Parametric Study of Magnesium Hydride Formation and Crystallographic Properties Changes

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Introduction

Mg is a silvery, white metal which has an atomic number of 12 and belongs to the 2A group of the periodic table.

is the seventh most abundant element in the earth's crush and average content is 2.1%

does not occur in nature in elemental form but in form of compounds in seawater, minerals, brines and rocks.

The prime raw material sources for magnesium extraction are the minerals dolomite ($CaCO_3.MgCO_3$), magnesite ($MgCO_3$), and brucite ($Mg(OH)_2$)

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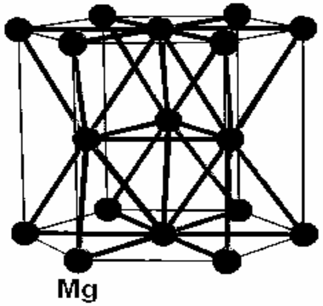
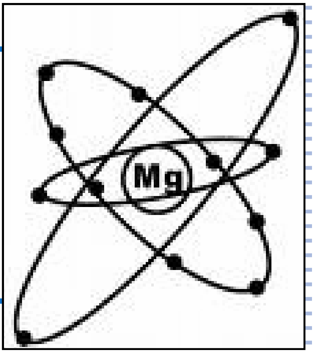
hexagonal crystal system

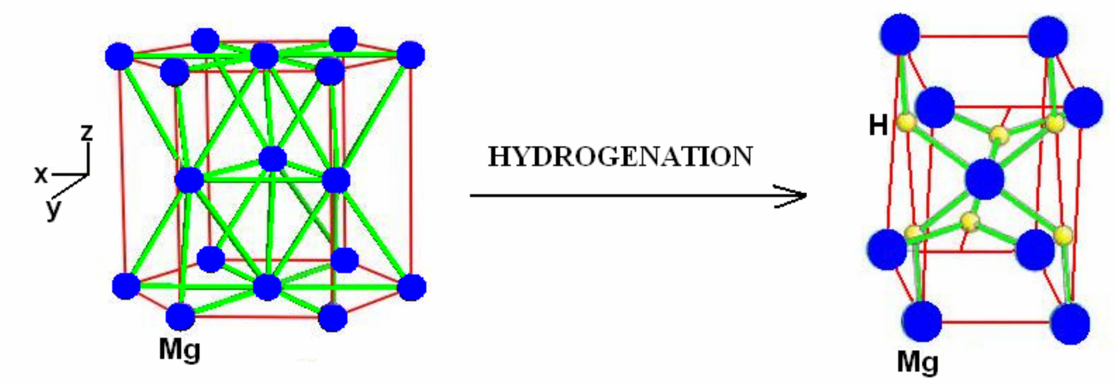


Magnesium is an attractive and promising material for hydrogen storage medium because it's high storage capacity with form of MgH_2 (up to 7.6 wt %).



Generally, MgH_2 is produced by a hydrogenation of magnesium under high temperature and hydrogen atmosphere.

$$Mg + H_2 \rightarrow MgH_2$$



However, it is necessary to explain how various factors effecting on hydrogen absorption to find an effective methods to improve the hydriding kinetics. The main concern of the present paper is identifying the effect of parameters (temperature, pressure, time) on crystal structure properties of MgH_2

EXPERIMENTAL PROCEDURE

Materials and Characterization

Magnesium powder with 99 % purity was purchased from Fluka.

The average powder size was 75 mesh and the all magnesium particles had similar size. Therefore, studies were carried out independently of the effects of microstructure and particular size of the powder particles on hydrogenation process.

Tetrahydrofuran (THF, 99%) as organic additives supplied from Riedel-de Haen, Sigma Aldrich, respectively. Also, chromium chloride ($CrCl_3$) as catalyst was purchased from Aldrich with 99 % purity.

The MgH_2 samples obtained were examined by X-Ray powder diffraction (XRD), using a Philips Panalytical X'Pert Pro diffractometer with Cu Kα radiation (λ=0.15418 mm) at operating parameters of 40 mA and 45 kV with step size 0.02° and speed of 1°/min. X-Ray diffraction patterns of powders were recorded at room temperature with a diffraction angle from 0° to 90°.

Magnesium Hydride Production

In order to determine the various factors affecting on magnesium hydride formation, samples of magnesium were exposed to various hydrogen gas pressure at different temperatures for several reaction time according to the reaction is given below:

$$Mg_{(s)} + H_{2(g)} \rightarrow MgH_{2(s)} \quad (1)$$

MgH_2 was produced in a stainless-steel autoclave with 2 lt volume, which was designed specifically for this study. Temperature can be controlled directly by control panel.

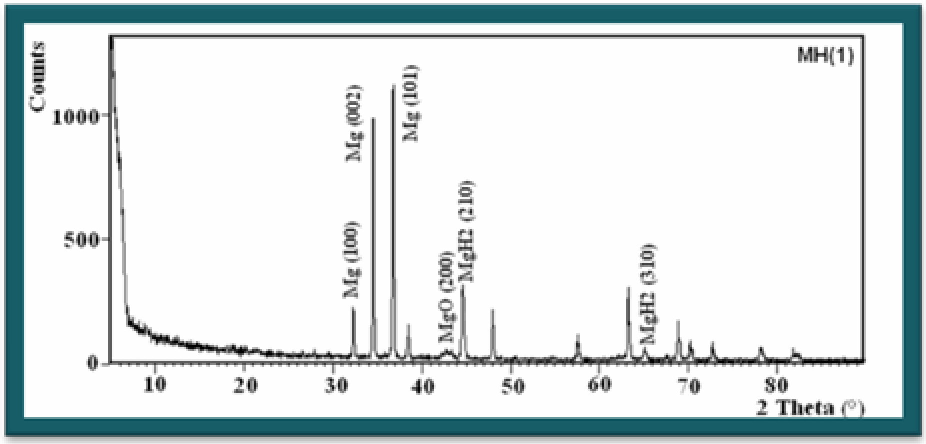
Sample no.	Mg particles	Initial pressure (bar)	Temperature (°C)	Time (hour)
MH (1)	Mg	10	350	8
MH (2)	Mg	10	350	24
MH (3)	Mg	15	450	24
MH (4)	Mg_{THF}	15	450	24
MH (5)	Mg_{THF}	26	100	24
MH (6)	$Mg_{THF}{:}CrCl_3$	26	100	24

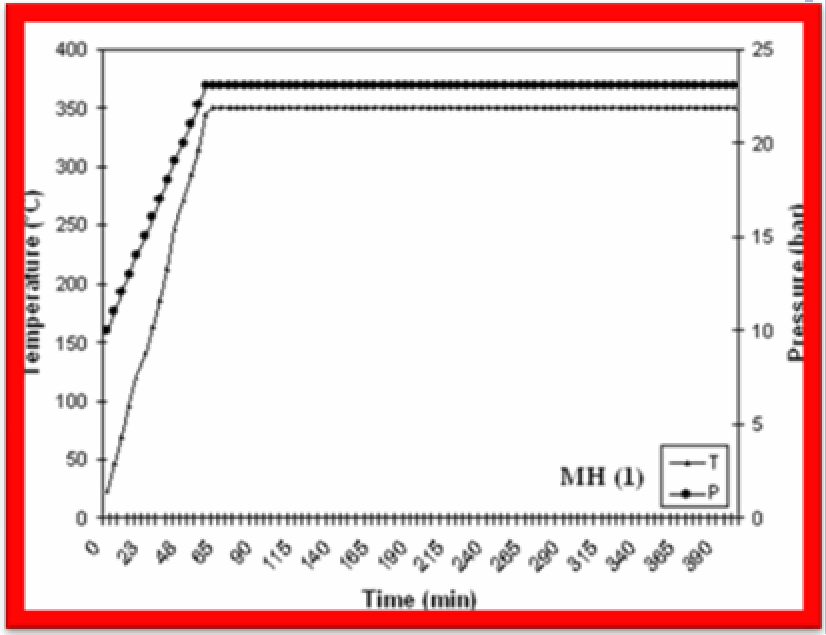
RESULTS AND DISCUSSION

Sample no.	Mg particles	Initial pressure (bar)	Temperature (°C)	Time (hour)
MH (1)	Mg	10	350	8

MH(1), peaks representative (1 0 0), (0 0 2) and (1 0 1) diffraction peaks corresponding to 32.34°, 34.52° and 36.74° diffraction angel respectively, which characterized metallic magnesium in the hexagonal crystal system and the tetragonal structure of MgH_2 was characterized with peaks occurred at 44.71° (2 1 0) and 65.38° (3 1 0) diffraction angels.

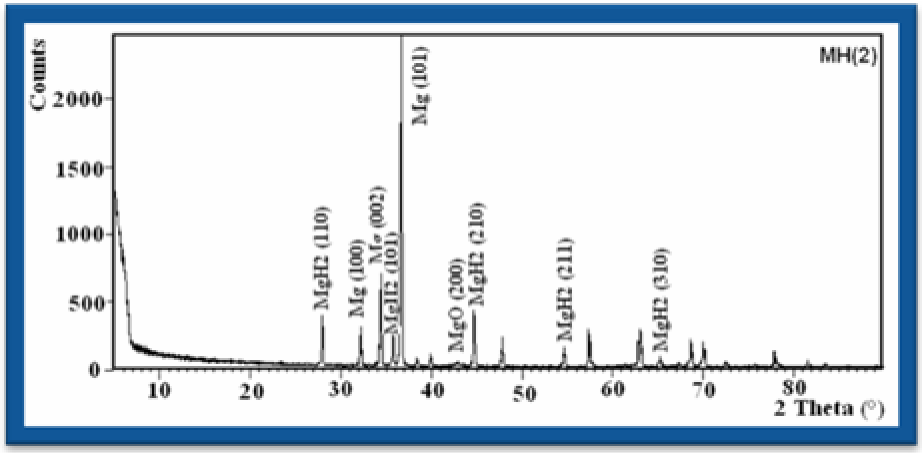
Mg powder transformed into MgH_2 with low conversion so that major phase is still metallic magnesium.

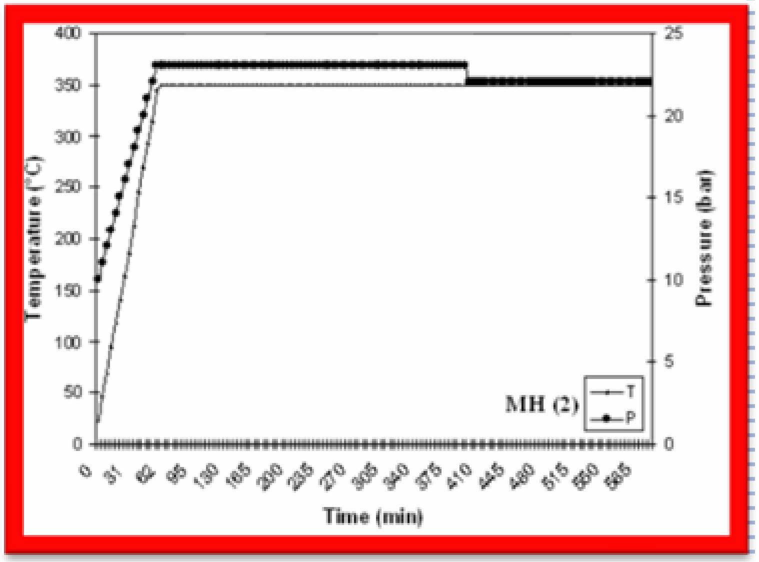




Sample no.	Mg particles	Initial pressure (bar)	Temperature (°C)	Time (hour)
MH (2)	Mg	10	350	24

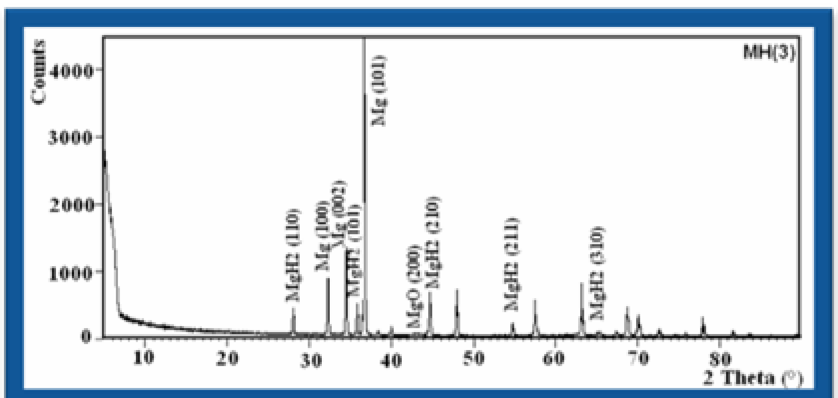
In order to increase hydrogenation of magnesium, the reaction time has been upgraded to 24 hour. By direct comparison of peaks intensity of MH(1) and MH(2), it can be seen that (2 1 0) of MgH_2 increase with reaction time increasing and at the same time (1 1 0), (1 0 1) and (2 1 1) of MgH_2 diffraction peaks corresponding to 27.96°, 35.76° and 54.56° diffraction angel respectively, which were disappeared in the X-ray diffraction pattern of MH(1), are formed. Intensities of (1 0 0) and (1 0 1) Mg peaks were increased and (0 0 2) Mg peak was reduced with increasing of reaction time, peaked at 32.23°, 34.42°, 36.65° respectively.

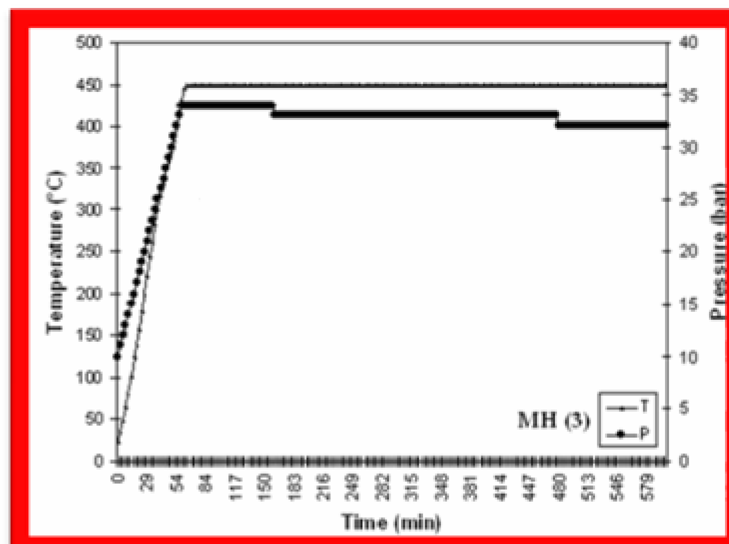




Sample no.	Mg particles	Initial pressure (bar)	Temperature (°C)	Time (hour)
MH (3)	Mg	15	450	24

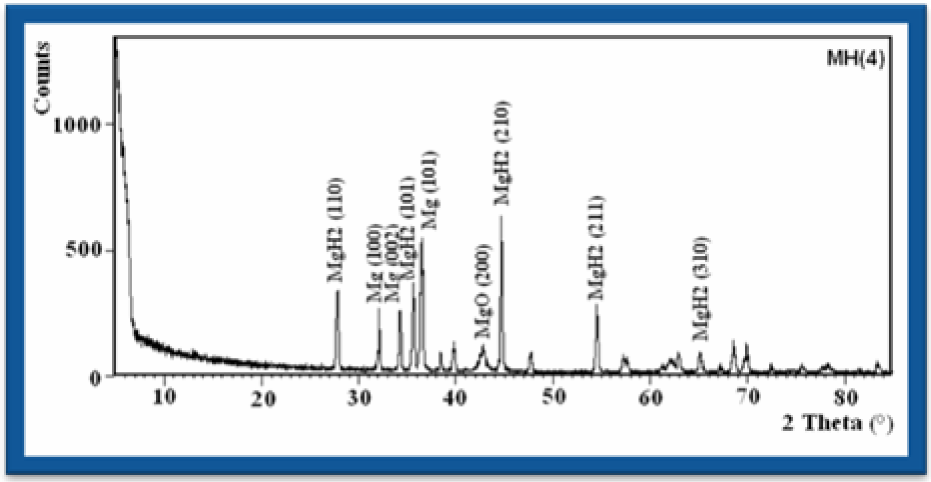
Three phases were observed in the powder, Mg, MgH_2 and MgO. (1 1 0), (1 0 1), (2 1 0) and (2 1 1) diffraction peaks corresponding to 28.10°, 35.83°, 44.64° and 54.75° diffraction angel matched with the characteristic peaks of magnesium hydride. With increasing pressure and temperature the intensity of (2 1 0) and (2 1 1) and (1 0 1) MgH_2 peaks increases while the intensity of (1 1 0) MgH_2 peak low decrease.

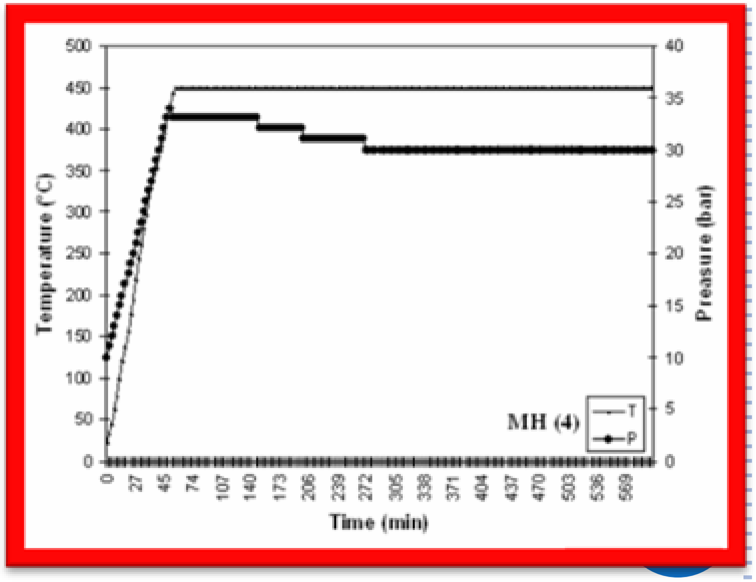




MH (4)	Mg_{THF}	15	450	24

X-Ray diffraction pattern indicated that the main phase in sample was MgH_2. There are some peaks that were related to residual Mg. Intensity of (1 0 1) and (2 1 1) MgH_2 peaks decreases while the (1 0 0), (0 0 2) and (1 0 1) Mg peaks reduced according to the peaks intensity of MH(3) sample (Fig 2). It was noted that, THF treaded Mg absorbs much more hydrogen than Mg powder at 450°C for 24 hours under 15 bar initial pressure. THF solution causes to form so many cracks inside the Mg particles and so that surface area of Mg was increased approximately three times according to the BET analysis.

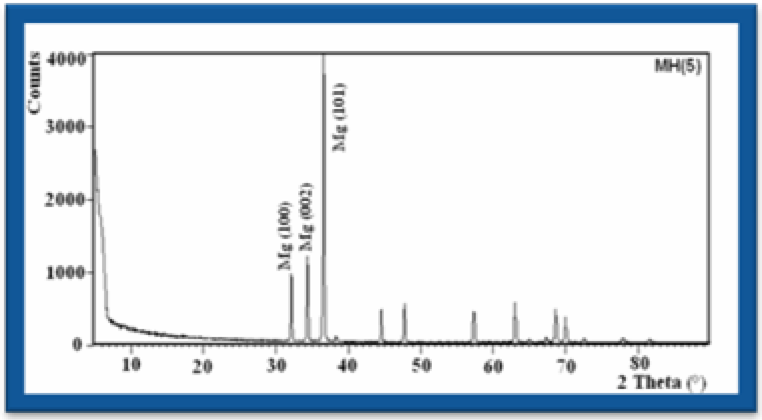


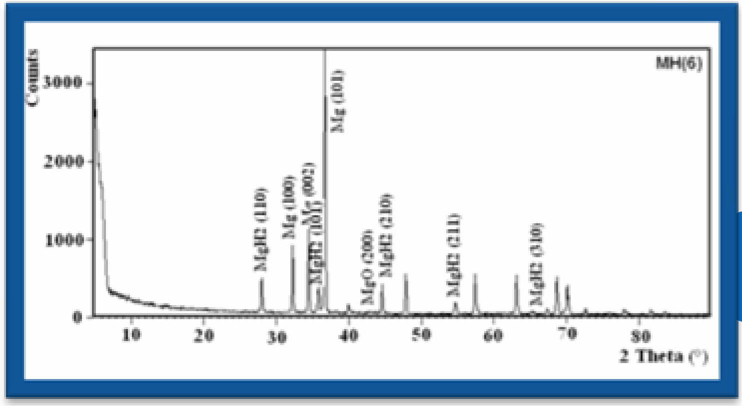


MH (5)	Mg_{THF}	26	100	24
MH (6)	Mg_{THF}:$CrCl_3$	26	100	24

MH(6) obtain by hydrogenation of THF treaded Mg particles in the presence of $CrCl_3$ catalyst (mole ratio of Mg:Anthracene:$CrCl_3$=100:1:1) at 100°C under an initial pressure of 24 bar. The product was filtered out, washed with THF solution and dried in a vacuum at room temperature to constant weight. MH(5) was obtained in the same way but without the addition of $CrCl_3$.

Comparison of the patterns indicate differences in main phase of the two samples and these differences were extremely clear. It is found that the reaction of hydrogenation does not occur at lower temperature in absence of catalyst. Hydrogenated at lower temperature in presence of catalyst, the intensity of (1 0 0), (0 0 2) and (1 0 1) Mg peaks reduced while characteristic peaks of MgH_2 to be formed.





CONCLUSION

1) At lower temperature catalyst effect was investigated.

Magnesium particles cannot be converted to magnesium hydride at low temperature without any catalytic effect. $CrCl_3$ improved the hydrogen storage capability of magnesium.

2) At 15 bar initial presure / 450C
Magnesim was conver to the MgH2.

We are working on the modeling the reaction parameters

SURFACE MODIFICATION + CATALYTS

THANK YOU
FOR YOUR KINDLY
INTEREST…