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1 Introduction

"Steam Iron" is an old process devoted to "chemically" store and release pure hydrogen [1] which experienced its golden age in the early twentieth century. It needs a solid, usually iron oxide, which changes its oxidation state easily and reversibly. The method roughly consists in a first step where a hydrogen-containing gas reduces the oxide. In a second step, the reduced oxide replenishes its oxygen taking it from a steam stream, releasing hydrogen.

$$3\ Fe_2O_3 + H_2 \rightarrow 2\ Fe_3O_4 + H_2O \qquad (r.1)$$
$$Fe_3O_4 + 4\ H_2 \leftrightarrows 3\ Fe + 4\ H_2O \qquad (r.2)$$

The reduced material could be maintained for some time at open air and ambient conditions, offering the possibility of hydrogen "virtual" storing. With pure hydrogen feed, the method then only serves as "gas storage". With gas mixtures, appropriate conditions are needed to avoid the other compounds to adsorb or react with the solid.

An interesting way of obtaining hydrogen from natural gas without CO_2 releasing is the catalytic pyrolysis, where H_2 and C are the only products [1, 2]. As leaving gas also contains unreacted methane, a further hydrogen separation is mandatory. Thus the "steam-iron" process could suit well the needs of hydrogen purification if hydrogen reacts with the oxide and the other gaseous component remains unaltered. Nevertheless, the appropriate conditions must be carefully chosen, otherwise, carbon deposits could be formed on the solid (oxidized or reduced state) so that the subsequent hydrogen release would contain carbon species as unaccepted impurities (e.g. CO in PEMFC applications [3]). Possible reactions from methane are:

$$CH_4 \leftrightarrows C + 2\ H_2 \qquad (r.3)$$
$$6\ Fe_2O_3 + CH_4 \leftrightarrows CO_2 + 4\ Fe_3O_4 + 2\ H_2 \qquad (r.4)$$
$$Fe_3O_4 + 2\ CH_4 \leftrightarrows 2\ CO_2 + 3\ Fe + 4\ H_2 \qquad (r.5)$$

In previous works, our research group has improved the iron oxide behavior by adding some other additives as aluminum and cerium oxides in small amounts [4]. This only fact rendered a considerable increase in the stability of the solid, since pure iron oxide loses its redox capacity quickly (in few cycles) [5]. Due to its low cost an iron oxide ore was also considered as testing material.

In this work these solids have used for carrying out the "steam-iron" process with a simulated gas coming from catalytic pyrolysis of natural gas. Hydrogen/methane ratio and temperature have been varied to determine the conditions to avoid the methane decomposition during the reduction stage.

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 81 wt% Fe_2O_3, with SiO_2 (6 %), Al_2O_3 (2.5 %) and CaO (2.5 %) as main impurities. The experiments have been carried out in a quartz fixed bed reactor (45 mm length and 13 mm inner diameter). The concentration and temperature radial profiles can be considered neglected. The solid samples consisted of 3.75 g of Fe_2O_3 regardless of the hematite content of the samples. This ensures that the quantity of active species keeps constant allowing a better comparison. In all cases, this mass conformed 75 wt% of the solid sample and was complemented with another 25 wt% of crushed quartz acting as solid diluent. The particle diameter ranged from 160 to 250 μm.

In the reduction stage, a mixture (50 mol%) of hydrogen and methane (with 40/10, 30/20, 15/35 and 10/40 ratios) and argon (50 mol%) was fed with a flow rate of 250 Nml/min (ensuring no external diffusional limitations). The temperatures chosen for testing were 500, 525, 550 and 575 ºC. Given the dimensions of the reacting zone, an isothermal behaviour could be expected. It was also experimentally confirmed. Oxidation stages were performed with diluted steam in argon (25:75 by vol.) at the same experimental conditions than in the reduction process. Gas analysis was performed by GC.

A thermodynamic study was carried out to determine if methane reactions can take place and to obtain the threshold condition for methane decomposition, depending on temperature and H_2/CH_4 partial pressure ratio in the feed.

3 Results

Detection limits for measurement of CO and CO_2 at GC were determined to be 60 vppm. During reduction step no CO_2 was observed under any condition, so the reactions (r.4) and (r.5) could be considered neglected. In fact, reaction 5 has $\Delta G>0$, so is not thermodynamically favored. However, reaction (r.4) shows $\Delta G<0$ above 200 ºC. Hematite reduction is more rapid than magnetite reduction, but we must effectively consider that kinetics of reaction 4 probably result in a very slow process. However, under some experimental conditions, CO and/or CO_2 formation during oxidation steps were observed (Table 1). It evidences previous decomposition of methane (r.3) during reduction. This effect is boosted at low H_2/CH_4 ratios and high temperatures, as expected. Thus, at 500 ºC, the 20/30 ratio does not cause coke deposition while the 15/35 exhibits coke formation and methane conversion during reduction, and CO and CO_2 formation under the subsequent oxidation.

Thermodynamic calculations determine that the decomposition of methane is favored above 590 ºC. However, experimental results show (Table 1) that at lower temperatures methane reacts, as CO_x is detected in oxidation step. The reason can be found in the fact that during oxide reduction, metallic iron is formed. This metal can catalyze the decomposition of methane [7], lowering the reaction temperature from thermodynamic (thermal decomposition) value. This is valid as some hydrogen is present at feed, since hydrogen reduces the solid at these temperatures. In the event of CH_4/Ar feeds (no hydrogen present), methane does not react up to higher temperatures.

Table 1: Results of CO_x formation during oxidation step with different temperatures and reduction feed ratios.

Feed mol% H_2/CH_4/Ar	10/40/50	15/35/50	20/30/50	30/20/50	40/10/50
Temperature	500 °C	500 °C	500 °C	500 °C	500 °C
Ternary	CO: yes CO_2: yes	CO: yes CO_2: yes	CO: no CO_2: no	CO: no CO_2: no	CO: no CO_2: no
Ore	CO: yes CO_2: yes	CO: yes CO_2: yes	CO: no CO_2: no	CO: no CO_2: no	CO: no CO_2: no
Feed mol% H_2/CH_4/Ar	40/10/50	40/10/50	40/10/50	40/10/50	-
Temperature	500 °C	525 °C	550 °C	575 °C	-
Ternary	CO: no CO_2: no	CO: no CO_2: no	CO: no CO_2: no	CO: no CO_2: no	-
Ore	CO: no CO_2: no	CO: no CO_2: no	CO: no CO_2: no	CO: no CO_2: no	-
Feed mol% H_2/CH_4/Ar	30/20/50	30/20/50	30/20/50	30/20/50	-
Temperature	500 °C	525 °C	550 °C	575 °C	-
Ternary	CO: no CO_2: no	CO: no CO_2: no	CO: yes CO_2: yes	CO: yes CO_2: yes	-
Ore	CO: no CO_2: no	CO: traces CO_2: no	CO: yes CO_2: no	CO: yes CO_2: yes	-

The equilibrium constant (Figure 1) determines @ 500 °C a H_2/CH_4 pressure ratio of 44/56. Ratios below it mean coke formation. Experimental results (ratio < 40/60) agree well with these calculations.

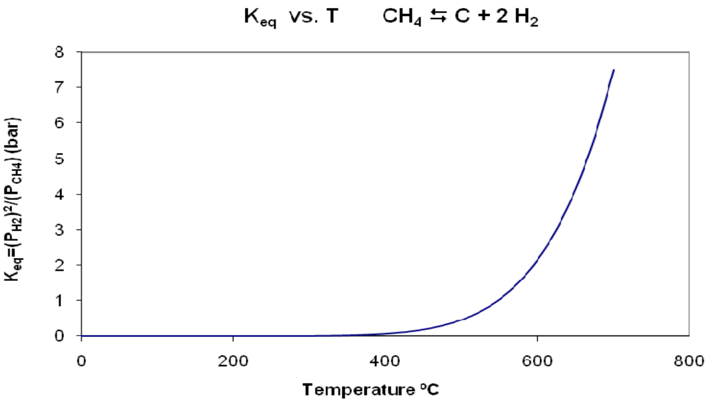

Figure 1: Equilibrium constant vs. temperature for the methane decomposition (r.3).

4 Conclusions

Gas from catalytic pyrolysis of natural gas (methane) has been proved to be suitable for use in the “steam-iron” process. This last can deal with hydrogen separation and purification (99.994 % in H_2 experimentally achieved along this work).

This is valid only under some feed and operating conditions. At 500 ºC, H_2/CH_4 ratios of 40/60 and above ensure no methane decomposition and hence hydrogen purification. Higher temperatures imply that this ratio must be also higher.

Typical streams from natural gas pyrolisis have a H_2/CH_4 ratio around 80/20 [2]. Therefore, operation temperatures up to 575 ºC are able to be used to purify hydrogen. This favors kinetics and shorter reaction times.

Small differences are found among the solids under study in separation/methane decomposition behavior. Both are useful for the pyrolysis gas streams.

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