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Characterization of new potassium-based solid sorbents prepared using metal silicates for post-combustion CO_2 capture

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ABSTRACT

Potassium-based sorbents prepared using metal oxides as supports or additive materials are commonly applied in fast fluidized bed reactors for post-combustion CO_2 capture. However, they have some disadvantages in terms of regeneration properties. To overcome these drawbacks, novel potassium-based sorbents, herein termed KAS, KCS, and KZS, prepared using aluminum silicate, calcium silicate, and zirconium silicate, respectively, were developed in this study. Unlike potassium-based sorbents prepared using metal oxides, the new sorbents exhibited high CO_2 capture capacities (90–96 mg CO_2/g sorbent) and excellent regeneration ratios of 90% or more during multiple tests, even at a the low regeneration temperature of 200 °C. These improved results were achieved because $KHCO_3$ alone is formed during CO_2 sorption without any by-product formation, and there is no loss of the active material (K_2CO_3) during preparation. Thus, metal silicates can be used to prepare potassium-based solid sorbents for CO_2 capture at low temperatures.

1. Introduction

CO_2 emitted from fossil fuel power plants causes global warming and climate change. Consequently, considerable research efforts are being made to reduce CO_2 emissions. One of the most effective techniques for removing CO_2 is CO_2 capture using solid sorbents. These solid sorbents require simple equipment for their application, have low capital and operating costs, produce less waste water, and are not susceptible to corrosion (Chae et al., 2016). It is especially worthy of mention that post-combustion CO_2 capture technology may be applied to both new and established fossil fuel power plants in the immediate future (Thiruvenkatachari et al., 2013; Zhao et al., 2010). Potassium-based sorbents are widely used for post-combustion CO_2 capture, removing CO_2 by the following reaction:

$$K_2CO_3 + CO_2 + H_2O \rightleftarrows KHCO_3$$

At temperatures between 50 and 70 °C, K_2CO_3 as the active material reacts with CO_2 and H_2O transforms to form $KHCO_3$. This $KHCO_3$ phase can be easily converted back to the original K_2CO_3 phase at temperatures below 200 °C (Hirano et al., 1995; Hayashi et al., 1998; Hoffman and Pennline, 2000; Lee et al., 2006). In general, these potassium-based solid sorbents are used in fast fluidized bed reactors. An ideal potassium-based solid sorbent for CO_2 capture in fast fluidized bed reactors should have high CO_2 capture capacity, excellent regeneration properties, and high attrition resistance (Lee et al., 2008; Lee et al., 2011; Yi et al., 2007). Thus, several studies have focused on the development of potassium-based solid sorbents using various supports (Zhang et al., 2011).

Metal oxides like gamma-alumina (γ-Al_2O_3), magnesium oxide (MgO), calcium oxide (CaO), titanium dioxide (TiO_2), and silicon dioxide (SiO_2) are used as supports or additive materials in the fabrication of potassium-based solid sorbents for CO_2 capture from flue gas (Jo et al. 2016; Lee et al., 2006; Okunev et al., 2000; Okunev et al., 2003). However, potassium-based sorbents prepared using metal oxides have certain disadvantages. Potassium-based sorbents prepared using γ-Al_2O_3 have high CO_2 capture capacities at 1 cycle. However, their CO_2 capture capacities are rapidly decreased by increasing the cycle numbers owing to the formation of by-products like $KAl(CO_3)(OH)_2$, during CO_2 sorption, because these by-products are not completely converted back to the active materials at temperatures below 200 °C (Esmaili and

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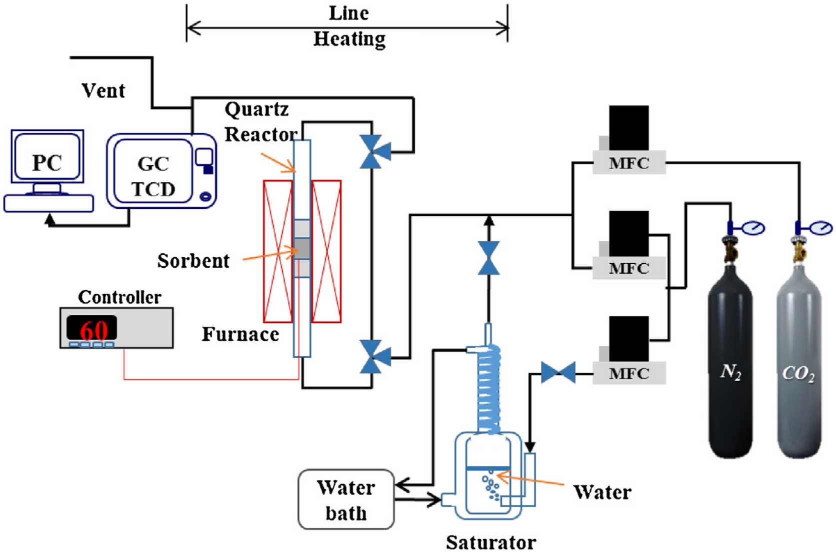

Fig. 1. Schematic of packed bed reactor system used for CO_2 absorption and regeneration experiments.

Ehsani, 2013; Jaiboon et al., 2015; Kim et al., 2012; Lee et al., 2014; Li et al., 2011; Zhao et al., 2010; Zhao et al., 2012a,b). In addition, the potassium-based sorbents prepared using MgO or CaO are also deactivated owing to the formation of by-products like $K_2Mg(CO_3)_2$, or $K_2Ca(CO_3)_2$, respectively, during CO_2 sorption, even though they have high CO_2 capture capacities at 1 cycle (Lee et al., 2006). Moreover, potassium-based sorbents prepared using TiO_2 or SiO_2 have low CO_2 capture capacities, even at 1 cycle. Hayashi et al. (1995) and Lee et al. (2010) reported that this is due to a decrease in the amount of active material (K_2CO_3) upon the formation of by-products such as potassium titanates and potassium silicates during calcination of the sorbents (Hayashi et al., 1995; Lee et al., 2010).

In this study, to address these disadvantages, novel potassium-based solid sorbents were developed by impregnation of metal silicates (instead of metal oxides) with 30 wt% K_2CO_3, and their CO_2 sorption and regeneration properties were investigated in a fixed bed reactor at the low-temperature range 60–200 °C. In addition, the morphologies and structural changes of the potassium-based sorbents were investigated using powder X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), and field emission scanning electron microscopy (FE-SEM), and their regeneration properties were analyzed using thermogravimetric analysis (TGA).

2. Experimental

2.1. Preparation of sorbents

The potassium-based sorbents used in this study were prepared by the impregnation of onto metal oxides or metal silicates, such as γ-Al_2O_3 (Aldrich), CaO (Aldrich), SiO_2 (Aldrich), $Al_6Si_2O_{13}$ (Aldrich), $CaSiO_3$ (Aldrich), and $ZrSiO_4$ (Duksan), with K_2CO_3 (30 wt%). First, 4.5 g K_2CO_3 was dissolved in 50 mL distilled water. Then, 10.5 g of the metal oxide or metal silicate was added to the solution containing dissolved K_2CO_3 in distilled water and stirred at ambient temperature for 12 h. The mixture was dried in a rotary evaporator under vacuum and calcined in a furnace under nitrogen flow (100 mL/min) for 5 h at 600 °C. The sorbents were denoted as KAl, KCa, KSi, KAS, KCS and KZS, where K, Al, Ca, Si, AS, CS, and ZS indicate K_2CO_3, γ-Al_2O_3, CaO, SiO_2, $Al_6Si_2O_{13}$, $CaSiO_3$, and $ZrSiO_4$, respectively.

2.2. Apparatus and procedures

Fig. 1 shows schematic of packed bed reactor system used for CO_2 absorption and regeneration experiments. CO_2 sorption performances were evaluated in a fixed-bed quartz reactor in the presence of 10 vol% CO_2 and 15 vol% H_2O at 60 °C under atmospheric pressure. The regeneration performances were evaluated in the presence of 100 vol% CO_2 at 200 °C. Moisture nitrogen was supplied to sorbents by using a circulator water bath and a saturator. The reactor was packed with 2 g of the sorbent. The total gas flow rate was 40 mL/min. The outlet gas was automatically analyzed every 4 min during reaction using a gas chromatographer (GC; Donam Systems Inc.) equipped with a thermal conductivity detector (TCD). A 1/8- inch stainless steel tube packed with Porapak Q was used as the column.

The physical properties of the potassium-based sorbents, including their morphologies and structural changes, were investigated by FT-IR (PerkinElmer Frontier), FE-SEM (ZEISS, SUPRA^{TM} 55VP) and XRD (using Cu Kα radiation) at the Korea Basic Science Institute (Daegu).

In addition, Nitrogen adsorption-desorption isotherms at −196 °C were measured with a Micromeritics ASAP 2020 instrument to obtain the textural properties of the sorbents. The weight losses upon phase transformation were determined using TGA and differential thermogravimetric (DTG) analysis, which were performed using a TA Instruments SDT-Q600. Nitrogen or CO_2 was used as the carrier gas, and the heating rate was 5 °C/min.

3. Results and discussion

3.1. CO_2 sorption and regeneration properties under process simulation conditions

To investigate the applicability of the new sorbents to post-combustion CO_2 capture, it is necessary to investigate the CO_2 sorption and regeneration properties of the potassium-based sorbents under process simulation conditions. Accordingly, CO_2 sorption tests were performed at 60 °C in the presence of 10 vol% CO_2 and 15 vol% H_2O. The regeneration tests were performed at 200 °C in the presence of 100 vol% CO_2.

Fig. 2 shows the CO_2 capture capacities of the KAl, KCa, KSi, KAS, KCS, and KZS sorbents during 3 cycles. Their CO_2 capture capacities were calculated from their breakthrough curves and represent