

Performance of optimized CO₂ solid sorbents for hydrogen production by Sorption-Enhanced Reforming (SER) in fluidised bed reactor

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One of the most promising new technologies to produce hydrogen with integrated CO₂ capture is the Sorption Enhanced Reforming (SER) of natural gas. Extensive work has been carried out during the last 15 years at IFE to develop this technology [1-3]. The SER technology is based on a high temperature solid cycle of a CaO-based CO₂ sorbent, mixed with a reforming catalyst. The system configuration involves two reactors with circulation of solids: the reformer, where methane conversion into hydrogen and CO₂ capture reactions occur simultaneously, and the calciner, where the sorbent - loaded with CO₂ - is heated up to evolve near-to-pure CO₂, ready for compression and further storage and/or utilization. Compared to conventional Steam Methane Reforming (SMR), the SER technology reduces significantly the number of process steps: from four steps (reforming, water-gas shift at high and low temperature, CO₂ separation) to one integrated system with only two interconnected fluidized bed reactors. Therefore, the SER technology has the potential to reduce the production cost of hydrogen by process intensification and energy savings, and can, on a medium term perspective, contribute to a more efficient and profitable production of hydrogen with integrated CO₂ capture.

CaO-based CO₂ sorbents are suitable materials in the SER technology because of their relatively low cost, high availability, fast kinetics and high CO₂ capture capacity [1-4]. The majority of the research carried out in the field of CaO-based CO₂ sorbents has focused on natural sorbents, such as limestone and dolomite. However, the CaO-containing natural materials suffer from rapid decrease in CO₂ uptake capacity over repeated carbonation/calcination cycles, due to sintering and pore closure effects [4-5]. In addition, natural CaO sorbents have sub-optimal mechanical properties leading to high attrition rates and consequently, elutriation of fine materials when used in fluidized bed reactor systems, as it is the case of SER. Advanced synthetic materials with improved chemical and mechanical stability compared to natural sorbents have the potential to reduce the capital and operation costs and therefore represent an important economic factor to bring the SER technology forward to up-scaling and commercialization.

Therefore, development of synthetic sorbents with high and stable CO₂-capacity over cycles has become an important research topic. Many new synthetic high temperature CaO-sorbents have been reported to overcome the sintering of CaO particles and to maintain cyclic carbonation conversion [5-6]. The introduction of inert materials as CaO supports - such as Al₂O₃, Ca₁₂Al₁₄O₃₃, ZrO₂ or CaTiO₃ - enhances the long-term stability of the material. Among those solid supports, mayenite (Ca₁₂Al₁₄O₃₃) is considered to be the most promising support for high-temperature CO₂ sorbents. Various synthesis methods for CaO/Ca₁₂Al₁₄O₃₃ sorbents have been reported in the literature. In a previous work, the authors presented a new synthesis for CaO/Ca₁₂Al₁₄O₃₃ sorbent based on the decomposition of Ca₃Al₂O₆ at high temperature. The sorbent prepared by a modified Pechini method showed a high CO₂ sorption capacity up to 29 g-CO₂/100g sorbent for more than 140 carbonation/calcination cycles [2]. However, the application of this material at large-scale might be uneconomic due to the costly preparation method and precursors. Therefore more recent efforts have been focused on the development of a simpler and more cost-effective synthesis method. The newly developed hydrothermal method results in high-performance CO₂-capture sorbents based on largely available and cheap calcium and aluminium hydroxide precursors [3]. Based on this hydrothermal method, synthetic sorbents can be easily prepared and show the desired combined composition of finely dispersed active CaO over mayenite (Ca₁₂Al₁₄O₃₃). Compared to natural limestone, hydrothermally-prepared synthetic sorbents exhibit much higher CO₂ capture capacity over multiple carbonation/calcination cycles, due to the mayenite support, that effectively prevents sintering of the CaO. The synthesis method and the agglomeration technique to produce particles with suitable size have been optimized. Thus, a synthetic sorbent with around 30 wt% CaO is considered to be optimum in terms of stable CO₂ capture capacity (23 g-CO₂/100g sorbent during 40 cycles), high sorption kinetics in presence of water vapour and high mechanical strength.

In the present work, a batch of the optimum sorbent has been synthesized and agglomerated at IFE. The material was characterized by XRD, PSD, TGA, mercury porosimetry and BET in collaboration with ICB-CSIC. Then, SER tests with the sorbent mixed with a commercial reforming catalyst have been performed in a fluidized bed reactor setup, at laboratory scale under relevant operating conditions, at ICB-CSIC facilities [5]. Different fluidization velocities, sorbent/catalyst ratios, steam/carbon ratios and regeneration conditions (with and without steam) have been studied.

The experimental set-up consists of a stainless steel fluidized bed reactor of 5.3 cm I.D., connected to mass flow controllers for CH₄, H₂, N₂ and steam, and equipped with on-line temperature, pressure and gas-composition analyzers. Initial amounts of calcined sorbent were pre-mixed with commercial catalyst at room temperature, matching calcined

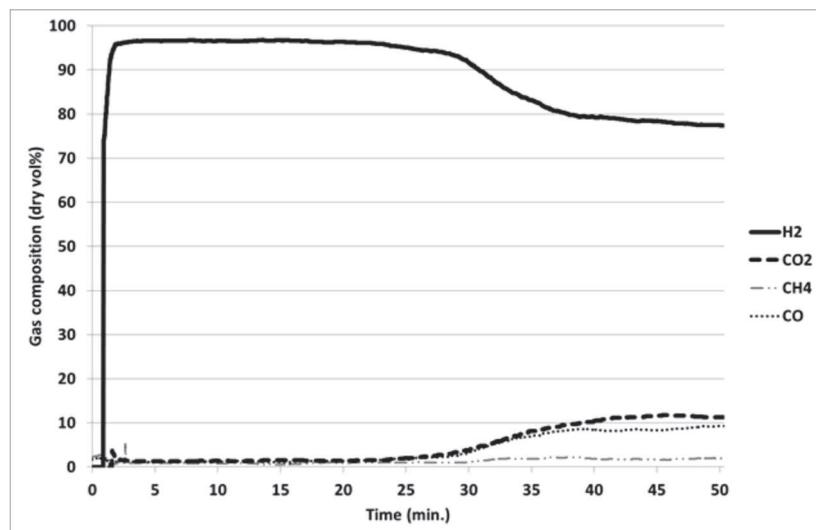


Figure 1. Measured vol. flow H₂, CO₂, CH₄ and CO (dry basis) during reforming reaction at 650 °C, 0.1 m/s gas linear velocity, sorbent/catalyst 3 (w/w), steam/carbon 4 (vol./vol.), solid inventory 225 g of IFE's synthetic sorbent and commercial catalyst tested at ICB's fluidized bed reactor

sorbent/catalyst ratios of 1; 3; 4 and 5 (w/w) for different tests, with a total solid inventory varying between 175 and 225 grams. For each cycle, the pre-selected total flow (for fluidization velocities of 0.06 and 0.1 m/s) and relative Steam/CH₄ flows (ratios 3 and 4 (vol./vol.)) were sent to the reactor at 650 °C. The feed flow was maintained until the saturation breakthrough curve of CO₂ was complete, i.e. until no further sorption enhancement effect occurred. After each reforming step, the saturated sorbent was regenerated either with or without the presence of steam at 850 °C. As an example of the obtained results, Figure 1 shows the evolution over time of the measured hydrogen, methane, carbon dioxide, and carbon monoxide concentrations during the sorption enhanced reforming reaction at 650 °C for a fluidization velocity of 0.1 m/s, a calcined sorbent/catalyst ratio of 3, a steam/carbon ratio of 4, a solid inventory of 225 grams and after 3 carbonation/calcination cycles.

Conclusions

In this work, optimized high temperature solid CO₂-sorbents for Sorption Enhanced steam Reforming (SER) were tested in a laboratory fluidized bed reactor at relevant operating conditions. Different fluidization velocities, sorbent to catalyst ratio, steam to carbon ratio and regeneration conditions (with and without steam) have been studied in the batch reactor. From this study, it can be concluded that the optimized hydrothermal sorbent is suited for the SER reaction at industry-relevant process conditions, showing remarkable performance in CO₂ sorption capacity and presenting good behavior in terms of chemical stability in fluidized bed reactor. The obtained results indicate an optimum sorbent/catalyst ratio of 3 for the specific commercial catalyst used in these tests. A steam/carbon ratio of 3 showed to be sufficient for the reaction to occur adequately. Over 95 vol% hydrogen yield (dry basis) has been achieved at fluidization velocity of 0.1 m/s, whilst low CO₂ concentrations (under 2.5 vol%) have been detected before the breakthrough saturation curve of the sorbent. Therefore, it can be concluded that the CaO-based synthetic sorbent prepared by the optimized hydrothermal method shows excellent performance for the SER reaction at industry-relevant process conditions. This work thus represents an important milestone in the development and upscaling of advanced low-cost sorbents for the efficient production of hydrogen with integrated CO₂ capture by SER technology.

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References

- [1] J. Meyer, J. Mastin, C. Sanz. Energy Procedia 63 (2014) 6800-6814.
- [2] J. Mastin, A. Aranda, J. Meyer Energy Procedia 4 (2011) 1184-1191.
- [3] Saima Sultana Kazi, Asunción Aranda, Julien Meyer, Johann Mastin. Energy Procedia 63 (2014) 2207-2215.
- [4] G.S. Grasa, J.C. Abanades. Ind.Eng.Chem. Res., 45 (2006) 8846-8851.
- [5] M. Aznar, A.L. García, G.S. Grasa and R. Murillo. Book of Abstracts Hydrogen Power Theoretical and Engineering Solutions International Symposium. Toledo, Spain, 2015.
- [6] S. Choi, J.H. Drese, C.W. Jones, ChemSusChem, 2 (2009) 796-854.