Iron oxide redox reaction with oxide ion conducting supports for hydrogen production and storage systems

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HIGHLIGHTS

- Oxide ion conducting supports such as YSZ and GDC improved reduction of Fe_2O_3 by H_2.
- High Reduction rates from FeO to Fe with CeO_2 and GDC supports were observed.
- CeO_2, YSZ and GDC improved oxidation reaction kinetics in steam-iron reaction.
- A positive correlation between rate constants and oxide ion conductivity in supports was observed.
- Oxygen vacancies in supports may have important role for the improvement of redox reaction.

ARTICLE INFO

ABSTRACT

Improvement of redox reaction kinetics is important for the application of metal oxide redox reactions in energy conversion systems such as chemical looping systems and hydrogen storage. In this study, we focused on physical properties in supports that can affect the redox reaction kinetics of metal oxides. The redox reaction of iron oxide by hydrogen and water vapor was studied with various support materials, ZrO_2, CeO_2, yttria-stabilized zirconia (YSZ) and gadolinia-doped ceria (GDC), which have different physical properties such as oxide ion and electronic conductivities. Oxide ion conductors such as YSZ and GDC clearly increased the rate of Fe_2O_3 reduction ($Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO \rightarrow Fe$). This result suggests that oxygen vacancies and good oxide ion transport properties in the supports may enhance removal of oxygen from iron oxide. In addition, CeO_2 and GDC significantly improved the reduction kinetics in the reduction step from FeO to Fe. Furthermore, it was found that these supports have an effect on the oxidation reaction kinetics of iron by water vapor in comparison with ZrO_2; that is, they increase the rate of the steam-iron reaction for hydrogen production. The mechanism of the improvement was discussed in terms of oxide ion and electronic conductivity in the supports and water dissociation on the support surfaces.

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1. Introduction

The development of energy storage systems with high energy density for storing renewable energy is essential for mitigating global warming and establishing a low-carbon society. Recently, redox reactions involving metal oxides have attracted great interest for applications in chemical looping systems and hydrogen production and storage (Adanez et al., 2012; Hossain and de Lasa, 2008). In chemical looping systems, metal oxide is reduced and reoxidized repeatedly. During these reactions, fuels are converted to CO_2 and form high-grade heat to produce electricity by means of a steam turbine. Additionally, a new energy storage system was proposed using the redox reaction of a metal oxide with a solid oxide fuel cell (SOFC) using H_2–H_2O as a mediator (Inoishi et al., 2012; Xu et al., 2011). In this system, metal oxide was utilized to store H_2. In the discharging process, H_2 is formed by the oxidation of metal by H_2O and is consumed in the SOFC to generate electricity and, finally, to form H_2O. In the charging process, H_2 generated by H_2O electrolysis in the SOFC reacts with the metal oxide to form metal. The energy densities of metal oxides such as Fe_2O_3, MnO_2 and CuO are higher than that of $LiCoO_2$, which is the representative positive electrode material for Li-ion batteries.

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Therefore, investigation of the mechanisms that promote the redox reactions of metal oxides is of great importance and may lead to highly efficient energy storage systems.

Redox reactions involving many kinds of metal oxides such as Fe_2O_3, NiO, MnO and CuO have previously been investigated (Adanez et al., 2012; Hossain and de Lasa, 2008). Among these, Fe_2O_3 has attracted much interest because of its low cost, low toxicity and high energy density. The redox reactions of Fe_2O_3 with H_2 and H_2O are expressed as follows:

$$Fe_2O_3 + 3H_2 \rightarrow 2Fe + 3H_2O \tag{1}$$

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2 \tag{2}$$

To improve system performance for practical applications, acceleration of the reduction reaction and prevention of degradation caused by sintering are required. The use of single- and double-metal additives to Fe_2O_3 to prevent degradation and accelerate the redox reaction was reported (Liu and Wang, 2010; Otsuka et al., 2003).

In this study, we focused on support materials such as oxide ion conductors to improve the redox reaction kinetics of the oxygen carrier. Ishida et al. reported that yttria-stabilized zirconia (YSZ) as a support material improved the reduction of NiO by H_2 (Ishida and Jin, 1994). Recently, Otomo et al. and Hedayati et al. reported that gadolinia-doped ceria (GDC) promoted the reduction of metal oxides such as NiO and Fe_2O_3 by CH_4 (Hedayati et al., 2012; Otomo et al., 2013). These results suggest that oxide ion conductors may promote the reduction of the metal oxide. However, the physical properties that influence the rate of reduction are not clearly understood because GDC has many specific characteristics, such as oxide ion conductivity, electronic conductivity in reducing atmospheres, and ease of reduction, which leads to loss of oxygen from bulk GDC. To determine which physical properties in support materials influence the rate of the reduction reaction of metal oxides, the redox reaction of iron oxide by H_2 and H_2O was conducted with various support materials: ZrO_2, CeO_2, $Zr_{1-x}Y_xO_{2-\delta}$ (YSZ) and $Ce_{1-x}Gd_xO_{2-\delta}$ (GDC). The crystal structures of the support materials are all fluorite-type structures but the physical properties such as oxide ion and electronic conductivity in these materials differ as listed in Table 1 (Kosacki et al., 2000; Lübke and Wiemhöfer, 1998; Madeyski and Smeltzer, 1968; Park and Blumenthal, 1989; Kharton et al., 2001). YSZ is a popular pure oxide ion conductor. By means of doping cations of different valence in the positions of zirconium, oxygen vacancies form and oxide ion conductivity results according to the following equation:
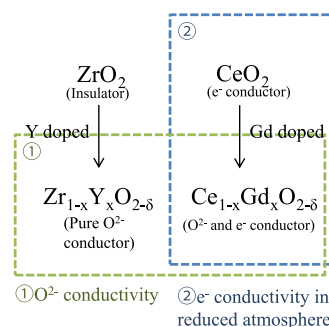
$$Y_2O_3 \xrightarrow{ZrO_2} 2Y'_{Zr} + V_O^{\cdot\cdot} + 3O_O^{\times} \tag{3}$$

Electronic conductivity in YSZ is very low: therefore, it is used as an electrolyte in SOFCs. On the other hand, oxygen is lost from CeO_2 depending on the oxygen partial pressure (Paier et al., 2013). In a reducing atmosphere, oxygen is lost from CeO_2 and the valence of cerium changes from $4+$ to $3+$. Therefore, CeO_2 has oxygen storage capacity and has been used in three-way catalyst in automobiles (Matsumoto, 2004). Furthermore, CeO_2 has electronic conductivity in a reducing atmosphere as shown in Table 1

Fig. 1. Different properties of the support materials used in this study.

(Kosacki et al., 2000). GDC also has high oxide ion conductivity and, in a reducing atmosphere, has both high electronic and oxide ion conductivity owing to loss of oxygen and change of Ce valence (Lübke and Wiemhöfer, 1998; Kharton et al., 2001). Differences in the physical properties of these support materials are summarized in Fig. 1. By comparing the redox reaction kinetics with these supports, the effect of oxide ion and electronic conductivity will be discussed. Furthermore, the effect of oxide ion conduction on the oxidation reaction of iron by water vapor (i.e., the steam-iron reaction for hydrogen production) was also investigated in the present study. It was found that the supports CeO_2, YSZ and GDC improved the rate of iron oxidation by water vapor. In a previous study, the steam-iron reaction with CeO_2 and an improvement of iron oxide reduction at low temperature determined by temperature-programmed reduction was reported (Li et al., 2013). To our knowledge, however, the present study is the first to report a correlation between oxide ion transport and the oxidation kinetics for iron oxidation by water vapor using oxide ion conductors such as YSZ and GDC. Kinetic analysis was conducted and an acceleration mechanism of the redox reaction was discussed based on the correlation between the oxide ion and electronic conductivity and the redox reaction kinetics.

2. Experimental

Fe_2O_3/support composites (30 wt%) were prepared by solid state reaction. First, the desired amount of Fe_2O_3 (Wako Pure Chemical Industries, Japan) and support materials, ZrO_2 (Wako Pure Chemical Industries, Japan), CeO_2 (Wako Pure Chemical Industries, Japan), $Zr_{0.8}Y_{0.2}O_{2-\delta}$ (Tosoh, Japan) and $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ (Daiichi Kigenso Kagaku Kogyo, Japan), were mixed with carbon powder to form pores and ethyl cellulose as a binder. Then, ethanol was added and the mixture was ball-milled for 20 h and dried at 90 °C. The obtained powders were pelletized at 3 t cm^{-2} and calcined at 1100 °C for 3 h to form Fe_2O_3/support cermet-like composites. The pelletized sample was ground and sieved to 150–300 μm to eliminate the influence of the diffusion of reaction gas in the pores of the Fe_2O_3/support samples.

The obtained Fe_2O_3/support composites were characterized using X-ray diffraction (XRD) spectroscopy (RIGAKU, Japan) and scanning electron microscopy (SEM, JEOL, Japan). The specific surface areas of the Fe_2O_3/support composites were also examined by the Brunauer–Emmett–Teller (BET) method with a NOVA2200e (Quantachrome Instruments, USA).

Measurements of reduction and oxidation reactions of the Fe_2O_3/support composites by H_2 and H_2O, respectively, were conducted by means of thermogravimetry (TG) (TG8120, Rigaku, Japan). Isothermal reduction and oxidation reactions of the Fe_2O_3/supports were conducted to evaluate the effect of the support materials on the reaction rate. Sieved Fe_2O_3/support samples were placed in an alumina pan and a gaseous mixture of H_2 and Ar

Table 1

Oxide ion conductivity, $\sigma_{O_2^-}$, and electronic conductivity, σ_{e^-}, at 600 °C in the support materials used in this study (Kosacki et al., 2000; Lübke and Wiemhöfer, 1998; Park and Blumenthal, 1989; Kharton et al., 2001).

	$\sigma_{O_2^-}$ (S cm^{-1})	σ_{e^-} (S cm^{-1}) ($p_{O_2} = 10^{-20}$ atm)
ZrO_2	–	–
CeO_2	4.0×10^{-5}	2.0×10^{-4}
YSZ	4.7×10^{-3}	6.8×10^{-11}
GDC	2.5×10^{-2}	6.3×10^{-4}