

Development and Evaluation of Iron Oxide-based Oxygen Carriers for Chemical Looping Combustion and Hydrogen Production

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Abstract

Concern over global warming has triggered an international effort to reduce CO₂ emissions. Among the available carbon capture and storage (CCS) technologies for power generation sector, Chemical Looping Combustion (CLC) is a promising approach in terms of efficiency, cost and environmental impact. One major challenge in CLC is the development of a stable 'Oxygen Carrier' (usually a solid metal oxide) which is prerequisite for the transport of oxygen in the CLC process. This dissertation is concerned with the i) synthesis of Ca- and/or Al- supported Fe-oxide oxygen carriers *via* a wide range of preparation methods, and ii) experimental studies of these prepared particles in thermogravimetric analyser and in fluidised bed reactor to evaluate their performance for chemical looping combustion and hydrogen production (CLCHP). Fe₂O₃-based oxygen carriers containing CaO and/or Al₂O₃, synthesised by mechanical mixing, wet impregnation and co-precipitation methods, were reduced and oxidised cyclically, at temperatures between 850 and 950 °C up to 50 cycles. The alternating redox cycles consist of: i) reduction of hematite to wüstite or mostly to metallic iron by H₂ or CO, ii) oxidation of the wüstite / iron to magnetite by steam or CO₂, and iii) finally, oxidation of the magnetite to hematite by air. The fresh and reacted oxygen carriers were characterised using a number of analysis *e.g.* X-ray diffraction, SEM, BET surface area measurements, ICP-AES, Temperature programmed reduction and oxidation (TPR and TPO).

CaO-modified iron oxides were synthesised by the addition of 2 - 66.7 mol.% of CaO to Fe₂O₃. Experiments showed that the addition of CaO conferred cyclic stability and additional capacity to produce hydrogen over many redox cycles, at the expense of reduced oxygen carrying capacity for CLC, owing to the formation of calcium ferrites. Less sintering and superior rates of reaction were observed during cyclic redox experiments with the developed particles in comparison to unmodified Fe₂O₃. Furthermore, the oxidation of the reduced product of Ca₂Fe₂O₅ by CO₂ or steam can reform the Ca₂Fe₂O₅ without air oxidation.

A modification of the co-precipitation method for the synthesis of Fe-Al-O oxygen carriers was proposed which made use of either NH₄OH or ion exchange resin as precipitant. 40 wt.% Al₂O₃ was required for a stable conversion during redox cycles. Doping of sodium into the developed particles was found to be beneficial owing to the suppression of hercynite formation along with providing additional stability in the amount of oxygen transferred over a redox cycle.

Using mechanical mixing and co-precipitation methods, composite particles containing different mass ratios of Fe₂O₃, CaO and Al₂O₃ were developed. For reduction to Fe, for stable redox cycles and the prevention of sintering, 40 wt.% CaO + Al₂O₃ (with a mass ratio of 0.67:1) support was required. Fe-Ca-Al-O oxygen carriers were found to be the best amongst the synthesised materials in this dissertation in terms of improved reactivity, stability and preventing sintering during redox cycles at 900 °C. However, the interaction of CaO and Al₂O₃ with Fe₂O₃ cannot be avoided.

In summary, the synthesised Fe₂O₃-based oxygen carriers demonstrated a promising performance in maximising the CO₂ capture and hydrogen production in CLC.