New Combined Materials for Calcium-Copper Chemical Looping Technology

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Calcium-Copper Chemical Looping Technology (“Ca-Cu Looping”) is a new and emerging concept for hydrogen production from natural gas with integrated CO₂ capture, combining Sorption-Enhanced Reforming (SER) and Chemical Looping Combustion (CLC) technology. The concept was originally proposed by the research group of J.C. Abanades, R. Murillo et al. in 2010 [1]. In this process, SER is combined with CLC using both a CaO-based CO₂ sorbent and a Cu-based material as oxygen carrier in order to achieve efficient hydrogen production alongside process intensification and simultaneous CO₂ capture. Ca-Cu Looping allows the production of a highly concentrated pressurized hydrogen stream and offers a solution to the challenge of efficient high temperature sorbent regeneration by including the exothermic Cu-CuO cycle in the process loop. The exothermic reduction of copper (II) oxide (CuO) by a suited fuel (natural gas, syngas, hydrogen) provides the thermal energy required for both sensible heating and calcination of CaCO₃ formed in the sorbent during CO₂ capture. Preliminary modelling of a fixed bed reactor system indicates theoretical CO₂ capture efficiencies in the order of 80 - 95% and total thermal efficiency of about 75% [2] [3].

Ca-Cu Looping is at an early stage of development and there is a need for research on materials that can meet the rather harsh process calcination requirements of ~1123 K in the presence of steam and reducing gases. The main challenges from a material point of view is to avoid sintering of CaO [4] [5] and copper sintering/migration during multi-cycling operation [6]. Typically, three individual solids are required to accomplish the different steps of the Ca-Cu Looping process: Ni-based catalyst, Cu-based O₂-carrier and CaO-based sorbent. The novelty proposed in this work is to combine CaO and CuO phases into one bi-functional material. This configuration has the potential to a) lower the inert fraction in the reactor bed and thus limit the sensible heating requirement in the reactor, and b) to promote close contact between the CaO and CuO phases, improving the heat and mass transfer compared to a segregated particle arrangement. Results from material synthesis, characterization and testing in a TGA under relevant process conditions, with focus on multi-cycling stability, will be presented and discussed.

Materials are primarily synthesized in powder form by a) reproducing stable CaO-based sorbent formulations reported in literature and b) introducing Cu in these materials through various methods. Promising sorbent materials include CaO/Ca₁₂Al₁₄O₃₃ (mayenite) prepared through a hydrothermal method [6], CaO/Al₂O₃ prepared by co-precipitation [7] and wet mixed CaO/CaZrO₃ [8]. CuO introduction is performed through chemical routes, i.e. directly in the sorbent synthesis, or through physical methods like sorbent impregnation, wet mixing and dry mixing with different CuO precursors (e.g. CuO, Cu(OH)₂ and Cu(NO₃)₂). The best performing material powders are then granulated using a high shear granulator to produce granules in the desired size range.
Synthesized powders/ granules are screened using process relevant TGA multi-cycle tests, SEM, XRD, ICP-MS and BET. The simulating TGA tests are performed by cycling 20 – 25 mg of material in 500 ml/min total flow between SER (T = 650°C, 15 vol% CO₂, 60 vol% N₂, 25 vol% H₂O), Cu oxidation (T = 650°C, 75 vol% CO₂, 20 vol% N₂, 5 vol% O₂), CaO calcination (T = 870°C, 40 vol% CO₂, 35 vol% N₂, 25 vol% H₂O) and CuO reduction (T = 870°C, 40 vol% CO₂, 15 vol% N₂, 25 vol% H₂O, 20 vol% H₂) conditions. The best performing material to date is a CaO-CuO-Ca₁₂Al₁₄O₃₃ material prepared through a hydrothermal method using Cu(NO₃)₂ as copper precursor (18.5 g/100g CO₂ and 8 g/100g O₂ capacity) (Figure 1, left). Preliminary results from combined CaO-CuO materials supported on CaZrO₃ have also shown good performance in terms of both CO₂ and O₂ capacity (21 g/100g material and 11 g/100g material, respectively) (Figure 1, right). Central to material performance is the CuO/CaO ratio which can be theoretically determined through thermodynamic calculations and more realistically established through transient heterogeneous reactor modelling. This oxide ratio should be as flexible as possible and a baseline requirement is presumed to be CuO/CaO ≥ 1.8.

Based on current results, future use of combined materials for the Ca-Cu Loping process for large scale H₂ production with integrated CO₂ capture seem plausible. To further improve these bifunctional materials, a full investigation with 50-100 TGA cycles of CaO-CuO/Al₂O₃, CaO-CuO/CaZrO₃ and CaO-CuO/Ca₁₂Al₁₄O₃₃ combined materials will be carried out. In addition, the use of characterization tools such as XRD (phase and relative crystallite size determination by Rietveld refinement), SEM (focus on possible Cu sintering and migration), BET surface area and porosity before and after test are to be presented and discussed.

References