



Research article

O₂ uncoupling behaviour of ilmenite and manganese-modified ilmenite as oxygen carriers

Zhenkun Sun^a, Dennis Y. Lu^{a,*}, Robin W. Hughes^a, Dimitrios Filippou^b^a Natural Resources Canada, CanmetENERGY-Ottawa, 1 Haanel Drive, Ottawa, Ontario K1A 1M1, Canada^b Rio Tinto Iron & Titanium, Technology Department, 1625 route Marie-Victorin, Sorel-Tracy, Québec J3R 1M6, Canada

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ABSTRACT

In this study, naturally occurring ilmenite and manganese-modified ilmenite were evaluated as oxygen carriers with respect to their O₂ uncoupling behaviour. The effects of temperature and pre-treatment on the O₂ uncoupling properties of manganese-modified ilmenite were also investigated. The experimental results indicated that both calcined ilmenite and manganese-modified ilmenite were capable of releasing gas-phase O₂ at certain temperatures with the amount of O₂ released by the manganese-modified ilmenite being much more than that of the calcined ilmenite. When the manganese-modified ilmenite was pre-treated by subjecting it to several cycles of chemical looping combustion with CH₄ as reductant, the Mn₂O₃ might react with iron species that had migrated outwardly, resulting in the formation of a ferrimanganic oxide which exhibits favourable thermodynamics for the oxidation reaction for the reduced oxygen carrier. As a result, the reduced pre-treated oxygen carrier could be easily re-oxidized and more O₂ could be released by the pre-treated oxygen carrier during every uncoupling steps than that by the untreated one. More gas-phase O₂ was released by the manganese-modified ilmenite when more redox cycles were performed during pre-treatment. The temperature of isothermal uncoupling-oxidation cycling showed a significant influence on the O₂ uncoupling behaviour for manganese-modified ilmenite. When temperatures were either higher or lower than 900 °C, less O₂ was released from manganese-modified ilmenite. 30%-Mn₂O₃/ilmenite released more O₂ than 15%-Mn₂O₃/ilmenite when the temperature was below 950 °C while the same amount of O₂ was released when the temperature was 1000 °C.

1. Introduction

Chemical looping combustion (CLC) is an emerging combustion technology which has been gaining considerable attention over the last two decades due to its high-efficiency in converting fuels to heat with inherent CO₂ separation [1,2]. CLC processes can be realized in dual-reactor systems consisting of an air reactor (AR) and a fuel reactor (FR). A metal oxide acting as an oxygen carrier (OC) is employed to transfer oxygen from the AR to the FR, thereby avoiding direct contact between fuel and air. As a result, CO₂ and H₂O are kept separated from the other flue gas components, and the costly and energy consuming separation of CO₂ is eliminated. For industrial applications, CLC processes depend on the availability of OCs with suitable chemical and physical properties [3]. The selection of OCs with high performance is a critical part of developing CLC technology. A suitable OC for CLC processes should be highly stable under repeated redox cycles at high temperatures, resistant to attrition and agglomeration, low-cost, environmentally friendly, and highly reactive with the selected fuel and oxidant [3,4].

During CLC processes, the full conversion of the fuels can be limited

due to inadequate gas-solid contacting or due to thermodynamic limits related to reaction between fuels and the lattice oxygen in OCs [5,6]. As a result, the flue gas produced from the FR will contain unconverted gases such as H₂, CO, and CH₄. The concentration of unconverted combustible gases in the flue gas must be limited in order to meet CO₂ pipeline specifications and to avoid wasting the fuel. There are several approaches that can be taken to achieve complete combustion. These include 1) the separation of unconverted gases including H₂, CO, and CH₄ from the CO₂ followed by the recirculation of these gases to the fuel reactor, and 2) the introduction of pure O₂ downstream of the FR to oxidize the remaining unconverted gases (oxygen polishing) [7]. Unfortunately, both of these measures are high-cost and energy-intensive due to the necessary gas separation unit operation. Another strategy to improve fuel conversion in the FR is the generation of gas-phase O₂ in the FR during the combustion of the fuels [7]. An alternative chemical looping concept, chemical looping with oxygen uncoupling (CLOU), provides a strategy to supply gaseous O₂ to the FR [8–10]. The CLOU approach can be regarded as an improvement of conventional CLC processes. The significant difference between CLOU and conventional

* Corresponding author.

E-mail address: Dennis.Lu@canada.ca (D.Y. Lu).

CLC processes is the mechanisms for oxidation of fuels in the FR. CLOU utilizes an OC that releases gas-phase O_2 under reducing conditions, and the fuels in the FR are oxidized by released O_2 via gas-gas (for gaseous fuels) or gas-solid (for solid fuels) reactions. In the AR, the OC is reoxidized by air, which is exactly the same as in conventional CLC processes. It has been observed that the rate of combustion by using OCs with O_2 uncoupling with CH_4 is significantly higher than in conventional CLC processes [3]. Thus, for a given fuel firing rate, the CLC processes using O_2 -uncoupling materials require smaller solids inventory, which in turn leads to smaller fuel reactors [11].

A series of studies has shown that oxidation and combustion of gaseous fuels, e.g. CH_4 , can proceed more completely when Fe-, Mn- or perovskite-based OCs exhibit an O_2 uncoupling property. Kallen et al. [12] prepared perovskite material $CaMn_{0.9}Mg_{0.1}O_{3-\delta}$ with O_2 uncoupling properties and examined its performance as an OC for CLC with CH_4 . They found that complete combustion of CH_4 was achieved with an oxygen concentration in the outlet stream from the fuel reactor of $> 1 \text{ vol}\%$, which suggests that a substantial part of the fuel is converted by gaseous O_2 released from the particles promoting the fuel conversion [12]. Given such high oxygen concentrations it should be noted that prior to CO_2 transport, any remaining O_2 present in the CO_2 produced by CLC systems with O_2 uncoupling will need to be removed to a concentration less than about 10 vppm in order to meet pipeline specifications that are in place to avoid pipeline corrosion [13]. This can be done through a number of methods including cryogenic separation and catalytic combustion. Shulman et al. developed a series of Mn/Fe composite OCs with O_2 release characteristics selected for CLC of CH_4 . They observed low CO formation during combustion which they attributed to O_2 uncoupling from the OCs [14]. Shulman et al. [15] also investigated O_2 uncoupling properties and reaction rates for CH_4 combustion in a fluidized bed reactor with various OC particles, produced from mixtures of Mn- and Mg-based oxides. They concluded that OC particles with enhanced O_2 release showed superior methane combustion properties achieving nearly complete conversion of the fuel. They believed O_2 uncoupling in commercial operations could facilitate very high or complete conversion of methane-rich fuels [15].

Although the CLOU approach largely relies on existing CLC technology configurations, the strategy presents the need for material development. A suitable OC for CLOU should be thermodynamically capable of releasing gas-phase O_2 at an appropriate temperature under relevant O_2 partial pressures in the FR (lower than $1.0 \times 10^{-5} \text{ atm}$ when considering the O_2 limit in CO_2 pipelines would be required to avoid oxygen removal in the CO_2 purification unit), and should exhibit a high enough oxygen releasing capacity to effectively oxidize the fuel gas. At the same time, the oxygen carrier's reduced form must be oxidized easily in the AR. Similar to conventional CLC processes, OCs for CLOU have to be mechanically stable, low-cost and environmentally acceptable. Thermodynamic analysis concludes that the most commonly proposed OCs formed with monometallic oxides based on Fe_2O_3 and NiO are incapable of releasing gas-phase O_2 at typical fluidized bed combustion (FBC) conditions [11]. OCs based on metal oxides such as CuO , Mn_2O_3 , and Co_3O_4 with appropriate equilibrium partial pressures of O_2 in the temperature range of 800 to 1200 °C are promising [11]. However, Co_3O_4 has not been widely considered as an OC due to its high cost and high toxicity [11,16]. CuO and Cu_2O are the most thoroughly examined oxide pair for CLOU and appears to be promising technically, but the fairly high cost of CuO and high possibility of sintering prompt us to look for alternates [17,18]. Mn_2O_3 is an abundant and inexpensive metallic oxide with a relatively low decomposition temperature favouring the release of gas-phase O_2 . However, assuming that the reduced oxygen carrier is regenerated with air, the decomposition temperature for Mn_2O_3 at 876 °C imposes a relatively low thermodynamic maximum temperature for the AR [11,19]. In other words, Mn_2O_3 will decompose into Mn_3O_4 when O_2 partial pressure is lower than or equal to 0.21 atm at atmospheric pressure. Therefore, at atmospheric pressure the maximum operation temperature of the AR

would need to be lower than 876 °C in practice to achieve rapid oxidation of Mn_3O_4 to Mn_2O_3 . As a result, directly using pure Mn_2O_3 or manganese ores as OCs for CLOU is unfavourable and impractical since excessively low AR operating temperatures result in low overall system efficiency.

Recent studies indicate that the temperature at which Mn_3O_4 oxidation proceeds can be increased by combining Mn species with other materials such as iron, nickel, silicon, magnesium and calcium resulting in mixed oxides with improved thermodynamic properties [19–22]. The most frequently investigated combinations are Fe_2O_3/Mn_2O_3 mixed oxides which exhibit superior O_2 uncoupling characteristics to Mn_2O_3 solely during reduction. The formation of bixbyite ($Mn_xFe_{1-x}O_3$) crystal phase enables the Mn species to be oxidized in the AR at high temperature and low oxygen partial pressure [23–25]. OCs containing Fe_2O_3/Mn_2O_3 mixed oxides employed in the majority of current studies are fully synthetic materials which show superior O_2 release capacity and improved oxidation behaviour. However, the mechanical integrity and attrition resistance of these synthetic particles are often unsatisfactory in continuous operation, which need a carefully design on the preparation method to improve their performance [26–29]. From an economic point of view, the use of these synthetic particles in practice, at current stage, is likely to be cost prohibitive even if the attrition resistance becomes comparable to the naturally occurring materials. This is due to the high cost of their precursors and their complicated production processes; as a result, an extreme high operational cost will be imposed even a low attrition rate is achieved. On the contrary, the lower cost of the naturally occurring materials can offset this operational cost when a reasonable attrition rate is achieved. Therefore, we believe that looking for OCs with suitable O_2 uncoupling behaviour based on low cost materials such as naturally occurring metal ores or minerals is still well worth considering.

Iron ores (e.g. hematite, mainly composed of Fe_2O_3) and titanium-iron ores (e.g. ilmenite ore, mainly composed of $FeTiO_3$) are two series of natural materials which have been extensively examined to act as low-cost OCs in various chemical looping processes. However, both pure oxides Fe_2O_3 and Fe_2TiO_5 ($FeTiO_3$ in oxidized form) should not be capable of releasing gas-phase O_2 during CLC-relevant temperatures below 1050 °C according to one thermodynamic study [30]. To enable O_2 uncoupling to proceed with iron ore, Haider et al. immobilized Mn_2O_3 on a Canadian iron ore resulting in a composite Fe_2O_3/Mn_2O_3 oxygen carrier [31]. They found that the impregnated iron ore exhibited significant O_2 uncoupling in an inert atmosphere and showed favourable oxidation kinetics in air. They concluded that the impregnated iron ore OC should facilitate efficient use of fuels for CLOU processes.

Ilmenite ore (titanium-iron) has been extensively investigated as an OC for CLC. Ilmenite is considered a highly promising OC for chemical looping applications due to its desirable thermodynamic properties, demonstrated attrition resistance, low-cost and its potential 100% combustion efficiency [32–37]. A recent study reported by Rydén et al. has shown that ilmenite is capable of releasing small amounts of gas-phase O_2 during chemical-looping combustion experiments at a temperature of $\sim 950 \text{ °C}$ [38]. They postulated that the reason for the O_2 release was due to the presence of small amounts of manganese in the sample or interactions between impurities and iron or titanium oxides [38]. Unfortunately, there is little else reported in the literature on the O_2 release behaviour of titanium-iron ore. The present research aims to understand the mechanism of O_2 uncoupling from ilmenite and to promote O_2 release.

In this paper, we report on an experimental investigation in which an ilmenite ore was modified by manganese species via an impregnation method. Evaluation of this manganese-modified ilmenite at relevant CLC conditions was performed in a thermogravimetric analyzer (TGA). In this study we sought to evaluate this material's O_2 uncoupling properties by measuring gas-phase O_2 release in an inert environment and by determining its feasibility during oxidation in air at different

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