Particle Clustering Phenomena on $SrCO_3$ Doped by Cu/Co During Thermochemical Energy Storage Cycles

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Abstract

Energy storage acquires great importance, since it allows to increase the efficiency of the processes to make possible the generation of energy even in periods of low solar irradiance or in its absence. Compounds such as carbonates and metal oxides are promising because they have high energy density, but particle clustering phenomena affect their stability during reactive cycles. In this work, the effects of doping $SrCO_3$ with Cu/Co have been studied by 2 synthesis methods: sol-gel and solid-state reaction methods, and the results have been compared with pure $SrCO_3$. It was concluded that the use of nitrates as precursors effectively improves the performance of $SrCO_3$, delaying the occurrence of particle clumping phenomena after 6 cycles, where the conversion of sol-gel synthesized $SrCuO_2$ was 0.89 and the gravimetric energy density was 1135.5 kJ/kg, compared to the conversion of 0.09 and the density of 197.3 kJ/kg of pure $SrCO_3$ powder.

Keywords: Thermochemical energy storage, clustering, high-temperature, strontium carbonate, sol-gel method, solid-state reaction method.

1. Introduction

There is currently greater awareness of the environmental effects of energy production using petroleum-based raw materials. For this reason, interest in transitioning to renewable energy sources has grown worldwide over the past few decades (Jarimi et al., 2019). The sun is an energy resource with enormous potential for various technological applications. Although photovoltaic energy has become commercially established as a viable technology, there are also solar thermal power plants that use heliostats to concentrate the sun's rays at a single point, converting them into heat, and generate electricity. Nevertheless, this technology has not yet reached the maturity necessary to be fully competitive due to factors such as solar intermittency, the alternation between day and night, the low efficiency of solar concentrators, and the costs associated with its implementation (Steinfeld and Palumbo, 2003; Yan et al., 2015; Peng et al., 2017).

Power can be generated from solar thermal energy collected by solar concentrators (SC) that can operate at high temperatures (>600°C). Thermal energy storage (TES) is a technology that can make more efficient performance of concentrated solar power (CSP) plants, extending the operation time that is reduced by the intermittency and cyclicity of the solar energy. In a specific case, thermochemical energy storage (TCS) allows a high capacity to accumulate energy longer than latent or sensible heat storage technologies. Carbonates such as calcium or strontium are promising materials because they have a high energy density, but they present clustering phenomena problems in their reaction cycles (Ortiz, 2021). Calcium carbonate is abundant in nature, which means it is inexpensive and readily available. Its main drawback is the deactivation of CaO due to sintering during the calcination/carbonation cycles, just as SrO shows a decrease in its conversion to $SrCO_3$ from the first reactive cycles (André et al., 2016; Wong, 2011; Santamaría and Romero-Paredes, 2023).

One of the main problems with the materials is the clustering of particles that occur due to temperature changes in their reactive dissociation/recombination cycles. Sintering and agglomeration generate, cycle after cycle, a decrease in conversion, affecting the stability and storage capacity of the material, which leads to lower efficiency in the system's energy storage process (Bagherisereshki et al., 2018). Physisorption and chemisorption in the carbonation reaction depend on the chemical nature of the gas and solid under specific energy storage operating conditions. Physical adsorption is mainly related to the surface area and porosity of the adsorbent material and equilibrium is quickly reached if there are no problems with mass transfer by diffusion through the pores. These problems may arise from changes in the partial pressure of the gas passing through the pores as well as the grouping of particles of the same structure as the adsorbent solid, known as agglomeration. On the other hand, sintering is the densification

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of the solid product of these adsorption phenomena, whereby the diameters and volume of the pores decrease, the solid becomes more compact, reducing its surface area, which causes a decrease in the active sites for chemisorption and a reduction in the diffusion channels of the gas through the solid in the case of physisorption (Wu et al., 2019). Fig. 1 shows the description of the phenomena mentioned above.

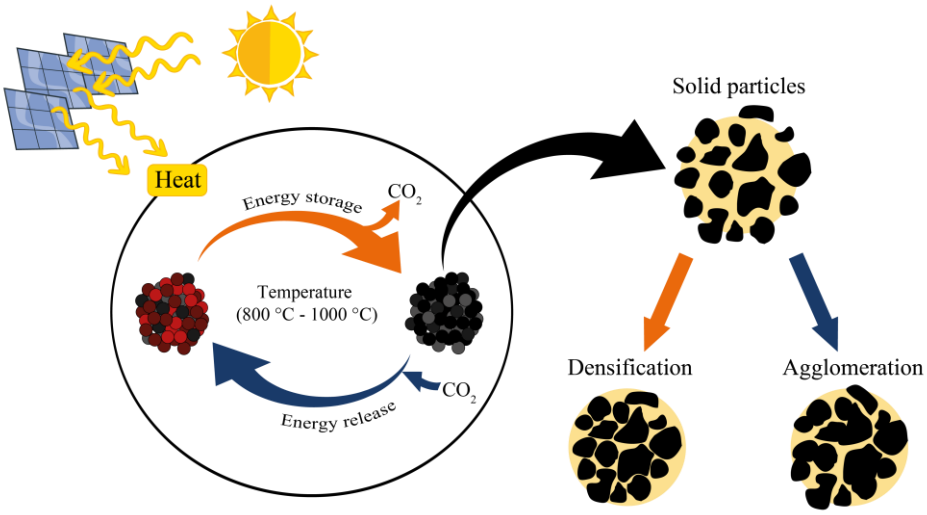

Figure 1: Particle clustering phenomena in carbonation/decarbonation cycles at high temperature.

Research conducted in recent decades on the application of composites in thermochemical energy storage processes has revealed a wide field to be explored to take advantage of the physical properties inherent in oxides and carbonates. Composites have been developed to improve the properties of pure components and reduce these phenomena since they are more stable, which would allow for greater use of the material (André and Abanades, 2020; Silakhori et alt. 2019; Yilmaz et alt. 2020; Gigantino et alt. 2020). The properties of the manufactured materials are intrinsically linked to the precursors and operating conditions applied at each stage of the process (Gigantino et al., 2019; Zhang et al., 2023).

This work presents a study of the reactivity of Cu/Co-doped strontium carbonate to understand the evolution of the clustering phenomena involved in the reversible reactions of $SrCO_3$ for TCS systems above 600 °C.

2. Methodology

Copper nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$, ACS reagent, Meyer), cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$, ACS reagent, Meyer) and strontium nitrate (ACS reagent, Meyer) were used as metal precursors for the sol-gel synthesis (SG). Cupric oxide (ACS reagent, Sigma-Aldrich) and strontium carbonate (>99.9% trace metals, Sigma-Aldrich) were employed as metal precursors by solid-state reaction synthesis (SSR). Deionized water was used as the physical medium for solutions. Citric acid monohydrate (ACS reagent, Meyer) was employed as chelating agent and ethylene glycol (ACS reagent, Meyer) was employed as polymerizing agent. All reagents were used without further purification. The procedure used in the methods for synthesizing doped SrCO3 is described in Fig. 2.

In the state-solid reaction method, CuO and $SrCO_3$ in solid state were physically mixed and ground in a molar ratio of Sr:Cu of 1:1 for 1 hour in an agate mortar. The mixture was dried at 100 °C for 12 hours. It was then calcined at 1000 °C for 1 hour in a Lindberg MOD 51894 furnace. The synthesized material was labeled as SCC-SSR (Strontium Copper Composite - State Solid Reaction) and stored in a desiccator in a closed vial. In the sol-gel method, the precursor nitrates (Sr-Cu or Sr-Co), both dissolved in deionized water, were mixed in a molar ratio of Sr:Cu of 1:1 and a molar ratio of Sr:Co of 1:1. Citric acid (CA) and ethylene glycol (Et) were then added in a molar ratio of CA:Et of 3:2, starting from a molar ratio of Sr:CA of 1:1. The solution was heated to 90 °C until gelation. It was then left to dry at 100 °C for 12 h. The first calcination was carried out at 300 °C for 3 h and the second calcination was carried out at 1000 °C for 10 min. The materials obtained were labeled as SCC-SG (Strontium Copper Composite - Sol-Gel) for the Cu precursor and SCoC-SG (Strontium Cobalt Composite - Sol-Gel) for the Co precursor and stored in a desiccator in a closed vial.

Figure 2: Schematic diagram of $SrCO_3$ composite preparation by sol-gel synthesis and ceramic method.

The crystalline structures were investigated by X-ray diffraction in a Bruker D8 Advance diffractometer with Cu K∝ radiation. The data were measured in the range from 10° to 80° in 2θ with a step size of 0.020414°, for 38.4 s per point. Thermogravimetric analysis. The experiments were conducted using a simultaneous TGA-DSC analyzer (STA 449 F3 Jupiter, NETZSCH) equipment with a high-sensitivity balance (<0.1 µg) and a silicon carbide furnace capable of reaching temperatures up to 1500 °C. This equipment was used to evaluate the performance as a thermochemical material, with which it was possible to know the behavior of the samples through their mass variation during the dissociation/recombination reactions. The clustering phenomena was performed using scanning electron microscopy (SEM). The data were obtained using a JEOL JSM 7600F microscope equiped operating at an acceleration voltage of 15 kV. Before analysis, the powder samples were deposited on a carbon tape that adhered to an aluminum holder and coated with a conductive gold layer of approximately 20 nm thick to enhance conductivity and image quality, to analyze the physical evolution of material after 6 reactive cycles.

The stability of the material was evaluated by calculating the effective conversion of SrO to $SrCO_3$ (Eq. 1).

$$X_{SrO} = \frac{\Delta n_{CO_2}}{m_{SrO}} M_{SrO} \qquad \text{(eq. 1)}$$

Where Δn_{CO2} is the mole number of CO_2 captured in each carbonation stage, which is equivalent to the mole number of SrO converted to $SrCO_3$, m_{SrO} is the mass corresponding to SrO within the material and M_{SrO} is the molar mass of SrO (Gigantino et al., 2019). The energy storage capacity of the material is determined by its gravimetric energy density (Eq. 2).

$$D_m = \frac{\Delta n_{CO_2}}{m_{in}} \cdot \Delta H_{r,298K} \qquad \text{(eq. 2)}$$

Where m_{in} is the total mass of the material after the previous decomposition stage and Δ_{Hr} is the standard heat of reaction (234 kJ/mol) (Ammendola et al., 2020).

3. Results and Discussion

Fig. 3 shows a preliminary particle size analysis of $SrCuO_2$ samples prior to cycling, obtained by digital microscopy. The particles synthesized via sol-gel route exhibit a more homogeneous size distribution and better dispersion compared with those produced by solid-state route. This observation is consistent with the improvement of surface morphology of the sol-gel material, which can provide a larger gas-solid contact area for carbonation reactions. Additionally, the sol-gel synthesized material shows particles approximately one order of magnitude smaller than those obtained by solid-state. This suggested that the use of nitrates precursors could promote a more refined microstructure compared to particles synthesized by the ceramic method and with the undoped compound.

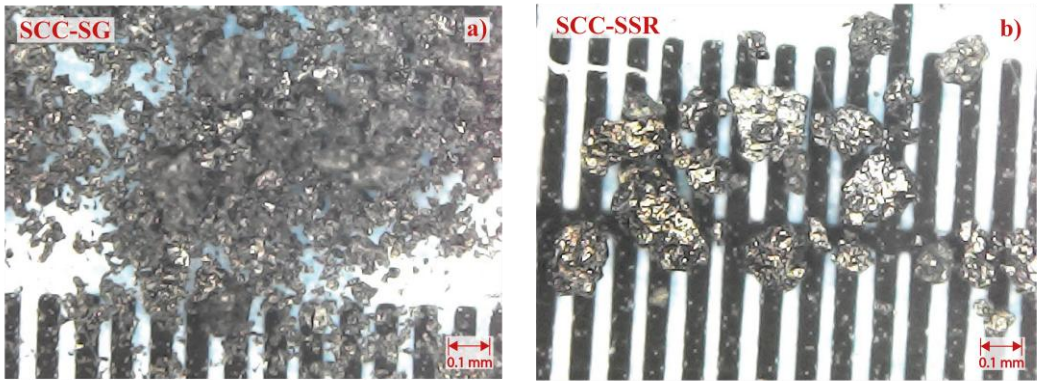

Figure 3: Digital microscopy images of $SrCuO_2$ particles synthesized by (a) sol–gel (SCC-SG) and (b) solid-state reaction (SCC-SSR) prior to thermochemical cycling.

X-ray diffraction patterns for synthesized SCC ($SrCuO_2$) and SCoC ($SrCoO_3$) were estimated in the range of $2\theta = 10°$ to 80° with a scanning step size of 0.020414. The results are shown in fig. 4. The peaks in the RXD pattern of SCC (left) indicate the highly crystalline nature of the synthesized powder. The positions of the diffraction peaks were identified and compared with standard reference patterns $SrCuO_2$: ICOD 381179. The XRD results successfully confirm that it was possible to obtain the target compound, $SrCuO_2$, by using both synthesis methods. In patterns observed in the SCoC sample, it was possible to identify 2 crystalline phases corresponding to $SrCoO_{2.5}$ (ICOD: 480875) and $SrCoO_{2.61}$ (ICOD: 470212), which were obtained during the synthesis of $SrCoO_3$.

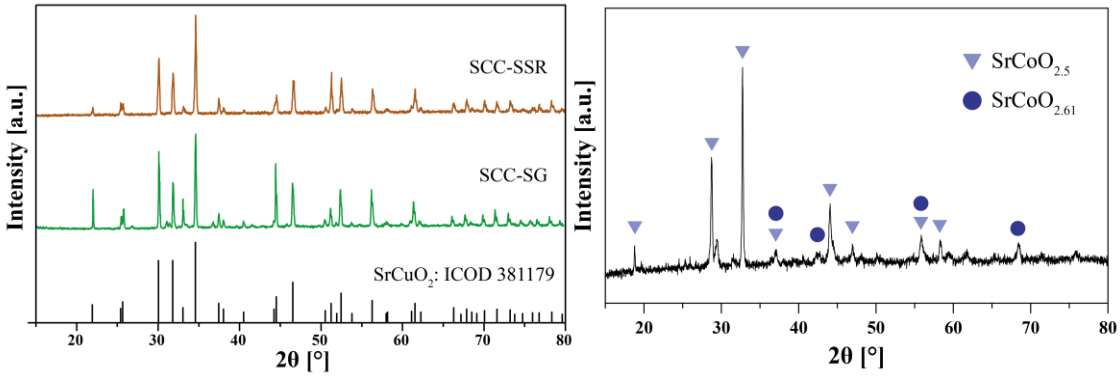

Figure 4: (Left) XRD patterns of $SrCuO_2$ synthesized, (right) XRD pattern of $SrCoO_3$ synthesized.

Thermogravimetric analyses were performed using 85 µL alumina open crucibles. The reference crucible was used empty. A blank test was performed with the empty sample crucible to eliminate the effect of buoyancy on the data obtained from the analysis. A sample of material was heated to 1000 °C at a heating rate of 10 °C/min in an Ar atmosphere (100%, 40 ml/min), cooled to 100 °C at a cooling rate of 30 °C/min, then heated to 1000 °C at a rate of 10 °C/min in a CO_2-Ar atmosphere (50%-50%, 40 ml/min) to determine the decarbonation and carbonation temperatures in the reversible cycles, which were set at 1000 °C and 940 °C, respectively. The curves shown in Fig. 5 indicate a higher conversion in the carbonation stage for materials obtained by the sol-gel method.

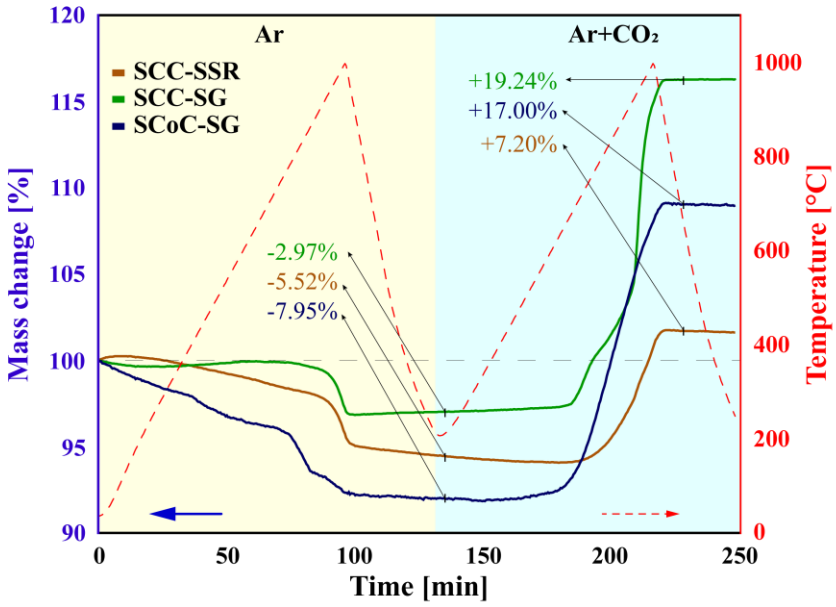

Figure 5: Comparative thermogravimetric analysis between $SrCuO_2$ and $SrCoO_3$.

To evaluate the occurrence or effect of agglomeration or sintering of the materials during reactive cycles, the decarbonation-carbonation cycles were carried out as follows: decomposition was performed in an Ar atmosphere with a flow of 40 ml/min at 1000°C with a heating rate of 20°C/min and an isotherm of 10 min; carbonation was carried out in an Ar-CO_2 (50:50) atmosphere with a flow of 40 ml/min at 940°C with an isotherm of 15 min. In the case of $SrCO_3$, decarbonation was carried out in an atmosphere with a flow of 40 ml/min at 1200°C with an increase of 20°C/min, and carbonation was carried out in an Ar-CO_2 (50:50) environment with a flow of 40 ml/min at 1000°C with a 10 min isotherm, parameters reported for optimal conditions for $SrCO_3$ (Santamaría et al., 2024).

The samples studied showed different performances during 6 cycles, attributable to morphological and textural properties of the samples. The results are shown on (Fig. 6). $SrCO_3$ exhibited an expected behavior because of clustering phenomena during the reactive cycles, which considerably reduces its conversion cycle after cycle (André and Abanades, 2017). In contrast, the composites show a more stable behavior. This fact confirms that synthesis method has a significant effect on the performance and stability of material during the reactive cycles studied and makes these synthesized materials ideal to be used in thermal energy storage processes. SCC-SG had the best performance with respect to the other samples studied and $SrCO_3$, which experienced a 91% drop.

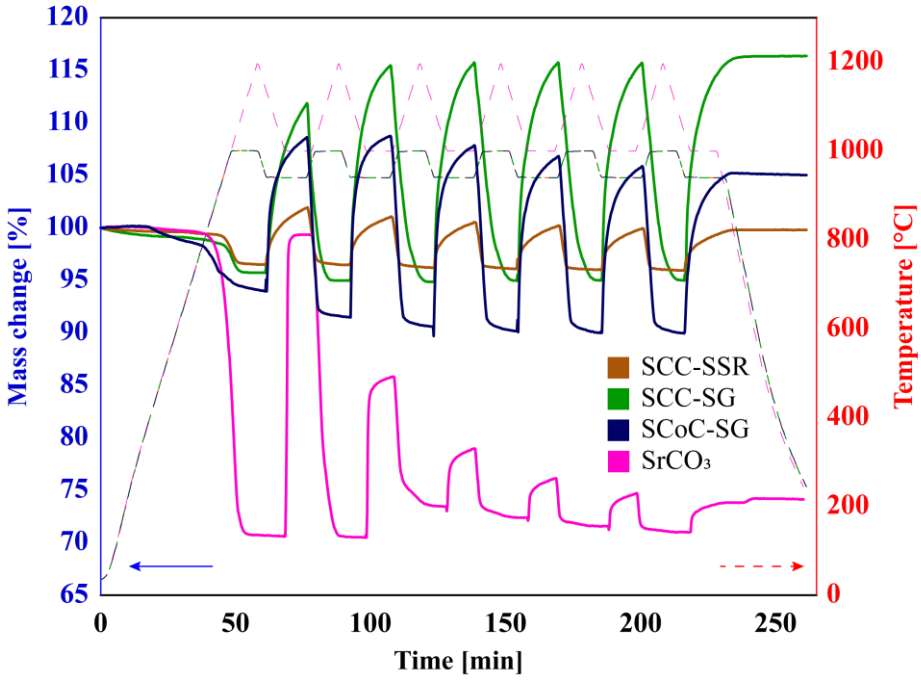

Figure 6: Thermogravimetric analysis for 6 calcination/carbonation cycles

Additionally, the stability was calculated in terms of effective conversion of SrO to $SrCO_3$ (Figure 7). On first cycle, $SrCO_3$ had $X_{SrO}=0.95$, compared to $X_{SrO} = 0.68$ for SCC-SG and $X_{SrO} = 0.23$ for SCC-SSR. Nevertheless, both pure material $SrCO_3$ and SCC-SSR, showed instability and exhibited a significant decrease in conversion after each successive cycle: $X_{SrO}=0.09$ for undoped $SrCO_3$ and $X_{SrO} = 0.16$ for SCC-SSR on 6th cycle. In contrast, for SCC-SG, the conversion was *0.89* (10 times the conversion rate compared to $SrCO_3$). The samples obtained by the sol-gel method show a significant mass gain, indicating a greater conversion of SrO to $SrCO_3$ compared to the sample obtained by the solid-state reaction. The value observed on the first SCC-SG cycle can be attributed to the stabilization of the material and the presence of SrC_2, which reduces the availability of Sr for the carbonation reaction. Although the SCoC-SG sample maintained a higher conversion ($X_{SrO} = 0.74$) value than that of undoped compound throughout the 6 cycles, a tendency toward reduced stability was observed. Since SCC-SSR didn't present good performance, it was considered unnecessary to evaluate the SCoC-SSR.

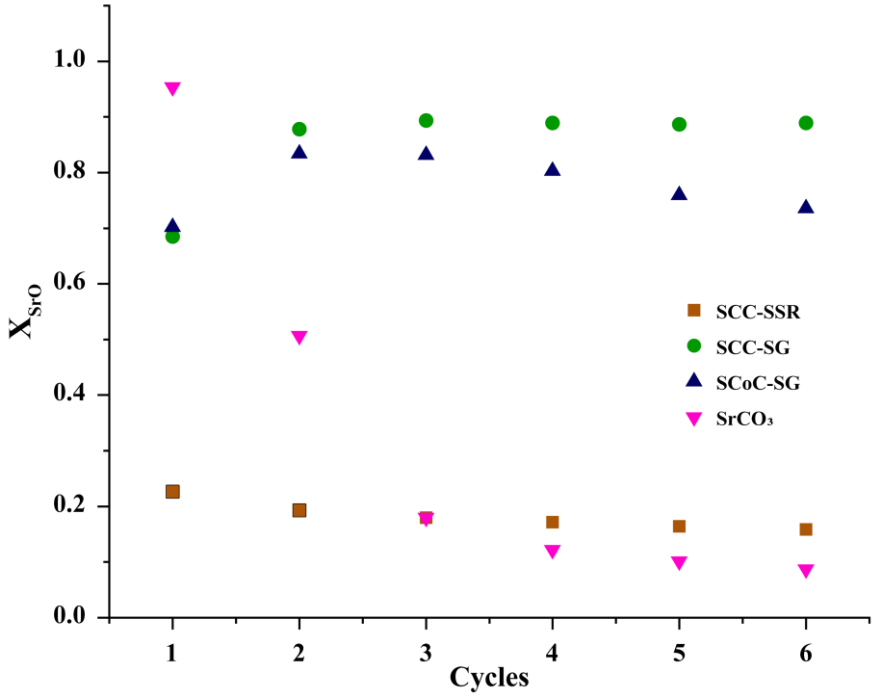

Figure 7: Effective conversion of SrO to $SrCO_3$ during six carbonation–calcination cycles for undoped $SrCO_3$, SCC-SSR (solid-state synthesis), and SCC-SG (sol–gel synthesis). Experiments were conducted under cyclic conditions at 1000 °C for calcination and 940 °C for carbonation.

The gravimetric energy density was calculated for all the materials during 6 cycles, and the results are shown on figure 8. SCC-SG showed a stable value of $D_m = 1135.5$ *kJ/kg* during the last 5 cycles compared to SCC-SSR and undoped $SrCO_3$, which showed a significant drop in capacity with values of $D_m = 203.2$ *kJ/kg* and $D_m = 197.3$ *kJ/kg*, respectively, in the last cycle. In the case of SCoC-SG sample, the value of gravimetric energy density was $D_m=885.9$*kJ/kg.* This finding confirms that the synthesis method has a significant effect on the performance and stability of the material during the reactive cycles, making the synthesized material an ideal candidate for thermal energy storage applications. The results indicate that Cu-doped $SrCO_3$ obtained by sol-gel method is a promising material for thermal energy storage.

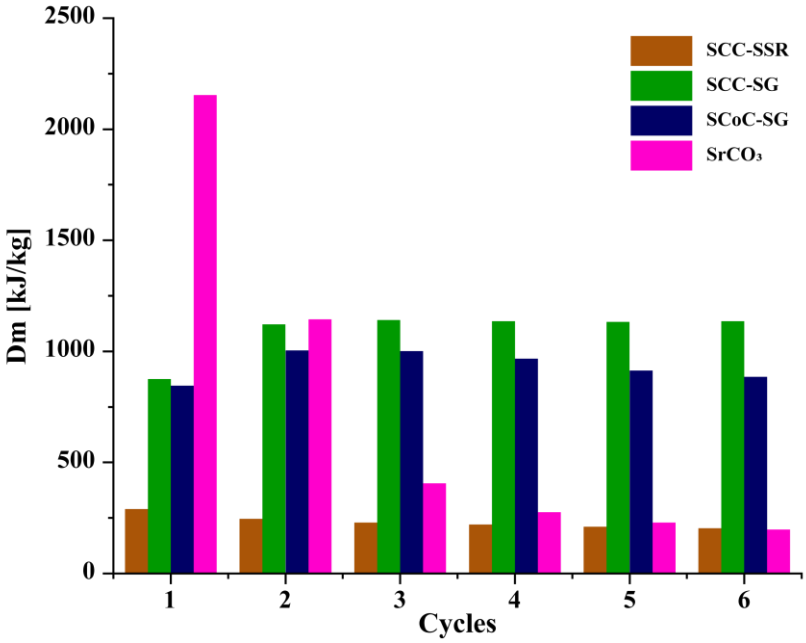

Figure 8: Gravimetric energy density for SCC-SS, SCC-SG and SrCO3 during 6 cycles

The behavior observed in the thermogravimetric analysis can be compared with the SEM images in Fig 9, which show micrographs of the SCC-SG and $SrCO_3$ samples before and after six consecutive calcination/carbonation cycles. In the SCC-SG sample before heat treatment, a porous and more irregular morphology is observed than that observed in Fig. 9c. The evolution of the structure and morphology of SCC-SG after 6 cycles shows that it preserves high porosity, and dispersion and particle size of the material allow greater diffusion of CO_2 within it. In contrast, $SrCO_3$ showed aggregate formation and pore coalescence (Fig. 9d) due to sintering, where the closure of the pore channels decreases the interaction between SrO and the diffused CO_2, causing a reduction in its stability during the reactive cycles.

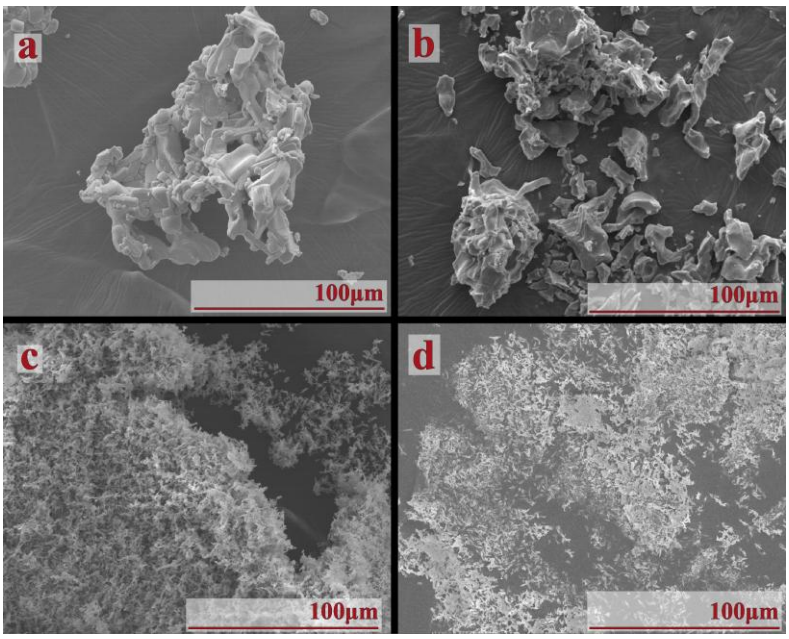

Figure 9: SEM of the materials before and after 6 thermochemical cycles: a-b) SCC-SG before and after, c-d) SrCO3 before and after

The best performance was observed in SCC-SG. It was evaluated under 10-cycles at the same conditions (Fig. 10), which remain to exhibit good stability ($X_{SrO}=0.88$), with a gravimetric energy density of 1120.5 kJ/kg. This behavior indicates an improvement in the performance of $SrCO_3$ as a potential thermochemical material for energy storage. The interaction between strontium and copper during the carbonation stage helps reduce the early onset of clustering phenomena in carbonate formation. These findings create a structure that is attractive for further deep investigation with other dopants to enhance the reactive stability in TCES at high-temperature.

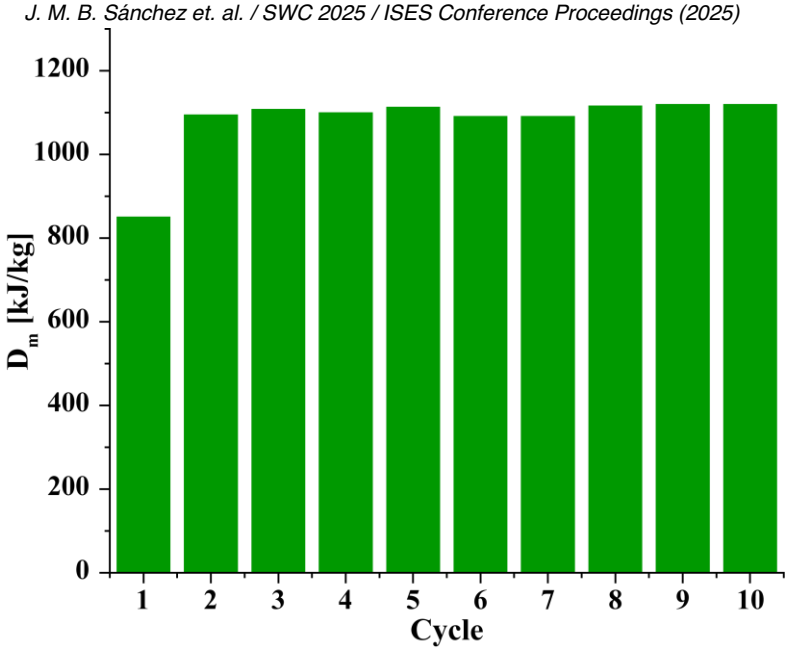

Figure 10: Gravimetric energy density for SCC-SG during 10 cycles

4. Conclusion

The effect of doping and synthesis method on the performance of $SrCO_3$ during thermochemical storage cycles was studied. It was determined that synthesis methods have a significant effect on the stability of the material during reactive cycles, as they delay the occurrence of particle clustering phenomena. The morphology and structural evolution of the materials provide insight into the transformation caused by heat treatment cycles, as well as the potential to expand theoretical studies on the control of reaction kinetics at active sites on the surface and within the material, and gas diffusion during the stage near the completion of maximum conversion in each cycle.

In terms of performance during thermochemical cycles, the materials synthesized by sol-gel exhibited the best behavior and stability. For sample SCC-SG, an effective conversion of 0.89 and a gravimetric energy density of 1135.5 kJ/kg were achieved after 6 reactive cycles, while sample SCoC-SG showed values of X_{SrO} = 0.74 and Dm=885.9 kJ/kg. In contrast, the material synthesized by solid-state reaction method exhibited a decrease in conversion to 0.16 (203.3 kJ/kg), and the undoped $SrCO_3$ reached a final conversion of 0.09 (197.3 kJ/kg). A 10-cycle test was conducted under the same conditions with SCC-SG, which continued to demonstrate stability with a gravimetric energy density of 1120.5 kJ/kg; demonstrating that Cu-doped $SrCO_3$ obtained via the sol-gel method is a promising material for thermal energy storage compared to pure $SrCO_3$ and Co-doped material.

Future work will focus on performing a larger number of cycles (~100) to confirm the stability of SCC-SG and SCoC-SG. To extend the evaluation research to other oxides and use them as strontium dopants, theoretical molecular dynamics studies will be conducted to identify the best options for experimental testing of the synthesized materials, based on theoretical results in thermochemical cycles at high temperatures.

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