

Validation of the H₂ production stage via SER under relevant conditions for the Ca/Cu reforming process practical application

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HIGHLIGHTS

- A reforming catalyst and CO₂ sorbent were tested for SER under suitable conditions for Ca/Cu process.
- The operational window for the materials has been determined.
- The system is able to process a CH₄ flow suitable for scaling up.
- The system is able to operate under pressure, and with aged materials.
- Experimental data have been successfully predicted by a pseudo-homogeneous reactor model.

ABSTRACT:

The joint performance of a CaO-based sorbent and a Ni-based commercial catalyst has been assessed under relevant conditions for the SER stage in the Ca/Cu H₂ production process. These conditions comprise processing CH₄ space velocities suitable for the scaling up of the process, operation of the system at pressure, and testing materials that had experienced up to 200 oxidation/reduction cycles. The system, catalyst and CaO-based sorbent, was able to fulfil the SER equilibrium composition up to 2.5 kg CH₄ h⁻¹ kg cat⁻¹, CH₄ space velocity that would allow the scaling up of the process. In this way, a gas stream containing up to 95% vol. H₂ was

obtained at 923 K, steam to carbon ratios of 3.2 and 4, sorbent to catalyst weight ratios from 4 to 15 and for operation pressures between 1 and 9 bar. The effect of oxidation/reduction cycles on catalyst performance was assessed, and the mixture sorbent and aged catalyst was able to process up to $2.5 \text{ kg CH}_4 \text{ h}^{-1} \text{ kg cat}^{-1}$, corroborating the operational limit determined for the fresh materials. The total operation pressure (from 1 to 9 bar) did not have an important influence on H_2 yield, and/or materials performance.

Sorbent carbonation reaction rates up to $4.42 \cdot 10^{-2} \text{ kmol h}^{-1} \text{ kg sorb}^{-1}$ were determined in the experiments, being this parameter responsible of the limit in CH_4 space velocity that can be successfully converted through this sorbent/catalyst system. The experimental results have been successfully described by a pseudo-homogeneous reactor model that incorporates the main kinetic expressions of the reactions involved in the SER stage.