

**SYNTHESIS OF MAGNESIUM HYDRIDE AND
SODIUM BOROHYDRIDE AT LOW
TEMPERATURES**

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**by
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ABSTRACT

SYNTHESIS OF MAGNESIUM HYDRIDE AND SODIUM BOROHYDRIDE AT LOW TEMPERATURES

In this study, experimental conditions for production of magnesium hydride and sodium borohydride by low temperature grinding are investigated. In the first set of experiments, it was attempted to confirm the information presented in the literature that magnesium hydride could be produced by heating at 350°C for 24 hours under 10 atmospheres of pressure. The results obtained in this study indicated that even a higher temperature heating at 400°C under 10 bar hydrogen pressure was insufficient for magnesium hydride formation.

Heating and grinding time were selected as the most effective parameters by which a full-factorial experimental design methodology was implemented. Statistical analysis results indicated that a combination of grinding and a 50°C heating was most effective. Hence, grinding was identified as the most significant factor effect on the production of magnesium hydride.

Two different mills were used, in this study, and it was found that disc mill was more effective than ball mill. Different combinations of dehydrated borax, sodium carbonate, magnesium, hydrogen gas, sodium hydride and sodium metaborate were tested without success to produce sodium borohydride. In the final set of experiments, sodium borohydride could be successfully produced by using trimethyl borate and sodium hydride in a disc mill at 50°C under 10 bars hydrogen pressure.

ÖZET

DÜŞÜK SICAKLIKLARDA MAGNEZYUM HİDRÜR VE SODYUM BORHİDRÜR SENTEZİ

Düşük sıcaklıklarda magnezyum hidrür ve sodyum borhidrür üretebilmek için yeni bir metot geliştirilmeye çalışıldı. Düşük sıcaklıklarda magnezyum hidrür üretimi ile ilgili optimizasyon çalışmaları sonucunda sıcaklık için 50°C, öğütme zamanı için 24 saat ve öğütme için 7,5 cm çapında öğütücü diskin en uygun koşulları sağladığı belirlendi.

Magnezyum hidrür sentezi için yapılan ön deneylerde 200- 400°C arası sıcaklık değerleri, 8-24 saat arası zaman aralıkları ve 10 bar hidrojen basıncı denendi. Literatürde magnezyum hidrür sentezi için gerekli minimum hidrojen basıncının 10 bar olması ve laboratuvar koşullarının en fazla 10 bar hidrojen basıncına izin vermesi sebebiyle tüm deneylerde hidrojen basıncı 10 barda sabit tutuldu. Ancak alınan sonuçlarda verimlerin çok düşük olması nedeniyle öğütme faktörünün magnezyum hidrür sentezi üzerine etkisi araştırıldı ve en etkili öğütme ortamının 7,5 cm çapında diskle öğütme yapan diskli değirmen olduğu saptandı.

Sodyum borhidrürden sentezi için, bilyeli değirmende ve diskli değirmende yapılan, başlangıç maddeleri olarak susuz boraks, sodyum karbonat, metalik magnezyum, hidrojen gazı ve susuz boraks, sodyum karbonat, sodyum hidrür kullanılan iki ayrı deney metodunun XRD analizleri sonucunda sodyum borhidrür saptanamadı. Başlangıç maddesi olarak boraks, sodyum hidroksit, su ve magnezyumun kullanıldığı deney metodunun birinci aşamasında, elde edilmesi gereken susuz sodyum metaborat, uygun verimle elde edildi. Ancak susuz sodyum metaborat, magnezyum ve hidrojen gazı basıncı altında gerçekleştirilen ikinci aşama sonunda gözlemeyi beklediğimiz magnezyum oksit ve sodyum borhidrürden sadece magnezyum oksit belirlendi.

Son olarak sodyum hidrür ve trimetil boratın 50°C'da diskli değirmende öğütülmesiyle yapılan 8 ve 16 saatlik deneylerin XRD analizleri sonucunda sodyum borhidrür sentezlendiği saptandı.

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CHAPTER 1

INTRODUCTION

1.1. Hydrogen Storage Systems

1.1.1. Hydrogen Energy

Hydrogen is the ultimate fuel. It is clean, efficient, and yields more energy per unit of weight than any other existing fuel. Because hydrogen is a major component of water and of hydrocarbons, it is in abundant supply “(Ovshinsky 2003)”.

Hydrogen is an energy carrier, an indirect source of energy, not a resource itself. In spite of this, hydrogen was at first foredetected as a substitute energy form, in particular to substitute coal, natural gas, oil, and any products derived from them. The reserves of fossil energy, in particular oil, are limited. This led to the belief that hydrogen could soon be used economically as a substitute energy form. The economic viability of the energy carrier hydrogen is enhanced by price advantage in transport over large distances and the possibility of energy storage. Hydrogen for use as a universal energy carrier can be generated by using all possible primary energy sources. Coal, nuclear energy including fusion (although still undeveloped), and solar energy have been named.

In addition to economic reasons for the introduction of new energy sources and new energy carriers, ecological reasons are becoming increasingly important, for example:

The increasing carbon dioxide content of the atmosphere, caused by the use of fossil energy sources and other human activities such as destruction of the tropical rain forests are predicted to lead to extensive climatic changes, e.g., a slow warming up of the atmosphere and the oceans, and melting of pole caps “(Bockris 1980)”. Because of the natural fluctuations in the climate this theory has not been proven beyond doubt. In particular, little is known about compensation effects.

Well-known scientists have been demanding for years (without success) that a "low-risk strategy" for the use of fossil resources should be followed “(Bach et al. 1980)”. The utilization of the energy carriers coal, oil (in the form of gasoline, diesel,

kerosene, etc.) and natural gas leads to emissions of sulfur dioxide, nitrogen oxides and hydrocarbons. In Europe, this has already led to the destruction of extensive wooded areas and to damage of the rest of the forests. The use of hydrogen as an energy carrier coupled with suitable utilization techniques could become particularly important for environmental protection.

Hydrogen competes with the conventional energy carriers hydrocarbons (methane, LPG, gasoline, etc.), coal, and electric power. Further energy carriers are those recovered from regenerable sources and from refuse: biogas, alcohols, and vegetable oils. For the suitability of an energy carrier, the following aspects are important: conversion efficiency of the primary energy carrier to the final use, availability, ease of storage, safety, and ecological and economic evaluation “(Ullmann 2002)”.

1.1.2. Hydrides

The hydrides are a large group of compounds with diverse structures and bonding types. They may be divided into four classes according to their bonding character:

- 1) Ionic hydrides
- 2) Polymeric covalent hydrides
- 3) Volatile covalent hydrides
- 4) Metallic hydrides.

The borders between the classes is not sharp; they merge into each other according to the electronegativities of the elements concerned. Arranging the binary hydrides as in the periodic table, the *ionic hydrides* are detected to be formed by the strongly electropositive alkali and alkaline earth metals. Beryllium hydride, which is partly covalent in character, is an exception. The elements that form *polymeric covalent hydrides*, apart from beryllium, belong to Groups 12 (zinc) and 13 (boron). Boron occupies a special position. It forms numerous volatile hydrides with unusual structures. The hydrides of Group 13 are electron deficient; saturation is achieved in the complex hydride ions such as BH_4^- and AlH_4^- . The covalent hydrides formed by the elements of groups 14 – 17 (carbon – fluorine) are characterized by high volatility. The polarity of the element – hydrogen bond changes with increasing electronegativity of

the elements. Whereas the hydrides of the metallic elements and of silicon contain hydridic (negatively polarized) hydrogen, those of the nonmetals contain acidic hydrogen, sometimes strongly so. The latter are not regarded as hydrides in the usual sense and are not discussed in the present article. Metallic hydrides are formed by the transition metals, the lanthanides, and the actinides. The structures of these hydrides are fundamentally similar to those of metals. The compositions of the metallic hydrides can vary and are frequently nonstoichiometric. Another class of hydrogen compounds, the transition metal hydride complexes, is becoming important. In these molecular complexes the hydrogen atoms are covalently linked to a transition metal. Economically, the most important hydrides are those of the alkali and alkaline earth metals and the complex hydrides of boron and aluminum. These are mostly produced in tonnage quantities and have a wide range of applications “(Ullmann 2002)”.

1.1.3. Metallic Hydrides

Hydrogen reacts with many metallic elements and alloys providing a range of metallic hydrides to choose for hydrogen storage. In general, the formation of metallic hydrides involves the dissociative chemisorption of H_2 onto the metal surface and then hydrogen atom diffusion into the crystal lattice. The formation of metallic hydrides is typically exothermic and hydrogen desorption from the hydrides can be achieved under certain temperature and pressure conditions. Over the years a number of alloys/intermetallics have been designed for a variety of applications. For mobile applications, the hydride should possess good hydriding/dehydriding properties, optimum kinetics at reasonably low temperatures (25- 100°C) and should undergo numerous thermal cycles. Metallic hydrides can be broadly classified into three categories: classical/interstitial, chemical, and complex light metal hydrides “(Chandra et al. 2006)”.

1.1.3.1. Classical / Interstitial Metallic Hydrides

Several intermetallics of AB_2 , A_2B , AB , and AB_5 types form hydrides that have been used for hydrogen storage; commonly used are AB_5 hydrides, where "A" is usually a lanthanide element (atomic numbers 57- 71), Ca, or mischmetal (rare earth metal

mixture), and "B" is Ni, Co, Al, Mn, Fe, Sn, Cu, Ti, etc. The hydrogen is stored interstitially in the lattice of the heavy atoms. These classical hydrides are remarkable due to the fact that their hydriding properties can be fine-tuned by microalloying "A" or "B" with the listed elements. These hydrides are reversible with good kinetics and are well suited for stationary applications. Although these classical hydrides have good volumetric H, densities ($\sim 130 \text{ kg H}_2/\text{m}^3$ for LaNi_5H_6 , γ), for on-board applications they suffer from the disadvantage of having low gravimetric density (1- 2 wt.% H_2), resulting in a large weight penalty "(Chandra et al. 2006)".

1.1.3.2. Chemical Hydrides

These are commonly known hydrides with high theoretical gravimetric weight density, such as methanol- CH_3OH (8.9 wt.%), methylcyclohexane- $\text{CH}_3\text{C}_6\text{H}_{12}$ (13.2 wt.%), ammonia- NH_3 (15.1 wt.%), ammonia borane- NH_3BH_3 (6 wt.% H), and other organic compounds (capacities do not include system weight). These compounds can be used for on-board reforming for generating hydrogen (e.g., steam reforming of CH_3OH for hydrogen production). The nonreversible nature of these hydrides coupled with increased pollution concerns is disadvantageous for vehicular applications "(Chandra et al. 2006)".

1.1.3.3. Complex Light Metallic Hydrides

Until recently, the light metal aluminohydrides, termed complex hydrides (so-called alanates), such as MAIH_4 and M_3AlH_6 ($\text{M} = \text{Na, Li}$), were not considered for hydrogen storage because they were considered to be non-reversible despite their high hydrogen content. NaAlH_4 could be reversibly dehydrided by the addition of transition-metal-based catalysts. The development of catalyzed light metal hydride complexes including borohydrides (Li, Na) BH_4 , Li-N based, and magnesium-based nanocomposites is the most active area of hydrogen storage research for on-board applications "(Chandra et al. 2006)".

1.1.4. Magnesium Hydride

Magnesium and magnesium-based alloys are amongst the most attractive materials for hydrogen storage, since their hydrogen capacity exceeds all known reversible metal hydrides. Magnesium forms a hydride (MgH_2) which provides nominally 7.6 wt.% of hydrogen. In addition, the enthalpy of hydride formation is large ($\Delta H = -75$ kJ/mole) making magnesium also attractive for thermal energy storage. These features, combined with the very low cost of magnesium, suggest an excellent potential for hydrogen-related applications. However, to date magnesium hydride remains of no practical use for hydrogen storage. The main reason is that the reaction for hydrogenation/dehydrogenation is very slow and occurs only at very high temperatures. In practice both absorption and desorption of hydrogen require a temperature of at least 350- 400°C and even then only occur over a time scale of hours. The pressure of hydrogen gas in equilibrium with magnesium hydride is low (1 bar at about 280°C) and therefore thermodynamically the hydride should form readily at room temperature. However, this never occurs in practice because of kinetic limitations. There are several factors that significantly reduce the rate of hydrogenation. One of them is the oxidation of magnesium surface and/or formation of magnesium hydroxide. Magnesium oxide forms easily on a Mg surface exposed to air. Usually oxide layers on the metal surface are not transparent to hydrogen molecules so that an MgO layer prevents hydrogen molecules from penetrating into the material “(Manchester and Khatamian 1988)”. To initiate hydrogen absorption the oxide layer on magnesium must be perforated or cracked, which is the essence of activation. Annealing causes cracking of the oxide layer and as a result bare metal surfaces are exposed to hydrogen. Activation usually consists of high-temperature cycling and most probably takes advantage of the different thermal expansion coefficient of magnesium and magnesium oxide at high temperatures. The oxide layer on a magnesium surface cracks only if the temperature of annealing exceeds 400°C. In addition, annealing at temperatures higher than 350°C causes magnesium hydroxide to decompose. Thus activation of magnesium consists of several cycles annealing at 400°C in vacuum and in hydrogen, followed by annealing for several hours at 400°C in vacuum “(Liang et al. 1995)”. However even after this procedure, hydride formation required the Mg to be exposed to hydrogen at 30 bar and at 400°C for several hours “(Liang et al 1995)”. Another reason for the very slow hydrogenation rate of magnesium (even after

activation) is the limited dissociation rate of hydrogen molecules on the metal surface “(Schlapbach 1992)”. A clean surface of magnesium is not active for the dissociation of gaseous hydrogen “(Zaluska et al. 1998)”.

The nucleation rate of magnesium hydride is dependent on hydrogen pressure. High hydrogen pressure increases hydrogenation rate by increasing the thermodynamic driving force of the reaction, but only up to a point. For pressures higher than about 30 bars, the absorption rate is again reduced. This effect occurs when initial hydrogenation is relatively fast and leads to the formation of a “surface shell” of magnesium hydride which blocks further hydrogen uptake. At this point hydrogenation is limited by the growth of the hydride. Although in general growth has been found to be faster than nucleation, growth limitations are usually responsible for reducing the final hydrogen capacity. Studies on hydrogenation kinetics showed that growth is controlled by diffusion of hydrogen atoms, which is very slow throughout magnesium hydride. Further experiments indicated that the growth is controlled by a slow migration of the interface between the hydride and magnesium, in particular by hydrogen diffusion along the hydride-metal interface and not throughout the hydride layer. In any case, hydrogenation of magnesium is normally almost impossible to complete, even at very high temperatures and pressures. It has also been observed that hydrogen uptake declines when the hydride nuclei start to coalesce on the magnesium surface to form a compact hydride layer and that the hydrogenation reaction diminishes completely when the hydride layer exceeds 30- 50 μm . For kinetic reasons the remaining magnesium cannot be further hydrogenated “(Zaluska et al. 1998)”.

The formation of a hydrogen-absorbing material by mechanical milling under hydrogen atmosphere simultaneously produces hydrogen uptake, mechanical deformation, defect formation and surface formation. These structural modifications can lead to the formation of metastable phases, refinement of the microstructure into the nanometer range, extension of solubility limits, development of amorphous phases. These effects produce important changes in the hydrogen-absorption and desorption properties. In order to understand the structural changes that occur during RMA (reactive mechanical alloying), the known phase of the system Mg-H should be analyzed first. The temperature-composition diagram of the Mg-H system consist of a hcp α -phase (interstitial solid solution) and a β -phase with tetragonal structure and a stoichiometric nominal composition of MgH_2 . When the tetragonal β - MgH_2 phase is subjected to high compressive stress, it partially transforms into the metastable

orthorhombic γ -phase. The transition $\beta \rightarrow \gamma$ was also observed at a pressure of 2.5 GPa. Both phases coexist up to a pressure of 8 GPa. The metastable γ phase reverts exothermically to the tetragonal β -phase by heating at 350°C, as measured by DTA between 300 and 350°C. Another metastable MgH_2 phase, the hexagonal (pseudocubic) δ -phase, has been observed after treatment of the β -phase at 2.8 to 8 GPa and 650 to 800°C. The thermal study of on a $\beta \rightarrow \delta$ - MgH_2 mixture showed an endothermic effect between 350 and 400°C. This effect was attributed either to $\delta \rightarrow \gamma$ or to $\delta \rightarrow \beta$ phase transitions “(Gennari et al. 2001)”.

1.1.4.1. Properties of Magnesium Hydride

Pure magnesium hydride is a white, nonvolatile powder. Although its properties are predominantly salt-like, it shows signs of a transition towards the covalent polymeric hydride structure of compounds such as beryllium and aluminum hydride. Its enthalpy of formation and thermal stability are considerably lower than those of the homologous calcium hydride. Magnesium hydride decomposes without melting at 280 °C. Its reactivity depends on the method of preparation. The product obtained by direct synthesis from the elements is stable in air. Nevertheless, if it is prepared by pyrolysis of dialkyl magnesium or by reaction of lithium aluminum hydride with dimethyl magnesium, the product is very pure and finely divided and ignites spontaneously on contact with air “(Ullmann 2002)”.

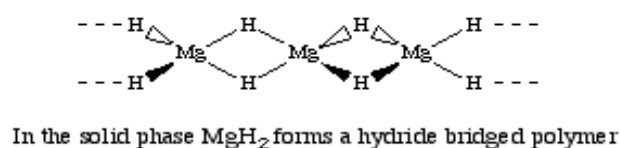
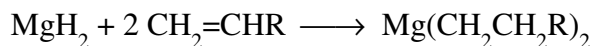


Figure 1.1. Solid Phase Form of MgH_2

1.1.4.2. Uses of Magnesium Hydride

Magnesium hydride contains a high proportion of hydrogen (7.65 wt%), which can be liberated by heat. The catalytically produced compound displays rapid rates of hydrogenation and dehydrogenation and it is therefore of interest as a hydrogen

reservoir. The high activity of catalytically produced magnesium hydride also enables it to take part in an addition reaction with 1-alkenes to form organomagnesium compounds “(Bogdanovic 1984)”.



These dialkyl magnesium compounds have become industrially important in the production of very active Ziegler catalysts. The Mg – H₂ system can also be used for the simultaneous removal and purification of pure hydrogen from gas mixtures “(Bogdanovic 1986)”. Magnesium hydride is also used as a drying agent for organic solvents and gases and in chemical syntheses.

1.1.4.3. Production Methods of Magnesium Hydride

1) Magnesium powders with a purity of 99.95% (Size:<75 μm) are hydrogenated at 350°C under 1 MPa (10 Bar). Hydrogenation rate of 60% were formed through 24-h hydrogenation “(Li et al. 2002)”.

2) MgH₂ are prepared by hydrogenation of pure Mg powder (purity:99%) under a hydrogen pressure of 7 MPa (70 Bar) at 300°C “(Noritake et al. 2003)”.

3) MgH₂ formation require the Mg to be expose to hydrogen at 3MPa (30 Bar) and at 400°C for several hours “(Liang et al. 1995)”.

4) Magnesium metal itself is hydrated with difficulty upon contact with hydrogen of 6 MPa (60 Bar) at 400°C “(Imamura et al. 1983)”.

5) Magnesium hydride are prepared by reaction ball milling. mechanically milling magnesium under hydrogen atmosphere with an initial pressure of ~ 1 MPa (10 Bar), followed by a long-period hydrogenation at 300°C. The process are repeated for three times to achive a hydrogenation ratio of ~80% “(Wu et al. 2006)”.

1.1.5. Borohydrides

Borohydrides are well-known reducing agents. They often have quite specific uses in organic and inorganic chemistry, where they may also be the sources of H⁻ other than simple reductants. Recently they have attracted more attention as a hydrogen

storage medium due to their high hydrogen storage capability. For example, NaBH₄ contains 10.6 wt.% hydrogen which is much more than what most hydrogen storage alloys have.

1.1.6. Sodium Borohydride

NaBH₄ is a white crystalline substance, completely stable in dry air and is nonvolatile. Solid state sodium borohydride, based on metal-hydrogen complexes which react with water releasing pure hydrogen. Sodium borohydride, first synthesized and identified in 1942. It is one of the most unique speciality inorganic chemical being manufactured today.

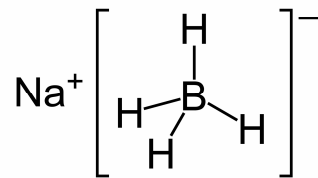
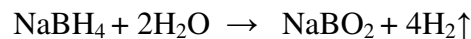


Figure1.2. Structure of NaBH₄

NaBH₄ contains hydrogen which is much more than what most hydrogen storage compounds have. Furthermore, the hydrolysis of sodium borohydride is of interest in hydrogen generation because half of the generated hydrogen is from the borohydride and the other half is from water. NaBH₄ can generate 10.8 wt.% of hydrogen based on the following hydrolysis reaction.



Its hydrogen generation rate, when using some catalysts, is rather high at room temperature compared with the hydrogen desorption rate of metal hydrides “(Li et al. 2003)”.

1.1.6.1. Physical and Thermodynamic Properties of Sodium Borohydride

Table 1.1. Thermodynamic Properties of Sodium Borohydride
(source: Wade 1980)

	Function	Value
Free Energy of Formation	ΔF°_{298}	-30.1 kcal/mole
Head of Formation	ΔH°_{298}	-45.53 kcal/mole
Entropy	S°	+24.26 cal/mole
Heat Capacity	C°_p	+20.67 cal/mole
Free Energy of Ionization	ΔF°_{298}	-5660 cal/mole
Borohydride Ion, $BH_4^-(aq)$		
Free Energy of Formation	ΔF°_{298}	+28.6 kcal/mole
Head of Formation	ΔH°_{298}	+12.4 kcal/mole
Entropy	S°_{298}	+25.5 cal/mole
Hydrolysis		
$BH_4^- + H^+ + 3H_2O(l) = H_3BO_3 + 4H_2(g)$	ΔF°_{298}	-88.8 kcal/mole
Oxidation		
$BH_4^- + 8OH^- = B(OH)_4^- + 4H_2O + 8e^-$	ΔF°_{298}	-228.9 kcal/mole
	E°_{298}	+1.24 volts

Table 1.2. Selected Physical Properties of Sodium Borohydride
(source: Wade 1980)

Property	
Formula	NaBH ₄
Molecular Wt	37.84
Purity	97+%
Color	White
Crystalline Form (anhydrous)	Face centered cubic a=6.15 A.U.
(dihydrate)	Exists below 36.4°C.
Melting Point	505°C. (10 atm. H ₂)
Thermal Stability	Decomposes above 400°C. in vacuum Will not ignite at 300°C. On hot plate Ignites from free flame in air, burning quietly
Density	1.074 g/cc.

1.1.6.2. Solubility of Sodium Borohydride

The solubility of sodium borohydride in water, the most commonly used solvent, has been accurately measured at different temperatures. 36.4°C is the equilibrium temperature of the two crystal forms NaBH₄ and NaBH₄·2H₂O. Below 36.4°C represents the solubility of the dihydrate, and above 36.4°C the solubility of anhydrous NaBH₄ “(Wade 1980)”.

1.1.6.3. Stability of Sodium Borohydride

Sodium borohydride is very stable thermally. It decomposes slowly at temperatures above 400 °C in vacuum or under a hydrogen atmosphere. Sodium borohydride absorbs water rapidly from moist air to form a dihydrate which decomposes slowly forming hydrogen and sodium metaborate. Decomposition in air is therefore a function of both temperature and humidity “(Wade 1980)”.

1.1.6.4. Chemical Properties of Sodium Borohydride

1.1.6.4.1. Organic Reductions of Sodium Borohydride

The first commercial uses for sodium borohydride were for the reduction of organic compounds containing carbonyl groups. Classical techniques for accomplishing these reductions have been developed.

Sodium borohydride attacks the carbon atom which has the largest positive charge. Because of this, any substituent which increases the fractional positive charge on the carbonyl carbon atom will increase the rate of reduction. If the fractional positive charge is decreased by substituents then the rate is slowed down.

Sodium borohydride is an attractive reducing agent for organic substrates because of its convenience as well as its selectivity and efficiency. The general techniques of its use are by now well known to the practitioner of organic synthesis, who also knows that modifications are sometimes dictated by the properties (solubility, thermal stability, pH sensitivity) of the material being reduced “(Wade 1980)”.

1.1.6.4.2. Reaction of Sodium Borohydride with Water

The reaction of sodium borohydride with water $\text{NaBH}_4 + 2\text{H}_2\text{O} \rightarrow \text{NaBO}_2 + 4\text{H}_2$ is of enormous practical importance. If this hydrolysis reaction occurs in competition with the reduction of an organic or inorganic compound, borohydride obviously is wasted and its utilization efficiency is lowered. On the other hand, sodium borohydride is a remarkably concentrated source of hydrogen. One gram,

dissolved in water will release 2.37 liters of molecular hydrogen. Important industrial use is made of this property.

Factors which control the rate of hydrolysis include concentration of BH_4^- , concentration of NaOH or base (pH) and temperature. The effect of these variables on the rate of hydrolysis has been extensively studied.

The times for complete hydrolysis of sodium borohydride solutions in water at 25°C which have been buffered at various pH's are shown in Table 1.3.

Table 1.3. NaBH_4 Hydrolysis Time vs pH
(source: Wade 1980)

pH	NaBH_4 Completely Hydrolyzed in
4.0	0.02 sec
5.0	0.22 sec
6.0	2.2 sec
6.25	3.9 sec
6.5	7.0 sec
6.75	12.4 sec
7.0	22.1 sec
8.0	3.7 min
9.0	36.8 min
10.0	6 hr 8 min

1.1.6.5. Industrial Applications of Sodium Borohydride

1)Pharmaceutical-Fine Chemical

*Vitamin A (Retinol)

*Isohumulone

*Pentazocine

2)Process Stream Purification

3)Pollution Control

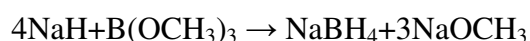
*Lead Pollution

*Mercury Pollution

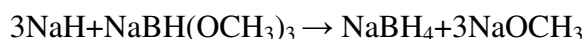
- *Silver-Cadmium from Photographic Film Manufacturers
- 4) Precious Metal Recovery
- 5) Catalyst Preparation
- 6) Magnetic Materials for Recording Tapes
- 7) Electroless Plating of Metals
- 8) Metals Coating of Window Glass
- 9) Pulp Brightening
- 10) Clay Leaching
- 11) Textile Applications–Vat Dye Reductions
- 12) Hydrogen Generation
- 13) Foamed Plastics
- 14) Hydri-pills
- 15) Preparation of Diborane and Derivatives

1.1.6.6. Production Methods of Sodium Borohydride

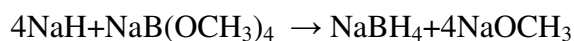
1) Sodium hydride and methyl borate in correct proportions undergo a rapid reaction at 225-275°C to produce sodium borohydride of 90-96% purity and in a yield as high as 94%, according to the equation “(Schlesinger et al. 1952)”.



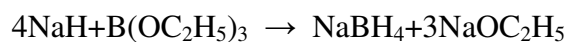
2) Reaction of Sodium Hydride with Sodium trimethoxy borohydride -Reaction at 250-270 °C and there maintained for 30 minutes. The crude product is extracted with isopropylamine. The product analysed 89% sodium borohydride, and the yield is 78% “(Schlesinger et al. 1952)”.



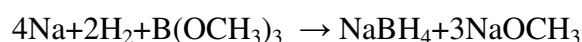
3) Reaction of Sodium Hydride with Sodium Tetramethoxyborohydride – Experiments and results are quite similar to trimethoxyborohydride. Sodium borohydride yield of 66% with 91% purity is obtained “(Schlesinger et al. 1952)”.



4) The methyl borate may also be replaced by higher esters, such as ethyl and n-butyl borate “(Schlesinger et al. 1952)”.

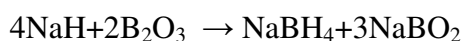


5) At higher temperatures (225-275°C) and with sodium, hydrogen and methyl borate in the approximate proportions:



Sodium borohydride is formed. The yields are relatively low, %15 “(Schlesinger et al. 1952)”.

6) At higher temperatures (330-350°C), sodium hydride and boric oxide react to produce up to 60% yields of sodium borohydride by the following reaction,

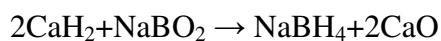


96% purity sodium borohydride is obtained “(Schlesinger et al. 1952)”.

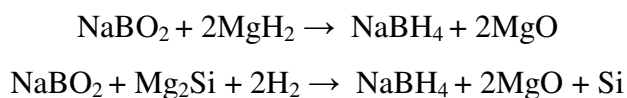
7) Sodium borohydride can also be synthesized by heating a mixture of dehydrated borax, quartz and sodium metal under hydrogen gas to higher temperatures of 450-500°C through the following reaction “(Schubert et al. 1963)”.



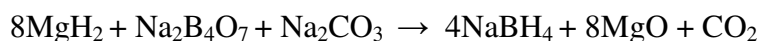
8) Besides sodium hydride, calcium hydride has been used to react with NaBO₂ to prepare NaBH₄ in the same temperature range “(Goerring et al. 1956)”.



9) Sodium borohydride is synthesized by reacting sodium metaborate (NaBO_2) with magnesium hydride (MgH_2) or magnesium silicide (Mg_2Si) by annealing (350-750°C) under high H_2 pressure. As the temperature and the pressure increases, the yield increases to have a maximum value (97-98%) at 550°C “(Kojima et al. 2003)”.



10) Sodium borohydride is prepared through a mechano-chemical reaction at room temperature. The mechano-chemical reaction is conducted by ball-milling a mixture of magnesium hydride, dehydrated borax and some Na compounds in a planetary ball mill at room temperature. MgH_2 is used as reducing agent to react with dehydrated borax “(Li et al. 2002)”.



1.2. Ball Milling

Ball Mills are a very efficient tool for grinding many materials into a fine powder. To use the Mill, the material to be ground is loaded into the barrel which contains grinding media. As the barrel rotates, the material is caught between the individual pieces of grinding media which mix and crush the product into a very fine powder over a period of several hours. Quite simply, the longer the Ball Mill is run, the finer powder will be. Ultimate particle size depends entirely on how hard the material you're grinding is, and how long the Ball Mill is run “(WEB_1 2006)”.

Mechanical milling is an effective technique for the preparation of fine metallic and ceramic powders and can also be used to drive a wide range of chemical reactions. Milling devices include planetary machines, attritors and vibrational mills; products include amorphous, nanocrystalline and quasicrystalline materials, supersaturated solid solutions, reduced minerals, high-surface-area catalysts and reactive chemicals “(Takacs and Suryanarayana 1996)”.

Mechanical Milling is a complex process and hence involves optimization of a number of variables to achieve the desired product phase and/or microstructure. Some

of the important parameters that have an effect on the final constitution of the powder are:

- Type of mill,
- Milling container,
- Milling speed,
- Milling time,
- Type, size, and size distribution of the grinding medium,
- Ball-to-powder weight ratio,
- Extent of filling the vial,
- Milling atmosphere,
- Process control agent, and
- Temperature of milling.

All these process variables are not completely independent. For example, the optimum milling time depends on the type of mill, size of the grinding medium, temperature of milling, ball-to-powder ratio “(Suryanarayana 2001)”.

1.2.1. Milling Process Parameters

Process parameters such as milling temperature, grinding ball diameter, ball-to-powder weight (charge) ratio, use of a process control agent, and relative proportion of the reactants seem to play an important role on the nature and kinetics of the product phase obtained by the displacement reactions. For example, a combustion reaction could be initiated during the reduction of copper oxide by iron; but the same reaction progresses gradually under slightly different milling conditions. Consequently, results from different laboratories can be effectively compared only if the exact conditions under which the reaction takes place are reported. These conditions need to be optimized for the best yield “(Suryanarayana 2001)”.

1.2.2. Temperature Rise during Milling

The intense mechanical deformation experienced by the powders leads to generation of crystal defects and this plus the balance between cold welding and fracturing operations among the powder particles is expected to affect the structural

changes in the powder. Another important parameter, the temperature experienced by the powder during milling, dependent on the kinetic energy of the balls, can also determine the nature of the final powder product. If the temperature generated is high, the associated higher diffusivity (higher atomic mobility) leads to processes resulting in recovery (and recrystallization). In such a case, a stable phase, e.g., an intermetallic, would form. On the other hand, if the temperature is low, then defect recovery would be less and an amorphous (or a nanocrystalline) phase would form“(Koch 1994)”.

The temperature of the powders during milling can be high due to two different reasons. Firstly, as mentioned above it is due to the kinetic energy of the grinding medium. Secondly, it is possible that exothermic processes occurring during the milling process generate heat. But, in practice, when the temperature of the powder or the milling container is measured, it is probably due to a combination of these two factors“(Koch 1994)”.

1.3. Mechanochemical Synthesis

Mechanical Milling could be used to induce a wide variety of solid–solid, liquid–solid and even solid–gas chemical reactions.

The mechanochemical reactions are characterized by a large negative free energy change and are therefore thermodynamically feasible at room temperature. The occurrence of these reactions at ambient temperatures is thus limited by kinetic considerations alone“(McCormick 1995)”.

A characteristic feature of all solid-state reactions is that they involve the formation of product phase(s) at the interfaces of the reactants. Further growth of the product phase involves diffusion of atoms of the reactant phases through the product phase, which constitutes a barrier layer preventing further reaction. Thus, these reactions require elevated temperatures to proceed at reasonable rates“(McCormick 1995)”.

Depending on the milling conditions, two entirely different reaction kinetics are possible:

1. The reaction may extend to a very small volume during each collision, resulting in a *gradual* transformation, or

2. If the reaction enthalpy is sufficiently high, a *self-propagating combustion reaction* can be initiated.

Mechanical energy can set off chemical changes in many different situations. For example, wear of a material involves chemical processes, corrosion is influenced by lattice defects created by plastic deformation, etc. We are primarily interested in mechanochemical reactions induced by high energy ball milling. The processes taking place in a ball mill are very complex. One of our primary goals is to understand their mechanism by separating and modelling their individual components “(Takacs 1992)”.

An interesting situation is when ball milling induces a self-supporting thermal reaction in a highly exothermic system. Investigating the conditions of ignition will be a useful tool to learn about the mechanism of mechanochemical reactions in general “(Takacs 1992)”.

Ball milling can also induce chemical changes in non-metallurgical systems, including silicates, minerals, ferrites, ceramics, and organic compounds. The research area of mechanochemistry developed to study and utilize these processes. As many mechanical alloying processes involve chemical changes, the distinction between mechanical alloying and mechanochemistry is often arbitrary “(Takacs 1992)”.

1.4. Mechanism of Amorphization

The mechanism of amorphization by Mechanical Milling (MM) is not clearly understood. The early investigators assumed that the powder particles melted because of the very high rate of plastic deformation, and consequent rise in the powder temperature. Subsequent quenching of the liquid by heat conduction into the less deformed, and hence cooler, interior regions of the particles, resulted in the formation of the amorphous phase (like in RSP). However, energy input calculations and temperature measurements suggest that the temperature rise is not large enough for the powder particles to melt. Additionally, if this mechanism were to be true, the glass-forming composition ranges in mechanically alloyed and rapidly solidified alloys should be the same; but this is not true as will be shown later. Researchers now believe that amorphization during MM is not purely a mechanical process and that a solid-state reaction similar to that observed in thin films occurs during MM. During MM, however, destabilization of the crystalline phase is thought to occur by the accumulation of

structural defects such as vacancies, dislocations, grain boundaries, and anti-phase boundaries. The continuous decrease in grain size (and consequent increase in grain boundary area) and a lattice expansion would also contribute to the increase in free energy of the system. It has been reported that the stored energy during MM can be about 50% of the enthalpy of fusion, whereas by cold rolling or wire drawing it is only a small fraction of it. These defects raise the free energy of the intermetallic system to a level higher than that of the amorphous phase and consequently, it becomes possible for the amorphous phase to form. It has been reported that amorphization occurs when the strain in the slow diffusing species reaches a maximum. In the case of ordered alloys, amorphization was reported to occur when the long-range order parameter is <0.6 with a corresponding volume of expansion of about 2% “(Ermakov et al. 1981)”.

Irradiation of crystalline materials by energetic particles and electrons has been known to cause amorphization when the following criteria are obeyed:

- The intermetallic compound has a narrow or zero homogeneity range,
- The order–disorder transition temperature of the intermetallic, T_c is higher than the melting temperature, T_m ,
- The two components (elements) are separated by more than two groups in the periodic table,
- The intermetallic has a complex crystal structure, and
- The fraction of A atoms ($f_A \geq f_B$) is $\geq 1/3$.

Intermetallics have also been amorphized by MM when the above criteria were generally followed. However, there have been several exceptions to the above empirical rules (too many to be ignored). For example, compounds with reasonably wide homogeneity ranges have also been amorphized. Further, a number of compounds with $f_A=1/4$ have been made amorphous. In view of these observations, it should be realized that the above criteria may only be used as guidelines and not that if they are obeyed, amorphization will be observed “(Eckert et al. 1992)”.

1.5. Characterization of the Solid Samples

Characterization of the solid samples was carried out by using X-Ray Diffraction, Scanning electron microscopy (SEM).

1.5.1. X-Ray Powder Diffraction

X-Ray powder diffraction finds frequent use in material science because sample preparation is relatively easy, and the test itself is often rapid and non-destructive. The vast majority of engineering materials is crystalline, and even those which do not yield some useful information in diffraction experiments.

The pattern of powder diffraction peaks can be used to quickly identify materials, and changes in peak width or position can be used to determine crystal size, and texture “(WEB_2 2006)”.

1.5.2. Scanning Electron Microscopy (SEM)

Scanning electron microscopy is the best known and most widely-used of the surface analytical techniques. High resolution images of surface topography, with excellent depth of field are produced using a highly-focused, scanning (primary) electron beam. The primary electrons enter a surface with an energy of 0.5 - 30 keV, and generate many low energy secondary electrons. The intensity of these secondary electrons is largely governed by the surface topography of the sample. An image of the sample surface can thus be constructed by measuring secondary electron intensity as a function of the position of the scanning primary electron beam. High spatial resolution is possible because the primary electron beam can be focused to a very small spot (<10 nm). High sensitivity to topographic features on the outermost surface (<5 nm) is achieved when using a primary electron beam with an energy of <1 keV “(WEB_3 2006)”.

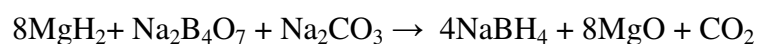
In addition to low energy secondary electrons, backscattered electrons and X-rays are also generated by primary electron bombardment. The intensity of backscattered electrons can be correlated to the atomic number of the element within the sampling volume. Hence, some qualitative elemental information can be obtained. The analysis of characteristic X-rays emitted from the sample gives more quantitative elemental information. Such X-ray analysis can be confined to analytical volumes as small as 1 cubic micron “(WEB_3 2006)”.

SEM, accompanied by X-ray analysis, is considered a relatively rapid, inexpensive, and basically non-destructive approach to surface analysis. It is often used

to survey surface analytical problems before proceeding to techniques that are more surface-sensitive and specialized “(WEB_3 2006)”.

1.6. Aim of This Work

The purpose of this work was to propose a new method for the synthesis of sodium borohydride at low temperatures. MgH_2 is used as a reducing agent to react with dehydrated borax. The sodium borohydride can be processed by the reaction as shown in the following equation.



However, magnesium hydride which is the starting material for this synthesis could not be obtained from the market, therefore metallic magnesium and hydrogen gas was used as the starting materials. Studies were also concentrated on the production of magnesium hydride.

For this purpose, several experimental procedures were tried, especially through milling. Characterization was mostly done by X-Ray powder diffraction.

CHAPTER 2

EXPERIMENTAL METHODS

2.1. Instrumentation and Apparatus

A Retsch S1000 series ball mill was used for the experiments. Emko ESM- 4410 series thermocouple was used to measure and also to control the temperature. As a reactor, we have modified our disc mill design. A 320 ml stainless steel grinding bowl with a stainless steel lid was built as a reactor. The lid has two valves for gas inlet and outlet and the cap was screwed to the main body with six screws so as not to leak hydrogen gas. A specially made copper gasket was used to prevent leakage. The grinding bowl had grooves outside to fit with specially made resistance for heating.

2.2. XRD, SEM Analysis

X-Ray powder diffraction (XRD) data were collected on a Philips X'Pert Pro diffractometer using $\text{CuK}\alpha$ radiation ($\lambda=0.154$ nm). Samples were prepared by compressing in the cassette sample holder without any adhesive substance.

SEM characterization was carried out using a Philips XL-30s FEG type instrument. Prior to analysis, the solid samples were sprinkled onto Al or C tapes which are adhesive and supported on metallic disks. Images of the sample surfaces were recorded at different magnifications.

2.3. MgH_2 Synthesis

Several procedures were tried for MgH_2 synthesis:



a. Some experiments were made by heating Mg to various temperatures under 10 bar H_2 pressure.

b. Some experiments were made by grinding Mg with a grinding disc at 100 rpm under 10 bar H_2 pressure at room temperatures.

c. Some experiments were made by putting Mg under 10 bar H₂ Pressure and grinding with a grinding disc at 100 rpm while heating.

2.3.1. Optimization of Parameters for MgH₂ Synthesis

In order to obtain accurate and reproducible results, the first part of the study was focused on the optimization of parameters for MgH₂ synthesis. Synthesis of MgH₂ is influenced by several factors such as the grinding media, temperature, H₂ pressure and grinding time effect. Variable and effective parameters were optimized.

2.3.1.1. Optimization of Grinding Conditions

The first parameter optimized was the setting of grinding materials. Since it is known that the yield of the MgH₂ synthesis is affected by Mg piece dimensions, it is important to find optimum grinding media to obtain the available optimum Mg particle dimensions. In order to increase the reaction surface, Mg pieces (Merck, 50-150 mesh) were put in the Ball Mill and ground for various time intervals with different size balls or discs.

a. Grinding was performed with the same diameter steel balls. However different size balls were used for different grinding to determine the optimum size. (all 2.5, 5, 10 or 20 mm diameter)

b. Grinding was also performed with a mixture of various diameter steel balls.

c. Grinding was performed with various size discs. (60 mm or 75 mm diameter discs)

2.3.1.2. Effect of H₂ Pressure

Hydride formation requires Mg to be exposed to a hydrogen pressure of at least 10 bar (Li 2002, Wu 2006). With our set up, we could maintain continuous 10 bar H₂ pressure. Therefore, continuously 10 Bar H₂ pressure was applied to the milling bowl either for various time intervals (8 to 24 hours) or for various grinding conditions (while grinding or not grinding) or for various temperature conditions (without heating or with heating from room temperature to 400°C).

2.3.1.3. Effect of Temperature

Various heating temperatures from room temperature to 400°C were tried for different time intervals.

In the literature, it is stated that heating up to 400°C and hydrogen pressures up to 70 bar gives good yields “(Imamura et al. 1983, Noritake et al. 2003)”. However, our experiments for heating up to 400°C and 10 bar hydrogen pressure gave very poor yields. Some good literature results up to 10 Bar and 350°C remains as a question mark for us.

2.3.1.4. Effect of Grinding Time

In our experiments various time intervals - from 8 to 24 hours - were tried for different temperatures under constant H₂ pressure (10 Bars). Only heating and H₂ pressure application was not enough for sufficient MgH₂ formation. Grinding especially with disc mill at 100 rpm increased the yield with a considerable amount.

It was rather surprising to see that grinding was more effective than heating for MgH₂ formation.

2.3.2. First Set of Experiments

Several experiments were tried for MgH₂ synthesis by heating Mg under 10 bar H₂ pressure:



During these experiments, 24 Hours heating at 200°C, 250°C, 300°C, 350°C and 400°C under 10 bar H₂ pressure was tried without grinding.

2.3.3. Experimental Design for MgH₂ Synthesis

Two main parameters showed to be very effective during the experiments. They were 1)Temperature and 2)Grinding time. Hydrogen pressure (10 bar) was kept

1) MgH_2 was not available from the market, so metallic magnesium and H_2 gas were used as starting materials instead of MgH_2 . Experiments were carried out with a ball mill at 100 rpm. Three time intervals - 8, 16 and 24 hours - were tried at room temperature. Ball diameters varied; (1 of 20mm, 3 of 10mm, 7 of 5mm, 3 of 2.5mm).



$$\text{Na}_2\text{B}_4\text{O}_7 = 10.06\text{g}$$

$$\text{Na}_2\text{CO}_3 = 5.30\text{g}$$

$$\text{Mg} = 9.72\text{g}$$

2) NaH was tried instead of H_2 gas. Experiments were carried with a ball mill at 100 rpm. Two time intervals, 8 and 16 hours were tried at room temperature. Ball Diameters; (1 of 20mm, 3 of 10mm, 7 of 5mm, 3 of 2.5mm).



$$\text{Na}_2\text{B}_4\text{O}_7 = 4.024\text{g}$$

$$\text{Na}_2\text{CO}_3 = 2.120\text{g}$$

$$\text{NaH} = 7.680\text{g}$$

2.4.2. Experiments with Disc Mill

The preliminary experiments did not give very satisfactory results with stainless steel balls, a new stainless steel disc mill with 5 cm height, and 10 cm diameter dimensions using a disk for grinding was purchased, and the experiments were carried out with this mill.

1) Experiments were carried at 100 rpm with the grinding disc. Three time intervals, 8, 16 and 24 hours were tried at room temperature and at 10 bar H_2 pressure.



$$\text{Na}_2\text{B}_4\text{O}_7 = 20.12\text{g}$$

$$\text{Na}_2\text{CO}_3 = 10.60\text{g}$$

$$\text{Mg} = 19.44\text{g}$$

2) Experiments were also carried out at two time intervals, 8 and 16 hours at 50 °C and at 10 bar H₂ pressure.



$$\text{Na}_2\text{B}_4\text{O}_7 = 20.12\text{g}$$

$$\text{Na}_2\text{CO}_3 = 10.60\text{g}$$

$$\text{Mg} = 19.44\text{g}$$

3) Experiments were carried by using NaH as the starting material. Two time intervals, 8 and 16 hours were tried at room temperature.



$$\text{Na}_2\text{B}_4\text{O}_7 = 4.024\text{g}$$

$$\text{Na}_2\text{CO}_3 = 2.120\text{g}$$

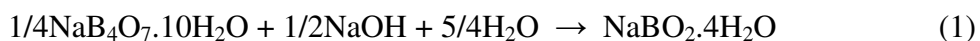
$$\text{NaH} = 7.680\text{g}$$

4) *Preparation of Anhydrous Sodium Metaborate (NaBO₂) as the Starting Material*

Experiments by using anhydrous sodium metaborate (NaBO₂) as the starting material were also carried out. The following simple processes were used to prepare the anhydrous sodium metaborate (NaBO₂):

a. From “Borax” as the abundant natural resource.

The process that starts from borax (Na₂B₄O₇·10H₂O) requires two parts of NaOH to make one part of NaBO₂. Na₂B₄O₇·10H₂O, NaOH and H₂O were put in the disc mill and grinded for 6 hours at 100 rpm for the process as given in Eq.(1);

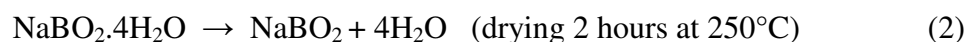


$$\text{NaB}_4\text{O}_7 \cdot 10\text{H}_2\text{O} = 19.1 \text{ g}$$

$$\text{NaOH} = 4 \text{ g}$$

$$\text{H}_2\text{O} = 4.5 \text{ g}$$

b. $\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$ is simply dried to yield anhydrous sodium metaborate as shown in Eq.(2);



Complete dehydration was accomplished with this process. Anhydrous sodium metaborate obtained, was used in the Dynamic Hydriding/Dehydriding Process to produce sodium borohydride by the reaction as shown in Eq.(3).

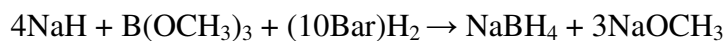


$$\text{NaBO}_2 = 6.6 \text{ g}$$

$$\text{Mg} = 4.8 \text{ g}$$

The reaction was carried out under constant temperature (250°C) and H_2 pressure (10 Bar) conditions for 8 hours. However the results were not satisfactory. Only MgO peaks were detected in the spectra but no NaBH_4 peaks.

5) Experiments were also carried by using NaH and $\text{B}(\text{OCH}_3)_3$ as starting materials. Two time intervals, 8 and 16 hours were tried for 50°C at 10 bar H_2 pressure.



$$\text{NaH} = 4.8\text{g}$$

$$\text{B}(\text{OCH}_3)_3 = 5.2\text{g}$$

CHAPTER 3

RESULTS and DISCUSSIONS

3.1. MgH₂ Synthesis

3.1.1. Optimization of Parameters for MgH₂ Synthesis

3.1.1.1. Optimization of Grinding Conditions

Aim of this study was to get smaller particles so as to obtain more and better products and to increase the yield.

From the experiments carried out, following results were deduced:

a. Grinding with same diameter steel balls but different size in each lot were used for grinding to determine the optimum size (all 2.5 or 5 or 10 or 20 mm diameter):

This procedure was not succesfull, since Mg pieces were stuck together.

b. Grinding with different diameter steel balls in the same lot:

This procedure was succesfull and approximated size Mg pieces were obtained.

c. Grinding with disc:

This procedure was more succesfull and approximated size Mg pieces were obtained. In Figure 3.1. effects of different grinding procedures are given.

3.1.1.2. Effect of H₂ Pressure

Hydride formation requires Mg to be exposed to a hydrogen pressure of at least 10 bar “(Li et al. 2002, Wu et al. 2006)”. With our set up, we could at most maintain continuous 10 bar controlled H₂ pressure therefore this pressure was used throughout the experiments.

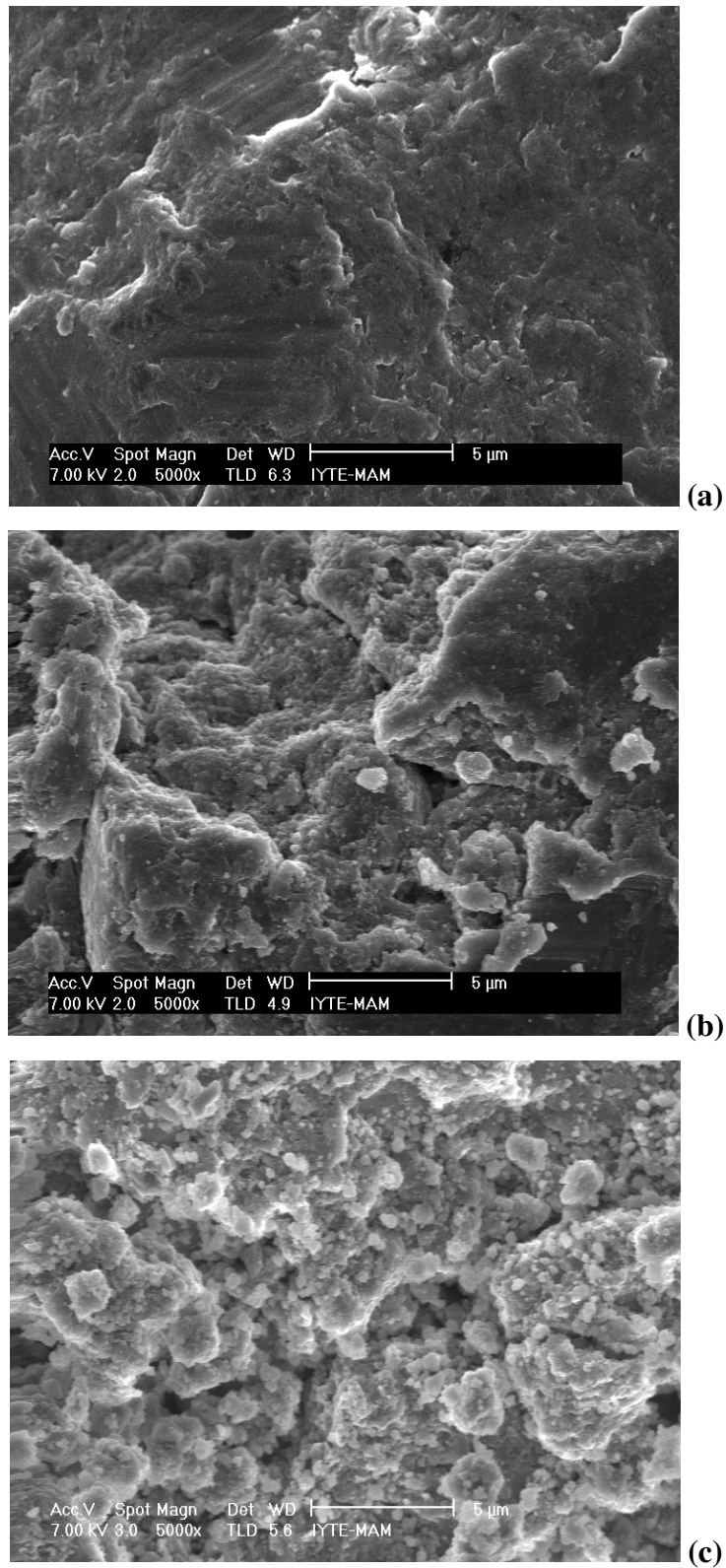


Figure 3.1. SEM back-scattered microimages of Mg at different grinding conditions
 (a): Grinding Mg with same diameter steel balls, (b): Grinding Mg with different diameter steel balls, (c): Grinding Mg with disc

3.1.1.3. Effect of Temperature

In our primary experiments, only heating under H₂ pressure, was not enough for sufficient MgH₂ formation. Our experiments up to 400°C and 10 bar hydrogen pressure gave very poor yields. Effect of temperature in our studies is given in Figure 3.2. MgH₂ formation starts after 300°C. There is a minor increase in the yield as the temperature is increased. More MgH₂ formation may be performed at even higher temperatures but NaBH₄ synthesis at high temperatures is beyond the aim of this study.

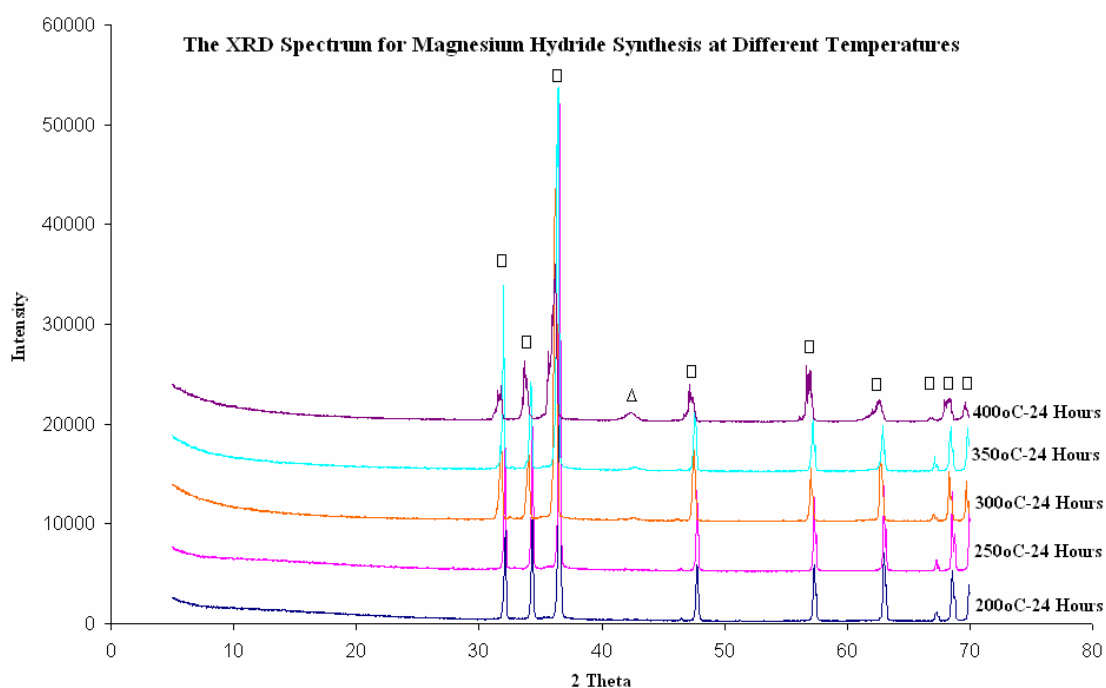


Figure 3.2. The XRD Spectra for MgH₂ Synthesis at Different Temperatures
Δ=MgH₂, □= Mg

3.3.1.4. Effect of Grinding Time

Grinding at room temperature, at 50°C and 100°C were performed for various time intervals. 8 hour grinding time was selected as optimum duration after experimental design results. Figure. 3.3 shows the results of 50 °C studies.

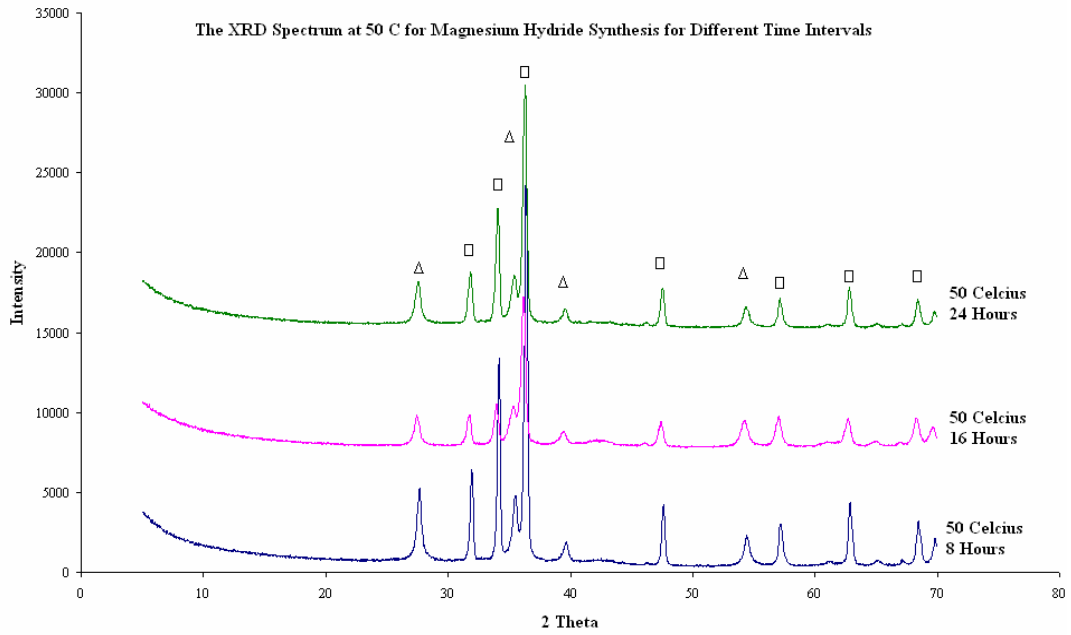


Figure 3.3. The XRD Spectra at 50 °C for MgH₂ Synthesis for Different Time Intervals Δ = MgH₂, \square = Mg

3.1.2. Experimental Design Results for MgH₂ Synthesis

To find the optimum conditions, two important parameters were selected and experiments were carried out for 3 levels. Experimental Design Results Scheme for MgH₂ Experiments are given in Table 3.1.

Table 3.1. Experimental Design Results Scheme for MgH₂ Experiments

Experiment Number	Temperature	Grinding Time	Peak Intensity Ratio I_{MgH_2}/I_{Mg}
1	1	1	0.127
2	1	0	0.078
3	1	-1	0.025
4	0	1	0.172
5	0	0	0.223
6	0	-1	0.173
7	-1	1	0.022
8	-1	0	0.017
9	-1	-1	0.016

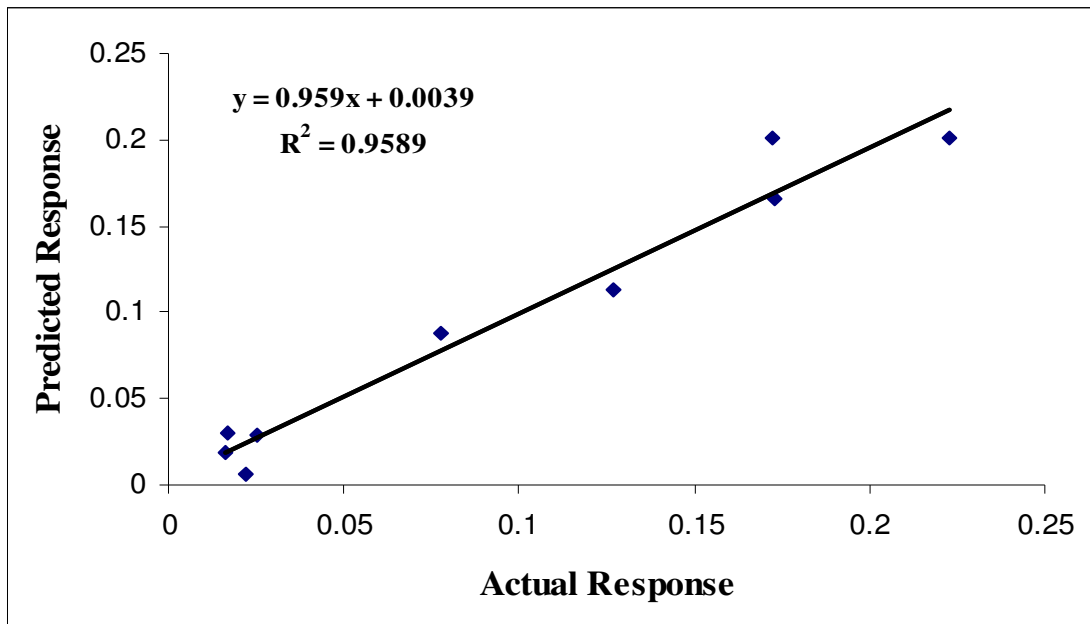


Figure 3.4. Nonlinear Model Predicted Response-Actual Response Plot

As detected from the comparison of the optimization plots of the linear and nonlinear models and also from the comparison of R^2 values which is shown in Figure 3.4. It can be predicted that the nonlinear model fits our experimental results.

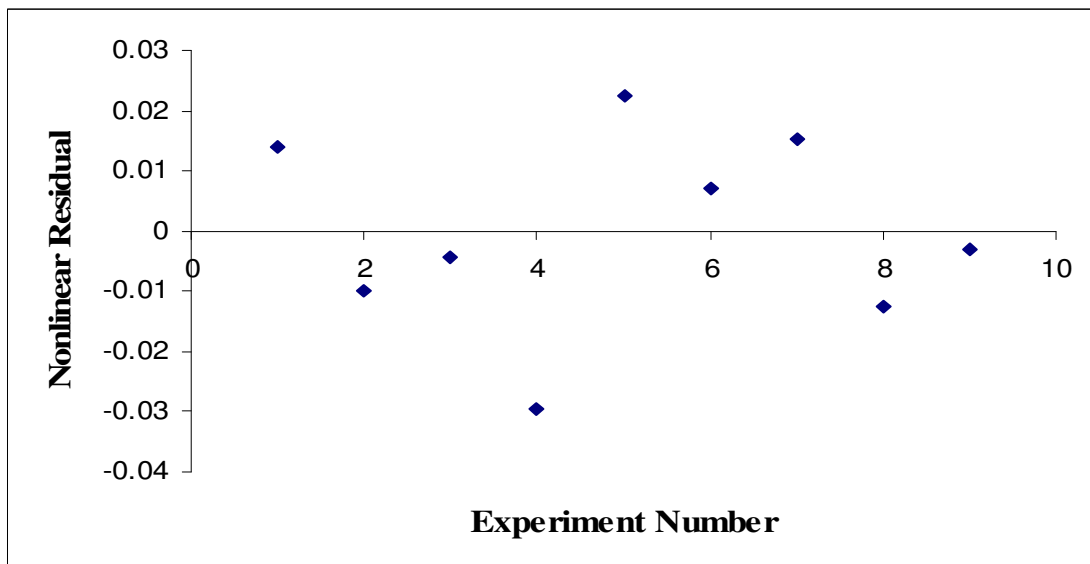


Figure 3.5. Nonlinear Model Residual-Experiment Number Plot

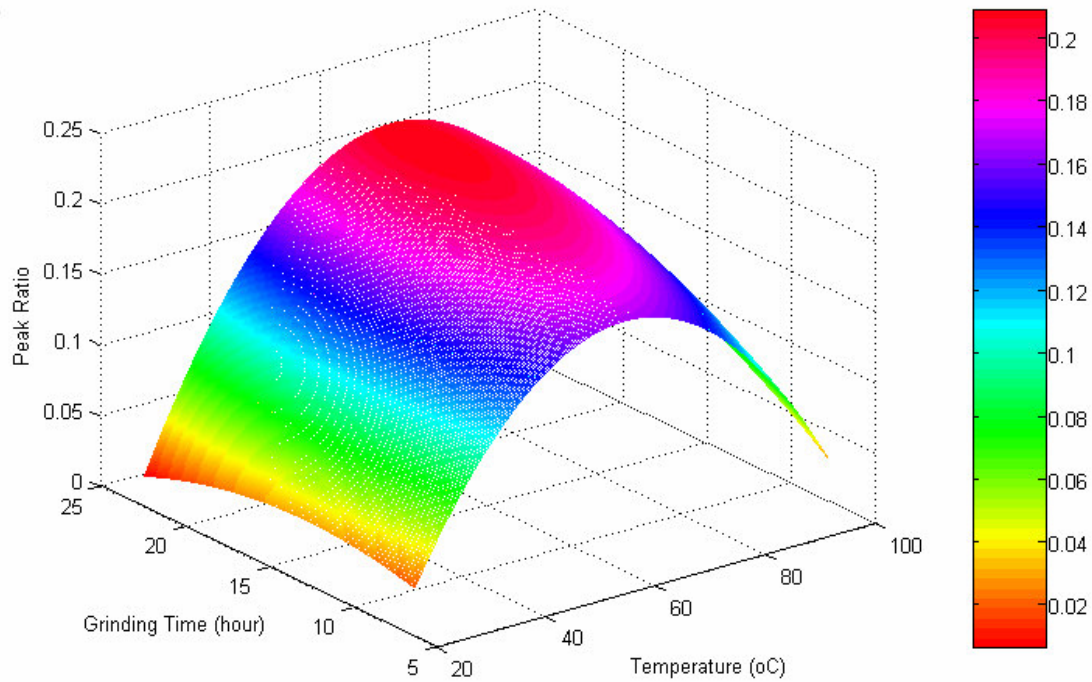
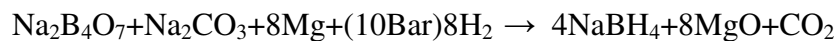


Figure 3.6. Nonlinear Model 3-D (Peak Intensity-Grinding Time-Temperature) Optimization Plot

3.2. NaBH₄ Synthesis

3.2.1. Experiments with Ball Mill

1) Metallic magnesium and H₂ gas were used as starting materials instead of MgH₂. Experiments were carried out with a ball mill at 100 rpm. Three time intervals - 8, 16 and 24 hours - were tried at room temperature.



Na₂B₄O₇, Mg and Na₂CO₃ peaks were identified in the XRD spectrum of 8 and 16 hours experiments, as detected in Figure 3.7. However Na₂B₄O₇ and Na₂CO₃ peaks disappeared in the spectrum for 24 hours experiments and NaBH₄ peaks are not present. We assume that crystallic structures of Na₂B₄O₇ and Na₂CO₃ are destroyed during 24 hours milling and they do not appear in the spectrum.

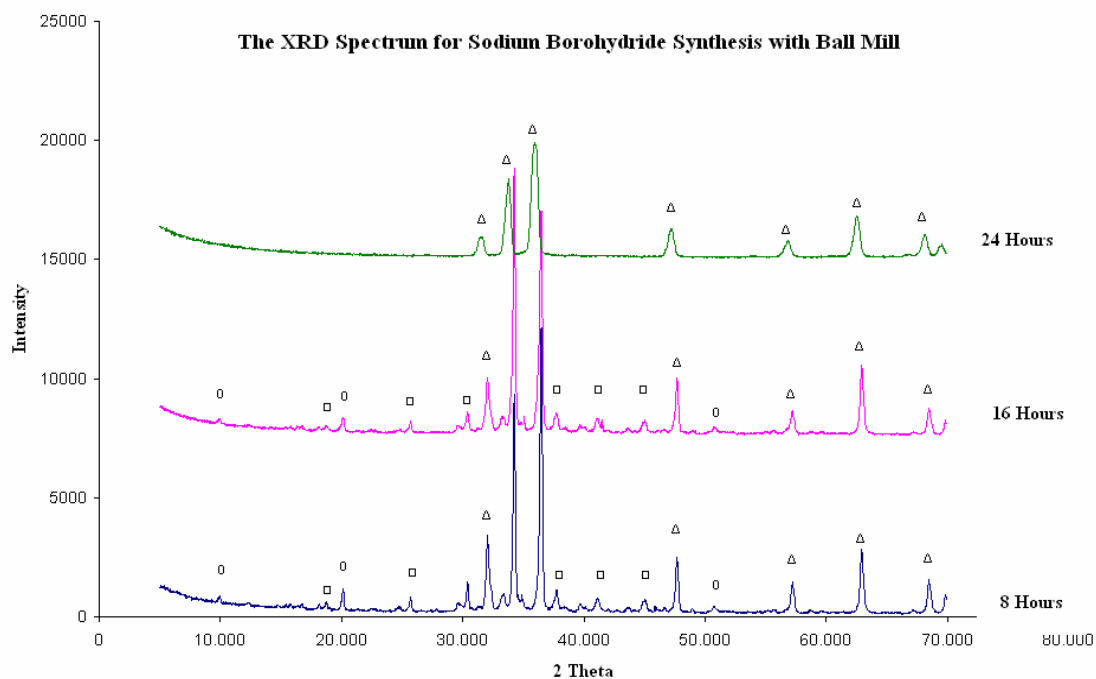


Figure 3.7. The XRD Spectra for Sodium Borohydride Synthesis Using H₂ Gas with Ball Mill at Room Temperature Δ= Mg, □=Na₂CO₃, 0=Na₂B₄O₇

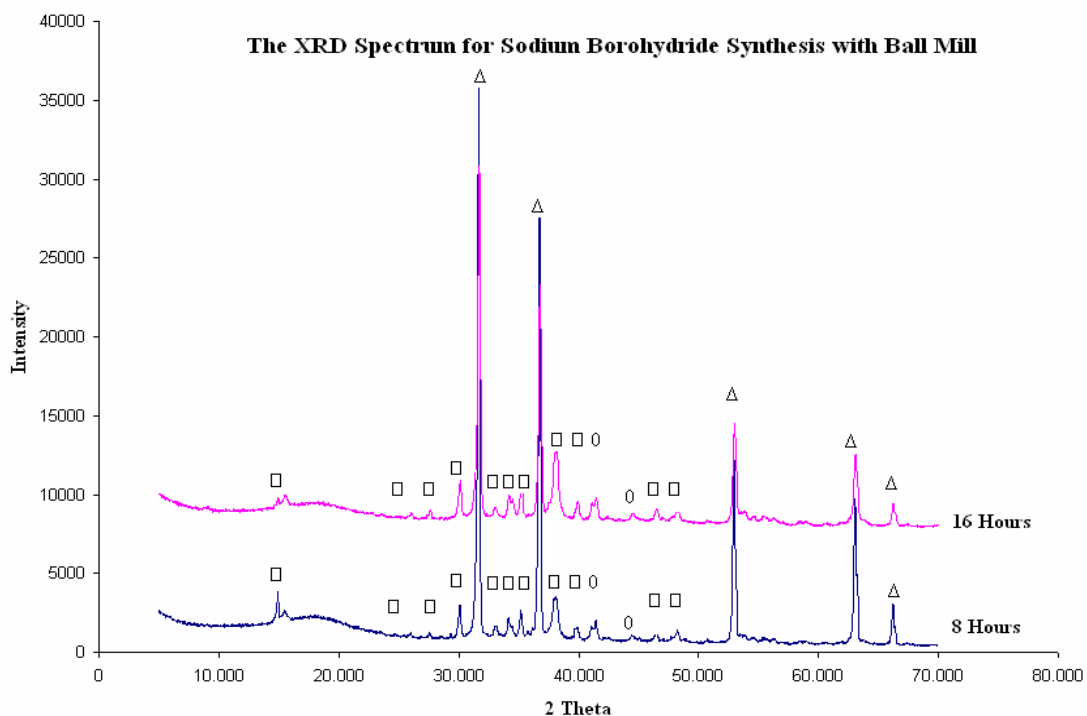
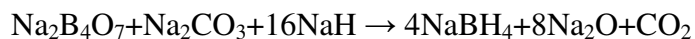


Figure 3.8. The XRD Spectra for Sodium Borohydride Synthesis Using NaH with Ball Mill at Room Temperature Δ= NaH, □=Na₂CO₃, 0=Na₂B₄O₇

2) NaH was tried instead of metallic magnesium and H₂ gas. Experiments were carried with a ball mill at 100 rpm. Two time intervals, 8 and 16 hours were tried at room temperature.



Na₂CO₃, NaH and small Na₂B₄O₇ peaks are detected at XRD spectra of 8 and 16 hours experiments which is given in Figure 3.8. Both spectra are nearly the same. No NaBH₄ peaks are observed.

3.2.2. Experiments with Disc Mill

1) Metallic magnesium and H₂ gas were used as starting materials instead of MgH₂. Experiments were carried out with a disc mill at 100 rpm. Three time intervals - 8, 16 and 24 hours - were tried at room temperature.



Mg and small Na₂CO₃ peaks were detected but Na₂B₄O₇ peaks disappeared at XRD spectrum of 8 and 16 hours experiments which is given in Figure 3.9. However Na₂CO₃ peaks also disappeared at 24 hours experiments' spectrum. No NaBH₄ peaks were detected at the XRD spectra.

2) Same experiments were carried with a grinding disc at 100 rpm. Two time intervals, 8 and 16 hours were tried for 50 °C at 10 bar H₂ pressure.



Mg and small Na₂CO₃ peaks were detected in Figure 3.10. at both XRD spectra. However Na₂B₄O₇ peaks disappeared. No NaBH₄ peaks are observed.

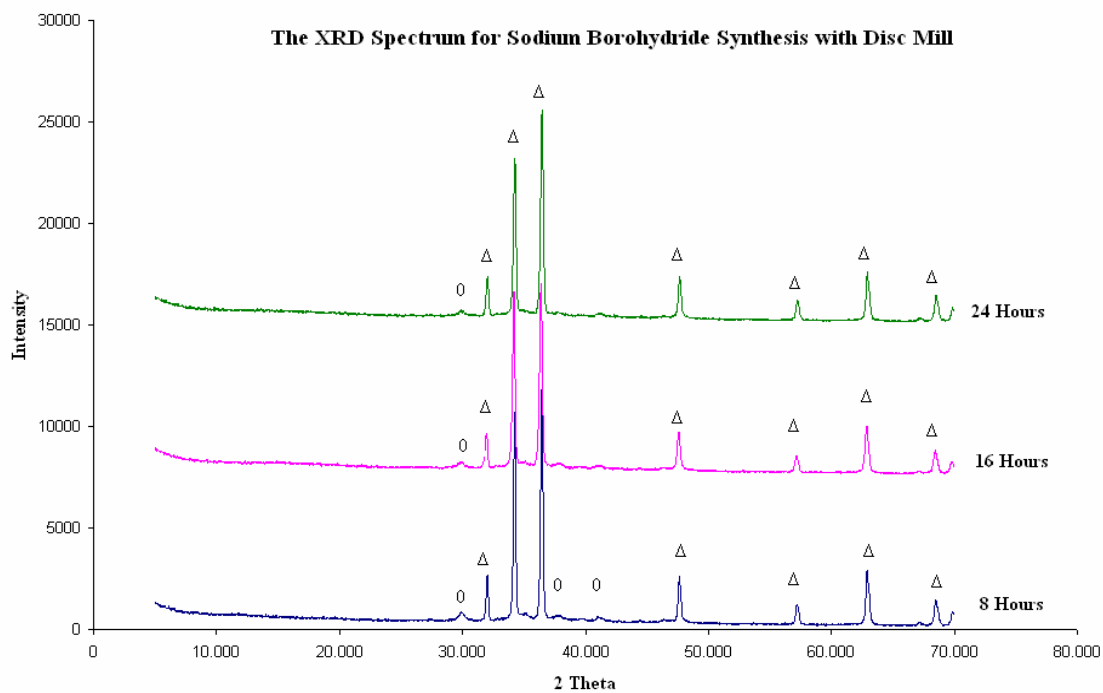


Figure 3.9. The XRD Spectra for Sodium Borohydride Synthesis Using H₂ Gas with Disc Mill at Room Temperature Δ= Mg, 0=Na₂CO₃

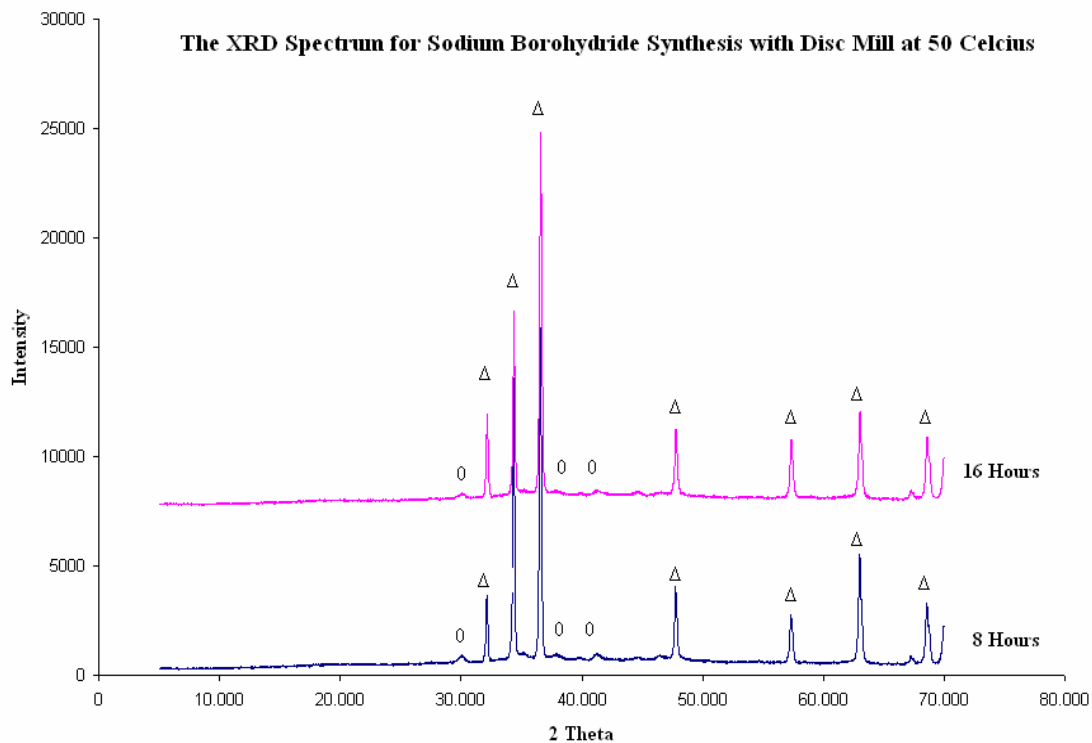


Figure 3.10. The XRD Spectra for Sodium Borohydride Synthesis Using H₂ Gas with Disc Mill at 50°C Δ= Mg, 0=Na₂CO₃

3) NaH was used as a source of H₂ gas. Experiments were carried with a grinding disc at 100 rpm. Two time intervals, 8 and 16 hours were tried at room temperature.



NaH and small Na₂CO₃ peaks were detected at both XRD spectra which are shown in figure 3.11. Na₂B₄O₇ peaks disappeared. No NaBH₄ peaks were observed.

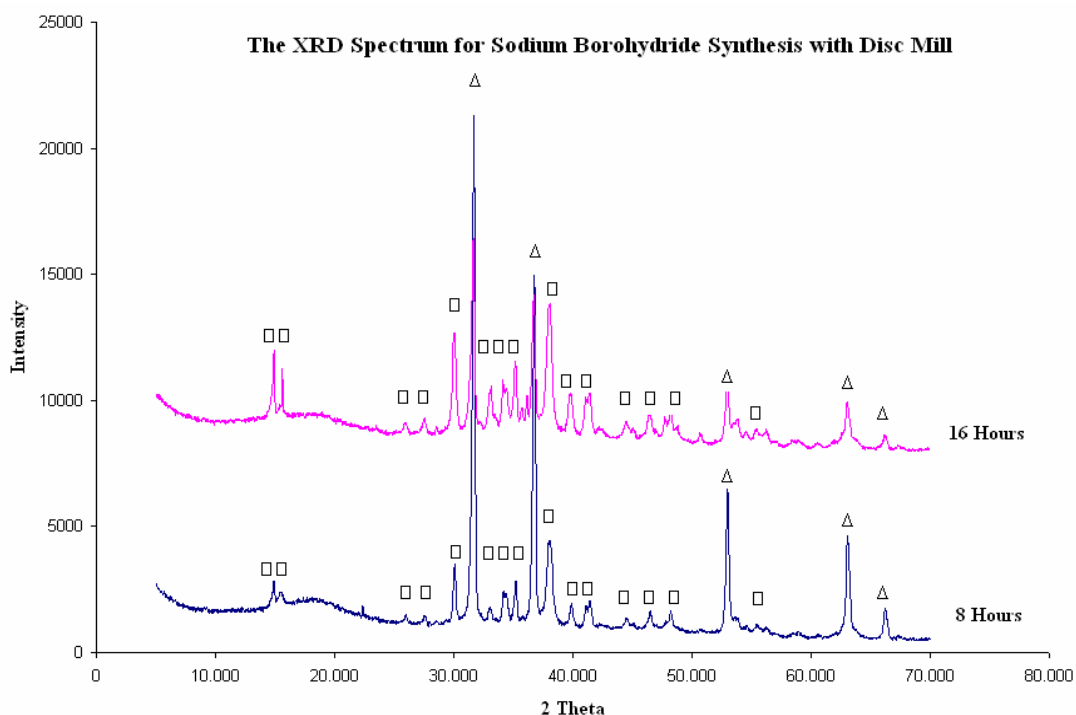


Figure 3.11. The XRD Spectra for Sodium Borohydride Synthesis Using NaH with Disc Mill at Room Temperature $\Delta = \text{NaH}$, $\square = \text{Na}_2\text{CO}_3$

4) a) The process that starts from Na₂B₄O₇·10H₂O requires two parts of NaOH to make one part of NaBO₂. Na₂B₄O₇·10H₂O, NaOH and H₂O were put in disc mill and grinded 8 hours at 100 rpm.



b) $\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$ is treated with a simple drying process to yield anhydrous sodium metaborate.

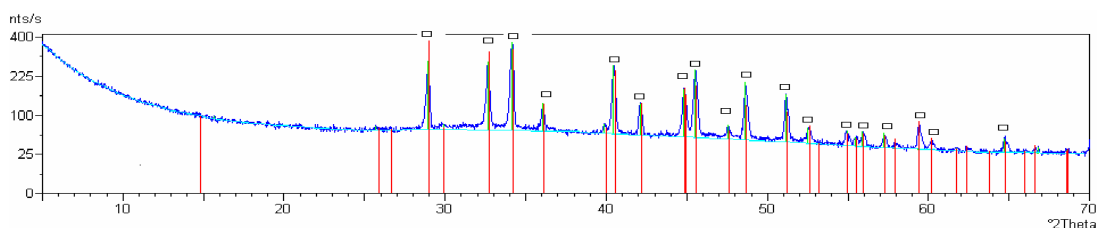
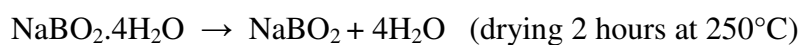


Figure 3.12. The XRD Spectrum for anhydrous sodium metaborate synthesis
 $\square = \text{NaBO}_2$

Anhydrous sodium metaborate (NaBO_2) was synthesised. Red peaks belong to the anhydrous sodium metaborate in Figure 3.12.

c) The sodium borohydride can be processed by the reaction as shown in equation, where the system is kept under constant temperature (250°C) and 10 Bar H_2 pressure conditions at 8 hours.



Small sodium borate hydroxide ($\text{Na}_2(\text{BO}_2(\text{OH}))$) and MgO peaks were detected at the XRD spectra as shown in Figure 3.13. But no NaBH_4 peaks were detected at the XRD spectra as shown in figure 3.13.

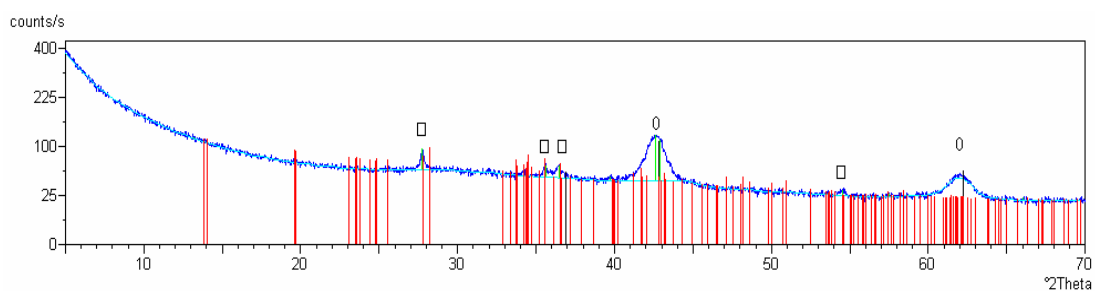
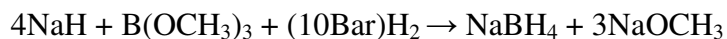


Figure 3.13. The XRD Spectrum for Sodium Borohydride Synthesis
 $\square = (\text{Na}_2(\text{BO}_2(\text{OH})))$, $\circ = \text{MgO}$

5) Experiments were carried using NaH and B(OCH₃)₃ as starting materials at 50 °C and 10 bar H₂ pressure with a grinding disc at 100 rpm. Two time intervals, 8 and 16 hours were tried.



The spectra are very different as shown in Figure 3.14. NaH, C₁₄H₈O₂ (alpha-9,10-Phenanthrenedione) and small NaBH₄ peaks appear in both spectra. NaBH₄ and C₁₄H₈O₂ peaks are more intense in the spectrum for 16 hours experiment, but NaH peaks are almost same as detected in Figure 3.14. The spectrum for 8 hours experiments has some excessive peaks. These peaks match with CaO but our samples do not contain Ca. CaO is probably an impurity from a previous XRD analysis. C₁₄H₈O₂ peaks may be due to the NaH solution because the chemical is bottled and transported in a mineral oil.

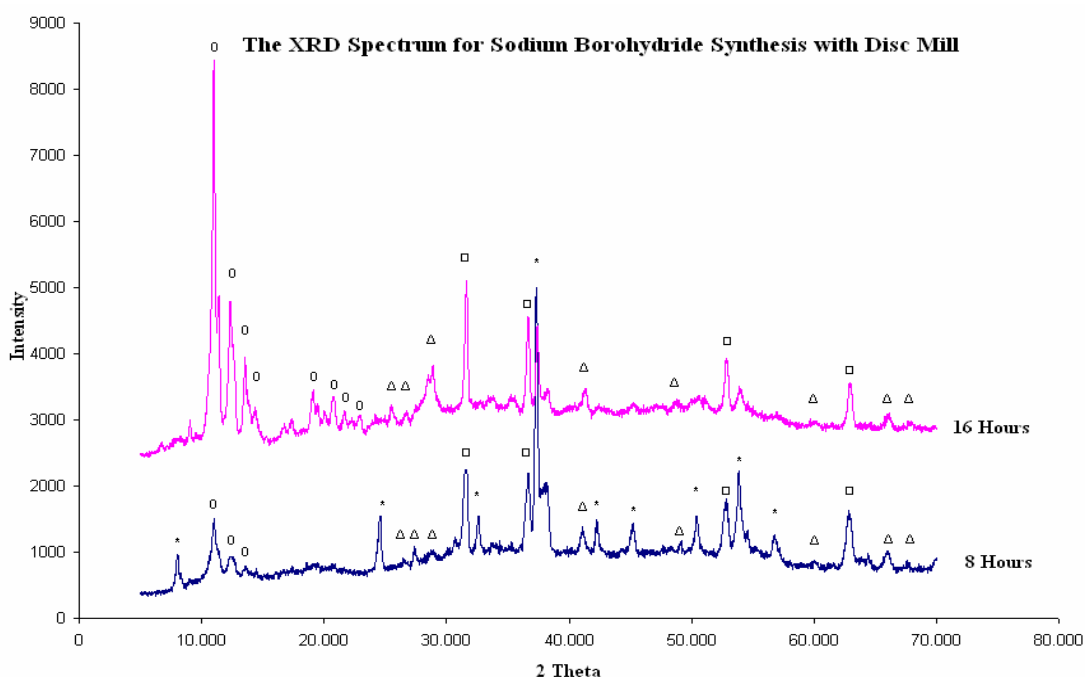


Figure 3.14. The XRD Spectra for Sodium Borohydride Synthesis Using H₂ Gas, NaH and B(OCH₃)₃ with Disc Mill at 50 °C Δ= NaBH₄, □=NaH, O= C₁₄H₈O₂, *=CaO

CHAPTER 4

CONCLUSION

The aim of this study was to develop a new method for the synthesis of sodium borohydride at low temperatures.

The most different part of this study is working at low temperatures and the more effective grinding instead of heating. In the literature studies at 50°C was not found.

Studies progressed at in two stages.

1) Experiments carried out for the production of MgH₂. Magnesium hydride which is the starting material for the synthesis of NaBH₄ could not be obtained from the market, therefore our experiments started with the production of MgH₂.

2) Experiments carried out for the production of NaBH₄.

Conclusions for MgH₂ production:

- Only heating and H₂ pressure application was not enough for sufficient MgH₂ formation.

- In the literature, it is stated that heating between 300°C to 400°C and hydrogen pressures between 10 to 70 bar “(Liang et al. 1995, Noritake et al. 2003, Wu et al. 2006)” gives satisfactory yields. Our studies for heating up to 400°C and 10 bar hydrogen pressure gave very poor yields. A literature result for 24 hours, 10 Bar and 350°C study with a yield of %60 “(Li et al. 2002)” is not consistent with our results. The only difference between this result and ours is the size of Mg particles. Their Mg powder size is stated as (<75 μm) while our starting Mg powder size was between (50 - 150 μm).

- Production of MgH₂ is possible at low grinding speeds, low temperatures and low H₂ pressures.

- Grinding is very important factor for magnesium hydride synthesis at low temperatures.

- Grinding especially with disc mill at 100 rpm increased the yield with a considerable amount.

- It was rather surprising to see that grinding was more effective than heating for MgH₂ formation. This effect is displayed in Figure 4.1.

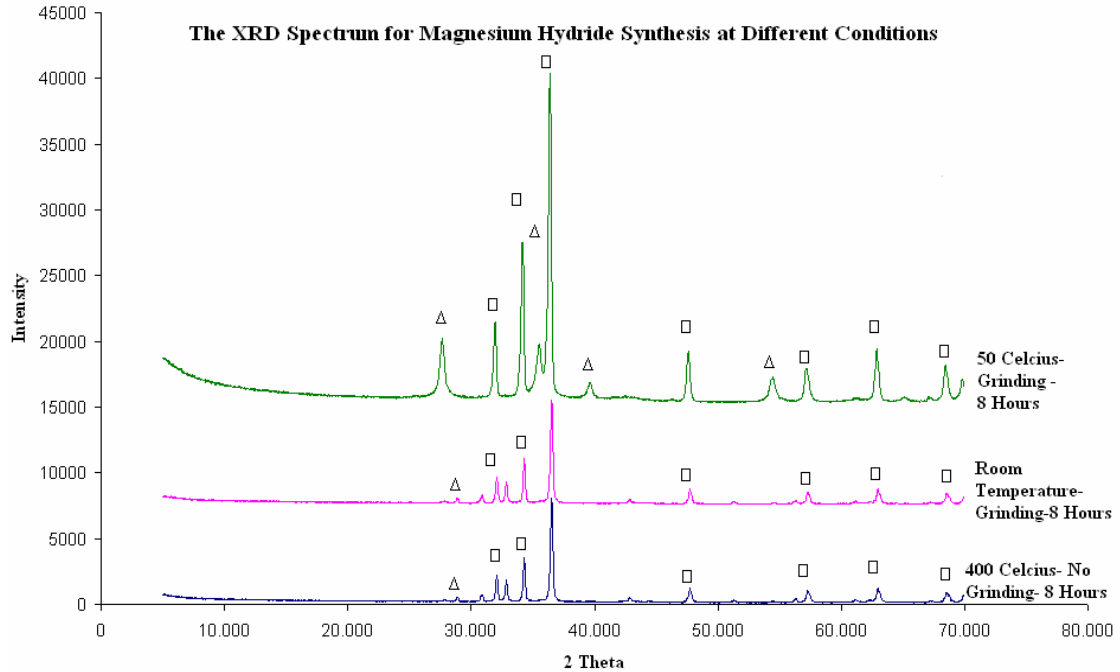


Figure 4.1. The XRD Spectra for MgH_2 Synthesis at Different Conditions $\Delta = MgH_2$, $\square = Mg$

- Most effective grinding is accomplished with a disc mill instead of ball mill. We think this is due to the big mass and therefore to the big momentum of the disc.

- Considerable MgH_2 production is possible even at 10 Bar H_2 pressures. The yield can be increased at higher H_2 pressures.

- Heating and grinding time were selected as the most effective parameters and experimental design set up was planned for these parameters. Heating at $50^\circ C$ and 24 hour grinding time was found as the optimal experimental conditions.

Conclusions for $NaBH_4$ production:

- MgH_2 production was accomplished which is used as starting material for the production of $NaBH_4$. However its purification was not completed so it could not be used as a starting material.

- $NaBH_4$ production using $Na_2B_4O_7$, Na_2CO_3 , Mg and H_2 gas as the starting materials at room temperature and at $50^\circ C$ under 10 bar H_2 pressure did not give satisfactory results.

- $NaBH_4$ production using $Na_2B_4O_7$, Na_2CO_3 and NaH as the starting materials at room temperature under 10 bar H_2 pressure did not give satisfactory results.

- NaBO_2 was produced from $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$. This NaBO_2 was used as a starting material for the production of NaBH_4 . However NaBH_4 could not be obtained.

- $\text{B}(\text{OCH}_3)_3$ and NaH was reacted in a disc mill at 50°C under 10 bar H_2 pressure. NaBH_4 peaks were observed in the XRD spectrum. Experiments at room temperatures and at 100°C were also fulfilled but their XRD spectra were not obtained.

Further studies will continue in two subjects.

a) Further studies will be carried to find the optimal conditions for MgH_2 synthesis. Studies will be carried at around 50°C to 80°C because our preliminary calculations gives 69°C as the optimal temperature. Our calculations also show the optimal grinding time as 21 hours, so the experiments will be carried between 20 to 24 hours. Longer grinding times, up to 30 hours will also be tried.

b) Studies on NaBH_4 production will continue in our future studies. $\text{B}(\text{OCH}_3)_3$ and pure NaH will be reacted in a disc mill between room temperature and 100°C under 10 bar H_2 pressure.

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**SYNTHESIS OF MAGNESIUM HYDRIDE AND
SODIUM BOROHYDRIDE AT LOW
TEMPERATURES**

**A Thesis Submitted to
the Graduate School of Engineering and Sciences of
İzmir Institute of Technology
in Partial Fulfillment of the Requirements for the Degree of**

MASTER OF SCIENCE

in Chemistry

**by
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ABSTRACT

SYNTHESIS OF MAGNESIUM HYDRIDE AND SODIUM BOROHYDRIDE AT LOW TEMPERATURES

In this study, experimental conditions for production of magnesium hydride and sodium borohydride by low temperature grinding are investigated. In the first set of experiments, it was attempted to confirm the information presented in the literature that magnesium hydride could be produced by heating at 350°C for 24 hours under 10 atmospheres of pressure. The results obtained in this study indicated that even a higher temperature heating at 400°C under 10 bar hydrogen pressure was insufficient for magnesium hydride formation.

Heating and grinding time were selected as the most effective parameters by which a full-factorial experimental design methodology was implemented. Statistical analysis results indicated that a combination of grinding and a 50°C heating was most effective. Hence, grinding was identified as the most significant factor effect on the production of magnesium hydride.

Two different mills were used, in this study, and it was found that disc mill was more effective than ball mill. Different combinations of dehydrated borax, sodium carbonate, magnesium, hydrogen gas, sodium hydride and sodium metaborate were tested without success to produce sodium borohydride. In the final set of experiments, sodium borohydride could be successfully produced by using trimethyl borate and sodium hydride in a disc mill at 50°C under 10 bars hydrogen pressure.

ÖZET

DÜŞÜK SICAKLIKLARDA MAGNEZYUM HİDRÜR VE SODYUM BORHİDRÜR SENTEZİ

Düşük sıcaklıklarda magnezyum hidrür ve sodyum borhidrür üretebilmek için yeni bir metot geliştirilmeye çalışıldı. Düşük sıcaklıklarda magnezyum hidrür üretimi ile ilgili optimizasyon çalışmaları sonucunda sıcaklık için 50°C, öğütme zamanı için 24 saat ve öğütme için 7,5 cm çapında öğütücü diskin en uygun koşulları sağladığı belirlendi.

Magnezyum hidrür sentezi için yapılan ön deneylerde 200- 400°C arası sıcaklık değerleri, 8-24 saat arası zaman aralıkları ve 10 bar hidrojen basıncı denendi. Literatürde magnezyum hidrür sentezi için gerekli minimum hidrojen basıncının 10 bar olması ve laboratuvar koşullarının en fazla 10 bar hidrojen basıncına izin vermesi sebebiyle tüm deneylerde hidrojen basıncı 10 barda sabit tutuldu. Ancak alınan sonuçlarda verimlerin çok düşük olması nedeniyle öğütme faktörünün magnezyum hidrür sentezi üzerine etkisi araştırıldı ve en etkili öğütme ortamının 7,5 cm çapında diskle öğütme yapan diskli değirmen olduğu saptandı.

Sodyum borhidrürden sentezi için, bilyeli değirmende ve diskli değirmende yapılan, başlangıç maddeleri olarak susuz boraks, sodyum karbonat, metalik magnezyum, hidrojen gazı ve susuz boraks, sodyum karbonat, sodyum hidrür kullanılan iki ayrı deney metodunun XRD analizleri sonucunda sodyum borhidrür saptanamadı. Başlangıç maddesi olarak boraks, sodyum hidroksit, su ve magnezyumun kullanıldığı deney metodunun birinci aşamasında, elde edilmesi gereken susuz sodyum metaborat, uygun verimle elde edildi. Ancak susuz sodyum metaborat, magnezyum ve hidrojen gazı basıncı altında gerçekleştirilen ikinci aşama sonunda gözlemeyi beklediğimiz magnezyum oksit ve sodyum borhidrürden sadece magnezyum oksit belirlendi.

Son olarak sodyum hidrür ve trimetil boratın 50°C'da diskli değirmende öğütülmesiyle yapılan 8 ve 16 saatlik deneylerin XRD analizleri sonucunda sodyum borhidrür sentezlendiği saptandı.

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CHAPTER 1

INTRODUCTION

1.1. Hydrogen Storage Systems

1.1.1. Hydrogen Energy

Hydrogen is the ultimate fuel. It is clean, efficient, and yields more energy per unit of weight than any other existing fuel. Because hydrogen is a major component of water and of hydrocarbons, it is in abundant supply “(Ovshinsky 2003)”.

Hydrogen is an energy carrier, an indirect source of energy, not a resource itself. In spite of this, hydrogen was at first foredetected as a substitute energy form, in particular to substitute coal, natural gas, oil, and any products derived from them. The reserves of fossil energy, in particular oil, are limited. This led to the belief that hydrogen could soon be used economically as a substitute energy form. The economic viability of the energy carrier hydrogen is enhanced by price advantage in transport over large distances and the possibility of energy storage. Hydrogen for use as a universal energy carrier can be generated by using all possible primary energy sources. Coal, nuclear energy including fusion (although still undeveloped), and solar energy have been named.

In addition to economic reasons for the introduction of new energy sources and new energy carriers, ecological reasons are becoming increasingly important, for example:

The increasing carbon dioxide content of the atmosphere, caused by the use of fossil energy sources and other human activities such as destruction of the tropical rain forests are predicted to lead to extensive climatic changes, e.g., a slow warming up of the atmosphere and the oceans, and melting of pole caps “(Bockris 1980)”. Because of the natural fluctuations in the climate this theory has not been proven beyond doubt. In particular, little is known about compensation effects.

Well-known scientists have been demanding for years (without success) that a "low-risk strategy" for the use of fossil resources should be followed “(Bach et al. 1980)”. The utilization of the energy carriers coal, oil (in the form of gasoline, diesel,

kerosene, etc.) and natural gas leads to emissions of sulfur dioxide, nitrogen oxides and hydrocarbons. In Europe, this has already led to the destruction of extensive wooded areas and to damage of the rest of the forests. The use of hydrogen as an energy carrier coupled with suitable utilization techniques could become particularly important for environmental protection.

Hydrogen competes with the conventional energy carriers hydrocarbons (methane, LPG, gasoline, etc.), coal, and electric power. Further energy carriers are those recovered from regenerable sources and from refuse: biogas, alcohols, and vegetable oils. For the suitability of an energy carrier, the following aspects are important: conversion efficiency of the primary energy carrier to the final use, availability, ease of storage, safety, and ecological and economic evaluation “(Ullmann 2002)”.

1.1.2. Hydrides

The hydrides are a large group of compounds with diverse structures and bonding types. They may be divided into four classes according to their bonding character:

- 1) Ionic hydrides
- 2) Polymeric covalent hydrides
- 3) Volatile covalent hydrides
- 4) Metallic hydrides.

The borders between the classes is not sharp; they merge into each other according to the electronegativities of the elements concerned. Arranging the binary hydrides as in the periodic table, the *ionic hydrides* are detected to be formed by the strongly electropositive alkali and alkaline earth metals. Beryllium hydride, which is partly covalent in character, is an exception. The elements that form *polymeric covalent hydrides*, apart from beryllium, belong to Groups 12 (zinc) and 13 (boron). Boron occupies a special position. It forms numerous volatile hydrides with unusual structures. The hydrides of Group 13 are electron deficient; saturation is achieved in the complex hydride ions such as BH_4^- and AlH_4^- . The covalent hydrides formed by the elements of groups 14 – 17 (carbon – fluorine) are characterized by high volatility. The polarity of the element – hydrogen bond changes with increasing electronegativity of

the elements. Whereas the hydrides of the metallic elements and of silicon contain hydridic (negatively polarized) hydrogen, those of the nonmetals contain acidic hydrogen, sometimes strongly so. The latter are not regarded as hydrides in the usual sense and are not discussed in the present article. Metallic hydrides are formed by the transition metals, the lanthanides, and the actinides. The structures of these hydrides are fundamentally similar to those of metals. The compositions of the metallic hydrides can vary and are frequently nonstoichiometric. Another class of hydrogen compounds, the transition metal hydride complexes, is becoming important. In these molecular complexes the hydrogen atoms are covalently linked to a transition metal. Economically, the most important hydrides are those of the alkali and alkaline earth metals and the complex hydrides of boron and aluminum. These are mostly produced in tonnage quantities and have a wide range of applications “(Ullmann 2002)”.

1.1.3. Metallic Hydrides

Hydrogen reacts with many metallic elements and alloys providing a range of metallic hydrides to choose for hydrogen storage. In general, the formation of metallic hydrides involves the dissociative chemisorption of H_2 onto the metal surface and then hydrogen atom diffusion into the crystal lattice. The formation of metallic hydrides is typically exothermic and hydrogen desorption from the hydrides can be achieved under certain temperature and pressure conditions. Over the years a number of alloys/intermetallics have been designed for a variety of applications. For mobile applications, the hydride should possess good hydriding/dehydriding properties, optimum kinetics at reasonably low temperatures (25- 100°C) and should undergo numerous thermal cycles. Metallic hydrides can be broadly classified into three categories: classical/interstitial, chemical, and complex light metal hydrides “(Chandra et al. 2006)”.

1.1.3.1. Classical / Interstitial Metallic Hydrides

Several intermetallics of AB_2 , A_2B , AB , and AB_5 types form hydrides that have been used for hydrogen storage; commonly used are AB_5 hydrides, where "A" is usually a lanthanide element (atomic numbers 57- 71), Ca, or mischmetal (rare earth metal

mixture), and "B" is Ni, Co, Al, Mn, Fe, Sn, Cu, Ti, etc. The hydrogen is stored interstitially in the lattice of the heavy atoms. These classical hydrides are remarkable due to the fact that their hydriding properties can be fine-tuned by microalloying "A" or "B" with the listed elements. These hydrides are reversible with good kinetics and are well suited for stationary applications. Although these classical hydrides have good volumetric H, densities ($\sim 130 \text{ kg H}_2/\text{m}^3$ for LaNi_5H_6 , γ), for on-board applications they suffer from the disadvantage of having low gravimetric density (1- 2 wt.% H_2), resulting in a large weight penalty "(Chandra et al. 2006)".

1.1.3.2. Chemical Hydrides

These are commonly known hydrides with high theoretical gravimetric weight density, such as methanol- CH_3OH (8.9 wt.%), methylcyclohexane- $\text{CH}_3\text{C}_6\text{H}_{12}$ (13.2 wt.%), ammonia- NH_3 (15.1 wt.%), ammonia borane- NH_3BH_3 (6 wt.% H), and other organic compounds (capacities do not include system weight). These compounds can be used for on-board reforming for generating hydrogen (e.g., steam reforming of CH_3OH for hydrogen production). The nonreversible nature of these hydrides coupled with increased pollution concerns is disadvantageous for vehicular applications "(Chandra et al. 2006)".

1.1.3.3. Complex Light Metallic Hydrides

Until recently, the light metal aluminohydrides, termed complex hydrides (so-called alanates), such as MAIH_4 and M_3AlH_6 ($\text{M} = \text{Na, Li}$), were not considered for hydrogen storage because they were considered to be non-reversible despite their high hydrogen content. NaAlH_4 could be reversibly dehydrided by the addition of transition-metal-based catalysts. The development of catalyzed light metal hydride complexes including borohydrides (Li, Na) BH_4 , Li-N based, and magnesium-based nanocomposites is the most active area of hydrogen storage research for on-board applications "(Chandra et al. 2006)".

1.1.4. Magnesium Hydride

Magnesium and magnesium-based alloys are amongst the most attractive materials for hydrogen storage, since their hydrogen capacity exceeds all known reversible metal hydrides. Magnesium forms a hydride (MgH_2) which provides nominally 7.6 wt.% of hydrogen. In addition, the enthalpy of hydride formation is large ($\Delta H = -75$ kJ/mole) making magnesium also attractive for thermal energy storage. These features, combined with the very low cost of magnesium, suggest an excellent potential for hydrogen-related applications. However, to date magnesium hydride remains of no practical use for hydrogen storage. The main reason is that the reaction for hydrogenation/dehydrogenation is very slow and occurs only at very high temperatures. In practice both absorption and desorption of hydrogen require a temperature of at least 350- 400°C and even then only occur over a time scale of hours. The pressure of hydrogen gas in equilibrium with magnesium hydride is low (1 bar at about 280°C) and therefore thermodynamically the hydride should form readily at room temperature. However, this never occurs in practice because of kinetic limitations. There are several factors that significantly reduce the rate of hydrogenation. One of them is the oxidation of magnesium surface and/or formation of magnesium hydroxide. Magnesium oxide forms easily on a Mg surface exposed to air. Usually oxide layers on the metal surface are not transparent to hydrogen molecules so that an MgO layer prevents hydrogen molecules from penetrating into the material “(Manchester and Khatamian 1988)”. To initiate hydrogen absorption the oxide layer on magnesium must be perforated or cracked, which is the essence of activation. Annealing causes cracking of the oxide layer and as a result bare metal surfaces are exposed to hydrogen. Activation usually consists of high-temperature cycling and most probably takes advantage of the different thermal expansion coefficient of magnesium and magnesium oxide at high temperatures. The oxide layer on a magnesium surface cracks only if the temperature of annealing exceeds 400°C. In addition, annealing at temperatures higher than 350°C causes magnesium hydroxide to decompose. Thus activation of magnesium consists of several cycles annealing at 400°C in vacuum and in hydrogen, followed by annealing for several hours at 400°C in vacuum “(Liang et al. 1995)”. However even after this procedure, hydride formation required the Mg to be exposed to hydrogen at 30 bar and at 400°C for several hours “(Liang et al 1995)”. Another reason for the very slow hydrogenation rate of magnesium (even after

activation) is the limited dissociation rate of hydrogen molecules on the metal surface “(Schlapbach 1992)”. A clean surface of magnesium is not active for the dissociation of gaseous hydrogen “(Zaluska et al. 1998)”.

The nucleation rate of magnesium hydride is dependent on hydrogen pressure. High hydrogen pressure increases hydrogenation rate by increasing the thermodynamic driving force of the reaction, but only up to a point. For pressures higher than about 30 bars, the absorption rate is again reduced. This effect occurs when initial hydrogenation is relatively fast and leads to the formation of a “surface shell” of magnesium hydride which blocks further hydrogen uptake. At this point hydrogenation is limited by the growth of the hydride. Although in general growth has been found to be faster than nucleation, growth limitations are usually responsible for reducing the final hydrogen capacity. Studies on hydrogenation kinetics showed that growth is controlled by diffusion of hydrogen atoms, which is very slow throughout magnesium hydride. Further experiments indicated that the growth is controlled by a slow migration of the interface between the hydride and magnesium, in particular by hydrogen diffusion along the hydride-metal interface and not throughout the hydride layer. In any case, hydrogenation of magnesium is normally almost impossible to complete, even at very high temperatures and pressures. It has also been observed that hydrogen uptake declines when the hydride nuclei start to coalesce on the magnesium surface to form a compact hydride layer and that the hydrogenation reaction diminishes completely when the hydride layer exceeds 30- 50 μm . For kinetic reasons the remaining magnesium cannot be further hydrogenated “(Zaluska et al. 1998)”.

The formation of a hydrogen-absorbing material by mechanical milling under hydrogen atmosphere simultaneously produces hydrogen uptake, mechanical deformation, defect formation and surface formation. These structural modifications can lead to the formation of metastable phases, refinement of the microstructure into the nanometer range, extension of solubility limits, development of amorphous phases. These effects produce important changes in the hydrogen-absorption and desorption properties. In order to understand the structural changes that occur during RMA (reactive mechanical alloying), the known phase of the system Mg-H should be analyzed first. The temperature-composition diagram of the Mg-H system consist of a hcp α -phase (interstitial solid solution) and a β -phase with tetragonal structure and a stoichiometric nominal composition of MgH_2 . When the tetragonal β - MgH_2 phase is subjected to high compressive stress, it partially transforms into the metastable

orthorhombic γ -phase. The transition $\beta \rightarrow \gamma$ was also observed at a pressure of 2.5 GPa. Both phases coexist up to a pressure of 8 GPa. The metastable γ phase reverts exothermically to the tetragonal β -phase by heating at 350°C, as measured by DTA between 300 and 350°C. Another metastable MgH_2 phase, the hexagonal (pseudocubic) δ -phase, has been observed after treatment of the β -phase at 2.8 to 8 GPa and 650 to 800°C. The thermal study of on a $\beta \rightarrow \delta$ - MgH_2 mixture showed an endothermic effect between 350 and 400°C. This effect was attributed either to $\delta \rightarrow \gamma$ or to $\delta \rightarrow \beta$ phase transitions “(Gennari et al. 2001)”.

1.1.4.1. Properties of Magnesium Hydride

Pure magnesium hydride is a white, nonvolatile powder. Although its properties are predominantly salt-like, it shows signs of a transition towards the covalent polymeric hydride structure of compounds such as beryllium and aluminum hydride. Its enthalpy of formation and thermal stability are considerably lower than those of the homologous calcium hydride. Magnesium hydride decomposes without melting at 280 °C. Its reactivity depends on the method of preparation. The product obtained by direct synthesis from the elements is stable in air. Nevertheless, if it is prepared by pyrolysis of dialkyl magnesium or by reaction of lithium aluminum hydride with dimethyl magnesium, the product is very pure and finely divided and ignites spontaneously on contact with air “(Ullmann 2002)”.

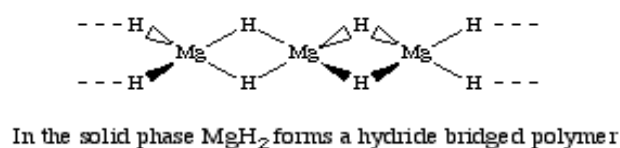
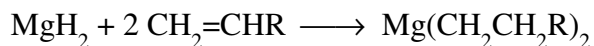


Figure 1.1. Solid Phase Form of MgH_2

1.1.4.2. Uses of Magnesium Hydride

Magnesium hydride contains a high proportion of hydrogen (7.65 wt%), which can be liberated by heat. The catalytically produced compound displays rapid rates of hydrogenation and dehydrogenation and it is therefore of interest as a hydrogen

reservoir. The high activity of catalytically produced magnesium hydride also enables it to take part in an addition reaction with 1-alkenes to form organomagnesium compounds “(Bogdanovic 1984)”.



These dialkyl magnesium compounds have become industrially important in the production of very active Ziegler catalysts. The Mg – H₂ system can also be used for the simultaneous removal and purification of pure hydrogen from gas mixtures “(Bogdanovic 1986)”. Magnesium hydride is also used as a drying agent for organic solvents and gases and in chemical syntheses.

1.1.4.3. Production Methods of Magnesium Hydride

1) Magnesium powders with a purity of 99.95% (Size:<75 μm) are hydrogenated at 350°C under 1 MPa (10 Bar). Hydrogenation rate of 60% were formed through 24-h hydrogenation “(Li et al. 2002)”.

2) MgH₂ are prepared by hydrogenation of pure Mg powder (purity:99%) under a hydrogen pressure of 7 MPa (70 Bar) at 300°C “(Noritake et al. 2003)”.

3) MgH₂ formation require the Mg to be expose to hydrogen at 3MPa (30 Bar) and at 400°C for several hours “(Liang et al. 1995)”.

4) Magnesium metal itself is hydrated with difficulty upon contact with hydrogen of 6 MPa (60 Bar) at 400°C “(Imamura et al. 1983)”.

5) Magnesium hydride are prepared by reaction ball milling. mechanically milling magnesium under hydrogen atmosphere with an initial pressure of ~ 1 MPa (10 Bar), followed by a long-period hydrogenation at 300°C. The process are repeated for three times to achive a hydrogenation ratio of ~80% “(Wu et al. 2006)”.

1.1.5. Borohydrides

Borohydrides are well-known reducing agents. They often have quite specific uses in organic and inorganic chemistry, where they may also be the sources of H⁻ other than simple reductants. Recently they have attracted more attention as a hydrogen

storage medium due to their high hydrogen storage capability. For example, NaBH₄ contains 10.6 wt.% hydrogen which is much more than what most hydrogen storage alloys have.

1.1.6. Sodium Borohydride

NaBH₄ is a white crystalline substance, completely stable in dry air and is nonvolatile. Solid state sodium borohydride, based on metal-hydrogen complexes which react with water releasing pure hydrogen. Sodium borohydride, first synthesized and identified in 1942. It is one of the most unique speciality inorganic chemical being manufactured today.

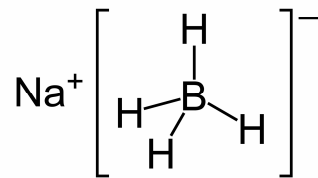
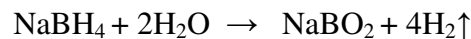


Figure1.2. Structure of NaBH₄

NaBH₄ contains hydrogen which is much more than what most hydrogen storage compounds have. Furthermore, the hydrolysis of sodium borohydride is of interest in hydrogen generation because half of the generated hydrogen is from the borohydride and the other half is from water. NaBH₄ can generate 10.8 wt.% of hydrogen based on the following hydrolysis reaction.



Its hydrogen generation rate, when using some catalysts, is rather high at room temperature compared with the hydrogen desorption rate of metal hydrides “(Li et al. 2003)”.

1.1.6.1. Physical and Thermodynamic Properties of Sodium Borohydride

Table 1.1. Thermodynamic Properties of Sodium Borohydride
(source: Wade 1980)

	Function	Value
Free Energy of Formation	ΔF°_{298}	-30.1 kcal/mole
Head of Formation	ΔH°_{298}	-45.53 kcal/mole
Entropy	S°	+24.26 cal/mole
Heat Capacity	C°_p	+20.67 cal/mole
Free Energy of Ionization	ΔF°_{298}	-5660 cal/mole
Borohydride Ion, $BH_4^-(aq)$		
Free Energy of Formation	ΔF°_{298}	+28.6 kcal/mole
Head of Formation	ΔH°_{298}	+12.4 kcal/mole
Entropy	S°_{298}	+25.5 cal/mole
Hydrolysis		
$BH_4^- + H^+ + 3H_2O(l) = H_3BO_3 + 4H_2(g)$	ΔF°_{298}	-88.8 kcal/mole
Oxidation		
$BH_4^- + 8OH^- = B(OH)_4^- + 4H_2O + 8e^-$	ΔF°_{298}	-228.9 kcal/mole
	E°_{298}	+1.24 volts

Table 1.2. Selected Physical Properties of Sodium Borohydride
(source: Wade 1980)

Property	
Formula	NaBH ₄
Molecular Wt	37.84
Purity	97+%
Color	White
Crystalline Form (anhydrous)	Face centered cubic a=6.15 A.U.
(dihydrate)	Exists below 36.4°C.
Melting Point	505°C. (10 atm. H ₂)
Thermal Stability	Decomposes above 400°C. in vacuum Will not ignite at 300°C. On hot plate Ignites from free flame in air, burning quietly
Density	1.074 g/cc.

1.1.6.2. Solubility of Sodium Borohydride

The solubility of sodium borohydride in water, the most commonly used solvent, has been accurately measured at different temperatures. 36.4°C is the equilibrium temperature of the two crystal forms NaBH₄ and NaBH₄·2H₂O. Below 36.4°C represents the solubility of the dihydrate, and above 36.4°C the solubility of anhydrous NaBH₄ “(Wade 1980)”.

1.1.6.3. Stability of Sodium Borohydride

Sodium borohydride is very stable thermally. It decomposes slowly at temperatures above 400 °C in vacuum or under a hydrogen atmosphere. Sodium borohydride absorbs water rapidly from moist air to form a dihydrate which decomposes slowly forming hydrogen and sodium metaborate. Decomposition in air is therefore a function of both temperature and humidity “(Wade 1980)”.

1.1.6.4. Chemical Properties of Sodium Borohydride

1.1.6.4.1. Organic Reductions of Sodium Borohydride

The first commercial uses for sodium borohydride were for the reduction of organic compounds containing carbonyl groups. Classical techniques for accomplishing these reductions have been developed.

Sodium borohydride attacks the carbon atom which has the largest positive charge. Because of this, any substituent which increases the fractional positive charge on the carbonyl carbon atom will increase the rate of reduction. If the fractional positive charge is decreased by substituents then the rate is slowed down.

Sodium borohydride is an attractive reducing agent for organic substrates because of its convenience as well as its selectivity and efficiency. The general techniques of its use are by now well known to the practitioner of organic synthesis, who also knows that modifications are sometimes dictated by the properties (solubility, thermal stability, pH sensitivity) of the material being reduced “(Wade 1980)”.

1.1.6.4.2. Reaction of Sodium Borohydride with Water

The reaction of sodium borohydride with water $\text{NaBH}_4 + 2\text{H}_2\text{O} \rightarrow \text{NaBO}_2 + 4\text{H}_2$ is of enormous practical importance. If this hydrolysis reaction occurs in competition with the reduction of an organic or inorganic compound, borohydride obviously is wasted and its utilization efficiency is lowered. On the other hand, sodium borohydride is a remarkably concentrated source of hydrogen. One gram,

dissolved in water will release 2.37 liters of molecular hydrogen. Important industrial use is made of this property.

Factors which control the rate of hydrolysis include concentration of BH_4^- , concentration of NaOH or base (pH) and temperature. The effect of these variables on the rate of hydrolysis has been extensively studied.

The times for complete hydrolysis of sodium borohydride solutions in water at 25°C which have been buffered at various pH's are shown in Table 1.3.

Table 1.3. NaBH_4 Hydrolysis Time vs pH
(source: Wade 1980)

pH	NaBH_4 Completely Hydrolyzed in
4.0	0.02 sec
5.0	0.22 sec
6.0	2.2 sec
6.25	3.9 sec
6.5	7.0 sec
6.75	12.4 sec
7.0	22.1 sec
8.0	3.7 min
9.0	36.8 min
10.0	6 hr 8 min

1.1.6.5. Industrial Applications of Sodium Borohydride

1)Pharmaceutical-Fine Chemical

*Vitamin A (Retinol)

*Isohumulone

*Pentazocine

2)Process Stream Purification

3)Pollution Control

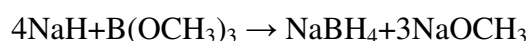
*Lead Pollution

*Mercury Pollution

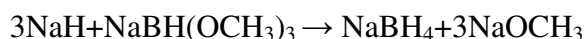
- *Silver-Cadmium from Photographic Film Manufacturers
- 4) Precious Metal Recovery
- 5) Catalyst Preparation
- 6) Magnetic Materials for Recording Tapes
- 7) Electroless Plating of Metals
- 8) Metals Coating of Window Glass
- 9) Pulp Brightening
- 10) Clay Leaching
- 11) Textile Applications–Vat Dye Reductions
- 12) Hydrogen Generation
- 13) Foamed Plastics
- 14) Hydri-pills
- 15) Preparation of Diborane and Derivatives

1.1.6.6. Production Methods of Sodium Borohydride

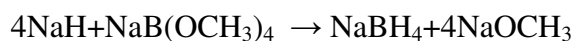
1) Sodium hydride and methyl borate in correct proportions undergo a rapid reaction at 225-275°C to produce sodium borohydride of 90-96% purity and in a yield as high as 94%, according to the equation “(Schlesinger et al. 1952)”.



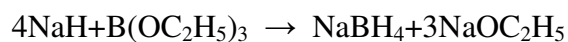
2) Reaction of Sodium Hydride with Sodium trimethoxy borohydride -Reaction at 250-270 °C and there maintained for 30 minutes. The crude product is extracted with isopropylamine. The product analysed 89% sodium borohydride, and the yield is 78% “(Schlesinger et al. 1952)”.



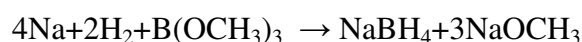
3) Reaction of Sodium Hydride with Sodium Tetramethoxyborohydride – Experiments and results are quite similar to trimethoxyborohydride. Sodium borohydride yield of 66% with 91% purity is obtained “(Schlesinger et al. 1952)”.



4) The methyl borate may also be replaced by higher esters, such as ethyl and n-butyl borate “(Schlesinger et al. 1952)”.

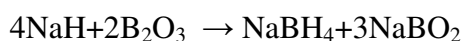


5) At higher temperatures (225-275°C) and with sodium, hydrogen and methyl borate in the approximate proportions:



Sodium borohydride is formed. The yields are relatively low, %15 “(Schlesinger et al. 1952)”.

6) At higher temperatures (330-350°C), sodium hydride and boric oxide react to produce up to 60% yields of sodium borohydride by the following reaction,

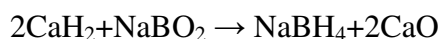


96% purity sodium borohydride is obtained “(Schlesinger et al. 1952)”.

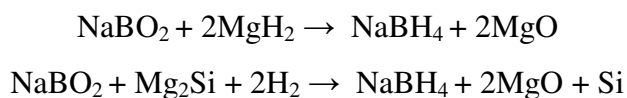
7) Sodium borohydride can also be synthesized by heating a mixture of dehydrated borax, quartz and sodium metal under hydrogen gas to higher temperatures of 450-500°C through the following reaction “(Schubert et al. 1963)”.



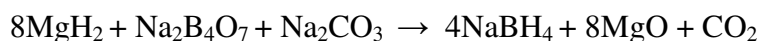
8) Besides sodium hydride, calcium hydride has been used to react with NaBO₂ to prepare NaBH₄ in the same temperature range “(Goerring et al. 1956)”.



9) Sodium borohydride is synthesized by reacting sodium metaborate (NaBO_2) with magnesium hydride (MgH_2) or magnesium silicide (Mg_2Si) by annealing (350-750°C) under high H_2 pressure. As the temperature and the pressure increases, the yield increases to have a maximum value (97-98%) at 550°C “(Kojima et al. 2003)”.



10) Sodium borohydride is prepared through a mechano-chemical reaction at room temperature. The mechano-chemical reaction is conducted by ball-milling a mixture of magnesium hydride, dehydrated borax and some Na compounds in a planetary ball mill at room temperature. MgH_2 is used as reducing agent to react with dehydrated borax “(Li et al. 2002)”.



1.2. Ball Milling

Ball Mills are a very efficient tool for grinding many materials into a fine powder. To use the Mill, the material to be ground is loaded into the barrel which contains grinding media. As the barrel rotates, the material is caught between the individual pieces of grinding media which mix and crush the product into a very fine powder over a period of several hours. Quite simply, the longer the Ball Mill is run, the finer powder will be. Ultimate particle size depends entirely on how hard the material you're grinding is, and how long the Ball Mill is run “(WEB_1 2006)”.

Mechanical milling is an effective technique for the preparation of fine metallic and ceramic powders and can also be used to drive a wide range of chemical reactions. Milling devices include planetary machines, attritors and vibrational mills; products include amorphous, nanocrystalline and quasicrystalline materials, supersaturated solid solutions, reduced minerals, high-surface-area catalysts and reactive chemicals “(Takacs and Suryanarayana 1996)”.

Mechanical Milling is a complex process and hence involves optimization of a number of variables to achieve the desired product phase and/or microstructure. Some

of the important parameters that have an effect on the final constitution of the powder are:

- Type of mill,
- Milling container,
- Milling speed,
- Milling time,
- Type, size, and size distribution of the grinding medium,
- Ball-to-powder weight ratio,
- Extent of filling the vial,
- Milling atmosphere,
- Process control agent, and
- Temperature of milling.

All these process variables are not completely independent. For example, the optimum milling time depends on the type of mill, size of the grinding medium, temperature of milling, ball-to-powder ratio “(Suryanarayana 2001)”.

1.2.1. Milling Process Parameters

Process parameters such as milling temperature, grinding ball diameter, ball-to-powder weight (charge) ratio, use of a process control agent, and relative proportion of the reactants seem to play an important role on the nature and kinetics of the product phase obtained by the displacement reactions. For example, a combustion reaction could be initiated during the reduction of copper oxide by iron; but the same reaction progresses gradually under slightly different milling conditions. Consequently, results from different laboratories can be effectively compared only if the exact conditions under which the reaction takes place are reported. These conditions need to be optimized for the best yield “(Suryanarayana 2001)”.

1.2.2. Temperature Rise during Milling

The intense mechanical deformation experienced by the powders leads to generation of crystal defects and this plus the balance between cold welding and fracturing operations among the powder particles is expected to affect the structural

changes in the powder. Another important parameter, the temperature experienced by the powder during milling, dependent on the kinetic energy of the balls, can also determine the nature of the final powder product. If the temperature generated is high, the associated higher diffusivity (higher atomic mobility) leads to processes resulting in recovery (and recrystallization). In such a case, a stable phase, e.g., an intermetallic, would form. On the other hand, if the temperature is low, then defect recovery would be less and an amorphous (or a nanocrystalline) phase would form“(Koch 1994)”.

The temperature of the powders during milling can be high due to two different reasons. Firstly, as mentioned above it is due to the kinetic energy of the grinding medium. Secondly, it is possible that exothermic processes occurring during the milling process generate heat. But, in practice, when the temperature of the powder or the milling container is measured, it is probably due to a combination of these two factors“(Koch 1994)”.

1.3. Mechanochemical Synthesis

Mechanical Milling could be used to induce a wide variety of solid–solid, liquid–solid and even solid–gas chemical reactions.

The mechanochemical reactions are characterized by a large negative free energy change and are therefore thermodynamically feasible at room temperature. The occurrence of these reactions at ambient temperatures is thus limited by kinetic considerations alone“(McCormick 1995)”.

A characteristic feature of all solid-state reactions is that they involve the formation of product phase(s) at the interfaces of the reactants. Further growth of the product phase involves diffusion of atoms of the reactant phases through the product phase, which constitutes a barrier layer preventing further reaction. Thus, these reactions require elevated temperatures to proceed at reasonable rates“(McCormick 1995)”.

Depending on the milling conditions, two entirely different reaction kinetics are possible:

1. The reaction may extend to a very small volume during each collision, resulting in a *gradual* transformation, or

2. If the reaction enthalpy is sufficiently high, a *self-propagating combustion reaction* can be initiated.

Mechanical energy can set off chemical changes in many different situations. For example, wear of a material involves chemical processes, corrosion is influenced by lattice defects created by plastic deformation, etc. We are primarily interested in mechanochemical reactions induced by high energy ball milling. The processes taking place in a ball mill are very complex. One of our primary goals is to understand their mechanism by separating and modelling their individual components “(Takacs 1992)”.

An interesting situation is when ball milling induces a self-supporting thermal reaction in a highly exothermic system. Investigating the conditions of ignition will be a useful tool to learn about the mechanism of mechanochemical reactions in general “(Takacs 1992)”.

Ball milling can also induce chemical changes in non-metallurgical systems, including silicates, minerals, ferrites, ceramics, and organic compounds. The research area of mechanochemistry developed to study and utilize these processes. As many mechanical alloying processes involve chemical changes, the distinction between mechanical alloying and mechanochemistry is often arbitrary “(Takacs 1992)”.

1.4. Mechanism of Amorphization

The mechanism of amorphization by Mechanical Milling (MM) is not clearly understood. The early investigators assumed that the powder particles melted because of the very high rate of plastic deformation, and consequent rise in the powder temperature. Subsequent quenching of the liquid by heat conduction into the less deformed, and hence cooler, interior regions of the particles, resulted in the formation of the amorphous phase (like in RSP). However, energy input calculations and temperature measurements suggest that the temperature rise is not large enough for the powder particles to melt. Additionally, if this mechanism were to be true, the glass-forming composition ranges in mechanically alloyed and rapidly solidified alloys should be the same; but this is not true as will be shown later. Researchers now believe that amorphization during MM is not purely a mechanical process and that a solid-state reaction similar to that observed in thin films occurs during MM. During MM, however, destabilization of the crystalline phase is thought to occur by the accumulation of

structural defects such as vacancies, dislocations, grain boundaries, and anti-phase boundaries. The continuous decrease in grain size (and consequent increase in grain boundary area) and a lattice expansion would also contribute to the increase in free energy of the system. It has been reported that the stored energy during MM can be about 50% of the enthalpy of fusion, whereas by cold rolling or wire drawing it is only a small fraction of it. These defects raise the free energy of the intermetallic system to a level higher than that of the amorphous phase and consequently, it becomes possible for the amorphous phase to form. It has been reported that amorphization occurs when the strain in the slow diffusing species reaches a maximum. In the case of ordered alloys, amorphization was reported to occur when the long-range order parameter is <0.6 with a corresponding volume of expansion of about 2% “(Ermakov et al. 1981)”.

Irradiation of crystalline materials by energetic particles and electrons has been known to cause amorphization when the following criteria are obeyed:

- The intermetallic compound has a narrow or zero homogeneity range,
- The order–disorder transition temperature of the intermetallic, T_c is higher than the melting temperature, T_m ,
- The two components (elements) are separated by more than two groups in the periodic table,
- The intermetallic has a complex crystal structure, and
- The fraction of A atoms ($f_A \geq f_B$) is $\geq 1/3$.

Intermetallics have also been amorphized by MM when the above criteria were generally followed. However, there have been several exceptions to the above empirical rules (too many to be ignored). For example, compounds with reasonably wide homogeneity ranges have also been amorphized. Further, a number of compounds with $f_A=1/4$ have been made amorphous. In view of these observations, it should be realized that the above criteria may only be used as guidelines and not that if they are obeyed, amorphization will be observed “(Eckert et al. 1992)”.

1.5. Characterization of the Solid Samples

Characterization of the solid samples was carried out by using X-Ray Diffraction, Scanning electron microscopy (SEM).

1.5.1. X-Ray Powder Diffraction

X-Ray powder diffraction finds frequent use in material science because sample preparation is relatively easy, and the test itself is often rapid and non-destructive. The vast majority of engineering materials is crystalline, and even those which do not yield some useful information in diffraction experiments.

The pattern of powder diffraction peaks can be used to quickly identify materials, and changes in peak width or position can be used to determine crystal size, and texture “(WEB_2 2006)”.

1.5.2. Scanning Electron Microscopy (SEM)

Scanning electron microscopy is the best known and most widely-used of the surface analytical techniques. High resolution images of surface topography, with excellent depth of field are produced using a highly-focused, scanning (primary) electron beam. The primary electrons enter a surface with an energy of 0.5 - 30 keV, and generate many low energy secondary electrons. The intensity of these secondary electrons is largely governed by the surface topography of the sample. An image of the sample surface can thus be constructed by measuring secondary electron intensity as a function of the position of the scanning primary electron beam. High spatial resolution is possible because the primary electron beam can be focused to a very small spot (<10 nm). High sensitivity to topographic features on the outermost surface (<5 nm) is achieved when using a primary electron beam with an energy of <1 keV “(WEB_3 2006)”.

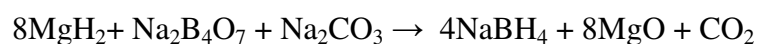
In addition to low energy secondary electrons, backscattered electrons and X-rays are also generated by primary electron bombardment. The intensity of backscattered electrons can be correlated to the atomic number of the element within the sampling volume. Hence, some qualitative elemental information can be obtained. The analysis of characteristic X-rays emitted from the sample gives more quantitative elemental information. Such X-ray analysis can be confined to analytical volumes as small as 1 cubic micron “(WEB_3 2006)”.

SEM, accompanied by X-ray analysis, is considered a relatively rapid, inexpensive, and basically non-destructive approach to surface analysis. It is often used

to survey surface analytical problems before proceeding to techniques that are more surface-sensitive and specialized “(WEB_3 2006)”.

1.6. Aim of This Work

The purpose of this work was to propose a new method for the synthesis of sodium borohydride at low temperatures. MgH_2 is used as a reducing agent to react with dehydrated borax. The sodium borohydride can be processed by the reaction as shown in the following equation.



However, magnesium hydride which is the starting material for this synthesis could not be obtained from the market, therefore metallic magnesium and hydrogen gas was used as the starting materials. Studies were also concentrated on the production of magnesium hydride.

For this purpose, several experimental procedures were tried, especially through milling. Characterization was mostly done by X-Ray powder diffraction.

CHAPTER 2

EXPERIMENTAL METHODS

2.1. Instrumentation and Apparatus

A Retsch S1000 series ball mill was used for the experiments. Emko ESM- 4410 series thermocouple was used to measure and also to control the temperature. As a reactor, we have modified our disc mill design. A 320 ml stainless steel grinding bowl with a stainless steel lid was built as a reactor. The lid has two valves for gas inlet and outlet and the cap was screwed to the main body with six screws so as not to leak hydrogen gas. A specially made copper gasket was used to prevent leakage. The grinding bowl had grooves outside to fit with specially made resistance for heating.

2.2. XRD, SEM Analysis

X-Ray powder diffraction (XRD) data were collected on a Philips X'Pert Pro diffractometer using $\text{CuK}\alpha$ radiation ($\lambda=0.154$ nm). Samples were prepared by compressing in the cassette sample holder without any adhesive substance.

SEM characterization was carried out using a Philips XL-30s FEG type instrument. Prior to analysis, the solid samples were sprinkled onto Al or C tapes which are adhesive and supported on metallic disks. Images of the sample surfaces were recorded at different magnifications.

2.3. MgH_2 Synthesis

Several procedures were tried for MgH_2 synthesis:



a. Some experiments were made by heating Mg to various temperatures under 10 bar H_2 pressure.

b. Some experiments were made by grinding Mg with a grinding disc at 100 rpm under 10 bar H_2 pressure at room temperatures.

c. Some experiments were made by putting Mg under 10 bar H₂ Pressure and grinding with a grinding disc at 100 rpm while heating.

2.3.1. Optimization of Parameters for MgH₂ Synthesis

In order to obtain accurate and reproducible results, the first part of the study was focused on the optimization of parameters for MgH₂ synthesis. Synthesis of MgH₂ is influenced by several factors such as the grinding media, temperature, H₂ pressure and grinding time effect. Variable and effective parameters were optimized.

2.3.1.1. Optimization of Grinding Conditions

The first parameter optimized was the setting of grinding materials. Since it is known that the yield of the MgH₂ synthesis is affected by Mg piece dimensions, it is important to find optimum grinding media to obtain the available optimum Mg particle dimensions. In order to increase the reaction surface, Mg pieces (Merck, 50-150 mesh) were put in the Ball Mill and ground for various time intervals with different size balls or discs.

a. Grinding was performed with the same diameter steel balls. However different size balls were used for different grinding to determine the optimum size. (all 2.5, 5, 10 or 20 mm diameter)

b. Grinding was also performed with a mixture of various diameter steel balls.

c. Grinding was performed with various size discs. (60 mm or 75 mm diameter discs)

2.3.1.2. Effect of H₂ Pressure

Hydride formation requires Mg to be exposed to a hydrogen pressure of at least 10 bar (Li 2002, Wu 2006). With our set up, we could maintain continuous 10 bar H₂ pressure. Therefore, continuously 10 Bar H₂ pressure was applied to the milling bowl either for various time intervals (8 to 24 hours) or for various grinding conditions (while grinding or not grinding) or for various temperature conditions (without heating or with heating from room temperature to 400°C).

2.3.1.3. Effect of Temperature

Various heating temperatures from room temperature to 400°C were tried for different time intervals.

In the literature, it is stated that heating up to 400°C and hydrogen pressures up to 70 bar gives good yields “(Imamura et al. 1983, Noritake et al. 2003)”. However, our experiments for heating up to 400°C and 10 bar hydrogen pressure gave very poor yields. Some good literature results up to 10 Bar and 350°C remains as a question mark for us.

2.3.1.4. Effect of Grinding Time

In our experiments various time intervals - from 8 to 24 hours - were tried for different temperatures under constant H₂ pressure (10 Bars). Only heating and H₂ pressure application was not enough for sufficient MgH₂ formation. Grinding especially with disc mill at 100 rpm increased the yield with a considerable amount.

It was rather surprising to see that grinding was more effective than heating for MgH₂ formation.

2.3.2. First Set of Experiments

Several experiments were tried for MgH₂ synthesis by heating Mg under 10 bar H₂ pressure:



During these experiments, 24 Hours heating at 200°C, 250°C, 300°C, 350°C and 400°C under 10 bar H₂ pressure was tried without grinding.

2.3.3. Experimental Design for MgH₂ Synthesis

Two main parameters showed to be very effective during the experiments. They were 1)Temperature and 2)Grinding time. Hydrogen pressure (10 bar) was kept

1) MgH_2 was not available from the market, so metallic magnesium and H_2 gas were used as starting materials instead of MgH_2 . Experiments were carried out with a ball mill at 100 rpm. Three time intervals - 8, 16 and 24 hours - were tried at room temperature. Ball diameters varied; (1 of 20mm, 3 of 10mm, 7 of 5mm, 3 of 2.5mm).



$$\text{Na}_2\text{B}_4\text{O}_7 = 10.06\text{g}$$

$$\text{Na}_2\text{CO}_3 = 5.30\text{g}$$

$$\text{Mg} = 9.72\text{g}$$

2) NaH was tried instead of H_2 gas. Experiments were carried with a ball mill at 100 rpm. Two time intervals, 8 and 16 hours were tried at room temperature. Ball Diameters; (1 of 20mm, 3 of 10mm, 7 of 5mm, 3 of 2.5mm).



$$\text{Na}_2\text{B}_4\text{O}_7 = 4.024\text{g}$$

$$\text{Na}_2\text{CO}_3 = 2.120\text{g}$$

$$\text{NaH} = 7.680\text{g}$$

2.4.2. Experiments with Disc Mill

The preliminary experiments did not give very satisfactory results with stainless steel balls, a new stainless steel disc mill with 5 cm height, and 10 cm diameter dimensions using a disk for grinding was purchased, and the experiments were carried out with this mill.

1) Experiments were carried at 100 rpm with the grinding disc. Three time intervals, 8, 16 and 24 hours were tried at room temperature and at 10 bar H_2 pressure.



$$\text{Na}_2\text{B}_4\text{O}_7 = 20.12\text{g}$$

$$\text{Na}_2\text{CO}_3 = 10.60\text{g}$$

$$\text{Mg} = 19.44\text{g}$$

2) Experiments were also carried out at two time intervals, 8 and 16 hours at 50 °C and at 10 bar H₂ pressure.



$$\text{Na}_2\text{B}_4\text{O}_7 = 20.12\text{g}$$

$$\text{Na}_2\text{CO}_3 = 10.60\text{g}$$

$$\text{Mg} = 19.44\text{g}$$

3) Experiments were carried by using NaH as the starting material. Two time intervals, 8 and 16 hours were tried at room temperature.



$$\text{Na}_2\text{B}_4\text{O}_7 = 4.024\text{g}$$

$$\text{Na}_2\text{CO}_3 = 2.120\text{g}$$

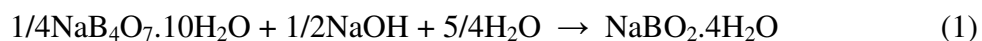
$$\text{NaH} = 7.680\text{g}$$

4) *Preparation of Anhydrous Sodium Metaborate (NaBO₂) as the Starting Material*

Experiments by using anhydrous sodium metaborate (NaBO₂) as the starting material were also carried out. The following simple processes were used to prepare the anhydrous sodium metaborate (NaBO₂):

a. From “Borax” as the abundant natural resource.

The process that starts from borax (Na₂B₄O₇·10H₂O) requires two parts of NaOH to make one part of NaBO₂. Na₂B₄O₇·10H₂O, NaOH and H₂O were put in the disc mill and grinded for 6 hours at 100 rpm for the process as given in Eq.(1);

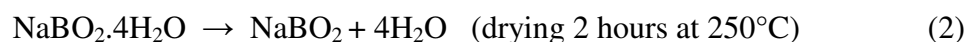


$$\text{NaB}_4\text{O}_7 \cdot 10\text{H}_2\text{O} = 19.1 \text{ g}$$

$$\text{NaOH} = 4 \text{ g}$$

$$\text{H}_2\text{O} = 4.5 \text{ g}$$

b. $\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$ is simply dried to yield anhydrous sodium metaborate as shown in Eq.(2);



Complete dehydration was accomplished with this process. Anhydrous sodium metaborate obtained, was used in the Dynamic Hydriding/Dehydriding Process to produce sodium borohydride by the reaction as shown in Eq.(3).

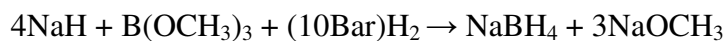


$$\text{NaBO}_2 = 6.6 \text{ g}$$

$$\text{Mg} = 4.8 \text{ g}$$

The reaction was carried out under constant temperature (250°C) and H_2 pressure (10 Bar) conditions for 8 hours. However the results were not satisfactory. Only MgO peaks were detected in the spectra but no NaBH_4 peaks.

5) Experiments were also carried by using NaH and $\text{B}(\text{OCH}_3)_3$ as starting materials. Two time intervals, 8 and 16 hours were tried for 50°C at 10 bar H_2 pressure.



$$\text{NaH} = 4.8\text{g}$$

$$\text{B}(\text{OCH}_3)_3 = 5.2\text{g}$$

CHAPTER 3

RESULTS and DISCUSSIONS

3.1. MgH₂ Synthesis

3.1.1. Optimization of Parameters for MgH₂ Synthesis

3.1.1.1. Optimization of Grinding Conditions

Aim of this study was to get smaller particles so as to obtain more and better products and to increase the yield.

From the experiments carried out, following results were deduced:

a. Grinding with same diameter steel balls but different size in each lot were used for grinding to determine the optimum size (all 2.5 or 5 or 10 or 20 mm diameter):

This procedure was not succesfull, since Mg pieces were stuck together.

b. Grinding with different diameter steel balls in the same lot:

This procedure was succesfull and approximated size Mg pieces were obtained.

c. Grinding with disc:

This procedure was more succesfull and approximated size Mg pieces were obtained. In Figure 3.1. effects of different grinding procedures are given.

3.1.1.2. Effect of H₂ Pressure

Hydride formation requires Mg to be exposed to a hydrogen pressure of at least 10 bar “(Li et al. 2002, Wu et al. 2006)”. With our set up, we could at most maintain continuous 10 bar controlled H₂ pressure therefore this pressure was used throughout the experiments.

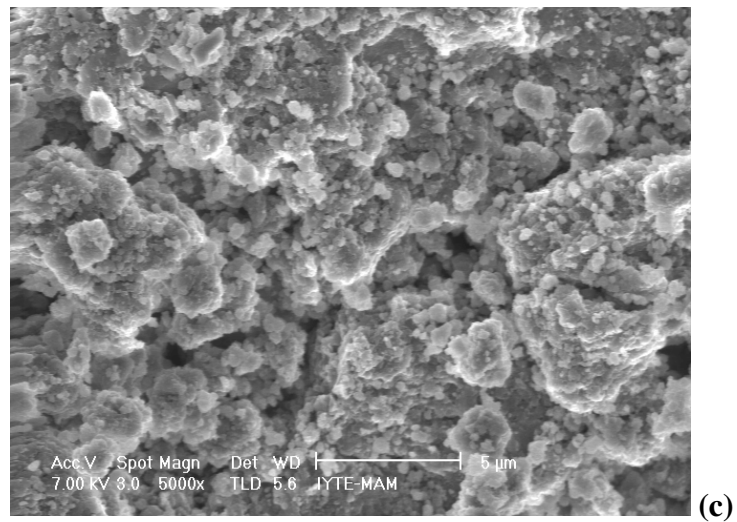
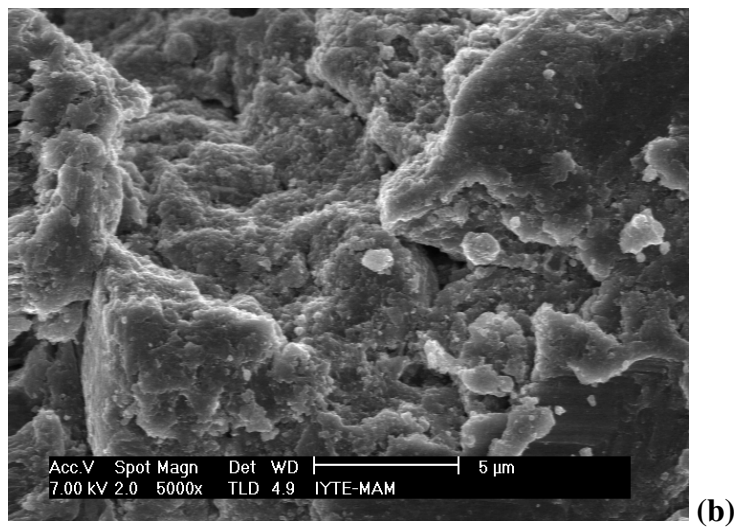
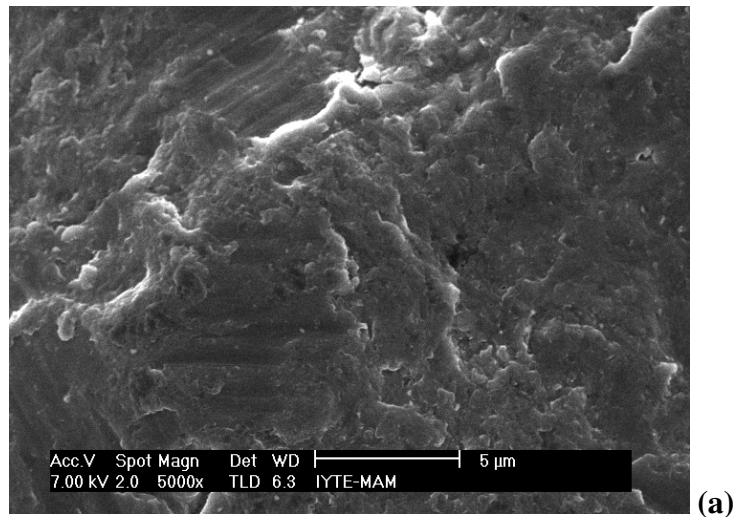


Figure 3.1. SEM back-scattered microimages of Mg at different grinding conditions
(a): Grinding Mg with same diameter steel balls, (b): Grinding Mg with different diameter steel balls, (c): Grinding Mg with disc

3.1.1.3. Effect of Temperature

In our primary experiments, only heating under H₂ pressure, was not enough for sufficient MgH₂ formation. Our experiments up to 400°C and 10 bar hydrogen pressure gave very poor yields. Effect of temperature in our studies is given in Figure 3.2. MgH₂ formation starts after 300°C. There is a minor increase in the yield as the temperature is increased. More MgH₂ formation may be performed at even higher temperatures but NaBH₄ synthesis at high temperatures is beyond the aim of this study.

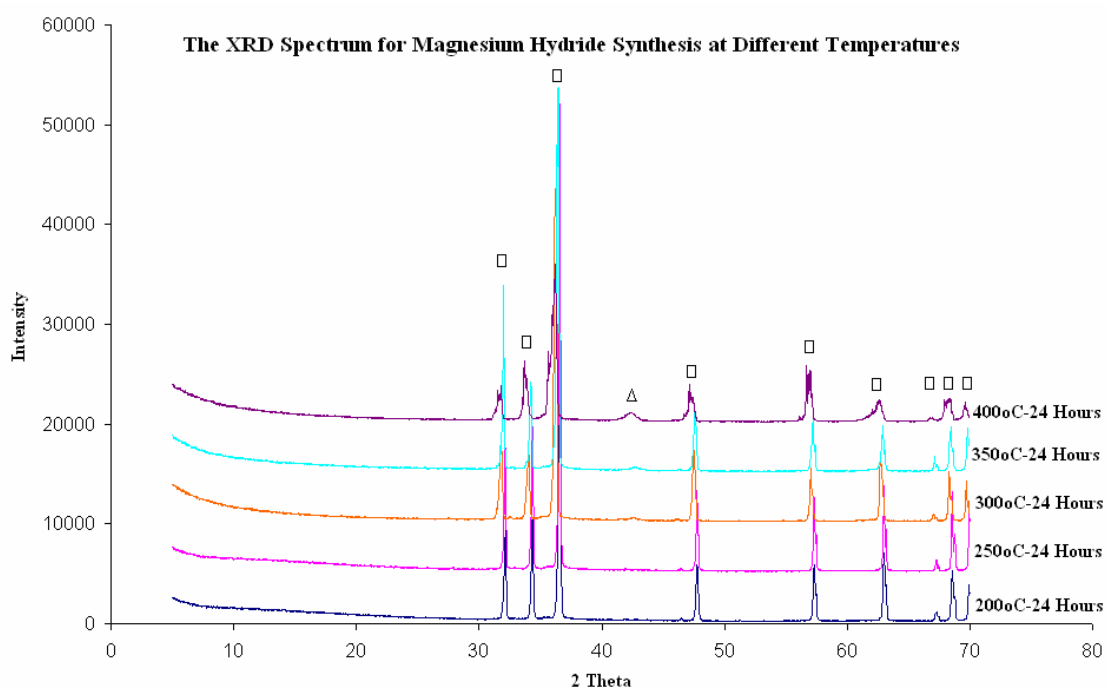


Figure 3.2. The XRD Spectra for MgH₂ Synthesis at Different Temperatures
Δ=MgH₂, □= Mg

3.3.1.4. Effect of Grinding Time

Grinding at room temperature, at 50°C and 100°C were performed for various time intervals. 8 hour grinding time was selected as optimum duration after experimental design results. Figure. 3.3 shows the results of 50 °C studies.

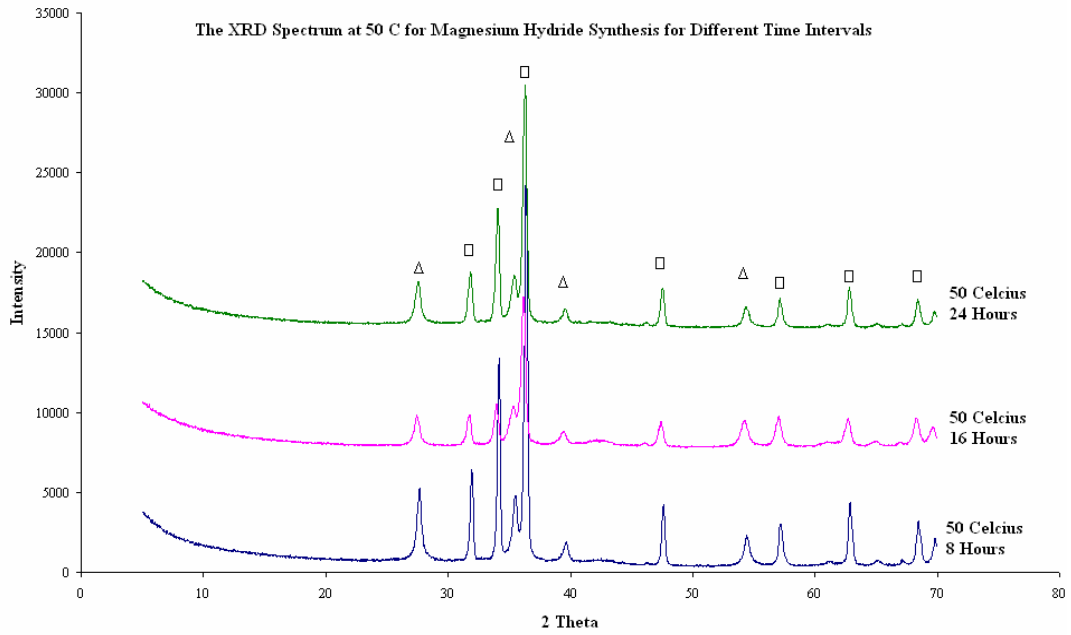


Figure 3.3. The XRD Spectra at 50 °C for MgH₂ Synthesis for Different Time Intervals Δ = MgH₂, \square = Mg

3.1.2. Experimental Design Results for MgH₂ Synthesis

To find the optimum conditions, two important parameters were selected and experiments were carried out for 3 levels. Experimental Design Results Scheme for MgH₂ Experiments are given in Table 3.1.

Table 3.1. Experimental Design Results Scheme for MgH₂ Experiments

Experiment Number	Temperature	Grinding Time	Peak Intensity Ratio I_{MgH_2}/I_{Mg}
1	1	1	0.127
2	1	0	0.078
3	1	-1	0.025
4	0	1	0.172
5	0	0	0.223
6	0	-1	0.173
7	-1	1	0.022
8	-1	0	0.017
9	-1	-1	0.016

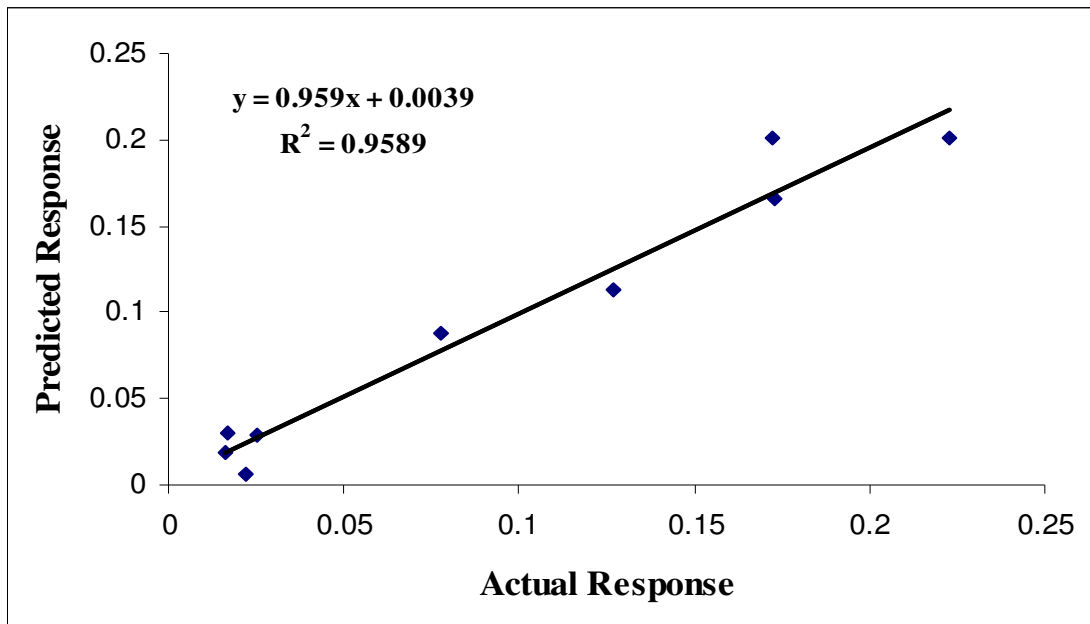


Figure 3.4. Nonlinear Model Predicted Response-Actual Response Plot

As detected from the comparison of the optimization plots of the linear and nonlinear models and also from the comparison of R^2 values which is shown in Figure 3.4. It can be predicted that the nonlinear model fits our experimental results.

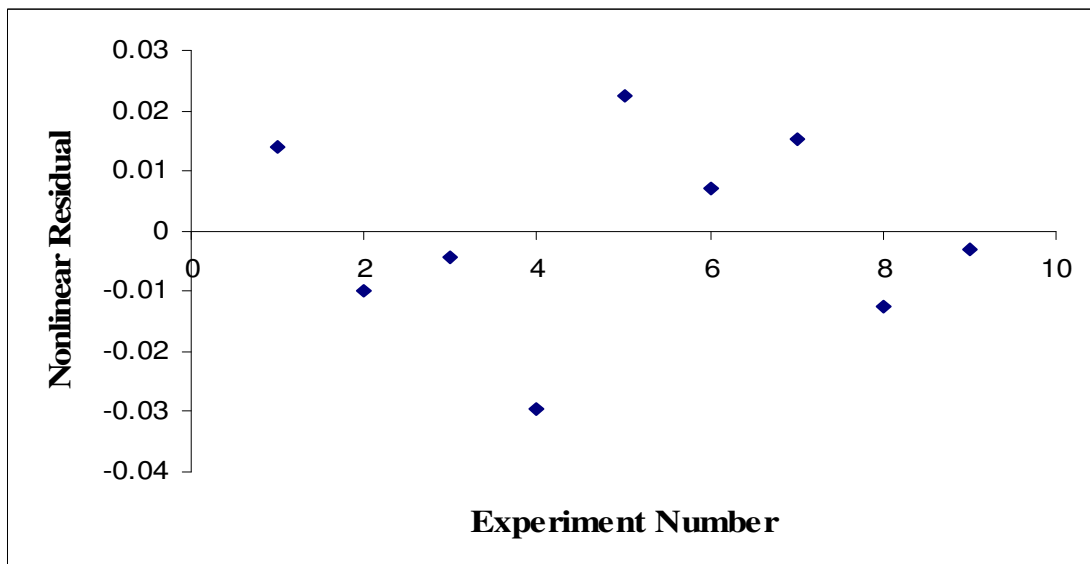


Figure 3.5. Nonlinear Model Residual-Experiment Number Plot

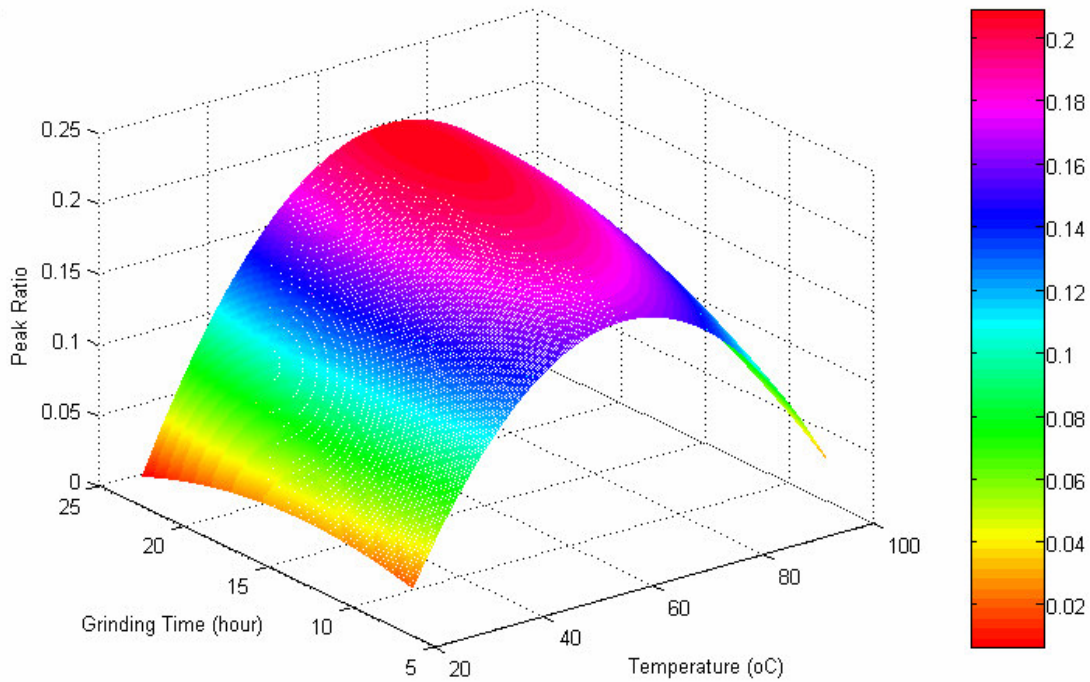
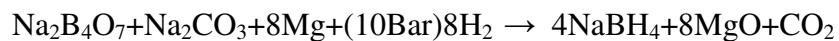


Figure 3.6. Nonlinear Model 3-D (Peak Intensity-Grinding Time-Temperature) Optimization Plot

3.2. NaBH₄ Synthesis

3.2.1. Experiments with Ball Mill

1) Metallic magnesium and H₂ gas were used as starting materials instead of MgH₂. Experiments were carried out with a ball mill at 100 rpm. Three time intervals - 8, 16 and 24 hours - were tried at room temperature.



Na₂B₄O₇, Mg and Na₂CO₃ peaks were identified in the XRD spectrum of 8 and 16 hours experiments, as detected in Figure 3.7. However Na₂B₄O₇ and Na₂CO₃ peaks disappeared in the spectrum for 24 hours experiments and NaBH₄ peaks are not present. We assume that crystallic structures of Na₂B₄O₇ and Na₂CO₃ are destroyed during 24 hours milling and they do not appear in the spectrum.

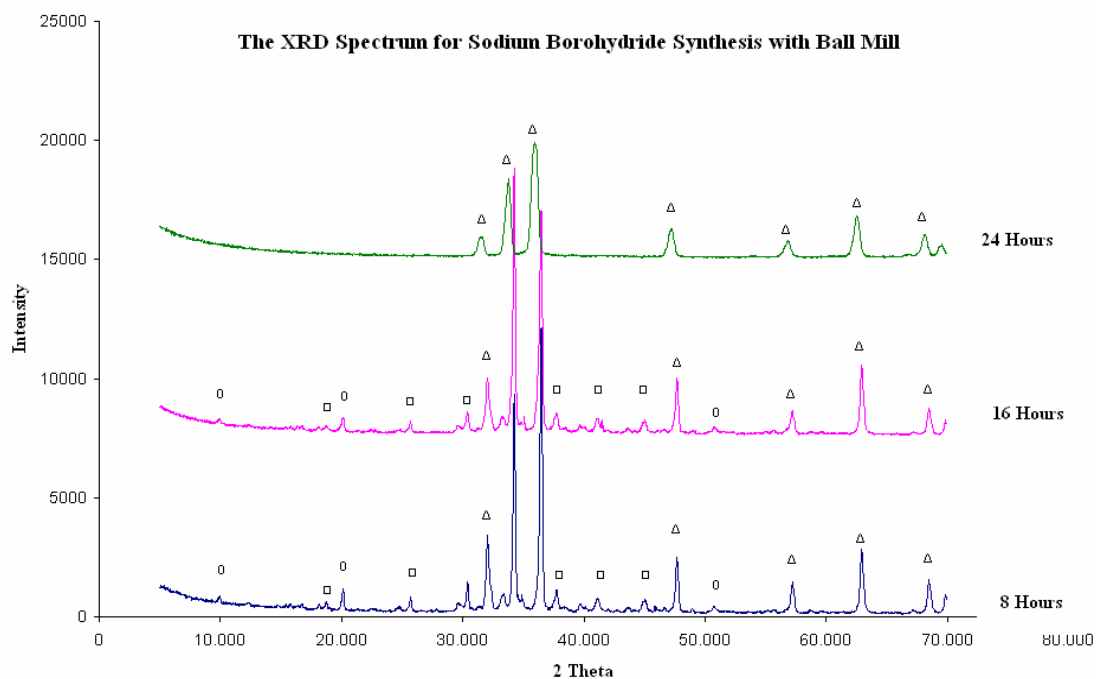


Figure 3.7. The XRD Spectra for Sodium Borohydride Synthesis Using H_2 Gas with Ball Mill at Room Temperature Δ = Mg, \square = Na_2CO_3 , \circ = $\text{Na}_2\text{B}_4\text{O}_7$

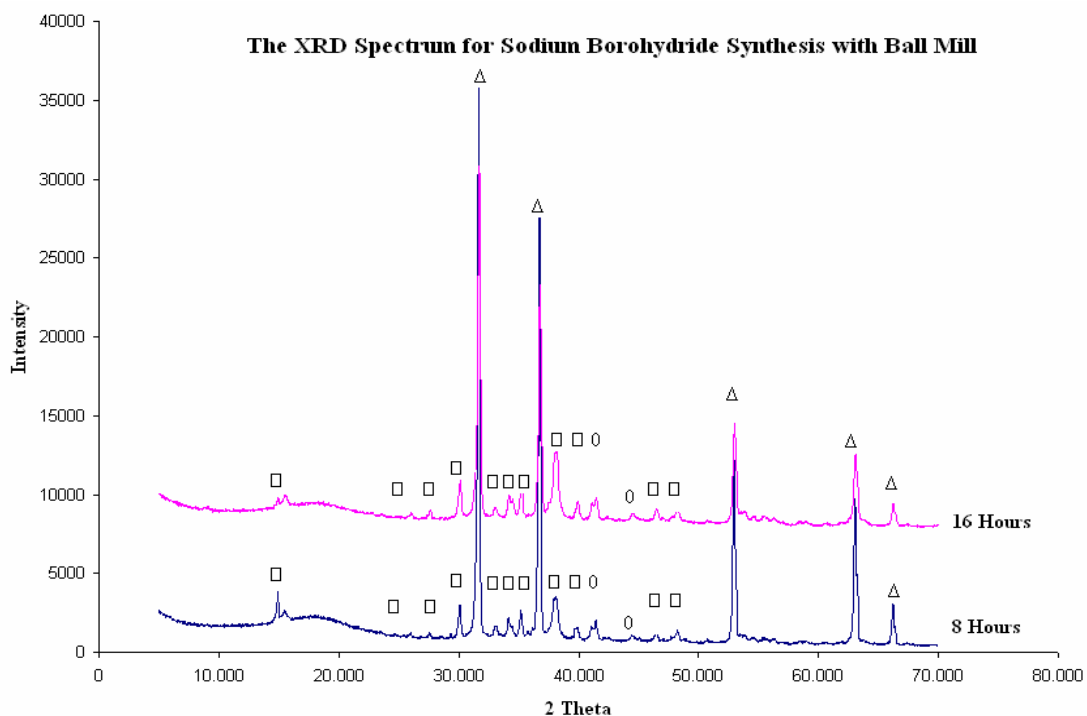
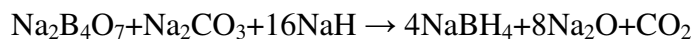


Figure 3.8. The XRD Spectra for Sodium Borohydride Synthesis Using NaH with Ball Mill at Room Temperature Δ = NaH, \square = Na_2CO_3 , \circ = $\text{Na}_2\text{B}_4\text{O}_7$

2) NaH was tried instead of metallic magnesium and H₂ gas. Experiments were carried with a ball mill at 100 rpm. Two time intervals, 8 and 16 hours were tried at room temperature.



Na₂CO₃, NaH and small Na₂B₄O₇ peaks are detected at XRD spectra of 8 and 16 hours experiments which is given in Figure 3.8. Both spectra are nearly the same. No NaBH₄ peaks are observed.

3.2.2. Experiments with Disc Mill

1) Metallic magnesium and H₂ gas were used as starting materials instead of MgH₂. Experiments were carried out with a disc mill at 100 rpm. Three time intervals - 8, 16 and 24 hours - were tried at room temperature.



Mg and small Na₂CO₃ peaks were detected but Na₂B₄O₇ peaks disappeared at XRD spectrum of 8 and 16 hours experiments which is given in Figure 3.9. However Na₂CO₃ peaks also disappeared at 24 hours experiments' spectrum. No NaBH₄ peaks were detected at the XRD spectra.

2) Same experiments were carried with a grinding disc at 100 rpm. Two time intervals, 8 and 16 hours were tried for 50 °C at 10 bar H₂ pressure.



Mg and small Na₂CO₃ peaks were detected in Figure 3.10. at both XRD spectra. However Na₂B₄O₇ peaks disappeared. No NaBH₄ peaks are observed.

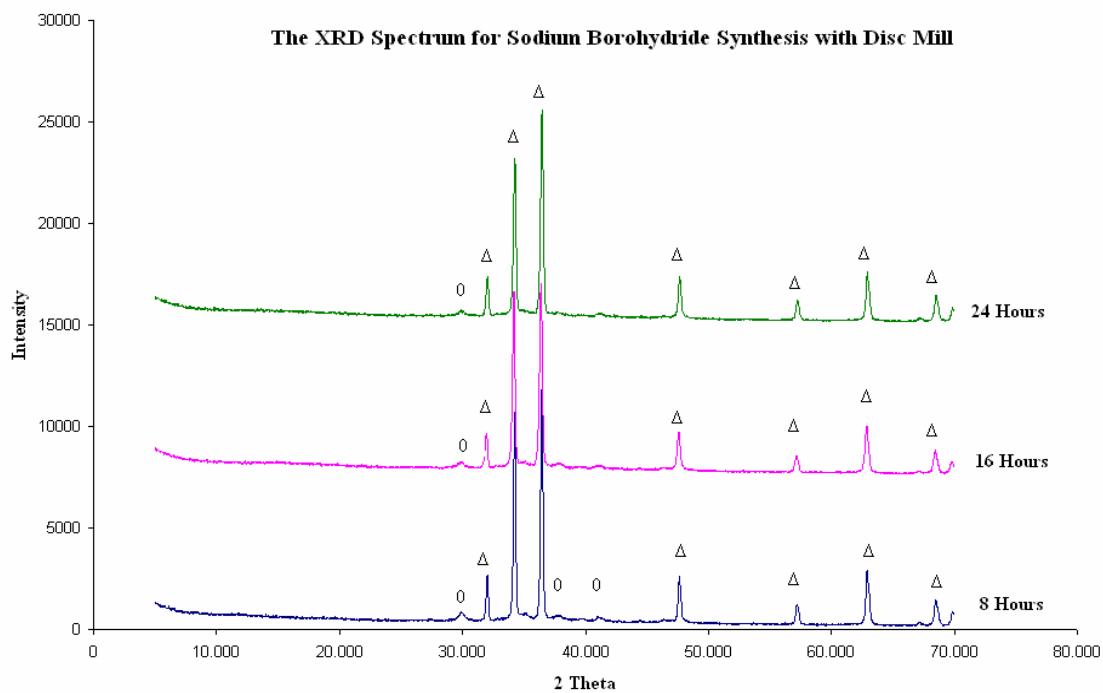


Figure 3.9. The XRD Spectra for Sodium Borohydride Synthesis Using H_2 Gas with Disc Mill at Room Temperature $\Delta = \text{Mg}$, $0 = \text{Na}_2\text{CO}_3$

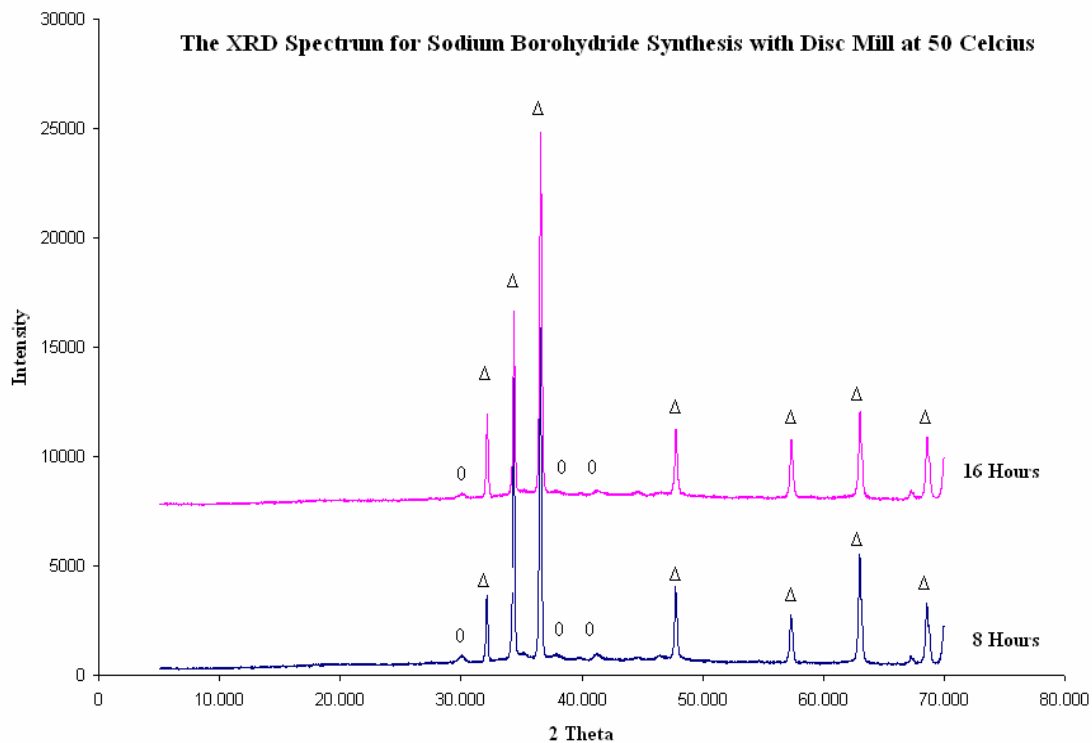


Figure 3.10. The XRD Spectra for Sodium Borohydride Synthesis Using H_2 Gas with Disc Mill at 50°C $\Delta = \text{Mg}$, $0 = \text{Na}_2\text{CO}_3$

3) NaH was used as a source of H₂ gas. Experiments were carried with a grinding disc at 100 rpm. Two time intervals, 8 and 16 hours were tried at room temperature.



NaH and small Na₂CO₃ peaks were detected at both XRD spectra which are shown in figure 3.11. Na₂B₄O₇ peaks disappeared. No NaBH₄ peaks were observed.

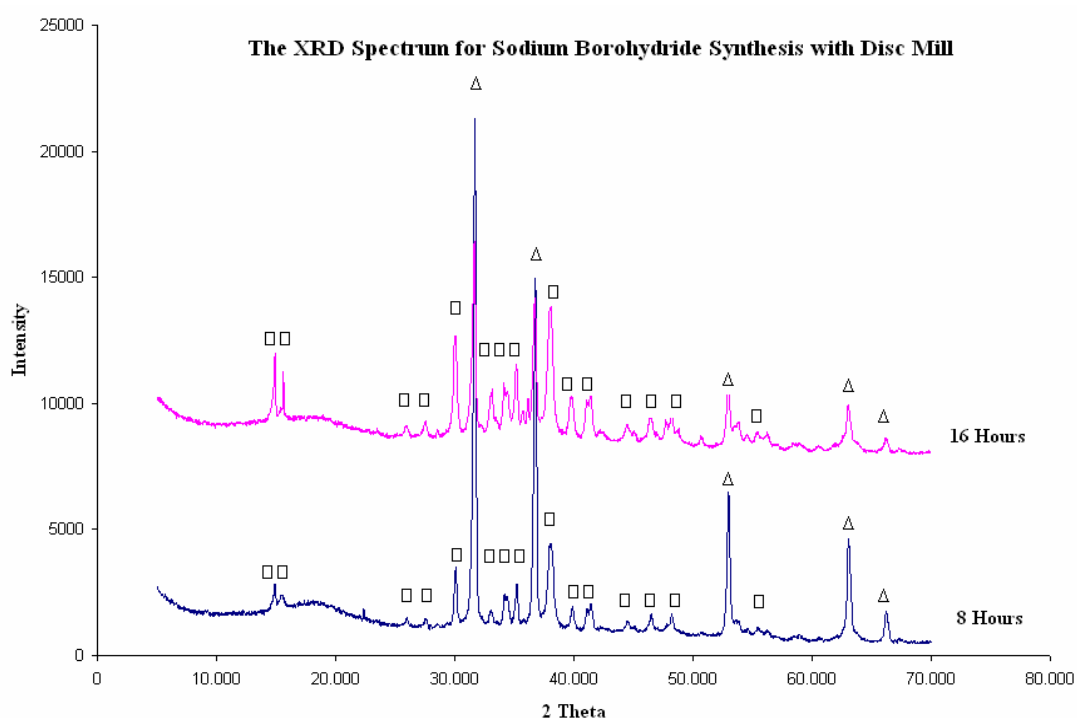


Figure 3.11. The XRD Spectra for Sodium Borohydride Synthesis Using NaH with Disc Mill at Room Temperature Δ= NaH, □=Na₂CO₃

4) a) The process that starts from Na₂B₄O₇.10H₂O requires two parts of NaOH to make one part of NaBO₂. Na₂B₄O₇.10H₂O, NaOH and H₂O were put in disc mill and grinded 8 hours at 100 rpm.



b) $\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$ is treated with a simple drying process to yield anhydrous sodium metaborate.

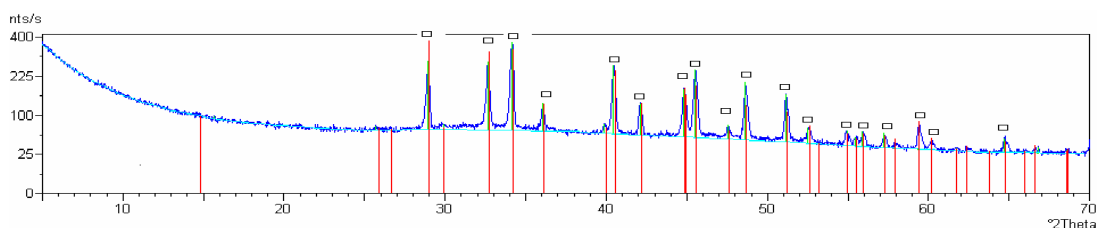
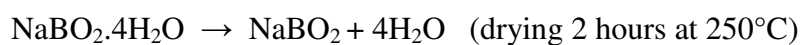


Figure 3.12. The XRD Spectrum for anhydrous sodium metaborate synthesis
 $\square = \text{NaBO}_2$

Anhydrous sodium metaborate (NaBO_2) was synthesised. Red peaks belong to the anhydrous sodium metaborate in Figure 3.12.

c) The sodium borohydride can be processed by the reaction as shown in equation, where the system is kept under constant temperature (250°C) and 10 Bar H_2 pressure conditions at 8 hours.



Small sodium borate hydroxide ($\text{Na}_2(\text{BO}_2(\text{OH}))$) and MgO peaks were detected at the XRD spectra as shown in Figure 3.13. But no NaBH_4 peaks were detected at the XRD spectra as shown in figure 3.13.

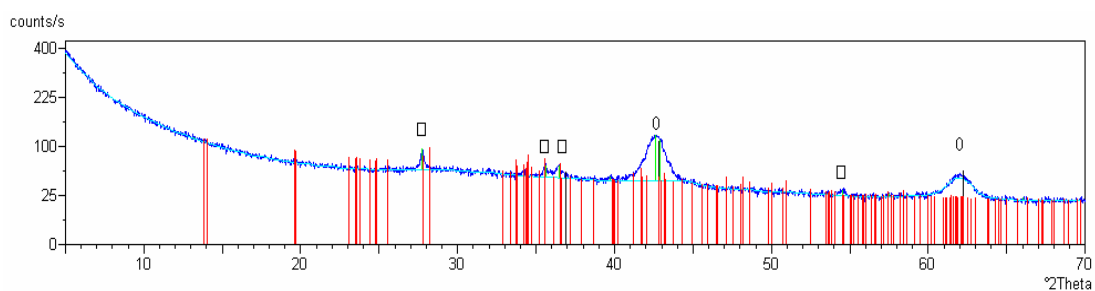
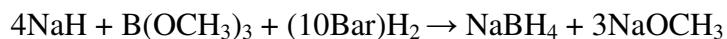


Figure 3.13. The XRD Spectrum for Sodium Borohydride Synthesis
 $\square = (\text{Na}_2(\text{BO}_2(\text{OH}))), 0 = \text{MgO}$

5) Experiments were carried using NaH and B(OCH₃)₃ as starting materials at 50 °C and 10 bar H₂ pressure with a grinding disc at 100 rpm. Two time intervals, 8 and 16 hours were tried.



The spectra are very different as shown in Figure 3.14. NaH, C₁₄H₈O₂ (alpha-9,10-Phenanthrenedione) and small NaBH₄ peaks appear in both spectra. NaBH₄ and C₁₄H₈O₂ peaks are more intense in the spectrum for 16 hours experiment, but NaH peaks are almost same as detected in Figure 3.14. The spectrum for 8 hours experiments has some excessive peaks. These peaks match with CaO but our samples do not contain Ca. CaO is probably an impurity from a previous XRD analysis. C₁₄H₈O₂ peaks may be due to the NaH solution because the chemical is bottled and transported in a mineral oil.

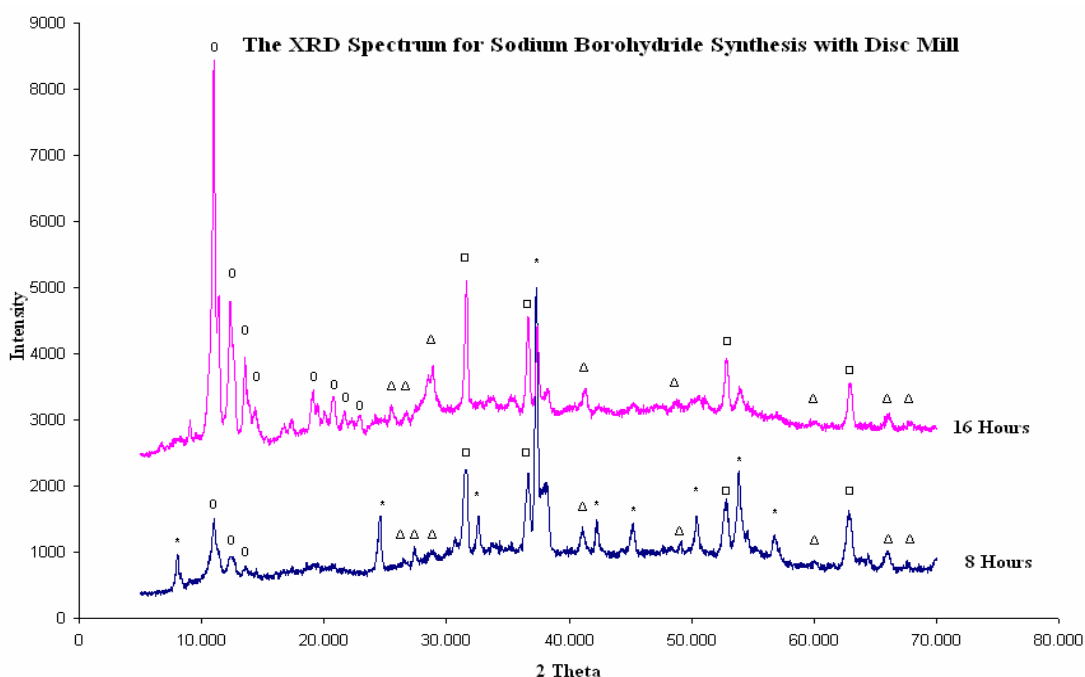


Figure 3.14. The XRD Spectra for Sodium Borohydride Synthesis Using H₂ Gas, NaH and B(OCH₃)₃ with Disc Mill at 50 °C Δ= NaBH₄, □=NaH, ○= C₁₄H₈O₂, *=CaO

CHAPTER 4

CONCLUSION

The aim of this study was to develop a new method for the synthesis of sodium borohydride at low temperatures.

The most different part of this study is working at low temperatures and the more effective grinding instead of heating. In the literature studies at 50°C was not found.

Studies progressed at in two stages.

1) Experiments carried out for the production of MgH₂. Magnesium hydride which is the starting material for the synthesis of NaBH₄ could not be obtained from the market, therefore our experiments started with the production of MgH₂.

2) Experiments carried out for the production of NaBH₄.

Conclusions for MgH₂ production:

- Only heating and H₂ pressure application was not enough for sufficient MgH₂ formation.

- In the literature, it is stated that heating between 300°C to 400°C and hydrogen pressures between 10 to 70 bar “(Liang et al. 1995, Noritake et al. 2003, Wu et al. 2006)” gives satisfactory yields. Our studies for heating up to 400°C and 10 bar hydrogen pressure gave very poor yields. A literature result for 24 hours, 10 Bar and 350°C study with a yield of %60 “(Li et al. 2002)” is not consistent with our results. The only difference between this result and ours is the size of Mg particles. Their Mg powder size is stated as (<75 μm) while our starting Mg powder size was between (50 - 150 μm).

- Production of MgH₂ is possible at low grinding speeds, low temperatures and low H₂ pressures.

- Grinding is very important factor for magnesium hydride synthesis at low temperatures.

- Grinding especially with disc mill at 100 rpm increased the yield with a considerable amount.

- It was rather surprising to see that grinding was more effective than heating for MgH₂ formation. This effect is displayed in Figure 4.1.

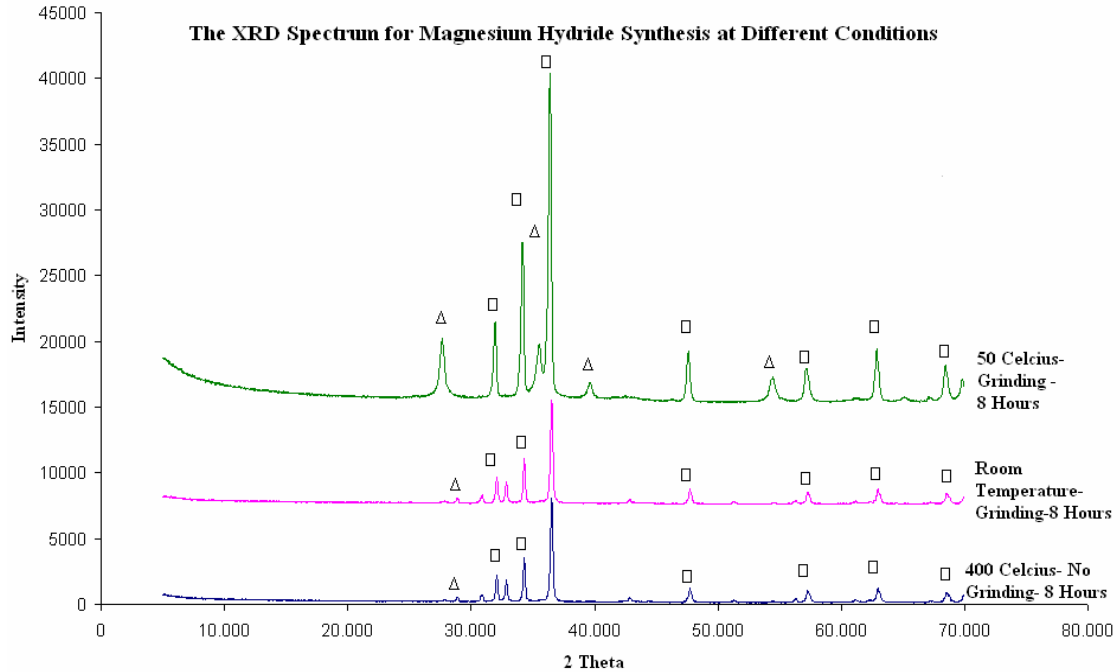


Figure 4.1. The XRD Spectra for MgH_2 Synthesis at Different Conditions $\Delta = MgH_2$, $\square = Mg$

- Most effective grinding is accomplished with a disc mill instead of ball mill. We think this is due to the big mass and therefore to the big momentum of the disc.

- Considerable MgH_2 production is possible even at 10 Bar H_2 pressures. The yield can be increased at higher H_2 pressures.

- Heating and grinding time were selected as the most effective parameters and experimental design set up was planned for these parameters. Heating at $50^\circ C$ and 24 hour grinding time was found as the optimal experimental conditions.

Conclusions for $NaBH_4$ production:

- MgH_2 production was accomplished which is used as starting material for the production of $NaBH_4$. However its purification was not completed so it could not be used as a starting material.

- $NaBH_4$ production using $Na_2B_4O_7$, Na_2CO_3 , Mg and H_2 gas as the starting materials at room temperature and at $50^\circ C$ under 10 bar H_2 pressure did not give satisfactory results.

- $NaBH_4$ production using $Na_2B_4O_7$, Na_2CO_3 and NaH as the starting materials at room temperature under 10 bar H_2 pressure did not give satisfactory results.

- NaBO_2 was produced from $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$. This NaBO_2 was used as a starting material for the production of NaBH_4 . However NaBH_4 could not be obtained.

- $\text{B}(\text{OCH}_3)_3$ and NaH was reacted in a disc mill at 50°C under 10 bar H_2 pressure. NaBH_4 peaks were observed in the XRD spectrum. Experiments at room temperatures and at 100°C were also fulfilled but their XRD spectra were not obtained.

Further studies will continue in two subjects.

a) Further studies will be carried to find the optimal conditions for MgH_2 synthesis. Studies will be carried at around 50°C to 80°C because our preliminary calculations gives 69°C as the optimal temperature. Our calculations also show the optimal grinding time as 21 hours, so the experiments will be carried between 20 to 24 hours. Longer grinding times, up to 30 hours will also be tried.

b) Studies on NaBH_4 production will continue in our future studies. $\text{B}(\text{OCH}_3)_3$ and pure NaH will be reacted in a disc mill between room temperature and 100°C under 10 bar H_2 pressure.

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