Synthesis of fly ash-based microporous copper silicate for CO₂ capture from humid flue gases

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Abstract−Conventional microporous adsorbents suffer from CO_2 adsorption capacity reduction due to the presence of water vapor in real flue gases. Therefore, development of low-cost moisture-insensitive adsorbents is of great significance. In the present work, microporous copper silicate was synthesized from waste fly ash for the first time. The synthesis conditions were further optimized to obtain copper silicates with high purities. The as-synthesized product was characterized in terms of structural morphology, chemical composition, and surface properties. The CO_2 and H_2O adsorption properties of the prepared copper silicate were also investigated by single-component isotherm measurements and dynamic CO_2/H_2O binary breakthrough experiments. The results show that the as-synthesized fly ash-based copper silicate exhibited excellent CO_2 adsorption properties even in the presence of water vapor, thus demonstrating promising potential as a moisture-insensitive adsorbent for directly capturing CO_2 from humid flue gases.

Keywords: Copper Silicate, Fly Ash, Water Vapor, CO_2 Capture, Humid Flue Gases

INTRODUCTION

The continuous increase in carbon dioxide concentration in the atmosphere has become a worldwide problem [1]. Consequently, a variety of CO_2 capture processes have been proposed, including cryogenic distillation [2,3], solvent-based chemisorption [4,5], membrane separation [6,7], pressure swing adsorption (PSA) [8], electrical swing adsorption [9], and temperature swing adsorption (TSA) [10,11]. Among them, the PSA technology has gained interest worldwide because of its low operating cost [12,13]. The high selectivity toward CO_2 against N_2 is an essential consideration for evaluating an adsorbent to capture CO_2 using the PSA technology [1]. Currently, the development of less expensive and more effective adsorbents is the most effective approach to reducing the cost of CO_2 capture.

Over the years, a large number of microporous materials have been developed as effective adsorbents, which can be applied to capturing CO_2 from flue gas streams [14-18]. However, the flue gas streams are usually wet or humid, and conventional adsorbents suffer from CO_2 sorption capacity reduction in the presence of water vapor [19,20]. To resolve this bottleneck, two different approaches were proposed: dehydrating the incoming gas stream [21], or adding a pre-layer for water removal. However, the ultimate strategy for eliminating the detrimental effect of water vapor is to use water-tolerant adsorbents [22]. Therefore, the search for such moisture-insensitive adsorbents with high CO_2 selectivity remains highly popular. Remarkably, Yoon et al. [21] developed a possible workaround using microporous copper silicate (SGU-29) that can capture CO_2 directly from humid flue gases. This material is the best adsorbent reported

to date that captures CO_2 in humid gas streams. Compared with the conventional adsorbents containing H_2O/CO_2-sharing sites, SGU-29 has H_2O-specific and CO_2-specific adsorption sites that do not interfere with each other. Owing to its unique structure, SGU-29 has a significantly high capacity of CO_2 adsorption from a flue gas in the presence of moisture; this provides a promising solution to the high costs of CO_2 capture from flue gases.

On the other hand, zeolite synthesis from fly ashes has seemed to be promising in recent years, which can effectively reduce the synthesis cost and protect the environment [23]. Thus, successful synthesis of SGU-29 from fly ash will offer considerable benefits economically and environmentally. In this study, for the first time, we investigated the synthesis of SGU-29 using waste fly ash. The feasibility of using the synthesized fly ash-based copper silicates as adsorbents for CO_2 capture from wet flue gases was assessed from the CO_2 adsorption isotherms and binary breakthrough experiments.

EXPERIMENTAL

1. Synthesis

The fly ash used in the study was primarily composed of SiO_2 (48.5 wt%), Al_2O_3 (40.8 wt%), Fe_2O_3 (2.0 wt%), and CaO (3.3 wt%). The copper silicate SGU-29 was synthesized by a two-step hydrothermal method. First, 60 g of fly ash and 50 g of NaOH were mixed with 150 g of water. The slurry was then heated at 120 °C for 2 h under continuous stirring. After centrifugation, a copper sulfate solution was added to the supernatant to adjust the ratio of silicon to copper. Dilute sulfuric acid (1 mol·L⁻¹) was added dropwise into the mixture under continuous stirring until the pH of the system reached a desired value (8.5-12.5). Then, 2 g of ETS-10 seeds, 18.5 g of NaCl, and 12 g of KCl were added to the resulting system under stirring for 30 min. The slurry was then transferred into an auto-

clave and hydrothermal reaction was carried out at 215 °C for different reaction times (1, 3, 5, and 6 d). The as-prepared solid was filtered and washed with deionized water three times. Finally, the copper silicate products were collected by drying at 100 °C for 10 h.

2. Characterizations

The crystal structure of the samples was examined using an X-ray diffractometer (XRD-7000, Shimadzu). The morphology of the synthesized copper silicates was investigated with a Zeiss Ultra Plus scanning electron microscope (SEM) operated at 15 kV. The BET surface area was measured on an ASAP2020 analyzer using N_2 as the probe gas at 77 K. The CO_2 adsorption isotherms of the synthesized copper silicates were recorded on a specific surface area and pore size analyzer (JW-BK112, JWGB Co., Ltd.). All the samples were degassed under vacuum (300 °C) for 8 h before measurements. H_2O/CO_2 binary breakthrough experiments were performed at 50 °C on a custom-built apparatus. The details of the experiments were reported in our previous study [24].

RESULTS AND DISCUSSION

1. Copper Silicate SGU-29 Synthesis

Alkalinity is an important factor for nucleation and crystal growth during the crystallization of zeolites [25]. To determine the effect of alkalinity on the crystallization of copper silicate SGU-29, an initial pH range of 8.5-12.5 was investigated to evaluate the influence of pH on the synthesis, and the as-synthesized products were analyzed by XRD (shown in Fig. 1). The crystalline phases of fly ash are mainly mullite and quartz [25]. In the XRD patterns of the prepared samples, the diffraction peaks of mullite and quartz disappeared, indicating that the structure of fly ash collapsed during copper silicate synthesis. When the pH was around 10.5, microporous copper silicate with high purity was obtained. The XRD pattern (Fig. 1(b)) shows distinct peaks, which are consistent with those reported for microporous copper silicate [21]. At a lower pH of 8.5, the XRD pattern (Fig. 1(c)) shows that the transformation of fly ash into copper silicate is incomplete, and thus, it is difficult to obtain high-purity microporous copper silicate SGU-29. On the contrary, at a higher pH of 12.5, the XRD pattern (Fig. 1(a)) of the product has many
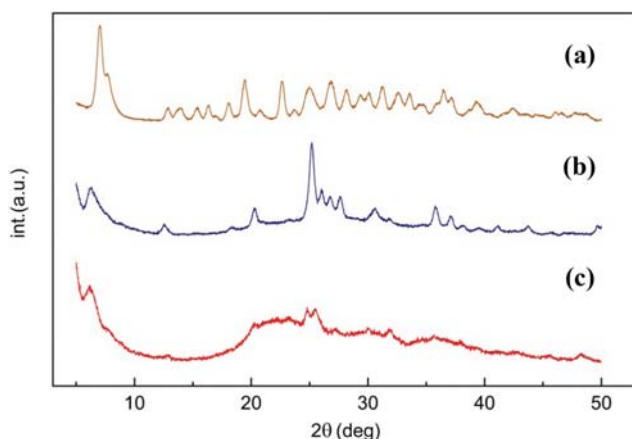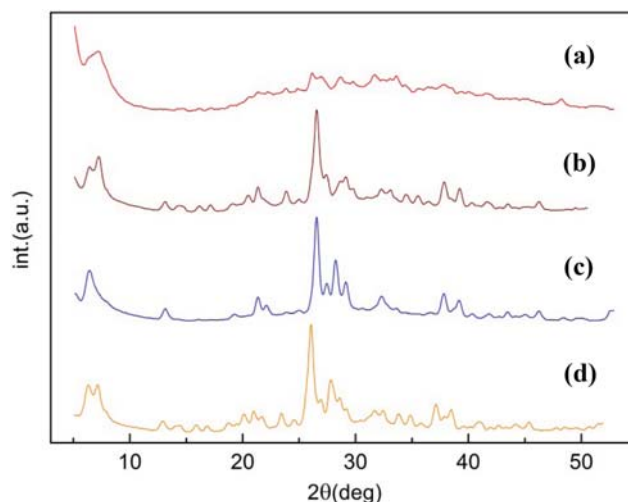

Fig. 2. XRD patterns of copper silicates obtained at different Si/Cu mole ratios: (a) 2.5, (b) 5, (c) 6 and (d) 8.

impurity peaks, suggesting that the copper silicate SGU-29 is heavily contaminated with large amounts of impurities.

To investigate the effect of Si/Cu molar ratios on the crystalline phase, Si/Cu mole ratios ranging from 2.5 to 8.0 were selected to synthesize pure copper silicate. Particularly, the Si/Cu mole ratio was controlled by adjusting the concentration of $CuSO_4$ solution added into the mixed system prior to the hydrothermal reaction. Fig. 2 shows the XRD patterns of the products that were synthesized with different Si/Cu ratios. According to the XRD patterns, copper silicate SGU-29 is the main phase of the sample prepared with a Si/Cu mole ratio of 6. For Si/Cu mole ratios higher or lower than 6, peaks corresponding to an unnamed copper silicate always appeared. In particular, when the Si/Cu mole ratio was 5, the unnamed copper silicate was the main phase. These findings show that the Si/Cu mole ratio is a key factor in the synthesis of copper silicate SGU-29. To obtain pure SGU-29, the Si/Cu mole ratio should be controlled carefully. Thus, the optimum Si/Cu mole ratio for obtaining a high-purity copper silicate SGU-29 is 6, and this optimal ratio was further used throughout the experiments.
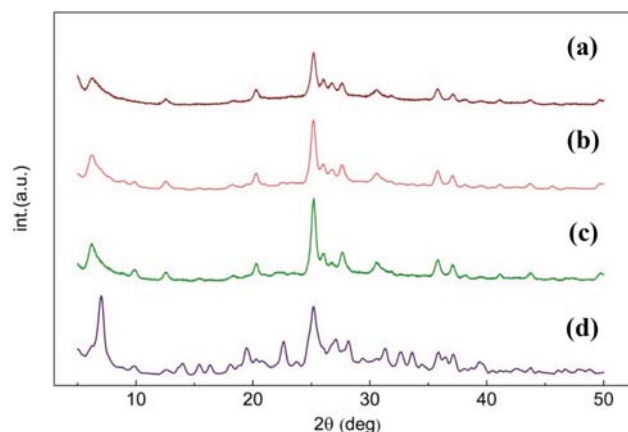

Fig. 1. XRD patterns of samples synthesized at different pH: (a) 12.5, (b) 10.5 and (c) 8.5.

Fig. 3. XRD patterns of samples synthesized at different crystallization times: (a) 1 d, (b) 3 d, (c) 5 d and (d) 6 d.
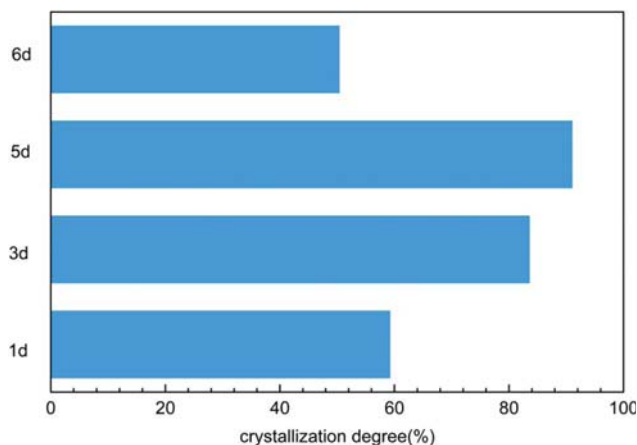
Fig. 4. Crystallinity of the prepared samples obtained at different crystallization times.

Hydrothermal reaction time is also a critical factor in controlling the purity of the synthesized microporous molecular sieves. To investigate the influence of hydrothermal reaction time on the copper silicate SGU-29 synthesis, time-dependent synthesis was carried out and the product purities were examined by XRD analysis. The results show that high-purity copper silicate SGU-29 could be obtained for a reaction time ranging from 1 to 5 d. When the reaction time was further increased to 6 d, the diffraction peak of the unnamed copper silicate was observed. This is probably because of the long crystallization time that led to the transformation of

SGU-29 into the unnamed copper silicate. The percent crystallinity was determined by dividing the total area of crystalline peaks by the total area of all the peaks. As shown in Fig. 4, the crystallinity of products first increased and then decreased with time. The best hydrothermal reaction time was 5 d, which was used in the rest of the study.

2. Morphological and Structural Analysis

The morphologies of fly ash and copper silicate are presented in Fig. 5. The SEM images of fly ash (Fig. 5(a) and (b)) show irregular or spherical particles with a broad size distribution. In contrast, the SEM images of the as-synthesized copper silicate SGU-29 (Fig. 5(c) and (d)) display typical truncated bipyramidal particles with a size of approximately 3 μm ($\pm$0.2)×1 μm ($\pm$0.1). Irregular or spherical particles can be hardly observed, which indicates that the fly ash underwent complete conversion. Therefore, the morphological analysis further confirmed the formation of high-purity copper silicate SGU-29.

The chemical composition of the product was analyzed by XRF spectroscopy. The prepared SGU-29 sample consists of Na, Si, Cu, Ti, K, and Al with content of 6.0, 28.5, 15.4, 3.4, 3.8, and 0.5 wt%, respectively. By comparing the aluminum content of the starting material and product, we can conclude that most of the alumina in the fly ash was converted during the process. The BET surface area and pore volume of the prepared SGU-29 measured at 77 K under a N_2 flow were 267 $m^2 \cdot g^{-1}$ and 0.16 $cm^3 \cdot g^{-1}$, respectively, which were close to those of SGU-29 reported in literature [21]. The structural analysis suggests that high-purity SGU-29 was successfully synthesized.
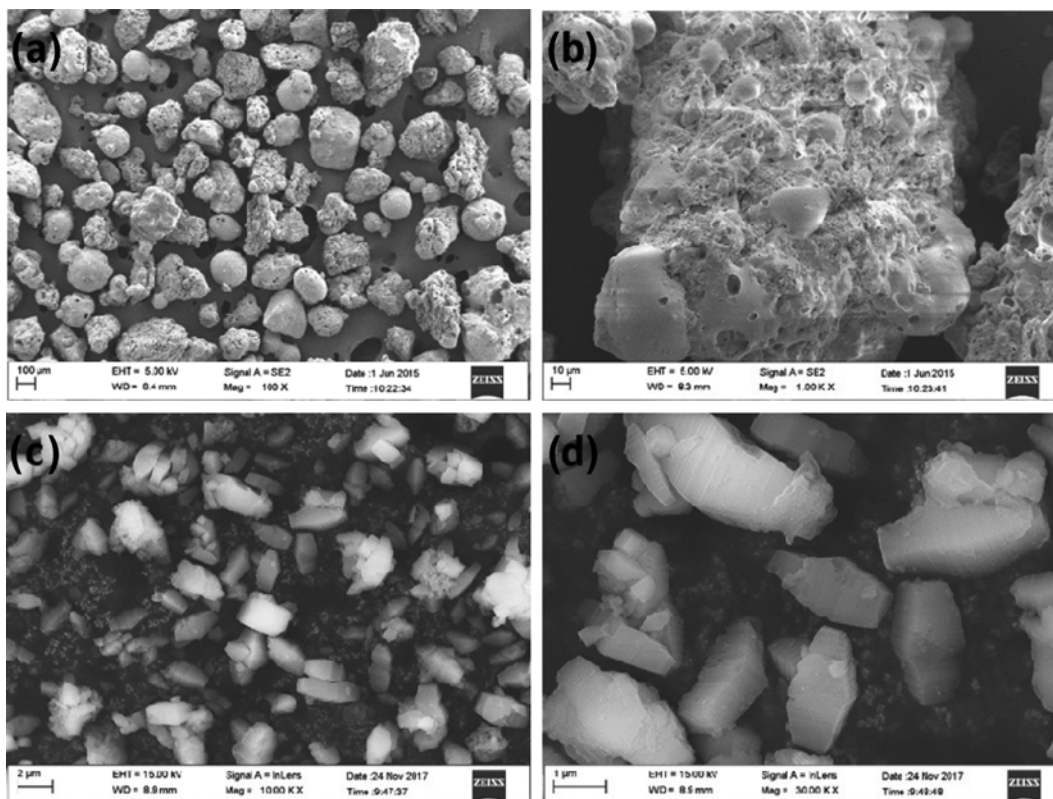

Fig. 5. SEM images of (a), (b) fly ash and (c), (d) as-synthesized SGU-29.
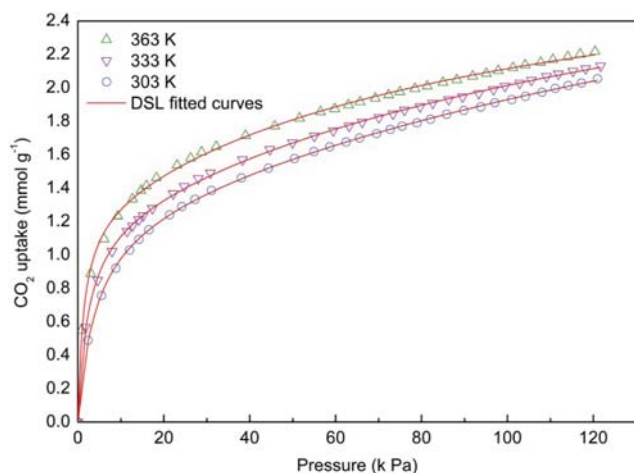
Fig. 6. CO_2 adsorption isotherms of the prepared SGU-29 at 303, 333 and 363 K.

Table 1. Fitting parameters of dual-site Langmuir model

	q_{m1}	b_1	q_{m2}	b_2	R^2
303 K	1.73	0.01	1.26	0.76	0.9985
333 K	1.22	0.43	2.21	0.06	0.9994
363 K	1.24	0.25	2.77	0.04	0.9998

Fig. 7. Calculated isosteric heat of CO_2 adsorption on the prepared SGU-29.

3. Adsorption Properties

3-1. Single-component CO_2 Adsorption

To understand the adsorption behavior of single-component CO_2 on the prepared SGU-29 more accurately, a physical adsorption apparatus was used to obtain the adsorption isotherms at 303, 333, and 363 K. The adsorption isotherms of SGU-29 (Fig. 6) showed the characteristics of type I curves, according to BDDT classification. At pressures below 20 kPa, the CO_2 adsorption capacities of SGU-29 increased rapidly with increasing pressure. When the pressure was increased to 20 kPa, the rate of adsorption of CO_2 on the prepared SGU-29 decreased, as SGU-29 is a microporous material whose inner surface area is larger than the outer surface area. When the pressure was increased to a certain level, the adsorption was mainly attributed to the adsorption on the outer surface; thus, the rate of adsorption on the prepared SGU-29 decreased. The adsorption energies at different adsorption sites vary in almost all adsorbents. The real adsorption behavior of adsorbents with heterogeneous surfaces cannot be described using the Langmuir equation. Thus, the adsorption isotherms of CO_2 on the synthesized SGU-29 were fitted by the dual-site Langmuir model (Eq. (1)).

Dual-Site Langmuir:

$$q = \frac{q_{m1}b_1p}{1+b_1p} + \frac{q_{m2}b_2p}{1+b_2p} \qquad (1)$$

Herein, two different adsorption sites (site 1 and site 2) are selected, and q_{m1} and q_{m2} are the saturation capacities (mmol·g^{-1}) and b_1 and b_2 are the adsorption equilibrium constants (kPa^{-1}) for site 1 and 2, respectively.

The correlation coefficients obtained were larger than 0.99, suggesting that the dual-site Langmuir equation could describe the adsorption behavior of CO_2 on the prepared SGU-29 accurately. The adsorption loading of CO_2 on the prepared SGU-29 at 303 K and 101 kPa was about 2.1 mmol·g^{-1}, which is comparable to that reported in literature [21]. This suggests that the synthesized fly ash-based copper silicate SGU-29 has similar adsorption properties of single-component CO_2 to the counterparts obtained with commercial sources.
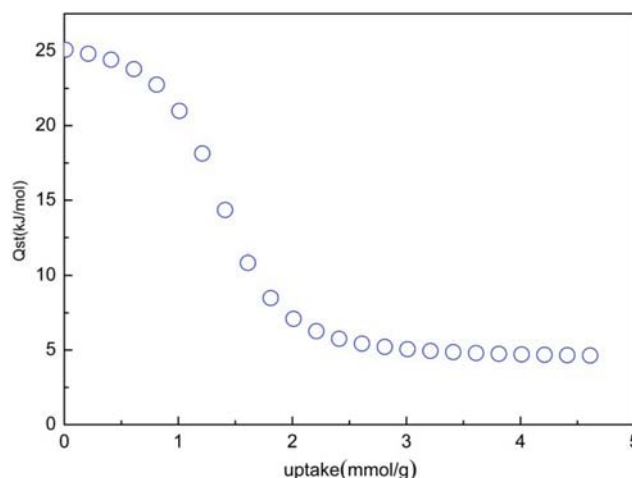
To explore the interaction mechanism between the prepared SGU-29 and CO_2 molecules, the Clausius-Clapeyron equation as well as the obtained dual-site Langmuir model parameters (Table 1) was applied to calculate the isosteric heat of adsorption, and the results are shown in Fig. 7. During CO_2 adsorption, the isosteric heat decreased with an increase in CO_2 loadings. The reason for this phenomenon is probably the interaction between the quadrupole moments produced by the CO_2 bonds and the extra cations in the framework of the as-synthesized SGU-29. When the adsorption loading is too low, the interaction between the quadrupole moment and the cation is strong. However, with an increase in adsorption loading, the interaction between the quadrupole moment and the cation decreases. The isosteric heat of CO_2 on the as-synthesized SGU-29 was between 5 and 25 kJ·mol^{-1}; therefore, physical adsorption plays the main role in single-component CO_2 adsorption on the prepared SGU-29.

3-2. Binary Adsorption Isotherms

Binary CO_2/H_2O adsorption experiments were carried out at 333 K on the fly ash-based SGU-29 to evaluate the influence of moisture on CO_2 adsorption. The concentration of CO_2 in the carrier gas was kept constant (10 wt%), while the concentration of water was varied in the relative humidity (RH) range of 0-70%. Fig. 8(a) displays the adsorption capacities of CO_2 and H_2O on the prepared SGU-29 based on the binary CO_2/H_2O breakthrough curves (Fig. 8(b)). At an RH of 0, the CO_2 adsorption capacity of SGU-29 at 101 kPa was about 1.3 mmol·g^{-1}, which is in good agreement with the CO_2 loading obtained from the physical adsorption apparatus. In the RH range of 0-30%, the CO_2 adsorption capacities remained almost constant (1.2 mmol·g^{-1}). When the RH was increased to 30%, the CO_2 adsorption capacities decreased with increasing RH.

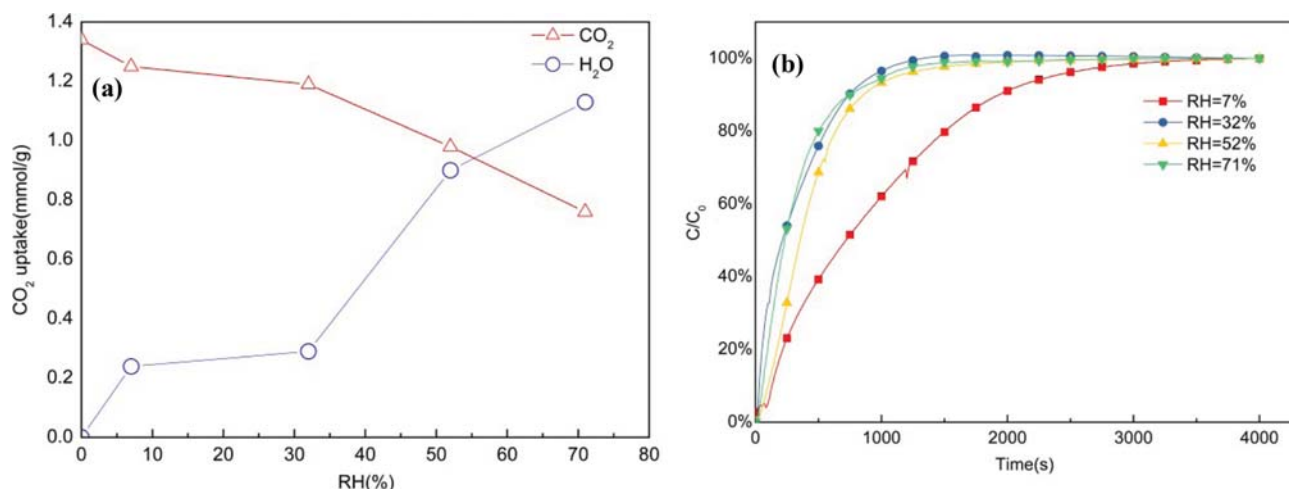**Fig. 8.** CO_2/H_2O breakthrough data for the prepared SGU-29 under different humidity conditions: (a) CO_2/H_2O adsorption capacities and (b) H_2O breakthrough curves.

The CO_2 adsorption capacity of the prepared SGU-29 was still above $0.8 \, mmol \cdot g^{-1}$ even at a high RH of 71%. The results suggest that the obtained SGU-29 has a much higher CO_2 adsorption capacity than that of the conventional adsorbents over a wide RH range [26]. As expected, the adsorption capacity of water on the as-synthesized SGU-29 increased with increasing RH. However, the H_2O loadings on the prepared SGU-29 were much lower than that on conventional adsorbents [26]. For instance, at a RH of 71%, the H_2O adsorption capacity was as low as $1.2 \, mmol \cdot g^{-1}$. Therefore, the prepared fly ash-based SGU-29 exhibited high CO_2 adsorption properties in the binary CO_2/H_2O gas streams. We can conclude that the prepared fly ash-based SGU-29 is a moisture-insensitive adsorbent that can be used to capture CO_2 directly from humid flue gases.

CONCLUSIONS

A novel strategy for synthesizing fly ash-based copper silicate was investigated. High-purity copper silicate could be obtained under the following synthesis conditions: pH of 10.5, Cu/Si mole ratio of 6, and hydrothermal reaction time of 5 d. The structural and adsorption properties of the fly ash-based copper silicate SGU-29 are similar to those of the counterparts obtained with commercial sources. Binary breakthrough experiments showed that the presence of water vapor has little effect on the adsorption behavior of CO_2 on the prepared fly ash-based SGU-29.

ACKNOWLEDGEMENTS

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