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Thermochemical cycles over redox structured reactors

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ABSTRACT

Structured bodies from redox materials are a key element for the implementation of thermochemical cycles on suitable reactors for the solar H_2O splitting. In the current work different configurations of nickel ferrite were investigated with respect to their performance in H_2O splitting: i) powder, ii) disk, iii) honeycomb flow-through monoliths. The structured bodies were prepared via pressing and extrusion techniques. The performance of the different structures was affected significantly by differences in the structural characteristics. Alternative approaches involving casting techniques for the structuring of nickel ferrite porous bodies were also investigated. This work constitutes a preliminary attempt towards tuning such characteristics to achieve enhanced and cycle-to-cycle stable production yields.

Introduction

Although the market is getting progressively open in "structuring" and establishing the set-up towards a hydrogen economy (e.g. realization of hydrogen vehicles and increase in the number of refueling stations), there is still much distance to be covered until all conditions are met for supporting a completely renewable hydrogen production and a relevant infrastructure.

The idea of exploiting solar energy for the implementation of thermochemical cycles for the production of hydrogen from the splitting of H_2O, is intensely investigated during the last years. Thermochemical cycles for hydrogen production via H_2O splitting can offer a practical solution to the very high temperature (typically > 2000 °C) of direct thermolysis reaction schemes. Numerous such cycles have been proposed [1–3], several have been reviewed and investigated [4–7] and the ones currently receiving the highest attention from the research community include sulfur-based cycles, the copper-chlorine, the zinc/zinc oxide system as well as two-step redox stoichiometric and non-stoichiometric cycles of single or mixed metal oxides. Despite operating at substantially lower temperatures in comparison to direct thermolysis reactions,

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most of such cycles still require elevated temperatures that can be achieved via technologies exploiting concentrated solar radiation. Solar tower and/or solar dish technologies are capable of meeting the requirements for driving such reactions. Solar energy exploitation enhances further the renewability of those reaction schemes. Exploitation of suitable metal oxides (typically, zinc oxide, iron oxides, ferrites, ceria-based and perovskite compositions), based on stoichiometric and non-stoichiometric thermochemical cycles [8–17], have been acknowledged as having the potential to convert/store solar energy into valuable chemicals. Stoichiometric approaches (i.e. reduction of all the metal cations of a metal oxide to a lower oxidation state, e.g. Fe_3O_4 to FeO), despite of somewhat higher theoretical efficiency, are currently facing the challenge of cyclic structural transitions and phase changes involved, which can result to notable challenges with consequent adverse effects on technical feasibility and long term stability of active materials. The general scheme of non-stoichiometric thermochemical cycles for H_2 production can be written as:

$$M_{x1}N_{x2}O_y \leftrightarrows M_{x1}N_{x2}O_{y-\delta1} + \delta_1/2O_2 \quad (1100-1500\,^\circ C) \tag{1}$$

$$M_{x1}N_{x2}O_{y-\delta1} + \delta_2H_2O \leftrightarrows M_{x1}N_{x2}O_{y-\delta1+\delta2} + \delta_2H_2 \quad (800-1200\,^\circ C) \tag{2}$$

where δ_1, δ_2 represent oxygen deficiencies referring to the thermal reduction step (δ_1) and the material after oxidation by H_2O (δ_2) respectively; M: metal; N: metal and $M_{x1}N_{x2}O_y$ typically corresponding to ferrite (e.g. $NiFe_2O_4$), ceria-based (e.g. $Ce_xZr_{1-x}O_2$) or perovskite (e.g $La_{1-x}Sr_xFeO_3$) structures.

A widely studied concept for the implementation of such cycles on solar reactors relates to structured bodies assemblies [16–25]. Such an approach is simple and in-principle capable of ensuring overall system durability in the course of hundreds of cycles. Such advantages are to some extent at the expense of heat recuperation, however the latter disadvantage can be mitigated significantly via careful overall optimized process design.

Key element of the structured reactors is the substrate, i.e. the inert structure that will accommodate the active materials. However, elimination of interactions of the substrate with the active redox material is quite challenging, especially at the elevated temperatures that are required by the above mentioned solar thermochemical reactions. Naturally, structured bodies shaped entirely from the active redox materials should provide, theoretically, an effective solution to this challenge. Yet, they should be designed to also ensure high gas-solid contact area, robustness and resistance to sintering phenomena induced by high temperatures especially in the course of multiple cycles. Currently the structured reactors are the only ones that have been scaled up to several dozens of kWs (100–750 kW level) [20,25,26].

The present study is an investigation of various structured morphologies based on nickel ferrite, prepared by different shaping techniques. Nickel ferrite was selected for the manufacturing of monolithic structures mainly because of the lower temperature that is required during the thermal reduction step compared for example to CeO_2-based structures, which have been previously materialized and tested for the same application [16,17], and require temperatures higher than 1500 °C to achieve significant reduction and consequently splitting activity. In addition, the color of Ni-ferrite (black) is most appropriate for structures that are developed as active components of solar absorbers, since it is expected that it will enhance the absorption of solar radiation compared to other lighter colored materials.

The whole development path is presented and the most promising approach is defined outlining further future optimization studies. Long-term exposure results are also presented.

Experimental–methods

Synthesis of redox material

The redox material selected for the development of porous ceramic structures was the $NiFe_2O_4$, which is a well-known and widely investigated composition [12,14,21,27,28]. $NiFe_2O_4$ has also been investigated via computational chemistry (DFT calculations, [29]) where it was shown that it is one of the state-of-the-art formulations in the family of ferrite materials. The nickel ferrite powder was synthesized via the Self-propagating High-temperature Synthesis (SHS) technique from a mixture of Fe, NiO and Fe_2O_3, according to the following reaction scheme:

$$Fe + NiO + 0.5\,Fe_2O_3 + (1.5/4)\,NaClO_4 \rightarrow (NiO)_{1.0}Fe_{2.0}O_3 + (1.5/4)\,NaCl \tag{3}$$

Details on the SHS technique can be found in Refs. [18,30].

Another synthesis route that was applied was the conventional solid state synthesis (SSS), where the raw oxide precursors (i.e. NiO and Fe_2O_3 at the appropriate ratio for the synthesis of nickel ferrite) were well homogenized into a mixture and calcined at 1400 °C to facilitate the formation of the ferrite.

Structuring into porous bodies

Two different structures were prepared; a porous disk geometry and a honeycomb monolithic geometry. Both structures consisted entirely of nickel ferrite. The disk geometry was prepared in order to have a porous structured body that is an intermediate step between the completely loose form of the powder and the well-organized form of a honeycomb monolith. For the preparation of the porous disk a mixture of nickel ferrite with a pore forming agent (i.e. an organic compound) was adequately pressed with the aid of a single-axis hydraulic press to form a dense disk that was further processed to achieve a degree of porosity according to the procedure followed in Refs. [31,32]. Extrusion of honeycomb structures is a process that is performed commercially for the manufacturing of numerous technical ceramics from different materials (e.g. Cordierite, SiC, Al_2O_3 etc) and for a variety of applications, most commonly involving water purification or automotive emission control. Ferrite materials are industrially shaped into structures like toroids, cylinders, tiles