
AIDIC
EFCE
ISCRE25
FLORENCE 2018
BRIDGING
SCIENCE & TECHNOLOGY
The 25th International Symposium
on Chemical Reaction Engineering
20-23 May 2018
Florence, Italy
www.aidic.it/iscre25

Evaluation of ZrO_2 promoted CaO-based sorbent for post-combustion CO_2 capture in a bench-scale fluidized bed reactor

Andy Antzara[1], Aitor Arregi[1,⊥], Eleni Heracleous[2], Angeliki A. Lemonidou[1]*

1 Department of Chemical Engineering, Aristotle University of Thessaloniki, University Campus, 54124 Thessaloniki, Greece; 2 School of Science & Technology, International Hellenic University (IHU), 14th km Thessaloniki – Moudania, 57001 Thessaloniki, Greece; ⊥ Permanent address: *Department of Chemical Engineering, University of the Basque Country UPV/EHU, P.O. Box 644, E48080 Bilbao, Spain*

**Corresponding author: alemonidou@cheng.auth.gr*

Highlights

- $CaO/CaZrO_3$ sorbent shows superior capacity and stability under fluidized bed conditions
- Steam addition improves both the sorption capacity and the stability of the sorbent.
- $CaO/CaZrO_3$ exhibited more than 5 times higher final capacity compared to limestone.
- The sorbent shows good attrition resistance with negligible elutriation of fines.

1. Introduction

Carbonate looping is a promising ex-situ post-combustion CO_2 capture technology based on the reversible gas-solid reaction of CaO with CO_2 [1]. CaO has been thoroughly studied as a CO_2 sorbent because of its high sorption ability [2]. Flue gases at high temperature are separated from CO_2, which is captured in the sorbent bed in the carbonator. After the sorbent's saturation, the material is led to the calciner where it is regenerated at higher temperatures and CO_2 is removed as pure stream, ready for sequestration. However the main drawback of this approach is the high temperature required for regeneration (up to 950°C), which leads to severe sintering of CaO and in rapid deactivation upon multiple cycles [3]. The use of dual fluidized bed reactors is considered the most suitable configuration for the process, however the problems of attrition and mechanical strength loss are common, especially for natural sorbents [4]. The key for successful commercialization of the process is the development of stable sorbents that can undergo multiple cycles without deterioration in their performance. In this work, we report the development of a stable CaO-based sorbent, prepared with an advanced technique and the evaluation of its performance in a fluidized bed reactor.

2. Methods

Material synthesis: The CaO-based sorbent was prepared via a sol-gel auto-combustion route, using citric acid as a combustion agent, $CaZrO_3$ as structural promoter and a constant 66wt% concentration of CaO [5]. After calcination the material was pelletized, crushed and sieved to obtain a particle size of $355 < d_p < 500 \mu m$.

Fluidized bed bench-scale experiments under carbonate looping conditions: The sorption capacity and stability of the sorbent was evaluated in a bench-scale fluidized bed reactor unit under different operating conditions such as fluidization velocity ($U/U_{mf} = 2.5, 3.8$), space velocity (2000-3500 h^{-1}), steam concentration during carbonation and calcination (0 or 20%), temperature of carbonation (650, 680°C) and calcination (750, 800, 920°C) and CO_2 partial pressure (0, 0.8) during calcination. The gaseous feed contained 10% CO_2/3.2%O_2/20%H_2O/N_2, simulating the composition of real flue gases from a natural gas-fired power plant.

3. Results and discussion

The $CaO/CaZrO_3$ sorbent demonstrated superior performance in CO_2 capture in preliminary TGA tests [5], and in fixed bed reactor testing under sorption enhanced chemical looping methane steam reforming conditions [6]. High carbonation conversion was recorded during the pre-breakthrough region (60-85%) under all investigated conditions. Testing of the material in the fluid bed reactor showed that the material maintains fast carbonation rates even at much higher space velocities, leading to a CO_2 capture from the flue gases of over 80% and 75% at carbonation temperatures of 650 and 680°C respectively. The addition of steam led to higher conversions, especially during pre-breakthrough, due to decreased diffusion resistance of CO_2 through the formed layer of $CaCO_3$. In addition, steam significantly enhanced the stability of the sorbent, leading to <16% deactivation after 20 consecutive cycles. The performance of the sorbent was further tested under lower temperature difference between carbonation and calcination (680 and 750°C respectively), a scheme more favourable for utilizing the heat of the highly exothermic carbonation reaction for the thermal demands of the calciner. The material displayed similar carbonation conversion but higher deactivation. Advanced characterization with in-situ XRD showed that even though the sorbent largely retains its initial high surface area and porous morphology, $CaCO_3$ decomposition is incomplete at 750°C, rendering a small fraction of the sorbent inactive for CO_2 capture.

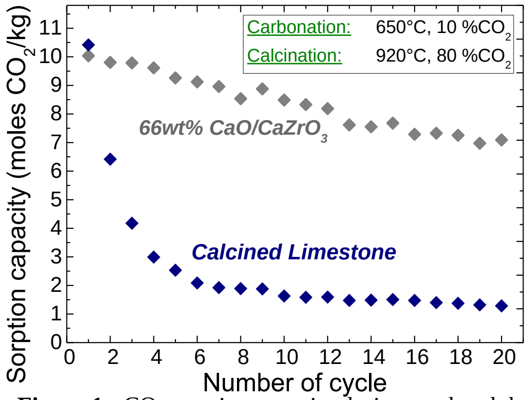

Figure 1. CO_2 sorption capacity during pre-breakthrough period versus number of cycles for limestone and $CaO/CaZrO_3$ sorbent under severe calcination conditions (*carbonation:* *650°C, 10% CO_2/3.2% O_2/20% H_2O/N_2;* *calcination:* *920°C, 20%H_2O/CO_2*).

Finally the material demonstrated an excellent performance, even when harsh calcination conditions were applied (i.e. calcination in high CO_2 partial pressure and higher temperature), maintaining more than 70% of its initial sorption capacity (7.1 moles of CO_2/kg) after 20 cycles (Fig. 1). Compared to a natural limestone that was used as a reference material, the final capacity of $CaO/CaZrO_3$ was almost 5.6 times higher. The synthetic sorbent also exhibited satisfactory mechanical strength. Even though almost 40% of the material shattered into smaller fragments in the presence of steam, attrition was limited to generation of particles in the range of 180-355μm, with no mass loss due to fines elutriating from the bed.

4. Conclusions

A Zr-promoted CaO-based CO_2 sorbent was tested in a fluidized bed reactor unit to determine its performance in cyclic CO_2 capture under various operating conditions. The material exhibited very high carbonation conversion (60-85%) during pre-breakthrough under all investigated conditions, with more than 75% CO_2 removal. The addition of steam in both the carbonation and calcination steps resulted, not only in higher conversions, but also in significantly enhanced cyclic stability with less than 16% deactivation after 20 cycles. Under realistic calcination conditions (920°C and 80% CO_2 concentration) the sorbent maintained more than 70% of its initial capacity, a value almost 6 times higher than natural limestone. Although the cost of the synthetic material would apparently be higher than that of a natural sorbent, the increased sorption capacity and stability, even under severe calcination conditions, are expected to lead to lower amount of material circulating in the fluidized bed reactor and lower sorbent make-up flow, balancing the increased cost.

References

[1] E.J. Anthony, Greenh. Gas Sci. Technol. 1 (2011) 36–47.
[2] C.S. Martavaltzi, A.A. Lemonidou, Ind. Eng. Chem. Res. 47 (2008) 9537–9543.
[3] J.C. Abanades, D.Alvarez, Energy & Fuels, 17 (2003) 308-315.
[4] D.Y. Lu, R.W. Hughes, E.J. Anthony, Fuel Process. Technol. 89 (2008) 1386–1395.
[5] A. Antzara, E. Heracleous, A.A. Lemonidou, Appl. Energy 156 (2015) 331–343.
[6] A. Antzara, E. Heracleous, A.A. Lemonidou, Appl. Energy 180 (2016) 457–471.

Keywords
Calcium looping; CaO-based sorbents; Zr promotion; Fluidized bed reactor.

CURRICULUM VITAE

Personal Information

Name	**Andy Antzara**
Address	Venizelou 52, 56334, Thessaloniki. Greece
Phone	Home number: +302310776911 Mobile number: +30670870035
e-mail address	aantzara@cheng.auth.gr
Nationality	Greek
Date of Birth	21/12/1987

Education

09/2006-11/2012	Diploma in Chemical Engineering, Department of Chemical Engineering, Aristotle University of Thessaloniki Diploma Thesis Title: Comparative feasibility study of a novel process for propylene glycol production and industrial process.
04/2013-today *(expected to receive PhD degree until 02/2018)*	PhD Candidate, Department of Chemical Engineering, Aristotle University of Thessaloniki Thesis Title: Intensification of sorption enhanced steam methane reforming for high-purity hydrogen production.

Short description

Andy Antzara received his Diploma in Chemical Engineering in 2012 from Aristotle University of Thessaloniki. He is currently a PhD student under the supervision of Professor Angeliki Lemonidou at the Laboratory of Petrochemical Technology in the Chemical Engineering Department. The title of his PhD thesis is “Intensifying sorption enhanced-chemical looping steam methane reforming for high purity hydrogen production”.

His research activities involve the development of a CaO-based CO_2 sorbents with high sorption capacity and stability of performance, including the synthesis, morphological and structural characterization, preliminary testing, and evaluation of the materials in bench scale tests under realistic conditions, which can be applied in high temperatures processes such as post-combustion CO_2 capture from power plant flue gases and steam reforming processes in terms of process intensification. On the above areas he has contributed with 7 publications in peer-review international scientific journals and more than 30 presentations in national and international conferences.

Selected publications in peer-review scientific journals

- **A. Antzara**, E. Heracleous, D.B. Bukur, A.A. Lemonidou, *Thermodynamic analysis of hydrogen production via chemical looping steam methane reforming coupled with in situ CO_2 capture*, Int. J. Greenh. Gas Control, 32 (2015) 115–128.
- **A. Antzara**, E. Heracleous, A.A. Lemonidou, *Improving the stability of synthetic CaO-based CO_2 sorbents by structural promoters*, Appl. Energy 156 (2015) 331–343.

- L. Silvester, **A. Antzara**, G. Boskovic, E. Heracleous, A.A. Lemonidou, D.B. Bukur, *NiO supported on* Al_2O_3 *and* ZrO_2 *oxygen carriers for chemical looping steam methane reforming*, Int. J. Hydrogen Energy 40 (2015) 7490–7501.
- **A. Antzara**, E. Heracleous, L. Silvester, D.B. Bukur, A.A. Lemonidou, Activity study of NiO-based oxygen carriers in chemical looping steam methane reforming, Catal. Today 272 (2016) 32–41.
- **A. Antzara**, E. Heracleous, A.A. Lemonidou, *Energy efficient sorption enhanced-chemical looping methane reforming process for high-purity* H_2 *production: Experimental proof-of-concept*, Appl. Energy 180 (2016) 457–471.
- L. Silvester, D. Ipsakis, **A. Antzara**, E. Heracleous, A.A. Lemonidou, D.B. Bukur, *Development of NiO-based oxygen carrier materials: Effect of support on redox behavior and carbon deposition in methane*, Energy & Fuels 30 (2016) 8597–8612.
- **A. Antzara**, A. Arregi, E. Heracleous, A.A. Lemonidou, *In-depth evaluation of a* ZrO_2 *promoted CaO-based* CO_2 *sorbent in fluidized bed reactor tests*, Appl. Energy 333 (2018) 697–711.