Development and Evaluation of Calcium Oxide Absorbent Immobilized on Fibrous Ceramic Fabrics for High Temperature Carbon Dioxide Capture

Man Su Lee^a, D. Yogi Goswami^{b,}, Nikhil Kothurkar^c, Elias K. Stefanakos^b*

^a CO₂ Project, Research Institute of Industrial Science & Technology, San 32 Hyoja-dong, Pohang 790-330, Republic of Korea

^b Clean Energy Research Center, University of South Florida, 4202 E Fowler Avenue Tampa, FL 33620, USA

^c Chemical engineering and Material Science, Amrita School of Engineering, Amrita University, Ettimadai, Coimbatore 641105, INDIA

entropy@rist.re.kr, goswami@eng.usf.edu, k_nikhil@cb.amrita.edu, stefanak@eng.usf.edu

Corresponding author, Tel: (813) 974-0956, Fax: (813) 974-2050, Email address: goswam@eng.usf.edu

ABSTRACT

Calcium oxide is an effective carbon dioxide absorbent, but the cyclic lifetime and durability of the absorbent are key issues for its practicability. When used as pellets, pore plugging and sintering of particles have been found to be the major causes of the degradation of the absorption capacity in cyclic

operation. In order to minimize these adverse effects, a simple and effective immobilization technique of the calcium oxide on fibrous ceramic-based fabrics (alumina and yttria) was developed. The prepared samples were characterized and evaluated by various analytical and experimental tools comprehensively. For a sample with 23 wt% calcium oxide on the alumina fabric, continuous cyclic carbonation conversions of about 75% were achieved over 13 carbonation-calcination cycles under mild calcination condition at 750°C and no CO₂ in N₂. Under more severe calcination condition at 850°C and 20 wt% CO₂ in N₂, the yttria fabric proved superior to alumina as a substrate of calcium oxide for carbon dioxide capture and the reactivity of the calcium oxide absorbent using the yttria fabric was maintained at the same level for 12 cycles.

Keywords: carbon dioxide, capture, calcium oxide, solid absorbent, ceramic fabric

1. Introduction

Carbon dioxide is one of the major greenhouse gases and considered as the major cause of global warming. The emissions from fossil fuel power plants are one of the largest sources of anthropogenic carbon dioxide emissions in the atmosphere. The carbon dioxide from the power plants can be separated from the sources via the following carbon dioxide capture processes: post-combustion, pre-combustion and oxyfuel combustion [1]. Among them, the pre-combustion process is considered as a feasible way to capture carbon dioxide in the clean coal gasification process or steam methane reformation (SMR) to produce hydrogen or electricity.

Conventional coal gasification and steam methane reforming consist of the following reactions.

Removal of carbon dioxide by the use of adsorbents causes a forward shift in the equilibrium of the water-gas shift reaction leading to higher hydrogen yields [2, 3]. Various absorbents have been introduced and studied, but calcium oxide based absorbents seem very promising, considering their operating temperature, pressure and CO₂ capture capacity [4].

The carbonation and calcinations reactions of calcium oxide described below illustrate the capture of CO₂ in the carbonation reaction and the regeneration of the adsorbent in the calcination reaction.

The use of calcium oxide as an absorbent has been and shown to improve the process efficiency while trapping the carbon dioxide in the biomass or coal gasification processes [5-12]. It was reported that the hydrogen yield increased more than five times over the conventional coal pyrolysis [8].

However, substantial changes in specific volume between the carbonate (36.9 cm³/mol) and oxide forms (16.9 cm³/mol) of the adsorbent are induced by these gas-solid reactions [14]. They lead to severe mechanical stresses in the porous adsorbent. Additionally, the calcination is carried out at elevated temperatures, which causes sintering of the particles. Thus during cyclic carbonation-calcination reactions there is a loss in the active surface area due to pore plugging and sintering of the particles of the absorbent. As a result, the performance of the absorbent was found to degrade seriously in the cyclic operation [15, 16]. This degradation should be overcome or minimized for the calcium oxide absorbent to be practical. For that reason, various forms of calcium oxide adsorbents with better structural integrity of the porous structure have been introduced and investigated to improve the cyclic performance of the absorbents for carbon dioxide capture. Some examples are dolomite (CaCO₃·MgCO₃) [17-19], CaO dispersed in porous inert calcium titanate (CaTiO₃) matrix [19], CaO impregnated in porous alumina granules [11] and titanium ethoxide [21], or mixed with mayenite (Ca₁₂Al₁₄O₃₃) [22, 23] or nano-sized alumina (Al₂O₃) particles [24], and core-in-shell catalysis/sorbent [24-26]. Luo et al. [27] suggested the manufacturing process of the CaO sorbent using a sol-gel process and confirmed the better cyclic performance of the sorbent. Most of these attempts showed better cyclic performance than pure calcium

oxide owing to the inert materials that help maintain the structure, but they bring with them other drawbacks such as complexity in preparation, high cost and lower content of calcium oxide in the adsorbent.

Lee et al. [12, 13] have developed and introduced a relatively simple and cost effective procedure to immobilize calcium oxide on the fibrous alumina mat. The new approach showed potential to improve the performance as well as simplify the procedure. In this paper, we have applied the method of immobilization of nano-sized calcium oxide particles on two fibrous ceramic fabrics, alumina and yttria, which act as a support of the calcium oxide adsorbent. The characteristics and cyclic performance of the proposed immobilized calcium oxide on the fabrics were examined with more practical conditions and compared with other results in the literature.

2. Experimental Procedure

Immobilization of calcium oxide on ceramic fabrics

A new process for the immobilization of calcium oxide on a fibrous mat has been introduced earlier [12, 13]. Calcium carbonate (CaCO_3) was selected as a starting material. Nano-sized calcium carbonate powder is inexpensive and readily available. In order to improve the homogeneity and dispersibility of the particles, precipitated nano-particulate calcium carbonate (PCC; average particle size = 70 nm), surface treated with stearic acid was procured from the manufacturer (Specialty Minerals, USA). A suspension of PCC in ethanol was prepared under mechanical stirring (10 min) and the suspension was ultrasonicated subsequently (Fisher Scientific Sonic Dismembrator MDL 100, 10 min) to improve dispersion and reduce agglomeration of the powders. The resultant suspension was dropped onto a dried ceramic fabric (**Felt type ALF-50(alumina) and YF-50(yttria) from Zircar Zirconia, Inc., USA**) using a transfer pipette. The impregnated fabric was dried in air at 100°C for 30 minutes and sintered at 800°C for 12 hours. The preparation steps are shown in brief in Fig. 1.

Figure 1

Characterization

The structure of the impregnated sample was examined under SEM. The observation focused on the structural changes over the cyclic reactions. The composition of the sample was investigated by XRD experiments to confirm the conversion of calcium oxide into calcium carbonate during carbonation and the regeneration of calcium oxide after calcination. The changes in the surface area during cyclic operation of the sample materials were measured by nitrogen adsorption in an AUTOSORB-1 instrument from Quantachrome Instruments.

Cyclic reaction experiment

The cyclic carbonation-calcination reactions were conducted in a Thermogravimetric (TG) Analyzer (TA Instruments Model: SDT-Q600). The cyclic experiments were performed in various conditions. The prepared samples were evaluated under isothermal conditions at 750°C for both carbonations and calcinations or by maintaining different temperatures (700°C and 850°C) for **20-minute** carbonations and **5-minute** calcinations respectively.

For severe calcination, 20 vol. % of carbon dioxide in nitrogen was supplied, while for mild calcination, pure nitrogen was supplied. The reaction conditions for the mild and severe calcinations are summarized in Table 1.

Table 1

The degree of carbonation (X) of the calcium oxide in the sample was defined as moles of calcium oxide reacted with carbon dioxide over moles of calcium oxide initially present (Eq. 5) :

$$X = \frac{n(\text{calcium oxide reacted with } CO_2)}{n(\text{initial calcium oxide})} \quad (5)$$

The moles of calcium oxide reacted with carbon dioxide was calculated from the weight change of the sample measured by the TG analyzer.

3. Results and discussion

The content of calcium oxide on the fabric increased in proportion to the number of the impregnation steps. Two samples with different calcium oxide contents, 23 wt% and 55 wt%, on the alumina fabric, were prepared and their maximum degrees of carbonation under the mild calcination condition were calculated (Fig. 2). The initial maximum degrees of carbonation were comparatively low, but the value increased and then remained constant for subsequent carbonation-calcination cycles. The sample with 23 wt% calcium oxide content attained about 75% degree of carbonation after 13 carbonation-calcination cycles and the sample with 55 wt% calcium oxide reached about 62% degree of carbonation after 10 cycles. The lower degree of carbonation in the sample with higher calcium oxide content may be caused by higher mass transfer resistance in the absorbent due to the high calcium oxide content.

Figure 2

The maximum amounts of reacted calcium oxide in the two samples **based on the total weight of the samples** were compared with those in pure calcium oxide forms from the previous researches in Fig. 3. Empirical curve fits of the experimental test data for various types of calcium oxide under different conditions from previous studies [15, 17, 20, 29, 30] have been reported by Silaban et al. [31] and Abanades et al. [32]. One of the curve fit equations [31] is given below, and it is also reproduced in Fig. 3 without actual experimental data points in order to compare our results with previous other studies.

$$X = 0.83 \times 0.77^N + 0.17 \quad (4)$$

The fitted curve of Silaban et al. dropped steeply with the number of cycles while the values of the samples in the present study gradually increased for the first few cycles, after which it remained stable. The absolute capacities of carbon dioxide capture of the sample with 55 wt% calcium oxide content exceeded that of conventional pure calcium oxide after the sixth cycle. The amount of carbon dioxide capture of the sample with 23 wt% calcium oxide is low due to low calcium oxide content in the

samples but the value of the sample is also expected to **even or** exceed the fitted curve approximately after the 15th cycle at this pace.

Figure 3

The surface areas of the sample with 23 wt% calcium oxide over several cyclic reactions are shown in Fig. 4. Considering the large difference in the molar volumes of calcium oxide and calcium carbonate, it was expected that the surface area would diminish during the carbonation reaction and would be regenerated after the calcination reaction. The fresh sintered sample began with a comparatively low surface area (9.2 m²/g). It decreased to 5.3 (m²/g) after carbonation due to the volume expansion of the particles as expected, but it increased drastically to about 18.3 m²/g after one cycle. After that, values of the surface area of the sample after calcination remained in the range of 16-19 m²/g. Based on the figure, it can be assumed that the big jump of the surface area in the initial stage was caused by the permanent partial structural breakage and void generation owing to the volume contraction from carbonate to oxide form.

Figure 4

Fig. 5 shows X-ray diffraction patterns of the sample (23 wt% CaO) (a) fresh sintered (b) after the 10th carbonation and (c) after the 10th calcination. In the fresh sintered sample, it was observed that the PCC was converted into calcium oxide during the sintering process by X-ray diffraction (XRD) analysis. The XRD data indicate that the samples after sintering and the 10th calcination contain only calcium oxide while calcium carbonate accounts for the major compound along with small quantities of unreacted calcium oxide after the 10th carbonation.

Figure 5

Fig. 6 shows the SEM images of the freshly sintered sample (23 wt% CaO) and the sample after the 10th carbonation and calcination reactions. From images (a) and (b), it can be observed that the calcium oxide particles which have a diameter of about 150 nm, are dispersed and interconnected on the alumina fabric. After the 10th carbonation reaction (c and d), the structure is comparatively closed-packed with

larger particles possibly due to the volume expansion of the particles. The structure after the 10th calcination in the images (e) and (f) seems to consist of more interconnected agglomerates of the calcium oxide particles with high surface area.

Figure 6

Practically, the severe condition for calcination reaction is preferable for carbon dioxide sequestration or utilization since higher concentration of carbon dioxide from carbonated absorbents can be recovered for various applications. However, it was observed that the severe calcination under higher temperature and presence of carbon dioxide pulled down the performance of the calcium oxide absorbents significantly [20-23, 29, 32]. Under the high temperature, it was found that the mixture of calcium oxide and alumina react to form a new compound, $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ [23, 24]. For this reason, yttria fabric was also introduced as a substrate along with alumina fabric. The cyclic carbonation-calcination experiments of the two samples using different fabric substrate materials were conducted under the severe calcination condition (Table 1) and the maximum conversion trends of the samples are illustrated in Fig. 7. As shown in the figures, the maximum degree of carbonation (about 55%) of the sample using yttria fabric as a substrate, showed no sign of degradation over the 12 cycles while those of the sample using alumina dropped by about eight percent from the maximum value (about 59%) after 12 cycles. Judging from these experiment results and the previous literature, it was concluded that the yttria fabric is superior to the alumina fabric as a substrate for calcium oxide absorbent at the severe calcination condition due to the possibility of the formation of $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ by the reaction between calcium oxide and alumina at temperatures over 800°C.

Figure 7

4. Conclusion

A new absorbent system consisting of calcium oxide dispersed and immobilized on fibrous ceramic mats was fabricated via a newly developed immobilization method. The procedure is straightforward and the materials are readily available. Based on the experimental data, it is possible to say that the use

of the fibrous ceramic fabric as a substrate minimized pore closure and particle sintering and preserved cyclic reactivity of calcium oxide compared to pure calcium oxide powder. Under the more severe calcination condition at 850°C and 20 wt% CO₂ in N₂ the cyclic reactivity of the calcium oxide sample using yttria fabric was maintained at the same level through the 12 cycles, while that of samples on alumina substrates deteriorated by about 8%. This indicates the yttria fabric is a superior substrate compared to the alumina fabric for the calcium oxide absorbent.

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Table 1. Mild and severe calcination conditions

	Carbonation			Calcination		
	Temperature	Gas feed	Duration	Temperature	Gas feed	Duration
Mild condition	750°C	20 vol. % of CO ₂ in N ₂	20 min	750°C	Pure N ₂	10 min
Severe condition	700°C	20 vol. % of CO ₂ in N ₂	30 min	Ramp 15°C/min from 700°C to 850°C	20 vol. % of CO ₂ in N ₂	10 min

Fig. 1. Preparation steps for immobilization of calcium oxide on the ceramic fabric

Fig. 2. Maximum conversions of carbonation reaction of two samples loaded different calcium oxide contents, 23 wt% and 55 wt%, with the number of cycles

Fig. 3. Maximum amounts of reacted calcium oxide in the carbonation reactions based on initial sample weight with the number of cycles

Fig. 4. Change of surface area in the sample over the several cyclic reactions

(a)

(b)

(c)

Fig. 5. XRD patterns of the samples (a) fresh, (b) after 10th carbonation, and (c) after 10th calcination (10 cycles)

(a)

(b)

(c)

(d)

(e)

(f)

Fig. 6. SEM pictures for the sample, (a and b) fresh, (c and d) after 10th carbonation, and (e and f) after 10th calcination (10 cycles)

Fig. 7. The cyclic maximum degree of carbonation of the samples using yttria and alumina as a substrate under the severe calcination condition at 850°C and 20 wt% CO₂