Physicochemical characterization of the performance of acidified modified eggshell cyclic adsorption of CO2

Hanhan Cheng1a*, Dehong Gong1b*, Ting Zhao1c*, Tingyi Wang1d*, Song Jiang1e

1 Electrical Engineering College, Guizhou University, GuiYang 550025, China

a*1451957862@qq.com, b*dhgong@gzu.edu.cn, c*1029994134@qq.com,
d*562424711@qq.com, e3242200143@qq.com

Abstract - The CO2 calcium based adsorbent was prepared by using citric acid monohydrate, L(+)-tartaric acid, glacial acetic acid and L(-)-malic acid modified eggshell. The cyclic calcination/carbonation reaction of the adsorbent before and after modification was carried out by thermogravimetric analyzer to investigate the attenuation characteristics of the cyclic CO2 absorption performance of the calcium-based adsorbent after modification. XRD, N2 adsorption analysis and other methods were used for physical and chemical characterization. The phase composition, morphology, specific surface area and porosity of the acidified calcium based adsorbent were investigated. The results showed that: during 20 cycles of calcination/carbonation after 900 °C pre-calcination, the maximum carbonation conversion of CIES900 modified with citric acid is significantly higher than that of the previous adsorbent, and its maximum carbonation conversion is 90.7%. The L(-)-malic acid modified adsorbent MAES900 significantly enhanced the carbonation cycle stability of the adsorbent before modification, and the cycle stability reached 92.9%.

1. Introduction

According to the latest information released by the World Meteorological Organization (WMO), the global average temperature in 2018 was 0.38°C higher than the 1981-2010 average and about 1°C higher than the pre-industrial average. The last five years (2014-2018) were the five warmest years since complete meteorological records began. The main cause of greenhouse effect is the emission of greenhouse gases such as CO2 produced by burning fossil fuels[1-2]. Since the 1980s, the scientific community's understanding of climate change has been deepening. The IPCC has issued five assessment reports, each more certain than the last that man-made activities are the main cause of global climate change[3]. Currently, there are three main routes of CO2 capture technology, which are pre-combustion capture technology, oxygen-rich combustion technology and post-combustion capture technology[4-6]. Among them, the post-combustion capture technology theory is mature and has a wide range of technical adaptability, mainly including absorption[7-8], adsorption[9], membrane separation[10-11] and low temperature distillation[12].

Calcium-based adsorbents are the most potential adsorbents in current carbon dioxide capture technologies[13]. In the process of cyclic calcination/carbonation reaction of calcium-based adsorbent, when the calcination temperature is greater than the corresponding Tammann temperature[14], the calcium-based adsorbent will be sintered at high temperature, particles will agglomerate, porosity will be reduced, collapse and blockage will occur, and CO2 will be prevented from entering the adsorbent, resulting in a decrease in carbonation conversion rate. A large number of scholars have studied the modification of calcium-based adsorbents, mainly including high temperature pretreatment, hydration...
activation, doping of high temperature resistant inert carriers and acidification\cite{15}. Manovic et al.\cite{16} found that the carbonation conversion rate of the heat-treated adsorbent was twice that of the unheat-treated adsorbent after calcination for 24h under the condition of N2 atmosphere at 1000°C. Zeman et al.\cite{17} found that calcium-based adsorbent can improve its cyclic CO2 capture performance by hydration activation after calcination. Hu et al.\cite{18} modified the calcium-based adsorbent with lactic acid, tartaric acid and malic acid, and found that after 26 cycles, the carbonation conversion rate of tartaric acid modified adsorbent was 36%, showing the best adsorption performance. However, the above studies are the intuitive characterization of the modified adsorption properties, and the influence of the microstructure of the adsorbent on the attenuation of cyclic adsorption properties is rarely explored. Based on waste, egg shell as calcium sorbents precursors, based on the sustainable utilization of solid waste recycling\cite{19}, both egg shell calcination rate, low heat resistance, high thermal stability, etc. With four kinds of organic acid modified preparation of CO2, calcium sorbents, egg shell through a variety of means such as XRD and N2 adsorption analysis to the physical and chemical characterization of adsorbent. In order to provide a theoretical basis for high carbonation rate and high stability of CO2, 20 cycles of calcination/carbonation reaction were carried out by thermogravimetric analyzer to study its cyclic adsorption characteristics.

2. Methods and Materials

2.1. Experimental samples and preparation

The egg shells, the precursor of the CO2 calcium-based adsorbent, were taken from a cake factory in Guizhou Province. The egg shells were soaked and cleaned in distilled water before calcination. After surface impurities were removed, the egg shells were placed in a blast drying oven at 105°C for 12 hours. Then take it out and grind it into powder, use a 140-mesh standard sieve to screen out qualified samples for bottling.

An appropriate amount of samples were taken out of the sample bottle and placed in the Muff furnace at 900°C for continuous calcination for 2h. After that, the samples obtained after calcination and cooling were ground, screened and bottled. The samples obtained before modification were labeled as ES900. The selected organic acids are citric acid monohydrate (C6H8O7•H2O), L(+)-tartaric acid (C4H6O6), glacial acetic acid (C2H4O2) and L(-)-malic acid (C4H6O5), all of which are provided by Sinopharm Chemical Reagent Limited The company produces and provides analytical reagents. The use of organic acid to modify the egg shell is used to obtain a CO2 calcium-based adsorbent with high carbonation rate and high stability. Take the citric acid monohydrate modified egg shell as an example. Take out the egg shell powder sample from the sample bottle and put it into a beaker, then add 150ml of distilled water. Ensure that the calcium carbonate in the sample is completely reacted. Place the reacted solution in a constant temperature magnetic stirrer at 100°C for continuous heating for 4 hours to ensure complete acidification. Then the liquid was placed in a quartz crucible in a drying oven at 105°C for 24h, and the dried powder was continuously calcined in a Muffle furnace at 900°C for 2h. After that, the samples obtained after cooling were ground, screened and bottled, and the modified samples were labeled as CIES900. The egg shell was modified by L(+) -tartaric acid, glacial acetic acid and L(-) -malic acid by the same procedure, and named TAES900, LAES900 and MAES900, respectively.

2.2. Carbonation reaction experiment and analysis method

The experiment uses an electronic analytical balance to weigh about 10 mg of sample and place it in an alumina crucible, and place it in a thermogravimetric analyzer STA409PC produced by NETZSCH in Germany. While purging with N2 at a flow rate of 60ml/min, heat the sample from room temperature to 900°C at a heating rate of 20K/min and maintain a constant temperature for 10 minutes, keeping the purging gas conditions unchanged, and at a cooling rate of 20K/min, make the temperature drop from 900°C to 765°C and keep constant temperature for 10 min. Start the cyclic calcination/carbonation experiment. Purge N2 and CO2 during the carbonation process. The purge rate is 60ml/min and 20ml/min respectively. Keep the temperature at 765°C for 40min, then close the CO2 valve and keep it at 765°C.
Calcined for 20 minutes, and cycled calcination/carbonation for 20 times.

The cyclic adsorption performance of the adsorbent can be characterized by carbonation conversion rate and cycle stability. The thermogravimetric analyzer can display and record the quality of the sample in real time. The change in sample quality is used to calculate the carbonation conversion rate and cycle stability of the adsorbent. The calculation formulas are shown in formula (1) and formula (2) respectively.

\[
X_N = \frac{m_N - m_0}{m_0 \times \alpha} \times \frac{M_{CaO}}{M_{CO_2}} \quad (1)
\]

\[
S_N = \frac{X_N}{X_1} \times 100\% \quad (2)
\]

Where \(m_0\) is the mass of the sample after calcination; \(m_N\) is the mass of the NTH sample after carbonation; \(\alpha\) represents the content of CaO after sample calcination; \(M_{CaO}\) is the molar mass of CaO 56g/mol; \(M_{CO_2}\) is the molar mass of CO\(_2\) 44g/mol; \(X_N\) is the carbonation conversion rate of adsorbent in the NTH cycle of carbonation and calcination. \(S_N\) is the cyclic stability of the adsorbent for the N cycle carbonation – calcination sample.

3. Experimental results and discussion

3.1. XRD analysis

The XRD analysis results of the adsorbent before and after egg shell modification are shown in Fig.1. Obvious diffraction peaks appear at \(2\theta = 32.3^\circ, 37.4^\circ, 53.9^\circ, 64.2^\circ\) and \(67.4^\circ\), but the characteristic peak of calcitate does not appear, indicating that all the precursors decompose into CaO after calcination at 900\(^\circ\)C for two hours. According to the principle of three main peaks, the average grain size of each adsorbent was calculated by Using the Scherrer formula. The calculation results are shown in Table 1. It is found from the data in the table that the crystal size modified by organic acid decreases in different degrees. The main reason for this is that the calcination process of organic acid salts will release a large amount of gas, resulting in a smaller crystal size.
Table 1 Crystal size

| Sample name | ES900  | LAES900 | TAES900 | MAES900 | CIES900 |
|-------------|--------|---------|---------|---------|---------|
| Crystal size (nm) | 52.03  | 32.65   | 25.46   | 20.48   | 13.28   |

3.2. \textit{N}_2 adsorption analysis

Natural egg shells are basically non-porous due to their close arrangement. Fig. 2 shows the \textit{N}_2 adsorption isotherms of the adsorbent before and after the high-temperature pre-calcination at \(-196^\circ\text{C}\) before and after the modification. It can be observed from the figure that even at lower pressures, the amount of \textit{N}_2 adsorbed has increased. This is mainly due to the precipitation of \textit{CO}_2 and other gases due to the high-temperature pre-calcination, which changes the pore structure of the egg shell and produces on its surface certain micropores and mesopores. The DFT method was applied to the experimental data of \textit{N}_2 adsorption at \(-196^\circ\text{C}\), and the pore size distribution diagram of the original and modified samples shown in Fig. 3 was obtained. From the figure, it can be seen that ES900 has more pore volume at 1-7 nm, and the modified sample has more pore volume at 7-100 nm. This phenomenon indicates that the sorbent with egg shell as the precursor changes from a non-porous or microporous structure to a mesoporous and macroporous structure after acidification modification. From the pore structure parameter table shown in Table 2, it can be seen that the specific surface area of the adsorbent before and after the modification is: CIES900>MAES900>TAES900>LAES900>ES900, which is the same as
the change trend of the pore volume. This shows that the acidification modification of organic acids further increases the specific surface area and pore volume of the adsorbent, and the acidification modification effect of CIES900 is better.

![Fig.2 N2 adsorption isotherm diagram](image1)

![Fig.3 Pore size distribution chart](image2)

### Table 2 Pore structure parameter table

| Sample     | BET Specific area(m²/g) | DFT Pore Volume(cm³/g) | Average pore size (nm) |
|------------|-------------------------|------------------------|------------------------|
| ES900      | 24.8                    | 0.081                  | 13.1                   |
| TAES900    | 34.3                    | 0.189                  | 22.0                   |
| CIES900    | 39.4                    | 0.247                  | 25.1                   |
| LAES900    | 29.7                    | 0.165                  | 22.2                   |
| MAES900    | 35.5                    | 0.201                  | 22.6                   |

**3.3. Cyclic calcination/carbonation reaction characteristics of different acidified modified egg shell adsorbents**

Fig.4 shows the adsorption performance curve of the adsorbent before and after modification for 20 cycles. The carbonation conversion rate of CIES900 in the first cycle is as high as 90.7%, and the
Carbonation conversion rate is maintained high in multiple cycles. At the twentieth cycle, the carbonation conversion rate dropped to 80.7%, and the cycle stability was 89%. The first cycle carbonation conversion rate of the other three acidified modified samples is a little lower than that of ES900. It can be seen from Figure 9 that the three acidified modified samples such as LAES900, MAES900 and TAES900 have slight particle agglomeration after high-temperature pre-calcination. The carbonation conversion rate is reduced. The carbonation conversion rates of LAES900, MAES900, and TAES900 in the first cycle were 85.1%, 85%, and 82.8%, respectively, and the carbonation conversion rates in the twentieth cycle were 58.7%, 79%, and 62.9%, respectively. The cycle stability was 69%, 92.9%, 76%. From these data, it can be concluded that the adsorbent modified by organic acid acidification has higher cycle adsorption stability than ES900, and the adsorbent modified by malic acid acidification MAES900 shows the highest cycle stability.

![Cyclic adsorption performance graph](image1)

**Fig.4 Cyclic adsorption performance graph**

![The relationship diagram of the maximum carbonation conversion rate](image2)

**Fig.5 The relationship diagram of the maximum carbonation conversion rate**
Fig. 6 shows the relationship between the crystal size and specific surface area and the maximum carbonation conversion rate. It can be seen from the figure that the maximum carbonation conversion rate of the calcium-based adsorbent has no obvious relationship with the specific surface area, and the adsorbent can also be found There is no obvious relationship between the maximum carbonation conversion rate and the size of the crystal particle size. It can be found that the maximum carbonation conversion rate of the adsorbent is caused by a variety of factors.

The carbonation cycle stability of the adsorbent is more important in engineering applications than the amount of CO₂ absorbed. Therefore, in the process of multiple cyclic calcination/carbonation experiments, the adsorbent is physically and chemically characterized, and the crystal size and crystal size of the adsorbent are explored. The relationship between specific surface area and cycle stability is shown in Fig. 6. It can be seen from the figure that the cycle stability of calcium-based adsorbents has a certain relationship with the crystal size and specific surface area. The adsorbent modified by organic acid has a larger specific surface area and a smaller crystal particle size of the adsorbent, the cycle stability can also be improved. This is because the adsorbent has a larger specific surface area and a smaller crystal size to maintain better anti-sintering ability during multiple cycles, inhibit particle agglomeration, not easily causes clogging of pores, and thus have better cycle stability.

4. Conclusion

Through XRD analysis, the CaO diffraction peaks of the adsorbent before and after the organic acid modification are obvious, indicating that the calcination is complete at 900°C and the CIES900 crystal size is the smallest, which makes the adsorption performance higher. BET results show that CIES900 has the largest specific surface area, and the pore size distribution obtained from DFT analysis data shows that CIES900 has the most mesopores.

Through the physical and chemical characterization of the adsorbent before and after the modification of organic acid, it was found that the acid modification can improve the specific surface area of the adsorbent, reduce the crystal size of the adsorbent, improve the sintering resistance of the adsorbent, prevent particle agglomeration and pore blockage, so as to improve the cyclic stability of the adsorbent.

After pre-calcining at 900°C for 20 cycles of calcination/carbonation reaction, the citric acid-modified adsorbent CIES900 has a significantly higher maximum carbonation conversion rate than the adsorbent before modification, and its maximum carbonation conversion rate reaches 90.7%. While the L(-)-malic acid modified adsorbent MAES900 has a significantly enhanced cycle stability up to 92.9% compared with the carbonation cycle stability of the adsorbent before modification.
Acknowledgments
This work was financially supported by the Natural Science Foundation of Guizhou Province, Guizhou Science foundation [2019]1059

References
[1] Manovic V, Anthony E J. Screening of binders for pelletization of CaO-based sorbents for CO2 capture[J]. Energy & Fuels, 2009, 23(10): 4797-4804.
[2] Aminu MD, Nabavi S A, Rochelle C A, et al. A review of developments in carbon dioxide storage[J]. Applied Energy, 2017, 208: 1389-1419.
[3] Wang T, Yu W, Le Moullec Y, et al. Solvent regeneration by novel direct non-aqueous gas stripping process for post-combustion CO2 capture[J]. Applied Energy, 2017, 205: 23-32.
[4] Rubin E S, Rao A B A. Technical, economic, and environmental assessment of amine-based CO2 capture technology for power plant greenhouse gas control[J]. Environmental Science & Technology, 2019, 36(20): 4467-4475.
[5] Wang, Huang, et al. Recent advances in solid sorbents for CO2 capture and new development trends[J]. Energy & Environmental Science, 2014, 7(11), 3478-3518.
[6] Dong Wang. Research progress of CO2 capture and resource utilization technology[J/OL]. Chemical Environmental Protection: 1-4[2021-07-02]. http://kns.cnki.net/kcms/detail/11.2215.X.20210617.1511.008.html
[7] Jie Xiong, Haibo Zhao, Zhaohui Liu, Chuguang Zheng, Meng Chen. Technical-economic evaluation of O2/CO2 circulating combustion system and MEA adsorption system based on thermo-economics[J]. Journal of Engineering Thermophysics, 2008(10): 1625-1629.
[8] Wu S F, et al. Behavior of CaTiO3/nano-CaO as a CO2 reactive adsorbent[J]. Industrial & Engineering Chemistry Research, 2010, 49(6): 2701-2706.
[9] Valverde J M, Perejon A, et al. Enhancement of fast CO2 capture by a nano-SiO2/CaO composite at Ca-looping conditions[J]. Environmental Science & Technology, 2012, 46(11): 6401-6408.
[10] Wilfredo, Anja, et al. CO2-Phlic polymer membrane with extremely high separation performance[J]. Macromolecules, 2010, 43(1): 326-333.
[11] Antzara A, Heracleous E, Lemonidou A A. Improving the stability of synthetic CaO-based CO2 sorbents by structural promoters[J]. Applied Energy, 2015, 156: 331-343.
[12] S Langè, Pellegrini L A. Energy analysis of the new dual pressure low-temperature distillation process for natural gas purification integrated with NGVs recovery[J]. Industrial & Engineering Chemistry Research, 2016: acs.iecr.6b00626.
[13] Shengping Wang, Hui Shen, Shasha Fan, Xinbin Ma. Research progress of solid carbon dioxide adsorbent[J]. Chemical Industry and Engineering, 2014, 31(01): 72-78.
[14] Aihara M, Nagai T, Matsushita J, et al. Development of porous solid reactant for thermal-energy storage and temperature upgrade using carbonation/decarbonation reaction[J]. Applied Energy, 2001, 69(3): 225-238.
[15] Yanxia Guo, Yiqi Geng, Biao Fan. Research progress on the capture of CO2 by CaO-based adsorbent and its anti-sintering modification[J/OL]. Journal of Fuel Chemistry and Technology: 1-16[2021-07-02]. http://kns.cnki.net/kcms/detail/14.1140.TQ.20210413.0901.016.html.
[16] Manovic V, Anthony EJ. Thermal activation of CaO-based sorbent and self-reactivation during CO2 capture looping cycles[J]. Environmental Science & Technology, 2008, 42(11): 4170-4174.
[17] Zeman F. Effect of steam hydration on performance of lime sorbent for CO2 capture[J]. International Journal of Greenhouse Gas Control, 2008, 2(2): 203-209.
[18] Hu Y, Liu W, Sun J, et al. Structurally improved CaO-based sorbent by organic acids for high temperature CO2 capture[J]. Fuel, 2016, 167: 17-24.
[19] Baláž Matej. Ball milling of eggshell waste as a green and sustainable approach: A review[J]. Advances in colloid and interface science, 2018, 256: 256-275.