Effective Factor on Catalysis of Niobium Oxide for Magnesium

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INTRODUCTION

Magnesium is a promising hydrogen storage material because of its high gravimetric hydrogen density of 7.6 wt %. However, the slow hydrogen desorption/absorption reaction kinetics is an issue that needs to be resolved. So far, various catalysts have been investigated to accelerate the processes. Among them, niobium(V) oxide (Nb$_2$O$_5$) is an excellent catalyst precursor, and mixing Nb$_2$O$_5$ with MgH$_2$ produces highly active materials in which the hydrogen absorption reaction proceeds even at $-50 \, ^\circ C$. A detailed catalytic mechanism has not yet been determined, although various studies have been conducted. Understanding the kinetics of the catalysis is difficult and involves a variety of factors, especially for solid catalysts on solid materials, such as Mg. The chemical properties of catalysts are important and affect the dissociation/recombination of H$_2$. In addition, physical properties such as initial particle size and crystal structure should also be considered because the dispersion degree of the catalyst on solid materials and/or formation of the catalytically active state strongly contribute to the reaction kinetics with H$_2$. However, identifying and controlling the physical properties of the catalyst are not easy. An understanding of these factors is essential so that the contribution of physical properties can be suppressed. The spray pyrolysis method is promising for producing fine particles because it is a simple, rapid, and continuous process and can be used to fabricate diverse materials with controllable sizes and compositions. Particles produced by conventional spray pyrolysis are highly uniform in size and chemical composition with a spherical shape and have agglomeration-free states because of the microscale reactions that proceed inside a droplet. Using the spray pyrolysis method, the physical properties of catalysts can be controlled, which is expected to lead to an essential understanding of the catalysis mechanism.

In this work, different types of Nb$_2$O$_5$ are synthesized both by spray pyrolysis and the simple calcination of ammonium niobium oxalate, and the products are characterized by structural analyses and microscopy. The catalysis of each oxide for the hydrogen absorption/desorption reactions of Mg are also investigated, including the chemical state variation of Nb during the deactivation and reactivation processes. From these results, the factors contributing to high catalytic efficiencies and improved kinetics for hydrogen desorption/absorption of Mg are discussed.

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RESULTS AND DISCUSSION

Figure 1 shows the X-ray diffraction (XRD) patterns of Nb$_2$O$_5$ prepared by spray pyrolysis at 500 and 1000 °C and the calcination method at 500 °C. In the spray pyrolysis method, ammonium niobium oxalate, NH$_4$[NbO(C$_2$O$_4$)$_2$(H$_2$O)$_2$]·10.5H$_2$O, was dissolved in water and sprayed droplets were heated in a furnace (Figure S1). The broad peaks observed in all the XRD patterns from 10 to 30° are caused by the grease used to fix the samples to the glass plate and the polyimide sheet used to cover the samples (see Figure S2). For Nb$_2$O$_5$ synthesized by spray pyrolysis at 1000 °C, a crystalline orthorhombic phase was clearly observed. On the other hand, Nb$_2$O$_5$ synthesized at 500 °C by spray pyrolysis and calcination methods were amorphous or nanocrystalline. The conversion process of Nb$_2$O$_5$ from NH$_4$[NbO(C$_2$O$_4$)$_2$(H$_2$O)$_2$]·10.5H$_2$O has been previously reported. During the heat treatment up to 600 °C, NH$_4$[NbO(C$_2$O$_4$)$_2$(H$_2$O)$_2$]·10.5H$_2$O decomposes to form Nb$_2$O$_5$, with endothermic reactions in the temperature range from 100 to 300 °C and an exothermic reaction at 580 °C under air flow (Figure S3). The total weight loss during heating up to 600 °C is 75%, which corresponds the theoretical one for the conversion of Nb$_2$O$_5$ from NH$_4$[NbO(C$_2$O$_4$)$_2$(H$_2$O)$_2$]·10.5H$_2$O to 1/2 Nb$_2$O$_5$. Although crystalline Nb$_2$O$_5$ is formed after heating at 600 °C, the solid material obtained after heating less than 500 °C is amorphous (Figure S4). In particular, the formation of crystalline Nb$_2$O$_5$ requires temperatures higher than 580 °C, and these observations are consistent with the results obtained in a previous report.

Figure 2 shows scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of the synthesized Nb$_2$O$_5$. The SEM image (Figure 2a) of the amorphous Nb$_2$O$_5$ synthesized by spray pyrolysis at 500 °C reveals homogeneous spherical particles with a diameter of about 180 nm; this shape is typical for particles synthesized by spray pyrolysis under moderate conditions. Polyhedral particles are observed for the crystalline Nb$_2$O$_5$ synthesized at 1000 °C (Figure 2c). Compared with the Nb$_2$O$_5$ prepared at 500 °C, a slightly wider size distribution and particles larger than 300 nm were found, although the average particle size was similar (Figure S5). Figure 2b,d shows TEM images and electron diffraction patterns of the Nb$_2$O$_5$ synthesized by spray pyrolysis. In TEM measurements of Nb$_2$O$_5$ prepared at 500 °C, particles exhibited a spherical hollow structure with shells surrounding empty spaces, and conventional spherical shapes were also observed. Only a halo pattern was found in the electron diffraction measurement, suggesting that the observed Nb$_2$O$_5$ particles were amorphous. The particles of Nb$_2$O$_5$ synthesized at 1000 °C were also spherical with a shell-like shape, but the walls were constructed by polyhedral particles. Various spots are observed in the electron diffraction pattern, suggesting that these particles were polycrystalline. These results are consistent with the XRD measurements. Additional TEM images for other particles observed for these two Nb$_2$O$_5$ samples are given in the Supporting Information (Figures S6 and S7). Using spray pyrolysis, the following particle growth process is expected. The Nb precursor solution is heated and condensed when sprayed through a furnace. Then, the spherical and amorphous Nb$_2$O$_5$ particles are formed at a low temperature of around 500 °C. When the furnace temperature is 1000 °C, the spherical Nb$_2$O$_5$ crystallizes into an orthorhombic structure. Figure 2e shows the SEM image of the Nb$_2$O$_5$ synthesized by simple calcination. Larger particles on the micrometer scale were observed using this method. On the basis of their structural features, the Nb$_2$O$_5$ samples synthesized by spray pyrolysis at 500 and 1000 °C and calcination at 500 °C are labeled A-Nb$_2$O$_5$, C-Nb$_2$O$_5$, and A$_{micr}$-Nb$_2$O$_5$, respectively.

Each synthesized Nb$_2$O$_5$ sample was distributed on the surface of MgH$_2$ by ball milling for 2 h. The hydrogen desorption properties of the MgH$_2$ samples were investigated by thermogravimetry–differential thermal analysis (TG–DTA), and the TG–DTA results are shown in Figure 3 together with the results of the pristine MgH$_2$. Here, the downward and upward peaks correspond to endothermic and exothermic reactions, respectively. The weight losses observed...
for all samples were almost identical and close to the theoretical hydrogen capacity, suggesting that MgH2 decomposed with a heating of up to 500 °C. The conversion from MgH2 to Mg was confirmed by XRD measurements for all samples (Figures S8 and S9). The hydrogen desorption temperature of MgH2 without additives by endothermic reaction was more than 400 °C. With the addition of Nb2O5, the dehydrogenation temperature decreased to less than 300 °C, suggesting that all the synthesized Nb2O5 had catalytic effects. The MgH2 with A-Nb2O5 desorbed H2 at the lowest temperature, with a peak centered at around 230 °C. In addition, the DTA curve showed a clear one-peak structure different from the MgH2 with A_micron-Nb2O5 and C-Nb2O5. The peak shape is strongly affected by the homogeneity of Nb2O5.1,8 If the catalytically active state is not homogenous because of a short milling time, the DTA curves contain a shoulder and two peaks in their DTA curves, is poor, while the highly homogeneous, catalytically active state can be generated for A-Nb2O5 by only 2 h of ball milling. It is noteworthy that the hydrogen desorption properties of the A-Nb2O5-loaded MgH2 is comparable to the best MgH2 activated by Nb2O5 reported in previous studies despite having only one-tenth of the milling time.6 It was generally expected that the Nb2O5 with smaller initial particle size would be highly dispersed on the MgH2 surface and/or form the catalytically active state; in fact, A-Nb2O5 showed better catalytic activity than A_micron-Nb2O5 although both Nb2O5 samples had the same amorphous structure. The results are understandable based on the initial particle size. However, the dehydrogenation temperature of MgH2 with A_micron-Nb2O5 is lower than that of Mg with crystalline Nb2O5, indicating that crystallinity is also an important factor for catalysis. In particular, A-Nb2O5 and A_micron-Nb2O5 are easily changed to the highly active state because of the unstable, amorphous state compared with the stable, crystalline one.

Figure 3. Hydrogen desorption profiles of pristine MgH2 and MgH2 with 1 mol % A-Nb2O5, A_micron-Nb2O5, and C-Nb2O5 prepared by ball milling for 2 h.

Figure 4 shows the hydrogen absorption curves of pristine Mg and Nb2O5-loaded Mg, which indicate that the Mg without catalysts did not absorb hydrogen at 40 °C. As it is suggested that the rate-determining step of hydrogenation below room temperature is hydrogen dissociation on the surface of Mg,5 this is a reasonable result. On the other hand, the hydrogen absorption of all the Nb2O5-loaded Mg proceeded at 40 °C under 0.1 MPa, suggesting that the synthesized Nb2O5 possessed significant catalytic effects, decreasing the activation energy of the surface reaction for the hydrogen absorption of Mg. The formation of MgH2 was confirmed by XRD measurements (Figure S10). The order of catalyst efficiency is A-Nb2O5 > A_micron-Nb2O5 > C-Nb2O5, which is the same trend as for the hydrogen desorption process. The efficiency difference between the three Nb2O5 catalysts can be understood by the homogeneity of the catalytically active state, similar to the desorption process. Note that the increase and anomaly around 6 min in the TG curves represent a background caused by switching the flow gas from Ar to H2.

To determine the dispersibility of Nb oxides with different crystallinities on the MgH2 surface and thus improve the kinetics for hydrogenation and dehydrogenation, TEM of the samples was carried out for the as-synthesized MgH2 with A-Nb2O5, A_micron-Nb2O5, and C-Nb2O5. Typical TEM images are shown together with the results of energy-dispersive X-ray spectroscopy (EDS) measurements (Figure S10). The contrast cannot only be formed as the high-contrast region with the results of EDS analyses for spot 1 in both samples. However, even for high-contrast regions, Nb was not observed from the results of EDS analyses for spot 3 in both samples. Thus, Nb was confirmed as the high-contrast region from the results of EDS analyses for spot 1 in both samples. However, even for high-contrast regions, Nb was not observed or the intensity was very low in some regions (such as spot 3 in Figure 5a), indicating that the contrast cannot only be attributed to the difference in elements. It has been reported that the catalytically active Nb species is nanoscale in size and highly dispersed on MgH2. In this case, it was difficult to distinguish Nb species even by TEM. A similar situation would occur for MgH2 with A-Nb2O5 and C-Nb2O5 because these Nb oxides have high activities. Thus, it is difficult to determine the differences in the dispersive state of Nb species in these samples; in other words, the dispersibilities of the Nb species are not very different for A-Nb2O5, A_micron-Nb2O5, and C-Nb2O5.

Figure 4. Hydrogen absorption profiles of pristine MgH2 and MgH2 with 1 mol % A-Nb2O5, A_micron-Nb2O5, and C-Nb2O5 after dehydrogenation. An anomaly around 6 min caused by switching the flow gas from Ar to H2 is indicated.
In addition to dispersibility, it is expected that the chemical state of the Nb species is an important factor in catalysis. Figure 6 shows Nb 3d X-ray photoelectron spectroscopy (XPS) spectra of the as-synthesized A-Nb2O5, C-Nb2O5, MgH2 + A-Nb2O5, and MgH2 + C-Nb2O5. Here, the XPS for O 1s was also carried out; however, it was impossible to distinguish the contribution of O originating from Nb oxides from other O peaks (i.e., adsorbed oxygen as background and oxide layers on Mg) because of the small amount of sample (1 mol %). The peaks corresponding to 3d (5/2) and 3d (3/2) were observed around 207 and 210 eV, respectively, in XPS spectra of both the synthesized Nb2O5, suggesting that Nb was in its fully oxidized state, Nb5+. After dispersion on the Mg surface by the ball-milling process, Nb is reduced to Nb4+, Nb2+, and Nb0. As shown in Table 1, the peak area ratio of (Nb0 + Nb2+)/Nb4+ for A-Nb2O5 is larger than that of C-Nb2O5, indicating that the amorphous Nb2O5 is easily reduced because of the structurally metastable state. In previous studies, it was clarified by X-ray absorption spectroscopy that Nb2O5 is reduced to NbO (Nb2+ state) during the ball-milling process via partial oxidation of Mg.10 The difference between the results reported in previous studies and those found in this one could be attributed to analytical differences or the synthesis process. Surface information is mainly obtained and emphasized in XPS spectra, while XAS shows average information of the bulk state. In fact, metallic Nb formation observed in XPS measurements was reported by Friedrichs et al.24 Moreover, if Nb in the samples after 2 h of milling is the intermediate state, the stable catalytic state might be formed after longer milling times. To fully understand the details, further analyses are required; however, from our results, it is clear that the structural stability affects the reduction process. In other words, the metastable amorphous state is possibly changed to the catalytically active state under mild conditions, such as short milling time.

The catalytic properties of A-Nb2O5, which is the best catalyst for hydrogen absorption/desorption among the Nb oxides investigated in this work, were further analyzed. Figure 7 shows the hydrogen desorption profiles of the MgH2 + A-Nb2O5 sample after storage for about 6 months in a glovebox. The hydrogen desorption temperature is changed from around 200 °C to more than 260 °C, and hydrogen is desorbed in a two-peak process, which is different from the single-peak process of the as-synthesized sample. Thus, the catalytically active state is unstable and degraded even under the glovebox conditions of low oxygen and water concentration. The hydrogen desorption profile was measured after rehydrogenation of the deactivated MgH2 + A-Nb2O5 sample. It is interesting that MgH2 desorbs H2 at a lower temperature than the as-synthesized sample, suggesting that the catalytic activity is enhanced (not only recovered) during the cycles of hydrogen desorption and absorption. Hanada et al. reported similar phenomena.4 The hydrogen desorption properties of MgH2 with Nb catalysts are further improved with the hydrogen desorption and absorption cycles. These observations indicate that the catalytic state after preparation is metastable, and high catalytic activity is reached after stabilization by the reactions with H2. Here, the weight loss for A-Nb2O5 is larger than that of C-Nb2O5, indicating that the amorphous Nb2O5 is easily reduced because of the structurally metastable state. In previous studies, it was clarified by X-ray absorption spectroscopy that Nb2O5 is reduced to NbO (Nb2+ state) during the ball-milling process via partial oxidation of Mg.10 The difference between the results reported in previous studies and those found in this one could be attributed to analytical differences or the synthesis process. Surface information is mainly obtained and emphasized in XPS spectra, while XAS shows average information of the bulk state. In fact, metallic Nb formation observed in XPS measurements was reported by Friedrichs et al.24 Moreover, if Nb in the samples after 2 h of milling is the intermediate state, the stable catalytic state might be formed after longer milling times. To fully understand the details, further analyses are required; however, from our results, it is clear that the structural stability affects the reduction process. In other words, the metastable amorphous state is possibly changed to the catalytically active state under mild conditions, such as short milling time.

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**Table 1. Peak Area Ratio of Nb5+, Nb4+, Nb2+, and Nb0 Estimated from the XPS Spectral Fitting Curves**

| sample | Nb5+ | Nb4+ | Nb2+ | Nb0 |
|--------|------|------|------|-----|
| A-Nb2O5 as-synthesized | 100 | 0 | 0 | 0 |
| MgH2 + A-Nb2O5 as-milled | 0 | 41 | 16 | 43 |
| | degraded | 0 | 54 | 11 | 35 |
| | re-hydrogenated | 0 | 20 | 22 | 58 |
| C-Nb2O5 as-synthesized | 100 | 0 | 0 | 0 |
| MgH2 + C-Nb2O5 as-milled | 0 | 20 | 20 | 60 |
After rehydrogenation, the XPS spectrum was fitted by the Nb$^0$, Nb$^{2+}$, and a small amount of Nb$^{4+}$. Namely, Nb was reduced during the hydrogen desorption/absorption process after degradation. It has been reported that hydrogen absorption/desorption affects the chemical state of Nb in the cycles.\textsuperscript{25,26} The variation in the redox state of Nb is consistent with the hydrogen desorption properties; in other words, the catalytically active state is the reduced Nb. It is noteworthy that the ratio of the Nb states is different between the as-synthesized and rehydrogenated samples. The peak intensity of the Nb$^{4+}$ state is drastically decreased and the Nb$^{2+}$ state is increased. Thus, the Nb catalyst is metastable after ball milling for 2 h, and the stable, catalytically active state is generated during the reaction with H$_2$. These results also suggest that the chemical state of Nb is an important factor for understanding the catalytically active state. The easy reactivation process is advantageous from an engineering point of view; in the case of conventional catalysts, a special reactivation process is required after degradation. On the other hand, the Nb catalysts can be preserved because the hydrogen absorption/desorption processes of Mg continuously activate the Nb species for reactions of Mg.

\section*{Conclusions}

In order to understand the important factors involved in Nb oxide catalysis for hydrogen desorption/absorption reactions of Mg, three types of Nb$_2$O$_5$ were synthesized by spray pyrolysis and a conventional calcination method. Nb$_2$O$_5$ prepared by spray pyrolysis at different temperatures consisted of homogeneous, spherical particles of almost the same size and different structural properties (i.e., amorphous and polycrystalline). From the investigation of hydrogen desorption properties, it is found that all Nb$_2$O$_5$ samples have catalytic effects. The amorphous Nb$_2$O$_5$ showed better catalysis, leading to a lower hydrogen desorption temperature in the DTA analyses. The hydrogen absorption rate was drastically improved by the Nb$_2$O$_5$ catalysts, with the best being amorphous Nb$_2$O$_5$ synthesized by spray pyrolysis. From the XPS analyses for Nb in the samples, it was confirmed that catalytic activity is high when the Nb species is more reduced. The catalytic state immediately after synthesis using the ball-milling process is metastable and degraded by oxidation over time, even in a glovebox, and the hydrogen desorption temperature is increased. During rehydrogenation, Nb in the samples is further reduced and shows the highest catalytic effects. Therefore, from the results obtained in this work, it is concluded that the chemical state of Nb is important for realizing high catalytic activity for hydrogen desorption/absorption reactions of Mg, and the initial structural stability of Nb$_2$O$_5$ affects the formation of the catalytically active state.

\section*{Experimental Section}

Ammonium niobium oxalate, NH$_4$[NbO(C$_2$O$_4$)$_2$(H$_2$O)$_2$]$·$10.5H$_2$O, was obtained from a reference catalyst (JRC-NBO-3AO), The Catalysis Society of Japan. Nb$_2$O$_5$ particles were prepared from solutions of NH$_4$[NbO(C$_2$O$_4$)$_2$(H$_2$O)$_2$]$·$10.5H$_2$O by the spray pyrolysis method using the experimental setup shown in Figure S1. The 0.01 M aqueous solution sprayed by an ultrasonic nebulizer passed through the furnace with an air flow of 1 L/min. In addition, Nb$_2$O$_5$ was synthesized by calcination of the NH$_4$[NbO(C$_2$O$_4$)$_2$(H$_2$O)$_2$]$·$10.5H$_2$O solid in a muffle oven. The temperature was

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure7}
\caption{Hydrogen desorption profiles of the as-synthesized, deactivated, and reactivated MgH$_2$ with 1 mol % A-Nb$_2$O$_5$.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure8}
\caption{Nb 3d XPS spectra (open circles) of the as-synthesized, deactivated, and reactivated MgH$_2$ + A-Nb$_2$O$_5$. The fitting curves (solid lines) are generated by the sum of each curve, corresponding to Nb$^{4+}$ (green dotted line), Nb$^{2+}$ (blue dotted line), and Nb$^{0}$ (red dotted line).}
\end{figure}
increased at 10 °C/min to the target temperature and maintained here for 3 h. Magnesium hydride (MgH2) powder (99.8% purity) was purchased from FUJIFILM Wako Pure Chemical Corporation. Mixtures of 300 mg of MgH2 and 1 mol % of each synthesized Nb2O5 (molar ratio of MgH2/Nb2O5 = 100:1) were placed into a chromium (Cr) steel pot (UMETOKU, 30 cm3 in volume) with 20 steel balls (SUJ-2, 7 mm in diameter). After introducing 1.0 MPa of H2 in the pot, milling was carried out by a Fritsch P7 ball mill at 370 rpm for 2 h. The samples were handled in a glovebox for about 6 months. To reactivate the catalysts, one cycle of hydrogen desorption with heating up to 400 °C under 0.1 MPa of Ar flow and hydrogen absorption with heating up to 250 °C under 0.1 MPa of H2 flow were carried out using the TG apparatus.

The structural properties of the samples were examined by XRD measurements (Rigaku RINT 2500, Cu Kα radiation), where the sample was covered by a polyimide sheet to avoid reactions with oxygen and moisture in the air. The synthesized Nb2O5 samples were characterized by SEM (HITACHI, S-4000) and TEM (JEOL, JEM-2010). The dispersion states of Nb oxides on the Mg were evaluated by TEM equipped with EDS. The dehydrogenation and hydrogenation properties were examined by TG–DTA (Rigaku, Thermo Plus TG8120). The dehydrogenation experiment was performed under 0.1 MPa of Ar flow with a 5 °C/min heating rate. The hydrogen absorption curves were measured under 0.1 MPa of H2 flow at around 40 °C for 30 min. The chemical states of the Nb oxides were investigated by XPS (Thermo Fisher Scientific, ESCALAB 250Xi, Al Kα radiation), where the powder samples were spread on carbon tape on the sample holder. Spectra were analyzed by fitting using a Lorentz/Gauss mixed function (Thermo Advantage). For fitting of the 3d peak of Nb, which shows two peaks corresponding to 3d (5/2) and 3d (3/2), peak positions were fixed to database values. In addition, the same values of half width, area ratio, and energy difference of 3d (5/2) and 3d (3/2) peaks were chosen for the fitting to minimize analytical flexibility.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c03101. Schematic image of the spray pyrolysis apparatus, XRD patterns of backgrounds, TG–DTA and XRD results of NH4[NbO(C2O4)2(H2O)2]·10SH2O, size distribution of Nb2O5, TEM images of Nb2O5, and XRD patterns of the as-synthesized, dehydrogenated, and rehydrogenated samples (PDF)

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Author Contributions

The manuscript was written with contributions from all authors. All authors have approved the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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