Chemical Engineering Journal 327 (2017) 257–267

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Improvements in reaction kinetics and stability of ilmenite as oxygen carrier by surface modification with calcium titanate in redox cycles of chemical-looping systems

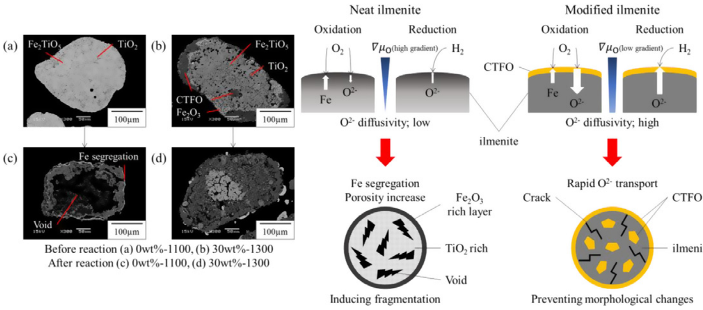
Kazuyuki Miya, Junichiro Otomo *

Department of Environment Systems, Graduate School of Frontier Sciences, The University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8563, Japan

HIGHLIGHTS

- Ilmenite was modified with iron-doped calcium titanate.
- Reduction kinetics of modified ilmenites were improved during redox cycles.
- Surface modification of ilmenite can prevent morphological changes.
- Control of ion transport can improve redox kinetics and stability of oxygen carriers.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 10 March 2017
Received in revised form 7 June 2017
Accepted 18 June 2017
Available online 19 June 2017

Keywords:
Chemical looping
Ilmenite
Oxide ion conductor
Redox reaction kinetics
Morphological change
Long lifetime

ABSTRACT

High reactivity and long-lifetime stability of the oxygen carriers in redox cycles are crucial in chemical-looping combustion systems. In this study, to improve the redox kinetics and prevent morphological changes during redox cycles, ilmenite was modified with a calcium additive to form iron-doped calcium titanate (CTFO), which is a mixed ionic and electronic conductor, on the ilmenite surface and interior. An ilmenite-core and CTFO-shell structure was formed and the structure changed depending on the calcination temperature. Use of the modified ilmenites improved the reduction kinetics in dry H_2 and wet CH_4 during redox cycles. Also, it was found that morphological changes of the modified ilmenites during redox cycles were prevented, although surface iron segregation and increased porosity were observed for neat ilmenite. The formation of a CTFO phase can induce rapid oxide ion transport at the ilmenite/CTFO interface and suppress the outward diffusion of iron cations. Prevention of morphological changes can increase the lifetimes of oxygen carriers in ilmenite. The present results provide strategies for developing oxygen carriers with high reactivities and stabilities.

1. Introduction

New technologies for effective chemical-energy-conversion systems are crucial targets in establishing a low-carbon society. Chemical looping (CL) is an attractive energy-conversion system, which involves CO_2 separation without any energy penalty [1–3]. In CL processes, the redox chemistry of metal oxides (i.e., oxygen carriers), which transport oxygen in the systems, plays a key role. The redox reaction cycles of metal oxides are performed in a fuel reactor (i.e., reduction of metal oxides and CO_2 separation) and an air reactor (i.e., oxidation of reduced metal oxides and high-grade heat generation) in CL systems. The development of oxygen carriers is important in improving the performances of CL systems,

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* Corresponding author.
E-mail address: otomo@k.u-tokyo.ac.jp (J. Otomo).

http://dx.doi.org/10.1016/j.cej.2017.06.089
1385-8947/

and providing environmental and economic advantages. Artificial oxygen carriers based on Fe_2O_3, CuO, and NiO have been widely investigated [4–9]. However, artificial oxygen carriers are generally expensive because of their production costs, and, for NiO in particular, the toxicity makes safe handling difficult. Oxygen carriers that have advantages in terms of available resources, safety, and economy are therefore needed. Natural ores such as iron ore and manganese ores are promising materials for use as oxygen carriers and their performances have been widely investigated [9–14].

Ilmenite is a natural ore that is a popular oxygen carrier and the suitability of ilmenite for CL systems has been investigated in terms of redox kinetics and stability [15–18]. The problems associated with ilmenite use are its low reactivity and stability during redox cycles. Early studies of ilmenite investigated the reactivity during redox cycles with reducing gases such as H_2, CO, and hydrocarbons, using thermogravimetry (TG) and a fluidized bed reactor [16,19–23]. The focus of these studies then switched to the use of solid fuels such as coal, petroleum coke, and syngas for 10 kW to 1 MW CL combustion (CLC) [24–31]. Operating models of CLC systems have been evaluated [32–39] and the environmental impacts of CLC systems have been assessed [40,41]. Morphological changes such as Fe segregation, sintering, and the formation of porous structures during redox cycles in CLC systems using ilmenite as an oxygen carrier have been reported [42]. Morphological changes shorten the lifetimes of oxygen carriers. However, there have been few studies focusing on changes in the morphology and composition of ilmenite particles during redox cycles [43–45]. Cuadrat et al. [43] reported that Fe segregation and increased porosity in ilmenite particles were observed after 100 redox cycles; this lowered the mechanical strength of the particles. Knutsson et al. [44] used scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX) to examine ilmenite particles after use in a 100 kW CLC system. Fe segregation inside and outside the particles and crack formation were observed, which would shorten the oxygen carrier lifetimes. Ridha et al. [45] studied pressurized CLC cycles using TG. They reported that the surface morphology of ilmenite was not affected by the total pressure and CO partial pressure. The formation of cracks and porous structures was observed with increasing number of redox cycles. Previous studies [43–45] have reported the morphological changes during redox cycles, but the prevention of morphological changes of ilmenite particles has not been studied.

In this study, we investigated the redox kinetics and morphological changes of ilmenite. In our previous studies, when yttria-stabilized zirconia (YSZ), gadolinia-doped ceria (GDC), and iron-doped calcium titanate (CTFO) were used as supports, the oxide ions and mixed ionic-electronic conductors acted as effective supports for oxygen carriers and improved the redox kinetics of the metal oxides [46–48]. Also, in our preliminary experiment, we found that ilmenite reacted with a calcium additive to form CTFO phase in the ilmenite particle and it accelerated the reduction kinetics [49]. In this study, therefore, we used a calcium additive to produce ilmenite surface-modified with CTFO to improve the reduction process on ilmenite and suppress morphological changes during redox cycles. The present report consists of three parts: (1) preparation of surface-modified ilmenites with CTFO and their characterization; (2) redox kinetic measurements of the surface-modified ilmenites; and (3) morphological changes in the surface-modified ilmenites during redox cycles. The mechanism of the suppression of morphological changes in the modified ilmenite particles is discussed in terms of oxygen transport phenomena in the particles. The present work provides guidelines for the design of oxygen carries with high reactivities and stabilities in CLC systems.

2. Materials and methods

2.1. Preparation and characterization of surface-modified ilmenite

Ilmenite surface-modified with CTFO ($CaTi_{1-x}Fe_xO_{3-\delta}$) was prepared using a wet impregnation method. First, ilmenite particles (Sibelco, Australia) were calcined in air at 950 °C for 24 h to obtain the highest oxidation state of ilmenite.

$$2FeTiO_3 + \frac{1}{2}O_2 \rightarrow Fe_2TiO_5 + TiO_2 \tag{1}$$

The desired amount of $Ca(NO_3)_2{\cdot}4H_2O$ (purity > 99.9%, Wako Pure Chemical Industries, Ltd., Japan) was dissolved in deionized water (20–25 mL). The calcined ilmenite particles were soaked in this solution. The solution was stirred and dried on a hot plate at 65–70 °C. The dried powders were calcined in air at given temperatures (1100, 1200, and 1300 °C) for 5 h to form CTFO around the ilmenite particles. Finally, the obtained samples were sieved to 150–300 μm. In this study, the Ca content of the ilmenite was expressed as the weight ratio of the equivalent amount of CaO, i.e., the Ca content was defined as the mass of CaO, m_{CaO}, per mass of the sample, m_{sample} [m_{CaO}/m_{sample} = equivalent CaO weight ratio (10, 20, 30 wt%)]. The samples are denoted by equivalent CaO weight ratio-calcination temperature (°C), e.g. 10 wt%-1100.

X-ray diffraction (XRD) patterns of the obtained samples were measured with SmartLab (Rigaku Co., Japan) using a Cu K_α source operating typically at 40 kV and 30 mA at a scan rate 3° 2θ min $^{-1}$ with an angular resolution 0.02° in the 2θ scans. The peak profiles were obtained from Cu K_α line-corrected data. Microstructures of neat and modified ilmenites and their compositions were observed by SEM (JSM-5600, JEOL Ltd., Japan) and EDX (Link ISIS, Oxford Instruments plc, UK). The ilmenite samples were mixed with epoxy resin, and then they were fixed on a slide glass. The fixed samples were polished using sandpapers and a grinding machine to observe the cross-sectional images. The specific surface areas of the samples were determined by the Brunauer–Emmett–Teller (BET) method with nitrogen using a NOVA2200e instrument (Quantachrome Instruments, USA). The relative pressure range between 0.05 and 0.3 (6-points measurement) was employed to measure the specific surface areas of the samples.

2.2. Kinetic measurements

Redox reactions of the CTFO-modified ilmenite samples, i.e., reduction of oxidized ilmenite with dry H_2 and wet CH_4 and subsequent oxidation of ilmenite with dry air, were performed at atmospheric pressure with TG (TG8120, Rigaku Corporation, Japan). A powdered sample of the CTFO-modified ilmenite was placed in an alumina pan, and then a gaseous mixture of H_2 and Ar (2:98) or CH_4, H_2O, and Ar (3:6:91) was introduced into the reaction chamber. After reduction, a gaseous mixture of O_2 and Ar (14:86) was introduced. The total flow rate was 300 mL/min. The redox reactions were cycled at constant temperature, 900 °C. To examine temperature dependences of reaction kinetics, reaction temperature was changed between 750 °C and 950 °C.

3. Results and discussion

3.1. Characterization of modified ilmenites

The components and morphological variations of the modified ilmenites were investigated using XRD, SEM-EDX, and the BET method. XRD patterns of the samples calcined at different temperatures are shown in Fig. 1a, b, and c. The ilmenite samples were calcined at 950 °C for 24 h in air before the redox kinetic