Investigation of Catalyst Development from Mg$_2$NiH$_4$ Hydride and Its Application for the CO$_2$ Methanation Reaction

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Received: 11 November 2020; Accepted: 29 November 2020; Published: 1 December 2020

Abstract: In current study various aspects of catalyst development for the Sabatier type methanation reaction were investigated. It was demonstrated that starting from 330–380 °C Mg$_2$NiH$_4$ hydride heating under CO$_2$ and H$_2$ gas flow initiates hydride decomposition, disproportionation and oxidation. These reactions empower catalytic properties of the material and promotes CO$_2$ methanation reaction. Detailed structural, colorimetric and thermogravimetric analysis revealed that in order to have fast and full-scale development of the catalyst (formation of MgO decorated by nanocrystalline Ni) initial hydride has to be heated above 500 °C. Another considerable finding of the study was confirmation that potentially both high grade and low grade starting Mg$_2$Ni alloy can be equally suitable for the hydride synthesis and its usage for the promotion of methanation reactions.

Keywords: Mg$_2$NiH$_4$; methanation; catalyst; CO$_2$; Sabatier
Second stage: $3\text{H}_2(\text{g}) + \text{CO}(\text{g}) \rightarrow \text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) \quad \Delta H_{298K} = -206 \text{ kJ/mol}$ \hfill (3)

Gao et al. \[9\] reported that based on free Gibbs energy calculations, the optimal temperature (in respect to $\text{CH}_4$ selectivity and $\text{CO}_2$ conversion) for the Sabatier reaction (1) is 300–400 °C. However, due to the endothermic reaction (2), relatively high activation barrier \[3\], and limited kinetics, at this temperature range significant methanation reaction is observed only with the presence of suitable catalyst \[10\]. The need for the catalyst is lessened when temperature exceeds 500°C and reverse water gas shift reaction (2) becomes exothermic. But at high temperatures the competing Bosch reaction takes place and the efficiency of methanation process (1) is starting to decrease \[9\]. The presence of conventional heterogeneous catalysts (for example Ni, Fe, Co or Ru \[11\]) do not help either because in addition to promoting CO methanation they also serve as catalytic drivers for the competing reaction (4) which produces elemental carbon and poisons the catalysts \[12\]:

$$\text{Bosch reaction: } 2\text{H}_2(\text{g}) + \text{CO}_2(\text{g}) \rightarrow \text{C}(\text{s}) + 2\text{H}_2\text{O}(\text{g})$$ \hfill (4)

Looking for the solutions to avoid carbon build up at elevated temperatures Gao et al. \[9\] and Jurgensen et al. \[12\] investigated the role of $\text{CO}_2$:H$_2$ and $\text{CO}_2$:H$_2$ gas ratios. The researchers determined that higher gas ratios have positive effects on lowering down carbon production and that preferable $\text{CO}_2$:H$_2$ gas ratios should be at least 1:6 \[9\]. Additionally, it was demonstrated that by increasing gas mixture pressure from 1 to 11 bars, the starting temperature for carbon generation rises from 365 to 515°C \[12\]. The other way to minimize carbon formation and the poisoning of the catalyst is to find new materials that have a higher selectivity for CH$_4$ production and do not support the Bosch reaction.

In 1990, Selvam et al. \[13\] investigated the interaction between CO$_2$, hydrogen storage alloys, and compounds including LaNi$_5$, CaNi$_5$, Mg$_2$Ni, Mg$_2$Cu, and FeTi. They reported that during exposure to air, all these compounds form surface oxides and hydroxides that, in turn, actively adsorb atmospheric CO$_2$ and favor the formation of carbonate species on the top few layers of the surface. In a subsequent study of air-exposed Mg$_2$NiH$_4$ hydride \[14\], Selvam et al. reached conclusion that later hydride also undergoes similar processes and forms surface carbonate species, especially in the presence of moisture.

Two decades later, Kato et al. \[6\] argued that the high absorptivity of CO$_2$ on an Mg$_2$NiH$_4$ surface could be beneficial for the Sabatier type methanation reaction. Their comprehensive study on the catalytic interactions of the hydride surface of Mg$_2$NiH$_4$ powder with CO$_2$ provided valuable insights into material disproportionation and oxidation during cyclic hydrogen absorption and hydrogen desorption under CO$_2$ (at temperatures up to 500 °C). Based on their findings, during the first few dehydriding cycles in a CO$_2$-containing atmosphere, the simultaneous disproportionation of Mg$_2$NiH$_4$ and the selective oxidation of Mg take place. As a result, a layered structure consisting of Mg$_2$NiH$_4$/Mg$_2$Ni/Ni/MgO was formed. According to the authors, when it was active, Ni helped to dissociate CO$_2$ and CO molecules and promoted methanation. Eventually, after approximately 20 cycles, Mg$_2$NiH$_4$ and Mg$_2$Ni were no longer formed and only MgO and Ni phases were observed.

In two more recent studies, Grasso et al. \[14\] reported experimental data on CO$_2$ methanation processes using as-sintered monoclinic \[15\] and as-milled cubic Mg$_2$NiH$_4$ \[16\] powders. In these studies, Mg$_2$NiH$_4$ powders served as the sole hydrogen sources and “providers” of catalytic sites for the promotion of the conversion of CO$_2$ to CH$_4$. To proceed with the experiments, a certain amount of hydride powder was placed into a stainless steel reactor connected to Sieverts volumetric equipment. The reactor was provided a specific CO$_2$ pressure and heated to 400 °C at a rate of 10 °C/min. The mass of the used Mg$_2$NiH$_4$ powder and the applied CO$_2$ pressure (approximately 1.2 bars \[16\]) were proportioned in such a way that the calculated total molar quantity of H$_2$ released by the complete decomposition of Mg$_2$NiH$_4$ would ensure an H$_2$:CO$_2$ molar ratio of 4:1. Interestingly, despite the nearly identical reaction conditions, the authors found evidence for two slightly different reaction mechanisms. After 10 h of the as-sintered monoclinic Mg$_2$NiH$_4$’s reaction with CO$_2$ at 400 °C, the complete decomposition of Mg$_2$NiH$_4$ was not reached, although CO$_2$ was totally consumed and...
no carbon deposition was observed [15]. Considering the intermediate reaction products that were obtained after 1 and 5 h (namely, Mg$_2$NiH$_4$, MgH$_2$, Mg$_2$Ni, MgO, and CO), Grasso et al. concluded that the methanation of CO$_2$ using Mg$_2$NiH$_4$ involves two simultaneous processes: (i) the catalytic conversion of CO$_2$ through reactions (2) and (3) and (ii) the direct reduction of CO$_2$ by the reducing effect of MgH$_2$ (Equation (5)).

$$2\text{MgH}_2(s) + \text{CO}_2(g) \rightarrow 2\text{MgO}_4(s) + \text{CH}_4(g) \quad (5)$$

The chemical activity of the as-milled cubic polymorph form of Mg$_2$NiH$_4$ was found to be considerably higher, and its reaction with CO$_2$ at 400 °C was completed in just 5 h [16]. The observed intermediate and final products of the methanation process were slightly different from the formerly described case. Therefore, the authors concluded that under a CO$_2$ atmosphere, as–milled Mg$_2$NiH$_4$ rapidly decomposes directly to the Ni-Mg$_2$Ni-Mg$_2$Ni$_2$/MgO (all of this phase remains after the reaction is complete) catalytic system Equation (6) which promotes the methanation reaction Equation (7).

$$2\text{Mg}_2\text{NiH}_4(s) + \text{CO}_2(g) \rightarrow 0.75\text{Mg}_2\text{Ni}_4(s) + 2\text{MgO}_4(s) + 0.25\text{Ni}_4(s) + 0.5\text{Mg}2\text{Ni}_2(s) + \text{C}_4(s) + 4\text{H}_2(g) \quad (6)$$

$$\text{C}_4(s) + 2\text{H}_2(g) \rightarrow \text{CH}_4(g) \quad (7)$$

Reports by Kato et al. [6] and Grasso et al. [15,16] provided clear evidence that during its interaction with CO$_2$ gas at 400–500 °C, Mg$_2$NiH$_4$ powder disproportionates into catalytically active compounds that efficiently promote the generation of methane. However, in all three studies, different reaction products were observed and divergent mechanisms were proposed. Grasso et al. assumed that at least some of the observed variations could have related to the specific forms and preparation methods of the Mg$_2$NiH$_4$ hydride [16].

Potentially, an Mg$_2$NiH$_4$ hydride-based CO$_2$ methanation reaction catalyst can be used in powder, as well as in the supported film (coating) form, but up to now, all of the reported studies were only conducted with Mg$_2$NiH$_4$ powders. Previous studies of Mg$_2$NiH$_4$ hydride films [17,18] indicated that characteristic strains caused by the film–substrate interaction can introduce noticeable changes of properties in comparison to corresponding powders. Therefore, there is a possibility that one form of Mg$_2$NiH$_4$ hydride might be better suited for CO$_2$ methanation catalysis than the other.

Accordingly, in the current study, we investigated the structural transformations of Mg$_2$NiH$_4$ hydride films under a CO$_2$ atmosphere and examined whether they correlated with the ones reported for Mg$_2$NiH$_4$ powders. In addition, our interest to investigate Mg$_2$NiH$_4$ films had two more motives. Firstly, film condensation from physical vapor allows one to synthesize very uniform samples with strictly controlled component ratios that prevent the formation of undesirable phases. This makes them particularly suitable as the subject for in-situ structural analysis, and this is useful for resolving discrepancies between the proposed reaction pathways. Secondly, films are eligible to be approximated as 1D objects, which is a clear advantage for the observation and evaluation of surface changes, including the analysis of surface region depth profiles.

In addition, we synthesized Mg$_2$NiH$_4$ in powder and investigated its efficiency for the methanation of CO$_2$ in order to compare processes in different forms of Mg$_2$NiH$_4$ hydride and to see how this material develops during the CO$_2$ methanation reaction.

2. Materials and Methods

2.1. Material Synthesis

Mg$_2$NiH$_4$ hydride films were formed by using magnetron sputtering to deposit metallic Mg$_2$Ni films and then hydriding them for 48 h under 20 bars of H$_2$ pressure at a temperature of 250 °C. The deposition of Mg$_2$Ni films was realized under a 6 × 10$^{-3}$ mbar Ar gas atmosphere inside a Kurt J. Lesker PVD-75 system (Jefferson Hills, PA, USA) by co-sputtering with two circular Torus 3 magnetrons. The nominal purities of Mg and Ni targets were 99.99% and 99.995%, respectively. By adjusting the
output power for individual magnetrons (196 W for Mg and 120 W for Ni), the Mg:Ni ratio in the films was tuned up to approximately 68:32 (as measured by EDS). A fraction that is slightly higher than the stoichiometric fraction of Mg has been proven to be beneficial for the synthesis of $\text{Mg}_2\text{NiH}_4$ hydride [3,19] because it prevents the crystallization of localized $\text{MgNi}_2$ phase nanoformations and makes full hydrogenation easier to attain. $\text{Mg}_2\text{Ni}$ films were deposited on $20 \times 20$ mm fused silica substrates. The approximate thickness of the films was 500 nm.

In previous studies [6,15,16], $\text{Mg}_2\text{NiH}_4$ catalysts were synthesized from high purity $\text{Mg}_2\text{Ni}$ powders that were prepared under controlled laboratory conditions. To extend the understanding of processes, in the current study, we chose to use a lower quality starting $\text{Mg}_2\text{Ni}$ material ($\text{Mg}_2\text{Ni}$ alloy granules of 99% purity obtained from American Elements) because it better reflected the potential conditions of $\text{Mg}_2\text{NiH}_4$ applications in commercial methanation reactors. At the same time, the usage of a less pure $\text{Mg}_2\text{Ni}$ alloy (both in elemental composition and phase) was expected to help to identify any significant material purity-related shortcomings of the methanation process. The average size of the initial $\text{Mg}_2\text{Ni}$ alloy granules was 3 mm. Prior to hydriding, the granules were mechanically ground down to a grain size of 20–50 µm. The obtained powders were placed into a stainless steel container and pumped down to a vacuum for several hours. The initial activation of the $\text{Mg}_2\text{Ni}$ powders [20,21] was achieved by applying 4 hydriding (16 h, 250 °C, and 20 bar $\text{H}_2$) and dehydriding cycles (8 h, 250 °C, vacuum). Final hydriding was conducted for 24 h under 20 bars of $\text{H}_2$ pressure at 250 °C. The specific surface areas of the unhydrided and hydrided $\text{Mg}_2\text{Ni}$ powders were estimated by the BET method and reached 1.59 and 2.69 m$^2$/g, respectively.

2.2. In-Situ XRD

The in situ XRD characterization of $\text{Mg}_2\text{NiH}_4$ films during annealing under a $\text{CO}_2$ atmosphere was performed with a Bruker D8 Discover (Hamburg, Germany) equipped with Mri TC-basic (Hamburg, Germany) chamber. For this type of experiment, $\text{Mg}_2\text{NiH}_4$ hydride films were placed on a Pt:Rh heating foil strip, and the temperature was monitored with an S-type thermocouple that was laser-welded to the backside of the foil. Prior to the heating, the chamber was abundantly flushed and filled up with $\text{CO}_2$ up to an absolute pressure of approximately 1.6 bar. From earlier reports by Kato et al. [6] and our own experience working with the in-situ heating of $\text{Mg}_2\text{NiH}_4$ films in air [22], it was known that at low temperatures (< 200 °C), the hydride remains satisfactorily stable. Therefore, in the beginning, XRD patterns were recorded with relatively large steps at temperatures of 30, 100, 150, and 200 °C. The heating rate between the steps was 1 °C/min, and at each temperature before pattern recording, samples were left for 60 min to reach thermal equilibrium with the heater. In temperature range from 200 to 500 °C, XRD patterns were recorded with 10 °C steps. The heating rate was kept to 1 °C/min, and the delay time was set to 30 min. The net measurement time for each pattern was approximately 90 min. Accordingly, below 200 °C, the total time samples were kept at each temperature step was 150 min, and an additional 50 min were used for heating. The corresponding values for the upper range measurements were 120 and 10 min, respectively.

2.3. Surface Characterisation Techniques

SEM measurements were performed using a Hitachi S-3400N (Tokyo, Japan) microscope. The surface depth profiles of the film samples was analyzed with an X-ray photoelectron spectrometer (PHI VersaProbe 5000, Boston, MA, USA) using monochromated 1486.6 eV Al radiation, 25 W of beam power, a 100 µm beam size, and a 45° measurement angle. Survey and high resolution XPS spectra were acquired using 187.85 eV and 23.5 eV band pass energies, respectively. An Ar$^+$ ion gun (a 4 kV accelerating voltage and a 2 × 2 mm sputtering area) was used for sputtering. XPS spectra processing and analysis was done using the MultiPak software.
2.4. Mass Changes and Thermal Effects

Differential scanning calorimetry (DSC) and TGA were performed with a NETZSCH STA 449 F3 Jupiter (Hamburg, Germany) analyzer with an SiC furnace. The heating program started at 45 °C and continued up to 580 °C at a heating rate of 10 °C/min. Argon gas (with a flow rate of 60 mL/min) was used as the inert atmosphere. The oxidizing environment consisted of carbon dioxide (with a flow rate of 25 mL/min) and argon (with a flow rate 35 mL/min). The TGA sample carrier with an S-type thermocouple was calibrated for 200 mg Al₂O₃ TGA crucibles. For each measurement, 8.4–8.8 mg samples were used.

2.5. Methanation

CO₂ methanation experiments were carried out with the custom build setup presented in Figure 1. For each CO₂ methanation experiment, 5 g of hydride powder were mixed with 5 g of fine Al₂O₃ powder (Sigma-Aldrich, 98% purity) and placed inside a cylindrical, high-temperature, stainless steel container (approximate length of 80 mm and internal diameter of 15 mm). From both ends, powder was closely packed by high purity quartz wool plugs. The container was heated up by a vertical high temperature tubular furnace, and the temperature of the powder was measured by an internal thermocouple probe that was inserted into the middle of the powder. The gas supply system consisted of three mass flow controllers (MFCs) dedicated to CO₂, H₂, and Ar gases. Flows from all MFC units were controlled by one digital gas controller manufactured by Brooks (Seattle, WA, USA). The controller was set up to maintain a total gas flow of 1 L/min while keeping the H₂:CO₂ gas flow ratio at 6:1 (following the suggestion by [9]). An automatic constant pressure regulator outside of the reaction vessel was used to maintain a constant pressure inside the reaction zone. A test pressure of 1 bar was selected to mimic the potential reaction conditions of the methanation reactor without any additional technical measures, whereas 10 bars of pressure were tested in order to limit the formation of carbon, as suggested by [12].

![Figure 1. Experimental scheme of CO₂ methanation set up.](image)

The supplementary inert Ar gas was used to maintain the recommended gas flow requirements of the on-line gas analyzer (VISIT 03H manufactured by Messtechnik EHEIM GmbH) and to transfer...
After hydriding, they became transparent and had a bright orange hue. Both of these features are characteristic for the low temperature (LT) phase of Mg$_2$NiH$_4$ [22–24]. The prevalence of the monoclinic LT phase of Mg$_2$NiH$_4$ was subsequently confirmed by XRD (Figure 2). In addition to the LT phase, small fractions of the so-called pseudo-cubic high temperature (HT) phase of Mg$_2$NiH$_4$ [17,25] were observed at room temperature.

3. Results and Discussions

As is typical for metallic films, the as-deposited Mg$_2$Ni coatings had mirror like appearances. After hydriding, they became transparent and had a bright orange hue. Both of these features are characteristic for the low temperature (LT) phase of Mg$_2$NiH$_4$ [22–24]. The prevalence of the monoclinic LT phase of Mg$_2$NiH$_4$ was subsequently confirmed by XRD (Figure 2). In addition to the LT phase, small fractions of the so-called pseudo-cubic high temperature (HT) phase of Mg$_2$NiH$_4$ [17,25] were observed at room temperature.

During the in-situ heating of the Mg$_2$NiH$_4$ film under the CO$_2$ atmosphere (Figure 2), several temperature ranges related to substantial composition changes could be identified. Starting from the room temperature up till 240 °C, the LT and HT phases of Mg$_2$NiH$_4$ co-existed, and their ratio in the film did not change noticeably. Above 240 °C, the fraction of LT phase gradually decreased, and at 300 °C, only the HT phase of Mg$_2$NiH$_4$ persisted. The initiation of Mg$_2$NiH$_4$ decomposition was observed at 350–360 °C when weak peaks attributed to Mg$_2$Ni arose. At 410 °C, the transition from Mg$_2$NiH$_4$ to Mg$_2$Ni was complete, and at 420 °C, only peaks of Mg$_2$Ni were observed. A further increase of the temperature was followed by the gradual disproportionation of Mg$_2$Ni and the crystallization of MgO. The crystalline MgO phase was at first observed at 450 °C and remained as the main phase at the end of the measurement at 500 °C.

Surface images made by SEM and the near surface region depth profile recorded by XPS complemented the findings of in-situ XRD and highlighted structural changes of the film that occurred due to the heating in the CO$_2$ atmosphere. More specifically, the SEM images (Figure 3) show that after heating in the CO$_2$ atmosphere, the surface of the films became considerably rougher, which indicated significant mass transfer processes within the film. At the same time, an XPS depth profile (Figure 3d) specified that the Ni concentration at the surface was less than 1/6 of Mg. This was clear evidence that during the disproportionation of Mg$_2$Ni, magnesium separated from Ni, oxidized, and had a tendency to segregate at the near surface region.
By comparing earlier reports by Kato et al. [6] and Grasso et al. [15,16], who worked with powders, with current in-situ XRD data that were observed for film, an outstanding feature was found: in the later case, there were no signs of the crystalline MgNi₂ and Ni phases. On one hand, this could be considered a sign of a slightly different reaction pathway for the film samples in comparison to the powder equivalent. On the other hand, it seems that a full-scale comparison does not provide substantial proof for that. For example, the observed quantitative concentration values, as well as their qualitative changes at the surface of the film (Figure 3d) in great proximity, resembled the data presented by Kato et al. [6], who measured the XPS depth profile of Mg₂NiH₄ powders that were cyclically exposed to a CO₂ atmosphere at a temperature of 500 °C. Furthermore, several tests with Mg₂NiH₄ powder that had an MgNi₂ phase (more details are provided in the following paragraphs) showed that there was a very close agreement between on-set process temperatures for powder and film samples. Altogether, we presume that the absence of MgNi₂ and Ni phases in in-situ XRD data was the result of insufficient crystallization rather than different reaction pathways.

![Figure 3. SEM surface images of Mg–Ni films: (a) as-deposited, (b) hydried, and (c) after it was analyzed by in-situ XRD in the CO₂ atmosphere. (d) XPS near surface region depth profile of the film presented in (c).](image)

XRD patterns of commercial Mg₂Ni powders that contained Mg and MgNi₂ components are provided in Figure 4a. After hydriding these powders, the crystal phases of Mg₂NiH₄, MgH₂, and MgNi₂ were obtained (Figure 4b). The XRD patterns of the hydrided powders had no peaks of unreacted Mg and Mg₂Ni phases, so we assume that the loss of hydrogen concentration (see DSC/TGA analyses below) was caused by the aggregate effect of hydrogen non-adsorbing phases like MgNi₂. MgO was not observed by XRD, but we nevertheless assume that it also contributed to the lower hydrogen concentration because commercial Mg–Ni grains were delivered in an air-containing canister and had successive handling in air.

The DSC analysis of hydrided powders under Ar flow indicated the presence of two distinct thermal events (Figure 5a). The first endothermal event started at approximately 235 °C and was attributed to the LT–HT phase transition of Mg₂NiH₄ [26,27]. Close to the beginning of the phase transition, the sample started to lose some mass (up to 0.2 wt.%), and this indicated the partial decomposition of Mg₂NiH₄. Proceeding further, most of the sample mass (∼2.6 wt.%) was lost during the second endothermal event starting at approximately 315–320 °C. This event represented the rapid hydrogen release during the supposedly full dehydriding of Mg₂NiH₄. Lastly, there was a lengthy mass loss of approximately 0.1 wt.% that led to a total mass loss of nearly 2.8 wt.%. Accordingly, we attributed the last phase of mass loss to the dehydriding of MgH₂.
with the LT–HT phase transition at 235 °C. This indicated that below the phase transition temperature, the activation barrier for Mg release of mass and a low intensity exothermic upswing was observed. Therefore, it is clear that the minimum of MgO transition, of MgNi2, MgNi2H4, Mg2NiH4, and Mg2Ni was reached at 400 °C. A nearly identical onset temperature and width of the Mg2NiH4 phase transition range (235–300 °C) were also observed for the Mg2NiH4 film (Figure 2) and powder samples (Figure 5a) that were tested under CO2 and Ar gas atmospheres, respectively. This indicated that below the phase transition temperature, the activation barrier for Mg2NiH4 hydride decomposition and/or oxidation was relatively high, and at near-atmosphere pressures, Mg2NiH4 hydride demonstrated enduring stability regardless of its form and surrounding gas phase composition.

Disparities between Mg2NiH4 hydride behavior under the inert and reactive gases arose soon after start of the LT–HT phase transition. Namely, under the CO2 and Ar gas flow, there were no mass change events up to approximately 330 °C. An analysis of the results of the in-situ XRD of Mg2NiH4 film heating under CO2 gas (Figure 2) suggested that at later temperatures, the dehydriding of Mg2NiH4 phase should have taken place. The decomposition reaction of Mg2NiH4 was expected to result in approximately 2.7 wt.% mass loss and a strong endothermic minimum in the TGA and DSC curves, respectively (Figure 5a). Instead, under the CO2 and Ar gas flow, a prolonged small (∼0.1 wt.%) decline of mass and a low intensity exothermic upswing was observed. Therefore, it is clear that the endothermal reaction (8) [28] was simultaneously accompanied by some additional reactions.

\[
\text{Mg}_2\text{NiH}_4(s) \rightarrow \text{Mg}_2\text{Ni}(s) + 2\text{H}_2(g) \quad \Delta H_{298K} = -63.5 \text{ kJ/mol} \tag{8}
\]

\[
\text{CO}(g) + \text{H}_2(g) \rightarrow \text{C}(s) + \text{H}_2\text{O}(g) \quad \Delta H_{298K} = -131.3 \text{ kJ/mol} \tag{9}
\]
we found a new catalyst with substantially di-

After MgH

◦

(Mg

(9)), and Boudouard Reaction (10) could potentially lead to solid carbon build up [29,30]. However,

powders significantly increased the hydrogen concentration in the gas flow. When the hydrogen

pressure was a stronger factor for the stabilization of Mg

2

phase by in-situ XRD. In this reaction pathway, finite oxygen adsorption compensated the mass

decrease in CO

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a low temperature region (prior to the temperature burst), there was a slight increase in H

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above-mentioned carbon production reactions, stabilized sample mass, and translated into severe

changes of the DSC curve. Instead, both curves maintained small increases, thus indicating the superior

role of other processes.

A strong endothermal event at 475 °C was accompanied by a 0.1% mass loss that was equal to the hydrogen desorption in the last section of the sample heating under Ar (Figure 5a). Accordingly, following the same reasoning as above, we attribute this event to the decomposition of MgH

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. The higher than usual decomposition temperature can be explained by two factors: (i) MgH

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 decomposition is usually kinetically limited [31] and the heating rate during DSC/TGA analysis was relatively high (10 °C/min); (ii) the dehydriding temperature is known to be postponed by surface oxides [15,32]. After MgH

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 decomposition, the powder reaction with CO

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 was finalized by some more thermal events, thus representing rapid oxidation of Mg that was produced by the dehydriding of MgH

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 and continued the disproportionation of Mg

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Ni and, eventually, MgNi

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.

The CO

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 methanation reaction dynamics at 1 and 10 bars of gas pressure are provided in Figure 6a,b, respectively. Both charts have temperature peaks that correspond to the fast decomposition of hydrides (Mg

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NiH

4
 and MgH

2
) and theoxidation of Mg

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Ni disproportionation products. After the heat burst, we found a new catalyst with substantially different properties.

By comparing methanation dynamics at different pressures, it could be noticed that at 1 bar in a low temperature region (prior to the temperature burst), there was a slight increase in H

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 (and a decrease in CO

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) concentration, whereas at 10 bars, the H

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:CO

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 ratio remained stable. At 1 bar of pressure, such behavior was not surprising because a similar hydrogen release was also observed in the TGA pattern (Figure 5a) and was attributed to the plateau pressure levels of Mg

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NiH

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 [33,34]. On the other hand, Mg

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NiH

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 stability at 10 bars of pressure demonstrated that high partial hydrogen pressure was a stronger factor for the stabilization of Mg

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NiH

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 than the oxidative potential of CO

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, even though at low pressure Mg

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NiH

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 decomposition and partial oxidation happened at the same time (see Figure 5b and comments above).

The second thing to notice from Figure 6 is that at 10 bars of pressure, the methanation reaction started at approximately 50 °C lower (330 °C versus 380 °C), and as soon as temperature reached 420–430 °C, there were almost no unreacted CO

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 or intermediate products from reaction (2), namely CO. A nearly 100% CO

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 conversion was maintained up to approximately 530 °C, with an estimated CH

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 yield of approximately 75%. On the other hand, methanation at 1 bar of pressure was able to reach a 100% CO

2
 conversion within a narrow time frame when the hydrogen desorption from powders significantly increased the hydrogen concentration in the gas flow. When the hydrogen source was depleted, the methanation reaction lost its temporarily boosted efficiency (approximately

2CO(g) → C(s) + CO2(g) \quad \Delta H_{298K} = -172.4 \text{ kJ/mol} (10)
90% at 500 °C) and maintained a downtrend as temperature rose to 550 °C. At both investigated pressures, CO\textsubscript{2} methanation by the reaction product of Mg\textsubscript{2}NiH\textsubscript{4} powder had lower CH\textsubscript{4} yields than were achieved with standard commercial Ni-based catalysts at 10 bar (H\textsubscript{2}:CO\textsubscript{2} ratio of 4:1) and 30 bar (H\textsubscript{2}:CO\textsubscript{2} ratio of 6:1) [9]. When operating at 10 bars of pressure, we did not detect CO or other carbon-containing species in gaseous reaction products; therefore, we assumed that relative difference between initial CO\textsubscript{2} and CH\textsubscript{4} product fluxes qualitatively reflected the actual solid C yields. This was quite surprising because theoretical and experimental study by Gao et al. [9] estimated that at the specifically used gas pressure and H\textsubscript{2}:CO\textsubscript{2} ratios, carbonization should have been prohibited. The cause of such a high carbon yield has not yet been identified and will be subject of our future studies.

Figure 6. CO\textsubscript{2} methanation dynamics: (a) at 1 bar and (b) at 10 bars of gas pressure. Hydrided Mg\textsubscript{2}Ni alloy powders were used as the starting catalyst material.

A study by Kato et al. [6] demonstrated that the properties of powder catalysts can be significantly improved after they are cycled through H\textsubscript{2} (25 bar and 350 °C), CO\textsubscript{2} (1 bar and 500 °C), and vacuum (500 °C). They reported that after 18 cycles, the methanation process was initiated at 250–260 °C, whereas an uncycled high purity Mg\textsubscript{2}NiH\textsubscript{4} catalyst initiated a methanation reaction at approximately 330–340 °C (in comparison to the current study with a relatively low grade Mg\textsubscript{2}NiH\textsubscript{4} catalyst that initiated methanation at 330 °C for 1 bar of pressure and 380 °C for 10 bars of pressure).

After considering the potential benefits of catalyst cycling after the first methanation run-up at 10 bars of pressure was finished, we gradually decreased furnace temperature down to 250 °C. During the cool-down period and 30 min after the target temperature was reached, the container was constantly flushed with hydrogen. Subsequently, the container was filled up with hydrogen to 10 bars of pressure and confined for 16 h at 250 °C. The next day, we repeated the methanation process (Figure 7) with same parameters as were used before (10 bars of pressure and H\textsubscript{2}:CO\textsubscript{2} ratio of 6:1). This time, the methanation reaction started immediately at 250 °C (close to the lowest reported values [35,36]), reached a 100% CO\textsubscript{2} conversion at 320–330 °C, and continued without the significant deterioration of CO\textsubscript{2} conversion up to the maximum tested temperature of 600 °C. The CH\textsubscript{4} yield at
500 °C was slightly higher and reached just over 80%. Looking at the methanation dynamics (Figure 7a), one can notice that there was no temperature burst or hydrogen concentration increase that could be attributed to the decomposition of Mg$_2$NiH$_4$ or MgH$_2$ hydride. This suggested that during the first methanation experiment, Mg$_2$NiH$_4$ and MgH$_2$ hydrides completely disproportionated, and only the MgO and Ni phases were formed. Accordingly, such a powder catalyst did not adsorb any additional hydrogen and was able to provide an enhanced performance after one just methanation cycle.

![Methanation dynamics](image)

**Figure 7.** Methanation with the developed powder catalyst: (a) product fraction of CO$_2$ methanation at different temperatures and (b) methanation dynamics.

A comparison of SEM images of the as-ground Mg$_2$Ni alloy grains (Figure 8b) and the final catalyst powder (Figure 8c) provided some more evidence regarding how specific features of hydrides could become beneficial for the formation of efficient catalysts for the methanation reaction. The initially ground Mg$_2$Ni alloy grains were relatively course, and their size ranged from 10 to 50 µm. During hydride formation (hydriding/dehydriding cycling), the catalyst material underwent huge volume changes (up to 30% [37]) that introduced large amount of structural defects, widened up grain boundaries, and ultimately fractured initial grains into sub-micrometer-size fine powders (Figure 8c). The first temperature run-up under CO$_2$ and H$_2$ gas flow promoted CO$_2$ methanation and initiated hydride decomposition and oxidation. These highly energetic chemical reactions empowered Mg$_2$Ni disproportionation and MgO–Ni phase separation (Figure 9). As the result, MgO particles decorated by nanocrystalline Ni were formed. Such a catalyst is able to promote CH$_4$ formation at a relatively low temperature (250 °C) and do this with a significantly higher CH$_4$ output than that not oxidized hydride powder. The superior catalytic properties of disproportionated MgO–Ni systems can be attributed to the role of MgO because MgO does not just work as an inert support for catalytic Ni nanoparticles but also actively changes the methanation pathway for Ni [38]. For example, studies have shown that MgO enhances the adsorption and activation of CO$_2$ [39]. On the other hand, MgO was also found to promote H$_2$O formation and its desorption from a catalyst [15].
In-situ XRD, TGA/DSC, and methanation reaction products analyses showed that in order for all these reactions to complete, it is recommended to heat a hydride powder above 500 °C (in a CO₂-containing atmosphere) or, for a short period of time, as high as 600 °C. When such high temperature conditioning is induced (or in the current study case, a spontaneous temperature burst is not suppressed), the full development of the catalyst can be obtained in one cycle within 1 h. Meanwhile, the catalyst development from a Mg₂NiH₄ powder kept below 500 °C might take more than 20 hydriding/dehydriding cycles [6] or up to 10-fold more time for the reaction to complete [15].

**Figure 8.** Optical and SEM images: (a) as received Mg₂Ni alloy grains, (b) Mg₂Ni grains after grinding, (c) catalyst–Al₂O₃ mixture after methanation test, and (d) EDS elemental mapping of catalyst–Al₂O₃ mixture after methanation test.

**Figure 9.** XRD pattern of catalyst–Al₂O₃ mixture after methanation test.

4. Conclusions

In the current study, various aspects of Mg₂NiH₄-based catalyst development for a Sabatier type methanation reaction were investigated. Based on the congruous data of reaction on set temperatures and other evidence, we conclude that despite some differences in the crystallization of MgNi₂ and Ni phases, both Mg₂NiH₄ hydride films and powders react with CO₂ equally. It was demonstrated that Mg₂NiH₄ hydride heating above 330–380 °C under a CO₂ and H₂ gas flow initiates hydride decomposition, disproportionation, and oxidation. These reactions empowered the catalytic properties of the material and promoted the CO₂ methanation reaction. However, structural and
Author Contributions: Conceptualization, M.L., M.U., and S.V.; methodology, M.U., S.V., and K.Z.; formal analysis, M.U.; investigation, M.U., S.V., and K.Z.; writing—original draft preparation, M.L.; writing—review and editing, M.U. and S.V.; visualization, M.U. and S.V. All authors have read and agreed to the published version of the manuscript.

Funding: This research has received funding from European Regional Development Fund (project No. 01.2.2-LMT-K-718-01-0005) under grant agreement with the Research Council of Lithuania (LMTLT).

Acknowledgments: Special thanks goes to the rest project team members: project manager Nerijus Striūgas; investigators: Andrius Tamošiūnas, Rolandas Paulauskas, Vilma Snapkauskienė.

Conflicts of Interest: The authors declare no conflict of interest.

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