni alloy via ultrasonic treatment[J]. J Magnesium Alloys, 2023, 11(3): 903–915.
- [26] REILLY J J, WISWALL R H. Reaction of hydrogen with alloys of magnesium and nickel and the formation of Mg₂NiH₄[J]. Inorg Chem, 1968, 7(12): 2254–2256.
- [27] SELVAM P, VISWANATHAN B, SWAMY C S, et al. Mg₂NiH: A new hydride phase in the Mg₂NiH₂ system[J]. Int J Hydrogen Energy, 1988, 13(12): 749–759.
- [28] STUCKI F. Hydriding and dehydriding kinetics of Mg₂Ni above and below the structural phase transition[J]. Int J Hydrogen Energy, 1983, 8(1): 49–51.
- [29] YANG H B, YUAN H T, JI J T, et al. Characteristics of Mg₂Ni_{0.75}M_{0.25} (M=Ti, Cr, Mn, Fe, Co, Ni, Cu and Zn) alloys after surface treatment[J]. J Alloys Compd, 2002, 330-332: 640–644.
- [30] SHAO H, WANG Y, XU H, et al. Preparation and hydrogen storage properties of nanostructured Mg₂Cu alloy[J]. J Solid State Chem, 2005, 178(7): 2211–2217.
- [31] ZLOTEA C, ANDERSSON Y. Microstructural modifications induced by hydrogen absorption in Mg₃Ga₂ and Mg₃Pd[J]. Acta Mater, 2006, 54(20): 5559–5564.
- [32] YAJIMA S, KAYANO H, TOMA H. Hydrogen sorption in La₂Mg₁₇[J]. J Less-Common Met, 1977, 55(1): 139–141.
- [33] POLANSKI M, NAWRA D, ZASADA D. Mg₂FeH₆ synthesized from plain steel and magnesium hydride[J]. J Alloys Compd, 2019, 776: 1029–1040.
- [34] GENNARI F C, CASTRO F J, ANDRADE GAMBOA J J. Synthesis of Mg₂FeH₆ by reactive mechanical alloying: Formation and decomposition properties[J]. J Alloys Compd, 2002, 339(1): 261–267.
- [35] KYOI D, SATO T, RNNEBRO E, et al. A new ternary magnesium-titanium hydride Mg₇TiH_x with hydrogen desorption properties better than both binary magnesium and titanium hydrides[J]. J Alloys Compd, 2004, 372(1): 213–217.
- [36] LIU L, HUANG Z N, GAO X, et al. Effect of novel La-based alloy modification on hydrogen storage performance of magnesium hydride: First-principles calculation and experimental investigation[J]. J Power Sources, 2022, 551: 232187.
- [37] LIU D M, TAN Q J, GAO C, et al. Reversible hydrogen storage properties of LiBH₄ combined with hydrogenated Mg₁₁CeNi alloy[J]. Int J Hydrogen Energy, 2015, 40(20): 6600–6605.
- [38] YANG X Y, WANG X Q, LIU R J, et al. Enhancing hydrogen storage performance of MgH₂ with hollow Bi₂Ti₂O₇ catalyst: Synergistic effects of Bi₂Mg₃ alloy phase and Ti polyvalency[J]. J Magnesium Alloys, 2025.
- [39] YOON M S, HUR J, PARK S H, et al. Role of solute elements in Mg-Mg₂Ni hydrogen storage alloys: A first-principles calculation study[J]. J Magnesium Alloys, 2024, 12(11): 4574–4593.
- [40] YU X, TANG Z, SUN D, et al. Recent advances and remaining challenges of nanostructured materials for hydrogen storage applications[J]. Prog Mater Sci, 2017, 88: 1–48.
- [41] DING S. Effect of novel nanostructured catalysts on hydrogen storage behavior of nanocrystalline MgH₂[D]. Qinhuangdao: Yanshan University, 2025.
- [42] WANG K. Preparation of Nb-based catalysts and their effects on hydrogen absorption/desorption properties of MgH₂[D]. Hangzhou: Zhejiang University, 2020.
- [43] PEZAT M, DARRIET B, HAGENMULLER P. A comparative study of magnesium-rich rare-earth-based alloys for hydrogen storage[J]. J Less-Common Met, 1980, 74(2): 427–434.
- [44] FERNNDEZ J F, SNCHEZ C R. Rate determining step in the absorption and desorption of hydrogen by magnesium[J]. J Alloys Compd, 2002, 340(1/2): 189–198.
- [45] REN L, LI Y, ZHANG N, et al. Nanostructuring of Mg-based hydrogen storage materials: Recent advances for promoting key applications[J]. Nano-Micro Lett, 2023, 15(1): 93.
- [46] AGUEY-ZINSOU K F, ARES-FERNNDEZ J R. Hydrogen in magnesium: New perspectives toward functional stores[J]. Energy Environ Sci, 2010, 3(5): 526–543.
- [47] DANAIE M, MITLIN D. TEM analysis and sorption properties of high-energy milled MgH₂ powders[J]. J Alloys Compd, 2009, 476(1): 590–598.
- [48] CHOI Y J, CHOI J W, SOHN H Y, et al. Chemical vapor synthesis of Mg-Ti nanopowder mixture as a hydrogen storage material[J]. Int J Hydrogen Energy, 2009, 34(18): 7700–7706.
- [49] WAGEMANS R W P, VAN LENTHE J H, DE JONGH P E, et al. Hydrogen storage in magnesium clusters: Quantum chemical study[J]. J Am Chem Soc, 2005, 127(47): 16675–16680.
- [50] CHEUNG S, DENG W Q, VAN DUIN A C T, et al. ReaxFF_{MgH} reactive force field for magnesium hydride systems[J]. J Phys Chem A, 2005, 109(5): 851–859.
- [51] DONG S, LI C, WANG J, et al. The “burst effect” of hydrogen desorption in MgH₂ dehydrogenation[J]. J Mater Chem A, 2022, 10(42): 22363–22372.
- [52] ZHANG M, XIAO X, LUO B, et al. Superior de/hydrogenation performances of MgH₂ catalyzed by 3D flower-like TiO₂@C nanostructures[J]. J Mater Chem A,

- 2020, 46: 191–198.
- [53] CHEN M, XIAO X, ZHANG M, et al. Highly dispersed metal nanoparticles on TiO₂ acted as nano redox reactor and its synergistic catalysis on the hydrogen storage properties of magnesium hydride[J]. *Int J Hydrogen Energy*, 2019, 44(29): 15100–15109.
- [54] NIELSEN T K, MANICKAM K, HIRSCHER M, et al. Confinement of MgH₂ nanoclusters within nanoporous Aerogel scaffold materials[J]. *ACS Nano*, 2009, 3(11): 3521–3528.
- [55] LI W, LI C, MA H, et al. Magnesium nanowires: Enhanced kinetics for hydrogen absorption and desorption[J]. *J Am Chem Soc*, 2007, 129(21): 6710–6711.
- [56] XIA G, TAN Y, CHEN X, et al. Monodisperse magnesium hydride nanoparticles uniformly self-assembled on graphene[J]. *Adv Mater*, 2015, 27(39): 5981–5988.
- [57] AGUEY-ZINSOU K F, ARES-FERNANDEZ J R. Synthesis of colloidal magnesium: A near room temperature store for hydrogen[J]. *Chem Mater*, 2008, 20(2): 376–378.
- [58] ÖLMEZ R, AKMAK G, ZTRK T. Combinatorial search for hydrogen storage alloys: Mg-Ni and Mg-Ni-Ti[J]. *Int J Hydrogen Energy*, 2010, 35(21): 11957–11965.
- [59] MAO J, GUO Z, YU X, et al. Enhanced hydrogen sorption properties of Ni and Co-catalyzed MgH₂[J]. *Int J Hydrogen Energy*, 2010, 35(10): 4569–4575.
- [60] YAO P, JIANG Y, LIU Y, et al. Catalytic effect of Ni@rGO on the hydrogen storage properties of MgH₂[J]. *J Magnesium Alloys*, 2020, 8(2): 461–471.
- [61] DAN L, WANG H, LIU J, et al. H₂ plasma reducing Ni nanoparticles for superior catalysis on hydrogen sorption of MgH₂[J]. *ACS Applied Energy Materials*, 2022, 5(4): 4976–4984.
- [62] DUAN C, SU Z, TIAN Y, et al. Mechanochemical assisted hydrogenation of Mg-CNTs-Ni: Kinetics modeling and reaction mechanism[J]. *Chem Eng J*, 2022, 441: 136059.
- [63] LIU J, TANG Q, ZHU Y, et al. Assisting Ni catalysis by CeO₂ with oxygen vacancy to optimize the hydrogen storage properties of MgH₂[J]. *J Mater Sci Technol*, 2023, 159: 62–71.
- [64] MA Z, PANDA S, ZHANG Q, et al. Improving hydrogen sorption performances of MgH₂ through nanoconfinement in a mesoporous CoS nano-boxes scaffold[J]. *Chem Eng J*, 2021, 406: 126790.
- [65] WANG Y, AN C, WANG Y, et al. Core-shell Co@C catalyzed MgH₂: Enhanced dehydrogenation properties and its catalytic mechanism[J]. *J Mater Chem A*, 2014, 2(38): 16285–16291.
- [66] YIN C, QIU S, WANG Y, et al. Promoted hydrogen storage properties of MgH₂ by Ti³⁺ self-doped defect-mediated TiO₂[J]. *J Alloys Compd*, 2023, 966: 171610.
- [67] CUI J, WANG H, LIU J, et al. Remarkable enhancement in dehydrogenation of MgH₂ by a nano-coating of multi-valence Ti-based catalysts[J]. *J Mater Chem A*, 2013, 1(18): 5603–5611.
- [68] TERZIEVA M, KHRUSSANOVA M, PESHEV P. Dehydrogenation kinetics of mechanically alloyed mixtures of magnesium with some 3d transition metal oxides[J]. *Int J Hydrogen Energy*, 1991, 16(4): 265–270.
- [69] SHI Q, GAO Y, ZHAO S, et al. Interfacial engineering of fluorinated TiO₂ nanosheets with abundant oxygen vacancies for boosting the hydrogen storage performance of MgH₂[J]. *Small*, 2024, 20(18): 2307965.
- [70] REN L, ZHU W, LI Y, et al. Oxygen vacancy-rich 2D TiO₂ nanosheets: a bridge toward high stability and rapid hydrogen storage kinetics of nano-confined MgH₂[J]. *Nano-Micro Lett*, 2022, 14(1): 144.
- [71] REN L, LI Y, LI Z, et al. Boosting hydrogen storage performance of MgH₂ by oxygen vacancy-rich H-V₂O₅ nanosheet as an excited H-Pump[J]. *Nano-Micro Lett*, 2024, 16(1): 160.
- [72] ZHANG J, WANG W, CHEN X, et al. Single-atom Ni supported on TiO₂ for catalyzing hydrogen storage in MgH₂[J]. *J Am Chem Soc*, 2024, 146(15): 10432–10442.
- [73] ZHU W J, ZHU H, ZHANG T Y, et al. Surface engineering of 2D metal-porphyrin metal-organic frameworks Z-scheme Heterostructure for boosting and stable photocatalytic hydrogen evolution[J]. *Small*, 2024: 2408806.
- [74] OELERICH W, KLASSEN T, BORMANN R. Metal oxides as catalysts for improved hydrogen sorption in nanocrystalline Mg-based materials[J]. *J Alloys Compd*, 2001, 315(1): 237–242.
- [75] HANADA N, ICHIKAWA T, HINO S, et al. Remarkable improvement of hydrogen sorption kinetics in magnesium catalyzed with Nb₂O₅[J]. *J Alloys Compd*, 2006, 420(1): 46–49.
- [76] WANG L, ZHONG T, WU F, et al. Anions intercalated two-dimension high entropy layered metal oxides for enhanced hydrogen storage in magnesium hydride[J]. *Chem Eng J*, 2025, 505: 159591.
- [77] KIDNAY A J, HIZA M J High pressure adsorption isotherms of neon, hydrogen, and helium at 76 K[C]//TIMMERHAUS K D. *Advances in Cryogenic Engineering*. Boston, MA: Springer, 1967, 12.
- [78] SU W, ZHOU Y P, WEI L F, et al. Effect of microstructure and surface modification on the hydrogen adsorption capacity of active carbons[J]. *New Carbon Materials*, 2007, 22(2): 135–140.
- [79] WANG X, LI Q, PAN H, et al. Size-controlled large-diameter and few-walled carbon nanotube catalysts for oxygen reduction[J]. *Nanoscale*, 2015, 7(47): 20290–20298.
- [80] LU X, ZHANG L, YU H, et al. Achieving superior hydrogen storage properties of MgH₂ by the effect of TiFe and carbon nanotubes[J]. *Chem Eng J*, 2021, 422: 130101.
- [81] JIA Y, CHENG L, PAN N, et al. Catalytic de/hydrogenation in Mg by Co-doped Ni and VO_x on active carbon: Extremely fast kinetics at low temperatures and high hydrogen capacity[J]. *Adv Energy Mater*, 2011, 1(3): 387–393.
- [82] LU X, YANG X, LIANG X, et al. TiO₂-ZnTiO₃ with carbon nanotubes catalytically improve the hydrogen storage characteristics of MgH₂[J]. *J Power Sources*, 2024, 623: 235455.
- [83] WANG Y, XIA Y, XU E, et al. Graphene oxide supported oxygen vacancy-rich Co₃O₄ and Ni nanoparticle for

- boosting the hydrogen storage properties of MgH_2 [J]. J Magnesium Alloys, 2025.
- [84] SINGH S, BHATNAGAR A, SHUKLA V, et al. Three-dimensional graphene aerogel decorated with nickel nanoparticles as additive for improving the hydrogen storage properties of MgH_2 [J]. Int J Hydrogen Energy, 2025, 107: 96–107.
- [85] YAN F, ALFONSN E M, NGENE P, et al. MgH_2 nanoparticles confined in reduced graphene oxide pillared with organosilica: A novel type of hydrogen storage material[J]. Nanoscale, 2024, 16(33): 15770–15781.
- [86] BU F, WAJID A, YANG N, et al. Fabrication of amorphous TiO_2 hydrogen channels and graphene wrappers to enhance the hydrogen storage properties of MgH_2 with extremely high cycle stability[J]. J Mater Chem A, 2024, 12(20): 12190–12197.
- [87] LIU M, XIAO X, ZHAO S, et al. Facile synthesis of Co/Pd supported by few-walled carbon nanotubes as an efficient bidirectional catalyst for improving the low temperature hydrogen storage properties of magnesium hydride[J]. J Mater Chem A, 2019, 7(10): 5277–5287.
- [88] DUNNE P W, LESTER E, WALTON R I. Towards scalable and controlled synthesis of metal-organic framework materials using continuous flow reactors[J]. React Chem Eng, 2016, 1(4): 352–360.
- [89] LI H, EDDAOUDI M, O'KEEFFEM, et al. Design and synthesis of an exceptionally stable and highly porous metal-organic framework[J]. Nature, 1999, 402(6759): 276–279.
- [90] NAVEEN K, MAHVELATI-SHAMSABADI T, SHARMA P, et al. MOF-derived Co/Zn single-atom catalysts for reversible hydrogenation and dehydrogenation of quinoline hydrogen carrier[J]. Appl Catal B: Environ, 2023, 328: 122482.
- [91] LAN Z, HONG F, SHI W, et al. Effect of MOF-derived carbon-nitrogen nanosheets co-doped with nickel and titanium dioxide nanoparticles on hydrogen storage performance of MgH_2 [J]. Chem Eng J, 2023, 468: 143692.
- [92] ZHENG L X, LI S, ZHANG L T, et al. A MOF derived multi-phase FeNi_3 -S catalyst for efficient hydrogen storage in magnesium hydride[J]. Chin Chem Lett, 2024: 110414.
- [93] LI F, HUANG Z, WANG Y, et al. Effect of MOF-derived nanoparticle-cumulated flower-like CoFe@C coated composites on hydrogenation/dehydrogenation performance of MgH_2 [J]. Chem Eng J, 2024, 485: 150008.
- [94] HU J Q, JIANG W, SI N, et al. MOF-derived carbon supported transition metal (Fe, Ni) and synergetic catalysis for hydrogen storage kinetics of MgH_2 [J]. Int J Hydrogen Energy, 2024, 86: 445–455.
- [95] YANG Z, WANG Y, LIN X, et al. Vanadium induces Ni-Co MOF formation from a NiCo LDH to catalytically enhance the MgH_2 hydrogen storage performance[J]. J Magnesium Alloys, 2025, 13(8): 4020–4031.
- [96] CHEN Y, SUN B, ZHANG G, et al. MOF-derived $\text{Ni}_3\text{Fe}/\text{Ni}/\text{NiFe}_2\text{O}_4/\text{C}$ for enhanced hydrogen storage performance of MgH_2 [J]. J Energy Chem, 2025, 101: 333–344.
- [97] AN Y, TIAN Y, FENG J, et al. MXenes for advanced separator in rechargeable batteries[J]. Mater Today, 2022, 57: 146–179.
- [98] LU H, LI J, ZHANG R, et al. Advances and perspectives of two-dimensional materials MXenes: Efficient catalysts for magnesium hydride[J]. Renewable Sustainable Energy Rev, 2025, 217: 115759.
- [99] DUAN X Q, LI G X, ZHANG W H, et al. Ti_3AlCN MAX for tailoring MgH_2 hydrogen storage material: From performance to mechanism[J]. Rare Met, 2023, 42(6): 1923–1934.
- [100] XIAO P, LIU J, GUO D, et al. High catalytic activity derived from TiNbAlC MAX towards improving the hydrogen storage properties of MgH_2 [J]. J Alloys Compd, 2023, 955: 170297.
- [101] ZHU W, PANDA S, LU C, et al. Using a self-assembled two-dimensional MXene-based catalyst ($2\text{D-Ni@Ti}_3\text{C}_2$) to enhance hydrogen storage properties of MgH_2 [J]. ACS Appl Mater Interfaces, 2020, 12(45): 50333–50343.
- [102] KIM M G, KANG S, WOOD B C, et al. Interfacial charge transfer driven by surface termination-controlled Ti_2C MXene for enhanced hydrogen storage in magnesium[J]. J Mater Chem A, 2024, 12(40): 27212–27219.
- [103] LAN Z Q, YANG J K, WEN X B, et al. An experimental and theoretical investigation of the enhanced effect of Ni atom-functionalized MXene composite on the mechanism for hydrogen storage performance in MgH_2 [J]. J Magnesium Alloys, 2024.
- [104] WANG Y, FENG D, MENG W, et al. Improvement of dehydrogenation kinetics of MgH_2 with VMnFeCoNi high-entropy alloy[J]. Fuel, 2025, 391: 134559.
- [105] DENG J, YUAN H P, SHANG X G, et al. Synergistic enhancement of hydrogen storage performance in Mg-based composites with high-entropy alloys[J]. Int J Hydrogen Energy, 2025, 137: 83–94.
- [106] LIU Y F, YUE M Y, GUO Y S, et al. Catalytic effect of carbon-supported NiCoFeCuMg high-entropy alloy nanocatalysts on hydrogen storage properties of MgH_2 [J]. J Magnesium Alloys, 2025, 13(3): 1232–1242.
- [107] WEI M X, LIU Y J, XING X F, et al. $(\text{TiVZrNb})_{83}\text{Cr}_{17}$ high-entropy alloy as catalyst for hydrogen storage in MgH_2 [J]. Chem Eng J, 2023, 476: 146639.
- [108] WANG L, ZHANG L T, LU X, et al. Surprising cocktail effect in high entropy alloys on catalyzing magnesium hydride for solid-state hydrogen storage[J]. Chem Eng J, 2023, 465: 142766.

镁基储氢材料改性方法研究进展

程 爽^{1,2,3}, 李 菲^{1,2,3}, 王玉琪^{1,2,3,*}, 王相依^{1,2,3}, 管司楠^{1,2,3}, 王 毅^{1,2,3},
王 玥^{1,2,3}, 欧观成^{1,2,3}, 徐 明^{4,5}

(1. 西北大学化工学院, 陕西 西安 710127; 2. 西安市绿色氢能制储用一体化重点实验室, 陕西 西安 710127;
3. 陕西省碳中和技术重点实验室, 陕西 西安 710127; 4. 西安科韦尔新材料有限责任公司, 陕西 西安 710086;
5. 陕西也方新材料有限公司, 陕西 西安 712021)

摘 要: 氢能作为最具发展潜力的新能源之一, 有望在 21 世纪全面进入“氢经济”时代。与传统高压气态与低温液态储氢方式相比, 固态化学储氢具有安全、高效、经济等显著优势。镁基轻质储氢材料因其高重量储氢密度(7.6%)与良好的可逆性而被广泛关注, 但其缓慢的反应动力学性能与苛刻的操作条件(放氢温度高达 350 °C、吸氢压力超过 4 MPa)使材料的应用面临巨大挑战。各国学者针对这些难题已开展了深入研究, 在镁基储氢合金改性领域取得了诸多研究进展。本工作阐述了主要改性工艺如合金化、纳米化、催化材料掺杂等方法, 深入分析梳理了各改性方法的优劣之处, 并结合当前理论与实验研究成果对未来镁基储氢材料的发展趋势做出了前景展望。

关键词: 氢化镁; 固态储氢; 改性; 热力学; 动力学

中图分类号: TB34; TG146.2

文献标识码: A

作者简介:



程爽(2001), 硕士, 研究方向为镁基储氢材料的性能研究, 2082827491@qq.com。



王玉琪(1974), 博士, 教授, 研究方向材料与能源化工、分离技术与反应工程, wangyuqi@nwu.edu.cn。