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High Thermal Stability Fe_2O_3-Al_2O_3 System to Produce Renewable Pure Hydrogen in Steam Iron Process

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The use of H_2 as fuel of the future is closely linked to the development of Fuel Cells, among them Proton Exchange Membrane Fuel Cells (PEMFCs) are the most attractive. To avoid the irreversible poisoning of the platinum-based catalyst placed on the PEMFC electrodes, pure H_2 (CO < 10 ppm) is required. Steam iron process (SIP) is a cyclical process which allows, at high temperature and low pressure, the direct production of pure H_2 by redox cycles of iron. Syngas is generally used as reducing agent while steam water is used to oxidize iron and to produce pure H_2. However, iron oxides powders suffer from deactivation in few redox cycles due to their low thermal stability. The aim of this study is to improve iron oxides resistance adding Al_2O_3 as high thermal stability material. Bioethanol is used as renewable sources of syngas to makes the process totally sustainable. To evaluate the effect of Al_2O_3 addition, different Fe_2O_3 / Al_2O_3 ratios were tested (40 wt%, 10 wt%, 5 and 2 wt%). The stability of the synthetized particles was evaluated with 10 redox cycles comparing the results with that of commercial Fe_2O_3 powders. Al_2O_3 does not behave as inert material in the process but it actively participates in the reduction step, catalysing coke formation due its acidity. With the sample 98 wt% Fe_2O_3- 2 wt% Al_2O_3 the best performances in terms of particles stability and hydrogen purity were obtained.

1. Introduction

Proton exchange membrane fuel cells (PEMFC) are electrochemical devices able to directly convert the chemical energy of the fuel into electricity. Using H_2 as fuel it is possible to generate electricity without pollutant emissions obtaining only water as by-product. To date, PEMFC has been chosen by many automotive companies as the power sources for the future vehicles thanks to its high energy density and fast activation times. However, their utilization is limited due to the excessive cost associated to the platinum catalyst of the cell electrode and the short life of the device (Chen et al.,2011). In addition, platinum-based catalyst is very sensitive to CO poisoning and before being powered to the cell, H_2 must be purified (CO below 10 ppm).

Steam iron process (SIP) is a non-conventional H_2 production technology which allows the generation of pure renewable H_2 to be directly fed to PEMFC. It is a cyclic process which exploits the redox properties of iron to produce H_2 by the oxidation of Fe metal with water. The starting material is generally hematite (Fe_2O_3) thanks to its abundance, low cost and environmentally friendly nature. The process consists in two steps: the reduction, in which iron oxides are reduced to metallic iron using syngas and the oxidation in which H_2 is produced feeding steam water. If a renewable source is used for the syngas generation, H_2 is totally green. In the author's previous work, renewable H_2 is obtained performing the reduction of iron oxides with bioethanol at elevated temperature and ambient pressure (675°C and 1 bar) (De Filippis et al.,2020). At the adopted operating conditions, ethanol was completely converted into syngas and traces of methane and ethylene (De Souza et al.,2012). These two last compounds are the responsible of the coke formation in the Fe_2O_3 particles and then of the production of CO in the oxidation step by coke gasification. Monitoring the reduction degree of iron oxides is a key parameter to avoid the carbon deposition. In the author's previous work (De Filippis et al., 2020) a relationship between the reduction degree of commercial Fe_2O_3 fine particles and the amount of the ethanol fed in the reduction step was reported.

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The activity of pure Fe_2O_3 is already studied in several works remarking its low thermal stability; at high number of redox cycles the amount of H_2 produced decreases, compromising the effectiveness of this technology. Using syngas in the reduction step, a positive effect in terms of powders stability and H_2 yields is obtained adding a support like Al_2O_3, MgO and ZrO_2 (Lou et al.,2018). For a future industrial application of this technology the enhancement of the chemical and thermal stability of the Fe_2O_3 particles is a key point which should be addressed.

The aim of this work is to enhance the performance of iron particles using aluminium oxide (Al_2O_3) as a structural promoter in the presence of bioethanol as reducing agent. It is well-known that Al_2O_3 has a very high thermal stability, however its acidity promotes the coke formation catalysing the cracking reactions (Bracciale et al., 2018). The Al_2O_3 - Fe_2O_3 particles are prepared by coprecipitation method adding different amount of Al_2O_3 (40 wt%,10 wt%,5 wt% and 2 wt%). The tests are carried out in a fixed bed reactor heated at constant temperature of 675°C and working at atmospheric pressure. The activity of Fe_2O_3 -Al_2O_3 is compared with commercial Fe_2O_3 particles (assay >99 wt%) focusing the attention on hydrogen yield and on the cyclic redox stability (10 redox cycles).

2. Experimental section

2.1 Materials

Commercial Fe_2O_3 was supplied by Sigma Aldrich (assay ≥ 99.0%, dp < 1 μm). Due to the very fine dimensions the particles tend to agglomerate, therefore before the tests they are sieved to the dimension of 0.150−0.300 mm. Iron (III) nitrate nonahydrate ($Fe(NO_3)_3{\cdot}9H_2O$, assay ≥ 98.0%) and Aluminum nitrate nonahydrate ($Al(NO_3)_3{\cdot}9H_2O$, assay ≥ 98.0%) were supplied by Sigma Aldrich and used as received.

2.2 Fe_2O_3- Al_2O_3 particles preparation

The Fe_2O_3- Al_2O_3 particles were prepared by coprecipitation method. The calculated amounts of precursor nitrates $Fe(NO_3)_3{\cdot}9H_2O$ and $Al(NO_3)_3{\cdot}9H_2O$ were dissolved in deionized water. The solution was mixed and heated with a magnetic stirrer till a temperature of 80 °C. Then a 30% ammonia solution was gradually introduced into the mixture to increase the pH until 9. It was then aged for 12 h under room temperature. The resulting precipitate was filtered and dried at 110 °C for 24 h. The solids obtained were subsequently subjected to decomposition at 350 °C for 2 h and sintered at 900 °C for 2 h in a muffle oven. Then the particles were crushed and sieved to get powders in the size range of 0.150−0.300 mm

2.3 Fe_2O_3 - Al_2O_3 particles characterization

Morphological analysis of Fe_2O_3-Al_2O_3 particles (before and after 10 redox cycles) was conducted by using a field emission gun-scanning electron microscopy (FEG-SEM) Tescan MIRA3 (EDAX) equipped with a Bruker EDS detector. X-ray powder diffraction (XRD) was implemented to study the crystal phase compositions before and after the tests. XRD patterns were acquired using a Philips Analytical PW1830 X-ray diffractometer, equipped with a Ni β-filtered Cu Kα (1.54056 Å) radiation, in the 2θ range from 5 to 90° with a step size of 0.02° and a time for step of 3.5 s. The data were collected with an acceleration voltage and applied current of 40 kV and 30 mA, respectively. The crystalline phases in the resulting diffractograms were identified through the COD database (Crystallography Open Database – an open access collection of crystal structures) (Gražulis S et al, 2009).

2.4 Experimental Set Up and Procedure

The tests were conducted in a bench scale plant reported in detail in the author's previous work (De Filippis et al., 2020). All the experiments were carried out in a fixed bed reactor, feeding alternatively ethanol and water in the presence of argon as carrier gas. The operative conditions are summarized in Table 1.

Table 1: Operative conditions for all tests.

Experimental parameters		
Solid bed (Fe_2O_3- Al_2O_3 particles)	2	g
Ethanol flowrate	4	mL/h
Water flowrate	4	mL/h
Argon flowrate	160	mL/min
Temperature	675	°C
Pressure	1	bar

3. Results and discussion

3.1 Determination of the optimal reduction time: effect of Al_2O_3 addition in the reduction step

As already demonstrated by the authors in the previous work (De Filippis et al., 2020), the monitoring of the reduction degree is essential to avoid the presence of CO in the oxidation step. In Figure 1 the volumetric composition of the gaseous mixture obtained from the reduction of 60 wt% Fe_2O_3- 40 wt% Al_2O_3 as a function of the ethanol feeding time is reported.

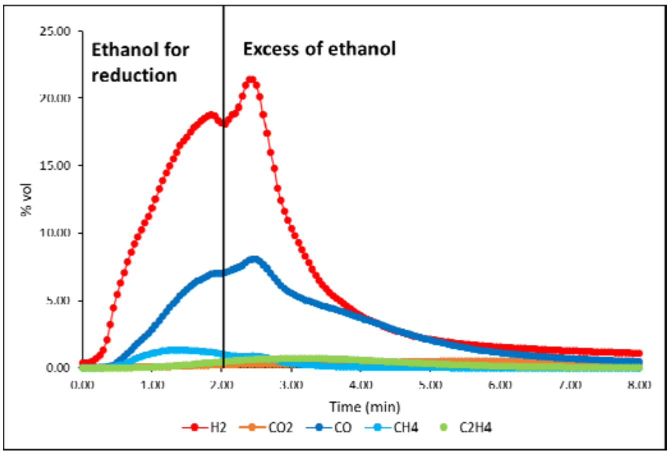


Figure 1: Volumetric composition of the gaseous mixture obtained from reduction of 60 wt% Fe_2O_3 – 40 wt% Al_2O_3 as a function of ethanol feeding time.

H_2 and CO curves present two peaks. The first one occurs at about 2 min and it corresponds to the reduction of the more accessible iron oxide sites, after this time the ethanol fed is used to reduce the less reactive sites. However, in this phase the kinetic of coke deposition catalyzed by Al_2O_3 is very fast, contributing to a high coke production. In order to limit this phenomenon and obtain a pure H_2 stream in oxidation, the optimal reduction time is fixed as the time in which only the reduction of the more accessible sites takes place even if a complete reduction of the iron oxides is not reached. This behavior is confirmed by the results reported in Table 2, which shows the optimal amount of ethanol in reduction and the amount of H_2 produced in oxidation for all the tested samples. When the load of Al_2O_3 increases the amount of hydrogen produced for 100 g di Fe_2O_3 decreases, meaning that the bed is not completely reduced. In fact, to avoid the coke deposition the degree of reduction must be contained to limit the effect of Al_2O_3 in the catalysis of the reactions of coke deposition (Keller M et al., 2020).

Table 2: Amount of ethanol fed and H_2 produced for each iron powders.

	Ethanol fed (mmol C_2H_5OH/g Fe_2O_3)	H2 (NL/100 g of Fe_2O3)
Commercial Fe_2O_3	3.422	9.621
98 wt% Fe_2O_3 -2 wt% Al_2O_3	2.921	7.305
95 wt% Fe_2O_3-5 wt% Al_2O_3	2.882	7.102
90 wt% Fe_2O_3-10 wt% Al_2O_3	2.851	3.449
60 wt% Fe_2O_3-40 wt% Al_2O_3	1.903	2.145

3.2 Effect of Al_2O_3 addition on particles stability for 3 redox cycles

In order to better understand the effect of alumina in the process a comparison between the H_2 yield obtained using 60 wt% Fe_2O_3- 40 wt% Al_2O_3 and commercial Fe_2O_3 particles (assay > 99 %) is reported in Figure 2. For each sample three redox cycles are performed.

As already explained in the previous section, Al_2O_3 catalysed the coke formation reactions thus, increasing its amount a lower reduction degree must be adopted determining a low H_2 yield. However, the better performance of commercial Fe_2O_3 particles is not only related to the better reduction degree but also to the smaller particle sizes.

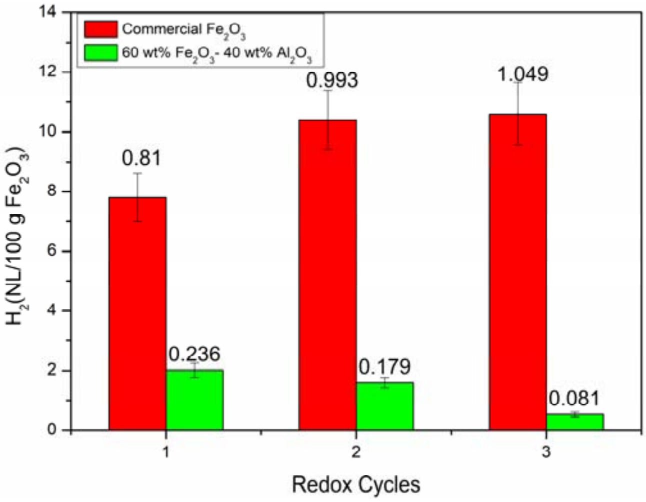


Figure 2: Comparison between H_2 produced in the oxidation step with commercial Fe_2O_3 and synthetized 60 wt% Fe_2O_3-40 wt% Al_2O_3 for three redox cycle.

It is clear from the figure that, in this case, the addition of Al_2O_3 does not produce the desired action that is the increase of stability. The 60 wt% Fe_2O_3 - 40 wt% Al_2O_3 is fastly deactivated in few redox cycles (from 2.012 NL /100 g of Fe_2O_3 to 0.656 NL /100 g of Fe_2O_3 in 3 redox cycles). These results can be attributed to the reduction of the active surface area of the Fe_2O_3-Al_2O_3 particles. This phenomenon can be related to the particles agglomeration which occur after several redox cycles or to the formation of high amount of coke which is only slightly gasified by the steam in the adopted operative conditions, being the temperatures too low. Thus, the coke is deposited on the surface of the iron particles inhibiting their activity. To make the use of bioethanol as reducing agent possible with Al_2O_3 as a structural promoter it is therefore fundamental to decrease the loads of Al_2O_3 in order to limit its catalytic activity on cracking reactions conferring, at the same time, improved structural properties to iron oxides.

3.3 Fe_2O_3 - Al_2O_3 particles stability for high number of redox cycles (10 redox cycles)

In order to assess the stabilizing effect of different amount of Al_2O_3 (40 %, 10 %, 5 % and 2 % wt) on the Fe_2O_3-Al_2O_3 particles, tests for high number of redox cycles are performed (10 cycles). The amount of hydrogen produced in each oxidation step is compared with the results obtained with commercial Fe_2O_3. The results are shown in figure 3.

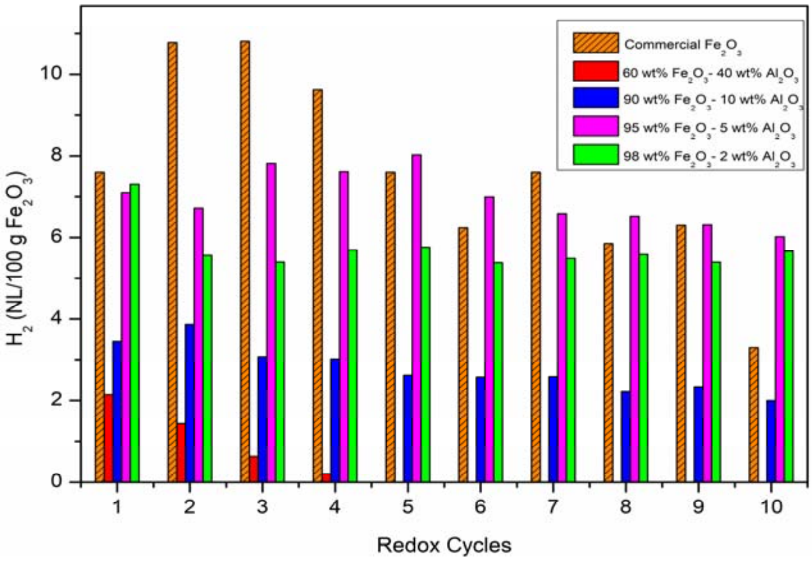


Figure 3: Stability tests for 10 cycles with the several samples.

In accordance with the results obtained with 60 wt% Fe_2O_3- 40 wt% Al_2O_3, Al_2O_3 is a strong catalyst for the production of carbon by ethanol cracking and thus decreasing its amount appears fundamental to control the stability of the process. Looking at figure 3, 60 wt% Fe_2O_3- 40 wt% Al_2O_3 is subjected to complete deactivation in only 4 redox cycles while reducing the amount of Al_2O_3 produces a positive effect on the stability of the powder with respect to the commercial one. Among the samples tested, the most stable production of H_2 for 10 redox cycles equal to 5.2 ± 0.2 NL / (100 g Fe_2O_3) is obtained using 98 wt% Fe_2O_3- 2 wt % Al_2O_3.

These results suggest that in order to achieve a stable production of H_2 using bioethanol in the reduction step it is essential to take into account two key factors strongly linked between them: the thermal stability of iron powder and the amount of coke deposition on the iron particle surface. The low thermal stability of the Fe particle after a long number of cycles results in the agglomeration of the particles and thus in decrease of the active surface area. Lower active surface area means lower “lattice” oxygens available for the combustion of coke during reduction. As a consequence, coke deposition is not prevented anymore.

The addition of 2 wt% of Al_2O_3 is the best choice conferring a higher thermal stability and consequently a stable H_2 production for high number of redox cycles.

3.4 Characterization of the Fe_2O_3-Al_2O_3 particles before and after stability test (10 redox cycles)

In order to better understand the behavior of the Fe_2O_3-Al_2O_3 particles, XRD and SEM analysis were also conducted.

From XRD analysis of the powders before the tests, alumina was detected only in 60 wt% Fe_2O_3-40 wt% Al_2O_3 sample. This result is due to the low concentration of Al_2O_3 in the other samples and to the non-formation of the crystalline Al_2O_3 phase. The only crystalline phase detected after stability tests in all samples is Fe_3O_4 (Figure 4).

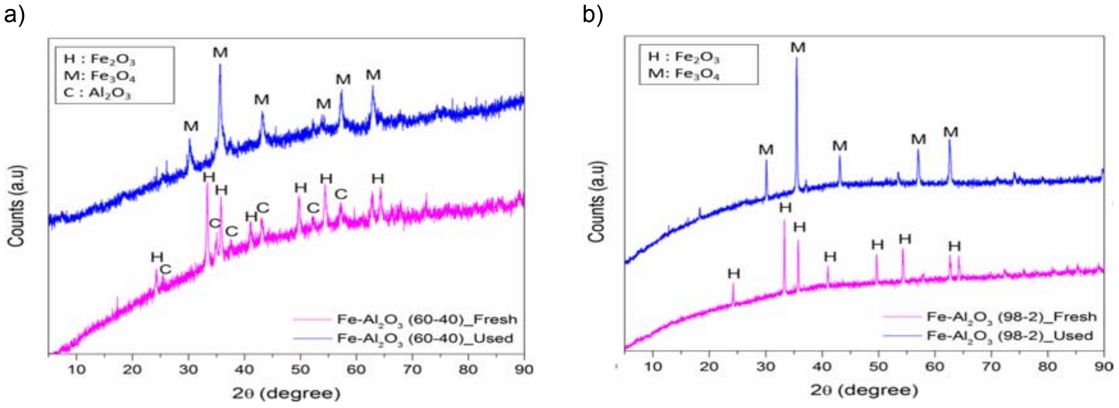
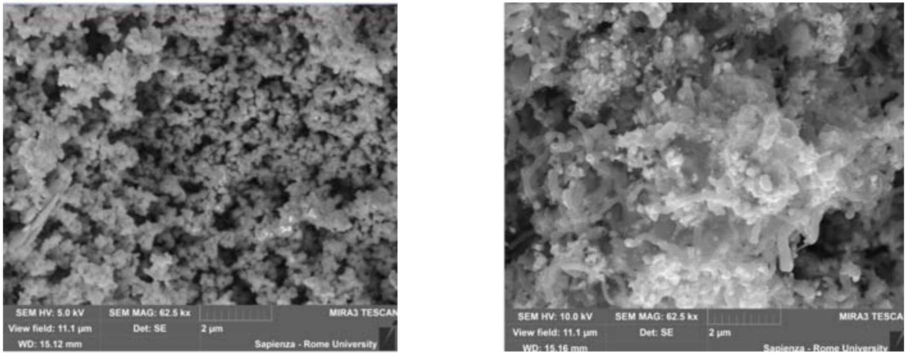


Figure 4: XRD patterns of 60 wt% Fe_2O_3 - 40 wt% Al_2O_3 (a) and 98 wt% Fe_2O_3- 2 wt% Al_2O_3 (b) before and after the stability tests.

SEM analysis of commercial Fe_2O_3 and 98 wt% Fe_2O_3- 2 wt% Al_2O_3 were also conducted. The results of the samples before and after the stability tests are collected in Figure 5. From the comparison of the figure 5 a and 5 c it is clear that commercial Fe_2O_3 is characterized by a lower particle dimensions corresponding to a higher surfaces exposed to the reaction, responsible to the major activity in the first redox cycles. However, the surface of the commercial Fe_2O_3 powders after 10 redox cycles as shown in figure 5 b, are for the most part covered by nanofilaments of carbon. As already explained in the previous section, this result is strongly related to the low thermal stability of this material. Iron oxides particles agglomerate after several redox cycles leading to a decrease of the active iron surface and therefore of the “lattice “oxygens available.

From the comparison of fresh and exhausted 98 wt% Fe_2O_3- 2 wt% Al_2O_3 particles (Figure 5 c and 5 d) the positive effect of Al_2O_3 on iron oxides stability is confirmed. In presence of 2 wt% of Al_2O_3 no modification of particle dimensions is registered after the stability test and only a very small amount of carbon is detected on the iron surfaces. The filamentous material visible in Figure 5 c is a glass wool residue used as a fixed bed support in the several tests.

a) Commercial Fe_2O_3 (fresh) b) Commercial Fe_2O_3 (10 redox cycles)



c) 98 wt% Fe_2O_3 - 2 wt% Al_2O_3 (fresh) d) 98 wt% Fe_2O_3-2 wt% Al_2O_3 (10 redox cycles)

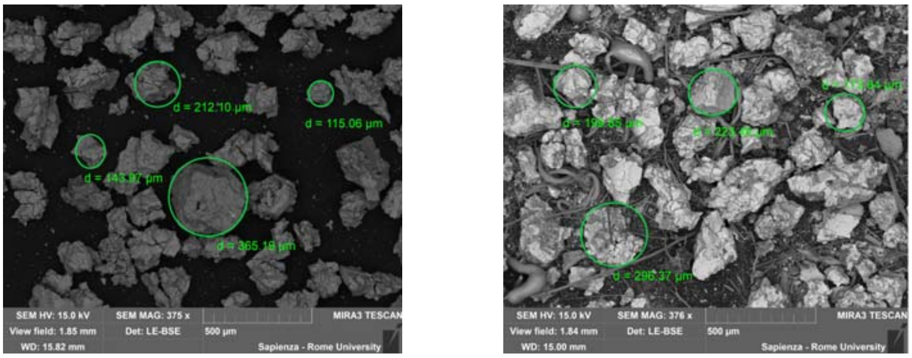


Figure 5: SEM images of commercial Fe_2O_3 and 98 wt% Fe_2O_3 -2 wt% Al_2O_3 before and after the stability tests.

4. Conclusion

Fe_2O_3-Al_2O_3 particles prepared by coprecipitation method were tested in a fixed bed reactor using bioethanol as reducing agent in steam iron process. The low iron oxides stability is one of the main issues of this technology and the addition of a high thermal stability material as Al_2O_3 is essential. In addition to ensuring the high purity of the H_2 produced the deposition of carbon during the reduction step must be avoided. The addition of different amount of Al_2O_3 to Fe_2O_3 demonstrated that Al_2O_3 is a strong catalyst of coke formation by ethanol cracking and thus its amount should be carefully controlled. 98 wt% Fe_2O_3-2 wt% Al_2O_3 showed the best performances, leading to a stable production of pure H_2 for at least 10 redox cycles. Therefore, the addition of Al_2O_3 can be an effective solution to enhance the process activity and stability by improving the thermal stability of the particles and consequently preventing their deactivation by the deposition of coke.

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