

EFFECT OF DIFFERENT CARBON MATERIALS ON THE HYDROGEN SORPTION PROPERTIES OF MgH₂

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ABSTRACT

The present study analyses the decomposition behaviour of MgH₂ in different mixtures of MgH₂ and carbon materials, including graphite (G), activated carbon (AC), multi-walled carbon nanotubes (MWCNTs), several carbon nanofibers (NFs) and activated carbon fibres (ACFs). The introduction of such carbon materials lowers the decomposition temperature of MgH₂ and improves its decomposition kinetics. The best results were achieved in the mixtures involving NFs and MWCNTs, with inorganic impurities, particularly nickel and iron, inherited from their synthesis. The peak temperatures for decomposition, from differential scanning calorimetry (DSC), were reduced to 322 and 341°C, respectively, for the two cases, compared with 360°C for milled MgH₂. Substantial improvement in the decomposition kinetics of MgH₂ was achieved particularly with the NF additions. Complete decomposition ended within 20 min. at 300°C with 5 wt% NF addition, compared with 240 min. for MgH₂ and this kinetics was maintained even after several hydriding-dehydriding cycles. X-Ray diffraction and TEM reveal some structural changes in the MgH₂-based materials after cycling: there is an increase in crystalline size of MgH₂, together with certain separation of the magnesium and carbon-supported phases, indicating a clear relationship between the decomposition temperature of MgH₂ and its structure.

INTRODUCTION

Recent studies analyse the use of carbon materials to enhance the decomposition properties of MgH₂ (Imamura et al., 2003; Huot et al., 2003; Shang and Guo, 2004; Wu et al., 2006). However, the issue with the stability of MgH₂ and the role of carbon on such decomposition remains unresolved and sometimes controversial. The aim of the present work is to further clarify the effect of carbon materials on the dehydriding properties of MgH₂, paying particular attention to the “novel” forms of carbon, such as carbon nanofibres and carbon nanotubes, in comparison with those of “conventional” carbon forms, such as activated carbon and graphite. In addition, the influence of the metals contained in those carbon materials is studied, which has rarely been investigated before in the literature. The metal particles may have a strong influence on the dehydriding step. For this purpose, carbon nanofibres containing nickel and iron were compared.

EXPERIMENTAL

Several carbon materials were selected for this study. Their porosity was characterised by physical adsorption of gases (N₂ and CO₂ at -196°C and 0°C, respectively) using an Autosorb 6-B apparatus (Quantachrome Corporation). Their inorganic content and composition was measured by X-Ray Fluorescence (XRF) using a Philips PW1480 XRF spectrometer. MgH₂ powder was purchased from Th. Goldschmidt AG, with a nominal composition of 95 wt.% MgH₂ and 5 wt.% Mg, and an average particle size of 50 µm. The hydride was pre-milled for 15 h in 4 bar argon atmosphere.

Each carbon material was mixed with pre-milled MgH₂ using a 5 wt% carbon composition. These samples were milled for 1/4 to 20 h in a high energy SPEX8000 mill under argon atmosphere.

The decomposition temperature of MgH₂ was determined by differential scanning calorimetry (DSC) (Setsys-Setaram). A heating rate of 5°C min⁻¹ was used and the experiments were performed in Ar (BOC gases, 99.999% purity) flow of 90 ml min⁻¹ using sample weights in the range of 2-4 mg. Hydrogen decomposition in the samples was performed using a volumetric equipment (PCT-Pro 2000, Hy-Energy) and high purity hydrogen (BOC gases, 99.999% purity). Each sample weighed around 100 mg. Desorption measurements were performed at 300°C and vacuum (0.1 kPa).

Morphology of the MgH₂/C samples was characterized by transmission electron microscopy (TEM) using a JEOL JEM-2010 high-tilt instrument operating at 200 kV. Structural properties were characterized by X-ray diffraction (XRD) using a Siemens D5000 powder diffractometer equipped with a Cu K α X-ray source, a graphite monochromator and an internal standard of silicon powder.

RESULTS AND DISCUSSION

Carbon materials

A wide range of carbon materials was selected for preparation of the MgH₂/C samples. Table 1 compares their porous texture showing that the samples under study strongly differ in terms of porosity, ranging from non-porous to highly-porous samples with BET surface areas of ~ 2000 m²/g.

Table 1. Porous texture characteristics of carbon samples.

Sample	Type of material	BET (m ² ·g ⁻¹)	DR N ₂ (cm ³ ·g ⁻¹)	DR CO ₂ (cm ³ ·g ⁻¹)
G	Graphite	13	0.01	0
MWCNT	Multiwalled carbon nanotubes	47	0.02	0
NF1	Carbon nanofibre	40	0	0
NF2	Carbon nanofibre	178	0.06	0.03
NF3	Carbon nanofibre	448	0.21	0.25
AC	Activated carbon	1757	0.67	0.36
ACF	Activated carbon fibre	1907	0.90	0.60

As expected, the carbon nanostructures incorporate some metal catalysts from their preparation. The presence of iron in the MWCNT is remarkable, as it also exists in NF1. NF2 was selected because of its nickel content. The AC incorporates phosphorus from its preparation (phosphoric acid activation).

Temperature programmed decomposition of MgH₂/C samples

Decomposition of pre-milled MgH₂ in argon was evaluated, leading to a clear endothermic DSC peak at 363°C. This sample was mechanically milled for different periods of time to use it as reference.

Table 2 shows that decomposition temperature of MgH₂ is slightly reduced with the incorporation of carbon, varying from 322 to 365°C depending on the carbon material used. In general, the decomposition temperature is lower for those milled for 1 or 2 h. Moreover, the addition of carbon avoids the formation of two overlapping peaks for 2 h. of milling, in contrast to the case for MgH₂.

Table 2. MgH₂ decomposition peak temperature (°C) for different MgH₂-based materials.

Milling time, h	MgH ₂	MgH ₂ /G	MgH ₂ /MWCNT	MgH ₂ /NF1	MgH ₂ /NF2	MgH ₂ /NF3	MgH ₂ /AC	MgH ₂ /ACF
0.25	361	363	346	358	328	358, 373	361	365
1.00	361	351	342	348	322	354	348	350
2.00	360, 376	348	341	348	322	354, 365*	354	352

* with a small shoulder

There appears no relationship between the surface area of the carbon materials and the decomposition temperature of MgH₂, since materials with relatively low porosity, e.g. graphite, and with well-developed surface area, e.g. AC and ACF, produce little added benefit to sorption temperature. However, the MWCNT and NF2 additions, both with low porosity but containing appreciable amounts of metals (iron and nickel, respectively) from their synthesis, lead to relatively large effects on the decomposition of MgH₂. Hence, this effective role of MWCNT and, especially, of NF2, should be attributed to the metallic particles that catalyse the decomposition process. Only with 5 wt% of NF2, decomposition of MgH₂ starts below 300°C, and peaks around 320°C. On the whole, the incorporation of the carbon materials can offer an additional benefit to the reduction and stability of the powder particle size (Liang et al., 1999; Güvendiren et al., 2004).

The other carbon materials, such as NF1 and NF3, show less marked effect on the decomposition temperature of MgH_2 . NF1 contains iron, although its content is lower than that in MWCNTs, whereas NF3 is a relatively pure material with only little quantities of magnesium, aluminium and other metals, which provide little activation. Phosphorus contained in AC shows little activity, since the incorporation of this carbon material does not appreciably modify the decomposition temperatures of MgH_2 .

Nonetheless, the DSC results show better effects of carbon on sorption kinetics than those shown in the literature (Imamura et al., 2003; Huot et al., 2003; Shang and Guo, 2004; Wu et al., 2006), due to the effect of metal impurities, in agreement with previous findings on pure alloying (Liang et al., 1999;). However, some previous results show that the addition of 5 wt % of Fe is catalytically more efficient than 5 wt% of Ni (Liang et al., 1999), contrary to what has been observed (comparing the performance of NF1 and NF2 with similar Fe and Ni contents, respectively). Different sizes of Fe and Ni particles could be responsible for such differences, though the actual activities may change for the carbon-supported metals.

Isothermal decomposition of MgH_2/C samples

Figure 1a shows that the addition of 5 wt% of selected carbon materials improves considerably the decomposition kinetics, reducing the decomposition time by 2 h in the case of AC. Although all the carbon materials improve MgH_2 decomposition kinetics, there is no clear correlation between the porosity in the carbon material (see Table 1) and the level of improvement in the dehydriding kinetics by the MgH_2/C system. For instance, the performance of the sample incorporating G, which presents no appreciable surface area (in the range of $13 \text{ m}^2/\text{g}$) shows little difference from that containing ACF, the most activated sorbent studied (BET surface area close to $2000 \text{ m}^2/\text{g}$).

Figure 1b plots the decomposition curves for other $\text{MgH}_2/\text{carbon}$ materials for nanomaterials, i.e. nanotubes and nanofibres, which contain metals from their preparation stages. The dehydriding kinetics varies considerably with the carbon material selected, which indicates the nanofiber morphology itself is not the only factor enhancing the desorption kinetics. In all the cases, these MgH_2/C materials perform much better than MgH_2 . With only 5 wt% addition of a nano-carbon, the decomposition time at 300°C can be reduced from 240 to 20 min., which makes these materials very promising for practical kinetic requirement in hydrogen-fuelled vehicles. The achieved kinetics is much faster than previously reported MgH_2/C samples with similar carbon contents (Wu et al., 2006).

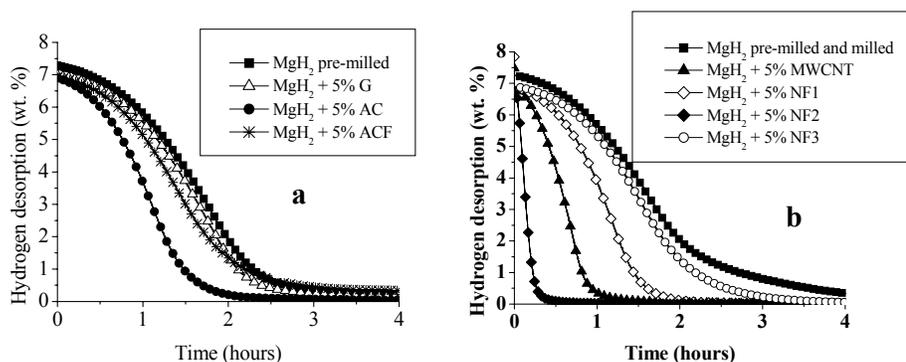


Figure 1. Comparison between the decomposition kinetics of MgH_2 and some selected $\text{MgH}_2/\text{carbon}$ systems which incorporate metals from the preparation stages of the carbon materials.

Results in Figure 1b emphasize that neither the porosity of the carbon materials nor their morphology has appreciable influence on the kinetics. For instance, $\text{MgH}_2/\text{NF3}$ shows the poorest decomposition kinetics, despite NF3 possessing the most developed surface area among the carbon materials in Figure 1b. Therefore, the large improvement must be essentially attributed to the metal particles in the carbon nanostructure (type, size and content). The most influential carbon is NF2, which contains nickel, in agreement with the DSC measurements. The iron-containing carbons (MWCNT and NF1) present an intermediate effect, whereas the poorest material, NF3, incorporates traces of other types of metals.

Modification of the dehydriding behaviour after cycling.

To evaluate the stability of these materials after cycling, DSC measurements were performed over selected samples after 5 dehydriding-hydriding cycles. Comparison between DSC curves of samples before and after cycling shows that the MgH₂ decomposition peak shifts towards slightly higher temperatures after cycling. The increase in temperature after cycling, previously reported for MgH₂ (Varin et al., 2006), seems to be associated with some structural change of the MgH₂ during cycling, also observed by colour changes in the samples.

Morphological and structural characterisations of the samples

Comparison of the XRD patterns of the Mg-based samples shows that there is an increase (or recovery) in the crystallinity of MgH₂ and a decrease in the amount of γ -MgH₂ phase after cycling. The level of increase in the crystallinity seems lower for the MgH₂ containing NF2, in comparison to other carbon-containing materials. Hence, the better decomposition characteristics of this sample is associated with the crystallinity of the milled samples and the introduction of NF2 seems to retard the recovery process of magnesium/MgH₂ particles.

Several differences can be observed by comparison of the TEM images of the MgH₂/C materials before and after cycling. Before cycling, carbon materials cannot be identified in the Mg matrix and crystalline Mg in the centre of these particles is noted, whereas the boundaries are mostly of amorphous Mg. However, the size of the crystalline Mg phases is greater after cycling, in agreement with what was observed by XRD. After cycling, the amorphous Mg phase on the surface seems rather fluffy or less dense around the surfaces than in the core, and the carbon phase can still be clearly identified.

CONCLUSIONS

The present study confirms that the dehydriding conditions of MgH₂ can be modified by the addition of carbon materials, particularly those that contain catalytic metal nanoparticles. The temperature programmed and isothermal decomposition experiments show that the addition of NF2, MWCNT and NF1, which contain nickel or iron, considerably improves the dehydriding kinetics, in comparison with the other carbon materials. The introduction of only 5 wt% of NF2 to the MgH₂-based materials reduces its decomposition time from 240 to only 20 min. at 300°C. These materials are stable and their decomposition kinetics remains unchanged at five dehydriding/rehydriding cycles.

Some changes are observed in the MgH₂-based materials after cycling: the XRD shows a certain level of increase in crystallinity of the MgH₂, with evident particle growth. However, this increase is lower for the carbon-containing samples, which is one of their beneficial effect. This crystalline growth is corroborated by TEM, together with the observation of some separation of carbon from the Mg phases. The gain in crystallinity and particle growth are responsible for the slight shift in decomposition peak towards a high temperature, as evidenced from the DSC results.

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ACKNOWLEDGMENTS

M.A. Lillo-Ródenas thanks GV for a postdoctoral fellowship (AEST06/002). The authors thank MEC (project CTQ2006-08958/PPQ), the EU (Feder), Hytrain (MRTN-CT-2004-512443) and the UK EPSRC (GR/S26965/01, GR/S52636/01) for financial support.