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The effect of V, VCl_3 and VC catalysts on the MgH_2 hydrogen sorption properties

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ABSTRACT

MgH_2 based composites processed by mechanical alloying with the addition of 5 wt.% of V, VC and VCl_3 were evaluated for their absorption/desorption hydrogen capacities at 300 and 350 °C. These composites were investigated by the following techniques: X-ray diffraction, XRD, Pressure–Composition Isotherms, PCI and Differential Scanning Calorimetry, DSC. It was observed that the addition of V, VC and VCl_3 compounds improves hydrogen absorption and desorption kinetics in comparison to the MgH_2. The MgH_2-5 wt.% VCl_3 composite showed the faster absorption kinetics which absorbed 6.0 wt.% of H_2 in 7.5 min at 350 °C. The desorption activation energy of the composite containing VCl_3 (47 kJ mol^{-1}) is smaller than VC (63 kJ mol^{-1}). This indicates that this catalyst is more effective to be used in hydrogen storage system.

1. Introduction

Over the past 40 years metal hydrides have been thoroughly investigated mainly in search of the development of high performance alloys with fast and elevated hydrogen absorption and desorption capacity that can be controlled. These are the requirements needed for enabling its use in hydrogen storage systems for stationary or mobile energy applications [1]. The design of intelligent reservoirs [2] makes Mg a promising candidate for use in storage systems. Mg can absorb high amounts of hydrogen and for this reason it was often considered one of the most promising candidates for this purpose. However, it presents slow kinetics and only releases H_2 at high temperature. Adding elements to an extent sufficient to promote the formation of intermetallic compounds such as Mg–Ni, Mg–Fe, Mg–Co, among others was initially a great motivation to several researchers [3]. Later researches have pointed to the use of transition elements in low amount to avoid the intermetallic compounds formation, such as light alloys. These additions contribute to decrease the temperature and pressure needed to break the hydrogen–metal bond. Nowadays, transition elements, intermetallic and organic compounds [4–7] are widely used as catalysts, especially combined with non-equilibrium thermodynamics processes in order to promote an energy excess, via the formation of defects in the metallic crystal structure and providing the refinement of the microstructure.

Vanadium has been widely used among the transition metals since it presents one of the best catalytic properties [8–11]. However it is a high cost material and easily oxidates, so alternatives to its use are widely investigated. For these reasons, the present study aims to comparatively evaluate the hydrogen absorption/desorption kinetics in the MgH_2 samples with addition of V, VCl_3 and VC produced by mechanical alloying.

2. Materials and methods

Commercial MgH_2 powder with a purity of 99.4%, purchased by Sigma–Aldrich, was pre-milled in a hermetically closed steel vial with tungsten carbide balls under H_2 atmosphere at 2 bar for 24 h using a Fritsch planetary mill with a rotation speed of 300 rpm. After that, the MgH_2 was ball milled for 20 min more with 5 wt.% of V, VCl_3 and VC catalysts. After milling, the samples structural properties were examined using X-ray diffraction measurements (Shimadzu XRD-6000, Cu Kα). Differential scanning calorimetric (DSC) measurements were performed using a DSC Sensys Evo (Setaram) under argon atmosphere at different heating rates equal to 10, 15, 20 and 25 K min^{-1}. The hydrogen sorption kinetics tests and pressure–composition isotherms (PCIs) were measured by an automatic Sievert's type apparatus designed by PCT-Pro 2000. The hydrogen absorption and desorption measurements were conducted at 1 MPa and 0.01 MPa of hydrogen pressure, respectively, at 300 and 350 °C. The samples were handled in a glove box under argon atmosphere.

3. Results and discussion

Fig. 1 shows the XRD patterns of MgH_2 with catalysts and pure MgH_2 after being ball milled. The peaks related to β-MgH_2 and γ-MgH_2 due to the initial grinding of MgH_2 are observed in all diffractograms. The metastable γ-MgH_2 phase is generated after mechanical milling due to the energy conditions created during processing. The sample containing 5 wt.% of V presents the $VH_{0.81}$ peaks besides the Mg hydride peaks as reported by Liang et al. [12]. The X-ray pattern of MgH_2 + 5 wt.% VC composite (Fig. 1) presents the peaks related to VC which indicates that the catalyst does not decompose with the processing performed. Even after hydrogen absorption and desorption cycles, the peaks related to the VC are identified which demonstrates the high stability of this

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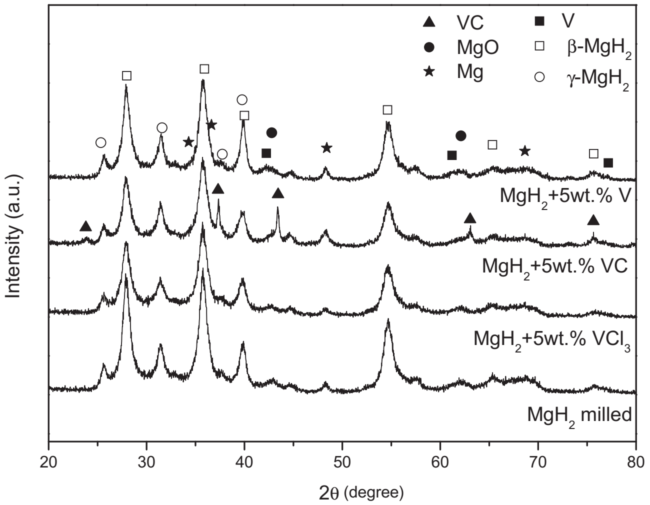

Fig. 1. XRD patterns of MgH_2 + 5 wt.% V, MgH_2 + 5 wt.% VC, MgH_2 + 5 wt.% VCl_3 and MgH_2 after milled.

composite at high temperature in the presence of MgH_2. The MgH_2 + 5 wt.% VCl_3 composite X-ray pattern presents peaks related to Mg hydride (β-MgH_2 and γ-MgH_2) and no reflection related to VCl_3 was identified, this occurs even after hydrogenation. This result contrasts with those observed by Malka et al. and Ma et al. [6,13] that observed traces of $MgCl_2$ formation after hydrogenation. The difference between the literature and the results obtained in the present study can be explained due to the lower VCl_3 concentration used in the latter. Besides this, the amount of V present in VCl_3 is smaller so the catalyst costs can be reduced.

Fig. 2a shows the absorption kinetics curves at 300 °C for MgH_2 samples with different catalysts under 1 MPa of H_2. MgH_2 + 5 wt.% VCl_3 and MgH_2 + 5 wt.% VC samples presented a similar kinetics at the beginning (until 5 min). However the sample containing VCl_3 reached the capacity of 6.0 wt.% of H_2 in 7.5 min while the sample with VC attained a capacity of 5.3 wt.% of H_2 in the same time interval. Despite the fact that the MgH_2 + 5 wt.% V sample achieved the capacity of 6.0 wt.% of H_2 it presented a slower kinetics compared to the other ones. This result obtained with VCl_3 showed an increase of 1 wt.% of H_2 capacity comparing to the one obtained with the same amount of another catalyst studied by Da Conceição et al. [4].

The desorption results at 300 °C (Fig. 2b) show that the best desorption kinetics was obtained for the MgH_2 + 5 wt.% VC composite. The desorption rate obtained at this temperature for the VC addition is 1.0×10^{-2} wt.% s^{-1} that is greater than the rates obtained for the VCl_3 and V addition, 6.5×10^{-3} wt.% s^{-1} and 3.1×10^{-2} wt.% s^{-1}, respectively.

Fig. 3 shows the hydrogen absorption and desorption kinetic curves at 350 °C for the different catalysts added to MgH_2. It is possible to notice that the absorption kinetics becomes slower than the ones obtained before but the addition of VCl_3 still exhibits the best kinetics. In Fig. 3b, it can be seen that the VCl_3 addition presents the fastest desorption kinetics. The desorption rate obtained at 350 °C for the VCl_3 addition is 2.7×10^{-2} wt.% s^{-1}, overcoming even the desorption rate of the sample containing VC (2.2×10^{-2} wt.% s^{-1}).

Fig. 4 shows the PCI curves for MgH_2 with different V-based catalysts at 300 °C. The MgH_2 milled with V and VCl_3 exhibited a maximum hydrogen capacity of 6.3 wt.%.

The hysteresis between hydrogen absorption and desorption of MgH_2 + 5 wt.% VCl_3 was smaller than MgH_2 + 5 wt.% V and this can be attributed to the decreased mechanical stress between the metal and the hydride phases [14,15].

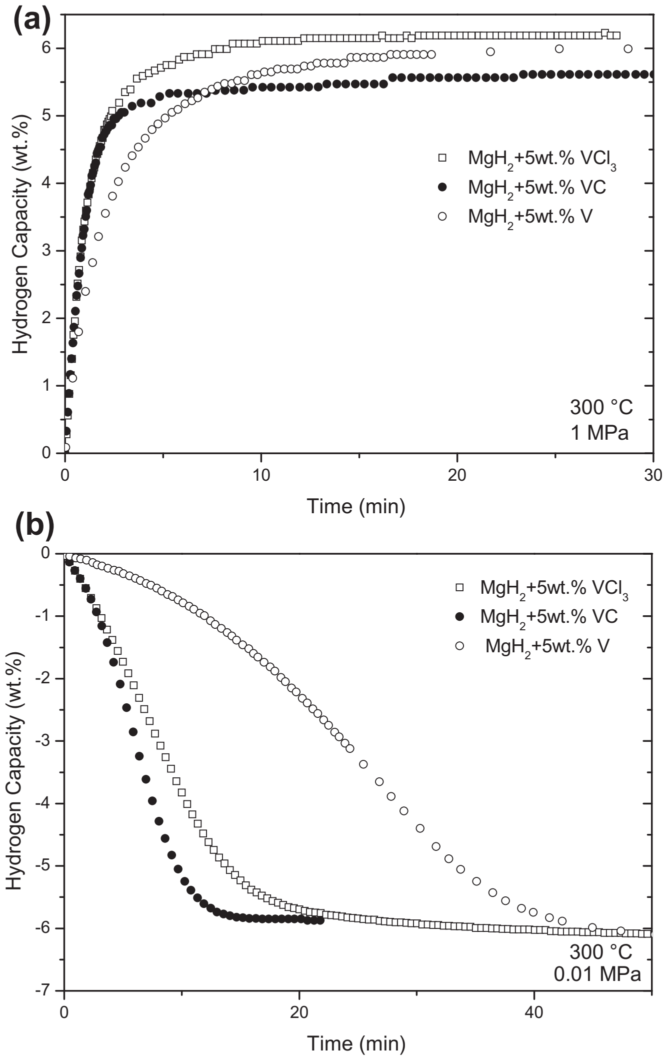

Fig. 2. Comparison of the sorption kinetics of MgH_2 containing 5 wt.% of V, VCl_3 and VC: (a) absorption and (b) desorption, both at 300 °C.

According to Shahi et al. [10] VCl_3 presents the best kinetics results when vanadium and V based compounds (VCl_3 and V_2O_5) are added to $Mg(NH_2)_2LiH$. They attributed this finding to the fact that this compound has unoccupied orbital and increased tendency to interact electronically with the electron pair from N-atoms of other compounds. This ability overcomes pure V and V_2O_5 and may explain the decrease in the binding energy of hydrogen with the Mg thereby facilitating the hydrogen absorption and desorption kinetics.

Fig. 5 shows the thermograms obtained by DSC for the MgH_2 mixed with different vanadium-based catalysts samples. For comparison purposes the typical peak value for the as-received MgH_2 sample is around 440 °C [16]. Regarding the addition of catalysts to MgH_2, the lowest peak temperature obtained was 375 °C for MgH_2 + 5 wt.% VCl_3 and for the other samples it was 387 °C (MgH_2 + 5 wt.% VC) and 400 °C (MgH_2 + 5 wt.% V). These values express the desorption temperatures of hydrogen and a lower peak temperature in a thermogram cannot be directly correlated with a fastest desorption kinetics, because DSC peaks do not always correspond to a higher reaction rate, since the exothermic and endothermic peaks can overlap and consequently shift the peak value [17].