



Magnesioferrites for solar thermochemical fuel production

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ARTICLE INFO

Keywords:

Thermochemical fuel production
Recyclability
Magnesium oxide doping
Sintering inhibitor

ABSTRACT

Solid solutions of iron oxide in MgO, prepared using the solid state reaction method (SSR), were investigated for solar thermochemical water splitting/carbon dioxide splitting (STC-WS/CDS). Experimental results show that 20 mole% magnetite (Fe₃O₄) in MgO has a hydrogen (H₂) production capacity of $6.12 \pm 0.22 \text{ cm}^3 \text{ g}_{\text{total material}}^{-1}$ when thermally reduced at 1450 °C (T_{red}) under an inert environment and oxidized at 1200 °C (T_{ox}) with excess steam. This compares favorably with cerium dioxide (CeO₂), which has proven to be an excellent STC-WS/CDS material, with H₂ production $2.91 \pm 0.15 \text{ cm}^3 \text{ g}_{\text{total material}}^{-1}$ at $T_{\text{red}} = 1450 \text{ °C}$ and $T_{\text{ox}} = 1200 \text{ °C}$, and $4.34 \pm 0.2 \text{ cm}^3 \text{ g}_{\text{total material}}^{-1}$ at $T_{\text{red}} = 1500 \text{ °C}$ and $T_{\text{ox}} = 1200 \text{ °C}$. 20 mole% Fe₃O₄ in MgO has advantages of lower operating temperature and higher production capacity. The partial pressure of oxygen (P_{O₂}) during thermal reduction is on the order of 10^{-4} atm, which can be achieved using existing industrial vacuum pump technology. These advantages make this material a viable option for further study in solar thermochemical fuel production applications.

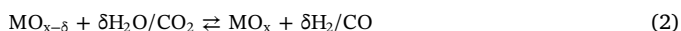
1. Introduction

An increase in the global demand for fuels and growing concern with emissions have given rise to the need for the development of novel methods for harnessing energy from sustainable resources. Solar energy is one such earth abundant renewable energy resource for which many different harnessing methods have been devised. Two-step solar thermochemical water splitting/carbon dioxide splitting (STC-WS/CDS) is a method employed to convert solar energy to fuels, such as hydrogen (H₂) and carbon monoxide (CO). In this application, metal oxides that undergo reversible redox reactions are heated to very high temperatures using concentrated solar radiation. Redox chemical reactions are executed cyclically to produce H₂ or CO, and such reactions for STCWS/CDS are described as:

Endothermic thermal reduction at temperature T_{red}



Water/carbon dioxide splitting at temperature T_{ox} , $T_{\text{ox}} \leq T_{\text{red}}$



Here MO_x is a metal oxide which is thermally reduced to MO_{x-δ}. The temperature required by STC-WS/CDS materials to reduce in air (at

high partial pressure of O₂; P_{O₂} ~ 0.21 atm) is generally greater than 2000 °C (Meredig and Wolverton, 2009). Designing solar reactors for carrying out STCWS/CDS that can withstand such high temperatures for thousands of cycles without degradation is not yet achievable. However, the thermal reduction temperature can be decreased substantially, near the vicinity of 1500 °C, by lowering the partial pressure of O₂ using an inert sweep gas, such as argon or nitrogen, or by vacuum pumping (Meredig and Wolverton, 2009; Siegel et al., 2013). This principle has been applied to investigate the performance of several materials (Roeb et al., 2012; Muhich et al., 2015). The earliest investigations began with Fe₃O₄-FeO systems as suggested by Nakamura (1977). Since the thermal reduction temperature of Fe₃O₄ to FeO is near the melting points of Fe₃O₄ (1535 °C) and FeO (1350 °C), extensive sintering occurs which decreases the active surface area of iron oxide, resulting in material deactivation (Sibieude et al., 1982). A method applied to overcome material deactivation is the formation of solid iron oxide solutions with other metal oxides to lower the thermal reduction temperature. Cation excess (Ni, Mn) ferrite spinels were studied by Tamaura et al. (1998) in the temperature range of 900–1100 °C. Similar investigations on manganese ferrites (Mn_xFe_{3-x}O₄) were carried out by Ehrensberger et al. (1995, 1996) in the temperature range of 400–900 °C. In these studies, the reduction temperatures were kept low to inhibit sintering. The drawbacks of very low required O₂ partial

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pressure (on the order of 10^{-7} atm) and very low H_2 yields due to limited cation non-stoichiometry were observed for these materials. Subsequently, these ferrite spinels were coated on zirconia based ceramic particles and foams to enable reduction at higher temperatures. Kodama and Gokon (2007), Kodama et al. (2008) and Gokon et al. (2009, 2008) reported stable H_2 production capacities in the temperature range of 1100–1400 °C for nickel, cobalt and manganese ferrites coated on zirconia particles and foams. They confirmed that the use of a passive zirconia support is highly effective in preventing sintering, thus stabilizing the reactive material. They reported that nickel ferrite is the most productive among the materials. Ishihara et al. (2008a,b) further improved on the findings of Kodama and Gokon by demonstrating stable H_2 production from solid solutions of iron oxide/nickel ferrite in 8YSZ (8 mole% Y_2O_3 in ZrO_2). Miller et al. (2006), Coker et al. (2011) and Allen et al. (2013) did similar studies on solid solutions of iron oxide and cobalt ferrite in 8YSZ in the temperature range of 1100–1450 °C and demonstrated stable fuel yields over multiple cycles. Scheffe et al. (2011) later showed that using Al_2O_3 as a support for $CoFe_2O_4$ also produces stable H_2 yields when oxidized and reduced in the temperature range of 1000–1350 °C.

The rate limiting step of the redox reactions is attributed to the surface reaction in the materials discussed above (Muhich et al., 2015). Slow reaction kinetics for these class of reactive metal oxides are the most significant limitation to the practical implementation of solar thermochemical fuel production. Hence, interest in these materials has waned with the demonstration of non-stoichiometric metal oxides which have higher H_2/CO production capacities, faster reaction kinetics and are morphologically stable over continuous cycling.

Ceria (CeO_2) is one of the first non-stoichiometric materials to be reported with appreciably high reaction rates. Abanades and Flamant (2006) first reported stoichiometric conversion of CeO_2 to Ce_2O_3 for STCWS/CDS at reduction temperatures as high as 1800 °C. Chueh and Haile (2010) suggested the utilization of O_2 vacancy formations in CeO_2 at lower temperature (~ 1500 °C) for fuel production and demonstrated the cyclic reactive stability; these results were later verified by Rhodes et al. (2015) and Gibbons et al. (2014). Several dopant incorporation studies on ceria were carried out to improve the productivity of the material. Kaneko et al. (2007, 2008) reported that the use of transition metal oxide dopants (Mn, Ni, Cu, and Fe) did not improve the H_2/CO productivity of ceria. Alkaline earth metal oxides (Ca and Sr) and Lanthanides (La, Sm, Gd and Pr) and transition ceramic oxides (Y, Sc, Hf and Zr) have been used as ceria dopants (Meng et al., 2011). Divalent and trivalent cations have been reported to increase the reaction rates but had no effect on the fuel production capacities. Tetravalent cations such as Zr^{4+} and Hf^{4+} has increased fuel production capacities at the expense of less favorable oxidation thermodynamics. A detailed survey of these materials has been provided in the review articles by Roeb et al. (2012), Muhich et al. (2015), Scheffe and Steinfeld (2014).

While ceria based materials are attractive from a kinetic and stability perspective, their fuel production capacity suffers compared to most ferrite based materials (Scheffe and Steinfeld, 2014). A new class of non-stoichiometric materials called perovskites ($ABO_{3-\delta}$) are under development. These materials have shown a greater extent of O_2 exchange capacities compared to ceria based ceramics. Evdou et al. (2008, 2010), Nalbandian et al. (2009) demonstrated the use of $La_{1-x}Sr_xMO_{3-\delta}$ ($M = Mn, Fe$) perovskites for membrane type reactors. Similar perovskite type materials were investigated by Scheffe et al. (2013), McDaniel et al. (2014), Yang et al. (2014) and Jiang et al. (2014) demonstrated considerably greater reduction extents (2–3 times higher than ceria at ~ 1500 °C reduction). Other perovskites such as $Ba_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ have been investigated by Demont et al. (2014). The fuel yields for these materials were 6–9 times that of ceria based materials when oxidized and reduced in the temperature range of 800–1400 °C. A major drawback with these materials is the less favorable oxidation thermodynamics resulting in incomplete oxidation, thus, demanding large quantities of oxidant for achieving high fuel yields.

It has been observed that reactive material re-oxidation is limited by the rate of reaction at the surface rather than the chemical diffusion of O_2 . The need for high surface area to achieve high fuel production rates presents a challenge for solar-driven redox cycles because the high temperatures required for reduction lead to sintering and a corresponding loss of surface area. Gibbons et al. (2014) studied redox reactions on ceria fibers and have emphasized the importance of maintaining high specific surface area for achieving high fuel yields. Long term reactive stability tests on ceria by Rhodes et al. (2015) support the findings of Gibbons et al. that sintering phenomenon and associated loss of surface area decreases reactivity over multiple redox cycles. The effect of loss in surface area is more prominent in ferrite based cycles where O_2 diffusion is much slower than non-stoichiometric cycles. Gokon et al. (2009, 2008) have reported surface area reduction from 10 to $13 \text{ m}^2 \text{ g}^{-1}$ to $\sim 1 \text{ m}^2 \text{ g}^{-1}$ in ferrites supported on YSZ after 10 cycles. Hence, there arises uncertainty as to whether zirconia based material supports are suitable sintering inhibitors for ferrites.

Zirconia (ZrO_2) and Yttria stabilized zirconia (YSZ) acting as inert supports for ferrites have high melting points ($T_{\text{melting}} > 2650$ °C) and high O_2 diffusion coefficients ($0(10^{-8}) \text{ m}^2 \text{ s}^{-1}$ at ~ 1400 °C (De González and García, 1990). Low H_2/CO productivity of ferrite spinel solutions in ZrO_2 or YSZ at high redox temperatures (> 1400 °C) indicates a high extent of sintering. Insight to this unusually high extent of sintering may be gained by referring to the phase diagrams of wustite (FeO) and Zirconia (ZrO_2) provided by Bechta et al. (2006) and Fabrichnaya and Pavlyuchkov (2016). These phase diagrams indicate the presence of a liquid phase in $FeO + ZrO_2$ solutions at temperatures above 1332 °C when the concentration of FeO is greater than 2.5 mole%. Fabrichnaya and Pavlyuchkov (2016) further showed the presence of a liquid phase in solutions of $Fe_3O_4 + ZrO_2$ above 1527 °C when Fe_3O_4 is greater than $\sim 2\%$. Since most of the ferrite solutions in ZrO_2 or YSZ tested for STCWS/CDS contain more than 10 mole% of ferrite, and thermal reduction temperatures are greater than 1400 °C (Roeb et al., 2012; Allen et al., 2013), it is most probable that traces of a liquid phase are formed during thermal reduction. The formation of a liquid phase with subsequent solidification will certainly destroy reactive surface area over multiple cycles which results in low H_2/CO yield.

This motivated us to examine ceramic oxides which do not form low temperature eutectic melts with iron oxide. One such oxide is magnesium oxide (MgO), which has a very high melting point of 2852 °C. Several investigations have been carried out to ascertain the composition, structure, and phase relations for an iron-magnesium- oxygen system. Phillips et al. (1961) studied the melting relations of $MgO-Fe_2O_3$ mixtures in air and reported temperatures higher than 1800 °C for 40% MgO in Fe_2O_3 . Lebrun and Fabrichnaya (2008) compiled available thermodynamic and structural data and developed phase diagrams for $Fe-Mg-O$ systems. Jung et al. (2004) used these experimental data to develop CALPHAD (CALculation of PHase Diagrams) models describing the Gibbs free energy of phases present at different temperatures and O_2 partial pressures. The phase diagrams of $Fe-Mg-O$ systems shown by Lebrun and Fabrichnaya (2008) and Jung et al. (2004) indicate that the liquid phase starts to appear at a temperature of 1500 °C when the concentration of FeO in MgO is greater than 30 mole%. The melting point of $FeO + MgO$ solution increases with decreasing FeO content. Analysis of the phase diagrams suggests that low concentration iron oxides in MgO may be more resistant to sintering compared to iron oxide solutions in ZrO_2 with similar molar concentrations. Furthermore, Blackman (1959) reported that MgO lowers the thermal reduction temperature of Fe^{3+} to Fe^{2+} due to preferential diffusion of iron.

Magnesium oxide reacts with iron (III) oxide to form magnesium-ferrite ($MgFe_2O_4$) spinel in oxidizing environments. Richard and White (1954) investigated the influence of temperature and composition on the rate of dissolution of FeO in mixtures of FeO , MgO and Fe_2O_3 and found that the O_2 loss is completely reversible, with relatively rapid rates of oxidation and dissolution. Cordischi et al. (1978) studied the

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