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# Study of the hydrogen production step of the $Mn_2O_3/MnO$ thermochemical cycle

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## ABSTRACT

In this work, a complete study of the second step of the  $Mn_2O_3/MnO$  thermochemical cycle for solar hydrogen production has been performed. It includes a complete thermodynamic calculation of the equilibrium phases between  $MnO$ ,  $NaOH$  and  $H_2$ , which shows that the reaction takes place theoretically at temperatures above  $75\text{ }^\circ\text{C}$ . However, the experimental results demonstrate that it is necessary at least  $450\text{ }^\circ\text{C}$  to achieve a satisfactory reaction rate. It indicates a dramatic influence of chemical kinetics and diffusion process, displacing the reaction to higher temperatures than those predicted by thermodynamics. The resultant solid of the reaction exhibits a phases distribution highly dependent on the temperature and the  $NaOH:MnO$  ratio and this is of great influence in the overall rate of the process. The kinetic study shows that the overall process involves not only the chemical reaction between  $MnO$  and  $NaOH$ , but also a number of physical processes (heat and mass transfer) and solid phase transformations. The apparent activation energy calculated is a composite value determined by the activation energies of those elementary processes.

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## 1. Introduction

The worldwide increasing energy demand and the need to reduce greenhouse gases emissions have promoted the study of alternative fuels and energy sources [1,2]. As a promising energy carrier, hydrogen could be a solution to store and transport renewable energy in a chemical form, helping to solve the problem of some greenhouse gases emissions and releasing the world from the current fossil fuel dependence. However 95% of hydrogen production is mainly derived from fossil fuels while only about 5% is produced from renewable energy [1,2]. It must be taken into account that only a massive hydrogen use is reasonable if renewable energy sources are

used for its production. At this point the ideal process would be the water thermolysis driven by solar energy concentrated in a chemical reactor where the dissociation of water into  $H_2$  and  $O_2$  occurs. However the high temperature required to reach reasonable values of dissociation (above  $4250\text{ }^\circ\text{C}$ ) and the need to separate  $H_2$  and  $O_2$  at high temperatures, to avoid recombination or explosive mixtures, have hindered the development of this process. For these reasons, water splitting by solar-driven thermochemical cycles that overcome those limitations represents a promising technology for this purpose [3].

The viability of a thermochemical cycle is based on different factors such as the number of reactions involved in the process, the required temperatures, the availability and

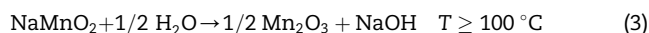
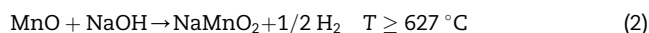
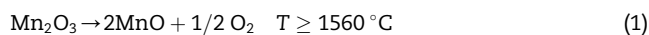
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cost of reactants, the corrosive power of the species involved in the process, etc. The most important features of a thermochemical cycle to be considered interesting are [4,5]: i)  $\Delta G_r = 0$  in an achievable range of temperatures; ii) minimum number of steps; iii) each step should be a fast reaction, without secondary reactions to avoid slow steps that slow the process down; and, iv) easily manageable intermediate species and minimum energetic requirement in any separation needed.

In recent years research has mainly focused on two-step metal oxide thermochemical cycles because of their simplicity and high efficiencies. However despite the advantages presented by these cycles, difficulties associated to the still high temperatures required for the process (1900–2200 °C) have diverted attention to other alternatives. Thus, new modified materials and operational conditions have been developed and proposed as alternatives for traditional two-steps cycles [5]. Besides that, thermochemical cycles based on more than two steps, which require lower temperatures, have been proposed attractive to be combined with concentrated solar energy [3]. In these cycles the direct reduction of water with the reduced oxide is not thermodynamically possible so a better oxidizing compound such as NaOH or KOH must be used for hydrogen production. Then, the oxidizing species and the initial oxide are recovered by reaction of the mixed oxide obtained in the hydrogen production step with water at low temperatures.

Sturzenegger and Nüesch proposed in 1999 a manganese-oxide-based cycle for the production of solar hydrogen [6]. This cycle consists of three steps (reactions 1–3).



The influence of different variables and the kinetics of the high-temperature reduction of  $\text{Mn}_2\text{O}_3$  to MnO have been previously studied in detail [7,8]. However, the hydrogen production step has been studied less thoroughly. From a theoretical point of view, Charvin et al. [9] couldn't developed the thermodynamic study for hydrogen production from MnO and NaOH due to the lack of thermodynamic data for  $\text{NaMnO}_2$ . Nevertheless they carried out the study for the production of hydrogen from  $\text{Fe}_3\text{O}_4$  and NaOH and they saw that an excess of NaOH in the initial mixture (10 mol NaOH/1 mol  $\text{Fe}_3\text{O}_4$ ) is enough to enhance the hydrogen production reaction, which is completed in the range of 100–1000 °C.

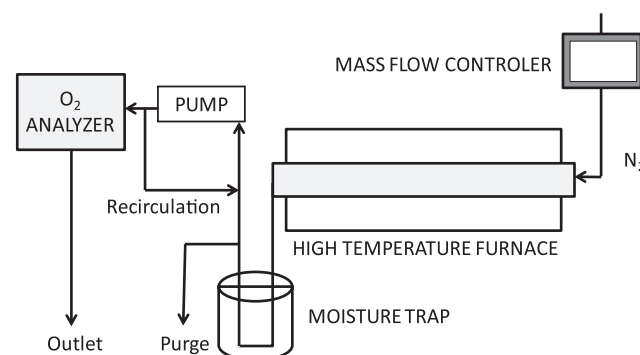
Experimentally, Sturzenegger et al. [10] proposed that hydrogen production from MnO and NaOH could be completed within ca. 75 min at temperatures of ca. 700 °C under reduced pressure. Kreider et al. [11] observed a full conversion after 3 h using a nitrogen purge, but only 30 min were required under vacuum at 850 °C. During those experiments vaporized sodium compounds reacted with the walls of the reactor (quartz or inconel metal alloy) and formed thermodynamically stable sodium silicate resulting in visible corrosion [9,11].

For these reasons the aim of this work is to carry out a thermodynamic study of the hydrogen production step in

order to get knowledge about the system behaviour and be able to compare with experimental results since predictions from thermodynamic data can be obviously limited by kinetics. Optimal operation conditions of the second step of the manganese-oxide thermochemical cycle will be determined to overcome all the difficulties reported in the literature (corrosion, high reaction times) and enhance and maximize the production of hydrogen.

## 2. Materials and methods

The hydrogen formation by reaction of MnO with NaOH was studied in a high temperature furnace as shown in Fig. 1. A Pt/Rh (90/10) crucible, resistant to NaOH corrosion and temperatures above 1300 °C, was placed inside as support for the MnO/NaOH mixtures. Stoichiometric MnO/NaOH mixtures and also an excess of twice NaOH respect to the stoichiometry of reaction 2 were studied. The reactants were milled before the reactions to homogenize the reactant mixture. The temperature was increased up to 1300 °C with different heating rates, from 2 to 20 °C/min. The  $\text{H}_2$  released from the reaction between MnO and NaOH was continuously removed with a purge of nitrogen (50 L/h). The gas flow from the reactor goes through a moisture trap in order to remove traces of condensed water that could interfere in the hydrogen detection. Then, part of the gas flow was released to the environment (Fig. 1, purge) whereas the other part was conditioned to a proper pressure (Fig. 1, pump and recirculation) for the analysis of the hydrogen in an Emerson Xstream analyser based on the thermal conductivity measurement principle and working at 50 °C. Since the hydrogen produced in the reaction is carried out from the reactor to the analyser with a nitrogen flow of 50 L/h, the response of the analyser is obtained as percentage of hydrogen in the flow with time. Integration of the graph obtained, taking into account the gas flow in the reactor (50 L/h plus the contribution of the hydrogen release during the reaction) and the simplification of the mixture as a perfect gas, allows the transformation of the response in total volume of hydrogen produced and the corresponding hydrogen mass. A standard gas mixture of 0.5% in  $\text{H}_2$  was used for the calibration of the equipment. The resultant solid material obtained after the reaction was characterized by X-Ray diffractometry using a PW3040/00 X'Pert MPD/MRD equipment.



**Fig. 1** – Schematic representation of the high temperature tubular furnace setup.

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