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Removal of low concentration CO_2 at ambient temperature using several potassium-based sorbents

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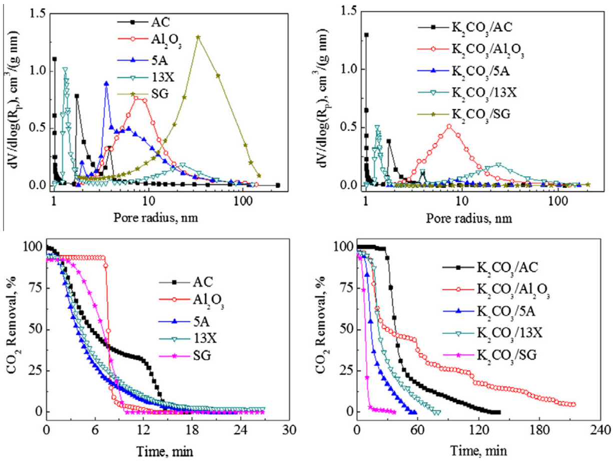
HIGHLIGHTS

- Several potassium-based sorbents were applied to low concentration CO_2 removal at ambient temperature.
- K_2CO_3/AC shows high carbonation conversion efficiency and CO_2 sorption capacity.
- K_2CO_3/5A, K_2CO_3/13X, and K_2CO_3/SG show low CO_2 sorption capacities.
- K_2CO_3/Al_2O_3 shows low carbonation conversion efficiency and needs high temperature of 350 °C to be regenerated.
- K_2CO_3/AC is a more efficacious choice for CO_2 removal in confined space.

GRAPHICAL ABSTRACT



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ABSTRACT

The requirement for long-duration human operation in a confined space has made removal of low concentration CO_2 a critical technology. The incorporation of organic amines into a porous support is thought to be a promising approach, but the low amine utilization ratio and the loss of amine components due to evaporation in regeneration process make it necessary to try new sorbents. As K_2CO_3 are more difficult to be decomposed than organic amine compound, potassium-based sorbents may be more effective for CO_2 removal in confined spaces. In this work, activated carbon (AC), Al_2O_3, zeolite 5A, zeolite 13X, and silica aerogels (SG) were chosen as the supports and K_2CO_3 was provided as the active component. An experimental demonstration of the CO_2 sorption performances of these sorbents was present in detail in the condition of ambient temperature and the CO_2 concentration of 5000 ppm. The CO_2 sorption capacities are calculated as 0.87, 1.18, 0.34, 0.53, and 0.15 mmol CO_2/g for K_2CO_3/AC, K_2CO_3/Al_2O_3, K_2CO_3/5A, K_2CO_3/13X, and K_2CO_3/SG, respectively. The reacted products are completely regenerated in the temperature range of 100–200 °C for K_2CO_3/AC and K_2CO_3/SG. Other sorbents, however, require a higher temperature of 350 °C in order to be regenerated. K_2CO_3/Al_2O_3 shows the highest CO_2 sorption capacity, while K_2CO_3/AC shows the highest bi-carbonation conversion efficiency. The CO_2 sorption capacities of K_2CO_3/5A, K_2CO_3/13X, and K_2CO_3/SG do not reach the expected values. Among these sorbents, K_2CO_3/AC is a new, more efficacious choice for CO_2 removal in confined space at ambient temperature.

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1. Introduction

The requirement for long-duration human operation in a confined space such as underground warehouses, mines, submarines and space capsules, has made removal of low concentration CO_2 a critical technology [1]. The primary method used to remove CO_2 from enclosed inhabited environments until the early 1990s was based on LiOH [2]. Although the CO_2 storage capacity of LiOH is high, the material cannot be practically regenerated. The long-term occupation of a space station or a submarine would require a CO_2 sorbent that can be easily regenerated to reduce launch weight and storage volume [3]. Recently, the incorporation of organic amines into a porous support is thought to be a promising approach, and this process has been widely studied by many researchers [4–31]. Various amine solutions were used as the active components. These divide into three categories: primary, secondary, and tertiary amine groups. The widely used supports include polymers [4–6], various silica material (SBA series [7–10], MCM series [11–15], Silica gel [16–20], and KIT series [21]), carbon materials [22–27], and zeolites [28–31]. Although various amine-based sorbents show high CO_2 sorption capacities, the utilization of amine compound is not high for all sorbents. Their amine utilization ratio was reported as only 20–67%. Another significant drawback for amine-based sorbents is loss of amine components due to evaporation when the sorbent is regenerated at a temperature higher than 100 °C. The requirement for solving these problems makes it necessary to test new sorbents.

Recently, carbon capture and storage is recognized as a promising option for CO_2 emission reduction [32–36], and alkali metal carbonates can be used to capture CO_2 in the presence of H_2O to form either sodium or potassium bicarbonate at temperatures below 100 °C [37]. A moderate temperature swing of 120–200 °C then causes the bicarbonate to decompose and release a mixture of CO_2/H_2O that can be converted into a "sequestration-ready" CO_2 stream by subsequently condensing the steam. Compared with the amine-based sorbent, alkali metal carbonates are more difficult to be decomposed; this is even the case if the temperature is increased to 800 °C. These sorbents may therefore be more effective for CO_2 removal in confined space. If the alkali metal-based sorbents are used for this technology, they should feature high sorption capacities at low CO_2 partial pressures and at ambient temperature. However, in previous studies most researchers have only examined the CO_2 capture behaviors of alkali metal-based sorbents under the reaction conditions of 50–100 °C, 5–20% CO_2, 5–20% H_2O [37–46]. It is unclear whether the carbonation reaction paths change when the temperature is the ambient temperature and the CO_2 concentration is lower than 1%. It is also unknown if their CO_2 sorption capacities keep high values in this situation.

Firstly, it was reported that K_2CO_3/AC [38–41,43,45] (activated carbon) and K_2CO_3/Al_2O_3 [42–46] had the potential to be employed as suitable sorbents for CO_2 capture in flue gas from fossil fuel-fired power plants due to their high CO_2 capture capacities and rapid carbonation reaction rates. Secondly, the zeolites [28–31,47–50] possess well-defined pore structures and their pore sizes are of the same magnitude as CO_2 molecules, they are therefore expected to have good affinities for CO_2 capture, and these pore sizes can accommodate both the immobilized alkali metal carbonates and the adsorbed CO_2. Thirdly, silica aerogels (SG) possessing an open pore structure, a high porosity, a high surface area and a low density, have a great potential for utilization as CO_2 adsorbents [16–20]. Nonetheless in order to reach high adsorption capacities, SG should be functionalized. Here, AC, Al_2O_3, zeolite 5A, zeolite 13X, and SG were chosen as the supports, and K_2CO_3 was chosen as the active component. An experimental demonstration of the CO_2 sorption performances of these sorbents was presented in detail in the condition of ambient temperature and the CO_2 concentration of 5000 ppm. Additionally, the CO_2 sorption capacities of these potassium-based sorbents were compared with other sorbents such as amine-tethered solid sorbents.

2. Experimental section

2.1. Samples

The supported potassium-based sorbents were prepared by impregnating K_2CO_3 on AC, Al_2O_3, zeolite 5A, and 13X, and SG, respectively. K_2CO_3 was provided as an analytical reagent. Al_2O_3 and AC were supplied by Research Institute of Nanjing Chemical Industry Group. Zeolite 5A and 13X were supplied by Shanghai Zeolite Molecular Sieve Co., LTD. SG was supplied by Shanghai Shangchen Industrial Co., LTD. The preparation process of these sorbents consisted of three steps as follows: (1) 10 g of support material were added to an aqueous solution of anhydrous K_2CO_3 in 100 ml of deionized water. Then it was mixed with a magnetic stirrer for 20 h at room temperature. (2) After stirring, the mixture was dried in a rotary vacuum evaporator at 105 °C for dehydration. (3) The dried samples were calcined in a furnace under a N_2 flow (100 ml/min) for 3 h at 300 °C.

All sorbents were prepared with theoretical K_2CO_3 loadings of 30%. However, the actual loadings are 12.49%, 28.5%, 11.2%, 16.2%, and 37.5% for K_2CO_3/AC, K_2CO_3/Al_2O_3, K_2CO_3/5A, K_2CO_3/13X, and K_2CO_3/SG, respectively.

2.2. Apparatus and procedure

The CO_2 sorption performances of these sorbents were assessed using a modified fixed bed reactor system coupled with a gas analyzer. This experimental setup is shown in Fig. 1.

The atmosphere was simulated by a constant flow of CO_2, H_2O and a balance of N_2. CO_2 and N_2 were obtained from high-purity cylinders and delivered to the experimental apparatus with mass flow controllers. H_2O was fed using a high-precision syringe pump and then heated to ensure complete vaporization. The fixed-bed reactor with an inner diameter of 0.05 m was made of stainless steel and was set in an electrically heated furnace. The electric heating was used to heat the reactor to the given temperature. A water pipe was buried in the cast copper. This water-cooling heat exchanger was used to keep the temperature constant, when the exothermic reaction occurred. A gravimetric sensor was used to detect the change of the sorbent's weight online. The Relative Humidity (RH) and temperature of the simulated atmosphere were also monitored online by a hygrothermograph. A gas analyzer was used to measure the CO_2 concentration of the outlet gas continuously. A total of 10 g of the sorbent was placed into the reactor, and the height of the material was 0.01 m. A simulated gas composition consisting of 5000 ppm CO_2 + 1.8% H_2O at a total flow rate of 0.05 m^3/h was used for the carbonation reactions. The reaction temperature is 20 °C. When the carbonation reaction was finished, the gas composition was changed to 100% N_2, and the reaction temperature was increased to 400 °C. In this way, the regeneration processes of these sorbents were carried out.

The amount of K_2CO_3 impregnated was determined by an Inductively Coupled Plasma Mass Spectrometer. An ASAP 2020 system with N_2 adsorption–desorption was used for surface area and pore structure determination.