High-temperature CO_2 Sorption using Sintering-Resistant CaO/Saffil Fibres Sorbents Prepared by Precipitation Method

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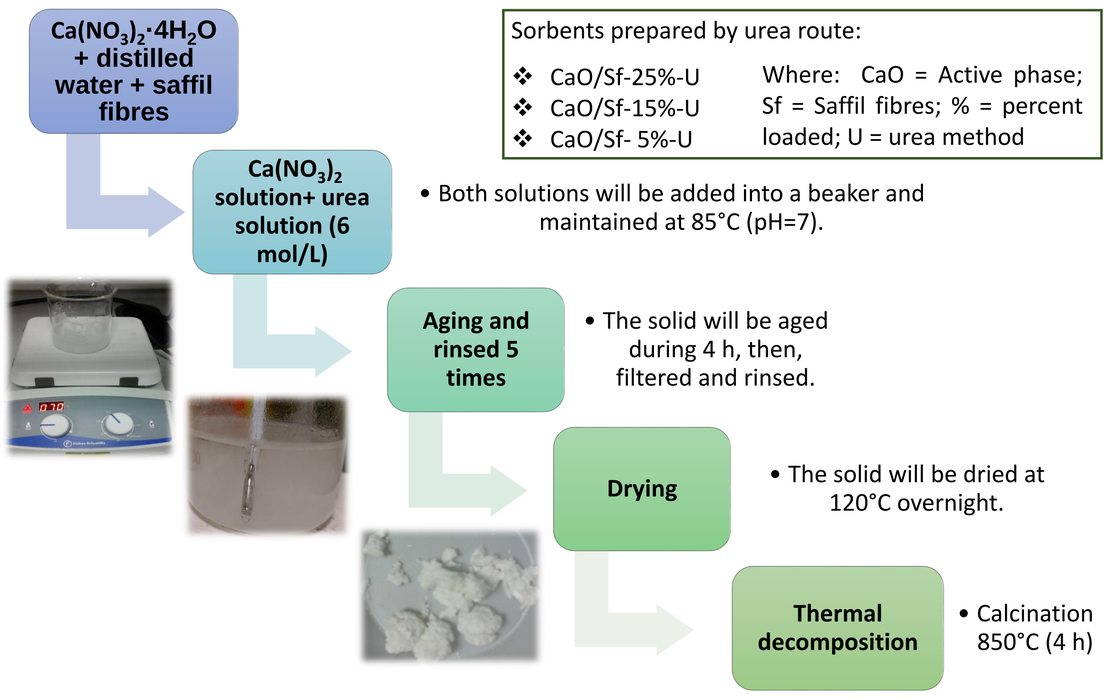
Introduction

Carbon capture and storage (CCS) has emerged as a promising approach for reducing or mitigate anthropogenic CO_2 emissions into the atmosphere [1]. A classification of the carbon capture technologies positioned pre-combustion capture (PCC) as a potential solution for separating CO_2 from a gasification or reforming process [2]. CO_2 removal at high temperature is conducted through solid sorbents that have the ability to be carbonated and regenerated by a simple reversible reaction. CaO has been conceived as the most cost-effective CO_2 sorbent owing to its high carrying capacity in regards to other sorbents such as Li_2ZrO_3 and Li_4SiO_4, etc., thermodynamics and low production cost [3, 4]. However, the main drawback of natural or synthetic CaO is the drastic reactivity loss over the progress of the carbonation and calcination cycles caused by microstructural changes arisen through sintering [5]. In order to cope this effect, this research proposed the use of a refractory material such as the Saffil fibres (δ-Al_2O_3 catalytic grade) to enhance the thermal properties of CaO ad thus inhibit or attenuate sintering.

Methodology

Ca/Sa-%-U sorbents were prepared by precipitation method using urea as precipitant agent. In order to conduct the synthesis method, Saffil fibres, calcium nitrate tetrahydrate ($Ca(NO_3)_2{\cdot}4H_2O$), urea and water were used as the raw materials. The procedure for loading CaO over the periphery of the Saffil fibres is described and schematized intuitively in the Figure shown below.



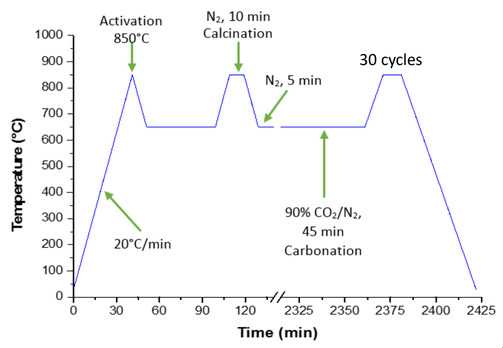
Sorbents prepared by urea route:

- CaO/Sf-25%-U
- CaO/Sf-15%-U
- CaO/Sf- 5%-U

Where: CaO = Active phase; Sf = Saffil fibres; % = percent loaded; U = urea method

Carrying Capacity Evaluation

A thermal profile that includes the operating parameters used for running 30 continuous carbonation-calcination cycles is presented. The conditions used in this program was settled up to evaluate the carrying capacity and thermal stability of the CaO/Sf-%-U sorbents at a harsh scenario.

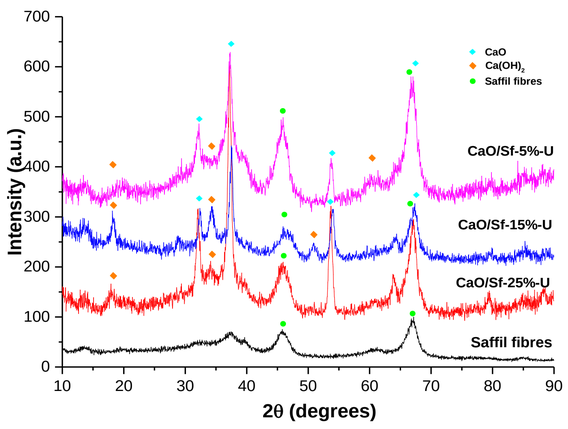


Results

Sorbents Characterization

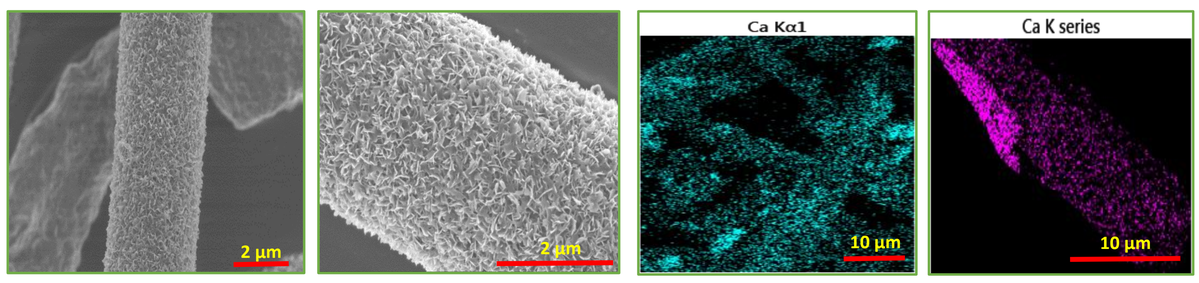
X-Ray Diffraction analysis

XRD patterns of the CaO/Sf-%-U sorbents registered in a 2θ range between 10 to 90°. The phase identification analysis elucidated that CaO and $Ca(OH)_2$ are the crystalline species obtained through the thermal decomposition of the CaO precursor .



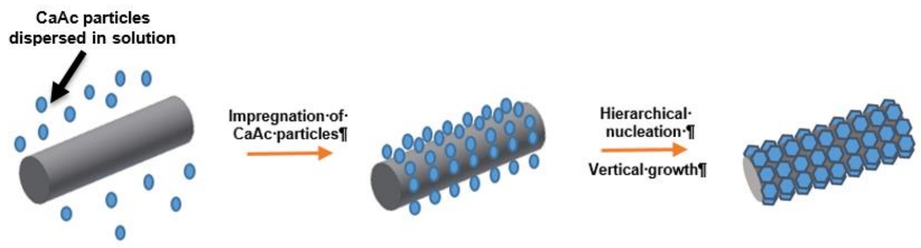
Scanning Electron Microscopy – Energy Dispersive X-ray Spectroscopy (SEM-EDS)

Morphological analysis of the CaO/SF-%-U sorbents loaded with 25% of CaO active phase and EDS mapping aimed to observe the distribution of CaO along the surface of the fibrous support.



Mechanism of Formation of the CaO over the Saffil Fibres

Apparent hierarchical crystallization process (nucleation and vertical growth) of CaO nano-layers over the Saffil fibres surface .

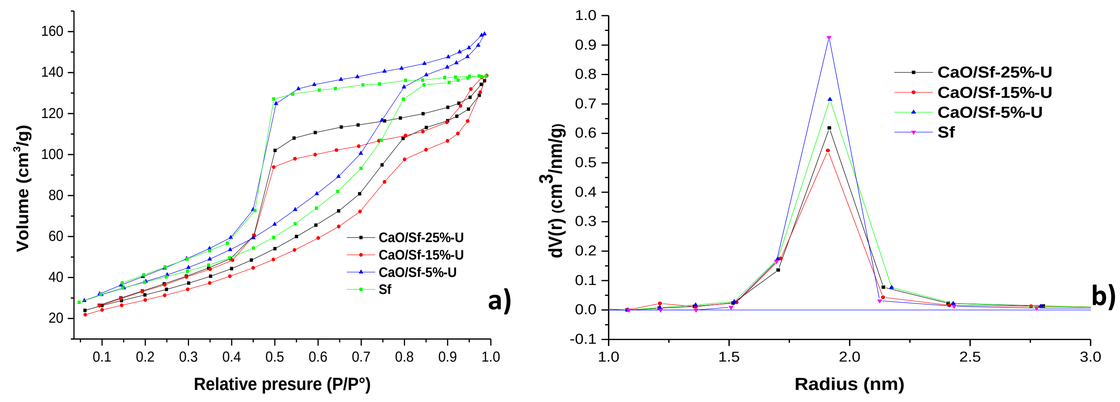


Surface Area and Pore Size Distribution

Specific surface area, pore volume and pore radius values obtained by BET and BJH methods in CaO/Sf-%-U sorbents prepared with different mass contents of CaO active phase.

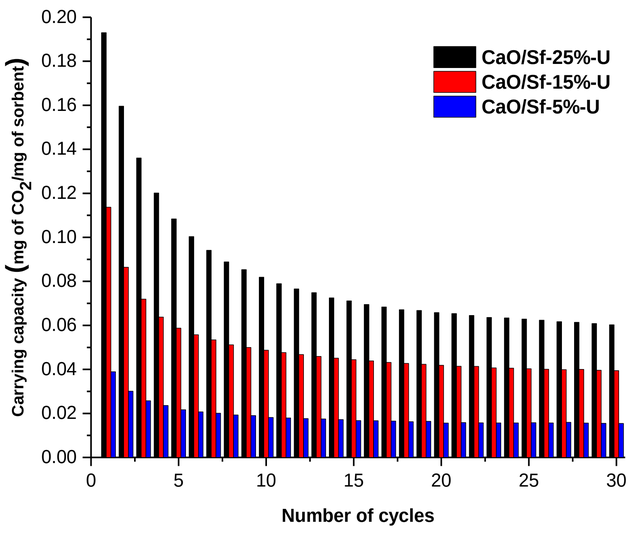
Sorbent	Surface area m^2/g	Pore volume cm^3/g	Pore radius nm
CaO/Sf-25%-U	96.2	0.223	1.909
CaO/Sf-15%-U	112.8	0.241	1.916
CaO/Sf-5%-U	123.2	0.285	1.919
Saffil fibres	138.5	0.249	1.915

Adsorption-desorption Isotherms and pore size distribution curves measured for CaO/Sf-%-U sorbents (**a)** and **c)**) by means of N_2 physisorption at 77 K.



Carrying Capacity Results

CO_2 carrying capacities measured in mg of CO_2/mg of sorbent in the CaO/Sf-%-U sorbents during repeated carbonation-calcination cycles.



Deactivation rate constants (k_1 and k_2) and residual reactivity values found by performing a non-linear curve fitting analysis.

Sorbent	Deactivation rate constant k_1	Deactivation rate constant k_2	Residual reactivity (mg CO_2/mg Sorbent)
CaO/Sf-25%-U	0.45724	0.105177	0.0647
CaO/Sf-15%-U	0.70448	0.10891	0.0411
CaO/Sf-5%-U	0.8600	0.14115	0.0160

Semiempirical equation (1) proposed by Grasa et al. to predict the residual carrying capacity in CaO sorbents.

$$a_N = \frac{1 - a_\infty}{(1 + kN)^n} + a_\infty$$

Double exponential model used to forecast the residual reactivity of the CaO-based sorbents prepared by the precipitation method.

$$a_{cc,N} = A_1 * e^{-k_1 * N} + A_2 * e^{-k_2 * N} + a_r$$

Non-linear curve fitting for the determination of residual carbonation capacities in the CaO/Sf-%-U sorbents considering a long series of cycles.

Conclusions

- The preparation of the sorbents via urea allowed the nucleation and growth of structures with a peculiar morphology such as nanosheets.
- The highest CO_2 capture capacity was attained by the sorbent loaded with 25 wt. % of CaO.
- An enhancement in the thermal stability of CaO was not only accomplished by using Saffil fibres as a sintering inhibitor but also by the CaO morphology acquired by means of the nucleation-growth mechanism.

References

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2. Leung, D.Y.C., G. Caramanna, and M.M. Maroto-Valer, *An overview of current status of carbon dioxide capture and storage technologies.* Renewable and Sustainable Energy Reviews, 2014. **39**: p. 426-443.
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4. Kumar, S. and S.K. Saxena, *A comparative study of CO_2 sorption properties for different oxides.* Materials for Renewable and Sustainable Energy, 2014. **3**(3): p. 1-15.
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