Examination of oxygen uncoupling behaviour and reactivity towards methane for manganese silicate oxygen carriers in chemical-looping combustion

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ABSTRACT

Cheap and environmental friendly Mn–Si oxygen carriers manufactured from Mn_3O_4 and SiO_2 by spray-drying have been investigated with respect to properties for chemical-looping combustion (CLC) and chemical-looping with oxygen uncoupling (CLOU). Fifteen oxygen carriers with SiO_2 content varying from 2 wt% to 75 wt% were prepared and calcined at 1050 °C and 1150 °C. The ability of material to release O_2 and their reactivity towards CH_4 were examined in the temperature range 900–1100 °C. Particles with a SiO_2 content of more than 45 wt% and calcined at 1150 °C showed limited CLOU behaviour and poor reactivity towards CH_4 at all temperatures investigated. The rest of the materials had significant CLOU properties and provided high conversion of CH_4 under the experimental conditions chosen. Increasing the temperature of operation enhanced the CLOU behaviour and reactivity towards CH_4. At temperatures above 950 °C, the CH_4 conversion was 90–100% for these materials. Crystalline phases identified by XRD in the oxidized samples with more than 45 wt% SiO_2 and calcined at 1150 °C were mainly rhodonite $MnSiO_3$. For materials with SiO_2 content below 45 wt%, braunite Mn_7SiO_{12} was detected as the main phase in most of the samples after oxidation. This indicates that braunite Mn_7SiO_{12} is the main active phase for oxygen transfer in CLC and CLOU, which is supported by thermodynamic calculations. The reactivity of all of the materials were also studied with syngas (50% CO and 50% H_2), showing complete gas conversion at 950 °C, except for materials with a SiO_2 content of more than 45 wt% and calcined at 1150 °C. The mechanical integrity and attrition resistance of the oxygen carriers were examined in a jet-cup attrition rig, and although the attrition rates varied, some reactive material showed low rates of attrition, making them very promising oxygen carrier materials for applications related to CLC and CLOU. However, measures should probably be taken to improve the crushing strength to some extent.

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1. Introduction

Global warming resulting from human activities is believed to cause irreversible damage to the earth's climate and ecosystems (Trenberth, 2005; Karl and Trenberth, 2003; McMichael et al., 2006). Among human activities, combustion of fossil fuels is regarded as the primary source contributing to global warming (Meinshausen et al., 2009; Vitousek, 1994). Fossil fuel combustion emits excessive amounts of CO_2 into the atmosphere every year. Only in 2010, over 30,000 million tons of CO_2 was released from fossil fuel combustion globally (International Energy Agency, 2013). To prevent the earth's temperature from increasing, suppressing the emission of CO_2 from fossil fuel combustion is of prime importance.

Carbon capture and storage (CCS) provides a possibility to rapidly reduce CO_2 emissions (Metz et al., 2005). In a CCS process, CO_2 produced from fossil fuel combustion is captured in concentrated form and stored in closed geological formations. Thus, instead of emitting CO_2 into the atmosphere, CO_2 is isolated in storage sites where it can be converted into carbonate minerals or other stable phases by natural processes over a long period of time (Metz et al., 2005).

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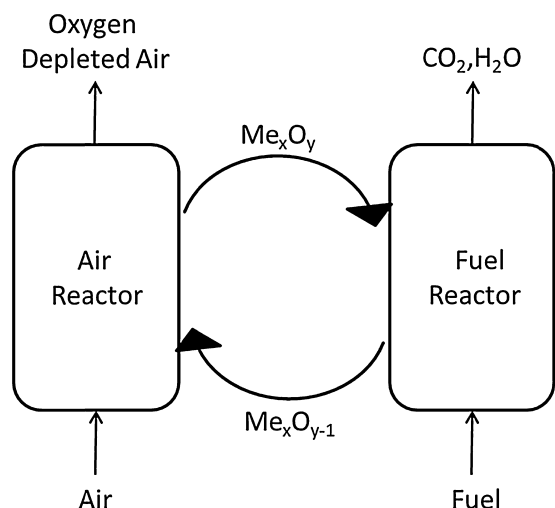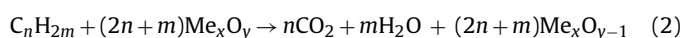E-mail address: dazheng@chalmers.se (D. Jing).

Fig. 1. Schematic representation of the CLC process.

For CCS to be feasible, a high purity CO_2 stream is required after the capture step. Chemical-looping combustion (CLC) is a CO_2 capture technique where pure CO_2 is obtained inherently during fuel oxidation without the need for any energy intensive gas separation step.

1.1. Chemical-looping combustion (CLC) and chemical-looping with oxygen uncoupling (CLOU)

In chemical-looping combustion (CLC) fuel and combustion air are not in direct contact with each other. As demonstrated by Fig. 1, a CLC unit consists of an air reactor and a fuel reactor (Ishida and Jin, 1996). Solid oxide particles, referred to as the oxygen carrier, circulate between the air reactor and the fuel reactor. In the CLC process, oxygen carrier particles are oxidized by air in the air reactor and are reduced by fuel in the fuel reactor according to reactions (1) and (2). In this way, the oxygen required for combustion is provided by the oxygen carrier through its redox cycling. Thus, direct contact of air and fuel does not occur. If fuel is fully converted, a pure CO_2 stream is obtained after condensation of steam to liquid water (Lyngfelt et al., 2001). There is no energy penalty for gas separation in CLC. This is a great advantage compared to other CO_2 capture techniques, which always include a gas separation unit (CO2 Capture Technologies, 2012; Wall, 2007). CLC can be realized in many ways, but the most commonly proposed and examined design involves circulating fluidized bed reactors with oxygen carrier particles as bed material. The overall design would be similar to conventional circulating fluidized bed boilers (Lyngfelt et al., 2001). Though the oxygen needed for combustion is transferred by the oxygen carrier, the heat produced in CLC is the same as for a normal combustion process, which is revealed by summing the following reactions:

$$O_2 + 2Me_xO_{y-1} \rightarrow 2Me_xO_y \tag{1}$$

$$C_nH_{2m} + (2n+m)Me_xO_y \rightarrow nCO_2 + mH_2O + (2n+m)Me_xO_{y-1} \tag{2}$$

In the fuel reactor, certain oxygen carriers have the ability to release gaseous O_2 according to reaction (3). Subsequently the O_2 released can be directly consumed by fuel according to reaction (4). This process is known as chemical-looping with oxygen uncoupling (CLOU) (Mattisson et al., 2009a) and oxygen carriers with the ability to release gaseous O_2 are referred to as CLOU materials. In the presence of a CLOU oxygen carrier, fuel is converted in a similar way as in normal combustion. There could be several advantages in using CLOU, and high gas conversion has been obtained in continuous units using solid, gaseous and liquid fuels (Mattisson, 2013).

The clearest advantage is likely obtained with solid fuels, where the slow gasification step for char conversion needed in CLC is avoided. Hence, the rate of fuel conversion can be greatly enhanced (Mattisson et al., 2009a). Using a CLOU material, it is reported that the rate of petroleum coke conversion could be increased about 45 times compared to a CLC oxygen carrier (Mattisson et al., 2009b; Leion et al., 2009a). With respect to gaseous or liquid fuel conversion, the O_2 released from a CLOU oxygen carrier enables fuel conversion in the freeboard above the solid bed, thus facilitating full conversion of fuel. Therefore, CLOU oxygen carriers could be favourable for both gaseous and solid fuels (Mattisson, 2013). The process in CLC and CLOU has been recently reviewed by several research groups (Fan, 2010; Lyngfelt, 2011; Adanez et al., 2012).

$$2Me_xO_y \rightarrow 2Me_xO_{y-1} + O_2 \tag{3}$$

$$C_nH_{2m} + (n+1/2m)O_2 \rightarrow nCO_2 + mH_2O \tag{4}$$
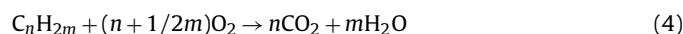
1.2. Oxygen carriers and combined manganese oxides

A key issue in CLC and CLOU is to develop appropriate oxygen carrier materials. Oxygen carriers typically are metal oxides capable of being oxidized and reduced when exposed to different conditions. For a metal oxide to be an oxygen carrier, there are some required properties. First of all, the metal oxide should have suitable thermodynamic properties and provide adequate reaction kinetics during combustion conditions. Since a CLC unit normally uses fluidized-bed technique, the oxygen carrier particles should fluidize well, meaning that they should not be prone to agglomeration or severe dust formation during operation. Oxygen carrier material is also required to have stable performance over a long time of operation. Moreover, oxygen carrier particles need to be benign to the environment and have a reasonable cost.

Oxides of Ni, Fe, Cu and Mn have been extensively examined (Adanez et al., 2005; Jerndal et al., 2006). With NiO material produced by spray-drying, high CH_4 conversion, stable performance and an expected oxygen carrier lifetime corresponding to over 30,000 h have been achieved in continuous CLC units (Linderholm et al., 2009; Kolbitsch et al., 2010). Though promising results have been obtained using such NiO-based materials, the cost of Ni, its toxicity and its thermodynamic restrictions for complete fuel conversion constitutes significant drawbacks (Jerndal et al., 2009). Fe-based oxides, which are environmentally friendly, have the ability to achieve high conversion of CO and H_2 to CO_2 and H_2O. But their reactivity towards CH_4 is relatively low (Abad et al., 2007a,b; Cho, 2005). Cu-based materials have the advantage of having oxygen uncoupling properties. In the fuel reactor of a CLC unit, CuO can decompose to Cu_2O while releasing substantial amount of O_2 for fuel combustion. It also has high reactivity towards gaseous fuels. Most of the CuO oxygen carriers in the literature had the ability to fully convert CH_4 to CO_2 (Forero et al., 2011; Gayan et al., 2012; Adánez-Rubio et al., 2012, 2013; de Diego et al., 2004; Arjmand et al., 2011, 2012). Upon high reduction degree to Cu, there is a risk for agglomeration during CLC operation as the melting temperature of Cu is only 1085 °C. It has also been found that CuO reacted with support material, such as Al_2O_3, forming other compound, resulting in a loss of its CLOU property (Arjmand et al., 2011, 2012). Mn-oxides can provide CLOU behaviour under relevant conditions (Leion et al., 2008a, b). However, oxidation of Mn_3O_4 to Mn_2O_3 is thermodynamic hindered above 800 °C when oxidizing with O_2 partial pressure of 0.15 bar (Zafar et al., 2007). At lower temperatures, where the oxidation reaction is thermodynamically favoured, oxidation of Mn_3O_4 to Mn_2O_3 is still hard to achieve, probably due to kinetic limitations (Zafar et al., 2007).

Another option for oxygen carrier materials for the CLOU process would be to combine Mn with other elements forming combined Mn-oxides. Several studies have shown that combined Mn-oxides