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# Development and performance of iron based oxygen carriers containing calcium ferrites for chemical looping combustion and production of hydrogen

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## ABSTRACT

Chemical looping combustion (CLC) is a cyclic process in which an oxygen carrier (OC), is firstly reduced by a fuel, e.g. syngas, and then oxidised in air to produce heat. If the OC is  $\text{Fe}_2\text{O}_3$ , the oxidation can take place in steam to produce hydrogen, i.e. chemical looping hydrogen production (CLH). This paper presents an investigation of CaO modified  $\text{Fe}_2\text{O}_3$  OCs for CLC and CLH. The performance of the mechanically mixed OCs were examined in a thermogravimetric analyser and a fluidised bed. It was found that the addition of CaO gives cyclic stability and additional capacity to produce hydrogen via CLH, at the expense of reduced oxygen carrying capacity for CLC, owing to the formation of calcium ferrites, such as  $\text{Ca}_2\text{Fe}_2\text{O}_5$ .

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## Introduction

Chemical looping combustion (CLC) combusts fuels using reduction–oxidation cycles of oxygen carriers to keep the products of combustion separate from the air used for combustion [1]. In some cases the oxygen carrier can directly release gas phase oxygen, leading to the chemical looping with oxygen uncoupling process (CLOU) [2]. The oxygen-

carrier requires sufficient and stable oxygen transport capacity over many cycles of oxidation and reduction. Oxides of Ni, Fe, Cu, Mn and Co are popular candidates for oxygen carriers for use in CLC [3].  $\text{Fe}_2\text{O}_3$  is cheap, widely available and environmentally benign and has been used in a number of studies [4–7]. The equilibria for the phase transitions for the Fe–O system are such that only the reduction of  $\text{Fe}_2\text{O}_3$  to  $\text{Fe}_3\text{O}_4$  will result in complete oxidation of a fuel [8]. The subsequent reductions to  $\text{Fe}_x\text{O}$  (i.e. wüstite where  $x \sim 0.95$  and can vary) and

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Fe, are also usually found to be much slower [9]. Chemical looping hydrogen (CLH) production [10] (also known as the cyclic-water gas shift [11] or the steam iron process [12–15]) uses steam during the oxidation stage to produce  $H_2$ . Whether a phase transition can be used to produce  $H_2$  depends on the equilibrium oxygen partial pressure ( $p_{O_2}$ ); reactions with  $p_{O_2}$  suitable for near complete combustion to  $H_2O$  cannot easily be reversed to produce  $H_2$ . The oxidation of Fe and, or  $Fe_xO$  to  $Fe_3O_4$  by steam can produce  $H_2$  [8,16,17]. The stoichiometry is such that the oxidation of iron to  $Fe_3O_4$  produces approximately four-times more  $H_2$  than that for  $Fe_xO$  to  $Fe_3O_4$ .

Unsupported metal oxides usually agglomerate, or lose their ability to transfer oxygen over many cycles [8,18,19]. Granulated  $Fe_2O_3$  was found to be stable over repeated cycles of conversion between  $Fe_2O_3$  to  $Fe_3O_4$  and  $Fe_2O_3$  to  $Fe_xO$ , but deactivated when reduced to Fe [8]. Thus, it is common to mix the iron oxide with support materials either to improve kinetics, or to improve the cyclic stability; e.g.  $Fe_2O_3$  on  $MgAl_2O_4$  [20,21],  $Fe_2O_3$  on  $Al_2O_3$  [22,23], various refractory (oxides of Mg, Al, Cr, Si etc.) dopants impregnated into granulated iron [24] or added during co-precipitation from metal nitrates [14]. Previous studies have shown that  $Fe_2O_3$  supported on  $Al_2O_3$  improved stability [22,23]. In contrast, a  $SiO_2$  support resulted in the formation of undesirable  $Fe_2SiO_4$ , which is unreactive under chemical looping conditions [21]. Iron oxide supported on  $Ce_{0.5}Zr_{0.5}O_2$  [11,25] or with  $ZrO_2$  [26] has been shown to be stable over many cycles. Support materials can also interact in ways which alter the redox chemistry, e.g.  $Al_2O_3$  forms various solid solutions with iron oxide and  $FeAl_2O_4$  during reduction [27,28].  $FeTiO_3$  ore has been suggested as a cheap oxygen carrier [29], in which the iron oxide is already supported by the titania. During chemical looping  $FeTiO_3$  oxidises to  $Fe_2TiO_5$ , and also segregates to give free iron oxide [30]; the material is often observed to become more reactive after a few cycles. For  $H_2$  production, the  $FeTiO_3$  must be reduced to metallic Fe; the kinetics of which have been found to be faster than those for reduction of wüstite; density functional theory calculations suggested that diffusion of  $O^{2-}$  through the  $FeTiO_3$  lattice facilitates reduction [31].

Oxygen carriers consisting of two active metal oxides have also been reported [32,33]. For CLOU combustion, in which the oxygen carrier releases gas phase oxygen, the iron + manganese oxide system has been proposed, with the mixed oxide phase showing favourable oxygen release equilibrium compared to  $Fe_2O_3$  or  $Mn_2O_3$  alone [2]. Svoboda et al. [32] suggested  $NiFe_2O_4$  and  $CoFe_2O_4$  as potential materials for CLH based on a thermodynamic feasibility study. They also suggested that additional  $H_2$  (per mole of Fe) can be produced if the reduced OCs are re-oxidised to spinel phases (e.g.  $NiFe_2O_4$  or  $CoFe_2O_4$ ) because the formation of spinels allows oxidation of more  $Fe^{2+}$  to  $Fe^{3+}$ . In contrast, it is practically impossible to oxidise iron oxide to an oxidation state higher than  $Fe_3O_4$  using steam. Other iron containing materials, based on perovskite structures [10,34] have also been proposed. Perovskite materials can accommodate significant oxygen non-stoichiometry, allowing oxidation or reduction without phase changes, potentially improving cyclic stability [10]. They also allow  $O^{2-}$  ion conduction, which should facilitate access to the oxidising or reducing species in the particle whether they are used as the actual looping material

themselves [32], or as a support, e.g. in composite oxygen carriers [35].

Thus, the support can interact with the active metal oxide in several ways, either by forming new phases with different redox equilibria (e.g. Fe–Mn carriers [2]), segregating or forming new phases during cycling (e.g.  $TiO_2$  [30],  $Al_2O_3$  [27,28]), providing porosity and separation between active metal grains, providing paths for ionic conduction (e.g.  $ZrO_2$  [26] or perovskites [35]), or altering the transport of ions within crystals by introducing defects or oxygen vacancies [36], either in the support or the active metal oxide phase.

The objective of this study is to investigate calcium oxide as the support material for  $Fe_2O_3$ . CaO, like  $Fe_2O_3$ , is cheap and environmentally benign and the thermodynamics of the Ca–Fe–O system is well known [37]. Calcium and iron oxide form a variety of calcium ferrite phases, with reduction/oxidation equilibria which differ from those of pure iron oxides. One such ferrite,  $Ca_2Fe_2O_5$  (i.e. a brownmillerite-type ferrite), has received particular attention owing to its structure which facilitates fast oxygen ion transport [38], leading to its use as a fuel cell cathode [39] or as a membrane material. At temperatures lower than those used for CLC some of the Fe can take on the +4 oxidation state within the brownmillerite structure, leading to very active oxygen species which can be used to catalyse combustion [40].  $Ca_2Fe_2O_5$  has also been suggested as catalyst for oxidation of CO,  $NH_3$  and hydrocarbons [41].

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## Thermodynamics

When CaO is added to  $Fe_2O_3$  various phases can form at equilibrium, depending on the equilibrium oxygen partial pressure (which is related to the ratio of  $CO_2$  to CO, or  $H_2O$  to  $H_2$  at equilibrium), temperature, and composition. Fig. 1 (calculated using MTDATA with the NPL oxide database [42]) shows the calculated phase boundaries for the Fe–Ca–O system at 1173 K. Various ferrite phases can form and are denoted as combinations of sub-lattice species with: C = CaO, F =  $Fe_2O_3$ , W = FeO; e.g., CF =  $CaFe_2O_4$  ( $CaO \cdot Fe_2O_3$ ) and  $C_2F$  =  $Ca_2Fe_2O_5$  ( $2CaO \cdot Fe_2O_3$ ). The form of the phase diagrams for other temperatures used are effectively the same, though with differing values of  $p_{O_2}$  for the phase transitions and with the region labelled as “ $C_2F + FeO$ ” disappearing below 1143 K.

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## Experimental

### Synthesis of oxygen carriers

Wet-granulated particles of unsupported iron oxide were prepared by spraying water into iron oxide powders (99 wt%, Sigma-Aldrich), while stirring the mixture. The resulting agglomerates were sieved to give 425–500  $\mu m$  particles and then sintered at 1273 K for 6 h and re-sieved. Particles with different ratios of  $Fe_2O_3$  to CaO (50, 57.3 and 66.7 mol% CaO) were prepared by mechanical mixing. Measured amounts of iron oxide and calcined CaO (97+%, Acros Organics) powders were mixed with a small amount of ethanol (99.8+%, Fisher Scientific) (to aid mixing) and ball milled (SFM-1, MTI Corporation) for 3 h at

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