Available online at www.sciencedirect.com

ScienceDirect

Solar Energy 129 (2016) 236–243

SOLAR ENERGY

www.elsevier.com/locate/solener

Influences of morphology and structure on Mn-based multi-step thermochemical H_2O splitting cycle

Zhenpan Chen [a,b], Qingqing Jiang [a], Jinhui Tong [a], Min Yang [a], Zongxuan Jiang [a], Can Li [a,*]

[a] State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian National Laboratory for Clean Energy, 457 Zhongshan Road, Dalian 116023, China
[b] University of the Chinese Academy of Sciences, Beijing 100049, China

Received 22 September 2015; received in revised form 27 December 2015; accepted 31 December 2015
Available online 18 February 2016

Communicated by: Associate Editor Michael EPSTEIN

Abstract

The multi-step thermochemical water splitting cycle based on $MnFe_2O_4$–Na_2CO_3 has emerged as an attractive process due to its relatively low reaction temperature. The main challenges are how to enhance its H_2/O_2 release rates and capacities. Herein, a series of $MnFe_2O_4$ with different microstructures synthesized by hydrothermal method were tested in H_2O splitting reaction. It was found that $MnFe_2O_4$ samples with smaller particle size and fine crystallinity exhibited higher H_2 production which was benefit from enhanced intimate contact between homogeneous particles and better ionic transport within fine crystals. In order to enhance the reaction kinetics of the O_2 release reaction, a hydrolysis treatment was introduced to the multi-step cycle. As a result, the lamellar structure of Na^+ extracted $Na_{1-x}(Mn_{1/3}Fe_{2/3})O_2$ oxide became unstable and collapsed into cubic $MnFe_2O_4$ spinel structure more easily under heating, a structure characteristic suitable for O_2 release reaction. Compared to direct O_2 release reaction between layered $Na(Mn_{1/3}Fe_{2/3})O_2$ oxide and CO_2, the hydrolysis treatment lead to much faster reaction rate.

Keywords: Solar energy; Multi-step H_2O splitting; Hydrogen; Manganese ferrite

---

1. Introduction

Solar energy is an infinite and clean renewable resource compared to fossil fuels (Lewis and Nocera, 2006). It is no doubt that solar energy resource will play an important role in the future energy system. Solar thermochemical H_2O/CO_2 splitting cycles based on metal oxide redox materials (Müller and Steinfeld, 2008; Steinfeld et al., 1999; Abanades and Flamant, 2006; Abanades et al., 2008; Chueh et al., 2010; Jiang et al., 2014) offer promising paths for solar energy conversion. Most of these thermochemical cycles are based on two-step redox reactions owing to their advantages of simplicity and easy manipulation, while the reduction temperature for oxygen evolution is too high, usually over 1300 °C, for most two-step thermochemical cycles. In order to reduce the reduction temperature of two-step thermochemical cycles, thermochemical process based on multicomponent compounds, such as $CoFe_2O_4$ (Arifin et al., 2012; Scheffe et al., 2013; Tong et al., 2015), $NiFe_2O_4$ (Gokon et al., 2013; Fernández-Saavedra et al., 2014), ABO_3 perovskites (Jiang et al., 2014) with better redox performance than simple oxides have received increasing attentions. Compared with two-step thermochemical cycles, multistep thermochemical cycles charac-

---

[*] Corresponding author. Tel.: +86 411 84379070; fax: +86 411 84694447.
E-mail address: canli@dicp.ac.cn (C. Li).

http://dx.doi.org/10.1016/j.solener.2015.12.051

terized by lower operation temperature (<1000 °C) appear to be another promising process. However, most multistep cycles, such as S–I (Machida et al., 2011), Cu–Cl (Ozbilen et al., 2014) and MnO–NaOH (Sturzenegger and Nüesch, 1999) cycles, are dependent on the aid of strong acid/base compounds (H_2SO_4, HCl, NaOH). These reactants bring strict requirements on reactor design and operation security considering their significant corrosion issues. Fortunately, metal oxide and mild base constituted thermochemical cycle, for example $MnFe_2O_4$–Na_2CO_3 cycle, is a promising multi-step process thanks to the mild chemical properties of its reactants.

The manganese ferrite thermochemical water splitting cycle is a multi-step cycle based on $MnFe_2O_4$–Na_2CO_3 interaction (Alvani et al., 2006, 2005; Tamaura et al., 1999). Water splitting occurs according to the following steps (Scheme 1):

In the first step, manganese ferrite ($MnFe_2O_4$) is oxidized by water under the participation of Na_2CO_3 to produce hydrogen. In the second step, Mn^{III} is reduced to Mn^{II} within sodium ferrimanganite ($Na(Mn_{1/3}Fe_{2/3})O_2$) compound under CO_2 atmosphere and the reactive material is regenerated simultaneously. As for the net reaction, the only input substance is H_2O and the outputs are H_2 and O_2. In the past decades, researches were focused on the oxygen release step (Scheme 1, step 2) of $MnFe_2O_4$–Na_2CO_3 system (Varsano et al., 2011; Seralessandri et al., 2009, 2008, 2006; Kaneko et al., 2001a,b). The oxygen release mechanisms have been extensively investigated, while no efficient strategy was developed to enhance the oxygen release rate and efficiency. Recently, $MnFe_2O_4$ synthesized by high-energy ball milling method and solid-state reaction method were tested in this cycle (Alvani et al., 2005). The results have shown that different synthesis methods influenced H_2 release rate and productivity. The literature results suggest that structure and morphology of $MnFe_2O_4$ are important to its reactivity and the oxygen release reaction kinetics is influenced greatly by the phase and structure of the H_2O oxidized sodium ferromanganese oxide ($Na(Mn_{1/3}Fe_{2/3})O_2$).

The reactivity of $MnFe_2O_4$ seems to be dependent on its micro-structure and morphology. Here, we applied a hydrothermal synthesis method to prepare $MnFe_2O_4$ and to investigate its influences on H_2O splitting reactivity in details. Furthermore, we developed a new method to enhance O_2 release rate and efficiency. Our results show that particle size and crystallinity of $MnFe_2O_4$ are important parameters to its performance in $MnFe_2O_4$–Na_2CO_3 thermochemical H_2O splitting cycle. Smaller particle size and fine crystallinity of $MnFe_2O_4$ lead to higher H_2 generation rate and production. The hydrolysis assisted O_2 release is proved to be more efficient than other routes, i.e. direct oxygen release reaction between layered $Na(Mn_{1/3}Fe_{2/3})O_2$ and CO_2 (Scheme 1) is relatively slow and takes more than 3 h to be finished (Varsano et al., 2011). It is noteworthy that both H_2 and O_2 release capacities and efficiencies can be improved by using the new preparation methods. These results demonstrated the possibilities for developing low temperature thermochemical cycles for overall water splitting. While, it should be clarified that this is an explorative study made to improve the multi-step Mn-based cycle but that at the present moment the cycle has not been completely closed, i.e. the parameters of the hydrolysis reaction (Scheme 2, step 2) should be further investigated.

$$\begin{aligned}&Step\ 1:\ 2MnFe_2O_4(s)+3Na_2CO_3(s)+H_2O(g)\xrightarrow{800\sim850\ ^{\circ}C}\\&\qquad 6Na(Mn_{1/3}Fe_{2/3})O_2(s)\ +\ 3CO_2(g)+H_2(g)\end{aligned}$$

$$\begin{aligned}&Step\ 2:\ 6Na(Mn_{1/3}Fe_{2/3})O_2(s)+3CO_2(g)\xrightarrow{600\sim800\ ^{\circ}C}\\&\qquad 2MnFe_2O_4(s)\ +\ 3Na_2CO_3(s)+1/2O_2(g)\end{aligned}$$

Scheme 1.

2. Experimental section

2.1. Materials synthesis

All reagents used in the experiments were of analytical grade and used without further purification. $MnFe_2O_4$ samples were synthesized by a modified hydrothermal method (Wang et al., 2004). In a typical synthesis process, 10 mmol manganese chloride ($MnCl_2{\cdot}4H_2O$) and 20 mmol ferric chloride ($FeCl_3{\cdot}6H_2O$) were dissolved in 200 ml deionized water under magnetic stirring. Appropriate amount of NaOH was dissolved into 30 ml deionized water. Then, the NaOH solution was slowly added to the mixed chloride salt solution drop by drop under magnetic stirring and further stirred for 30 min to get a uniform pre-reaction mixture. At last, the brown reaction mixture was transferred to a 300 ml teflon-lined autoclave and hydrothermal reacted at designed conditions. Finally, the obtained products were separated by filtration and washed several times with distilled water, then dried at 60 °C in vacuum oven.

2.2. Materials characterization

The synthesized $MnFe_2O_4$ and used samples were characterized by powder X-ray diffraction (XRD) on a Rigaku D/Max-2500/PC powder diffractometer using Cu Kα radiation with operating voltage of 40 kV and operating current of 200 mA. The scan rate of 5° min^{-1} was applied to record the XRD patterns in the range of 5–80° at a step size of 0.02°. Scanning Electron Microscopy (SEM) images technique (a Quanta 200FEG scanning electron microscope) was used to characterize the morphology and particle size of the samples. The metal (Na, Mn, Fe) contents are measured by inductively coupled plasma spectroscopy (Shimadzu ICPS-8100).

2.3. Reactivity test

The reactivity test was carried out in an temperature programmed erect quartz reactor ($\Phi = 20$ mm) equipped