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Chemical looping oxygen transfer properties of Cu-doped lanthanum oxysulphate

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ABSTRACT

$\text{La}_2\text{O}_2\text{SO}_4$ was investigated as a candidate high capacity oxygen carrier for Chemical Looping processes based on the occurrence of the redox cycle of sulphur from S^{+6} to S^{-2} leading to the reversible formation of the corresponding lanthanum oxysulphide ($\text{La}_2\text{O}_2\text{S}$). The effect of the addition of copper (1% wt.) on the redox properties and thermal stability of $\text{La}_2\text{O}_2\text{SO}_4$ during high temperature reduction/oxidation cycles was also studied.

Temperature Programmed Reduction and Oxidation experiments were carried out cyclically at temperatures up to 1027 °C respectively with 2% H_2/Ar and 0.5% O_2/He mixtures. Fresh and used carriers were characterized by ICP-MS, XRD, BET and SEM analysis. Regardless of copper doping the material reversibly changed from $\text{La}_2\text{O}_2\text{SO}_4$ to $\text{La}_2\text{O}_2\text{S}$ and vice versa restoring each time the corresponding crystalline structure with a complete oxygen recovery. Copper addition decreased the peak temperature for both reduction and oxidation, likely due to the enhanced oxygen mobility in the La-oxysulphate/oxysulphide structures.

For comparison purposes, CaSO_4 tested under identical conditions dramatically lost its Oxygen Storage Capacity across each redox cycle due to irreversible formation of CaO instead of CaS.

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Introduction

Chemical looping technology is becoming an established “clean combustion technology” due to its highly efficient inherent CO_2 capture and ultralow NO_x formation [1–3], and can be safely used also with H_2 (or syngas) fuel [1,3,4]. The reaction engineering principle behind chemical looping – i.e. the splitting of a reaction into two spatially separated reaction half-steps which are coupled through the periodic oxidation and reduction of an “oxygen carrier” – has recently been

applied to further fuel conversion reactions beyond combustion, such as hydrogen production via steam reforming or syngas production via partial oxidation [1,2].

The successful development of Chemical Looping Combustion (CLC) and of all these emerging chemical looping processes depends on the properties of the oxygen carrier. It should have enough reactivity in both the oxidation and the reduction reaction to limit solid inventory, good selectivity for the desired (total or partial) oxidation of the fuel, negligible carbon deposition, high resistance to attrition to minimize losses of elutriated solid, no agglomeration tendency,

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environmental friendly properties, and, above all, high oxygen storage capabilities and long lifetime over high temperature redox cycles [1,2].

The most investigated materials for CL processes are the transition metal oxides (CuO, Fe₂O₃, NiO, Mn₃O₄ or CoO) supported on Al₂O₃, MgAl₂O₄, SiO₂, TiO₂, ZrO₂ [1,5–8].

Ni-based oxygen-carriers have shown very high reactivity with almost complete CH₄ conversion [1,9]. Dispersion of nickel on Al₂O₃ avoids carbon deposition under CLC conditions and also reduces problems of attrition and agglomeration. Nevertheless, formation of NiAl₂O₄ spinel at high temperature depresses the activity requiring NiO excess in the carrier [1,10] or alumina doping with alkaline earth elements [11]. Formation of aluminates was also observed for Al₂O₃ supported Cu, Fe and Mn based carriers [5–8], although a large number of solutions have been proposed to avoid the major issues of sintering and agglomeration [1,9,12], such as the use of sol–gel technique for the preparation of Fe-based carriers on Al₂O₃ [13,14] or promoting Cu-based carrier with lanthanum [15].

Also the use of a more thermally stable support such as barium hexa-aluminate has been reported to improve the carrier performance [2]. In particular, the porous nano-structure of the hexa-aluminate promotes a fast transfer of reactants and products and suppresses metal particles sintering at the same time. This support was also successfully used for Fe-based carrier in CL steam reforming process [2]. Use of reducible supports (CeO₂, La₂O₃) was also proposed for Ni-based carrier providing improved performances and stability [16].

Metal oxides are generally prone to sulphur poisoning which represents an important issue especially when using carbon or biomass-derived fuels [1,5–8,17,18]. Fe and Cu based carriers, although less active are more sulphur-tolerant [19]. Moreover, dispersion of metals as Cu on a proper support can avoid S-poisoning by promoting in the fuel reactor the oxidation of H₂S to SO₂ which is then recovered in the air reactor [2].

Mixed oxides with perovskite-type and spinel structures have been intensively investigated because of their enhanced redox behaviour and better stability as compared to conventional monometallic oxygen carriers [1 and ref. therein, 4,20]. Fe–Ni alloy has been also proposed to enhance Fe activity [16].

A different class of CL carriers does not operate on the basis of the redox cycle of the metal cation: in particular CaSO₄ has been extensively tested as oxygen carrier for CLC due to the very high oxygen storage capability of sulphur [1,21,22]. Indeed, compared to metal oxides providing a storage capacity generally below 0.5 mol O₂ mol⁻¹ (change in the oxidation number of the metal ≤ 2), sulphate compounds can have an oxygen storage capacity up to 2 mol O₂ mol⁻¹, thanks to the change of the redox number of sulphur from +6 (in sulphate form SO₄²⁻) to -2 (in sulphide form S²⁻) [21–23]. In addition, calcium sulphate is a stable and cheap material, widespread as natural sulphate. However CaSO₄ exhibits high reduction reaction rate only at $T > 1000$ °C, but at such high temperatures SO₂ is also produced in concentrations as high as 6% vol. [22]; moreover carbon deposition and agglomeration are known issues that must be carefully controlled through a suitable choice of the operating conditions [21,22]. The

addition of CaCO₃ has been reported to improve the regeneration ability of CaSO₄ through the formation of CaO (inert carrier) that can adsorb large amounts of SO₂ emissions [21].

Lanthanum oxysulphate (La₂O₂SO₄), has been proposed as oxygen storage promoter in the formulation of three-way automotive exhaust catalysts [23,24]. This compound undergoes reversible redox cycles of sulphur (La₂O₂SO₄/La₂O₂S), thus providing the same theoretical storage capacity of CaSO₄ but, in contrast with it, no H₂S or SO₂ were detected during its redox cycles [24]. Recently lanthanide oxysulphide/oxysulphate materials have been reported as highly active, stable and S tolerant catalysts for the high temperature water gas shift reactions [25].

Moreover, Machida et al. [24] also showed that the addition of small amounts of a noble metals (Pt or Pd) significantly reduced the temperature of reduction from 730 °C down to 550–600 °C.

The use of transition metals as promoters for La oxysulphates has not been explored and could represent a more affordable alternative to noble metals. Those materials with the adequate choice of the metal could meet performance requirements for oxygen carriers in chemical looping processes.

In this paper we set out to investigate the effect of the addition of small amounts of copper to La₂O₂SO₄ by performing repeated reduction/oxidation cycles in order to evaluate the possibility to use this compound as an effective and durable oxygen carrier, intrinsically tolerant to S-poisoning, and with an affordable cost in view of the absence of precious metals. The stability of this new material to redox cycles was evaluated especially as concerns the temperature delay of both reduction and oxidation processes induced by the progressive thermal ageing.

TPR/TPO cycles using H₂ and O₂ containing mixtures were carried out in order to easily compare the thermo-chemical behaviour of the novel oxygen carriers with that of the commonly used CaSO₄.

Experimental

Preparation of carrier

La₂(SO₄)₃ from Aldrich (99.99% purity) was treated at 1027 °C for 5 h under helium flow in order to convert the sulphate into its corresponding oxysulphate (La₂O₂SO₄). It was previously reported [26,27] that this transformation takes place starting from 900 to 950 °C.

A fraction of the La₂O₂SO₄ powder was impregnated with a water solution of Cu(NO₃)₂·2.5H₂O from Aldrich (98%) to obtain a nominal copper loading of 1 wt.%. The sample (Cu/La₂O₂SO₄) was then dried for 12 h at 120 °C in a stove and finally calcined in He at 900 °C for 2 h.

Commercial anhydrous CaSO₄ supplied by Carlo Erba (99% purity) was used for comparative analysis with lanthanum oxysulphate.

Physical and chemical characterization of carrier

The copper content was quantitatively determined using an ICP-MS Agilent 7500 instrument after microwave digestion of

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