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Thermal and mechanical behaviour of oxygen carrier materials for chemical looping combustion in a packed bed reactor

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HIGHLIGHTS

- Ilmenite-based oxygen carriers were developed for packed-bed chemical looping.
- Addition of Mn_2O_3 increased mechanical strength and microstructure of the carriers.
- Oxygen carriers were able to withstand creep and thermal cycling up to 1200 °C.
- Ilmenite-based granules are a promising shape for packed-bed reactor conditions.

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ABSTRACT

Chemical looping combustion (CLC) is a promising carbon capture technology where cyclic reduction and oxidation of a metallic oxide, which acts as a solid oxygen carrier, takes place. With this system, direct contact between air and fuel can be avoided, and so, a concentrated CO_2 stream is generated after condensation of the water in the exit gas stream. An interesting reactor system for CLC is a packed bed reactor as it can have a higher efficiency compared to a fluidized bed concept, but it requires other types of oxygen carrier particles. The particles must be larger to avoid a large pressure drop in the reactor and they must be mechanically strong to withstand the severe reactor conditions. Therefore, oxygen carriers in the shape of granules and based on the mineral ilmenite were subjected to thermal cycling and creep tests. The mechanical strength of the granules before and after testing was investigated by crush tests. In addition, the microstructure of these oxygen particles was studied to understand the relationship between the physical properties and the mechanical performance.

It was found that the granules are a promising shape for a packed bed reactor as no severe degradation in strength was noticed upon thermal cycling and creep testing. Especially, the addition of Mn_2O_3 to the ilmenite, which leads to the formation of an iron–manganese oxide, seems to results in stronger granules than the other ilmenite-based granules.

1. Introduction

Fossil fuel power plants are major emitters of greenhouse gases, which leads to an increase of CO_2 concentration in the atmosphere and as such, contribute to the global warming problem [1]. One possible method to reduce these CO_2 emissions is to capture the carbon, which can then be transported for use or storage [2–4]. There are different technologies available or currently under development which accomplish the capture of CO_2 from combustion sources, i.e. pre-combustion, post-combustion or oxyfuel combustion. Pre-combustion capture avoids production of CO_2 in combustion by transforming the carbon based component of the fuel to hydrogen which only produces water when burned. As such, CO_2 is separated before combustion when it is much more concentrated. Post-combustion capture tackles the problem by installing a separation process to treat flue gases, so no or only minor

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modifications are needed to the existing production processes. Nevertheless, post-combustion CO_2 capture systems have a significant impact on the energy production total costs [5]. On the other hand, oxy-combustion strongly increases the concentration of CO_2 in the flue gas by replacing air with oxygen for burning the fuel. Currently, the CO_2 capture technologies consist of very energy intensive steps, resulting in an increase in the cost of energy production and efficiency losses. In order to reduce energy losses, some authors are analysing methods and systems to combine powder production and CO_2 capture in a single step, as for example the fuel cell MCFC-based CO_2 capture system applied on small scale CHP plants [6].

One interesting capture route that is getting increased attention to overcome these disadvantages of the existing ones, is chemical looping combustion (CLC) [7–9]. This innovative technology combines power production and CO_2 capture in a single step and produces a pure CO_2 stream without any separation step or need of additional energy [10,11]. In this method, oxygen is transported from the air to the fuel via an oxygen carrier, which is based on a metal oxide. This oxygen exchange is carried out in cycles of two steps. During the first step, the fuel reacts with an oxygen carrier, a metal oxide (MeO), to form CO_2 and H_2O. This metal oxide is then reduced to a metal (Me) or a reduced form of MeO, so this first step is called the reduction step. In the second step, the oxygen carrier is oxidized with air. After this oxidation step, the regenerated material is ready to start a new cycle. The flue gas leaving the oxidation step contains N_2 and unreacted O_2. The exit gas during the reduction step contains only CO_2 and H_2O. After water condensation, almost pure CO_2 can be obtained.

There are different types of reactor configurations for chemical looping combustion, such as a fluidized bed or a packed bed reactor. The fluidized bed reactor concept is most often studied in literature [11]. For example, Mendiara et al. studied the behaviour of oxygen carriers based on bauxite waste in a 500 W_{th} CLC unit. High combustion efficiencies (around 90%) were obtained in the fuel reactor with coal without agglomeration problems [12]. Even tests in larger fluidized bed installations have been performed. Mattisson et al. developed and tested calcium manganite oxygen carriers in a 10 kW and a 120 kW reactor [13]. Complete combustion was achieved in both reactors using these calcium based oxygen carriers, which were fabricated by spray drying. However, another interesting concept is the packed bed reactor, which has as main advantages an easy design and the possibility to work under pressure to have a higher efficiency compared to a fluidized bed concept, but the packed bed concept requires high temperature gas switching valves [14]. Kimball et al. confirmed that packed bed chemical looping combustion is a feasible configuration for CO_2 capture. The inherent separation of the CO_2 from the depleted air stream in a packed bed concept can even give a lower efficiency penalty than in fluidized beds [15]. In addition, Zhang et al. found a superior reactivity performance in fixed-bed mode compared to fluidized-bed mode, which resulted in higher values of CO_2 concentration and oxygen carrier conversion in pressurized chemical looping combustion of coal [16].

As oxygen carriers for chemical looping combustion, different ores and low cost materials such as ilmenite are recently being investigated [17,18]. The performance of ilmenite oxygen carriers in a 300 W CLC reactor were investigated by Moldenhauer et al. [19]. They reached CO_2 yield above 99% and noticed an increased reactivity of the oxygen carrier in the presence of sulfur. On the other hand, Mayer et al. determined the syngas conversion in a 10 kW_{th} bubbling fluidized bed reactor for ilmenite particles, while Leion et al. investigated the reactivity of ilmenite oxygen carriers in a laboratory fluidized-bed reactor system [20,21]. The reactivity with both gaseous and solid fuels was also studied by Bidwe et al. They conducted a parametric study and found that ilmenite works well for the conversion of syngas when it is fully oxidized, but that reactivity reduces as ilmenite is reduced [22]. Besides testing in fluidized bed reactors, ilmenite was also tested in a packed bed reactor by Schwebel et al. [23]. The fixed bed reduction showed higher gas conversion by using coarser ilmenite particles than fluidized bed reduction, but some particle sintering occurred during oxidation. Furthermore, Cuadrat et al. studied the use of ilmenite as oxygen carrier for CLC of coal regarding the conversion of gaseous products from char gasification in a lab fluidized bed reactor [11]. In addition, they determined the porosity and the crushing strength of ilmenite particles in function of the amount of redox cycles [24]. As such, almost all studies deal with the reactivity of the oxygen carriers and the fuel conversion, but very few information is available on the mechanical properties of the oxygen carriers. Nevertheless, it is an important aspect since strong particles are needed in the reactor to assure a good chemical looping performance. Furthermore, there is almost no existing information on which type of microstructure is needed to obtain strong oxygen carriers. Therefore, in this study, the mechanical properties of ilmenite particles are investigated for their use as oxygen carriers in a packed bed CLC reactor. Particles in the shape of a granule with different compositions were subjected to thermal cycling, creep tests and crush tests in order to investigate the behaviour of these oxygen carriers under packed bed conditions. In addition, the microstructure of these oxygen particles was studied to understand the relationship between the physical properties and the mechanical performance.

2. Experimental

2.1. Materials

For a packed bed reactor, the ideal oxygen carrier material has a high activity through high and accessible surface area, a high selectivity and is resistant to poisoning. In addition, the structural integrity of the oxygen carrier is important for a good multi-cycle performance and a long service life [25]. An interesting naturally occurring material with proven performance in a fluidized bed reactor and with a low cost is ilmenite ($FeTiO_3$). Ilmenite is a mineral and it is mainly composed of $FeTiO_3$, with iron oxide as active phase. In order to avoid a large pressure drop in a packed bed reactor, larger oxygen carrier particles are needed such as granules. For this study, five different compositions based on ilmenite and an additive in the shape of granules were produced via extrusion by CTI. As additives, titanium oxide, manganese oxide, nanosized titanium oxide and bentonite were used [26]. The granules have a length of 7, 15 or 25 mm long with a diameter of 3–4 mm (Fig. 1). The compositions of the granules are given in Table 1.

2.2. Characterization

In order to study the microstructure of the different granules, SEM and XRD analysis were performed on granules G1, G4 and G5. XRD spectra were recorded on a Philips X'Pert diffractometer, while microscopic images and elemental analyses were carried out on the cross sections using a JEOL JSM-6340F field emission scanning electron microscope (FESEM) with an energy dispersive spectroscopy (EDS) system and using a FEI NOVA Nanosem 450. For these images, the granules were cut and embedded in epoxy resin, which is then cured at room temperature. Afterwards, these embedded granules were grinded and polished so that the different phases in the cross section are clearly visible. In addition, the pore size distribution of the granules was measured with mercury intrusion porosimetry (Pascal 140-240 series, Thermo Electron Corporation). In this technique, the pore size was calculated using