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Hydrogen storage properties of a destabilized MgH_2–Sn system with TiF_3 addition

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ABSTRACT

The MgH_2–Sn system is considered a promising reactive metal composite for hydrogen storage. Several ratios of MgH_2–Sn (2:1, 3:1 and 4:1) destabilized system were investigated experimentally using a ball milling method. Based on the temperature-programme desorption results, the onset dehydrogenation temperature of the MgH_2–Sn composite was consisted of two steps in the range of 235–250 °C and 325–340 °C. TiF_3 catalyst was introduced to enhance the desorption temperature of the MgH_2–Sn (4:1) system. The onset dehydrogenation temperature of the $4MgH_2$–Sn-10 wt% TiF_3 composite was reduced to approximately 100 °C and 205 °C compared to the MgH_2–Sn (4:1) and the as-milled MgH_2. The Kissinger analysis established that the apparent activation energy for the first stage of the $4MgH_2$–Sn composite was reduced from 149.0 kJ/mol to 114.0 kJ/mol after adding 10 wt% TiF_3. However, the addition of TiF_3 did not result in improvement of the absorption process. The improvement of the dehydrogenation properties of the MgH_2–Sn composite with the addition of TiF_3 was due to the formation of Ti-containing and F-containing species. These species played a catalytic role in improving the dehydrogenation properties of the MgH_2–Sn system.

1. Introduction

Hydrogen is one of the most valuable energy carriers in view of the current demand for pollution-free energy systems. One of the keys to effective hydrogen storage is to store enough hydrogen for automobile on-board applications. The current research and development of high capacity hydrogen storage materials are drawing intensive attention among investigators in the energy material field [1]. As an energy carrier, hydrogen is a proximate ideal because it can be generated from a diverse number of feedstocks and can be converted to the desired form of energy without releasing harmful emissions at the point source, thus reducing greenhouse gas emissions, criteria pollutants and dependence on fossil fuels [2]. Hydrogen can be stored in several forms: as a compressed gas, cryogenic liquid and solid-state. Hydrogen storage in solid-state form has been extensively studied compared to compressed gas and cryogenic liquid forms. Several classes of solid-state hydrogen storage materials have been developed, such as metal hydrides [3], complex hydrides [4–7] and carbon nanomaterials [8,9]. Metal hydrides have largely been investigated due to their benefits. Among the metal hydrides, the Mg-based hydride, MgH_2, meets many of the technological demands, such as large gravimetric hydrogen density (7.6 wt% H_2), abundant resources, low cost and good reversibility [10,11], but its sluggish kinetics of hydrogen sorption and high thermodynamic stability have delayed commercial application of this material. Intensive efforts have been devoted to overcome these barriers, such as the use of ball milling [12,13], adding catalysts [14–20] and combining with metal or other hydrides [21–27], to enhance the MgH_2 hydrogen sorption properties.

The combination of MgH_2 with other metals, also known as the destabilization concept has attracted the attention of many researchers with several studies conducted for the MgH_2–Sn system [28–31]. Based on the results of a study by Imamura et al. [30,31], it was found that the addition of Sn as a destabilizing agent to form the MgH_2–Sn composite significantly improved its hydrogen sorption properties. Even though the desorption temperature of the MgH_2–Sn system was reduced, it still did not meet the desired requirement for practical applications. Therefore, in order to improve the desorption temperature, a catalyst was introduced to the MgH_2–Sn system. There are no studies on the effect of the

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catalyst on the storage properties of the MgH_2–Sn system. Therefore, it is an important issue for future research to discover any catalyst or additives that can improve the hydrogen storage properties of the MgH_2–Sn system. To the best of the authors' knowledge, no study has been conducted to classify the effect of TiF_3 as an additive on the hydrogen storage properties of MgH_2–Sn. Recently, Ismail et al. [32] stated that the formation of Ti-containing and F-containing active species plays a catalytic role in the MgH_2–⊜ $NaAlH_4$–TiF_3 system, which may promote the interaction of $NaAlH_4$ and MgH_2, and thus enhance the dehydrogenation of the MgH_2–$NaAlH_4$ system. The effect of TiF_3 on the dehydrogenation properties of MgH_2 was investigated by Ma et al. [33] who suggested that TiH_2 and MgF_2, formed in situ, played an important role in the enhancement of the dehydrogenation properties of MgH_2. Therefore, the present study hypothesised that the hydrogen storage properties of MgH_2–Sn could be improved by doping using the TiF_3 additive.

In this article, the addition of TiF_3 to improve the hydrogen storage properties of the MgH_2–Sn composite by ball milling was investigated for the first time. The hydrogen sorption properties of the MgH_2–Sn composite in the presence of TiF_3 were investigated by Sievert-type pressure-composition-temperature (PCT) apparatus and differential scanning calorimetry (DSC). To determine the particle's size and to clarify the reaction mechanism of the composite during the de/rehydrogenation process, scanning electron microscopy (SEM) and X-ray diffraction (XRD) were used, respectively. Next, the possible mechanism from the catalytic effect of TiF_3 in the MgH_2–Sn composite was discussed.

2. Experimental details

The initial materials, MgH_2 (hydrogen storage grade with 98% purity), Sn and TiF_3 were purchased from Sigma Aldrich and were used directly without any further purification. The milling experiments were performed in a planetary ball mill (NQM-0.4) by milling for 15 min, resting for 2 min and milling for another 15 min. This process was conducted in three cycles in a different direction at a rotation speed of 400 rpm using hardened stainless steel milling tools. The molar ratios of MgH_2 and Sn in this study were 2:1, 3:1 and 4:1. These composites are referred to as $2MgH_2$–Sn, $3MgH_2$–Sn and $4MgH_2$–Sn for simplicity. TiF_3 (10 wt%) was mixed with $4MgH_2$–Sn under the same conditions to investigate the catalytic effects. Pure MgH_2 was also prepared under the same conditions for comparison purposes. All handling of the powders, including weighing and loading, was performed in an argon atmosphere MBraun Unilab glove box.

For the temperature-programmed-desorption (TPD) and the sorption measurements, the sample was loaded into a sample vessel and sealed inside a glove box. The experiments were performed in a Sieverts-type pressure-composition-temperature (PCT) apparatus (Advanced Materials Corporation). This system covers the temperature range from room temperature to 500 °C at hydrogen pressures up to 10 MPa. The heating rate for the TPD measurement was 5 °C/min, and samples were heated in a vacuum chamber from room temperature to 450 °C.

Differential scanning calorimetry (DSC) analysis of the dehydrogenation process was performed on a Mettler Toledo thermogravimetric analysis/differential scanning calorimeter (TGA/DSC) 1. The sample was loaded into an alumina crucible in the glove box. The crucible was then placed in a sealed glass bottle to prevent oxidation during transportation from the glove box to the DSC apparatus. An empty alumina crucible was used as the reference. The samples were heated from room temperature to 500 °C under an argon flow of 30 ml/min, and different heating rates were used.

The samples for scanning electron microscopy (SEM) and X-ray diffraction (XRD) were also prepared in the glove box. The SEM samples were placed on carbon tape and coated with gold spray under a vacuum. The morphology of the samples was characterized using a scanning electron microscope (SEM; JEOL JSM-6360LA). In addition, the samples before and after desorption, as well as after the rehydrogenation stage, were characterized by a Rigaku Mini-Flex X-ray diffractometer with Cu Ka radiation. The patterns were scanned over diffraction angles from 20° to 80° with a speed of 2.00°/min. To avoid exposure to air during the measurement, the sample was spread uniformly on the sample holder and covered with plastic wrap.

3. Results and discussion

3.1. Dehydrogenation temperature

Fig. 1 shows the TPD (temperature-programmed desorption) results for the as-received MgH_2, the as-milled MgH_2 and the MgH_2 with Sn added (2:1, 3:1 and 4:1 M ratios). The as-received MgH_2 started to release hydrogen at approximately 434 °C and desorbed approximately 7.5 wt% hydrogen (7.6 wt% H_2 was theoretically released). After milling, the onset desorption temperature of the MgH_2 was reduced to approximately 355 °C, indicating that the milling process also influenced the onset decomposition temperature of the MgH_2. The ball milling technique is an effective way to activate magnesium or form composites for hydrogen storage [34] and influences the onset desorption temperature of MgH_2, as claimed by Huot et al. [12]. The as-milled MgH_2 released approximately 7.4 wt% hydrogen after 420 °C. After combining with Sn, there are two stages of dehydrogenation during the heating process. The first stage occurs within the temperature range from 235 to 250 °C, and the second dehydrogenation stage starts at approximately 325–340 °C and is completed at 380 °C. The first step at low temperature is due to the reaction of MgH_2 with Sn to irreversibly form the Mg_2Sn intermetallic compound (Reaction (1)), and the second step at relatively high temperature is due to hydrogen desorption from the remaining MgH_2 (Reaction (2)). This process is already known from the previously reported properties of the MgH_2–Sn system [30,31]. The onset decomposition temperature of the MgH_2 decreased dramatically after combining with Sn and was 100 °C and 164 °C lower than for the as-milled and as-received MgH_2, respectively. The total amount of hydrogen released

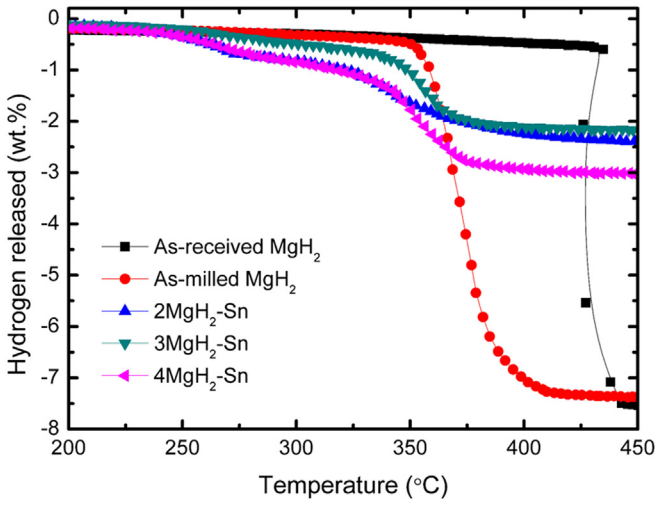

Fig. 1. TPD patterns for the dehydrogenation of the as-received MgH_2, as-milled MgH_2 and the MgH_2–Sn mixture with ratios of 2:1, 3:1, and 4:1.