



HOKKAIDO UNIVERSITY

Title	Investigation on Catalytic Effect and Transformation Process in Mg/MgH ₂ System [an abstract of dissertation and a summary of dissertation review]
Author(s)	馬, 涛
Degree Grantor	北海道大学
Degree Name	博士(工学)
Dissertation Number	甲第11123号
Issue Date	2013-09-25
Doc URL	https://hdl.handle.net/2115/53845
Rights(URL)	https://creativecommons.org/licenses/by-nc-sa/2.1/jp/
Type	doctoral thesis
File Information	Ma_Tao_abstract.pdf, 論文内容の要旨



学 位 論 文 内 容 の 要 旨

DISSERTATION ABSTRACT

博士の専攻分野の名称 博士（工学） 氏名 馬 涛

学 位 論 文 題 名

Title of dissertation submitted for the degree

Investigation on Catalytic Effect and Transformation Process in Mg/MgH₂ System

(マグネシウム系水素貯蔵材料における触媒効果と変態の研究)

Mg/MgH₂ system is a promising candidate for hydrogen storage materials due to its high hydrogen capacity (7.6 wt%) and low cost; Yet the main obstacle impeding its application lies in the limitation of kinetics and thermodynamics. In respect to these problems, two significant issues, the catalytic effect and Mg→MgH₂ transformation process, were studied in this thesis, as a contribution to further development on the system.

A brief introduction, as well as the state-of-the-art in hydrogen storage materials, was made in Chapter 1. Especially the Mg/MgH₂ system for hydrogen storage was reviewed in three aspects: nanocrystallization, catalyst modification, and Mg↔MgH₂ transformation process. Then the main purpose of this work, to study the mechanism of catalysis and the transformation process, serving as two important issues for developing the system, was mentioned.

The experimental procedures were mentioned in Chapter 2. The devices and methods used in this work, including ball-milling, evaporation, X-ray diffraction (XRD), thermal desorption spectroscopy (TDS), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and transmission electron microscopy (TEM), were described in detail. The principle and the operating procedures were described separately.

In Chapter 3, the catalytic effect of Nb₂O₅ was investigated in the MgH₂–Nb₂O₅ composites ball-milled for 0 (hand mixed), 0.02, 0.2, 2, and 20 h. An improvement on the desorption properties with the increase of ball-milling time were confirmed by TDS. Then we estimated by the Kissinger method the activation energies (E_a) during dehydrogenation, revealing that E_a decreased as the ball-milling proceeded, in accordance with the improved desorption properties. Especially, a significant decrease in E_a was achieved after the composite was ball-milled for 0.2 h. In the following XRD measurement and TEM observations, it was confirmed that the particle size of the additive was gradually refined during ball-milling. More importantly, XPS measurements revealed that Nb₂O₅ was partially reduced after been milled for 0.2 h. Therefore, the reduced Nb compounds may act as an essential catalyst improving the desorption properties and decreasing the activation energy.

Next, in order to find out the essential catalyst in the system, the state of the catalyst in $\text{MgH}_2\text{--Nb}_2\text{O}_5$ composite was investigated during the full cycle, written in Chapter 4. Its reduced counterparts, Nb and NbO, were also investigated for comparison. The results showed that a transition of $\text{Nb}_2\text{O}_5 \rightarrow \text{NbH}_2 \rightarrow \text{Nb} \rightarrow \text{NbH}$ was confirmed in the Nb_2O_5 -doped sample during ball-milling, dehydrogenation, and rehydrogenation, respectively. A similar transition, $\text{Nb} \rightarrow \text{NbH} \rightarrow \text{Nb} \rightarrow \text{NbH}$, was found in the Nb-doped sample. The similarity in the composition suggests that the catalytic effect in both samples follows the same mechanism, the Nb-gateway model, in which Nb facilitates the hydrogen transportation from MgH_2 to the outside, and accelerates the recombination of hydrogen molecules during the process. By contrast, NbO remained during the full cycle. The promoted dehydrogenation may either be attributed to the catalytic effect of NbO itself or the existence of the $\text{MgNb}_2\text{O}_{3.67}$ phase. In addition, we found that the Nb_2O_5 -doped sample tended to be refined in size, compared to the Nb-doped and NbO-doped ones, due to the hard and brittle features of Nb_2O_5 . This size effect partially leads to a better dehydrogenation property in the sample. NbH_2 and Nb, with 10–20 nm in size, were also observed in the composite doped by 1 mol% Nb_2O_5 , validating the Nb-gateway model in the $\text{MgH}_2\text{--Nb}_2\text{O}_5$ system. As the essential catalyst, tiny crystals of Nb worked as the gateway facilitating hydrogen transportation and hence improving dehydrogenation properties.

In Chapter 5, $\text{Mg} \rightarrow \text{MgH}_2$ transformation process was investigated by means of TEM observation. It was found that the hydrogenation took place along the specific orientation relationship, $\text{MgH}_2(101) \parallel \text{Mg}(002)$, as well as $\text{MgO}(200) \parallel \text{Mg}(002)$ during the inevitable oxidation process. It was indicated that the transformation process of Mg during hydrogenation and oxidation occurs following the sequence that $\text{MgH}_2(101)$ or $\text{MgO}(200)$ single layers form on the surface of $\text{Mg}(002)$ and then grow along these certain directions from the surface to the inside, as well as enlarge the range of each layer at the same time. A structural model, in which the Mg–Mg distance is adjusted according to the introduction of H or O, and correspondingly the Mg layers shift slightly, was proposed to demonstrate the transformation process.

Chapter 6 is the conclusions of the whole work. Based on the aforementioned results, an aspect was made in further development on the system. Future work may either put on generating ultra-fine nanoparticles of transition metals as catalysts, or making multi-layers of Mg and transition-metal catalysts with specific crystal orientation.