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A novel solid-solution MXene $(\text{Ti}_{0.5}\text{V}_{0.5})_3\text{C}_2$ with high catalytic activity for hydrogen storage in MgH_2

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ABSTRACT

A novel solid-solution MXene $(\text{Ti}_{0.5}\text{V}_{0.5})_3\text{C}_2$ is successfully synthesized by exfoliating a solid-solution MAX phase $(\text{Ti}_{0.5}\text{V}_{0.5})_3\text{AlC}_2$, and its catalytic effect on the hydrogen storage reaction of Mg is systemically evaluated for the first time. Typical layer morphology is observed for the prepared $(\text{Ti}_{0.5}\text{V}_{0.5})_3\text{C}_2$, which exhibits a better catalytic activity than that of Ti_3C_2 . The addition of 10 wt% $(\text{Ti}_{0.5}\text{V}_{0.5})_3\text{C}_2$ remarkably reduces the dehydrogenation onset temperature of MgH_2 by 70 °C, from 266 to 196 °C. At 250 °C, approximately 5.0 wt% H_2 is released from the 10 wt% $(\text{Ti}_{0.5}\text{V}_{0.5})_3\text{C}_2$ -containing MgH_2 within 20 min. The dehydrogenated sample rapidly absorbs 4.8 wt% H_2 within 5 s at 120 °C; these hydrogenation kinetics are much more superior even to the well-studied Nb_2O_5 catalyst. The apparent activation energy is calculated to be 77.3 kJ/mol for the MgH_2 -10 wt% $(\text{Ti}_{0.5}\text{V}_{0.5})_3\text{C}_2$ sample, which is only around half of that of the pristine MgH_2 (153.8 kJ/mol). This is responsible for the remarkably reduced dehydrogenation operating temperature. Moreover, the chemical states of $(\text{Ti}_{0.5}\text{V}_{0.5})_3\text{C}_2$ during dehydrogenation are also analysed and discussed.

1. Introduction

Interest in the development of Mg-based hydrides as hydrogen storage materials is still active in the last few decades because of their high capacity, excellent reversibility, natural abundance and low cost [1–5]. MgH_2 contains 7.6 wt% of hydrogen; however, two significant disadvantages, namely its high thermodynamic stability with dissociation enthalpy change of 75 kJ/mol- H_2 and sluggish reaction kinetics with activation energy of 140–220 kJ/mol, must be overcome before it can be practically used as storage material for stationary application or for concentrating solar power systems [6–8]. Numerous attempts have been made to address these important issues by alloying, catalysing and nanostructuring [9–34]. In addition, there are several works that aim at reducing the cost of Mg-based hydrogen storage system by producing them from waste Mg alloys because it is very important for large scale mobile or stationary applications [35,36].

Specifically, doping with selected catalysts to form nanocomposite powders has been quite effective at reducing the operating temperatures and enhancing the reaction kinetics for hydrogen storage in MgH_2 by considering the fact that hydrogen release from bulk MgH_2 parti-

cles generally followed a multiple nucleation and growth model [19]. A wide range of pure metals, intermetallic compounds, metal oxides, metal halides, metal carbides, metal nitrides and metal hydrides has been screened and evaluated [20–34], and the results indicate that Ti- and V-based species are very promising catalysts for hydrogen storage in MgH_2 because of their high activity toward the dissociation of hydrogen molecules. For example, an early work by Liang et al. in 1999 reported the catalytic effects of 3-d transition metal powders of Ti, V, Mn, Fe and Ni by ball milling with MgH_2 powders [21]. Their results showed that Ti and V were much more effective at catalysing the hydrogen release from MgH_2 and subsequent uptake of hydrogen compared to Ni. The favourable effects of Ti and V compounds on enhancing the hydrogen absorption/desorption kinetics of Mg/ MgH_2 were further confirmed by adding a minor amount of TiO_2 and V_2O_5 to the MgH_2 as hydrogen was fully desorbed from $\text{MgH}_2/(\text{TiO}_2)_{0.01}$ and $\text{MgH}_2/(\text{V}_2\text{O}_5)_{0.01}$ within 7 min at 300 °C [22]. Wang et al. even observed 2.5 wt% of hydrogen uptake for the Mg-20 wt% TiO_2 sample within 10 min at 160 °C and 20 bar of hydrogen pressure [23]. A structural characterization revealed that Ti-substituted MgO was the main reaction product for the ball-milled MgH_2 - TiO_2 mixture, which causes MgO to become an active built-in catalyst [24,25]. The catalytic

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effectiveness of TiF_3 was much superior to that of TiO_2 as the onset dehydrogenation temperature of the MgH_2 - TiF_3 system was reduced to 173 °C, whereas it was 216 °C for the TiO_2 -doped sample [26]. The 5 wt% TiF_3 -containing MgH_2 desorbed 4.5 wt% hydrogen in 6 min at 300 °C and absorbed 4.2 wt% hydrogen in 1 min under 20 bar of hydrogen at room temperature [27]. Reversible hydrogen sorption was even achieved below 150 °C by introducing a small amount of TiH_2 into the MgH_2 [29,30]. In addition, a synergetic effect on the dehydrogenation of MgH_2 was also observed by the co-addition of TiO_2 and TiH_2 . As reported by Daryani and co-workers, the dehydrogenation temperature of a MgH_2 - TiH_2 - TiO_2 nanocomposite (molar ratio: 84:10:6) was dramatically reduced by 100 °C [31]. Cui et al. observed a similar phenomenon by preparing a Ti, TiH_2 , TiCl_3 and TiO_2 composite-coated Mg powder [32]. In their case, the multiple-valence Ti sites facilitated electron transfer among them and consequently greatly enhanced hydrogen absorption/desorption by MgH_2 . More importantly, recent studies revealed that TiN and TiC could offer a catalytic effect similar to that of Nb_2O_5 , which has been generally accepted as one of the most effective catalysts for hydrogen storage in MgH_2 at present [33]. We have previously found that a novel 2D MXene Ti_3C_2 prepared by the exfoliation of a Ti_3AlC_2 MAX phase exhibited superior catalytic effects towards the hydrogen storage reaction of MgH_2 as the 5 wt% Ti_3C_2 -containing MgH_2 releases 6.2 wt% H_2 within 1 min at 300 °C and absorbs 6.1 wt% H_2 within 30 s at 150 °C [34]. This was attributed to its unique layered structure and the good dispersion of active Ti species formed in situ. These results sufficiently proved that the 2D layered MXene compound Ti_3C_2 was an advanced catalyst for improving the reaction kinetics of hydrogen storage in MgH_2 . As a result, the further enhancement of the catalytic activity of Ti_3C_2 should be of scientific interest and practical importance for the improvement of MgH_2 . However, no attempt has been made in this respect until now.

In this work, we demonstrate a novel solid-solution MXene $(\text{Ti}_{0.5}\text{V}_{0.5})_3\text{C}_2$ by taking the high catalytic activity of the elements Ti and V and systematically evaluating its catalytic effectiveness in the hydrogen storage reaction of MgH_2 . The results showed that adding 10 wt% $(\text{Ti}_{0.5}\text{V}_{0.5})_3\text{C}_2$ induced a significant reduction in the onset dehydrogenation temperature of MgH_2 from 266 to 196 °C. In the isothermal mode, approximately 5.0 wt% H_2 was released from the 10 wt% $(\text{Ti}_{0.5}\text{V}_{0.5})_3\text{C}_2$ -containing MgH_2 within 20 min at 250 °C, and the dehydrogenated sample absorbed 4.8 wt% H_2 within 5 s at 120 °C. The chemical states of $(\text{Ti}_{0.5}\text{V}_{0.5})_3\text{C}_2$ additive before and after dehydrogenation were analysed and are discussed on the basis of XRD, EDS and XPS characterizations.

2. Experimental section

2.1. Sample preparation

Commercial Ti (Aladdin, purity 99%), V (Beijing Xing Rong Yuan, purity 99%), Al (Alfa-Aesar, purity 99%) and graphite (Alfa-Aesar, purity 99.8%) powders were purchased and used. A solid-solution MAX phase compound with a composition of $(\text{Ti}_{0.5}\text{V}_{0.5})_3\text{AlC}_2$ was first prepared by sintering a Ti-V-Al-C mixture with a molar ratio of 1.5:1.5:1.7:2 following the procedure reported previously [37]. Here, an additional 0.7 mol Al was used to compensate for the volatilization loss at high temperature because of the relatively low melting temperature of Al (~660 °C). The powders of Ti, V, Al and graphite were first mixed by ball milling in a planetary ball mill (QM-3SP4, Nanjing) at 300 rpm for 12 h. The ball-to-sample weight ratio was approximately 10:1. After mixing, the powders were placed in alumina crucible and heated at rate of 5 °C/min under Ar flow in a pit type cold-wall retort furnace (SVHT 2/30-GR, Nabertherm, Germany). After furnace cooling, the resulting lightly sintered porous compacts were mechanically crushed and ground to a powder finer than 200 mesh. After that, the prepared $(\text{Ti}_{0.5}\text{V}_{0.5})_3\text{AlC}_2$ powder was immersed in a 48% HF solution for 72 h at room temperature. The resulting suspension was washed 3 times with deionized water and finally filtered to obtain the 2D layered

$(\text{Ti}_{0.5}\text{V}_{0.5})_3\text{C}_2$. MgH_2 was synthesized in our own laboratory by heating Mg powder (Macklin, purity 99%) at 340 °C for 8 h under 20 bar of hydrogen. The prepared $(\text{Ti}_{0.5}\text{V}_{0.5})_3\text{C}_2$ was mixed with the prepared MgH_2 in anticipation of catalysis studies by ball milling on a QM-3SP4 planetary ball mill (Nanjing) at 500 rpm for 24 h under 50 bar of hydrogen. The designed sample composition was MgH_2 -x wt% $(\text{Ti}_{0.5}\text{V}_{0.5})_3\text{C}_2$ (x=0, 5, 7, 10 and 12). The ball-to-sample-weight ratio was set to be approximately 120:1. The milling process was conducted by alternating 12 min of milling and 6 min of rest to minimize the increase in temperature. Samples related to MgH_2 were handled in a glove box (MBRAUN, Germany) filled with pure argon to prevent contamination from moisture and oxygen. The H_2O and O_2 concentrations were kept below 1.0 ppm.

2.2. Structural and compositional characterization

X-ray diffraction (XRD) data were collected in a 2θ range of 5–90° with 0.02°-step increments at room temperature using an X-ray diffractometer (MiniFlex600, Rigaku) with Cu $K\alpha$ radiation (40 kV, 15 mA). The powder samples were sealed in a custom-designed container covered with Scotch™ tape to prevent air and moisture contamination. Raman analyses were performed on a confocal Raman microscope (Via-Reflex, Renishaw plc, UK) at a laser excitation wavelength of 532 nm. The sample morphologies were observed with scanning electron microscopy (SEM, Hitachi, S-4800) and transmission electron microscopy (TEM, Tecnai, G2 F20 S-TWIN). An energy-dispersive X-ray spectrometer (EDS) was attached to the SEM facility to characterize the distribution of the elements Mg, Ti and V in the samples. X-ray photoelectron spectroscopy (XPS) data were recorded on a Thermo Scientific ESCALAB 250Xi system equipped with an Al $K\alpha$ (1486.6 eV) X-ray source. The binding-energy spectra were fitted by XPSPEAK software.

2.3. Property evaluation

Quantitative hydrogen desorption/absorption properties were measured with a volumetric method on a homemade Sieverts-type apparatus. A sample of approximately 70 mg was loaded into a stainless steel tube reactor in a MBRAUN glove box (Germany) and then placed in a tube furnace. Both isothermal and non-isothermal approaches were adopted. For isothermal examination, the sample was quickly heated to the pre-set temperature and maintained at that temperature during the entire test. In the non-isothermal mode, the sample was gradually heated to a desired temperature at 2 °C/min under a primary vacuum (approximately 10^{-3} Torr) for dehydrogenation and at 1 °C/min with an initial hydrogen pressure of 50 bar for hydrogenation. A homemade temperature-programmed desorption (TPD) system with an online gas chromatograph (GC) was used to qualitatively measure temperature-dependent hydrogen desorption behaviours. A sample of approximately 40 mg was heated from room temperature to 400 °C at a heating rate of 2 °C/min with constantly flowing pure argon as the carrier gas. Differential scanning calorimetry (DSC) experiments were conducted on a NETZSCH DSC 200F3 unit, which was set up inside an argon-filled glove box. Approximately 2 mg of sample was heated in an Al crucible from 50 to 400 °C at 2 °C/min.

3. Results and discussion

First, $(\text{Ti}_{0.5}\text{V}_{0.5})_3\text{AlC}_2$, a solid-solution MAX phase compound reported recently [37], was prepared by calcining a Ti-V-Al-C mixture at 1450 °C for 2 h under an Ar atmosphere. The XRD results confirmed the formation of a single-phase $(\text{Ti}_{0.5}\text{V}_{0.5})_3\text{AlC}_2$ because the observed reflection (the bottom of Fig. 1(a)) was in good agreement with the previously reported pattern [37]. After that, the prepared $(\text{Ti}_{0.5}\text{V}_{0.5})_3\text{AlC}_2$ powders were etched using a HF solution at room temperature, and the resultant product was characterized by XRD, SEM and TEM. As shown in

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