STUDY OF CuO-BASED MATERIALS FOR Ca/Cu REFORMING PROCESS

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The Ca/Cu looping process for H_2 production is currently under development under the umbrella of the FP7 ASCENT project, and makes use of a Cu/CuO chemical loop to solve the problem of the endothermic $CaCO_3$ calcination and to release the CO_2 captured during the production of H_2 by a sorption enhanced reforming (SER) of CH_4. The general scheme of this process includes the following main steps: -The production of a hydrogen-rich stream by the sorption enhanced catalytic reforming of CH_4 with steam, and the simultaneous carbonation of CaO with the CO_2 resulting from the reforming reaction. -The oxidation of Cu to CuO with air, in conditions such that no major decomposition of $CaCO_3$ takes place (this will be favoured by high pressure operation, low temperatures and the partial recycling of the N_2 product gas as a way to lower O_2 partial pressures).-The calcination of $CaCO_3$ and the reduction of CuO with a fuel in order to obtain most or all of the heat necessary for calcination.

Functional materials with the right proportions of Cu and CaO have to be developed to ensure that all the reactions take place in the different reaction stages. Since the reactions involving Cu and CaO in the SER step and the Cu oxidation step are proceeding independently of each other, the Cu/Ca molar ratio in the material is best defined on the basis of the heat requirements in the calcination step [1].

Focussed on the Cu-based materials, solids with Cu loads ranging between 60 %wt. and 75%wt. have been synthesised by Johnson Matthie following diverse routes as: co-precipitation, deposition-precipitation, spray drying and mechanical mixing over Al_2O_3, also in parallel diverse commercial JM's CuO based materials on to different supports (SiO_2, ZnO, ZnO-MgO) have been also evaluated as possible candidates for the process. The chemical and mechanical stability of the materials was determined via thermo gravimetric analysys (TGA) in multicyclic operation. Up to 100 oxidation/reduction cycles were carried out to every individual material, at 870 ºC. The samples have been characterized (fresh and after TGA) to determine the crystalline species (XRD); to determine the reducible species with a Temperature programmed reduction test (TPR). Some materials have been tested in powder and pellet form.

In general, the materials presented high chemical and mechanical stability with constant oxygen transport capacities, slow oxygen release due to oxygen uncoupling and highly repetitive oxidation/reduction conversion curves with fast kinetics. Co-precipitation was one of the synthesis routes that provided the best chemical and mechanical results for the solids prepared. Besides, CuO/Al_2O_3 solids prepared by mechanical mixing by JM's company also proved appropriated in TGA tests.

References

[1] Abanades J.C., Murillo R., 2009, PCT/ES2010/070585200