FINAL REPORT

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Title: Development of a New Solid Sorbent for CO_2 Separation

Submitted to

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EXECUTIVE SUMMARY

Introduction

The concentration of CO_2 in atmosphere has increased considerably in last 100 years, especially in last 50 years. Industries, especially power industry, are the large anthropogenic CO_2 emitters. On one hand, these fossil fuels, including coal, oil and natural gas, are expected still to be the major energy resources in the foreseeable future. On the other hand, people want to limit the emission of CO_2 to the atmosphere because CO_2 is possibly linked to the increasingly concerned global warming. To meet the needs of both environmental protection and industrial development, capture of CO_2 from its large emitters such as coal based power plants has become increasingly important.

A number of technologies have already been developed for separation of CO_2 generated by coal-fired power plants, which include amine solutions. These technologies use the reversibility of the reactions between alkaline chemicals and CO_2 for CO_2 separation amines. The obvious advantage of the aqueous CO_2 separation methods is their high CO_2 sorption efficiencies. However, they are too energy intensive due to use of water. Consequently, other processes need to be developed.

Supported solid sorbents are promising CO_2 separation materials from perspectives of improvement of CO_2 adsorption rate and reduction of energy demand for CO_2 capture. For example, in recent years, people are increasingly interested in using solid sorbents synthesized with amines and solid supports or grafting materials for CO_2 separation in coal-fired power plants. Compared to aqueous amines, solid sorbents have several advantages when used for separation of CO_2 from flue gases in power plants. The first one is that solid amine sorbents

consumes less energy than aqueous counterparts to perform the same CO_2 separation tasks, which is mainly due to their avoidance of H_2O with high specific-heat-capacity and heat of vaporization. Additionally, it is easy to handle and transport solid sorbents in coal-fired power plants.

Different from conventional monoethanolamine (MEA) immobilization approaches, a semi-immobilization to use amine for CO_2 separation has been studied in this research. In other words, MEA is immobilized during the CO_2 sorption step while it is mobilized during CO_2 desorption step. More specifically, immobilized MEA reacts with CO_2 in a sorption reactor, but is transported to another reactor during the CO_2 desorption process due to the use of higher temperatures. The proposed technology is also developed based on the idea that the practical supporting materials for MEA should be inexpensive, widely available, and light in densities to reduce the overall cost of using the MEA based sorbent for CO_2 separation. Many supporting materials including TiO_2, Al_2O_3, SiO_2, $FeOOH$ and $TiO(OH)_2$ have been considered. TiO_2, $FeOOH$ and $TiO(OH)_2$ are three compounds rarely used by other researchers. However, we finally use TiO_2 as a support for MEA to separate CO_2 due to its wide availability and lower price compared to $FeOOH$ and $TiO(OH)_2$. The MEA utilization approach studied in this research is expected to considerably reduce CO_2 separation energy consumption and costs. The resultant saving is expected much larger than that needed for compensation of the added sorbent cost due to the use of TiO_2. Several major factors potentially affecting the CO_2 sorption capacities of the proposed MEA utilization method were investigated. The results obtained in the research could be used for further development or optimization and eventually commercialization of the MEA based CO_2 separation technology.

Project Objectives

The first objective of the proposed project is to develop an alternative method for using monoethanolamine (MEA) in CO_2 separation from the viewpoints of the MEA-CO_2 reaction environment and the process of spent sorbent regeneration MEA-TiO_2 (MT). The second one is to evaluate the factors affecting the performance of the MT sorbent on CO_2 separation to achieve high CO_2 sorption capacity. Another objective is to investigate the regenerable ability of MT sorbent. The final objective is to establish the kinetic model of the CO_2 desorption associated with the new MEA based CO_2 separation technology.

Project Outcomes

Sorbent Preparation

An inexpensive MEA/TiO_2 (hereafter named as MT) based sorbent using MEA and nanoporous widely available TiO_2 has been developed. TiO_2 can be prepared by using a predetermined amounts of $Ti(OC_2H_5)_4$ and water, filtering the resultant precipitate and washing it with deionized water, and drying it at 393 K for a given period of time, although commercial TiO_2 can be used. The prepared supporting material (TiO_2) can be characterized with a physisorption analyzer to determine its surface area, average pore size, and pore volume, and a powder X-ray diffraction (XRD) analyzer for its structure.

CO_2 Separation

An experimental set-up which can be used for evaluation of the performance of MT CO_2 sorbent is successfully designed and tested. The set-up mainly consists of N_2 cylinder, CO_2

cylinder, flow meters, syringe pump, heat tape, temperature controller for heat tape, temperature controller for furnace, quartz wool, sorbent bed, furnace, reactors, cooling water, cooling water temperature controller, water vapor removal unit, a multi-gas analyzer, and a data collection unit. CO_2 sorption tests can be performed in a bottom reactor. The sorbent bed in the bottom reactor is prepared by loading MT sorbent between two bed holders made from quartz wool. The bottom reactor can be held in a tube furnace whose temperature can be controlled with a temperature controller. A syringe pump can be used to generate the water vapor used in moisture-containing gas streams. Temperature controlled thermo-tapes can be used to heat the inlet gas tubes to prevent condensation of water vapor prior to entering the bottom reactor. The effluent gas stream from the bottom reactor passes through a sorbent bed (consisting of the support material for MT sorbent, TiO_2) in the top reactor to condense the MEA vaporized from the bottom reactor using cooling water circulating through a spiral copper pipe and held at 12°C by a small refrigeration unit. The effluent gas from the top reactor enters a water removal unit and then an infrared gas analyzer for measurement of the concentration of CO_2 in the outlet gas stream. The CO_2 sorption profiles are collected using a data collection unit.

Factors Affecting CO_2 Separation of MT

MEA Loading

The CO_2 sorption capacity of the MT sorbent is affected by the loading of MEA on TiO_2. The sorption capacity of the MT sorbent is 1.09 mol-CO_2/kg-MT at 45 wt% MEA, although an optimum of 40 wt% MEA loading was chosen for most of the sorption tests.

Moisture

The CO_2 sorption capacities of MT are affected to some degrees but not significantly by the concentration of H_2O in gas stream during the initial CO_2 sorption periods within which the outlet CO_2 concentrations of the gas streams are 0 vol% or all the CO_2 molecules in gas streams are completely adsorbed on MT.

Sorption Temperature

Effects of sorption temperature on the total CO_2 sorption capacity of MT sorbents were evaluated in the temperature range of 25-65 ^{o}C. The CO_2 sorption capacity of MT increases with temperature in the range of 25 to 45°C, but decreases with the further increases of temperature from 45 to 65 ^{o}C.

Desorption Temperature

Effects of CO_2 desorption temperature on the total CO_2 sorption capacity of the MT sorbent regenerated for next cycle of sorption and desorption were evaluated in the temperature range of 80-110 ^{o}C. CO_2 desorption tests were performed at 80°C, 90°C, 100°C and 110°C to evaluate the effect of temperature on CO_2 sorption capacity of the MT sorbent. The intermediate temperatures, 90°C and 100°C, are better based on the sorption capacities obtained in the next sorption-desorption cycle. However, due to the higher energy consumption at 100°C, 90°C was chosen as the CO_2 desorption temperature for all other MT evaluation tests. Actually, CO_2 desorption at a lower temperature not only reduce the energy needed for overall CO_2 separation process but also is favorable to the structure stability of MEA, and environmental protection.

Alternative Support Materials for MEA

An alternative Ti based support material is $TiO(OH)_2$. It can be easily prepared at low temperatures compared to TiO_2. It is stable even at 400°C. Its performance as a support for MEA is better than TiO_2 to some degree during most of the sorption period. $TiO(OH)_2$ can probably accelerate CO_2 sorption to some degree due to its structure. Among many other possible highly porous and inexpensive MEA support materials is FeOOH. FeOOH is thermally stable under the operation conditions used in this research. The CO_2 sorption results with the pure MEA supported with FeOOH indicate that FeOOH is better than TiO_2, but not as good as $TiO(OH)_2$.

Sorbent regeneration

Industrial sorbents are required not only to be highly active and selective, but also regenerable. Therefore, five-cycle CO_2 sorption-desorption tests with MT sorbents were run under conditions with and without moisture. The average adsorption capacities for five-cycle tests at 45°C under dry and humid (1 vol% H_2O) sorption conditions are 1.04 and 1.09 mol-CO_2/kg-MT, respectively, indicating MT can be used in both dry and wet environments for effective CO_2 separation.

The capacities of MT under the two different environments are higher than that of aqueous MEA, which can absorb 0.82 mol-CO_2/kg-aqueous-MEA. In addition, they are also higher than those of the sorbents recently reported in literature. The regeneration temperatures of those sorbents varied from 80 to 120°C and increased by 10°C with each subsequent sorption-desorption cycle compared to the constant 90°C used for the spent MT regeneration. The quantities of CO_2 immobilized on MT during the sorption period and CO_2 desorbed from spent MT during the desorption process are very close. In other words, the CO_2 sorption capacities of MT do not fluctuate considerably from one sorption-desorption cycle to another.

Conclusions

An alternative method for using monoethanolamine (MEA) in CO_2 separation has been developed from the viewpoints of the MEA-CO_2 reaction environment and the process of spent sorbent regeneration. MT sorbent is synthesized using pure MEA and TiO_2. The performance of the MT sorbent on CO_2 separation was investigated in tubular reactors under various experimental conditions. The sorption capacity of the MT sorbent reached 1.09 mol-CO_2/kg-MT. Temperature affected the CO_2 sorption capacity considerably, with optimum values of 45°C for adsorption and 90°C for regeneration, while humidity has a small positive effect. The MT sorbent is regenerable, with a multi-cycle sorption capacity of ~ 0.91 mol-CO_2/kg-MT. MT is a promising CO_2 sorbent. Like any other CO_2 separation technologies, CO_2 desorption from MT is the most energy-intensive step in the overall CO_2 separation process. The presence of water during CO_2 desorption process leads to a significant increase in energy consumption. The activation energy of the CO_2 desorption is 80.79 kJ/mol. The kinetic characteristics of the CO_2 desorption are much superior to those associated with aqueous MEA based CO_2 separation. The energy saving is not only due to voiding the use of water but also the favorable desorption kinetics of MT based CO_2 separation. Therefore, the proposed technology could significantly reduce the energy needed for CO_2 separation.