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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.

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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 $MgH_2 + 0.05$ 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.

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 $NiCl_2$, Fig. S1b, consisted of thin, sharply faceted hexagonal flakes on the order of 50–1000 nm 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 Pulverisette 6 planetary ball mill for 1 h 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 O_2 and H_2O 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 $K\alpha$ x-rays was employed for powder X-ray