

Nickel oxide redox processes with oxide ion conductor-supported nickel oxide in dry and humidified methane: Effect of oxide ion conductors on induction period in nickel oxide reduction and subsequent hydrogen production

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HIGHLIGHTS

- ▶ Oxide ion conductors were investigated as oxygen carrier supports in a chemical looping process.
- ▶ Induction period in NiO reduction by dry and humidified methane was observed.
- ▶ A longer induction period was observed under a humid condition than under a dry condition.
- ▶ The induction period was decreased when the oxide ion conductors were used as supports.
- ▶ The performance of NiO redox cycle strongly depends on support materials of oxide ion conductors.

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ABSTRACT

NiO redox processes and hydrogen production from dry and humidified methane were investigated by chemical looping combustion (CLC) and chemical looping reforming (CLR) using NiO as an oxygen carrier. To achieve a lower operating temperature in the NiO reduction process, oxide ion conductors such as gadolinia doped ceria (GDC) and strontium doped lanthanum aluminate (LSA) were investigated as the support materials of NiO. Hydrogen rich gas products were obtained by the CLC and CLR processes but a prolonged induction period for the NiO reduction by methane (i.e., induction period for CO₂ formation from methane) was observed at relatively low operating temperatures in both processes. NiO/GDC and NiO/LSA lead to a decrease in the induction period of NiO reduction by comparison with the reference NiO/ZrO₂. Upon repeating the NiO reduction–oxidation cycles, we also found that the induction period for NiO/GDC became shorter with an increase in the redox cycle number. However, for NiO/LSA this time became longer, which may result from the strong interaction between Ni and the support materials. This NiO reduction behavior on the oxide ion conductors is discussed together with the autocatalytic reaction mechanism for NiO reduction, which provides new insights into the efficient use of lattice oxygen in CLC and CLR.

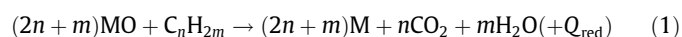
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1. Introduction

Hydrogen production technology can assist the industrial community to realize CO₂ emission reduction. For the widespread application of this technology, the development of cost effective processing and multiple adaptations for renewable and non-renewable energy sources are indispensable. The concept of chemical looping combustion (CLC) has been proposed as an efficient method to reduce the irreversibility of the combustion process over a quarter of a century ago [1]. In general, the CLC system

consists of a pair of reactors (fuel reactor and air reactor) wherein oxygen carrying species are reduced by fuels such as coal, biomass and carbonaceous waste materials as well as gas and liquid fuels (i.e., the consumption of lattice oxygen in the oxygen carrying species by the fuels in the fuel reactor) and the reduced species are subsequently oxidized by air in a continuous loop (i.e., regeneration of the oxygen carrying species in the air reactor) to obtain a high grade heat. The relevant reactions including oxygen carrier (i.e., metal oxide) are given below.

Reduction of the metal oxide (MO) by carbonaceous fuels (C_nH_{2m}):



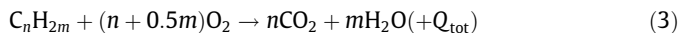
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Oxidation of the metal (M):

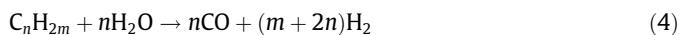


Total reaction:



For the MO reduction (Eq. (1)), endothermic low grade heat, Q_{red} , is supplied and exothermic high grade heat Q_{ox} is obtained in the subsequent oxidation process (Eq. (2)). The net gain is therefore: $Q_{tot} = Q_{red} - Q_{ox}$. A thermodynamic study of a power generation system combined with a CLC system suggests a high energy conversion efficiency [2]. To date, the CLC and the related lattice oxygen utilization have been widely examined in terms of oxygen carrier materials development, kinetics and system evaluations [3–19] (a detailed history of CLC development is well documented in Refs. [3,4]).

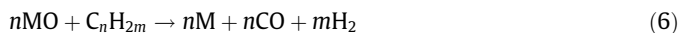
As for hydrogen production, chemical looping reforming (CLR) has been also proposed [5].



The generated CO reacts with water to form hydrogen (water gas shift reaction).



Additionally, auto-thermal reforming should also be considered for hydrogen production [5].



In CLC and CLR systems, efficient usage of the lattice oxygen in the metal oxides is important. For a further improvement in system performance, an important step is the initial reduction process of the metal oxide. To enhance the initial reduction process, oxygen carrier support materials should be investigated as well as metal oxides (e.g. NiO, Fe_2O_3 , CuO and Mn_3O_4 [6–11]). Support materials can influence physicochemical characteristics such as dispersivity, durability, conversion and selectivity. Therefore, investigations into support materials such as Al_2O_3 , SiO_2 , TiO_2 , ZrO_2 , yttria stabilized zirconia (YSZ), spinel (e.g., $MgAl_2O_4$, $NiAl_2O_4$) and perovskite (e.g., $La_xSr_{1-x}Fe_yCo_{1-y}O_{3-\delta}$) have been conducted [12–16] and they are continuing.

In this study we focus on the functions of oxide ion (O^{2-}) conductors ($Ce_{0.9}Gd_{0.1}O_{2-\delta}$ and $La_{0.9}Sr_{0.1}AlO_{3-\delta}$) as oxygen carrier (NiO) support materials for CLC and CLR. Gadolinia doped ceria, $Ce_{1-x}Gd_xO_{2-\delta}$ (GDC), which has a fluorite structure is known to be a fast oxide ion conductor as well as YSZ [20]. Trivalent cation (e.g., Gd^{3+} , Y^{3+} , Sm^{3+}) doped ceria is chemically stable as a functional catalyst or an electrolyte in reduction and oxidation atmospheres and it is used as a component in materials such as the electrodes and electrolytes of solid oxide fuel cells [21,22]. Therefore, fluorite-type oxide ion conductors are interesting oxygen carrier support materials including YSZ. We employed GDC as a representative material of a fluorite structure in this study. Strontium doped lanthanum aluminate, $La_{1-x}Sr_xAlO_{3-\delta}$ (LSA), is a perovskite-type oxide ion conductor [23]. $LaAlO_3$ has previously been examined as a catalyst support material. For example, Ni/ $LaAlO_3$ has high catalytic activity and durability during the steam reforming of methane [24]. Generally, in oxide ion conductors, oxide ion hopping conduction occurs via oxygen vacancies (V_o^\bullet), which form by multivalent cation doping into the oxide ion conductors [20]. In terms of the surface reaction, it has been reported that the oxygen species originate from oxygen molecules or water molecules in the gas phase that are generated on the surface of oxide ion conductors by an interaction with V_o^\bullet . Consequently, an oxygen exchange reaction of the oxygen molecules or water molecules with lattice oxygen in the oxide ion conductor proceeds via V_o^\bullet [25]. These generated active oxygen species may enhance the oxidative

reaction with carbonaceous fuels, which is our main concern in the present CLC and CLR systems.

NiO reduction kinetics in CLC and CLR is thus investigated with relevant oxide ion conducting support from the fundamental aspect, which is related to the performance of the fuel reactor, i.e., the system efficiency is related to heat generation and hydrogen production. Recently, in our previous study [26], a prolonged induction period for NiO reduction by methane has been observed at relatively low temperatures. Observing the induction period for NiO reduction will provide data to suggest how to efficiently operate the CLC and CLR. A shorter induction period will result in faster reduction kinetics and a lower temperature for the operation of a fuel reactor. Lowering operating temperature may improve life time of oxygen carrier particles since it can suppress sintering of particles and reaction between oxygen carrier and contaminants such as ash formed in a fuel reactor. In addition, hydrogen production in pyrolysis and steam gasification may increase with a decrease in temperature [12]. Furthermore, the present kinetics study and the development of relevant support materials may provide a hint for effective operation at high temperatures (around 900 °C), which is also an important issue. We believe that the kinetic data obtained in this work will include knowledge developing fast kinetics under a high temperature operating condition. Therefore, to guide the design of an efficient NiO reduction system, the induction period for NiO reduction is a specific index for the efficient operation of CLC and CLR.

This article mainly deals with (1) a product analysis of the methane fuel and an investigation of the induction period for NiO reduction with the metal oxide support materials ZrO_2 , GDC and LSA; (2) the dependence of the NiO reduction–oxidation cycle behavior on the oxide ion conductors; and (3) a discussion of the NiO reduction mechanism on oxide ion conducting support materials, which will be dealt with in combination with the autocatalytic reaction mechanism. We used methane as a fuel to investigate fundamental reduction kinetics with oxide ion conducting supports in CLC and CLR systems. Also, methane is supposed as a direct fuel (i.e., LNG is utilized as fuel) for heat and power generations in CLC systems. The experiments and observations provide new insights for the efficient use of lattice oxygen in CLC and CLR with the appropriate use of oxide ion conducting materials.

2. Experimental

2.1. Preparation and characterization of oxygen carrier

Metal oxide-supported NiO oxygen carriers were prepared by a wet impregnation method. In this study, 35 wt% NiO-loaded metal oxide powders were prepared and used for the NiO reduction experiments. ZrO_2 was used as supplied from Tosoh (Tokyo, Japan). $Ce_{0.9}Gd_{0.1}O_{2-\delta}$ (GDC) was also used as supplied from AGC Seimi Chemical (Kanagawa, Japan). $La_{0.9}Sr_{0.1}AlO_{3-\delta}$ (LSA) was prepared by a solid state reaction method: $La(NO_3)_3 \cdot 6H_2O$ (purity > 99.5%, Kanto Chemical, Tokyo, Japan), $Sr(NO_3)_2$ (purity > 99%, Kanto Chemical, Tokyo, Japan) and $Al(NO_3)_3 \cdot 9H_2O$ (purity > 99%, Kanto Chemical, Tokyo, Japan) were calcined in air at 1173 K for 5 h and then at 1423 K for 10 h. The 35 wt% NiO-loaded metal oxide powders were prepared by a wet impregnation method with nickel nitrate (purity > 99.5%, Kanto Chemical, Tokyo, Japan) and with metal oxide powders followed by calcination in air at 673 K for 4 h and then at 1073 K for 4 h. The obtained powders were characterized using transmission electron microscopy (TEM, JEM 2010F, JEOL, Japan) and X-ray diffraction spectroscopy (XRD, M03X HF22, MAC Science, Japan). The specific surface areas of the metal oxides were also examined by the Brunauer–Emmett–Teller (BET) method with a Gemini 2360 (Shimadzu, Japan).

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