Preparation of the New Low-Cost K_2CO_3/Al_2O_3 Sorbent for CO_2 Capture at Flue Gas Operating Conditions

Javad Esmaili (Corresponding author), Mohammad Reza Ehsani

Department of Chemical Engineering, Isfahan University of Technology, Isfahan, 84156-83111, Iran
javad_esmaili@ce.iut.ac.ir

Abstract: In this study, the preparation of the new low-cost potassium carbonate on alumina support sorbents prepared by impregnating K_2CO_3 on industrial grade of Al_2O_3 support was investigated. The CO_2 capture capacity was measured in the presence of H_2O in a fixed-bed reactor at CO_2 capture temperature of 60°C using breakthrough curves. The sorbent developed showed the adsorption capacity of 75.4 $mgCO_2$/g sorbent. The stability of sorbent capture capacity is higher than the reference sorbent. The changes in the pore volume and surface area are $0.020 cm^3$/g and $5.5 m^2$/g, respectively after 5 cycles adsorption and regeneration. The small changes occur in the pore size distribution and surface area of sorbent after 5 cycles. This sorbent can be considered for large-scale applications.

1. Introduction:

Global warming increasingly thought to be associated with the atmospheric emission of greenhouse gases. Carbon Dioxide is a major greenhouse gas that is released into the atmosphere due to the use of fossil fuels. Large amounts of CO2 are emitted in diluted streams at atmospheric pressure, for instance, in flue gases from power stations, as the fuel is usually burned in air. It can be removed from these streams by various methods such as membrane separation, amine scrubbing, and using molecular sieves [1-3]. These methods however are costly and energy intensive.

Solid sorbent processes for CO_2 capture are also under study. The use of solid sorbents can be a highly cost-effective and energy efficient way to remove CO_2 [4-7]. Sorbents containing alkali and alkaline-earth metals like potassium carbonate and calcium oxide are investigated for this commercial feasibility [8].

Alkaline-earth method-based sorbents such as MgO and CaO are applicable at much higher adsorption and regeneration temperatures [7]. Alkali metal-based sorbents were employed in CO_2 adsorption at low temperatures (50-70°C) with thermal regeneration easily occurring at low temperatures (<200°C). CO_2 capture using a dry sodium-based sorbent was also reported [9,10]. However, when CO_2 reacted with Na_2CO_3, the global carbonation reaction rate was rather slow [11]. The CO_2 adsorption and regeneration of potassium-based sorbents with several supports such as activated carbon [4,5,12], TiO_2, SiO_2, MgO, ZrO_2, CaO and Al_2O_3 were studied [6,9,13,14]. Al_2O_3 is one of the most proper materials used as sorbent support. An

Ideal dry sorbent must have a high CO_2 capture capacity, high adsorption rate, excellent regeneration property, and high attrition resistance to remove CO_2 from the flue gas.

In all of the previous works, initial materials used were from high pure materials that have low impurities and high costs. The objective of this work is to develop a low-cost, high-capacity CO_2 sorbent and to demonstrate its technical and economical potentials for post-combustion CO_2 capture. For synthesis of this sorbent industrial grade of alumina (that has the highest cost in sorbent preparation) was used and some of the important specifications of the prepared sorbent such as, capture capacity at single and multiple cycles, surface area, and structural properties are obtained in this work.

2. Experimental

Preparation of Sorbents. The potassium-based sorbents used in this study were prepared by impregnating K_2CO_3 (Merck) on Alumina of industrial grades as support. Twenty (20.0) g of Al_2O_3 was added to 100 ml of an aqueous solution of anhydrous potassium carbonate with 9wt% concentration in deionized water. Then, it was mixed with a magnetic stirrer at room temperature for 24 hours. After that, the mixture was dried in a rotary vacuum evaporator at 60 °C. The dried samples were calcined in a furnace under the N_2 flow (100 cc/min) for 4 hours at 300 °C. The amount of K_2CO_3 loaded was 23.2% and the sorbent had an apparent density of 2.44 g/cm^3.

Apparatus and Procedures. A fixed-bed Stainless-Steel reactor (diameter of 15 mm), which was placed in an electric furnace under atmospheric

pressure was used for adsorption process. Two (2.0) g of the sorbent was packed into the reactor. In order to prevent condensation of water vapor injected into the reactor and the GC column, the temperatures of the inlet and outlet lines of the reactor were maintained above 100 °C. The column used in this analysis was a 1/8 in. stainless tube packed with Porapak Q. When the CO_2 concentration of the outlet gas reached the same level as that of the inlet gas in the CO_2 adsorption process, process was stopped. The outlet gas from the reactor was automatically analyzed every 5 min by a thermal conductivity detector (TCD), which was equipped with an auto sampler (Valco online valve). Schematic diagram of the fixed-bed reactor is shown in Fig. 1.

The feed stream comprises of Nitrogen, carbon dioxide and water. The liquid water flow rate was controlled using a piston pump and the water was vaporized before entering the column. Both CO_2 and N_2 flow rates were controlled by independent mass flow controllers and these gases are were mixed with the vaporized water inside the oven where experiments were done. All the CO_2 sorption tests were performed following the same procedure.

The CO_2 capture capacity of the sorbent was evaluated by the breakthrough curve for CO_2 adsorption. In this study, the CO_2 capture capacity of sorbent was calculated from its breakthrough curve during CO_2 adsorption in the presence of 9.0 vol.% H_2O and 1 vol.% CO_2. The CO_2 capture capacity describes the amount of CO_2 absorbed until the output concentration of CO_2 reached 1 vol.%, which is the same value as that of the inlet. Adsorption and regeneration processes were carried out at 60 °C and 200 °C, respectively.
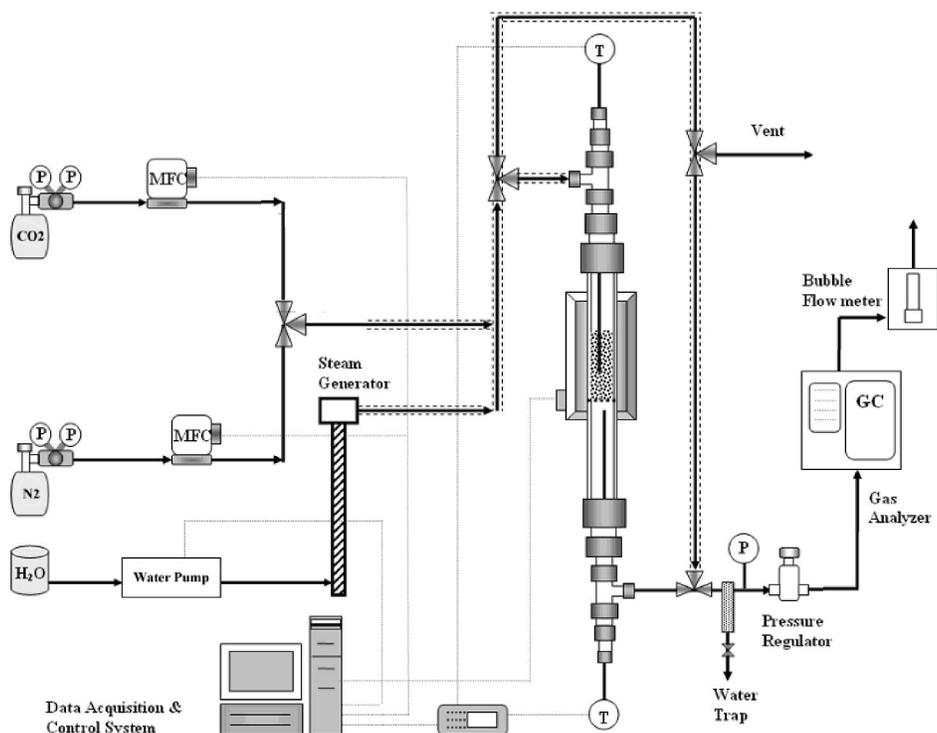
Fig 1. Schematic Diagram of the fixed-Bed Reactor

3. Results and Discussion

Fig. 2 shows the CO_2 Breakthrough Curve (CO_2 concentration changes during adsorption step at the bed outlet) for new developed sorbent. The CO_2 concentration was nearly zero for about first 10 min, indicating that CO_2 was completely adsorbed. The CO_2 concentration then slowly increased to 1% after 180 min indicating the complete conversion of available K_2CO_3 in sorbent at this time.
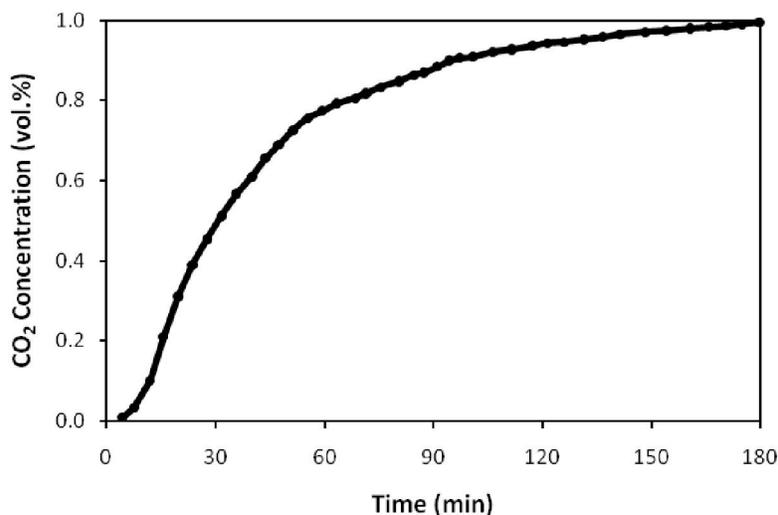
Fig 2. Change of the CO_2 Concentration during adsorption

Fig. 3 shows the total CO_2 capture capacities of the new low-cost sorbent as well as those obtained [15] as a function of cycle number. In this figure both adsorption and regeneration are considered as a one-cycle process. As shown in Fig. 3, the total capture capacity of the new low-cost sorbent was about 75.4 mg CO_2/g sorbent at the first cycle. This amount is lower than the value of the reference sorbent at the first cycles; but the stability of capture capacity is higher because, after 5 cycles, capture capacity decreases by 35% that is lower than the reference sorbent. These results show that new low-cost sorbent developed in this study is more suitable for multiple cycle operations necessary for industrial applications.
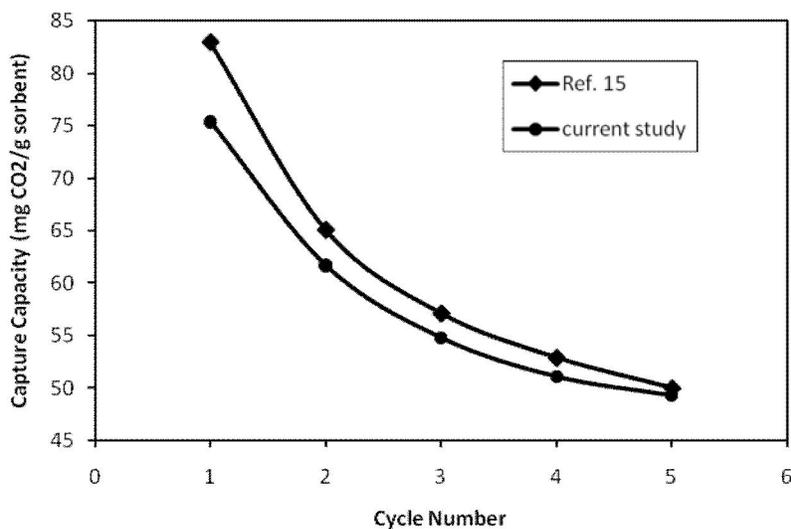
Fig 3. The CO_2 capture capacity of the sorbents as function of cycle number

For study on Sorbent structure change during adsorption and regeneration process three samples (0.5 g) were taken after the 1st, 3rd, and 5th cycles, respectively, and the surface area and pore volume were measured with N_2 adsorption method. The pore volume and the surface area of the samples are shown in Fig. 4. The surface area and pore volume of sorbent decrease as the number of cycles increases.
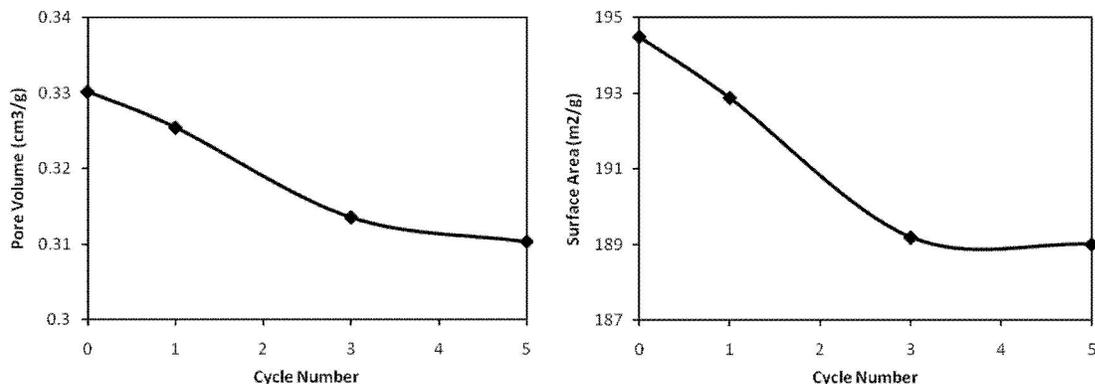
Fig 4. Changes of the pore volume and surface area with the cycle number

As shown in Fig. 5, for 80% of pores of the fresh sorbent, the pore size distribution range from 1.8 to 20.0 nm. The maximum value of the pore volume appears at 5.4 nm. There is a little change in pore size distribution after 5 cycles.
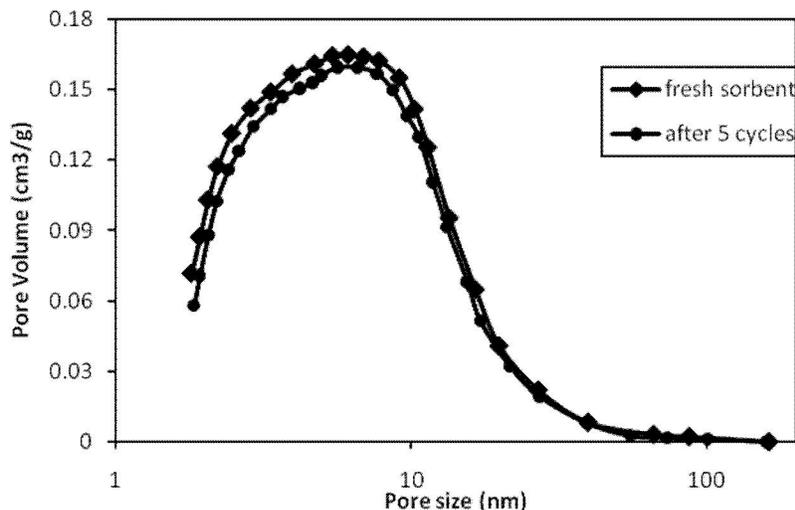
Fig 5. Pore size distribution of sorbent

The SEM images for fresh sorbent and sorbent after 5 cycles are shown in Fig. 6. The SEM images confirm that the change in the structure is minimal after 5 cycles.
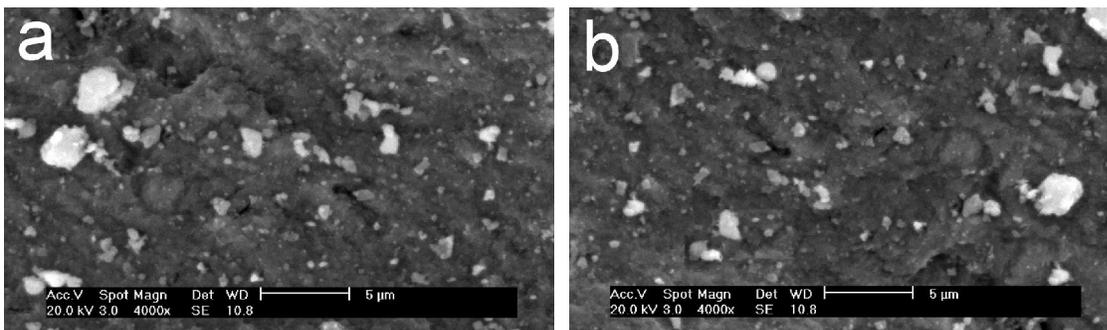
Fig 6. Scanning electron micrographs of sorbent: (a) fresh sorbent; (b) after 5 cycles

4. Conclusion

The low-cost sorbent developed in this study showed 75.4 mgCO_2/g sorbent in present of 1.0% CO_2 and 9.0 vol.% H_2O at 60°C. The capture capacity of sorbent as a function of cycle number was investigated in a fixed-bed reactor. The stability of sorbent capture capacity is higher than the reference sorbent. The changes in the pore volume and surface area are 0.020cm^3/g and 5.5m^2/g, respectively. Small changes occur in the pore size distribution and surface area of the prepared sorbent. This sorbent could be used for an industrial CO_2 capture processes with fixed-bed reactors. To investigate this purpose, a dual fixed-bed reactor is needed for operating at real cyclic steady-state condition.

References

[1] Hagewiesche, Ashour, S. S., Al-Ghawas, H. A., Sandall, O. C., "Absorption of Carbon Dioxide into Aqueous Blends of Monoethanolamine and N-methyldiethanolamine", *Chem. Eng. Sci.*, 50 (7), 1071–1079, 1995.

[2] Mavroudi, M., Kaldis, S. P., Sakellaropoulos, G. P., "Reduction of CO_2 Emissions by a Membrane Contacting Process", *Fuel*, 82, 2153–2159, 2003.

[3] Siriwardane, R. V., Shen, M. S., Fisher, E. P., Poston, J. A. "Adsorption of CO_2 on Molecular Sieves and Activated Carbon", *Energy Fuels*, 15, 279–284, 2001.

[4] Hayashi, H., Taniuchi, J., Furuyashiki, N., Sugiyama, S., Hirano, S., Shigemoto, N., Nonaka, T., "Efficient Recovery of Carbon Dioxide from Flue Gases of Coal-Fired Power Plants by Cyclic Fixed-Bed Operations over K2CO3-on-Carbon", *Ind. Eng. Chem. Res.*, 37, 185–191, 1998.

[5] Shigemoto, N., Yanagihara, T., Sugiyama, S., Hayashi, H., "Material Balance and Energy Consumption for CO_2 Recovery from Moist Flue Gas Employing K_2CO_3-on-Activated Carbon and Its Evaluation for Practical Adaptation", *Energy Fuels*, 20 (2), 721–726, 2006.

[6] Lee, S. C., Choi, B. Y., Lee, S. J., Jung, S. Y., Ryu, C. K., Kim, J. C. "CO_2 Absorption and Regeneration using Na and K based sorbents", *Studies in Surface Science and Catalysis,* 153, 527–530, 2004.

[7] Lee, S. C., Choi, B. Y., Lee, T. J., Ryu, C. K., Ahn, Y. S., Kim, J. C., "CO_2 "Absorption and regeneration of alkali metal-based solid sorbents", *Catal. Today*, 111, 385–390, 2006.

[8] Hoffman, J.S., Pennline, H.W., "Study of Regenerable Sorbents for CO_2 Capture", *First National Conference on Carbon Sequestration*, Washington, 2001.

[9] Liang, Y., Harrison, D. P., Gupta, R. P., Green, D. A., McMichael, W. J., "Carbon Dioxide Capture Using Dry Sodium-Based Sorbents", *Energy Fuels*, 18, 569–575, 2004.

[10] Seo, Y. W., Jo, S. H., Ryu, C. K., Yi, C. K., "Effects of water vapor pretreatment time and reaction temperature on CO_2 capture characteristics of a sodium-based solid sorbent in a bubbling fluidized-bed reactor", *Chemosphere*, 69, 712–718, 2007.

[11] Zhao, Chu, Chen, X., Zhao, Cha., "CO_2 absorption using dry potassium-based sorbents with different supports", *Energy Fuels*, 23, 4683–4687, 2009.

[12] Hirano, S., Shigemoto, N., Yamaha, S., Hayashi, H., "Cyclic Fixed-Bed Operations over K_2CO_3-on-Carbon for the Recovery of Carbon Dioxide under Moist Conditions", *Bull. Chem. Soc. Jpn.*, 68, 1030-1035, 1995.

[13] Okunev, A. G., Sharonov, V. E., Aistov, Y. I., Parmon, V. N., "Sorption of Carbon Dioxide from Wet Gases by K_2CO_3-in-Porous Matrix: Influence of the Matrix Nature", *Reaction Kinetics and Catalysis Letters*, 71 (2), 355–362, 2000.

[14] Okunev, A. G., Sharonov, V. E., Gubar, A. V., Danilova, I. G., Paukshtis, E. A., Moroz, E. M., Kriger, T. A., Malakhov, V. V., Aistov, Y. I., "Sorption of carbon dioxide by the composite sorbent: potassium carbonate in porous matrix", *Russ. Chem. Bull., Int. Ed.*, 52 (2), 359–363, 2003.

[15] Lee, S. C., Chae, H. J., Lee S. J., Park, Y. H., Ryu, C. K., Yi, C. K., Kim, J. C., "Novel Regenerable Potassium-Based Dry Sorbents for CO_2 Capture at Low Temperatures", *J. Mol. Catal. B: Enzym.*, 56, 179-184, 2009.

5/17/2013