

Preliminary screening of SrO-based composites for thermochemical energy storage

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In the framework of the thermochemical energy storage (TCES) for concentrating solar power (CSP) applications, the reversible calcination/carbonation of metal carbonates is receiving increasing interest. In this context, the SrCO₃/SrO system is one of the most promising solution due to its high energy density (4 GJ m⁻³) and working temperatures (up to 1200 °C). In analogy to the well-known CaCO₃/CaO system, also SrO suffers from a dramatic drop of reactivity when subjected to cycling operations due to sintering. Therefore, it is necessary to focus the research activity to the material characterization and improvement of its multicycle conversion and stability.

In this work, different materials (containing Al, Ca, P or Zr) have been incorporated in the SrO/SrCO₃ system as agglomeration/sintering inhibitors. The multi-cyclic stability and performances of all the synthesized SrO-based composites have been studied in thermobalance and the materials, have been characterized from the morphological and chemico-physical point of view (SEM-EDS, XRD).

1. Introduction

Among all renewable energy resources, solar radiation is the most abundant persistent one and it could, indeed, provide enough energy to meet the world annual demand (Raganati et al., 2020). In particular, solar energy can be converted into heat and electricity by means of a concentrated solar power (CSP) plant, thus completely avoiding the use of fossil fuels and the CO₂ emission in the atmosphere (Rhodes et al., 2015). The main challenge to increase the share of solar energy, characterized as most of the renewable energy sources by the intermittency of power production, in the global energy mix is represented by the energy storage. In this framework, thermochemical energy storage (TCES) can be a viable technological solution to accomplish high-energy storage efficiency in concentrating solar power (CSP) plants (Raganati et al., 2019). TCES uses the high temperatures achievable by CSP to drive an endothermic chemical reaction; then, the reaction products are stored separately and employed, when needed, to carry out the exothermic reverse reaction, which releases the heat previously accumulated (Ortiz et al., 2019).

Among all the available TCES systems (metallic hydrides, carbonates, hydroxides, redox system), alkaline-earth metal carbonates are recognized to be one of the best alternatives, especially due to the high reaction enthalpy, storage temperature and energy density (Karasavvas et al., 2018). In this framework, the SrCO₃/SrO system is recently receiving great research interest due to its high energy density (4 GJ m⁻³) and working temperatures (up to 1200 °C) (Bagherisereshki et al., 2018). In analogy to the more extensively investigated CaCO₃/CaO couple, one of the main problem of SrO is that particle sintering causes a dramatic drop of its reactivity over multiple carbonation/calcination cycles (Miccio et al., 2016). Therefore, great research effort must be devoted to the material characterization and improvement of its multicycle conversion and stability. One promising solution is represented by the incorporation of refractory inert materials serving as sintering inhibitors (Al₂O₃, La₂O₃, MgO, SiO₂, TiO₂, Y₂O₃, ZrO₂) (Gigantino et al., 2019). In particular, we showed in previous works (Ammendola et al., 2021, 2020), that Al₂O₃ can be successfully used as sintering inhibitor to improve the multicyclic performances of the SrO/SrCO₃ system (Ammendola et al., 2020). Besides that, it was shown that

Al₂O₃ serves also as agglomeration inhibitor, thus making the SrO-based composite applicable in fluidized bed operations (Ammendola et al., 2020).

This paper represents a further development of the above-mentioned research activity. In particular, the incorporation of different materials containing Al, Ca, P or Zr, as sintering inhibitors, has been considered besides alumina. The stability and performance of the synthesized SrO-based materials over multiple carbonation-calcination cycles has been studied in thermobalance in order to select the most promising material for future lab-scale reactor tests. The thermogravimetric (TG) results have been correlated with microstructural and chemico-physical characterization (SEM-EDS, X-Ray Diffractometry).

2. Experimental

Materials – Strontium carbonate based mixtures have been prepared mixing commercial powder of SrCO₃ (Carlo Erba, purity >99.9 %) with 30 wt% of other compounds (Ammendola et al., 2020), namely Al₂O₃ (Martoxid KMS-96, purity 96,0 %), Hydroxyapatite (Calcium phosphate hydroxide, Riedel de Haen), ZrO₂ (3YB Tosoh), ZrO₂ Al₂O₃ (Tosoh) and Sr-substituted Hydroxyapatite (Istec, lab-made with Sr/Ca molar ratio = 0.2). Since the powders agglomerate naturally due to air humidity, the composite mixtures have been dried at 80°C and noted as Sr-A, Sr-HA, Sr-Z, Sr-ZA Sr-SrHA, respectively. The additional phases have been used for testing as sintering/agglomeration inhibitor during calcining/carbonation cycles.

Fresh and cycled samples have been characterized as needed by:

- Morphological characterization - by scanning electron microscopy coupled with Energy Dispersive X-Ray Spectrometry (Zeiss SEM-FEG-EDS instrument).
- XRD - qualitative crystallographic analysis has been performed by X-Ray Diffraction (Powder Diffractometer Bruker D8 Advance with CuKα radiation, Karlsruhe, Germany D) in air atmosphere using a Si sample holder, dedicated to low amount specimens.

Cycling carbonation/calcination tests - The carbonation/calcination cycles have been performed in a STA 449 Jupiter (Netzsch Geraetebau, Selb, Germany) thermo-balance. The sample (80-100 mg) is heated up to the desired reaction temperature (1050 °C) at 30 °C/min in an inert atmosphere (Ar). Then, 10 calcination/carbonation cycles have been performed alternatively flowing either Ar or CO₂ (40 ml min⁻¹ STP) gas at atmospheric pressure. The SrO carbonation conversion, X, has been calculated from the sample mass variation:

$$X = \frac{\Delta m}{w} \frac{M_{SrO}}{m_i M_{CO_2}} \quad (1)$$

where Δm is the variation of sample mass during the i-th carbonation, m_i is the mass of sample at the beginning of the i-th carbonation, w is the mass fraction of SrO in the sample, and M_{SrO} and M_{CO₂} are the molecular weights of SrO and CO₂, respectively.

3. Results and discussions

Figure1 shows the comparison of the TG curves of the tested composites, including the heating before the carbonation/calcination cycles at 1050 °C.

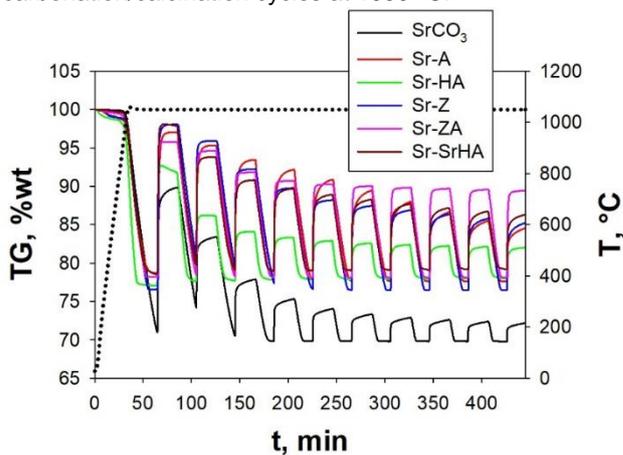


Figure 1. TG cycles of carbonation and calcination at 1050°C performed respectively under CO₂ and Ar flowing.

Then the TG curves have been elaborated in order to evaluate the weight gain percentages and the carbonation conversion, X_c , reported in Table 1 and Figure 2, respectively.

Table 1: Sample weight gain percentages obtained in the 1st, 2nd and 10th cycles.

	$\Delta m/m_i$, %wt		
	1 st cycle	2 nd cycle	10 th cycle
SrCO ₃	26.41	6.05	3.45
Sr-A	23.65	16.83	9.01
Sr-HA	20.21	6.54	5.24
Sr-Z	28.18	15.05	11.48
Sr-ZA	22.53	15.54	14.52
Sr-SrHA	24.79	12.56	9.05

Clearly, the first weight loss accounts for the weight ratio between SrCO₃ and the additional phase. As regards the calcination step, it is always complete, since the signal always achieves the baseline. On the contrary, as regards the carbonation step, it is clear that pure SrCO₃ is characterized by a fast decay of the carbonation conversion with the increasing number of cycles. Indeed, SrCO₃ starts with a percentage weight gain as high as 26.41 % (Table 1), corresponding to $X_c = 0.62$ (Figure 2a), and after just one cycle its carbonation performances are characterized by a dramatic drop, which continues down to a very low residual conversion $X_c = 0.08$ at the 10th carbonation (Figure 2).

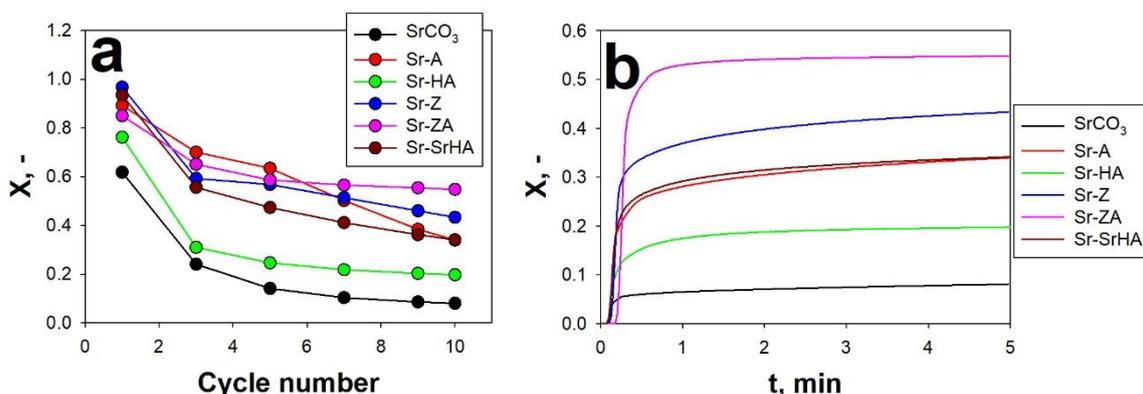


Figure 2. a) Carbonation conversion degree as function of the cycle number. b) Time evolution of the conversion degree in the 10th carbonation.

In contrast to the pure SrCO₃, it can be observed that all the synthesized composites are characterized by more stable performances, i.e. the incorporation of all the selected sintering/agglomeration inhibitors makes it possible to limit the loss of carbonation reactivity with cycling. In particular, among all the tested inhibitors, HA is the one providing the slightest improvement in the cycling behavior of SrCO₃; besides, it also leaves quite unaltered the calcination rate. The other additional phases behave remarkably better. Indeed, as clearly shown in Table 1 and Figure 2, all the other the composites show a much slower decay in the carbonation extent moving toward higher number of cycles and, in addition, slower calcination rate. In particular, it can be inferred that the Sr-ZA is the composite providing the best multicyclic performances, showing a residual carbonation conversion as high as 0.55 (Figure 2).

The visual inspection of the sample in the TG crucible after the test confirmed the comparison results. The better TG behaviors are associated with samples that underwent less volumetric contraction.

The XRD analysis on the cycled materials (Figure 3) evidences, besides Sr carbonate and hydroxide hydrates, the presence of the added phases (Alumina, zirconia, calcium phosphates and/or of new formed mixed compounds, such as strontium aluminates (card #24-1187 Sr₃Al₂O₆), zirconates (card #44-0161 SrZrO₃), Sr enriched phosphate hydroxides (cards #34-0477 Ca₂Sr₈(PO₄)₆(OH)₂, #34-0481 Ca₄Sr₆(PO₄)₆(OH)₂). In the last case, the substitution of Ca with more Sr in the hydroxyapatite lattice results in the formation of calcium oxide. The added phases do not behave as completely inert phases towards Sr carbonate/oxide but a partial reaction occur, until a stable condition is achieved at different number of carbonation/calcination cycles for the different mixtures, as shown by TG curves.

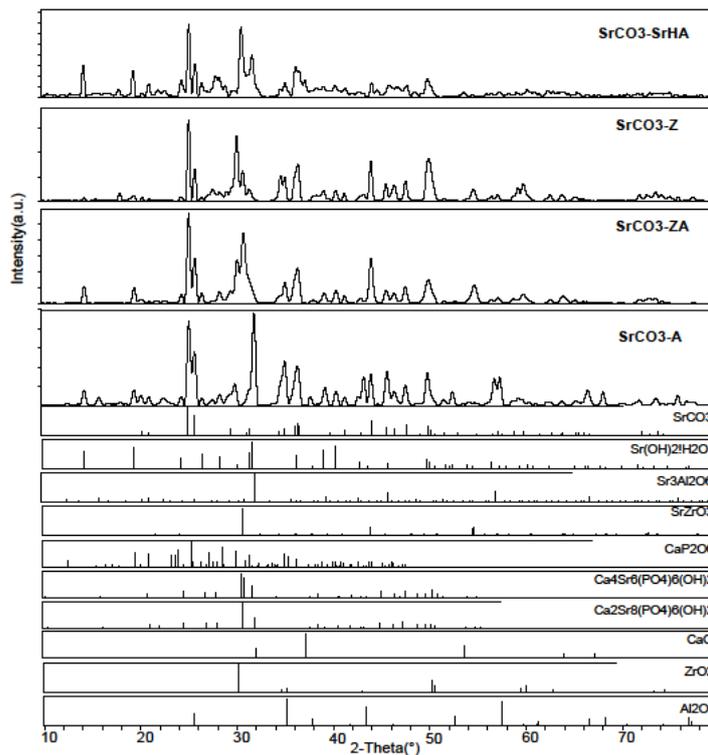


Figure 3. XRD spectra.

The SEM microstructure images (Figure 4) confirm the different grade of volumetric shrinkage the different materials had during the cycling. SrCO₃ along with Sr-HA show a more compact microstructure compared to the other composite materials. Sr-ZA and Sr-Z are the most efficient composites in hindering the material compaction.

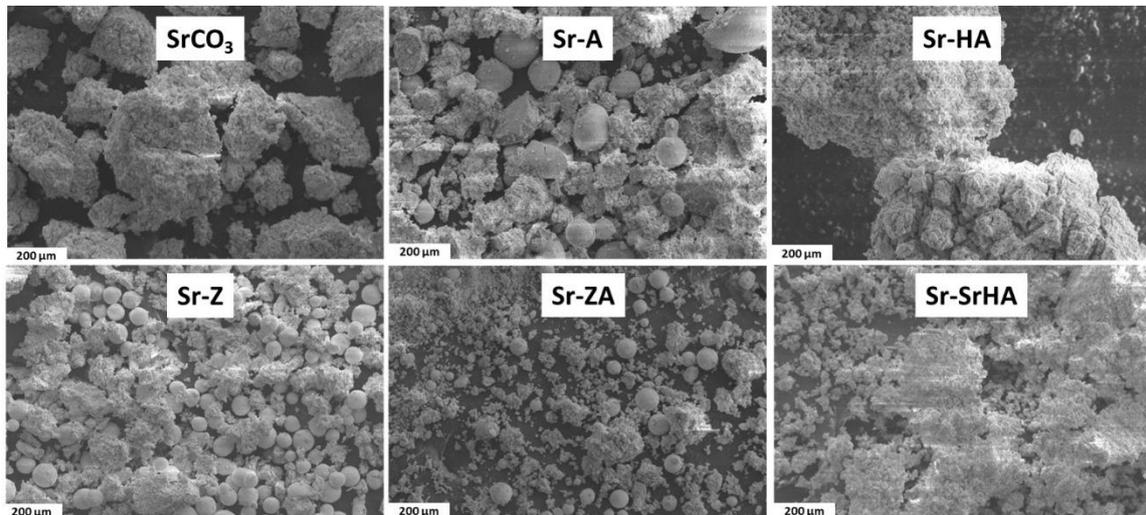


Figure 4. SEM microstructures of the cycled samples.

SEM analysis through the element mapping (Figure 5) evidenced that in some cases the added phase, due to its peculiar morphology or composition, is clearly distinguishable from the Sr-carbonate/oxide matrix, while in others it is uniformly and more homogeneously distributed in the material. At higher magnification, the microstructures of the cycled samples show the presence of pores, that again accounts for the different

contractions that the samples experienced. A diffuse interconnected porosity with evidence of pores mainly located in the range of tens of microns, can be responsible of the better performance in carbonation of the composites.

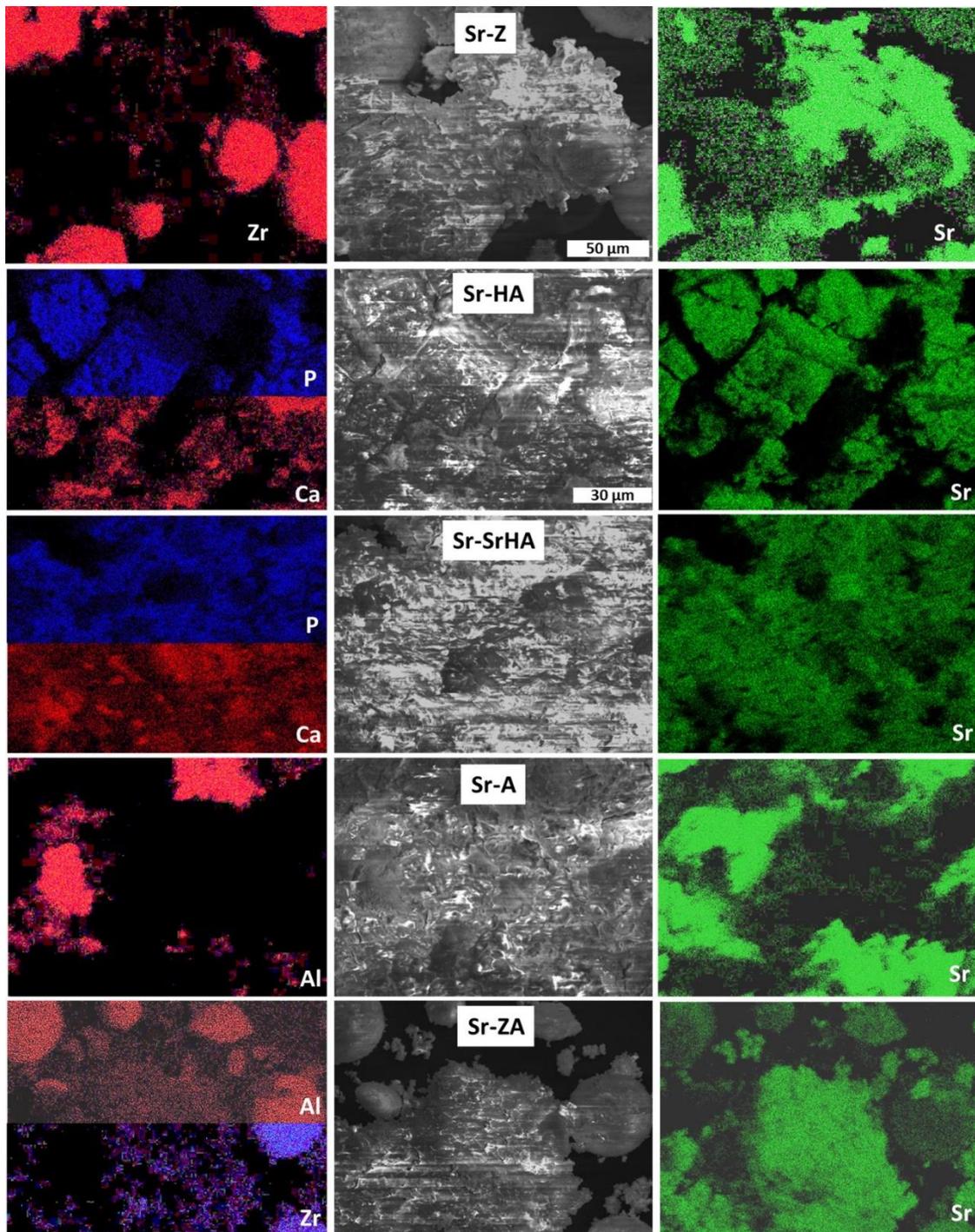


Figure 5. SEM images and EDS maps of the cycled composites.

4. Conclusions

In this work, the reversible carbonation-calcination reaction of SrO/SrCO₃ system has been studied for the thermochemical storage of energy at high temperature (> 1000 °C). Aiming at increasing the cycling stability of this system, which is characterized by a dramatic drop of reactivity due to sintering when subjected to cycling

operations, different materials (Al_2O_3 , Hydroxyapatite, ZrO_2 , $\text{ZrO}_2/\text{Al}_2\text{O}_3$ and Sr-substituted Hydroxyapatite) have been incorporated in SrO/SrCO₃ system and screened as possible sintering/agglomeration inhibitors. All the synthesized composites have been tested in thermobalance in 10 consecutive carbonation/calcination cycles in order to assess their multicyclic performances.

The results obtained showed that, except for HA, which provides just a minor improvement with respect to SrCO₃, all the other composites showed much more stable performances, i.e. the decay in the carbonation conversion with increasing number of cycles is remarkably limited with respect to SrCO₃. In particular, among all the tested composites, Sr-ZA is the one providing the best multicyclic performances, showing a residual carbonation conversion as high as 0.55.

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