



Synthesis of Alkali Metal/CaO Sorbent for CO₂ Capture at Low Temperature

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ARTICLE INFO

Article history:

Received 23 August 2010

Received in revised form

23 September 2010

Accepted 26 September 2010

Available online

26 September 2010

Keywords:

potassium carbonate;
decarbonation process;
Thermogravimetric
Analyser;

ABSTRACT

In order to improve their CO₂ absorption capacity at low temperature, alkali-based sorbents were prepared by impregnation method. It was found that supported CaO modified with a K/Ca molar ratio of 3 kept the most favorable stability and CO₂ uptake capacity among the proposed K₂CO₃-stabilized samples. The result showed that the total CO₂ capture capacity of 3K/CaO was 3.84 mg CO₂/g sorbent at 50°C. The X-ray diffraction (XRD) result revealed the new structure was formed during CO₂ adsorption such as CaCO₃ and K₂Ca(CO₃)₂.

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1. Introduction

Carbon dioxide (CO₂) in the atmosphere is approximately 300 ppm while humans can live in an atmosphere of CO₂ up to 5,000 ppm. After the air is taken into the lung, oxygen will be absorbed and CO₂ will be desorbed. It can cause toxicity to the body when one gets it in large quantity. The accumulation of CO₂ occurs in confined and poorly ventilated spaces, such as in the vault or in diving activities. As a result, the body gets the excess CO₂. This will cause rapid breathing, rapid heartbeat, dizziness, and can be fatal. CO₂ can be removed by various methods such as membrane separation, absorption with a solvent, and adsorption using molecular sieves (Lee, *et al.*, 2009). However, these methods are costly and consume high energy.

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One of the improved techniques for CO₂ removal is the chemical absorption of CO₂ with solid sorbents. The use of solid sorbents containing alkali and alkali-earth metals for CO₂ absorption has been reported in many literatures (Gupta and Fan, 2002; Lee, *et al.*, 2008). Among the materials studied, calcium oxide (CaO) has attracted most attention because of its low cost, high capture capacity, and suitable reaction kinetics. However, the lack of long-term stability, mainly due to the unstable structures upon high-temperature decarbonation is still an important drawback in industrial applications. Currently, many researches focus on the performance improvement of CaO-based sorbents by increasing the porosity and improving the stability. In the past, several studies regarding the efficient chemical absorption over K₂CO₃ supported on carbon (Lee, *et al.*, 2006) employed alkali metal carbonate in CO₂ absorption at low temperatures (50-60°C) with thermal regeneration easily occurring at a low temperature.

One objective of this work was to develop a new solid sorbent for being used to absorb CO₂ at low temperatures below 60°C. The CO₂ capture capacities of several potassium-based sorbents were studied in TGA reactor using multiple tests. The role of support in CO₂ absorption at low temperatures was also investigated. In addition, the changes in the physical properties of the sorbents before/after CO₂ absorption and its mechanism were investigated with the aid of power X-ray diffraction (XRD) and Temperature Program Desorption (TPD).

2. Methodology

2.1 Catalyst preparation

The alkali metal-based sorbent used in this study was prepared by the impregnation method. A typical preparation procedure for the sorbent supported on the calcium oxide (99% CaO, Aldrich) is as follows: 5.0 g of supports were added to an aqueous solution containing 2.5 g of potassium carbonate (K₂CO₃, Aldrich) in 25 ml of deionized water and the percentage weight ratio of K:CaO was studied at 3, 5, 10, 20, and 30, respectively. Then, the content was mixed by using a magnetic stirrer for 24 h at room temperature. The dried samples were calcined in a furnace with N₂ flow for 2 h at 450°C and 750°C. The ramping rate of the temperature was maintained at 3°C/min.

2.2 Characterization of the catalyst

The specific surface area and total pore volume were determined by nitrogen adsorption method at 77 K on the ASAP 2010 analyzer (Micromeritics, USA) using a Burnauer-Emmrtt-Teller (BET) theory. X-ray diffraction (XRD, Bruker D8 advance, USA) was used to find the

chemical composition and the crystallographic structure with Cu α K radiation in an angular range (2θ) and the scanning range from 5° to 80° with 40 mA and 40 kV. The functional groups of components in a mixture and interfacial bonding mechanism of Ca and C were characterized by using Fourier transform infrared spectroscopy (FTIR, Bruker Tensor 27), with the sample mixed in KBr pellet at room temperature, Spectra were got over the range of $400-4,000\text{ cm}^{-1}$

2.3 Reaction study

Carbon dioxide adsorption on the prepared powders was studied using a TGA. The weight losses of the substance were calcined to analyze in a furnace under a N_2 flow (100 mL/min) at 450°C and 750°C . The ramping rate of the temperature was maintained at $3^\circ\text{C}/\text{min}$. Decarbonation/carbonation experiments were conducted with thermogravimetric analyzer (TGA). All the steps of carbonation and decarbonation experiments, sample heating, sample cooling, and gases shifting between CO_2 and nitrogen were programmable. A small amount of sorbent was placed in an alumina crucible and heated to the decarbonation temperatures (50 , 70 and 100°C) at a ramp rate of $20^\circ\text{C}/\text{min}$ under nitrogen with 2-hour temperature maintaining. During the entire process, the sorbent weight and the temperature were continuously recorded.

3. Results and discussion

The calcium oxide sorbents in the present study were subjected to thermogravimetric (TGA) analysis. The thermograms obtained between 30 and 750°C are shown in Figure 1. In general, the TG profiles of calcium oxide exhibit a three-step weight-loss system. Firstly, the weight loss with the temperature range of $30-340^\circ\text{C}$ occurred on account of dehydration. Secondly, the weight loss of adsorbent was changed to about 21% within the temperature range of $380-440^\circ\text{C}$, at which $\text{Ca}(\text{OH})_2$ was complete changed to CaO (Lu, *et al.*, 2006; Karami and Mahinpey, 2012) as expressed in Equation (1).



A little weight of adsorbent was changed within the temperature range of $450-750^\circ\text{C}$ due to the stable structure. This is because the reaction (1) is completed at low temperature.

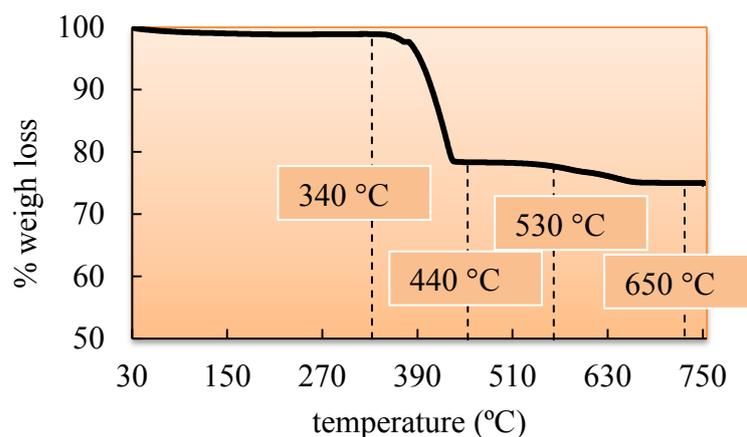


Figure 1: The relationship between weight changes with temperature by TGA.

Therefore, the temperatures were select at 450°C and 750°C to study the adsorbent calcinations before CO₂ adsorption because these temperatures stimulated the structure of the adsorbent. Figure 2 shows that the calcination temperature of 450°C presents the higher ability to absorb CO₂ than that of 750°C about 1 mg/g, because the calcination temperature at 750°C caused the adsorbent breakdown and the structure decimation. This negatively impacts the ability to decrease the absorption. To compare the adsorption capacity of CaO and 30K/CaO, they were calcined at the both calcination temperature mentioned above. Similarly, at the temperature of 450°C, CaO and 30K/CaO have the higher ability to absorb CO₂ than that of 750°C. In addition, at the calcination temperatures of 450°C, 30K/CaO had higher adsorption capacity than CaO by 30% as depicted in Figure 2.

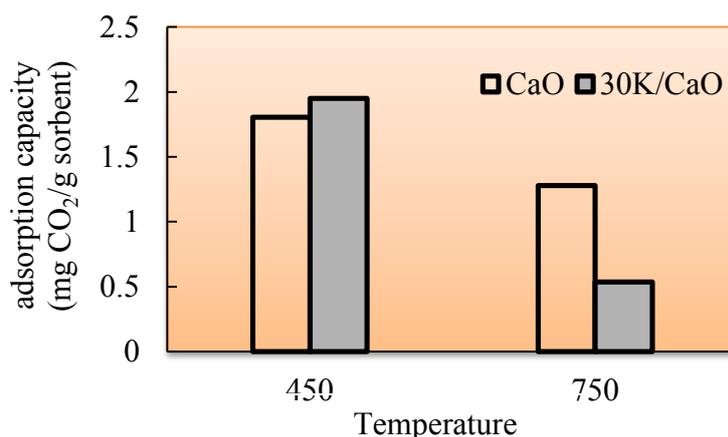


Figure 2: The CO₂ absorption capacity of the sorbents burned at different temperatures

FTIR technique provides information about vibrational state of adsorbed molecules and hence the nature of surface complexes. The FTIR spectra of CaO impregnated with potassium carbonate can be seen from Figure 3, where the bands due to hydroxyl and carbonate are

distinctly displayed in the spectrum. The strong band at $3,643\text{ cm}^{-1}$ corresponds to the O-H bonds from the remaining hydroxide. The bands at $1,417\text{ cm}^{-1}$ and 866 cm^{-1} correspond to the C-O bond. The wide and strong bands at around 418 cm^{-1} and 578 cm^{-1} correspond to the Ca-O bonds (Roy and Bhattacharya, 2011), while the peak found of potassium carbonate at $1,776\text{ cm}^{-1}$ (Hilliard, 2008) were indicative of the increment of functional groups by K_2CO_3 impregnation on CaO.

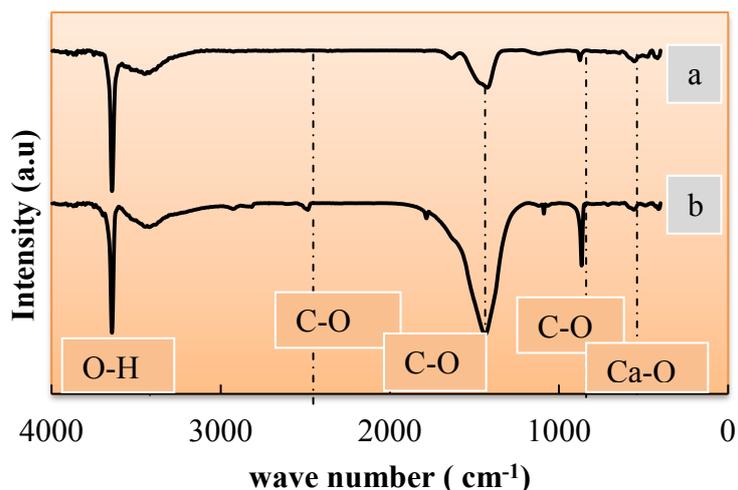


Figure 3: IR spectra of samples: (a) CaO (b) 30K/CaO.

The surface areas of various alkali metal/CaO sorbent were depicted in Table 1. The BET surface area of commercial calcium oxide ($4.96\text{ m}^2/\text{g}$) is lower than that of K/CaO because potassium carbonate entering the structure of CaO increases the surface area. The highest surface area was 3K/CaO which showed a maximum of $24.88\text{ m}^2/\text{g}$. Meanwhile, the increasing amount of potassium carbonate enhanced the surface area. However, an excessive amount of potassium carbonate could damage the mesoporous structure since it aggregated with K_2CO_3 and blocked the pore structure of CaO.

Figure 4 shows the carbonic dioxide adsorption ratio of 3K/CaO, 30K/CaO and CaO at 50°C , 0-120 minutes. It is found that, in this temperature range at the initial 0-3 minutes, there is no CO_2 absorption because CO_2 disseminates into the absorbed surface area. As time increases to 4-10 minutes, the adsorption rapidly occurs and is constant at 10 minutes onwards. The period of 7 minutes gives the highest absorption. In this research, the

absorbents are able to absorb CO₂ quickly within 10 minutes, while the research of Lee, *et al.*, 2009 took the time to absorb more than 100 minutes to reach equilibrium. The 3K/CaO has the absorption ability of 3.84 mg/g, whereas 30K/CaO and CaO have the absorption ability of 1.95 and 1.8 mg/g, respectively, as presented in Figure 4.

Table 1: The surface area of CaO and potassium carbonate supported on CaO

Type sorbent	% wt potassium	BET (m ² /g)
CaO	-	4.96
3K/CaO	3	24.88
5K/CaO	5	22.41
10K/CaO	10	18.97
30K/CaO	30	5.90

It has been found from the experiments that the 3K/CaO sorbent is the best and the burning temperature before the absorption of the catalyst is at the temperature of 450°C. Therefore, 3K/CaO was used to study the effects of temperature for adsorbing carbon dioxide at various temperatures of 50, 70 and 100°C with the time spent in absorbing of 120 minutes.

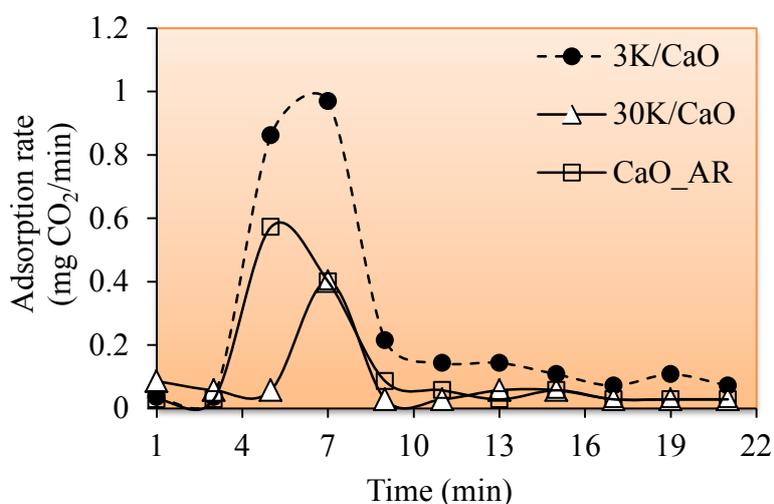


Figure 4: The adsorption rates at time adsorption, calcined in a furnace under a N₂ flow of 100 mL/min at 450°C

The potassium increased ability to absorb carbon dioxide decreased, while 3K/CaO had higher CO₂-absorbing ability than that of 30K/CaO by 50%. Since the addition of potassium in excessive amounts to the catalyst support could cause clogging of the pores of CaO and porosity, the surface area of the adsorbent decreased. Similarly, the surface area decreased with the increasing amount of potassium as shown in Figure 4. For the first four minutes of running, the CO₂-absorbing ability was low; but during 6-20 minutes, the ability increased.

Then, it took 80 minutes to be constant and steady continuously until 120 minutes. As in Figure 5, when comparing the absorption temperature, the best absorption was at 50°C, followed by 70 and 100°C, with the absorbing ability of 3.84, 3.68, 3.66 mg/g, respectively. It has been found that the adsorption temperature of 70°C and 100°C had the decreasing CO₂-absorbing ability to 4.16 and 4.68%, respectively.

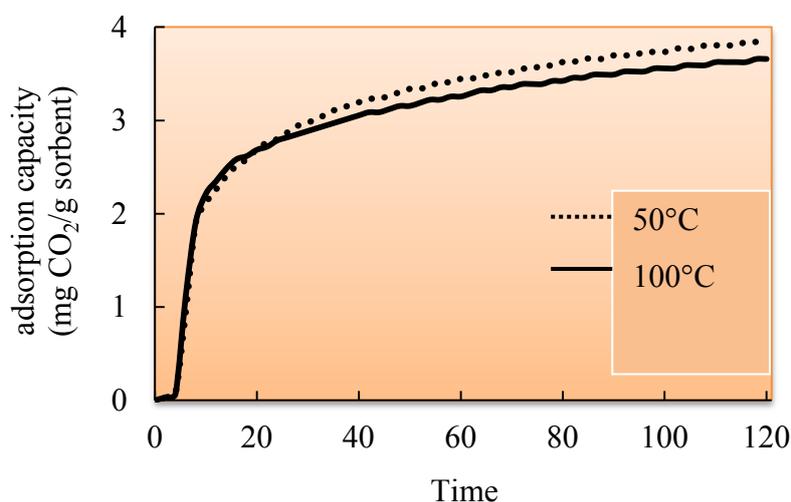


Figure 5: The adsorption capacity at 50°C and 100°C, calcined in a furnace under a N₂ flow of 100 mL/min at 450°C

Due to the breakdown of the bond between the burning structures, the study of Lee, *et al.*, 2009 found that the burning of adsorbent at higher temperatures would decrease potassium calcium carbonate coating on the surface. The results showed that the adsorbents calcined at 450°C would have higher CO₂-absorbing ability than that of the burning temperature of 750°C.

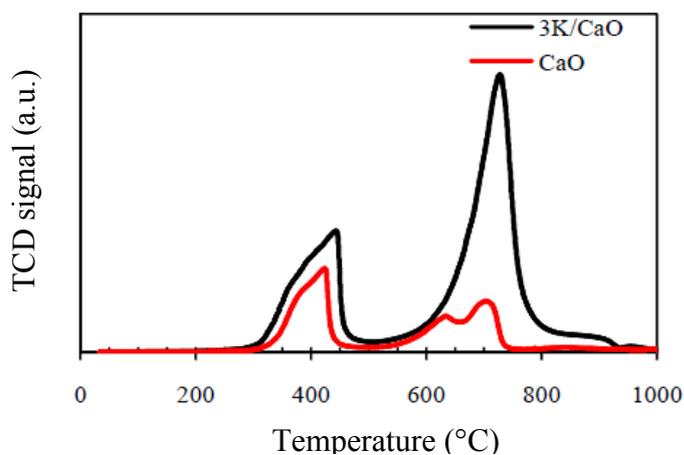


Figure 6: CO₂ Temperature-Programmed Desorption (CO₂-TPD).

From the study of the base sorbent with Chemisorptions Analyzer by TPD, it has been found that the highest temperature causing CO₂ desorption of CaO and 3K/CaO was 450°C, the absorption is due to bonding weak. While at 725°C, the adsorbents were strongly base resulting in the difficulty exothermic adsorption of CO₂ due to the chemical bonding.

The CO₂-TPR graph indicated that the base value of adsorbent of 3K/CaO was higher than that of CaO, showing that carbonic dioxide adsorption was a chemical bond. It could be concluded from TPD curves that CaO and 30K/CaO had 2 period bases. The temperature range of 250-450°C for weak bases and the range of 600-800°C during the period of strong bases were presented in Figure 6. It was found that the strong bases had higher CO₂-absorbing ability than the weak bases up to 2-3 times.

For 3K/CaO, the area under the graph was more than that of CaO by 43%. It could be concluded that the addition of potassium carbonate on supports resulted in increasing base of sorbent. Meanwhile, the absorbing ability increased. The results confirmed that of 3K/CaO has higher carbon-dioxide-adsorbing ability than that of CaO by 52%. The optimum temperature of the sorbent regeneration was at 450°C because at 750°C the structure of the adsorbent was destroyed.

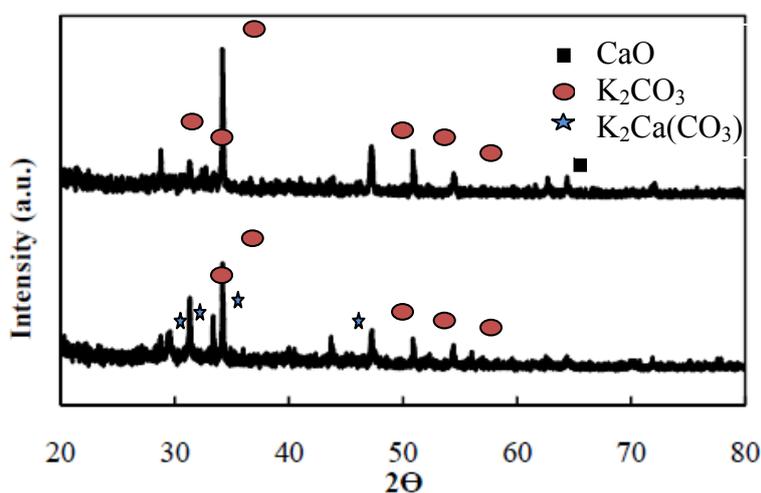


Figure 7: XRD patterns of 30K/CaO sorbents
(a) before and (b) after CO₂ adsorption

Analysis of structural changes in the adsorbent after adsorption showed that the adsorption of CaO formed the new compounds, CaCO₃, following the reaction (2). And after adsorption, 30K/CaO adsorbent also incarnated the new compounds, K₂Ca(CO₃)₂, (present in Figure 7) due to the addition of potassium carbonate which reacted with CaO to support and

absorb carbon dioxide during the process of equation (3).



4. Conclusion

It has been found that K_2CO_3 supported on CaO results in the most promising sorbents for CO_2 . Total carbon dioxide capture capacity of 3K/CaO was 3.84 mgCO_2/g sorbent mostly abundant in all conditions. The enhanced performance could be attributed to the high surface area and large pore volume of the sorbent with the appropriate amounts of K_2CO_3 . For higher K_2CO_3 loadings, the performance did not improve further due to the formation of paracrystalline K_2CO_3 on the CaO support surface. The CO_2 -TPD indicated that there was a chemical reaction between the sorbent and the adsorbate. Considering the regeneration capacity as an important factor in addition to the CO_2 -capture capacity, 3K/CaO could be used as a sorbent that had the potential for CO_2 absorption.

5. Acknowledgements

The authors express their thanks to Department of Chemical Engineering, Faculty of Engineering, and Graduate School of Khon Kaen University for the financial supports.

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Peer Review: This article has been internationally peer-reviewed and accepted for publication according to the guidelines in the journal's website. Note: Original version of this article was accepted and presented at the Third International-Thai Chemical Engineering and Applied Chemistry (TIChE) Conference, jointly organized by Department of Chemical Engineering, Faculty of Engineering, Khon Kaen University and Thai Institute of Chemical Engineering and Applied Chemistry, at Pullman Khon Kaen Raja Orchid Hotel, Khon Kaen, THAILAND, October 17-18, 2013.