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## Study on reaction mechanism of dehydrogenation of magnesium hydride by *in situ* transmission electron microscopy

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*In situ* observation on dehydrogenation of  $\text{MgH}_2$  was performed by using transmission electron microscope (TEM). The dehydrogenation of  $\text{MgH}_2$  with 1 mol %  $\text{Nb}_2\text{O}_5$  and formation of nanosized Mg particles were observed at 150 °C.  $\text{Nb}_2\text{O}_5$  was not confirmed in diffraction patterns and TEM images probably due to wide dispersion. On  $\text{MgH}_2$  with 10 mol %  $\text{Nb}_2\text{O}_5$ , the high resolution TEM could recognize the dehydrogenation at the interface between  $\text{MgH}_2$  and  $\text{Nb}_2\text{O}_5$ , proceeding with increasing temperature. This suggests that hydrogen atoms could diffuse from  $\text{MgH}_2$  phase to the interface between Mg and  $\text{Nb}_2\text{O}_5$ , resulting in formation of hydrogen molecules at the interface.

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Mg has been regarded as a promising candidate for a base metal of hydrogen storage alloys, which have large capacity for hydrogen storage.<sup>1-3</sup> However, one of disadvantages is its slow reaction speed of hydrogenation and dehydrogenation. Recently, it has been suggested that oxide catalyst is effective for improving the hydrogenation and dehydrogenation kinetics of Mg. Barkhordarian *et al.* reported that  $\text{Nb}_2\text{O}_5$  had the best effect on the hydrogen storage properties of Mg and  $\text{MgH}_2$  as an oxide catalysts.<sup>4-6</sup> Hanada *et al.* made some composite materials of  $\text{MgH}_2$  catalyzed with transition metals and oxides by ball milling method, and reported that  $\text{MgH}_2$  with 1 mol % of  $\text{Nb}_2\text{O}_5$  has superior dehydrogenation characteristics.<sup>7-9</sup> However, the detail of the catalytic reaction has not been understood yet. In this study, the change in the high resolution image before and after dehydrogenation was observed by using with TEM to examine the details of the catalytic reaction.

In this study, two kinds of samples with 1 and 10 mol % of  $\text{Nb}_2\text{O}_5$  were prepared. For  $\text{MgH}_2$  catalyzed with 1 mol %  $\text{Nb}_2\text{O}_5$ ,  $\text{MgH}_2$  powder (Alfa Aesar), and  $\text{Nb}_2\text{O}_5$  powder (mesoporous: Sigma-Aldrich) were ball-milled under the hydrogen atmosphere of 1.0 MPa for 20 h. On the other hand, for

$\text{MgH}_2$  catalyzed with 10 mol %  $\text{Nb}_2\text{O}_5$ ,  $\text{MgH}_2$  powder, and  $\text{Nb}_2\text{O}_5$  powder (single-crystalline: Kojundo chemical Laboratory) were mixed by agate mortar in a glovebox filled with Ar gas. The samples were handled without exposure to air in whole process. The sample powder was placed on a micro-grid and the grid was set into a heating specimen holder in the glove box under Ar atmosphere. The heating specimen holder was put into a plastic bag under Ar atmosphere and loaded into TEM equipment in order to prevent the oxidation. The samples were observed from room temperature to 200 °C by using a TEM (JEOL-2010; 200 kV), and high resolution images of a 10 mol % catalyzed sample were obtained by using high voltage electron microscope (HVEM, JEM-ARM1300; 1250 kV). With respect to temperature control for *in situ* TEM observation, the temperature was rapidly raised up and kept at 100, 150, or 200 °C. The TEM images were analyzed by the selected area electron diffraction pattern (SADP), fast Fourier transformation (FFT), and inverse fast Fourier transformation (IFFT).

At the first step, observation by using a conventional TEM (200 kV) was carried out for  $\text{MgH}_2$  catalyzed with 1 mol %  $\text{Nb}_2\text{O}_5$ , which showed a remarkable catalytic effect.<sup>10</sup>

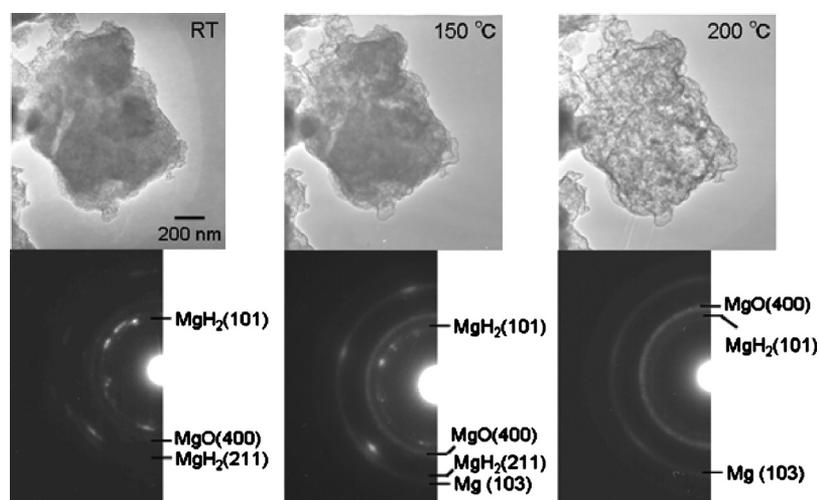


FIG. 1. BF images and diffraction pattern of 1 mol % catalyzed sample at room temperatures, 150 and 200 °C.

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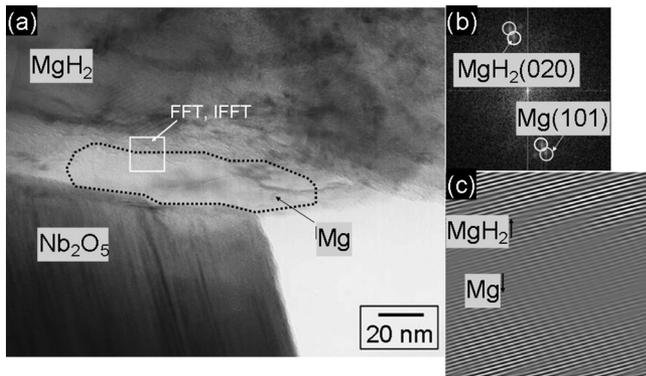


FIG. 2. BF image (a), FFT (b), and IFFT (c) from 10 mol % catalyzed sample at room temperature.

Fig. 1 shows the bright field (BF) images and SADP of  $\text{MgH}_2$  catalyzed with 1 mol %  $\text{Nb}_2\text{O}_5$  at RT, 150 and 200 °C. In case of RT, the diffraction rings and patterns of  $\text{MgH}_2$  and  $\text{MgO}$  were confirmed.  $\text{MgO}$  could be considered as an impurity in the starting material of  $\text{MgH}_2$ . At 150 °C, the diffraction ring of  $\text{MgH}_2$  became weak and the diffraction ring of  $\text{Mg}$  appeared. Therefore, it was confirmed that the decomposition of  $\text{MgH}_2$  and the formation of  $\text{Mg}$  started from around 150 °C. In the case of 200 °C, the diffraction ring of  $\text{MgH}_2$  almost disappeared and the Debye ring of  $\text{Mg}$  developed, meaning that the  $\text{Mg}$  crystal was formed with several 10 nm in size. On the other hand,  $\text{Nb}_2\text{O}_5$  was not identified by both BF images and SADP. In BF images, the shape of sample hardly changed while the contrast became weak with increasing temperature, indicating that the density of the particle decreased due to formation of voids.

In order to identify microstructure of interface between  $\text{MgH}_2$  and  $\text{Nb}_2\text{O}_5$ ,  $\text{MgH}_2$  catalyzed with 10 mol %  $\text{Nb}_2\text{O}_5$  was observed by using high resolution microscopy with HVEM (1250 kV). On the desorption kinetics, the dehydrogenation characteristics of the  $\text{MgH}_2+1$  mol %  $\text{Nb}_2\text{O}_5$  is superior to that of  $\text{MgH}_2+10$  mol %  $\text{Nb}_2\text{O}_5$  due to a larger amount of interface volume between  $\text{MgH}_2$  and catalyst. Figure 2 shows (a) BF image, (b) FFT image, and (c) IFFT image at RT. As shown in Fig. 2(a), it was confirmed that upper and bottom parts are  $\text{MgH}_2$  and  $\text{Nb}_2\text{O}_5$ , respectively. Meanwhile  $\text{Mg}$  formation is confirmed near the interface. Figures 2(b) and 2(c) are FFT and IFFT images from square in (a), showing phases of  $\text{MgH}_2$  and  $\text{Mg}$ . It was indicated that the initial decomposition from  $\text{MgH}_2$  to  $\text{Mg}$  occurred at the interface between  $\text{MgH}_2$  and  $\text{Nb}_2\text{O}_5$  even at RT. The reason why the decomposition started even at RT was probably due to an effect of electron-beam irradiation. Here, the effect of electron-beam irradiation on the decomposition should be considered. By electron-beam irradiation, the temperature would be locally increased. The decomposition could be caused by this local heating. However, despite the electron-beam irradiation could affect the entire sample; the results showed that  $\text{Mg}$  phase appeared at the interface. From this consideration, it can be recognized that the decomposition started at the interface due to the catalytic effect. The size of  $\text{Mg}$  phase, as shown in the dotted line in Fig. 2(a) was approximately 60 nm. Figure 3 shows BF image and related FFT and IFFT images at 100 and 200 °C. The  $\text{Mg}$  phase grew up with increasing temperature. Conclusively, we successively observed the growth of  $\text{Mg}$  phase started at the

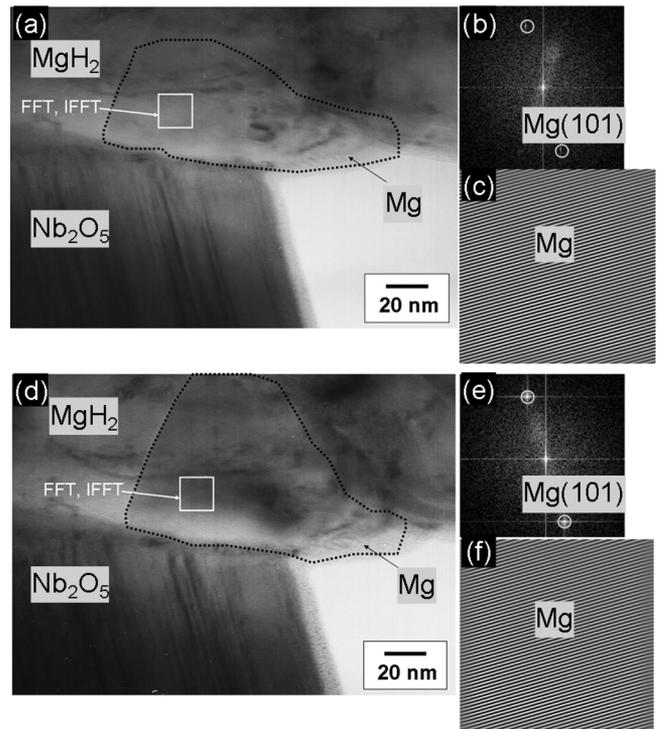


FIG. 3. BF image (a), FFT (b), and IFFT (c) from 10 mol % catalyzed sample heated to 100 °C BF image (d), FFT (e), and IFFT (f) from 10 mol % catalyzed sample heated to 200 °C.

interface between  $\text{MgH}_2$  and  $\text{Nb}_2\text{O}_5$  and proceeded with increasing temperature. Here, it should be noticed that  $\text{Mg}$  phase appeared and grew up between  $\text{MgH}_2$  and catalyst, indicating that  $\text{MgH}_2$  phase did not touch the catalyst any longer. In that case, it should be considered that how the catalyst does work. In general, surface reaction is regarded as the rate determining step of the decomposition of  $\text{MgH}_2$ . On the surface, hydrogen molecules form with hydrogen atoms. The catalyst should rescue the activation energy of the surface reaction. So, it can be recognized that hydrogen molecules emitted at the interface. As a result, it can be suggested that hydrogen atoms diffuse from  $\text{MgH}_2$  phase to the interface through  $\text{Mg}$  phase, as shown in Fig. 4. With respect to state of hydrogen atoms, initially hydrogen is as atoms in

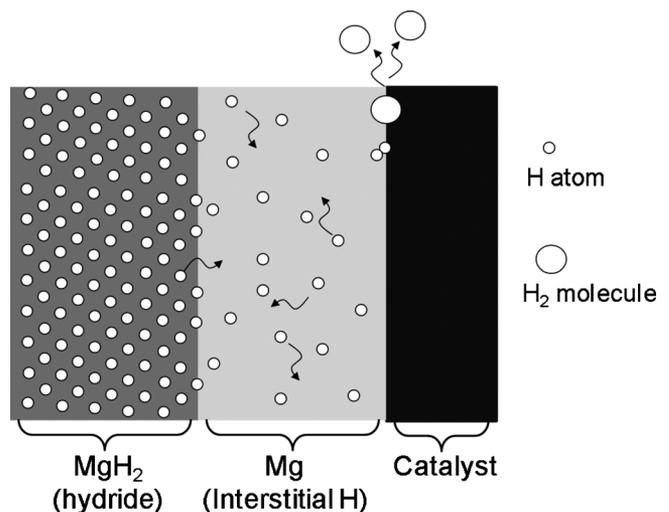


FIG. 4. Schematic of dehydrogenation process of  $\text{MgH}_2$ .

hydride, next hydrogen atoms randomly diffuse in interstitial sites, and finally hydrogen atoms are combined to be hydrogen molecule at the interface between Mg and catalyst.

In conclusion, it was confirmed that the dehydrogenation of MgH<sub>2</sub> catalyzed with 1 mol % Nb<sub>2</sub>O<sub>5</sub> started at 150 °C, and then nanosize Mg was formed by SADP. In the case of MgH<sub>2</sub> catalyzed with 10 mol % Nb<sub>2</sub>O<sub>5</sub>, it was indicated that the dehydrogenation of MgH<sub>2</sub> started at interface between Nb<sub>2</sub>O<sub>5</sub> and MgH<sub>2</sub>. And it can be assumed that hydrogen probably diffuse from MgH<sub>2</sub> to surface of Nb<sub>2</sub>O<sub>5</sub> through Mg phase. The real catalyst, which might exist on the interface of Nb<sub>2</sub>O<sub>5</sub> and MgH<sub>2</sub> could not be identified either. Hanada *et al.*<sup>11</sup> reported the catalyst of Nb–O binary oxides in MgH<sub>2</sub> was characterized to be NbO by x-ray absorption fine structure (XAFS). NbO was generated by ballmilling MgH<sub>2</sub> with Nb<sub>2</sub>O<sub>5</sub>. On the other hand, Porcu *et al.*<sup>12</sup> observed Nb<sub>2</sub>O<sub>5</sub>, Nb<sub>2</sub>O, and MgNb<sub>2</sub>O<sub>3.67</sub> by TEM. Still several candidates can be considered for the most effective catalyst. Near future, we plan to observe the interface between MgH<sub>2</sub> and Nb<sub>2</sub>O<sub>5</sub> by using scanning transmission electron microscope electron energy-loss spectroscopy (STEM-EELS), which can be a proper method to determine the real catalyst at the interface.

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