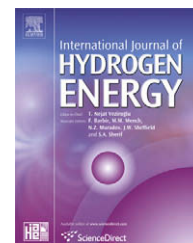


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The oxygen-releasing step in the water splitting cycle by $\text{MnFe}_2\text{O}_4\text{--Na}_2\text{CO}_3$ system

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ABSTRACT

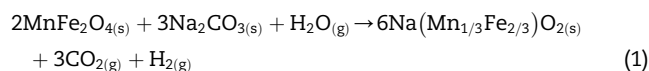
Investigation of the feasibility of the thermochemical two-step water splitting cycle based on $\text{MnFe}_2\text{O}_4/\text{Na}_2\text{CO}_3$ system is reported. Influence of temperature and carbon dioxide pressure on the oxygen-releasing step was investigated. XRD analysis was applied to obtain phase identification of reacted powders at investigated experimental conditions. Different sodium sub-stoichiometric $\text{Na}_{1-\delta}(\text{Mn}_{1/3}\text{Fe}_{2/3})\text{O}_{2-\delta/2}$ compounds were observed and their structure determined by using Rietveld analysis. Selected experimental conditions permitted to define a T/p_{CO_2} phase diagram, showing different solid phases coexistence regions. Experimental conditions that permit complete regeneration of the initial $\text{MnFe}_2\text{O}_4/\text{Na}_2\text{CO}_3$ mixture were identified (field I in the reported diagram), demonstrating the possibility of full chemical cyclical operation of the system.

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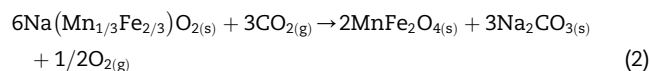
1. Introduction

In recent years several efforts have been done in order to develop chemical systems and solar reactor technology suitable for hydrogen production by CO_2 free processes [1–5]. In particular a special interest was aroused by thermochemical cycles able to perform water splitting at temperatures lower than that required by direct water thermolysis [6–10].

The manganese ferrite thermochemical cycle [11,12] is a two-step water splitting process based on a $\text{MnFe}_2\text{O}_4/\text{Na}_2\text{CO}_3$ reactive mixture. Water thermolysis occurs according to the following reaction sequence: in the first step (1) the reacting mixture $\text{MnFe}_2\text{O}_4/\text{Na}_2\text{CO}_3$ is oxidized by water producing hydrogen, sodium ferrimanganite $\text{Na}(\text{Mn}_{1/3}\text{Fe}_{2/3})\text{O}_2$ and releasing CO_2 .



In the second step, $\text{Mn}^{\text{III}}\text{--Mn}^{\text{II}}$ reduction in sodium ferrimanganite $\text{Na}(\text{Mn}_{1/3}\text{Fe}_{2/3})\text{O}_2$ and O_2 release occur in CO_2 atmosphere and initial materials are restored according to the following reaction (2):



While hydrogen evolution has been studied in details and proved to be stoichiometric [13–15], some doubtful aspects concerning the oxygen evolution yield in reaction (2) were reported [16,17].

With the aim to obtain a better understanding on factors limiting a full $\text{Na}(\text{Mn}_{1/3}\text{Fe}_{2/3})\text{O}_2$ conversion, influence of temperature and carbon dioxide pressure on sodium manganese ferrite disproportionation (2) was investigated. XRD analysis performed on reacted powders showed that the reaction (2) can evolve toward unexpected mixture compositions as a function of different reaction conditions [18]. In this paper

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identification of reaction products observed in different T/p_{CO_2} experimental conditions is pursued and additional information on the structure of the observed phases are obtained by applying Rietveld analysis on collected XRD patterns.

2. Materials and methods

All solid reactants used were of analytical grade and were supplied by Carlo Erba. Gaseous reactants were supplied by Alpha Gaz, Ar (Alpha Gaz2), O₂ (Alpha Gaz2), CO₂ (N 20). The sodium ferrimanganite reduction was performed at different carbon dioxide pressures ($p_{\text{CO}_2} = 0.1, 0.2, 0.5, 0.8$ and 1.0 atm) and temperatures ($T = 600, 700, 750$ and 800 °C), performing a whole cycle. Stoichiometric mixtures of MnFe₂O₄ and Na₂CO₃ were oxidized at 750 °C for 2 h in Ar/O₂ (40/10) flow (50 cc/min). Oxygen was then removed from the reactor by flowing Argon (50 cc/min) for 30 min. The resulting oxidation product Na(Mn_{1/3}Fe_{2/3})O₂ was successively exposed to a flow (50 cc/min) of CO₂ diluted in Ar, to obtain different partial pressures, at different temperatures. With the aim to complete reaction (2), CO₂ treatments were carried on for 12 h. All cycles were performed inside a Netzsch STA 409 thermobalance. A schematic demonstrating the experimental set-up is reported in Fig. 1.

Reacted powders were analyzed by using X-ray diffraction (XRD) analysis. Samples were sealed in glass capillary (0.1 mm) to limit air exposure. Samples were analyzed by a Siemens D500 diffractometer (Mo K_{α1} radiation) in the angular range $4 < 2\theta < 40^\circ$. Phase identification was obtained by comparison with JCPDF-ICDD database [19]. Structural characterization and chemical composition of detected phases were obtained by applying Rietveld analysis on collected XRD patterns [20,21]. This procedure consists in minimising the difference function between the observed data and a profile calculated on the basis of structural models. Several quality of fit indexes can be adopted to evaluate the obtained results [22]. In this work conventional guidelines were adopted [22] and the refinement procedure results were considered

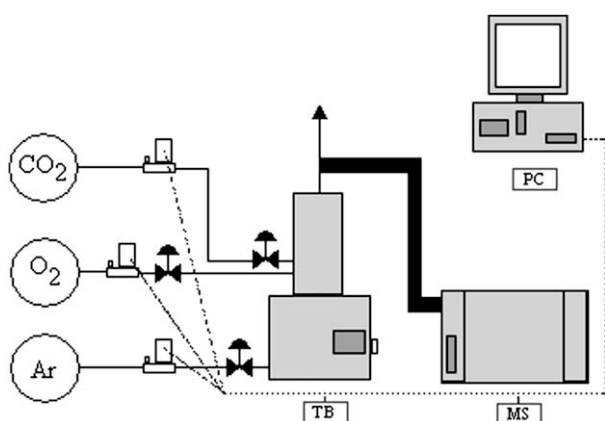


Fig. 1 – Scheme of the experimental set-up utilized for thermal analysis measurements. Netzsch STA 409 Thermobalance (TB) is coupled to a Balzer quadrupole Mass Spectrometer (MS). Computer controlled flow-meters regulate Argon, oxygen and carbon dioxide flows.

acceptable for weighted residual pattern index R_{wp} value less than 10%. In detail, $R_{wp} = (\sum w_i(y_{oi} - y_{ci})^2 / \sum w_i y_{oi}^2)^{1/2}$ where y_{oi} , y_{ci} and $w_i = 1/y_{oi}$ are respectively the observed intensity, the calculated intensity and the weight of the intensity observed at the i th step. As a supplementary verification of the goodness of results obtained by the refinement, the metal ratio (Na:Mn:Fe = 3:1:2) in the calculated final phases composition was checked (chemical validation). Rietveld analysis was performed by using GSAS (General Structure Analysis System) [23] software. Structural models were obtained from ICSD database [24] or developed on the basis of chemical considerations.

3. Results and discussion

In Fig. 2 conversion degree values of reaction (2) are reported as a function of T and p_{CO_2} conditions. As shown in the figure, Na(Mn_{1/3}Fe_{2/3})O₂ readily reacts with carbon dioxide. In the

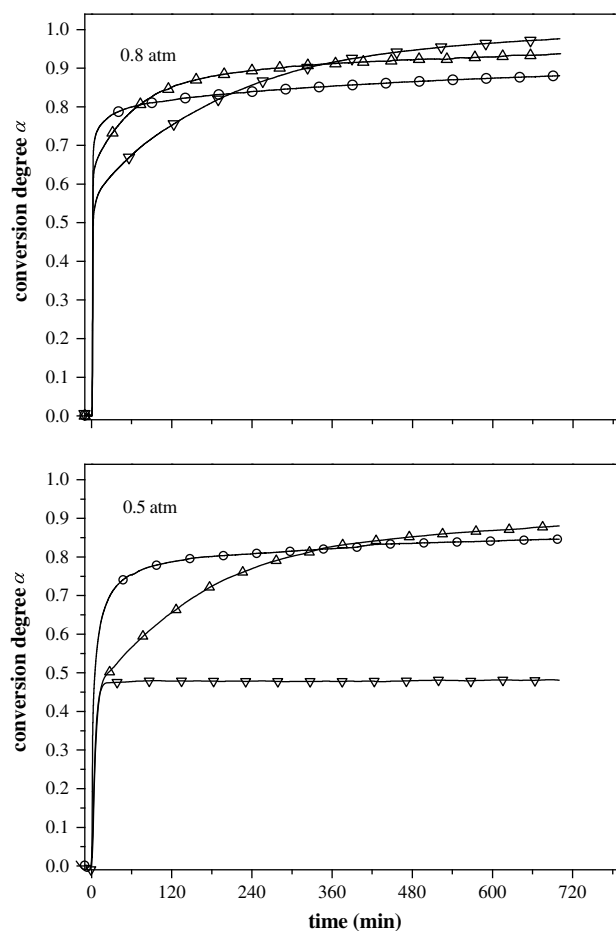


Fig. 2 – Conversion degree values from thermogravimetric curves observed for reduction step (2) performed at $p_{\text{CO}_2} = 0.8$ and 0.5 atm and $T = 600$ °C (○), 750 °C (△) and 800 °C (▽). Mass gains are reported as conversion degree $\alpha = wt_{\text{obs}}/wt_{\text{exp}}$, where wt_{obs} is the observed weight gain and wt_{exp} the expected one for a complete regeneration of the MnFe₂O₄/Na₂CO₃ initial mixture (17.49%).

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