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# Optimized Dehydrogenation of Magnesium Hydride with Fe and Cu Additives

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#### **Abstract**

Solid state hydrogen storage using of MgH<sub>2</sub> has gained widespread attention because of its good reversible storage capacity. This metal hydride however slowly releases hydrogen at high temperatures ranging between 325 – 375 °C. An important feature required of MgH<sub>2</sub> is its ability to commence hydrogen release at a fast rate and reduced temperature. Transition metal-containing alloys/compounds having either Fe or Cu as the principal element have been used to improve the dissociation of hydrogen from MgH<sub>2</sub>. Studies involving the use of each metal in its elemental form as an additive are minimal. This study investigated the catalytic effects of elemental Fe and Cu on the hydrogen release performance of MgH<sub>2</sub> for potential applications in transportation and power generation. It was observed that MgH<sub>2</sub>/Fe had a better dehydrogenation performance; the temperature of onset of MgH<sub>2</sub>/Fe and MgH<sub>2</sub>/Cu dehydrogenation were 205, and 215 °C which were 98 and 88 °C lower than that for as-received MgH<sub>2</sub>. The highest amount, 1.9 wt. % H<sub>2</sub> was released by MgH<sub>2</sub>/Fe while 1.44 wt. % H<sub>2</sub> was released by MgH<sub>2</sub>/Cu. The activation energy for dehydrogenation was reduced from 150.5 kJ/mol for as-received MgH<sub>2</sub> to 89.8 and 79.8 kJ/mol in MgH<sub>2</sub>/Cu and MgH<sub>2</sub>/Fe respectively. It took 18.8 min for as-received MgH<sub>2</sub> to commence dehydrogenation while that for MgH<sub>2</sub>/Fe and MgH<sub>2</sub>/Cu composites started from 12.2 and 13.4 min respectively. The in-situ formed Fe and Cu in MgH<sub>2</sub> after milling acted as active catalytic sites for its improved dehydrogenation with MgH<sub>2</sub>/Fe behaving better.

**Keywords**: Hydrogen storage, Hydrogenation, Dehydrogenation, MgH<sub>2</sub>/Cu, MgH<sub>2</sub>/Fe

### 1. Introduction

One of the major issues that frequently debilitate the social and environmental aspects of every nation is the challenges of climate change [1], [2]. It is not farfetched that the rising rate of greenhouse gas emissions that occupy the atmosphere is deeply rooted in everyday human activities. Globally, it is a conventional assessment that the growth of any economy is profoundly beefed up by fossil fuel consumption for generation in the domestic, agricultural, and transportation sectors [3], [4], [5]. Leaders of nations have therefore been inundated with the task of striking a balance between economic growth and overreliance on fossil fuels for energy production, storage, and transportation. Clean energy is a prominent alternative where renewable resources are been exploited.

Renewable secondary energy such as hydrogen energy maintains a leading position in modern-day energy-inclined researches because its distribution and storage are eco-friendly in addition to its high energy content [6]. Successful hydrogen energy use can be achieved by ensuring a safe storage mode that will aid its effective transportation and consumption. Storage of hydrogen in the solid state with the use of metal hydride such as magnesium hydride (MgH<sub>2</sub>) has been a promising technology because it possesses the capacity to store up to 7.6 wt. % H<sub>2</sub> and 110 kg/m<sup>3</sup> density [7], [8]. The use of this metal hydride for solid state hydrogen storage, however, faces some difficulties in its

applications of which hydrogen release kinetics is a major one [9]. This has necessitated attempts to ensure that its dehydrogenation is enhanced via nanostructuring and the introduction of additives [10]. Desorption of hydrogen from MgH<sub>2</sub> is endothermic as the reaction requires the application of heat for its activation according to the reaction:

$$MgH_2 + heat \leftrightarrow Mg + H_2$$
 (i)

This process has been reported to occur between 325 – 375 °C [11], [12], [13], [14]. The reverse reaction – absorption can take place when hydrogen is no longer in use and it has to be stored in its combined solid state. An important feature required of MgH<sub>2</sub> is its ability to commence the release of hydrogen at a fast rate and reduced temperature. The energy needed to dissociate hydrogen from MgH<sub>2</sub> during this thermal event is often quantified in terms of activation energy. As low hydrogen desorption temperature connotes improved performance, the same can also be said about the activation energy - a reduced magnitude implies that less energy will be required to break the Mg - H bond [15].

Our previous review (including other related works) affirms that the use of transition metals or transition metal-based compounds/composites as additives is a practicable way of modifying the hydrogen storage performance of MgH<sub>2</sub> [16], [17]. A conventional way of doping MgH<sub>2</sub> with these additives is via high energy ball milling. This is often done to enhance improved metallurgical bonding (cold welding) between/among combining materials. High-energy ball milling has been reported to promote grain refinement, lower reaction activation energy, and reduced temperature for chemical reactions [18], [19]. Depending on the time allowed during ball milling (0.5 h  $\leq$  time  $\leq$  12 h), an earlier review inferred that one of the following reactions would take place:

$$MgH_2 + A \rightarrow MgH_2 + A$$
 (ii)

$$MgH_2 + AB \rightarrow MgH_2 + AB$$
 (iii)

$$MgH_2 + AB \rightarrow MgB + AH_2$$
 (iv)

$$MgH_2 + AB \rightarrow \frac{1}{2}MgB_2 + \frac{1}{2}Mg + AH_2$$
 (v)

From the reactions above, A represents a transition metal; B could be one of hydrogen (H), carbon (C), oxygen (O), sulphur (S), or any group VII element in the periodic table. For simplicity, the reactions above only fit an elemental or a single transition metal-based

compound. Reactions (ii) and (iii) imply that each combining material may still exist after milling while (iv) and (v) suggest possible reactions that could take place after milling. These have been proven to facilitate the de-bonding of MgH<sub>2</sub> on the application of heat during dehydrogenation.

Transition metal-containing materials having either Fe or Cu as the principal element have been used to improve the dissociation of hydrogen from MgH<sub>2</sub>. Density functional theory (DFT) and molecular dynamic (MD) simulations have proven that there lies a stable surface on doping MgH<sub>2</sub> with Cu [20]. This surface imparts stronger hydrogen adsorption effects than undoped MgH<sub>2</sub>. In addition, the surface could act as a catalytic site for more hydrogen adsorption. Copper has been used in combined form with other metals or transition metals to improve the hydrogen storage properties of MgH<sub>2</sub> [21], [22], [23]. When used as one of the combining elements in a carbon-supported high entropy alloy (NiCoFeCuMg), a reversible catalytic phase Mg2Ni(Cu)/Mg2Ni(Cu)H4, was formed after hydrogenation/dehydrogenation reactions and this was investigated to have improved the hydrogen storage ability of MgH<sub>2</sub> [24]. Sometimes when doped with MgH<sub>2</sub> in a chemically combined form, it forms an intermetallic phase with Mg. This was exemplified in the works of Wang et al. [17] where CuS2 was ball milled with MgH<sub>2</sub>. In-situ formation of the MgCu<sub>2</sub> phase was found to be beneficial for MgH2 dehydrogenation. In an earlier study where a ternary combination of Mg, Ni and Cu was ball- milled in the presence of H<sub>2</sub>, Milanese et al. [25] reported that MgH<sub>2</sub> and MgCu<sub>2</sub> were formed. The MgCu<sub>2</sub> intermetallic provided a helpful impact by increasing the desorption partial pressure of MgH<sub>2</sub> which eventually yielded Mg<sub>2</sub>Cu. It has also been reported that Mg<sub>2</sub>Cu could be formed as a result of dehydrogenating MgH<sub>2</sub> doped with 10 wt. % CuFe<sub>2</sub>O<sub>4</sub> at 450 °C [26]. It was reported that the positive influence of CuFe<sub>2</sub>O<sub>4</sub> on the hydrogen storage properties of MgH<sub>2</sub> was based on a catalytic influence of Mg<sub>2</sub>Cu formed dehydrogenation. Copper has played a key role in the capability of Ni-Cu solid solution to act as a good additive to modify the hydrogen storage properties of MgH<sub>2</sub> [27]. With an equal content of 50 wt. %, the catalytic mechanism of the alloy was attributed to the existence of Mg<sub>2</sub>Ni(Cu) which aided the desorption and absorption of H<sub>2</sub>. Iron, on the other hand, is a cheap and

the most abundant transition metal on the earth's crust [28].

Most investigations have focused on its use as an alloying element (with other metals), compound, or composite with other non - metal-based materials. When doped with MgH<sub>2</sub> via high-energy ball milling, it was reported to remain stable after the process including hydrogenation and dehydrogenation [29]. The stability of Fe, according to the researchers, played a catalytic role in the hydrogen desorption from Mgh<sub>2</sub>. The valence state transition of Fe (combined with hollow carbon spheres) from +3 to +2 was concluded to be responsible for the fast dehydrogenation kinetics of MgH<sub>2</sub>. [30]. When in compound form with electronegative elements, its valence state could be converted to 0 (i.e. it remains an elemental Fe) after milling and/or cycle(s) of hydrogenation/dehydrogenation. In the works of Cheng et al. [31], Fe<sub>7</sub>S<sub>8</sub> was doped with MgH<sub>2</sub> to improve its hydrogen sorption properties. The reaction was confirmed to have taken place during milling as MgS and Fe were formed. The elemental Fe (coupled with MgS) was reported to have acted as a catalyst for the enhancement of MgH2 desorption. These studies, however, have shown that Cu and Fe play major catalytic roles when present in combined phases including complex compounds, alloys and intermetallic as additives in modifying the hydrogen storage properties of MgH<sub>2</sub>. Both transition metals occur naturally (with Fe being cheaper) and it is believed that using each as an additive in the elemental form should be cheaper than when used in their combined states as these may involve further complex processes. Information arising from the investigations involving the use of these metals in their elemental form is very limited.

In this study,  $MgH_2$  is separately doped elemental Cu and Fe via high- energy ball milling. The effects of these additives on the hydrogen release performance of  $MgH_2$  are investigated.

### 2. Materials and Methods

Powders used for this study are MgH<sub>2</sub> (Xi'AN 98% purity), Fe (TLS Technik 99.8% purity) and Cu (Sigma Aldrich, 99.9 % purity). A Retsch PM 100 CM planetary ball mill was used. At different times, Fe and Cu powders were separately mixed with MgH<sub>2</sub> in a ratio of

90:10 (MgH<sub>2</sub> being the matrix). A total of 15 g powder and 5 stainless steel balls of 15 mm diameter were used resulting in a 10:1 ball-to-powder mass ratio. Milling was run for 5 h at 300 rpm.

Microstructural and elemental composition was carried out using VEGA 3 TESCAN Scanning Electron Microscope (SEM) equipped with an Energy Dispersion X-ray Spectrometer (EDX). X-Ray diffraction was carried out using Bruker D8 X-Ray diffractometer, with Cu K $\alpha$  radiation. Thermogravimetric analysis (TGA) was performed with the use of PerkinElmer TGA 4000 while Micometrics AutoChem 2950 was used to perform Temperature Programmed Desorption (TPD) analysis. For both thermal analyses, the heating rate of 10 °C/min was used.

## 3. Results and Discussions

# 3.1. Morphology and structure

Figure 1a shows the micrograph of un-milled MgH<sub>2</sub> with dispersed particles (although few aggregated particles are present). After 5 h ball milling, the morphology of MgH<sub>2</sub> becomes characterized with more fractions of loose finer dispersed sub-particles (Figure 1b) compared to as-received MgH<sub>2</sub>. This may be attributed to the period of high-energy ball milling operation which has culminated in the fracturing of particles. Larger sponge-like agglomerates dispersed fine particles are formed in the micrograph of ball-milled MgH<sub>2</sub> + 10 wt. % Fe (Figure 1c); this could have occurred as a result of the milling parameters chosen and the addition of Fe used for this study. Observation from MgH<sub>2</sub> + 10 wt. % Cu micrograph (Figure 1d) informs that agglomerated particles appear angular, porous-like and devoid of dispersed fine particles as noticed for MgH<sub>2</sub> + 10 wt. % Fe particles. The EDX justifies the existence of elements in each sample. The calculated average particle size of asreceived MgH<sub>2</sub> is 0.053 µm (Figure 2a). Milling agglomerates these particles and from the distribution curve shown in Figure 2b; the average particle size (agglomerate) of MgH<sub>2</sub> after 5 h milling is 0.747 µm. The average particle sizes of milled MgH<sub>2</sub> + 10 wt. % Fe and  $MgH_2 + 10$  wt. % Cu are 0.179 and 0.274 µm respectively (Figure 2c and Figure 2d). This shows that Fe and Cu powders restrict particle agglomeration (when compared to milled MgH<sub>2</sub>).

The XRD patterns of as-received  $MgH_2$  with milled  $MgH_2+10$  wt. % Fe and  $MgH_2+10$  wt. % Cu are presented in Figure 3. No additional compound is formed

as Cu and Fe remain un-oxidized or reduced after 5 h milling. This, therefore, shows that they will play a role in easing or aggravating the dehydrogenation of MgH<sub>2</sub>.

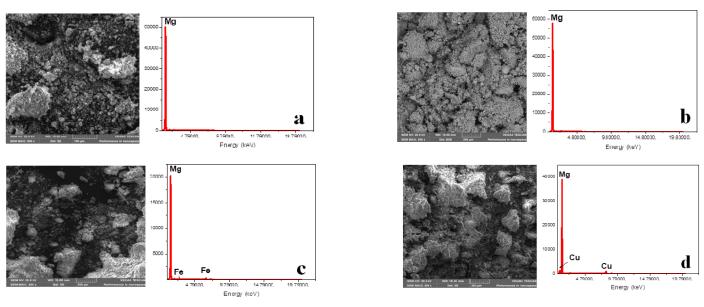


Figure 1. SEM/EDX of (a) as-received MgH<sub>2</sub> (b) milled MgH<sub>2</sub> (c) milled MgH<sub>2</sub> + 10 wt. % Fe (d) milled MgH<sub>2</sub> + 10 wt. % Cu.

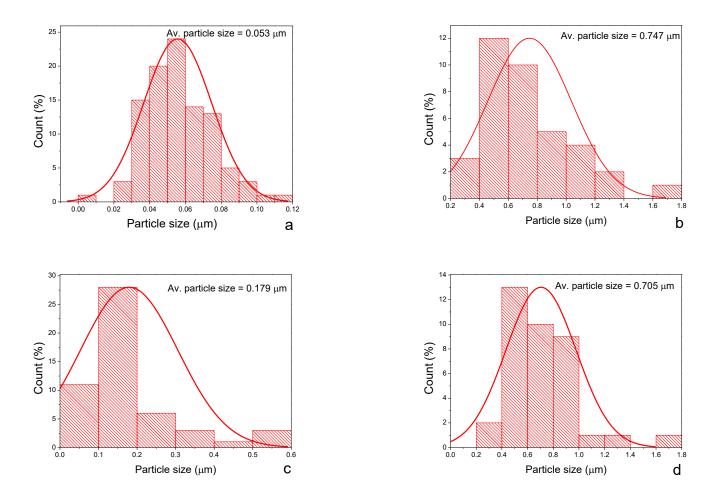


Figure 2. Average particle size distribution for (a) as-received  $MgH_2$  (b) milled  $MgH_2$  (c) milled  $MgH_2 + 10$  wt. % Fe (d) milled  $MgH_2 + 10$  wt. % Cu.

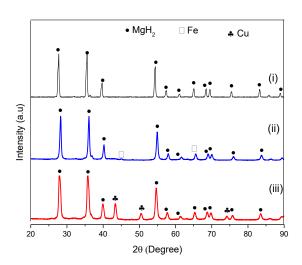
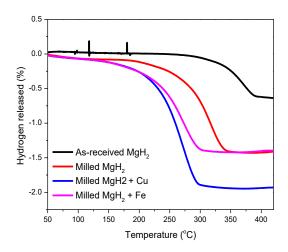


Figure 3. X-ray Diffraction patterns of as-received MgH<sub>2</sub>, milled MgH<sub>2</sub> + 10 wt. % Fe and milled MgH<sub>2</sub> + 10 wt. % Cu.

# 3.2. Effects of each additive on dehydrogenation property of MgH<sub>2</sub>

In order to investigate the amount (wt. %) of H<sub>2</sub> released, TGA was carried out. As illustrated in Figure 4, as-received MgH<sub>2</sub> displays the highest temperature from which dehydrogenation commences (303 °C) with the least content of hydrogen released (0.6 wt. %). After 5 h milling, initial hydrogen desorption drops to 233 °C and 1.4 wt. % H<sub>2</sub> is released. This shows that milling positively influences the hydrogen storage property of MgH<sub>2</sub>. The formation of agglomerated (loose-like) fine particles created by the milling process may have created a better energetically favorable site for easier desorption.



**Figure 4**. TGA of as-received MgH<sub>2</sub>, milled MgH<sub>2</sub>, milled MgH<sub>2</sub> + 10 wt. % Fe and milled MgH<sub>2</sub> + 10 wt. % Cu.

The figure has also shown that Fe and Cu have imparted catalytic effects on  $MgH_2$  dehydrogenation. The onset dehydrogenation temperature for Fe-doped  $MgH_2$  is 205 °C while 215 °C is recorded for  $MgH_2$  doped with Cu. Both  $MgH_2$  / Cu and milled  $MgH_2$  release the same amount of hydrogen (1.4 wt. %) but it is evidenced from the figure that the rate at which the former achieves this is faster as it also completes its dehydrogenation at 42 °C lower. The highest content of hydrogen (1.9 wt. %) is released from  $MgH_2 + 10$  wt. % Fe composite and this is expected to have been done the easiest as the dehydration is completed at the least temperature (297 °C).

In this study, the ease of dehydrogenation is expressed by the magnitudes of activation energy Ea which was calculated from the TGA thermogram of each sample from the expression given in Eq. (1) [32] and this has also been adopted by Gbenebor *et al.* [33] in calculating Ea:

$$Ln(-Ln(1-X)) = -Ea/RT + Const.$$
 (1)

From the expression, T (K) is the absolute decomposition temperature and the activation energy for the thermal event is Ea (kJ/mol); the universal gas constant is R with a value of 8.314 J/mol·K. Decomposition degree (X) has the expression given in Eq. (2):

$$X = [(W_o - W_i) / (W_o - W_f)]$$
 (2)

The initial and instantaneous weights are represented by Wo and Wi respectively; The slope Ea/R of the fitted curve is obtained from a straight line graph of Ln (- Ln (1- X)) against 1/T.

The Ea required for dehydrogenation is 150.5, 115.6, 79.8 and 89.8 kJ/mol for as-received MgH<sub>2</sub>, milled MgH<sub>2</sub>, milled MgH<sub>2</sub> + 10 wt. % Fe and milled MgH<sub>2</sub> + 10 wt. % Cu respectively (Figure 5 a-d). The least magnitude of Ea calculated from Fe-doped MgH<sub>2</sub> TGA implies that it possesses the fastest dehydrogenation rate.

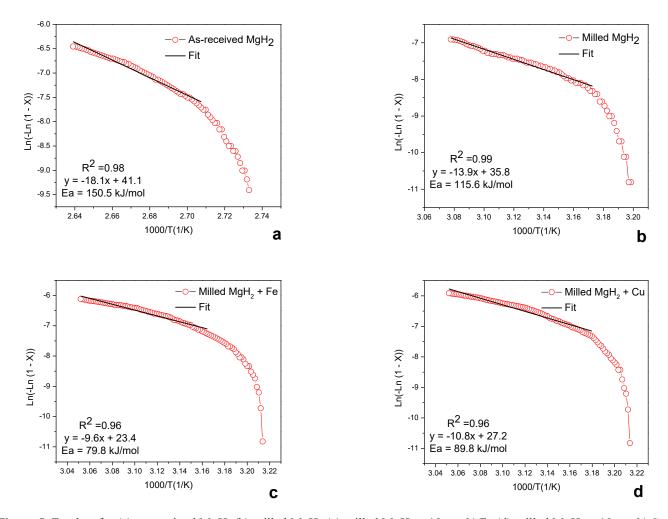
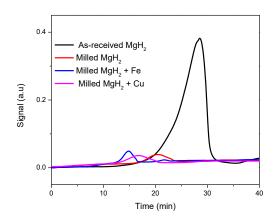


Figure 5. Ea plots for (a) as-received MgH<sub>2</sub>(b) milled MgH<sub>2</sub> (c) milled MgH<sub>2</sub> + 10 wt. % Fe (d) milled MgH<sub>2</sub> + 10 wt. % Cu.

The time involved during hydrogen desorption from each hydride sample was determined from the TPD result (Figure 6). After approximately 19 min, asreceived MgH2 begins to release hydrogen. The time at which this reaction attains its maximum rate is on the 29th min and completed after 31.4 min. It takes 15. 2 min for milled MgH<sub>2</sub> to commence hydrogen release and this is completed earlier than as-received MgH<sub>2</sub> as this reaction takes place within 25.3 min. This further justifies the reduction in onset temperature and Ea of milled MgH<sub>2</sub> compared to the as-received. Hydrogen is released with more ease when Fe and Cu additives are used; within 15 min, MgH<sub>2</sub> + 10 wt. % Fe composite completes its dehydrogenation (after commencing from 12.2 min) while it takes 17.3 min for  $MgH_2 + 10$  wt. % Cu composite to complete its dehydrogenation after commencing from 13.4 min.



**Figure 6.** TPD of as-received MgH<sub>2</sub>, milled MgH<sub>2</sub>, milled MgH<sub>2</sub> + 10 wt. % Fe and milled MgH<sub>2</sub> + 10 wt. % Cu.

### 4. Conclusion

In this work, the effects of elemental Fe and Cu additives on the dehydrogenation of MgH2 have been investigated and compared. Results show that after 5 h ball milling, both Fe and Cu remain un-reacted and their existence have acted as catalytic sites which has positively influenced the hydrogen release performance of MgH<sub>2</sub> (MgH<sub>2</sub> doped with Fe displayed better dehydrogenation). There is a reduction dehydrogenation temperature from 303 °C in as-received MgH<sub>2</sub> to 233 °C in as-milled MgH<sub>2</sub>. This also shows that ball milling plays a positive role in the hydrogen release performance of MgH<sub>2</sub>; 1.4 wt. % H<sub>2</sub> is released from milled MgH<sub>2</sub>, which is 0.8 wt. % more than what asreceived MgH<sub>2</sub> could attain. The highest amount (1.9 wt. % H<sub>2</sub>) is released from MgH<sub>2</sub> + 10 wt. % Fe composites whose temperature of onset of dehydrogenation is 205 °C. Although MgH<sub>2</sub> + 10 wt. % Cu composite releases a similar amount of hydrogen as the milled MgH<sub>2</sub> (1.4 wt. % H<sub>2</sub>), it does this at a lower temperature (215 °C). The Ea associated with the dehydrogenation of as-received MgH<sub>2</sub> is 150.5 kJ/mol and this is greater than that calculated for milled MgH<sub>2</sub> (115.6 kJ/mol). Ease and rapid dehydrogenation are exemplified in doped samples as much lower Ea is required for hydrogen release; 79.8 and 89.8 kJ/mol are calculated for MgH<sub>2</sub> + 10 wt. % Fe and MgH<sub>2</sub> + 10 wt. % Cu composites respectively. While it takes 18.8 min for as-received MgH2 to commence hydrogen release, dehydrogenation of MgH<sub>2</sub> + 10 wt. % Fe and  $MgH_2 + 10$  wt. % Cu composites start from 12.2 and 13.4 min respectively. The in-situ formed Fe and Cu in MgH<sub>2</sub> have acted as active catalytic sites for its improved dehydrogenation with MgH<sub>2</sub> + 10 wt. % Fe behaving better. These composites can find potential applications in transportation, power generation and fuel cells. For easy handling and ensuring effectiveness during application, some of our future works entail the following:

- Discs of these samples will be processed via compaction at different loads. With this, the effects of particle features on the mechanical properties (hardness, compressive and impact strengths) of these compacted discs will be studied.
- Thermal cycles of hydrogenation —dehydrogenation of compacted discs will be studied to investigate their thermal and mechanical stabilities.

### **Conflict of Interest Statement**

We the authors (Gbenebor O.P and Popoola A.P.I) declare that we have no known conflicts of financial interests or personal relationships that could have influenced the work reported in this article.

# **Data Availability Statement**

No data or additional materials were utilized for the research described in the article. All findings in this study have been presented in the discussion section.

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