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# Improved kinetic model for water splitting thermochemical cycles using Nickel Ferrite

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## ABSTRACT

In a previous work of the authors (*AIChE Journal* 2013; 59(4): 1213–1225) on the characterization of the performance of redox material compositions during two-step thermochemical splitting of water, it was observed that fitting of the obtained hydrogen and oxygen concentration profiles with a reaction model based on simple first order reaction rates could describe adequately only the first part of the evolution curves. This suggested that more complicated reaction models taking into account the structure of the redox material are needed to describe the whole extent of the experimental data. Based on the above, a minimum set of experiments for water splitting thermochemical cycles over a Nickel-ferrite was designed and performed involving an increased duration of the reaction steps. A new extended model was derived for the water splitting and thermal reduction reactions, which considers two oxygen storage regions of the redox material communicating to each other by a solid state diffusion mechanism. The inclusion of two state variables instead of one has a significant effect on the reaction dynamics and renders the model capable to explain the dynamics of the convergence of the thermochemical cycles to a periodic steady state, observed experimentally in the previous work.

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## 1. Introduction

During the last years the subject of hydrogen production by employing water splitting thermochemical cycles is examined intensively in the literature [1,13]. The efficient implementation of the process in practice requires the appropriate (optimal) redox material, an optimized reactor design and an optimized operation strategy [14,15]. In order to be able to scale-up the results from the testing of redox materials in

laboratory reactors to the production reactor the kinetics of the reactions must be derived. This kinetics can be incorporated in the mathematical models of the application reactor, which will be used to optimize the reactor design and the operation strategy. In this spirit an effort is made to derive a descriptive reaction kinetic model for a particular redox material, a Ni-ferrite, which was found to be an active water-splitting material.

The thermochemical production of hydrogen from water splitting based on redox-pair cycles comprises of two

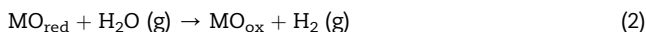
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reactions, the thermal reduction (regeneration of the material) (Reaction (1)) and the water splitting reaction (oxidation of the material) (Reaction (2)):



where  $\text{MO}_{\text{ox}}$  is the oxidized form of the redox material and is usually the higher-valence oxide of a metal exhibiting multiple oxidation states. The thermal reduction step is the higher-temperature step during which the oxidized form of the material releases a quantity of oxygen and “falls” to a more reduced (lower-valence) state. During the water splitting step the reduced material is oxidized from water back to the higher-valence state by taking oxygen from water and producing hydrogen, establishing thus a cyclic process.

Among the compositions that have been extensively tested for such applications are the ferrites [16–21]. However, it is observed that the conditions that are employed for the synthesis and the characterization of the materials, such as the temperature, are moderate when compared to the water splitting and the thermal reduction cyclic operation of the materials. This may lead to phenomena such as sintering of the materials causing a modification of their structure and some times also reduction of their surface area which subsequently leads to the degradation of the performance of the material. In addition, evaluation conditions that are not representative of the actual application may obstruct the proposal of appropriate reaction mechanisms or the extraction of reliable water splitting – thermal reduction kinetic data.

In Ref. [13], a variety of redox materials were synthesized and then calcined under air and under nitrogen at 1400 °C to establish a common background for relevant comparisons. It was found – and corroborated by other studies reported in the literature [18–21] – that among the many ferrite materials tested for the targeted application, Zn-containing ones exhibit Zn-volatilization problems and Mn-containing ones suffer from phase stability problems under air atmosphere at high temperatures. These facts practically leave only  $\text{NiFe}_2\text{O}_4$  and  $\text{CoFe}_2\text{O}_4$  as the most “robust” among the ferrites, capable to operate reliably at the real conditions of a solar-aided process. Between these two,  $\text{NiFe}_2\text{O}_4$  was the first material selected as a “model system” for a thorough parametric study of the water splitting – thermal reduction reactions in order to quantify the effects of various operating parameters presented and to extract reaction kinetics. In Ref. [22] a simple mathematical model was formulated describing the water splitting – thermal reduction cyclic studies with  $\text{NiFe}_2\text{O}_4$  redox materials via the heterogeneous surface reactions of water vapor with the redox powder material, from which, in conjunction to the experiments above, the kinetic parameters of the water splitting and thermal reduction reactions were extracted. The effective water splitting kinetic constant exhibited weak temperature dependence between 700 and 1100 °C.

Fitting of the hydrogen and oxygen evolution profiles from these experiments with simple first order reaction rates could not describe adequately the entire profile. The inability of the model to describe the whole extend of the experimental data

was attributed to relatively short reaction times (i.e. the duration of activation, water splitting and thermal reduction steps) that led to insufficient: i) exhaustion of the oxygen uptake capability of the material and ii) liberation of the oxygen storage sites, during the water splitting and the thermal reduction steps respectively.

In order to be able to describe the experimental data with an extended reaction model,  $\text{NiFe}_2\text{O}_4$  was employed for the realization of experiments that involved an increased duration of the reaction steps. In this way, the hydrogen and oxygen concentration evolution curves corresponding to conditions close to the exhaustion of the storage sites were obtained. These long-term experiments were carried out at different combinations of water splitting and thermal reduction temperatures. The structure of the present work is the following: At first the kinetic model is described. Then the experimental conditions and results are presented. The strategy followed to fit the model to the experimental results is explained in detail. Finally a parametric study of the model is performed in order to demonstrate the effect of several parameters such as the cycling period and the initial state of the redox material.

## 2. Kinetic model description

There are two basic approaches for the derivation of rate expressions of water splitting and the corresponding regeneration (thermal reduction) reactions. The first approach is based on the consideration of kinetic expressions from works conducted in the field of solid phase reactions [23,24]. The expressions are fitted to the experimental rate-conversion curves to find the optimum expression and subsequently the mechanism that dominates the reaction rate. The disadvantage in this case is that the experimental results are typical for partial conversion and since the dominant reaction mechanisms (like the shrinking core one [25] or the three dimensional diffusion dominated [26]) have non-linear rates, a question about the validity of the approach arises. Other solid state reaction mechanisms proposed for the water splitting/thermal reduction reactions is the simple constant radial retraction rate [27] and the two-dimensional growth of nuclei model [28].

A linear reaction rate (the second approach) does not have the disadvantage associated to the incomplete conversion however the actual data do not support such a linear rate [22]. On the other hand the initial period of the reaction can be approximated by a linear form up to a point of 30% reduction of the initial rate. At longer reaction times the actual rate deviates from the linear behavior implying that there is a second reaction step which sustains the reaction. A phenomenological model will be developed here to be valid for the whole reaction duration met in the experiments. The new model does not cancel the previous linear model described in Ref. [22] but naturally extends it to longer reaction times.

The general idea is that the redox material can be considered to consist of two distinct regions. The first region is in contact with the gas phase (outer region). This region includes the pore structure that is filled with gas. It is noted that the

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