Multicycle sorption enhanced steam methane reforming with different sorbent regeneration conditions.

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Highlights

- Successful synthesis and characterization of CSCM for SESMR
- CSCM works for 205 SESMR/mild-regeneration (N_2, 850 °C) cycles
- CSCM deactivates in 140 SESMR/severe-regeneration (CO_2, 925 °C) cycles
- TGA study on sorbent regeneration conditions

1. Introduction

Sorption enhanced steam methane reforming (SESMR), i.e. steam methane reforming (SMR) with in-situ CO_2 sorption by a high-temperature CO_2 solid sorbent, can lead to a sustainable and economical exploitation of natural gas for high-purity H_2 production, avoiding greenhouse gases emissions [1]. CO_2 capture pushes water gas shift equilibrium (WGS, Reaction 2), and then SMR (Reaction 1), towards additional H_2 production [2]. CaO-based sorbents are generally preferred for CO_2 capture (Reaction 3), as well as Ni for SMR catalysis (Reactions 1 and 2) [3,4].

$CH_{4(g)} + H_2O_{(v)} \leftrightarrow CO_{(g)} + 3H_{2(g)}$	$\Delta H^0_{298K} = 206.2$ kJ/mol	Reaction 1
$CO_{(g)} + H_2O_{(v)} \leftrightarrow CO_{2(g)} + H_{2(g)}$	$\Delta H^0_{298K} = -41.2$ kJ/mol	Reaction 2
$CO_{2(g)} + CaO_{(s)} \leftrightarrow CaCO_{3(s)}$	$\Delta H^0_{298K} = -178.2$ kJ/mol	Reaction 3

This research work studies combined sorbent-catalyst materials (CSCM) based on Ni and CaO supported on mayenite ($Ca_{12}Al_{14}O_{33}$), focusing on effects of different regeneration strategies in multicycle processes.

2. Methods

Ni-CaO-mayenite CSCM are synthesized by wet mixing and wet impregnation methods, presented and validated in [4].

Multicycle SESMR/regeneration tests are carried out by a fully automated, bench scale packed-bed rig (~10 g). The conditions chosen for SESMR are 650 °C, 1 atm, inlet molar steam/carbon = 3, weight hourly space velocity = 0.24 $Nl_{CH4,in}$ h^{-1} $g_{packed\text{-}bed}^{-1}$. Regenerations are performed, choosing different gases (N_2 or CO_2) at different temperatures (within the range 850-925 °C).

Thermogravimetric analyses (TGA) are used for multicycle carbonation (30 min, 650 °C, 15 vol% of CO_2 in N_2)/calcination tests on CSCM, applying several kinds of regenerations, within the range of multicycle SESMR/regeneration tests. In addition, pre- and post-test characterizations are performed by: XRD, SEM-EDS, TEM-EDS, BET/BJH.

Experimental data are also employed as a reference for SESMR and CO_2 capture mathematical simulations, by already developed particle grain model (PGM) [5] and axial dispersion plug flow reactor (ADPFR) dynamic model [6].

3. Results and discussion

CaO15Ni10, a CSCM with 10 wt% of Ni derived from wet impregnation of a CaO-mayenite sorbent with 15 wt% of free CaO, underwent two multicycle SESMR/regeneration tests: the first with a mild regeneration (pure N_2, 850 °C, Figure 1a), the second with a severe one (pure CO_2, 925 °C, Figure 1b).

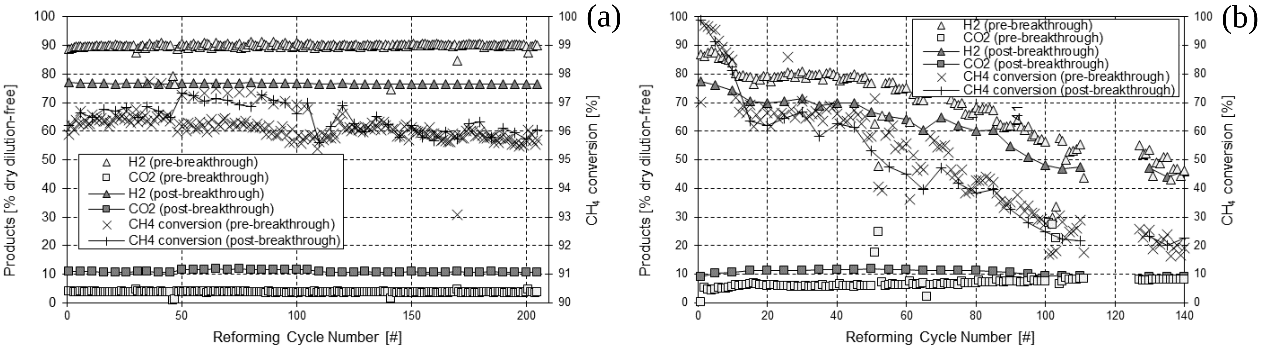

Figure 1. Multicycle SESMR/regeneration tests on CaO15Ni(N)10, with mild (N_2, 850 °C) (a) or severe (CO_2, 925 °C) regenerations.

Results from the first test depicted a very stable performance, in terms of H_2 outlet purity (about 90 vol% dry, dilution-free basis), CH_4 conversion (96-97 %) and CO_2 capture, throughout 205 cycles (Figure 1a). In the second test, the only change of the regeneration procedure caused a deactivation of the same CSCM, with CH_4 conversion close to 20 % at the 140th cycle; post-test characterization allowed to associate this deactivation with a decrease of surface area and pores specific volume (BET/BJH methods), and a rearrangement of Ni in coarse spheroidal structures (SEM-EDS).

Breakthrough curves from the first test were also used as a reference for the fitting of numerical results from simulations of the same test by the ADPFR model.

TGA multicycle tests are currently ongoing on the same CSCM, applying several regeneration strategies, e.g. pure N_2 at 850 °C, pure CO_2 at 925 °C, pure N_2 at 925 °C, or other intermediate conditions, so to identify effects from temperature and regenerative gas, and to locate new regeneration conditions for further multicycle SESMR/regeneration tests.

4. Conclusions

A CSCM suitable for a multicycle SESMR/regeneration process was synthesized by wet mixing and wet impregnation methods. Its performances strongly depend on the used regeneration procedure. A TGA study is expected to locate regeneration conditions suitable for the CSCM and as far as possible close to those of a hypothetical industrial SESMR, in which CO_2 could be reused as a process fluid for the regeneration. Mathematical models are also employed as a tool in this study.

References

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Keywords
Sorption enhanced steam methane reforming; Multicycle CO_2 capture; Combined sorbent-catalyst materials; Sorbent regeneration