Article

Catalytic Effect of Nb$_2$O$_5$ in MgH$_2$-Nb$_2$O$_5$ Ball-Milled Composites

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Abstract: We report a study on the desorption properties, crystallography and chemical state of MgH$_2$ and 1 mol% Nb$_2$O$_5$ ball-milled composites. Desorption temperatures of the composites decreased with increase of ball-milling time. Size of MgH$_2$ crystallites decreased during ball-milling. Reduction of Nb$_2$O$_5$ after ball-milling was confirmed by tracing the chemical state of Nb and was further supported by TEM observation. The reduced phases may act as more effective catalysts improving the desorption properties.

Keywords: MgH$_2$; Nb$_2$O$_5$; catalytic effect; ball-milling

1. Introduction

Facing the energy crisis as we are in the 21st century, many contributions have been made to develop new energy resources. Hydrogen is a promising alternative energy carrier that has been highly regarded because of its prominent advantages such as high energy density (142 MJ/kg [1]), great variety of potential sources, light weight, and environmental friendliness. Besides the application of hydrogen energy, many kinds of hydrogen storage materials have been studied in the past decades, such as lithium compounds [2,3], ammonia borane [4,5], as well as the hydrides of light metals [6,7]. Magnesium hydride is one of promising candidates for hydrogen storage materials due to its high hydrogen capacity

(7.6 wt%), which fulfills the ultimate target of 7.5 wt% [8] set by the Department of Energy, USA. However, the absorption and desorption reaction of Mg/MgH_2 itself is too slow. Recently, scientists found out that the composite of MgH_2 and transition metal compounds prepared by ball-milling showed improved kinetics for both hydrogen absorption and desorption [9–13], which can be seen as a good indicator for practical application. Barkhordarian *et al.* reported that Nb_2O_5 had a superior catalytic effect for absorption and desorption, compared to other metal oxide catalysts. The magnesium hydride catalyzed with 0.5 mol% Nb_2O_5 and ball-milled for 100 h finished full desorption within 90 s under vacuum conditions at 300 °C. The desorbed products could also absorb roughly 7 wt% of hydrogen within 60 s under 8.4 bar of hydrogen at 300 °C [12]. Hanada *et al.* reported that the composite, MgH_2 with 1 mol% Nb_2O_5 milled for 20 h, was able to absorb ∼4.5 wt% of hydrogen after full desorption even at room temperature, under a pressure lower than 1.0 MPa within 15 s [13]. The exciting achievements reflect a glorious prospect for future application.

On the other hand, the catalytic mechanism of Nb_2O_5 has also been well investigated. According to the progress so far, the potential mechanism may rest in some aspects. The first possibility should be the refinement of the material size. In the recent Transmission Electron Microscope (TEM) observations on MgH_2-Nb_2O_5 ball-milled composites, the size of both the hydride and the additive was found to be within nanoscale. The refinement of size and the consequently homogeneous distribution may lead to the fast kinetics [14,15]. The second possibility comes to the phase changes of Nb_2O_5 brought by high energy ball-milling. Hanada *et al.* performed X-ray absorption spectroscopy for investigating the valences of metal oxide additives. The results showed that Nb_2O_5 had been reduced by ball-milling with MgH_2 for 20 h. Therefore, they suggested that the improvement of desorption properties was caused by the catalytic effect of reduced niobium oxides [16]. Meanwhile, some complex compounds, such as $MgNb_2O_{3.67}$, have been discovered by another group [15]. Finally, the increased defects in the ball-milled composites may act as the hydrogen pathway facilitating the transportation of hydrogen. Friedrichs *et al.* proposed their "pathway" model, in which Mg-Nb-O ternary phases diffuse through MgH_2 and form a pathway for hydrogen desorption [17]. However, the completion of the exact mechanism in MgH_2-Nb_2O_5 needs more effort and investigation.
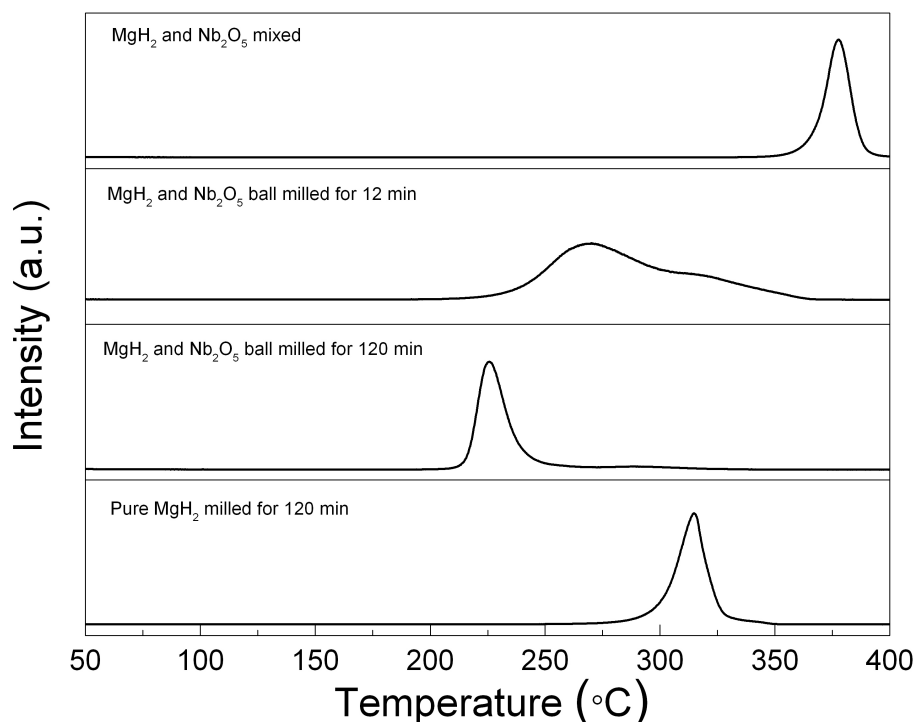
In the present work, we did a series of ball-milling using MgH_2 and 1 mol% Nb_2O_5 composites. The desorption properties were evaluated by the Thermal Desorption Spectroscopy (TDS). Moreover, the crystallography and chemical state were investigated in order to discuss the catalytic mechanism.

2. Results and Discussion

Thermal desorption properties of the ball-milled composites are shown in Figure 1. The peak temperatures of desorption for the composites ball-milled for 0 min (hand mixed), 12 min, 120 min, as well as the pure MgH_2 ball-milled for 120 min turned out to be 378 °C, 268 °C, 226 °C and 315 °C, respectively. It can be seen that the desorption properties have been improved with the increase of ball-milling time. This milling time dependence reveals the fact that the catalytic effect can be activated gradually by ball-milling. In the sample milled for 12 min, a very wide peak with a shoulder around 310 °C was obtained. It suggests that Nb_2O_5 in the sample is not well-distributed yet, so that only parts of the sample have been affected by the catalyst during thermal desorption. On the other hand, by

comparing the catalyzed and pure MgH$_2$ ball-milled for 120 min, we can see a decrease of 89 °C in the peak temperature. This significant improvement of the desorption properties should be ascribed to the addition of Nb$_2$O$_5$.
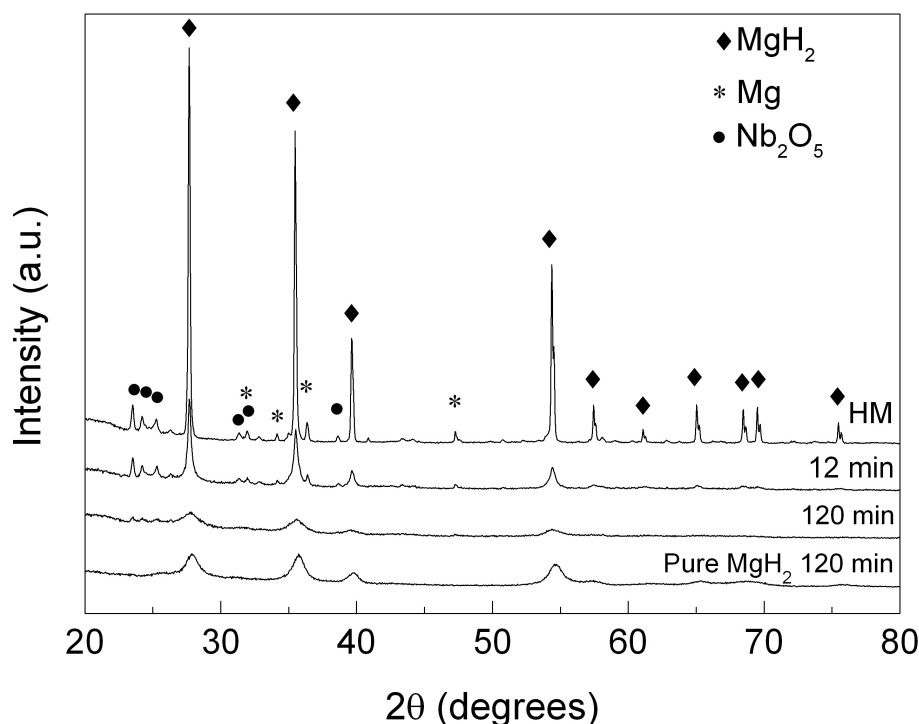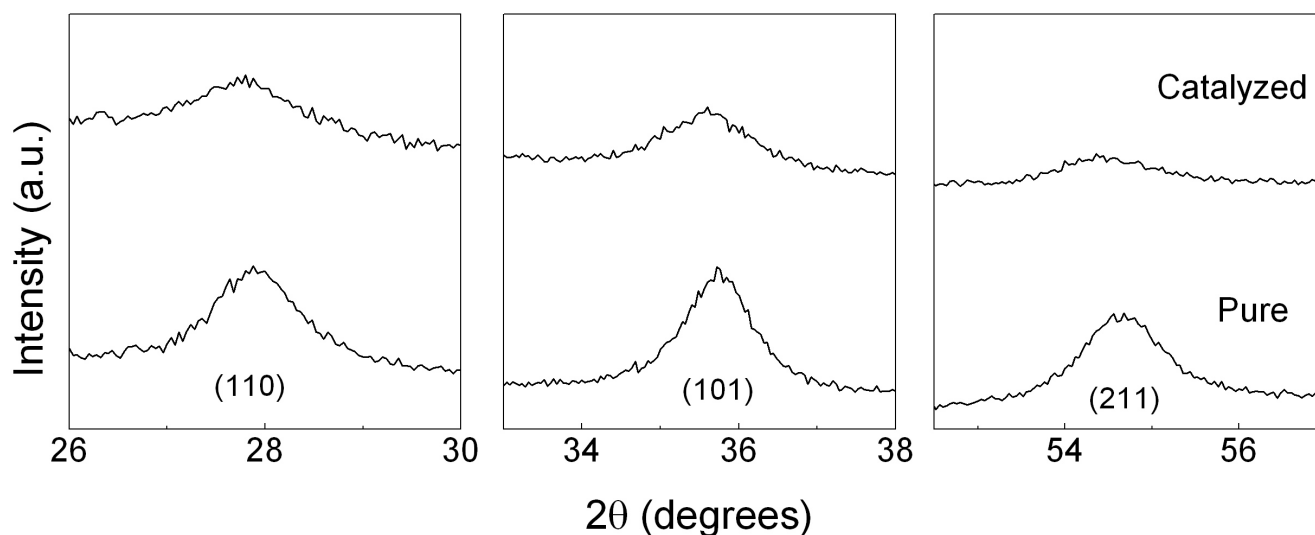
Figure 1. Profiles of TDS of hydrogen for the hand mixed and ball-milled samples.

The XRD patterns of the samples were obtained in order to evaluate the crystalline information, as presented in Figure 2. The peaks widened and the intensity drastically decreased after the samples were milled for a long time. It indicates that the crystallites become smaller during ball-milling. This refinement of size may suggest a better distribution of catalyst in the samples, leading to an improvement on the catalytic effect. The size of crystallites can be estimated using Sherrer Equation:

$$\tau = \frac{K\lambda}{\beta cos\theta}$$

where K is the shape factor, typically 0.89, λ is the X-ray wavelength, 1.54 Å for Cu radiation, β is the full width at half maximum (FWHM), θ is the Bragg angle, and τ is the mean size of the crystallites [18]. We selected the three strongest peaks of the catalyzed and pure MgH$_2$ milled for 120 min, shown in Figure 3, to apply the equation and listed the results in Table 1. It can be seen that the crystalline size of the catalyzed composites is a little smaller than the pure MgH$_2$ after ball-milling. It seems Nb$_2$O$_5$ with ceramic feature acts as abrasive facilitating the refinement of MgH$_2$. However, the difference of several ten angstroms is not so sufficient to bring the obvious improvement on the desorption properties. There should be other more essential factors.

Figure 2. X-ray diffraction profiles of the hand mixed and ball-milled samples.

Figure 3. Three strongest peaks of XRD pattern for the catalyzed and pure MgH_2 milled for 120 min.
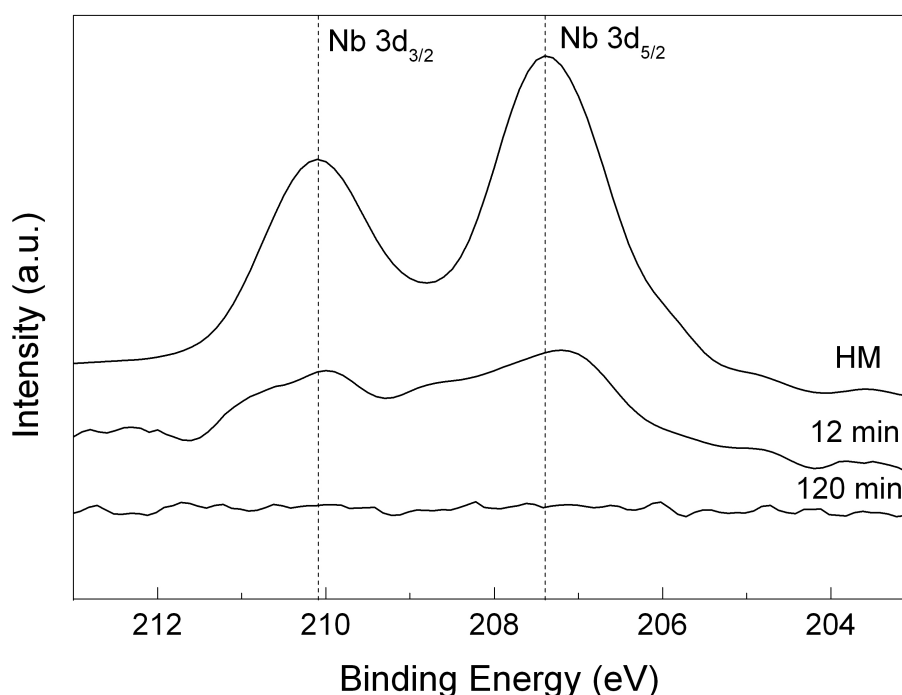

In order to clarify the mechanism of catalytic effect, XPS measurements were carried out to evaluate the chemical state of Nb on the surface of the catalyst. Niobium 3d spectra were drawn in Figure 4. An obvious decrease of the signal was presented in the composites milled for 12 min, while the signal completely disappeared after the composites were milled for 120 min. The phenomena could be explained as the milled MgH_2 particles gradually covered the surface of Nb_2O_5, preventing the detector from getting enough signal from inside. Yet it still can be seen that the peaks in the composites that was milled for 12 min broadened evidently, and the apex slightly shifted to the lower energy side. It provides

the evidence that the chemical state of Nb in this sample has changed. Perhaps new phases, at least on the surface, have been generated during ball-milling, in which the valence of Nb is less than +5, because of the decrease in binding energy. In another word, Nb_2O_5 has been partially reduced during ball-milling. The detailed analysis on peak separation has been reported in another article, which concluded the existence of a certain or a complication of Nb_2O_{5-x} phase(s) that may act as a more effective catalyst to improve the kinetics of desorption [19]. In our previous work, we have confirmed that hydrogen desorption started on the interface between MgH_2 and Nb_2O_5, where hydrogen was recombined and released with the assistance of the essential catalyst on the surface of Nb_2O_5 [20]. Confirmation of the reduction of Nb_2O_5 reasserts and supports the above mechanism of desorption. The reduced phases on the catalyst surface are likely to be the essential catalyst facilitating the completion of desorption.

Table 1. Crystalline size (τ; in Å) of catalyzed and pure MgH_2 ball-milled for 120 min.

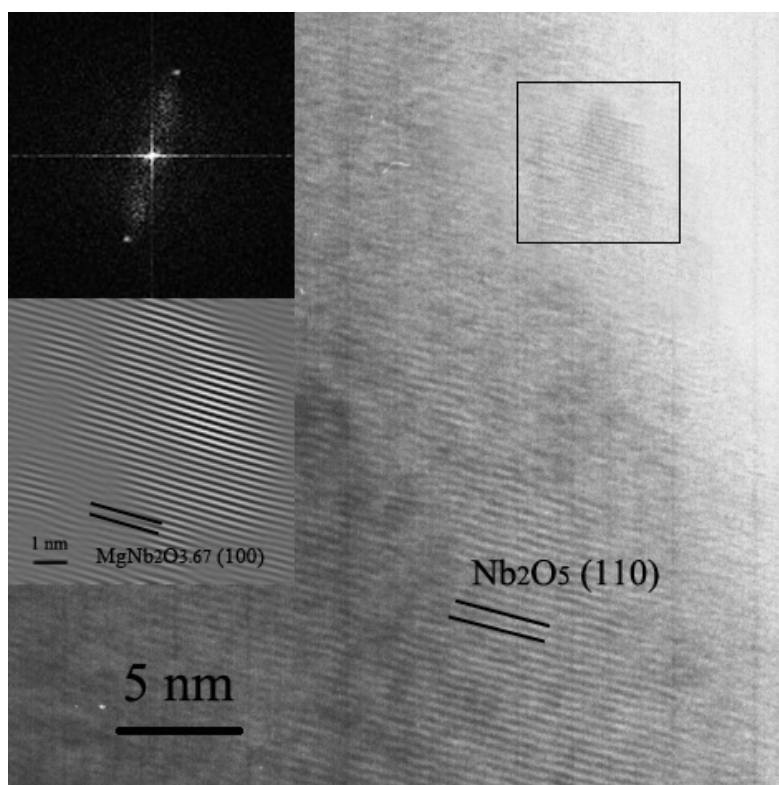| **Catalyzed**				**Pure**			
Plane	**$2\theta(°)$**	**FWHM (°)**	**τ (Å)**	**Plane**	**$2\theta(°)$**	**FWHM (°)**	**τ (Å)**
(110)	28.0	1.26	73.9	(110)	27.9	0.813	103
(101)	35.8	1.35	72.8	(101)	35.7	0.795	104
(211)	54.6	1.32	78.5	(211)	54.6	0.839	105

Figure 4. XPS spectra of Nb3d for the catalyzed samples.

Taking advantage of high resolution electron microscopy, we were able to find out one possible state of the reduced niobium phases. The lattice image of Nb_2O_5 particle in the composites milled for 120 min is shown in Figure 5. When we performed the fast Fourier transformation (FFT) and the inverse fast

Fourier transformation (IFFT) on the selected area near the edge of Nb_2O_5 particle, we obtained the lattice image with the d-spacing of 2.13 Å, which matches the value of $MgNb_2O_{3.67}$ (100). The existence of this ternary phase has also been reported elsewhere [15,21]. Nevertheless, the results so far still can not draw a clear conclusion on the catalytic effect of this ternary phase. Further investigation on the phase change of Nb_2O_5 is still on the way in order to make a clear understanding on the mechanism of the catalytic effect in Nb_2O_5 catalyzed MgH_2 composites.

Figure 5. High resolution image of Nb_2O_5 catalyzed MgH_2 composites ball-milled for 120 min. The insets are the FFT and IFFT images obtained from the selected area, marked by the square.

3. Experimental Procedures

MgH_2 (98%, from Alfa Aesar) and Nb_2O_5 (99.99%, $\sim 1\mu m$, from Kojundo chemical Laboratory) powder were used as purchased. Ball-milling was performed using a Fritsch P7 device. Mixtures of 300 mg MgH_2 and 1 mol% Nb_2O_5 were ball-milled with 20 steel balls (7 mm in diameter) for 12 min and 120 min. The ball-to-powder ratio was set to 100:1. The hydrogen pressure inside the milling spot was 1 MPa and the rotating speed was 400 rpm. Pure MgH_2 powder was also ball-milled for 120 min under the same condition. Hand-mixed (HM) sample with the same composition was prepared using agate mortar. The desorption properties were examined by thermal desorption spectroscopy (TDS) with a heating rate of 1 °C/min under a highly pure helium flow. X-ray diffraction (XRD) was performed using JEOL JDX-3500 powder diffractometer with Cu K_α radiation. X-ray Photoelectron Spectroscopy (XPS) was carried out using a JPS-90MX photoelectron spectrometer with Mg K_α radiation. The energy scale of the spectrometer was calibrated by setting oxygen (O1s) peak to 532 eV. TEM observation

was performed under a 1250 kV High Voltage Electron Microscope (JEM-ARM1300). Plastic bag method [22] was used to prevent oxidation of the sample during transport into the TEM instruments.

4. Conclusions

In summary, we performed a study on the Nb_2O_5 catalyzed MgH_2 ball-milled composites, as well as the pure MgH_2 which serves for comparison. Improved desorption properties were reached by ball-milling with the presence of Nb_2O_5. Especially the peak temperature of the catalyzed composites milled for 120 min was decreased to 226 °C, even 89 °C lower than the pure MgH_2 milled for the same duration. XRD spectra indicated a refinement of crystallites during ball-milling, suggesting a better distribution of Nb_2O_5 in the composites. The estimation of crystalline size using Sherrer equation showed Nb_2O_5 as ceramics acts as abrasive facilitating the size decreasing of MgH_2. Reduction of Nb_2O_5 was confirmed by tracing the chemical state of Nb in the samples, arising the possibility that the reduced phases act as more effective catalysts to improve the desorption properties. We were able to find $MgNb_2O_{3.67}$ existing near the edge of Nb_2O_5 particle via TEM, providing further evidence for the reduction of Nb_2O_5 and raising the further investigation on the phase transition of Nb_2O_5 during ball-milling.

Acknowledgments

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