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Effect of Impurities of the Solid on the Subsequent Hydrogen Release in Steam-Iron Process

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1 Introduction

The greenhouse effect and the progressive fossil fuels depletion are the main motivations for searching new energy sources, which could replace the actual dependency to carbon based fuels. These sources must be green and renewable in a long term. Until this moment arrives, other substitutive must be found to lead the transient.

The hydrogen economy concept so explains that a large part of the generated energy must be obtained using hydrogen previously produced without greenhouse gas emissions [1]. The long-term objective of this study is the implantation of an alternative system to obtain, separate and storage, hydrogen without CO_2 added production, using for instance, streams from renewable sources like biogas, bio-oils or biomass pyrolysis gases.

The use of fuel cells is being proposed as an important possibility for automotive, where a high purity hydrogen feed is needed, since minimum gas impurities (e.g. CO) results in poisoning on the cell anode.

The “Steam-iron” process has been claimed as an interesting way to achieve this purity, and also to store hydrogen much safer than others storage methods. The process consists of a first step where a solid oxide is reduced by a H_2-rich stream. The reduced solid can then be stored for some time at open air and room conditions. When hydrogen is required, feeding steam to the solid containment can release hydrogen regenerating the former oxide.

The global reactions for this process will be:

$$3\,Fe_2O_3 + H_2 \leftrightarrow 2\,Fe_3O_4 + H_2O\,(g) \quad \text{Hematite to Magnetite} \quad \text{(r. 1)}$$
$$Fe_3O_4 + 4\,H_2 \leftrightarrow 3\,Fe + 4\,H_2O\,(g) \quad \text{Magnetite to Iron} \quad \text{(r. 2)}$$

Among the best suitable solids, iron oxides are proposed for this process, due to their high redox capacity, availability, and in addition their economic feasibility [2]. They have also a relatively low molecular weight, and the high oxidation state of the metal allows an interesting hydrogen storage density.

After proving the viability for this process [3], a strong decay in red-ox capacity has been evidenced when using pure hematite along the redox cycles [4]. Although some additives were considered [5], a ternary sample containing small amounts of alumina and ceria with Fe_2O_3 was prepared. Due to its low cost an iron oxide ore was also considered.

This work deals with the experimental study of steam-iron viability for these solids. Also in order to gain know about the process, kinetics of reduction and oxidation reactions were calculated from experimental data. These were better fit to an Avrami-based model.

2 Experimental

The ternary oxide (98 mol% Fe_2O_3–1.5 % Al_2O_3–0.5 % CeO_2) was prepared in laboratory using the citrate method [6]. The ore contains ~80 wt% Fe_2O_3, and SiO_2, Al_2O_3 and CaO as main impurities.

The experiments have been carried out in a thermogravimetric system (C.I. Electronics, MK2). The solid samples and flow conditions were chosen to ensure no external diffusional limitations. Reaction extent was measured as weight loss during reduction and gain at oxidation.

For studying the whole process, up to 7 red-ox cycles were carried out. Mixtures of hydrogen and nitrogen at 1 bar with different hydrogen partial pressures (0.1 to 0.9 bar) simulating the ones coming from a pyrolysis gas were checked, at 450 ºC and with a total flow rate of 750 Nml/min and P_{H2O}=0.05 bar in oxidations. Methane was checked out to exhibit an inert behavior in these experimental conditions. Also, with P_{H2}=0.5 bar different experiments were carried out at temperatures 400, 425, 450, 475 and 500 ºC. Oxidation reaction was studied conducting 7 red-ox cycles with P_{H2}=0,5 bar (in reduction steps) at 450 ºC for several steam partial pressures (0.01, 0.02, 0.05, 0.1 and 0.15 bar).

Weight loss or gain were fit to the Johnsson-Mehl-Avrami-Kolmogorov (JMAK) model [4]

$$X=1-\exp(-k*t^N) \qquad \text{(eq. 1)}$$

to obtain the characteristic parameters of the kinetics of reduction and oxidation. It were allowed to depend on temperature and reactant partial pressures. X is the solid conversion, k is the kinetic constant, t is the time, and N is the Avrami exponent (related to the nucleation grade and the characteristic dimension of morphologic growing). The constant k is expressed as:

$$k=k_0*\exp(-E_a/RT)*P_{gas}^n \qquad \text{(eq. 2)}$$

where P_{gas} is the partial pressure of reactant gas and n is the partial reaction exponent. The fittings were set for the second reduction (r.2, magnetite to iron) since r.1 (hematite to magnetite) is inhibited after the first reduction because of thermodynamic limitations at the used conditions of temperature and pressure.

3 Results

For the 7 red-ox cycles runs performed, the lab-made ternary solid exhibited a great stability, improving substantially the behavior of a pure hematite sample which lost its red-ox capacity quickly [4].

Weight losses and gains showed a strong effect of temperature and hydrogen partial pressure in reductions (Figure 1) in both solids. However, the stability of ternary solid was well maintained in the whole range of studied conditions, proving the good behavior of additives.

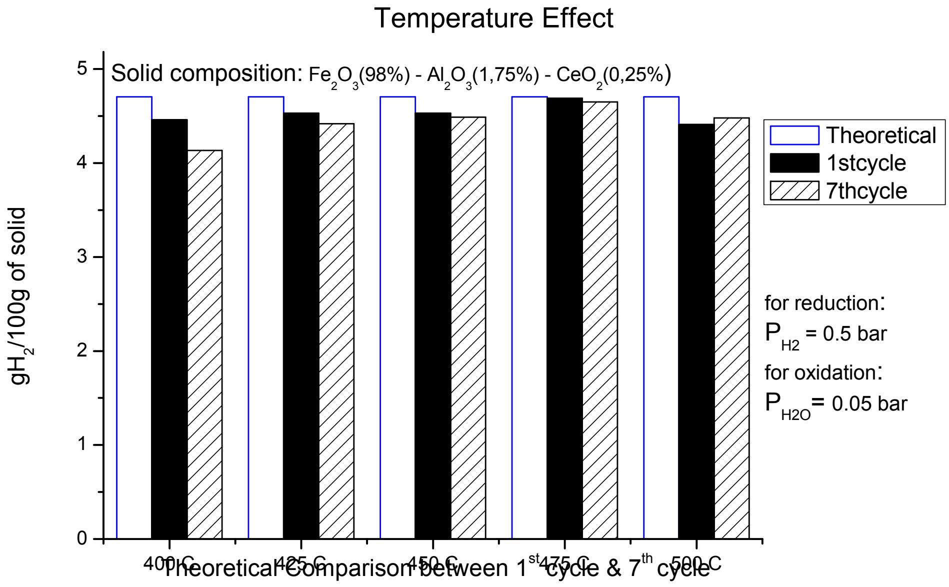

Figure 1: Hydrogen yield at different red-ox cycles vs. temperature in ternary oxide.

With the ternary oxide, nearly constant k values for each cycle were found in the same experiment (Table 1), which is in accordance to the solid red-ox stability. Reduction data showed an increase in k values at higher temperature and higher H_2 partial pressures, as expected. On the contrary, an increase in k values after each cycle at the same experiment is observed for the ore solid data fit (not shown here). This is due to the decay in red-ox capabilities with cycles (the maximum is reached at lower times, with apparent higher kinetics).

Data fit at different steam partial pressures showed similar behavior, increasing k values at higher partial pressures. However, oxidation results were fitted with decreasing k values at higher temperatures. This could be due to internal diffusion limits for water molecule (greater than hydrogen one) inside the particles.

Table 1: Parameters obtained from data fitting of the experimental red-ox cycles at different temperatures.

Reduction	k	Error	N	R^2
T = 400 ºC				
2	0.04436	±1,127E-4	1.396	0.99829
8	0.05567	±2,160E-4		0.99688
T = 425 ºC				
2	0.06802	±2,764E-4	1.440	0.99721
8	0.06999	±3,178E-4		0.99678
T = 450 ºC				
2	0.08467	±3,967E-4	1.463	0.99676
8	0.0872	±4,556E-4		0.99604
T = 475 ºC				
2	0.13073	±6,722E-4	1.517	0.99717
8	0.12792	±8,083E-4		0.9958
T = 500 ºC				
2	0.30821	±0,0018	1.517	0.99742
8	0.31512	±0,0023		0.99705

4 Conclusions

Ternary iron oxide-based solid showed a great stability after 7 red-ox cycles, strongly enhancing the pure iron oxide behavior. The ore also improved the pure iron oxide but some deactivation was not avoided.

Kinetics obtained for the ternary solid and the natural solid allow validate the proposed kinetic model in order to further simulation of same solids-based reactors.

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