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Research article

CO_2 sorbents derived from capsule-connected Ca-Al hydrotalcite-like via low-saturated coprecipitation

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ABSTRACT

This work presents the synthesis of Ca-Al mixed oxides derived from Ca-Al-CO_3 layered double hydroxides (LDHs), which were prepared using a low-saturated coprecipitation method at high constant pH. Compared to the high-saturated coprecipitation method, a better CO_2 adsorption capacity and stability were obtained from the mixed oxides. This was attributed to the novel capsule-connected structure of LDHs nanoparticles, smaller crystal size of CaO, and uniform distribution of CaO and Al_2O_3. The effect of the coprecipitation temperature, Ca/Al ratio and methanol modification on the CO_2 capture performance of Ca-Al mixed oxides was also investigated. The mixed oxides with 2:1 Ca/Al ratio modified by methanol showed a much greater stability with carbonation capacity of about 56.7 wt% after 30 carbonation/calcination cycles. A double exponential model was fitted to the CO_2 adsorption curves, providing a good explanation for the disparity between CO_2 uptakes with different Ca/Al ratios.

1. Introduction

Recently, CO_2 capture and separation from high-temperature flue gases in fossil-fuel power plants has been considered as a promising technology to mitigate global warming in the medium to long term [1]. In comparison with liquid adsorbents, solid adsorbents such as alkaline metal carbonates and alkaline earth oxides show great potential in CO_2 capture systems because of their use in a wide temperature range and their limited pollution to the environment [2]. Alkaline metal carbonate sorbents such as K_2CO_3 and Na_2CO_3 sorbents have been paid more attention for CO_2 capture in the last decade years [3–5]. Typically, their CO_2 capture takes place within the temperature range of 50 °C–100 °C, while regeneration occurs in the range of 120 °C–200 °C, enabling them potentially applicable to the capture of CO_2 from existing fossil fuel-fired power plants. However, the main problems of this type of sorbent are the slow carbonation reaction rate and low adsorption capacity, etc. [6]. As for the sorbents based on alkaline earth metals, MgO sorbents absorb CO_2 in the temperature range of 200 °C–400 °C and can be regenerated at relatively low temperatures (400 °C–500 °C). They have the advantages of relatively moderate operating temperature and low energy requirement for regeneration, and it is widely employed in the process of pre-combustion capture to adsorb and remove CO_2 [7]. However, because of its relatively low CO_2 sorption capacity and slow sorption kinetics, the practical application of MgO as a CO_2-sorbent is limited. Lithium silicates have been investigated as high-temperature CO_2 adsorption sorbents. While when the adsorption temperature is low than 600 °C, the kinetics of the CO_2 capture reaction is relatively low [8].

CaO-based sorbents have been recognized as one of the best candidates for CO_2 capture due to their advantages of high theoretical adsorption capacity, wide availability and low cost [9]. However, the main challenge for CaO-based materials is their loss-in-capacity throughout multiple carbonation/calcination cycles due to the serious sintering and physical aggregation of sorbent particles [10,11]. To improve the long-term durability of the CaO-based sorbents, many methods have been adopted, including changing morphology and microstructure [12–14], sorbent modification by chemical treatments [15,16] and adding inert support materials of high-temperature resistance [17–19]. Among the proposed stabilizers, aluminum compounds have shown outstanding performance in improving the stability of the sorbents [20–22].

Mixed oxides derived from Ca-Al layered double hydroxides (LDHs) are also promising adsorbents at high temperatures. In these mixed oxides, CaO is the active ingredient while the aluminum-containing components serve as inert supports to improve the dispersion of CaO particles and the sintering-resistant property of the sorbents. Although a series of methods has been developed to prepare Ca-Al-LDHs, the Ca-Al mixed oxides by decomposition of these LDHs showed relatively low

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CO_2 uptake compared to other calcium based sorbents, with the highest value of 48.5 wt% after 30 cycles via the high-saturated coprecipitation technique at the adsorption temperature of 600 °C [23–26].

On the other hand, low-saturated coprecipitation method has attracted much attention in the synthesis of LDHs for intermediate-temperature CO_2 capture, considering that different coprecipitation condition could render different morphology of LDHs, such as plate-like or sand-rose, which would further affect the CO_2 adsorption performance of their derived mixed oxides. In particular, if the preparation of LDHs was proceeded at low-saturated coprecipitation condition with high enough pH (pH > 10), the reaction between LDH nanoparticles and anions would be hindered, and the growth of the LDH particles would be prevented, so a distinct morphology of LDHs would be formed. For example, Wang et al. developed a nanoscale spherical $Mg_3Al–CO_3$ LDHs using a low-saturated coprecipitation method at a pH value of 12. Compared to the conventional coprecipitation method, a higher CO_2 adsorption capacity of 0.58 mmol g^{-1} was obtained at 200 °C for the LDHs derived mixed oxides owing to a small crystal size (20 nm) [27]. However, this promising preparation method has not been applied into the synthesis of Ca-Al-LDHs. Especially, the influence of coprecipitation condition on the CO_2 adsorption performance of Ca-Al-LDHs derived sorbent has not been studied thus far. So it is still necessary to carry out the extensive research on the pH controlled synthesis of Ca-Al-LDHs for CO_2 capture.

In this paper, Ca-Al-CO_3 LDHs with the novel capsule-connected structure were synthesized through a low-saturated coprecipitaton method at high constant pH. The influence of coprecipitation temperature and Ca/Al ratio on the CO_2 capture performance of Ca-Al mixed oxides derived from Ca-Al-CO_3 LDHs was investigated. To explain the different adsorption ability of the mixed oxides with different Ca/Al ratio, a double exponential model is proposed to fit the CO_2 adsorption curves. Furthermore, methanol modification was adopted to gain sorbents with higher adsorption capacity and better stability.

2. Experimental

2.1. Sorbent synthesis

2.1.1. Synthesis of LDHs

Ca-Al-CO_3 LDHs precursors were synthesized via a low-saturated coprecipitation method at a high constant pH level [27]. In a typical preparation, a mixed metal solution A (1 M) was added drop-wise to a basic solution B (100 mL) containing 0.05 mol Na_2CO_3. The pH value of solution B was kept constant at a high value by adding a solution C (50 mL) containing 0.17 mol NaOH. The resulting mixture was then aged at room temperature for 24 h, after which the products of LDHs were collected by filtration, washed with deionized water, and dried at 100 °C overnight. In comparison, the high-saturated coprecipitation method was also adopted, in which the solution A was quickly added to the mixed solution B and C. Finally, the resulting LDHs were calcined at 600 °C for 1 h in a muffle furnace to obtain the derived mixed oxides as CO_2 sorbents.

2.1.2. Methanol modification

The methanol modified Ca-Al-CO_3 LDHs was also prepared via the low-saturated coprecipitation method as described above except that the water washed LDHs slurry was re-dispersed in methanol and stirred at room temperature for 1 h. After that, the LDH was filtered and washed thoroughly with methanol again. Finally the product was dried at 75 °C overnight. Similarly, the obtained LDHs were calcined at 600 °C for 1 h in a muffle furnace.

2.2. Materials characterization

2.2.1. TGA

The thermogravimetric analysis was carried out by a thermal analysis system (STA449F3, NETZSCH). The experiment was performed in a flow of air (50 mL/min) with a heating rate of 10 °C/min and a final temperature of 800 °C.

2.2.2. XRD

Powder XRD analysis was conducted using a Bruker D8 Focus operating at 40 kV and 40 mA equipped with a nickel-filtered Cu K_α radiation (λ = 1.54056 Å) and operating in a 2θ range of 5–90° at a scanning rate of 0.02 °/s.

2.2.3. SEM

The morphologies of the LDHs and the derived mixed oxides were observed using scanning electron microscopy analysis. SEM/EDX was conducted on a Hitachi S4800 field emission microscope at 10.0 kV.

2.3. CO_2 adsorption analysis

The cyclic carbonation/calcination performance of the Ca-Al-CO_3 LDHs derived mixed oxides was measured using thermogravimetric analysis (TGA, NETZSCH STA 449F3). A small amount of sorbent (~10 mg) was placed in a quartz sample pan and heated to a carbonation temperature of 600 °C at a rate of 10 °C/min under N_2 atmosphere at atmospheric pressure. Next, the carbonation proceeded for 45 min in 50 mL/min of CO_2 reactant gas along with 50 mL/min of N_2 purge gas. After carbonation, a pure N_2 flow (50 mL/min) was introduced into the thermogravimetric analyzer instead of CO_2 and the calcination was performed at 700 °C for 20 min.

3. Results and discussion

3.1. Effect of coprecipitation method

The crystal identity of the Ca-Al-CO_3 LDHs prepared via low-saturated and high-saturated coprecipitation method (annotated as LDH-L and LDH-H, respectively) was examined using powder X-ray diffraction. As shown in Fig. 1(a), both of the LDHs exhibited the same reflection peaks at the angle of 11.9° and 23.6°, which corresponded to the basal planes of (003) and (006), indicating a well-formed crystalline layered structure. It was noted that the peak of LDH-L at $2\theta = 11.9°$ was broader and of weaker intensity than that of LDH-H, indicating the lower degree of crystallinity and smaller crystal size of LDH-L. The crystal size of LDH-H and LAH-L are 37.0 nm and 32.1 nm, respectively. In addition, the intense diffraction peaks of $CaCO_3$ phase (JCPDS no. 47–1743) appeared at 2θ = 23.3°, 29.8°, 32.0°, 36.0°, 39.8°, 42.8°, 43.8°, 46.4°, 48.2°, 48.7°, 57.4°, 61.0°, demonstrating that Ca^{2+} and ${CO_3}^{2-}$ were inclined to combine directly because of the incompatibility of the ionic sizes of Al and Ca (6.2 vs. 10.6 nm) and the higher solubility product constant Ksp of $CaCO_3$ [24]. In addition, two weak peaks of AlOOH (JCPDS no. 49-0133) were also detected.

After being thermally treated at a high temperature of 600 °C, both LDH-L and LDH-H were transformed into Ca-Al mixed oxides (annotated as sorbent-L and sorbent-H, respectively). As displayed in Fig. 1(b), CaO phase with diffraction peaks at 32.1°, 37.3°, 53.8°, 64.1°, 67.3°, 79.6°, 88.4° (JCPDS no. 48-1467) were detected for both sorbent-L and sorbent-H. Additionally, $CaCO_3$ was still observed which may have resulted from the incomplete decomposition of $CaCO_3$. Moreover, sorbent-L and sorbent-H exhibited weak peak reflections attributed to Ca-Al spinel such as $Ca_{12}Al_{14}O_3$, $Ca_3Al_2O_6$ and $CaAl_2O_4$. Finally, as calculated from the plane (200) by the Scherrer equation, the grain size of CaO in sorbent-L was only 29.5 nm, which was smaller than that of sorbent-H with 36.0 nm.

Fig. 2 presented the TGA analysis of LDH-L and LDH-H, both of which showed three-stage weight loss. The first step in the range of 30–200 °C is due to the removal of physisorbed and inter-layer water; the second step in the range of 200–450 °C is attributed to the removal of hydroxyls on the layer and the decarbonation of carbonate anions