

METAL RECOVERY FROM SEWAGE SLUDGE ASH FOR CLC OXYGEN CARRIERS PRODUCTION

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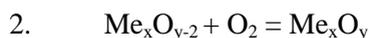
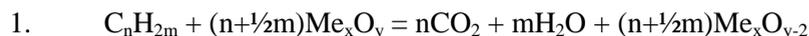
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Abstract

Metals like Fe, Ca, Mn present in sewage sludge ash have been deposited on high surface γ -alumina with high mechanical resistance used as bed materials during sewage sludge fluidized bed combustion to produce low-cost CLC oxygen carriers. The produced oxygen carriers have been characterized using ICP-MS, X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) and surface area (BET) analysis. H_2 Temperature Programmed Reduction (TPR) experiments have been performed to study the redox behaviour of the oxygen carrier and reduction/oxidation cycles have been carried out to assess the carrier stability. The performances of the oxygen carrier in methane combustion/air regeneration cycles in a fluidized bed reactor have been evaluated.

Introduction

Chemical looping combustion (CLC) is a promising strategy to produce energy from fossil fuel coupling the CO_2 sequestration [1,2]. The CLC process is typically realized adopting two interconnected fluidized beds with a solid, the oxygen carrier, circulating between them. The solid, i.e. the oxygen carriers (OC), promotes fuel oxidation without direct contact with atmospheric oxygen. Typical OCs consist of an active phase, which could be a suitable metal oxide, supported on an inert material for ensuring chemical, thermal and mechanical stability [3-5]. The process involves two cyclic reactions which take place alternately in the Fuel Reactor (reaction 1) and in the Air Reactor (reaction 2):



where C_nH_{2m} is a generic fuel, while Me_xO_y and Me_xO_{y-2} are the metal oxide in the oxidized and reduced form, respectively.

The oxygen carriers should have high reactivity with gaseous fuels and oxygen and oxygen transport capacity, low fragmentation, attrition and agglomeration tendency and high stability to a large number of redox cycles. However, the choice of the proper oxygen carrier is still open and it deserves further investigations. Usually the oxygen carrier is made of a metal oxide. Among transition metals, Fe-based oxygen carriers are considered an attractive option for the chemical looping combustion owing to their low cost, abundance and environmental compatibility

[4,5]. The aim of this work is the production of low-cost CLC oxygen carriers by sewage sludge fluidized bed combustion. In particular, the metals (Fe, Ca, Mn) present in sewage sludge ash have been deposited during sewage sludge fluidized bed combustion on high-surface γ -alumina which is characterized by high mechanical resistance and it was used as bed material. The produced oxygen carrier has been characterized using ICP-MS, X-ray diffraction (XRD), Scanning Electron Microscopy (SEM-EDX) and surface area (BET) analysis. The redox behaviour of the oxygen carrier has been investigated using H_2 reduction experiment. Reduction/oxidation cycles have been performed to assess the stability of the systems. The reactivity of the carriers and their oxygen transport capacity have been also evaluated under repeated cycles of methane combustion/air regeneration carried out in a fluidized bed reactor.

Methods

The metals (Fe, Ca, Mn) present in sewage sludge ash and identified by ICP analysis have been deposited on porous γ - Al_2O_3 particles (1mm in diameter) supplied by Sasol used as bed material during sewage sludge fluidized bed combustion. Different amount of metals have been loaded on the support changing the duration (45, 90, 220 minutes) of the combustion test.

The experimental apparatus consisted of a 110mm ID stainless steel fluidized bed combustor 2.7m high. Bed temperature was measured by means of a chromel-alumel thermocouple placed 3cm above the distributor. The gas distributor is of conical shape and is equipped with a port and a valve at its bottom in order to enable rapid discharge of the bottom ash and bed material. A high efficiency cyclone for the capture of fine particles generated during combustion and elutriated in the exit gasses is present. A data acquisition unit is used to process signals from pressure transducers, from the thermocouples and from the on-line gas analyzers (O_2 , CO, CO_2 , SO_2 and NO_x).

Bed inventory was 3 kg of porous γ - Al_2O_3 particles (diameter 1mm, $U_{mf} = 0.223$ m/s @ 20°C) supplied by Sasol, corresponding to a static bed height of about 0.3m. The experiments were carried out at a fluidization velocity of 1m/s and at an air excess of 47%. The gas was fed to the column via high-precision digital mass flow-meters. The fuel, fed under-bed, consists of semi-dried sludge particles of about 1-3mm, whose proprieties are reported in table 1 in terms of proximate and ultimate analysis, of lower heating value and of inorganic elemental analysis. The heating value and the proximate (TGA 701 LECO) and ultimate analyses (elemental analyzer CHN 2000 LECO) were based on standard ASTM procedures. The inorganic elemental analysis of the sewage sludge and the prepared oxygen carriers was accomplished by ICP-MS using a Agilent 7500CE instrument after dissolving the fuel samples by means of microwave-assisted acid digestion according to US-EPA 3051 and 3052 methods. The experimental campaign consists of steady combustion tests with continuous feeding of the sludge particles. The gaseous and particulate emissions were monitored during both the start-up

stage and once steady state conditions were reached.

Table 1. Sewage sludge properties

Fuel		Sewage sludge							
Moisture, % by mass		26.1							
Volatiles, % by mass		43.7							
Fixed carbon, % by mass		6.4							
Ash, % by mass		23.8							
Carbon, % by mass dry		32.3							
Hydrogen, % by mass dry		4.8							
Nitrogen, % by mass dry		6.6							
Oxygen, % by mass dry		1.2							
Stoichiometric air, kg/kg		3.51							
Lower heating value (dry), MJ/kg		13.3							
Inorganic elemental analysis of sewage sludge (as received), mg/kg									
Al	Ca	Cu	Fe	Mg	Mn	K	Na	Ni	Zn
4931	10320	171	14170	2210	122	1404	268	41	303

The possible presence of different crystalline species has been detected by X-ray diffraction (XRD) analysis using a PW 1100 Philips diffractometer.

The redox behaviour of OCs has been analyzed performing H₂ temperature programmed reduction (TPR) experiment with a Micromeritics Autochem II TPD/TPR analyzer reducing about 110 mg OC with a 2% H₂/Ar mixture (50 Ncm³ min⁻¹) at 10 °C min⁻¹ up to 850 °C. The fresh OC was pre-treated 1 h in air (50 Ncm³ min⁻¹) at 850 °C before the experiment. The cyclic process has been simulated in fluidization conditions using a 30mm ID fluidized bed reactor, figure 2B, and switching between two different feeds the first containing CH₄ (1.6 % vol.) in N₂ and the second containing air at 850°C.

Methane combustion and catalyst oxidation were carried out using 40 g of material at a superficial gas velocity of 0.4m/s, corresponding to two times the value of the minimum fluidization velocity. A symmetric period (300 seconds) of combustion time and oxidation has been chosen. Between the two steps pure N₂ has been fluxed for 120 s. During each test, the time-resolved profiles of bed temperature and of concentration of different analyzed species have been recorded. An ABB

continuous analyzer equipped with IR detectors for CO, CO₂, and CH₄ and a thermal conductivity detector (TCD) for H₂ has been used for analysis of the concentration of gases.

Results

The deposition of metals present in the ash of the sewage sludge on the γ -Al₂O₃ particles is confirmed by the red color of the bed material collected during the combustion tests at 45, 90 and 220 min (Figure 1). According to the results of ICP analysis the more abundant element is iron followed by Ca, Na and Zn. Increasing the duration of the combustion run (45, 90, 220 minutes) the load of the metal dispersed on the support increases and an intensification of the red color of the sample has been observed (Figure 1). It is noteworthy that the total amount of each metal deposited on the alumina support is, in every case, lower than that of the sewage sludge.

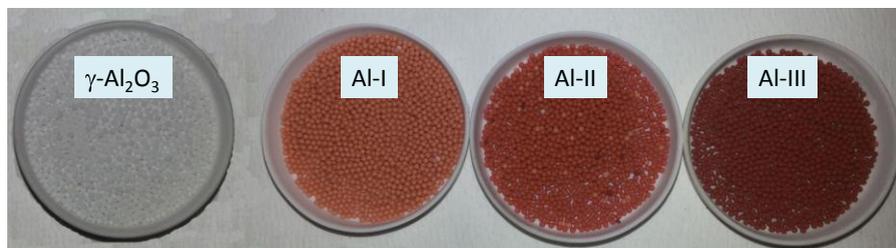


Figure 1. Images of fresh Al sample compared to Al-x samples

The XRD spectra obtained for the different samples are very close to that obtained for the γ -Al₂O₃ suggesting that no oxide cluster formation, detectable at XRD, takes place.

A very low value of surface area (around 20 m²/g) in comparison to that of starting alumina (140m²/g) is obtained by BET analysis for the Al-III. Since XRD analysis does not show neither the formation of metal cluster, neither the alumina transition phase, the reduction of the surface could be associated to the decrease of the alumina porosity.

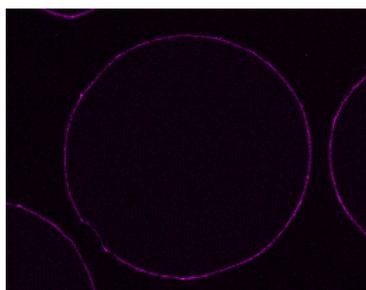


Figure 2. SEM-EDX micrographs of Al-III section: Fe distribution.

Pore occlusion could be related to metal deposition on the alumina external surface. This hypothesis is confirmed by the SEM-EDX of the internal section of the OCs. The Fe (more abundant metal and chosen as representative) is prevalently present on the external surface of the support (figure 2).

The amount of hydrogen consumed during the TPR experiments (Table 2) increases with the increase of the duration of the deposition phase confirming that an accumulation of reducible metals (mainly Fe) occurs during the combustion of the sewage sludge, in agreement with the observed increase of the metal concentration shown by ICP analysis.

Table 2. H₂ uptake, H₂/g_{sample} and H₂/Fe ratio from H₂ TPR experiments.

Sample	H ₂ uptake (μmol)	H ₂ /g _{sample} (mg/g)	H ₂ /Fe (mol/mol)
Al-I (45 min)	18.09	0.33	4.12
Al-II (90 min)	22.86	0.42	2.69
Al-III (220 min)	20.19	0.37	0.97

A lower H₂ uptake, has been obtained for the sample Al-III (220min) even if a higher amount of iron is present in the sample suggesting a detrimental effect due to pore occlusion.

In order to have a preliminary information on the material stability, four reduction/oxidation cycles have been performed on the sample Al-III. A modification of the TPR profile after the first reduction oxidation cycle occurs even if not coupled with a different value of H₂ uptake. After the second cycle the sample is stable and no further modification has been observed. This finding suggests that only a rearrangement of the different species occurs but the global reducibility of the sample is not influenced, confirming the good stability of the sample in cyclic processes.

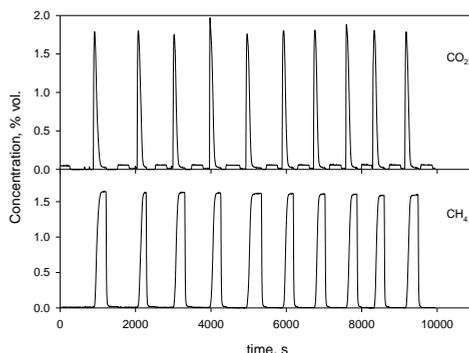


Figure 3. CO₂ and CH₄ profiles during the cyclic process in fluidized bed. Combustion time (300 s) regeneration time (300 s); N₂ washing time 120 s. Gas compositions: CH₄ (1.6% vol.) in N₂ and air; T =850°C; WOC= 40 g; U=0.4m/s.

The CLC cyclic process has been simulated in fluidized conditions switching between two different fluidizing gases, the first containing methane (1.6% vol.) and nitrogen and the second air. A symmetric time interval (300 seconds) of combustion time and oxidation has been chosen. The results obtained are reported in Figure 3. A stable CO₂ production has been observed after ten combustion/oxidation cycles, confirming a good stability of the tested oxygen carrier. The oxygen transport capacity, RO, of the sample Al-III has been calculated from the integration of data reported in figure 3. A reasonable oxygen transport capacity (0.83) of the sample Al-III, has been obtained even if it is lower than that of a low cost ores materials, like Ilmenite (oxygen carrying capacity of about 4%). This limitation is probably due to low concentration of the metals loaded in the material.

Conclusions

These results suggest that the adopted strategy is suitable for the recovery of the metals present (Fe, Ca, Mn) present in sewage sludge ash and their subsequent dispersion on a support even if prevalently on its external surface area. The obtained system shows a promising redox properties and the oxygen carrier activity of these material is unchanged after ten methane/air combustion reduction cycles. The oxygen transport capacity and the reactivity of the produced materials are comparable with systems based on Cu, Ni, and Fe, already reported in literature. However, further studies are required in order to improve the amount of the metals loaded on the support.

References

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