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Thermodynamic Changes in Mechanochemically Synthesized Magnesium Hydride Nanoparticles

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Abstract: The thermodynamic properties of magnesium hydride nanoparticles have been investigated by hydrogen decomposition pressure measurements using the Sieverts technique. A mechanochemical method was used to synthesize MgH_2 nanoparticles (down to ~7 nm in size) embedded in a LiCl salt matrix. In comparison to bulk MgH_2, the mechanochemically produced MgH_2 with the smallest particle size showed a small but measurable decrease in the decomposition reaction enthalpy (ΔH decrease of 2.84 kJ/mol H_2 from $\Delta H_{bulk} = 74.06 \pm 0.42$ kJ/mol H_2 to $\Delta H_{nano} = 71.22 \pm 0.49$ kJ/mol H_2). The reduction in ΔH matches theoretical predictions and was also coupled with a similar reduction in reaction entropy (ΔS decrease of 3.8 J/mol H_2/K from $\Delta S_{bulk} = 133.4 \pm 0.7$ J/mol H_2/K to $\Delta S_{nano} = 129.6 \pm 0.8$ J/mol H_2/K). The thermodynamic changes in the MgH_2 nanoparticle system correspond to a drop in the 1 bar hydrogen equilibrium temperature ($T_{1\ bar}$) by ~6 °C to 276.2 ± 2.4 °C in contrast to the bulk MgH_2 system at 281.8 ± 2.2 °C. The reduction in the desorption temperature is less than that expected from theoretical studies due to the decrease in ΔS that acts to partially counteract the effect from the change in ΔH.

Introduction

Magnesium hydride has a high gravimetric hydrogen storage capacity (7.7 wt %) and has been studied in detail over the past 50 years.[1] However its use as a commercial hydrogen storage material has been impeded by a high thermal stability and poor sorption kinetics. Recently the kinetics issue has largely been overcome by introducing catalytic oxides during ball milling,[2,3] but to the authors' knowledge no alterations to the thermodynamics of pure MgH_2 have been experimentally achieved to date. Some studies in the literature utilize Differential Scanning Calorimetry (DSC) to measure changes in the desorption temperature of MgH_2.[4−6] However these studies often overlook the fact that the DSC signal contains both a thermal and kinetic component[7] and in many hydride systems (including MgH_2) the onset temperature can be determined by kinetics, leading to problems with this method of thermodynamic determination.[8]

Recent theoretical work[9] suggests that a reduction in MgH_2 particle size below 10 nm can result in thermodynamic destabilization of the hydride phase with a consequent lowering of the desorption temperature. This effect is expected to be pronounced for particles below 3 nm in diameter.[9−12] As a result of the promising theoretical investigations a number of recent attempts have been made to experimentally synthesize Mg or MgH_2 nanoparticles in this size range which include the following: a melt infiltration technique being applied to synthesize <5 nm[13] Mg nanocrystallites or <30 nm Mg nanoparticles[14] supported in carbon frameworks, the sonoelectrochemical production of Mg particles reported to be 4 nm,[15] the formation of MgH_2 embedded within a carbon aerogel scaffold by deposition of a dibutylmagnesium precursor,[16] and the

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formation of 5 nm colloidal Mg[17] that appears to be stabilized by an adduct.[18] Despite the number of nano-Mg and nano-MgH_2 synthesis methods there is still no experimental evidence of the thermodynamic destabilization of the Mg-H system being attributed solely to particle size effects.

Herein, MgH_2 nanoparticles were produced using a mechanochemical method, allowing for control over the size of the MgH_2 particles produced by the addition of an inert LiCl buffering material.[18] Mechanochemical synthesis involves a chemical reaction that is initiated using mechanical milling. Usually a reaction byproduct phase is also formed during milling that can act to separate the desired reaction product. The phase separation can be enhanced by the addition of large quantities of a buffer material to the chemical reagents leading to product particle sizes down to 4 nm.[19] The buffer is often chosen as the reaction byproduct phase for simplicity and to facilitate its extraction if so desired. The MgH_2 samples and the effect of the buffering material (LiCl) on the microstructure evolution have previously been characterized by synchrotron X-ray Diffraction and Transmission Electron Microscopy.[18]

Experimental Details

All handling of chemicals and sealable milling canisters was undertaken in an argon-atmosphere glovebox to minimize oxygen ($O_2 < 1$ ppm) and water ($H_2O < 1$ ppm) contamination. LiH (Sigma-Aldrich, 95%), $MgCl_2$ (Sigma-Aldrich, ≥98%), and LiCl (Sigma-Aldrich, ≥99%) were used as starting reagents. The reagents were all individually milled for 3 h using a ball to powder ratio (B/P) of 30:1 prior to use. Ball milling was performed at room temperature with a custom-made 316 stainless steel ball milling canister (650 cm^3 internal volume) attached to a Glen Mills Turbula T2C shaker mixer. All samples were milled for 18 h using a 90:1 B/P with equal numbers of 7.9 mm and 12.7 mm 316 stainless steel balls in 5−10 g batches.

Magnesium hydride was synthesized mechanochemically at room temperature according to the following reaction:

$$2\mathrm{LiH} + \mathrm{MgCl_2} \rightarrow \mathrm{MgH_2} + 2\mathrm{LiCl} \quad \Delta_r G_{298\mathrm{K}} = -72.8\ \mathrm{kJ/mol} \tag{1}$$

To promote nanoparticle production a LiCl reaction buffer was used to separate the as-synthesized MgH_2 particles. The amount of LiCl added to each sample corresponded to 0 (sample MgH_2-A), 1.05 (sample MgH_2-B), 2.62 (sample MgH_2-C), and 6.82 (sample MgH_2-D) mol of LiCl added to the left-hand side of eq 1. A purchased MgH_2 (Sigma-Aldrich, ≥96.5%) powder sample was also ball milled without LiCl for 18 h using a B/P of 90:1 for use as a MgH_2 reference material, designated forthwith as MgH_2-Purchased. Further synthesis details can be found in Sheppard et al.[18]

Transmission electron microscopy (TEM) was conducted on a JEOL 3000F FEGTEM instrument operating at 300 kV. Samples were loaded onto 200 mesh copper grids with holey carbon support films dropwise via suspension in toluene. Samples must be exposed to air before being loaded into the TEM column; however the air-exposure time was kept as short as possible (up to a few minutes).

X-ray diffraction (XRD) on MgH_2-Purchased was performed using a Bruker D8 Advance diffractometer (Cu Kα radiation) with a 2θ range of 10°−100° using 0.02° steps with 0.8 s of count time per step with operating conditions of 40 kV and 40 mA. The XRD instrument was equipped with a LynxEye 3° linear position sensitive detector (PSD) with 192 pixels. The instrumental line broadening is taken into account using a fundamental parameters approach in Topas (Bruker AXS) that was verified using a NIST 660a LaB_6 reference standard. The sample was loaded into an XRD sample holder in an argon glovebox and sealed with a poly(methylmethacrylate) (PMMA) airtight bubble to prevent oxygen/moisture contamination during data collection. The crystallite sizes were determined from an LVol-IB method (volume averaged column height calculated from the integral breadth)[20] that provides a good measure of the volume-weighted average crystallite size.

Table 1. Summary of Thermodynamic Data for MgH_2 Decomposition Available in the Literature

Source	Temperature Range (°C)	Enthalpy (ΔH, kJ/mol H_2)	Entropy (ΔS, J/mol H_2/K)
Stampfer 1960[21]	314−576	74.4 ± 0.3	135.1 ± 1.9
Reilly 1968[22]	276−350	77.4 ± 4.2	138.3 ± 2.9
Pedersen 1983[23]	303−390	70	126
Friedlmeier 1988[24]	280−370	74.3 ± 0.5	136 ± 1
Klose 1995[25]	270−345	81.86	146.1
Shao 2004[26]	350−400	75.0	135.6

Hydrogen sorption experiments were performed in a manometric apparatus. The digital pressure gauge (Rosemount 3051S) had a precision and accuracy of 14 mbar, while room temperature measurements were recorded using a 4-wire platinum resistance temperature detector (RTD). The determination of correct thermodynamic properties requires measurements with high levels of accuracy and precision. The Sieverts apparatus that was utilized allows for small thermodynamic changes to be discerned due to the high precision pressure and temperature data that are collected. Due to limitations with extremely slow kinetics full pressure−composition isotherms were not generated. As such, equilibrium pressure data were collected over the hydrogen equilibrium plateau between hydrogen to metal ratios (H/M) of 0.8 to 1.8 in the temperature range 300 to 360 °C. Due to the flat nature of the equilibrium plateau in the Mg-H system, repeat equilibrium measurements over this range were found to be equivalent within reported uncertainties. For example, at 360 °C equilibrium pressures of 8.05 ± 0.02 bar and 8.06 ± 0.03 bar were measured at H/M ratios of 1.28 and 1.78 respectively for a given sample. Further details are provided in the Supporting Information on the hydrogen sorption apparatus and on the methods and uncertainties involved in equilibrium measurements and thermodynamic calculations.

Results and Discussion

Bulk MgH_2 Thermodynamic Properties. The generally accepted thermodynamic properties for the Mg-H system were provided by Stampfer, J. F., Jr. et al. in 1960[21] (see Table 1). Stampfer's data are often preferred due to the large number of data points collected over a wide temperature range.[1] However it must be noted that the accuracy of this data set is quite low. Listed equilibrium pressure values vary by up to 9% at the same sample temperature. The percentage error in Stampfer's pressure data is lower at high temperatures, but repeated equilibrium pressures still vary by 3 bar at 444 °C. The thermodynamic data from a number of sources provided in Table 1 illustrate the wide spread in the reported decomposition enthalpy (ΔH) and entropy (ΔS) data for MgH_2 as measured under similar temperature conditions. The large discrepancies between the determined ΔH and ΔS values are likely a result of the poor MgH_2 desorption kinetics not being adequately accounted for in some studies. If the Mg-H system does not reach a true

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equilibrium pressure then the resultant thermodynamic values calculated from these pressures will be biased.

Hydrogen equilibrium pressure measurements can be used to determine thermodynamic quantities using the van't Hoff relationship for hydrogen desorption:

$$\ln\left(\frac{f_{eq}}{f_0}\right) = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \qquad (2)$$

where f_{eq} is the fugacity of hydrogen under equilibrium at a given temperature T, f_0 is a reference fugacity of 1 bar, and R = 8.3145 J/K/mol H_2 is the gas constant. The fugacity is the activity of the real gas which provides a better representation of the chemical potential of the system than pressure. In turn, the fugacity (and hence pressure) can be calculated from ΔH and ΔS using the exponential of eq 2 as follows (where f_0 = 1):

$$f_{eq} = e^{\left(-\frac{\Delta H}{RT} + \frac{\Delta S}{R}\right)} \qquad (3)$$

The determination of ΔH and ΔS from a van't Hoff plot (ln f_{eq} against $1/T$) relies upon a straight line fit to the experimental data. The thermodynamic parameters are only weakly temperature dependent[27] allowing the linear approximation to be valid over a limited but large temperature range.[28] The pressure and fugacity can be related when the compressibility of hydrogen is taken into account by using[29]

$$\ln\left(\frac{f}{p}\right) = \int_0^p \left(\frac{V_m}{RT} - \frac{1}{p}\right)\mathrm{d}p \qquad (4)$$

where V_m is the molar volume of H_2 which is calculated from an equation of state (EOS) for hydrogen. The Hemmes equation of state (EOS)[30] and the method of McLennan and Gray[31] were used to account for the compressibility of hydrogen. The fugacity is often assumed to be equal to pressure due to the small deviation from the ideal gas law at low pressures. However, for our equilibrium measurements at 360 °C the difference between the measured pressure and the fugacity was of a similar magnitude to the uncertainty in the measured pressure. Consequently all measured pressures were converted to their fugacities using eq 4 to provide higher accuracy thermodynamic data.

The requirement of fugacity in determining thermodynamics from a van't Hoff plot is especially important when dealing with higher pressure data. For example Stampfer, J. F., Jr. et al.[21] utilize the Beattie–Bridgeman EOS[32] to account for the compressibility of hydrogen and to calculate the fugacity of hydrogen at a given pressure and temperature. Stampfer's pressure data extend up to ~280 bar where the compressibility of hydrogen is vital in determining accurate fugacity values. Reprocessing Stampfer's pressure data reveals that the fugacity values that were calculated using the Beattie–Bridgeman EOS do not match fugacities calculated using more recent EOS models.[30,33] The disparity leads to a change in Stampfer's reported ΔH and ΔS values from 74.4 ± 0.3 kJ/mol H_2 and 135.1 ± 1.9 J/mol H_2/K to 76.2 ± 1.1 kJ/mol H_2 and 137.4 ± 1.4 J/mol H_2/K respectively. The uncertainties for the reprocessed data were calculated using the weighted least-squares method explained in the Supporting Information. Given the large ~2% difference in calculated ΔH and ΔS values by using different EOS models, it can be seen that an accurate fugacity is essential in determining accurate thermodynamics from a van't Hoff plot, especially when dealing with high measured pressures. Reilly and Wiswall[22] also calculated the decomposition thermodynamics of the Mg-H system as shown in Table 1. Although they report that the enthalpy and entropy are converted to 25 °C, reprocessing their data shows that these thermodynamic properties are in fact not converted and are valid at their temperature range midpoint (313 °C). Reprocessing of Reilly's raw pressure data using fugacity (calculated using a modern EOS) also results in different enthalpy and entropy values (ΔH = 78.8 kJ/mol H_2 and ΔS = 140.9 J/mol H_2/K) than those originally reported in Table 1.

Table 2. Summary of MgH_2 Particle and Crystal Size Information As Determined by TEM and XRD[18]

	TEM average particle size	XRD average crystallite size
MgH_2-A	1−2 μm	10.1 ± 0.3 nm
MgH_2-B	15−40 nm	7.6 ± 0.3 nm
MgH_2-C	12−20 nm	6.7 ± 0.4 nm
MgH_2-D	2−7 nm[a]	6.7 ± 0.7 nm
MgH_2-Purchased	N/A	6.4 ± 0.1 nm

[a] Only crystallites could be discerned from the homogeneous sample.

MgH_2 Samples. Four samples of MgH_2 were mechanochemically synthesized according to eq 1 using various amounts of LiCl buffer added to premilled starting reagents prior to milling. Large quantities of LiCl buffer act to separate the synthesized MgH_2 particles, essentially restricting particle growth and promoting nanoparticle formation. The LiCl is also essential in forming a barrier to particle growth during thermodynamic investigations where samples are heated up to 360 °C. Each of the four mechanochemically synthesized samples differed dramatically in its structural features as investigated with transmission electron microscopy (TEM) in the synthesis study.[18] MgH_2 particle and crystal sizes are provided in Table 2 for all of the samples analyzed.

The MgH_2 particle size decreases from several micrometers in size for MgH_2-A to 12−20 nm for MgH_2-C. Comparison of the particle size from TEM of MgH_2-C with its crystallite size from XRD suggests that the MgH_2 particles consist of a few individual crystallites. TEM of MgH_2-D was largely homogeneous with no obvious particle morphology. Thus only crystallite

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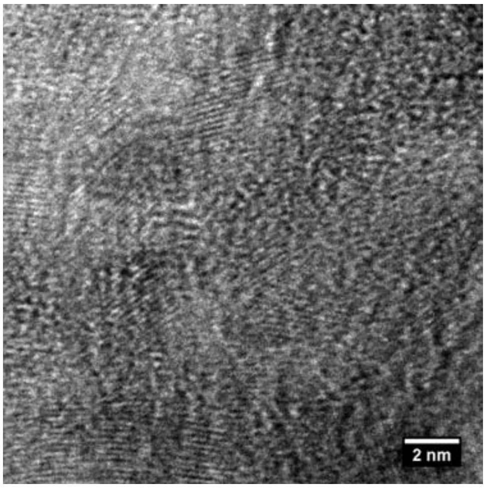

Figure 1. Transmission electron microscope (TEM) micrograph of lattice fringing in MgH_2-D occurring from the MgH_2 *hkl* = 020 plane. The crystallites are 2−7 nm in size.

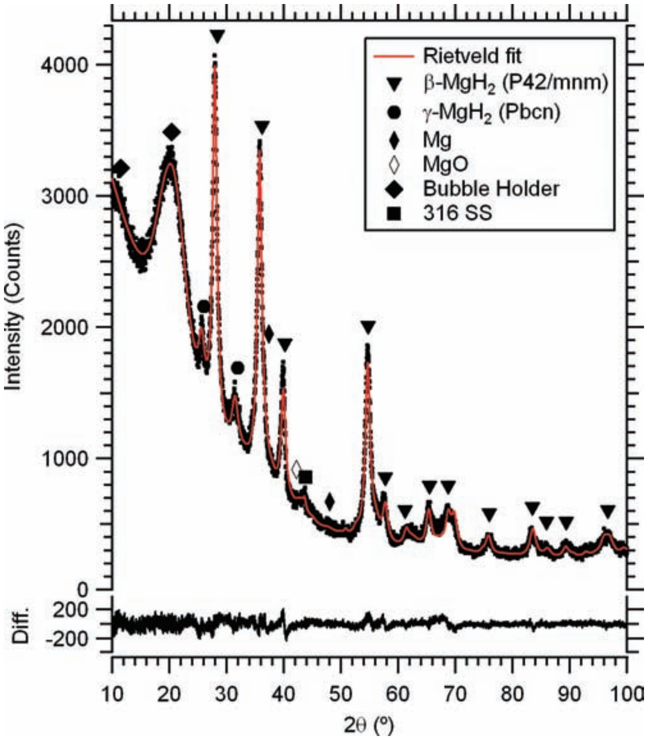

Figure 2. X-ray diffraction (XRD) pattern for MgH_2-Purchased after 18 h of ball milling with 90:1 B/P. A Rietveld fit to the data is shown along with a difference plot.

sizes could be determined from high magnification lattice fringing as shown in Figure 1. Of note is that only the *hkl* = 020 plane of MgH_2 could be discerned from TEM. It may be possible that there is MgH_2 crystal growth along a preferred crystallographic axis in the mechanochemically synthesized nanoparticles.

The MgH_2-Purchased sample was analyzed with XRD after being ball milled for 18 h as shown in Figure 2. Two MgH_2 crystalline phases (β and γ) were detected along with small quantities of MgO and Mg impurities. The γ-MgH_2 phase has previously been shown to form during ball milling.[34] The Rietveld fit to the XRD data for MgH_2-Purchased does not adequately model the peak intensities from the γ-MgH_2 phase unless the preferential cleavage along particular γ-MgH_2 crystal planes is taken into account.

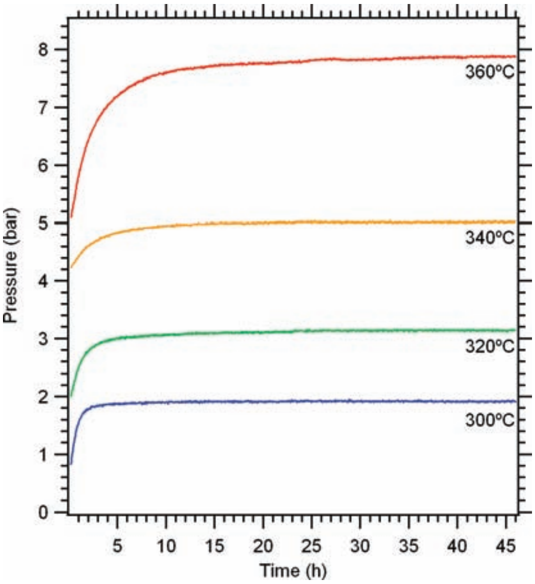

Figure 3. Kinetic hydrogen desorption data for MgH_2-D illustrating that equilibrium was reached at all temperatures.

Thermodynamics. Thermodynamic investigations were undertaken by measuring hydrogen desorption equilibrium pressures at 300, 320, 340, and 360 °C for each of the mechanochemically synthesized samples in addition to the MgH_2-Purchased sample. Kinetic pressure and temperature data was collected at 120 s intervals for every measurement, and very long collection times ($\geq$48 h) were implemented to ensure true Mg-H equilibrium was reached in each case. It is often ambiguous as to whether MgH_2 data presented in the literature are actually at equilibrium or whether data collection was ceased prematurely. Certain studies present pressure−composition isotherms (PCIs) that appear to be severely affected by kinetics.[26] PCI curves often display large amounts of hysteresis that could simply be due to an inadequate measurement time. If one does not wait until true equilibrium is met, then measured absorption pressures will be higher than the true equilibrium and measured desorption pressures will be lower than the true equilibrium, leading to an apparent hysteresis. Kinetic plots allow for an assessment of whether true equilibrium is met. Certain PCI features such as a shortened equilibrium plateaux at low temperatures can also indicate that the true equilibrium has not been met. These features can be due to the slower kinetics at low temperatures and the slower kinetics at extreme hydrogen to metal ratios not being accounted for adequately. In our research, care was taken in an effort to provide high quality equilibrium data for MgH_2 to provide accurate bulk thermodynamic data and to study the variation in thermodynamics with changes in MgH_2 particle size.

The kinetics of decomposition are quite slow for the mechanochemically synthesized MgH_2 samples. This can be attributed to the fact that the MgH_2 particles are embedded within a LiCl salt byproduct matrix. Kinetic hydrogen desorption data are provided in Figure 3 that illustrates the majority of decomposition occurs within 2−5 h; however minor but significant changes in pressure are still evident until 24 h have passed. It is likely that small MgH_2 nanoparticles that are not embedded within a LiCl matrix would present very fast hydrogen sorption kinetics. However removal of the LiCl byproduct phase has proven

Table 3. Measured Equilibrium Pressures and Thermodynamic Properties for Mechanochemically Synthesized and Purchased MgH_2 Samples[a]

	MgH_2-Purchased	MgH_2-A	MgH_2-B	MgH_2-C	MgH_2-D
Pressure at 300 °C (bar)	1.636 ± 0.020	1.622 ± 0.018	1.671 ± 0.019	1.824 ± 0.017	1.919 ± 0.018
Pressure at 320 °C (bar)	2.789 ± 0.019	2.763 ± 0.019	2.837 ± 0.020	3.146 ± 0.018	3.134 ± 0.020
Pressure at 340 °C (bar)	4.581 ± 0.021	4.506 ± 0.022	4.622 ± 0.021	5.086 ± 0.017	5.019 ± 0.019
Pressure at 360 °C (bar)	7.196 ± 0.019	7.092 ± 0.027	7.370 ± 0.020	8.053 ± 0.023	7.862 ± 0.044
Decomposition enthalpy (ΔH, kJ/mol H_2)	74.06 ± 0.42	73.92 ± 0.45	74.75 ± 0.42	74.15 ± 0.37	71.22 ± 0.49
Decomposition entropy (ΔS, J/mol H_2/K)	133.4 ± 0.7	133.1 ± 0.7	134.7 ± 0.7	134.5 ± 0.6	129.6 ± 0.8
Calculated 1 bar H_2 equilibrium temperature ($T_{1\,bar}$) (°C)	281.8 ± 2.2	282.2 ± 2.2	281.7 ± 2.1	278.1 ± 2.1	276.2 ± 2.4

[a] Uncertainties are calculated with a 95% confidence interval with further details provided in the Supporting Information.

difficult due to the reactivity of MgH_2 with a range of solvents capable of dissolving LiCl. For example, the ball-milled MgH_2-Purchased as well as the mechanochemically synthesized MgH_2 showed obvious gas evolution on addition to tetrahydrofuran unlike the early work of Ashby[35] in synthesizing MgH_2 in tetrahydrofuran and diethyl ether. If the LiCl phase was removed however, it is also very likely that the MgH_2 nanoparticles would agglomerate into much larger particles, especially at the high temperatures required for decomposition.

Given the slow kinetics of desorption, the hydrogen equilibrium pressures were determined by averaging the final 6 h of pressure data as presented in Table 3, with uncertainties calculated with a 95% confidence interval from the 180 averaged data points. It is evident that there is a change in the hydrogen equilibrium pressures between the samples analyzed. The equilibrium pressures for MgH_2-A and MgH_2-B are similar to the pressures obtained for MgH_2-Purchased at all measured temperatures. The similarity in equilibrium pressures is expected for MgH_2-A due to the large MgH_2 particle size (1−2 μm) which is effectively bulk MgH_2. However the similarity between the equilibrium pressures of MgH_2-B and MgH_2-Purchased is interesting as the MgH_2-B particle size from TEM was found to be in the range of 15−40 nm. The result indicates that MgH_2 particle sizes smaller than this are required to observe measurable thermodynamic changes, as is predicted by theoretical studies. An appreciable increase in the equilibrium pressure is found for both MgH_2-C and MgH_2-D in comparison to MgH_2-Purchased at all measured temperatures (Table 3). It can be deduced that the change in equilibrium pressure is a result of thermodynamic changes within the Mg/MgH_2 system due to nanoscopic particle size, as this is the only variable between the mechanochemically synthesized samples.

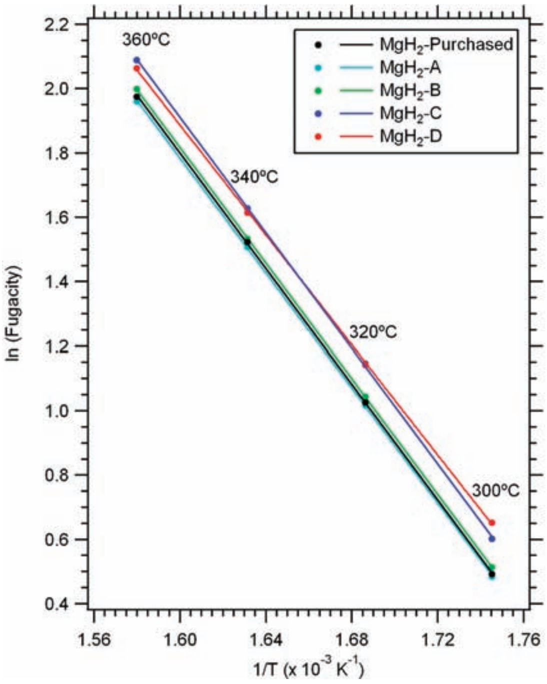

Figure 4. van't Hoff plot for the decomposition of MgH_2 in the four mechanochemically synthesized samples as well as the bulk reference (MgH_2-Purchased).

A van't Hoff plot was constructed as shown in Figure 4 that illustrates the change in measured pressures for MgH_2-C and MgH_2-D that have average particle sizes below 20 nm. The decomposition reaction enthalpy (ΔH) and entropy (ΔS) were calculated by a weighted least-squares method (explained in detail in the Supporting Information) and are provided in Table 3. ΔH for MgH_2-Purchased is equivalent to ΔH for MgH_2-A, MgH_2-B, and even MgH_2-C within uncertainty; however a reduction in ΔH of 2.84 kJ/mol H_2 is determined for MgH_2-D in contrast to the bulk. The measured change in ΔH for MgH_2-D is similar to theoretical predictions for ∼4 nm MgH_2 nanoparticles by Kim et al.[9] The average MgH_2 particle size in MgH_2-D cannot be smaller than the average crystallite size (6.7 ± 0.7 nm) as determined by XRD. The small difference between the experimentally measured minimum particle size (6.7 nm) and the theoretically predicted particle size (4 nm) for the given change in ΔH may simply relate to minor inaccuracies in the theoretical model. However it is also likely that some MgH_2 particle size polydispersity exists within MgH_2-D. If significant levels of polydispersity exist, the hydrogen equilibrium pressure will be controlled by certain MgH_2 particle sizes at different H/M ratios. Desorption measurements for each sample began at H/M = 2. It follows that initially the particles with the smallest size will contribute to the equilibrium pressure (above the bulk value) due to their larger change in ΔH and hence higher inherent equilibrium pressure. As the hydrogen in the smallest particles is exhausted, the elevated equilibrium pressure will no longer be maintained and the equilibrium pressure will begin to approach the bulk value. In the present work the equilibrium pressure was found to be repeatable (within uncertainty) at the different H/M ratios (0.8−1.8) in which measurements were taken. Given the change in ΔH measured for MgH_2-D, it is likely that the equilibrium pressure in this H/M range is controlled by small MgH_2 particles while larger particles (with larger crystallite sizes) may dominate equilibrium pressures at lower H/M ratios.

Figure 5a provides a visual representation of the calculated ΔH and ΔS quantities for each of the samples analyzed. There is an interesting correlation between ΔH and ΔS where a lower

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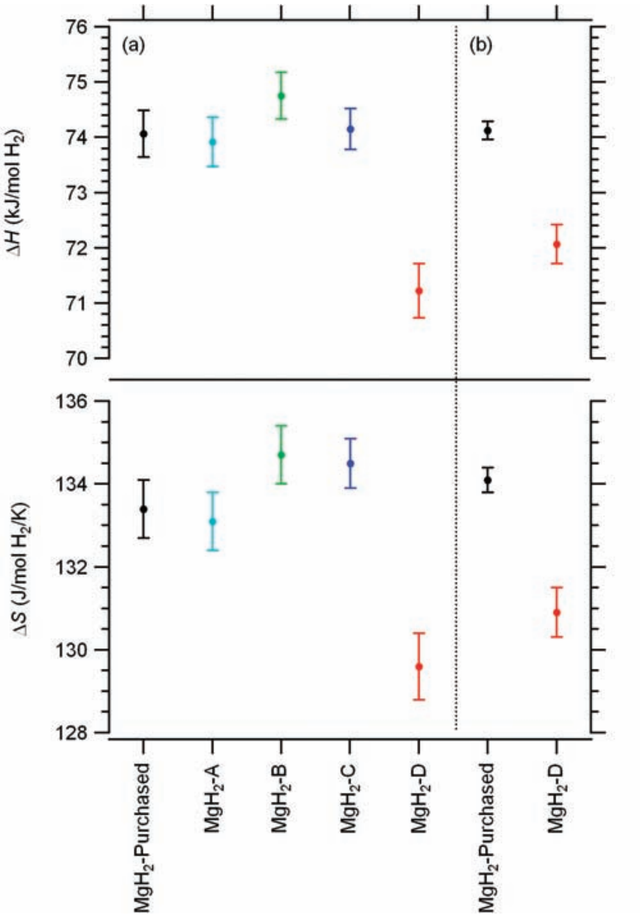

Figure 5. (a) Calculated thermodynamic values for MgH_2 decomposition from the van't Hoff plot in Figure 4. (b) Calculated thermodynamic values from repeat measurements on freshly synthesized MgH_2-Purchased and MgH_2-D. Uncertainties are calculated with a 95% confidence interval as described in the Supporting Information.

decomposition reaction enthalpy in MgH_2-D is matched by a lower reaction entropy, and even subtle changes in enthalpy are closely matched by corresponding changes in entropy. Mg and MgH_2 particles that have nanoscopic sizes contain a large number of atoms that are influenced by the particle surface.[36] The influence of the particle surface affects the Mg and MgH_2 phases to different degrees resulting in a reduction in the overall MgH_2 decomposition reaction enthalpy (ΔH). The same phase-preferred destabilization also appears to apply to ΔS (between Mg and MgH_2). Given the contentious claim of a measured change in the thermodynamics of nanosized MgH_2 particles, the thermodynamic measurements of MgH_2-Purchased and MgH_2-D were repeated by synthesizing two completely new batches of these samples. The values for the enthalpy and entropy of the freshly synthesized samples both agree, within uncertainties, of the original measurements (Figure 5b). This is particularly encouraging given (1) ball milling does not produce perfectly homogeneous samples and (2) the desorption equilibrium pressures at each temperature were measured at different H/M ratios for each sample. This confirms that the measured changes in enthalpy and entropy for MgH_2-D are real and not an artifact of the measurement technique.

Changes in ΔS are not considered in the theoretical investigations, and instead constant bulk ΔS quantities are assumed when predicting the 1 bar desorption temperature.[9,11] Recently Fichtner[37] noted that nothing had been reported to date on whether changes in ΔS with particle size would positively or negatively affect equilibrium pressures. In a bulk system the reaction entropy (ΔS) upon $MgH_2 \rightarrow Mg + H_2$ at 25 °C can be expressed as S_{Mg} (32.5 J/mol H_2/K) + S_{H_2} (130.0 J/mol H_2/K) − S_{MgH_2} (31.1 J/mol H_2/K) = ΔS (131.4 J/mol H_2/K).[38] S_{H_2} is not affected by alterations in the particle structure, but it can be seen that a disproportionate change in the entropy of Mg and MgH_2 with particle size would lead to a change in ΔS. A lower ΔS will be generated if the entropy of a MgH_2 nanoparticle increases by a greater quantity than the entropy for a Mg nanoparticle as particle size is reduced.

The measured thermodynamics for MgH_2-D acts to lower the 1 bar hydrogen equilibrium temperature ($T_{1\,bar}$) (see Table 3) as predicted by theoretical investigations.[9−12] However, the measured reduction in $T_{1\,bar}$ is not in line with the magnitude of the changes predicted. Herein $T_{1\,bar}$ is reduced by ~6 °C for MgH_2-D in contrast to the bulk (MgH_2-Purchased). A reduction in $T_{1\,bar}$ of ~4 °C is also found for MgH_2-C even though its enthalpy was found to be close to that of the bulk. The result indicates that entropy also plays a large part in determining changes in $T_{1\,bar}$. Given the change in ΔH determined for MgH_2-D (2.84 kJ/mol H_2) a reduction in $T_{1\,bar}$ is theoretically predicted to be ~15 °C[9] when using a constant bulk ΔS. This result is in contrast to the calculated ~6 °C reduction in $T_{1\,bar}$ because of the change in ΔS relative to the bulk. The fact that a decrease in $T_{1\,bar}$ is still observed indicates that the change in ΔH due to particle size reduction has a larger impact on $T_{1\,bar}$ than the corresponding change in ΔS.

Conclusions

Hydrogen equilibrium pressure measurements have been used to determine the decomposition enthalpy and entropy for MgH_2 nanoparticles that were mechanochemically synthesized. A reduction in both the decomposition enthalpy and entropy was found for ~7 nm MgH_2 nanoparticle in relation to bulk MgH_2. The consequence of this thermodynamic destabilization is a drop in the 1 bar hydrogen equilibrium temperature of ~6 °C. The temperature drop is not as large as theoretical predictions due to the effect of the decrease in reaction entropy which partially counteracts the decrease in reaction enthalpy. It is not known if the thermodynamics of smaller nanoparticles will be dominated by changes in either the reaction enthalpy or entropy. Further theoretical and experimental studies on MgH_2 nanoparticles will need to be performed with a focus on reaction entropy changes to accurately quantify the thermodynamic destabilization of the Mg-H nanoparticle system to determine whether large reductions in the 1 bar hydrogen equilibrium temperature are possible. Though the mechanochemical synthesis of MgH_2 is a suitable method for producing nanosized particles and comparing their thermodynamics to theoretical predictions, the minor thermodynamic alterations achievable do not justify the added level of synthesis complexity or the hydrogen density penalties for its use as a hydrogen storage solution.

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Supporting Information Available: Detailed information is provided regarding the Sieverts apparatus, the associated uncertainty calculations, and the reproducibility of the acquired data. This material is available free of charge via the Internet at http://pubs.acs.org.

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