

Nickel ferrite supported on calcium-stabilized zirconia for solar hydrogen production by two-step thermochemical water splitting

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Solar hydrogen production by thermochemical cycles from water using oxide redox pairs represents a promising technology at medium-long term to storage intermittent solar irradiation. Redox oxides based on nickel ferrite supported on modified zirconia have been prepared and studied for renewable H₂ production from water by two-step thermochemical cycles. We report herewith a new material based on nickel ferrite supported on Ca-doped zirconia substrate that presents high efficiency for hydrogen production, which is ascribed to a high active phase dispersion promoted by the inclusion of part of Fe cations in the support lattice and by the formation of calcium zirconate, acting as a physical barrier that hinders sintering.

Keywords:

Hydrogen production, two-step thermochemical water splitting, nickel ferrite, calcium-stabilized zirconia

1. Introduction

The production of renewable hydrogen by the splitting of water molecule is a sustainable energy source for the future. Ideally, the simplest process would be to use concentrated solar energy in a chemical reactor to perform the direct decomposition of water into hydrogen and oxygen. The direct decomposition of water into hydrogen and oxygen needs extremely high temperatures to reach a reasonable yield. Moreover, after the water splitting process, it is necessary to separate hydrogen and oxygen, which raise the operation cost and the technological difficulty. Another method is water splitting by thermochemical cycles, using a series of reactions which have the net result of decomposing the water molecule into oxygen and hydrogen. The use of these cycles for water splitting involves two advantages: a decrease in the operation temperature and the production of hydrogen and oxygen at separate stages, thus being a convenient way to overcome the above stated drawbacks [1].

One of the most promising solar thermochemical water splitting cycles is the two-step cycle using non-volatile materials such as the iron oxide redox pair [2],[3]. This process, originally proposed by (Nakamura, 1977) involves two reactions:



The first thermal-reduction (T-R) step of Fe_3O_4 to FeO (Eq. (1)) is highly endothermic and thermodynamically favourable at high temperature (above 2200 °C under a pressure of 1 bar), whereas the second water-decomposition (W-D) step (Eq. (2)) is slightly exothermic and it is feasible at moderate temperatures. In order to avoid the recombination of FeO and O_2 , the T-R is carried out under an inert gas flow. Even in this case, to avoid oxidation back of FeO to Fe_3O_4 , quenching would be necessary and this is not practical. On the other hand, another drawback of this redox pair is related to the melting point of FeO , which is below the temperature required for its T-R step. This fact promotes sintering, being necessary to extract and grind the reduced material before proceeding with W-D step. Therefore the use of materials with a melting point larger than the required T-R temperature is imperative. Solid solution redox systems based on

$M_xFe_{3-x}O_4$ (M : Mn, Co or Ni; $x = 0 - 1$) are outstanding candidates for this purpose, requiring $1400^\circ C$ for T-R and having a melting point above this temperature [4].

Previous works in the literature have shown the $NiFe_2O_4$ system as one of the most investigated composition with promising efficiency for H_2 production via 2-step water splitting thermochemical cycles [5]-[9]. The reduction and oxidation steps on $NiFe_2O_4$ have been also investigated and modelled via computational chemistry [10] and their structuration for use in solar reactors was also recently addressed [11].

One of the problems associated to $M_xFe_{3-x}O_4$ is the rapid deactivation of iron oxide particles during the cyclic reaction because of the high-temperature and subsequent sintering, which results in a rapid drop of exposed iron oxide surface area [12]. In order to solve this problem, it is essential to support the active redox oxide on a refractory substrate, such as ZrO_2 , which alleviates sintering, increasing the cyclability of the supported materials [4]-[13]. The Zr^{4+} cation is too small to withstand the cubic fluorite structure and only forms either at high temperatures or when the zirconium ion is partially substituted with another (usually larger) cation. Doping is usually performed by substituting lower valence cations into the lattice, which introduces oxygen vacancies to maintain the overall charge neutrality. These oxygen vacancies supply the equivalent sites allowing the oxygen ions to migrate [14].

Thus, an effective approach may be to combine two materials to get the desirable properties of each, such as the fast oxygen transport associated with doped zirconia and the thermodynamically favorable redox chemistry of iron [15].

It has been reported an improvement in hydrogen yield and cyclability using stabilized zirconia, by the addition of yttria (YSZ), that stabilizes the high temperature cubic phase during the cooling to room temperature [16]. The improvement in hydrogen production on ferrite/YSZ materials is associated with the redox transition of some Fe^{2+} - Fe^{3+} ions in the YSZ lattice, which alleviates the deactivation of the redox oxide due to sintering at a high-temperature [2],[17],[18]. When doped- ZrO_2 stabilized in the cubic polymorph was used as support for $NiFe_2O_4$, the Fe^{2+} ions from ferrite could be dispersed into the cubic zirconia lattice during the thermal reduction step. These Fe^{2+} ions atomically

dispersed in the zirconia lattice reacts with steam in the subsequent oxidation step improving the generation of hydrogen respect to the unsupported ferrites [16].

Taking into account that zirconia can be also stabilized by doping with Ca^{2+} ions [16],[19], in this work we explore a new approach to improve the efficiency of nickel ferrite for hydrogen production by 2-step thermochemical cycles supporting NiFe_2O_4 on zirconia doped with Ca, which is also compared with other samples based on nickel ferrite supported on zirconia and zirconia doped with Y. The synthesis method chosen, coprecipitation, is the simplest to implement of the wet chemistry synthesis methods, and allows a significant molecular mixing and thus a more homogenous material [20]. The incorporation of the nickel ferrite on this new Ca-zirconia doped support notably improves the hydrogen production and cyclability respect the conventional supports such as zirconia and YSZ. The improvement in activity on Ca-zirconia doped support was associated with the reactivity between ferrite and support as derived from the characterization by different techniques (N_2 adsorption-desorption, X-ray diffraction, XPS, Raman spectroscopy, Scanning and Transmission Electron Microscopy). Experimental details can be found in the Supporting Information (SI).

2. Experimental

2.1 Samples preparation

The preparation of samples $\text{NiFe}_2\text{O}_4/\text{ZrO}_2$, $\text{NiFe}_2\text{O}_4/\text{Zr}_{0.9}\text{Y}_{0.1}\text{O}_2$, $\text{NiFe}_2\text{O}_4/\text{Zr}_{0.9}\text{Ca}_{0.1}\text{O}_2$ (25% NiFe_2O_4 , weight) has been carried out by coprecipitation and refluxing at 60°C under inert atmosphere (He flow), pH 8.5, using NaOH as precipitant. The precursors used were $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$. Then, the precipitate is aged under stirring for 1 h. After, the ageing is completed overnight without stirring. The separation and cleaning of the precipitate was done by three centrifugation-washing cycles. After, the solid was dried at 60°C for 12 h and sieved between 0,21-0,42 mm. In order to get the final material consisting on NiFe_2O_4 supported on zirconia, YSZ or CSZ, the solid was calcined under N_2 flow at 600°C for 1 h (ramp 6.4°C/min).

2.2 Samples characterization

The specific BET area of the samples was determined from the nitrogen adsorption-desorption isotherms at 77 K, recorded with a Micromeritics ASAP 2020 apparatus. Prior to adsorption the samples were degassed at 413 K under vacuum for 4 h.

X-ray diffraction (XRD) of prepared samples before and after the redox cycles were recorded using a X'Pert Pro PANalytical X-ray diffractometer and nickel-filtered Cu K α radiation. For each sample, Bragg angles between 4° and 90° were scanned with a step size of 0.04°. The mean crystallite size was estimated from X-ray line width broadening using the Scherrer equation with the most intense and least overlapped peak.

The x-ray diffraction patterns were analyzed with the Rietveld method [21], using the Fullprof program [22]. For the refinement of the profile, a pseudo-Voigt function was used to simulate the peak shape, and the background was fitted with a sixth-degree polynomial function. In the final run we refined the scale factor, background coefficients, zero-point error, positional coordinates, cell parameters and overall thermal factor.

Raman spectra were recorded at room temperature with a Renishaw in Via Raman Microscope spectrometer equipped with a laser beam emitting at 532 nm and 0.5 mW output power. The photons scattered by the sample were dispersed by a 1800 lines/mm grating monochromator and simultaneously collected on a CCD camera.

The morphology of the samples before and after the reaction cycles was analyzed by Scanning Electron Microscopy, SEM (Hitachi TM-1000) coupled with an energy dispersive X-ray analyzer (INCAx-sight, Oxford Instruments), in order to analyze chemically the samples. Acceleration voltage was 15 kV.

A Philips Tecnai 20 T transmission electron microscope operated at 200 kV was employed to conduct high resolution transmission electron microscopy (HR-TEM) analyses. The TEM was equipped with a EDX Genesis detector.

Photoelectron spectra were acquired with a VG ESCALAB 200R spectrometer equipped with a hemispherical electron analyzer and an Al K α 120 W X-ray source. The pressure in the ion-pumped analysis chamber was below $3 \cdot 10^{-9}$ mbar during data acquisition. Intensities were estimated by calculating the integral of each peak after smoothing and subtraction of the S-shaped background and fitting of the experimental

curve to a mixture of Lorentzian and Gaussian lines of variable proportions. All binding energies (BE) were referenced to the adventitious C 1s line at 284.6 eV.

2.3 Redox activity tests

The materials prepared were used for the two step water splitting the reactions. The supported ferrite (0.5–1.0 g) was placed on a Pt-Ir tray in the middle of the reactor tube (made of recrystallized alumina, 48 mm of internal diameter and 120 cm of length) heated by an electric oven. Thermal-reduction (T-R) step was performed while passing N₂ gas (5 mL/min) (internal standard for GC analysis of products) and He (100 mL/min). The sample was heated to 1000°C (10°C/min) and then up to 1500°C (5°C/min) and keep at this temperature for 1 h. Finally, the sample was cooled to room temperature. After the T-R step, the thermally reduced solid sample was subjected to the water-decomposition (W-D) step. A H₂O/N₂/Ar gas mixture (31% vol. H₂O, by means of a saturator placed inside a heater) was introduced into the reactor. The reactor was heated up to 1100°C (5°C/min) for 2 hours. To determine the amounts of oxygen and hydrogen evolved during the T-R and W-D steps, the reactor effluent was analyzed by gas chromatography (Varian 3800), using helium as carrier gas for T-R and argon for W-D.

3. Results and discussion

The evolution of the hydrogen production in 3 consecutive thermal reduction-hydrolysis cycles on the samples prepared in this study: nickel ferrite supported on zirconia (F-Z), nickel ferrite supported on Y-stabilized zirconia (F-YSZ) and the nickel ferrite supported on the new Ca-doped zirconia (F-CSZ) is shown in Figure 1.

Total amount of hydrogen produced in each cycle per gram of ferrite and per gram of material together with ferrite conversions are reported in Table 1. Ferrite conversions were estimated from the amounts of hydrogen that were produced, assuming that the wustite phase formed in the T-R step was completely reoxidized to ferrite in the subsequent W-D step.

As derived from consecutive thermal reduction-hydrolysis tests, all the samples suffer some deactivation with cycles, following the trend: F-Z > F-YSZ > F-CSZ. Analysing quantitatively the hydrogen production obtained for these samples, it can be verified that Y- or Ca-doped zirconia, increases the activity, being calcium widely the most effective zirconia dopant. This is also shown in the values found for ferrite conversion.

It is worth mentioning that hydrogen production is notably increased for all supported nickel ferrites respect to non-supported nickel ferrite (table 1) which produces 0.234 milimol of H₂/g ferrite in the first redox cycle. Hydrogen production obtained on supported ferrites depends on the type of support, being the sample supported on Ca-doped zirconia (F-CSZ) the most efficient. This sample shows, in the first cycle, a hydrogen production more than five times higher than that achieved for the unsupported ferrite.

As derived from data depicted in Figure 1, the deactivation of nickel ferrite also depends on the type of support. Nickel ferrite supported on zirconia (F-Z) showed strong deactivation after the 3rd cycle. The deactivation was lower when the ferrite was supported on Y-stabilized zirconia while the ferrite supported on Ca-doped zirconia (F-CSZ) shows very stable behaviour after the three consecutive thermal reduction-hydrolysis tests.

As observed in figure 1, the on-set temperature is also influenced by the kind of support. Thus, for the sample F-CSZ the on-set temperature is slightly shifted to higher temperatures with consecutive cycles, from around 680°C, for the first hydrolysis to around 720°C for the third one. On the contrary, the sample supported on YSZ shows a higher increase of the on-set temperature from 825°C for the first hydrolysis up to 1020°C for the third one. The behaviour is different for the sample supported on zirconia (F-Z), for which is observed a decrease of the on-set temperature from 800°C for the first hydrolysis to around 670°C for the second and third hydrolysis stages.

The efficiency of F-CSZ samples for hydrogen production has been compared with the results reported in literature for materials based on transition metal ferrites supported on zirconia or doped-zirconia, choosing those works for which the experimental conditions of redox cycles have been similar to those used in this study. The evolved hydrogen amount in the third W-D step for the sample

supported on CSZ (0.27 milimol H₂/g material, 1.07 milimol H₂/g ferrite) is some lower the values reported for a sample based on NiFe₂O₄/ZrO₂^[16], (around 0.54 milimol H₂/gram of material for the third cycle) and in the order of a sample based on manganese or cobalt ferrite supported on zirconia (around 0.3 milimol H₂ per gram of material, for the third cycle)^[23]. However, for these last reported works, it has to be considered that the W-D step has been carried out over a ground sample by using a pestle and a mortar (after T-R step), which alleviates the agglomeration suffered during the T-R step. In our work, the 3 reduction-hydrolysis cycles are carried out over a sample that is not taken out from the reactor at any time. On the other hand, it has to be highlighted that hydrogen production per mass of nickel ferrite is much higher for F-CSZ sample when compared to unsupported NiFe₂O₄ (0.38 mmol H₂ g)^[24].

Next, different characterization results are presented, attempting to identify the physicochemical properties that make the CSZ-supported sample more active and stable.

In all supported ferrites the specific surface area (Table S1), dramatically decreased after thermal cycles due to the sintering suffered by particles associated to the high reduction temperatures. The BET surface area is barely higher only in sample doped with Ca, after redox cycles.

At structural level, for the fresh powder samples, the main diffraction lines (Figure S1, SI) correspond to NiFe₂O₄ and tetragonal phases of ZrO₂ and ZrO₂ containing Y or Ca. The stability of the tetragonal phase is attributed to the presence of oxygen vacancies, which are generated because the samples are thermally treated under N₂ flow^[25]. Diffraction profiles confirm the insertion of Y³⁺ and Ca²⁺ ions into the ZrO₂ lattice, which is evidenced by a shift of the diffraction peaks toward small angles respect to the XRD pattern of F-Z, due to an increase of the cell parameter (figure S2) derived from the substitution of Zr⁴⁺ (0.84 Å) by Y³⁺ (1.02 Å nm) or Ca²⁺ (1.12 Å). The observed peak shift was smaller for the calcium-doped support, indicating the lower substitution of Ca²⁺ ions than in the case of Y³⁺ ones, as a consequence of its bigger size and divalent oxidation state that hampers its inclusion into the zirconia lattice.

As derived from XRD analyses, after the thermochemical cycles (fig S1), in F-Z and F-CSZ samples, tetragonal ZrO₂ evolves towards a monoclinic phase, while

in F-YSZ, the cubic zirconia phase is formed. The stabilization of zirconia with yttrium in a cubic phase verifies the successful incorporation of Y^{3+} into ZrO_2 lattice. On the contrary, the sample F-CSZ does not form detectable crystals of cubic phase. This formation of a single monoclinic phase after heating and cooling is in accordance with studies previously published in the bibliography [26]. The identification of monoclinic and cubic zirconia phases in samples after the thermochemical cycles was confirmed by Raman spectroscopy (Fig S3).

Mean crystallite size of nickel ferrite and zirconia phases, determined by the Scherrer equation (Table S2), showed an increase of their average crystallite size after the thermochemical cycles. Although the weight amount of nickel ferrite is considerably high (25%), the average size of its domain size is rather low. This is ascribed to the synthesis method used in this research: coprecipitation of all the cations of the samples, both Fe and Ni as the corresponding to the support (Zr, Ca and Y).

By Rietveld refinement we also confirmed the crystal structures (Fig. S4) and determined the proportion of Fe in the support lattice. As observed in table 2, although the cubic phase was found in the support of the F-YSZ sample, Rietveld analysis did not show any Fe occupying metal lattice positions in the support. On the contrary, for the Ca-doped sample, 7% Fe is occupying Zr ion positions in the support lattice (table 2). As previously commented, this fact would enhance the activity and stability, by maximizing the active phase dispersion and by avoiding sintering of this lattice stabilized Fe cations [16],[17]. Since the size of Fe^{3+} ($r_{\text{VIII}} = 0.78 \text{ \AA}$) is slightly smaller than Zr^{4+} ($r_{\text{VIII}} = 0.84 \text{ \AA}$), we could expect a reduction of the lattice in comparison to F-Z sample, however this is not appreciable because the increment of the cell due to the introduction of Ca^{2+} ($r_{\text{VIII}} = 1.12 \text{ \AA}$) implies a greater effect [27]. On the other hand, it is worth mentioning that in F-Z sample, the third line of Bragg reflections correspond to 1-2 % of Zr_3NiO_x impurity (figure S4).

Morphological characterization of the samples before and after thermochemical cycles by SEM (Figure 2) reveals large differences between fresh and used samples and among the used samples. The comparison between micrographs corresponding to the fresh and used samples clearly shows the agglomeration of particles.

For the final samples (after 3 consecutive thermochemical cycles), nickel ferrite and support are differentiated by EDS analyses performed in different zones. It is clearly observed that the grain size considerably changes among the supported samples. For the sample F-YSZ, it should be highlighted the formation of a material in which both ferrite and YSZ support phases seem as molten, being not possible to differentiate the relief of the grains. In the case of the sample F-CSZ, the grain size corresponding to the support is considerably smaller than in the case of F-Z and F-YSZ samples and the particles of nickel ferrite and CSZ support appear more separated than in the other samples.

The sample supported on Ca-doped zirconia also showed high and increasing oxygen production along the consecutive thermochemical cycles (Table S3 and figure S6). This improved production of oxygen in the thermal reduction step could be related to the formation of CaZrO_3 by solid state reaction between CaO and ZrO_2 entities. It has been reported in literature that calcium zirconate presents high oxygen ion conductivity at very low oxygen partial pressures and high temperatures. These low oxygen partial pressure and very high temperature are the conditions used during the thermal reduction stage [28],[29]. In accordance with the stoichiometry of the nickel ferrite redox cycle, the number of oxygen moles produced in the reduction step should be half of the moles of hydrogen produced in the hydrolysis step (table 1 and table S3). However, it has to be considered that during the reduction step, oxygen produced by the reduction of Fe^{3+} to Fe^{2+} can be introduced into the matrix of $\text{Zr}_{1-x}\text{Ca}_x\text{O}_{2-\delta}$, filling the oxygen vacancies and forming segregated CaO , decreasing the evolved oxygen amount. Thus, the high temperature and inert gas used during the thermal reduction implies secondary state reactions that modify the expected outcoming gases. In the third cycle the oxygen that evolves is slightly higher than what would be expected from stoichiometry. This excess is explained by high oxygen ion conductivity of calcium zirconate at very high temperature and very low oxygen partial pressure.

Calcium zirconate was not observed by XRD, probably because the percentage is very low or the particles are too small to have an appreciable diffraction. The formation of CaZrO_3 on used F-CSZ sample was observed by HRTEM. Figure 3 shows representative HRTEM images for F-CSZ sample, before and after the thermochemical cycles, being possible to differentiate between ferrite and support

particles. The comparison of micrographs corresponding to both initial and final samples reveals an enlargement of nickel ferrite particle size. It is also found and corroborated by EDX the presence of CaO particles in F-CSZ sample before the thermochemical cycles and the formation of CaZrO₃ after redox cycles.

The elemental oxidation states on the surface of F-CSZ, fresh and used samples were analysed by XPS. The X-ray photoelectron spectra of O 1s, Ca 2p3/2, and Zr 3d5/2, Ni 2p3/2 and Fe 2p3/2 are presented in Figure S5 (SI).

The corresponding binding energy values and different atomic ratios are presented, respectively, in Tables S4 and S5.

The binding energy of Zr 3d5/2 level for ZrO₂ is observed at 182.0 eV and the formation of Zr mixed oxides will give to an increase in binding energy [30]-[32]. On the other hand, the spin-orbit distance (3d5/2 – 3d3/2 splitting) for CaZrO₃ species is around 2,4 eV [33]. The comparison of XPS spectra for initial and final Ca-doped sample shows an increase of binding energy from 182,5 to 183.0 eV as well as an increase in 3d5/2 – 3d3/2 splitting from 2,2 to 2,5 eV. These facts support the formation of CaZrO₃ along the cycles, as well as the slight decrease of binding energy for Ca 2p core level in the sample in comparison to its fresh counterpart [31]. From XPS results (Table S5, SI) can be also extracted that Fe and Ni surface exposure decreases moderately after redox cycles in the Ca-doped zirconia sample, due to the sintering of nickel ferrite particles suffered during the thermochemical cycles, which produced a slight decrease in evolved hydrogen amount with consecutive cycles (table 1). The lesser loss of surface Fe compared to surface Ni is attributed to the inclusion of some proportion of iron into the zirconia lattice.

The evolution of the hydrogen production along 3 consecutive thermal reduction-hydrolysis cycles on the samples prepared in this study showed that both hydrogen production and deactivation with cycles were notably improved when nickel ferrite was supported on Ca-doped zirconia, F-CSZ (Figure 1, Table 1). Structural characterization of the Ca-doped zirconia sample showed the insertion of Fe ions from the ferrite occupying Zr ion positions in the support lattice (table 2). The presence of these Fe ions into the ZrO₂ lattice could be related with the improvement of hydrogen production observed in the Ca-doped zirconia sample because, as indicated in the introduction section, the Fe ions atomically dispersed

in the zirconia lattice avoid sintering [34]-[36] and they reduce/react with inert/steam in the reduction/oxidation steps improving the generation of hydrogen respect to unsupported ferrites [16]. The existence of calcium zirconate particles detected by TEM (Figure 3) and XPS (Figure S5 and table S4) could also participate in the improvement in stability observed for the F-CSZ sample. Calcium zirconate particles, derived from the solid state reaction between ZrO_2 and segregated CaO entities (formed from Ca^{2+} ions not inserted into the ZrO_2 lattice), can form a physical barrier between the nickel ferrite particles which can hinder the thermal sinterization of ferrite particles [31] maintaining the active surface area during the thermal cycles. The formation of these segregated calcium zirconate particles could be also responsible for the higher oxygen production capacity observed on the sample supported on Ca-ZrO_2 (Figure S6).

4. Conclusion

Nickel ferrite supported on calcium-doped zirconia shows high values of ferrite conversion and hydrogen production from water splitting via 2-step thermochemical cycles when is compared with un-supported nickel ferrite and with nickel ferrite supported on zirconia and on yttrium-doped zirconia. The improved behaviour of this formulation is associated with the presence of Fe ions, atomically dispersed into the zirconia lattice, which can reduce/react with inert gas/steam along the reduction/oxidation steps improving the generation of hydrogen. On the other hand, the formation of calcium zirconate particles by solid state reaction between ZrO_2 and CaO particles can form a physical barrier between the nickel ferrite particles which hinders their sintering, improving their stability for water-splitting thermochemical cycles.

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