Transition metal-based materials and their catalytic influence on MgH₂ hydrogen storage: A review

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Abstract. The dependence on fossil fuels for energy has culminated in its gradual depletion and this has generated the need to seek alternative source that will be environmentally friendly and sustainable. Hydrogen stands to be promising in this regard as energy carrier which has been proven to be efficient. Magnesium hydride (MgH₂) can be used in storing hydrogen because of its availability, light weight and low cost. In this review, monoatomic, alloy, intermetallic and composite forms of Ti, Ni, V, Mo, Fe, Cr, Co, Zr and Nb as additives on MgH₂ are discussed. Through ball milling, additive reacts with MgH₂ to form compounds including TiH₄, Mg2Ni, Mg2NiH₄, V2O, VH₄, MoSe, Mg2FeH₆, NbH and NbO which remain stable after certain de/hydrogenation cycles. Some monoatomic transition metals remain unreacted even after de/hydrogenation cycles. These formed compounds, including stable monoatomic transition metals, impart their catalytic effects by creating diffusion channels for hydrogen via weakening Mg - H bond strength. This reduces hydrogen de/sorption temperatures, activation energies and in turn, hastens hydrogen desorption kinetics of MgH₂. Hydrogen storage output of MgH₂/transition metal-based materials depend on additive type, ratio of MgH₂/additive, ball milling time, ball –to-combining materials ratio and de/hydrogenation cycle. There is a need for more investigations to be carried out on nanostructured binary and ternary transition metal-based materials as additives to enhance the hydrogen storage performance of MgH₂. In addition, the already established compounds (listed above) formed after ball milling or dehydrogenation can be processed and directly doped into MgH₂.

Keywords: Dehydrogenation; Fossil fuel; Hydride; Hydrogenation; Transition metal

Introduction

Rapid growth in human productive engagements (aimed at improving standards of living) over the years have brought about urbanization. This has led to drastic population growth and placed a huge stress on energy generation and its utilization globally. The world community at large has been plagued with consequences of global warming owing to its large dependence on fossil fuels since the emergence of industrial revolution. These non-renewable resources have largely played a dominant role in energy production, maintenance and transportation. It has been reported by the United States Environmental Protection Agency (US EPA) that carbon dioxide (CO₂) maintains the highest constituent (Figure 1a) among the greenhouse gases (US EPA, 2023). This gas is often released during burning of fossil fuels such as oil, coal, natural gas (Stephen, 2005), deforestation (Van der Werf et al. 2009) and other industrial/manufacturing activities (Figure 1b). It causes global warming and other health issues through hypercapnia (Yu et al. 2013; Shigemura et al. 2017; Taghizadeh-hesary et al. 2021). The basic source of energy for instance, as reported by Singh et al. (2021) entails the combustion of fossil fuels which yields the release of CO₂ before (pre-combustion) or after (post-combustion) to the atmosphere. Globally, economic growth has been seen as a catalyst for greenhouse gas existence and its emission is mostly prevalent in China (Yang et al. 2020). African countries largely depend on fossil fuels for energy storage and use. In a model developed by Olubusoye and Musa, (2020), it was predicted that gradual economic growth rise in African countries will engender more greenhouse gas emissions. In South Africa for instance, Oladunni et al. (2022) reported that economic and population growths are the two major elements that have triggered the emission of greenhouse gas, most especially in the transport sector.

Efforts therefore are being made to produce renewable and sustainable energy that is friendly to the ecosystem. Hydrogen energy stands out as a renewable secondary energy which is clean, sustainable and can be used as an energy carrier and fuel cells. It is not like gas, coal or oil that serves as a primary energy source; hydrogen needs to be produced from another energy source (preferably from renewable sources in this case) such as biomass, wind, solar, hydro and geothermal. As the most abundant element in the universe, hydrogen is affirmed to be the ideal energy source in the 21st century that can be synthesized via water electrolysis with no pollutant released (Hou et al. 2021).

2. Hydrogen storage

Hydrogen is often stored as compressed gas, cryogenic liquid or in solid state. Liquid hydrogen is used as fuel for low temperature rockets and mobile applications (Al Ghafr...
It has been reported that cryogenic liquid hydrogen can be stored at -253 °C and 1 bar (Krishna et al. 2012). At this temperature, it maintains a density approximately 71 gL⁻¹ (Edwards, et al. 2007). In the sphere of energy and space missions, the main tools to consider in liquid hydrogen storage are materials for transportation vessels and cryogenic storage. Alloys of titanium (Madina & Azkarate, 2009), steel (Krainz, et al. 2004) and aluminum-lined composites (Aceves et al. 2000; Aceves et al. 2010) have been used for the storage and transportation of cryogenic liquid hydrogen but drawbacks have been witnessed in their impact strength, ductility and toughness at low temperatures. Design and development of highly effective low temperature materials for cryogenic liquid hydrogen storage is being advocated for (Qiu et al. 2021). A methodical insulation needs to be devised in other to maintain hydrogen in its liquid phase because of its low boiling point in this cryogenic state. Storage in the compressed gaseous form is another common method to store hydrogen. Materials such as steel (Zhang et al. 2008) and aluminum-carbon fiber composites (Takeichi et al. 2003) have been used in designing vessels that can store and transport hydrogen compressed at high pressure. Unlike the liquid storage, compressed gas can be stored at room temperature (Zheng et al. 2012). The density of hydrogen stored in the compressed gaseous state is lower compared to that of cryogenic liquid; a lower energy per unit volume has also been affirmed to be witnessed in pressurized gas (Zhang et al. 2016). Although both storage methods allow easy accessibility of hydrogen, there are draw backs that have bedeviled its storage and transportation. Cryogenic liquid hydrogen for instance, can only be stored for a short period to avoid the risk of steady boiling (Prabhukhot et al. 2016; Edalati et al. 2018). The low specific gravity of hydrogen creates an issue for its storage in compressed form as it requires huge magnitude of energy to achieve this, though much energy is needed for the storage of hydrogen in the liquid form compared to when compressed in gaseous state (Krisha, et al. 2012). In the solid state form, hydrogen molecules combine with other materials; a little volume of material can store large}

Fig 1. (a) Percentage constituents of greenhouse gas (US EPA, 2023) (b) Major activities that result to CO₂ emission.
hydrogen content than the two methods earlier discussed. A solid state hydrogen storage material easily adsorbs/absorbs and desorbs hydrogen at temperatures close or equal to room temperature. Storing hydrogen in the solid-state addresses issues of safety; boil off loss, heavy vessel weights and liquefaction energy associated with pressurized and liquid hydrogen storage. The volumetric and gravimetric densities of hydrogen storage methods are presented in Figure 2.

Hydrogen can physically or chemically combine with a solid material and when needed, it is made to desorb or dissociate from the material on involvement of thermal energy or any other means such as hydrolysis as discussed by Hou et al. (2021). In the physical process (physiabsorption), molecules of hydrogen adsorb on the material surface while a chemical bond is formed when hydrogen molecules chemically react with the material (also called chemisorption as material absorbs hydrogen molecules in this case). When hydrogen adsorbs on a material, there often exists weak van der Waals interactions between its molecules and the surface of the storage material. This implies that an appropriate material surface area will be required to achieve a remarkable hydrogen storage capacity. It is being reported that low activation energy is required to execute adsorption and desorption of hydrogen molecules in this case and this is responsible for fast ad/desorption kinetics (Prabukhrot et al. 2016). Materials with porous structures including activated carbon, graphene, carbon nanotubes (CNTs), porous aromatic frame works (PAFs), metal organic frame works (MOFs) and zeolites have been used (see Table 1).

A chemical bond is formed when a material absorbs hydrogen molecules into its structure. Many metals fall into this category as they reversibly react with hydrogen to form hydrides which serve as a hydrogen storage material. The ease of hydride formation and dissociation is different among metal hydrides based on the strength of bond formed between the metal and hydrogen. For a metal hydride to be classified as suitable for hydrogen storage for energy use, it needs to possess High volumetric and gravimetric densities. Fast hydrogen release (during dissociation) at a reduced temperature and adequate pressure is also a key feature required of a metal hydride as this saves time and energy. Aluminum hydride (AlH₃) for example, is affirmed to decompose into its constituent elements rapidly at room temperature and 700 bar with enthalpy of formation ranging between -6 to 7.6 kJ/mol (Zidan, 2010). This implies that it has fast dehydrogenation kinetics which qualifies it as a good storage material. Jieng et al. (2021) highlighted the high pressure (700 bar) as an issue when considering hydrogen storage on a large scale. Another class of hydride called complex hydride contains a counter ion with a coordination complex where hydrogen is covalently bonded. Electropositive Li⁺ for instance, reacts with BH₃ to form Li(BH₄). Prabukhrot et al. (2016) gave the complex hydride representation as AₓMeₓHₙ where elements in the first and second groups in the periodic table fit into “A” while “Me” is often occupied by aluminum or boron. Some other complex

![Figure 2](https://example.com/figure2.png)

**Figure 2.** Hydrogen storage methods with their volumetric and gravimetric densities (Edwards et al. 2007)

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### Table 1

Hydrogen adsorption capacities of some activated carbon, metal organic frame works, porous aromatic frame works and zeolites

<table>
<thead>
<tr>
<th>Material</th>
<th>H₂ storage capacity (%)</th>
<th>ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated carbon</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.88% at 2 bar and 77 K</td>
<td>(Wang et al. 2009)</td>
<td></td>
</tr>
<tr>
<td>4.85% at 10 bar and 77 K</td>
<td>(Chen et al. 2008)</td>
<td></td>
</tr>
<tr>
<td>2.96% at 1 bar and 77 K</td>
<td>(Sethia &amp; Sayar, 2016)</td>
<td></td>
</tr>
<tr>
<td>2.85% at 1 bar and 77 K</td>
<td>(Wrobel-Iwancie et al. 2015)</td>
<td></td>
</tr>
<tr>
<td>2.50% at 1 bar and 77 K</td>
<td>(Liu et al. 2014)</td>
<td></td>
</tr>
<tr>
<td>0.2% at 30 bar and room temp.</td>
<td>(Doğan et al. 2020)</td>
<td></td>
</tr>
<tr>
<td>Carbon nanotubes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>19% at 100 bar and 77 K</td>
<td>(Assfour et al. 2011)</td>
<td></td>
</tr>
<tr>
<td>14.15% at 70 bar and 77 K</td>
<td>(Farha et al. 2010)</td>
<td></td>
</tr>
<tr>
<td>5.5% at 100 bar and 300 K</td>
<td>(Assfour et al. 2011)</td>
<td></td>
</tr>
<tr>
<td>Graphene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.7% at room temp. And 25 bar</td>
<td>(Yuan et al. 2011)</td>
<td></td>
</tr>
<tr>
<td>1.47% at 1 bar and 77 K</td>
<td>(Huang et al. 2017)</td>
<td></td>
</tr>
<tr>
<td>Zeolite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.07% at 0.016 bar and 77</td>
<td>(Dong et al. 2007)</td>
<td></td>
</tr>
<tr>
<td>8.33% at 20 bar and 77 K</td>
<td>(Dong et al. 2007)</td>
<td></td>
</tr>
<tr>
<td>2.6% at 1 bar and 77 K</td>
<td>(Yang et al. 2007)</td>
<td></td>
</tr>
<tr>
<td>0.07% at 0.1 bar and 303 K</td>
<td>(Nishihara et al. 2009)</td>
<td></td>
</tr>
<tr>
<td>2.2% at 0.3 bar and 303 K</td>
<td>(Nishihara et al. 2009)</td>
<td></td>
</tr>
<tr>
<td>2.19% at 15 bar and 77 K</td>
<td>(Langmi et al. 2005)</td>
<td></td>
</tr>
<tr>
<td>Porous aromatic frame works</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6% at 50 bar and 77 K</td>
<td>(Lan et al. 2010)</td>
<td></td>
</tr>
<tr>
<td>3% at 50 bar and 150 K</td>
<td>(Lan et al. 2010)</td>
<td></td>
</tr>
<tr>
<td>2.09% at 1 bar and 77 K</td>
<td>(Ben et al. 2011)</td>
<td></td>
</tr>
<tr>
<td>2.7% at 1.2 bar and 77 K</td>
<td>(Konstas et al. 2012)</td>
<td></td>
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<tr>
<td>Metal organic frame works</td>
<td></td>
<td></td>
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<tr>
<td>17.8% at 80 bar and 77 K</td>
<td>(Furukawa et al. 2010)</td>
<td></td>
</tr>
<tr>
<td>4.5% at 20 bar and 77 K</td>
<td>(Nathaniel et al. 2003)</td>
<td></td>
</tr>
<tr>
<td>1.0% at 0.8 bar and room temp.</td>
<td>(Nathaniel et al. 2003)</td>
<td></td>
</tr>
<tr>
<td>4.5% at 0.8 bar and 77bK</td>
<td>(Rosi, et al. 2003)</td>
<td></td>
</tr>
<tr>
<td>10% at 56 bar and 77 K</td>
<td>(Rosi, et al. 2003)</td>
<td></td>
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Magnesium hydride (MgH₂) has been used as a storage material for hydrogen owing to its availability, light weight, huge storage capacity (7.6 wt.%), low cost of processing, good reversibility and high volumetric capacity (109 g H₂/L) (Shahi et al. 2015; hongtan et al. 2018). Low sorption kinetics has been recorded to be an issue with this material; Reaction of Mg with hydrogen to form MgH₂ (absorption) is exothermic and occurs between 250-370 °C (Figure 3); heat therefore needs to be supplied to the system for hydrogen desorption to occur.

To improve the hydrogen storage properties of the hydride, composites comprising combination of MgH₂ with one or more of carbonaceous materials (Ródena et al. 2008), intermetallics (Lu et al. 2018) oxides and hydrides of metals (including complex hydrides) have been used as catalysts.

3. Alloys compounds and composites of transition metals as catalysts

Numerous transition metals in their single forms, compounds and alloys have been used as catalysts to improve the hydrogen storage properties of MgH₂. Researchers have also entailed doping MgH₂ with other non-metallic materials such as grapheme, activated carbon, carbon nanotubes and metal organic frameworks to form composites. In this section, researches on the use of transition metals in the single or monometallic forms, alloys (binary, tertiary and multicomponent) and composites with non-metallic materials as catalysts are reviewed.

3.1. Titanium (Ti)

Having established that dehydrogenation of MgH₂ will occur between 300 - 350 °C (Jin et al. 2007a; Croston et al. 2010; Li et al. 2013), it is expected that MgH₂-based composites should release hydrogen at a lower temperature and the activation energy required for this should reduce. Additives used impart their catalytic effects by remaining stable (unreacted) or form a new stable phase (owing to a chemical reaction) when exposed to de/hydrogenation temperatures. This boosts the hydrogen storage potency of MgH₂. Lu et al. (2009) employed an ultra-high pressure reactive milling on MgH₂ and TiH₂ powders for 4 h at room temperature. Nanostructured combination of MgH₂ and TiH₂ were maintained after milling as no additional phase was formed. Composites remained stable after 80 cycles of dehydrogenation and hydrogenation at 300 °C. Existence of TiH₂ phase uniformly distributed in MgH₂/TiH₂ nanocomposite was reported to cause reduction in hydrogenation and dehydrogenation enthalpies. This was an additional claim to justify that aside grain size reduction, existence of well distributed stable additives will improve hydrogen storage performance of MgH₂. Twenty hours continuous milling however, culminated in the transformation of Mg and Ti to MgH₂ and TiH₂ when Shao et al. (2011) doped 0.1 wt.% Ti into MgH₂. Dehydrogenation of MgH₂/TiH₂ as determined by TGA/DTG curves was faster than as-milled MgH₂; the former occurred at 342 °C which was 100 °C lower than the latter (as-milled MgH₂). Unlike findings of Shao et al. (2011), Dehouch et al. (2003) earlier reported that Mg, MgO, Ti, V and Fe₂O₃ phases were formed after MgH₂ was ball milled with Ti and V. Although the milling time and temperature were not stated, it could be deduced here that the milling process engendered the dissociation of Mg from H atoms which later got oxidized to MgO on reacting with oxygen in the air. Milling condition was also sufficient to yield the formation of Fe₂O₃, which was notified as an impurity that arose from the oxidation of the steel mill balls; Ti and V remained unreacted. On cycling (de/hydrogenation cycles) at 300 °C in the presence of hydrogen-containing moisture after milling, there was an increase in hydrogen storage capacity and absorption kinetics between 500 and 1000 cycles for the composite; after the 1000th cycle, an additional phase Mg(OH)₂ was formed. The moisture acting as a contaminant in the hydrogen was affirmed to have engendered structural relaxation in the composite which led to its improved absorption kinetics. On the other hand, the structural modification retarded the hydrogen desorption kinetics after cycling. The investigators attributed this low kinetics to modifications that occurred on the surface of the composites. Although information regarding the mechanism involved in this surface modification was not detailed, one may suppose that Mg (OH)₂ and Fe₂O₃ may have a role to play in this. To further elucidate on the Findings of Lu et al. (2009), Hao & Scholl, (2012) deduced the mechanism responsible for the reduction in MgH₂/TiH₂ composite’s enthalpy of reaction compared to single MgH₂ by adopting the first principles density functional calculations. This was used to distinguish the interfaces that could exist between MgH₂ or Mg and TiH₂. Calculations explained that strong equiaxial surfaces could exist between the low surface energy faces of MgH₂ (or Mg) and TiH₂. These interfaces induced strain on MgH₂ and Mg which was identified to be responsible for the low dehydrogenation enthalpy. Addition of 0.05, 0.1, 0.25 and 0.5 wt.% Ti, to MgH₂ and milling for 2 h have produced Mg, MgH₂ and Ti phases.
(Pukazh selvan et al. 2020). Magnesium hydride, Ti and TiH2+x (nonstoichiometric hydride) were identified when MgH2 /0.25 wt.% Ti composite was milled for 15 h. When composites were dehydrogenated at 315 °C and 5 bars H2 pressure after 1, 5 and 10 cycles, Ti/TiH2+x was further hydrogenated to TiH2. Titanium additive remained unreacted under 2 h (mild milling condition as defined by the researchers) milling; it was partially hydrogenated when the milling was severe (15 h) and got completed after de/hydrogenation cycles. For the strong milled composite, XPS (X-ray Photoelectron Spectroscopy) indicated that Ti existed in mixed valence states (TiIV, TiI+, TiII+, TiIV). It was believed that TiI+ (oxidation state of Ti in TiO2) present in both samples (mild and strong milling) may have occurred as a result of surface oxidation on exposure to air. It was thus concluded that catalytic influence of Ti/TiH2 would only be effective if MgH2 would be milled long enough. Formation of TiH2 during strong milling reduced the dehydrogenation activation energy of MgH2 to 89.4 kJ/mol from 153 kJ/mol displayed by as-received MgH2. This further justified the findings of Hao & Scholl, (2012), who suggested that when there is an equiaxial contact between Mg/MgH2 and TiH2, the latter would induce strain on Mg/MgH2 contact surface which would end up lowering its dehydrogenation enthalpy. It has also been reported by Patelli et al. (2017) and Bhatnagar et al. (2018) where TiH2 was confirmed to improve the sorption kinetics of MgH2 by lowering the activation energy. This was also attributed to the imposition of lattice strain on MgH2 by TiH2 Malahayati et al. (2021) observed that 1 h ball milling may not be sufficient enough to induce reaction between MgH2 and Ti powders as no change of phase was noticed after the process. Agglomerations of combining powders with increased diameter only existed during this time. After 12 h of milling, both MgH2 and Ti still existed but this time, in nanosized form, which was attributed to the effect of energy induced by the milling process. The Ti phase disappeared after milling for 18 h while broad peaks of MgH2 remained. It was not mentioned in the report what happened to Ti but it could be assumed that Ti was oxidized to TiH2 which may have also led to the broadening of MgH2 peaks that was initially narrow. The composite (MgH2/Ti) absorbed hydrogen at 300 °C and 10 bar while desorption happened at 350 °C and 50 mbar. Both processes took place within 7 min and from previous findings of researchers, it can be deduced that TiH2 may be responsible for the much fast kinetics compared to additive –free MgH2. These temperatures however were outlined by the authors to be high for application purpose. Berezovets et al. (2022) observed that TiH2 phase was formed using Ti nanopowder additive which led to the increase in hydrogen storage capacity of MgH2 (6.7 wt.% H2) (Figure 4). Milling Mg and TiO2 nanopowders after 5 h, TiO2 remained unreacted and this led to a low storage capacity of 5.7 wt.% H2; it may be assumed here that the milling time was insufficient for TiO2 to get reduced. As illustrated in Figure 4, both additives facilitated hydrogenation compared to pure Mg which implied that they aided the crystallization of MgH2. More improved hydrogenation was realized on milling Mg powder with a suboxide of Ti2Fe2O5 (x = 0.3, 0.5) in the presence of hydrogen pressure. The suboxide additives promoted hydrogen dissociation and the Ti4Fe2O5:H phase formed after milling was responsible for its highest hydrogen storage capacity (6.76 wt.% H2). Presence of Ti, Fe and O in the suboxide created diffusion pathways for hydrogen to or from Mg/MgH2 system during de/hydrogenation.

Titania (TiO2) has also been proven to be a good additive for MgH2. Titania. MgH2 and rock salt (Ti dissolved MgO) were reportedly formed when MgH2 was milled with 10 wt.% TiO2 for 5 h (Pukazh selvan et al. 2017a). A reduced phase, TiO was yielded when TiO2 was milled with 10 wt.% MgH2 for 30 h. A single phase rock salt was formed when MgH2 was milled with TiO2 in ratio 2:1. The Ti/Mg/O phase in the rock salt was confirmed to make the additive impact of TiO2 effective on hydrogen storage properties of MgH2. The single phase rock salt formed after milling 2MgH2 + TiO2 system for 30 h had the least dehydrogenation activation energy (110.9 kJ/mol). Further works of Pukazh selvan et al. (2017b) established that TiO2 transformed as an inbuilt rock salt catalyst during dehydrogenation and its content depended on the variation of Mg/Ti. The proportion of Mg/Ti according to the researchers was assumed to cause e passivation of active rock salt. Shao et al. (2022) prepared three-dimensionally ordered macroporous (3DOM) TiO2 via colloidal crystal template technique. After 10 h ball milling with MgH2, the composite absorbed 4.17 wt.% H2 at 100 °C within 1800 s and released 5.75 wt.% H2 at 300 °C within 1000 s. Improvement in the hydrogen storage properties of MgH2 arose from the combined structure and electronic interactions as TiO2 was reduced by MgH2 and multiple valence Ti (TiII, TiIV and TiV) were formed. These destabilized MgH2 and weakened Mg - H bonds. In addition, TiO2 nanoparticles were wrapped and uniformly distributed in carbon layer; this aided de/absorption of hydrogen in MgH2. Titanium and TiO2, each of 0.4 g and 0.2 g of nitrogen-doped graphene (XFNANO) was ball milled for 1 h to obtain TiO@N-C (Hong et al. 2023). The additive (0.1 g TiO@N-C) was mixed with 0.9 g of MgH2 and milled for 5 h. The composite completely dehydrogenated hydrogen at 350 °C within 4 min and its dehydrogenated form absorbed 5.1 wt.% H2 in 4 min at 175 °C. There was a reversible reaction of Ti and TiH2 on Mg/H2 surface during de/hydrogenation which made hydrogen molecules dissociate and diffuse easily; the stability of MgH2 was also reduced by weakening of Mg - H bonds triggered by TiO2. Nitrogen-doped graphene was covered on MgH2 surface which impeded the agglomeration of MgH2 particles. In addition, carbon structural defects that existed in nitrogen-doped graphene acted as nucleation sites which promoted diffusion of hydrogen. These were responsible for the hydrogen storage performance of MgH2. Multi-phase interface comprising Ti, TiO2, TiO and MgH2 has been established to provide more diffusion paths for hydrogen and more nucleation sites for Mg/MgH2. This finding substantiates the investigations of Liu et al. (2021) who doped graphene-supported TiO2 nanoparticles.

Fig 4. Hydrogen absorption capacities of Mg/Ti-based composites as a function of ball milling time (Berezovets et al. 2022)
(TiO$_2$@rGO) into MgH$_2$. Asides the fact that Mg$_2$ was surrounded by the catalyst; partial reduction of Ti$^{4+}$ to Ti$^{3+}$ existed. This propelled charge transfer that advanced the de/hydrogenation kinetics of MgH$_2$. In addition, Ren et al. (2022) recorded that multi-phase interfaces that comprised multi-valence Ti (Ti$^{4+}$, Ti$^{3+}$) and MgH$_2$ existed when flower-like MgH$_2$/TiO$_2$ heterostructure synthesized from 2D TiO$_2$ nanosheets with oxygen vacancies. The multi-phases aided electron and hydrogen diffusion and created more nucleation sites for MgH$_2$/Mg. Magnesium rod, Ni sheet and Ti pellets were melted in a vacuum induction levitation furnace to process MgNi-Ti and MgTiNi ingots (Li et al. 2018). The alloy ingots were crushed and mechanically ground to 200-mesh powder. When milled, Ni-Ti and NiTi phases were observed in both alloys. New phases- MgNiH$_4$ and TiH$_2$ were formed after 100 cycles of hydrogenation and dehydrogenation. These I, phases were responsible for 5.22 and 3.23 wt.% H$_2$ recorded for Mg-Ni-Ti and MgTiNi alloys, respectively. Amorphous TiMgVN$_5$ produced via Induction melting of Ti, Ni and V powders, has been used as a catalyst on MgH$_2$ (Hu et al. 2022). After 100 h of milling, of cast TiMgVN$_5$, 10 wt.% was further milled with MgH$_2$ for 10 h under 5 MPa H$_2$ pressure. The separate hydride (Ti) and (Ti,Mg,V,Ni)H$_2$ were formed after milling. When MgH$_2$ / TiMgVN$_5$ composite underwent 2 cycles of hydrogenation and dehydrogenation, a homogenous distribution of (Ti),V$_2$H$_3$ and MgNiH$_4$ nanoparticles formed on the surface of MgH$_2$; these were responsible for its fast hydrogen desorption Magnetic levitation melting has been used in preparing TiV based BCC alloy (Ti$_{56}$Cr$_{15}$Mn$_{15}$V$_{10}$) which was mechanically pulverized into particles as an additive for MgH$_2$ (Yu et al. 2010). Some alloy powders were water quenched while others were hydrogenated at 20 bars H$_2$ for 2 h at room temperature. Alpha- MgH$_2$, y-MgH$_2$ and HBCC were formed after milling. The BCC contributed to the improvement of atomic diffusivity of hydrogen as well as its ease of dissociation and recombination. Hydrogenated BCC appeared to impart the most effective followed by quenched BCC. Solid BCC (ingot) offered the least effect. EI-Eskandarany et al. (2019) milled MgH$_2$ with 10 wt.% TiMn$_2$ master alloy powders for 50 h under 70 bar H$_2$ pressure. The composite formed was further consolidated (compaction) in circular buttons of 1.2 and 2 cm diameter and thickness respectively. The consolidation enabled the TiMn$_2$ nanopowders get embedded in the micro/nanopores of MgH$_2$ grains which acted as a good hydrogen diffusion path during hydrogenation and dehydrogenation. The buttons could absorb and desorb 5.8 wt.% H$_2$ at 225 °C within short periods of 150 s and 500 s, respectively.

Titanium carbide (TiC) nanoparticles was formed on the grain boundaries of MgH$_2$ when both underwent cryo-milling (using N$_2$ to enant freezing) for 8 h followed by high energy ball milling (at room temperature) for 16 h. (Tan & Shang, 2012). The formation of the additive on the grain boundary shortened the diffusion length and weakened the Mg-H bond which lowered the desorption temperature and activation energy to 190 °C and 235 to 104kJ/mol respectively. Sandwich-like Ti$_5$C$_3$/TiO$_2$(A-C) was processed via facile gas-solid approach and doped into MgH$_2$ by 10 h ball milling (Gao et al. 2020). X-Ray diffraction results showed that MgH$_2$, with few contents of Mg and MgO were formed after milling. From their investigation, incomplete hydrogenation or dehydrogenation of MgH$_2$, was suggested to have culminated in the formation of Mg while the reaction between MgH$_2$ and TiO$_2$ resulted in the formation of MgO. The composite could absorb 5 wt.% H$_2$ at 250 °C within 1700 s (42.32 kJ/mol) and within 800 s, 4 wt.% H$_2$ was desorbed at 125 °C (77.69 kJ/mol). Multiple valence Ti compounds of Ti$^{4+}$, Ti$^{3+}$, Ti$^{2+}$ and Ti$^0$ as observed by XPS and synergetic effects between the layered structure were reported to be the mechanism of the catalytic influence of Ti$_5$C$_3$/TiO$_2$(A-C). A modified wet chemical method used in fabricating sandwich-like Ni/TiC$_3$ catalysts, was introduced to MgH$_2$ to improve its hydrogen storage performance (Gao et al. 2021). A strong electronic interaction existed between nanoparticles of Ni and Ti3C$_2$. This was affirmed to be responsible for the improved hydrogen absorption feature of MgH$_2$. Catalytic effect of NiTi$_2$C$_3$ was influenced by the electron transfer in the multiple valences of Ti (Ti$^{4+}$, Ti$^{3+}$, Ti$^{2+}$ and Ti$^0$). Works of Gao et al. (2021) justify earlier works (Cui et al. 2013) where it was claimed that Ti3C$_2$ derived its catalytic influence from electron transfer in multi-valence Ti which triggered the transformation of Mg$^{2+}$ and Mg$^+$ and H$^+$ and H.

3.2. Nickel (Ni)

A common Ni- based intermetallic compound – Mg$_2$Ni has been synthesized and reported over the years to be a good hydrogen storage material (Zaluski et al. 1995a; Zaluski et al. 1999b). Recently, Baroutaj et al. (2022) summarized that another Mg-Ni based compound - Mg$_2$NiH$_4$ can be realized (together with Mg) when Mg$_2$Ni directly interacts with MgH$_2$. It can boost Mg$_2$H$_4$ hydrogen storage feature when both materials interact (Lu et al. 2022). These two Mg-Ni based compounds have played important roles on MgH$_2$ hydrogen storage features and they can also be formed on reacting pure Ni or Ni based compounds with MgH$_2$. Hanada et al. (2005) concluded that observing de/hydrogenation cycle of 2% mol Ni nanoparticle - doped MgH$_2$ at 200 °C, hydrogen desorption properties of the composite degraded as a result of Mg$_2$Ni which formed at that temperature. Here, the Ni content and/or the composite processing method (15 h ball milling under 1 MPa H$_2$ pressure) may have been responsible for the limiting impact of Mg$_2$Ni. Using Ni in uncombined form could have also been responsible. It was reported by Liang et al. (2000) that milling Mg and 30 wt.% LaNi$_5$ intermetallic mechanically for as long as 40 h would not yield chemical reaction unless when hydrogenated. At this point, the intermetallic decomposed and a composite comprising MgH$_2$, LaH$_3$ and MgNiH$_4$ phases was formed. When MgH$_2$ and 30 wt.% LaNi$_5$ were ball milled prior to hydrogenation, part of MgH$_2$ and LaNi$_5$ decomposed to form Mg$_2$NiH$_4$ while some part was reduced by La to form stable LaH$_3$ and Mg. After hydrogenation, Mg$_2$H$_4$/ LaH$_3$/ MgNiH$_4$ system similar to that observed on milling Mg powder with LaNi$_5$ was formed. Milling LaNi$_5$ with MgH$_2$ was preferable to Mg because the former facilitated ease of powder size reduction, which enhanced absorption properties of MgH$_2$ and not desorption. Magnesium absorption kinetics was improved by the presence of LaH$_3$ beyond 373 K. Mg$_2$Ni imparted a better catalytic effect. Hydrogen storage kinetics has been improved by doping MgH$_2$ with 5 wt.% SiC (Ranjbar et al. 2009a) but addition of 10 wt.% Ni further enhanced this property because it improved composite’s surface area and reduced the concentrations of defects (Ranjbar et al. 2009b). In addition, hydrogen desorption reaction was influenced by bulk nucleation and 3D growth of the existing Mg nuclei; finely dispersed Ni nanoparticles increased the amount of nucleation sites.

Mao et al. (2010) ball milled MgH$_2$ with 10 wt.% NiCl$_2$ for 2 h. Magnesium hydride phase was observed after milling without a trace of Ni; this could be attributed to the little milling time employed or content of additive used. After hydrogenation and dehydrogenation cycles, more phases were formed which followed the suggested reaction:

$$3\text{MgH}_2 + \text{NiCl}_2 \rightarrow \text{MgCl}_2 + \text{MgNi} + 3\text{H}_2 \quad (1)$$
Magnesium chloride and Mg-Ni acted as catalyst on MgH₂. It was also noted that the additive removed nucleation barrier which enabled hydrogen desorption occur at a low driving force. Within 60 s, 5, 17 wt.% H₂ was absorbed at 300 °C for MgH₂/NiCl₃ composite while it took 400 s to absorb 3.51 wt.% H₂ at the same temperature for undopped ball milled MgH₂. Furthermore, dehydrogenation activation energies of 158.5 and 102.6 kJ/mol were calculated for MgH₂ and MgH₂/NiCl₃ composite respectively. Nano Ni powders produced via Ni carboxyl process was ball milled with high enthalpy MgH₂ (Wronski et al. 2011) Acting as a catalyst, the powders reduced desorption temperature of the metal halide as low as 100 °C at low hydrogen partial pressure The catalyst was affirmed to provide adequate surface area with carbon and oxygen (impurities formed during the carboxyl process) coating which was also responsible for activation energy reduction for hydrogen desorption. The activation energy for desorption reduced from 167 kJ/mol (unactivated MgH₂) to 78 kJ/mol for nano Ni-catalyzed MgH₂ between 325 – 350 °C. Cui et al. (2014) also reported that formation of MgNi improved the hydrogenation and dehydrogenation kinetics of Mg-Ni system. In their work, MgH₂ ball milled with Ni nanoparticles which were uniformly dispersed and anchored on reduced graphene oxide (Ni@rGO) for 2, 5, 10 and 20 h under 1MPa H₂ pressure. A high surface area of 161.4 m²/g possessed by Ni@C nanorods mixed with MgH₂ was investigated to absorb 6.4 wt.% H₂ within 10 min and 300 °C (An et al. 2014). Here, it was suggested that Ni@C composites had the capacity to create interface with MgH₂ to form catalytic site for hydrogen diffusion. When the combination of SrTiO₃ and Ni were used as additive for MgH₂ (Yanya & Ismail, 2018), MgNi and MgNiH₄ were formed after dehydrogenation and hydrogenation respectively. The two phases were concluded to be active in improving the hydrogen storage properties of MgH₂. The phase SrTiO₃ remained unreacted throughout the process but its catalytic influence was imparted in the modification of the composite's microstructure. This created an additional advantage ahead of using only SrTiO₃. Nano Ni particles were dispersed in nanoporous carbon material (CMk-3) prepared by impregnation reduction and 10 wt.% of the combination was added to MgH₂ (Chen et al. 2018). Under 3 MPa H₂ pressure and 150 °C, the composite MgH₂/Ni/CMK-3 absorbed 3.1 wt.% H₂ after 360 s while 5.7 wt.% H₂ was absorbed with 2400 s. At 328 K, and 3 MPa, H₂ pressure, 3.9 wt.% H₂ was absorbed. Nickel nanoparticles played an active role in lowering the decomposition enthalpy of MgH₂ by forming MgNi and Mg₆Ni. Combined effect of activation and destabilization from Ni was responsible for the enhanced performance of MgH₂. Ma et al. (2018) employed carbonization process to synthesize carbon supported nano-Ni (Ni@C) additive for MgH₂. Inclusion of 5 wt.% of the additive promoted MgH₂ the hydrogen storage display. After 10 cycles, average grain size of MgH₂ grew to 35.5 nm and this was reported to be responsible for its reduced storage capacity at that instant. Furthermore, MgNiH₄ also appeared after 10 cycles and was suggested to have a negative impact on the composite’s hydrogen performance. Increase in milling time up to 10 h has led to gradual reduction in crystallite and grain sizes of MgH₂/ nano Ni anchored on reduced graphene oxide (Ni@rGO) composite (Yao et al. 2020). On the other hand, prolong milling up to 20 h led to the welding and agglomeration of particles which made them brittle. Catalytic effect of the additive was influenced by the formation of MgNi/MgNiH₄ phase which was formed after rehydrogenation. Milling for 5 h offered the best result as the composite could absorb 5 wt.% H₂ in 20 min at 100 °C and within 15 min, 6.1 wt.% H₂ was released at 300 °C. It was easier for MgNiH₄ to release H₂ with ease. The rGO created hydrogen diffusion channels and active catalytic site, which was responsible for the lowering of dehydrogenation temperature and kinetics. Solid solution of Ni-Cu powders has created a platform for enhanced MgH₂ nucleation and de/hydrogenation by reducing the bond strength of Mg-H (Zhang et al. 2020). At 300 °C, the composite could eject 5.14 wt.% H₂ after 15 min while within 30 min, 4.37 wt.% H₂ was absorbed at 250 °C Magnesium hydride hydrogen storage display was elevated by the formation of Mg₃Ni(Cu), which allowed hydrogen molecules to dissociate and recombine to MgH₂. Ball milling of Mg powder and MgNi alloy followed by hydrogen combustion synthesis technique was devised by Fu et al. (2020) to synthesize MgH₂/MgNi3 composite. Majority of the Mg were transformed to MgH₂ after hydrogenation while some reacted with MgNi to form Mg₂NiH₆ that later transformed to MgNi during dehydrogenation. These two phases enhanced hydrogen adsorption and desorption of MgH₂ as 2.5 wt.% H₂ was absorbed at 200 °C while at 300 °C, 2.6 wt.% H₂ was released. Magnesium hydride was investigated to be capable of absorbing 5.3 wt.% H₂ at 300 °C within 5 min when doped with 2mol% nano Ni powders of approximately 90 nm via high pressure ball milling under 10 MPa H₂ pressure (Bahwanato et al. 2021). The nano Ni powders provided adequate reaction surface for MgH₂ during milling. Li et al. (2021) doped Ni/ Ni/tubular g-C₃N₄ (TCN) into Mg by milling for 5 h and under 4 MPa H₂ pressure, the milled sample was kept for 40 h to form MgH₂/Ni/TCN composite. During milling, the additive coated the Mg surface and Ni particles reacted with Mg to form a phase that comprised Mg, Ni and H. The C atom, being a good conductor of heat and electron, was considered good for the behavior of the composite when hydrogenated and dehydrogenated at 400 °C; it also prevented the growth of particles. Reversible conversion from Mg to MgH₂ and reaction between MgNiH₄ and Mg₂NiH₆ was realized during de/hydrogenation of the composite. The C coating on Mg and the formation of Mg-Ni-H phases (MgNiH₄ and MgNiH₆) improved the hydrogen storage properties of Mg₃Ni(Cu). Tricarboxybenzene was used by Shao et al. (2021) to process Ni-MOF (N-MBTSC300), which was calcined at 300 °C as catalyst for MgH₂. The additive displayed uniformly dispersed and bonded metal ions, which improved the hydrogenation and dehydrogenation kinetics of MgH₂. With the addition of 10 wt.% Ni-MOF, composite could release 5.14 wt.% H₂ at 300 °C. This was better than additive free MgH₂ that released 0.09 wt.% H₂ after 15 min at the same temperature. Good cyclic behavior of composite was attributed to the robust structure of MOF. Rods of Ni – based oxide, NiMoO₄, was incorporated into MgH₂ by 6 h ball milling (Huang et al. 2021). The composite still contained NiMoO₄ and MgH₂ after milling while Mg, Mo, MoO and MgNi phases were formed after complete desorption at 300 °C, which indicated that NiMoO₄ reacted with MgH₂ in the process according to the reaction:

\[
6\text{MgH}_2 + \text{NiMoO}_4 \rightarrow \text{Mg}_4\text{Ni} + 4\text{MoO}_3 + \text{Mo} + 6\text{H}_2
\] (2)

Magnesium hydride and Mg-NiH₄ were formed after hydrogenation at 150 °C and 3.2 MPa H₂ pressure. Within 10 min, MgH₂/NiMoO₄ was able to desorb 6 wt.% H₂ at 300 °C and adsorb 5.5 wt.% H₂ at 150 °C after 10 min. The exceptional de/hydrogenation kinetics was ascribed to the formation of MgNi and Mo after reaction of MgH₂ with NiMoO₄, while Mo encouraged the removal of hydrogen atoms from MgH₂ under less severe ball milling. A reversible phase evolution among Mg₄Ni,Mg₂NiH₆ and C6H₆ was reported to exist after hydrogenation and dehydrogenation of ball milled Ni@CeO₂/MgH₂ composites (Yu et al. 2023) These phases
enhanced the hydrogen storage properties of MgH₂ as they were finely dispersed in its matrix.

3.3. Vanadium (V)

Mechanically ball milling MgH₂ with V for 20 h was observed to yield βMgH₂, γMgH₂, and VH₀.₃ after hydrogenation (Liang et al. 1999). Hydrogen was completely desorbed after 2000 s at 800 K with MgH₂/5 wt.% V. The nanocomposite absorbed 2 wt.% H₂ within 1000 s at 10 MPa H₂ pressure and 302 K; at 373 K, 4 wt.% H₂ was absorbed after 100 s and at 473 K, 6.5 wt.% H₂ was absorbed in 250 s. The microstructure of composite with V inclusion improved the hydrogenation kinetics. Vanadium (5 wt.%) was added to MgH₂ powders and mechanically ball-milled for 100 h to nano scale (Rivoirard et al. 2003). At 253 K MgH₂ absorbed hydrogen slowly while that activated with V was faster. Fine grains of MgH₂ formed were also responsible for its enhanced hydrogen absorption kinetics. At 603 K the absorption kinetics was reduced because it was noticed that at that temperature, δVH₂ which was formed after ball milling became unstable. They concluded that nature of combining materials would not only contribute to hydrogen absorption properties of MgH₂; particle size reduction, distribution and agglomeration would also play key roles. After mechanically milling Mg and V powders for 20 h, MgV₀.₃₃ was formed and this improved the hydrogen storage property of Mg (Schimmel, et al. 2005). At the onset of hydrogenation, MgH₂→c phase was formed and there was much hydrogen vacancies which enabled the phase have higher diffusion coefficient. This was responsible for the improved hydrogenation kinetics of the nanocomposite. Conceição et al. (2014) compared the effects of pure V, vanadium chloride (VCl₃) and vanadium carbide (VC) catalysts on the hydrogen storage properties of MgH₂. Adding 5 wt.% separately of each additive to MgH₂, VCl₃ showed the best catalytic effect in terms of hydrogen storage capacity and dehydrogenation kinetics. It was reported that considering the same content for all additives (wt.%), the amount of V in VCl₃ was the least compared to that in VC and pure V. Vanadium carbide could enhance desorption of MgH₂ but its high stability contributed to its retarded desorption kinetics. According to Kadri et al. 2(015), catalyzed V synthesized from vanadium hydride, VH₃ could act as a hydrogen splitting agent which could hasten dissociation of hydrogen from MgH₂. Catalytic influence of bismuth vanadate (BiVO₃) on MgH₂ hydrogen storage properties via ball milling has been investigated (Xu et al. 2017). At 150 °C, and 3 MPa H₂ pressure, the composite composed of MgH₂/16.7 wt.% BiVO₃ had the capacity to absorb 1.99 wt.% H₂ while additive-free MgH₂ had 0.94 wt.% H₂ absorbed under the same conditions of temperature and pressure (Figure 5a). At 400 °C, 1.1 wt.% H₂ was desorbed within 1200 s (Figure 5b). Catalytic influence of BiVO₃ was attributed to the formation of V-containing compounds (Mg₆V₂O₇ and V₂O₅) that were formed during dehydrogenation at 400 °C.

Vanadium oxide supported on cubic carbon nanoboxes (nano-V₂O₅/C) has been ball milled with MgH₂ (Wang et al. 2018). Within 10 min, MgH₂/9 wt.% V₂O₅/C composite could release 6.0 wt.% H₂ while additive – free MgH₂ desorbed 0.4 wt.% H₂ within this time. The metallic V formed from V₂O₅ during milling and at the initial stage of heating was responsible for the fast dehydrogenation kinetics of MgH₂; it elongated Mg-H bond length and weakened its strength. Vanadium chloride was reduced to metallic V when milled with MgH₂ (Kumar et al. 2018). The metallic V imparted a good catalytic effect on MgH₂ hydrogenation and dehydrogenation kinetics. This was achieved by MgH₂ grain refinement and crystallite size reduction that eventually created the diffusion path for hydrogen. In the investigations of Liu et al. (2021), 7 wt.% of V nanoparticles was added to MgH₂. Within 10 min, 6.5 wt.% H₂ was released at 300 °C (MgH₂ could not achieve this at this time). Fully dehydrogenated composite had the potency of absorbing hydrogen at room temperature and 5.6 wt.% H₂ at 150 °C. Vanadium remained stable all through hydrogenation and dehydrogenation processes. Well dispersed Ni and vanadium trioxide nanoparticles in nanoporous carbon (Ni/V₂O₅/C) has been used as catalyst on MgH₂ (Lan et al. 2022). There was a partial transformation of V₂O₅ to VO during milling while MgH₂, V₂O₅, VO, and V remained unreacted during hydrogenation and dehydrogenation. In contrast, Ni reacted with Mg to form MgNi and this further reacted with hydrogen to form MgNiH₄. The MgNi/MgNiH₄ particles acted as hydrogen pump as it was observed to be coated on Mg/MgH₂, this aided diffusion and dissociation of hydrogen. The presence of carbon (C) enhanced the catalytic effect, promoted MgH₂/Mg lattice expansion and held up their crumbling during hydrogen de/absorption, which ended improving MgH₂ cyclic stability. It was concluded that a multicomponent catalyst comprising V, VO, V₂O₅, C, and MgNi/MgNiH₄ will improve the hydrogen
performance of MgH₂. Two dimensional nanocarbid (V,C) MXene has been added to MgH₂ to improve its hydrogen desorption kinetics (Lu et al. 2022). Improved cyclic stability was not only caused by the additive; low hydrogen desorption temperature (from 318 °C in MgH₂ to 198 °C in MgH₂/V/C composite) was also enhanced. The V/C played a role of reducing Mg H bond length to hasten desorption kinetics of MgH₂. Tian et al. (2023) ball milled hydrothermally synthesized V- based catalysts (V₂O₅, FeVO₃, and NiV₂O₅) with MgH₂ to improve its hydrogen storage properties. Dehydrogenation behaviour of MgH₂/FeVO₃ displayed the best performance followed by MgH₂/V₂O₅. During this process, the Fe-V complex oxide reduced elemental Fe and V which eventually lowered Mg-H bond strength. This hastened the absorption and desorption of MgH₂. It was concluded that Fe would improve the catalytic effect of V₂O₅ while Ni will not. Structured V- based MOFs (MOFs-V) synthesized by facile hydrothermal reaction and calcination has been doped with MgH₂ via ball milling to modify its hydrogen storage properties (Lu et al. 2023). It was observed by Scanning Electron Microscope (SEM) that the MOFs composed of bullet-like V₂O₅. The desorption temperature of composite containing 5 wt.% MOFs was 199.8 °C which was 142 °C lower than catalyst-free MgH₂ increasing the content of MOFs to 7 and 9 wt.% further lowered the desorption temperatures to 190 and 186 °C respectively. During ball milling, MOFs-V was reduced to metallic V which created a catalytic effect. Catalytic effect of vanadium disulphide (VS₃) on MgH₂ was investigated by Verma et al. (2023). The composite began to release hydrogen at 289 °C which was 87°C lower than MgH₂. Hydrogen desorption activation energy barrier required to reduce MgH₂ to Mg in the presence of VS₃ was lower (98.09 kJ/mol) than in catalyst-free MgH₂. Du et al. 1(997) had earlier reported that V in VS₃ could be reversibly converted from V⁴⁺ to V⁶⁺ during de/hydrogenation. The existence of V in its variable oxidation form would weaken Mg-H bond and thus trigger fast de/hydrogenation kinetics.

3.4. Molybdenum (Mo)

Jia et al. (2013) reported that molybdenum disulphide (MoS₂) had more effect in improving the absorption and desorption kinetics of MgH₂ than molybdenum oxide (MoO₃). During ball milling, the following reactions were investigated to have taken place as indicated from XRD patterns:

\[ 2\text{MgH}_2(s) + \text{MoS}_2(s) \rightarrow 2\text{MgS}(s) + \text{Mo(s)} + 2\text{H}_2(g) \] (3)

\[ 2\text{MgH}_2(s) + \text{MoO}_2(s) \rightarrow 2\text{MgO}(s) + \text{Mo(s)} + 2\text{H}_2(g) \] (4)

Considering similar ball milling conditions, reaction (3) was observed to be faster than reaction (4). As-milled MgH₂ could absorb 90% of its hydrogen storage capacity within 72 min; MgH₂/MoO₃ could attain this within 31 min while it took 13 min for MgH₂/MoS₂ to achieve this. Formation of MgS/Mo and MgO/Mo in each reaction was suggested to have been responsible for the absorption/desorption kinetics of MgH₂. Addition of 10 wt.% MoS₂ to Mg particles according to Han et al. (2016) would be enough to prevent agglomeration and cold welding of particles as it acted as a dispersant and lubricant. The 2 milling process reduced crystallite size of MgH₂ to a little below 38.8 nm and this was sustained all through milling because MoS₂ confined its growth. The reduction in crystallite size was responsible for the reduced dehydrogenation temperature of MgH₂. During MgH₂ decomposition, crystal of Mg was reported to grow by three dimensions controlled by interface transformation. The researchers concluded that MoS₂ had a weak catalytic influence on the decomposition of MgH₂. Rather than use bulk MoS₂, Setjadi et al. (2016) synthesized MgH₂ nanoparticles using delaminated MoS₂ through a simple hydrolysis route which involved the decomposition of di-n-butylmagnesium. The delaminated additive led to the formation of Mg worm-like structures that collapsed and recrystallized during hydrogen cycling. Thermodynamic features of Mg/MgH₂ reaction was strongly influenced by the additive through destabilization of the Mg-H bond.

Han et al. (2017) observed that after ball milling Mg/C (combination of magnesium and crystalline carbon) with Mo for 3 h under 1 MPa H₂ pressure, MgH₂ was formed. Molybdenum and crystalline carbon offered a synergistic effect on improving the hydrogenation kinetics of MgH₂ in the reactive ball milling process. Enhanced dehydrogenation rate of MgH₂ was attributed to the conductive capacity of Mo The use of 2% mol. MoO₃ was researched to have a positive impact on hydrogen storage performance of MgH₂ (Dan et al. 2019). During hydrogenation and dehydrogenation, MoO₃ was an active site for hydrogen absorption and desorption; the oxide was observed to also create a fast diffusion pathway for hydrogen atoms. Formation of MoO₂ during hydrogenation (reduction of MnO₂ to Mn), which was affirmed to reduce the catalytic effect of MoO₃ on the long run. Synthesized nanosheets of NiMoO₃ were ball milled with MgH₂ (Chen et al. 2020). After activation, MoNi and MgNi nanoparticles were formed, which created reaction surfaces and hydrogen diffusion channels. Synergic effects of MoNi on MgH₂ increased hydrogenation and dehydrogenation kinetics than the use of mono atomic Mo and Ni on MgH₂. The MoNi possessed high hydrogen absorption capacity which was able to dissociate hydrogen from MgH₂ by breaking Mg-H bonds. Magnesium hydride has been separately milled with 10 wt.% MoSe@FeNi hollow nanospheres, FeNi₃, and MoSe₂ particles (Gao et al. 2020). All additives showed improved catalytic influence on the hydrogenation and dehydrogenation reactions of MgH₂ but MoSe₂@FeNi offered the best performance. The combination of FeNi₃, and MoSe₂ was responsible to its excellent catalytic performance. Dehydrogenation of 10 wt.% MoSe₂@FeNi₃-doped MgH₂ composite commenced from 194 °C; it could absorb 5.8 wt.% H₂ within 0.5 min at 150 °C. The combined additive propitiated the formation of active MgSe, Fe, MgNi and Mo species that were uniformly distributed on the surface of NiMoO₃. They were reported to have engendered the de/hydrogenation stability of MgH₂. Furthermore, MgNi turned MgH₂ to an effective pathway for hydrogen absorption and desorption. Molybdenum flakes have been used in improving the hydrogen storage capacity of MgH₂ (Cheng et al. 2023). Adding 7 wt.% Mo flakes to MgH₂ powder, hydrogen desorption commenced at 250 °C, which was 100°C lower than ordinary MgH₂ (350°C). The composites released 6.5 wt.% hydrogen for 20 min at 325 °C. At room temperature, the composite began to absorb hydrogen and 6 wt.% was absorbed at 250 °C within 10 min. Lamellar surfaces possessed by the flakes provided more diffusion pathways and contact surfaces which hastened diffusion of hydrogen at Mg/MgH₂ interfaces. Molybdenum remained stable during de/hydrogenation cycles and this made it impart an active catalytic effect on MgH₂.

3.5. Chromium (Cr)

Prolonged hydrogenation-dehydrogenation cycling was devised by Dehouche et al. (2002) to determine the thermal stability of MgH₂/0.2 mol % Cr₂O₃ nacoasposite. At 350 °C, the composite possessed the best absorption kinetics after 17 cycles and it witnessed the least kinetics after 1000 cycles at 300 °C. Absorption rate of 47 kW/kg was maintained at 300 °C after 1000 cycles while desorption rate reduced to 4.5 kW/kg. During the cycling process, the crystallite size which was initially 21 nm
grew to 84 nm after 1000 cycles at the same temperature; the coarsening of the composites microstructure was responsible for the slow desorption rate. Coarsening of the microstructure was maintained up to 350 °C. Cycling effects on MgH₂/10 wt.% Cr₂O₃ nanopowder composites was studied by Polanski et al. (2011). At 325 °C, the ball milled nanocomposite was put through 150 de/absorption cycles. Progressive reduction of nanocomposite’s hydrogen storage capacity was witnessed after every 25 cycles; this ranged from 5.1 wt.% H₂ after the 1st cycle to 4.6 wt.% H₂ on the 150th cycle. This reduction in nanocomposite’s hydrogen storage capacity upon cycling was ascribed to the formation of agglomerates that arose from the sintering (as a result of long term cycling) of combining powders (MgH₂ and Cr₂O₃), reduction of Cr₂O₃ to Cr with formation of MgO and existence of Cr₂O₃ particles in Mg interface. Bimetallic Cr-V was confirmed effective for hydrogen sorption kinetics of MgH₂ within room temperature and 300 °C (Zahiri et al., 2011). Within 1 h, 5 wt.% H₂ was absorbed at room temperature and 8 bar; the composite remained stable beyond 225 cycles with reduced degradation kinetics at 200 and 300 °C. The stability was attributed to positioning of nanocrystalline bimetallic Cr-V catalyst at Mg/MgH₂ grain boundaries which ended up coating the surface. With increasing cycling, the coating potency of Cr-V was dwindled and limited the cycling stability of MgH₂/Cr-V composite.

3.6. Iron (Fe)

Iron is regarded as an inexpensive and the most abundant transition metal on earth (Du et al., 2015). Several studies have proven that Fe can upgrade the hydrogen storage properties of MgH₂ in its pure form, as an alloy compound and in composite with other materials. Yavari et al. (2005) ball milled MgH₂ with 3 wt.% iron (III) fluoride (FeF₃) nanoparticles. There was a partial transfer of fluorine (F) which formed protective intergranular MgF₂ with fine dispersed Fe nanoparticles in Mg or MgH₂, according to reaction (5). The catalytic effect could have come from the Fe formed.

3MgH₂ + 2FeF₃ + 3MgF₂ (intergranular) + 2Fe + 3H₂

Bassetti et al. (2005) reported that when MgH₂ was ball milled with Fe particles in ball to powder ratios (BPR) of 1:1, 3:1 and 10:1, MgH₂, MgO and Mg were formed. When BPR was increased to 20:1, additional phase Mg₂FeH₆ was formed. Optimum microstructure that showed a uniform distribution of micron and submicron-sized Fe particles in the MgH₂ matrix was achieved at high milling energy (BPR of 10:1 and 20:1). Also, 10 wt.% Fe was the optimum catalyst concentration because contents lower than this led to the formation of poorly catalyzed regions; concentrations beyond this value yielded no improvement either. Ten weight percent of Fe and Iron (III) oxide (Fe₂O₃) were separately ball milled with MgH₂ for 3 h under 0.3 MPa H₂ pressure (Baum et al., 2007). Although mechanism of the improved adsorption/desorption properties of MgH₂ was not fully established, Fe acted as an active site for hydrogen sorption (Fe₂O₃ was also reduced to Fe). Iron (III) oxide displayed a better catalytic effect. It could be assumed here that a more reduced crystallite size offered by Fe₂O₃ may be responsible for this. Santos et al. (2014) discovered that using elemental Fe nanoparticles would give a better catalytic effect on MgH₂ hydrogen sorption performance than nanoparticles of FeNb (ferrominion alloy) during milling. During milling, it was observed that nanointerfaces comprising Mg (MgH₂)/Fe and Mg (MgH₂)/FeNb alloy were formed which acted as diffusion paths for hydrogen into the bulk particle. These interface according to the researchers, possessed high chemical interfacial energies. Formation of NbO₂ and Nb₂O₅ when milled with the alloy may have been responsible for its lower sorption kinetics. The catalytic effect of as-synthesized graphene sheet templated Fe₅O₇ nanoparticles (Fe₅O₇@GS) on MgH₂ was examined by (Bhatnagar et al., 2016). The structure of as milled composite (MgH₂/Fe₅O₇@GS) contained MgH₂, Fe, Fe₅O₇, MgO and Mg₂FeH₆. Graphene sheet prevented the agglomeration of Fe nanoparticles (formed by reduction of Fe₅O₇), increased the surface area, durability and cycle stability (after 25 cycles of de/hydrogenation) of MgH₂. It was investigated that the layer of MgO was punctured by Mg₅Fe₀ which created hydrogen diffusion pathway through its layer. In addition, electron transfer between Mg²⁺ and H² during de/hydrogenation was engendered by the multiple valence of Fe. Surfactant-assisted solvothermal method was used in preparing Fe₅S₃ micro-spheres which was ball milled with MgH₂ (Zhang et al., 2018). Adding 16.7 wt.% of the additive, the following reactions were confirmed to have taken place after milling:

2MgH₂ + Fe₂S₃ → 2MgS + Fe + 2H₂

2MgH₂ + Fe + H₂ → Mg₂FeH₆

After hydrogenation at 350 °C, MgH₂ and Mg₂FeH₆ appeared as the major phases while their decomposition yielded metallic Mg and Fe after dehydrogenation at the same temperature. The composite could release 1.24 wt.% H₂ at 350 °C within 1400 s while pure MgH₂ could release 0.18 wt.% H₂ under similar condition. The composite absorbed 3.71 wt.% H₂ within 1400 s at 250 °C, compared with 1.03 wt.% H₂ of the as-milled pure MgH₂. Mg₂FeH₆ and MgS created diffusion pathway for H₂ diffusion. Sazelee et al. (2018) confirmed that MgO, Fe and Ba were formed after milling MgH₂ with 10 wt.% BaFe₆O₁₉ and these imparted synergic effects on hydrogen storage properties of MgH₂. Onset decomposition temperature for composite was 237 °C which was as-milled MgH₂ was 340 °C. At 150 °C, its absorption capacity was 4.5 wt.% H₂ after 10 min while for the additive-free MgH₂, it was 3.5 wt.% H₂. The composite could release 4.2 wt.% H₂ in 30 min while additive-free MgH₂ could do 3.4 wt.% H₂ within the same time. Iron based MOFs has been synthesized and introduced to MgH₂ by ball milling. (Ma et al., 2019). The improved hydrogen storage of the composite was ascribed to the formation of nano α-Fe particles which was uniformly distributed on de/hydrogenated Mg/MgH₂ surface. Ball milling was employed in creating homogenous dispersion of the individual catalyst: Fe, Fe₂O₃ and Fe₃O₄ in MgH₂ powders (Gattia et al., 2019). Activation energy for decomposition as calculated by Kissinger plots showed that 10 h ball milled MgH₂/5 wt.% Fe possessed the least magnitude of 220.69 kJ/mol. Vales recorded for MgH₂/5 wt.% Fe₂O₃ and MgH₂/5 wt.% Fe₃O₄ was 230.90 and 304.45 kJ/mol respectively. Low activation energies maintained using Fe and Fe₂O₃ compared to that of uncatalyzed MgH₂ (241.46 kJ/mol) indicated that these two materials gave good catalytic effects on desorption kinetics of MgH₂. Gao et al. (2019) doped MgH₂ with 270 °C iron bullet (FeB) by dry milling and wet milling (with cyclohexane) at room temperature. Both milling techniques improved the hydrogenation and dehydrogenation performance of MgH₂ compared to additive-free MgH₂ as the in situ formed Fe and B served as active species during the process. Wet milling yielded smaller particles than dry milling and this was responsible for its better performance. Iron nanosheets have been synthesized to act as catalyss at MgH₂. (Zhang et al., 2019). Adding 5 wt.% Fe nanosheets made the activation energy for the dehydrogenation reaction to be 40.7 kJ/mol, which was 85.2 kJ/mol lower than the catalyst-free MgH₂. Within 10 min, 6 wt.% H₂ was absorbed by the composite at 200 °C while 2.3 wt.% H₂ was taken up after 45 min at the same temperature. It was noticed that during the first
hydrogenation and dehydrogenation processes, the Fe nanosheets became ultrathin nanoparticles on MgH2, this created more active sites in the cycles that followed. At the onset of adding Fe nanosheets, Mg-H bond was broken. Catalytic influence of nanostructured Co3S8 (pyritesite) on hydrogen sorption properties of MgH2 was studied by Cheng et al. (2021). Doping the parent hydride with 16.7 wt.% Fe3S8 and ball milling, 4 wt.% H2 was absorbed at 200 °C within 1800 s; undoped MgH2 had the capacity to absorb 1.847 wt.% H2 at the same temperature and time. Also, within 1800 s and 350 °C, 4.403 and 2.479 wt.% H2 were released by MgH2/Fe3S8 composite and MgH2 respectively. The Fe3S8 catalyzed MgH2 composite began to desorb hydrogen at a much lower temperature (147 °C) compared to as milled MgH2 (437 °C). Improvements on the hydrogen storage performance of MgH2 by the catalyst was credited to the formations of MgS and Fe from the reacting materials that occurred during ball milling. Synthesized Fe nanoparticles were ball milled with MgH2 to tailor its hydrogen storage performance (Song et al. 2022). Magnesium hydride remained dominant after ball milling and hydrogenation while Mg phase was formed in the dehydrogenated phase. The existence of stable Fe in the three stages was responsible for the enhanced absorption and desorption of Mg/H2 system as it acted as an active catalytic site during these processes. The composite retained 93.4% of its hydrogen capacity after the 20th cycle. At this point, grain growth in MgH2 and Fe catalyst occurred which was responsible for capacity loss and kinetics reduction. Soni et al. (2023) reported effect of Fe nanoparticles and hollow carbon spheres composite on the hydrogen storage properties of MgH2. During hydrogenation and dehydrogenation cycles, the valence state of Fe was converted from +3 to +2 and this was responsible for the improved hydrogen storage properties of MgH2.

3.7. Cobalt (Co)

The modification of MgH2 hydrogen sorption potency has been achieved by doping with combined oxides of Co and Ni (Cabo et al. 2011). Addition of 5 wt.% mesoporous NiO increased the desorption rate 7 times greater than MgH2 with reduced sorption activation energy. Addition of nanoporous Co3O4 showed a minimal improvement while nanoporous NiCo3O4 imparted property that was in between MgH2/NiO and MgH2/Co3O4. The role of CoFe2O4 nanoparticles on the dehydrogenation of MgH2 was demonstrated by Shan et al. (2014). Ball milled MgH2/7 mol% CoFe2O4 composite began to desorb hydrogen at 160 °C and this was 200 °C less than the onset desorption temperature of additive-free MgH2. It was observed that during dehydrogenation, CoFe2O4 reacted with MgH2 to form a ternary combination of CoFe, MgO and Co; these were affirmed to catalyze the decomposition of MgH2. Hierarchical Co@NC nanoflowers have been reported to create more hydrogen diffusion channels and active catalytic sites that aided the reduction of hydrogen desorption temperature of MgH2 (Li et al. 2017). The hierarchical Co@CN nanoflowers were synthesized by employing a simple route that was based on a low temperature solid-phase reaction; it was milled with MgH2 for 5 h under 1 MPa H2. Onset desorption temperature of the composite (201 °C) was 99 °C lower when compared with as-milled MgH2. Within 30 min, the composite released 5.74 wt.% H2 within 30 min and at 300 °C, 6.08 wt.% H2 was released in 60 min. On the other hand, as-milled MgH2 could release 0.37 wt.% H2 within 30 min; at 300 °C, 1.20 wt.% H2 was released in 60 min. Gao et al. (2020) used 10 wt.% CoFe/B/CNTs as an additive to improve dehydrogenation behaviours of MgH2. This was actualized by in situ formed stable Co/Mg/C, Fe, CoFe and B which created active nucleation sites for dehydrogenation reactions. In addition to the formation of these phases, uniform distributions of Co, B, Fe and C in the composite contributed to its good cyclic stability. Hydrolysis of MgH2 in the presence of 2.5 – 10 wt.% CoCl2 to produce hydrogen was executed by Filiz (2021). It was concluded that the best performance in terms of kinetics of hydrogen generation was displayed using CoCl2 solution with a concentration of 6.55 wt%. Core-shell CoNi@C bimetallic nanoparticles (MOFs) were introduced to MnH2 to improve its hydrogen storage properties (Zhao et al. 2021). During dehydrogenation, Mg2Co and Mg2Ni were formed as the composite desorved 5.83 wt.% H2 at 275 °C within 1800 s. During hydrogenation, Mg2Co and Mg2Ni were transformed to Mg2CoH4 and Mg2NiH4. The composite could absorb 4.83 wt.% H2 within 1800 s at 100 °C. Hydrogen dissociation and recombination were hastened as a result of the reversible phase transitions of Mg2Co/ Mg2CoH4 and Mg2Ni/Mg2NiH4. Heat conduction during the thermal cycles was facilitated by the good thermal conductive feature of carbon and this hindered agglomeration of nanoparticles. Carbon also provided a confinement effect which also aided the stability of MgH2 during dehydrogenation cycles. Ali et al. (2022) doped MgH2 with 10 wt.% CoTiO3. Hydrogen was desorbed at 270 °C, which was lower than that of MgH2 that occurred at 340 °C. Within the first 10 min, 6.4 wt.% H2 was adsorbed. Activation energy of MgH2 was measured to be 135 kJ/mol while on adding CoTiO3, it reduced to 104.6 kJ/mol. In situ formation of MgTiO3, CoMg2, CoTi, and MgO formed during heating elevated the hydrogen storage performance of MgH2. Clusters of Mg2NiH4/Mg2CoH4 interfaces were reportedly formed after mechanically milling MOF-derived bimetallic CoNi@C catalyst with MgH2 for 6 h (Zhang et al. 2022a). The interfaces were formed on the surface of MgH2 and they were confirmed to create low energy barrier hydrogen diffusion channels which culminated in rapid release and uptake of hydrogen. Zhang et al. (2022b) doped Co particles into MgH2 via 2 h ball milling. Cobalt particles were uniformly distributed on the surface of MgH2 and this created active sites and paths for hydrogen diffusion. Dehydrogenation kinetics of MgH2 was hastened as a result of Mg2Co/Mg2CoH4 phase change that existed during hydrogenation and dehydrogenation. When 10 wt.% CoMoO4/rGO nanosheets was milled with MgH2 for 4 h (Zhang et al. 2022c), these three components – Mo, CoMoO4 and MgO were formed. They had a synergic catalytic effect on improving the hydrogen storage capacity of MgH2. The composite began to release hydrogen at 204 °C, while as-milled MgH2 commenced desorption at 330 °C. The combined catalytic effect of the generated components was also responsible for accelerated hydrogen diffusion.

3.8. Zirconium (Zr)

Hydrogen storage features of MgH2 separately catalyzed with 7 wt.% ZrF4 and NbF5 after series of cyclic loading were researched by Malla et al. (2011). At 325 °C, MgH2/ZrF4 maintained 5 wt.% H2 after 30 cycles while MgH2/NbF5 could hold 4.5 wt.% H2; thus implied that the former composite possessed a better hydrogen sorption stability at this temperature. Existence of stable ZrF4 nanoparticles in the structure of MgH2 was found responsible for a better hydrogen storage capacity. Reduction in the stability of MgH2/ZrF4 however was attributed to the gradual grain size increase by virtue of extended number of cycling. At this point, it was reported that more stable MgH2/Mg phases were formed and contributed to formation of large grain sizes. Shahi et al. (2015) introduced ZrF4 and its hydride (ZrFeH4) to investigate hydrogenation features of MgH2 by producing MgH2/ZrFe, and MgH2/ZrFeH4 nanocomposites after milling. Intermetallic...
ZrFe, was converted to fine powders of ZrFeH3 via hydrogenation; it was noted to be a more useful catalyst as it was more homogenously distributed after milling. Desorption temperatures for as received MgH2, MgH2/ZrFe, and MgH2/ZrFeH3 were 410, 368 and 290 °C respectively. At 280 °C and 2MPa H2 pressure, ball-milled MgH2 could absorb 4.5 wt.% H2 after 1 h while MgH2/ ZrFe and MgH2/ZrFeH3 nanocomposites could absorb 4.6 and 5.2 wt.% H2 respectively under the same condition; it was further confirmed that MgH2/ZrFeH3 absorbed 4.7 wt.% H2 within the first 20 min. The catalytic hydride was also found to be responsible for a reduced activation energy (61.4 kJ/mol) because it facilitated easy dissolution of hydrogen molecules to atoms and transferred it to it Mg/ZrFe2H4. Kumar et al. (2027) reported that when ZrCl3 was used as a catalyst in improving on hydrogen sorption kinetics of MgH2 via milling, metallic Zr or ZnCl2 was formed. Either phase according to the researchers modified the surface of MgH2 which was responsible for its hydrogenation and dehydrogenation kinetics. Activation energies of 40 and 92 kJ/mol were recorded for MgH2/ZrCl2 hydrogenation and dehydrogenation respectively while 70 kJ/mol (hydrogenation) and 150kJ/mol (dehydrogenation) were observed for catalyst-free MgH2. Refined grains possessed by catalyzed MgH2 (via the use of ZnCl2) was also noted to be responsible its improved hydrogenation and dehydrogenation kinetics. The refinement of grains occurred during ball milling and dehydrogenation. The product 2ZrH/MgO nanoparticles were confirmed to be formed after ball milling of MgH2 and ZrO2 for 20 h (Pukazhselvan et al. 2022). This phase was known to be responsible for the improvement of MgH2 sorption kinetics and stability.

3.9. Niobium (Nb)

A metastable NbH was formed by the hydrogenation and dehydrogenation of Mg from a 20 h ball milled MgH2/5 wt.% Nb composite (Huot et al. 2003). The formation of NbH decreased the energy barrier for MgH2 dehydrogenation. Effects of cyclic heating on milled MgH2/20% NbO2 was carried out by Friedrichs et al. (2006). After hydrogen had desorbed from MgH2, NbO2 was added to Nb; dissociated Mg reacted with oxygen from the additive (NbO2) to form MgO and MgNbO2. These three components prevented MgH2 grain growth during heating and thus improved its hydrogen sorption kinetics. Jin et al. (2007b) ball milled MgH2 with 1 mol. % of niobium (V) fluoride (NbF5) for 15 min. The additive was reported to have melted during the milling period and a liquid-solid reaction between the two combining materials led to the formation of thin-like NbH layers along nanocrystalline MgH2 grain boundaries. The grain growth of nanocrystalline MgH2 was subdued by the NbH layers and this sustained the additive’s catalytic effect up to 10 de/hydrogenation cycles. Role of F in MgF2 product (during dehydrogenation reaction) or Mg−F−F solid solution in the de/hydrogenation kinetics of MgH2, according to the researchers, needed further investigations. Niobium (V) fluoride was confirmed by Luo et al. (2008) to have a profound influence on the de/hydrogenation kinetics and storage capacity of MgH2. The composite which was processed by milling MgH2 together with 2 mol % NbF5 for 5 h could absorb 56 wt.% H2 in 60 min and within the same period, it could desorb 5 wt.% H2. Results from XRD and XPS proved that Nb species with varying valence states between 0 and +5 was responsible for the improved kinetic performance of the composite. Further investigations on the active species and influence of F in the de/hydrogenation reactions were recommended. Porcu et al. (2008) employed transmission electron microscopy (TEM) - based techniques to identify the structure and reaction between MgH2 and NbO2. The TEM analysis showed that during milling, NbO2 broke into fragments and were embedded within MgH2. The smallest fragments stuck to the MgH2 grains and got embedded within the grain boundaries. This happened after the grains were welded into larger particles. Heating the two compounds yielded reduction of NbO2 to Nb2O and MgO was formed. Inter diffusion of MgO and NbO2 yielded formation of the mixed oxide- MgNb2O6.7 Bi- metallic Nb-V film catalyst added to MgH2 was recorded to enhance its cycling stability, even beyond 500 de/hydrogenation cycles without causing sorption kinetics distortions (Tan et al. 2012). To achieve this, investigators claimed that the surface catalyst distribution and its stability determined the cyclic stability of MgH2. Ball milling was employed in doping nanosized amorphous NbHx nanoparticles into MgH2 (Zhang et al. 2015). The composite absorbed 4 wt.% H2 at 100 °C while at a higher temperature (300 °C), it absorbed 3.3 wt.% H2. It was reported that the nanosized amorphous NbHx acted as charge transfer between Mg2+ and H+, which played a major role in the improved hydrogen storage performance of MgH2. Hydrogen storage of MgH2/NbOx composite was investigated by Pukazhselvan et al. (2016). Two different milling media- zirconia and steel, were used and the system was processed by mechanochemically reacting the combining compounds for 30 h. The product was characterized with Nb - dissolved MgO, which provided a catalytic effect on the hydrogen storage properties of MgH2. Influence of high energy ball milling (HEBM) with isothermal catalytic synergetic behaviour of 10 wt.% Nb2O3 and TiF4 on dehydrogenation of MgH2 was investigated by Zhang et al. (2016). Dehydrogenation temperature of MgH2/TiF4 was 341 °C which was 76 °C lower than as-received MgH2; addition of Nb2O3 to MgH2 resulted in hydrogen being released at a reduced temperature of 336 °C. A combination of these two catalysts to MgH2 culminated in 310 °C desorption temperature. The non-isothermal synergetic catalytic effect of TiF4 and Nb2O3 was attributed to electronic exchange reactions with hydrogen molecules, which improved the recombination of hydrogen atoms during dehydrogenation. A two-dimensional Nb2C/Ti (Mxene) synthesized via chemical exfoliation has been introduced to MgH2 (Liu et al. 2019). Adding 5 wt.% of the additive to the matrix demonstrated good sorption kinetics. The simulated surface structure showed OH-terminated regions and F terminations were generated on the surface of the additive. NbH2 was formed after ball milling and de/hydrogenation cycles. The NbH2 was found to be evenly dispersed in the matrix. Onset temperature for ball milled MgH2, was approximately 297 °C while that of the composite was recorded as 151 °C. Within 800 °C, the composite releases H2 completely within 800 s. Yahya et al. (2018) ball milled 1-20 wt.% K3NB3F12 with MgH2 powders. The composite comprising MgH2/5 wt.% K3NB3F12 was the most effective as it lowered the dehydrogenation temperature of MgH2 to 225 °C. This composite absorbed 5.1 wt.% H2 after 43 s at 320 °C while as-milled could absorb this quantity within 76 s at the same temperature. At lower temperature, the composite absorbed 4.7 wt.% H2 after 30 min while as-milled MgH2 could absorb 0.7 wt.% at the same time. The active species that led to the improvement of MgH2 hydrogen storage properties were KH and Nb that were formed during the process. Hollow spherical α-Nb2O5 made of 50 nm wall thickness and mossy surfaces was synthesized and ball milled with MgH2 for 24 h to improve its hydrogen storage properties (Zhang et al. 2020). The composite (MgH2/7 wt.% α-Nb2O5) desorbed 6.4 wt.% H2 at 195 °C; at room temperature, the dehydrogenated composite began to reabsorb hydrogen, and 5.7 wt.% H2 was achieved at 150 °C. It was reported that high valence Nb5+ state of Nb2O5 was gradually lowered to Nb4+ and Nb2+ and finally Nb+ during
milling followed by first dehydrogenation cycle. It was concluded that the in situ formed low-valence Nb acted as de facto catalytic species which lowered the kinetic barriers of MgH₂ hydrogen sorption. This culminated in its decreased dehydrogenation/hydrogenation temperatures. Nanoparticles of V₂Nb₂O₁₀ have been synthesized to aid the catalytic effect of Nb₂O₅ on MgH₂ hydrogen storage properties (Meng et al. 2022). Desorption temperature of MgH₂ was reduced to 225 °C, synergistic effect between both V⁵⁺ and Nb³⁺ improved hydrogen desorption properties of MgH₂. When MgH₂ was doped with 5 wt.% Nb nanocatalyst (prepared via surfactant assisted ball milling technique), stable NbH was formed; this acted as active catalytic unit diminished the energy obstacle and boost MgH₂ kinetics (Nyahuma et al. 2022). The composite began to release hydrogen at 186.7 °C, while additive-free s MgH₂ stated hydrogen release at 347 °C. Niobium (V) oxide nanoparticles grafted on MOF (NbO₅@MOF) has been synthesized and doped into MgH₂ (Zhang et al. 2023). A slight loss in composite’s hydrogen storage capacity was attributed to the formations of MgO and NbO emanating from the reactions between MgH₂ and Nb₂O₅. However, there was a synergistic effect between Nb₂O₅ and MOF which enhanced hydrogen drift between Mg/MgH₂ boundaries; it also prevented Mg/MgH₂ from agglomeration and growth. Ultrafine and steadily dispersed NbC (niobium carbide) nanoparticle composites synthesized via carbon adsorbent (NbC/C) has been consumed via carbon thermal shock method and ball milled with MgH₂ (Jia et al. 2023). Particles of MgH₂ were refined by NbC while the substrate (carbon) destabilized Mg-H bond. In addition, multi valence electron transfer existed between positively charged Nb ions and NbH₅ (formed in situ). In addition, the electron transfer also occurred between Mg and H atoms which influenced Mg/MgH₂ reversible transformation. These were the outcomes of the catalytic influence of NbC/C.

4. Summary and Conclusion

Researches involving the use of Ti, Ni, V, Mo, Fe, Cr, Co, Zr and Nb in their monoatomic forms, alloys (with transition or other metals), intermetallics and composites to better MgH₂ hydrogen storage features have been reviewed. These transition metal-based additives are often doped in MgH₂ via ball milling in the presence or absence of hydrogen. Depending on the milling time and other conditions considered, reaction often occurs during milling which culminates in the formation of new phase(s) (see Figure 6); in situations where combining materials remain unchanged after milling, transformation occurs during de/hydrogenation which engenders the existence of new phase(s). Besides causing uniform distribution of additives throughout MgH₂ matrix, mechanical milling has also been proven to create suitable surface area that acts as catalyst sites. In addition to the prevalence of some monoatomic transition metal after hydrogenation-dehydrogenation cycles, phases such as TiH₂, Mg₄Ni, Mg₃NiH₆, V₅O₁₂, VH₂, MoSe₂, Mg₆FeH₁₀, NbH and Nb₂O₅ have imparted catalytic effects through creation of diffusion channels for hydrogen by weakening Mg – H bond strength. This reduces hydrogen de/sorption temperatures, remove energy barrier for de/hydrogenation (which results to activation energy reduction) and in turn, hastens MgH₂ hydrogen absorption and desorption kinetics. Grain growth of MgH₂ can also be prevented by the catalysts during heating to improve its hydrogen storage capacity. Transition metals such as Ti, Fe and Nb can exist in multiple valence states and they often aid charge transfer between Mg⁺ and H to positively influence hydrogen sorption kinetics. It is also observed that the hydrogen storage operation of MgH₂/transition metal – based materials will depend on the kind of additive used (including formulations), MgH₂/additive mixing ratio, ball milling time, ball-to-combining materials ratio and de/hydrogenation cycle.
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