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Effective hydrogen production by hydrolysis of Mg wastes reprocessed by mechanical milling with iron and graphite

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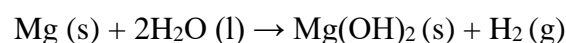
Keywords: Hydrogen production, Hydrolysis, Magnesium alloys, Mechanical milling

Abstract

The reprocessing by mechanical milling of Mg scraps from the manufacturing of sacrificial anodes to produce H₂ by hydrolysis is discussed. In particular, the effects of iron and graphite as additives to improve the hydrolysis reaction are presented. It has been found that by pre-milling the scraps under air atmosphere for 10 h with 1.5 wt% of Fe followed by an extra milling of 1 h with 5 wt% of graphite produces the best results. Fe contributes to speed up the reaction rate by inducing microgalvanic coupling with Mg, and graphite plays a significant role as process control agent during milling inducing a significant size reduction of the material. As the shape of the hydrolysis curves is compatible with a kinetic process controlled by volume contraction, the acceleration of the movement of the Mg/Mg(OH)₂ interphase induced by the galvanic coupling, and the reduction in size both contribute to a faster H₂ production. Additionally, the performance of the material favorably compares with similar materials reported in the literature producing 775(24) mL/g of H₂ in 5 minutes, and 780(24) mL/g when the reaction finishes (80(2) % yield).

1 Introduction

Hydrogen is widely considered as the energy carrier of the future, due to its environmental friendliness, high energy density and versatility [1]. However, several challenges continue to block its large-scale application. Indeed, scientific, technological and economic issues need to be solved for a hydrogen-based energy paradigm to become a reality [1-2]. The storage of hydrogen is one of them [2]. One alternative to overcome it is simply to produce hydrogen on demand. In this way, small portable devices could be recharged and short-range assisted vehicles could be powered. One way to produce hydrogen for these applications is the hydrolysis reaction. For light metals like Mg or Al this reaction is a relatively simple process that has a high theoretical hydrogen yield of 933 mL/g and 1245 mL/g, respectively, and in principle spontaneously occurs at ambient temperature and pressure [3-4]. In the case of Mg the hydrolysis reaction is:



For the reaction to proceed at a fast and continuous rate some processing and conditioning of the material has to be done. This is needed to minimize the formation of a compact Mg(OH)₂ layer that practically stops the reaction. One effective way to do this is by processing the materials by mechanical milling to simultaneously reduce size, change morphology and incorporate additives that favor reactivity [3-4]. Many elements or compounds have produced a speed up of the

hydrolysis reaction in the past years when incorporated to Mg as additives [3-4]. The focus is, in this Section, on the effect of transition metals and carbon. Kravchenko *et al.* [5] have studied the effect of different amounts of Ni, Cu, Co and Fe on Mg hydrolysis by preparing mixtures by fusion or mechanical milling. They have found that the incorporation of all these metals considerably increases the hydrolysis rate, and that this effect is more pronounced in the mechanically alloyed materials. In this case, hydrogen yields of the order of 80 % were obtained after 20 minutes of reaction, with the higher rates following the sequence: Co > Ni > Fe > Cu. Wang *et al.* [6] have studied the hydrolysis properties of Mg – Al – Fe mixtures prepared by mechanical milling. They have found that increasing the milling time and the amount of Fe improves both the rate of the process and the hydrogen yield (disregarding the loss due to the presence of the non-reacting Fe). The effect is attributed to the formation of micro-galvanic cells that improve reactivity. In these mixtures both Mg and Al are hydrolyzed. By using different aqueous solutions, they have also found that the presence of cations with strong affinity to OH⁻ anions (Ca²⁺ or Mg²⁺) affects the yield of the reaction by reducing the alkalization effect that promotes Al hydrolysis. Awad and coworkers [7] have studied the hydrolysis properties of Mg and MgH₂ mixtures with Fe, Ni, graphite, and other additives incorporated by mechanical milling. They have found that when using single additives the best performance occurs for the mixtures with C, followed by Ni and Fe. However, faster kinetics were observed when milling the transition metals simultaneously with C. The improvements have been attributed to a synergetic effect between the lubricating effect of C during milling and the formation of microgalvanic cells. Sevastyanova *et al.* [8] have studied the hydrolysis of Mg-Fe and Mg-Cu “mechanical alloys” in different chlorides solutions. They have reported that the incorporation of Fe or Cu noticeably improves the hydrolysis properties of Mg compared with a material milled without additives. The amount of transition metal incorporated does not have a measurable effect on hydrogen yield, but have it on the rate. Additionally, they have shown that solutions of Ni, Co or Cu chlorides are more reactive than NaCl solutions. More recently Ma and coworkers [9] have studied the hydrolysis of Mg powder mixed with expandable and expanded graphite. The mixtures have been prepared by conventional planetary ball milling and by plasma-assisted ball milling. They have found that the morphology of graphite and the type of milling have an effect on the hydrolysis properties of the materials, with the best results corresponding to the mixture prepared with expanded graphite by plasma-assisted milling.

Regarding the raw material, if Mg-based industrial wastes are used instead of pure alloys to produce H₂, another advantage is added: the reduction of an environmental liability. Effectively, the small chips generated by machining during industrial processes that use Mg alloys cannot be efficiently recycled and constitute an environmental problem due to Mg’s pyrophoricity. As the industrial use of Mg alloys has recently increased thanks to Mg’s light weight, good mechanical properties and economic convenience, there are plenty resources of Mg scraps available. For these reasons several papers have recently reported hydrogen generation from the hydrolysis of Mg wastes [10-20]. Cho *et al.* [10] have studied the hydrolysis of Ni-rich AZ91D alloys. They have used recycled ingots discarded for having Ni contents in excess of the ASTM B93 standard. These inexpensive waste materials were useless for industrial applications but very convenient for hydrogen production, as the Ni excess increases the corrosion rate by two orders of magnitude, improving the hydrolysis properties of the material. Uan *et al.* have explored hydrogen production from low-grade Mg wastes using catalytic nets [11-13]. In [11] they have studied the effect of a Pt-coated Ti net. They have found that by grinding the net against the surface of remelted Mg wastes H₂ can be produced at a stationary rate, whereas the production stops once a passive Mg(OH)₂ layer forms on the surface if the net is statically loaded. In [12] they compare a Pt-coated Ti net and a 304 stainless-steel net embedded in remelted Mg scraps. Both nets produce H₂ at a steady rate, but the Pt-coated Ti net produces a greater amount of H₂ per unit time. In [13] they report that H₂ can be efficiently produced by the addition of citric acid to natural seawater with or without stainless-steel catalytic nets. Matsuzaki *et al.* [14] have produced H₂ by hydrolysis during mechanical milling of Mg or AZ91 commercial alloy chips. The mechanical process effectively removes the Mg(OH)₂ layers formed during the reaction and exposes fresh surface, thus yielding a more efficient hydrogen

production process compared with a stationary process. Al Bacha and coworkers have explored the effect of Ni, C and AlCl₃ as additives on the hydrolysis of Mg-based alloys wastes [15-17]. In [15] and [16] wastes from the manufacturing of sacrificial anodes have been processed by mechanical milling using two different devices (Fritsch-Pulverisette P6 and Uni-Ball Mill II), with inert (Ar) or reactive (H₂) atmospheres and employing C and AlCl₃ as additives. The main results of these studies are: 1) the materials milled under Ar have in general better yield than those prepared under H₂, despite the formation of MgH₂, 2) the incorporation of additives clearly improves the hydrolysis performance of the materials, with the sequential incorporation of 5 wt% C followed by 5 wt% AlCl₃ being the best strategy, and 3) the materials processing could be successfully scaled up from a small scale device (P6) to an intermediate scale device (Uni-Ball). In [17] the hydrolysis of wastes of the WE43 Mg commercial alloy has been studied. The material was also processed by mechanical milling, but in this case C and Ni have been used as additives. The sequential incorporation of Ni and then C has been identified as the processing that gave the best results, with a full reaction in less than 10 minutes. Akbarzadeh *et al.* have reported a “waste plus waste to hydrogen” method that produces hydrogen by the hydrolysis reaction of Mg wastes in a solution made with wastewater from a brewery and acetic acid [18]. The highest hydrogen generation rate observed was around 1 NL/min using a solution with 30 wt% of acetic acid at 50°C. Hou and coworkers have explored hydrogen production from wastes of different Mg-based commercial alloys using (Mg₁₀Ni)₉₀Ce₁₀ as additive [19]. They have found that the hydrolysis performance improves when the wastes are mechanically milled and further improves if the additive is used. With the addition of 20 wt% of additive they have produced 81 % of the theoretical capacity of the material after 2 minutes of reaction at 55°C. Recently, in our lab we have explored the reprocessing of scraps from the manufacturing of sacrificial anodes by milling under air atmosphere and using no additives [20]. We found that H₂ can be successfully produced with good kinetics and yield, and studied the effects on hydrolysis of milling time, particle size, and presence of different phases. In this work we improve the performance of the same Mg wastes by optimizing their reprocessing throughout the incorporation of graphite and iron by mechanical milling under air atmosphere. Graphite was selected for its lubricating effect during milling (process control agent) [21] and positive effects on hydrolysis [7, 9, 15-17, 22], and iron was chosen for the formation of galvanic pairs with Mg and the consequent improvement of the hydrolysis reaction [5-8]. We show that by a reprocessing scheme consisting of first milling the starting material with 1.5 wt% of iron for 10h followed by 1 h of extra milling with 5 wt% of graphite produces a material with excellent kinetics and yield. It produces 775 (24) mL/g of H₂ in 5 min, and a total yield of 80 (2) %. The milling process is carried out under air atmosphere, a fact that considerably simplifies the process and also constitutes an economic advantage considering the potential scaling up of the process. Additionally, the abundance and low cost of the selected additives also contribute to the cost effectiveness of the process.

2 Experimental

The starting material (Fig. 1) were Mg scraps from the manufacturing of sacrificial anodes¹. The scraps are in fact a mixture of ASTM alloy AZ31 chips and Al scraps with a global composition estimated at 90 wt% Mg, 9 wt% Al and minor amounts of Zn, Cu and Mn. The additives used were graphite powder (99 % Aldrich, < 20 μm) and Fe powder (99 % Riedel-de Haën, < 212 μm). The materials were processed by mechanical milling using a Fritsch-Pulverisette P6 device. The milling conditions were a ball to powder ratio of 40:1, air atmosphere, 400 RPM and cycles of 10 minutes of milling followed by 20 minutes of rest. The milling sequence and the type and amount of additives used for the different studied materials are detailed below.

¹ Provided by Roberto Cordes S.R.L.

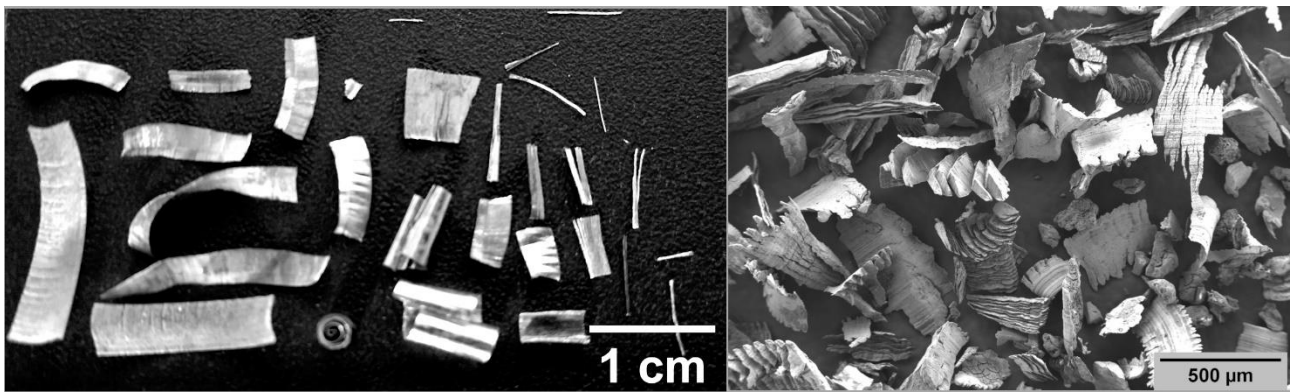


Figure 1: Images of the starting material. Left: bigger size fraction (optical microscope), right: smaller size fraction (SEM).

Structural characterization has been done by X-ray diffraction (XRD) using a Bruker Advance D8 instrument with a Cu anode operated at 40 kV and 40 mA and a Lynxeye detector. Diffraction data have been Rietveld-refined using Fullprof [23]. The morphology of the materials has been analyzed by Scanning Electron Microscopy (SEM) using a Zeiss Crossbeam 340 microscope. The hydrolysis reaction has been studied using a custom made instrument described in detail in [24]. Briefly, H_2 generation has been quantified by weighing the amount of water displaced by the H_2 produced. The reaction has been carried out with around 25 mg of sample in 50 mL of a 0.6 M $MgCl_2$ aqueous solution whose temperature is kept constant at 24 °C by means of a thermal bath. Once the reaction practically stopped, 10 mL of 0.5 M HCl were added to the solution to ensure the completion of the reaction.

3 Results and discussion

3.1 Milling strategy optimization

The best milling strategy for milling with graphite and iron was selected after several tests in which the performance of the materials with additives was compared with those of the scraps milled without additives, as detailed below. A careful analysis of the hydrolysis properties of this last material can be found in [20].

3.1.1 Graphite

When the materials are prepared by milling the raw Mg scraps with graphite from the start, the efficiency of milling is reduced compared with the material obtained by milling without additive. As a consequence of this, a smaller size reduction, a diminished microstructural and morphological evolution, and a slower hydrolysis reaction are observed (results not shown here). The effect is attributed to the well-known lubricating effect of graphite during milling [21]. For this reason, it was decided to explore the effects of graphite addition to pre-milled Mg scraps. In this section the effects of the quantity of graphite used and the milling time after the incorporation of the additive are discussed. Based on the results of [20] the Mg scraps were pre-milled for 10 h and only the fraction that passed through a 100 μm sieve was kept. The mixing with different graphite amounts has been done manually using a mortar and pestle under air atmosphere for a total duration of 15 minutes. This process does not produce significant changes on the morphology and size of the material, but produces a noticeable effect on the hydrolysis curves (Fig. 2, 5 wt% C).

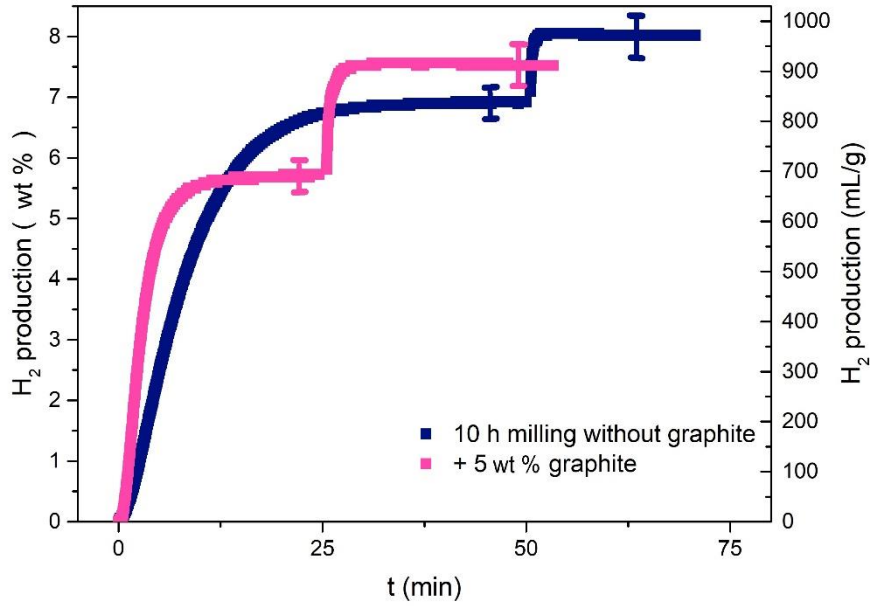


Figure 2: Effect of graphite on the hydrolysis reaction. By adding 5 wt% of graphite the hydrolysis reaction takes less time. The yields after acid addition are similar in both cases. Error bars correspond to estimated errors before and after acid addition.

Effectively the incorporation of graphite improves kinetics, but also reduces the yield before acid addition. The kinetic improvement can be attributed to a faster corrosion rate of Mg in the presence of C [22]. This faster reaction with many nucleation sites could also produce a continuous and compact layer of $\text{Mg}(\text{OH})_2$ that eventually stops the reaction, thus explaining the lower yield before acid addition. When acid is added, the hydroxide layer is dissolved and similar yields are observed for both materials taking into account the small reduction in H_2 generation due to the incorporation of the non-hydrolyzable C.

Fig. 3 compares the kinetics and yield of the materials with 1 wt%, 2.5 wt%, 5 wt% and 10 wt% of graphite. Kinetics is evaluated by the time taken to reach a H_2 production of 3 wt%.

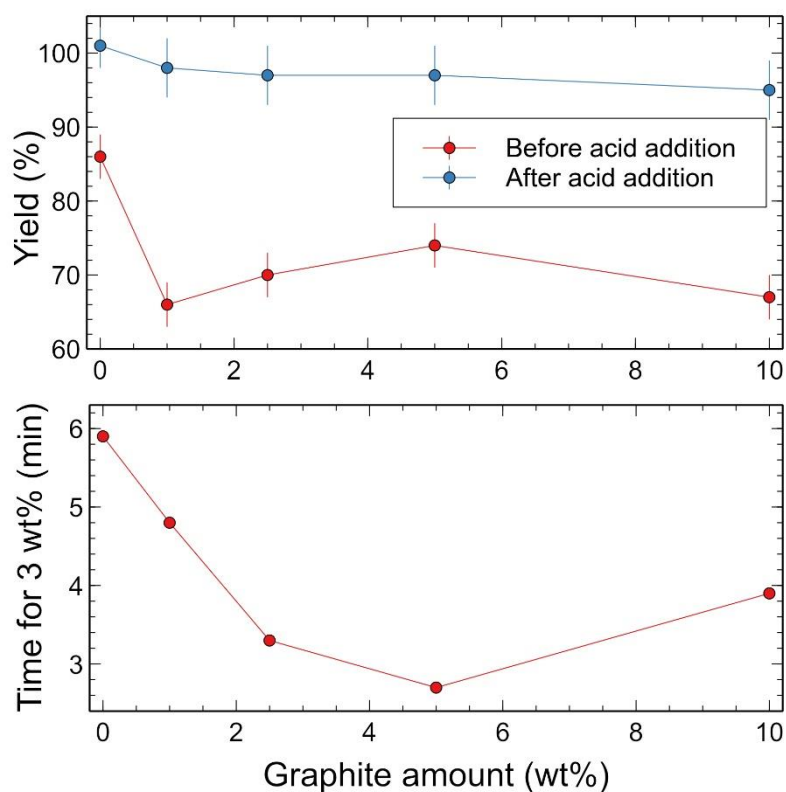


Fig. 3: Kinetics and H₂ yield with different amounts of graphite. The incorporation of 5 wt% of graphite produces the best kinetics and yield.

The material with 5 wt% of graphite shows the best kinetics (characteristic time reduced to less than a half) and yield before acid addition. As expected, after acid addition yields are all similar.

After having identified an optimal amount of graphite, the effect of incorporating this quantity of graphite to the 10 h pre-milled mixture by mechanical milling different times was explored. To this end, 5 wt% of graphite has been added to the pre-milled material and the mixture was further milled different intervals. A single batch was prepared and samples were extracted after milling 5 min, 10 min, 20 min, 1 h, 2 h and 5 h². For simplicity, the extraction process has been done under air. The extracted material has been size selected by using a 200 μ m sieve.

Milling with graphite induces important changes in the size of the material. The SEM images of Fig. 4 show that size continuously decreases when milling up to 1 hour. After that, the agglomerates size starts to increase. The initial decrease in size is attributed to the lubricant effect of graphite. When milling up to 1 hour, graphite is mainly located on the surface of the material and significantly reduces the cold welding phenomena thus producing a size reduction. After 1 hour of milling graphite starts to be incorporated in the bulk and the lubricating effect is gradually lost, with the consequent increase in size. More evidence of the movement of graphite from the surface to the bulk with milling time can be seen in the amount of MgO quantified by Rietveld refinement of the XRD patterns of the samples. The successive openings of the milling chamber to extract the samples increased the amount of MgO in the material. In Fig. S1 the quantity of MgO in the material is plotted as a function of the number of openings. It can be seen that the jumps in the amount of MgO from one opening to the other are smaller up to 10 - 20 minutes of milling and increases reaching a constant value of around 2.3(3) wt% from 1 h of milling on. This behavior can be explained by considering that graphite is on the surface of the material for shorter milling times

- 2 After having extracted a sample for a predefined milling time, the milling chamber was closed under air atmosphere and the material was further milled to obtain the next sample. As a consequence of this, the amount of MgO in the material monotonically increased with milling time.

and thus protects the material against oxidation [15]. As milling time increases, it is incorporated into the bulk and its protective effect diminishes³.

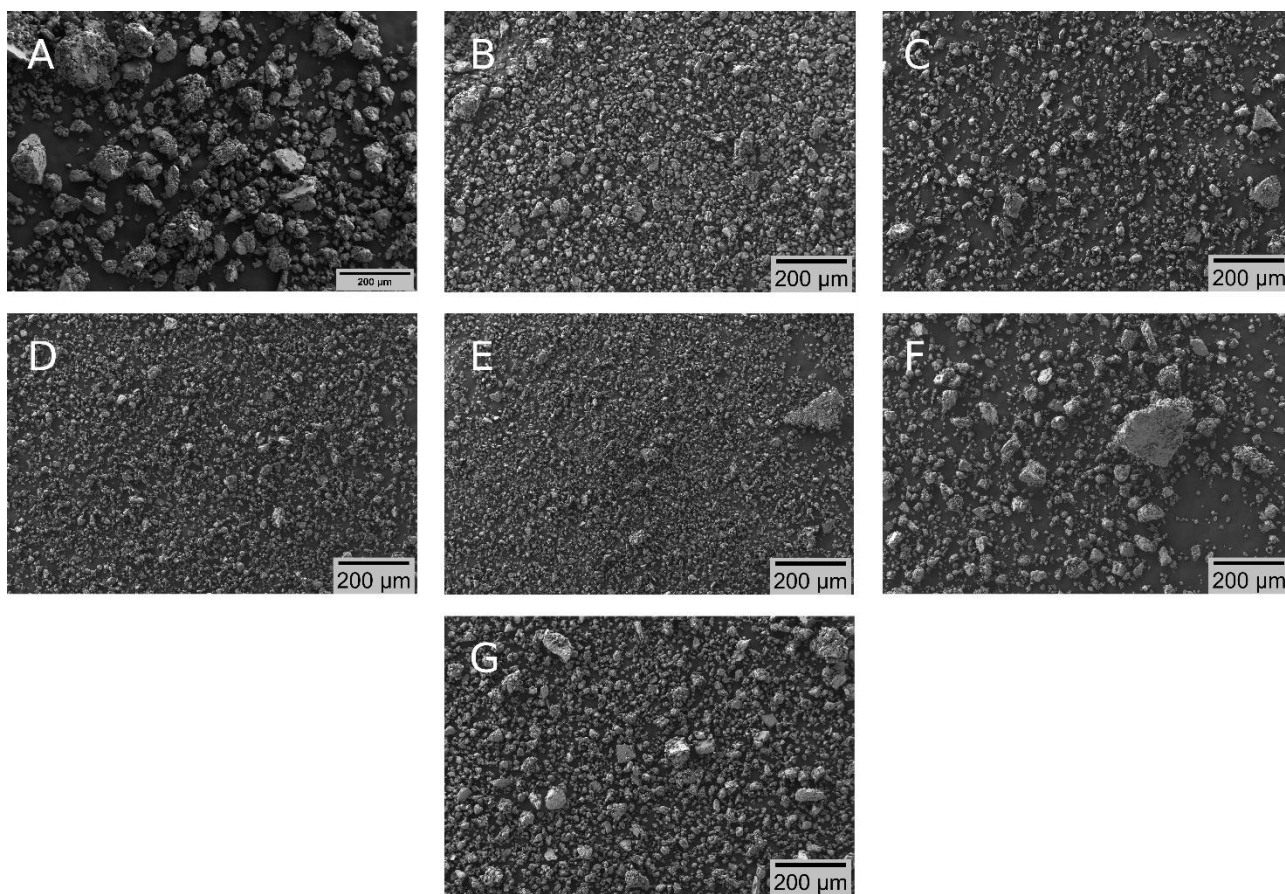


Fig. 4: SEM images of the materials milled without graphite (A) and with 5 wt% of graphite during 5 min (B), 10 min (C), 20 min (D), 1h (E), 2 h (F) and 5 h (G).

From the hydrolysis point of view, the best kinetics is obtained for the 1 h-milled material. Fig. 5 compares the hydrolysis curves of the material without graphite and the one milled 1 h. The time taken to produce 3 wt% of H₂ is reduced fourfold from 20 minutes to 5 minutes. In this case the yield is also reduced by the greater proportion of non-hydrolyzable MgO accumulated during the previous milling steps (9.2 ± 0.4 wt%).

3 The stationary increase in the amount of MgO of 2.3(3) wt% after 20 minutes of milling is similar to the 1.8 wt% estimated considering that all the O₂ in the milling chamber is consumed to form MgO during milling (an extra contribution may arise from the exposure of the milled material to air when opening the chamber).

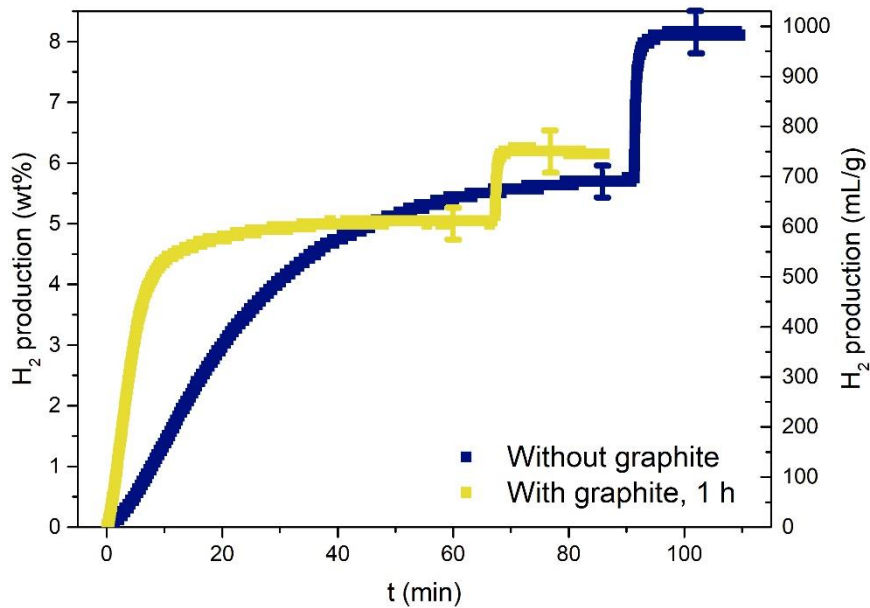


Fig. 5: Hydrolysis curves of the material without graphite and with 5 wt% of graphite and milled 1h.

3.1.2 Iron

The incorporation of Fe has been done from the start of the milling, as Fe does not have a substantial effect as process control agent. Besides the already cited literature reports that show the effects of rather high amounts of Fe enhancing Mg hydrolysis [5-7] the positive effect induced by small amounts of Fe incorporated in the material by contamination from the milling tools during mechanical processing has been observed by us. To have more control on its amount, and taking into account that the quantity of Fe incorporated by contamination was around 1.0 wt%, it was decided to include 1.5 wt% of Fe to the scraps in the pre-milling stage. To see the positive effect of this additive on the hydrolysis reaction Fig. 6 presents the curves of the material obtained by milling 10 h the scraps with 1.5 wt% Fe (2.5 wt% total Fe amount, the extra contribution comes from contamination) and the material obtained by milling just the raw scraps 10 h (total Fe content 0.7 wt%, from contamination).

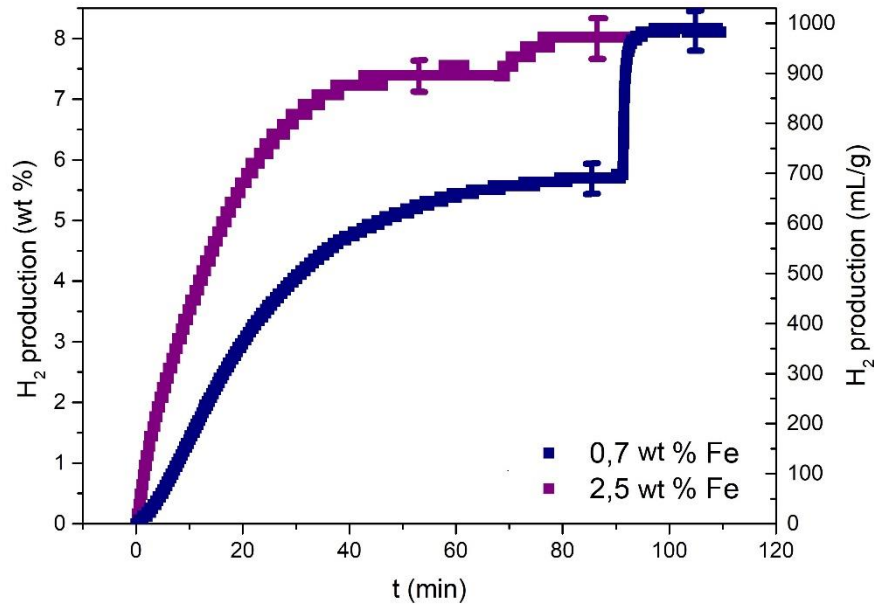


Fig. 6: Hydrolysis curves of two materials with different Fe content. The purple one corresponds to the material with 2.5 wt% Fe (1.5 wt% included in the mixture, the rest comes from contamination from the milling tools) and the blue curve to the material milled without intentionally including Fe (the content of 0.7 wt% arises from contamination).

It can be seen that kinetics is considerably enhanced by the greater quantity of Fe present in the material. Fe forms a galvanic pair with Mg and favors Mg corrosion (the open circuit potentials of Fe and Mg respect to a saturated calomel electrode are -0.7 V and -1.65 V, respectively). The kinetic improvement is attributed to Fe, as size, morphology, microstructure and abundance of the other phases are all similar in both materials (see Fig. 7 below and Table S2 in the supplementary material).

3.2 Effect of additives

Based on the results of the previous Section, the selected processing strategy consist of a pre-milling step of 10 h with the raw scraps and 1.5 wt% Fe followed by milling with 5 wt% C for 1 h. In this Section the material obtained following this processing is described and compared with a material milled 10 h without additives.

3.2.1 Morphology and composition

Fig. 7 shows the marked differences in size by milling with or without graphite. The images correspond to materials that have been previously sieved by a 100 μm sieve. Effectively, the incorporation of Fe does not produce any substantial effect on size or morphology, but on the contrary, the addition of graphite and just 1 h of milling considerably reduces the characteristic size of the agglomerates.

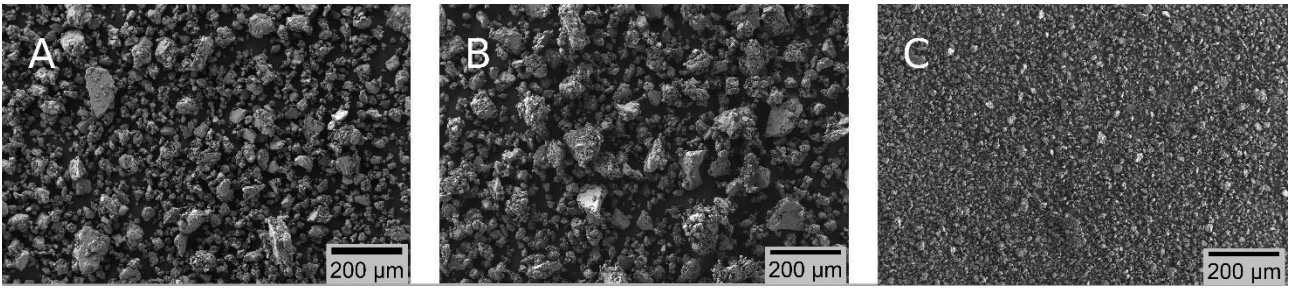


Fig. 7: SEM images of the materials milled 10 h without additives (A), 10 h with Fe (B), and 10 h with Fe + 1 h with graphite (C).

A rough estimate of size distribution was obtained by sieving the milled materials with 100 μm and 200 μm sieves. Fig. 8 shows the fractions of the materials with characteristic sizes below 100 μm , between 100 μm and 200 μm , and above 200 μm . It can be seen that the incorporation of Fe from the start reduces the amount of agglomerates with sizes above 200 μm , and the incorporation of graphite produces agglomerates with sizes practically entirely below 100 μm .

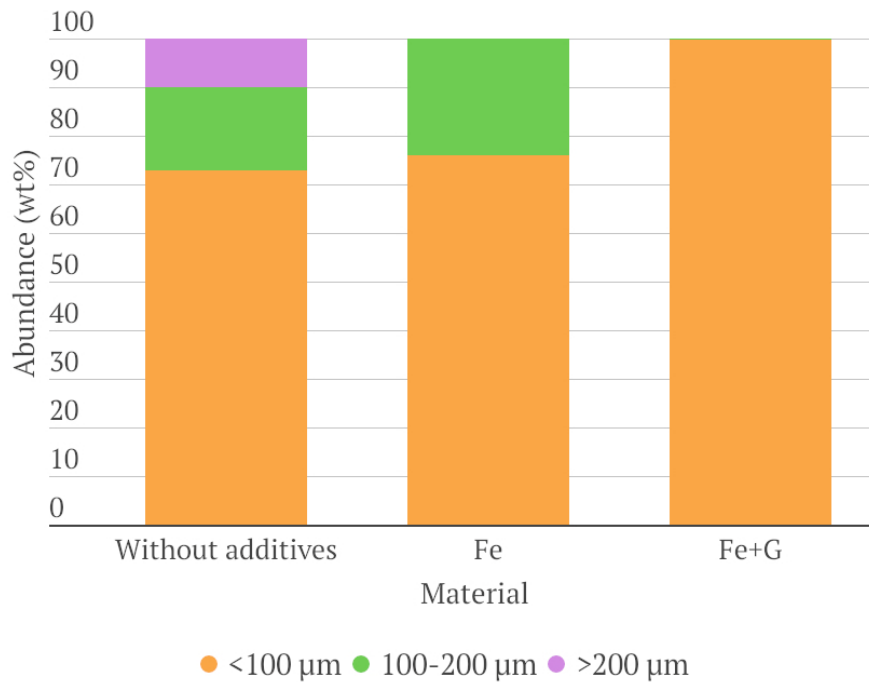


Fig. 8: Size distribution obtained by sieving the milled materials with 100 μm and 200 μm sieves.

By XRD diffraction it is observed that with additives a weak C peak appears and more intense Fe peaks are seen (Fig. 9). Table 1 presents the results of phase quantification and microstructural characterization by Rietveld refinement.

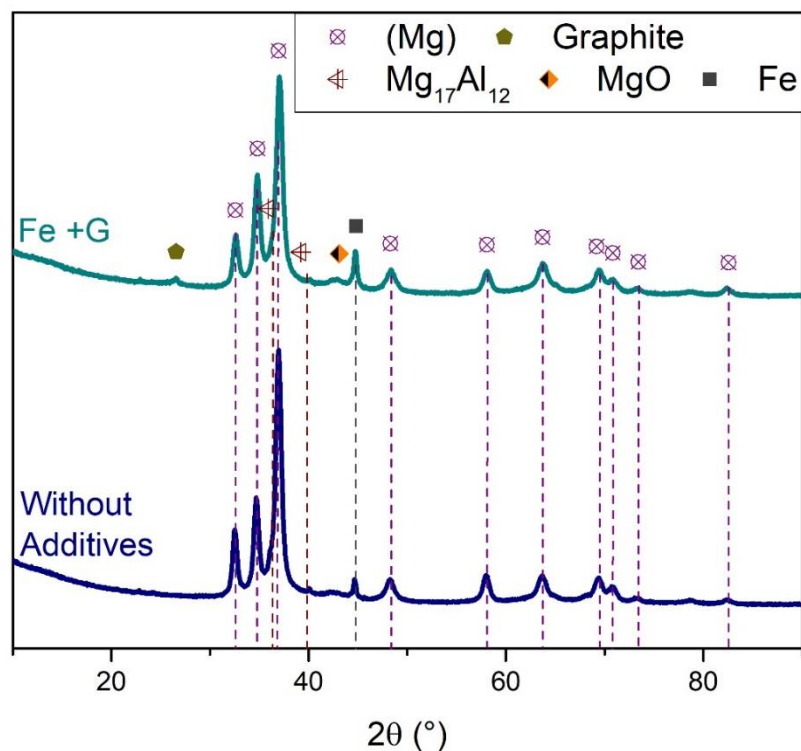


Fig. 9: XRD patterns of the materials milled with or without additives.

It can be seen that the main differences between both materials are the presence of C, the greater abundance of Fe, and a higher amount of MgO in the sample with additives due to the additional opening of the milling chamber to incorporate the graphite (Fig. S1). Crystallite size and microstrain are very close.

	Without additives	With 1.5 wt% Fe + 5 wt% C
(Mg) crystalline	72(1)	62(2)
(Mg) nanocrystalline	19(1)	19(2)
Al	-	-
Mg ₁₇ Al ₁₂	4.0(2)	4.1(1)
MgO	4.7(2)	7.3(3)
Fe	0.7(1)	2.6(1)
C	-	5
Al in (Mg) [wt%]	7.2(2)	6.9(2)
Crystallite size [nm]	19(5)	23(5)
Microstrain [%]	0.8(1)	0.9(1)

Table 1: Phase abundance and microstructural characterization from Rietveld refinement of the diffractograms. Two (Mg) contributions have been included in the refinement, one regular and another one nanocrystalline that takes into account the amorphous-like contribution between Mg main peaks. The amount of C has been fixed at 5 wt% in the material with additives because the weakness of the C peak does not allow a good quantification of this phase.

3.2.2 H₂ production

The hydrolysis curves of the materials with and without additives are compared in Fig. 10. The marked improvement in kinetics due to the presence of the additives is observed, together with the small reduction of capacity due to the incorporation of non hydrolyzable additives. The total H₂ production before acid addition is 850(20) mL/g (82(2) % yield) for the material without additives and 780(24) mL/g (80(2) % yield) for the material with Fe and C. After acid addition the material without additives completes H₂ production releasing 975(20) mL/g (yield of 96(2) %) whereas the material with additives produces 850(40) mL/g (87(2) % yield). The time taken to produce 3 wt% of H₂ is reduced from 11 minutes to 1.2 minutes.

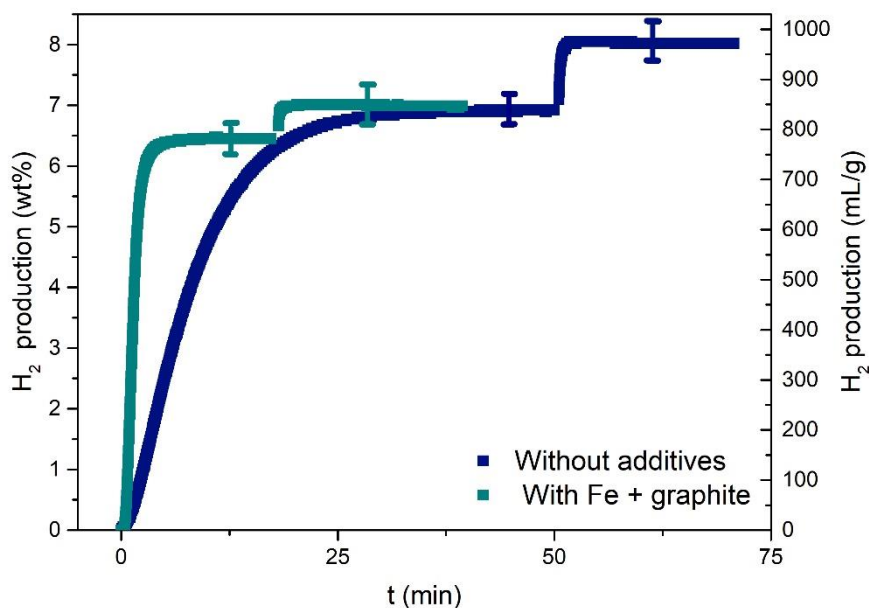


Fig. 10: Hydrolysis curves of the materials with and without additives. In the case of the material with Fe and graphite 3 M HCl acid was added to obtain the final capacity due to a greater abundance in this material of the hydroxide Mg₆Al₂(OH)₁₈, more resistant to acid.

In order to get information about the mechanism that controls the kinetics of the hydrolysis reaction and to analyze the effect of the additives, the shape of the curves was fitted with the traditional kinetic models described in [25]. Table 2 shows the values of R², the square of the correlation coefficients obtained after fitting the relationships between conversion fraction (α) and time for each model. For details of this fitting procedure see [20]. The best fit (R² 0.999 and 0.997 for the materials without and with additives, respectively) corresponds to the R3 model, that describes a reaction controlled by the contracting volume of the particles. A comparison between the measured and best-fit curves is presented in Fig. 11. The small differences between the measured and best-fit curve in the case of the material milled with additives could be due to a non-uniform particle size distribution. The fact that both curves are satisfactorily fitted with the same reaction model means that the kinetic improvement is not due to a mechanism change. The effective rate constant of the R3 model, k_0 , is in fact the quotient of the rate of advance of the interphase (k) and a characteristic size of the particles (r), $k_0 = k/r$ [25]. The improvement in kinetics, consequence of the incorporation of additives, can be interpreted as the combined effect of a faster rate of advance (greater k) due to the increased corrosion rate of Mg induced by the galvanic pair formation with Fe (and C), and a smaller particle characteristic size consequence of the lubricating effect of C during milling (smaller r). Hence, the effects of Fe and C combine in a sort of synergy that contributes to a faster H₂ production rate.

Model	w/o additives	with additives
R2 (Contracting area)	0.997	0.992
R3 (Contracting volume)	0.999	0.997
D1 (1-D diffusion)	0.997	0.988
D2 (2-D diffusion)	0.990	0.985
D3 (3-D diffusion-Jander)	0.956	0.960
D4 (Ginstling-Brounshtein)	0.981	0.980
F1 (First order)	0.993	0.994
F2 (Second order)	0.878	0.896
F3 (Third order)	0.705	0.737

Table 2: R^2 for the different kinetic models considered. The best three values for each milling time are highlighted.

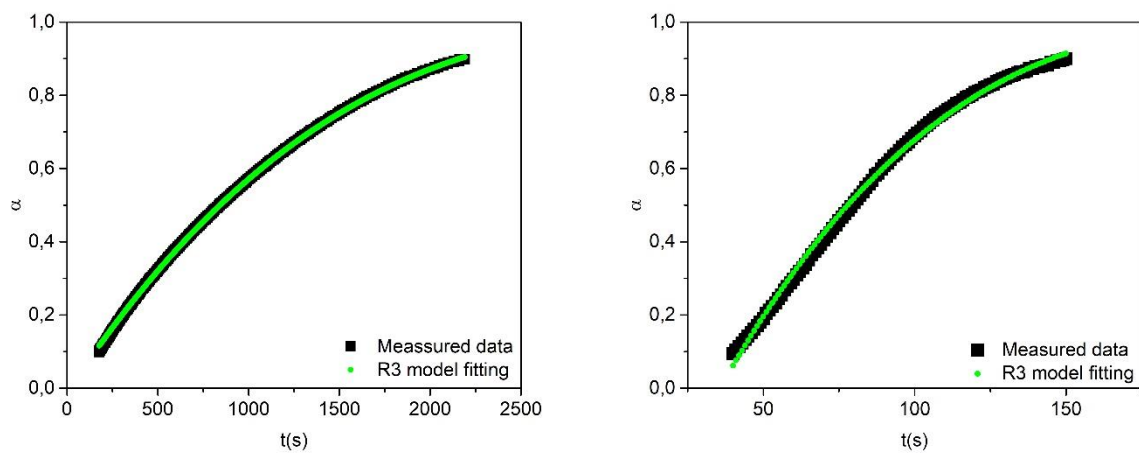


Fig. 11: Fitting of the hydrolysis curves with the R3 model. Left: material without additives, right: material with Fe and graphite.

To put this material in context its hydrolysis performance is compared to that of similar materials reported in the literature (Table 3).

Starting material	Processing	Additive	Reaction solution	Reaction T [°C]	H ₂ after 5 min [mL/g]	H ₂ yield [mL/g]	Ref
Mg alloy sacrificial anodes scraps	5h milling under Ar	5 wt% C	MgCl ₂ 0.6 M	24	791(24)	840(24)	[15]
Mg alloy sacrificial anodes scraps	5h milling under H ₂	5 wt% C	MgCl ₂ 0.6 M	24	694(24)	888(24)	[16]
AZ91 scraps	5h milling under Ar	5 wt% C	NaCl 3.5 wt%	RT	292(24)	691(24)	[26]
AZ91 scraps	Hydrolysis during milling	-	Seawater	20	47	798	[14]
Mg powder	10h plasma assisted milling under Ar	20 wt% C	NaCl 3.5 wt%	45	156	634	[9]
Mg-Mg ₂ Si composite scraps	12 h milling under Ar	-	MgCl ₂ 0.5 M	25	397	820	[27]
Mg powder	3 min milling under Ar	10 wt% Fe	CoCl ₂ 0.032 M	24	815	815	[8]
Mg alloy scraps	-	-	Wastewater + acetic acid 30 wt%	50	494	526	[18]
AZ91 scraps	45 min milling under Ar	(Mg ₁₀ Ni) ₉₀ Ce ₁₀	NaCl 3.5 wt%	55	600	620	[19]
Mg alloy sacrificial anodes scraps	10 h pre-milling with Fe + 1 h milling with C under air	1.5 wt% Fe 5 wt% C	MgCl ₂ 0.6 M	24	775(2)4	780(24)	This work

Table 3: Some results from the literature and from this work.

Al Bacha *et al.* have prepared a material based on the same raw scraps but milling with 5 wt% of graphite from the start and using Ar or H₂ atmospheres [15-16]. The material milled under Ar has a greater H₂ yield and similar kinetics. And the material milled under H₂ exhibits higher yields (due to the contribution of the hydrolysis of the MgH₂ formed during milling) but slower kinetics. In other paper [26] Al Bacha *et al.* use the same milling strategy in scraps of Mg alloy AZ91. In this case the results reported here are slightly better in kinetics and yield. Comparing with the H₂ production reported by Matsuzaki *et al.* [14] obtained during the mechanical milling of AZ91 scraps with seawater it is observed that the yields are similar, but their rate of H₂ production during milling is considerably lower. However, it is important to take into account the differences in scales between both processes (mg in our case, g in Matsuzaki's process). Something similar is observed when comparing our results with those of Ma *et al.* [9], though in this case their yield is also smaller, despite hydrolyzing the materials at 45 °C. The yields obtained here are slightly below those reported by Tan *et al.* [27] and Sevastyanova *et al.* [8], but kinetics are faster than Tan's results and a bit slower than Sevastyanova's. Akbarzadeh *et al.* [18] reported the hydrolysis of Mg-alloys scraps without processing using wastewater with acetic acid at 50 °C, and Hou *et al.* [19] hydrolyzed AZ91 scraps with a Mg-Ni-Ce catalyst at 55 °C. In both cases the rate of H₂ production and the yield obtained in this work overcome the performance obtained by these authors. Summarizing, our results show yields and H₂ production rates that are above the average, with the additional advantage of having prepared the materials under air atmosphere and using cheap and abundant additives. However, comparisons have to be taken with care because the materials are not strictly comparable, due to the differences in the starting materials, processing methods, hydrolysis

solution, etc. By only considering kinetics and yield as figures of merit, the performance is above the average.

4 Conclusions

Mg scraps from the manufacturing of sacrificial anodes have been successfully reprocessed by mechanical milling to produce H_2 by hydrolysis. The best reprocessing strategy found was the pre-milling of the scraps for 10 h with 1.5 wt% of Fe followed by 1 h of extra milling with the addition of 5 wt% of C (graphite). Both millings have been done under air atmosphere. The incorporation of Fe leads to faster corrosion rates due to the formation of microgalvanic pairs with Mg, and the addition of C mainly contributes to a significant size reduction due to the lubricating effect during milling (reduction of the cold welding process). The shape of the hydrolysis curves matches that of a kinetic process limited by volume contraction, i.e. by the advance of the interphase between the unreacted material and the hydrolyzed material. The positive effects on kinetics of the formation of microgalvanic pairs and the reduction in particles size are compatible with reaction being controlled by the movement of the interphase.

The hydrolysis of the material milled with additives is considerably better than that of the scraps milled without them. The time to produce 3 wt% of H_2 is reduced tenfold from 11 minutes to 1.2 minutes, and the yield in saline solution and after acid addition is only reduced by the amount expected taking into account the incorporation of non-hydrolyzable additives. The best material produces 775(24) mL/g of H_2 in 5 minutes and 780(24) mL/g (80(2) % yield) when the reaction stops before acid addition, and with the incorporation of acid yields a final value of 850(40) mL/g of H_2 (87(2) % yield).

The comparison of the performance of the material reported here with that of similar materials from the literature is positive. The obtained yield and the rate are above the average, with the advantage that this process involves cheap additives and a mechanical processing under air atmosphere.

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