Impact of Initial Catalyst Form on the 3D Structure and Performance of Ball-Milled Ni-Catalyzed MgH_2 for Hydrogen Storage

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ABSTRACT

Although it has been shown that the hydrogen storage kinetics of metal hydrides can be significantly improved by the addition of transition metal-based catalysts, relatively little attention has been paid to the impact that the form in which these catalysts are introduced during synthesis has on the resulting structure and how this alters performance. Two mixtures of MgH_2 doped with Ni were prepared via high-energy ball-milling under identical conditions, one using a pure Ni nanopowder catalyst and the other using anhydrous NiCl_2 . The resulting Ni catalyst particles of the NiCl_2 -doped material were 10-100 times smaller, as well as more uniform in size and shape. Electron tomography revealed that the additive form also altered its incorporation and 3D spatial distribution, with Ni particles limited to the outer surface in the NiCl_2 -doped case. The significantly lower desorption performance measured in the NiCl_2 -doped material is attributed to regions of MgCl_2 acting as barriers between the MgH_2 and Ni, hindering the ability of the latter to effectively catalyze the reactions. This work demonstrates the hazards in assuming different catalyst forms produce similar final structures and highlights the potential of catalyst form as a synthesis tool for optimizing the material structure and performance.

KEYWORDS: Metal hydrides, Hydrogen storage, Transmission electron microscopy, Electron tomography, In situ TEM, High-energy ball-milling

1. INTRODUCTION

The requirements placed on the hydrogen storage systems in H_2 -powered fuel cell vehicles are demanding [1]. Complex metal hydrides – e.g., Al, Ca, Li, Mg, and Na – are attractive candidates for lightweight, onboard regenerative storage due to their high gravimetric

and volumetric storage densities [2-5]. The promise of these materials, however, is challenged by their thermodynamic stability and poor hydrogen sorption kinetics, leading to restrictively high reaction temperatures. Significant improvement in de/hydrogenation behavior has been demonstrated through high-energy ball-milling – to reduce particle size, increase surface area, and create defects – and by doping the hydride with a suitable catalyst. These catalysts are typically transition metals either in their pure form [6-8] or as oxides [9-11], halides [12, 13], hydrides [14, 15], or intermetallics [16-18].

Beyond the catalytic species selected, experimental and computational efforts have shown that the effectiveness of the catalyst at enhancing the hydrogen sorption kinetics depends on its size, shape, and residence with respect to the hydride – e.g., in surface, interfacial, or interior positions and whether it is well-dispersed or agglomerated [19-24]. Knowing the location of the catalyst is vital due to the low concentrations required to achieve the benefit, typically only a few atomic percent. Additionally, some studies suggest that the preferential location of catalyst particles can enhance the cyclic stability, such as by hindering grain boundary movement to limit grain growth [25]. Most efforts made thus far to identify catalyst location in these systems have relied on conventional characterization approaches yielding ambiguous results [8, 13, 14, 26-31], e.g., due to the depth information lost in TEM micrographs, which are two-dimensional projections through three-dimensional structures. In a previous work, however, we demonstrated that the three-dimensional dispersion of catalyst in these material systems can be determined by using electron tomography [32]. The impact that the form in which a given catalyst is introduced during synthesis has on the resulting structure, morphology, and catalyst dispersion in high-energy ball-milled hydride materials still remains uncertain. In particular, no studies of whether – and if so, to what degree – the initial form of the catalytic additive impacts

the incorporation and dispersion of the catalyst in 3D have been performed. To facilitate the improvement of hydride storage systems through the determination of optimal synthesis conditions and the rational selection of hydride-catalyst combinations, the connection between the synthesis, structure, and performance must be better understood.

The current study explores this issue by examining the high-energy ball-milled $\text{MgH}_2 + 0.05 \text{ Ni}$ system, in which the materials have been prepared identically except for the initial form of the catalyst: a pure Ni nanopowder and anhydrous NiCl_2 . Magnesium hydride, MgH_2 , is one of the most promising storage hydrides due to its attractive gravimetric (7.6 wt%) and volumetric (110 g/L) hydrogen storage densities, low cost, and non-toxicity. Fortunately, the high dehydrogenation temperatures (350-400 °C) and sluggish kinetics (necessitating temperatures in excess of 300 °C and pressures of around 20 bar for hydrogenation) [33-38] of MgH_2 can be significantly improved through high-energy ball-milling [26, 39-41] and a wide variety of catalytic additives [6-18]. Although its kinetic enhancement is well-documented [35, 36, 42, 43], Ni was selected as the catalyst for this study because the hydrogen desorption temperatures were found to increase with increasing milling duration [8, 32]. While longer milling time is the typical approach for reducing catalyst particle size, it was of additional interest to explore whether initial catalyst form might offer an alternative method. NiCl_2 was chosen for testing, as it was expected to decompose to form MgCl_2 , leaving the Ni behind.

The effects of the different forms of Ni were investigated in this work using electron microscopy (TEM, STEM, and SEM), diffraction (electron and X-ray), and energy-dispersive X-ray spectroscopy; the 3D distribution of catalyst was determined by using electron tomography. The dehydrogenation performance of the two systems was compared by thermogravimetric analysis, while the changes in structure and catalyst dispersion during hydrogen desorption were

probed via *in situ* TEM/STEM heating experiments. The results of this work demonstrate the inadequacy of assuming disparate catalyst forms produce similar final structures and highlights the potential of catalyst form as a tool for tailoring the catalyst size, shape, and dispersion.

2. MATERIAL AND METHODS

The storage materials for this study were prepared from 20:1 mixtures of MgH_2 (from Gelest, 95% purity) and one of two Ni catalysts: Ni nanopowder (from Argonide Corp.) or anhydrous NiCl_2 (from Sigma Aldrich, 99.999% purity). The Ni nanopowder was observed to be spheres 10-80 nm in diameter, with an average diameter of 50 nm, Supplementary Material S1a, while the anhydrous NiCl_2 , Figure S1b, consisted of thin, sharply faceted hexagonal flakes on the order of 50-1000 nanometers across (typically hundreds) and approximately 20-60 nm thick. Regardless of the Ni catalyst used, mixtures were prepared under identical conditions inside an argon-atmosphere glovebox with O_2 and H_2O concentrations <1 ppm. Approximately 1 g of material was high-energy ball-milled under argon gas in a Fritsch Pulversette 6 planetary ball mill for 1 hour at 400 rpm in an 80 cm^3 hardened steel milling vessel packed with 30 chrome-steel 7 mm-diameter milling balls. The Ni nanopowder-catalyzed material is the same batch examined in one of our previous works that investigated the effect of ball-milling duration on catalyst morphology and incorporation and the resulting hydrogen storage behavior of Ni-doped MgH_2 . [32] The 1-hr milled specimen was selected for further analysis in the current study since it showed the highest performance.

The hydrogen release properties of 17-20 mg samples of the storage materials were characterized with a Shimadzu TGA-50 thermogravimetric analyzer (TGA) installed inside an

Ar-filled glovebox with O₂ and H₂O levels <0.5 ppm. The specimens were heated under 50 ml/min flowing argon up to 550 °C at a rate of 5 °C/min.

A Siemens-Bruker D-5000 x-ray diffractometer with monochromated Cu K α x-rays was employed for powder x-ray diffraction (XRD) analysis of the as-milled material. A low-background quartz holder with a 200 mm³ cavity was packed in an argon environment and sealed with Kapton tape to prevent reaction of the sample with air. The XRD spectra were collected over the angular range $2\theta = 20-80^\circ$ using a 0.02° step size and a scan speed of $0.25^\circ/\text{min}$. Although a slight expansion of the Kapton tape cover by the pure Ni-doped specimen occurred sometime after 2 hours, the cover remained airtight and no alteration in powder color was observed in either material.

Characterization of the structure, morphology, and catalyst dispersion of the hydride systems was carried out using various electron microscopy and spectroscopy techniques. Conventional transmission electron microscopy (TEM) was used for imaging and selected area electron diffraction (SAED), while high-angle annular dark-field scanning TEM (HAADF-STEM) was used to collect HAADF images and perform energy-dispersive x-ray spectroscopy (EDS) compositional analysis. The primary TEM was a JEOL 2010 while the primary STEM was a JEOL 2010F equipped with an atmospheric thin-window EDS spectrometer from Oxford Instruments. An FEI Tecnai F20ST S/TEM equipped with an EDAX Sapphire Si (Li) ultra-thin window energy spectrometer was used to acquire the tilt series for tomography and additional EDS. All S/TEM analysis was performed at a 200 keV operating voltage. A JEOL 7000F scanning electron microscope (SEM) operated at 15 keV was used for topographical characterization.

All sample storage and preparation was carried out inside an MBraun Ar-atmosphere glovebox maintained at O₂ and H₂O concentrations < 0.1 ppm. Microscopy specimens were prepared via dry application of the powdered material to holey carbon coated Cu TEM grids. A Gatan HHST 4004 environmental vacuum cell transfer stage was used for all S/TEM experiments performed on the JEOL microscopes in order to minimize exposure of the specimens to air. By employing this stage, the specimens experienced only either a purified argon atmosphere or a roughing pump vacuum prior to insertion into the microscope column. A Model 1000F single-tilt tomography holder from Hummingbird Scientific was used for the analysis performed with the Tecnai F20 S/TEM. The samples for SEM examination were mounted on an aluminum stub. In both cases, atmospheric exposure of the specimens during transfer and loading was kept to less than 10 minutes.

In situ heating experiments to explore how the systems evolve during the dehydrogenation process were performed using the vacuum transfer stage. The samples were heated to a nominal temperature of 300 °C at a ramp rate of 5-6 °C/min, held for 25 minutes to allow for hydrogen desorption, and then cooled at a rate of approximately 10 °C/min. During observation prior to heating, the locations of selected hydride particle aggregates were recorded to enable their reexamination after each heating increment without the need to keep them continually under the electron beam. To supplement these tracked aggregates, new aggregates that had not been previously imaged or scanned were examined after each heating step.

During the first minute of exposure to the electron beam during S/TEM, limited changes were observed in the MgH₂, consisting of contrast fluctuations, the formation of small voids, and the appearance of Mg diffraction spots in selected area electron diffraction (SAED) patterns. After one minute of exposure to the electron beam, the material stabilized, as long as the

operating magnification was kept < 100 kX (and the beam broadened in TEM), no further changes were observed. This suggests that the effect of beam exposure was beam-heating-induced decomposition of MgH_2 to Mg. Despite altering the surrounding MgH_2 , electron beam effects produced no observable change in the size, shape, or position of the Ni catalyst particles. No significant differences in morphology were noted between the tracked and new particles.

3. RESULTS

3.1 Dehydrogenation Performance

The hydrogen desorption behavior of the two materials, measured via TGA, is shown in Figure 1a as the fractional weight loss curves for dehydrogenation and in Figure 1b as the derivative weight loss ($\text{wt\%/}^\circ\text{C}$). The onset temperatures for hydrogen release and the total weight of desorbed hydrogen from these measurements are included in Table 1. The values listed in parentheses are from a second set of samples run for confirmation. In both cases, the NiCl_2 -doped material exhibited significantly poorer dehydrogenation performance than the Ni-doped specimen. The onset of hydrogen desorption occurred at a temperature roughly 60°C higher, and released only 4.5 wt% of hydrogen by 325°C , whereas the Ni-doped material had already completed its dehydrogenation, releasing 5.9 wt%. The final quantity of hydrogen released by the NiCl_2 system was lower by ~ 0.4 - 0.7 wt%. To further analyze this behavior, the desorption curves of Figure 1b were fitted as multiple thermally stimulated desorption processes, detailed in reference [32]. The resulting fits are included in Supplementary Material S2-S3; Table 2 summarizes the peak positions and fitting parameters. This fitting indicates that while two desorption processes took place in the Ni-doped specimen, each with an activation energy on the order of 1.8 ± 0.1 eV, only a single process took place in the NiCl_2 -doped specimen, with a similar

but slightly lower activation energy around 1.7 ± 0.1 eV, albeit at a much higher temperature. The higher temperature and lower activation energy indicates a lower attempt frequency for H release, consistent with a different catalytic activation process. The gradual onset of desorption in the Ni-doped material suggests a continuously increasing activation energy and so that region was not fitted in this analysis.

Table 1. Hydrogen desorption values derived from TGA experiments.

Milling Duration	Onset Temp (°C)	Total Weight % loss
Ni	222 (215) ± 1	5.90 (5.92) ± 0.04
NiCl₂	281 (269) ± 1	5.24 (5.50) ± 0.04

The values listed in parentheses are from the second set of samples.

Table 2. Peak positions and fitting parameters for the curve fits to the derivative weight loss TGA measurements, Figure 1b.

Peak Position (°C)	Ea (eV)	Prefactor^A	Peak Height (wt%)	
			Ni	NiCl₂
255 ± 5	1.8 ± 0.1	9.0 $\times 10^{14}$	4.4 ± 0.2	n/a
295 ± 5	1.8 ± 0.1	5.0 $\times 10^{13}$	1.0 ± 0.1	n/a
310 ± 5	1.7 ± 0.1	2.1 $\times 10^{12}$	n/a	5.7 ± 0.3

“n/a” means that component is not present in the desorption curves for that material. ^AThe prefactors were about ten times smaller for Ea values 0.1 eV lower, and ten times larger for Ea values 0.1 eV higher.

3.2 Morphology and Catalyst Dispersion as a Function of Catalyst Form

The full XRD spectra acquired from the Ni- and NiCl₂-doped materials are labeled in Figure 2, along with a background spectrum of an empty sample holder covered with the Kapton tape. The same α -MgH₂ and Ni diffraction peaks are present in both specimens, as identified using the MDI JADE software package. The MgH₂ peaks are sharper and more intense for the NiCl₂-doped specimen, indicating a larger grain size, and the peaks do not exhibit the doublet structure of the Ni-doped material, Figure 3a. The doublets, attributed to off-stoichiometry material preceding intermetallic formation, are discussed in detail in reference [32]. An average grain size of 25.5 nm was estimated from the NiCl₂-doped MgH₂ peaks using the Williamson-

Hall method [44]. While the doublets prevented a good estimate for the Ni-doped material, a comparison of the diffraction peaks suggests a smaller, but not dramatically smaller, grain size. In contrast, the Ni diffraction peaks of the NiCl_2 -doped material, Figure 3b-c, are significantly broader and shallower than in the Ni-doped spectrum, indicating catalyst particles of a much smaller (nanometer) size. A very low-intensity feature corresponding to the primary (200) MgO diffraction peak was present in both spectra with no discernible difference in size or shape between them. Two additional small, broad peaks, shown in Figure 3c-d, were observed only in the NiCl_2 -doped spectrum. The closest matches for these features are the MgCl_2 (110/113) and the MgCl_2 (012), respectively. The primary MgCl_2 peak (104) was not observed; its position, however, marked by an arrow in Figure 3a, lies on the tail of the large MgH_2 (200) peak, which may obscure it.

Both materials were composed of particle aggregates with a similar size range after ball-milling, from <100 nm up to a few micrometers. The aggregate morphologies, however, were noticeably different, as seen in the SEM micrographs in Figure 4. Whereas the constituent particles of the Ni-doped aggregates, Figure 4a, were round and distinct, those in the NiCl_2 -doped material, Figure 4b, were more angular and appear to be in greater contact with each other, as though they had begun to fuse.

In both instances, a nanocrystalline MgO layer covers the outside of the aggregates, visible in the TEM micrographs of Figure 5. The MgO rings are indicated in the corresponding SAED patterns, along with the primary diffracting planes of the Mg- and Ni-based phases present in the patterns. The oxide grain size, ~1.2-3 nm, and layer thickness were comparable in both specimens, though the oxide layer in the NiCl_2 -doped material was smoother.

The post-milling catalyst particle morphology and dispersion differed significantly depending on the initial catalyst introduced. In the Ni-doped specimens, Figure 6a, the Ni particles possessed a variety of shapes and sizes. Particles ranging in shape from round (spherical or ovoid) to elongated (plate-like or more irregularly shaped) were observed, most being tens of nanometers across. Round particles ranged from 3 nm to 86 nm in diameter. Aspect ratios for the elongated particles were typically 2 to 9, although ratios as high as 17 were measured. In contrast, the catalyst particles in the NiCl_2 -doped specimens, Figure 6b-c, were 10-100 times smaller and were much more uniform in size. The largest Ni catalyst particle observed was around 10 nm and the smallest 2 nm although there may well be smaller ones; poorer contrast rendered particles below 2 nm difficult to distinguish. The Ni particles were also more finely dispersed in the NiCl_2 -doped than in the Ni-doped material, spanning areas up to hundreds of nanometers across, Figure 6c, in which the clearly distinguishable individual particles had not sintered into larger ones. The retained individuality of the nanoparticles and their more uniform size is corroborated by TEM, as in the small patch of Ni nanoparticles magnified in the inset of Figure 5b.

EDS mapping revealed that the Ni in the Ni-doped samples, Figure 7a, was predominantly localized into the discrete Ni nanoparticles. Likewise, the Ni distribution in the NiCl_2 -doped samples, Figure 7b, corresponded with the patches of Ni nanoparticles seen in the STEM micrographs. The Cl distribution was found to be similar to that of Ni but more diffuse, suggesting that upon decomposition of the NiCl_2 , the Ni stayed relatively stationary as nano-sized particles while the Cl diffused away into or onto the MgH_2 . While some NiCl_2 particles remained, Supplementary Material S4, most decomposed, leaving behind Ni particles, indicated by the white arrow, and a more uniform background level of Cl.

Electron tomography was used to determine how the 3D dispersion and spatial residence of the catalyst particles with respect to the magnesium hydride were affected by catalyst form. A tilt series of HAADF-STEM micrographs was acquired from a particle aggregate from each specimen. An image was acquired every 2° over the angular range $+76^\circ$ to -72° for the Ni-doped series and -72° to $+74^\circ$ for the NiCl_2 -doped series. Movies of the aligned tilt series are included in Supplementary Material M1 and M2, respectively. The tilt series were reconstructed using EM3D [45] and TomoJ [46] and visualized using UCSF Chimera [47] and ImageJ [48]. A micrograph from each tilt series along with corresponding images of the resulting reconstructions are shown in Figure 8. Full movies of the visualized tomograms are included in Supplementary Material M3 and M4. The tomograms reveal that the form of catalyst introduced significantly impacts its 3D distribution. In the Ni-doped material, Figure 8a-e, most of the Ni particles reside on the MgH_2 surface or in shallow sub-surface positions (less than or equal to the size of the particle). The larger, more spherical or ovoid particles tended to be found in these exterior positions, either partially recessed into the surface or nestled into interstices between MgH_2 particles. Some particles, however, were entirely embedded inside the MgH_2 . These exhibited primarily smaller or more irregular morphologies, presumably from having experienced more extensive deformation during the milling process. The depths and positions of the catalyst particles were measured from orthogonal slices through the reconstruction. The orthogonal slices for three example Ni particles, labeled on the tomogram in Figure 8b, are included in Figure 8c-e: (c) a small, round interior particle, (d) a large, ovoid exterior/interstitial particle, and (e) a plate-like interior/near-sub-surface particle. In the NiCl_2 -doped material, however, Figure 8f-j, the Ni catalyst particles were limited to the exterior surface of the MgH_2 ; none were found to be fully encased in MgH_2 . This is exemplified by three particles labeled in Figure 8g and their

corresponding orthogonal slices, Figure 8h-j: (h) an isolated particle, (i) a small cluster of nanoparticles, and (j) a larger patch of nanoparticles. The greater uniformity of catalyst shape and size is also apparent.

In both tilt series and their corresponding tomographic reconstructions, the voids and channels visible inside the MgH_2 particles (appearing here as darker regions) are the products of beam damage, likely the result of thermal decomposition of the MgH_2 induced by beam-heating. Their formation occurred prior to acquisition of the tilt series and had no effect on the size, morphology, or location of the Ni particles.

3.3 Morphology and Catalyst Dispersion Changes with Dehydrogenation

To explore any differences in the evolution of the as-synthesized structures, samples of both materials were examined during dehydrogenation under vacuum via *in situ* STEM and TEM heating to 300 °C. As seen in the post-heating SEM images of Figure 9, while the overall MgH_2 aggregate shape did not differ appreciably in the Ni-doped case after heating, the initially angular NiCl_2 -doped aggregates were much smoother, suggesting agglomeration.

The STEM micrographs, Figure 10a-b, reveal both recession of the underlying MgH_2 in the Ni-doped material from the outer oxide layer, attributable to its decomposition to the lower-volume Mg, and the formation of large interior voids. This MgH_2 recession can also be seen in some SEM images, such as the inset of Figure 9a. These phenomena were not as evident in the NiCl_2 -doped specimens although some degree of shrinkage was still observed, Figure 10c-d. The higher temperature required for complete dehydrogenation of MgH_2 in the NiCl_2 sample suggests that had the *in situ* heating been ramped to a higher temperature the recession would have become more pronounced. Recession of the Mg away from the outer oxide layer was also

evident in the post-heating TEM micrographs, Figure 11. No noticeable changes in the oxide, in thickness or shape, were observed as the MgH_2 receded. Coarsening of grain size during dehydrogenation is implied by more uniform and larger-scale mottling combined with a drastic reduction in non-MgO spots in the corresponding SAED patterns for both specimens.

In contrast, the Ni catalyst in the two specimens exhibited dramatically different behavior. The Ni in the Ni-doped material underwent a redistribution during dehydrogenation, with the discrete Ni particles partially decomposing, growing diffuse (Figure 10a-b) and forming the intermetallic compound Mg_2Ni ; see reference [32] for further information. No significant changes in the Ni particles of the NiCl_2 -doped material were observed during the heating, though this may be due MgCl_2 inhibiting any Mg/Ni interaction, as is discussed in the next section.

4. DISCUSSION

The results of the current work demonstrate that the nature of the catalyst precursor affects the hydrogen discharge kinetics, nanostructure, and distribution of the catalyst particles; that the components of the catalyst precursor (Cl here) may remain in the storage medium after ball milling; and that the stability and cyclability of the storage material may be affected by that precursor. We begin the discussion of these results by considering the impact of species introduced with the catalyst material in the precursor.

Here we studied the use of anhydrous NiCl_2 as a precursor, compared against pure Ni nanopowder. In this case the Cl diffused and reacted with the MgH_2 forming MgCl_2 . This compound is energetically favorable, with a standard enthalpy of formation of -641.3 kJ/mol , even more negative than MgO , -601.6 kJ/mol [49], which we have found present on the surface of the storage material. Thus, it is expected that all or almost all of the Cl released from

decomposed NiCl_2 quickly formed MgCl_2 (verified by XRD). MgCl_2 , is not a hydrogen storage material and is interposed between the Ni and the remaining MgH_2 . We propose that this material forms a barrier between the catalyst and the hydride, limiting their interaction and hindering the ability of the Ni to function as an effective catalyst in the hydrogen reactions.

We note that the two catalyst precursors studied here show desorption processes with roughly the same activation energy (1.8 ± 0.1 eV), which suggests that the rate limiting step for reaction is the same for both catalysts. This is consistent with the idea that Ni is the active catalyst in both cases. The difference in prefactor in the desorption rate indicates that the Cl-containing material has a reduced attempt frequency for hydrogen extraction, consistent with the MgCl_2 site blocking mechanism proposed above. Although the Ni catalyst particles produced are smaller and more numerous, most are hindered from acting as useful catalysts by the MgCl_2 barriers.

It is possible that further milling of the material may separate the MgCl_2 and Ni, putting the Ni into contact with fresh MgH_2 , but this runs the risk of transforming the Ni into $\text{Mg}_2\text{Ni}/\text{Mg}_2\text{NiH}_4$, as was observed in the Ni-nanopowder system [32]. This concern is also relevant to the possible reaction of the catalyst with the storage material after dehydrogenation. In this case the storage material is converted to metallic Mg after dehydrogenation, which may react irreversibly to form Mg_2Ni (verified by SAED). We suggest that forming the intermetallic compound is inevitable [32] and needs to be considered in selection of a catalyst. For example, in this case Mg does not form intermetallics with Ti, suggesting that this may be a better choice for a cyclable catalyst compared to Ni, although the overall catalytic activity also needs to be considered.

Despite the performance degradation that resulted from the addition of NiCl_2 specifically, the current work demonstrates that the form of the catalyst introduced during synthesis has a significant impact on the resulting size, morphology, and spatial residence of the catalyst particles. Using anhydrous NiCl_2 instead of pure Ni nanopowder resulted in much finer and more uniformly sized Ni particles for identical milling durations, and impacted not only the 2D spatial distribution, but also its 3D integration into the hydride (determined via tomography). This indicates that initial catalyst form can be treated as another tool for tailoring the structure of these systems, aiding optimization of the synthesis process by allowing greater flexibility in method – e.g., the ability to use shorter milling times – to achieve a given final material structure.

We also suggest that analysis of TGA measurements, as described here, as a function of number cycles of the storage medium can demonstrate how the mechanism is changing as the catalyst and microstructure of the structure evolves. Total absorbed hydrogen is related to factors such as reactions of the catalyst with the dehydrogenated storage material. Activation energy changes may relate to microstructure (as here where a range of values were observed for the large and variously distributed Ni nanoparticles from the Ni nanoparticle precursor), while the prefactor describing the desorption can reflect the presence of blocking layers or disconnection of the catalyst from the storage medium.

5. CONCLUSIONS

Based on the results of this study, we conclude that the chemical nature of the dopant used to produce catalytic nanoparticles is critical to their performance. Far from being something to be chosen arbitrarily, it is a variable that can and should be used to optimize the structure and performance of the catalyzed system. After preparation via high-energy ball-milling under

identical conditions, the Ni catalyst particles resulting from doping MgH_2 with a pure Ni nanopowder exhibited a wide range of sizes and morphologies, while those produced from anhydrous NiCl_2 were 10-100 times finer and much more uniform in both size and shape. The initial form of the catalyst also influenced its location on and in the MgH_2 . The catalyst particles occupied surface, interstitial, and fully interior positions in the Ni-doped material, whereas the Ni in the NiCl_2 -doped material was restricted to the exterior surface – no Ni was found inside the MgH_2 . Introducing the Ni catalyst in the form of anhydrous NiCl_2 as opposed to Ni nanoparticles was found to negatively impact the desorption of hydrogen, as gauged via TGA. Despite the smaller size of its catalyst particles, the NiCl_2 -doped material released a lower quantity of hydrogen and required a significantly higher temperature to do so. We attribute this degradation of sorption kinetics to the observed formation of MgCl_2 interposed between the MgH_2 bulk and Ni particles, inhibiting the ability of the Ni to catalyze the dehydrogenation reaction. These results demonstrate that selection of initial catalyst form can be a tool for tailoring material structure and catalyst dispersion, offering greater flexibility in synthesis methods, but that optimizing the size and distribution of the catalyst nanoparticles is not always sufficient to avoid degradation due to secondary reactions. They also emphasize the hazards of assuming that different catalyst forms will produce similar structures when otherwise prepared identically, and highlight the need for multi-probe analysis to fully understand the influence of processing on the distribution of catalyst particles and the resulting performance.

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Figure 1. TGA (a) weight loss and (b) derivative weight loss curves from the first run of the Ni- (black) and NiCl₂-doped (gray) specimens. The dehydrogenation onset temperatures and total weight losses for both runs are included in Table 1.

Figure 2. Indexed powder XRD spectra for the Ni- and NiCl₂-doped specimens. Also included is a “background” spectrum from an empty holder with only the Kapton tape covering. The spectra have been offset vertically for ease of viewing.

Figure 3. Enlargements of selected XRD peaks from Figure 2. The identity of each peak is included above its position. The MgH₂ peaks (a) of the NiCl₂-doped specimen (gray) are sharper than the corresponding features in the Ni-doped specimen (black) and do not display the doublets of the latter. Conversely, the Ni peaks (b-c) are significantly broader and shallower in the NiCl₂-doped specimen. Small MgCl₂ features (c-d) are visible in the spectra for the NiCl₂-doped specimen, though the primary MgCl₂ peak – the triangle in (a) – is likely obscured by the nearby MgH₂ (200) peak.

Figure 4. SEM micrographs of (a) Ni- and (b) NiCl₂-doped MgH₂ aggregates after ball-milling but prior to dehydrogenation.

Figure 5. TEM micrographs of example aggregates of (a) Ni- and (b) NiCl₂-doped. The corresponding electron diffraction patterns, with the primary diffracting planes of the Mg- and Ni-based phases indexed where present, are shown to the right. The inset in (b) shows a higher-magnification view of a patch of Ni catalyst particles.

Figure 6. HAADF-STEM micrographs of (a) Ni- and (b) NiCl₂-doped specimens prior to dehydrogenation. A close-up of the boxed region in (b) is shown in (c), where the individual Ni particles comprising the “patch” can be easily distinguished.

Figure 7. EDS spectral maps of the (a) Ni- and (b) NiCl₂-doped specimens. Maps showing the elemental distribution of Mg, Ni, and Cl are included, along with the dark-field intensity. All maps are 3.5 μm across.

Figure 8. (a,f) Micrographs from the HAADF-STEM tilt series of a (a-e) Ni- and (f-j) NiCl₂-doped aggregate, respectively. The matching views from the reconstructed tomograms are shown in (b) and (g), with MgH₂ colored blue and Ni colored yellow. (c-e) and (h-j) are orthogonal

slices through the tomograms of selected catalyst particles, labeled with white triangles in (b) and (g). The large yellow stripe in (g), indicated by a black arrow, is a reconstruction artifact.

Figure 9. SEM micrographs of (a) Ni- and (b) NiCl₂-doped aggregates following *in situ* STEM heating to 300 °C. The inset of (a) shows a region of the aggregate where the recession of the Mg surface (solid line) from the outer oxide shell (dotted line) can be clearly seen.

Figure 10. HAADF-STEM micrographs of (a-b) Ni- and (c-d) NiCl₂-doped aggregates (a,c) before and (b,d) after *in situ* STEM heating to 300 °C. (a) Voids (e.g., dotted black lines) were formed in the MgH₂ during dehydrogenation, as MgH₂ decomposed to lower-volume Mg. The inset of (b) shows a higher magnification view of a region where the underlying Mg surface (solid white line) has clearly receded from the outer oxide layer (dotted white line). Although some recession of the underlying Mg/MgH₂ and void formation can be observed in (d), the effect is not as pronounced. No appreciable change in the Ni catalyst particles was observed during heating in the NiCl₂-doped material.

Figure 11. TEM micrographs and corresponding diffraction patterns of the same (a) Ni- and (b) NiCl₂-doped aggregates shown in Figure 5, following *in situ* TEM heating to 300 °C. No change in the MgO rings was observed. The inset in (a) shows an example of where recession of the underlying Mg from the outer oxide shell can be seen.