IMPROVEMENT OF MgH$_2$ SORPTION KINETICS BY CARBON-SUPPORTED NICKEL CATALYSTS

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ABSTRACT

The present study analyses MgH$_2$ decomposition catalysed by nickel-based materials, showing that some parameters (i.e. catalyst content, composition, preparation method and milling time) strongly affect their activity. Carbon-supported catalysts have shown superior performance than those prepared by physical mixing and, especially those only containing Ni. This emphasizes the role played by carbon on their activity. Selected catalysts give rise to a reduction in the decomposition temperature of MgH$_2$ by 150ºC. However, comparison among carbon-supported materials of different Ni sizes shows little difference in their isothermal decomposition kinetics. Suitable selection of the preparation conditions leads to the MgH$_2$ being fully decomposed in just 9 min. at 300ºC, in comparison to 240 min. for the undoped MgH$_2$.

INTRODUCTION

Magnesium hydride satisfies most of the requirements for hydrogen storage, although its practical use is impeded by its high decomposition temperature and slow kinetics. Numerous works have studied the use of catalysts. Literature compiles different Mg-based systems effectively catalysed by nickel (Bogdanovic et al., 1999; Liang et al., 1999; Berlouis et al., 2000; Tessier et al., 2000; Bobet et al., 2001; Jensen et al., 2006; Varin et al., 2007a; Varin et al., 2007b; Hanada et al., 2005; Kojima et al., 2006 ; Yoo et al., 2006).

In the present study we are focusing on Mg-based systems which incorporate carbon-supported Ni, encouraged by previous results (Lillo-Ródenas et al., 2007) and by the scarce literature data about the use of carbon-supported catalysts for this purpose. Thus, the improvement of nickel dispersion using a wide range of carbon materials and the beneficial role shown by carbon are analysed.

EXPERIMENTAL

MgH$_2$ powder was purchased from Th. Goldschmidt AG (95 wt.% MgH$_2$ and 5 wt.% Mg and an average diameter of 50 μm). Table 1 summarises the nomenclature and some features of the carbon materials selected. Ni(NO$_3$)$_2$•6H$_2$O (Fluka, p.a.) was used as the Ni precursor. Elemental nickel (3 μm size, Sigma-Aldrich), was used for the preparation of some samples and is referred to as micrometric nickel.

Table 1. Summary of the carbon samples used in the present study.

Sample	Type of material	Commercial reference	Company
G	Graphite	General purpose	Fisher Chemicals
MWCNT	Multiwalled carbon	(Andrews et al., 1999)	CAER, University
NF	Carbon nanofibre	GANF	Grupo Antolín
AC	Activated carbon	A1100 10x25	Mead Westvaco
ACF	Activated carbon fibre	ACT-25	Nippon Kynol Inc.

Carbon supports were characterised by physical adsorption of gases, N$_2$ and CO$_2$ at –196ºC and 0ºC, respectively, (Rodríguez-Reinoso et al., 1988) using an Autosorb 6-B (Quantachrome Corporation).

Carbon-supported Ni catalysts were prepared by impregnation, using Ni(NO$_3$)$_2$•6H$_2$O, on the supports previously oxidised by H$_2$O$_2$ (whose nomenclature include "-ox"). All the catalysts were reduced in pure H$_2$ up to 500ºC, held for 5 h and characterized by transmission electron microscopy (TEM) using a JEOL JEM-2010 high-tilt instrument operating at 200 kV.

Before mixing and milling MgH_2 and the different catalysts, the hydride was pre-milled in Ar for 15 hours. Then, different MgH_2-catalyst mixtures were milled up to different times (from 5 min. to 20 h.) in a high energy SPEX 8000 mill under argon atmosphere. Three types of MgH_2 samples containing nickel were prepared: 1st type, containing carbon-supported nickel catalysts, 2nd type of samples containing micrometric nickel and 3rd type, comprising micrometric Ni and carbon physically mixed.

Decomposition temperature of MgH_2 was determined by differential scanning calorimetry (DSC) (Setsys-Setaram). A heating rate of $5°C\ min^{-1}$ was used and the experiments were performed under flowing Ar (BOC gases, 99.999% purity) of $90\ ml\ min^{-1}$. Sample weights in the range of 2-4 mg were used. The hydrogen titration in the different samples was performed at 300°C and 0.1 kPa using a volumetric equipment (Pct-Pro 2000, Hy-Energy) and high purity hydrogen (BOC gases, 99.999% purity). Around 100 milligrams of sample were used.

RESULTS AND DISCUSSION

Carbon supports
Table 2 shows that the carbon supports under study strongly differ in terms of porosity, covering materials from no apparent porosity to BET specific surface areas in the range of 2000 m^2/g.

Table 2. Textural characterisation of the carbon samples used.

Sample	BET $(m^2 \cdot g^{-1})$	DR $N_2\ (cm^3 \cdot g^{-1})$	DR $CO_2\ (cm^3 \cdot g^{-1})$
G	13	0.01	0
MWCNT	47	0.02	0
NF	178	0.06	0.03
AC	1757	0.67	0.36
ACF	1907	0.90	0.60

Carbon-supported nickel catalysts
Figure 1 compiles some of the obtained TEM images showing that, as expected, nickel dispersion is very different depending on the porosity of the carbon support. Thus, the mean Ni particle size is in the range of 50 nm, for G-ox, around 15 nm, for MWCNT-ox and NF-ox supports, and in the range of 8 nm for samples supported on AC and ACF.
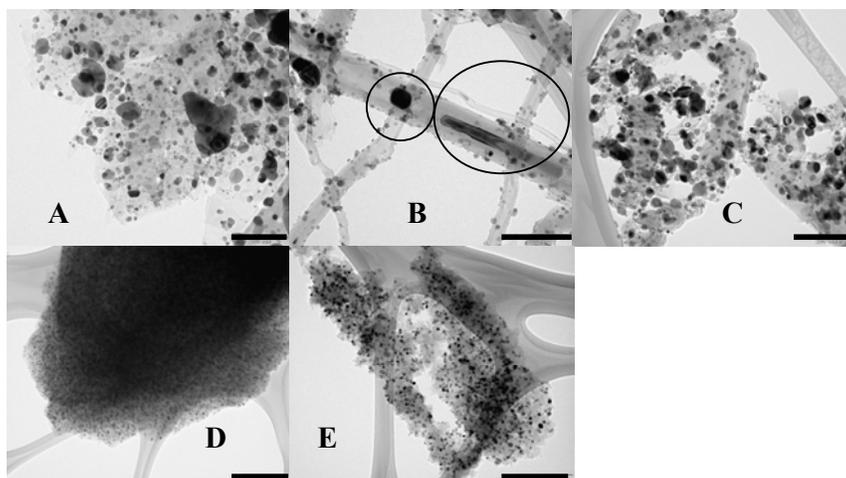
Figure 1. TEM images of the different carbon-supported nickel catalysts: a) Ni/G-ox, b) Ni/MWCNT-ox, c) Ni/NF-ox, d) Ni/AC-ox and e) Ni/ACF-ox (the bar corresponds to 200 nm).

Temperature programmed decomposition

The information obtained is compiled in Table 3, which presents the temperatures for the decomposition of MgH_2 followed by DSC, for samples prepared in different conditions. MgH_2 is used as a reference. For MgH_2, milling for longer than 2 h. leads to two overlapped DSC peaks. The appearance of shoulders or two peaks in the decomposition of MgH_2 has been previously reported in the literature as

Sample	Type of material*	DSC decomp peak at 15 min milling time (ºC)	DSC decomp peak at 60 min milling time (ºC)	DSC decomp peak at 120 min milling time (ºC)
MgH_2	Ref.	361	361	360, 376**
1%Ni/4%G-ox/MgH_2	1	286**, 345	291	293
1%Ni/4%NF-ox/MgH_2	1	267	275	293
1%Ni/4%AC-ox/MgH_2	1	302**, 335	270	292
1%Ni/4%ACF-ox/MgH_2	1	337, 371**	300**,365	275**, 345
2%Ni/8%G-ox/MgH_2	1	277	279	283
2%Ni/8%MWCNT-ox/MgH_2	1	217	245	270
2%Ni/8%NF-ox/MgH_2	1	242	263	286
2%Ni/8%AC-ox/MgH_2	1	260	260	290
1%Ni+MgH_2	2	328, 366**	308**, 363	318**, 363
2%Ni+MgH_2	2	318, 364**	309**, 375	309, 367[a]
2%Ni+8%G-ox+MgH_2	3	324, 370**	306**, 342	298

due to bimodal distribution of particle sizes in the initial stages of milling (Shang and Guo, 2004).

Table 3. Temperature for the DSC decomposition peak(s) of samples milled for different times (wt.% of MgH_2 is the difference up to 100%).

* According to the description in the experimental section
** Most intense peak, [a] both peaks have the same intensity.

The introduction of carbon-supported nickel catalysts with 1 wt.% Ni leads to a relevant decrease in the decomposition temperature of MgH_2, especially remarkable for the AC-ox, NF-ox or G-ox-supported catalysts. Comparison between these data and those for sample 1%Ni+ MgH_2 (2nd type) shows that for a similar nickel content, the decomposition temperatures for MgH_2 are lower when incorporating the carbon-supported nickel catalysts, underlining the role played by carbon.

By increasing the amount of nickel to 2 wt.%, lower decomposition temperature is achieved. Thus, a decomposition temperature as low as 217ºC is observed for the Ni/MWCNT-containing sample. Such important decrease followed by DSC has never been reported neither by the addition of carbon materials, as concluded in a previous publication (Lillo-Ródenas et al., 2007), nor by the addition of different Ni-based catalysts (Berlouis et al., 2000; Tessier et al., 2000; Jensen et al., 2006 ; Varin et al., 2007a; Varin et al., 2007b; Yoo et al., 2006).
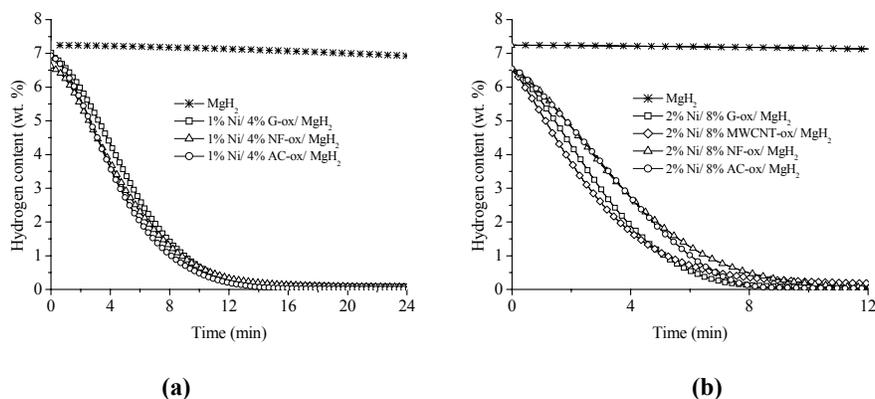
Decomposition temperature of MgH_2 in samples containing 2 wt.% Ni supported on carbon has been compared to that in a sample prepared using 2 wt.% micrometric nickel and MgH_2. Although the introduction of micrometric Ni lowers the decomposition temperature of the hydride, in agreement with published data (Berlouis et al., 2000; Tessier et al., 2000; Jensen et al., 2006), this temperature is even lower when the carbon-supported catalysts are incorporated.

An additional material was prepared by mixing 2 wt.% micrometric nickel, 8 wt.% G-ox and MgH_2 (3rd type). However, decomposition temperatures for MgH_2 are much lower for the carbon-supported nickel sample, what confirms the important role played by the size of nickel used as catalyst in the decomposition temperature of MgH_2 or by the interaction between nickel and carbon when the catalyst is supported. In this sense, the literature shows that the amount of H_2 chemisorbed on a Ni-carbon material is strongly dependent on the nickel size and on the method of preparation, being the mechanical mixture of nickel and graphite that showing poorer results (Zhong et al., 2002).

Isothermal decomposition

Figure 2a presents the decomposition kinetics at 300ºC for samples containing 1 wt.% nickel supported on three different carbon materials. Decomposition kinetics of MgH_2 in these samples is much faster that in MgH_2. Thus, only 15 min. are required for complete decomposition of the hydride at 300ºC and the amount of H_2 recovered agrees with what is theoretically expected considering their composition. In contrast, four hours are required for complete decomposition of the pure hydride at 300ºC.

Results for samples supported on different carbon materials show that only slight differences in the decomposition of the hydride exist, despite the difference in the surface area of the supports and, especially, in the size of the nickel particles deposited on them, as observed in Figure 1. This implies that, in this range of Ni particles sizes, from 8 to 50 nm, no important differences in the activities exist.

(a) **(b)**

Figure 2. Comparison between decomposition kinetics of MgH_2 in samples containing: a) 1 wt.% Ni supported on carbon, milled for 60 min., b) 2 wt. % Ni supported on carbon (Samples using MWCNT-ox and NF-ox milled for 15 min., those containing G-ox and AC-ox milled for 60 min.).

The effect of the increase in the amount of the carbon-supported nickel catalyst on the decomposition kinetics has also been studied, according to the better results previously shown in the DSC measurements. Thus, supported materials containing 2 wt. % Ni, 8 wt.% carbon and MgH_2 were tested. Figure 2b shows that MgH_2 decomposition kinetics in these samples is very fast. Only 9 min. are required for the total decomposition of the hydride, a substantial decrease in time in comparison to samples containing 1 wt.% Ni/ 4wt.% carbon/ MgH_2. Note that best milling time for each support was selected according to the results obtained in the DSC measurements (Table 3).

Figure 3 compiles the MgH_2 isothermal decomposition for samples prepared using the same Ni contents, but different methods and compositions. MgH_2 and MgH_2+ 5 wt. % G-ox are presented as reference. This figure shows that the best sample is that in which nickel was supported on G-ox (mean Ni particle size around 50 nm). For that prepared using a physical mixture with the same composition of micrometric size Ni, G-ox and MgH_2, decomposition kinetics of the hydride is slower, underlying the importance of the nickel size or the carbon-nickel interaction in its catalytic properties. The mean size of the micrometric Ni added is 3 μm, although it might be reduced as a result of the milling process.
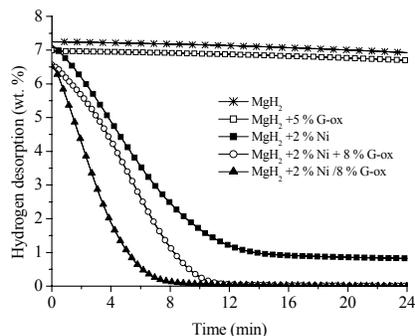
Figure 3. Comparison between the decomposition kinetics of MgH_2 and samples containing 2 wt.% Ni prepared in different conditions.

The sample prepared using 2 wt. % micrometric Ni in absence of G-ox shows much slower decomposition kinetics. Moreover, not complete recovery of the H_2 is achieved after 2 h. These results remark the beneficial effect not only of the catalyst, but also of the presence of carbon.

Decomposition kinetics of MgH_2-doped nickel has been previously studied in the literature. Varin et al. (2007a) reported the desorption of 5 wt.% H_2 in 16 min. at 300ºC in their 2 wt.% Ni-based materials, whereas Yoo et al. show that around 12 min. are required for 6 wt. % hydrogen recovery for some of their materials at the same temperature. Berlouis and co-workers checked that Mg-based materials containing different amounts of nickel deactivate after cycling, what is in agreement with the low hydrogen desorption from our 2 wt.%Ni + MgH_2 sample. Very good kinetic results have been reported for systems containing Ni-nanoparticles (Hanada et al., 2005) or for nano-composite material containing nano-Ni, Al_2O_3 and C (Kojima et al., 2006).

Additionally, it must be emphasized that the behaviour of the samples containing carbon-supported nickel catalysts is stable after five cycles and total hydride decomposition takes place.

CONCLUSIONS

Carbon-supported catalysts perform much better than the non-supported Ni or the samples without the metal. Those with unsupported nickel show the highest MgH_2 decomposition temperatures and the slowest kinetics. The fact that the introduction of carbon by physical mixture improves the kinetics outlines the importance of the composition of such catalysts and the fact that carbon must be one of their components.

Porous texture of the supports has shown, as expected, an important effect on the mean size of the Ni particles. However, this has little effect on the catalytic role of the nickel in this range of sizes.

The amount of nickel supported on carbon, from 1 to 2 wt.%, has also shown some effect on the decomposition of MgH_2. Thus, small amounts of carbon-supported Ni catalysts improve the decomposition of MgH_2, reducing decomposition time at 300ºC from 4 h to 9 min. or the DSC decomposition peak temperature by up to 150ºC. The prepared samples are stable after five cycles and the hydride is completed decomposed in each cycle.

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