

## Article

# Potassium-Based Solid Sorbents for CO<sub>2</sub> Adsorption: Key Role of Interconnected Pores

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**Abstract:** Industrial CO<sub>2</sub> emissions contribute to pollution and greenhouse effects, highlighting the importance of carbon capture. Potassium carbonate (K<sub>2</sub>CO<sub>3</sub>) is an effective CO<sub>2</sub> absorbent, yet its liquid-phase absorption faces issues like diffusion resistance and corrosion risks. In this work, the solid adsorbents were developed with K<sub>2</sub>CO<sub>3</sub> immobilized on the selected porous supports. Al<sub>2</sub>O<sub>3</sub> had an optimum CO<sub>2</sub> adsorption capacity of 0.82 mmol g<sup>-1</sup>. After further optimization of its pore structure, the self-prepared support Al<sub>2</sub>O<sub>3</sub>-2, which has an average pore diameter of 11.89 nm and a pore volume of 0.59 cm<sup>3</sup> g<sup>-1</sup>, achieved a maximum CO<sub>2</sub> adsorption capacity of 1.12 mmol g<sup>-1</sup> following K<sub>2</sub>CO<sub>3</sub> impregnation. Additionally, the relationship between support structure and CO<sub>2</sub> adsorption efficiency was also analyzed. The connectivity of the pores and the large pore diameter of the support may play a key role in enhancing CO<sub>2</sub> adsorption performance. During 10 cycles of testing, the K<sub>2</sub>CO<sub>3</sub>-based adsorbents demonstrated consistent high CO<sub>2</sub> adsorption capacity with negligible degradation.

**Keywords:** CO<sub>2</sub>; potassium carbonate; adsorbent; aluminum oxide



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## 1. Introduction

The increasing concentration of CO<sub>2</sub> in flue gas from coal-fired power plants, a critical driver of the greenhouse effect, has led to the recognition that Carbon Capture and Storage (CCS) technology, particularly post-combustion capture, is regarded as a promising solution for the reduction of carbon dioxide emissions [1–6]. Although the liquid amine absorption method has been widely utilized in post-combustion capture, it still faces several challenges, including corrosiveness to containment vessels, potential amine volatility leading to environmental contamination, and significant mass transfer resistance within the liquid phase [7–10]. Recently, the incorporation of organic amines into porous supports has been extensively studied by many researchers [11–24]. Solid amine adsorbents, utilizing materials with high porosity such as polymers [11–13], carbon materials (e.g., carbon nanotube [14,15], activated carbon [16,17], and mesoporous carbon [18]), and mesoporous molecular sieves (e.g., SBA-15 [19–21], MCM-41 [22,23], and KIT-6 [24]), have been a focal point of research. These adsorbents incorporate various amine groups (e.g., primary, secondary, and tertiary amines) to enhance CO<sub>2</sub> capture capabilities [25]. However, despite their high adsorption capacity, the surface utilization rate of amine groups is still quite low. This is mainly because the organic amine has high viscosity and large molecular diameter, making it hard to penetrate evenly in the pores, which can lead to aggregation, pore blockage, and ultimately fewer active sites on the surface. Furthermore, there is significant amine loss during the adsorption–desorption cycles due to the facts that amines are inherently volatile organic compounds. Thus, it is necessary to develop innovative technologies or materials to overcome the current limitations in efficiency and cost.

In recent years, numerous studies have reported the use of potassium carbonate as an active component impregnated onto support materials to fabricate  $K_2CO_3$ -based adsorbents, which serve as a substitute for amine-based adsorbents for  $CO_2$  capture [26–28]. Alkali carbonate-based adsorbents exhibit superior stability and are free from issues of secondary environmental pollution. They are more difficult to decompose, even when the temperature is increased to 800 °C. Generally, a temperature of 350 °C is adequate to fully regenerate the adsorbent. The inherent alkalinity of potassium carbonate confers a significantly enhanced  $CO_2$  adsorption capacity upon the adsorbent, particularly effective for the capture of low-concentration  $CO_2$ , such as the 10–15% found in flue gasses. Current research on  $K_2CO_3$ -based adsorbents predominantly focuses on the in-depth exploration of the underlying reaction mechanisms and the selection of appropriate support materials [29–43]. The carbonation reaction induced by  $K_2CO_3$ -based sorbents was found to consist of two steps: first, the hydration reaction takes place, and then the produced  $KHCO_3$  reacts rapidly. During the  $CO_2$  sorption process, the carbonation reaction coexists with the adsorption process, indicating that both chemical and physical adsorption occur [28]. The support material in  $K_2CO_3$ -based sorbents facilitates not only physical  $CO_2$  adsorption but also the dispersion of alkaline active sites. Consequently, the choice of support material and the optimization of its pore structure are crucial for enhancing the  $CO_2$  adsorption performance of the sorbents.

Activated carbon was first considered as a superior support material due to its high surface area, abundant porosity, and controllable pore structure. It was reported that the  $K_2CO_3/AC$  sorbent exhibits high  $CO_2$  capture capacities and rapid carbonation reaction rates [28–30]. Zeolites have also been widely investigated because they possess well-defined pore structures that can accommodate both the immobilized alkali metal carbonates and the adsorbed  $CO_2$  [31–38]. In addition, activated alumina, with its high porosity, large surface area, and diverse pore channels, also has great potential for use as a support material [39–43]. Zhao et al. [40–43] have conducted extensive research on the supports for  $K_2CO_3$ -based sorbents. They impregnated potassium carbonate onto several supports and compared the conversion rates using thermogravimetric analysis (TGA) and a bubbling fluidized-bed reactor. However, the pore structure of the support materials requires additional refinement to optimize performance. There is an imperative to elucidate the correlation between the pore structural attributes and  $CO_2$  adsorption efficacy, which is pivotal for informing the strategic design of advanced support materials. In this study, the performance of adsorbents prepared with various support materials was systematically compared, and the pore structure was further improved by strategically selecting the most suitable support. Additionally, the research endeavored to delineate the principal factors that influence  $CO_2$  adsorption capacity.

## 2. Materials and Methods

### 2.1. Acquisition of the Support Materials

The porous solid materials, including ZSM-5, zeolite 5A, zeolite  $\beta$ , zeolite NaY, and MCM-41, served as supports and were obtained from Nanjing XFNANO Materials Tech Co., Ltd., Nanjing, China. The activated carbons, namely, CSAC and CAC, were purchased from Kecheng Activated Carbon Co., Ltd., Beijing, China. Aluminum oxide ( $Al_2O_3$ ) was supplied by J&K Scientific. Moreover, two additional aluminum oxide supports were self-synthesized using the following procedures:

Scheme 1 [44]: In the preparation of  $Al_2O_3$ -1, 2.38 g of sodium aluminate, 20.23 g of urea, and 1 g of F127 were combined and dissolved in 70 mL of distilled water under vigorous stirring to form a homogeneous solution. This solution was subsequently transferred to a 100 mL Teflon-lined stainless steel autoclave, sealed, and subjected to hydrothermal treatment at 140 °C for 24 h. After that, the autoclave was cooled to ambient temperature, and then a white precipitate was formed. The resulting white precipitate was isolated from the supernatant and extensively washed with deionized water followed by ethanol in a sequential manner. The precipitate was then dried in a vacuum oven at 80 °C for 12 h.

Finally, the dried powder was calcined at 450 °C for 4 h in static air to yield the desired  $\gamma$ - $\text{Al}_2\text{O}_3$  product.

Scheme 2 [45]: For the synthesis of  $\text{Al}_2\text{O}_3$ -2, a mixture of  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (0.014 mol) and  $\text{CO}(\text{NH}_2)_2$  (0.028 mol, 0.021 mol, or 0.056 mol) was dissolved in 70 mL of distilled water and stirred vigorously for 30 min to form a clear solution. The solution was then poured into a 100 mL Teflon-lined autoclave and heated at 180 °C (160 °C or 200 °C) for 4 h (3 h or 5 h), followed by natural cooling to room temperature. The resulting white precipitate was collected by vacuum filtration, washed sequentially with distilled water and anhydrous alcohol, and dried at 80 °C for 12 h in a vacuum oven. The boehmite precursor was calcined at 550 °C for 4 h, with a heating rate of 4 °C  $\text{min}^{-1}$ , to yield the final  $\gamma$ - $\text{Al}_2\text{O}_3$  product.

All the reagents used in the two schemes were of analytical grade without any further purification.

### 2.2. Preparation of $\text{K}_2\text{CO}_3$ -Based Adsorbents

To prepare  $\text{K}_2\text{CO}_3$ -based sorbents, designated as x  $\text{K}_2\text{CO}_3$ /support, where x represents the weight percentage of  $\text{K}_2\text{CO}_3$  in the adsorbents, a given amount of  $\text{K}_2\text{CO}_3$  was first dissolved in 40 mL of methanol with stirring for 30 min at room temperature. Then, 2 g of the supports was added into the above  $\text{K}_2\text{CO}_3$  methanol solution. After that, it was mixed with a magnetic stirrer at 40 °C until most of the methanol evaporated. Finally, the resultant x  $\text{K}_2\text{CO}_3$ /support adsorbents were further dried at 80 °C for 12 h under vacuum.

### 2.3. Characterization of the Self-Synthesized $\text{Al}_2\text{O}_3$

X-ray diffraction (XRD) spectra were obtained by an X'Pert PRO diffractor (PANalytical, Almelo, Holland, Cu  $\text{K}\alpha$ ,  $\lambda = 0.15406$  nm, 40 kV, 40 mA). The micro-morphology of the  $\text{Al}_2\text{O}_3$  supports was observed by a scanning electron microscope (SEM, Hitachi SU8010, Tokyo, Japan). Before the measurements, the samples were degassed at 100 °C for 12 h under vacuum. Nitrogen adsorption–desorption isotherms were measured at 77 K using a Tristar II 3020 analyzer (Micromeritics, Norcross, GA, USA). The Brunauer–Emmett–Teller (BET) method was utilized to calculate the specific surface area. The total pore volume and pore size distribution were derived from the isotherm desorption branches using the Barrett–Joyner–Halenda (BJH) model. A thermogravimetric analysis (TGA, Netzsch STA 449F5, Selby, Germany) of samples was performed in a highly pure  $\text{N}_2$  atmosphere at a flow rate of 70 mL/min. About 10 mg of the sample was heated at a constant rate of 10 °C/min from room temperature to 600 °C.

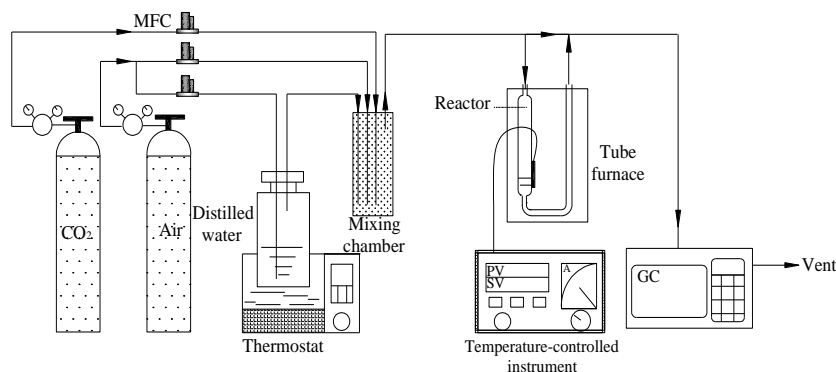
### 2.4. Evaluation for $\text{CO}_2$ Adsorption over $\text{K}_2\text{CO}_3$ -Based Adsorbents

A fixed-bed flow sorption system, equipped with gas flow controllers and an integrated online gas chromatograph, was designed and constructed for the purpose of evaluating adsorbent performance in  $\text{CO}_2$  adsorption, as depicted in Figure 1. The process involved packing 2 g of adsorbent into a U-shaped quartz reactor, which was placed in a programmable furnace for precise temperature control. Prior to each measurement, the sample was heated to 100 °C in a highly pure Ar stream at the flow rate of 100 mL  $\text{min}^{-1}$  for 60 min to eliminate the physically adsorbed  $\text{H}_2\text{O}$  and  $\text{CO}_2$ , and then the sample was cooled to 25 °C. The gas stream was rapidly switched to the 10%  $\text{CO}_2$ /air with 30% relative humidity (RH) at the desired flow rate of 10 mL  $\text{min}^{-1}$ . The moisture was produced by bubbling air into water, and the relative humidity was measured using a hygrometer. The flow rate of the gas was controlled by electronic flow control instruments. The concentrations of  $\text{CO}_2$  at the inlet and outlet of the reactor were monitored by an online gas chromatograph (GC-7890II, Techcomp, Beijing, China) equipped with a methane converter, and the flame ionization detector was used. The sorption capacity of the adsorbent was calculated by the

integration of the area above the breakthrough curve, and the integral equation is displayed in Equation (1)

$$q_s = \frac{1}{W} \times \left[ \int_0^t Q \times \frac{C_0 - C}{1 - C} dt \right] \times \frac{T_0}{T} \times \frac{1}{V_m} \quad (1)$$

where  $q_s$  is the saturated adsorption capacity of  $\text{CO}_2$ ,  $\text{mmol g}^{-1}$ .  $W$  is the weight of the adsorbent, g.  $Q$  is the gas flow rate  $\text{mL min}^{-1}$ .  $C_0$  and  $C$  are the influent and effluent  $\text{CO}_2$  concentration, respectively, vol%.  $t$  denotes the adsorption time, min.  $T_0$  is 273K.  $T$  is the gas temperature, 273K.  $V_m$  is  $22.4 \text{ mL mmol}^{-1}$ .  $q_s$  is defined as the adsorption capacity of  $\text{CO}_2$  when  $C$  is equal to  $C_0$ ; i.e.,  $C/C_0$  is equal to 1.0.

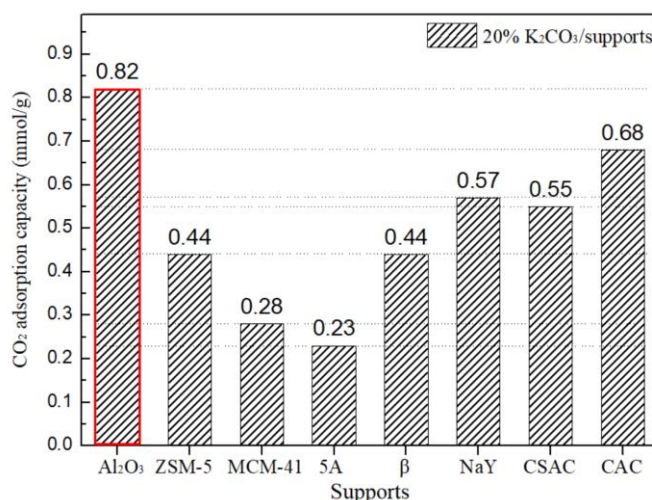


**Figure 1.** Schematic diagram of the experimental setup for  $\text{CO}_2$  adsorption assessment.

### 3. Results and Discussion

#### 3.1. $\text{CO}_2$ Sorption Performances of Different $\text{K}_2\text{CO}_3$ -Based Adsorbents

A series of  $\text{K}_2\text{CO}_3$ -based adsorbents were synthesized using the impregnation method, uniformly incorporating a 20% mass percentage of  $\text{K}_2\text{CO}_3$  onto various support materials. The supports selected included aluminum oxide ( $\text{Al}_2\text{O}_3$ ), coconut shell activated carbon (CSAC), coal-based activated carbon (CAC), and a series of molecular sieves, namely, zeolite ZSM-5, zeolite MCM-41, zeolite 5A, zeolite  $\beta$ , and zeolite NaY. The loading amount of  $\text{K}_2\text{CO}_3$  was determined according to the literature [46,47], and the supports were chosen for their heterogeneous pore texture and abundant porosities. A comparison of the  $\text{CO}_2$  adsorption capacities for these adsorbents, each loaded with 20%  $\text{K}_2\text{CO}_3$ , was conducted under identical conditions, as depicted in Figure 2.

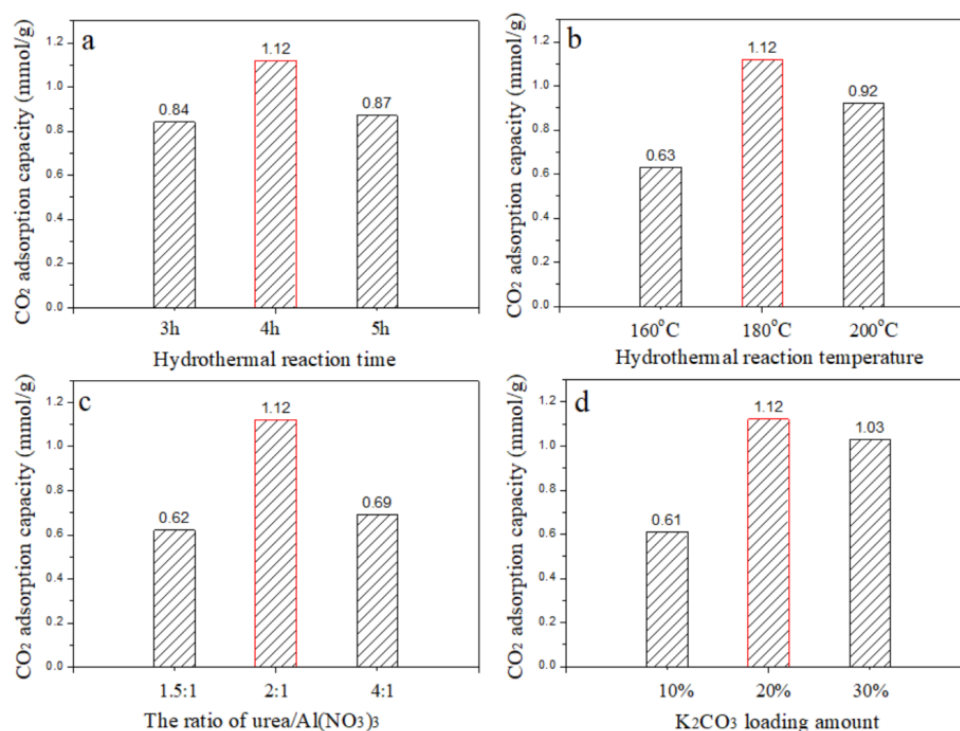


**Figure 2.**  $\text{CO}_2$  adsorption capacities of the 20%  $\text{K}_2\text{CO}_3$ /supports under the conditions: 10 vol%  $\text{CO}_2$  in air, 298 K adsorption temperature.

Porous solid materials are primarily characterized by the physical adsorption of  $\text{CO}_2$ . Given that our study focuses on a low concentration of  $\text{CO}_2$  at 10%, the physical adsorption effect results in a low adsorption capacity, which can fall below the detection limit of gas chromatography. Consequently, the  $\text{CO}_2$  adsorption capacity of the supports is not depicted here. For the adsorbents with 20%  $\text{K}_2\text{CO}_3$  loading, the 20%  $\text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3$  adsorbent exhibits a higher  $\text{CO}_2$  adsorption capacity compared to the other adsorbents. This superior performance may be attributed to the unique pore structure of  $\text{Al}_2\text{O}_3$ , which facilitates a homogeneous distribution of  $\text{K}_2\text{CO}_3$  and promotes efficient contact between  $\text{CO}_2$  and the alkaline adsorption sites.

Due to its excellent performance, the pore structure and morphology of the  $\text{Al}_2\text{O}_3$  support were further optimized by using different preparation conditions. Two types of  $\text{Al}_2\text{O}_3$  were synthesized using different precursor solutions, as described in the experimental section. In Scheme 1,  $\text{Al}_2\text{O}_3$ -1 was formed by adding urea and F127 to sodium aluminate as the aluminum source. In Scheme 2,  $\text{Al}_2\text{O}_3$ -2 was produced by incorporating urea into a solution containing aluminum nitrate as the aluminum source. Both  $\text{Al}_2\text{O}_3$ -1 and  $\text{Al}_2\text{O}_3$ -2 were then subjected to impregnation with 20%  $\text{K}_2\text{CO}_3$ , resulting in  $\text{CO}_2$  adsorption capacities of  $0.69 \text{ mmol g}^{-1}$  and  $1.12 \text{ mmol g}^{-1}$ , respectively.

The 20%  $\text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3$ -2 adsorbent exhibited a significantly higher  $\text{CO}_2$  adsorption capacity than 20%  $\text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3$ -1. Thus, further adjustments were made to the  $\text{Al}_2\text{O}_3$ -2 support, including varying the hydrothermal reaction time, temperature, and the molar ratio of urea to aluminum nitrate nonahydrate ( $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) during the hydrothermal process. The obtained results are presented in Figure 3.



**Figure 3.** (a–d)  $\text{CO}_2$  adsorption capacities of 20%  $\text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3$ -2 adsorbents by varying preparation conditions.

Figure 3a,b show the effects of hydrothermal reaction time and temperature on the preparation process, respectively. Clearly, either an excessively short reaction time or an undesirably low temperature can hinder the formation of  $\text{Al}_2\text{O}_3$  crystals with perfection. Conversely, an excessively long reaction time or high temperature can damage the pore structure, affecting the  $\text{CO}_2$  adsorption performance of  $\text{Al}_2\text{O}_3$  after  $\text{K}_2\text{CO}_3$  loading. Figure 3c illustrates the optimization of the urea/ $\text{Al}(\text{NO}_3)_3$  ratio. Proper amounts of urea and  $\text{Al}(\text{NO}_3)_3$  are crucial for precise  $\text{Al}_2\text{O}_3$  formation; excess amounts can lead

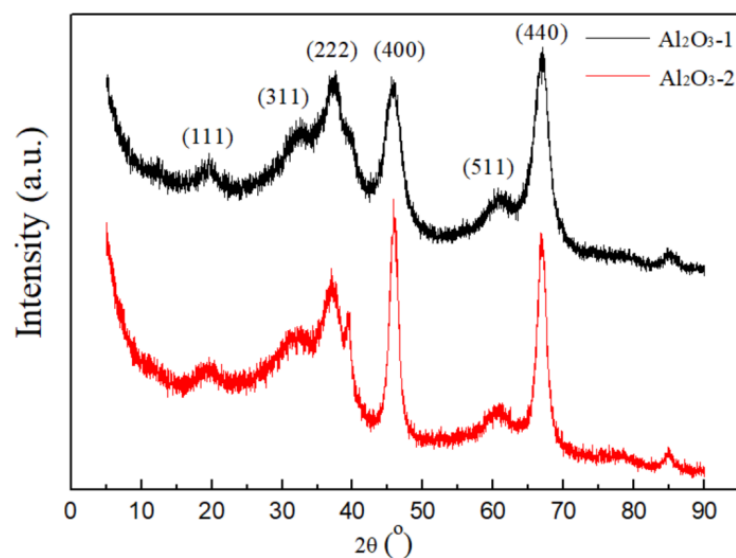
to impurities, reducing the product's purity and performance. Therefore, the optimal preparation conditions were determined to be a 2:1 molar ratio of urea to  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  in the precursor solution, with a hydrothermal reaction at 180 °C for 4 h.

Figure 3d exhibits the effect of varying the  $\text{K}_2\text{CO}_3$  loading amount, indicating that the optimal loading is 20%. At a 10% loading, there are insufficient alkaline active sites on the adsorbent surface, resulting in lower  $\text{CO}_2$  adsorption capacity. Conversely, at a 30% loading, an excess of  $\text{K}_2\text{CO}_3$  may block the pores, leading to the uneven dispersion of active sites, which in turn results in a lower utilization rate and a subsequent decrease in  $\text{CO}_2$  adsorption capacity.

Based on the optimal adsorption capacity attained, which was  $1.12 \text{ mmol g}^{-1}$ , the utilization rate of  $\text{K}_2\text{CO}_3$  was evaluated. Theoretical calculations, derived from the chemical reaction equation  $\text{K}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2 \rightleftharpoons 2\text{KHCO}_3$ , suggest that each gram of the adsorbent is capable of potentially adsorbing up to  $1.45 \text{ mmol g}^{-1}$  of  $\text{CO}_2$ . As a result, the calculated maximum utilization rate for  $\text{K}_2\text{CO}_3$  is approximately 77%.

### 3.2. Characterization of Self-Prepared $\text{Al}_2\text{O}_3$

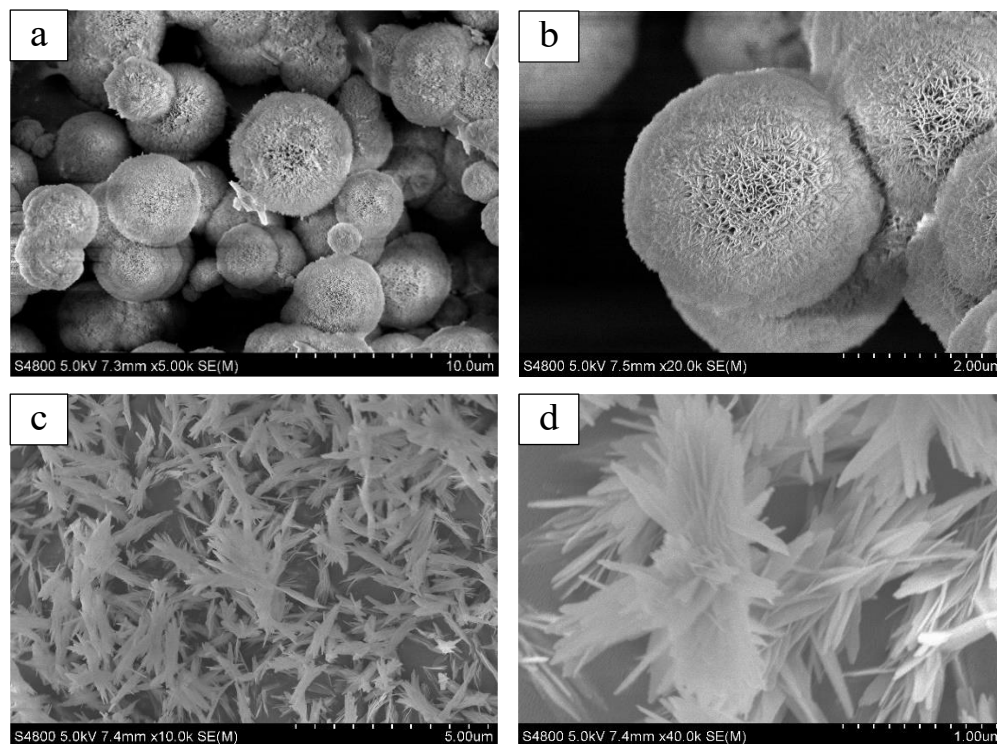
The  $\text{Al}_2\text{O}_3$  powders, synthesized using two different precursor solutions, have been subjected to comprehensive characterization and analysis. The X-ray diffraction (XRD) patterns for the  $\text{Al}_2\text{O}_3$ -1 and  $\text{Al}_2\text{O}_3$ -2 samples are presented in Figure 4. The patterns show that the reflective peaks observed in both samples are definitively attributed to cubic  $\gamma$ - $\text{Al}_2\text{O}_3$  [48], indicating a complete transformation achieved through the calcination process. In addition, the absence of any characteristic peaks from other crystalline impurities suggests that the samples exhibit an exceptionally high degree of purity. Notably,  $\text{Al}_2\text{O}_3$ -2 exhibits narrower diffraction peaks and relatively elevated peak intensities, indicating superior crystallinity and enhanced crystal quality. High crystallinity  $\gamma$ - $\text{Al}_2\text{O}_3$  may exhibit fewer defects and structural distortions, which is beneficial for improving the pore structure of the support and achieving a uniform distribution of surface active-sites [49].



**Figure 4.** XRD patterns of  $\text{Al}_2\text{O}_3$ -1 and  $\text{Al}_2\text{O}_3$ -2.

The morphologies of  $\text{Al}_2\text{O}_3$ -1 and  $\text{Al}_2\text{O}_3$ -2 were examined using scanning electron microscopy (SEM). The spherical morphologies of  $\text{Al}_2\text{O}_3$ -1 are clearly observable in Figure 5a,b. It has been reported that hydrogen bonds between the surface of aluminum hydroxide (the precursor to  $\gamma$ - $\text{Al}_2\text{O}_3$ ) and the structure-directing agent molecules can reduce the free energy of the crystals, leading to the formation of low-dimensional nanosheets [50]. These nanosheets tend to aggregate to minimize the exposed area and thus reduce surface energy. Consequently, hierarchical porous  $\gamma$ - $\text{Al}_2\text{O}_3$  particles with a similarly spherical structure were formed through the directed self-assembly mediated by F127. The hierarchical porous

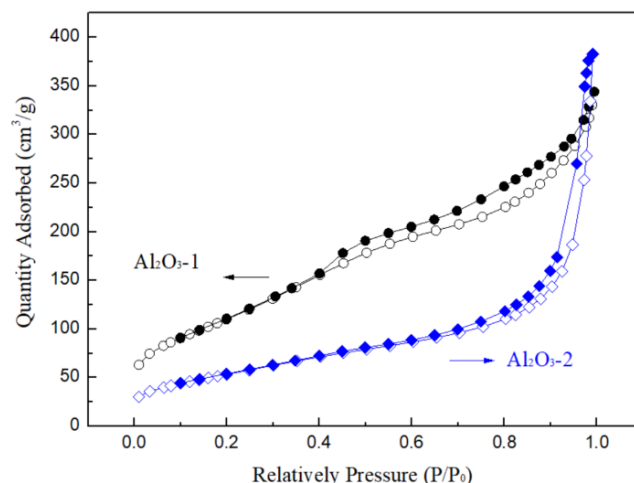
structure not only accommodates  $K_2CO_3$ , providing basic active sites for  $CO_2$  adsorption, but also provides diffusion channels for  $CO_2$ . Figure 5c depicts a low-magnification SEM image of  $Al_2O_3$ -2, showing that the sample is composed of well-dispersed spindle-like aggregates, and the irregular agglomerates are almost negligible, indicating the high quality and purity of the spindle-like aggregates. Figure 5d, a high-magnification SEM image, reveals that the three-dimensional spindle-like particles consist of well-aligned nanoplates with spindle-like edges and rough surfaces.



**Figure 5.** SEM images of  $Al_2O_3$ -1 (a,b) and  $Al_2O_3$ -2 (c,d).

Obviously, compared to the spherical structure of  $Al_2O_3$ -1, the three-dimensional spindle-shaped pore structure in  $Al_2O_3$ -2 may be more conducive to the impregnation and uniform dispersion of  $K_2CO_3$ . It is likely that the spindle-like porous structure not only facilitates the entry of  $K_2CO_3$  but also enables the accommodation and dispersion of more of it. After the loading of  $K_2CO_3$ , there is sufficient space for  $CO_2$  diffusion to be captured by active sites. In contrast, the pore size of the spherical structured  $Al_2O_3$ -1 appears relatively narrower, and after  $K_2CO_3$  loading, it is prone to blockage, leading to greater resistance to  $CO_2$  diffusion within its interior.

The hierarchical structures of the two as-prepared  $Al_2O_3$  samples were characterized using  $N_2$  adsorption–desorption isotherms, as shown in Figure 6. It is evident that the nitrogen adsorption isotherms for both materials have been classified as type IV according to the International Union of Pure and Applied Chemistry (IUPAC) [51], signifying the basic characteristic of mesoporous materials. The hysteresis loop exhibited by  $Al_2O_3$ -2 is typically characterized as type H1, which is a feature commonly observed in mesoporous materials with a relatively uniform pore size distribution. The weakly pronounced condensation steps, indicative of small mesopores, and the narrow hysteresis loop observed at high relative pressures reflect the textural larger pores that are formed between plate-like particles. It is documented in the literature that small mesopores, with diameters less than 4 nm, are formed between primary crystallites, while larger mesopores, with diameters greater than 20 nm, are formed between the secondary aggregated particles [52].



**Figure 6.** N<sub>2</sub> adsorption (hollow) and desorption (solid) isotherms of Al<sub>2</sub>O<sub>3</sub>-1 and Al<sub>2</sub>O<sub>3</sub>-2.

The Al<sub>2</sub>O<sub>3</sub>-1 curves display a type H3 hysteresis loop, characterized by the absence of a clear saturation adsorption platform. These curves indicate the presence of weak condensation steps, which are associated with the formation of larger slit-like mesopores between plate-like particles [45]. Additionally, a slightly wider hysteresis loop is observed within the relative pressure range of 0.4 to 1.0. The wider hysteresis loop is attributed to the irregularity of the pore structure. Generally, the width of the hysteresis loop is indicative of the connectivity between pores: a wider loop may suggest a lower degree of connectivity, while a narrower loop indicates a higher degree of connectivity between the pores. Obviously, the superior connectivity of the pore structure in Al<sub>2</sub>O<sub>3</sub>-2 is more favorable for the loading of K<sub>2</sub>CO<sub>3</sub> solution. Super connectivity allows for the uniform dispersion of K<sub>2</sub>CO<sub>3</sub> within the pore channels, preventing channel blockage and, in turn, facilitating the diffusion of CO<sub>2</sub>. The enhanced connectivity also promotes contact with a greater number of active sites, thereby increasing the adsorption capacity for CO<sub>2</sub>.

The pore structure parameters of the samples, including specific surface area, pore volume, and average pore size, are listed in Table 1. It can be seen that Al<sub>2</sub>O<sub>3</sub>-1 exhibits a higher BET surface area; however, this does not necessarily imply that more active sites would be exposed to CO<sub>2</sub> after K<sub>2</sub>CO<sub>3</sub> loading. The relatively small average pore diameter may lead to significant pore blockage, resulting in the loss of a large number of active sites. In contrast, Al<sub>2</sub>O<sub>3</sub>-2, which has a similar total pore volume to Al<sub>2</sub>O<sub>3</sub>-1, exhibits a much larger average pore diameter and better pore connectivity, as inferred from Figure 6. Consequently, this facilitates the uniform dispersion of K<sub>2</sub>CO<sub>3</sub>, the exposure of alkaline active sites, and the reduction of CO<sub>2</sub> diffusion resistance, thereby further enhancing the utilization rate of active sites and the CO<sub>2</sub> adsorption capacity.

**Table 1.** Textual characteristics of Al<sub>2</sub>O<sub>3</sub>-1 and Al<sub>2</sub>O<sub>3</sub>-2.

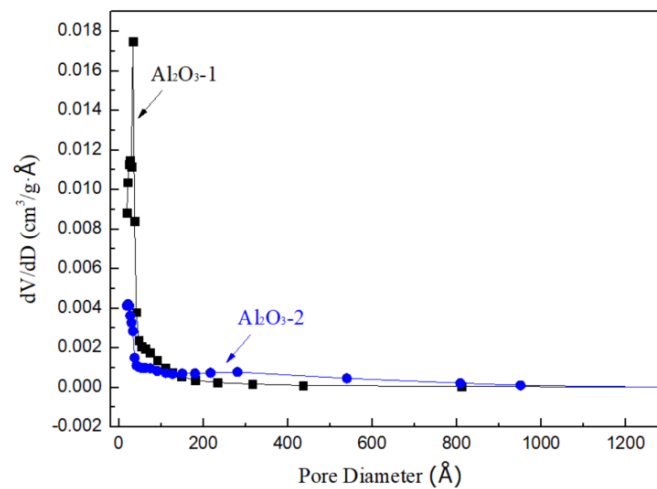
Preparation Method	BET Surface Area (m <sup>2</sup> g <sup>-1</sup> )	Pore Volume (cm <sup>3</sup> g <sup>-1</sup> )	Average Pore Diameter (nm)
Al <sub>2</sub> O <sub>3</sub> -1	417	0.53	4.9
Al <sub>2</sub> O <sub>3</sub> -2	196	0.59	11.89

Figure 7 reveals that Al<sub>2</sub>O<sub>3</sub>-1 has a higher BET surface area and a smaller average pore diameter due to its abundance of micropores, whereas Al<sub>2</sub>O<sub>3</sub>-2, with a greater number of mesopores and macropores, has a lower BET surface area and a larger average pore diameter.

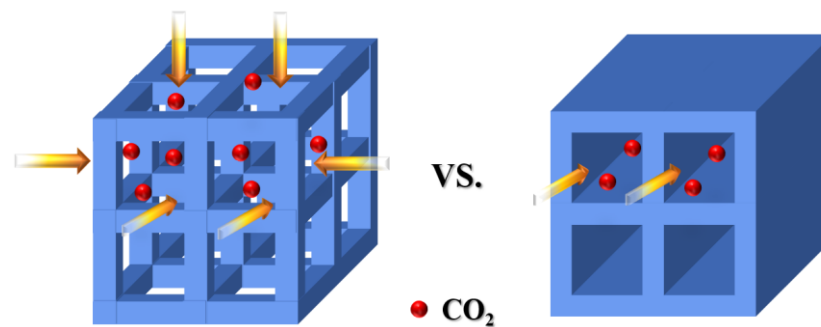
In summary, the connectivity of the pores and the large pore diameter of the support are deduced as key factors for achieving high CO<sub>2</sub> adsorption capacity. The comparative schematic of CO<sub>2</sub> diffusion in the interconnected and non-interconnected pore channels is



depicted in Figure 8. It is evident that the interconnected pores significantly facilitate the diffusion of  $\text{CO}_2$ .

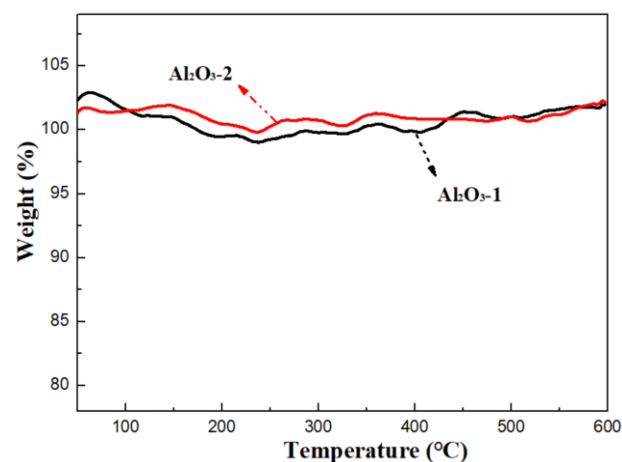


**Figure 7.** Pore size distributions of  $\text{Al}_2\text{O}_3$ -1 and  $\text{Al}_2\text{O}_3$ -2.



**Figure 8.** A comparative schematic of  $\text{CO}_2$  diffusion in interconnected and non-interconnected pore channels. The arrow represents the direction of molecular diffusion.

The thermal stability of  $\text{Al}_2\text{O}_3$ -1 and  $\text{Al}_2\text{O}_3$ -2 was examined using TGA, as depicted in Figure 9. Neither of the two aluminum oxide samples exhibited weight loss or endothermic peaks throughout the temperature-programmed process, suggesting that the aluminum oxide support is thermally stable at the adsorption and desorption temperatures of  $25\text{ }^\circ\text{C}$  and  $350\text{ }^\circ\text{C}$ . Consequently, the  $\text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3$  sorbents have the potential to be reused multiple times without losing amine sites.



**Figure 9.** TGA curves of  $\text{Al}_2\text{O}_3$ -1 and  $\text{Al}_2\text{O}_3$ -2.

### 3.3. Recycling Performance

The regeneration performance of the adsorbent was evaluated and is depicted in Figure 10. Typically, after the CO<sub>2</sub> sorption process in a closed-loop environmental control system, adsorbents are regenerated by increasing the temperature or introducing high-temperature steam. In our experiment, the used adsorbents were regenerated at 350 °C, a temperature at which the reacted products can be completely regenerated [46]. After 10 cycles, the CO<sub>2</sub> adsorption capacity of the 20% K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> sorbent showed virtually no decline, demonstrating that the prepared sorbent can be reused repeatedly while maintaining its CO<sub>2</sub> adsorption capacity.

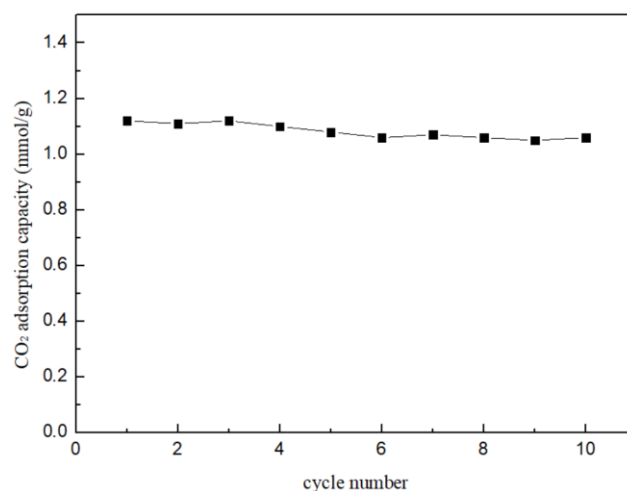


Figure 10. Recycling performance of 20% K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>-2 adsorbent after 10 cycles.

## 4. Conclusions

A series of K<sub>2</sub>CO<sub>3</sub>-based adsorbents were synthesized in this work. The CO<sub>2</sub> sorption performance was investigated in detail under ambient temperature conditions and at a CO<sub>2</sub> concentration of 10% using a fixed-bed flow sorption system, equipped with gas flow controllers and an integrated online gas chromatograph system. A 20 wt.% loading of K<sub>2</sub>CO<sub>3</sub> was impregnated onto various supports, including Al<sub>2</sub>O<sub>3</sub>, zeolites ZSM-5, MCM-41, 5A, β, and NaY, CSAC, and CAC. Among these supports, Al<sub>2</sub>O<sub>3</sub> was identified as the superior support, leading to further optimization of its pore structure by varying the preparation conditions to enhance CO<sub>2</sub> adsorption capacity. The sorbent of 20% K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>-2 achieved the maximum CO<sub>2</sub> adsorption capacity of 1.12 mmol g<sup>-1</sup>, and the utilization rate of K<sub>2</sub>CO<sub>3</sub> was 77%. The pore volume and pore size distribution were found to significantly influence CO<sub>2</sub> adsorption, as larger, interconnected pores enabled the uniform dispersion of the alkaline active sites, thereby enhancing the utilization of K<sub>2</sub>CO<sub>3</sub>. Moreover, the optimum adsorbent demonstrated full regenerability at 350 °C, highlighting its excellent recyclability. The K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> sorbent may be an excellent choice for CO<sub>2</sub> removal in coal-fired power plants.

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