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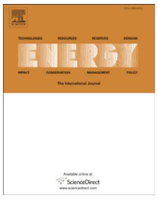

Bench scale study of CO_2 adsorption performance of MgO in the presence of water vapor

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ABSTRACT

The CO_2 adsorption performance of MgO in the presence of water vapor is of great importance for CO_2 capture and was studied in a fixed bed in this work. With the relative humidity at 50 °C increased from 30% to 70%, the CO_2 adsorption capacity of MgO increased from 0.82 mol/kg to 3.42 mol/kg correspondingly. The CO_2 adsorption capacity could reach as high as 3.54 mol/kg at adsorption temperature of 75 °C and a concentration of water vapor of 8.547% v/v. But the time to equilibrium increased due to the restrained CO_2 diffusion caused by the condensation of water vapor. Results on cycle experiments implied that condensed water would accelerate the aggregation of MgO particles. It was also found that when the temperature was higher than 100 °C, the condensation of water vapor would not happen and the porous structure would keep stable in the cycling adsorption. When the adsorption temperature is between 100 °C and 110 °C, the degradation of porous structure could be eliminated and the increase of CO_2 adsorption capacity could be achieved at the same time. This work indicates that MgO is a promising candidate for CO_2 capture from wet flue gas.

1. Introduction

Due to the economic development, fossil fuel consumption has increased sharply since the industrial revolution. The corresponding environmental problems caused by the large-scale usage of fossil fuel are gaining more and more attention. One of the main issues is the large emission of CO_2, which is the major anthropogenic greenhouse gas. To eliminate the detrimental effect of greenhouse phenomenon, extensive strategies have been proposed to reduce the CO_2 emission. CO_2 capture technologies seem to be one of the most effective ways to reduce CO_2 emission. Among these technologies, adsorption method is particularly promising owing to its superior advantages, such as no liquid waste, low energy consumption and wide range of operating temperature [1]. Hence, numerous efforts have been paid to develop effective adsorbents like carbon-based materials [2], zeolites [3], metal oxides [4], metal organic frameworks (MOFs) [5], aerogels based materials [6–8] and so on. Among these adsorbents, MgO is one of the promising candidates because Mg-contained minerals are widely available in nature, which can be prepared in large amount with low cost. MgO can adsorb CO_2 below 200 °C and be regenerated at relatively low temperature compared with CaO [4,9]. Moreover, water vapor in flue gas is favorable for the CO_2 adsorption of MgO, which make it suitable for CO_2 capture in fossil fuel power plants [10].

While, due to the low specific surface, the CO_2 adsorption capacity of pure MgO is fairly small (~2 wt%) [11]. Synthesis of porous MgO with high specific surface area seems to be an effective way to enhance the CO_2 performance of MgO. Because it would decrease the particle size and increase the active sites such as edges and corners on the crystalline structure [12]. Hence, extensive works have been done to synthesize MgO with high CO_2 adsorption performances [13–15]. Bian et al. prepared mesoporous MgO via the thermal decomposition of anhydrous magnesium acetate [16]. The MgO sample exhibited enhanced CO_2 adsorption capacity relative to commercially available MgO nanoparticles. Bhagiyalakshmi et al. synthesized mesoporous MgO using mesoporous carbon CMK-3 as exotemplate [11]. The MgO sample showed a high specific surface area and a CO_2 adsorption capacity of 10 wt% at 100 °C. To weaken the aggregation of MgO nanoparticles and increase the accessibility of basic sites for CO_2, a strategy utilizing carbon insertion was used

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to synthesize porous MgO [17]. The prepared sample showed a high surface area and a high CO_2 adsorption capacity at 200 °C. More recently, porous MgO was also used as sorbent for CO_2 capture at intermediate temperatures [18–20]. For instance, Kumar et al. examined the CO_2 capture capacity of mesoporous MgO as a potential pre-combustion CO_2 adsorbent [21]. The results showed that 96.96% of MgO was converted to $MgCO_3$ at 350 °C and CO_2 pressure of 10 bar. Vu et al. synthesized mesoporous MgO sorbent promoted with KNO_3 using an aerogel method and investigated its CO_2 adsorption performance in the intermediate temperature range of 250–400 °C [22]. The MgO sample showed a high CO_2 adsorption capacity of 13.9 wt% at 325 °C and 120 min. According to previous research it could be seen that MgO shows higher CO_2 adsorption performance after modification and is a promising adsorbent for CO_2 capture.

For industrial applications in fossil fuel power plants, the flue gas often contains a certain amount of water vapor. Especially for those units with the wet desulfurization, the flue gas leaving the wet scrubber is nearly saturated with water vapor. Meanwhile, the concentrations of SO_x and NO_x are very low (<100 ppm) at this time and thus their effects on the CO_2 adsorption can be neglected. In this case, the CO_2 capture unit is suitable to be located after the wet desulfurization unit because its interference on the technological process of fossil fuel power plant is ignorable and the CO_2 capture cost will then be reduced. Under such an operating system, the CO_2 adsorption characteristics of adsorbent in the presence of water vapor become important for the design of adsorption process and technology. Until now, different adsorbents have been investigated under this condition to verify their CO_2 adsorption performances in practical application. For instance, Plaza et al. investigated the effect of water vapor on CO_2 adsorption of a coffee-based micro-porous carbon through breakthrough experiments [23]. It was shown that the adsorption of CO_2 was not hindered by H_2O at short adsorption time and but the adsorption capacity would be reduced by the co-adsorption of H_2O at long adsorption time. Ruiz et al. studied the effect of water vapor on the CO_2 adsorption of zeolite by bench scale test [24]. They found that the addition of water had a detrimental effect on the CO_2 adsorption and the CO_2 breakthrough curve shifted to shorter time due to the competitive adsorption of H_2O. Liu et al. investigated the CO_2 adsorption of MIL-101(Cr) in the presence of water vapor [25]. Results showed that the adsorption capacity increased slightly at 10% RH, but decreased from 10% RH to 100% RH. The authors attributed the increased CO_2 adsorption capacity to the electrostatic interaction and the decrease to the competitive adsorption of water vapor. In addition, previous studies also indicate that water vapor is favorable for the CO_2 adsorption of MgO [10,26,27]. However, to the best of our knowledge, there is no bench scale study concerning the CO_2 adsorption of MgO in the presence of water vapor in the packed bed. Besides, the adsorption behavior and cycle stability of MgO in the presence of water vapor is also unknown.

In this work, hence, the CO_2 adsorption performance of MgO in the presence of water vapor was studied on a fixed bed adsorption system. The breakthrough curves under different adsorption conditions were obtained and the CO_2 adsorption capacity was calculated. The MgO samples before and after CO_2 adsorption were characterized by X-Ray Diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM) and surface area and porosity analysis. The influence of water vapor on the CO_2 adsorption behavior, adsorption mechanism, cycle stability and porous structure of MgO was discussed. Better understanding of the CO_2 adsorption of MgO in the presence of water vapor will be provided.

2. Materials and methods

2.1. Adsorbents

Porous MgO was obtained through the calcination of basic magnesium carbonate (Sigma-Aldrich, AR, light). Basic magnesium carbonate was heated at 450 °C with a temperature rising rate of 10 K/min and kept for 4 h under a N_2 (99.99%) flow rate of 30 mL/min.

2.2. Adsorption experiments

The experimental setup for the CO_2 adsorption of MgO developed by our group is shown in Fig. 1 and the detail information of experimental setup is given in Supporting Information. During the CO_2 adsorption test, the adsorption column was firstly heated to 400 °C and kept for 1 h with a N_2 flow rate of 100 mL/min to remove the adsorbed impurities. Then the temperature decreased to a fixed value and the moist flue gas flowed into the column. In this work, 15% CO_2 concentration in dry flue gas was used to simulate the real flue gas from the coal-fired power plant (12–15%) [28]. After adsorption, the effluent gas stream entered the purification device to remove the water vapor and the CO_2 concentration was measured by CO_2 analyzer. The CO_2 concentration of outlet was recorded continuously until it reached 14.5%.

To eliminate the pseudo adsorption capacity caused by the volume of pipeline, a similar breakthrough curve with no adsorbent packed was undergone and the pseudo adsorption capacity was calculated. The real adsorption capacity of MgO was then equal to the total capacity subtracted the pseudo capacity.

To test the cycle stability of MgO under different adsorption conditions, 10 continuous adsorption tests were performed. The adsorption process was the same as the above description. After adsorption, the adsorption column was heated to 400 °C and kept for 1 h under a purge gas of N_2 (100 mL/min). Then the temperature decreased to the adsorption temperature and the subsequent adsorption process began.

2.3. Characterization of materials

Powder X-ray diffraction measurement was performed using a Rigaku D/max-1200 X-ray diffractometer (Japan) with Cu radiation. The adsorption mechanism of MgO was examined by Fourier transform infrared spectroscopy (Perkin-Elmer Spectrum 100 Series FTIR instrument (USA) with a horizontal attenuated total reflectance (HATR) sampling accessory). MgO powders were placed on the top of a ZnSe crystal with a high refractive index. The spectrum was collected from 650 cm^{-1} to 4000 cm^{-1} with a resolution of 4 cm^{-1}. The morphologies were observed by S-4800 field emission scanning electron microscope (Hitachi, Japan). The adsorption-desorption isotherm for N_2 was measured at 77 K through an ASAP 2020 surface area and porosity analyzer (Micromeritics, USA). BET specific surface area was calculated according to the Brunauer-Emmett-Teller (BET) model. Pore size distribution was determined from the adsorption branch of the isotherm using the Barrett-Joyner-Halenda (BJH) method. Total pore volume was calculated according to the N_2 amount adsorbed at a relative pressure of 0.97.

3. Results and discussion

3.1. CO_2 adsorption in the absence of water vapor

Prior to the experimental study on the effect of water vapor, the CO_2 adsorption performance of MgO under dry condition was