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Characterization of a sol–gel derived $CuO/CuAl_2O_4$ oxygen carrier for chemical looping combustion (CLC) of gaseous fuels: Relevance of gas–solid and oxygen uncoupling reactions

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ABSTRACT

A new sol–gel $CuO/CuAl_2O_4$ material was characterized in a thermogravimetric analyzer (TGA) for chemical looping combustion (CLC) with gaseous fuels, including the relevance of the oxygen uncoupling mechanism in oxygen transference was considered. This material possesses high reactivity and oxygen transport capacity, which combines the best features of the previously reported impregnated and spray-dried materials. During the cycles with N_2 and air, CuO was fully decomposed into Cu_2O in N_2 and then regenerated to CuO in air, similarly to chemical looping with oxygen uncoupling (CLOU) for solid fuels. Decomposition of $CuAl_2O_4$ to $CuAlO_2$ was quite slow, and the followed regeneration cannot be accomplished. Subsequently, the adequate and stable reaction rates of this material were examined in high numbers of cycles (>50 cycles) with gaseous fuels. The material undergone such cycles with gaseous fuels was then subjected to cycles with N_2 and air. Segregation of CuO from Al_2O_3 in the $CuAl_2O_4$ was observed during gaseous fuels combustion, which produced more available oxygen for CLOU than the initial material. Finally, the relative importance of gas–solid reactions in CLC against oxygen uncoupling in CLOU was examined with the appearance of gaseous fuel.

1. Introduction

The greenhouse gas CO_2 has greatly increased its concentration over the past decades as a result of the dependence of energy produced from fossil fuels. It was reported that the global mean concentration of CO_2 had risen to 395 ppm in 2013 [1], which was increased more than 12% compared to the 1980s. Strategies are urgently needed to control the emission of CO_2, especially from the combustion of fossil fuel which provides 80% of the overall world consumption of energy. Analysis made by IPCC and IEA [2,3] showed that the carbon capture and storage (CCS) could attribute 15–55% to the cumulative mitigation effort worldwide until 2100, to mitigate climate change to a reasonable cost. In this context, chemical looping combustion (CLC) has been suggested among the best alternatives for the capture of CO_2 with low cost [4]. CLC concept based on the rationale of generating pure CO_2 was first proposed by Lewis and Gilliland [5]. This concept was recovered by Richter and Knoche in the 1980s as a highly efficient process for energy generation [6]. In CLC technology, combustion is split into separate reduction and oxidation: oxygen needed for the combustion of fuel is provided by one solid oxygen carrier, such as a metal oxide; and air is used to regenerate the oxygen carrier. Generally in CLC, the oxygen carrier circulates between interconnected fluidized-bed reactors to provide continuous oxygen source for the fuel combustion [7]. In one of the reactors, i.e. fuel reactor, the oxygen carrier is reduced and in another reactor, i.e. air reactor, the previously reduced oxygen carrier was continuously regenerated. As an alternative in CLC technology, chemical looping with oxygen uncoupling (CLOU), which was first proposed by Mattisson and coworkers [8], preserves the feasibilities of the CLC technology, but gaseous oxygen being generated in the fuel reactor. Thus, direct reaction between fuel and oxygen carrier particles is not required. In addition to the properties of conventional CLC, the CLOU process gives higher conversion rates and efficiencies for the solid fuel combustion [9].

A schematic description of CLC technology, valid also for CLOU, is shown in Fig. 1 where the oxygen carrier, oxidized form MeO_x and reduced form MeO_{x-1}, circulates between the air and fuel reactors to provide the oxygen source for combustion. In the fuel reactor, the oxygen carrier MeO_x reacts with fuel (C_nH_{2m}) via reaction (1). Ideally, the outlet gas stream from the fuel reactor contains only CO_2 and H_2O

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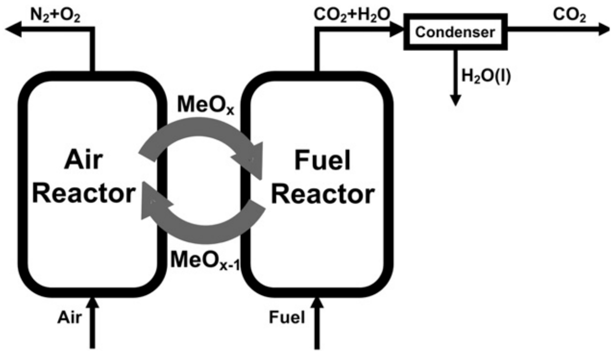

Fig. 1. Schematic layout of generic CLC process.

(steam), where CO_2 can be easily separated by relatively inexpensive condensation of H_2O in the condenser. The reduced oxygen carrier MeO_{x-1} is subsequently transferred to the air reactor where it is regenerated for new cycles via reaction (2) by capturing O_2 from air. In CLC, the separation of CO_2 is inherently accomplished with low energy penalty and low cost. The concentrated CO_2 from CLC can be used for industrial purpose and the permanent underground storage [3]. In brief, the CLC technology provides a prospective technical strategy to address the global increasing of CO_2 emission.

$$\text{Fuel reactor:} \quad C_nH_{2m} + (2n+m)MeO_x \rightarrow (2n+m)MeO_{x-1} + n\ CO_2 + m\ H_2O \tag{1}$$

$$\text{Air reactor:} \quad MeO_{x-1} + 1/2O_2(g) \rightarrow MeO_x \tag{2}$$

The cornerstone of CLC and CLOU is the oxygen carrier used. Along with many other properties, the oxygen carrier must maintain the reactivity during long-term operation. In CLOU, special oxygen carriers are required to provide gaseous oxygen for the combustion of fuels [8,10]. Based on the thermodynamic, the pairs CuO/Cu_2O, Mn_2O_3/Mn_3O_4, and Co_3O_4/CoO, can release and absorb oxygen at proper temperatures [8]. Among these oxides, CuO is highlighted for its high oxygen transport capacity, 10% with respect to 3% for Mn_2O_3 and 6.6% for Co_3O_4. Moreover, the reactions in fuel reactor and air reactor are exothermic when using the Cu-based materials, which is beneficial to the heat balance over the global system [8,11].

The earliest experimental investigation of CLOU was given by Mattisson et al. [12] by using a CuO supported on ZrO_2 material in a batch fluidized bed. In their experiments, petroleum coke burned quickly with the gaseous O_2 released from CuO/ZrO_2 particles. The average combustion rate of the petroleum coke varied between 0.5 and 5%/s depending on the temperature. This material was further demonstrated for its use in CLOU by combustions of six solid fuels (Mexican petroleum coke, South African coal, Indonesian coal, Colombian coal, German lignite and Swedish wood char) in the same batch fluidized bed reactor [13].

Researchers from ICB-CSIC developed Cu-based oxygen carriers with low attrition rate and high resistance to agglomeration both for CLC [14,15] and for CLOU [16,17]. For CLC, impregnated CuO/Al_2O_3 materials were extensively investigated in units ranging from 0.5 to 10 kW_{th}, even with sulfur containing gases [18–23]. These materials showed a complete combustion of fuel gases due to the high reactivity with CH_4, H_2 and CO. In addition, agglomeration was avoided by maintaining the CuO content below 20 wt.% [14]. However, these impregnated CuO/Al_2O_3 materials have no or little CLOU properties [17].

For CLOU, more than 25 oxygen carriers prepared through various techniques were screened based on the following criterions: crushing strength, reactivity, resistance to attrition and agglomeration. After long-term tests, CuOs supported on $MgAl_2O_4$ or ZrO_2 prepared by mechanical mixing followed by pelletizing by pressure were selected as suitable materials for CLOU. Subsequently, a similar material was demonstrated for the long-term use on CLOU in a 1.5 kW unit [11] with a bituminous coal as fuel. Later, combustion tests for several solid fuels, including anthracite, lignite and pine wood, were done [24–26]. Totally, 40 h for continuous combustion under various conditions was accomplished. Complete combustion of the solid fuel was reached in all the cases and CO_2 capture rates higher than 95% were usually obtained.

Mei et al. recently developed a $CuO/CuAl_2O_4$ oxygen carrier by sol–gel [27,28]. During their tests in batch fluidized bed reactor, the oxygen carrier composed of 60 wt.% CuO and 40 wt.% $CuAl_2O_4$ showed satisfactory properties for the combustion of different coals within 850–950 °C [28]. This oxygen carrier showed good properties to be used in the CLOU process. The sol–gel derived $CuO/CuAl_2O_4$ oxygen carrier maintained the porous structure after the tests with all the coals, which suggests that the sintering was avoided.

Additionally, the use of low-cost Cu based mineral as oxygen carrier would be very attractive. However, these materials agglomerated easily during fluidized bed operation, which makes it difficult to find a proper mineral, excepting the recent work by Zhao et al. [29].

In the CLOU process with solid fuels, an excess of oxygen must be provided for the combustion in order to keep high carbon capture efficiency. This requirement was evidenced by the fact that small amount of O_2 was always mixed with the CO_2 stream outlet from the fuel reactor. In this sense, Adánez-Rubio et al. identified the operational regions to give a mapping of the gas distribution under different solid inventories [30]. When the solid inventory was higher than 58 kg/MW_{th}, substantial O_2 was detected in the flue gas from fuel reactor meanwhile the full conversion to CO_2 was achieved. Decreasing the solid inventory to 32–58 kg/MW_{th}, the reduction of O_2 was attained; however, part of CO was not converted to CO_2. Moreover, CO in the exhaust gas increased together with the depletion of oxygen, when oxygen carrier inventory in the fuel reactor was lower than 32 kg/MW_{th}. The results illustrate that there is a compromise between low oxygen carrier inventory and high purity of CO_2 in the CLOU combustion of coal. Thus, minor amount of either O_2 or CO would be in the CO_2 stream. However, the actual solid inventory must also consider the combustion reactivity of solid fuel in order to get high CO_2 capture rates. Thus, preliminary calculations using kinetics for oxygen uncoupling reaction and coal combustion were performed. The results suggested that the solid inventory in the fuel reactor could be higher than 600 kg/MW_{th} to reach CO_2 capture higher than 95% for the lignite combustion [31]. Thus, an excess of oxygen would be expected in gas stream from fuel reactor, if both high CO_2 capture and complete fuel combustion were desired.

The oxygen uncoupling property of an oxygen carrier can be also exploited for gaseous fuel combustion [32–34]. It has been found that the CLC process can be highly improved when an oxygen carrier with CLOU properties and the appropriate operation windows was applied [34].

This work deals with the characterization of a new sol–gel derived $CuO/CuAl_2O_4$ oxygen carrier for its use in CLC of gaseous fuels, where the oxygen uncoupling involved in CLOU was studied as well. A thermogravimetric analyzer (TGA) was introduced to carry out the related experimental tests. The objectives of this work are: (*i*) a new material combining the best features of previously developed impregnated and spray-dried materials was characterized; (*ii*) a new way based on TGA test was detailed to determine the composition of the oxygen carrier; (*iii*) high numbers of cycles with gaseous fuels were performed for the new material; (*iv*) the oxygen uncoupling property of this new material was examined; (*v*) preliminary mechanistic of the segregation of CuO from Al_2O_3 in the $CuAl_2O_4$ was studied; (*vi*) identification of the relative significance of CLC and CLOU effects was done when applying an oxygen-releasable material to gaseous fuel combustion.