Application of core-shell-structured K₂CO₃-based sorbents in post-combustion CO₂ capture: Statistical analysis and optimization using response surface methodology

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Abstract

This study investigates the effect of core-shell-structured supports prepared with alumina as the core on the CO₂ capture performance of K₂CO₃. One main issue in using alumina-based-supported K₂CO₃ is the high moisture uptake of the sorbent, which converts active sites of K₂CO₃ to hydrated by-products with a very low CO₂ capture capacity. To address this issue, the support was shelled with a less hydrophilic material using a core-shell technique. Six core-shell-structured supports were prepared using alumina-based cores (γ -alumina and Boehmite), and TiO₂, ZrO₂ and SiO₂ shells. K₂CO₃ was impregnated on each support and tested in a thermogravimetric analyzer over ten cycles. K₂CO₃/Boehmite/TiO₂ showed the lowest moisture uptake and the highest surface area, and thus the best CO₂ capture performance. A semi-empirical model was developed using a response surface methodology

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to optimize the CO₂ capture capacity of K₂CO₃/Boehmite/TiO₂. The optimal amounts of the operating parameters including carbonation temperature, carbonation time and H₂O-to-CO₂ flowrate ratio, were 61 °C, 40 min and 1.15, respectively. The maximum CO₂ capture capacity at the optimal point was 6.61 mmol CO₂/g K₂CO₃, which is equal to 92 percent of the theoretical value. Therefore, the use of K₂CO₃/Boehmite/TiO₂ at the obtained optimal condition is proposed as a suitable option for post-combustion processes.

Keywords: CO₂ capture; K₂CO₃-based sorbents; core-shell technique; characterization; optimization; kinetic model

1. Introduction

Greenhouse gases (GHGs) have been increasing since the beginning of the industrial revolution, roughly the year 1750 [1]. Among the various GHGs, carbon dioxide is the main contributor to the greenhouse effect due to its huge emission amount [2]. The rapid increase in the concentration of CO₂ would lead to severe environmental issues such as sea-level rise, climate change, ocean acidification and species extinction [3]. According to the Intergovernmental Panel on Climate Change (IPCC), about 75 percent of the increase in the anthropogenic CO₂ emission is attributed to fossil fuel power plants [4]. To mitigate the threatening effect of CO₂, carbon capture and sequestration (CCS) technologies have been employed widely in recent years [5]. CCS provides a temporary solution to alleviate the harmful environmental impacts of fossil fuels until renewable energy technologies prosper [6]. In a CCS system consisted of capture, compression, transport and storage processes; 70-90 percent of the total cost is disbursed in the CO₂ capture unit [7,8]. For the combustion processes, three main CO₂ capture techniques have been proposed, namely, post-combustion, pre-combustion and oxyfuel combustion [9]. Post-combustion is the most commonly used

CO₂ capture technique as it can be readily retrofit into the existing power plants [10]. In this process, CO₂ is separated from flue gas using different methods including adsorption, absorption, membrane separation, hydrate-based separation and cryogenic distillation [11]. Multiple advantages have been reported for the adsorption by solid sorbents including high CO₂ selectivity, high adsorption capacity and low required regeneration energy [12]. Chemical adsorption of CO₂ over alkali-metal-based solid sorbents such as K₂CO₃ (Reaction 1) is a promising method for the selective capture of diluted CO₂ from the huge amount of nitrogen existing in the flue gas [13–15].

To improve CO₂ capture performance, K₂CO₃ is commonly supported by a stable and porous material [16]. Al₂O₃ has been employed frequently as a support due to its high surface area and physical strength [7,16]. The presence of moisture in the inlet gas has been observed to adversely affect the CO₂ capture capacity of Al₂O₃-supported K₂CO₃ [17,18]. The high amount of moisture adsorbed by the supported K₂CO₃ converts the active sites of the sorbent to hydrated by-products having a very low CO₂ capture capacity [18]. The hydration reaction (Reaction 2) occurs in parallel with Reaction 1 during the carbonation process. According to Reaction 2, an increase in the moisture uptake increases the hydrated by-products' formation. Regeneration of the by-products to the original K₂CO₃ requires a temperature of over 300 °C, whereas the regeneration temperature of the carbonated K₂CO₃ is about 150 °C [19,20]. Providing a high regeneration temperature would increase the operating cost of the process. Thus, as an alternative solution, the hydrophilicity of the sorbent should be reduced to lower the moisture uptake and the formation of by-products. One approach to reducing the hydrophilicity is to modify the structure of Al₂O₃ by shelling it with less hydrophilic material and forming a core-shell composite. To the best of authors' knowledge, this is the first study that investigates the effect of core-shell-structured supports on the hydrophilicity of the

supported K₂CO₃. Lee et al. (2006) [21] studied the cyclic CO₂ capture performance of γ -Al₂O₃-supported K₂CO₃ at different regeneration temperatures. They observed the formation of by-products during the carbonation process. To regenerate the by-products to the original K₂CO₃, they had to increase the regeneration temperature to 400 °C, which increases the operating cost of the system. Lee et al. (2013) [22] investigated the effect of alumina's phases on the formation of by-products like KAl(CO₃)(OH)₂ in an alumina-supported K₂CO₃ sorbent. According to their study, sorbents prepared by α -Al₂O₃ showed better regeneration properties compared to γ -Al₂O₃ due to less by-products' formation. α -Al₂O₃-supported K₂CO₃ showed high CO₂ capture performance at a low regeneration temperature of 130 °C. Chool et al. (2014) [23] prepared different phases of alumina by calcining Al₂O₃ at different temperatures including 300, 600, 950 and 1200°C. They found that sorbents calcined at higher calcination temperatures produced less by-products and showed better regeneration properties. To produce more efficient alumina phases, it should be calcined at a high temperature. However, calcination at a high temperature reduces the surface area, which adversely affects the adsorption capacity. For this reason, core-shell-structured supports were proposed in this work to lower the regeneration cost and produce more efficient sorbents with high surface area.

Response surface methodology (RSM) is a useful tool to optimize the effect of operating parameters with the minimum number of experiments [24,25]. RSM evaluates the interaction of operating parameters using an experimental design such as full factorial, central composite and Box Behnken [26]. The experimental points defined by the experimental design are applied to develop a model for the system [27]. Using the model, the response values are predicted at the specific ranges of the variables and the optimal amount of each variable is calculated. Using RSM the combination effect of main operating parameters was investigated

on the CO₂ capture capacity of K₂CO₃/Boehmite/TiO₂ and a model was developed to find the optimum carbonation condition.

To investigate the effect of core-shell-structured supports on the rate of CO₂ adsorption, three kinetic models were applied including pseudo-first order, pseudo-second order and Avrami's models. Avrami's model considers multiple adsorption pathways and is a suitable choice to study complex adsorption mechanisms on the surface of the sorbent [28,29].

The present study investigates the synthesis of efficient core-shell-structured support for use in the CO₂ capture process. The synthesized material was utilized as support of K₂CO₃ by employing an impregnation technique. To the extent of the authors' knowledge, this is the first work that examines the effect of core-shell-structured support in the post-combustion CO₂ capture process. In addition; kinetic analysis, optimization and modelling of the system by RSM have not been investigated in the scientific literature.

2. Experimental section

2.1. Material

γ-alumina and Boehmite were purchased from Sasol company. Potassium carbonate (ACS reagent, ≥ 99.0%), titanium propoxide, tetra ethyl ortho silicate, zirconium butoxide, PEG-PPG-PEG Pluronic® P-123 surfactant, ethanol and acetylacetone were all received from Sigma Aldrich. All materials were used as received.

2.2. Preparation method

Core-shell-structured K₂CO₃-based sorbents were prepared in two steps: first, the support was synthesized using core-shell technique and then K₂CO₃ was impregnated on it. To synthesize core-shell supports, γ-alumina and Boehmite were used as cores; and titanium propoxide,

tetra ethyl ortho silicate and zirconium butoxide were used to prepare shells. Thus, six different core-shell-structured supports such as γ -alumina/TiO₂, γ -alumina/ZrO₂, γ -alumina/SiO₂, Boehmite/TiO₂, Boehmite/ZrO₂ and Boehmite/SiO₂ were synthesized and employed in the preparation of the sorbents.

In the synthesis of the supports, the following amounts of components were used per mole of the shell precursor: 0.05 moles P-123 surfactant, 5 moles deionized water, 40 moles ethanol, 1 mole acetylacetone and 0.02 moles nitric acid. First, ethanol and shell precursor were mixed and stirred for a few seconds. Then, the required amount of P123 surfactant was added and stirred vigorously for 20 mins to obtain a clear solution. Afterwards, acetylacetone was added dropwise to the solution while stirring. A mixture of nitric acid and water was prepared in a separate beaker and added slowly to the solution obtained in the previous step. Using a steel basket, the alumina powder (core) was soaked in the solution for 1 min and dried in an oven for 10 min at 80 °C. The process of soaking and drying was repeated three times to ensure the uniform shelling of alumina. The sample was calcined at 550 °C for 3 hours to get the final support material. K₂CO₃ was impregnated on the obtained material based on 50 wt% K₂CO₃/support using an impregnation method. In this method, 2 gr K₂CO₃ was dissolved in 1.68 ml deionized water and stirred for 5 mins. Afterwards, the support was mixed gradually in the solution. The obtained solution was dried for one day at room temperature and then calcined at 300 °C for 4 hours. The sorbents had a spherical shape with particle size ranging from 5 μ m to 10 μ m.

2.3. Characterization

Pore morphologies of the sorbents were analyzed using scanning electron microscopy (SEM, Phenom ProX Desktop SEM). Elemental composition was determined by energy dispersive X-ray spectroscopy (EDS) in the SEM analyzer. Surface area was calculated by a

micromeritics 2020 volumetric adsorption analyzer using Brunauer-Emmett-Teller (BET) analysis method. In the analyzer, samples were first degassed at 150-450 °C for 2 hours and then analyzed using pressure values ranging from 1 to 760 mmHg. Pore size distribution was calculated using Barrett-Joyner-Halenda (BJH) pore size and volume analysis method.

2.4. Experimental setup and procedure

CO₂ capture capacity of the sorbents was quantified in a Thermmax 500 thermogravimetric analyzer (TGA), as shown in Figure 1. The sorbents were analyzed over ten carbonation and regeneration cycles. For carbonation, N₂, H₂O and CO₂ were the inlet gases and the temperature varied between 40 °C and 80 °C. N₂ and H₂O flowrates were fixed at 152.85 std ml min⁻¹ and 3.40 std ml min⁻¹, respectively. The CO₂ flowrate varied between 1.70 std ml min⁻¹ and 6.80 std ml min⁻¹ to provide different H₂O-to-CO₂ flowrate ratios. The ratios were defined in three levels including 0.5, 1.25 and 2 based on Box Behnken Design (BBD) of experiments. For regeneration, the sample was subjected to a stream of pure N₂ at 150 °C. To provide H₂O in the inlet gas, nitrogen gas was humidified using a water bubbler. A psychrometric chart was used to obtain relative humidity of nitrogen and flowrate of H₂O. The composition of CO₂ in the outlet gas was monitored using a mass spectrometer (MS) to calculate the mass of adsorbed CO₂. The total weight change due to the adsorption of CO₂ and H₂O was calculated using the TGA data. The amount of adsorbed H₂O in each cycle was calculated by subtracting the amount of adsorbed CO₂ from the total weight change.

Figure 1. Schematic of the experimental setup

2.5. Experimental design and mathematical models

The optimal amounts of the main operating parameters, namely, carbonation temperature, carbonation time and H₂O-to-CO₂ flowrate ratio were found using a model developed by response surface methodology (RSM). For this purpose, seventeen sets of experiments were designed in three levels (coded as -1, 0 and +1) by BBD, as shown in Table 1.

Table 1. Experimental ranges and levels of variables for CO₂ capture capacity of the sorbent

Variables	Ranges and levels		
	-1	0	+1
Carbonation temperature (°C, A)	40	60	80
Carbonation time (min, B)	15	30	45
H ₂ O-to-CO ₂ flowrate ratio (C)	0.5	1.25	2

By conducting the experiments at BBD experimental points, a second-order equation was developed by Design Expert software Version 9.0.3.

$$Y = \beta_0 + \beta_1 A + \beta_2 B + \beta_3 C + \beta_{12} AB + \beta_{13} AC + \beta_{23} BC + \beta_{11} A^2 + \beta_{22} B^2 + \beta_{33} C^2 \quad (3)$$

Where, Y is the predicted CO₂ capture capacity (mmol CO₂ per g K₂CO₃), and A, B and C are carbonation temperature (°C), carbonation time (min) and H₂O-to-CO₂ flowrate ratio, respectively. $\beta_0, \beta_1, \beta_2, \beta_3, \beta_{12}, \beta_{13}, \beta_{23}, \beta_{11}, \beta_{22}$ and β_{33} are the coefficient parameters.

2.6. Kinetic model

Adsorption kinetic was evaluated using pseudo-first order, pseudo-second order and Avrami's kinetic models according to the following equations:

$$q_t = q_e [1 - \exp(-K_1 t)] \quad (4)$$

$$q_t = \frac{K_2 q_e^2 t}{1 + K_2 q_e t} \quad (5)$$

$$q_t = q_e \left[1 - \exp\left(-\frac{(K_a t)^n}{n}\right) \right] \quad (6)$$

Where, q_t and q_e are the CO₂ uptakes (mmol CO₂ per g K₂CO₃) at time t (min) and equilibrium, respectively; and K_1, K_2, K_a and n are the models' constants.

Avrami's kinetic model has been applied successfully in different processes, including adsorption of Hg²⁺ on chitosan membranes, adsorption of anionic dyes on a silica-based material, adsorption of reactive dyes on chitosan microbeads and adsorption of CO₂ on solid sorbents [29,30]. The main advantage of the model is its ability to interpret complex systems having multiple adsorption mechanisms [29,31,32].

3. Results and discussion

3.1. Carbonation performance

According to Reaction 1, the ideal molar ratio for the adsorbed H₂O-to-CO₂ is one. Table 2 shows the adsorbed H₂O-to-CO₂ molar ratio for the synthesized sorbents in the first carbonation cycle. K₂CO₃/γ-alumina/TiO₂ showed the lowest ratio, which was attributed to less hydrophilicity of TiO₂ than the other shells. The contact angle of TiO₂, SiO₂ and ZrO₂ with water was reported 132°, 75° and 49°, respectively [33]. Larger contact angles (>90) correspond to lower hydrophilicity [33,34]. Hence, TiO₂ has the lowest and ZrO₂ the highest hydrophilicity among the shells used in the preparation of the sorbents. As seen in Table 2, K₂CO₃/γ-alumina/TiO₂ and K₂CO₃/Boehmite/TiO₂ showed the lowest adsorbed H₂O-to-CO₂ molar ratio among the sorbents. The adsorbed H₂O-to-CO₂ molar ratio for K₂CO₃/γ-alumina/ZrO₂ and K₂CO₃/γ-alumina/SiO₂ was higher than K₂CO₃/γ-alumina, whereas this ratio for K₂CO₃/Boehmite/ZrO₂ and K₂CO₃/Boehmite/SiO₂ was lower than K₂CO₃/Boehmite. This is because γ-alumina has less hydrophilicity than ZrO₂ and SiO₂, whereas the hydrophilicity of Boehmite is higher than ZrO₂ and SiO₂ [33]. The contact angle of γ-alumina and Boehmite with water was reported 91° and 12°, respectively [35–37].

Excess water adsorption increases the formation of hydrated by-products and lowers the proportion of fresh K₂CO₃ in the sorbent [17–19]. It also causes pore blockage by the formation of liquid films and increases the mass transfer resistance [29].

Table 2. Adsorbed H₂O-to -CO₂ molar ratio for the synthesized sorbents (carbonation time = 30 min, carbonation temperature = 50°C and H₂O-to-CO₂ flowrate ratio = 0.91)

Sorbent	Adsorbed H ₂ O-to-CO ₂ molar ratio
K ₂ CO ₃ /γ-alumina	1.53
K ₂ CO ₃ /γ-alumina/TiO ₂	1.24
K ₂ CO ₃ /γ-alumina/ZrO ₂	1.62
K ₂ CO ₃ /γ-alumina/SiO ₂	1.59
K ₂ CO ₃ /Boehmite	2.96
K ₂ CO ₃ /Boehmite/TiO ₂	1.31
K ₂ CO ₃ /Boehmite/ZrO ₂	2.28
K ₂ CO ₃ /Boehmite/SiO ₂	2.13

Figure 2 displays the cyclic CO₂ capture capacity for K₂CO₃/γ-alumina, K₂CO₃/γ-alumina/TiO₂, K₂CO₃/γ-alumina/ZrO₂ and K₂CO₃/γ-alumina/SiO₂ in 30 min, at carbonation temperature of 50°C and H₂O-to-CO₂ flowrate ratio of 0.91. The CO₂ capture performance of K₂CO₃/γ-alumina improved significantly after shelling the support with TiO₂, which is ascribed to the low hydrophilicity of the sorbent. Shelling γ-alumina with ZrO₂ and SiO₂ did not improve the CO₂ uptake due to higher H₂O-to-CO₂ adsorption capacity of K₂CO₃/γ-alumina/ZrO₂ and K₂CO₃/γ-alumina/SiO₂ than K₂CO₃/γ-alumina. Surface area (Table 3) also plays a role in the CO₂ capture performance. For the sorbents possessing low hydrophilic properties, an increase in the surface area would enhance the CO₂ capture capacity [18]. K₂CO₃/γ-alumina has a higher surface area than K₂CO₃/γ-alumina/ZrO₂ and K₂CO₃/γ-alumina/SiO₂, but lower hydrophilicity, thus its CO₂ capture performance is higher. The BET surface areas of K₂CO₃/γ-alumina and K₂CO₃/γ-alumina/TiO₂ are in the same range; however, K₂CO₃/γ-alumina has higher hydrophilicity, thus lower CO₂ capture capacity.

Figure 2. Cyclic CO₂ capture performance of the sorbents prepared by γ-alumina/shell supports (carbonation time = 30 min, carbonation temperature = 50°C and H₂O-to-CO₂ flowrate ratio = 0.91)

Table 3. BET surface area of the sorbents

Sorbent	BET surface area (m ² /g)
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K ₂ CO ₃ /γ-alumina	48.9
K ₂ CO ₃ /γ-alumina/TiO ₂	49.1
K ₂ CO ₃ /γ-alumina/ZrO ₂	33.4
K ₂ CO ₃ /γ-alumina/SiO ₂	39.0
K ₂ CO ₃ /Boehmite	15.9
K ₂ CO ₃ /Boehmite/TiO ₂	62.8
K ₂ CO ₃ /Boehmite/ZrO ₂	51.0
K ₂ CO ₃ /Boehmite/SiO ₂	63.4

Figure 3 displays the cyclic CO₂ uptake of the sorbents prepared by Boehmite as the core. According to the figure, K₂CO₃/Boehmite/TiO₂ represented the greatest cyclic uptake. The CO₂ capture performance varied in the following order: K₂CO₃/Boehmite/TiO₂ > K₂CO₃/Boehmite/SiO₂ > K₂CO₃/Boehmite/ZrO₂ > K₂CO₃/Boehmite and the adsorbed H₂O-to-CO₂ molar ratio varied in the opposite direction, which agrees well with the previous findings. As displayed in Figures 2 and 3, the CO₂ capture performance of K₂CO₃/γ-alumina/TiO₂ and K₂CO₃/Boehmite/TiO₂ is similar, and the CO₂ uptake of both sorbents is about 90 percent of the theoretical value in each cycle. Although the regeneration temperature was low (150 °C) compared to similar works on K₂CO₃/alumina-based sorbents, the CO₂ capture capacity did not reduce by increasing the number of cycles. Most of the studies on the alumina-supported K₂CO₃ were carried out at a high regeneration temperature (more than 300 °C) to completely regenerate the produced by-products to the original K₂CO₃ [14,38,39]. By-products usually are formed due to interactions at the interface of K₂CO₃ and alumina. In this work, a layer was created between alumina and K₂CO₃ by the core-shell technique to lower the interactions. A high regeneration temperature will increase the operating cost of the process. There are few works in the literature, which examined a K₂CO₃/alumina-based sorbent at a regeneration temperature of less than 300 °C. Lee et al. [21] used a regeneration temperature of 200 °C to investigate the CO₂ capture performance of K₂CO₃/γ-alumina. The carbonation capacity of the sorbent reduced to 52 percent of the theoretical value after five carbonation/regeneration cycles. Jaiboon et al. [14] tested K₂CO₃/γ-alumina at a regeneration

temperature of 150 °C. The CO₂ capture capacity of the sorbent after five cycles reached 31 percent of the theoretical value, whereas the CO₂ capture capacity of K₂CO₃/γ-alumina/TiO₂ and K₂CO₃/Boehmite/TiO₂ was about 90 percent after ten cycles. Since K₂CO₃/γ-alumina/TiO₂ and K₂CO₃/Boehmite/TiO₂ showed the best performance among the prepared sorbents, they were chosen for further characterization analyses.

Figure 3. Cyclic CO₂ capture performance of the sorbents prepared by boehmite/shell supports (carbonation time = 30 min, carbonation temperature = 50°C and H₂O-to-CO₂ flowrate ratio = 0.91)

3.2. Characterization

The adsorption branch of the BJH pore size distribution for K₂CO₃/γ-alumina/TiO₂, K₂CO₃/Boehmite/TiO₂, K₂CO₃/γ-alumina and K₂CO₃/Boehmite is depicted in Figure 4. As seen in the figure, the pore diameters were in the range of mesoporous materials (between 2nm and 50nm). According to Figure 4a, K₂CO₃/γ-alumina/TiO₂ and K₂CO₃/γ-alumina showed practically the same pore size distribution; however, K₂CO₃/Boehmite/TiO₂ and K₂CO₃/Boehmite were quite different. This is attributed to the partial dissolution and peptization of non-modified Boehmite in the alkaline solution of K₂CO₃ during the synthesis process. Dissolution and peptization of non-modified Boehmite caused a great reduction in

the surface area and pore volume of the sorbent due to pore blockage and the creation of inaccessible active sites. By shelling Boehmite with TiO_2 , the physical properties of the sorbent were improved significantly. BET surface area and pore volume of the pure Boehmite were found to be $275.7 \text{ m}^2/\text{g}$ and $0.38 \text{ cm}^3/\text{g}$, respectively. After supporting it with K_2CO_3 , the BET surface area and the pore volume reduced to $15.9 \text{ m}^2/\text{g}$ and $0.02 \text{ cm}^3/\text{g}$, respectively. Whereas, $\text{K}_2\text{CO}_3/\text{Boehmite}/\text{TiO}_2$ showed $62.8 \text{ m}^2/\text{g}$ BET surface area and $0.21 \text{ cm}^3/\text{g}$ pore volume, indicating the positive impact of TiO_2 on the reduction of partial dissolution and peptization effects. γ -alumina has lower chemical reactivity toward moisture compared to Boehmite, thus maintains its physical properties during the synthesis process. For this reason, the pore size distribution of $\text{K}_2\text{CO}_3/\gamma$ -alumina did not change significantly after shelling γ -alumina with TiO_2 .

Figure 4. BJH pore size distribution of the sorbents prepared by γ -alumina (a) and Boehmite (b)

Figure 5 displays SEM images of $\text{K}_2\text{CO}_3/\gamma$ -alumina/TiO₂, $\text{K}_2\text{CO}_3/\text{Boehmite}/\text{TiO}_2$, $\text{K}_2\text{CO}_3/\gamma$ -alumina and $\text{K}_2\text{CO}_3/\text{Boehmite}$. The surface morphology of $\text{K}_2\text{CO}_3/\gamma$ -alumina/TiO₂ is like $\text{K}_2\text{CO}_3/\gamma$ -alumina, and the surface structure did not change significantly after shelling γ -alumina with TiO₂ (Figures 5a and 5b). However, shelling Boehmite with TiO₂ improved evidently the pore morphology of the sorbent. As mentioned above, due to less hydrophilicity and reactivity of γ -alumina compared to Boehmite, it had less dissolution in the alkaline solution of K_2CO_3 and maintained its physical structure during the impregnation process.

Hence, the pore morphology of K_2CO_3/γ -alumina and K_2CO_3/γ -alumina/ TiO_2 were almost the same. Due to the dissolution and peptization of Boehmite in the K_2CO_3 solution and agglomeration of the materials during the drying step, a nearly flat and non-porous surface was formed (Figure 5c) [18]. Shelling Boehmite with TiO_2 worked very well to modify the physical properties and reduce the dissolution and peptization effects (Figure 5d).

Figure 5. SEM images of K_2CO_3/γ -alumina (a), K_2CO_3/γ -alumina/ TiO_2 (b), K_2CO_3 /Boehmite (c) and K_2CO_3 /Boehmite/ TiO_2 (d)

To verify the presence of Ti in the structure of K_2CO_3/γ -alumina/ TiO_2 and K_2CO_3 /Boehmite/ TiO_2 , EDS analysis was performed, and the elemental composition of Ti was found to be 0.57 and 0.74 wt%, respectively. Distribution of the selected elements K, Al and Ti on the surface of the sorbents is represented in the EDS mapping images of Figure 6.

The uniform spatial distribution of Ti is observed in both sorbents indicating the successful coating of γ -alumina/TiO₂ and Boehmite/TiO₂ on K₂CO₃.

K₂CO₃/Boehmite/TiO₂ demonstrated outstanding physical properties, including high BET surface area, high porosity and uniform distribution of components. As shown in Table S1 (Supporting Information), the BET surface area and pore volume of the sorbent did not change significantly after ten carbonation/regeneration cycles. The cyclic CO₂ capture capacity of K₂CO₃/Boehmite/TiO₂ was higher than the other sorbents prepared in this work. In addition, no new phases were detected in the XRD pattern of the sorbent (Figure S1); thus, no interactions occurred between alumina and K₂CO₃. Therefore, this sorbent was selected for further analyses and modelling of the system in the following section.

Figure 6. EDX mapping images for elements K (red), Al (yellow) and Ti (orange) of samples K₂CO₃/ γ -alumina/TiO₂ (a) and K₂CO₃/Boehmite/TiO₂ (b)

3.3. Modeling

To improve the CO₂ capture performance, the effect of main operating parameters including carbonation temperature, carbonation time and H₂O-to-CO₂ flowrate ratio was studied on the performance of K₂CO₃/Boehmite/TiO₂. Table 4 shows seventeen sets of experiments

designed by BBD along with the actual and predicted values of the CO₂ capture capacity. Each experiment indicated in Table 4 was conducted using a fresh sample. By applying BBD, an empirical second order polynomial (Equation 7) was developed for the response variable (CO₂ capture capacity) as a function of carbonation temperature, carbonation time and H₂O-to-CO₂ flowrate ratio.

$$Y = -13.59 + 0.37A + 0.29B + 4.85C + 7.42 * 10^{-4}AB + 0.02AC + 8.22 * 10^{-3}BC - 3.55 * 10^{-3}A^2 - 4.49 * 10^{-3}B^2 - 2.52C^2 \quad (7)$$

Where Y represents the CO₂ capture capacity (mmol CO₂/g K₂CO₃) and A, B and C are carbonation temperature (°C), carbonation time (min) and H₂O-to-CO₂ flowrate ratio, respectively. Using the equation, the predicted values of the response were calculated as shown in Table 4.

Table 4. RSM predicted results along with actual values of the response.

Run	A: Carbonation temperature (°C)	B: Carbonation time (min)	C: H ₂ O-to-CO ₂ flowrate ratio	CO ₂ capture capacity (mmol CO ₂ /g K ₂ CO ₃)	
				Actual	Predicted
1	60	30	1.25	6.13	6.05
2	60	30	1.25	6.01	6.05
3	60	30	1.25	5.90	6.05
4	60	30	1.25	5.88	6.05
5	60	45	2	4.83	4.87
6	80	30	0.5	2.52	2.86
7	60	15	0.5	2.61	2.57
8	40	30	0.5	3.86	3.69
9	60	15	2	2.12	2.26
10	80	15	1.25	2.35	2.05
11	80	45	1.25	5.13	4.92
12	60	45	0.5	4.95	4.81
13	40	15	1.25	2.56	2.77
14	40	45	1.25	4.45	4.75
15	60	30	1.25	6.35	6.05
16	80	30	2	3.13	3.29
17	40	30	2	3.35	3.01

Table S1 (Supporting Information) shows the statistical analysis of the data performed by analysis of variance (ANOVA). The model had an F-value of 37.79 and the corresponding P-value was found to be < 0.0001 . This meant that there was only a 0.01% chance that the F-value occurred due to noise; thus, the model was highly significant [40,41]. The lack of fit of the F-value was not significant because the corresponding P-value was 0.0700 and higher than 0.0500 [42,43]. The lack of fit of the F-value should not be significant for a successful prediction of the response [43]. The F-values and P-values of the model's variables were used to compare the impact of each variable on the final response. Smaller P-values and larger F-values indicate the higher impact of the corresponding variables on the response [25,44]. For instance, carbonation time had smaller P-value and larger F-value than the other independent variables, thus, caused a higher impact on the CO₂ capture capacity. The interaction effect of carbonation temperature and H₂O-to-CO₂ flowrate ratio is higher than the other variables, according to their P-values and F-values. The actual values of the CO₂ capture capacity were plotted versus the predicted values in Figure 7. The high values of the regression coefficient ($R^2=0.97$) and the adjusted regression coefficient ($R^2_{adj}=0.95$) verified the adequate accuracy of the model to predict the response.

Figure 7. Plot of the predicted versus actual CO₂ capture capacity

To further investigate the adequacy of the model, the normal probability plot of the internally studentized residuals was depicted in Figure S2. The residual points were well distributed along the straight line indicating no violation of the assumptions underlying the model [45]. According to this figure, errors were normally distributed and independent. Figure 8 shows the plot of the internally studentized residuals versus the predicted response. The experimental points were scattered randomly within the constant horizontal lines of ± 3.00 , implying the adequacy of the proposed model and confirming the constant variance assumption [44].

Figure 8. plot of the internally studentized residuals versus the predicted response

To investigate the combination effect of the operating parameters and find the optimal condition points, the response surface analysis was carried out. 3D response surface plot and the corresponding contour plot for the combination effect of carbonation time and H₂O-to-CO₂ flowrate ratio are depicted in Figures 9 and S3 (Supporting Information), respectively. At each carbonation time, an optimal point of around one was observed for the H₂O-to-CO₂ flowrate ratio. According to Equation 1, an ideal H₂O-to-CO₂ flowrate ratio of one is required for the carbonation reaction to go forward [8]. When the flowrate ratio is less than one, the required amount of moisture does not reach the surface of the sorbent and reduces the carbonation capacity. On the other hand, at high concentrations of the moisture, the formation

of by-products increases and adversely affects the performance of the sorbent [19]. Also, excess water adsorption forms liquid films at the pore endings and increases the mass transfer resistance [29]. Figures 10 and S4 display the combination effect of carbonation temperature and carbonation time on the CO₂ uptake. At constant carbonation temperatures, by increasing the carbonation time, the CO₂ capture capacity improved. The rate of the improvement was not constant and approached to zero at the end of the carbonation time. As shown in Figures 10 and S4, the carbonation temperature had an optimal point at different reaction times. By exceeding the optimal point, the CO₂ capture capacity reduced which was attributed to the exothermic behavior of the carbonation reaction [16,46]. According to Figures 9 and 10, for the carbonation reaction to being complete, a minimum carbonation time of about 30 min was required. The combination effect of H₂O-to-CO₂ flowrate ratio and carbonation temperature is illustrated in Figures 11 and S5. The optimal condition occurred in the middle of the range of each variable, at about 60°C for the carbonation temperature and about 1 for the H₂O-to-CO₂ flowrate ratio. In general, the variables studied in this work affected the CO₂ capture capacity in an almost independent way and the interaction effects were not significant. For example, in Figure 11, at different amounts of H₂O-to-CO₂ flow ratio, the optimum amount of carbonation temperature remained almost the same.

Figure 9. 3D response surface of the CO₂ capture capacity versus H₂O-to-CO₂ flow ratio and carbonation time.

Figure 10. 3D response surface of the CO₂ capture capacity versus carbonation time and carbonation temperature

Figure 11. 3D response surface of the CO₂ capture capacity versus H₂O-to-CO₂ flow ratio and carbonation temperature

3.4. Optimization of the variables

The obtained second order polynomial was used to find the maximum CO₂ capture capacity for K₂CO₃/Boehmite/TiO₂ (symbolized by Y) at the optimal amounts of the operating parameters (symbolized by X_i). Since the second order polynomial was obtained empirically, the ranges of the operating parameters should be considered in the optimization process to avoid extrapolation. Hence, the optimization problem was defined as below:

Maximize Y

Constraints on the parameters X_i:

$$-1 < X_i < +1, i = 1, 2 \text{ and } 3$$

The numerical optimization method provided by Design Expert software Version 9.0.3 was utilized to find the optimal point. Table 5 shows the optimal values of carbonation temperature, carbonation time and H₂O-to-CO₂ flowrate ratio. At the optimal condition, the CO₂ capture capacity was predicted 6.39 mmol CO₂/g K₂CO₃. To confirm the accuracy of the predicted value, three replicate experiments were conducted at the optimal point. The average CO₂ capture capacity was found to be 6.61 mmol CO₂/g K₂CO₃, which is very close to the predicted value.

Table 5. Optimal values of carbonation temperature, carbonation time and H₂O-to-CO₂ flowrate ratio

Operating parameters	Optimal values
Carbonation temperature (°C)	61
Carbonation time (min)	40
H ₂ O-to-CO ₂ flowrate ratio	1.15

3.5. Kinetic model

In this section, the kinetic behavior of fresh K₂CO₃/Boehmite/TiO₂ was investigated in the first carbonation/regeneration cycle. The reason to study kinetic behavior is to obtain useful information about adsorption capacity versus carbonation time. The required time for sorbents to complete the carbonation process is important for industrial purposes. The kinetic study also provides essential information about adsorption mechanisms and reaction pathways.

Different kinetic models, including pseudo-first order, pseudo-second order and Avrami, were applied to analyze the kinetic behavior of the sorbent and find the adsorption mechanism. The pseudo-first order kinetic model is suitable for the diffusion-controlled adsorption processes [47]. The second-order kinetic model was proposed for the reaction-

controlled adsorption processes [29]. It was reported that both models can be used to describe gas-solid kinetic performance; however, the pseudo-first order model gives accurate predictions only at the early stage of the adsorption process [29]. The pseudo-second order model can successfully be applied for the whole range of the process. K₂CO₃-based sorbents showed complex kinetic behaviors, because CO₂ can be captured by both chemical and physical adsorption mechanisms through different reaction pathways [28]. For this reason, the pseudo-first order and pseudo-second order models might show limitations in describing the adsorption mechanism. Avrami's kinetic model was reported to propose accurate predictions since the model considers different adsorption mechanisms [29,30]. This model was applied in different CO₂ adsorption systems including CO₂ sorption over amine-functionalized mesoporous silica, CO₂ sorption over K₂CO₃-modified silica aerogels and adsorption of CO₂ over alumina-aerogel-supported K₂CO₃ sorbent [18,30].

The linear form of the pseudo-first order kinetic model is given as follows:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (8)$$

Where, q_t (mmol CO₂/g K₂CO₃) is the CO₂ capture capacity at time t (min), q_e (mmol CO₂/g K₂CO₃) is the CO₂ capture capacity at equilibrium and K_1 (min⁻¹) represents the rate constant of the pseudo-first order kinetic model. The value of K_1 can be obtained by plotting $\ln(q_e - q_t)$ versus t , as shown in Figure S6. Since the model can describe the system only at the early stage of the process, by increasing the reaction time, the values of $\ln(q_e - q_t)$ deviated from the straight line. Table 6 shows the regression coefficient (R^2) and the kinetic constant of the model, which were found to be 0.94 and 0.136 min⁻¹, respectively.

Table 6. Regression coefficients and kinetic constants for pseudo-first order, pseudo-second order and Avrami's kinetic models (carbonation temperature = 61°C, H₂O-to-CO₂ flowrate ratio = 1.15 and N₂ flowrate = 152.85 std ml min⁻¹)

Kinetic model	Kinetic constant	R^2
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Pseudo-first order	$k_1=0.136 \text{ min}^{-1}$	0.94
Pseudo-second order	$k_2=0.001 \text{ g mmol}^{-1} \text{ min}^{-1}$	0.97
Avrami	$k_a=0.114 \text{ min}^{-1}$ $n=1.104$	0.99

Equation 9 represents the linear form of the pseudo-second order model.

$$\frac{1}{q_t} = \frac{1}{q_e} + \left(\frac{1}{k_2 q_e^2}\right) \frac{1}{t} \quad (9)$$

Where, q_t (mmol CO₂/g K₂CO₃) and q_e (mmol CO₂/g K₂CO₃) are the CO₂ capture capacity at time t (min) and equilibrium, respectively, and K_2 (g mmol⁻¹ min⁻¹) is the rate constant. To find the kinetic constant of the model, $\frac{1}{q_t}$ was plotted versus $\frac{1}{t}$ as shown in Figure S7. From the slope and the intercept of the obtained trendline, K_2 was calculated as 0.001 g mmol⁻¹ min⁻¹. R^2 of the model was found to be 0.97, which indicates the higher accuracy of the model compared to the pseudo-first order kinetic model.

The following equation shows the linear form of the Avrami's kinetic model.

$$\ln \left[\ln \left(1 - \frac{q_e}{q_t} \right)^{-1} \right] = n \ln t + (n \ln k_a - \ln n) \quad (10)$$

In this Equation, q_t and q_e have the same definition as in Equation 7, and K_a and n are the kinetic constants. Figure S8 displays the linear relationship between $\ln \left[\ln \left(1 - \frac{q_e}{q_t} \right)^{-1} \right]$ and $\ln t$. The values of n and K_a were calculated using the slope and the intercept of the obtained trendline as 1.104 and 0.114 min⁻¹, respectively. The accuracy of the model to predict the kinetic behavior of the sorbent was investigated by calculating the R^2 value, as shown in Table 6. As seen in the table, the Avrami's model represented the highest R^2 value among the models, which was attributed to the ability of the model to consider different adsorption mechanisms.

Conclusion

In this study, a group of core/shell-structured K_2CO_3 -based sorbents were synthesized and applied for the post-combustion process, among which $\text{K}_2\text{CO}_3/\text{Boehmite}/\text{TiO}_2$ showed the highest CO_2 capture performance. The effect of operating parameters was investigated on the carbonation capacity of $\text{K}_2\text{CO}_3/\text{Boehmite}/\text{TiO}_2$ by Response Surface Methodology and Box Behnken Design of experiments. The optimal values for carbonation temperature, carbonation time and H_2O -to- CO_2 flowrate ratio were found 61°C , 40 min and 1.15, respectively. The CO_2 capture capacity of $\text{K}_2\text{CO}_3/\text{Boehmite}/\text{TiO}_2$ at the optimal condition reached the significant value of $6.61 \text{ mmol CO}_2/\text{g K}_2\text{CO}_3$, which is close to the theoretical CO_2 capture capacity of K_2CO_3 ($7.20 \text{ mmol CO}_2/\text{g K}_2\text{CO}_3$). $\text{K}_2\text{CO}_3/\text{Boehmite}/\text{TiO}_2$ was tested over ten cycles at a low regeneration temperature (150°C) and the CO_2 capture capacity of the sorbent was about 90 percent of the theoretical value in each cycle, which is a significant improvement compared to studies available in the literature. Statistical analysis showed that carbonation time had a higher impact on the CO_2 uptake compared to the carbonation temperature and H_2O -to- CO_2 flowrate ratio. Three kinetic models were applied to investigate the adsorption rate of the sorbent, and Avrami was the best-fit model with $k_a=0.114 \text{ min}^{-1}$ and $n=1.104$. In future work, the pelletized $\text{K}_2\text{CO}_3/\text{Boehmite}/\text{TiO}_2$ will be synthesized using different binding agents and pelletization techniques.

Supporting information

BET surface area and pore volume of $\text{K}_2\text{CO}_3/\text{Boehmite}/\text{TiO}_2$, XRD pattern of $\text{K}_2\text{CO}_3/\text{Boehmite}/\text{TiO}_2$, ANOVA for the proposed quadratic model; plot of the normal probability versus internally studentized residuals; contour plot of the CO_2 capture capacity versus H_2O -to- CO_2 flow ratio and carbonation time; contour plot of the CO_2 capture capacity versus carbonation time and carbonation temperature; contour plot of the CO_2 capture capacity versus H_2O -to- CO_2 flowrate ratio and carbonation temperature; linearized plots for the pseudo-first order kinetic model; linearized plots for the pseudo-second order kinetic model; linearized plots for the Avrami's kinetic model

Nomenclature

q_t = CO₂ capture capacity at a specific time, mmol CO₂/g K₂CO₃

q_e = Equilibrium CO₂ capture capacity, mmol CO₂/g K₂CO₃

t = Time elapsed in the carbonation step, min

K_1 = Kinetic constant for pseudo-first order model, min⁻¹

K_2 = Kinetic constant for pseudo-second order model, g mmol⁻¹ min⁻¹

K_a = Kinetic constant for Avrami model, min⁻¹

n = Kinetic constant for Avrami model

Y = CO₂ capture capacity (mmol CO₂/g K₂CO₃)

A = Carbonation temperature (°C)

B = Carbonation time (min)

C = H₂O-to-CO₂ flowrate ratio

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