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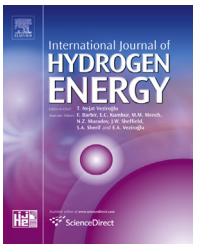

Thermochemical hydrogen production using manganese cobalt spinels as redox materials

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ABSTRACT

Mn and Co spinels ($Mn_{3-x}Co_xO_4$) were thermally reduced and subsequently oxidized showing successful hydrogen production from water splitting by a three-step thermochemical cycle involving sodium hydroxide (NaOH). The spinel materials overcome the main limitation of the Mn_2O_3/MnO redox cycle, reducing the required temperatures from 1300–1400 °C to 850–1050 °C. Additionally, the reduction process takes place through a single step reaction, avoiding the formation of intermediate species that makes much more complex the chemistry of the Mn_2O_3 redox cycle. On the other hand, the subsequent reaction with NaOH allows a hydrogen production of 52.5 cm^3 STP/$g_{material}$·cycle, which is comparable to the obtained with other spinel-oxide cycles at similar temperature. The cyclability and stability of the hydrogen production with these materials after operation of several cycles have been assessed in a high temperature tubular furnace.

Introduction

World energy consumption grows every year and more than 85% of the global energy demand is still covered by fossil fuels such as coal, oil and natural gas. This fossil fuel dependence has important economic and environmental implications like the high and volatile prices, the depletion of oil reserves and the emission of greenhouse gases. These problems have motivated the research of other fuels and energy sources, and in this context, hydrogen has been proposed as a promising zero-emission energy carrier for the future, primarily for the transport sector but also for energy storage [1].

As energy vector, hydrogen can be obtained for several routes and it has been produced for industrial applications for many decades by steam reforming of fossil fuels fractions [2]. However these routes for hydrogen production do not release the world from the fossil fuel dependence. In addition to that, those systems require a carbon sequestration to purify the obtained hydrogen. Therefore, a massive hydrogen use is reasonable only if renewable energy sources are used for its production. In this context, solar driven water splitting and electrolysis of water are the most promising and environmental friendly alternatives for carbon-free hydrogen production [3,4].

Water electrolysis implies the electrochemical splitting of water into hydrogen and oxygen using a conductive electrolyte like salts, acids, bases [5] or solid oxides [6]. However, a great amount of electric energy is required and this energy should come from renewable sources like wind or sun. But

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due to the high energy demand it does not seem consistent to use part of the electricity production for obtaining hydrogen [3]. On the other hand, direct splitting of water using concentrated solar energy is the most direct and cleanest method to obtain hydrogen. However the required temperature is 4250 °C, far over the maximum temperatures achievable in modern solar concentrating systems of around 2700 °C [1]. There are also other problems associated to this technology such as the huge radiation losses which are proportional to the fourth power of the absolute temperature, and the need to separate the hydrogen and the oxygen to avoid explosive mixtures at lower temperatures. For those reasons, water splitting by solar-driven thermochemical cycles represents a promising technology for this purpose because of their lower temperature requirements and the fact that hydrogen and oxygen are obtained at different steps thus eliminating the need to separate them [4].

Thermochemical cycles are processes that decompose water into oxygen and hydrogen. They consist of two or more chemical reactions where a metal oxide is first thermally reduced (R1) and then oxidized with water (R2), being the overall reaction the splitting of water in ½ mol of O_2 per mol of H_2.

$$M_xO_y \rightarrow M_xO_{y-1} + \tfrac{1}{2}O_2 \quad \text{(R1)}$$

$$M_xO_{y-1} + H_2O \rightarrow H_2 + M_xO_y \quad \text{(R2)}$$

A large number of these redox cycles have been examined in the literature, being current research efforts mainly focused on thermochemical cycles based on iron [7–9] or zinc oxides [10,11]. Despite their apparent simplicity, there are difficulties associated to the high temperatures required for the thermal reduction step (between 1600 and 2230 °C) [12–17] so the attention has diverted to other thermochemical cycles, which require lower temperatures [18]. Consequently, alternative cycles such as the Mn-oxide or Co-oxide cycles have been proposed. In this context, the Mn-oxide cycle is the most studied one. Unfortunately, water-splitting reactions with MnO are not thermodynamically favorable, with negligible hydrogen production [18,19]. A possible solution to this inconvenience is the substitution of water with a better oxidizing compound, such as sodium hydroxide, which may enhance the oxidation of the reduced material during the hydrogen production reaction. However, despite the advantages presented by this cycle, the required temperature for the process is still very high (1450–1575 °C) [20]. Aiming for a decrease in this operating temperature, different kind of spinels of the iron [21,22] and aluminum [23,24] families have been studied. These materials show a significant sintering degree which implies a lack of cyclability limiting their application for long-term H_2 production by thermochemical cycles [25]. Co_3O_4 requires lower temperatures to perform the reduction step but it is toxic and expensive [26]. Moreover, the generation of hydrogen by reaction with water or NaOH is not thermodynamically feasible for the Co_3O_4/CoO redox pair. In contrast, a combination with less harmful and inexpensive metal oxides, like Mn_2O_3, will be advantageous. On the other hand, the combination of Mn_2O_3 with other metal oxides with lower reduction temperatures, like Co_3O_4, may be positive due to a decrease in the operational temperature. Thus, a study of the thermochemical cycle for hydrogen production of oxides that combine both metals seems relevant, as it could result in an economic and efficient material for this application.

In this work, a novel study on the use of Mn and Co spinels ($Mn_{3-x}Co_xO_4$) redox cycle for water splitting is presented, evaluating the required temperatures for the reduction and oxidation steps, their viability for hydrogen production and the cyclability behavior of these materials.

Materials and methods

Materials

Mn and Co spinels ($Mn_{3-x}Co_xO_4$) were synthesized starting from a physical mixture of the respective pure metal oxides (Mn_3O_4 with a particle size of 44 μm, and Co_3O_4 with a particle size of 37 μm) purchased from Sigma–Aldrich and Alfa Aesar respectively. The mixture was heating up to 800 °C with a rate of 10 °C/min and calcined at that temperature during 5 h under air flow of 92 cm^3 STP·min^{-1} [25].

Physicochemical characterization

The elemental composition of the spinels was determined by a Varian Vista AX inductive coupled plasma-atomic emission spectrometer (ICP-AES), and their crystal structure by X-Ray diffractometry (XRD) using a PW3040/00 X'Pert MPD/MRD equipment. Morphology of materials was observed by Scanning Electron Microscopy (SEM) using a Philips Scanning Electron Microscope XL30 FEG with an accelerating voltage of 5.00 kV and a magnification of 60,000.

H_2-TPR experiments of the synthesized spinels and the pure metal oxides were performed by a Micrometrics (Norcross, GA, USA) Autochem 2910 equipment. The samples were previously degasified in flowing argon (32 cm^3 STP·min^{-1}) for 2 min at 100 °C with a heating rate of 5 °C/min. Afterward, the H_2-TPR profile was obtained by flowing 10% H_2 in Ar (32 cm^3 STP·min^{-1}) from 100 °C to 1000 °C with a heating rate of 10 °C/min.

Thermogravimetric measurements

A thermochemical cycle comprises the release of oxygen by reduction of the metal oxide and its subsequent uptake in the oxidation step, involving both steps a mass variation. The cyclability of the different Mn and Co spinels synthesized has been firstly analyzed by checking the reversibility of the mass variations along different cycles using a thermobalance. Thermogravimetric experiments (TGA) were carried out in a TGA/DSC1 STARe System (Mettler, Toledo) with a maximum operation temperature of 1600 °C. Three consecutive cycles were performed to evaluate the re-oxidation capacity of the synthesized materials. For these experiments, air flow (92 cm^3 STP·min^{-1}) was used to maintain an oxidant environment around the sample which was placed in an alumina crucible of 0.15 cm^3 of total volume. First, the temperature was ramped up to 1400 °C with a heating rate of 10 °C/min. The weight loss measured is consequence of the thermal reduction and the

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