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Hydrogen production by two-step thermochemical cycles based on commercial nickel ferrite: Kinetic and structural study

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ABSTRACT

One of the promising routes for hydrogen production consists of the dissociation of the water molecule through two-step thermochemical cycles based on iron oxides, i.e., ferrites. In a previous work, our group evaluated the activity of five commercial ferrites for this purpose, being Ni ferrite the one that exhibits the highest hydrogen production. In this work, the results obtained after a more exhaustive study of the thermochemical cycle based on a commercially available Ni ferrite are presented. Structural characterization of $NiFe_2O_4$ after each step of the thermochemical cycle is shown, as well as oxygen and hydrogen production over several cycles. In addition, kinetic parameters of this cycle are also studied, fitting the experimental data obtained under isothermal conditions to the most appropriate model among those ascribed to gas–solid non-catalytic multistep reaction systems.

1. Introduction

During the last century fossil fuels have been considered as the primary energy source. Nevertheless, they present important disadvantages such as the lack of fossil resources and limitations on the release of greenhouse effect gases during their combustion. Therefore, since the oil crisis of 1973, significant progress has been made in the search for alternative energy sources. In this sense, hydrogen is considered a sustainable and clean energy carrier that could potentially replace the use of fossil fuels. Thus, huge efforts are focused on the development of new techniques for massive hydrogen production [1–3].

Nowadays, one of the routes being developed for obtaining hydrogen is based on its generation from water splitting through solar thermochemical cycles. One-step or direct water splitting for H_2 production (1) is theoretically simple, but it requires high temperatures to get a significant hydrogen production yield (17% at $T \geq 2800$ °C and 0.01 bar) and an efficient separation method of the formed gases in order to prevent their recombination [4]. These two factors imply severe technological drawbacks that can be avoided by dividing the splitting process into different partial reactions, each

performed at a lower temperature than the direct thermolysis. Thus, thermochemical water splitting consists on the conversion of water into hydrogen and oxygen by a series of endothermic and exothermic chemical reactions. They constitute a practical way to overcome the above mentioned limitations, since, the operation temperature is reduced and hydrogen and oxygen are produced at separate stages. Endothermic reactions can be driven by concentrated solar energy [5–7].

$$H_2O \Rightarrow H_2 + \frac{1}{2}O_2 \quad T > 2800°C \tag{1}$$

Among the great number of water splitting thermochemical cycles proposed, two-step processes based on metal oxides are considered as one of the most appropriate candidates for their use with concentrated solar radiation. These cycles involve the endothermic reduction of the oxide at high temperature (activation) (2), followed by the exothermic oxidation of the reduced oxide, which reacts directly with steam for hydrogen generation (hydrolysis) (3) [5].

$$MO_x \Rightarrow MO_{x-\delta} + \frac{\delta}{2}O_2 \quad T > 1300°C \tag{2}$$

$$MO_{x-\delta} + \delta H_2O \Rightarrow MO_x + \delta H_2 \quad T < 1000°C \tag{3}$$
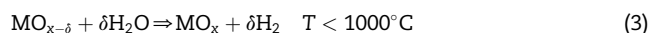
One of the metallic oxide cycles proposed for solar water splitting is based on the redox pair Fe_3O_4/FeO [8,9]. Although relatively high theoretical hydrogen yields are obtained, this system presents a disadvantage associated with the high temperature required for the activation step ($T > 2800$ °C). A reduction of this temperature can be obtained by using partially substituted ferrites of the type MFe_2O_4 (M: metal), spinel ferrites. Therefore, they are considered as promising materials for solar hydrogen production by two-step thermochemical cycles [10,11].

Studies on water splitting with different synthetic ferrites have been reported in the literature [11–15]. In a previous work, our group has evaluated the activity of several commercial ferrites, concluding that Ni ferrite is the most promising ferrite for solar hydrogen production [16]. This paper describes the results of a kinetic study carried out to gain insight into the reduction and oxidation steps of the process so as to obtain data for further design of a suitable reactor and establish the optimal reaction conditions for such a purpose.

2. Experimental procedures

Commercially available $NiFe_2O_4$ ferrite nanopowder ($\geq$98%) was purchased from SIGMA–ALDRICH. This material was chemically characterized by XRF (PANalytical AXIOS). Powder X-Ray diffraction (XRD) patterns were obtained by means of a PANalytical X'Pert PRO diffractometer operating in $\theta-\theta$ configuration, with Cu K_α radiation. BET surface area was also calculated from N_2 adsorption isotherms (Micromeritics 2100) measured at 77 K over samples previously degassed at 140 °C. Thermal characterization of the cycle was performed by two units: a Seiko TG/DTA 6300TGA for the activation step and a NETZSCH STA 449 Jupiter equipped with an electric furnace suitable for the hydrolysis reaction at several He flow rates

and water concentrations (maximum working temperature of 1350 °C and maximum heating rate of 20 °C min^{-1} are imposed by the equipment). Thermochemical cycles were carried out in a laboratory scale testing bench based on a tubular reactor placed inside an electric furnace as displayed in Fig. 1 [16]. In the experimental study, a fixed-bed reactor layout was used and the reactor characteristics allowed the control of the heating rate and temperature, enabling the determination of kinetic laws. Mullite and quartz tubes (both 20 mm outer and 17 mm inner diameters) were used for the activation and hydrolysis reactions, respectively. About 0.7 g of powder sample was placed in a Pt/Rh (90:10) crucible inside the tubular reactor (Fig. 1). Activation reaction was studied at temperatures between 1350 and 1450 °C, keeping this temperature for 4 h and hydrolysis reaction was carried out at temperatures between 650 and 950 °C, keeping this temperature for 5 h. The sample was heated under a 100 mL min^{-1} Ar flow to the desired temperature at a rate of 50 °C min^{-1} and then held isothermally. Steam for the hydrolysis step was generated by passing Ar through deionized water at 80 °C, so that the water mole fraction in the feeding gas was 0.5, i.e., about 100% relative humidity. The effluent gas was analysed by a micro-gas chromatograph (Varian CP4900) which automatically samples gas aliquots from the reactor outlet every ca. 2 min. Numerical integration of the obtained molar flow–time curves provides the total amount of oxygen and hydrogen evolved.

3. Results and discussion

3.1. Characterization of the as-received ferrite

A $Ni_{0.99}Fe_{2.01}O_{4.00}$ stoichiometric formula was obtained by chemical characterization of the $NiFe_2O_4$ commercial ferrite by XRF (Table 1). XRD diffraction patterns show that this material is mainly composed of a spinel-type crystalline phase, with a lattice parameter a_0 (8.32 Å) in agreement with that encountered in the *International Centre for Diffraction Data* (*ICDD*) database used by our group [16,17]. This ferrite also exhibits a high surface area value associated with a small crystal size (Table 1). Thermal characterization of $NiFe_2O_4$ under N_2 flow was performed in order to study the behaviour of this material during the activation step. Fig. 2 shows the thermal analysis of an original $NiFe_2O_4$ sample and a $NiFe_2O_4$ sample after a first thermochemical cycle. At a temperature below 1350 °C, the original $NiFe_2O_4$ sample shows a higher weight loss than that subjected to a first thermochemical cycle. This fact could be explained by the presence of oxygen
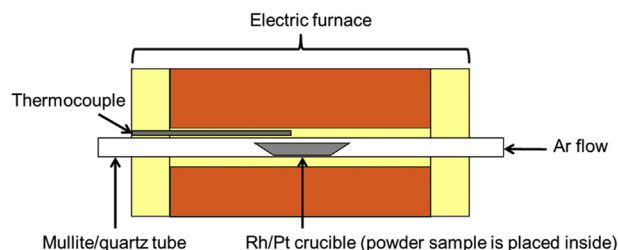

Fig. 1 – Reactor setup.