

論文の要旨 (Thesis Summary)

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Modification of Kinetics and Thermodynamics by Various Oxides Addition and Composite Formation for Magnesium-Hydrogen System

The search for hydrogen as an energy carrier is a key center of research worldwide to make an alternative energy source to replace carbon byproducts. Hydrogen storage, transportation, and conversion into electricity are still challenges for new generation scientists. The development of suitable host materials with versatile properties like volumetric density, gravimetric density, thermodynamic, kinetic, reversibility, and efficiency is a main target for researchers today. This research thesis consists of five chapters: Introduction/research background, purpose, experimental, results/discussion, and conclusion. The outline of each chapter is summarized below.

Chapter 1 Summarize existing technologies for hydrogen energy storage. The use of renewable energy is essential for the world to realize a carbon dioxide (CO₂)-free and sustainable society without depending on fossil fuels. Hydrogen is a promising energy carrier that has been highly regarded because of its advantages, such as high energy density (142 MJ/kg), great variety of potential sources, lightweight, and environmental friendliness. Hydrogen is not a primary energy source; it stores, transports, and delivers energy. An efficient and effective hydrogen storage method must be developed to realize a hydrogen-based energy system. Magnesium has always been the center of extensive investigations for its potential use as a medium for storing hydrogen as a basic technology for next-generation hydrogen transportation and increasing the amount of hydrogen flow because it can store up to 7.6 mass % of hydrogen. In this work, the kinetic and thermodynamic alteration of MgH₂ was performed using various kinds of oxides and composites.

Chapter 2 Purpose of the thesis has been explained in this chapter. In this study, we performed the kinetic and thermodynamic modification of MgH₂ using various types of oxides and composite. Basically, we performed the kinetic modification with various oxides, namely as purchased single phase of TiO₂, ZrO₂, HfO₂, V₂O₅, Nb₂O₅, Ta₂O₅, CrO₃, MoO₃, and WO₃ (Nb₂O₅ and its neighboring oxide) with Mg-MgH₂ system were investigated.

Various kinds of research and development are going on in the search for the newest and best catalysts. We often need middle properties or some suitable properties or some suitable combination of materials as per our need for application purposes. We have synthesized and taken various types of single phase transition metal ternary oxide catalysts for the Mg-H system to know the catalysis as well as catalytic mechanism. The replacement of any one of the transition metal element from transition metal ternary oxide with other elements of periodic table like alkali or alkaline or other column elements will give a new class of ternary oxide with single phase for Mg-H system.

In sequence with this study, we synthesize various types of Nb and Ta gel oxides using solution gel method to synthesize highly activated Mg for faster kinetics of hydrogen sorption by reducing the synthesis time 10 times shorter than the conventional method. Further, the thermodynamic alteration of MgH₂ can be achieved by introducing CaH₂ in the ratio of 2:1 respectively by the formation of 2MgH₂-CaH₂ composite.

Chapter 3 This chapter is all about experimental techniques as well as analysis related to the samples. All samples dealt inside the glovebox, filled with high purity Ar gas. All the sample syntheses were done using the planetary ball milling machine. The variation of crystal structure of the MgH₂ with different catalysts after ball milling and hydrogen sorption processes are analyzed by X-ray diffraction (XRD). The microstructural analysis of oxides and synthesized MgH₂ samples have been performed using scanning electron microscope (SEM). The measurements of

gravimetric storage capacity and reaction temperatures for MgH₂ systems were performed using thermogravimetry-differential thermal analyses connected with mass spectroscopy (TG-DTA-MS). The chemical state of each oxide catalyst with and without MgH₂ is determined using X-ray photoelectron spectroscopy (XPS).

Chapter 4

All the single phase of TiO₂, ZrO₂, HfO₂, V₂O₅, Nb₂O₅, Ta₂O₅, CrO₃, MoO₃, and WO₃ oxides ball milled with MgH₂. In case of TiO₂, V₂O₅, Nb₂O₅, CrO₃, ZrO₂, and MoO₃ oxide, we found high dispersion state on Mg surface whereas for HfO₂, Ta₂O₅, WO₃ we found almost no/less dispersion state. The hydrogen desorption peak temperature for pristine MgH₂ was found around 425 °C. The high catalysis was found in case of TiO₂, ZrO₂, V₂O₅, Nb₂O₅, and CrO₃ respectively yields dehydrogenation peak temperature reduced around 200 °C. On the other hand, low catalysis was found in case of HfO₂, Ta₂O₅, WO₃, and MoO₃. Among all the samples, the MgH₂ with Nb₂O₅ showed the highest hydrogen absorption rate, and the catalysis of other oxides was better in the order of ZrO₂ > TiO₂ > V₂O₅ > MoO₃ > CrO₃ > WO₃ > HfO₂ > Ta₂O₅ for isothermal hydrogen absorption. On the other hand, the hydrogen absorption was completely changed at higher temperatures due to change in hydrogenation reaction as heating rate was continuously increasing with 5 °C/min till 250 °C, reported in detail. As catalysis of MoO₃ can't be explained by dispersion state of oxide as well as transmission electron microscope so we performed surface analysis using X-ray photoelectron spectroscopy. The detailed surface analysis of each oxide and its reduction state was briefly explained in the thesis. We concluded that +3 and +2 oxidation state is responsible for catalytic active state.

In search of the newest and best catalysts, the Single-phase of TaVO₅, Nb₉VO₂₅ and Nb_{0.6}Cr_{0.4}O₂ ternary oxide were successfully synthesized. For all the ternary oxides, characteristic catalysis (hydrogen desorption temperature) was observed as-MgH₂+TaVO₅ (250 °C) which is in the middle of its individual oxide MgH₂+V₂O₅ (213 °C) and MgH₂+Ta₂O₅ (288 °C) respectively. Though, in the case of MgH₂+Nb₉VO₂₅ hydrogen desorption peak temperature was found as 250 °C which is higher compared to its individual oxide MgH₂+V₂O₅ (220 °C) and MgH₂+Nb₂O₅ (225 °C), respectively. However, in the case of MgH₂+Nb_{0.6}Cr_{0.4}O₂ hydrogen desorption peak temperature was found as 300 °C which is higher compared to its individual oxide MgH₂+Nb₂O₅ (222 °C) and MgH₂+CrO₃ (206 °C) respectively.

Various types of amorphous Nb and Ta gel oxides were synthesized via simple sol-gel method. These oxides are dispersed on the MgH₂ surface by ball milling for 2h, which is ten times shorter than that of the previous synthesis process using ball milling. All the oxides evidently reveal catalysis for the hydrogen desorption and absorption reactions of Mg. The synergetic effects of the synthesized Nb₂O₅-Ta₂O₅ mixed oxide are not found for catalysis; however, it is indicated that the mixed oxide state such as solid solution or ternary oxide (Nb-Ta-O) synthesized by the sol-gel methods shows characteristic catalytic effects differently from that of each oxide. The detailed work is reported in the thesis.

The MgH₂ and CaH₂ have been ball milled in the ratio of 2:1 to form a composite, further ZrCl₄ has been added as a catalyst. The ball-milled sample showed the individual MgH₂ and CaH₂ peaks in XRD. The dehydrogenation of 2MgH₂-CaH₂ composite with and without catalysts was performed up to 550 °C. The dehydrogenated product has shown the formation of Mg₂Ca intermetallic which favored the hydrogenation-dehydrogenation process. However, for catalyzed

sample, the peak shift in the case of $ZrCl_4$ could be possible, if $ZrCl_4$ is electrochemically interacting with MgH_2 and as consequence, the 3d electron is in the diffused state. On the other hand, the peak shift of Zr^0 could be due to doping of zirconium over the MgH_2 - CaH_2 - $ZrCl_4$ sub-surface. The detailed thermodynamic alteration is reported in the thesis.

Chapter 5 The dispersion state is one of the key factors talked about the catalysis of MgH_2 . The detailed surface analysis of each oxide and its reduction state was briefly explained in the thesis. We concluded that +3 and +2 oxidation state is responsible for catalytic active state. In the case of +3 ~ +2 oxidation state, as outer 4s electrons are left, and valence electron is changed to d electrons as per basic inorganic chemistry, possibly responsible for high catalytic activity in transition metal oxide.

The search of new catalyst with transition metal ternary oxide with single-phase was achieved, the new direction of catalysis and its tuning was achieved for Mg-H system.

The highly activated Mg surface is obtained by using synthesized oxide by simple solution gel method, milling time is drastically reduced, 10 times compared to previously reported work.

The thermodynamic alteration of MgH_2 was achieved with CaH_2 by the formation of Mg_2Ca phase after dehydrogenation at 550 °C.