International Journal of Economy, Energy and Environment
2019; 4(6): 132-135
http://www.sciencepublishinggroup.com/j/ijeee
doi: 10.11648/j.ijeee.20190406.13
ISSN: 2575-5013 (Print); ISSN: 2575-5021 (Online)

Modification of Waste-derived CaO Using Organic Acids for CO_2 Capture

Azra Nawar[1], Majid Ali[1], Rashid Khan[2], Mariam Mahmood[1]

[1]US-Pakistan Centre for Advanced Studies in Energy (USPCAS-E), National University of Sciences and Technology (NUST), Islamabad, Pakistan

[2]School of Environment, Tsinghua University, Beijing, China

Email address:

Azranawar@gmail.com (A. Nawar), majidali@uspcase.nust.edu.pk (M. Ali), mrashid1987@yahoo.com (R. Khan), mariam@uspcase.nust.edu.pk (M. Mahmood)

[*]Corresponding author

To cite this article:

Azra Nawar, Majid Ali, Rashid Khan, Mariam Mahmood. Modification of Waste-derived CaO Using Organic Acids for CO_2 Capture. *International Journal of Economy, Energy and Environment.* Vol. 4, No. 6, 2019, pp. 132-135. doi: 10.11648/j.ijeee.20190406.13

Received: MM DD, 2019; **Accepted**: MM DD, 2019; **Published**: January 6, 2020

Abstract: Calcium looping is a widely used CO_2 capture technology, where calcium oxide (CaO) is used as a sorbent. However, it has many drawbacks such as expensive raw material and reduction in sorbent capacity over multiple cycles. This study is aimed at developing economic as well as environment friendly sorbents for CO_2 capturing. For this purpose, chicken eggshells were collected from household municipal waste as a CaO sorbent for CO_2 capture. The eggshell sorbent was characterized using different techniques such as SEM-EDS, XRD and TGA. Three different organic acids were used to improve the conversion of eggshell sorbents i.e., lactic, oxalic and tartaric acid. The results showed that one out of three acids i.e., lactic acid (ES LA-10%) showed improved conversion and stability over a period of 20 cycles as compared to other acids. In terms of CaO conversion ES LA-10% displayed the maximum performance of 47.8% and had improved cyclic stability during 20 cycles. Hence, this study showed that modifying sorbent (eggshells) by using acid is a better sorbent in comparison with other natural and synthetic sorbent, therefore reducing waste and cost simultaneously.

Keywords: Eggshell, Organic Acids, CaO Based Sorbent, CO_2 Capture

1. Introduction

Worldwide increase in energy demand and more perception about the environmental conservation have led to search for sustainable energy sources to reduce CO_2 emissions [1]. Carbon capture and storage (CCS) technology is widely utilized in power plants, having major CO_2 emissions, leading to efficient option for CO_2 emissions reduction. During CCS process, CO_2 capturing is the utmost demanding and costly one. Presently, the amine based scrubbing technology is marketable technology for CO_2 Capture. This technology is however, energy intensive, costly consequences due to deterioration of the expensive solvent [2]. Calcium looping cycle consists of two reactors: carbonator (here CO_2 adsorption occurs) and calciner (for CaO regeneration). Carbonator and calciner operate at 650℃ and 900℃ respectively, which follows the following reaction [3, 4]:

$$CaCO_3 \leftrightarrow CaO + CO_2$$

Limestone is recognised as a feasible source of CaO due to widely available and cheaper than other sorbents [5]. For the carbon capturing process to be economically feasible and environmental friendly, regenerability of the sorbent and possess high cyclic stability. However, many studies presented in literature shows that the capability of CaO-based sorbents decreased sharply due to two processes i.e., sintering and attrition [6, 7]. In order to reduce this loss of capacity and to improve the capacity over excessive number of cycles, various methods have been suggested like (a) reactivation through hydration of CaO (b) attaining CaO from new calcium precursors sources (c) utilization of inert support for CaO improving resistance for sintering [8], also including treatment of limestone sorbents with organic acids

[2, 8-10].

In this study, eggshell derived CaO based sorbent were used to capture CO_2 and was characterized using SEM and XRD. It was further modified with organic acids to improve its conversion and stability over multiple cycles.

2. Materials Preparation

Eggshells were collected from the household waste. Impurities were removed from eggshells by washing it with distilled water and drying in open air. Eggshells were then crushed, grinded and sieved to produce powder. Eggshell were calcined at 850℃ for 2h to produce CaO based sorbent. After that three different organic acids were used for modification process which include formic acid (98%), *L*-(-)-malic acid (97%) and oxalic acid. CO_2 and N_2 gases (with 99.8% purity) were used in this study to improve CaO conversion.

2.1. Methodology

The eggshell powder was placed in desiccator to prevent moisture adsorption. Calcination of samples were performed for 2 hours 850°C in a tube furnace using nitrogen gas to obtain calcium oxide. For acid modification of samples: 20 mL (1M) of formic acid and lactic acid with 10% volume was slowly added into the flask with 2.5g of CaO obtained from the eggshell under the fume hood while being stirred.

The sample was heated in a water bath to obtain a consistent sample. The sample was dried at 105°C in an oven. The sample was re-calcined in a tube furnace. The alphabet used for the modified sorbents is as follows: ES-A-10 where ES stand for eggshell based CaO, A is the alphabet of the matching acids and number represents volume fraction (%). The original CaO (ES-CaO) sorbent prepared from eggshell was also used for comparison purposes.

2.2. Sample Characterization

For sample's characterization, following instruments were used. Morphology of the samples were investigated through scanning electron microscopy (SEM) (VEGA 3), using sputter-coating with gold, while energy dispersive X-ray spectrometry (EDS) analysed the compositions of the prepared samples.

The phase composition of the samples was determined using X-ray diffraction (X'pert 1, Philips). 2θ was recorded ranging from 10–80°. The average crystallite size (D) was calculated by Debye-Scherer's formula.

$$D = (k \times \lambda)/(\beta \times \cos\theta) \tag{1}$$

2.3. Cyclic CaO Conversion Test

CO_2 was measured using TGA (Q50). In TGA, 10 mg of sample was placed where it was carbonated at 650°C, 15% CO_2 (balance N_2), 30 min whereas calcination was performed at 850°C, 5 min, N_2.

A whole 20 cycles were performed which were suitable for analysis purposes. The sorbents modified by acids were analysed by means of the same operating conditions as mentioned above. Two parameters were calculated to determine the CO_2 capture performance of the sorbents: CO_2 uptake (Ci, g CO_2 per g sorbent, Eq.2 and CaO conversion rate (Xi, %, Eq.3) [11]:

$$C_i = (m_{\max i} - m_{\min i})/m_{\min i} \tag{2}$$

$$X_i = \frac{C_i \times M_{CaO}}{W_{CaO} \times M_{CO_2}} \times 100 \tag{3}$$

3. Results and Discussion

The XRD diffractogram of the original sorbent i.e. original eggshell (ES- CaO) and acid modified sorbents is presented in Figure 1. The original eggshell (ES CaO) sample shows diffraction peaks index according to the cubic phase with major peaks corresponding to CaO (referred from JCPDS No 37-1497) [12]. The XRD shows the results as reported by Witoon *et al* [8]. All the peaks of the acid modified samples in the pattern resemble to that of CaO (JCPDS 37-1497) development as a result of calcination of respective organic salts [13].

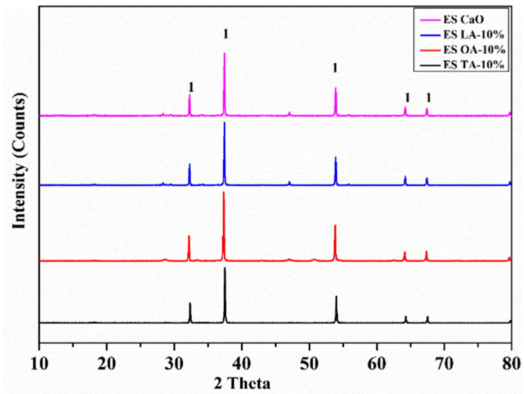

Figure 1. *XRD diffractogram of the fresh original sorbent (ES CaO) and acid modified sorbents.*

Figure 2 shows the CaO conversion of acid modified samples along with un modified eggshell sample (ES CaO). CaO conversion of ES CaO was 84% at first cycle and then decreased rapidly to 29.2% after 20 cycles. Conversion of Acid modified sorbents followed the order: ES TA-10%>ES LA-10%>ES OA-10% at the first cycle with conversion rate, X_i of 57.2%, 47.8% and 33.7%, respectively. ES TA-10% conversion decreased rapidly over the period of 20 cycles with conversion reduces to 5.7% from first cycle. ES OA-10% also followed a similar decreasing trend with conversion reducing to 4.9% after 20 cycles. ES LA-10% maintained the capacity over a period of 20 cycles i.e., 34%.

Among all the sorbents, ES LA-10% maintained the conversion and also the last 4 cycles gave higher conversion than that of original sorbents (ES- CaO). This can be justified as acidification of sorbents leads to a more porous structure, hence resulting in higher conversion rate, whereas the stability of sorbents over the periods can also be improved. Thus on the basis of this analysis, ES LA-10% was nominated as the suitable sorbent for CO_2 capture [14]. Liu *et al* [8] used limestone as a source of CaO along with using of 8 different organic acids to modify it during their study. Lactic acid, Tartaric acid and oxalic acid achieved higher conversion of 62%, 82% and 75% respectively. There was a reduction in conversion over a period of 20 cycles and reduced to around 30-40%. As compared to our studies, lactic acid modified sorbent achieved higher stability over the 20 cycles. Even the modification process in both studies was same but the source of CaO was changed which was the main reason for improved stability.

Historically, different organic acids have been used for last few decades, a large number of organic acids has been studied. Li *et al* [10] used propionic acid for CO_2 capture where modified sorbent had higher conversion than that of original one. Anthony *et al* [9] utilized formic acid to alter it, attaining a higher CO_2 uptake of 0.6 g of CO_2/g of sorbent. Lin *et al* [15] prepared sorbent using acetic acid by stirring at different interval i.e., 12, 48 and 72 hours. Sorbent modified with acetic acid stirring for 24 hours showed the highest CO_2 capacity of 53.8 wt % after 10 cycles. Ridha *et al* [2] used different acids such as acetic, vinegar, formic and oxalic acid, out of which oxalic acid showed 35% conversion as compared to other acids after 20 cycles. Zhao *et al* [16] used acetic acid to modified dolomite, having a conversion of 0.61. Fan *et al* [17] used eggshell as a source of CaO, in which regeneration of sorbent was performed by using acetic acid.

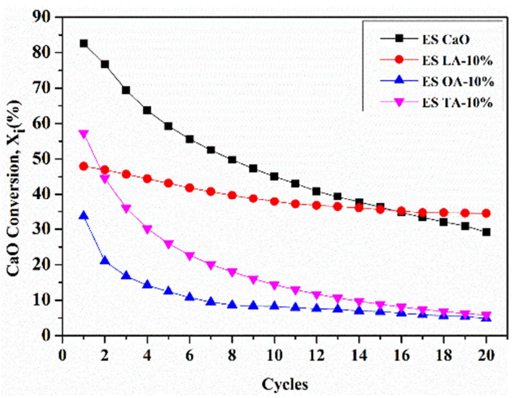

Figure 2. *CaO conversion of sorbents modified by acids under conventional N_2 condition (as mentioned in section 2.3).*

The SEM micrographs of the original sorbent (ES CaO) and Lactic acid modified sorbent (ES LA-10%), before and after 20 cycles are displayed in Figure 3. Figure 3(a) and (c) present the porous morphology of the sorbents before the multi cyclic test i.e., ES- CaO and ES LA-10%.

Morphology of the sorbents after 20 cycles is presented in figure 3(b) and (d). Figure 3(b) shows that there is reduction in pores in case of ES CaO after 20 cycles; however still it had some pores. Figure 3(d) shows the structure of ES LA-10% after 20 cycles with particle agglomerated but still having a porous structure leading to maintaining the conversion over the 20 cycles.

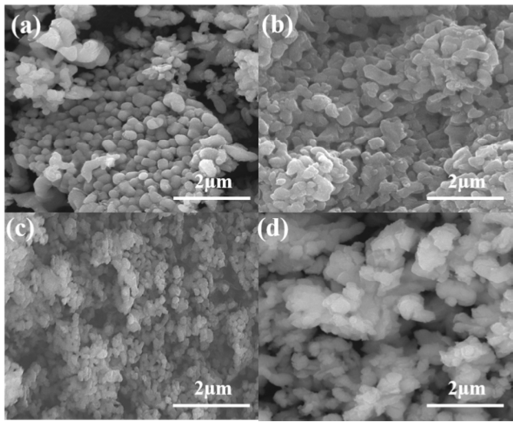

Figure 3. *Surface micromorphology of the sorbents: before 20 cycles (a) ES CaO, (c) ES LA-10% and after 20 cycles (b) ES CaO, (d) ES LA-10%.*

The obstruction of pores in original samples i.e., ES CaO after 20 cycles decreased the route of CO_2 after the multiple cycles. Therefore, the conversion of sorbent decreased rapidly with the extension over cycles. In case of ES LA-10%, after 20 cycles it has been observed that there are many pores as presented in figure 3(d). This type of morphology is benefical for CO_2 capture. Acidification of sorbents made it more porous due to release of acetone and CO_2 [13].

In order to reduce the cost of the acid modified sorbent instead of synthetic acids, waste acids should be used as previously reported by Zhao *et al* [13], Li *et al* [18], Du *et al* [19].

4. Conclusion

The research work aimed to reutilize the waste derived eggshells into environmental friendly and cost effective sorbents for CO_2 capture. CaO was obtained from eggshell by calcining at 850°C for 2h. Three different organic acids i.e., lactic, oxalic and tartaric acid were used to enhance the conversion and cyclic stability of eggshell sorbents.

Structural and morphological analysis demonstrated that Lactic acid modified sorbent achieved higher conversion and stability as compared to original sorbent and sorbents treated with oxalic and tartaric acid. Surface morphology of sorbent also shows that after 20 cycles the sintering phenomena can be seen but still the structure is porous up to some extent, thus maintaining the CaO conversion.

Hence, this research work highlights the potential of eggshell as a substitute to the commercial sorbents for Calcium Looping process (CaL). This will offer the advantage of economic and sustainable method of CO_2 capturing for developing nations.

Nomenclature

K = Scherrer constant

λ and β = wavelength of the electron beam

FWHM = full width at half maximum of the peak

θ = the Bragg's angle of diffraction.

m_{max-i} = maximum weight at cycle *i*

m_{min-i} = minimum weight at cycle i

M_{CaO} and M_{CO2} are the molecular weight of CaO and CO_2 W_{CaO} = CaO weight fraction.

Acknowledgements

We would like to thank USPCAS-E, NUST for providing the experimental facilities to perform this research work.

References

[1] Poortinga, W., et al., Climate change perceptions and their individual-level determinants: A cross-European analysis. Global Environmental Change, 2019. 55: p. 25-35.

[2] Ridha, F. N., et al., Assessment of limestone treatment with organic acids for CO_2 capture in Ca-looping cycles. Fuel Processing Technology, 2013. 116: p. 284-291.

[3] Chen, J., L. Duan, and Z. Sun, Accurate Control of Cage-Like CaO Hollow Microspheres for Enhanced CO_2 Capture in Calcium Looping via a Template-Assisted Synthesis Approach. Environmental Science & Technology, 2019. 53 (4): p. 2249-2259.

[4] Azimi, B., et al., Multicycle CO_2 capture activity and fluidizability of Al-based synthesized CaO sorbents. Chemical Engineering Journal, 2019. 358: p. 679-690.

[5] Jiang, B., et al., An environment-friendly process for limestone calcination with CO_2 looping and recovery. Journal of Cleaner Production, 2019. 240: p. 118147.

[6] Teixeira, P., et al., Enhancement of sintering resistance of CaO-based sorbents using industrial waste resources for Ca-looping in the cement industry. Separation and Purification Technology, 2020. 235: p. 116190.

[7] Pi, S., et al., Investigation of Y2O3/MgO-modified extrusion–spheronized CaO-based pellets for high-temperature CO_2 capture. Asia-Pacific Journal of Chemical Engineering, 2019. 0 (0): p. e2366.

[8] Hu, Y., et al., Structurally improved CaO-based sorbent by organic acids for high temperature CO_2 capture. Fuel, 2016. 167: p. 17-24.

[9] Ridha, F. N., et al., Post-combustion CO_2 capture by formic acid-modified CaO-based sorbents. International Journal of Greenhouse Gas Control, 2013. 16: p. 21-28.

[10] Sun, R., et al., Enhancement of CO_2 capture capacity by modifying limestone with propionic acid. Powder Technology, 2013. 233: p. 8-14.

[11] Zhao, M., et al., Zirconia incorporated calcium looping absorbents with superior sintering resistance for carbon dioxide capture from in situ or ex situ processes. Sustainable Energy & Fuels, 2018. 2 (12): p. 2733-2741.

[12] Yin, X., et al., Biodiesel production from soybean oil deodorizer distillate usingcalcined duck eggshell as catalyst. Energy Conversion and Management, 2016. 112: p. 199-207.

[13] Li, Y., et al., Modified CaO-based sorbent looping cycle for CO_2 mitigation. Fuel, 2009. 88 (4): p. 697-704.

[14] Ridha, F. N., et al., Pelletized CaO-based sorbents treated with organic acids for enhanced CO_2 capture in Ca-looping cycles. International Journal of Greenhouse Gas Control, 2013. 17: p. 357-365.

[15] Lin, K. H., et al., Acidic Treatment of CaO-Based Materials for Medium-High Temperature CO_2 Capture. Key Engineering Materials, 2015. 656-657: p. 18-22.

[16] Li, Y.-j., et al., Cyclic calcination/carbonation looping of dolomite modified with acetic acid for CO_2 capture. Fuel Processing Technology, 2008. 89 (12): p. 1461-1469.

[17] Sacia, E. R., et al., Synthesis and Regeneration of Sustainable CaO Sorbents from Chicken Eggshells for Enhanced Carbon Dioxide Capture. ACS Sustainable Chemistry & Engineering, 2013. 1 (8): p. 903-909.

[18] Li, Y., et al., CO_2 capture efficiency and energy requirement analysis of power plant using modified calcium-based sorbent looping cycle. Energy, 2011. 36 (3): p. 1590-1598.

[19] Ni, C., et al., Facile recovery of acetic acid from waste acids of electronic industry via a partial neutralization pretreatment (PNP) – Distillation strategy. Separation and Purification Technology, 2014. 132: p. 23-26.