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$La_{1-x}Sr_xM_yFe_{1-y}O_{3-\delta}$ perovskites as oxygen-carrier materials for chemical-looping reforming

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ABSTRACT

The use of perovskites with the general formula $La_{1-x}Sr_xM_yFe_{1-y}O_3$ (M = Ni, Co, Cr, Cu) as oxygen carriers for syngas generation from methane by Chemical Looping Reforming is investigated in the present work. The experimental study concerns the oxidation of a fuel, using the oxygen from a solid oxygen carrier, instead of oxygen from air. Subsequent oxidation of the reduced solid is performed either with gaseous oxygen or with water. In the latter case additional hydrogen is produced, which is very pure and therefore appropriate to be used in fuel cell applications. The performance of the candidate materials is ranked by taking into account the hydrogen and carbon monoxide yields during the fuel oxidation step as well as the amount of oxygen per mole solid (δ) that can be delivered reversibly to the fuel. The effect of the materials composition and of NiO addition is examined. The best performance was obtained with the $La_{0.7}Sr_{0.3}Cr_{0.1}Fe_{0.9}O_3$ sample mixed with 5% NiO. The H_2 yield was up to 90%.

1. Introduction

It has been established that CO_2 emissions resulting from human activity have led to an increase in the atmospheric CO_2 concentration, from a pre-industrial level of 280–450 ppm [1]. This results in a mean annual temperature increase at the earth's surface which is commonly known as global warming.

One possible approach to minimize CO_2 emissions is to enhance the use of renewable energy resources, such as biomass, solar and wind energy. These alternative energy sources have the intrinsic advantage of not generating CO_2 or contributing with zero net CO_2 emissions. However, in their current state of development and/or availability, alternative energy technologies cannot fully replace the existing fossil fuels-based energy production.

A way to reduce CO_2 emissions in the medium-term, that receives increasing interest, is the CO_2 sequestration. This consists of capturing CO_2 in an emission source and storing it. It is therefore prevented from reaching the atmosphere. Sequestration could involve, for example, CO_2 capture in flue gases from combustion processes, and CO_2 storage in geological formations such as depleted oil and gas fields or deep saline aquifers [2].

There are currently a number of available processes for CO_2 capture. Increasing interest among them is being gained in the recent years by the Chemical Looping Combustion (CLC) technology [3]. CLC involves the use of a metal oxide as an oxygen carrier. This process is configured with two interconnected fluidized bed reactors: an air reactor and a fuel reactor. The solid oxygen carrier is circulated between the air

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and fuel reactors. In CLC, the gaseous fuel is fed into the fuel reactor where it is oxidized by the lattice oxygen of the metal oxide. Complete combustion in the fuel reactor produces CO_2 and water vapor. The CO_2 formed can be readily recovered by condensing the water vapor and the water-free CO_2 can be sequestrated or/and used for other applications. The technology has recently been successfully demonstrated for more than 1000 h and at scales of up to 140 kW [4–6]. Ni/NiO, usually supported on alumina, has so far been selected by many investigators [3–6] as the most suitable oxygen carrier (OC) material for chemical-looping processes since it delivers high reactivities for oxygen exchange.

Carbon sequestration has the potential to greatly reduce CO_2 emissions from large point sources such as power plants and industries. However, CO_2 capture applications for small mobile emission sources such as cars, trucks and airplanes seem implausible. This is noteworthy because the transportation sector alone is responsible for about one-quarter of the global CO_2 emissions, and this share has a clear tendency to increase.

A promising option is the use of H_2 as a fuel to reduce the CO_2 emissions. Hydrogen production from renewable sources is the most appropriate environmental solution for long-term sustainable hydrogen production. The thermochemical water splitting, in particular when combined to solar energy supply is one of the most promising routes for long-term sustainable hydrogen production [7,8]. However, the technologies are still not mature and of high cost. Therefore, existing technologies based on hydrogen production from fossil-fuel sources (e.g. steam reforming of natural gas) are expected to continue to dominate also in the coming decades. Presently, hydrogen is produced mostly by reforming of natural gas (i.e. methane), partial oxidation of heavy oils and naphtha and gasification of coal [9,10]. Natural gas is an ideal source for hydrogen production since its hydrogen/carbon ratio is roughly twice as much as that of oil.

A promising alternative for H_2 production from natural gas is the "Chemical Looping Reforming (CLR)" process [11]. In CLR a suitable oxide catalyst is circulated between two reactors as in CLC. In the first reactor methane is oxidized to synthesis gas by the lattice oxygen of the oxide, and in the second reactor, the reduced oxide is re-oxidized by air. In this way the products are undiluted with N_2. A schematic diagram of the CLR and/or the CLC process is presented in Fig. 1a.

One big concern in Chemical Looping processes generally and of the CLR specifically is the recirculation of the solid materials between the two reactors. Besides the energy consumption to provide the driving force for the circulation of particles between the two reactors, large recirculation rates of oxygen carrier also result in the breakage and attrition of particles in the air reactor, which excludes many materials with good oxygen transfer capacity from being suitable as oxygen carriers due to their high attrition indices.

In order to overcome these problems the dense membrane reactor concept (Fig. 1b) is proposed in this work. It is based on the use of a dense mixed-conducting membrane reactor to perform the reduction and oxidation steps simultaneously at either membrane side. It is composed of two compartments gas tightly separated by the dense membrane. A hydrocarbon (e.g. natural gas) is oxidized in the "Fuel" compartment in the absence of gaseous oxygen, by pulling oxygen atoms from the solid. Due to chemical potential difference, oxygen is transferred through the membrane from the opposite "oxidation" side. If air is added in the "oxidation" compartment, gaseous oxygen molecules decompose on the membrane surface and the oxygen atoms fill the oxygen vacancies of the membrane. Alternatively, water can be added in this compartment, which decomposes on the membrane surface into gaseous hydrogen

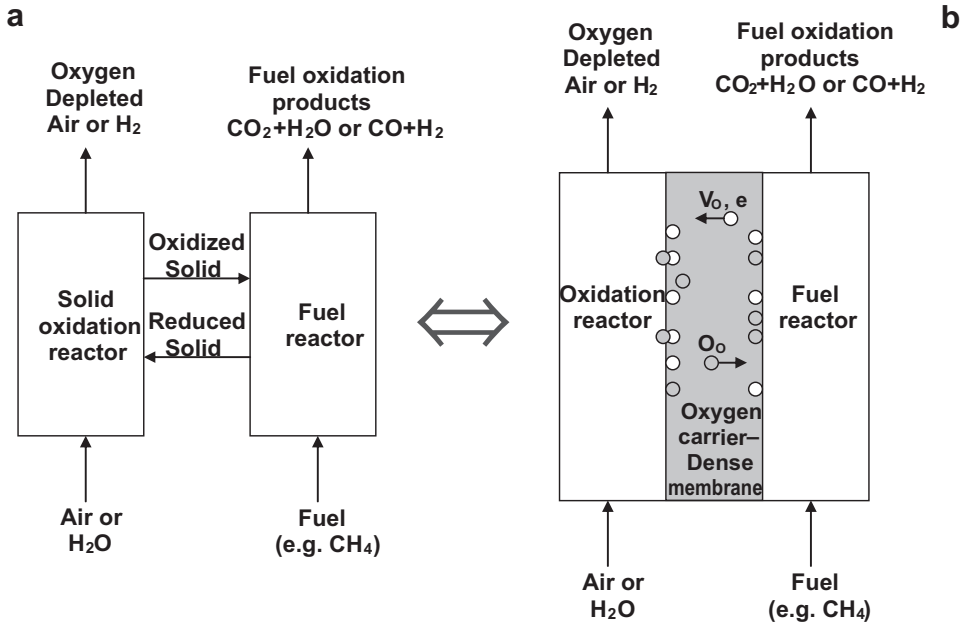

Fig. 1 – (a) Schematic diagram of the Chemical Looping Combustion (CLC) and/or the Chemical Looping Reforming (CLR) process (b) Dense Membrane Reactor–Chemical Looping Combustion (DMR–CLC) and/or Dense Membrane Reactor–Chemical Looping Reforming (DMR–CLR).