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Note: *Coiled magnesium sheets and magnesium ingots. This work has been released into the public domain by author Mark Fergus (CSIRO). The file was taken from Wikimedia Commons from the following location: https://en.wikipedia.org/wiki/File:Mg_sheets_and_ingots.jpg*

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The Chemist (Established in 1923)

Editorial

Innovations in Chemistry

David Devraj Kumar

Florida Atlantic University

Innovations in chemistry continue as many products that impact our life could be traced back to chemical discoveries (1). Examples include penicillin, protective fabrics, renewable energy, information technologies (computer chips, organic light emitting diodes), and fertilizers. Some chemistry innovations capture public attention and some do not. Regardless, chemistry innovations continue to impact the world. In this context, the cadre of articles appearing in this issue of *The Chemist* is an indication of continuing innovations in chemistry at various domains.

A novel method of synthesizing risedronic acid, avoiding environmentally hazardous halogenating agents is the focus of the study by Rafal Tomczak and co-authors. Considering the pharmaceutical applications of the sodium salt of risedronic acid this study is significant. Lei Zhang and co-author report a study of the effect of RF magnetron sputtering parameters on the electro-optical properties of amorphous indium zinc thin films. Their study shows that the maximized transparency and conductivity of IZO thin films are same as those of ITO thin films. Adeola Ibikunle and co-author present the results of modeling and kinetics studies of doped magnesium borohydrides. In another study, they address the effects of additives on the dehydrogenation of Magnesium borohydrides.

Todd Houston shows how to make chemistry more interesting and engaging, by using a membrane permeability visual demonstration that is easy to carry out. Demonstrations such as this are excellent vehicles for promoting public understanding of chemistry.

By Volume 90 and Issue Number 2 *The Chemist* has completed six years since it was re-introduced in its current format and mission as the official refereed online journal of The American Institute of Chemists. I would like to acknowledge the members of the Review Board for their timely input and valuable service to maintain the quality of manuscripts appearing in *The Chemist*. Also acknowledgments are due to the editorial assistants Debora Cate, Vanessa Hotchkiss and Chelsea Dittrich for their invaluable technical and language help.

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Influence of RF Magnetron Sputtering Parameters on the Electro-Optical Properties of Amorphous Indium Zinc Thin Film

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Abstract: Transparent Conducting Oxide (TCO) thin films have been extensively used in optoelectronic applications such as flat panel displays, touch screen devices, and photovoltaics. In this project we deposited amorphous Indium–Zinc Oxide (IZO) thin films by Radio Frequency (RF) magnetron sputtering from a In_2O_3–10 wt. % ZnO sintered ceramic target and optimized RF power, argon gas flow rate, thickness of film, and substrate tilt angle of microscope slide substrates to maximize conductivity and transparency in visible and near infrared regions. The results indicated that the maximized conductivity and transparency of IZO thin films are the same as ITO's conductivity and transparency.

Key Words: amorphous indium–zinc oxide, RF sputtering, Electro-optical properties.

INTRODUCTION

Transparent Conducting Oxide (TCO) films such as impurity-doped indium oxide, tin oxide, and zinc oxide systems have been widely used as transparent conductors for numerous optoelectronic applications, such as flat panel displays, touch screen devices, and photovoltaics [1 – 4]. Among these transparent conducting oxides, Indium Tin Oxide (ITO) is one of the most widely used because of its low resistivity and high optical transparency in the visible region. However, ITO is relatively expensive, brittle, unstable, and inflexible. Moreover, ITO transparency drops rapidly for wavelengths above 1,000 nm and requires a higher deposition temperature [5]. Indium Zinc Oxide (IZO) thin film has been reported to have an excellent conductivity, high optical transparency, and low deposition temperature [6-7]. Most importantly, the smooth surface and high etching rate of amorphous IZO thin films have been discussed [8].

A variety of techniques such as DC sputtering, RF sputtering, Pulsed Laser Deposition (PLD), Metal Organic Chemical Vapor Deposition (MOCVD), and spray pyrolysis have been used to deposit IZO films [9]. In this paper, we report on the factors controlling the surface morphology and electro-optical properties of ITO (10 wt. % ZnO + 90 wt. % In_2O_3) films deposited on microscope slide (Fisher Scientific Inc.) substrates with RF magnetron sputtering deposition. The electrical and optical properties of the IZO samples were examined as a function of the top IZO thickness, sputtering power, Argon gas flowing rate, and substrate tilt angle to optimize the conductivity and optical transparency of the IZO layer. In addition, surface morphology of the top IZO layer was evaluated by Scanning Electron Microscopy (SEM).

EXPERIMENTS

An IZO (10 wt. % ZnO + 90 wt. % In_2O_3, 2.00″ diameter, 0.125″ thick, 99.99% pure) ceramic target (Kurt J. Lesker company) was placed at a distance of 50 mm from the main chamber of an AJA RF/DC magnetron sputtering system. The main chamber was equipped with a load-lock system and a diffusion pump which had a base pressure of 1.5×10^{-6} torr. The microscope slide substrates (1″ x 1″)

were cleaned in an ultrasonic bath of acetone at room temperature for 5 minutes, rinsed in deionized water in the ultrasonic bath for another 5 minutes, and then dried under N_2 gas. The substrates were treated in Ultraviolet light for 15 minutes right before they were placed in the center of main chamber via the load-lock system from the side chamber of the sputtering system for being sputtered. The sputtering was carried out at room temperature and at a pressure between 8×10^{-3} and 2×10^{-4} torr in pure argon gas with varying sputtering parameters such as sputtering power, argon gas flow rate, and deposition thickness.

Thickness of each deposited IZO layer was estimated by deposition rate from the sputtering system and was also measured by a thickness profilometer (Surfcorder ET-3000, Kosaka Laboratory Ltd.). Surface morphology of the top IZO layer was analyzed by a Scanning Electron Microscope (SEM). The optical transmittance was measured in the wavelength range of 300 – 1100 nm by UV/VIS/NIR spectrophotometer (Shimadzu Corp.)

RESULTS & DISCUSSIONS

Table 1 shows the sheet resistances of deposited IZO thin films varied with the RF sputtering powers applied with fixed 100 nm top IZO film thickness and 251 gas flowing rate. The lowest sheet resistance, 265 Ω/Sq, was found at 20 watts sputtering power. As the crystallinity of the IZO films increased with sputtering power, the grain size and surface roughness of the films increased, and electrical resistivity decreased. However, in this work, as the sputtering power increased beyond 25 W, electrical resistivity also increased. This might be due to a change in its phase or crystal structure as film deposition rate varied [10]. It also demonstrated a small influence of sputtering power on the optical transmittance at wavelength regions of 300 to 1100 nm.

Table 1. Process conditions for depositing IZO thin films - IZO thickness: 100 nm, Ar. flow rate: 250

Power	Ω/Sq
8	5000
10	625
15	295
20	265
25	375
40	25000

Table 2 shows the sheet resistances of deposited IZO films as a function of argon gas flow rate with fixed 100 nm top IZO film thickness and 20 W sputtering power. The best electrical conductivity of the film was measured at an argon gas flow rate of 51.

Increasing argon flow rates lead to increases in the thickness and the crack size on the films surface, which might have resulted in higher sheet resistance [11]. However, higher sheet resistance was also observed at very low argon flow rates. It might be due to decreasing the carrier concentration of the IZO films at low argon flow rates and decreasing the films growth rate. There were no observed significant differences for optical transmittance at wavelength regions of 300 to 1100 nm.

Table 2. Process conditions for depositing IZO thin films - power: 20 W, IZO thickness: 100 nm.

Ar. Flow Rate	Ω/Sq
300	670
250	265
187	290
125	210
100	85
51	65
30	95

Table 3 shows that the sheet resistances of deposited IZO films decrease when the thickness increases with fixed 20 W sputtering power and 51 argon gas flow rate. The sheet resistance at 150 nm was 51 Ω/sq which is close to ITO's at the same thickness (around 35 Ω/sq). However, an increasing IZO deposited thickness resulted in a decrease of optical transmittance at ultraviolet wavelength regions of 300 to 400 nm, although a slight optical transmittance fluctuation was noticed at visible and near infrared regions of 400 to 1100 nm, as shown in Figure 1. The Figure also shows that ITO had a better optical transmittance performance in the ultraviolet region than IZO's.

Table 3. Process conditions for depositing IZO thin films - power: 20 W, Ar. flow rate: 51

Thickness (nm)	Ω/Sq
100	65
150	51
200	39
300	25

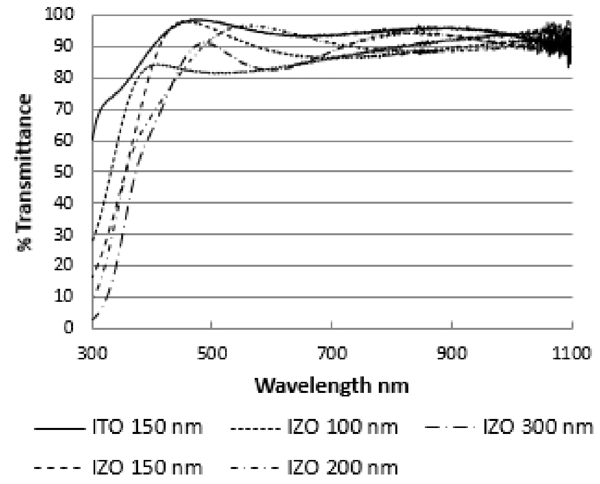

Fig 1. Transmittance curves with 51 Argon gas flowing rate, and 20 W sputtering power.

Table 4 shows the minimal sheet resistances 35 Ω/sq at 70° tilt angle. The sputtering with tilt angles produced a columnar structure which reduced film stress induced by the defect variations in ZnO films [12], and thus at a 70° tilt angle sheet resistance decreases. Figure 2 shows the transmittance profile at the minimal sheet resistance did not make any noticeable changes compared with the profile with no tilt angles, a bit lower before 420 nm and a bit higher after 420 nm.

Table 4. Process conditions for depositing IZO thin films - power: 20 W, IZO thickness: 150 nm, Ar. flow rate: 51

Tilt angle	Ω/Sq
45°	150
60°	109
67.5°	90
70°	35
75°	72
80°	125
90°	175

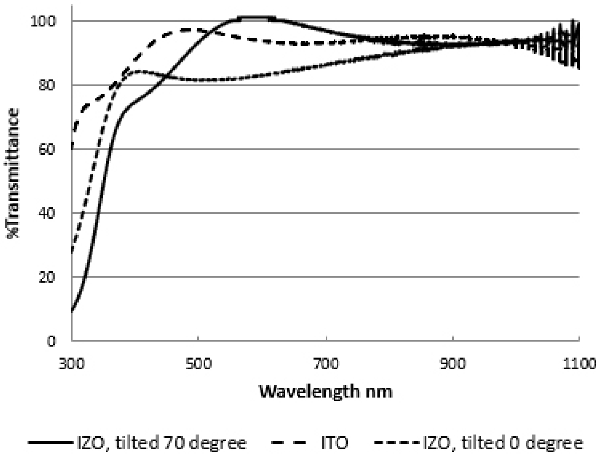

Fig 2. Transmittance curves with different title angles at 51 Argon gas flowing rate, 20 W sputtering power, and 150 nm thickness.

Figures 3 and 4 show AFM Images of surface topology of the top IZO layer with 100nm and 300 nm thickness under the processing condition of 51 argon flow rate and 20 watts sputtering power. In the case of the 300-nm-thick IZO layer (Figure 4), the AFM image is fairly smooth and featureless without defect crack pinholes, cracks, or protrusions on the surface of the top IZO layer. The RMS roughness of the area, excluding particulates, was Sq = 3.3 Å. In the case of the top IZO layer with a thickness of 100 nm (Figure 3), the AFM surface image had uniform defect crack pinholes and cracks. The RMS roughness of the area, excluding particulates, was Sq = 4.2 Å. The figures indicated that the surface of the top IZO layer got smoother with the increased thickness, and in the meanwhile, the sheet resistance would be reduced because the pinhole-like IZO layer was covered by the top IZO layer [5].

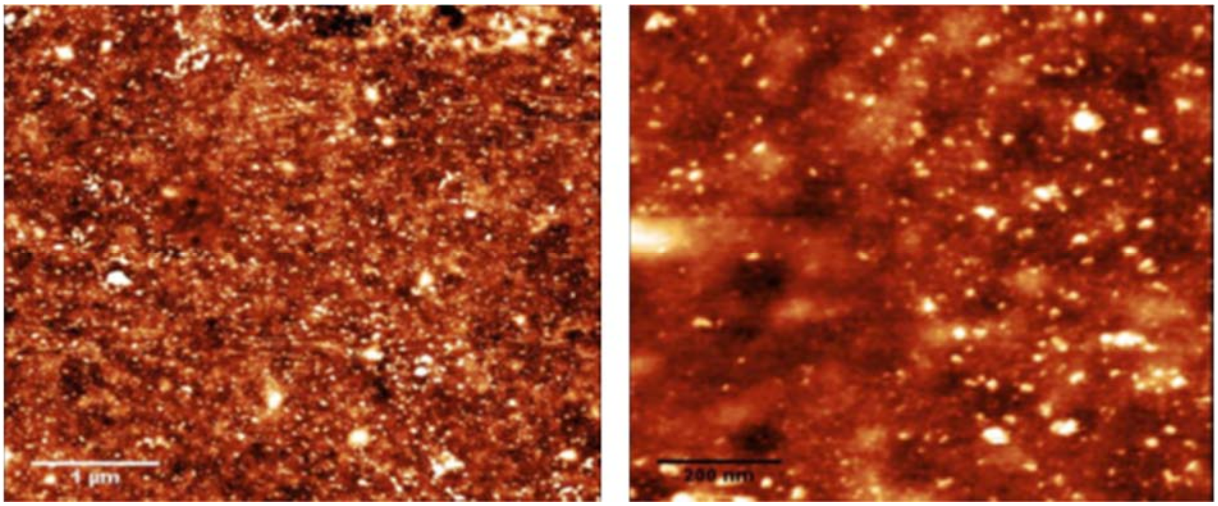

Fig 2. AFM Images of surface topology of IZO with 100 nm thickness, 51 Argon flow rate, and 20 W power. RMS roughness of area in (right) excluding particulates is Sq = 4.2Å.

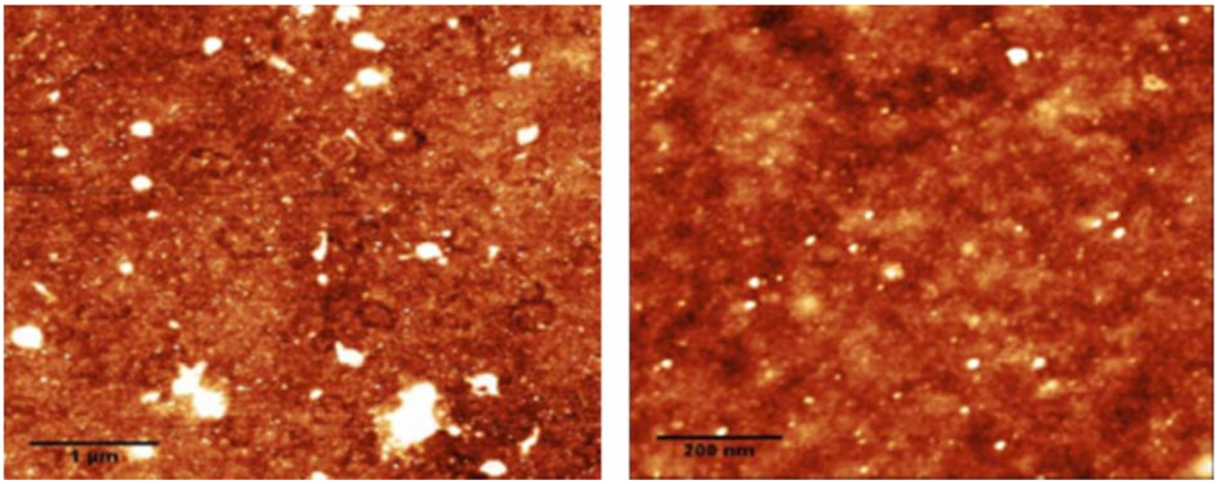

Fig 3. AFM Images of surface topology of IZO with 300 nm thickness, 51 Argon flow rate, and 20 W power. RMS roughness of area in (right) excluding particulates is Sq = 3.3Å.

CONCLUSION

In this work, amorphous Indium Zinc Oxide (IZO) thin films were deposited on the microscope slide substrates by using RF magnetron sputtering technique. We investigated the electrical and optical properties of these IZO thin films under different process conditions. We found the conductivity and optical transparency of the deposited IZO thin film very close to ITO's under the process condition at a 51 Argon flow rate, 20 W sputtering power, 150 nm thickness, and 70° substrate tilted angle.

ACKNOWLEDGMENTS

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Modeling & Kinetics Studies of Doped Magnesium Borohydrides

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Abstract: $Mg(BH_4)_2$ is a potential solid state hydrogen storage material with high gravimetric hydrogen holding capacity. The effects of mechanical milling of $Mg(BH_4)_2$ with CaH_2 and CaH_2/NaH on its rate of hydrogen desorption were investigated at constant thermodynamic driving force. There is at least a two fold increase in the hydrogen desorption kinetics of $Mg(BH_4)_2$ resulting from the two additives. The rate of hydrogen release from the $Mg(BH_4)_2/CaH_2$/NaH system is twice as fast as that of $Mg(BH_4)_2/CaH_2$. Modeling studies, based on a shrinking core model, showed that reaction at the phase boundary is the rate-limiting process in the hydrogen desorption from $Mg(BH_4)_2/CaH_2$ up to 70% of the reaction. In the $Mg(BH_4)_2/CaH_2$/NaH systems, reaction at the phase boundary is the rate controlling process up to about 90% of the reaction.

Key Words: Magnesium borohydride; Plateau pressure; Opposing pressure; Kinetics; Modeling.

INTRODUCTION

The desire to have a clean atmosphere has led to an increased urge to develop alternative sources of energy. The greatest challenge with the use of hydrogen as a source of fuel is the unavailability of suitable storage mechanisms. For solid state hydrogen storage in automobiles, complex metal hydrides that are lightweight, low cost, and high in hydrogen density are potential candidates [1,2]. The use of $Mg(BH_4)_2$ as a potential storage material has been gaining popularity in recent times due to its high gravimetric hydrogen content of 14.9 wt% [3-11]. The hydrogen, however, cannot be easily harnessed due to thermodynamic and kinetic barriers. Studies have shown that in complete dehydrogenation, $Mg(BH_4)_2$ should produce MgB_2 and 4 moles of hydrogen gas, according to equation (1) [12,13].

$$Mg(BH_4)_2 \rightarrow MgB_2 + 4H_2 \qquad (1)$$

A popular way of improving the hydrogen storage properties of hydride compounds, first developed by Reilly and Wiswall [14], is mixing/destabilizing with other additives. Vajo et al. [15,16] showed that addition of MgH_2 to $LiBH_4$ reduces its desorption temperature by changing the reaction pathway. The mixture also became reversible under moderate conditions. Similarly, a mixture of CaH_2 and $LiBH_4$ was predicted by Alapati et al. [17,18] to release 11.7 wt% of hydrogen, according to equation (2). They also calculated the enthalpy of the reaction to be 47 kJ/mol H_2.

$$LiBH_4 + CaH_2 \rightarrow 6LiH + CaB_6 + 10H_2 \qquad (2)$$

Studies showed that the system released hydrogen at a lower temperature than pure $LiBH_4$ [19-24]. Pinkerton and Meyer [21] reported that samples of $6LiBH_4 + CaH_2 + 0.25\ TiCl_3$, prepared by ball milling, released about 9.1 wt% of hydrogen during a TGA scan and that samples were successfully rehydrogenated under 83 bar H_2 and 400^{o}C.

Severa et al. [8] found that it was possible to reversibly store about 11 wt% hydrogen in $Mg(BH_4)_2$. This was achieved under extreme conditions by direct hydrogenation of MgB_2 at a pressure of 900 bar and a temperature of 400°C. The addition of catalyst/additives has also been reported to improve the hydrogen storage properties of $Mg(BH_4)_2$ [25 - 28]. For instance, Yang et al. [26] reported the reduction of the onset temperature for hydrogen release to 150°C by the addition of LiH. It was also shown by Bardaji et al. [12] that a composite mixture of $LiBH_4$ and $Mg(BH_4)_2$ releases about 7 wt% of hydrogen at lower temperature than that of the individual borohydrides. A theoretical study by Ozolin et al. [29] using DFT calculations identified some reaction schemes that have the potential of reversibly storing hydrogen. Some of these reactions schemes that have been studied by our group are highlighted in equations (3)-(5).

$$5Mg(BH_4)_2 + Ca(BH_4)_2 \rightarrow CaB_{12}H_{12} + 5MgH_2 + 13H_2 \quad (3)$$

$$3Mg(BH_4)_2 + CaH_2 \rightarrow 3MgH_2 + CaB_6 + 10H_2 \quad (4)$$

$$3Mg(BH_4)_2 + CaH_2 + 3NaH \rightarrow 3NaMgH_3 + CaB_6 + 10H_2 \quad (5)$$

In previous studies, we determined the hydrogen properties of these systems [10]. We also found that the mixture of $Mg(BH_4)_2$ and $Ca(BH_4)_2$ releases hydrogen at a faster rate than either of the components [11].

In this present study, we present the kinetics and modeling studies of hydrogen desorption of systems in reaction schemes (4) and (5).

EXPERIMENTAL

CaH_2 and NaH were obtained from Sigma-Aldrich and were used without further treatment. Unsolvated $Mg(BH_4)_2$ was prepared from MgH_2 and triethylamine borane, as described by Chłopek et al. [9]. All sample preparations were carried out in an argon-filled Vacuum Atmospheres glove box with oxygen and moisture levels below 1 ppm. The sample mixtures were ball-milled for 10 h using a SPEX 8000D mixer/mill. PCT isotherms were determined for each sample using an Advanced Materials Corporation Gas Reaction Controller PCI unit. This unit was fully automated and was controlled by a Lab View-based software program. Kinetics measurements were done in an all stainless steel Sieverts apparatus. This apparatus is described in Fig. 1. It contained a back pressure regulator for controlling the pressure that was applied to the sample. Pressure transducers were used to monitor the pressure in the reservoirs and the sample reactor. Kinetics measurements were done at the same temperature and thermodynamic driving force. The thermodynamic driving force, denoted as the N-Value, is defined as the ratio of the mid plateau pressure, P_m, to the opposing pressure, P_{opp} (i.e., $N=P_m/P_{opp}$). The experiments were all carried out at 450 °C and N =10. Further details about the technique of constant pressure thermodynamic forces are published elsewhere [10, 11, 23, 24, 30, 31].

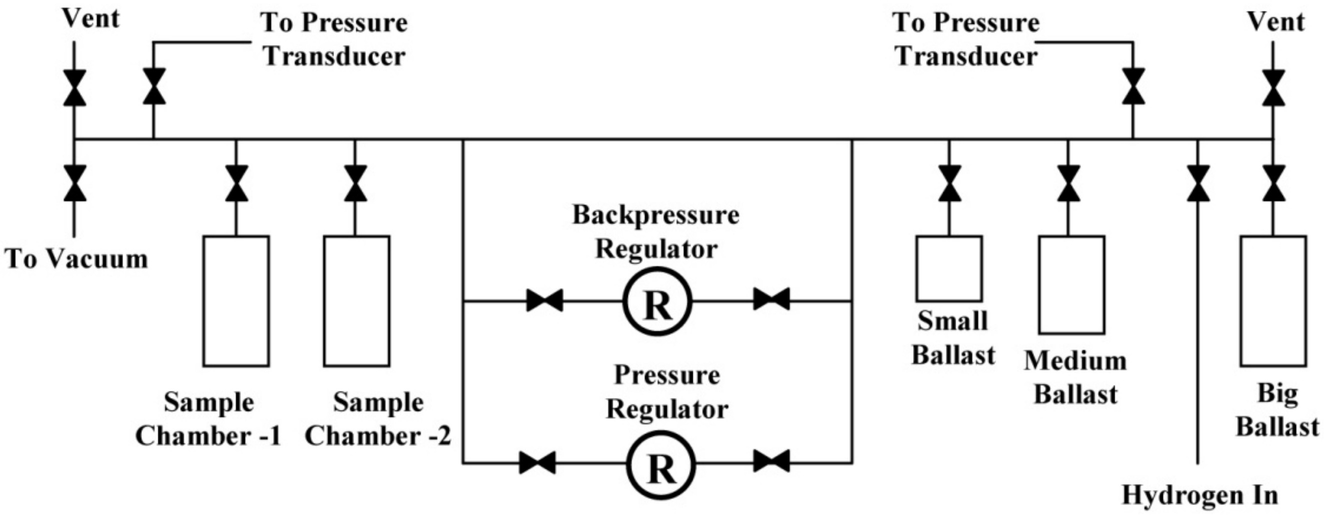

Fig 1: Schematic diagram of the apparatus used for kinetics measurements.

RESULTS & DISCUSSIONS

Desorption kinetics of the $Mg(BH_4)_2/CaH_2$ and $Mg(BH_4)_2/CaH_2/NaH$ mixtures as well as that of the pure $Mg(BH_4)_2$ components were performed at 450 °C (Fig. 2). These measurements were carried out at a constant pressure thermodynamic driving force of N=10. In order to accomplish this, it was first necessary to determine a PCT isotherm for each sample. The PCT isotherms of $Mg(BH_4)_2$ and the mixtures at 450 °C have been reported [10,30]. The opposing pressures determined for the mixtures from the isotherms are shown in Table 1.

Table 1: Plateau pressures, opposing pressures, & Reaction times to reach 90 %, T_{90} completion for borohydride systems at N=10 and 450°C.

System	Plateau pressure (atm)	Opposing pressure (atm)	T_{90}(min)
$Mg(BH_4)_2$	62.0	6.2	12.0
$Mg(BH_4)_2/Ca(BH_4)_2$	64.0	6.4	4.0
$Mg(BH_4)_2/CaH_2$	57.0	5.7	5.0
$Mg(BH_4)_2/CaH_2/NaH$	56.0	5.6	2.5

All of the reactions are faster than that of pure $Mg(BH_4)_2$. All of the reactions except $Mg(BH_4)_2$, reached 90% completion on or before 5 minutes. Table 1 shows the time taken for the hydrogen desorption reactions to reach 90% completion (T_{90}). It takes about 12 min for the pure $Mg(BH_4)_2$ to reach T_{90}, while the mixtures take between 2.5 - 4.0 mins to reach 90% completion. All the mixtures have also been reported to have higher desorption temperatures than the pure $Mg(BH_4)_2$, except the $Mg(BH_4)_2/CaH_2/NaH$ mixture [30].

Modeling studies were done to determine the process controlling the rates of hydrogen desorption from the systems. A set of equations used by Smith and Goudy [31] in modeling the $LaNi_{5-x}Co_x$ hydride system were used. The models were used to determine whether the hydrogen desorption process is controlled by a reaction occurring at phase boundary or hydrogen diffusion.

$$\frac{t}{\tau} = 1 - (1 - X_B)^{1/3} \qquad (6)$$

Where

$$\tau = \frac{\rho_B R}{b k_S C_{Ag}}$$

$$\frac{t}{\tau} = 1 - 3(1 - X_B)^{2/3} + 2(1 - X_B) \qquad (7)$$

Where

$$\tau = \frac{\rho_B R^2}{6 b D_e C_{Ag}}$$

The various terms in the equations are defined as follows: t = time at a specific point in the reaction; X_B = fraction of the material reacted; R = initial radius of the sample particles; b = stoichiometric coefficient of the material; C_{Ag} = the gas phase concentration of the reactant; D_e = the effective diffusivity of the hydrogen atoms in the material; ρ_B = the density of the material; and k_S = a rate constant. In the modeling studies, the experimental kinetics data of the systems were statistically fitted with theoretically generated data based on equations (6) and (7).

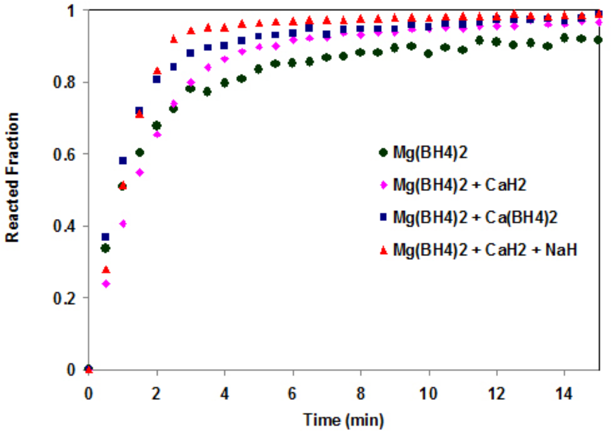

Fig 2. Combined plots of reacted fraction versus time for $Mg(BH_4)_2$, $Mg(BH_4)_2/Ca(BH_4)_2$, $Mg(BH_4)_2/CaH_2$ and $Mg(BH_4)_2/CaH_2/NaH$ mixtures at 450°C and N = 10

Values of τ were selected that minimized the difference between the experimental and theoretical curves. The parameters (R, b, De, ρB, and ks) were not used to determine τ in the equations and we don't have their values. Tau (τ) is essentially a fitting parameter. The values of τ for each reaction were determined statistically by minimizing the standard deviation between the experimental and theoretical curves. Equation (6) corresponds to a situation in which the rate is controlled by diffusion, while equation (7) is that of a process where the rate is controlled by reaction at the phase boundary.

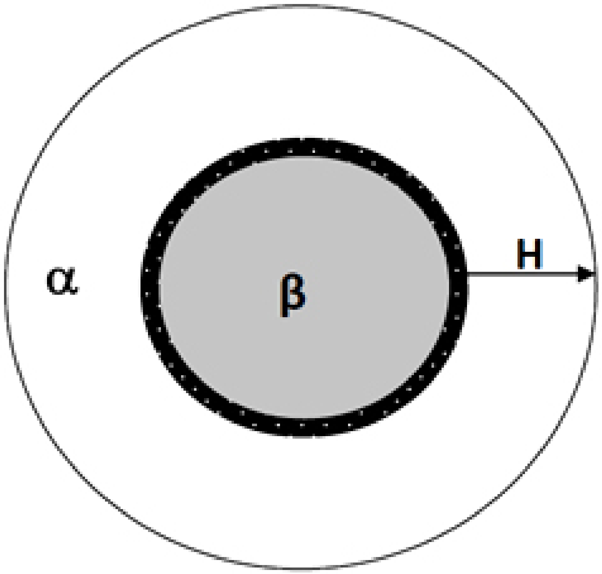

Fig 3: The shrinking core model.

Equations (6) and (7) are based on a shrinking core model in which desorption begins from a fully hydrided sphere. As hydrogen desorbs from the particle, an outer layer of dehydrided material begins to cover the sphere. The outer dehydrided layer grows as hydrogen desorption continues and the inner sphere shrinks. A phase boundary separates the outer and inner spheres. A schematic of this shrinking core model is shown in Fig. 3. Hydrogen desorption occurs at the phase boundary and hydrogen atoms diffuse through the outer dehydrided layer. The two processes occur simultaneously throughout the entire desorption process. The kinetics may be limited by the rate of reaction at the phase boundary or by the rate of hydrogen diffusion through the outer dehydrided layer, depending on which is slower.

The plot in Fig. 4 for $Mg(BH_4)_2/CaH_2$ shows that the phase boundary controlled model fits the experimental curve up to 70% of the reaction, while the diffusion controlled model fits between 75 and 85%. Above that region, none of the two models fits. Therefore, the system rate determining step changes during the course of the reaction. The results correspond to those reported earlier for the $Mg(BH_4)_2/Ca(BH_4)_2$ system [11]. The CaH_2 changed the rate determining process of the mixture from that of pure $Mg(BH_4)_2$ controlled by the diffusion process [11].

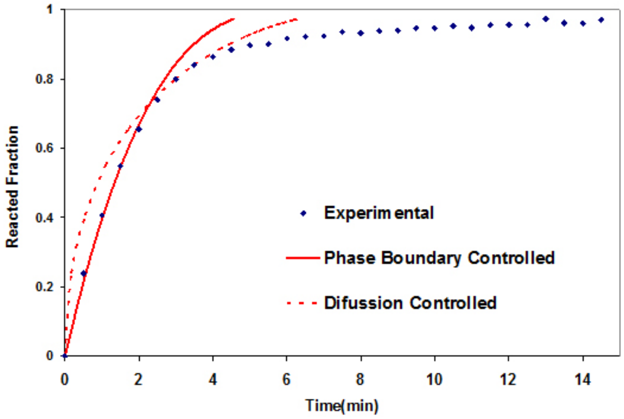

Fig 4: Modeling curves for the $Mg(BH_4)_2/CaH_2$ mixture.

The modeling curve of the $Mg(BH_4)_2/CaH_2/NaH$ mixture is shown in Fig. 5. Model fitting for the $Mg(BH_4)_2/CaH_2/NaH$ mixture shows a good fit of the phase boundary controlled model with the experimental up to about 90% of the reaction. The diffusion controlled model does not fit at all for this process. Therefore, the rate limiting process in the dehydrogenation of $Mg(BH_4)_2/CaH_2/NaH$ system is a reaction at the phase boundary. It can be seen that the mixture containing NaH released hydrogen at the fastest rate of any system under study. It may be that the Na^+ enhances the rate of hydrogen diffusion in the system, thereby resulting in an increase in the overall reaction kinetics. The high desorption temperature of $Mg(BH_4)_2/CaH_2/NaH$, the highest of the three mixtures involving $Mg(BH_4)_2$, can be attributed to the high reactivity of the Na in the system [30].

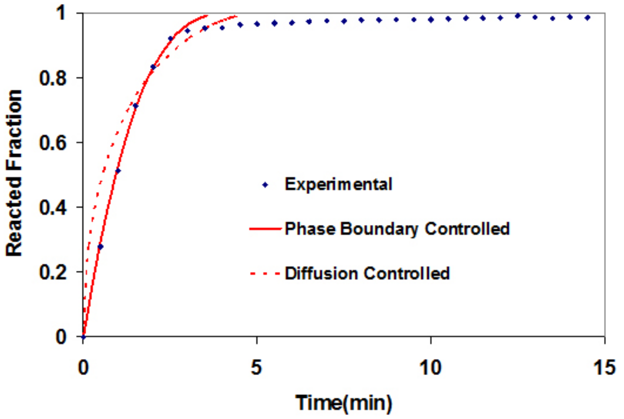

Fig 5: Modeling curves for the $Mg(BH_4)_2/CaH_2/NaH$ mixture.

CONCLUSION

The studies have shown that the rate of hydrogen desorption from $Mg(BH_4)_2$ can be increased by destabilization. The mechanical alloying of $Mg(BH_4)_2$ with CaH_2 and CaH_2/NaH improved the rate of hydrogen desorption, with the ternary mixture having the fastest kinetics. Modeling studies also show that the rate of hydrogen desorption from $Mg(BH_4)_2/CaH_2$ is controlled by reaction at the phase boundary in first 75% of the reaction, and changed to diffusion in 75-85% of the reaction. Furthermore, hydrogen desorption from $Mg(BH_4)_2/CaH_2/NaH$ is controlled by the reaction at the phase boundary up to 90% of the reaction based on the shrinking core model.

ACKNOWLEDGMENTS

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A New Way to Obtain Risedronic Acid

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Abstract: A novel, facile, and convenient protocol for the synthesis of risedronic acid was developed involving two sequential reactions performed at room temperature. One of the main benefits of this approach is avoiding the use of hazardous and environmentally harmful halogenating agents. The mild reaction conditions and unexpectedly high catalytic activity of DMAP (4-dimethylaminopyridine) are the key elements that set this reaction apart from the majority of previous reports. The synthesis of risedronic acid was carried out in 76% yield and excellent purity (⩾99.9%). The sodium salt of this compound is one of the most frequently prescribed drugs used for the treatment of osteoporosis and other bone-related disorders.

Key Words: Green chemistry; Medicinal chemistry; Organocatalysis; Synthesis design; Synthetic methods

INTRODUCTION

Recent years of intensive research studies have proved that bisphosphonates (compounds based on a phosphorous-carbon-phosphorous spine) are gaining increasing interest in organic chemistry. This is a direct result of their unique chemical properties that make them affordable and suitable for many medical purposes. In general, their action to prevent the loss of bone mass is considered to be a key pharmacological effect in clinical use for the treatment of osteoporosis, Paget's disease, hypercalcemia, and others. It bears emphasizing that these compounds are able to prevent several types of cancer from spreading to the bone. Some bisphosphonates exhibit direct apoptotic effects on cancer cells activating the γδ-T cell population which makes them attractive for the treatment of a broad spectrum of tumors [1].

The increased usage of these compounds underscores the research efforts aiming, in particular, to find useful and convenient methods for the formation of the crucial P-C-P moiety [2]. Since α-hydroxy-1,1-bisphosphonates were officially recognized as the most potent suppressors of bone resorption, many attempts have been made to obtain such compounds in a direct and efficient way. The traditional procedure involves the formation of an acyl chloride from the corresponding carboxylic acid using highly toxic PCl_3, PCl_5, $POCl_3$, or $(COCl)_2$, followed by a direct reaction with phosphorous acid [3] or trialkyl phosphite with acidic hydrolysis [4]. The latter requires high temperatures (100–150 °C) and a harsh acidic environment to occur. The final, high-purity product is sometimes difficult to obtain since there is a number of side reactions that are also possible [5].

Recently, many attempts have been made to optimize the synthesis of N-heterocyclic dronic acids. Risedronic acid was synthesized by Keglevich et al. using phosphorous trichloride as the main reagent [6]. The final product was obtained after a short reaction time without using phosphorous acid. This method was presented in a review concerning the 'greener' synthesis of bisphosphonic acid derivatives [7]. However, the optimal reaction conditions still require the use of toxic PCl_3 and high temperatures.

Another approach resulting in the synthesis of α-hydroxy-1,1-bisphosphonates was presented by Mustafa et al. The use of microwave irradiation in the place of conventional heating made it possible to reduce the reaction time to minutes instead of hours [8]. Although this method appears promising for large-scale industrial processes, it is relatively expensive.

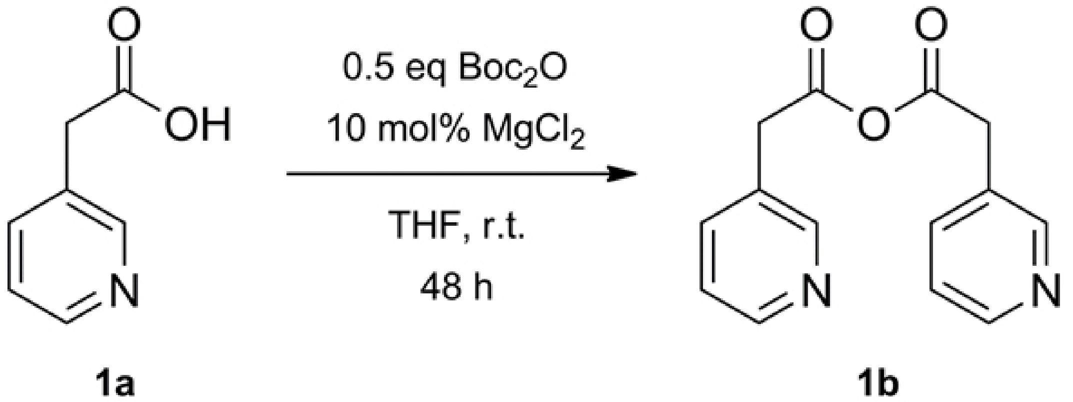
An alternative synthetic procedure, proposed by Lecouvey et al., proceeds with the use of tris(trimethylsilyl) phosphite and an acyl chloride [9]. Although this one-pot reaction was effective for a wide variety of starting substrates in producing unsymmetrical α-hydroxy-1,1-bisphosphonates, an initial preparation of an acyl chloride puts the safety and general validity of this method at risk. A need to use toxic and harmful halogenating agents in large amounts makes it a questionable choice for 'going green' and creating a convenient, sustainable method for the synthesis of bisphosphonates.

A particularly interesting approach toward the formation of α-hydroxy-1,1-bisphosphonic acids was made by Egorov et al. in 2011 [10]. It is still the only current method that provides these compounds without using any halogenating agents. They use 1.1, 2.1, or 3.1 equivalent amounts of catecholborane followed by an addition of tris(trimethylsilyl) phosphite, which gave the expected product after smooth methanolysis and purification in 51-86% yields. However, there are some downsides of this reaction that make it a less than an ideal choice. First, catecholborane is highly flammable, reacts violently with water, and may cause severe burns upon skin contact. It must be added in at least stoichiometric amounts and cannot be reused under reaction conditions. Second, gaseous hydrogen is formed in the first step of this reaction, which is what makes it even more dangerous and flammable. Finally, Egorov et al. proved that the use of any other nucleophile than the expensive tris(trimethylsilyl) phosphite does not lead to the expected product.

Prompted by this background, we proposed a simple method for the preparation of risedronic acid starting from corresponding carboxylic acid. Following the approach described by Bartoli et al. [11], we obtained 3-pyridylacetic anhydride and examined its reactivity with phosphorous acid as a simple, cheap, and insensitive nucleophile after the activation with 4-(dimethylamino)pyridine (DMAP) used in catalytic amounts.

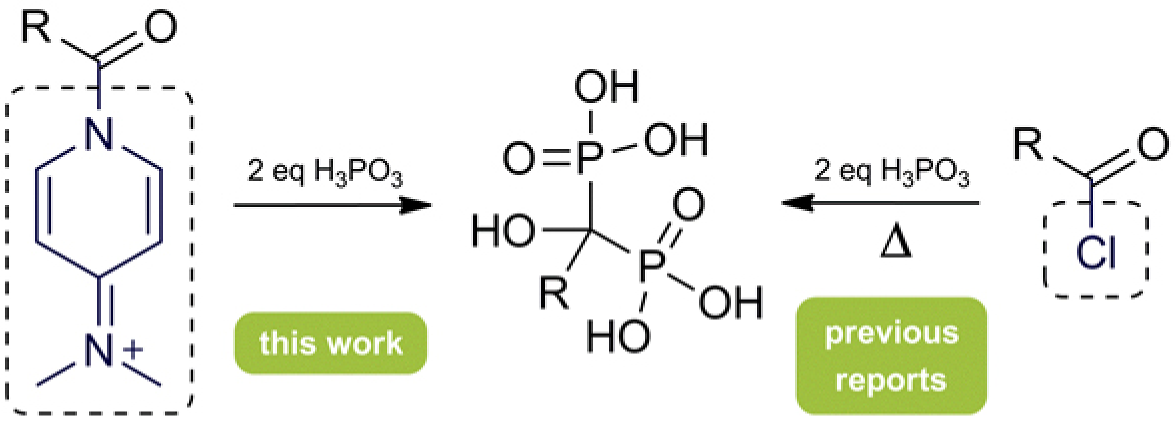
RESULTS & DISCUSSION

We used 3-pyridylacetic acid as the starting material since there was no 3-pyridylacetyl halide commercially available. At first, we synthesized 3-pyridylacetic anhydride **1b** based on the reaction of 3-pyridylacetic acid **1a** with di-*tert*-butyl dicarbonate in the presence of catalytic amounts of anhydrous magnesium chloride [11] (Scheme 1). Tetrahydrofuran was chosen as the solvent to maximize the product yield by minimizing the possibility of ester formation. As the reaction time elapsed, the mixture was then filtered and the crude product was washed successively with THF to remove soluble by-products (e.g., alcohol) that might have a negative impact on the second step of this process.



Scheme 1. Synthesis of 3-Pyridylacetic Anhydride Based on the Method Proposed by Bartoli et al. [11]

In our ongoing program on the synthesis of bisphosphonates from carboxylic acids, we required a simple method to obtain such compounds without using any halogenating agents. We achieved this by employing catalytic amounts of DMAP, which acts as a strong nucleophile and an acyl transfer reagent in a number of different applications [12]. As observed in the related process, i.e., Yamaguchi esterification [13], the newly formed intermediate is susceptible to nucleophilic acyl substitution under mild conditions; it is suggested that the reason for this is that DMAP reacts with anhydrides, leading to reactive amides (Scheme 2).



Scheme 2. Nucleophilic Acyl Substitution with H_3PO_3

Prompted by the similarity of the chemical structure of the intermediate and an acyl chloride used in the typical α-hydroxy-1,1-bisphosphonic acid synthesis, we explored the effects of the nucleophilic substitution on the intermediate with phosphorous acid. In view of the fact that DMAP adds to an acyl group to form a much better leaving group than any of the halogens, and that phosphorous acid is a stronger nucleophile than alcohol, we assumed that no heat was necessary for this process to occur. As a result, we allowed the reaction to reach completion at room temperature. The use of cheap and widely accessible phosphorous acid made it possible to afford the expected product in 76%.

The product was washed with cold water and ethanol to eliminate the remaining impurities according to the method presented by Kieczykowski et al. [14]. This step allowed us to obtain a white powder which was identified by using ^{1}H NMR (^{1}H Nuclear Magnetic Resonance) and ^{31}P NMR (^{31}P Nuclear Magnetic Resonance). The ^{31}P NMR spectrum shows a single peak at 16.28 ppm which corresponds with that observed for risedronic acid by other authors. What is more, the chemical shifts in the ^{1}H NMR and ^{31}P NMR spectra seem concordant with those reported by Srinivasa Rao et al. [15]. The ^{1}H NMR and ^{31}PNMR spectra were measured at pH 5.5. The purity of the final product (⩾99.9%) was confirmed by using high-performance liquid chromatography. The insights gained from the FTIR (Fourier Transform Infrared Spectroscopy) and HRMS (High Resolution Mass Spectrometry) studies are complemented. The findings of this work suggest that our reaction provides better solutions than the existing approaches, in terms of both energy consumption and environmental impact.

CONCLUSIONS

In summary, our results are of interest for a few reasons. First, we synthesized risedronic acid in a simple, room temperature reaction starting from corresponding carboxylic acid. Second, the elimination of harmful halogenating agents, which react violently with water, provides a cost-effective and environmentally benign technique that meets criteria of industrial ecology. The main, second step of this process is the DMAP-catalyzed activation of the anhydride followed by the reaction with phosphorous acid as the mild phosphorous-containing nucleophile. The addition of a second equivalent of H_3PO_3 results in the formation of the desired product in 76%.

Finally, the promising results encourage us to follow this method in further studies. Future work will focus on the synthesis of risedronic acid by using a polymer-bound equivalent of DMAP (e.g., commonly used PS-DMAP), which has been employed as a catalyst for acylation and related reactions [16]. This would lead to the formation of the desired product by a simple 'Catch and Release' approach, eliminating the problem of removing DMAP from the solution. The application of the polymer-bound DMAP catalyst, thanks to its high reusability, could help to minimize the amount of chemical waste. We believe that this unique combination would provide a valuable contribution towards making the synthesis of risedronic acid even greener.

EXPERIMENTAL

All chemicals were purchased from Sigma-Aldrich (Poland) as high or the highest purity grade and were used without further purification. The melting point was measured using a Stuart Scientific SMP10 melting point apparatus. The FTIR spectrum was recorded on a Bruker VERTEX 70 spectrophotometer in KBr. ^{1}H NMR spectra were measured at pH 5.5 and ambient temperature on a Bruker Ascend™ 400 MHz spectrometer using TMS as the internal standard and D_2O as the solvent. Data was recorded as follows: chemical shifts in ppm on the δ scale, number of equivalent nuclei (by integration), multiplicity (s – singlet; d – doublet; t – triplet; m – multiplet), and coupling constant. The ^{31}P NMR spectrum was performed at pH 5.5 and ambient temperature on a Bruker Ascend™ 600 MHz spectrometer using D_2O as the solvent. Mass spectrometry data was determined using an API 4000 QTRAP triple quadrupole mass spectrometer from AB Sciex. High-performance liquid chromatography was carried out on an Hypersil™ ODS C18 column (250 mm × 2.1 mm, particle size 5 µm) (Thermo Fisher Scientific) using an HP Agilent 1100 (Hewlett Packard) HPLC (High-Performance Liquid Chromatography). The temperature of the column was maintained at 24 °C in all cases.

General Procedure

3-Pyridylacetic acid hydrochloride (5.76 mmol), anhydrous magnesium chloride (0.576 mmol), and tetrahydrofuran (10 mL) were charged to a 50 mL two neck flask equipped with a stirring bar. After 10 min of stirring at room temperature, di-*tert*-butyl dicarbonate (2.88 mmol) was added through a dropping funnel. Then, the mixture was stirred at room temperature for 48 h at air atmosphere.

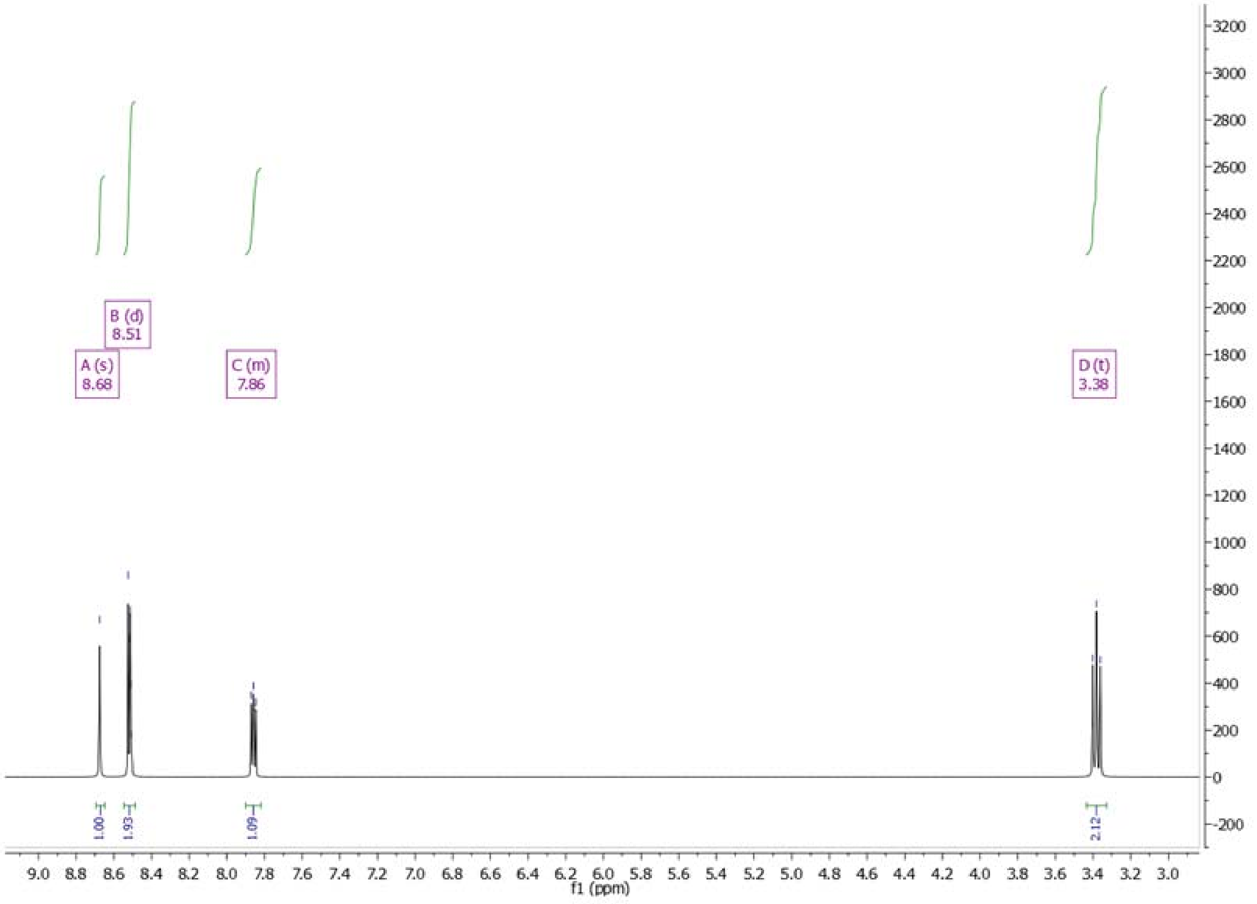


Fig 1. ^{1}H NMR Spectrum of the Synthesized Product

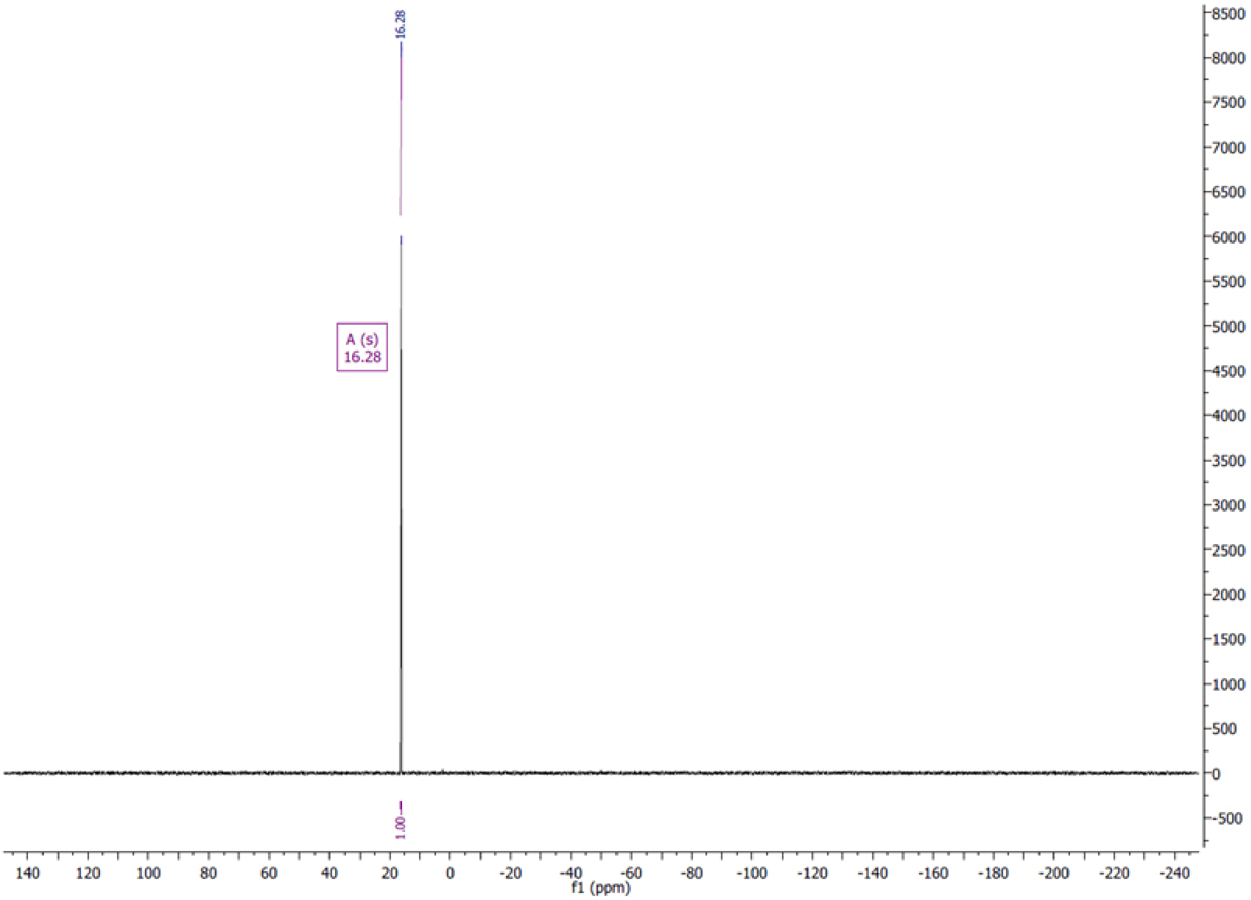


Fig 2. ^{31}P NMR Spectrum of the Synthesized Product

After this time, the crude product was separated by vacuum filtration and washed twice with tetrahydrofuran (2 × 2.5 mL). The resulting powder was charged with 4-(dimethylamino)pyridine (DMAP, 0.461 mmol) and tetrahydrofuran (10 mL) to a 50 mL two neck flask and stirred for 10 min. As the time elapsed, phosphorous acid (11.52 mmol) was added while stirring vigorously. After 24 h, the product was filtered and washed with cold water and ethanol according to the method applied by Kieczykowski et al. [14]. Finally, the purified white powder was dried under air atmosphere at 80 °C.

1-Hydroxy-2-(3-pyridyl)ethylidene bisphosphonic acid (risedronic acid) [15,17]. Obtained as white powder in 76% yield; m.p.: 225-228 °C, HPLC purity: ⩾99.9%. **FTIR** (KBr, cm^{-1}) 3379, 309, 2149, 2035, 1637, 1566, 1475, 1446, 1396, 1332, 1213, 1072, 1026, 933, 889, 815, 800, 692, 667, 628, 607, 563, 532. **^{1}H NMR** (400 MHz; D_2O; Me_4Si) δ 8.68 (s, 1H), 8.51 (d, J=7.7 Hz, 2H), 7.86 (m, 1H), 3.38 (t, J=12.1 Hz, 2H). **^{31}P NMR** (600 MHz; D_2O) δ 16.28. **HRMS** m/z 284.3 ([M+H]$^+$, 100%; calculated: 284.12)

Risedronic acid is a well-known compound and was characterized by comparing the FTIR, ^{1}H NMR (Figure 1), ^{31}P NMR (Figure 2), and HRMS spectroscopic data with authentic samples reported in the literature.

HPLC Condition Methods

HPLC Condition Method I. The optimized mobile phase was composed of methanol (solvent A), acetonitrile (solvent B), and 25 mM dibasic sodium phosphate/citrate buffer, pH 3.5 (solvent C) and was delivered by a gradient mode. A flow rate of 0.6 mL/min and injection volume of 1 μL were used for this experiment. UV detection was performed at 264 nm. A single peak at the retention time of 0.85 min was reported.

HPLC Condition Method II. The optimized mobile phase was composed of methanol (solvent A), 20 mM ammonium acetate in 80% aqueous acetonitrile (solvent B), and 25 mM dibasic sodium phosphate/citrate buffer, pH 3.5 (solvent C) and was delivered by a gradient mode.

A flow rate of 0.5 mL/min and injection volume of 1 µL was used for this experiment. UV detection was performed at 264 nm. A single peak at the retention time of 1.037 min was reported.

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Effect of Some Dopants on Hydrogen Storage Behaviors of Magnesium Borohydrides

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Abstract: Access to high gravimetric hydrogen content of $Mg(BH_4)_2$ is hampered by its thermodynamic stability, which has hindered its utilization as a hydrogen storage material. The destabilizing effects of silicon, carbon, and NaH on $Mg(BH_4)_2$ was investigated using TPD (temperature programmed desorption) and XRD. Mechanically milled $Mg(BH_4)_2$/NaH has a lower onset temperature and desorbs about 6 wt% hydrogen below 350 ^oC. XRD analysis showed formation of a new phase. The new phase accounts for the change in the hydrogen desorption path of the mixture resulting in the low onset desorption temperature of the mixture containing Si and carbon had no effect on the desorption temperature; they only increased the overall weight of the mixture resulting in a lower amount of hydrogen. XRD analysis also showed the presence of Si and carbon in the as-milled and de-hydrided mixtures. The products of dehydrogenation of $Mg(BH_4)_2$/CaH/Si are similar to those of $Mg(BH_4)_2$/CaH and those of $Mg(BH_4)_2$/C and they resemble those of $Mg(BH_4)_2$.

Key Words: Magnesium borohydride, Desorption, Mechanical milling, Additives.

INTRODUCTION

Complex metal hydrides with high gravimetric hydrogen content such as amides, alanates, and borohydrides are being considered as potential candidates for hydrogen storage [1-6]. Notable among the challenges of using borohydrides as hydrogen storage materials are their high dehydrogenation temperatures, diborane production, poor reversibility, as well as cycle life [6-11]. The study of $Mg(BH_2)_4$ as a potential hydrogen storage material is gaining more attention due to its light weight and high gravimetric hydrogen content. Konoplev and Bakulani reported some of its properties in 1971 [12]. Theoretical studies predict $MgB_{12}H_{12}$ and MgB_2 to be the only energetically stable and possible decomposition products of $Mg(BH_4)_2$ [13]. Thermal analysis showed that most of the hydrogen loss from the decomposition of $Mg(BH_4)_2$ occurs between 300 to 400 ^oC [14]. Decomposition started at 290 ^oC and about 13 wt% hydrogen was released up to 500 ^oC with a minimal trace of B_2H_6. At 290 ^oC, MgH_2, MgB_2, and Mg were observed while at 450 ^oC and above, Mg, MgB_2, and an unknown phase were detected.

The effect of ball milling and several additives on the decomposition of $Mg(BH_4)_2$ have been investigated [15-29]. Ball milling does not have any effect on the decomposition temperature [15-16]. The sample becomes amorphous during ball milling but is recrystallized to the α-phase after heating to about 150 ^oC. Li et al. reported the reduction of the onset desorption temperature of $Mg(BH_4)_2$ from 262 ^oC to 88 ^oC by addition of $TiCl_3$ [16]. They proposed that the improvement is due to the formation of more stable TiB_2 or less stable MgTi-based borohydride. Badaji et al. also investigated $Mg(BH_4)_2$ mechano-chemically alloyed with several metal chlorides [15] and found that combined Nb-Ti additives lowered the onset temperature by up to 125 ^oC. However, none of the additives were able to improve the reversibility of the material.

There have been reports on studies involving destabilization of $Mg(BH_4)_2$ with hydrides, borohydrides, and amides [20-26]. Studies have shown that the system consisting of $Mg(BH_4)_2$ and $LiBH_4$ possess superior hydrogen storage properties to either of the constituents [20-22]. Similarly, Temperature Programmed Desorption, TPD, analyses have shown that the desorption temperature of $Mg(BH_4)_2$ can be lowered by ball milling with $Ca(BH_4)_2$ [26]. The resulting mixture absorbed and released hydrogen with a well-defined plateau region in the pressure composition isotherm (PCI). This mixture has also been reported to release hydrogen at a faster rate [27]. In the present study, the effect of NaH, silicon, and carbon on the hydrogen storage properties of $Mg(BH_4)_2$ is presented.

EXPERIMENTAL

The materials used in this research were obtained from Sigma Aldrich; they were hydrogen storage grade and were hence used without further purification. The $Mg(BH_4)_2$ was prepared from MgH_2 and triethylamineborane, as described by Chłopek et al. [14]. All sample handling, weighing, and loading were performed in a Vacuum Atmospheres argon-filled glove box with oxygen and moisture levels below 1 ppm, to prevent contamination from air and moisture. The glove box was vacuum cleaned several times using purified argon gas to remove air and moisture. The mixture of the samples were mechanically mixed for 10 hrs using a SPEX 8000M Mixer Mill that had a stainless steel milling pot, which contained four small and two medium sized stainless steel balls. X-ray powder diffraction, XRD, analysis was used to determine whether new phases were formed by milling the different substances. A Panalytical X'pert Pro MPD Analytical X-ray Diffractometer Model PW 3040 Pro was used for these analyses. The samples were covered with a Kapton film to protect them from air and moisture. Temperature Programmed Desorption, TPD, was done in a gas reaction controller-PCI unit to evaluate the hydrogen desorption properties of each reaction mixture. This apparatus was manufactured by the Advanced Materials Corporation. The unit was fully automated and was controlled by a Lab View-based software program. An in-situ XRD analysis was also carried on the mixture at different temperatures to determine the species that were present during the dehydrogenation of the mixtures.

RESULTS & DISCUSSION

$$3Mg(BH_4)_2 + CaH_2 + 1.5Si \rightarrow 1.5Mg_2Si + CaB_6 + 13H_2 \quad (1)$$

$$2Mg(BH_4)_2 + NaH \rightarrow NaMgH_3 + 3MgB_4 + 7H_2 \quad (2)$$

$$2Mg(BH_4)_2 + C_2 \rightarrow MgB_2C_2 + 4H_2 \quad (3)$$

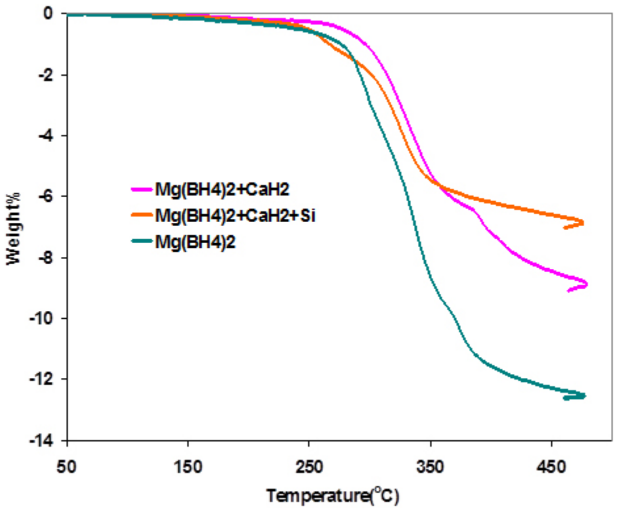

Fig 1: Combined TPD curves of $Mg(BH_4)_2/CaH_2$ and $Mg(BH_4)_2/CaH_2/Si$ and $Mg(BH_4)_2$

The TPD curve of $Mg(BH_4)_2/CaH_2/Si$ is shown in Fig. 1 along with those of pure $Mg(BH_4)_2$ and $Mg(BH_4)_2/CaH_2$. It has been shown that the decomposition temperature of hydrides could be lowered by alloying with silicon [28, 29]. The addition of silicon reduced the onset temperature of the $Mg(BH_4)_2/CaH_2$ mixture, but the overall decomposition temperature is still higher than that of $Mg(BH_4)_2$. The silicon also reduced the total amount of hydrogen desorbed by increasing the overall weight of the mixture.

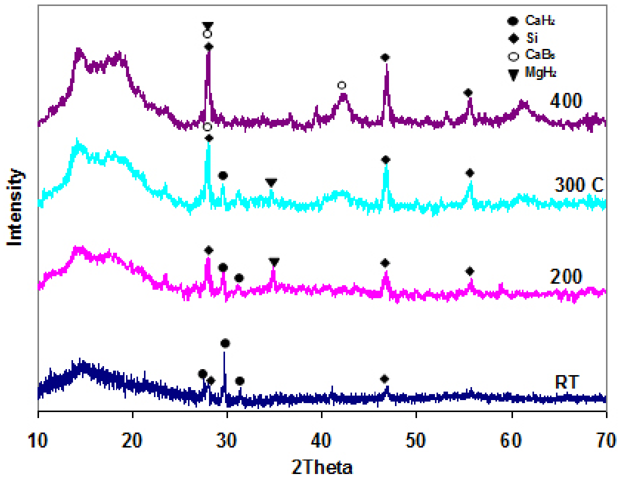

Fig 2: XRD pattern of $Mg(BH_4)_2/CaH_2/Si$ mixture.

From the results of the XRD studies shown in Fig. 2, it is clear that the silicon did not form any alloy with CaH_2. It only remains in the mixture throughout the dehydrogenation reaction. The expected product of dehydrogenation of this mixture, Mg_2Si according to equation 1, as predicted by Alapati et al. [30] and Ozolin et al. [31] is conspicuously absent in the XRD pattern. The products of the dehydrogenation are also similar to those of the mixture involving only $Mg(BH_4)_2$ and CaH_2 (i.e., MgH_2 and CaB_6 shown in Fig. 3).

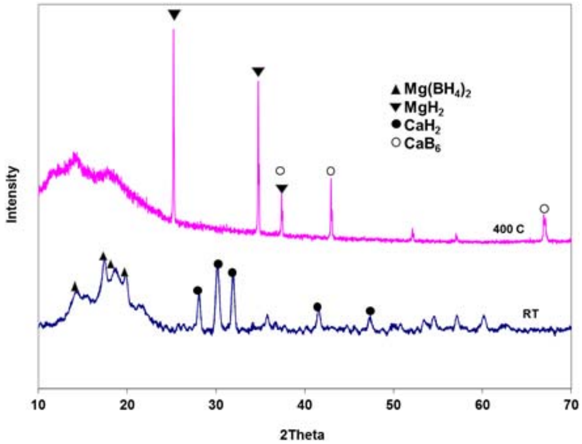

Fig 3: XRD pattern of $Mg(BH_4)_2/CaH_2$ mixture.

In Fig. 4, the TPD curve of $Mg(BH_4)_2$/NaH shows a big reduction in the onset temperature of $Mg(BH_4)_2$, releasing about 6 wt% of hydrogen below 350 °C. This shows that NaH is better at destabilizing the $Mg(BH_4)_2$ than either CaH_2 or a mixture of CaH_2 and NaH.

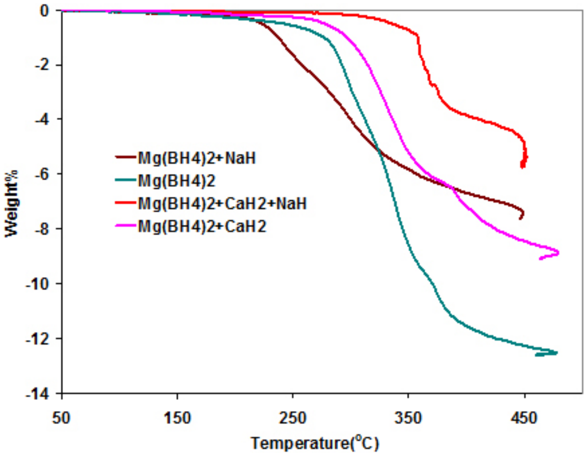

Fig 4: Combined TPD curves of $Mg(BH_4)_2$, $Mg(BH_4)_2$/NaH, $Mg(BH_4)_2/CaH_2$/NaH, and $Mg(BH_4)_2/CaH_2$.

In the XRD analysis of the $Mg(BH_4)_2$/NaH shown in Fig. 5, neither the peaks of $Mg(BH_4)_2$ nor NaH were present in the as-milled sample at room temperature. This suggests that a new species might have been formed during ball milling. The appearance of some new peaks, which become persistent even after heating to 300°C, indicates the presence of a new phase.

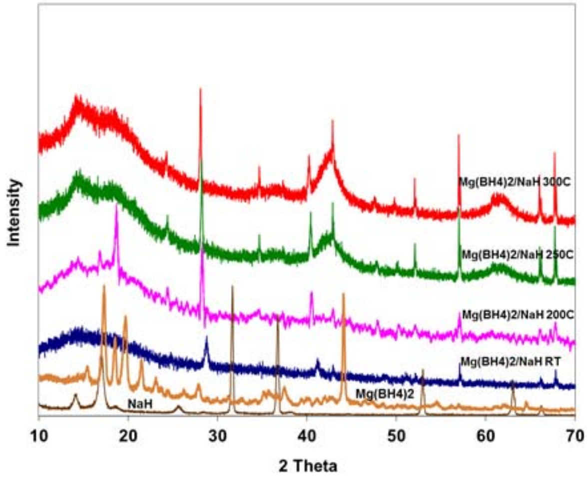

Fig 5: XRD pattern of $Mg(BH_4)_2$/NaH mixture.

Fig. 6 contains the TPD curve of the $Mg(BH_4)_2$/C system alongside that of pure $Mg(BH_4)_2$. It can be deduced from the curve that the presence of carbon does not affect the desorption temperature of the mixture. However, the amount of hydrogen released was reduced and this can be ascribed to the physical presence of carbon adding to the overall weight of the mixture. Further evidence from of the XRD analyses shows that carbon is just passive in the mixture.

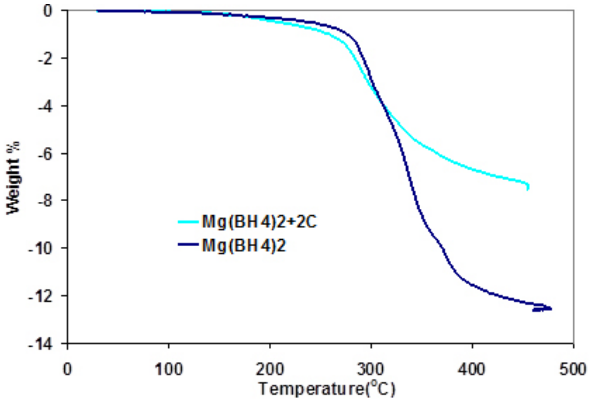

Fig 6: Combined TPD curves of $Mg(BH_4)_2$/C and pure $Mg(BH_4)_2$.

In Fig. 7, the major peaks of carbon were persistent throughout the analysis. No peak for the expected product of dehydrogenation (MgB_2C_2) according to equation 2 was detected. MgB_2 is the only species identified as the product after dehydrogenation.

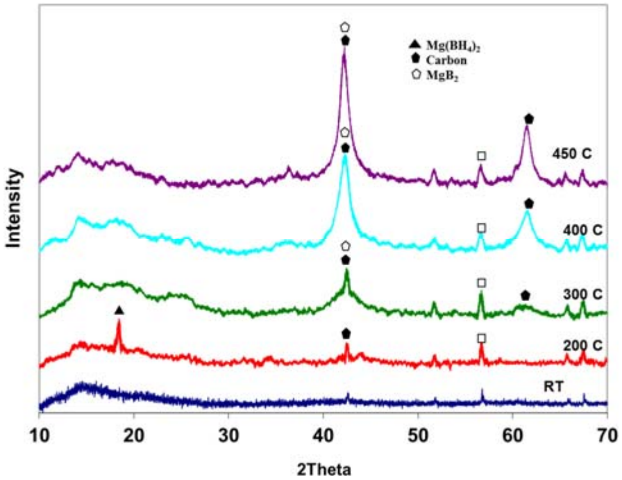

Fig 7: XRD pattern of $Mg(BH_4)_2$/C mixture

The TPD curves of the rehydrogenated samples are shown in Fig 8. All the mixtures released just about 1 wt% hydrogen in the second dehydrogenation cycle, showing that reversibility of these mixtures are very poor. Attempts to obtain the isotherms for the mixtures were unsuccessful as no clear plateau region was observed, also indicating that their reversibility is poor.

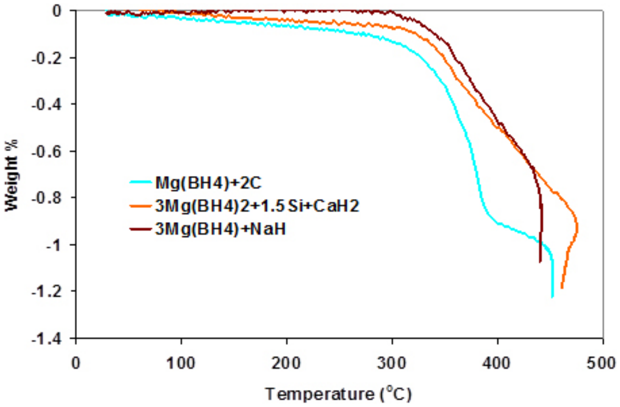

Fig 8: TPD curves of Rehydrided Magnesium Borohydride Mixtures.

CONCLUSION

The results from this study have shown the effects of various additives on the dehydrogenation of borohydrides. Of all the various ball milled mixtures of $Mg(BH_4)_2$ and additives, NaH is the only one that effectively lowers the desorption temperature of $Mg(BH_4)_2$. This may be due to the formation of new borohydride species during ball-milling of the mixture. Other additives did not have any effect on the desorption temperatures, but rather reduced the amount of hydrogen released due to their physical presence increasing overall weight of the mixture. The mixtures also showed poor reversibility, releasing much lower amounts of hydrogen in the second dehydrogenation.

ACKNOWLEDGMENTS

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A SIMPLE VISUAL DEMONSTRATION OF MEMBRANE PERMEABILITY

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Iodine is a useful topical antiseptic due in part to its ability to dissolve in both hydrophobic and hydrophilic media. It has broad spectrum antimicrobial activity and its ability to readily pass through cell membranes plays an important role [1]. Iodine is also a useful catalyst in carbohydrate chemistry for a range of transformations [2]. Using it in such a capacity certainly makes traditional synthetic chemistry more colorful, as solutions of iodine are intensely colored, ranging from blue to violet to deep red depending on the solvent and other solutes. Iodine can be readily converted to colorless iodide solutions by the addition of sodium thiosulfate or sodium metabisulfite. Because iodine can pass between an organic/aqueous interface (Figure 1), this property offers an obvious visual demonstration of membrane permeability that is related to the distribution of molecules in living organisms. This simple protocol can be carried out using readily available household chemicals.

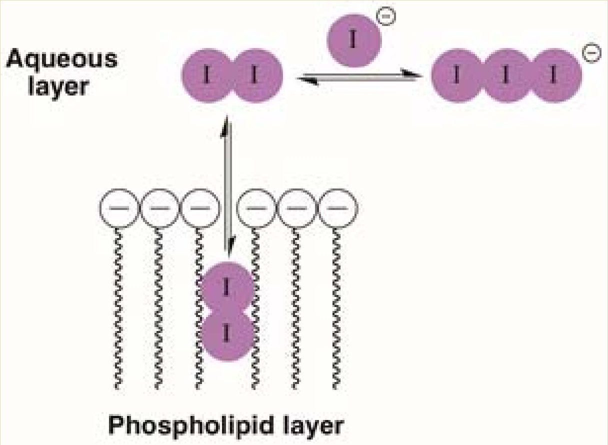

Fig 1. Iodine distribution at a biological membrane.

Commercially, iodine solutions are often sold in a complex with the polymer povidone as a topical antiseptic. Iodine can be dissolved in an aqueous solution by adding iodide salts to form the I_3^- anion (Figure 1); this is also used to make a tincture of iodine. When an aqueous solution of iodine/iodide or iodine-HI-povidone complex is partitioned with an organic solvent such as ethyl acetate or cyclohexane, coloration of the organic layer occurs almost immediately (see test tube 1, Figure 2). This results from free iodine passing into the organic solvent and eventually the top layer will achieve a steady level of coloration. Once this has occurred, a reducing agent such as sodium metabisulfite can be added. This will dissolve only in the aqueous layer and quickly reduce iodine to iodide, removing color from the bottom layer (see test tube 2, Figure 2). Still, a small cloud of iodine color can be seen settling back into the bottom layer as iodine passes back into the aqueous layer from the organic layer. If this bilayer is mixed for extended periods of time, eventually all color from the iodine will be removed if enough metabisulfite is used. This offers a simple look at the partitioning of iodine and its removal using an aqueous based reaction. Each stage demonstrates iodine's ability to dissolve in both organic and aqueous media, while using chemistry that takes place only in the water layer makes this more obvious.

Details of Demonstration

Sourcing components:

1. Povidone-iodine is sold commercially under trade names such as Betadine. Aqueous iodine solutions can also be made from I_2/NaI.
2. Ethyl acetate is available commercially as nail polish remover usually labeled "acetone-free". However, this can also contain alcohol and water.
3. Sodium metabisulfite is sold for a variety of purposes such as sterilization of brewing equipment.

Fig 2. Iodine solution partitioned between water and ethyl acetate either (1) before or (2) after addition of sodium metabisulfite.

Method shown in Figure 2:

Approximately 2 mL of commercial iodine solution was diluted with an equal volume of distilled water and ca. 4 mL of ethyl acetate was added by pipette, which was also used to mix the two layers. The povidone-iodine solution should be diluted with water, as it often contains a mixture of ethanol and water which can interfere with partitioning. [Note: cyclohexane offers a more vibrant color than ethyl acetate, but is less commonly available.] Once steady color in the organic layer was obtained, 50 mg sodium metabisulfite was added with stirring to facilitate reduction. Vigorous mixing will remove color from both layers, while avoiding any agitation after the addition of metabisulfite will allow for a very slow dissipation of iodine color.

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  Table 1. Bond Lengths (Å) of 2-aminophenol

- **Figure legends** should be in numerical order as they appear in the text. Legends should be limited to 250 words.

  Figure 1. PVC Melt Flow Characterized by Analytical Structural Method

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  Booth DE, Isenhour TL. *The Chemist*, 2000, 77(6), 7-14.

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  Turner GK in *Chemiluminescence: Applications*, ed. Knox Van Dyke, CRC Press, Boca Raton, 1985, vol 1, ch. 3, pp 43-78.

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  McCapra F, Tutt D, Topping RM, UK Patent Number 1 461 877, 1973.

- **Reports and bulletins, etc. -** For example:

  Smith AB, Jones CD, *Environmental Impact Report for the US*, final report to the National Science Foundation on Grant AAA-999999, Any University, Philadelphia, PA, 2006.

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  Smith AB. Presented at the Pittsburgh Conference, Atlantic City, NJ, March 1983, paper 101.

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Announcements

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